Chapter 2

Methodology

2.1 Introduction

Over the past twenty years, one of the major developments in the physical and biological sciences is the use of computer modelling. For example, impressive achievements have been made in molecular biology [6,7], protein science [8], polymer science [9,10], physical chemistry [11], liquid crystals [12, 13] and solid-state materials [14, 15]. Previously, computer modelling has been concerned with reproducing experimental data; in essence it has been trying to prove itself. However, it is increasingly becoming a predictive tool, and is moving towards more realistic and accurate predictions of complex systems [16]. Much of this advancement is a consequence of the rapid increase in computational resources available, which is illustrated by the continued increase in the number density of transistors incorporated on an integrated circuit, still in accordance Moore's Law [17].

The modelling methodologies, which are used within the field of solid-state physics,

fall into two categories, those that rely upon the use of a simple description of interatomic forces, and those that take a quantum mechanical approach by solving Schrödinger's equation [14]. Interatomic potentials are numerical functions that attempt to describe the variation in energy of an atomic or ionic interaction as a function of separation. Such potentials can be used to perform either static [14, 18] or dynamic calculations.

This thesis utilises static-lattice calculations, and these are described in more depth later. Molecular dynamics (MD) calculations are methods that allow the crystal lattice to vibrate, where this vibration is described by Newtonian laws [14]. One popular method for quantum molecular dynamic (QMD) calculations is based on the Car-Parrinello approximation [19] and use Density Functional Theory (see Section 2.7) to calculate the energy of the system, and thus, the interatomic forces. Monte Carlo (MC) methods have their basis in statistical physics and make changes to the system by randomly swapping components and then deciding whether to accept or reject the change via a set of rules. MC can be used in conjunction with energy minimization to evolve structures by swapping ions within a lattice in a random fashion and decision criterion is the evaluation of the energy via energy minimization, this is then compared to the previous result [20].

Molecular dynamics calculations are more computationally intensive than the staticlattice approach. They are limited by the very short time-scales they can predict (typically nanoseconds). The timestep between calculations must be on a scale smaller than the characteristic time of any important process in the system (e.g. an atomic vibration), hence a value of the order of 10^{-15} s is typically used [14]. A technique recently proposed by Voter [21] may help to resolve this timescale problem by running the simulation at elevated temperatures in order to accelerate the system dynamics. The electronic structure calculations that attempt to solve Schrödinger's equation are even more computationally expensive. They are however, considered less reliant on empirical approximations and so may yield more accurate results. One important role of highly accurate quantum mechanical calculation is in determining reliable parameters for interatomic potentials [16].

The calculations presented in this study employ predominantly the static-lattice, energy minimization approach whilst some use a quantum mechanical approach. The minimum energy configuration is determined by an iterative relaxation of the atom positions with respect to the forces acting on them.

Static-lattice simulations are very versatile and have been extended to a wide range of applications and provide a good working description of many important properties of ionic crystals [18, 22–28]. Nevertheless they do have limitations in their scope, for example, they are unable to model any property that depends explicitly on electronic structure. They can, however, model charged defects, from which an electronic defect can be inferred [14], for example, a lattice ion can be ionized (a hole) or can assume an extra charge (a small polaron or localized electron).

2.2 Crystal Data

Initial crystallographic data were obtained by a search of research literature using the Inorganic Crystal Structure Data file (ICSD), which is part of the Chemical Data Service at Daresbury [29]. These data are presented in Tables 3.6, 3.7, and 3.8.

Effective ionic radii were taken from Shannon [30]. The 12 co-ordinate effective radii

were not available for all ions, thus for these the radii were calculated by fitting a function to the changes in ionic radius as the co-ordination increased from 6 to 8 and then applying this to the increase from 8 to 12. Predictions were then validated against known 12 coordinate radii. The ionic radii used for this work are given in Tables 2.1 and 2.2 and the relationship between 8 and 12 coordinated ionic radii is shown in Figure 2.1 where it can be seen that there is good correlation between the predicted and experimental ionic radii.



Figure 2.1: Comparison of predicted and ionic radii with those of Shannon.

Cation	Effective ionic radius Å
Sc^{3+}	1.0503
In^{3+}	1.1044
Lu^{3+}	1.1509
Yb^{3+}	1.1578
Er^{3+}	1.175
Ho^{3+}	1.1857
Y^{3+}	1.1897
Dy^{3+}	1.198
Tb^{3+}	1.2122
Gd^{3+}	1.227
Eu^{3+}	1.2424
Sm^{3+}	1.24*
Nd^{3+}	1.27*
Pr^{3+}	1.3147
Ce^{3+}	1.34*
La ³⁺	1.36*

 Table 2.1: 12 co-ordinate effective cation radii.

* Ionic Radii from Shannon [30].

Table 2.2: 6 co-ordinate effective cation radii [30].

Cation	Effective ionic radius Å
Al^{3+}	0.535
Cr^{3+}	0.615
Ga^{3+}	0.62
Fe^{3+}	0.645
Sc^{3+}	0.745
In^{3+}	0.8

2.3 The Perfect Lattice

Static lattice calculations are based on the classical Born model [31, 32] of ionic solids in which the lattice is constructed from an arrangement of spherical, charged ions. A pair-potential description of the forces between ions is used [18], in which the interaction energy between the ions is a function of their separation (and hence atomic position). These forces can be resolved into two components (Figure 2.2): (i) long-range Coulombic interactions and (ii) short-range interactions.



Figure 2.2: The long and short range interactions of the total forces (adapted from Harding [33]).

Since there are many atoms interacting with each other within the lattice, the total interaction can be expressed as a series summation, with increasing numbers of ions such that:

$$\Phi = \Phi_0 + \sum_{ij} \Phi_2(r_{ij}) + \sum_{ijk} \Phi_3(r_{ijk}) + \sum_{ijkl} \Phi_4(r_{ijkl}) + \dots$$
(2.1)

In this sum, Φ_0 is a function of the local environment, and is traditionally ignored since it is differences in energies that are usually of importance, i.e. it defines the energy zero. $\Phi_2(r_{ij})$ is the interaction acting over ion pairs, $\Phi_3(r_{ijk})$ is the interaction acting over ion triplets etc. For ionic materials, the pair interactions are usually assumed to be dominant and all higher interactions are considered to be negligible [33]. Consequently we only include the two body $\Phi_2(r_{ij})$ terms and choose to ignore three body $\Phi_3(r_{ijk})$ and higher terms explicitly. This is the *pair potential approximation* [33]. The total energy (E_T) for the interaction between two ions (*i* and *j*) takes the form [34]:

$$E_T = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \phi_{sr} \tag{2.2}$$

where the first term represents the long range Coulombic interaction; q_i , q_j are the charge on ions *i* and *j*; r_{ij} is the ionic separation; and ϵ_0 is the permittivity of free space. The second term, ϕ_{sr} , is the short-range interaction energy (described in Section 2.3.2). All interactions in a lattice can be summed to give the total lattice energy (E_L) :

$$E_L = \sum_{j>i} \sum_i \left(\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + \phi_{sr} \right)$$
(2.3)

2.3.1 The Long Range Interaction: The Ewald Summation

A significant computational problem exists in the summation of the long range Coulombic forces. The issue is that these forces typically fall off as r^{-d} , where d is the system dimensionality [35, 36]. It therefore proves very difficult to sum the forces to determine the true interaction energy of the system. Consequently, a new mathematical approach was needed to facilitate the summation: the first such method was provided by crystallographer Paul Ewald in 1921 [37].

The Ewald summation technique was derived to calculate the electrostatic interaction between one ion and all remaining ions in the crystal lattice. The formal mathematical derivation is rather complex and a detailed explanation is beyond the scope of this thesis. Therefore, the following section describes the important aspects of the summation method; a similar abridged derivation can be found in early editions of Kittel's book, Introduction to Solid State Physics [38], and is attibuted to an unpublished paper by Ewald and Shockley. Later editions of Kittel's book (e.g. [39]) introduce a structure factor into the derivation for the case where the unit cell contains more that one ion. A third good derivation is given by Tosi [40].

In deriving the Ewald sum, an assumption is made that the lattice is constructed of spherical ions with charges of the same magnitude (whether positive or negative) and that they do not overlap. With this in mind, the total potential, ψ , experienced at a specific reference lattice point, \vec{r} , can be partitioned into two distinct, but related components, one in reciprocal space, ψ_1 (Figure 2.3), and one in real space, ψ_2 (Figure 2.4).

$$\psi = \psi_1 + \psi_2 \tag{2.4}$$

The potential ψ_1 is that of a lattice with a Gaussian distribution of charges fixed at each lattice point with the same signs as the ions occupying those lattice points in the real crystal. The potential ψ_2 is that of a lattice of point charges, with the addition of a Gaussian distribution of opposite sign superimposed upon the point charges. The reason for the splitting of the potential into two components, is that by choosing a suitable parameter, η , for the width of the Gaussian peaks, both parts can be made to converge rapidly at the same time. A highly optimal value for this width parameter has been determined by Catlow and Norgett [41] and is given by:

$$\eta = \left(\frac{N\pi^3}{V_c^2}\right)^{\frac{1}{6}} \tag{2.5}$$

where N is the total number of species and V_c is the unit cell volume. When the two component potentials are summed, the overall potential reduces to the original set of point charges, i.e. Gaussian distributions cancel, and the overall potential is independent of parameters, such as the width parameter, used during the convergence of the components ψ_1 and ψ_2 .

The definition of the Madelung constant mandates that the charge distribution on the reference point is not considered to contribute to the potentials ψ_1 or ψ_2 , i.e. ions cannot experience their own electrostatic potential as illustrated in Figure 2.3. It follows that the potential ψ_1 can be described as the difference between two potentials, ψ_a , being the potential of a continuous series of Gaussian distributions and ψ_b , being the potential of the single Gaussian distribution of the reference point.

$$\psi_1 = \psi_a - \psi_b \tag{2.6}$$



Figure 2.3: The development of the potential as a consequence of the definition of the Madelung constant, from a lattice of Gaussian distributions and a Gaussian charge distribution at the reference point.



Figure 2.4: Graphical representation of ψ_2 of the Ewald summation.

In order to calculate the potential of the continuous Gaussian distribution, ψ_a , it and its associated charge density, ρ , are expanded in terms of a Fourier series:

$$\psi_a = \sum_k c_k \exp(i(\vec{k} \cdot \vec{r})) \tag{2.7}$$

$$\rho = \sum_{k} \rho_k \exp(i(\vec{k} \cdot \vec{r})) \tag{2.8}$$

where c_k and ρ_k are coefficients and \vec{k} is 2π times the reciprocal lattice vectors. The series converges with increasing \vec{k} and decreasing c_k and ρ_k . The charge density is related to the electrostatic potential via the Poisson equation [35]:

$$\nabla^2 \psi_a = -4\pi\rho \tag{2.9}$$

so that

$$\rho_k = \frac{c_k k^2}{4\pi} \tag{2.10}$$

The Gaussian charge density for a single ion of charge q_i with half width $\sqrt{\frac{\ln 2}{\eta}}$ is:

$$\rho = q_i \left(\frac{\eta}{\pi}\right)^{\frac{3}{2}} \exp(-\eta \bar{r}^2) \tag{2.11}$$

It is possible to evaluate the charge density, ρ_k , by multiplying both sides of Equations (2.8) and (2.11) by $e^{-i\vec{k}\cdot\vec{r}}$, and integrating (2.8) over the unit cell volume, V_c , and (2.11) over the whole crystal. These two integrations should result in identical charge densities, so that:

$$\int_{V_{\infty}} q_i \left(\frac{\eta}{\pi}\right)^{\frac{3}{2}} \exp(-\eta \vec{r}^2) \exp(-i\vec{k} \cdot \vec{r}) dr = \rho_k \int_{V_c} \exp(i\vec{k} \cdot \vec{r}) \exp(-i\vec{k} \cdot \vec{r}) d\vec{r} = V_c \rho_k$$
(2.12)

Integrating over the unit cell results in a charge distribution that originates from both the lattice point within the cell, and the tails of the distributions from all other lattice points.

It is then possible by considering Equations (2.7) and (2.10) and combining with the above result to derive,

$$\psi_a = \sum_k \frac{4\pi}{k^2 V_c} \int \left(\frac{\eta}{\pi}\right)^{\frac{3}{2}} \exp(i\vec{k}\cdot\vec{r}) \exp(-\eta r^2) \exp(-i\vec{k}\cdot\vec{r}) d\vec{r} \qquad (2.13)$$

which can be integrated to yield

$$\psi_a = \frac{4\pi}{V_c} \sum_k \frac{\exp(i\vec{k} \cdot \vec{r} - \frac{k^2}{4\eta})}{k^2}$$
(2.14)

When $\vec{k} = 0$, the potential ψ_a tends to infinity. However, since it is assumed that the overall charge of a neutral unit cell is zero, this term can be ignored.

The potential at the reference point in the lattice, (i.e. at $\vec{r} = 0$) is ψ_b ; the contribution of this to the field is due to the central Gaussian distribution:

$$\psi_b = \int_0^\infty \frac{1}{\epsilon_0} r^2 \frac{\rho}{\vec{r}} d\vec{r} = \frac{1}{2\epsilon_0} q_i \frac{\eta^{\frac{1}{2}}}{\pi^{\frac{3}{2}}}$$
(2.15)

Therefore, combining Equations (2.14) and (2.15) it is possible to obtain an expression for ψ_1 :

$$\psi_1 = \frac{4\pi}{V_c} \sum_k \frac{\exp(i\vec{k}\cdot\vec{r} - \frac{k^2}{4\eta})}{k^2} - \frac{1}{2\epsilon_0} q_i \frac{\eta^{\frac{1}{2}}}{\pi^{\frac{3}{2}}}$$
(2.16)

The remaining contribution to the net potential, ψ_2 , must now be evaluated at the reference point, this is non zero since it has a contribution due to the tails of the Gaussian distributions from the other lattice points overlapping the reference point. The potential has three contributions from each lattice point: the point charge associated with the ion j, the Gaussian distribution contained within the sphere of radius r_{ij} at the j lattice point and the Gaussian distribution occurring outside the same sphere.

$$\psi_2 = \frac{1}{4\pi\epsilon_0} \sum_j q_j \left[\frac{1}{r_j} - \frac{1}{r_j} \int_0^{r_j} \rho d\vec{r} - \int_{r_j}^\infty \frac{\rho}{\vec{r}} d\vec{r} \right] = \frac{1}{4\pi\epsilon_0} \sum_j \frac{q_j}{r_j} \operatorname{erfc}(\eta^{\frac{1}{2}}r_j) \quad (2.17)$$

Now, with expressions for ψ_1 and ψ_2 determined, it is possible to expand Equation (2.4) by combining Equations (2.16) and (2.17):

$$\psi = \frac{4\pi}{V_c} \sum_k \frac{\exp(i\vec{k}\cdot\vec{r} - \frac{k^2}{4\eta})}{k^2} - \frac{1}{2\epsilon_0} q_i \frac{\eta^{\frac{1}{2}}}{\pi^{\frac{3}{2}}} + \frac{1}{4\pi\epsilon_0} \sum_j \frac{q_j}{r_j} \operatorname{erfc}(\eta^{\frac{1}{2}}r_j)$$
(2.18)

2.3.2 The Short Range Interaction

The short-range interaction energy has both repulsive and attractive components. The repulsive interactions occur due to an increase in nuclear repulsion through electron cloud overlap between the ions as they approach; this only acts over small separations. The attractive force operates over intermediate distances and results from the formation of instantaneous dipoles between the ions (one type of the van der Waals interaction). The magnitude of the attractive force is determined by the charges on the ions. In theory, there should not be a problem in defining a potential since, as an energy surface exists, an algorithm that describes it will constitute the potential. Many different models exit, and are useful for different approaches, for instance the Lennard-Jones potential is very popular for molecular dynamics simulations. Early attempts at determining empirical potentials were overly simplistic such as that determined by Kapustinskii [42, 43] and required no information about the crystal structure in order to yield the lattice energy (see Equation 2.19).

$$\Delta U = -\frac{1.07 \times 10^5 v \mid q_i \mid \mid q_j \mid}{r_{ij}}$$
(2.19)

where U is the system lattice energy, v is the number of ions in the molecule, q_i, q_j are the ionic charges and r_{ij} is the ion separation.

The first attempt to describe a true interionic potential was by Born and Landé [44] who described the functional form:

$$\phi_{sr}(r_{ij}) = \frac{b}{r_{ij}^n} \tag{2.20}$$

where b and n are constants that are chosen to reproduce the equilibrium interionic separation and r_{ij} is the nearest distance between two unlike ions. This form, though very simple, works well for very highly ionic materials such as the alkali halides. To account for the new information from quantum mechanics, Born and Mayer [32] introduced a short range repulsive function of the form:

$$\phi_{sr}(r_{ij}) = A_{ij} \exp(\frac{-r_{ij}}{\rho_{ij}}) \tag{2.21}$$

where A_{ij} and ρ_{ij} are adjustable parameters. An attractive term of the form $C_{6,ij}/r_{ij}^6$, was also then added to Equation 2.20 to account for the van der Waals interaction which had just been determined via work from van der Waals, London and Margenau [45–48]. This combination results in the aforementioned Lennard-Jones potential [49–51]:

$$\phi_{sr}(r_{ij}) = \frac{b}{r_{ij}^n} - \frac{C_{6,ij}}{r_{ij}^6}$$
(2.22)

When the short range repulsive and the attractive van der Waals terms are combined, the Buckingham potential model is formed:

$$\phi_{sr}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{6,ij}}{r_{ij}^6}$$
(2.23)

where the A_{ij} parameter can be approximated as a measure of the number of electrons within the ion; ρ_{ij} can be approximated as a measure of the electron density; and $C_{6,ij}$ is an approximate description of the polarisability of the ion. It is however, important to note that the potential terms are purely numerical in nature, and whilst comparison with physical properties may be possible (and helpful) for some cases, caution should be exercised. The $C_{6,ij}$ term takes the correlation effect into consideration and as such has an intermediate-range effect. The justification for the $C_{6,ij}$ term inclusion in the short-term potential form is that it is small beyond a few lattice spacings and so the contribution to the system energy is minimal. As such, the $C_{6,ij}$ term is subjected to a cut-off of 20 Å. The $C_{6,ij}$ parameter was calculated via the Slater-Kirkwood formula [52]:

$$C_{6,ij} = \frac{\frac{3}{2}\alpha_i\alpha_j}{\left(\frac{\alpha_i}{P_i}\right)^{\frac{1}{2}}\left(\frac{\alpha_j}{P_j}\right)^{\frac{1}{2}}}$$
(2.24)

where α_i , α_j are the static polarisabilities of ions *i* and *j*, and P_i , P_j are the number of electrons that contribute significantly to the polarisability of ions ions *i* and *j*, i.e. the effective electron numbers of ions *i* and *j*. Consequently, $C_{6,ij}$ a function of the ionic radius, and as such depends on the coordination of the ions.

The determination of the $C_{6,ij}$ term requires knowledge of the in-crystal radius and the polarisability, α_D , of the relevant ions and was calculated using Equation 2.25 [53,54]. The polarisabilities and $C_{6,ij}$ are presented in Tables 2.3 and 2.4

$$\alpha_D = \frac{8}{9} a_0 \left(2\ell + 1\right) \left[a_0 < r^2 > \right]^2 \tag{2.25}$$

where ℓ is the orbital angular momentum quantum number of the electron subshell concerned, i.e. the outermost occupied/paritially occupied electron shell, the factor $[a_0 < r^2 >]^2$ is a form of mean square radius of the outer electron orbit (r is the radius in dimensionless atomic units and a_0 is the radius of the first Bohr orbit in hydrogen).

The Buckingham potential model has proved to be successful in simulating many oxide systems [55, 56] and other ionic solids [57, 58]. On this justification, this was the potential model implemented to describe the short-range interactions in this study, however a significant problem with the Buckingham potential is that the energy tends to minus infinity as the ion separation goes to zero (see Figure 2.5)); this region must be inaccessible by making the barrier sufficiently large, this is particularly problematic in molecular dynamics [43].

Ion	Radius	Modified Crystal	Polarisability,	Effective No. of	$C_{6,ij}$
Interaction	(CN8) (Å)	Radius, r (Å) [53, 54]	$\alpha_D (\mathrm{\AA}^3)$	Electrons, P [53, 54]	$(eVÅ^6)$
$0^{20^{2-}}$	1.42	1.20	2.01	5.93	5.20
$Ce^{3+}-O^{2-}$	1.14	1.21	6.15	17.86	15.86
$\mathrm{Dy}^{3+}\mathrm{-}\mathrm{O}^{2-}$	1.03	1.11	4.07	13.99	10.94
$\mathrm{Er}^{3+}\mathrm{-}\mathrm{O}^{2-}$	1.00	1.09	3.81	13.64	10.34
$\mathrm{Eu}^{3+}\mathrm{-}\mathrm{O}^{2-}$	1.07	1.15	4.53	14.64	12.00
$\mathrm{Jd}^{3+}\mathrm{-}\mathrm{O}^{2-}$	1.05	1.14	4.37	14.35	11.62
$H_0^{3+}-O^{2-}$	1.02	1.10	3.97	13.93	10.72
$La^{3+}-O^{2-}$	1.16	1.23	6.07	17.00	15.51
$Lu^{3+}-O^{2-}$	0.98	1.06	3.64	13.74	10.01
$\mathrm{Nd}^{3+}\mathrm{-}\mathrm{O}^{2-}$	1.11	1.18	5.01	15.23	13.07
$P_{T}^{3+}-O^{2-}$	1.13	1.19	5.32	15.97	13.83
$Pu^{3+}-O^{2-}$	I	1.20	4.67	13.80	12.10
$5m^{3+}-O^{2-}$	1.08	1.16	4.74	15.03	12.49
$\Gamma b^{3+}-O^{2-}$	1.04	1.12	4.25	14.33	11.37
${\rm Yb^{3+-}O^{2-}}$	0.99	1.07	3.58	13.34	9.81

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Ion	Radius	Modified Crystal	Polarisability,	Effective No. of	$C_{6,ij}$
raction	(CN8) (Å)	Radius, r (Å) [53, 54]	$\alpha_D ({ m \AA}^3)$	Electrons, P [53, 54]	$(eVÅ^6)$
$^{+}-0^{2-}$	0.54	0.74	0.79	6.22	2.54
$+-0^{2-}$	0.62	0.82	1.45	9.28	4.47
$^{+}-O^{2-}$	0.65	0.85	2.29	13.64	6.96
$^{3+}-O^{2-}$	0.62	0.82	1.50	9.49	4.62
$^{+}-O^{2}-$	0.80	1.00	2.62	11.14	7.40
$^{+}-0^{2-}$	0.75	0.95	2.81	13.38	8.14
$^{+}_{-}O^{2-}$	0.90	1.10	3.81	13.39	10.30



Figure 2.5: The form of the Buckingham Potential for $O^{2-}O^{2-}$ interaction illustrating how the energy tends to minus infinity as the ion separation tends to zero (see Table 2.6 for parameter values).

2.3.3 Electronic Polarisability

It is noteworthy that the Buckingham potential is a pair-potential model, i.e. it operates between two ions at a time (i and j). Other interactions may occur that operate between three or more ions at a time (many-body interactions). A many body term is included, through the shell model since the two-body interactions operate between shells (or shell to the core of those ions that are treated as without a shell). Since the position of the shell (relative to the core) depends on the assumed electro-static interactions from all ions in the crystal, the two-body forces are mediated via a many-body shell position.

The electronic polarisability of species was determined using the Shell Model which was originally developed by Dick and Overhauser [59] while Faux and Lidiard [60] proved its value to defect calculations. The ion is described as having a massless shell (usually for static lattice calculations, for MD a shell can be assigned a mass) around a central massive core. The core and shell are linked by an isotropic, harmonic spring with a force constant, k (Figure 2.6). When an electric field is applied to the ion, the shell is allowed to move relative to the core in such a way that it develops a dipole and thus simulates the dielectric polarisability of the lattice. The core and the shell are assigned positive $(X \cdot e)$ and negative $(Y \cdot e)$ charges respectively such that the sum is equal to the charge on the ion $((X + Y) \cdot e)$. The polarisability, α_e , of an isolated ion is given by:

$$\alpha_e = \frac{1}{4\pi\epsilon_0} \left(\frac{Y^2}{k}\right) = 14.3994 \left(\frac{Y^2}{k}\right) \tag{2.26}$$

where Y is the shell charge in electronic charge units, ϵ_o is the permittivity of free space, α_e and k are in units of Å³, and eVÅ⁻² respectively. For this work, only the



Figure 2.6: A schematic of the shell model.

oxygen ion is treated as polarisable, and the parameters for this are presented in Table 2.8.

2.3.4 Cauchy Violation

One of the assumptions made in this model is that the potential is merely a function of the separation of the ions and not their direction [33]. In other words this is a centrosymmetric model. This is clearly an approximation since it implies that the elastic constants c_{12} and c_{44} are equal (for a cubic crystal); this is known as the Cauchy relationship [61]. Unfortunately this is not found experimentally, and for many materials the difference between the elastic constants is quite considerable.

The centrosymmetric nature of the model is also manifested in the Shell Model since this assumes that only dipolar distortions to spherical symmetry are allowed. Modifications can be made to the shell model in order to model the Cauchy violation. Schroder allowed the shell to distort in a spherical manner, adjusting the radius of the shell to create what is known as the *breathing shell* [62]. The problem with this model is that it is only able to account for cases where $c_{12} < c_{44}$. Sangster developed a further modification to describe the case where $c_{12} > c_{44}$ by allowing the shell to distort in an ellipsoidal manner [63]. However, these models are hard to parameterise due to the limited amount of data available. Fortunately for calculating defect properties and parameters, the centrosymmetric shell model approximation has proven very successful [33].

2.3.5 Potential Parameters: Fitting

There are two types of approach for determining valid interatomic potentials. These are empirical fitting (to match experimental data) and energy surface fitting. In the latter approach, a high quality quantum mechanical technique is used to predict the interaction energy between ions as a function of ion separation. Parameters are then chosen to reproduce this energy surface. Throughout this work only potentials determined empirically were used.

Empirical potential derivation consists of a least squares procedure, whereby the difference between observed (experiment) and calculated properties are minimized, i.e.:

$$F = \sum [f_{observable} - f_{calculated}]^2 \tag{2.27}$$

Almost all properties of the material can be used in the derivation process, including elastic and dielectric constants, lattice energy and phonon data. The prerequisite, however, is a knowledge of the crystal structure, including the ionic positions and lattice parameters. Care must be taken when phonon modes are included in the derivation process since their order can change during the fitting, thus they are commonly used only to used to ensure that the minimum energy structure is stable (i.e. all the phonons are positive). It is often the case with empirical fitting that only the crystal structure is known with any degree of certainty.

Often, more than one set of parameter values can reproduce the physical properties of the material [64]. However, the test of a successful potential model is the transferability of the parameters to systems not included in the initial parameter selection. If the potential set is only able to reproduce the structure for which it was fitted against, then it is of little use.

The transferability and reliability of the potentials can be improved by including as much information about the structure as possible (e.g. high frequency and static dielectric constants, bulk modulus and elastic constants) in the fitting procedure. Unfortunately, a potential may reproduce such perfect lattice properties, and yet when defect calculations are performed, its shortcomings become evident. Experience suggests that such problems are generally avoided if the potential is fitted over a broad range of interionic separations to allow for the consideration of interstitial and vacancy defects which alter the equilibrium separation (see Figure 2.2). A useful method for accomplishing this is to use multi-fitting. Here a cation - anion interaction is determined against a large number of related compositions with varying ion separations. This has the added benefit that any errors in the experimental crystal properties are minimized (see Table 2.5 for examples).

When a range of compositions and interactions are to be studied, it is possible to impose a self-consistency between them. For example, in this work where the rare earth elements were to be modelled, the potential parameters were required to vary in a smooth manner. This is due to the steady decrease in the size of the ions with increasing atomic number accompanied by a corresponding increase in the number of electrons in the 4f orbital (the lanthanide contraction). This smooth order can be imposed onto the potential parameters as a function of the radius of the ion for which they describe. This imposed order can be seen in the smooth transitions in the A_{ij} (Figures 2.7(a)), ρ_{ij} (Figure 2.7(b)) and $C_{6,ij}$ (Figure 2.7(c)) terms.



(c)

Figure 2.7: The smooth change in ion radius due to the lanthanide contraction allows for an imposed order onto the potential parameters (a) A_{ij} , (b) ρ_{ij} and (c) $C_{6,ij}$.

The potential parameters used for this study are presented in Tables 2.6 and 2.7 and were derived via a multi-structure empirical fitting procedure. The A_{ij} and ρ_{ij} terms of the Buckingham potential were altered in such a way that they gave good agreement to the crystallographic properties taken from experimental observations,

Table 2.5: The percentage agreement with experimental unit cell volumes for thecompounds used for the derivation of the cation - anion potentials.

	B Cation							
		Ga	\mathbf{Cr}	Al	Sc	Fe	\mathbf{Pr}	Averages
	La	100.47	100.57	101.00	-	99.76	_	100.45
	\mathbf{Ce}	100.48	98.44	100.73	-	-	-	99.89
	\mathbf{Pr}	100.97	97.95	101.37	-	99.90	-	100.05
I	\mathbf{Nd}	100.11	100.49	101.19	-	99.88	-	100.42
tio	\mathbf{Sm}	-	98.49	101.37	-	100.62	-	100.16
Ca	$\mathbf{E}\mathbf{u}$	-	-	-	100.10	-	-	100.10
A	Gd	99.91	100.65	-	100.33	100.01	-	100.23
	\mathbf{Tb}	-	-	100.22	-	99.95	-	100.09
	$\mathbf{D}\mathbf{y}$	-	100.70	-	-	99.84	-	100.27
	Ho	-	-	100.17	-	100.15	-	100.16
	\mathbf{Er}	-	100.33	-	-	100.06	-	100.19
	Yb	-	-	-	-	100.15	-	100.15
	$\mathbf{L}\mathbf{u}$	-	-	-	-	100.46	99.99	100.22
	Averages	100.39	99.70	100.86	100.21	100.07	99.99	-

in particular, the aim was that the average unit cell volume was fitted to within 1% over the series, both horizontal and vertical, to ensure that the relative Madelung energies of the lattices were correct. It is important that the potentials are able to reproduce experimental data so that when they are used to predict structures for which there is no experimental data, confidence in the model predictions is maintained. Similar fitting methods have been used by Binks *et al.* [34] and Minervini *et al.* [5,26]. The terms in the Shell model were taken from Minervini *et al.* (Table 2.8) [5]. A more detailed explanation of the fitting procedure used and a discussion of the merits of this and other potential fitting methods is given by Gale [43].

2.3.6 Potential Model Variation

The results presented in this thesis were based on Buckingham pair potentials (Equation 2.23). However, in order to improve crystal structure predictions (Figure 3.10) the potential model was altered. Such modifications were however, within the scope of the Buckingham model and involved changes in and extensions to the standard Buckingham model by simple additions to its functional form as follows:

- Changes in the co-ordination dependency of the $C_{6,ij}$ term.
- The addition of a double exponential term for the oxygen-oxygen interaction.
- The addition of a damped coulombic interaction.

Species	A_{ij} (eV)	ρ_{ij} (Å)	$C_{6,ij}$ (eVÅ ⁶)
$O^{2-}-O^{2-}$	9547.96	0.2192	32.0
$Al^{3+}-O^{2-}$	1365.79	0.30096	2.538
$\mathrm{Ce}^{3+}\text{-}\mathrm{O}^{2-}$	2034.18	0.34380	15.86
$\mathrm{Cr}^{3+}\mathrm{-O}^{2-}$	1452.25	0.30918	4.472
$Dy^{3+}-O^{2-}$	1767.64	0.33770	10.94
$\mathrm{Er}^{3+}-\mathrm{O}^{2-}$	1678.21	0.33781	10.81
$\mathrm{Eu}^{3+}\text{-}\mathrm{O}^{2-}$	1886.71	0.33975	11.997
$\mathrm{Fe}^{3+}-\mathrm{O}^{2-}$	1478.98	0.31306	6.960
$Ga^{3+}-O^{2-}$	1456.72	0.30988	4.616
$\mathrm{Gd}^{3+}\text{-}\mathrm{O}^{2-}$	1868.75	0.33880	11.62
$\mathrm{Ho^{3+}\text{-}O^{2-}}$	1726.29	0.33776	10.72
$\mathrm{In^{3+}-O^{2-}}$	1595.65	0.32960	7.402
$La^{3+}-O^{2-}$	2051.32	0.34585	15.51
$Lu^{3+}-O^{2-}$	1561.36	0.33854	10.01
$\mathrm{Nd}^{3+}-\mathrm{O}^{2-}$	1979.11	0.34148	13.07
$Pr^{3+}-O^{2-}$	2025.54	0.34270	13.83
$\mathrm{Sc}^{3+}-\mathrm{O}^{2-}$	1587.95	0.32190	8.143
$\mathrm{Sm}^{3+}-\mathrm{O}^{2-}$	1944.44	0.34080	12.49
$\mathrm{Tb}^{3+}\text{-}\mathrm{O}^{2-}$	1818.00	0.33845	14.33
$Y^{3+}-O^{2-}$	1721.23	0.33821	10.29
$Yb^{3+}-O^{2-}$	1616.68	0.33798	13.34

Table 2.6: Short-range potential parameters used for perovskite materials.

 Table 2.7: Short-range potential parameters used for fluoride materials.

Interaction	$A_{ij} \ (eV)$	ρ_{ij} (Å)	$C_{6,ij}$ (eVÅ ⁶)
F^F^-	1317.50	0.27530	13.8
Li^+-F^-	574.80	0.25530	0.0
$\mathrm{Zn}^{2+}\text{-}\mathrm{F}^{-}$	918.41	0.28481	0.0

Co-ordination Dependency of $C_{6,ij}$

The value of the $C_{6,ij}$ term is determined via calculation by using the Slater-Kirkwood equation (Equation 2.24). This approach requires the use of the in crys-

Table 2.8: Shell Parameter for O^{2-} [5,34]

Species	Y (e)	$k \; (eV Å^{-2})$
O^{2-}	-2.04	6.3

tal ion radius. The $C_{6,ij}$ derived for this work used an effective ionic radius for all cation - anion potentials. This effective ionic radius was taken from Grimes and Grimes [53,54]. However, cations at different lattice sites were subjected to different anion coordinations and consequently exhibited different cationic radii (the A cation being 12 fold oxygen co-ordinated has a larger radius than a B cation which is 6 fold coordinated). The values of Grimes and Grimes [53,54] represent an average (roughly 6 co-ordinate). It was therefore pertinent that the potential should reflect this difference between the A and B cation co-ordination. As such, a co-ordination specific model was determined, whereby the cation radii were chosen to match the coordinate radius is larger than the corresponding 6 co-ordinate radius. This coordination specific radius was then used to determine a modified value for $C_{6,ij}$ and then in turn, the A_{ij} and ρ_{ij} potential parameters were re-derived (the site specific $C_{6,ij}$ potentials are shown in Table 2.9). The effective co-ordinate and co-ordinate specific $C_{6,ij}$ values are shown in Table 2.10.

Double Exponential Oxygen

The next step was to consider altering the $O^{2-}O^{2-}$ Buckingham potential although, of course this interaction affects all others in the system. There have been many different oxygen interactions used, however one that has proved successful is that used by Catlow [2]. In order to incorporate this Catlow oxygen interaction into the

Species	A_{ij} (eV)	ρ_{ij} (Å)	$C_{6,ij} \; (\mathrm{eV} \mathrm{\AA}^6)$
$O^{2-}-O^{2-}$	9547.96	0.2192	32.0
$Al^{3+}-O^{2-}$	1365.79	0.30096	1.499
$\mathrm{Ce}^{3+}\text{-}\mathrm{O}^{2-}$	2034.18	0.34380	18.30
$Cr^{3+}-O^{2-}$	1452.28	0.30918	2.827
$Dy^{3+}-O^{2-}$	1767.64	0.33770	12.24
$\mathrm{Er}^{3+}-\mathrm{O}^{2-}$	1678.21	0.33781	11.59
$\mathrm{Eu}^{3+}\text{-}\mathrm{O}^{2-}$	1886.71	0.33975	13.53
$\mathrm{Fe}^{3+}-\mathrm{O}^{2-}$	1478.98	0.31306	6.127
$\mathrm{Ga}^{3+}\text{-}\mathrm{O}^{2-}$	1456.72	0.30988	2.930
$\mathrm{Gd}^{3+}\text{-}\mathrm{O}^{2-}$	1868.75	0.33880	13.013
$\mathrm{Ho^{3+}\text{-}O^{2-}}$	1726.29	0.33776	12.00
$\mathrm{In}^{3+}\text{-}\mathrm{O}^{2-}$	1595.65	0.32960	5.211
$La^{3+}-O^{2-}$	2051.32	0.34585	17.70
$\mathrm{Lu}^{3+}\text{-}\mathrm{O}^{2-}$	1561.36	0.33854	11.32
$\mathrm{Nd}^{3+}-\mathrm{O}^{2-}$	1979.11	0.34148	14.96
$Pr^{3+}-O^{2-}$	2025.54	0.34270	16.05
$\mathrm{Sc}^{3+}-\mathrm{O}^{2-}$	1587.95	0.32190	5.581
$\mathrm{Sm}^{3+}\text{-}\mathrm{O}^{2-}$	1944.44	0.34080	14.15
$\mathrm{Tb}^{3+}\text{-}\mathrm{O}^{2-}$	1818.00	0.33845	12.76
$Y^{3+}-O^{2-}$	1721.23	0.33821	7.550
$Yb^{3+}-O^{2-}$	1616.68	0.33798	11.55

Table 2.9: Short-range potential parameters used for perovskite materials based on the site dependent $C_{6,ij}$ term.

oxygen interaction already in use for this work, a double exponential oxygen model was introduced. The form of this can be seen in Equation 2.28.

$$V(r_{ij}) = \left(\frac{A_{ij}}{2}\right) \exp\left(\frac{-r_{ij}}{\rho_{ij,1}}\right) + \left(\frac{B_{ij}}{2}\right) \exp\left(\frac{-r_{ij}}{\rho_{ij,2}}\right) - \frac{C_{6,ij}}{r_{ij}^6}$$
(2.28)

Here, the A_{ij} and $C_{6,ij}$ terms are those taken from the Binks oxygen potential [1],

T	Effective	Site Specific
Interaction	Co-ordination	Co-ordination
$O^{2-}-O^{2-}$	32.0	32.0
$Al^{3+}-O^{2-}$	2.538	1.499
$Ce^{3+}-O^{2-}$	15.86	18.300
$Cr^{3+}-O^{2-}$	4.472	2.827
$Dy^{3+}-O^{2-}$	10.94	12.240
${\rm Er}^{3+}{\rm -O}^{2-}$	10.81	11.590
$\mathrm{Eu}^{3+}\text{-}\mathrm{O}^{2-}$	11.997	13.530
$\mathrm{Fe}^{3+}-\mathrm{O}^{2-}$	6.960	6.127
$\mathrm{Ga}^{3+}\text{-}\mathrm{O}^{2-}$	4.616	2.930
$\mathrm{Gd}^{3+}\text{-}\mathrm{O}^{2-}$	11.62	13.013
$\mathrm{Ho}^{3+}\text{-}\mathrm{O}^{2-}$	10.72	12.000
$\mathrm{In}^{3+}\text{-}\mathrm{O}^{2-}$	7.406	5.211
$La^{3+}-O^{2-}$	15.51	17.700
$Lu^{3+}-O^{2-}$	10.01	11.320
$\mathrm{Nd}^{3+}\text{-}\mathrm{O}^{2-}$	13.07	14.96
$Pr^{3+}-O^{2-}$	13.83	16.05
$\mathrm{Sc}^{3+}-\mathrm{O}^{2-}$	8.143	5.581
$\mathrm{Sm}^{3+}\text{-}\mathrm{O}^{2-}$	12.49	14.15
$\mathrm{Tb}^{3+}\text{-}\mathrm{O}^{2-}$	14.33	12.76
$Y^{3+}-O^{2-}$	10.29	7.550
Yb ³⁺ -O ²⁻	13.34	11.55

Table 2.10: Comparison between the effective radius and co-ordinate specific radius $C_{6,ij}$ value (eVÅ⁶).

while the B_{ij} is the A_{ij} term from the Catlow potential [2]. The two potentials are shown in Table 2.11 and the forms are shown in Figure 2.8(a).

Potential	A_{ij} (eV)	ρ_{ij} (Å)	$C_{6,ij} \; (eV Å^6)$
Binks	9547.96	0.2192	32.0
Catlow	22764.3	0.1490	27.8

Table 2.11: Comparison between the Binks [1] and Catlow $O^{2-}-O^{2-}$ potentials.

 Table 2.12: Short-range potential parameters used for perovskite materials based

 on the double exponential oxygen term.

Species	A_{ij} (eV)	ρ_{ij} (Å)	$C_{6,ij} (eV Å^6)$
$O^{2-}-O^{2-}$	4773.98	0.21910	32.00
$O^{2-}-O^{2-}$	11382.15	0.14900	0.0
$Al^{3+}-O^{2-}$	1412.20	0.30096	2.538
$\mathrm{Ce}^{3+}-\mathrm{O}^{2-}$	2032.94	0.34380	15.86
$\mathrm{Cr}^{3+}\mathrm{-O}^{2-}$	1500.68	0.30918	4.472
$Dy^{3+}-O^{2-}$	1778.50	0.33770	10.94
$\mathrm{Er}^{3+}-\mathrm{O}^{2-}$	1700.81	0.33705	10.34
$\mathrm{Eu}^{3+}\text{-}\mathrm{O}^{2-}$	1888.10	0.33974	11.997
$\mathrm{Fe}^{3+}-\mathrm{O}^{2-}$	1510.00	0.31306	6.960
$\mathrm{Ga}^{3+}\text{-}\mathrm{O}^{2-}$	1488.22	0.30988	4.616
$\mathrm{Gd}^{3+}\text{-}\mathrm{O}^{2-}$	1854.73	0.33880	11.62
$\mathrm{Ho^{3+}\text{-}O^{2-}}$	1735.99	0.33776	10.72
$In^{3+}-O^{2-}$	1600.35	0.32960	7.402
$La^{3+}-O^{2-}$	2040.50	0.34572	15.51
$Lu^{3+}-O^{2-}$	1625.65	0.33680	10.01
$\mathrm{Nd}^{3+}-\mathrm{O}^{2-}$	1985.63	0.34095	13.07
$Pr^{3+}-O^{2-}$	2015.13	0.34258	13.83
$\mathrm{Sc}^{3+}\mathrm{-O}^{2-}$	1610.47	0.32190	8.143
$\mathrm{Sm}^{3+}-\mathrm{O}^{2-}$	1925.16	0.34080	12.49
$\mathrm{Tb^{3+}\text{-}O^{2-}}$	1815.81	0.33900	14.33
$Y^{3+}-O^{2-}$	1708.82	0.33821	10.29
$Yb^{3+}-O^{2-}$	1658.86	0.33695	13.34



(b)

Figure 2.8: (a) Comparison between the $O^{2-}-O^{2-}$ potentials from Binks [1], Catlow [2] and the double exponential model; (b) modification of the $Al^{3+}-O^{2-}$ interaction energy.

Damped Coulombic Potential

This potential model aims to better account for the large amount of electronic overlap between the cations and the oxygen ions at the short interatomic separations that occur at lower coordination states (e.g. 5 and 7 coordination with respect to the 6 and 12 coordination for the classical perovskites see Chapter 3) Physically, this reduces the coulomb interaction between formal charged ions at short separations. The coordination states should thus be biased toward Pnma from P6₃cm. For this purpose, a potential model was developed by Grimes and Redfern and termed a "damped Coulombic Potential" [65]. In essence, this model is equivalent to the standard partial charge model at short separations however at larger distances, the effect of the dampening is negligible and ions interact as formal charged species. For this model, the scale of the electrostatic interaction between ions decreases exponentially with decreasing ionic separation. The general form of the potential is:

$$V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \left(1 - \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right)\right)$$
(2.29)

Since this new potential form is not one of the standard "classical" potential forms included for use with GULP, the damped coulombic model has to be modified such that it fits the GULP general potential model:

$$V(r_{ij}) = D_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) r_{ij}^{-m} - Cr_{ij}^{-n}$$

$$(2.30)$$

It is clear how this is achieved if Equation 2.29 is expanded as;

$$V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} - \left(\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}\right) exp\left(\frac{-r_{ij}}{\rho_{ij}}\right)$$
(2.31)

The initial coulombic interaction term is then the standard coulombic interaction and is treated as usual within the code. The remaining "damped coulombic" term is rearranged such that it fits a general potential model (Equation 2.30):

$$V(r_{ij}) = \frac{D_{ij}}{r_{ij}} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right)$$
(2.32)

The damped coulombic term of the potential can now be compared to this new general potential form in order to elucidate the constant terms:

$$-\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) = \frac{D_{ij}}{r_{ij}} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right)$$
(2.33)

In Equation 2.30, the C value is set to zero, the exponent m is set to 1, and the D_{ij} term is:

$$D_{ij} = -\frac{q_i q_j}{4\pi\epsilon_0} \tag{2.34}$$

thus, the only variable input into the general potential equation is the ρ_{ij} which here is fixed so that the damped coulombic contribution to the total energy is only 1% at the sum of the six coordinate ionic radii $(R_i + R_j)$, i.e.:

$$\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) = 0.01|_{r_{ij}=(R_i+R_j)}$$

$$(2.35)$$

Tables 2.13 and 2.14 show a limited set of parameters that were used for the general potential. Figure 2.9 shows a comparison of the effective co-ordination potential and the damped coulombic potential for the $La^{3+}-O^{2-}$ interaction. It is clear that the energy minima is translated to higher separations, thus biasing the high co-ordinations. The motivation for the derivation of this model was an attempt to predict the dissociation of the perovskite into two distinct garnet phases.

Table 2.13: Damped coulombic model parameters for input into the general poten-tial for GULP.

Inte	rac	tion	D_{ij}	$ ho_{ij}$
Al^{3+} core	-	$O^{0.04+}$ core	-0.10785	0.42018
Al^{3+} core	-	$O^{2.04-}$ shell	5.50038	0.42018
Al^{3+} core	-	Al^{3+} core	-8.08880	0.34027
Al^{3+} core	-	La^{3+} core	-8.08880	0.34027
La^{3+} core	-	$O^{0.04+}$ core	-0.10785	0.52810
La^{3+} core	-	$O^{2.04-}$ shell	5.50038	0.52810
La^{3+} core	-	La^{3+} core	-8.08880	0.34027
$O^{0.04+}$ core	-	$O^{0.04+}$ core	-0.00144	0.60801
$O^{0.04+}$ core	-	$O^{2.04-}$ shell	0.07334	0.60801
$O^{2.04-}$ shell	-	$O^{0.04+}$ core	0.07334	0.60801
$O^{2.04-}$ shell	-	$O^{2.04-}$ shell	-3.74026	0.60801

 Table 2.14: Short-range potential parameters used for perovskite materials based

 on the damped coulombic model.

Species	A_{ij} (eV)	ρ_{ij} (Å)	$C_{6,ij} \; (eV Å^6)$
$O^{2-}-O^{2-}$	9547.96	0.21910	32.00
$Al^{3+}-O^{2-}$	1359.79	0.30096	2.538
$\mathrm{La}^{3+}\text{-}\mathrm{O}^{2-}$	2044.32	0.34572	15.51



Figure 2.9: Comparison of the effective co-ordination and damped coulombic potentials for the $La^{3+}-O^{2-}$ interaction.

Cation Shell Model

In addition to predicting the crystal structure of the wide range of perovskite compositions, a potential model should also be able to predict dielectric properties. An important contribution to the dielectric constant of a material is from the electronic behaviour. This is modelled using the shell model. In order to improve predictions of the dielectric constant, the shell model was investigated and shells were added to the cations (leaving the oxygen shell unaltered). The addition of these cation shells was designed to increase the contributions to the dielectric constant.

The rationale behind the decision to define the shell charge as negative (with a positive core) lies with the make-up of the atom. This consists of a positive nucleus surrounded by a negative cloud of electrons, therefore it was logical to translate this to the shell model. The value assigned to the shell charge was determined from the the ratio of the effective electron number taken from Grimes and Grimes [53, 54]

to the shell charge on the oxygen ion. Therefore the shell charges are consistent throughout. These modified effective electron numbers (shell charges) are shown in Tables 2.3 and 2.4. The shell spring constant was also determined in a consistent manner, and is related to the ionic polarisability taken again from Grimes and Grimes [53, 54]. The shell parameters for these potentials are shown in Table 2.15, with the Buckingham potentials corresponding to those shown in Table 2.16.

Species	Y (e)	$k \; (eV Å^{-2})$
Al^{3+}	-0.193	275.1
Ce^{3+}	-0.56	292.42
Cr^{3+}	-0.293	333.73
Dy^{3+}	-0.44	270.2
Er^{3+}	-0.427	274.4
Eu^{3+}	-0.46	265.82
Fe^{3+}	-0.427	456.4
Ga^{3+}	-0.3	337.23
Gd^{3+}	-0.453	264.77
Ho^{3+}	-0.44	274.57
In^{3+}	-0.353	266.17
La^{3+}	-0.53	267.4
Lu^{3+}	-0.43	291.37
Nd^{3+}	-0.48	260.05
Pr^{3+}	-0.5	269.32
Sc^{3+}	-0.42	357.87
Sm^{3+}	-0.473	267.75
Tb^{3+}	-0.453	271.42
Y^{3+}	-0.453	264.42
Yb^{3+}	-0.453	279.3

 Table 2.15: Cation shell parameters.

Species	A_{ij} (eV)	ρ_{ij} (Å)	$C_{6,ij} \; (eV Å^6)$
$O^{2-}-O^{2-}$	9547.96	0.2192	32.0
$Al^{3+}-O^{2-}$	1765.52	0.2873	2.538
$\mathrm{Ce}^{3+}-\mathrm{O}^{2-}$	1080.51	0.3815	15.86
$\mathrm{Cr}^{3+}\mathrm{-O}^{2-}$	1292.28	0.31646	4.472
$Dy^{3+}-O^{2-}$	840.00	0.3866	10.94
$\mathrm{Er}^{3+}-\mathrm{O}^{2-}$	790.926	0.388	10.34
$\mathrm{Eu}^{3+}\text{-}\mathrm{O}^{2-}$	925.00	0.386	11.997
$\mathrm{Fe}^{3+}-\mathrm{O}^{2-}$	1505.98	0.312	6.960
$\mathrm{Ga}^{3+}\text{-}\mathrm{O}^{2-}$	1335.72	0.315	4.616
$\mathrm{Gd}^{3+}\text{-}\mathrm{O}^{2-}$	900.25	0.385	11.62
$\mathrm{Ho^{3+}\text{-}O^{2-}}$	820.77	0.387	10.72
$In^{3+}-O^{2-}$	775.81	0.37954	7.402
$La^{3+}-O^{2-}$	1115.79	0.38147	15.51
$\mathrm{Lu}^{3+}\text{-}\mathrm{O}^{2-}$	710.81	0.3932	10.01
$\mathrm{Nd}^{3+}\text{-}\mathrm{O}^{2-}$	1002.47	0.3819	13.07
$Pr^{3+}-O^{2-}$	1050.00	0.3813	13.83
$\mathrm{Sc}^{3+}-\mathrm{O}^{2-}$	754.43	0.37183	8.143
$\mathrm{Sm}^{3+}\text{-}\mathrm{O}^{2-}$	950.664	0.3848	12.49
$\mathrm{Tb^{3+}\text{-}O^{2-}}$	870.00	0.3868	14.33
$Y^{3+}-O^{2-}$	825.00	0.3862	10.29
$Yb^{3+}-O^{2-}$	750.008	0.391	13.34

 Table 2.16: Short-range potential parameters used for perovskite materials with cation shells.

2.4 The Defective Lattice

In order to efficiently simulate the lattice relaxation around defects, a multi region approach is adopted which stems from the work of Mott and Littleton [33,66]. The lattice is partitioned into concentric spherical regions centred on the defect (Figure 2.10). The area surrounding the defect is termed Region I, here lattice relaxation is



Figure 2.10: Representation of the Multi Region Approach

large, so all interactions are calculated explicitly, while all ions are relaxed to zero force using a Newton-Raphson minimization procedure [18]. Beyond Region I, the lattice relaxation is smaller and as such a more approximate approach can be used. This region is termed Region II, here the interaction is treated as arising from the net charge effect of the defect.

The size of Region I was chosen such that a further increase yields no appreciable change (less than 0.1 eV for an increase in region size of 1 Å) in the defect energy, whilst being small enough for computational efficiency (see Figure 2.11).

Within the two-region approach the defect formation energy, E_d , can be expressed as [25, 67]:



Figure 2.11: Defect energy variations with changing region size for an antisite defect, A_B^X .

$$E_d = E_I(\bar{r}) + E_{I-II}(\bar{r}, \bar{\zeta}) + E_{II}(\bar{\zeta})$$
(2.36)

where E_I is the energy due to the interactions of ions in region I while \bar{r} is their displacement vector; E_{II} is the energy of region II for which the displacement vector is $\bar{\zeta}$; and E_{I-II} is the energy of the interaction between regions I and II. Since region II extends to infinity, E_{II} is the summation of an infinite number of displacements and as such cannot be solved exactly. If, however, it is assumed that all displacements within region II are small, then the quasi-harmonic approximation is valid, such that:

$$E_{II} = \frac{1}{2}\overline{\zeta}.A.\overline{\zeta} \tag{2.37}$$

where A is the force constant matrix. Substituting Equation 2.37 into Equation 2.36, and differentiating with respect to $\overline{\zeta}$, the equilibrium displacements in region II are given by:

$$\frac{\delta E}{\delta \overline{\zeta}} = \frac{\delta E_{I-II}(\overline{r}, \overline{\zeta})}{\delta \overline{\zeta}}|_{\overline{\zeta} = \overline{\zeta_e}} + A \overline{\zeta_e}$$
(2.38)

where $\overline{\zeta_e}$ is the equilibrium value of $\overline{\zeta}$ corresponding to \overline{r} . When this is substituted into Equation 2.37 and then into Equation 2.36, the explicit dependence of E_d on energy of region II, E_{II} , is removed allowing a far more convenient solution:

$$E_d = E_1(\overline{r}) + E_{I-II}(\overline{r}, \overline{\zeta}) - \frac{1}{2} \frac{\delta E_{I-II}(\overline{r}, \overline{\zeta})}{\delta \overline{\zeta}} \Big|_{\overline{\zeta} = \overline{\zeta_e}} \cdot \overline{\zeta_e} \cdot \overline{\zeta_e}.$$
(2.39)

Original versions of this method only partitioned the lattice into two regions. However, in order to ensure a smooth transition between Region I and Region II, Region II is split into areas called Region IIa and Region IIb. In Region IIa, which acts as a transition region between Region I and Region IIb, the Mott-Littleton approximation [33, 66] is used to calculate the polarisation, P, at a distance, r, from the defect of charge, q:

$$P(r) = \frac{q\overline{r}}{4\pi r^3} \left(1 - \frac{1}{\epsilon_0}\right) \tag{2.40}$$

where ϵ_0 is the static dielectric constant of the crystal (note: the above uses atomic units). Within Region IIa the displacements of the ions are calculated via direct summation, using the Mott-Littleton approximation due to all defect components within Region I.

2.5 Energy Minimization

Once a model has been adequately validated, in order to be made useful in a predictive manner, it must be combined with energy minimization. This reduces the system to a state of mechanical equilibrium. The criterion used for determining the accuracy of the model is that the ion displacements in the optimised structure from the experimental configuration are minimal. During energy minimization, all ionic interactions are calculated and each ion moves a distance proportional to the force acting on it through an iterative process.

Two conditions exist to minimize the lattice energy at equilibrium: constant volume and constant pressure (it is also possible to equilibrate under constant stress conditions but this is not discussed further.). Under constant volume minimization, the lattice energy is minimized only by varying the internal coordinates of the ions within the unit cell relative to the strains on individual ions, whilst the lattice parameters are not allowed to change. Under constant pressure minimization, the unit cell dimensions are also adjusted, accounting for the strains on both the individual ions and the unit cell. Since there are fewer degrees of freedom for the constant volume calculations, they are computationally faster. Consequently, most early calculations were constant volume. Due to the increase in computation power available, nearly all modern calculations are of the constant pressure type, including all those included in this thesis.

If the lattice energy (U_L) of a system with N ions with coordinates, r, is $U_L(r)$, then after one minimization step, the lattice energy at a new set of coordinates, r' is:

$$U_L(r') = U_L(r) + \vec{g} \cdot \vec{\delta} + \frac{1}{2} \vec{\delta} \cdot \mathbf{W} \cdot \vec{\delta}$$
(2.41)

where **W** is a matrix that contains the corresponding second derivatives (Equation 2.45); $\vec{\delta}$ is a generalised strain vector with 3N displacement components; $\vec{\delta r}$, and 6 independent bulk strain components; $\vec{\delta \varepsilon}$ of the symmetric strain matrix **E**, which is the Voigt matrix representation of the vector $\vec{\delta \varepsilon}$:

$$\mathbf{E} = \begin{pmatrix} \delta \varepsilon_1 & \frac{1}{2} \delta \varepsilon_6 & \frac{1}{2} \delta \varepsilon_5 \\ \frac{1}{2} \delta \varepsilon_6 & \delta \varepsilon_2 & \frac{1}{2} \delta \varepsilon_4 \\ \frac{1}{2} \delta \varepsilon_5 & \frac{1}{2} \delta \varepsilon_4 & \delta \varepsilon_3 \end{pmatrix}$$
(2.42)

therefore the set of new coordinates, r' is related to the original set, r, by:

$$r' = \mathbf{E} \cdot (r + \delta r) \tag{2.43}$$

The vector \vec{g} , refers to the first derivative of the lattice energy with respect to the ion displacements and strain components;

$$\vec{g} = \left(\frac{\partial U_L}{\partial r}, \frac{\partial U_L}{\partial \delta \varepsilon}\right) \tag{2.44}$$

while the matrix **W** contains the corresponding second derivatives;

$$\mathbf{W} = \begin{pmatrix} \frac{\partial^2 U_L}{\partial r \cdot r} & \frac{\partial^2 U_L}{\partial r \cdot E} \\ \frac{\partial^2 U_L}{\partial E \cdot r} & \frac{\partial^2 U_L}{\partial E \cdot E} \end{pmatrix} = \begin{pmatrix} W_{rr} & W_{rE} \\ W_{Er} & W_{EE} \end{pmatrix}$$
(2.45)

The system is then relaxed iteratively, adjusting the coordinates of the ions until the forces on the ions are zero. Since the first derivative of the lattice energy with respect to distance (coordinates) is the force, it is possible to write this convergence aim as:

$$\frac{\partial U_L}{\partial r} = F = 0 \tag{2.46}$$

in practice, the minimization proceeds for a pre-set number of iterations or until a point where at subsequent steps, the total energy of the system changes by less than a predetermined value.

2.6 Ion Migration Activation Energies

The bulk transport properties of intrinsic defects can be calculated very simply by performing numbers of static lattice defect calculations at different points throughout the lattice. This method is only applicable when the migration process is controlled via a thermally activated hopping mechanism. When this is the case, then the energy difference between a migrating ion at a saddle point (local energy maximum, see Figure 2.12) and an isolated ion represents the energy barrier for migration of that ion. The location of this saddle point is determined by compiling contour plots of defect energies between the start and end points of the migration. It is then assumed that the defect will follow a lowest energy pathway, and hence the migration path and saddle point energy can be determined. The saddle point is confirmed by carrying out energy calculations perpendicular to the migration pathway.



Figure 2.12: Example ion migration plot.



Figure 2.13: Schematic of ion migration calculations in ZnF_2 .

In order to calculate this energy contour, the migrating defect is rastered across a plane parallel to the direction of migration and to ensure that a valid minimum is located, planes either side of this are also calculated, and one perpendicular. An example of this approach, whereby an interstitial defect is migrating in the (100) of a ZnF₂ lattice, is shown in Figure 2.13, and the associated contour plot is shown in Figure 2.14 (the results are discussed in Chapter 6).



Figure 2.14: Migration energy contour plot for ion migration in ZnF₂

Other more automated techniques such as nudged elastic band methods [68, 69] maybe used in the future. However they are far more computationally expensive.

2.7 Quantum Mechanical Calculations

2.7.1 General Considerations

Quantum mechanics provides a reliable method to calculate the total energy of an ensemble of electrons and atomic nuclei in a perfect or defective lattice. One of the postulates of quantum mechanics is that the state of a system can be fully described by a mathematical function $\Psi(r_1, r_2, ..., t)$ where r_1, r_2 are the spacial coordinates of particles 1, 2 etc. that constitute the system and t is the time. This is known as the wavefunction of the system and can be evaluated by solving a wave equation, known as the Schrödinger equation [70]. All the properties of the system can be evaluated from the wavefunction. Such analysis can involve calculations based on fundamental quantum mechanical relationships so that the Schrödinger's equation is solved without the use of prior chosen parameters to describe the electrons in that material. However, even in this case the equations are usually subject to approximations such as the Born-Oppenheimer [71]. In that case, the positions of the nuclei can be considered static and only the electrons are considered subject to the static field of the nuclei (this is based on the assumption that the electron velocity is so much higher than that of the nuclei that the position of the latter is effectively fixed). The problem with such *ab initio* approaches is that exact solutions are immensely computationally demanding for a system involving anything other than a single electron in a simple potential. This is due to the complex interactions between electrons.

In general, the problem is handled by approximating electron interactions so that each electron is assumed to be in an effective potential generated by all the other electrons and the nuclei. The specific interactions are thus managed in an average manner within this potential so that one electron is dealt with at a time, i.e. the interactions are decoupled and the wave function is now:

$$\Psi(\vec{r_1}, \vec{r_2}, \vec{r_3}, ..., \vec{r_n}) = \Psi(\vec{r_1})\Psi(\vec{r_2})\Psi(\vec{r_3})...\Psi(\vec{r_n})$$
(2.47)

where Ψ_n are the *n* one-electron wavefunctions. This reduces the problem to solving a series of coupled one-electron Schrödinger equations of the form:

$$H\Psi_n = \left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ext} + V_{eff}\right)\Psi_n = \epsilon_i\Psi_n \tag{2.48}$$

where V_{ext} is the external potential, either due to the nuclei and/or other applied field and V_{eff} is the effective potential. In general, calculations of this type involve writing part of the electron-electron interaction in terms of a mean-field. The difference between this average approach and one in which electron motions are able to take explicit account of each other is called the correlation (i.e. where the electron paths are correlated).

There are two possible descriptions of the wavefunction, local orbital and planewave. In the local orbital approach, the wavefunctions are located at single atomic nuclei and was originally developed for molecules. This approach was not used in these studies.

The plane-wave approach describes an infinite periodic system, in other words a perfect solid. The plane-wave approach has the benefits that all space is treated the same, it is mathematically simple, and does not depend upon the atomic positions. However disadvantages also exist, such that empty space is treated to the same level as an area of importance for property determination such as electron overlap. The quality of the calculation depends on a single energy cut-off parameter. This parameter is expressed as the energy of a free electron whose wavefunction has the same wavevector as the smallest plane wavevector. All plane waves of energy less than this cut-off energy are used in the calculation [72].

Problems occur with both approaches when defects are involved, i.e. when there is a local defect placed within an infinite solid. For such calculations neither approach is perfect but here calculations of the plane-wave variety were chosen for this work.

2.7.2 The Hartree-Fock approach

An early approach for the development of a computational method was developed by Hartree [73, 74] who set V_{eff} to the average of the Coulomb potential between an electron and all other electrons in the system. The Hartree method neglects exchange and correlation, and therefore yields somewhat poor results. Exchange is a result of the indistinguishability of electrons and results from the fact that the wavefunction describing the pair must be anti-symmetric [75] (a requirement of the Pauli exclusion Principle [76]). When Fermi statistics are added to this approach, the Hartree-Fock (HF) method is formed. This now calculates the exchange energy exactly, however, it still neglects the correlation energy. This technique has enabled many advances, and is often the platform from which more accurate calculations are built.

2.7.3 Density Functional Theory

A subtly different approach to HF is that of density functional theory (DFT). The popularity of DFT is due to the fact that it is less computationally demanding than HF calculations and that predictions for systems involving d-block metals agree more closely to experiment than those for HF [77]. This technique was initially developed by Hohenberg, Kohn and Sham [78–80], and resulted in a Nobel prize for chemistry in 1998 for Walter Kohn and John Pople [72]. DFT is based on two simple principles [72, 78]. First, the total energy of a system of electrons and nuclei is a unique functional of the electron probability density, i.e. the density uniquely determines the potential acting on the electrons. The second principle, is that the variational minimum of the energy is exactly equivalent to the true ground state. The variation principle seeks the parameter values that minimize the energy, with the resulting wavefunction being the optimum wavefunction of the selected form [81]. The concept of the density functional for the energy is the basis of early approximate models such as the Fermi-Thomas method [82, 83] and the Hartree-Fock-Slater method [84]. It was not until 1964 that a formal proof was derived to show that the ground state electronic properties can be uniquely determined by the electron density [78]. However, these do not suggest the form that any functional should take, only that one exists.

The benefit of DFT is that no attempt is made to calculate the many-body wavefunction. The energy is instead simply written in terms of the electron density. This, in effect, removes with the huge complexity of a multidimensional wavefunction. Although the simplification is immense, the theory remains general. The energy is then written:

$$E = E[\rho(r)] = \int dr V_{ext}(r)\rho(r) + F[\rho(r)]$$
 (2.49)

where $\rho(r)$ is the charge density function and F is a universal functional of the charge density and a function of the electron kinetic energy, Hartree Coulomb term, and the exchange-correlation functional. The method works so long as the energy of Equation 2.49 is a minimum for the correct density function.

The problem remains that a value for the exchange-correlation energy (E_{xc}) is unknown. The benefit of DFT is that very simple approximate functionals work. A widely used approximation is the local-density approximation (LDA). LDA states that E_{xc} can be calculated by assuming that for each infinitesimally small element, the E_{xc} is that of a uniform electron gas. This is clearly inadequate since the charge density is highly non-uniform about an atom. However, LDA is a very effective method for calculating E_{xc} and hence, LDA methods yield good results and works for many cases [85,86]. Instances where this approximation are poor are generally due to spatial variations in the charge density. As such, the generalized-gradient approximation (GGA) is used which includes the gradient dependence of the density [85].

It is important to note that despite the successes of DFT through LDA and GGA, these are still far from ideal and rely on not only an assumption but also parameters for the functionals. The functionals for E_{xc} are the major approximation and are postulated from physically reasonable assumptions, and their use is justified *a posteriori* by their success.

2.8 Simulation Codes

Two simulation codes were employed to conduct static lattice calculations, CAS-CADE (Cray Automatic System for the Calculation of Defect Energies) [87] and GULP (General Utility Lattice Program) [88, 89]. CASCADE was originally developed at the Daresbury Laboratory for the CRAY-1 computer and was based on the original HADES (Harwell Automatic Defect Examination System) code [90,91]. GULP was written as an improved code and incorporates automatic empirical potential fitting routines and calculation of phonon spectra. GULP was used for simultaneous multi-structure fitting of potential parameters.

The CASTEP code [72] was used for all quantum mechanical calculations, and is a part of the Accelrys Materials Studio Package.

2.9 Contour Plots

Due to the nature of many of the results presented in this thesis, contour plot representations of the data have been employed as they facilitate easy identification of regions of compositional interest. An example contour plot is given in Figure 2.15. The plots are generated by ordering the A and B cation radii along x and y axes, respectively. Compounds for which a property has been calculated therefore form a grid of points. The materials property of interest (the independent variable) is displayed by the contours of varying colour. Warm colours represent high values, whilst cool colours represent low values. The compositions for which calculations have been performed are shown by different points overlaid on the plot. The contour lines themselves connect equal property values. In order to facilitate comparisons between different crystal structures, all results are plotted against the VI coordinate ionic radii taken from Shannon [30] so that a full set of consistent ionic radii are available. The ionic radii are simply used as an order parameter.

Data values that fall between simulation results were interpolated via the Kriging method. The Kriging method is a modified weighted average interpolation approach. The weights are calculated by solving sets of linear equations based on the variance of the data being interpolated [92,93]. The benefit of the Kriging method over that of other interpolation schemes, is that the original dataset remains unchanged after the interpolation has been performed. The Kriging method has its roots in geology and the analysis of maps.

The data interpolation and the generation of the resulting contours were performed using MicroCal Origin Pro 6.1 [94].



Figure 2.15: Example contour map used to display results presented in this thesis.