COMPUTATIONAL STUDIES
of PEROVSKITE-STRUCTURED
ION CONDUCTORS

by

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This thesis describes the application of advanced computational techniques to the detailed study of the defect chemistry and ion transport properties of mixed metal oxides. In particular, we investigate the perovskite-type oxides based on the general formula LaBO₃, (where B = Cr, Mn, Fe, Co) which have important applications in solid oxide fuel cells, and as effective heterogeneous catalysts. For the four compounds considered, a common set of interatomic potentials was derived that correctly reproduces their observed cubic structures. The simulations consider intrinsic disorder and find minimal deviation from ideal stoichiometry. We examine the energies of solution for a range of alkaline-earth and alkali metal dopants on the cation sites, and also investigate dopant-vacancy clusters. Both static lattice and molecular dynamics methods are used to study oxygen ion diffusion. The results support models in which diffusion is mediated by oxygen vacancies, with the calculated diffusion coefficients and migration energies in good agreement with available experimental values. We also explore protons in these perovskite oxides and find that the dissolution of water is an exothermic process. The mechanism and energetics of proton migration are investigated by \textit{ab initio} quantum mechanical calculations. Finally, lattice simulations are performed on another important family of metal oxides, bismuth molybdates, which find use as selective oxidation catalysts. We successfully reproduce the complex structure of Bi₂Mo₂O₉ and investigate key redox processes, oxygen migration mechanisms and surface structures. The reduction reaction involving loss of oxygen is predicted to be the most favourable process, which is consistent with the observed catalytic behaviour.
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Chapter 1

INTRODUCTION
Perovskite-structured oxides of the general formula LaBO₃, where B is a transition metal ion, comprise a rich family of compounds which have attracted much fundamental and technological interest. These materials find use in various solid state electrochemical processes such as fuel cells, electrolysis, gas sensors and gas separation membranes [1-6]. LaBO₃ perovskite oxides have also received considerable attention as efficient heterogeneous catalysts, for example, in the oxidation of CO and reduction of NOₓ for use in auto-exhaust treatment [7-11]. Other catalytic reactions include the oxidative coupling of methane to C₂ hydrocarbons, a process of much importance in utilising the abundant resources of natural gas [12-15]. In general, the basic ABO₃ perovskite structure (illustrated in figure 1.1) forms the ‘building block’ for many compounds, including the high temperature cuprate superconductors [16-19]. It has been noted that the wide range of perovskite-type metal oxides and of properties, appears to be as “variable as the colours of a chameleon” [16].

The fact that this class of materials can have properties tailored to meet the often stringent requirements of the applications outlined above, provides just one of the many reasons for the ever increasing interest in perovskite oxides. The need to develop environmentally-friendly methods of power generation has largely influenced the rapid growth in novel and exciting technologies. In particular, fuel cell technology has benefited immensely from the need to make more efficient use of existing fuel sources and also reduce the amount of harmful pollutants.
Fuel cells convert up to 80% of the fuel directly into usable energy with virtually none of the noxious emissions such as CO$_2$, NO$_x$, SO$_x$ and particulates, produced by conventional power generators [2,20]. There are several types of fuel cell, characterised by their electrolyte material, all of which are based on the same principles first discovered by Sir William Grove in 1839 [21]. A cell consists of an electrolyte sandwiched between porous electrodes; a schematic of which is presented in figure 1.2. The fuel, usually hydrogen, is fed to the anode where it is oxidised and electrons released to the external circuit. The oxidant, typically oxygen, is fed to the cathode.
where it is reduced and electrons are accepted from the external circuit. The circuit is completed by a flow of ions across the electrolyte that separates the fuel and oxidant, while direct current electricity is produced by the flow of electrons from the anode to the cathode through the external circuit. Cells are combined in series and in parallel to increase the power output, and a series of cells is referred to as a stack, with adjoining cells separated by an interconnect material. Metal oxides are of common use in the construction of these devices, and hence they are often termed solid oxide fuel cells (SOFC). Typical components include a zirconia based electrolyte, a porous cermet anode (ceramic/metal complex), and doped perovskite oxides as the cathode ($\text{LaMnO}_3$) and interconnect ($\text{LaCrO}_3$).

![Cross section of an individual fuel cell.](image)

The structural features of perovskites, discussed below, mean that oxygen mobility is much more likely and energetically favoured than cation mobility. In contrast to other metal oxides, such as corundum or spinel oxides which adopt a close packing
arrangement of oxygen ions, the perovskite structure has a cubic close packing of the A site cations and anions. Appreciable ionic conductivity in these compounds will, therefore, require the introduction of defects, in particular oxygen vacancies. Typically, these materials are doped at the La\(^{3+}\) site with aliovalent ions (e.g. Sr\(^{2+}\)) which leads to charge compensation by the formation of ionic and electronic defects. The type of defect depends on the nature of the dopant, the oxygen partial pressure and the temperature [3,16,22-24]. At low oxygen partial pressure (or low oxygen activity) the predominant defects in acceptor-doped LaBO\(_3\) perovskites are oxygen vacancies, given by the following defect equation:

$$\text{MO} + \text{La}_{\text{La}}^{\text{\#\#}} \leftrightarrow \text{M}_{\text{La}}^{\text{\#\#}} + \frac{1}{2} \text{V}_{\text{O}}^{\text{\#\#}} + \frac{1}{2} \text{La}_{2}0_{3}. \quad (1.1)$$

where \(M_{\text{La}}^{\text{\#\#}}\) is the dopant substitution and \(V_{\text{O}}^{\text{\#\#}}\) is the oxygen vacancy. Therefore, the oxygen ion conductivity increases with decreasing oxygen partial pressure, whereas hole conductivity decreases. As the oxygen activity increases oxygen vacancies become occupied, with charge compensation through hole formation; therefore, the material passes through a state of mixed (ionic/electronic) conductivity, until a point is reached where hole conductivity predominates, and described by:

$$\text{V}_{\text{O}}^{\text{\#\#}} + \frac{1}{2} \text{O}_{2(\text{g})} \leftrightarrow \text{O}_{0}^{\text{\#\#}} + 2h^{\#}. \quad (1.2)$$

where \(h^{\#}\) represents a hole species. A schematic (Brouwer diagram [1]) of the oxygen content, vacancy concentration and hole conductivity as a function of oxygen activity is given in figure 1.3.
The ability of these materials to stabilise grossly oxygen deficient phases while conserving the basic perovskite structure, explains the ease with which oxygen ion conduction can occur. The importance of understanding the ion transport behaviour in these materials has resulted in numerous studies of oxygen diffusion [25-34], employing a range of techniques including; ac/dc ionic conductivity, secondary ion mass spectrometry (SIMS) and potentiostatic step methods.

Under certain conditions perovskite oxides have been shown to be protonic conductors, which are also important in electrochemical applications [35-39]; for
example, perovskite electrolytes exhibiting excellent protonic conductivities offer the prospect of fuel cells operating at intermediate temperatures (600-800°C). Iwahara [36] first demonstrated the existence of proton conduction in ABO₃ perovskites; and it has since been shown that many ABO₃ perovskite type oxides, in particular those based upon cerates, zirconates (where A²⁺ = Sr, Ba, Ca and B⁴⁺ = Ce, Zr), and also KTaO₃, can possess appreciable levels of protonic conductivity. There is, however, uncertainty surrounding the nature of the proton migration mechanism in these materials.

The development of materials for use in these technologically important applications is essential, and investigation at a fundamental level is primary. The variable composition and properties of perovskite oxides has prompted extensive studies into their challenging structure-composition-property relationships [16,23,24,40-43]. A few studies have attempted to develop a framework to identify perovskite-type materials with high ionic conductivity. For example, Cook and Sammells [44] have proposed various criteria for selecting new solid electrolytes, such as lattice “free volume” and the critical radius of the opening at the saddle point. In addition, computer simulations have demonstrated that the low-vacancy migration energies in fluorite-type oxygen ion conductors are due to a balance between several factors, principally electrostatic, short-range, and polarisation energies [45].

However, many crucial and yet basic questions are still unanswered, including aspects of the defect chemistry and transport properties of these compounds. It is clear that for a full understanding of these problems we require further insight at the fundamental
level. In this thesis, we therefore use a variety of computational methods, to explore the defect chemistry and transport phenomena of perovskite-structured oxides. The reliability of such a theoretical approach has been demonstrated by similar studies applied to a wide range of inorganic material such as halides [46-48], spinel oxides [49,50], high T_C superconductors [51-55], zeolites [56,57] and metal oxides [58-62], and are now well established tools for probing solid state properties at the atomic level.

We start in Chapter 2 by discussing the classical simulation methods employed which are based on the Born model approach to the cohesion of the solid. We introduce perfect lattice techniques, including the summation and energy minimisation procedures which are readily incorporated into modern computer codes. The simulation of defective solids is performed by the two-region strategy of Mott and Littleton [63], and methods of modelling solid surfaces are also considered. Finally, an overview of molecular dynamics (MD) is presented, where valuable information can be obtained on transport phenomena by analysing the time evolution of the system.

The energetics and mechanism of proton conduction in perovskites are modelled using ab initio quantum mechanical (QM) cluster calculations. Chapter 3 gives a brief outline of the methods employed, namely Hartree Fock theory including electron correlation effects. The choice of basis set is crucial to the reliability of the model, as is the representation of the crystal environment which is simulated using an array of point charges constructed to reproduce the correct electrostatic potential.
Chapter 4 examines the defect chemistry and oxygen ion migration in the LaBO$_3$ (where B = Cr, Mn, Fe, Co) perovskite oxides. The effects of aliovalent doping, particularly by alkaline earth ions, are essential to the properties of these materials, and are investigated by lattice simulations. In addition, we have explored various mechanisms of oxygen ion migration, as well as trends in migration energy as a function of cation size.

The study of oxygen ion conduction is continued in Chapter 5, where molecular dynamics (MD) techniques are used to investigate the effects of temperature and of dopant concentration on oxygen diffusion in LaMnO$_3$ and LaCoO$_3$. MD also provides further information on oxygen diffusion coefficients and migration mechanisms, including the ability to visualise the ions in motion.

In Chapter 6 we discuss the application of both classical simulations and \textit{ab initio} methods to the incorporation and conduction of protons in perovskite oxides. Atomistic simulation methods are used to calculate the energy required to incorporate protons into the materials, and to examine possible orientations of the hydroxyl group in the structure. The conduction of protons is investigated using \textit{ab initio} calculations; in particular we calculate the energy barrier to proton transfer between two adjacent oxygen ions, and discuss the effects of charge redistribution and lattice relaxation. In addition, muon implantation studies are performed to help elucidate the proton site and migration in perovskite type oxides, as positive muons have been shown to emulate protons both chemically and physically.
Finally we turn to another important family of metal oxides, the bismuth molybdates, and consider their application as oxidation catalysts in Chapter 7. In particular they are used as catalysts in selective allylic oxidation processes, including ammoxidation to the corresponding nitrile. There are several bismuth molybdate phases, but only three are known to be catalytically active, namely $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ (α phase), $\text{Bi}_2\text{Mo}_2\text{O}_9$ (β phase), and $\text{Bi}_2\text{MoO}_6$ (γ phase). Structural aspects play an important role in their catalytic behaviour, although it is clear that the defect chemistry and surface properties are not well characterised. In an attempt to clarify these issues, we apply atomistic simulation methods to the highly active $\text{Bi}_2\text{Mo}_2\text{O}_9$ (β) phase in order to elucidate bulk and surface properties of this commercially important catalyst.
Chapter 2

SIMULATION METHODS

2.1 INTRODUCTION

2.2 POTENTIAL MODEL
    2.2.1 Coulombic Interactions
    2.2.2 Short-range Interactions
    2.2.3 Three Body Terms
    2.2.4 Ionic Polarisability

2.3 PERFECT LATTICE SIMULATION
    2.3.1 Energy Minimisation
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2.4 DERIVATION OF INTERATOMIC POTENTIALS
    2.4.1 Empirical Fitting
    2.4.2 Theoretical Methods
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2.5 MODELLING OF DEFECTS

2.6 SURFACE SIMULATION

2.7 MOLECULAR DYNAMICS
    2.7.1 Methodology
    2.7.2 Periodic Boundary Condition (PBC)
    2.7.3 Transport Properties
2.1 INTRODUCTION

Atomistic simulation techniques are well established as important tools in the field of solid state chemistry. These methods have been successfully used in the investigation of defect and transport properties of materials ranging from superconductors to catalysts [45-62,64,65]. The reliability of any such study is highly dependent upon the ability of the computational model to represent the structural and physical properties of the system in question. Indeed, the description of the energy of a system as a function of atomic co-ordinates, i.e. the potential model, is the basis behind most of the computer simulation techniques used in this thesis.

We now give a brief description of the methods used and their application within this study, since comprehensive details have been given elsewhere by Norgett, Catlow and Mackrodt [66-69].

2.2 POTENTIAL MODEL

The simulations are formulated within the framework of the Born model, in which ionic crystals may be regarded as being comprised of discreet ions. The lattice energy ($U_L$) of the crystal; the energy required to bring the ions from an infinite separation to form the crystal, can be calculated from a knowledge of the interatomic potential, and written as:
\[ U_L = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \sum_{i,j} V(r_{ij}) + \sum_{i,j,k} V(\Theta_{ijk}), \]  

where the summations refer to all pairs of ions \( i,j \) and all trios \( i,j,k \) in the crystal.

### 2.2.1 Coulombic Interactions

The first term of equation (2.1) represents the Coulombic interactions between the ions in the crystal. Its value is dependent upon the structural arrangement of the ions, and the value of the ion charges. Summation of this term is relatively straightforward due to an ingenious method developed by Ewald [70], a good description of which is given by Tosi [71]. The Coulombic potential varies as \( 1/r \), which if summed conventionally is extremely slow to converge, as there is significant contribution to the Coulomb energy at long distances.

The Ewald method divides the summation into two rapidly convergent parts, one in real space, the other in reciprocal space. To each Bravais lattice (real and reciprocal) a Gaussian distribution of the charge is superimposed to create a smoothly variant function. The sign of the reciprocal space function is opposite to that of the real space, so upon summation the functions cancel each other (see figure 2.1). The \( 1/r \) term is expressed in integral form with the summation from zero to infinity divided into the two spatial parts by a parameter \( \eta \),

\[ \frac{1}{r} = \frac{2}{\pi^{1/2}} \left\{ \int_{0}^{\eta} \exp(-r^2 t^2) dt + \int_{\eta}^{\infty} \exp(-r^2 t^2) dt \right\} \]  

(2.2)
where \( r \) is the separation, and \( t \) the half-height width of the Gaussian function. The value of \( \eta \) is calculated from a knowledge of the unit cell volume, and the number of species in the unit cell, so as to achieve maximum efficiency in the convergence. In the final expression of the required potential, the Fourier representation of the potential generated by the first component (\( 0 \) to \( \eta \) summed over reciprocal space) is combined with the potential of the second (\( \eta \) to \( \infty \) summed over real space) to give the electrostatic potential of the lattice. The result is a rapidly convergent and reliable method for the summation of the Coulombic potential.

Figure 2.1. (i) Charge distribution of a 1-D Bravais lattice. The vertical lines represent the point charges at the lattice sites, and the horizontal line the neutralising uniform distribution of charge. (ii) The Ewald components of the charge distribution, each Gaussian is centred on a lattice site and normalised to unity.
2.2.2 Short-range Interactions

The second term in equation (2.1) refers to short range interactions in the crystal, both attractive and repulsive. They arise from the fact that ions are not point charges, but are comprised of positively charged nuclei surrounded by electron clouds. As the ions approach one another overlap of electron clouds causes repulsion between the ions, for two reasons: firstly, interpenetration of the electron clouds reduces the effective shielding, and hence increases the Coulombic repulsion of the nuclei; secondly, as a result of the Pauli exclusion principle there is a repulsion between the interacting closed shell charge clouds.

The form of this short range interaction is commonly expressed by use of the Born-Mayer equation:

\[ V(r_{ij}) = A \exp\left(-\frac{r}{\rho}\right). \]  

(2.3)

Electron clouds in close proximity also undergo concerted, correlated motions of the van-der Waals type, leading to the formation of dipoles which interact to add an attractive term to the short-range potential of the order \( r^{-6} \). These interactions are small and dependent upon the polarisability of the ions, and therefore, they are often only included for interactions involving large polarisable ions, such as \( \text{O}^{2-} \).
Combination of the repulsive and attractive terms gives the short-range interactions between the ions, and is modelled through the use of the analytical function known as the Buckingham potential:

\[ V(r_{ij}) = A \exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}. \]  

Summation of the short range interactions presents few difficulties particularly as the potential decreases rapidly with increasing distance, and is generally terminated at a set cut-off. However, the potential is highly dependent upon obtaining suitable values for the parameters \( A, \rho, \) and \( C. \) Their derivation forms a crucial part of the construction of the potential model, and is discussed in more detail in section 2.4.

### 2.2.3 Three Body Terms

The third expression of equation (2.1) represents the three body 'bond-bending' terms. Materials with increasing deviation from ionic bonding may require the addition of an three-body term which provides a degree of directionality. This bond-bending term takes the form of a single harmonic function:

\[ V(\theta_{ijk}) = \frac{1}{2} k_b (\theta - \theta_o)^2, \]  

where \( \theta_o \) is the ideal equilibrium angle and \( k_b \) is the harmonic force constant. Potentials including three-body terms have been successful in modelling zeolites [57] and \( \text{La}_2\text{CuO}_4 \) [72].
2.2.4 Ionic Polarisability

Many of the properties that we would wish to obtain from our model, such as dielectric constants and optical phonon modes, require the treatment of ionic polarisation. Reproduction of these properties is, moreover, essential if the response of the lattice to charged defects is to be modelled effectively and reliably.

There are several methods available for the treatment of ionic polarisation, but by far the most successful of these is the shell model, originally developed by Dick and Overhauser [73]. This model includes vital coupling between polarisation and the short range repulsion, which is often omitted by other models such as the point polarisable ion model. Short-range repulsion, as previously discussed, is a result of overlap of electron clouds, and is affected by polarisation, in which there is a distortion of these electron clouds. Omission of this coupling generally leads to an overestimation of the polarisation, which in turn reflects directly upon the calculated physical properties.

The shell model is a simple mechanical representation of the ionic dipole as illustrated in figure 2.2. Each ion is represented by a massive core of charge $X$, connected to a massless shell of charge $Y$, by a harmonic spring of force constant $k$. The formal charge of the ion is then $X+Y$, and polarisation occurs through displacement of the shell relative to the core. The polarisability of the free ion is given by,

$$\alpha = \frac{Y^2}{k}$$

(2.6)
where $Y$ and $k$ are variables and derived along with the short range potential parameters $A$, $\rho$, and $C$. Coupling between the short range forces and the polarisation is achieved by allowing the short range potentials to interact between shell species only.

![Diagram of shell model](image)

**Figure 2.2.** Schematic representation of the shell model.

The Coulombic interactions take place between all species, except core and shell of the same ion. Short range repulsive interactions take place between shell species, with van-der Waals forces usually limited to interactions involving anions.

### 2.3 PERFECT LATTICE SIMULATION

Given high quality interatomic potentials, we may simulate structural and defect properties of crystals using energy minimisation techniques, in which we calculate the equilibrium geometry of the structure i.e. the minimum energy configuration of the crystal with respect to the ion co-ordinates. Comparison of the computed and
experimental structural and physical properties provides a good test of the reliability of the potentials.

2.3.1 Energy Minimisation

The concept of energy minimisation is simple: structural parameters including the ionic co-ordinates are adjusted until a minimum energy configuration is attained. There are however, several procedures available and careful consideration is required in the choice of method to be employed. Perhaps the most widely used methods, due to their efficiency and speed of convergence, are gradient techniques which involve the use of the first derivatives of the energy function with respect to the structural parameters (e.g. ion co-ordinates).

The simplest of the gradient techniques is the steepest descent method, where parameters are adjusted iteratively through the use of an expression of the form:

\[ X^{(p+1)} = X^{p} - g^{p} \delta \]  

(2.7)

where \( X^{(p+1)} \) is a vector the components of which are variables for the \((p+1)^{th}\) iteration, \( X \) and \( g \) are variables and their gradients for the \( p^{th} \) iteration, and \( \delta \) a scalar parameter chosen so as to obtain rapid convergence. More sophisticated techniques are generally employed, based upon a similar strategy, of which the conjugate gradient method is most notable.
The technique in common use in minimisation studies is the Newton-Raphson method, which introduces second as well as first derivatives of the energy function, to give a greatly accelerated convergence. The lattice energy (\( U_L \)) of a new set of co-ordinates (\( r' \)) which have changed from an initial set (\( r \)) is updated as,

\[
U_L(r') = U_L(r) + g^T.\delta + \frac{1}{2}\delta^T . W . \delta ,
\]

where \( \delta \) is a vector of dimensions \( 3N+6 \), \( N \) being the number of species in the unit cell, and \( g \) is a vector of the first derivatives of the lattice energy with respect to the ion displacements and the strain components:

\[
g = \left( \frac{\partial U}{\partial r} , \frac{\partial U}{\partial \delta \varepsilon} \right)
\]

\( \delta (\delta = r' - r) \) is the strain vector incorporating the \( x,y,z \) displacements of the ions, and the bulk strain components \( \delta \varepsilon \). \( W \) is the second derivative matrix of the lattice energy function,

\[
W = \begin{pmatrix}
\frac{\partial^2 U}{\partial r . r} & \frac{\partial^2 U}{\partial r . E} \\
\frac{\partial^2 U}{\partial E . r} & \frac{\partial^2 U}{\partial E . E}
\end{pmatrix} = \begin{pmatrix}
W_{rr} & W_{rE} \\
W_{Er} & W_{EE}
\end{pmatrix}
\]

and \( E \) is the symmetric strain matrix formed from the components of \( \delta \varepsilon \).

\[
E = \begin{pmatrix}
\delta \varepsilon_1 & \frac{1}{2} \delta \varepsilon_6 & \frac{1}{2} \delta \varepsilon_5 \\
\frac{1}{2} \delta \varepsilon_6 & \delta \varepsilon_2 & \frac{1}{2} \delta \varepsilon_4 \\
\frac{1}{2} \delta \varepsilon_5 & \frac{1}{2} \delta \varepsilon_4 & \delta \varepsilon_3
\end{pmatrix}
\]
The new set of co-ordinates \((r^1)\) are related to the initial set \(r\) by

\[
r^1 = E(r + \delta r)
\]  \(\text{(2.12)}\)

where \(\delta r\) is the change in the co-ordinates, scaled accordingly. The minimisation can be performed under both constant volume and constant pressure conditions. With constant volume the bulk strain components are neglected, with removal of only strain due to the ionic co-ordinates. Constant pressure calculations include the removal of bulk strains through adjustment of the unit cell (lattice) parameters.

In each case the initial step is to update the co-ordinates according to the formula,

\[
r^{(p+1)} = r^p - g^p \cdot H^p
\]  \(\text{(2.13)}\)

where \(H^p = (1/W_{rr})^p\) and commonly known as the Hessian matrix. Complications arise with the computing power required to invert and store the \(W_{rr}\) matrix. However, explicit calculation of the Hessian matrix at each cycle is deemed unnecessary due to an approximation made by Fletcher and Powell [74]. This method requires the updating of the forces at each cycle, but only performs the full matrix inversion at predetermined intervals to enhance convergence rates given by,

\[
H^{p+1} = H^p + \frac{\delta r . \delta r^T}{\delta r . \delta g^T} - \frac{H^p . \delta g . \delta g^T . H^p}{\delta g^T . H^p . \delta g}
\]  \(\text{(2.14)}\)
where $\delta r = r^{(p+1)} - r^{p}$ and $\delta g = g^{(p+1)} - g^{p}$. The storage of the large $3N \times 3N$ matrix is simplified through the use of symmetry constraints, whereby only symmetry independent sites are necessary. For constant volume calculations this step of adjusting ionic co-ordinates is repeated until an energy minimum is attained. Under constant pressure conditions an additional step is required in the iterative process. Following the adjustment of the ion positions, the bulk strains are also minimised by relaxation of the cell vectors. Thus removal of bulk and basis strains is obtained through a two step process within each iteration.

### 2.3.2 Physical Properties

Through the calculation of the first and second derivatives of the lattice energy with respect to the ionic co-ordinates and cell vectors, several physical properties can be evaluated. Elastic constants are defined as the second derivatives of the lattice energy with respect to strain, normalised to the cell volume ($V$),

$$ C = \frac{1}{V} \left( W_{EE} - W_{Er} \cdot W^{-1}_{rE} \cdot W_{rE} \right), $$

where $C$ is the elastic constant matrix. Dielectric constants which depend upon the polarisabilities, and are given by the following equation;

$$ k^{\alpha\beta} = \delta^{\alpha\beta} + \frac{4\pi}{V} q^T \left[ W^{-1}_{rE} \right]^{\alpha\beta} \cdot q, $$
where $k^{\alpha \beta}$ is the dielectric tensor, $\delta^{\alpha \beta}$ ion displacement, $V$ unit cell volume, and $q$ the charge. The calculation of these physical properties [66] and others is an easy method of testing the potential model as well as providing predictive values in cases where experimental data is unavailable.

2.4 DERIVATION OF INTERATOMIC POTENTIALS

As previously discussed the reliability of the simulation is highly dependent upon the quality of the potential model. The short-range potential and ionic polarisability include variable parameters, the values of which need to be determined for the system in question. A significant component of the present study has concerned the derivation of the short-range parameters $A$, $\rho$, and $C$, and the shell model parameters $Y$ and $k$ for the interactions investigated. There are two main methods available for the derivation of potential parameters; empirical and theoretical, which are now discussed in detail.

2.4.1 Empirical Fitting

The empirical method is perhaps the most widely used as it allows the derivation of short range and shell model parameters appropriate to the system under investigation. Quite simply the potential parameters are adjusted so as to obtain the best agreement between calculated and experimental properties, which is achieved by a combination of perfect lattice simulation methods and a least squares fitting routine to change
iteratively the parameters until the best fit is attained. This procedure has been implemented in the GULP (General Utility Lattice Program) code written by Gale [75]. It is desirable to have a wide range of crystal properties including structural, elastic, dielectric and phonon data, though this is often not possible and commonly only structural data are available.

Empirical fitting procedures have been used successfully for a large number of halide and oxide materials [76-78]. There is however, an inherent weakness in empirically derived potentials, due to the inability to extract information about the potential at interatomic spacings different from those in the perfect lattice. The method relies on the validity of the analytical form of the potential over a considerable range of inter-nuclear separations. It should be noted though, that potentials derived in this manner have proven successful in modelling defects positioned at non-lattice spacings e.g. interstitials, for these halide and oxide materials [47,48,50,52].

The reliability of potentials derived by empirical methods is greatly improved when knowledge of the potential is available over a wider range of inter-atomic separations. This can be achieved by; simultaneous fitting of several structures containing the same interaction, or when a material contains a range of distances for the interacting ions, as is commonly available in complex low symmetry structures. In each case, simultaneous fitting and fitting to low symmetry structures, we are able to sample the potential energy surface at several points, and so decrease the dependence of the analytical function to reproduce the correct potential starting from only one point, a schematic of
this is shown in figure 2.3. When no such experimental information is available derivation must proceed through the use of non-empirical, theoretical methods.

Figure 2.3. Schematic representation of empirical fitting to a potential energy surface, with (a) one point, and (b) several points.

2.4.2 Theoretical Methods

Quantum mechanical methods can be used in the derivation of potential parameters, by calculating the energy of interaction between ions as a function of their separation. A potential form can then be fitted to the resulting energy surface, which should be valid over a wide range of separations. \textit{Ab initio} Hartree Fock methods can be employed, but are computationally expensive for all but the 'lighter' ions. Therefore, more approximate theoretical methods have been developed, of which electron gas techniques, developed by Wedephol, and Gordon and Kim [79,80], are the most notable.
The approximations are based on the following procedure:

(i) The electron densities of the interacting ions are obtained by calculating their wavefunctions, usually by a Hartree Fock method.

(ii) The interaction energy $\Phi_{ij}(r_{ij})$ is then given as a function of the total electron density of a pair of ions $i$ and $j$.

$$\Phi_{ij}(r_{ij}) = E_N + E_C + E_X + E_{KE},$$  \hspace{1cm} (2.17)

where $E_N$ represents the nuclear repulsion, $E_C$ the coulomb exchange, $E_X$ the exchange function, and $E_{KE}$ the kinetic energy incorporating a limited correlation contribution. Consideration of the Madelung potential is required in calculating electron densities, particularly for highly polarisable ions such as $O^2$ where the second electron is not bound in the free state, but is held only by the Madelung potential.

There are also several assumptions made, which include the neglect of distortion of the interacting ions as they approach one another; the total electron density is simply the sum of the isolated ionic densities. Moreover, there is no consideration of dispersion or relativistic effects, and at present these methods are unable to calculate shell model parameters.
2.4.3 Shifted Electron-Gas Method

Where possible the potentials used in this study have been derived using empirical procedures, but in some cases experimental data are unavailable and we resort to theoretical techniques. Work by Butler et al [58] has shown that it is inappropriate to mix potentials obtained from different sources. The shifted electron gas procedure overcomes the incompatibility of mixed potentials by adjustment of calculable empirical potentials, through the use of electron gas potentials which are available for all species. This procedure is best described through the use of an example.

In Chapter 4, potentials are derived using empirical techniques for the perovskite oxide LaCoO$_3$, where both cations are trivalent. Experimental studies have shown that under certain conditions the Co$^{3+}$ ion will oxidise to Co$^{4+}$. To investigate the energetics of the oxidation process a potential for the Co$^{4+}$...O$^2-$ interaction is required. However, Co$^{4+}$ is an uncommon oxidation state for a pure cobalt oxide and there is no suitable experimental data which would allow empirical methods to be used. Therefore, the shifted electron gas procedure is employed (shown schematically in figure 2.4), the method proceeds as follows:

(i) Using empirical methods a Co$^{3+}$...O$^2-$ potential is obtained, based on the LaCoO$_3$ perovskite oxide.

(ii) Electron gas methods are used to calculate potentials for both the Co$^{3+}$...O$^2-$ and Co$^{4+}$...O$^2-$ interactions.
The difference between the two electron gas potentials is then used to adjust the empirically derived Co\(^{3+}\)...O\(^{2-}\) potential, resulting in a compatible Co\(^{4+}\)...O\(^{2-}\) potential.

![Schematic representation of the shifted electron gas procedure.](image)

Figure 2.4. Schematic representation of the shifted electron gas procedure.

The difference between the two electron gas potentials is used to adjust the Co\(^{3+}\) potential derived by empirical methods, to give a Co\(^{4+}\) potential, compatible with the empirical Co\(^{3+}\) potential.

### 2.5 MODELLING OF DEFECTS

Defect calculations introduce one vital feature in addition to the perfect lattice methods previously mentioned, that is the relaxation of the lattice ions around the defect species. In ionic crystals the perturbation caused by the defect is mainly Coulombic in origin; its effects are generally extensive and apparent over a long range. Defect simulations must include an accurate description of this relaxation. One such procedure which has proven itself in the simulation of defective materials is the two-region strategy based on
the Mott-Littleton method [63]. The crystal is divided into two main regions, shown in figure 2.5.

Explicit relaxation (usually by the use of Newton-Raphson procedures) is performed on all ions within the inner region (region I), to obtain the minimum energy configuration. The close proximity of the ions in region I to the defect species mean that the forces exerted on them by the defect are strongest, and hence it is necessary to treat the relaxation as accurately as possible. However, relaxation of these inner ions in response to the defect species acts to dampen the effect of the defect forces over longer distances, effectively shielding the outer ions from the defect. The remainder of the lattice (region II) which extends to infinity can, therefore, be treated using more approximate methods.
The Mott and Littleton technique, based on the two region strategy, is now of common use in defect modelling [81,82], and incorporated into the CASCADE code [83]. The method assumes that the response of region II is essentially a dielectric response to the effective charge of the defect. A simple result of continuum dielectric theory can then be used, which gives the polarisation of the crystal $P$, per unit cell, at a distance $r$, from the defect as:

$$P = \frac{V}{4\pi} \frac{qr}{r^3} \left(1 - \frac{1}{\varepsilon_0}\right),$$  

where $V$ is the unit cell volume, $q$ the effective charge of the defect, and $\varepsilon_0$ the static dielectric constant. The total defect formation energy following the division of the crystal into two regions is expressed as:

$$E = E_1(x) + E_2(x,y) + E_3(y),$$  

where $E_1$ is a function of the co-ordinates $(x)$, and dipole moments of the ions solely in region I. $E_2(x,y)$ arises from the interaction between region I and II, where in practice it is found necessary to include an interface region (region IIa), to produce a smoother convergence during minimisation. Ions in region IIa are displaced according to the forces determined by the Mott-Littleton approximation, but interactions which displace region I ions are calculated explicitly.

$E_3$ depends solely upon the displacement $(y)$ of the ions within region IIb according to the approximation. The explicit dependence of the defect energy on region IIb can be
removed, and providing region I is of sufficient size (typically $\geq 100$ ions) the calculation of the defect formation energy can be performed reliably and efficiently. The minimum size of region I required to obtain a reliable result, is usually determined by plotting the defect formation energy as a function of the region I size, and finding the point at which the defect energy converges.

The defect calculation will proceed as:

(i) The energy minimisation in region I is performed yielding equilibrium values of $\langle x \rangle$.

(ii) The displacements of ions in region IIa are calculated as a direct response to those in region I, by use of the Mott-Littleton method.

(iii) Calculation of $E_1(x)$ by explicit summation.

(iv) $E_2$ and its derivatives are calculated explicitly for all ions within region IIa.

(v) Calculation of displacements in region IIb, which are used to calculate $E_2$ and its derivatives.

2.6 SURFACE SIMULATION

The techniques used to simulate surfaces and interfaces are similar to those used in bulk simulations with differences which arise due to the fact the crystal is no longer infinite in all three dimensions, but is terminated in one direction. The normal procedure is to describe the crystal as a stack of planes which are periodic in two dimensions.
Calculation of the self potential of the crystal requires a consideration of the loss of periodicity in all dimensions, which is achieved through use of a method developed by Parry [84-85]. It is also necessary to describe relaxation of the ions as a result of their close proximity to the surface. The methods used are similar to those employed in bulk simulations which divide the crystal into different regions, as illustrated in figure 2.6.

![Figure 2.6. Surface simulation, crystal terminated in one direction, and divided into regions.](image)

The unrelaxed surface is created by termination of the relaxed (equilibrated) bulk. The stacks of planes below the surface are split into two regions. Ions in the region directly below the surface (region A) are relaxed explicitly using Newton Raphson procedures. Ions in the region further from the surface (region B), which represent the bulk of the
lattice, are held fixed. Region B is required to reproduce the correct potential in region A; the procedure allows us to calculate the surface energy as,

$$E_\gamma = \sum_{i=1}^{N} \frac{E_s - \frac{1}{2} E_b}{\text{Area}}$$

(2.20)

where $E_\gamma$ is the surface energy per unit area, $E_s$ the energy of the free surface, and $E_b$ the bulk lattice energy.

Defective surfaces are treated using a two region strategy as in bulk calculations. The main differences being that the regions (I and IIa) are now hemispherical in shape, and procedures are required to deal with the modification of interplanar spacings in the surface region. In addition, for small crystals grown under equilibrium conditions, the morphology of the crystallite can be directly related to the relative energetics of the component crystal faces. The crystal, therefore, will grow in a manner which minimises the total surface energy at a given volume. The relative surface energetics for a variety of crystal surfaces can be obtained from the surface simulations, and then can be used by Wulff's \[86\] theorem to define the morphology of the crystallite.

### 2.7 MOLECULAR DYNAMICS

The simulation methods previously discussed have been concerned solely with the calculation of potential energies of the system, and are performed using a static
description of the lattice corresponding to a zero temperature limit (which maybe of zero-point motion). Molecular dynamics (MD) is a method which explicitly includes the kinetic energy term, and introduces the effects of ion motion (lattice vibration), and temperature.

2.7.1 Methodology

Molecular Dynamics (MD) simulations assume that once a reliable potential model has been defined, classical mechanics can provide an accurate description of the underlying dynamics of the system. The system is allowed to evolve in time by solving in an iterative fashion the classical Newtonian equations of motion using the specified interatomic potentials.

The Hamiltonian function which dictates the time evolution of the system through use of the equations of motion has the form,

\[
H (r, p) = V(r) + T(p)
\]  

(2.21)

where \( V \) is the potential energy of the system with co-ordinates \( r \), and \( T \) is the kinetic energy with respective momenta \( p \).

Initially the ions are assigned positions \( r_i \) and velocities \( v_i \). For solids, the positions are normally those observed in crystallographic studies; the velocities of the ions are
normally taken as random in direction and of a magnitude corresponding to the kinetic energy appropriate to the temperature such that:

\[
\sum_i m_i \langle v_i^2 \rangle = 3Nk_b T
\]

where \(N\) is the number of ions in the simulation 'box' and \(k_b\) is the Boltzmann constant.

MD simulations are performed via the use of a numerical scheme to update the positions and momenta of the ions, over a chosen timestep \((\Delta t)\) which should be sufficiently small so that all the motions of the system can be adequately reproduced. The equations themselves are based on power series expansions for short times \(\Delta t\) around the current time, \(t\), for co-ordinates, velocities and accelerations,

\[
\begin{align*}
\mathbf{r}_i (t + \Delta t) &= \mathbf{r}_i (t) + \Delta t \mathbf{v}_i (t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i (t) + ... \\
\mathbf{v}_i (t + \Delta t) &= \mathbf{v}_i (t) + \Delta t \mathbf{a}_i (t) + \frac{1}{2} \Delta t^2 \mathbf{b}_i (t) + ... \\
\mathbf{a}_i (t + \Delta t) &= \mathbf{a}_i (t) + \Delta t \mathbf{b}_i (t) + \frac{1}{2} \Delta t^2 \mathbf{c}_i (t) + ...
\end{align*}
\]

where \(\mathbf{b}_i\) and \(\mathbf{c}_i\) are the third and fourth time derivatives of the positions, respectively. There are two main types of algorithms available for the updating procedure, predictor-corrector (gear), and Verlet, of which the latter has been utilised throughout this study and incorporated into the DL_POLY code [87]. An example of the Verlet type
algorithm is the leap-frog procedure, which will be briefly explained here; for greater
details of updating algorithms refer to [88].

The Verlet leap-frog algorithm takes its name from the way in which the co-ordinates
and velocities jump ahead of each other as the simulation progresses. If we rewrite the
co-ordinate expression of equation (2.23) as,

$$r_i (t + \partial t) = r_i (t) + \partial t [v_i (t) + 1/2 \partial t a_i (t)]$$  \hspace{1cm} (2.24)

and then expand the velocities but in terms of a 1/2\partial t (half-step), and disregard terms
higher than the first order

$$v_i (t + 1/2 \partial t) = v_i (t) + 1/2 \partial t a_i (t)$$  \hspace{1cm} (2.25)

the velocity expression can be substituted into the co-ordinate expression to give

$$r_i (t + \partial t) = r_i (t) + \partial t v_i (t + 1/2 \partial t)$$  \hspace{1cm} (2.26)

The velocities can be expanded backwards in time to give an expression for the
velocities at a half step, from which we obtain an expression for calculating $v_i (t)$

$$v_i (t + 1/2 \partial t) = v_i (t - 1/2 \partial t) + \partial t a_i (t)$$  \hspace{1cm} (2.27)
The iterative procedure is as follows,

(i) The accelerations of the ions at time $t$, are calculated from a knowledge of the forces acting upon the ions.

(ii) Using equation (2.27) the half step velocities are calculated using the previously attained values of the accelerations.

(iii) The co-ordinates can now be updated by use of equation (2.26), and the procedure repeated to obtain the desired trajectories.

The updating procedure is repeated several thousand times, which allows study of the time evolution of the system. In the initial stages of the simulation, the system equilibrates and achieves a Maxwellian distribution of velocities. The observation of a constant temperature may, in general, be safely taken as the criteria for equilibrium.

2.7.2 Periodic Boundary Condition (PBC)

In the simulation of crystal solids, the initial configuration consists of a supercell which in the present study contains approximately 2500 ions, located at their perfect lattice positions. Periodic boundary conditions are applied which repeat the simulation cell to infinity, thus generating an unbounded system to eliminate the effects of surfaces, shown in figure 2.7. PBC ensures that all the ions can be considered to be embedded in the system under bulk conditions, and so, if a particle leaves the ‘box’ it re-enters on the opposite face with the same trajectory.
Figure 2.7. Periodic boundary conditions. The simulation cell (full lines) is surrounded by images of itself (dotted lines), repeated to infinity, to produce an unbounded system with no surfaces.

Simulations maybe performed under different ensembles [89-92]. The simplest ensemble is the microcanonical ensemble (NVE) where the number of species (N), volume (V) and total energy (E) are conserved within the simulation, i.e. there is no interaction of the system with the surrounding environment. The ensemble used for our study is that of Berensden [89] (NPT) corresponding to conditions of constant temperature (T) and constant pressure (P), which allows the exchange of energy between the ions in the simulation cell with the surroundings, and also the modification of the cell dimensions to maintain a constant pressure. The number of species within the cell is kept constant through the use of the PBC. The concept of NPT ensemble is analogous to that of the
idea of an ideal gas contained within a box of variable dimensions, submersed in a temperature and pressure ‘bath’. Energy is free to transfer into or out of the simulation box and has the effect of keeping the system at constant temperature but still allows for localised changes where potential energy is transferred to kinetic energy. This is equivalent to heat exchange with the surrounding environment. The pressure is caused by the particles colliding with the sides of the box resulting in a net force exerted on the box. If this net force is greater than a theoretical force on the outside of the box (i.e. air pressure) the box will expand, and visa versa.

It should be noted that the inclusion of ionic polarisabilities in the simulation would substantially increase the computing time required for the simulation, as the treatment of shell species requires careful consideration. Either, the relaxation of the shells is required for each time step so as to calculate the new forces, therefore, increasing the number of calculations per time step, or the shell is given a small mass and the positions updated accordingly, but with a significantly smaller time step required to conserve energy. The interatomic potentials used in these simulations are, therefore, rigid-ion. The potential parameters are derived by empirical methods and are compatible with the potentials used within the static lattice simulations.

2.7.3 Transport Properties

The data from MD can be used to provide insight into the microscopic dynamics of the system. Two valuable properties are the Radial Distribution Functions (RDF), and the
Mean Square Displacements (MSD). The RDF measures the distribution of distances between pairs of ions and provides extensive structural information. MSD are time dependent single particle averages which describe the average displacement of an ion species from its initial position over a set period of time, given by,

$$\langle r_i^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2$$  \hspace{1cm} (2.28)

where $N$ is the total number of ions. MSD are an important property as they can be related directly to the diffusion of an ion(s) through the lattice. If the MSD of one ion type increases linearly with time then diffusion of that ion type is indicated. The diffusion coefficient ($D_i$) can be obtained from the gradient of the plot of the MSD with time, according to the relationship:

$$\langle r_i^2 \rangle = 6D_i t + B_i$$  \hspace{1cm} (2.29)

where $B_i$ is the thermal (Debye-Waller) factor arising from lattice vibrations of ions.

Structural information can be extracted from Radial Distribution Functions (RDF) which provide a measure of the long-range order; or in our case termed the partial pair distribution function, $g(r)$, written as,

$$g_{ij}(r) = \frac{\langle n_{ij}(r) \rangle}{4\pi r^2 (n_in_j)^{1/2}}$$  \hspace{1cm} (2.30)
where \( <n_{ij}(r)> \) is the ensemble average of the number of species of type \( j \) in a radial shell of \( r \) to \( r + dr \) with a central ion of type \( i \); \( n\) is the bulk density of ion type \( i \). The RDF of the mobile sublattice in fast-ion conductors is often more liquid like than those of normal solids.

In summary, this Chapter describes the atomistic simulation methods which are employed in the investigation of perovskite-structured oxides and bismuth molybdates, in Chapters 4 and 7 respectively. In particular, the lattice simulations are used to study defect chemistry and mechanisms of anion migration. Molecular dynamics techniques are applied to investigate oxygen ion diffusion as a function of temperature in the perovskite oxides, LaMnO\(_3\) and LaCoO\(_3\), in Chapter 5.
Chapter 3

QUANTUM MECHANICAL METHODS

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3.1 INTRODUCTION

The classical simulation methods previously discussed, although very powerful, are restricted in their range of applications. To model the diffusion of a proton through a perovskite oxide we require a technique, that allows investigation of bond breaking and formation, which is beyond the scope of classical simulations. Chemical bonding of the proton with the oxygen ions has a large influence on the migration of the proton; the mechanism may involve transport of the proton by 'hopping' from one lattice ion to another, or migration may occur via a carrier mechanism whereby the proton moves with an associated, bonded ion. *Ab initio* quantum mechanical techniques are ideally suited, and have proven so in similar investigations [93-96], of the mechanisms involved as they can model chemical bonding and polarisation effects explicitly.

A brief overview of quantum mechanical (QM) methods [97-101] is now presented; more specifically, the QM cluster methods used in this study to investigate proton migration in perovskite oxides. Hartree-Fock theory forms the basis of the techniques discussed, with additional levels of accuracy added through perturbation theory.

The CADPAC (Cambridge Analytical Derivatives PACkage) code [102] which incorporates Hartree-Fock techniques, is used throughout this study, to perform the QM cluster calculations.
Chapter 3 QUANTUM MECHANICAL METHODS

3.2 THE ELECTRONIC PROBLEM

3.2.1 The Schrödinger Equation

One of the central problems in quantum chemistry is to describe the motion of electrons in the field of nuclear charges. We are concerned with finding approximate solutions of the non-relativistic time-independent Schrödinger equation,

$$H\Psi = E\Psi,$$  \hspace{1cm} (3.1)

where $H$ is the Hamiltonian operator, $\Psi$ is the wavefunction, and $E$ the corresponding energy of the eigen equation. The Hamiltonian for a system containing $N$ electrons of charge $e^-$ and mass $m_e$, and $V$ nuclei of charge $Z_A$ (atomic number of nucleus A) and mass $M_A$ is,

$$H = \sum_{A=1}^{V} \frac{-\hbar^2}{8\pi^2 M_A} \nabla_A^2 + \sum_{i=1}^{N} \frac{-\hbar^2}{8\pi^2 m_e} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{V} \frac{Ze^2}{4\pi\varepsilon_o r_{iA}} + \sum_{i>j=1}^{N} \frac{e^2}{4\pi\varepsilon_o r_{ij}} + \sum_{A>B=1}^{V} \sum Z_A Z_B e^2 \frac{1}{4\pi\varepsilon_o R_{AB}}$$  \hspace{1cm} (3.2)

where $\hbar$=Planck’s constant, $\nabla$ is the Laplacian operator (involves differentiation with respect to co-ordinates $\{\partial/\partial x, \partial/\partial y, \partial/\partial z\}$). The first two terms of equation 3.2 represent the motion of the nuclei (A,B) and electrons (i,j) respectively. The remaining terms are the Coulomb attraction between electrons and nuclei, Coulomb repulsion...
between electrons, and finally between nuclei. R and r are the distances between the relevant species.

3.2.2 The Born-Oppenheimer Approximation

The Hamiltonian (equation 3.2) contains terms that describe the motion of electrons and also the motion of nuclei with respect to each other. Solution of the Schrödinger equation incorporating this Hamiltonian presents a formidable problem, and one, which is insoluble analytically for all but the simplest systems i.e. a one electron atom. Separation of electronic and nuclear motion through use of the Born-Oppenheimer approximation provides a simplified version of the problem, and is possible due to the relative masses of the electrons and nuclei. The nuclei are considerably heavier than the electrons and, therefore, move much more slowly, which allows the motion of the electrons to be described with respect to fixed nuclei. The Hamiltonian for the motion of the electrons in this fixed nuclei approximation is:

\[ H = -\frac{\hbar^2}{8\pi^2 m_e} \sum_{i=1}^{N} \nabla_{i}^2 \pm \text{[Coulomb terms]} \]  (3.3)

Therefore solution of the corresponding Schrödinger equation is performed in two stages: first the electronic problem is addressed, and secondly the dynamics of the nuclear motion are treated using the potential energy surface obtained from the solution of the Schrödinger equation for fixed nuclei with a range of separations. We
note that the Born-Oppenheimer approximation is not always valid, for example, it is inappropriate for systems exhibiting Jahn-Teller distortion.

3.2.3 Variation Principle

As already stated, except for the simplest cases it is not possible to obtain an exact solution to the Schrödinger equation, we therefore, find approximate solutions. The variation principle states that given any N-electron wavefunction that satisfies the necessary boundary conditions, an upper bound to the exact ground state energy $E_0$ is,

$$E = \frac{\int \Psi^* \mathcal{H} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} \geq E_0 \quad (3.4)$$

where $\Psi^*$ is the complex conjugate of the wavefunction $\Psi$, and the product $(\Psi^* \Psi \, d\tau)$ is the probability of finding the electron in a volume element. The boundary conditions which the wavefunction must satisfy are; that the wavefunction is continuous, single valued, finite and has a continuous first derivative. Equation 3.4 shows that the energy of the evaluated wavefunction will always be greater than the exact ground state energy. The form of the wavefunction usually includes a number of variable parameters and these functions are commonly written as a linear superposition of the form:

$$\Psi = C_1 \Phi_1 + C_2 \Phi_2 + \ldots + C_n \Phi_n = \sum_{j=1}^{n} C_j \Phi_j \quad (3.5)$$
where $C_j$ are coefficients for the N-electron functions $\Phi_j$, which also satisfy the same boundary conditions as the wavefunction $\Psi$. In addition, the wavefunction must be antisymmetric i.e. if the co-ordinates of two particles are interchanged the sign of the corresponding wavefunction changes. In our case, the orbitals are defined as Slater determinants and, to ensure antisymmetry, are arranged in a multi-determinantal wavefunction. It follows then that the best possible approximation to the exact solution of the Schrödinger equation will be obtained by minimisation of the energy $E$ with respect to the $n$ coefficients,

$$\frac{\partial E}{\partial C_j} = 0 \quad (j = 1, 2, \ldots, n) \quad (3.6)$$

There are $n$ possible solutions to this energy,

$$E_1 \leq E_2 \leq E_3 \quad \ldots \quad \leq E_n \quad (3.7)$$

each having a wavefunction,

$$\Psi_i = \sum_{j=1}^{n} \Phi_j C_{ji} \quad (3.8)$$

A consequence of this result is that increasing the number of coefficients gives a better approximation to the exact ground state energy. However, an exact solution is still unfeasible as it would require an infinite number of parameters, but the larger the number of component functions the closer we can approach to the hypothetical limit.
3.3 ORBITALS and BASIS FUNCTIONS

3.3.1 Orbital Representation

The most common representation of atomic and molecular orbitals is as linear combinations of known one electron functions. Thus for molecules we use a Linear Combination of Atomic Orbitals to give Molecular Orbitals (LCAO-MO) [103]:

\[ \Psi_i = \sum_{u=1}^{n} \Phi_u C_{ui} \]  \hspace{1cm} (3.9)

where \( \Psi_i \) is the \( i \)-th molecular orbital, \( C_{ui} \) are the coefficients, \( \Phi_u \) is the \( u \)-th atomic orbital, and \( n \) is the number of atomic orbitals. The (LCAO-MO) equation follows the same format as equation 3.8 utilised in the Variation principle, and therefore solutions to the wavefunction can be attained by a similar procedure.

The atomic orbitals (AO) are solutions of the Hartree-Fock equations for the atom i.e. the form of the orbitals is based upon the exact solution to the one electron problem, for example, hydrogen. Slater type orbitals (STO) are the most accurate representation of the atomic orbitals due to their similarity with the atomic orbitals of hydrogen. However, STO functions are unsuitable for polyatomic systems due to the time required to evaluate electron interaction integrals; hence, Gaussian type orbitals (GTO) are used almost exclusively for the representation of molecular orbital wavefunctions,
as Gaussian functions allow rapid and efficient evaluation of electron interaction integrals. Gaussian functions have the form,

\[ \phi(\alpha, l, m, n; x, y, z) = N e^{-\alpha r^2} x^l y^m z^n, \]

where \( N \) is a normalisation constant, and \( \alpha \) is the exponent. The \( x, y, z \) are Cartesian coordinates, and \( l, m, n \) are integral exponents of the Cartesian coordinates where \( r^2 = x^2 + y^2 + z^2 \). One of the main advantages of using Gaussian functions is that the product of two Gaussian functions, is a third Gaussian function, see figure 3.1.

![Figure 3.1](image)

Figure 3.1. The product of two Gaussians centred on sites \( A \) and \( B \), is a third Gaussian centred on site \( P \).

Therefore, although Gaussian functions are not optimum basis functions, especially in the region close to the nucleus, they allow complicated two electron integrals to be
evaluated much more rapidly. The normal procedure is to use combinations of Gaussian functions or ‘contractions’ i.e. we write

\[ \Psi_G = \sum C_g \psi_g \]  

(3.11)

where \( \psi_g \) are individual Gaussians and the \( C_g \) (coefficients) are held constant once optimised for an atom in a given environment. The aim is to obtain resulting functions \( \psi_G \) which approximate to Slater type functions, or any other set of functions desired. Nevertheless, they still allow integral evaluation with only primitive Gaussian functions. Functions that approximate Slater type orbitals are termed STO-nG functions, where \( n \) is the number of Gaussian functions fitted to the STO.

3.3.2 Basis Sets

The basis set is the totality of the functions (Slater, contractions or primitive Gaussians) used to construct the wavefunction. The choice of basis set is, therefore, crucial to the accuracy of the calculation, but also greatly influences the time required for the calculation, as the computational expense in a Hartree-Fock calculation is proportional to the 4th power of the number of basis functions. A minimal basis set such as STO-3G is relatively inexpensive as it uses the least number of functions i.e. one contraction per orbital, to describe the orbitals. It does however, require considerable care in evaluating the contraction parameters.
Improvement of a minimal basis set is achieved by increasing the number of basis functions used to represent each orbital and are termed double-zeta (two contractions per orbital), and triple-zeta (three contractions) basis sets. We note that increasing the number of functions per orbital increases the time required for the overall calculation. However, since valence orbitals of atoms are generally of greater importance to chemical properties, increasing the number of functions per orbital is usually confined to the outer valence orbitals, which reduces the overall number of functions required. These representations are strictly not double-zeta, triple-zeta functions, but are known as split-valence functions, an example of which is 6-31G. Here, a contraction of six Gaussian primitives are used to represent the core orbitals, and then the valence orbitals are split, the inner valence orbital is a contraction of three Gaussian primitives, and the outer valence orbital one Gaussian primitive.

There is a limit to the number of functions the orbital can be represented by, and usually it is not plausible to go beyond a triple-zeta function. Further improvement on the basis set is attained by adding polarisation functions, which acts to increase the angular momentum quantum number, for example, by adding p-type functions to hydrogen and d-type functions to the first row atoms. Addition of these usually unoccupied orbital functions contributes further flexibility to the basis set, necessary when an atom or ion is placed in a field as for a molecular, or more particular crystalline, environment. The addition of a * to the basis set label, i.e. 6-31G* indicates the inclusion of polarisation functions on non-hydrogens.
3.4 HARTREE-FOCK THEORY

The Hartree-Fock approximation is central to many approaches of finding and describing approximate solutions to the electronic Schrödinger equation. It also provides a suitable starting point for more sophisticated solutions. The ground state of an N-electron system can be described by a single Slater determinant,

$$\Psi = | \phi_1, \phi_2, \ldots, \phi_n |$$  \hspace{1cm} (3.12)

with orthonormal spin orbitals $\phi_n$. This represents the simplest anti-symmetric wavefunction, with the lowest possible energy being the expectation value (variation principle) of the Hamiltonian:

$$E_0 = \int \Psi^* H \Psi \delta \tau$$  \hspace{1cm} (3.13)

By minimising $E_0$ with respect to the choice of spin orbitals we obtain the Hartree-Fock equation, which determines the optimal spin orbitals $\chi$,

$$f(i) \chi(i) = e \chi(i)$$  \hspace{1cm} (3.14)

where $f(i)$ is an effective one electron operator called the Fock operator. It is the sum of a core Hamiltonian operator $h(i)$ and an effective one electron potential called the Hartree-Fock potential $V^{HF}(i)$. The core Hamiltonian $h(i)$ represents the kinetic and potential energy for attraction to the nuclei of a single electron,
and $\mathcal{V}^{HF}(i)$ represents the Coulomb and exchange operators for electron-electron interaction,

$$\mathcal{V}^{HF} = \sum J_b(i) - K_b(i)$$  \hspace{1cm} (3.16)$$

In an exact theory, the Coulomb interaction is simply the two electron operator $1/r_{ij}$. In Hartree theory, it is represented by a Hartree product wavefunction rather than an antisymmetrized (Slater determinant) wavefunction. The Coulomb operator $J_b(i)$ is, therefore, a one electron operator that is the total averaged potential acting on an electron, arising from the presence of all other (N-1) electrons.

The exchange term $K_b(i)$ arises from the antisymmetric nature of the single determinant. It does not have a simple interpretation but represents the interaction of two electrons in the 'exchange' charge distribution i.e. correlation energy for electrons of same spin.

The Fock operator thus takes the form,

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \mathcal{V}^{HF}$$  \hspace{1cm} (3.17)$$
where $V^{\text{HF}}(i)$ is the average potential (Coulomb and exchange) experienced by the $i$-th electron due to the presence of all other electrons. The essence of the Hartree-Fock approximation is to replace the complicated many electron problem by a one electron problem, in which electron-electron interaction is treated in an average manner.

3.4.1 Self Consistent Field (SCF) Calculations

The Hartree-Fock equation is not strictly an eigenvalue equation, since the Hamiltonian $h(i)$ is a function of the unknown spin orbitals. Thus the Hartree-Fock equation is non linear and must be solved iteratively. The procedure for solving the Hartree-Fock equation can be summarised as,

\[ \ldots \phi^n(i) \rightarrow h(i) \rightarrow \phi^{n+1}(i) \rightarrow h^{n+1}(i) \ldots \]  

and is called the Self Consistent Field (SCF) method. Solution starts by making an initial guess at the spin orbitals, which then allows the average field as seen by each electron to be calculated. Subsequently the eigen-equation can be solved, which leads to a new set of spin orbitals, and thus a new eigen-equation. The procedure is repeated until the solution is self consistent; that is, until the fields no longer change and the calculated eigenfunctions are the same.

The result is a set of orthonormal Hartree-Fock, $N$ occupied spin orbitals, and an infinite number of virtual (unoccupied) spin orbitals. In practice a finite set of basis
functions is used, the larger and more complete the set of functions the lower will be the expectation value of the energy. Larger and larger basis sets will reduce the energy further, until we reach the 'Hartree-Fock limit.' We should note that the limit reached is not the energy corresponding to an exact solution of the Schrödinger equation, but is a limit of the Hartree-Fock Hamiltonian (approximation).

3.4.2 Constrained and Extended Hartree-Fock

Assumptions are commonly made which simplify the calculation and interpretation of the wavefunctions, which lead to constraints being placed on the form of the wavefunction and thus effect the eigenfunctions/values. The restricted Hartree-Fock (RHF) model assumes double occupancy and a symmetry constraint, that implies that the orbitals occur in sets of spatially degenerate symmetrical orbitals. A totally symmetric contribution is made to the Hartree-Fock operator, when every member of the set is singly occupied and is associated with the same spin $\alpha$ or $\beta$. When associated with both $\alpha$ and $\beta$ spin factors the corresponding degenerate orbitals are said to form a shell, and when every orbital is doubly occupied the shell is said to be closed.

These assumptions constrain the spatial description of a $1s\,\alpha$ electron to be identical to that of a $1s\,\beta$ electron. The $1s\,\alpha$ electron will interact with other $\alpha$ electrons (Coulomb and exchange operators) but only by Coulomb interaction with $\beta$ electrons and visa versa (Pauli principle). Unrestricted Hartree-Fock (UHF) techniques remove the
constraint by using different orbitals for the different spin factors (α or β), which results in a lower energy solution to the problem.

3.4.3 Electron Correlation

The Hartree-Fock method is in modern work often used as a starting point to more accurate solutions of the Schrödinger equation. An eigenvalue of the non relativistic Hamiltonian is divided into two parts. Firstly the Hartree-Fock energy, and secondly a part which adds a correction term related to electron correlation. The energy for such a system would be,

$$ E = E^{\text{HF}} + E^C $$

(3.19)

where $E$ is the total non relativistic energy, $E^{\text{HF}}$ is the Hartree-Fock energy, and $E^C$ is the correlation energy. As $E^{\text{HF}}$ is an upper bound to the exact ground state energy the correlation energy will be negative. The more accurate the Hartree-Fock energy the smaller will be the correlation term. Nevertheless, the correlation term is often of the same order of magnitude as the chemical energies of interest, and so forms a vital part of the calculation. The correlation energy will contain contributions which, could be obtained by the relaxation of the double occupancy and symmetry constraints (similar to UHF). For example, for the 1s ground state of helium, the RHF wavefunction is,

$$ \Psi_{\text{RHF}} = | 1s \alpha, 1s \beta | $$

(3.20)
Both electrons occupy the same spatial orbital, and the probability of finding either electron at a position \((r)\) is independent of the position of the other electron. Obviously, this is incorrect, as Coulomb repulsion between the electrons will affect their positions, the consequence of which is to reduce the probability of finding an electron at \((r)\) as the other electron approaches the same position.

There are two main effects incorporated into this: the radial correlation, whereby the electrons have a tendency to be at different distances from the nucleus, and secondly, angular correlation, whereby the electrons have a tendency to be on opposite sides of the nucleus. Due to the Pauli principle the wave function vanishes when two electrons with like spins approach the same position in space, which is already accounted for in the Hartree-Fock approximation. Therefore, the greater part of the correlation energy is associated with electrons having opposite spins.

There are several methods available for the calculation of the correlation energy. Perhaps the most simple method conceptually, but not computationally, is the method of configuration interaction (CI). Once we have obtained a single determinant wavefunction, for example by solution of the Hartree-Fock problem, we may now construct determinantal wavefunctions, other than the Hartree-Fock function, by replacing one or more of the occupied spin orbitals by virtual spin orbitals. In full CI a trial wavefunction is used, where all the orbitals are substituted, and unknown coefficients are then determined by the variational method. A complete basis set would, therefore, give the exact energies of all the states in the system (ground and
excited). However, in practice, the length of the CI expansion is truncated leading to a more approximate solution.

A different procedure for calculating the correlation energy, and the one of use in this study, is perturbation theory. Here, the difference between the 'exact' model, as represented by the Hamiltonian $H$, and the Hartree-Fock model is treated as a perturbation on the Hartree-Fock model. The theorem was originally developed by Rayleigh and Schrödinger, but was first applied to $N$ electron systems, using Hartree-Fock as the zeroth order operator, by Möller and Plesset [104]. Therefore, it is often known as Möller Plesset perturbation theory, a good review of which is given by Hehre et al [105].

The basic assumption is that the energy and wavefunction for the perturbed state may be expanded as power series in $\lambda$ about the energy and wavefunction of the unperturbed state. The Hamiltonian ($H$),

$$H = H_0 + \lambda V$$  \hspace{1cm} (3.21)

where $H_0$ is the unperturbed operator, $V$ is the perturbation (of the property of interest e.g. energy or wavefunction) and $\lambda$ is the ordering parameter. The eigenvalues and eigenfunctions are therefore,

$$E = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ....$$

$$\Psi = \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} ....$$  \hspace{1cm} (3.22)
where $E_i^{(n)}$ is the n-th order eigenvalue, and $\Psi_i^{(n)}$ the n-th order eigenfunction. Providing $\lambda V$ is small enough we obtain a set of equations which can be solved in sequence to give progressively more accurate solutions to the Schrödinger equation.

3.4.4 Cluster Methods

A limiting factor for these quantum mechanical calculations, is the availability of suitable computing facilities. Restrictions are imposed on the calculations due to the excessive amount of CPU time and memory required for quantum mechanical calculations. It is not feasible to attempt to model every ion in a periodic system, as for a crystal, using a full quantum mechanical description.

One solution is to use cluster calculations where a small number of ions are modelled explicitly using QM methods; with these ions then embedded into an array of point charges simulating the remainder of the crystal. These charges are situated at the relevant lattice sites of the crystal, and have the formal charge of the ion they represent. Charges at the surface of the array are adjusted, so that the cluster experiences an electrostatic field identical to that which would be produced by an infinite lattice, which is the essential role of the charge array. A schematic of this is shown in figure 3.2.

The calculations performed on the cluster will, therefore, produce results which are meaningful to the crystal as a whole, and not simply relevant to the cluster in question,
which means that once a suitable cluster has been chosen the results should be consistent with models where the entire crystal is considered explicitly.

Figure 3.2. Schematic representation of a cluster of ions, described using quantum mechanical methods, surrounded by an array of point charges representing the crystal environment.

Ab initio quantum mechanical cluster methods are used in Chapter 6 to model the diffusion of a proton in the LaBO$_3$ perovskite structured oxides. One of the properties we are interested in is the influence of the migrating proton on the charge of the lattice ions in close proximity. The charges of the ions in the cluster are calculated using a Mulliken population analysis [105,106], which involves a partitioning of the total
charge distribution into atomic orbital contributions, and can be used for any molecular wavefunction constructed from atomic orbitals centred on the nuclei. We note that there is no unique definition of charge, but the Mulliken method is widely used.

In conclusion, we have presented a brief outline of the QM methods employed, in Chapter 6, in the investigation of the energetics and mechanism of proton conduction in perovskite-structured oxides. We also note, that the Hartree-Fock molecular orbital method is not the only way of solving the Schrodinger equation, and we now give a short account of alternative procedures, namely Density Functional methods.

3.5 DENSITY FUNCTIONAL THEORY

These methods differ from those discussed above in that the energy of the system is written directly as a function of the electron density; they aim to obtain the variation in the local electron density $\rho(r)$ as a function of the nuclear co-ordinates. The fundamental basis of the approach is the theorem of Hohenberg and Kohn [107] which showed that the ground state energy of a system is a unique function of the electron density. The method has been widely applied to the study of perfect solids, and can give good values for the ground state properties of crystals, including structural, cohesive and lattice dynamical properties; further details of the method and applications are given in a review article by Cohen [108].
Chapter 4

DEFECT CHEMISTRY and

OXYGEN MIGRATION in LaBO$_3$

4.1 INTRODUCTION

4.1.1 LaBO$_3$ Structure and Potentials

4.2 INTRINSIC ATOMIC DEFECTS

4.2.1 Redox Processes

4.3 DOPANT SUBSTITUTION

4.2.1 Oxidation of Doped LaBO$_3$

4.2.2 Dopant-Vacancy Clusters

4.3 OXYGEN ION MIGRATION

4.3.1 Migration Mechanism and Energetics

4.3.2 Variation in Ion Size

4.4 CONCLUSIONS
4.1 INTRODUCTION

It is recognised that the defect chemistry and the facile diffusion of oxygen are vital in controlling the physical properties (e.g. electrical conductivity, catalytic activity) of LaBO$_3$ (where B = Cr, Mn, Fe, Co) perovskite structured oxides. Consequently, the importance of understanding the defect and ion transport behaviour in these oxides, as well as their fuel cell and catalyst applications, has resulted in numerous studies [16,22-34,40-44,109-115].

The properties of the LaBO$_3$ oxides are sensitive to oxygen deficiency and the A-site composition. Studies on these materials show that the oxygen vacancy concentration in the pure oxides is small, even at sufficiently low oxygen activity, as the native non-stoichiometric defects are cation vacancies (oxygen excess) and electron holes [3,23,43]. Oxygen defects are, however, much more mobile than cation species, and therefore, ionic conductivity is enhanced by increasing the oxygen vacancy concentration, which is achieved by the partial substitution of the La$^{3+}$ site with low-valent cations (e.g. Sr$^{2+}$). This type of 'acceptor' doping leads to charge-compensation by an increase in the valence of the B-site transition-metal (as positive holes) and/or by the formation of oxygen vacancies. The predominant disorder is largely a function of the oxygen partial pressure with the concentration of oxygen vacancies and, therefore, the oxygen ion conductivity, increasing with decreasing Po$_2$. 
Clearly, the role of defects and dopants, as well as the nature of redox reactions to create electronic (hole) species are crucial to the fundamental understanding of the behaviour of the LaBO$_3$ materials. We attempt to shed light on these problems by using atomistic simulation techniques which are now well established tools in solid state chemistry. We focus on doped materials in which there is, as noted, enhanced hole formation with an increase in the oxygen vacancy concentration, and oxygen transport. In particular, we examine the mechanism of oxygen diffusion, as well as the relationship between the ion size and the activation energy for oxygen migration, a key problem in the design of new materials with improved performance.

4.1.1 LaBO$_3$ Structure and Potentials

The short-range potential parameters assigned to each ion-ion interaction were derived, using the procedures outlined in Chapter 2, by empirical fitting to observed structural properties. The LaBO$_3$ compounds adopt the ideal cubic perovskite structure (shown in figure 4.1) at the elevated temperatures at which diffusion experiments are normally carried out. As shown in figure 4.1, La occupies the cube corners, B the body centre and O the face centres of the unit cell, in which, the La ion is in a 12 co-ordinate cubo-octahedral site, and B an octahedral position. The structure can also be related to the corner sharing network of BX$_6$ octahedron of ReO$_3$, with the La and O ions forming a close packed arrangement in the {111} plane.
For all four compounds considered, namely \( \text{LaCrO}_3 \), \( \text{LaMnO}_3 \), \( \text{LaFeO}_3 \) and \( \text{LaCoO}_3 \), the potential parameters for the \( \text{La}^{3+}..\text{O}^{2-} \) and \( \text{O}^{2-}...\text{O}^{2-} \) interactions were fitted simultaneously resulting in a common set of interatomic potentials. This approach enables some information concerning the curvature of the energy surface to be included and has the added advantage of improved transferability.

The methodology of fitting to multiple lattices has been implemented in the program GULP [75], the potentials and shell model parameters used in this study are listed in table 4.1. We note that our pair-potentials were found to be more appropriate for the present study than the alternative set reported recently by Bush et al [78]; their potentials, although excellent for modelling perfect lattices of metal oxides, are found to be less suitable to simulation of defects in the \( \text{LaBO}_3 \) systems.
Table 4.1. Interatomic potentials for the LaBO$_3$ perovskites.

(i) Short-range

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>$\rho$ (Å)</th>
<th>C (eVÅ$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$...O$^{2-}$</td>
<td>1545.21</td>
<td>0.3590</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr$^{3+}$...O$^{2-}$</td>
<td>1690.90</td>
<td>0.3010</td>
<td>0.0</td>
</tr>
<tr>
<td>Mn$^{3+}$...O$^{2-}$</td>
<td>1267.50</td>
<td>0.3214</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe$^{3+}$...O$^{2-}$</td>
<td>1156.36</td>
<td>0.3299</td>
<td>0.0</td>
</tr>
<tr>
<td>Co$^{3+}$...O$^{2-}$</td>
<td>1329.82</td>
<td>0.3087</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^{2-}$...O$^{2-}$</td>
<td>22764.3</td>
<td>0.1490</td>
<td>43.0</td>
</tr>
</tbody>
</table>

(ii) Shell model$^a$

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (e)</th>
<th>k (eVÅ$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>-0.25</td>
<td>145.0</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.97</td>
<td>67.0</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>3.00</td>
<td>95.0</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>4.97</td>
<td>304.7</td>
</tr>
<tr>
<td>Co$^{3+}$</td>
<td>2.04</td>
<td>196.3</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>-2.39</td>
<td>42.0</td>
</tr>
</tbody>
</table>

$^a$Y and k refer to the shell charge and harmonic force constant respectively

Note: Potential Cut off = 12.0Å; Region I = 250 ions
Prior to carrying out the defect calculations, the unit cell dimensions and ion positions are equilibrated under constant pressure conditions. The calculated bond distances and lattice parameters, and their comparison with experimental values are listed in tables 4.2 and 4.3. Examination of the differences shows a good agreement between observed and simulated structures. Unfortunately, there are no additional experimental data on dielectric and elastic properties which would be useful for further validation and refinement of the potential model.

Table 4.2. Calculated and experimental bond distances.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Distance</th>
<th>expt (Å)</th>
<th>calc (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO₃</td>
<td>La...O</td>
<td>2.7393</td>
<td>2.7394</td>
</tr>
<tr>
<td></td>
<td>Cr...O</td>
<td>1.9370</td>
<td>1.9370</td>
</tr>
<tr>
<td></td>
<td>O...O</td>
<td>2.7393</td>
<td>2.7394</td>
</tr>
<tr>
<td>LaMnO₃</td>
<td>La...O</td>
<td>2.7605</td>
<td>2.7605</td>
</tr>
<tr>
<td></td>
<td>Mn...O</td>
<td>1.9520</td>
<td>1.9520</td>
</tr>
<tr>
<td></td>
<td>O...O</td>
<td>2.7605</td>
<td>2.7605</td>
</tr>
<tr>
<td>LaFeO₃</td>
<td>La...O</td>
<td>2.7761</td>
<td>2.7761</td>
</tr>
<tr>
<td></td>
<td>Fe...O</td>
<td>1.9630</td>
<td>1.9630</td>
</tr>
<tr>
<td></td>
<td>O...O</td>
<td>2.7761</td>
<td>2.7761</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>La...O</td>
<td>2.7011</td>
<td>2.7029</td>
</tr>
<tr>
<td></td>
<td>Co...O</td>
<td>1.9100</td>
<td>1.9113</td>
</tr>
<tr>
<td></td>
<td>O...O</td>
<td>2.7011</td>
<td>2.7029</td>
</tr>
</tbody>
</table>
Table 4.3. Calculated and experimental [116] lattice parameters.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( a_0^{\text{exp}} ) (Å)</th>
<th>( a_0^{\text{calc}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO(_3)</td>
<td>3.874</td>
<td>3.874</td>
</tr>
<tr>
<td>LaMnO(_3)</td>
<td>3.904</td>
<td>3.904</td>
</tr>
<tr>
<td>LaFeO(_3)</td>
<td>3.926</td>
<td>3.926</td>
</tr>
<tr>
<td>LaCoO(_3)</td>
<td>3.820</td>
<td>3.823</td>
</tr>
</tbody>
</table>

4.2 INTRINSIC ATOMIC DEFECTS

Initial calculations were performed on the energies of isolated point defects (vacancies and interstitials) for the four compounds LaCrO\(_3\), LaMnO\(_3\), LaFeO\(_3\), and LaCoO\(_3\), with the results presented in table 4.4. For vacancies, the energy corresponds to removing a lattice from the perfect crystal to infinity; likewise, the interstitial energy corresponds to introducing an ion from infinity into the perfect lattice. We note that the most stable interstitial site in the LaBO\(_3\) lattice, in relation to figure 4.1, was found to be at (1/2,0,0), and the energies reported in table 4.4 are for ions placed at this site. Also it is important to stress that all calculations employed full lattice relaxation around the defect in the energy minimisation procedure, as discussed in Chapter 2.

Combination of isolated point defect energies with the appropriate lattice energies, allows the calculation of formation energies for Schottky and Frenkel disorder. These disorders are represented by the reactions, shown in equations 4.1 to 4.6, using Kroger-
Vink notation. Formation energies for Schottky-type and Frenkel disorders are reported in table 4.5.

Table 4.4. Calculated energies of isolated point defects.

<table>
<thead>
<tr>
<th>Defect</th>
<th>LaCrO$_3$</th>
<th>LaMnO$_3$</th>
<th>LaFeO$_3$</th>
<th>LaCoO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>42.21</td>
<td>41.93</td>
<td>41.58</td>
<td>42.82</td>
</tr>
<tr>
<td>B$^{3+}$</td>
<td>59.06</td>
<td>57.80</td>
<td>56.43</td>
<td>60.10</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>18.33</td>
<td>17.85</td>
<td>16.84</td>
<td>19.31</td>
</tr>
<tr>
<td>Interstitial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>-25.67</td>
<td>-23.74</td>
<td>-25.97</td>
<td>-21.83</td>
</tr>
<tr>
<td>B$^{3+}$</td>
<td>-46.52</td>
<td>-40.96</td>
<td>-41.66</td>
<td>-41.76</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>-11.76</td>
<td>-11.51</td>
<td>-11.99</td>
<td>-10.50</td>
</tr>
</tbody>
</table>

Reactions representing Schottky-type and Frenkel disorder,

Schottky-type disorder:

$$\text{La}_{\text{La}}^x + \text{B}_{\text{B}}^x + 3\text{O}_0^x \leftrightarrow \text{V}_{\text{La}}^{\text{III}} + \text{V}_{\text{B}}^{\text{III}} + 3\text{V}_0^{\text{**}} + \text{LaBO}_3 \quad (4.1)$$

$$2\text{La}_{\text{La}}^x + 3\text{O}_0^x \leftrightarrow 2\text{V}_{\text{La}}^{\text{III}} + 3\text{V}_0^{\text{**}} + \text{La}_2\text{O}_3 \quad (4.2)$$

$$2\text{B}_{\text{B}}^x + 3\text{O}_0^x \leftrightarrow 2\text{V}_{\text{B}}^{\text{III}} + 3\text{V}_0^{\text{**}} + \text{B}_2\text{O}_3 \quad (4.3)$$
Frenkel disorder:

\[
\begin{align*}
\text{La}^{x}_{\text{La}} & \leftrightarrow V^{\text{III}}_{\text{La}} + \text{La}^{\text{+++}}_{i} \quad (4.4) \\
\text{B}^{x}_{\text{B}} & \leftrightarrow V^{\text{III}}_{\text{B}} + \text{B}^{\text{+++}}_{i} \quad (4.5) \\
\text{O}^{x}_{\text{O}} & \leftrightarrow V^{\text{++}}_{\text{O}} + \text{O}^{\text{++}}_{i} \quad (4.6)
\end{align*}
\]

where the symbols indicate the type of defect, i.e. V for vacancy, i for interstitial and the superscripts, • (positive), / (negative) indicate the charge of the defect relative to the normal site.

The calculated formation energies, presented in table 4.5 for all LaBO$_3$ systems, clearly show the most favourable intrinsic disorder is of the La$_2$O$_3$ Schottky-type, which is consistent with available experimental results, where Tofield and Scott [109] observed, from structure refinement data, the elimination of La$_2$O$_3$ in LaMnO$_3$. However, this elimination process was not detected in subsequent neutron diffraction studies and was, therefore, attributed to extremely low defect concentrations, as is suggested by the magnitude of our calculated formation energies. Other experimental results [23,43] also report that the concentration of intrinsic disorder is small.

The relatively high formation energies for Frenkel disorder are consistent with previous observation of the defect structure, where interstitial formation was believed to be unfavourable due to the close packed LaBO$_3$ perovskite structure.
Table 4.5. Calculated formation energies for intrinsic disorder.

<table>
<thead>
<tr>
<th>Disorder*</th>
<th>LaCrO₃</th>
<th>LaMnO₃</th>
<th>LaFeO₃</th>
<th>LaCoO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky-type</td>
<td>2.91</td>
<td>2.72</td>
<td>2.00</td>
<td>3.55</td>
</tr>
<tr>
<td>LaBO₃ (4.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La₂O₃ (4.2)</td>
<td>2.42</td>
<td>2.02</td>
<td>1.28</td>
<td>3.26</td>
</tr>
<tr>
<td>B₂O₃ (4.3)</td>
<td>3.27</td>
<td>3.42</td>
<td>4.97</td>
<td>4.01</td>
</tr>
<tr>
<td>Frenkel</td>
<td>8.27</td>
<td>9.10</td>
<td>7.81</td>
<td>10.50</td>
</tr>
<tr>
<td>La (4.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B (4.5)</td>
<td>6.27</td>
<td>8.42</td>
<td>7.39</td>
<td>9.17</td>
</tr>
<tr>
<td>O (4.6)</td>
<td>3.29</td>
<td>3.17</td>
<td>2.43</td>
<td>4.41</td>
</tr>
</tbody>
</table>

A further point to be taken from these results is the effect of the B-site cation on the formation energies. Although, the magnitude of the formation energies for the intrinsic disorder models are dependent upon the nature of the B-site cation, the trends in stability between the different disorder reactions are very similar.

4.2.1 Redox Processes

The LaBO₃ perovskite structured oxides exist in three states, oxygen deficient, stoichiometric, and oxygen excess; in which the oxygen content is a function of temperature and oxygen partial pressure [23,43,111]. The defect chemistry of LaBO₃...
has, therefore, been the subject of extensive study, for example a recent series of studies by van Roosmalen et al [23] has investigated several aspects of LaMnO$_{3+\delta}$.

We use lattice simulations to model the non-stoichiometric behaviour of LaBO$_3$. Our approach is similar to that used previously for transition metal oxides, and the oxide superconductors [57,117,118]. Calculations are first performed on the hole centres (B$^{4+}$, O$^-$), and the defect electron (B$^{2+}$) substitutionals. Short-range interactions for the hole and electron species are derived using the shifted electron-gas procedure outlined in Chapter 2. The change in Coulombic forces are effected by altering the shell charge of the ions; a full list of these potentials is reported in Appendix A. All calculations are performed including full relaxation around the defect; the resulting energy, therefore, corresponds to a small polaron, where the electronic defect is localised and self trapped by its own polarisation field. To estimate the polaron energy, the appropriate ionisation or electron affinity energy [119] is added to the lattice energy term. The energies for these electronic defects are presented in table 4.6.

We note that in Appendix B, we investigate the second-electron affinity for oxygen in the perovskite structure, and calculate an energy of 10.30eV, which is used in evaluating our oxidation/reduction energies. In addition, there were problems with modelling LaCrO$_3$, in particular the calculation of the Cr$^{4+}$ hole energy which will have an effect upon the results, dependent on this term.
Table 4.6. Formation energies for electronic defects.

<table>
<thead>
<tr>
<th>Defect</th>
<th>LaCrO$_3$</th>
<th>LaMnO$_3$</th>
<th>LaFeO$_3$</th>
<th>LaCoO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}^{2+}$ electron ($e'$)</td>
<td>2.87</td>
<td>0.04</td>
<td>2.68</td>
<td>0.70</td>
</tr>
<tr>
<td>$\text{B}^{4+}$ hole ($h^*$)</td>
<td>1.69</td>
<td>4.33</td>
<td>3.28</td>
<td>3.11</td>
</tr>
<tr>
<td>$\text{O}^-$ hole ($h^*$)</td>
<td>3.85</td>
<td>4.79</td>
<td>4.05</td>
<td>4.20</td>
</tr>
</tbody>
</table>

The oxidation/reduction reactions, presented in the following equations, represent the defect models which lead to the formation of non-stoichiometric compounds:

(i) oxidation to form holes ($h^*$) with oxygen interstitial compensation (oxygen excess compound).

$$ \frac{1}{2} \text{O}_2 (g) \rightarrow \text{O}^{2+} + 2h^* $$  \hspace{1cm} (4.7)

(ii) oxidation to form holes ($h^*$) with cation vacancy compensation (metal deficient compound). Note that the compound can be deficient in La or B cations.

$$ \frac{1}{2} \text{O}_2 (g) \rightarrow \frac{2}{3} \text{V}_{\text{La}}^{\text{III}} + 2h^* + \frac{1}{3} \text{La}_2\text{O}_3 $$  \hspace{1cm} (4.8)

(iii) reduction to form electron states ($e'$) with oxygen vacancy compensation (oxygen deficient compound).

$$ \text{O}_0 \rightarrow \frac{1}{2} \text{O}_2 (g) + V_{\text{O}}^{**} + 2e' $$  \hspace{1cm} (4.9)
(iv) reduction to form electron states \( e' \) with cation interstitial compensation (metal excess compound). Note that the compound can have La or B excess.

\[
\text{B}_B + O_0 \rightarrow \frac{1}{2} O_2 (g) + \frac{2}{3} \text{B}_i^{***} + 2e' \\
(4.10)
\]

(v) disproportionation of transition metal ion.

\[
2\text{B}^{3+} \rightarrow \text{B}^{2+} + \text{B}^{4+} \\
(4.11)
\]

The energies for these reactions are listed in Table 4.7 and are derived using the relevant defect energies and intra-atomic energy terms.

Table 4.7 Calculated energies for oxidation/reduction processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Energy (eV)</th>
<th>LaCrO₃</th>
<th>LaMnO₃</th>
<th>LaFeO₃</th>
<th>LaCoO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O excess (4.7)</td>
<td>3.03</td>
<td>8.56</td>
<td>5.98</td>
<td>7.13</td>
<td></td>
</tr>
<tr>
<td>La deficient (4.8)</td>
<td>0.50</td>
<td>5.59</td>
<td>3.26</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>B deficient (4.8)</td>
<td>2.23</td>
<td>7.92</td>
<td>5.31</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td><strong>Reduction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O deficient (4.9)</td>
<td>12.66</td>
<td>6.52</td>
<td>10.79</td>
<td>9.30</td>
<td></td>
</tr>
<tr>
<td>La excess (4.10)</td>
<td>19.65</td>
<td>15.27</td>
<td>19.07</td>
<td>17.87</td>
<td></td>
</tr>
<tr>
<td>B excess (4.10)</td>
<td>15.25</td>
<td>12.05</td>
<td>16.46</td>
<td>14.84</td>
<td></td>
</tr>
<tr>
<td><strong>Disproportionation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{B}^{3+} \rightarrow \text{B}^{2+} + \text{B}^{4+} ) (4.11)</td>
<td>4.56</td>
<td>4.37</td>
<td>5.96</td>
<td>3.81</td>
<td></td>
</tr>
</tbody>
</table>
Owing to the uncertainties in the free ion terms, we must be cautious in giving detailed interpretations. Nevertheless, the calculated energies for the oxidation/reduction reactions show oxidation, with cation vacancy compensation, to be the most favourable process, which is in accord with experimental results [23,43,109]. The magnitude of these energies indicates that the deviation from stoichiometry will be small, which is also in accord with experiment where it is known that these materials are largely resistant to oxidation/reduction; this resistance being an important factor in their technological applications.

4.3 DOPANT SUBSTITUTION

It has been established that the addition of dopant ions to the LaBO$_3$ oxides is crucial to promoting catalytic activity and high conductivity [1,3,14]. These materials are commonly 'acceptor' doped with low-valent cations (e.g. Sr$^{2+}$) which substitute for La$^{3+}$; this reduction of the effective valence of the A site cations leads, as argued above, to the formation of a compensating population of oxygen vacancies at low oxygen partial pressures. The increased oxygen vacancy concentration gives rise to the observed high ionic conductivity. The corresponding substitution reaction can be represented by the following defect equation for alkaline-earth dopants:

$$\text{MO} + \text{La}_\text{La}^+ \rightarrow \text{M}_{\text{La}}^\prime + \frac{1}{2}\text{V}_0^{**} + \frac{1}{2}\text{La}_2\text{O}_3$$  \hspace{1cm} (4.12)
where \( M_{La}^{'} \) represents the dopant substitution. Alkali-metal doped \( \text{LaBO}_3 \) lead to exsolved dopant oxide, which may 'poison' the oxide surface, effectively reducing catalytic activity, as has been suggested for \( \text{La}_2\text{O}_3 \) [61,118]. Therefore, we also investigate alkali-metal substitution, which can be represented by the following reaction:

\[
\frac{1}{2} M_2\text{O} + \text{La}^{x}_{La} \rightarrow M^{''}_{La} + V^{**}_O + \frac{1}{2}\text{La}_2\text{O}_3 \quad (4.13)
\]

The energies of these 'solution' reactions can be evaluated by our simulation approach in which we combine appropriate defect and lattice energy terms.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{Mg}^{2+} )</th>
<th>( \text{Ca}^{2+} )</th>
<th>( \text{Sr}^{2+} )</th>
<th>( \text{Ba}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LaCrO}_3 )</td>
<td>4.35</td>
<td>1.06</td>
<td>0.37</td>
<td>3.97</td>
</tr>
<tr>
<td>( \text{LaMnO}_3 )</td>
<td>4.20</td>
<td>0.73</td>
<td>-0.02</td>
<td>3.53</td>
</tr>
<tr>
<td>( \text{LaFeO}_3 )</td>
<td>3.92</td>
<td>0.35</td>
<td>-1.17</td>
<td>2.31</td>
</tr>
<tr>
<td>( \text{LaCoO}_3 )</td>
<td>4.60</td>
<td>1.54</td>
<td>1.18</td>
<td>5.26</td>
</tr>
</tbody>
</table>

We note that the interatomic potentials for the dopant species are exactly those of the corresponding binary metal oxides [76], as they are consistent with our potentials and
have been successfully applied to similar studies of dopant substitution in the YBa$_2$Cu$_3$O$_7$ superconductor [54,55] and the La$_2$O$_3$ methane coupling catalyst [118].

Our calculated energies of solution for alkaline-earth dopants are presented in table 4.8 and are also shown as a function of ion radius in figure 4.2. Examination of the results reveals that the most favourable solution energy and hence the highest solubility is predicted for Sr$^{2+}$ in all the LaBO$_3$ hosts. The relatively high solubility of Sr$^{2+}$ in LaBO$_3$ is clearly illustrated in figure 4.2 which shows a strong correlation between the solution energy and the dopant size with a minimum at Sr$^{2+}$ (close to the La$^{3+}$ radius of 1.06 Å).

![Figure 4.2. Energies of solution (La site) for alkaline-earth dopants, as a function of dopant radius (lines are guides to the eye).](image)

Our results accord well with experimental studies which have demonstrated how the addition of Sr (and, to a lesser extent, Ca) leads to an increase in the oxygen diffusion
coefficient [1,3] and to high catalytic activity [8,14,22]. The calculations also show that solution of MgO and BaO is appreciably endothermic, in line with the observed low solubility.

The correlation between dopant size and solution energy is further shown by our results for substitution of the smaller B-site cation; the results for alkaline-earth dopants at the B-site are reported in table 4.9. For the larger dopant ions (Ca, Sr and Ba) substitution at the B-site is shown to be highly unfavourable, whereas, the smaller Mg ion preferentially substitutes at the B-site.

Table 4.9. Energies of solution for alkaline-earth dopants
(substituting for B) with oxygen vacancy compensation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Sr$^{2+}$</th>
<th>Ba$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$_3$</td>
<td>2.67</td>
<td>4.23</td>
<td>7.42</td>
<td>13.01</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>2.36</td>
<td>4.32</td>
<td>4.98</td>
<td>12.92</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>0.44</td>
<td>1.20</td>
<td>3.23</td>
<td>7.77</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>3.11</td>
<td>5.07</td>
<td>7.60</td>
<td>13.29</td>
</tr>
</tbody>
</table>

The results for the alkali-metal dopants, presented in figure 4.3, show that in general, the solution energy of alkali ions in LaBO$_3$ is appreciably less favourable than the alkaline-earth ions, in line with their observed low solubility. This is in agreement with
the idea that the properties of alkali-metal doped LaBO₃ are associated with exsolved dopant oxide, thus poisoning the oxide surface.

![Figure 4.3. Energies of solution (La site) for alkali-metal dopants, as a function of dopant radius.](image)

Perhaps, the most important conclusion of this section is, however, provided by the results summarised in table 4.8 showing that Sr-solubility in LaBO₃ oxides is expected to be high owing to the low heat of solution of SrO in these materials. Moreover, the solution of Sr will enhance oxygen diffusion owing to the increase in the concentration of oxygen vacancies.

### 4.2.1 Oxidation of Doped LaBO₃

It is generally believed that the catalytic behaviour and the oxygen transport through fuel cell materials are partly controlled by the exchange between gas-phase oxygen and
lattice oxygen of the doped LaBO\textsubscript{3} systems. The defect reaction responsible for this process involves the filling of oxygen vacancies by molecular oxygen to form electronic holes; such an oxidation reaction involves the dissociation of O\textsubscript{2} and can be written as,

\[ V_0^{\text{**}} + \frac{1}{2} O_2 (g) \rightarrow O_0^\text{=} + 2h^*, \quad (4.14) \]

We note that the oxygen vacancies have already been introduced into the lattice by dopant (e.g. Sr\textsuperscript{2+}) substitution. Our studies have favoured (on energetic grounds) B\textsuperscript{4+} holes in LaBO\textsubscript{3} (where B = Cr, Mn, Fe and Co). Indeed, an important aspect of the behaviour of several perovskites arises from the fact that a transition metal ion at the B site can readily change its oxidation state. This often allows the reversible addition and removal of oxygen, which enables the oxide to act as an oxygen store in catalytic reactions. The energies of the oxidation reaction (4.14) were calculated for all four systems and are reported in table 4.10.

Due to uncertainties in the precise hole energies it is difficult to make detailed conclusion, however, the results do indicate trends and lead to two main points. First, oxidation of the doped LaCrO\textsubscript{3} and LaCoO\textsubscript{3} is exothermic indicating a thermodynamically favourable reaction. Thus, except at low oxygen partial pressures, we would expect holes (B\textsuperscript{4+}) to predominate over vacancies and that oxidation will enhance the solubility of the dopant in the host. These results are consistent with experimental findings [1] which show mixed (electronic and ionic) conductivity and that the p-type conductivity increases with increasing oxygen activity.
Table 4.10. Calculated energies of oxidation reaction (4.14) in doped compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$_3$</td>
<td>-3.54</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>2.22</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>1.13</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>-1.68</td>
</tr>
</tbody>
</table>

In addition, recent structural studies of La$_{0.5}$Sr$_{0.5}$CoO$_3$ have found evidence for ordering effects involving both Co$^{4+}$ and oxygen vacancies [120]. Secondly, we calculate an endothermic energy for LaMnO$_3$ and LaFeO$_3$ but significantly less favourable than that for LaCrO$_3$ or LaCoO$_3$. While no measured values are available for direct comparison, these results are consistent with isotope experiments that find a sign difference in oxygen exchange behaviour (kinetics) between LaCoO$_3$ and LaMnO$_3$ [30]. It has been noted previously by Steele et al [1,30] that a key factor is the relative "redox stability" of the transition metal cation occupying the B-site, where the stability of Mn$^{3+}$ is inherently greater than of Co$^{3+}$. Our oxidation energies are in accord with this trend in stability. In this context, it is also interesting to note that LaCoO$_3$ exhibits the highest catalytic activity of these systems [7,8,14], and may be attributed to the relative ease of oxidation with the creation of Co$^{4+}$. 
Our analysis has included all the key terms in the solution and redox processes. There are, however, uncertainties in the absolute values due to the free-ion energies employed. However, our concern here is to understand how hole species may form; for this task our modelling methods have proved to be reliable. We should note that redox reactions involving oxygen vacancies in other oxide materials (for example, CeO$_2$ and La$_2$O$_3$) are found to be more favourable at the surface than in the bulk, which is an obvious topic for further study.

4.2.2 Dopant-Vacancy Clusters

It is well established that for the fluorite-structured ion conductors, such as Y doped CeO$_2$, the conductivity is controlled by the extent of dopant-vacancy interactions [121,122]. These can be described in terms of formation of simple pair clusters for low dopant concentrations, which add a binding energy term to the Arrhenius energy of the ionic conductivity. Both experiment and calculations have shown that the elastic strain interaction between the dopant and the oxygen vacancy is at least as important as the electrostatic term [25,121,122].

Consequently, we have considered pair, and neutral (trimer) defect clusters, as shown in figure 4.4, in the LaBO$_3$ systems, comprised of nearest-neighbour dopant substitutionals and oxygen vacancies. We have already found the solution of Sr more favourable than other cations; moreover, Sr is the most commonly used dopant for the LaBO$_3$ hosts. We will, therefore, focus our attention on the formation of $\text{Sr}_{\text{La}}-\text{V}_{\text{O}}$ clusters. The
calculated binding energies with respect to the component isolated defects are reported in table 4.11.

![Figure 4.4. Schematic of defect clusters: Sr substitutes for La (Sr_La) and □ represents an oxygen vacancy (V_o).](image)

The results reveal that the clusters are bound only in the LaCoO_3 material (LaCrO_3 exhibits a negligible binding energy for cluster i) which would inhibit the oxygen mobility in this system, and the neutral trimer, cluster (i), is shown to be the most favourable of the configurations. However, these results suggest that, with the exception of LaCoO_3, there will be little tendency towards clustering at low dopant concentrations, although it is possible that other types of aggregate could have greater stability. We note that our calculated oxygen migration energies, presented in the next section, accord well with the experimental activation energies. This may indicate that binding energy terms are not significant in these materials at low dopant content, a view that is consistent with our cluster calculations.
It is interesting to note that we find a strong correlation between the binding energy and the calculated static dielectric constant which suggests that, as expected, dielectric screening effects are important. The most favourable binding energy is calculated for LaCoO$_3$ which also has the lowest value for the dielectric constant (table 4.11).

Table 4.11. Binding energies for defect clusters, and calculated static dielectric constants.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cluster / Binding energy (eV)</th>
<th>static dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pair</td>
<td>trimer (i)</td>
</tr>
<tr>
<td>LaCrO$_3$</td>
<td>0.03</td>
<td>-0.03</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>0.35</td>
<td>0.27</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>1.10</td>
<td>0.62</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>-0.19</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

*refer to figure 4.4 for schematic of cluster.

While we have included all of the key terms we should note, however, that there are uncertainties in the absolute values of the binding energies due to their sensitivity to the choice of O-O potential parameters. However, our main concern here is to understand how defect clusters may form; for this task our modelling procedures have proved to be reliable.
4.3 OXYGEN ION MIGRATION

4.3.1 Migration Mechanism and Energetics

Although, as noted, there have been several reports on oxygen diffusion in LaBO$_3$ materials [25-34] the amount of information on migration activation energies and fundamental mechanistic features is rather limited. It is generally accepted that oxygen diffusion is based on rapid transport of vacancies which migrate by a conventional hopping mechanism, although this has not been confirmed by experiment.

We have investigated these problems by an extensive search of the potential energy surface. The energy profiles are mapped out by calculating the defect energy of the migrating ion along the diffusion path, and allowing relaxation of the lattice at each position. In this way the saddle-point configuration can be identified from which the energy barrier to migration is derived. An example of an energy profile is shown in figure 4.5. The resulting activation energies are reported in table 4.12 together with the available values from experiment.

Examination of the results confirms migration of oxygen ion vacancies as the lowest energy path. Indeed, vacancy migration is further verified by additional defect calculations which find high energy barriers (>1.5 eV) to interstitial migration. For comparison, the corresponding energy for interstitial migration in fluorite-structured
ThO$_2$ is about 0.9 eV [45,121]. Hence our results confirm that ion diffusion in perovskite-type LaBO$_3$ arises from mobility of oxygen ion vacancies.

![Energy profile for vacancy migration between nearest-neighbour anions in LaMnO$_3$. The x-scale indicates equidistant positions along the migration path.](image)

Figure 4.5. Energy profile for vacancy migration between nearest-neighbour anions in LaMnO$_3$. The x-scale indicates equidistant positions along the migration path.

The calculated values, for vacancy migration, accord well with experimental activation energies, although direct comparison is not straightforward since the observed values show significant variation. This scatter may reflect differences in experimental conditions and oxygen stoichiometry, as well as problems with phase purity. We should note that the calculated energies in table 4.12 relate to intrinsic migration of oxygen defects and do not include formation or association energy terms, a point which was discussed previously.
Table 4.12. Migration Activation Energies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{calc}}$ (eV)</th>
<th>$E_{\text{expt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$_3$</td>
<td>0.48</td>
<td>--</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>0.86</td>
<td>0.73$^a$</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>0.50</td>
<td>0.77±0.25$^b$</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>0.61</td>
<td>0.62±0.21$^c$, 0.78±0.22$^d$</td>
</tr>
</tbody>
</table>

$^a$Belzner et al [28]. $^b$Ishigaki et al [27]. $^c$Carter et al [30]. $^d$Ishigaki et al [26].

An important result of our search of the potential energy surface is that we find a small deviation from the direct path for vacancy migration; this is shown schematically in figure 4.6 and as a contour map in figure 4.7.

Figure 4.6. Schematic representation of the curved path for oxygen migration.
It has commonly been assumed that the migrating ion takes a direct linear path long the <110> edge of the BO₆ octahedron into an adjacent vacancy, for which the saddle-point is located midway between the two anion sites. However, the calculations reveal a curved route with the saddle-point away from the neighbouring B site cation resulting in a significantly lower energy barrier to oxygen migration.

Figure 4.7. Contour plot (contours are ≈0.2eV apart) of the potential energy surface for oxygen vacancy migration, showing the curved path between adjacent anion sites of a BO₆ octahedron.
The magnitude of the deviation, from a straight path, for each LaBO$_3$ compound is shown in figure 4.8 and listed in table 4.13. A clear trend with B site radius does not emerge partly due to the small range of cation sizes investigated. Nevertheless, the greatest deviation corresponds to the largest cation at the B site.

Figure 4.8. Migration energy as a function of the ion position normal to the mid-point of a linear path between nearest-neighbour anions.

Table 4.13. Deviation from direct linear path for vacancy migration.

<table>
<thead>
<tr>
<th>Compound</th>
<th>B radius (Å)$^a$</th>
<th>Deviation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO$_3$</td>
<td>0.63</td>
<td>0.42</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>0.65</td>
<td>0.43</td>
</tr>
<tr>
<td>LaFeO$_3$</td>
<td>0.65</td>
<td>0.43</td>
</tr>
<tr>
<td>LaCoO$_3$</td>
<td>0.61</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$^a$Shannon and Prewitt [123].
In the saddle-point configuration, the migrating ion must pass through the opening of a triangle defined by two A site (La$^{3+}$) ions and one B site ion (figure 4.9). Clearly the repulsive interactions can be reduced by the outwards movement of the nearest cations.

![Figure 4.9. Saddle-point configuration for oxygen ion migration, indicating the cation relaxation.](image)

The simulation approach is able to model lattice relaxation and generate valuable information on local ion movements. It is also worth recalling that ionic polarisability has been treated in our simulations by the shell model. From our analysis we find average displacements of the La$^{3+}$ and B$^{3+}$ ions of 0.08Å and 0.07Å respectively, away from the mobile oxygen ion (shown in figure 4.9). These results emphasise that neglecting lattice relaxation effects at the saddle-point may be a serious flaw in previous ion size approaches based on a rigid hard-sphere model, in which the 'critical radius' of the opening is derived [44].
4.3.2 Variation in Ion Size

It is clear that the radius ratio of the A to B cations in the perovskite structure is an important factor in controlling ionic conductivity. A simple geometric analysis of the saddle-point configuration, as illustrated by figure 4.9, has been employed before in the context of defining selection criteria for good ion conductors [44]. Here we further examine the relationship between migration energy and cation size using our simulation procedure.

Our approach is to change systematically our interatomic potential model so as to calculate the vacancy migration energy as a direct function of the ionic size of the A and B cations. To model ion-size changes we vary the exponential Born-Mayer function which enables the short-range repulsive energy to be related to ionic radii, as suggested by Fumi and Tosi [124]. The form of the potentials are as follows:

\[
A_{A-O} = a \cdot \exp\left(\frac{r_A + r_o}{\rho}\right) \\
A_{B-O} = a \cdot \exp\left(\frac{r_B + r_o}{\rho}\right)
\]  

(4.15)  
(4.16)

where \(A_{A-O}\) and \(A_{B-O}\) are the pre-exponential parameters of the short-range potential for the A and B cation to anion interactions; \(r_A\), \(r_B\) and \(r_o\) are the ionic radii of the A cation, B cation and oxygen ion respectively, and \(a\) is a scaling parameter. Using these potentials we were able to calculate the migration energies of the vacancy jump for a range of A and B cation radii, which are illustrated in figure 4.10. The starting point in
each case corresponds to the parameters for the LaMnO$_3$ system where the size of A is varied with B fixed at the Mn$^{3+}$ radius (0.65 Å) and similarly, the size of B is varied with the A value set at La$^{3+}$ (1.06 Å).

Figure 4.10. Calculated migration energy as a function of cation size; (a) the A site (b) the B site.
The results indicate two main points. First, the calculations exhibit a clear trend towards lower migration energies with smaller A site cations. There is an optimum value of about 0.95 Å below which the migration energy rises steeply. This result is in accord with the limited amount of experimental evidence and with results of similar calculations on lanthanide aluminates (LnALO$_3$) [25]. Second, as is evident from figure 4.10 (b), there is a decrease in energy with increasing size of the B cation with a minimum at 0.75 Å. However, the plot also shows a discontinuity at about 0.55 Å. A likely explanation is that this reflects the B cation size approaching the tolerance limit for a stable perovskite structure. Indeed, lattice dynamics (using the GULP [75] code) calculations are consistent with this view as they reveal the presence of negative phonon frequencies at this point which indicates a structural instability.

It is well established that simple geometrical limits for cation radii on the A and B sites can be defined by the so-called Goldschmidt Tolerance Factor [16] given by:

$$ t = \frac{(r_A + r_O)}{\sqrt{2}} \left( \frac{r_B + r_O}{r_A + r_O} \right) $$

(4.17)

where we note that, nominally, the perovskite structure is stable for $1.0 > t > 0.75$. To assess our results further, we consequently examined the relationship between the tolerance factor and our calculated migration energies. The results are illustrated in figure 4.11. As can be seen, a degree of correlation exists with a clear minimum at $t = 0.81$. Using ionic radii from Shannon and Prewitt [123] we derive, for example, a $t$ value of 0.85 for LaMnO$_3$ which is the most commonly used cathode material in fuel
cell technology. Our calculations, therefore, suggest that materials with a $t$ value of about 0.81 may lead to lower migration energies and faster diffusion, a result with practical consequences for oxidation catalysis and for operating fuel cells at lower temperatures and at higher rates. By using the same set of radii we find that this value of the tolerance factor would encompass various perovskite electrolytes such as PrMnO$_3$ and GdMnO$_3$, as well as NdGaO$_3$. Indeed, a recent study by Ishihara et al [32] reported high levels of oxygen diffusion in Ga-doped NdAlO$_3$.

![Figure 4.11. Calculated migration energy as a function of the tolerance factor (from both A and B site simulations).](image)

We can attempt to rationalise our results in terms of lattice relaxation effects. As the mobile oxygen ion approaches the saddle-point it must pass through the centre of a triangle of cations (shown in figure 4.9). Our calculations have already shown that the
repulsive overlap interactions can be reduced by the outwards relaxation of these cations. It appears, that the minimum in the tolerance factor corresponds to the most effective balance of the relaxation of the A and B cations at the saddle-point position. In other words, the even distribution of relaxation between the cations is an important factor for low energy barriers to oxygen ion migration.

4.4 CONCLUSIONS

The present chapter demonstrates how computer modelling techniques can be used to examine the defect chemistry and oxygen transport properties in perovskite-type oxides, that are relevant to their use in oxidation catalysis, fuel cells, and separation membranes. It is clear that analogous modelling procedures could be applied to other non-stoichiometric systems, including the oxides of the general formula ABO$_3$,$_5$. The following conclusions have emerged from our discussion:

1. The concentration of intrinsic disorder in these materials is small, and they are found to be resistant to oxidation and reduction. This is in direct agreement with experiment and supports their application in harsh operating environments.

2. The most favourable dopant substitution is predicted for Sr$^{2+}$ in all the LaBO$_3$ hosts, which accords well with observation. The creation of oxygen vacancies by such doping suggests that the net flux of oxygen through the solid will be
high. In addition, the binding energies indicate that there is little tendency toward cluster formation except for LaCoO$_3$.

(3) We find clear trends between the calculated solution energies and the dopant size with minima near the La$^{3+}$ radius. However, the relatively unfavourable energies for alkali-metal dopants in LaBO$_3$ suggest that their properties are associated with exsolved dopant oxide.

(4) The simulations have examined the oxidation reaction in which molecular oxygen is incorporated into the lattice at oxygen sites to form hole species. The oxidation energies are found to be relatively favourable for all four systems, with an exothermic energy for LaCrO$_3$ and LaCoO$_3$. It is worth noting that LaCoO$_3$ is observed to exhibit the highest catalytic activity of these materials which may be related to the ease of oxidation and oxygen exchange.

(5) Oxygen diffusion is mediated by hopping of oxygen-ion vacancies along the anion octahedron edge, but not in a linear fashion; rather migration takes place via a curved path, resulting in a significantly lower energy barrier. Our calculated migration energies are in accord with the available experimental data.

(6) The calculations demonstrate the importance of lattice relaxation effects at the migration saddle-point, which were previously neglected by the ion size arguments based on a simple hard sphere approach.

(7) Finally, we find a clear trend toward lower migration energies with smaller A site cations and larger B site cations. The calculations also exhibit a strong relationship between our calculated migration energy and the perovskite tolerance factor, with a minimum at around $t=0.81$. 
Chapter 5

MD STUDIES of OXYGEN DIFFUSION in LaBO$_3$

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5.1 INTRODUCTION

The method of molecular dynamics (MD) was originally developed for the simulation of liquids [125], but in recent years has found extensive application in the field of solid state chemistry [51, 56, 60, 126-129]. MD studies have been complementary to the static lattice simulations by providing valuable information on the mechanisms of diffusion in a range of materials, especially fast-ion conductors such as Li₃N [126], Na β-Al₂O₃ [127] and CaF₂ [128]. Whereas, static lattice methods are used to probe the energetics and pathway of a single migrating ion, MD can view the time evolution of the whole system. The temperature and concentration of charge carriers are important aspects of ion diffusion in perovskite oxides, and these factors can be investigated through the use of MD; the results obtained from such a study are also directly comparable to experimental diffusion data. The use of MD to study oxygen ion diffusion in perovskite oxides is, therefore, a natural progression from the static lattice simulations.

5.2 SIMULATION MODEL

In the present simulations a supercell is constructed of 8x8x8 perovskite unit cells, approximately 30Å in dimension, and containing 2560 ions. This cell is repeated using periodic boundary conditions (PBC) to generate an unbounded system with no surfaces and, as with most simulations to date, the interactions are treated using a rigid ion model. Four systems were studied, chosen in relation to available diffusion data; these
were $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (where $x=0.2$ and 0.5), and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (where $x=0.1$ and 0.2). The rigid ion potentials were derived by empirical methods to be compatible with the shell model potentials, and are given in table 5.1.

An initial study was performed using static lattice calculations with these rigid ion potentials for direct comparison with the shell model results (table 5.2). Obviously it is not possible to reproduce the perfect lattice properties that are dependent solely upon polarisability effects ($\varepsilon_{\infty}$), but where direct comparison is possible there is good accord between the two sets of potentials. In particular, we note the good agreement between the oxygen migration activation energy calculated using the shell model and rigid ion potentials.

The MD simulations were performed under conditions of constant pressure and temperature (NPT ensemble), using the method of Berendsen [89]. The pressure was set to 1 atm, and the temperature varied between simulations from 800 to 2000K. We should note that simulations were performed at temperatures below 800K, but even after extended run times they generated unsatisfactory statistics, probably due to insignificant levels of diffusion at these temperatures. In most cases the simulations were run for a total period of 10ps, with the system allowed to equilibrate in the first 4ps. The time step ($\delta t$) was 1fs ($1x10^{-15}$s), therefore, a 10ps run would consist of a total of 10,000 iterations. The data collected for subsequent analysis was over a period of 6ps, which was found to be satisfactory for simulations at these temperatures.
### Table 5.1. Rigid ion interatomic potentials used in the MD study.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Short-range rigid ion parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A) (eV)</td>
</tr>
<tr>
<td>(\text{Co}^{3+}...\text{O}^{2-})</td>
<td>636.35</td>
</tr>
<tr>
<td>(\text{La}^{3+}...\text{O}^{2-})</td>
<td>1516.30</td>
</tr>
<tr>
<td>(\text{Mn}^{3+}...\text{O}^{2-})</td>
<td>1235.87</td>
</tr>
<tr>
<td>(\text{O}^{2-}...\text{O}^{2-})</td>
<td>22764.3</td>
</tr>
<tr>
<td>(\text{Sr}^{2+}...\text{O}^{2-})</td>
<td>774.18</td>
</tr>
</tbody>
</table>

### Table 5.2. Properties calculated using the shell model, and rigid ion potentials.

<table>
<thead>
<tr>
<th>Property</th>
<th>(\text{LaCoO}_3)</th>
<th>(\text{LaMnO}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shell</td>
<td>Rigid ion</td>
</tr>
<tr>
<td>Lattice energy (eV)</td>
<td>-143.07</td>
<td>-139.74</td>
</tr>
<tr>
<td>Lattice parameter (\text{\AA})</td>
<td>3.823</td>
<td>3.820</td>
</tr>
<tr>
<td>(C_{11}) (dyne/cm²)</td>
<td>41.81</td>
<td>34.68</td>
</tr>
<tr>
<td>(\varepsilon_o)</td>
<td>22.99</td>
<td>22.95</td>
</tr>
<tr>
<td>(\varepsilon_{\infty})</td>
<td>2.35</td>
<td>---</td>
</tr>
<tr>
<td>(E_{\text{act}}) (eV)</td>
<td>0.62</td>
<td>0.67</td>
</tr>
</tbody>
</table>

\(^*\)Activation energy for oxygen ion migration.

\(^*\)Negative curvature in minimisation.
5.3 UNDOPED PEROVSKITE OXIDES

Preliminary simulations were performed on the undoped perovskite oxides \( \text{LaMnO}_3 \) and \( \text{LaCoO}_3 \), at a temperature of 1000K. The results from these simulations were used to check the validity of the model, and to determine variable parameters in the dataset controlling the simulation, for example, Ewald parameters controlling the Coulombic summation. The time evolution of several physical properties during these simulations is presented in figure 5.1.

Examination of the results reveals that the temperature attains the predefined equilibrium value after a relatively short time span and deviates by only a small margin. Moreover, the mean values for all the calculated properties during the simulations are acceptable. The volume of the supercell increases during the equilibration period of the simulation, indicating an increase in the lattice parameter from the initial crystallographic value. It is noted that the interatomic potential parameters for the cubic structure are effectively derived at 0K, and so expansion of the material is expected at higher temperatures.

5.3.1 Structural Information

Structural information on the undoped \( \text{LaMnO}_3 \) and \( \text{LaCoO}_3 \) can be extracted using Radial Distribution Functions (RDF. The partial pair distribution function \( g(r) \), defined in Chapter 2, is calculated for like-like ion pairs, and shown in figures 5.2 and 5.3.
Figure 5.1. Time evolution of calculated properties (total energy, temperature, pressure and lattice parameter) for undoped LaMnO$_3$ at 1000K.
Figure 5.2. Radial distribution functions for undoped LaMnO$_3$. 
Figure 5.3. Radial distribution functions for undoped LaCoO$_3$. 
Examination of the cation-cation radial distribution functions reveals well defined peaks corresponding to the successive nearest neighbour distances with cubic symmetry. In addition, they fall to approximately zero between peaks, which is typical of an ordered solid. By contrast, the oxygen-oxygen pair functions for both undoped systems (LaMnO$_3$ and LaCoO$_3$) show weak structure which indicates loss of long-range order for the oxygen sublattice, which is probably a result of distortion of the oxygen octahedron arrangement, and not of oxygen diffusion.

Further evidence for possible distortion of the oxygen ion octahedron is found in the nearest-neighbour (nn) distances presented in tables 5.3 and 5.4. The La-O distances cover a wide range of values about a mean value roughly equivalent to the crystallographic (nn) distance, which is consistent with distortion of the anion octahedron.

Table 5.3. Calculated (from the MD simulation) and crystallographic nearest-neighbour distances, for undoped LaMnO$_3$.

<table>
<thead>
<tr>
<th>Ion pair</th>
<th>Calculated (Å)</th>
<th>Cryst. (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La...La</td>
<td>3.92</td>
<td>3.90</td>
</tr>
<tr>
<td>La...Mn</td>
<td>3.39</td>
<td>3.38</td>
</tr>
<tr>
<td>La...O</td>
<td>2.34 - 3.15</td>
<td>2.76</td>
</tr>
<tr>
<td>Mn...Mn</td>
<td>3.92</td>
<td>3.90</td>
</tr>
<tr>
<td>Mn...O</td>
<td>2.03</td>
<td>1.95</td>
</tr>
<tr>
<td>O...O</td>
<td>2.84</td>
<td>2.76</td>
</tr>
</tbody>
</table>
Table 5.4. Calculated (from the MD simulation) and crystallographic nearest-neighbour distances, for undoped LaCoO₃.

<table>
<thead>
<tr>
<th>Ion pair</th>
<th>Calculated (Å)</th>
<th>Cryst’ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La...La</td>
<td>3.87</td>
<td>3.82</td>
</tr>
<tr>
<td>La...Co</td>
<td>3.33</td>
<td>3.31</td>
</tr>
<tr>
<td>La...O</td>
<td>2.47 - 3.01</td>
<td>2.70</td>
</tr>
<tr>
<td>Co...Co</td>
<td>3.87</td>
<td>3.82</td>
</tr>
<tr>
<td>Co...O</td>
<td>1.94</td>
<td>1.91</td>
</tr>
<tr>
<td>O...O</td>
<td>2.48</td>
<td>2.70</td>
</tr>
</tbody>
</table>

5.3.2 Ion Displacement

The mean square displacements (MSD) for all the ions in both the undoped manganate and cobaltate systems are presented in figures 5.4 and 5.5.

Figure 5.4. Mean square displacements for undoped LaMnO₃ at 1000K.
Figure 5.5. Mean square displacements for undoped LaCoO$_3$ at 1000K.

The figures show that following equilibration the MSD of all the ions are constant with time. The results for the undoped perovskite oxides, therefore, indicate that there is no diffusion of any species through the lattice. Moreover, the pure stoichiometric materials i.e. systems without defects, would not exhibit ionic diffusion, which is consistent with their observed low ionic conductivities.

5.4 Sr-DOPED PEROVSKITE OXIDES

The preliminary MD study of the undoped perovskite oxides clearly shows that defects are essential for appreciable diffusion in these materials. As discussed in the previous chapter, these perovskites are 'acceptor' doped on the La$^{3+}$ site with aliovalent cations such as Sr$^{2+}$, leading to a compensating population of oxygen vacancies at low oxygen
partial pressures. Therefore, following the creation of the supercell for the perfect system, a set concentration of dopant ions are now introduced, with the corresponding number of oxygen ions removed for charge compensation.

The systems studied are La$_{1-x}$Sr$_x$MnO$_3$ ($x=0.2$, $0.5$) and La$_{1-x}$Sr$_x$CoO$_3$ ($x=0.1$, $0.2$) as they relate directly to available experimental data. First, the required number of La$^{3+}$ ions are replaced in a random fashion by the Sr$^{2+}$ ions, and then half this number of oxygen ions are removed. The simulations were performed at several temperatures ranging from 800 to 2000K for a total period of 10ps including 4ps equilibration. It would be desirable to run the simulations for longer periods but they are computationally demanding. Nevertheless, the linear nature of the MSD plots suggests that for the purpose of calculating diffusion coefficients, the present simulations are satisfactory.

5.4.1 Structural Information

The RDF for the oxygen pair functions calculated for both doped systems at 800 and 2000K are given in figures 5.6 and 5.7. The oxygen-oxygen pair functions again show weak structure at all temperatures indicating loss of long range order on the mobile oxygen sublattice. As the temperature increases to 2000K, the first peak decreases in height, while the general profile broadens indicating a greater degree of disorder (in addition to that normally observed) at higher temperatures associated with enhanced
oxygen diffusion. It is worth noting that this behaviour is also found for the oxygen-oxygen pair functions as a function of dopant concentration.

Figure 5.6. Oxygen-oxygen pair functions for La_{1-x}Sr_{x}MnO_{3}. 
Figure 5.7. Oxygen-oxygen pair functions for La$_{1-x}$Sr$_x$CoO$_3$.

The calculated nearest-neighbour distances for all the pair functions for these simulations at the highest and lowest temperatures, are given in table 5.4. As expected an increase in temperature results in an expansion of the cell due to an increase in the pressure exerted on the cell by the lattice ions.
Table 5.4. Nearest-neighbour separations (Å), for simulations performed at 800 and 2000K, for all systems.

(a) La$_{1-x}$Sr$_x$MnO$_3$

<table>
<thead>
<tr>
<th>Ion pair</th>
<th>La$<em>{0.8}$Sr$</em>{0.2}$MnO$_3$ 800K (temp)</th>
<th>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$ 800K (temp)</th>
<th>La$<em>{0.8}$Sr$</em>{0.2}$MnO$_3$ 2000K</th>
<th>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$ 2000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>La...La</td>
<td>3.89</td>
<td>3.94</td>
<td>3.87</td>
<td>3.89</td>
</tr>
<tr>
<td>La...Mn</td>
<td>3.38</td>
<td>3.40</td>
<td>3.35</td>
<td>3.38</td>
</tr>
<tr>
<td>La...O</td>
<td>2.39 - 3.20</td>
<td>2.41 - 3.25</td>
<td>2.38 - 3.10</td>
<td>2.39 - 3.15</td>
</tr>
<tr>
<td>Mn...Mn</td>
<td>3.92</td>
<td>3.94</td>
<td>3.87</td>
<td>3.89</td>
</tr>
<tr>
<td>Mn...O</td>
<td>1.98</td>
<td>2.00</td>
<td>1.96</td>
<td>1.98</td>
</tr>
<tr>
<td>O...O</td>
<td>2.84</td>
<td>2.86</td>
<td>2.81</td>
<td>2.84</td>
</tr>
</tbody>
</table>

(b) La$_{1-x}$Sr$_x$CoO$_3$

<table>
<thead>
<tr>
<th>Ion pair</th>
<th>La$<em>{0.9}$Sr$</em>{0.1}$CoO$_3$ 800K (temp)</th>
<th>La$<em>{0.8}$Sr$</em>{0.2}$CoO$_3$ 800K (temp)</th>
<th>La$<em>{0.9}$Sr$</em>{0.1}$CoO$_3$ 2000K</th>
<th>La$<em>{0.8}$Sr$</em>{0.2}$CoO$_3$ 2000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>La...La</td>
<td>3.85</td>
<td>3.87</td>
<td>3.83</td>
<td>3.85</td>
</tr>
<tr>
<td>La...Co</td>
<td>3.33</td>
<td>3.35</td>
<td>3.33</td>
<td>3.35</td>
</tr>
<tr>
<td>La...O</td>
<td>2.45 - 2.99</td>
<td>2.50 - 3.10</td>
<td>2.45 - 3.05</td>
<td>2.48 - 3.10</td>
</tr>
<tr>
<td>Co...Co</td>
<td>3.85</td>
<td>3.87</td>
<td>3.83</td>
<td>3.85</td>
</tr>
<tr>
<td>Co...O</td>
<td>1.94</td>
<td>1.94</td>
<td>1.89</td>
<td>1.89</td>
</tr>
<tr>
<td>O...O</td>
<td>2.75</td>
<td>2.77</td>
<td>2.75</td>
<td>2.77</td>
</tr>
</tbody>
</table>

Note: separations involving Sr are approximately equivalent to La.
Furthermore, there is a reduction in the cell dimension with an increasing level of dopant concentration, which is due to the loss of oxygen as the Sr dopant ion is of approximately the same ionic radii as the La ion. The reduction in cell size is most noticeable for the highly doped manganate system. A plot of the variation in unit cell size with respect to temperature and dopant concentration is given in figure 5.8. The creation of oxygen vacancies in these systems is, therefore, accompanied with a contraction of the lattice surrounding the vacant site.

![Figure 5.8. Variation in unit cell parameter with temperature and dopant concentration.](image)

5.4.2 Ion Displacement

Turning now to the dynamics of the ions, the mean square displacements (MSD) of all the host and dopant ions for all four doped systems at 2000K are shown in figures 5.9
and 5.10. We note that, the basic features of the plots are similar for all the temperatures considered, namely 800, 1000, 1200, 1500 and 2000K, although there is clearly a dependence of the oxygen diffusivity with temperature.

Figure 5.9. MSD of all ion species in La_{1-x}Sr_xMnO_3 at 2000K.
Examination of the results reveals that the cation function tends to a constant value which confirms that the cations do not diffuse. In contrast, the oxygen ion function increases with time, as expected for diffusing ions. Focusing on the anion sub-lattice, the MSD for the oxygen ions in the acceptor doped LaMnO$_3$ and LaCoO$_3$ systems over the wide range of temperatures studied are presented in figures 5.11 and 5.12.
Figure 5.11. Mean square displacements of oxygen ions for La$_{1-x}$Sr$_x$MnO$_3$

($x = 0.2, 0.5$), calculated at temperatures 800 to 2000K.
Figure 5.12. Mean square displacements of oxygen ions for La$_{3-x}$Sr$_x$CoO$_3$

($x = 0.1, 0.2$), calculated at temperatures 800 to 2000K.
From the slope, we obtain the oxygen diffusion coefficient \( D_o \) according to the Einstein relation:

\[
\langle r_0(t)^2 \rangle = B_o + 6D_o t ,
\]  

(5.1)

where \( B_o \) is the thermal (Debye-Waller) factor arising from atomic vibrations. The diffusion coefficients derived from these plots are given in tables 5.5 and 5.6, where they are compared with results obtained from diffusion experiments.

**Table 5.5. Calculated rates of diffusion for \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \).**

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>( D_o ) (( \text{cm}^2 \text{s}^{-1} ))</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x=0.2 )</td>
<td>( x=0.5 )</td>
<td>Experimental*</td>
</tr>
<tr>
<td>800</td>
<td>( 1.51 \times 10^{-8} )</td>
<td>( 5.32 \times 10^{-8} )</td>
<td>( 1.0 \times 10^{-7} - 3.8 \times 10^{-7} ) (973K)</td>
</tr>
<tr>
<td>1000</td>
<td>( 6.23 \times 10^{-8} )</td>
<td>( 1.48 \times 10^{-7} )</td>
<td>( 1.7 \times 10^{-7} - 6.5 \times 10^{-7} ) (1033K)</td>
</tr>
<tr>
<td>1200</td>
<td>( 1.08 \times 10^{-7} )</td>
<td>( 5.52 \times 10^{-7} )</td>
<td>( 7.4 \times 10^{-7} - 1.2 \times 10^{-6} ) (1133K)</td>
</tr>
<tr>
<td>1500</td>
<td>( 4.21 \times 10^{-7} )</td>
<td>( 9.17 \times 10^{-7} )</td>
<td>-----</td>
</tr>
<tr>
<td>2000</td>
<td>( 3.41 \times 10^{-6} )</td>
<td>( 9.25 \times 10^{-6} )</td>
<td>-----</td>
</tr>
</tbody>
</table>

*Belzner *et al [28], results for \( \text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \) at temperatures stated.

The calculated diffusion coefficients for the manganate system are in good agreement with the experimental results of Belzner *et al* [28], though the calculated results for the cobaltate system are an order of magnitude greater to those obtained by Carter *et al* [30]. Nevertheless, the MD simulations clearly show the greater mobility of oxygen
ions in the cobaltate system in comparison to the manganate system, which is consistent with the experimental diffusion data. Moreover, the diffusion coefficients for both doped LaMnO$_3$ and LaCoO$_3$ indicate the high mobility of oxygen ion, which is of importance for their fuel cell and catalytic applications.

Table 5.6. Calculated rates of diffusion for La$_{1-x}$Sr$_x$CoO$_3$.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$D_0$ (cm$^2$ s$^{-1}$)</th>
<th>Experimental$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x=0.1$</td>
<td>$x=0.2$</td>
</tr>
<tr>
<td>800</td>
<td>$1.47\times10^7$</td>
<td>$1.92\times10^7$</td>
</tr>
<tr>
<td>1000</td>
<td>$3.02\times10^7$</td>
<td>$4.05\times10^7$</td>
</tr>
<tr>
<td>1200</td>
<td>$4.83\times10^7$</td>
<td>$1.12\times10^6$</td>
</tr>
<tr>
<td>1500</td>
<td>$2.03\times10^7$</td>
<td>$3.65\times10^6$</td>
</tr>
<tr>
<td>2000</td>
<td>$3.61\times10^6$</td>
<td>$1.25\times10^5$</td>
</tr>
</tbody>
</table>

$^*$Carter et al [30], results for La$_{0.8}$Sr$_{0.2}$CoO$_3$ at stated temperatures.

The calculated diffusion coefficients also suggest that the doped LaCoO$_3$ system would give higher levels of oxygen ion conductivity for use in SOFC. However, the doped LaMnO$_3$ system is preferred owing to greater stability in the operating environment [2,130]. Nevertheless, an important point which can be drawn from the MD simulations, is the need to create higher vacancy concentrations in the manganate system to enhance the rate of anion diffusion.
The MD simulations show that the diffusion takes place by a conventional 'hopping' mechanism involving discrete jumps of the oxygen ions, which allows us to evaluate an activation energy for oxygen migration using the standard Arrhenius relation,

\[ D = A \exp \left( \frac{-E_{\text{act}}}{kT} \right) \]  

(5.2)

where \( D \) is the diffusion coefficient, \( E_{\text{act}} \) the activation energy, \( k \) the Boltzmann constant, and \( A \) a pre-exponential factor. Figures 5.13 and 5.14 show the Arrhenius plots for the manganate and cobaltate systems, on which the experimental diffusion coefficients are also included. The activation energies can be derived from the slope of these plots and are presented in table 5.7. It should be noted that these values were derived from the higher temperature simulations (excluding the 800K simulation) due to better statistics.

Figure 5.13. Arrhenius plot for La\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x=0.2, 0.5), with comparable experimental data.
Figure 5.14. Arrhenius plot for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.1, 0.2$), with comparable experimental data.

The Arrhenius plots for the manganate systems further demonstrate the good agreement between the calculated and experimental diffusion coefficients, both in their magnitude and in their function of temperature dependence. The results for the cobaltate system confirm the difference in magnitude between the calculated and experimental diffusion coefficients, but clearly show consistency in the temperature dependence, and hence, activation energies. Indeed, the calculated activation energies accord well with the experimental values, presented in table 5.7.

The dopant concentration, which directly determines the population of anion vacancies, has a direct effect upon the activation energy. An increase in dopant concentration for the manganate system leads to an increase in the rates of diffusion and a decrease in the activation energy.
By contrast, an increase in the activation energy is found at higher dopant levels for the cobaltate system, which suggests the formation of defect clusters. Indeed, lattice simulations (presented in Chapter 4), found that (Sr$\text{La}^{\prime} - V_o^{-})$ clusters (pair and neutral) are bound only in the LaCoO$_3$ material with binding energies of -0.19 to -0.35eV. It is well established [121,122] that the aggregation of defects involving the migrating species, adds a binding energy term to the Arrhenius energy of the ionic conductivity. Our binding energy for the cobaltate system is consistent with the variation in activation energies between the two doped cobaltate (La$_{0.9}$Sr$_{0.1}$CoO$_3$ and La$_{0.8}$Sr$_{0.2}$CoO$_3$) systems.

Table 5.7 Calculated and experimental activation energies for oxygen ion migration.

<table>
<thead>
<tr>
<th>System</th>
<th>Activation energy (eV)</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$MnO$_3$</td>
<td>0.70</td>
<td>0.70*</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$</td>
<td>0.67</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.9}$Sr$</em>{0.1}$CoO$_3$</td>
<td>0.51</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.8}$Sr$</em>{0.2}$CoO$_3$</td>
<td>0.59</td>
<td>0.62±0.2*</td>
<td></td>
</tr>
</tbody>
</table>

*Blezner et al [28]  
*# Carter et al [30]
5.4.3 Migration Mechanism

A significant thrust of basic transport studies has been the determination of the atomistic mechanisms controlling bulk transport phenomena. Detailed examination of the individual configurations of the simulations allows us to extract information concerning the mechanism of oxygen ion migration. During the progress of a simulation a vast amount of information is produced, so we concentrate on two simulations: the $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ performed at 1000K. From these simulations we focus on a box containing approximately 70 ions, and animate the motion of the ions using the Insight II package [131].

Analysis of the trajectory information using animation confirmed the existence of extensive motion of the oxygen sub-lattice, as already indicated by the MSD and RDF results. In contrast, the cation motion is restricted to a small volume about their lattice sites, verifying the retention of an ordered crystal structure as shown by the RDF. The animations also confirm the distortion of the anion octahedron due to the motion of the oxygen ions. The distortion is particularly apparent in close proximity to a vacant site, where all neighbouring oxygen ions are drawn towards the vacancy, probably due to both elastic and Coulombic interactions.

Anion diffusion occurs by discrete hops of oxygen ions to neighbouring vacant sites with no indication of correlated motion. Figure 5.15 shows a schematic representation of the migration of an oxygen ion as simulated using MD.
From our analysis of the saddle point position, we find significant outward relaxation of the cations away from the mobile oxygen ion. The pathway is along the edge of an anion octahedron, passing through a saddle point position defined by three cations, as previously shown in figure 4.9. Moreover, the migration pathway observed in the MD simulations is in direct agreement with the pathway calculated using the static lattice simulations. The motion of all ion species, within a specified volume of the simulation 'box', can be presented two-dimensionally by way of 'scatter' plots. We should note that the plots do not represent one single plane of the unit cell but the direction at which the cell is viewed, as shown in figure 5.16. The scatter plots given in figures 5.17, 5.18 and 5.19 show the position of the lattice ions for one unit cell every 10 time steps, over a period of 2ps, superimposed onto one figure. Therefore, a plot of the cation positions viewed into the x,y face would include all 9 cations from the three z planes of the unit cell.
Figure 5.16. Diagram illustrating the view presented in a scatter plot.

Figure 5.17. Scatter plot of cation positions for (a) La_{0.5}Sr_{0.5}MnO_{3} (b) La_{0.8}Sr_{0.2}CoO_{3}. Each point on the plot represents the position of a cation (as shown in the schematic); the box represents the unit cell.
The dense clustering of the points for the cation distributions verifies the comparatively small magnitude of vibration for these ions, with no evidence of diffusion. In contrast, the oxygen distributions are more diffuse, showing considerable motion of the oxygen ions.

Figure 5.17. Scatter plot of oxygen positions for La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\).

Each point on the plot represents the position of an oxygen ion (as shown in schematic); the box represents the unit cell.
Figure 5.18. Scatter plot of anion positions for La$_{0.8}$Sr$_{0.2}$CoO$_3$.

Each point on the plot represents the position of an oxygen ion (as shown in schematic); the box represents the unit cell.

The diffusion of an oxygen ion is illustrated by the spread of points between neighbouring lattice sites which occurs along the octahedron edge in only two directions, and thus confirming a planar migration pathway. The distortion of the
anion octahedron is also apparent by the diffuse distribution of all the oxygen ions, which is particularly marked in the plane of the migration pathway, and probably due to local relaxation about the vacancy.

A plot of the x,y,z co-ordinates of the migrating oxygen ion, for the manganate and cobaltate systems, are presented in figures 5.19 and 5.20. The migration shown for the manganate system occurs in the y-z plane, with the x co-ordinate invariant for the duration of the simulation. The hop occurs after approximately 0.6ps of the simulation and is immediately followed by a hop back to the original lattice site.

![Graph showing variation in x,y,z co-ordinates for the migrating oxygen ion in La₀.5Sr₀.5MnO₃.](image)

**Figure 5.20.** Variation in x,y,z co-ordinates for the migrating oxygen ion in La₀.5Sr₀.5MnO₃.

For the cobaltate system the migration shown occurs in the x-z plane after a period of 0.8ps, with no further hops observed (for these ions) for the remainder of the
simulation. In both cases, manganate and cobaltate, the hop from one site to the neighbouring site requires approximately 0.2 ps. However, it is also evident that the migrating oxygen ion is never situated exactly on the perfect lattice site, but occupies an off site position located towards the saddle point due to local relaxation about the oxygen vacancy.

Figure 5.20. Variation in x, y, z co-ordinates for the migrating oxygen ion in $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$.

5.5 CONCLUSIONS

The MD simulations accord with the static lattice calculations on oxygen ion migration, and several key points are evident:
(1) Oxygen ion diffusion is not observed in the undoped \( \text{LaMnO}_3 \) and \( \text{LaCoO}_3 \) materials, further demonstrating that interstitial migration is unfavourable.

(2) For the doped materials, the oxygen sub-lattice is shown to be highly mobile, with calculated diffusion coefficients indicating rapid diffusion. Furthermore, the rates of diffusion are in general accord with available oxygen diffusion data.

(3) Diffusion is shown to occur by a conventional hopping mechanism involving discrete jumps of the oxygen ions, with no indication of correlated motion.

(4) Calculated activation energies for anion migration are in excellent agreement with experiment.

(5) The migration pathway is shown to be along the edge of an anion octahedron and passing through a saddle point position defined by three cations.

Finally we note that the complementary use of static lattice and MD simulations can produce reliable and predictive information relating to ion diffusion in metal oxides.
Chapter 6

PROTONS in PEROVSKITE-STRUCTURED OXIDES

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6.5 CONCLUSIONS (162)
6.1 INTRODUCTION

High temperature proton conductors have a large potential for use in electrochemical processes such as fuel cells, steam electrolysis and hydrogen gas sensors [35-39]. Iwahara [36] first demonstrated the existence of proton conduction in ABO$_3$ perovskites; and several studies [36-39,132-140] have shown that many ABO$_3$ perovskite type oxides in particular those based upon cerates, zirconates (where A$^{2+}$ = Sr, Ba, Ca and B$^{4+}$ = Ce, Zr), and also KTaO$_3$, can possess appreciable levels of protonic conductivity. There is however, uncertainty surrounding the nature of the proton migration mechanism in these materials. This chapter will examine the fundamental features of proton conduction in oxides using a range of computational techniques. Our study will focus on 'LaBO$_3$' (B = trivalent cation) materials, where there has been work by Iwahara [141] investigating Ca-doped LaYO$_3$, and where recently Larring and Norby [142] have shown that under certain conditions LaErO$_3$ is a proton conductor.

As with other perovskites, doping is essential to the uptake of protons. Indeed it has been shown for some systems [136,143] that pure stoichiometric samples are not charged with protons. For LaBO$_3$ systems the La$^{3+}$ ion is commonly substituted by Sr$^{2+}$, resulting in charge compensating oxygen vacancies, represented in Kroger-Vink notation by the defect equation:

\[
\text{La}_{La} + \text{SrO} \rightarrow \text{Sr}_{La}^{'} + \frac{1}{2} V_{O}^{**} + \frac{1}{2} \text{La}_2\text{O}_3\quad (6.1)
\]
In the presence of water vapour these vacancies are readily filled by hydroxyl ions; the defect is described as a hydroxyl ion as the interstitial proton associates strongly with the neighbouring oxide ion. The water incorporation reaction can be described as follows:

\[ \text{H}_2\text{O}_\text{(g)} + V_{\text{O}_0}^* + O_{\text{O}_0}^x \rightarrow 2\text{OH}^* \]  

(6.2)

Improving our understanding of transport properties and the nature of proton migration have been the impetus behind many investigations [144-148]; this includes the study of the EMF in electrochemical cells and IR absorption measurements investigating isotope effects between proton and deuteron migration. The results have been interpreted in terms of the migration of the proton via hopping from one oxide ion to the next, although the exact mechanism is still uncertain.

The main objectives of this chapter are to study two specific problems by the use of contemporary computational techniques. First, the energetics of incorporating protons in the lattice and the position of this proton are investigated using atomistic simulation techniques; secondly, we study the mechanism and energetics of proton migration by quantum mechanical cluster calculations. Both techniques have been successfully applied to other related materials [52-56,93-96], although the present study presents the first detailed modelling study of the behaviour of protons in perovskite-structured oxides.
Finally, we present some experimental work using muon implantation techniques to investigate the site and mobility of a muon in perovskite type oxides. The chemical and physical characteristics of the muon are comparable to that of the proton and so these studies will aim to elucidate by way of experiment the properties we are trying to simulate.

6.2 ATOMISTIC SIMULATION OF PROTONS

Lattice simulations were employed to determine the orientation of the hydroxyl group in the high temperature cubic form of the perovskite LaMnO₃, as depicted in figure 6.1, potential parameters are those from table 4.1. In addition, the O-H interaction is modelled using an attractive Morse potential:

\[ V_{(O)} = D \{ 1 - \exp[-\beta(r - r_0)] \}^2 \]  

(6.3)

The parameters were developed by Saul et al [149] using *ab initio* quantum mechanical cluster calculations, with a point charge representation of the surrounding lattice; these parameters are presented in table 6.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( D ) (eV)</th>
<th>( \beta ) (Å⁻¹)</th>
<th>( r ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0525</td>
<td>2.1986</td>
<td>0.9845</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1. Parameters for the Morse potential of the O-H interaction.
Charges on the hydroxyl species were distributed across both ions to give an overall charge of -1 with O assigned -1.4263 and H +0.4263, which reproduces the correct dipole moment of the O-H group. We note that this charge distribution compares favourably with the QM results presented later.

6.2.1 O-H Configuration

As the incorporated protons are present as OH- centres, IR absorption due to O-H stretching modes provides direct evidence for the presence of protons in the lattice. It can also provide information regarding the orientation of the O-H group. Indeed several groups have used spectroscopic techniques to examine possible sites for the proton in perovskite oxides [139,150-153]. Kapphan [150] suggested there may be a need for a specific model for the O-H centre in each ABO₃ compound. These studies however have centred mainly upon the SrTiO₃, BaTiO₃ and KTaO₃ systems; there has been no similar study on LaMnO₃.

The results from previous work led to the identification of several possible orientations for the OH- ion. These positions are shown in figure 6.1, and indicated by the labels i-iv. The configurations relate to different positions of the proton in which (i) the proton lies between two neighbouring oxide ions of an octahedron, (ii) the proton is situated parallel to one of the <100> axes of the unit cell, (iii) the proton points along a <110> axes, (iv) the proton lies on the face of an anion octahedron. Our simulation techniques can be used to probe the proton position and determine the most
energetically favourable site(s) within LaMnO$_3$. Since there is no available experimental data for LaMnO$_3$ it was thought necessary to establish results for a perovskite system which could be directly compared to experimental data, and hence we also report results for SrTiO$_3$. The potential parameters for SrTiO$_3$ were taken from Ahktar [62].

![Cubic perovskite structure, with proton positions shown (i-iv).](image)

Figure 1. Cubic perovskite structure, with proton positions shown (i-iv).

Calculations (using the CASCADE code [83]) were first performed on the relative energies of each of the aforementioned OH configurations in LaMnO$_3$. This was carried out by fixing the proton in positions (i)-(iv) at various distances from the oxide ion, and the energy ($E_{OH}$) for each configuration evaluated allowing the remainder of the lattice to relax. The results from these calculations are presented in table 6.2 (region I size of 250 ions). The lowest energy orientation for the hydroxyl group in LaMnO$_3$ was calculated for configuration (ii) in which the proton lies along a $<100>$ axis of the
perovskite structure, with an equilibrium O-H distance of 0.94 Å. Our results in table 6.2 indicate the relative stability in order of increasing energy as (ii) < (i) < (iv) < (iii). It is noted that although the difference in energies between orientations (i) and (ii) is relatively small, the magnitude is still significant.

Table 6.2. Calculated values of $E_{\text{OH}}$ for the four O-H configurations (figure 6.1), in LaMnO$_3$ and SrTiO$_3$.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$E_{\text{OH}}$ (eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LaMnO$_3$</td>
</tr>
<tr>
<td>(i)</td>
<td>14.90</td>
</tr>
<tr>
<td>(ii)</td>
<td>14.53</td>
</tr>
<tr>
<td>(iii)</td>
<td>18.69</td>
</tr>
<tr>
<td>(iv)</td>
<td>16.40</td>
</tr>
</tbody>
</table>

*energies incorporate D parameter of Morse potential.

Similar calculations were carried out for SrTiO$_3$ (also given in table 6.2) and resulted in the order (i) < (ii) < (iv) < (iii). This relative stability is in accord with high resolution IR experiments on SrTiO$_3$ [151] that find a proton site comparable to that of configuration (i), which they term the octahedron model.
6.2.2 Energy of Incorporation

The calculations presented above were performed constraining the hydroxyl group to adopt configurations corresponding to models (i) to (iv) in figure 6.1. We now allow full relaxation of the OH group in order to obtain the optimum geometry which is used to calculate the energy of incorporation of water into the system ($E_{\text{react}}$) represented by equation (6.2). The results from these calculations on LaMnO$_3$ gave the minimised geometry for the hydroxyl group as shown in figure 6.2. This relaxed position lies between the two models (i) and (ii), with an O–H distance of 0.95 Å.

![Figure 6.2. Geometry optimised position for proton in the LaMnO$_3$ lattice, with comparison to configurations (i) and (ii).](image)

The energy for the incorporation of water into the acceptor-doped material ($E_{\text{react}}$) is evaluated using the following equation:

$$E_{\text{react}} = 2E_{\text{OH}} - E(V^{\ddagger \ddagger}_O) + E_{\text{PT}}$$  

(6.4)
where $E_{\text{OH}}$ is the energy associated with substitution by the hydroxyl group, $E_{V_o^-}$ the energy of an isolated oxygen vacancy, and $E_{\text{PT}}$ the energy of the hypothetical gas phase proton transfer reaction: $\text{O}^2^- + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$. This term can be estimated from the difference between the proton affinities of $\text{O}^2^-$ and $\text{OH}^-$ and is discussed in greater detail elsewhere [46,154]. We note that the proton affinity of $\text{O}^2^-$ is in turn estimated using a value for the second electron affinity of the oxygen atom ($E_{A2}$). These component energies and the calculated values of $E_{\text{react}}$ are given in Table 6.3.

Table 6.3. Terms used in the calculation of the energy of incorporation of water ($E_{\text{react}}$).

<table>
<thead>
<tr>
<th>Energy term</th>
<th>LaMnO$_3$</th>
<th>SrTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{OH}}$</td>
<td>14.37</td>
<td>14.61</td>
</tr>
<tr>
<td>$E(V_o^-)$</td>
<td>17.85</td>
<td>18.17</td>
</tr>
<tr>
<td>$E_{\text{PT}}$</td>
<td>-11.77</td>
<td>-11.77</td>
</tr>
<tr>
<td>$E_{\text{react}}$</td>
<td>-0.88</td>
<td>-0.72</td>
</tr>
</tbody>
</table>

The main uncertainty in evaluating $E_{\text{react}}$ is associated with $E_{\text{PT}}$ which as noted depends upon the second electron affinity energy for the oxygen atom. Harding and Pyper [155] have recently shown that the true second electron affinity of an oxide ion in a crystal is dependent upon both the chemical composition and the structure of the crystal. Therefore ab initio calculations have been performed to re-evaluate $E_{A2}$ for oxygen.
within the perovskite structure. Our approach is to calculate the difference in energy between an $O^-$ and $O^{2-}$ ion embedded in a point-charge array of lattice ions which represent accurately the electrostatic potential of the lattice. The calculations were performed at a high level of accuracy: open shell, SCF UHF with MP2 correlation and a high quality oxygen basis set (O 8-411G). The CADPAC [102] code was used for all these studies. Further details of our calculations of these electron affinity terms are reported in Appendix B.

EA$_2$ for oxygen within LaMnO$_3$ was calculated to be 10.30 eV, in contrast with the value of 8.27 eV based on the thermochemical data of Waddington [156]. This calculated value of EA$_2$ gives a figure of -11.77 eV for E$_{PT}$. The energy of incorporation of water (E$_{react}$) is then calculated to be negative and hence exothermic (see table 6.3); this clearly agrees with experimental data [35,136,142], showing that the dissolution of protons from a H$_2$O atmosphere is favourable in these perovskite-structured oxides. We should note that the precise proton concentration is dependent on the temperature and the partial pressure of water vapour and oxygen.

6.3 QM STUDIES OF PROTON TRANSFER

Our next concern is the calculation of the proton transfer between oxide ions. Quantum Mechanical techniques, discussed in Chapter 3, and embodied in the CADPAC [102] code are used to investigate this process, specifically to derive the
energy barrier to the reaction \( \text{OH} + \text{O}^2- \rightarrow \text{O}^2- + \text{OH} \). In a review article by Catlow [157], calculations of this energy were reported for two \( \text{O}^2- \) ions at different separations embedded in an array of point charges simulating the remainder of the lattice. We now extend this treatment to a cluster of 13 lattice ions, as shown in figure 6.3, with the remainder of the lattice represented by an array of point charges which reproduce the correct electrostatic potential.

![QM cluster used in the calculation of energy barriers to proton transfer.](image)

Y ions lie (± 1/2 lattice units) above and below plane of diagram.

The calculations were based upon the LaAlO\(_3\) system, with high quality basis sets, Al 8-511G, O 8-411G, and H 6-311G. The Al and O basis sets were optimised for Al\(_2\)O\(_3\) [158] and therefore particularly applicable to the present system; La is represented by the use of a model pseudopotential based upon Y [159]. The psuedopotential was used
as it gives a superior description than a formal charged point ion representation, and therefore the central cluster is better described as YAlO$_3$. The calculations were performed at the SCF HF level, and then single point correlation effects were included by the addition of Moller-Plesset perturbation theory to the second order, the MP2 technique.

The energy barrier to the proton transfer is evaluated as the difference in energy between two states: (i) the ground state in which the hydrogen is effectively bound to an oxide ion, and (ii) the barrier state in which the hydrogen is equidistant between both the adjacent oxide ions, which is illustrated in figure 6.4. The calculations were performed for a series of increasingly sophisticated treatments, and the resulting energies presented in table 6.4.

![Diagram of ground and barrier states](image)

**Figure 6.4.** Schematic of the geometries of the ground and barrier states in the transfer of a proton between adjacent oxide ions. Dashed lines indicate the perfect lattice geometry, and full lines their energy minimised positions.
Series 1 allowed only the proton and two neighbouring oxide ions (O4, O5) to relax, series 2 included relaxation of the central Al ion (Al1), in series 3 a polarisation function was added to the proton, and series 4 included polarisation functions for both the proton and oxygen ions. For calculations at the SCF HF level the barrier energy decreases with increasing sophistication of the calculation.

Table 6.4. Calculated barrier energies for the proton transfer process, with an initial O...O spacing of 2.67Å. The calculations were performed at varying levels of sophistication, as described in the text.

<table>
<thead>
<tr>
<th>SERIES</th>
<th>Eb (eV)</th>
<th>SCF HF</th>
<th>+ MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.38</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.32</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.27</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.29</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

We also note the appreciable difference in $E_b$ between these results and those obtained by Catlow [157], showing the dependence of the barrier energy on the surrounding lattice environment. In each case inclusion of correlation effects lowers $E_b$ by approximately 0.2 eV. Indeed all energies after inclusion of correlation are small, the lowest of $\sim 0.02$ eV is comparable to thermal energies. All subsequent calculations
described below were performed at a level of sophistication equivalent to that of series 4, in which we include polarisation functions for the proton and oxygen ions.

An important factor in the proton transfer process is the O...O separation. Kreuer [145] has proposed that for fast proton transfer the oxide and hydroxyl group must approach each other to a separation of less than 2.5Å. We have therefore calculated the energy of proton transfer as a function of O...O spacings; the results are presented in table 6.5. $E_b$ increases with increasing separation between the two oxide ions at the SCF HF level of calculation, but inclusion of correlation effects reduces $E_b$ significantly. The energy required to break the O-H bond is in the order of 4eV, so the proton transfer takes place through a mechanism in which bond formation accompanies bond breaking, which shows the importance of electronic interactions between the ions, particularly in the barrier state configuration.

Table 6.5. Variation in the energy barrier ($E_b$) with initial O...O spacing, at the SCF HF level, and including correlation effects by the MP2 technique.

<table>
<thead>
<tr>
<th>Initial separation O...O (Å)</th>
<th>$E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SCF HF</td>
</tr>
<tr>
<td>2.67</td>
<td>0.29</td>
</tr>
<tr>
<td>2.76</td>
<td>0.40</td>
</tr>
<tr>
<td>2.90</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Further information on the mechanism for proton transfer comes from a Mulliken population analysis, discussed in Chapter 3; the calculated charges for the atoms in the cluster are presented in table 6.6. They indicate electronic interaction between the proton and both neighbouring oxide ions for both the initial and saddle point configurations. We note that the charges for the O-H group are also in good agreement with those used in the atomistic simulation work.

Table 6.6. Calculated charges for atoms in the QM cluster.

<table>
<thead>
<tr>
<th>ATOM</th>
<th>Configuration / charge</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ground state (i)</td>
<td>Barrier state (ii)</td>
</tr>
<tr>
<td>Al (1)</td>
<td>2.72</td>
<td>2.71</td>
</tr>
<tr>
<td>Al (2,3)</td>
<td>2.96</td>
<td>2.96</td>
</tr>
<tr>
<td>O (4)</td>
<td>-1.34</td>
<td>-1.62</td>
</tr>
<tr>
<td>O (5)</td>
<td>-1.85</td>
<td>-1.62</td>
</tr>
<tr>
<td>O (6,7)</td>
<td>-1.97</td>
<td>-1.97</td>
</tr>
<tr>
<td>H</td>
<td>0.50</td>
<td>0.57</td>
</tr>
</tbody>
</table>

*For ion positions and labels, refer to figure 6.3.

In the ground state the proton and nearest oxide ion (labelled as O4) adopt a charge distribution comparable to a hydroxyl group, however, there is also a reduction of the effective charge of the adjacent oxide ion (O5). Upon displacement to the barrier state (ii) both neighbouring oxide ions (O4 and O5) are drawn towards the proton position,
and the charge becomes evenly distributed over the ions. The charge distribution of both configurations is consistent with the proposal that bond breaking is unnecessary in the proton transfer process.

As already mentioned, the QM calculations can also probe the preferred geometry of the hydroxyl group and neighbouring ions, as shown in figure 6.4. The resulting geometry is very similar to that obtained in our atomistic simulation work, where in the initial ground state configuration the hydroxyl group lies in a position between models (i) and (ii) (figure 6.2). The relaxed geometry of the barrier state configuration shows the importance of the O...O separation in the transfer process. In each case, starting from the initial separation the oxide ions are drawn together so as to allow transfer to occur, which is consistent with the study by Kreuer [145]. Table 6.7 presents the initial and final (calculated) O...O separations for the barrier state configuration, which show that in each case the separation reduces to a value well below 2.5Å.

Table 6.7. Initial and final (calculated) O...O separations for the barrier-state configuration in the proton transfer process.

<table>
<thead>
<tr>
<th>Initial separation (Å)</th>
<th>Final separation (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.67</td>
<td>2.32</td>
</tr>
<tr>
<td>2.76</td>
<td>2.35</td>
</tr>
<tr>
<td>2.90</td>
<td>2.38</td>
</tr>
</tbody>
</table>
6.3.1 Lattice Relaxation Effects

We note that experimental values for the activation energy ($E_{act}$) in ABO$_3$ perovskites are in the range 0.35 - 1.1eV [37,133-140,142,145]. Our calculated energy barriers are obviously well below these energies, suggesting that the activation energy for proton migration depends on other energy terms. For the proton transfer process our QM calculations yield the energy and geometry of the ground and barrier state configurations. However, they provide no information concerning the relaxation of the surrounding lattice which would accompany the proton migration. Moreover, if protons migrate by a 'barrier-less' hop or by a tunnelling process it will be essential that lattice relaxation achieves an equivalent environment around each oxygen site before transfer can occur. Migration would thus occur via the process shown schematically in figure 6.5.

![Figure 6.5](image)

Figure 6.5. Schematic representation of the migration process showing equilibration of the energy levels of the oxide ions prior to proton transfer.
We propose that the energy required to obtain this intermediate state which precedes
the proton transfer, is the major constituent of the proton migration activation energy.
We have used atomistic simulations to evaluate this 'equivalencing' energy; i.e. the
energy required to move from the initial ground state with the proton bound to one
oxide ion to the intermediate state where the oxide ions are in equivalent environments
and separated by less than 2.5Å. The energy of the ground state configuration is simply
$E_{\text{OH}}$, the energy of substituting an oxide ion with a hydroxyl group which is given in
table 6.3. To obtain a value for the intermediate state we require a more complex
approach, and is calculated as follows.

First, we require the energy-minimised positions of the lattice ions when the proton
and adjacent oxide ions are in the barrier state configuration as attained from our QM
cluster calculations. These positions are then utilised in a calculation in which the
proton is placed at a site adjacent to one oxide ion, with both the oxide ions held in
their barrier state locations i.e. the proton is now 'bound' to one oxide ion only. Then
a calculation is performed using the CASCADE [83] code allowing only the shells of
each lattice ion to relax. In this way we obtain the polarisation effects associated with
the lattice energy of the intermediate state. The procedure is as follows:

(i) Calculate the energy of dissolution of water to the oxide, i.e. $E_{\text{OH}}$ the energy of
the proton in the ground state configuration.

(ii) Using QM methods find the lowest energy positions for the proton and
neighbouring oxygen ions in the barrier state configuration.
(iii) Using the positions generated in (ii), use lattice simulations to calculate the relaxed geometries of the ions in the crystal, with respect to the barrier state configuration of the proton and neighbouring oxygen ions (i.e. the proton and neighbouring oxygen ions are held in position).

(iv) The relaxed geometries from (iii) are retained, and the proton placed in a position bound to one oxygen ion only. A calculation is then performed allowing only the shell species of the ions to relax, to give the energy $E_{\text{int}}$.

(v) The difference in energy between (iv) and (i) is the energy associated with obtaining the intermediate state configuration, i.e. the energy needed to generate equivalent environments about the two adjacent oxygen ions.

Table 6.8. Energy terms associated with the lattice relaxation needed to generate equivalent environments about two adjacent oxide ions.

<table>
<thead>
<tr>
<th>Energy State</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{OH}}$</td>
<td>7.34</td>
</tr>
<tr>
<td>$E_{\text{int}}$</td>
<td>8.03</td>
</tr>
<tr>
<td>$E_{\text{relax}}$</td>
<td>0.69</td>
</tr>
</tbody>
</table>

The relaxation energy ($E_{\text{relax}}$) or activation energy for proton migration is calculated as the difference in energy between the intermediate state ($E_{\text{int}}$) as described above and the ground state ($E_{\text{OH}}$). The results for this series of calculations and the value of $E_{\text{relax}}$ are
given in table 6.8. It is significant that we find a value of 0.69eV for $E_{\text{relax}}$ which accords well with experimental data and fully supports our basic model for the proton migration mechanism. This result strongly suggests that a key step preceding proton transfer is the energy required for the neighbouring oxide ions to acquire equivalent lattice environments. We now turn to an alternative approach in the investigation of proton site and mobility in perovskite oxides. The chemical and physical characteristics of the muon are comparable to that of the proton, and so we now use muon implantation studies to further our understanding of protons in perovskite oxides.

6.4 MUON IMPLANTATION STUDIES

6.4.1 Introduction

The positive muon is a unique microscopic probe which can provide a wealth of structural and dynamical information at the atomic scale. When implanted into a material the evolution of its spin polarisation may be readily monitored to give information on the crystallographic site it occupies, the local fields it experiences and the time dependence of these fields. Moreover, once stopped or thermalised within a material, positive muons play the role of lightweight protons which is the reason behind our interest.

The muon, symbol $\mu$, can adopt several charge states including that of the cationic state $\mu^+$ which has physical and chemical characteristics directly comparable to
protons. Positive muons and protons are both fermions carrying spin $1/2$, have unit positive charge with similar magnetic moments, the main difference between $\text{Mu}^+$ and $\text{H}^+$ is the mass of the species, the muon is approximately $1/9^{th}$ the weight of the proton. Nevertheless, despite their mass difference, muons are heavy enough to adopt the same localised sites as protons, however, in diffusion studies they are light enough to show quantum effects. Therefore, muons can model the local structure i.e. static aspects of proton behaviour, but to compare dynamical aspects (interstitial diffusion) we require a mass-dependent model. For these reasons it is possible to model experimentally the behaviour of protons in materials using muon implantation techniques. Further details of the theory and application of muon implantation studies are given by Cox [160], and so only a brief discussion will be presented in this thesis.

6.4.2 \(\mu\)SR

The experimental technique known as \(\mu\)SR, where the initials stand for muon spin rotation, relaxation or resonance, is based on magnetic interaction of the muons, via the evolution of spin polarisation with their host environment. Muons are unstable particles and disintegrate spontaneously by $\beta$ decay with a lifetime of 2.2$\mu$s, the positive muons decaying to form positrons. The rapid decay of the muon allows their polarisation to be monitored since the $\beta$-emission is most intense in the direction of the polarisation. We utilise both muon spin rotation and muon spin relaxation techniques. In the former technique, precession signals are obtained where the frequency of the signals provides a measure of the magnetic field that the muon experiences (applied or
internal), and relaxation functions characterise the variation of these local fields. Muon spin rotation implies that the detection of precession in a field is transverse to the initial muon polarisation. Muon spin relaxation is used to denote studies of the evolution of polarisation parallel to the initial direction. An illustration of the muon spin rotation technique is given in figure 6.6. Implantation is depicted in part (a), where initially the muon beam is longitudinally polarised and usually retains this polarisation in the actual implantation and thermalisation.

![Diagram of muon experiment](image)

Figure 6.6. Schematic representation of the muon experiment, showing (a) implantation, (b) precession in transverse field, and (c) detection of positrons at the scintillator.

Subsequent evolution of the muon polarisation within the sample is monitored, as the muon indicates its spin direction by emission of a positron at the instant of decay. The precession of the muons about a magnetic field which is not parallel to the initial
polarisation is shown in part (b) and (c) of figure 6.6; the decay of the muons is then monitored by the detection of positrons at the scintillator.

If the muons occupy equivalent sites within the lattice and experience identical fields, they will precess in phase and preserve the magnitude of the initial polarisation during rotation. However, if there is variation in the local field experienced, for example, as a consequence of different locations, there will be a gradual decrease in the polarisation as the muons become out of phase. The progressive loss in the polarisation can be monitored and is described by a relaxation function. Measurement of the frequency and relaxation function constitutes the spectroscopic nature of the technique.

The major interest in longitudinal studies (muon spin relaxation) has focused on the form of the relaxation function, which is the time evolution of the polarisation measured parallel to the initial direction. Here, fields are applied parallel (experiments can be performed with zero field) to the initial muon polarisation, and usually in the direction of the muon beam. In addition to studying the relaxation function, a longitudinal field may be required to account for reduction of the precession signal in transverse field. If for some unknown reason there is a reduction of the asymmetry measured in transverse field, valuable information regarding the chemical nature of the 'missing fraction' may be gained from longitudinal field experiments.

A 'pulsed' beam is employed for all the studies, where muons are implanted in intense sharp bursts, so that there is a common start signal. The bursts are short in duration
but repeated over a long interval, with respect to the muon lifetime. In principle, a histogram may be attained for each burst and high statistics accumulated by summation of the histograms from successive bursts.

The objectives of the muon implantation studies performed in this thesis, are as follows:

(i) Determine the site of the muon in perovskite type oxides, for comparison to the simulation studies on the proton position.

(ii) Examine the muon charge state, and muon mobility to help elucidate the proton transfer mechanism.

6.4.3 Experimental

The muon implantation studies were all performed using the pulsed beam muon source at ISIS, Rutherford Appleton Laboratory. The \( \mu \)SR technique is dependent upon the interaction of the muon with the spins of the ions within the sample, and so samples are required which contain ion types possessing suitable magnetic moments. Also the beam can be focused to a diameter of approximately 20mm and the sample needs to be of sufficient size to intercept a significant proportion of the muon beam. The materials studied in this implantation study are LaAlO\(_3\), La\(_{0.8}\)Sr\(_{0.2}\)CoO\(_3\) and La\(_{0.8}\)Ca\(_{0.2}\)MnO\(_3\) in powder form, and a single crystal sample of LiNbO\(_3\). It was useful to extend our study to LiNbO\(_3\) because of its resemblance to the perovskite structure, and the availability of a suitable single crystal.
The studies were performed over a wide range of temperatures (15K to 833K) using an oven and cryostat facilities. The LiNbO₃ sample was mounted on a rotateable holder to allow the orientation dependence of the precession signal to be monitored. The powder samples of the perovskite oxides were used to investigate both the muon state and its mobility, though we should note that the magnetic characteristics of the two doped materials will have a direct effect upon the results obtained. For each of the samples studied, both transverse and longitudinal fields of variable magnitude were applied.

6.4.4 Muon State and Mobility in LaAlO₃

Muon implantation studies were performed on a powder sample of the perovskite-structured oxide LaAlO₃ at temperatures ranging from 15K to 833K. The precession signals obtained, for data collected at 15K, 200K and 833K, with an applied transverse field of 100 Gauss, and shown with fitted Gaussian functions, are given in figure 6.7.

The initial amplitude of a precession signal is a measure of the decay anisotropy, commonly characterised by the effective asymmetry parameter $a$. After suitable calibration it yields the proportion of muons observed in a particular state. The maximum amplitude of the precession signal at the muon Larmor frequency is approximately 0.22. The amplitude obtained for LaAlO₃ at all the temperatures studied indicated a 'missing' fraction, with a minimum amplitude of 0.07 at a temperature of 200K.
Figure 6.7. Precession signals for LaAlO$_3$ at 15, 200 and 833K.
The variation of the asymmetry with temperature is presented in figure 6.8, and suggests that not all of the muons implanted into the material reach a diamagnetic state, i.e. a state with no unpaired electron spins nearby. Therefore, only some (varies from 40 to 70%) of the muons occupy sites comparable to a proton in a hydroxyl group. The variation of asymmetry with temperature indicates that the charge state is temperature dependent, although further μSR experiments were unable to provide additional information on the state of the ‘missing’ fraction, and the unusual temperature dependence.

![Figure 6.8. Temperature dependence of asymmetry for LaAlO₃.](image)

The Gaussian depolarisation function fitted to the signal, is appropriate to the distribution of static dipolar fields from spins on a regular lattice, as would be experienced in a crystal environment. The amplitude of the precession signal decreases over the collection period, for all temperatures, indicating a narrowing of the signal either from fluctuation of the host spins or, more probably, from the mobility of the
muon in the material. A gradual loss of amplitude, with time, is evident in the precession signals presented in figure 6.7. The variation of the damping constant or linewidth (which is the Fourier transform of the damping of the precession signal), with temperature is given in figure 6.9.

![Figure 6.9. Temperature dependence of linewidth (damping parameter) for LaAlO$_3$.](image)

As nuclear spin lattice relaxation is expected to be slow on the timescale of the muon lifetime, the dynamical narrowing observed can be attributed to diffusion of the muon through the lattice. The muon is shown to be mobile at all temperatures, but with a sudden decrease in mobility below 150K. The change in damping below 150K suggests the loss of long range diffusion. Above 150K the damping is constant, but never reaches zero, indicating that the limiting factor in the rate of diffusion of muons through the perovskite lattice is not temperature dependent. There are several steps involved in proton diffusion through the lattice, an important factor being the relaxation of the
lattice ions to accommodate proton migration. It is likely that the lattice relaxation effects will be temperature dependent and below a certain temperature the material is no longer able to facilitate long range diffusion of the proton/muon. Due to the close separation of neighbouring oxygen ions in LaAlO₃ there is rapid proton transfer between them; these studies suggest that this transfer is occurring even at the lowest temperatures.

6.4.5 Muon State and Mobility in Doped Perovskite Oxides

The muon state and mobility in La₀.₈Ca₀.₂MnO₃ and La₀.₈Sr₀.₂CoO₃ were investigated in the temperature range 15K to 300K, and the temperature dependence of the asymmetry for each sample are given in figure 6.10. At 300K both materials retain full polarisation, and therefore, full asymmetry of the precession signal, but show behavioural differences in the asymmetry at lower temperatures. The materials are paramagnetic at room temperature, with magnetic ordering occurring at lower temperatures. The onset of magnetic ordering in a sample should reduce the asymmetry observed in the precession signal by approximately two thirds, as the internal field generated by the magnetism reduces the magnitude of polarisation. However, no reduction in asymmetry is evident for the manganate system; this suggests that either their is an overall cancellation in the field experienced by the muon at the site it occupies or the muon is diffusing rapidly between sites such that the local field is zero on average. The cobaltate system experiences a reduction in the asymmetry of the signal reflecting the onset in magnetic ordering in the sample. Moreover, the
reasons for the retention in asymmetry for the manganate system can not be valid for the cobaltate.

\[ \text{Figure 6.10. Temperature dependence of asymmetry for } \text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3 \text{ and } \text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3. \]

The temperature dependence of the linewidth for each system is shown in figure 6.11. The linewidth is initially small at 300K indicating rapid diffusion of the muon through the perovskite oxides. Below a temperature of around 250K the linewidth undergoes a steady increase in magnitude until the temperature reaches approximately 50K, where a sharp increase in the linewidth occurs. However, the pronounced variation of the linewidth with temperature can not be interpreted explicitly, as it is difficult to separate the effects of magnetism and muon mobility. Nevertheless, the magnitude of the linewidth (as for LaAlO\(_3\)) never reaches a value to indicate that the muon had become stationary, which confirms the diffusion of muons through perovskite type oxides at low temperatures.
Figure 6.11. Temperature dependence of linewidth (damping parameter) for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$.

6.4.6 Muon State and Mobility in LiNbO$_3$

Muon spin rotation experiments on LiNbO$_3$ produced precession signals of maximum amplitude at the muon Larmor frequency. All implanted muons, therefore, reach a diamagnetic state and maintain this state over the temperature range studied, as shown in figure 6.12. The damping of the signals is consistent with the expected distribution of local fields from dipolar nuclei neighbouring the muon site(s), with some dynamical narrowing. Again the narrowing is attributed to interstitial diffusion of the muon through the LiNbO$_3$ lattice. The temperature dependence of the damping parameter is consistent to that of the perovskite oxides, showing no indication that the muon becomes stationary at low temperature (figure 6.12).
Figure 6.12. Temperature dependence of asymmetry and linewidth (damping parameter) for LiNbO$_3$. We note, that due to the small size of the sample the maximum asymmetry was calculated to be approximately 9% and not 22%.

The original aim of the experiment was the determination of the muon site based on the orientation dependence of the linewidth. The experiment was performed using a rotatable sample holder to allow the orientation of the single crystal to be varied with
respect to the muon beam. The precession signals indicate no variation of the linewidth with orientation. The linewidth is constant for all the orientations studied, (as shown in figure 6.13), even at very low temperatures, where we would expect reduced motion of the muon and a site preference. The mobility of the muon at all temperatures, and the complexity of the structure (with several muon sites available) has, therefore, made it difficult to elucidate the orientation dependence of the linewidth.

![Graph showing orientation dependence of linewidth for LiNbO₃.](image)

Figure 6.13. Orientation dependence of linewidth for LiNbO₃.

6.5 CONCLUSIONS

The work discussed in this Chapter demonstrates that the complementary use of atomistic simulation and \textit{ab initio} techniques can assist in providing fundamental details of proton transport in perovskite-type oxides. In addition, \mu SR techniques are used to elucidate the nature of incorporating protons and their transport.
Our discussion has drawn attention to five main results:

1) The predicted orientation of the O-H group (by lattice simulation) has the proton site close to the direction of an adjacent oxide ion. The *ab initio* study yields a relaxed O-H geometry that is very similar to the atomistic simulations, providing additional support for our potential model.

2) The calculated energy of incorporating water into both LaMnO$_3$ and SrTiO$_3$, involving O$^{2-}$ vacancy sites, is found to be exothermic, clearly indicating that the dissolution of water into the acceptor-doped material is an energetically favourable process, in accord with experiment.

3) The *ab initio* cluster calculations find a very low energy barrier to proton transfer between neighbouring oxide ions. This supports models in which rapid proton transfer occurs by a "barrier-less" or a non-classical (tunnelling) process. The calculations also illustrate the importance of including correlation effects in the quantum mechanical approach.

4) A critical step for proton migration, we believe, is the energy required for the neighbouring oxide ions to acquire equivalent lattice environments preceding proton transfer. Indeed, for LaMnO$_3$ we calculate an energy of 0.69eV associated with the lattice relaxation needed to generate such an environment, which is compatible with experimental activation energies for proton conduction.

5) $\mu$SR experiments indicate rapid diffusion of muons through the perovskite lattice which is analogous to rapid diffusion of protons in these oxides. Similar experiments on LiNbO$_3$ also indicate persistence of proton mobility at low temperatures.
Chapter 7

DEFECT CHEMISTRY of

$\text{Bi}_2\text{Mo}_2\text{O}_9$
7.1 INTRODUCTION

Bismuth molybdates are widely utilised as catalysts in selective allylic oxidation processes, including ammoxidation to the corresponding nitrile [161,162]. The effectiveness of these materials as catalysts is associated with a dual-site concept, where bismuth is thought to be responsible for the conversion of a chemisorbed hydrocarbon to an allylic intermediate species; this is followed by further reaction at a molybdenum site to the required product. The procedure involves sequential reduction and reoxidation of the catalyst, placing stringent requirements on the suitability of such a material. Rapid oxygen diffusion is required from bulk to surface as lattice oxygen is used in the oxidation of the hydrocarbon, the catalyst is then required to reduce gaseous oxygen which is incorporated into the vacant oxygen sites.

Several studies have investigated the reduction/reoxidation properties of bismuth molybdates, and have also discussed the mechanistic aspects of the process [161-167]. There are three, main active phases of these materials: Bi$_2$Mo$_3$O$_{12}$ (α), Bi$_2$Mo$_2$O$_9$ (β) and Bi$_2$MoO$_6$ (γ). The selectivity and effectiveness of each as a catalyst has been measured with respect to bulk and surface properties. Bi$_2$Mo$_2$O$_9$ is found to be the most active of the three materials, although it should be noted that following partial reduction it resembles the α phase probably due to a disproportionation process.

It is clear, however, that the defect chemistry and surface properties are not well established and are crucial to the proper understanding of these materials. In an attempt
to clarify this we have applied computer simulation techniques in the investigation of
the $\beta$ phase bismuth molybdate ($\text{Bi}_2\text{Mo}_2\text{O}_9$), in order to elucidate solid state properties
of this commercially important catalyst.

### 7.1.1 Structure and Potentials

As noted above, there are several bismuth molybdates phases, but only three of these
are known to show high activity and selectivity in the oxidation/ammonoxidation
process: $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ ($\alpha$), $\text{Bi}_2\text{Mo}_2\text{O}_9$ ($\beta$) and $\text{Bi}_2\text{MoO}_6$ ($\gamma$). The $\alpha$ and $\beta$ phases adopt
‘fluorite’ related structures with tetrahedral co-ordination of the molybdenum, whilst
$\text{Bi}_2\text{MoO}_6$ ($\gamma$) has a layered structure with distorted octahedral co-ordination of the
molybdenum.

We focus on the $\beta$ phase ($\text{Bi}_2\text{Mo}_2\text{O}_9$), which has a monoclinic cell, and space group P 1
$21/N 1$ [168]. The cations occupy $8/9^{th}$ of a body-centred arrangement leaving large
cavities (vacancies) which are surrounded by oxygens. The structure consists of regular
$\text{MoO}_4$ tetrahedra, with Bi occupying eight co-ordinate sites. There are four unique sites
for the Bi ions, of which three form part of the $\text{Bi}_3\text{O}_2$ chains which run parallel to the
$b$-axis. A schematic representation of the structure is shown in figure 7.1.

Potential derivation was carried out empirically, by a least squares fitting routine to
adjust simultaneously the potential parameters so as to achieve the best possible
agreement between calculated and experimental crystal properties. Due to the
complexity of the structure we were able to sample the potential energy surface at several points and so obtain a more reliable set of potential parameters. The resulting parameters for $\text{Bi}_2\text{Mo}_2\text{O}_9$ are given in table 7.1.

Figure 7.1. Structure of $\text{Bi}_2\text{Mo}_2\text{O}_9$ projected in the a-c plane. $\text{Bi}_3\text{O}_2$ chains are shown along the b axis, with the $\text{MoO}_4$ groups shown as the tetrahedra.
Table 7.1. Interatomic potentials for Bi$_2$Mo$_2$O$_9$

(i) Short-range

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>$\rho$ (Å)</th>
<th>C (eVÅ$^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$^{3+}$...O$^{2-}$</td>
<td>49529.35</td>
<td>0.2223</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo$^{6+}$...O$^{2-}$</td>
<td>767.43</td>
<td>0.4386</td>
<td>0.0</td>
</tr>
<tr>
<td>O$^{2-}$...O$^{2-}$</td>
<td>9547.96</td>
<td>0.2192</td>
<td>32.0</td>
</tr>
</tbody>
</table>

(ii) Shell model

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (e)</th>
<th>k (eVÅ$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$^{3+}$</td>
<td>-5.51</td>
<td>359.55</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>5.89</td>
<td>7.69</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>-2.04</td>
<td>6.3</td>
</tr>
</tbody>
</table>

$^a$Y and k refer to the shell charge and harmonic force constant respectively.

Note: Potential Cut off = 12.0 Å; Region I = 250 ions.

Using these potentials, energy minimisation techniques successfully reproduced the complex structure of the β phase Bi$_2$Mo$_2$O$_9$, shown in figure 7.1. Table 7.2 presents a comparison between calculated and experimental properties, whilst table 7.3 gives the bond distances. It is clearly seen that the calculated structure agrees extremely well with the experimental structure, which in itself is a significant achievement for a complex
structure such as Bi$_2$Mo$_2$O$_9$, particularly as only two-body pair potentials are used with no three-body 'angle-dependent' terms.

The successful reproduction of the complex β phase suggests that it should also be possible to model the α phase (Bi$_2$Mo$_3$O$_{12}$) using similar, if not the same set of potentials. However, it is likely the γ phase (Bi$_2$MoO$_6$) will require an alternative set of potentials due to the different co-ordination of the Mo ions. The MoO$_6$ distortion suggests a high degree of covalency which may require additional angle dependent terms.

Table 7.2. Calculated and experimental lattice parameters of Bi$_2$Mo$_2$O$_9$.

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>Calc</th>
<th>Expt*</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>11.989</td>
<td>11.972</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.823</td>
<td>10.813</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.886</td>
<td>11.899</td>
</tr>
<tr>
<td>α=γ</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>β</td>
<td>90.43</td>
<td>90.13</td>
</tr>
</tbody>
</table>

* Chen et al [168]

7.2 INTRINSIC DEFECTS

Defect calculations were first performed on the energies of isolated point defects, such as vacancies where an ion is removed from the lattice to infinity, and interstitials where an ion is taken from infinity to a non perfect lattice position.
<table>
<thead>
<tr>
<th>Bond</th>
<th>expt</th>
<th>calc</th>
<th>Bond</th>
<th>expt</th>
<th>calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(1)-O</td>
<td>2.154</td>
<td>2.152</td>
<td>Mo(1)-O</td>
<td>1.755</td>
<td>1.695</td>
</tr>
<tr>
<td></td>
<td>2.209</td>
<td>2.168</td>
<td></td>
<td>1.760</td>
<td>1.721</td>
</tr>
<tr>
<td></td>
<td>2.474</td>
<td>2.515</td>
<td></td>
<td>1.778</td>
<td>1.748</td>
</tr>
<tr>
<td></td>
<td>2.481</td>
<td>2.533</td>
<td></td>
<td>1.780</td>
<td>1.764</td>
</tr>
<tr>
<td></td>
<td>2.578</td>
<td>2.562</td>
<td>Mo(2)-O</td>
<td>1.708</td>
<td>1.687</td>
</tr>
<tr>
<td>Bi(2)-O</td>
<td>2.202</td>
<td>2.137</td>
<td></td>
<td>1.747</td>
<td>1.733</td>
</tr>
<tr>
<td></td>
<td>2.239</td>
<td>2.145</td>
<td></td>
<td>1.752</td>
<td>1.747</td>
</tr>
<tr>
<td></td>
<td>2.337</td>
<td>2.369</td>
<td></td>
<td>1.776</td>
<td>1.758</td>
</tr>
<tr>
<td></td>
<td>2.575</td>
<td>2.475</td>
<td>Mo(3)-O</td>
<td>1.729</td>
<td>1.696</td>
</tr>
<tr>
<td>Bi(3)-O</td>
<td>2.394</td>
<td>2.348</td>
<td></td>
<td>1.754</td>
<td>1.706</td>
</tr>
<tr>
<td></td>
<td>2.409</td>
<td>2.411</td>
<td></td>
<td>1.757</td>
<td>1.747</td>
</tr>
<tr>
<td></td>
<td>2.480</td>
<td>2.455</td>
<td></td>
<td>1.792</td>
<td>1.778</td>
</tr>
<tr>
<td></td>
<td>2.494</td>
<td>2.458</td>
<td>Mo(4)-O</td>
<td>1.719</td>
<td>1.688</td>
</tr>
<tr>
<td></td>
<td>2.543</td>
<td>2.516</td>
<td></td>
<td>1.761</td>
<td>1.725</td>
</tr>
<tr>
<td></td>
<td>2.549</td>
<td>2.535</td>
<td></td>
<td>1.763</td>
<td>1.746</td>
</tr>
<tr>
<td>Bi(4)-O</td>
<td>2.127</td>
<td>2.180</td>
<td></td>
<td>1.778</td>
<td>1.759</td>
</tr>
<tr>
<td></td>
<td>2.173</td>
<td>2.181</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.428</td>
<td>2.468</td>
<td>(average)</td>
<td>1.757</td>
<td>1.731</td>
</tr>
<tr>
<td></td>
<td>2.475</td>
<td>2.483</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.410</td>
<td>2.435</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Chen et al [168].
As there are several crystallographic sites for each of the Bi, Mo, and O ions, we present the lowest calculated energy for each of the defect species in table 7.4, with a full list of the energies given in Appendix C. We note that due to the close packed nature of the structure there is limited possibility for interstitial ions, and only one such site was investigated.

Table 7.4. Calculated energies of isolated defect energies.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy</td>
<td></td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>52.40</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>174.25</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>16.43</td>
</tr>
<tr>
<td>Interstitial</td>
<td></td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>-36.83</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>nc</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>-11.51</td>
</tr>
</tbody>
</table>

*nc: no convergence in minimisation.*

The full results, presented in Appendix C, show that there is considerable variation in the energy required to create an oxygen vacancy at each of the non-equivalent lattice sites, which is a consequence of the structural variation of each site; for example, oxygen ions (1,2) which form the Bi$_3$O$_2$ chains have relatively low vacancy energies. These results are also in line with the existence of two types of Bi ion, those which are
in the Bi$_3$O$_2$ chain, Bi(1,2,4), and Bi(3) which are situated between the MoO$_4$ tetrahedra. The energy required to remove Bi(3) from the lattice is 3eV lower than to remove Bi(1,2,4), which indicates the existence of crystallographically distinct lattice sites for the Bi ion in Bi$_2$Mo$_2$O$_9$.

The individual point defects can be combined to give formation energies for Frenkel and Schottky-type disorder; the resulting energies are presented in table 7.5.

Table 7.5. Formation energies for intrinsic disorder.

<table>
<thead>
<tr>
<th>Disorder</th>
<th>Energy/defect (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Schottky-type</strong></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$Mo$_2$O$_9$</td>
<td>3.19</td>
</tr>
<tr>
<td>Bi$_2$Mo$<em>3$O$</em>{12}$</td>
<td>11.04</td>
</tr>
<tr>
<td>Bi$_2$MoO$_6$</td>
<td>4.19</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>2.94</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>nc</td>
</tr>
<tr>
<td><strong>Frenkel</strong></td>
<td></td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>7.8</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>nc</td>
</tr>
<tr>
<td>O$_2^-$</td>
<td>2.46</td>
</tr>
</tbody>
</table>

nc: no convergence in minimisation.
Examination of the formation energies for intrinsic disorder reveals that the thermodynamically most favourable defects are that of the oxygen Frenkel type (2.5eV) and the Schottky-type leading to the formation of Bi$_2$O$_3$ (2.9eV). It has been observed [163] that Bi$_2$Mo$_2$O$_9$ undergoes partial reduction to form the α phase (Bi$_2$Mo$_3$O$_{12}$), which is consistent with the loss of Bi$_2$O$_3$. However, these energies suggest that these processes will not play a major role in the defect chemistry of the β phase, and will only be present in low concentrations. Hence, it is likely that dopant substitution will enhance the defect concentration.

7.2.1 Redox Processes

Under reaction conditions the catalyst undergoes reduction and subsequent reoxidation. We therefore use lattice simulations to model the redox processes in Bi$_2$Mo$_2$O$_9$. First we calculate the energy required to change the oxidation state of each lattice ion. These terms are then combined with the appropriate ionisation or affinity energies to give the necessary electron (\(e'\)) and hole (\(h^*\)) formation energies required in the redox reactions; calculated energies of electronic defects are reported in table 7.6. It should be noted that we have derived the short-range potential parameters for these new species using the shifted electron gas approach; a list of these potential parameters is also given in Appendix C.

Examination of table 7.6 reveals that the formation of hole species is found to be energetically unfavourable, for both the Bi ion and the oxygen ion. In addition, the
results suggest that the formation of Mo\textsuperscript{5+} (e') is highly unlikely, although, reduction of Mo\textsuperscript{6+} to Mo\textsuperscript{4+} (e''') is energetically favourable, which is consistent with the oxidation states of Mo.

Table 7.6. Formation energies of electronic defects.

<table>
<thead>
<tr>
<th>Process</th>
<th>Lattice site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi\textsuperscript{3+} to Bi\textsuperscript{4+} (h*)</td>
<td>Bi(3)</td>
<td>16.76</td>
</tr>
<tr>
<td>Bi\textsuperscript{3+} to Bi\textsuperscript{2+} (e')</td>
<td>Bi(3)</td>
<td>2.48</td>
</tr>
<tr>
<td>Mo\textsuperscript{6+} to Mo\textsuperscript{5+} (e')</td>
<td>Mo(1)</td>
<td>14.34</td>
</tr>
<tr>
<td>Mo\textsuperscript{6+} to Mo\textsuperscript{4+} (2e')</td>
<td>Mo(1)</td>
<td>-5.47</td>
</tr>
<tr>
<td>O\textsuperscript{2-} to O\textsuperscript{-} (h*)</td>
<td>O(1)</td>
<td>7.33</td>
</tr>
</tbody>
</table>

The redox processes can be represented by the following equations:

(i) oxidation to form holes (h*) with oxygen interstitial compensation (oxygen excess compound).

\[
\frac{1}{2} O_2 (g) \rightarrow O_1^{''} + 2h^* \quad (7.1)
\]

(ii) oxidation to form holes (h*) with cation vacancy compensation (metal deficient compound). Note that the compound can be deficient in Bi or Mo cations.

\[
\frac{1}{2} O_2 (g) \rightarrow \frac{2}{3} V_{Bi}^{''''} + 2h^* + \frac{1}{3} Bi_2 O_3 \quad (7.2)
\]

(iii) reduction to form electron states (e') with oxygen vacancy compensation (oxygen deficient compound).

\[
O_0 \rightarrow \frac{1}{2} O_2 (g) + V_{O}^{''''} + 2e' \quad (7.3)
\]
reduction to form electron states (\(e^'/\)) with cation interstitial compensation (metal excess compound). Note that the compound can have Bi or Mo excess.

\[
\text{Bi}_{\text{Bi}} + O_0 \rightarrow \frac{1}{2}O_2 (g) + \frac{2}{3}\text{Bi}_{i}^{***} + 2e'
\]  
(7.4)

In association with the point defect energies we can then calculate the energetics of each of the reduction and oxidation reactions, the results of which are reported in table 7.7.

<table>
<thead>
<tr>
<th>Redox process</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation</td>
<td></td>
</tr>
<tr>
<td>O excess (7.1)</td>
<td>12.54</td>
</tr>
<tr>
<td>Bi deficient (7.2)</td>
<td>12.48</td>
</tr>
<tr>
<td>Mo deficient (7.2)</td>
<td>nc</td>
</tr>
<tr>
<td>Reduction</td>
<td></td>
</tr>
<tr>
<td>O deficient (7.3)</td>
<td>1.58</td>
</tr>
<tr>
<td>Bi excess (7.4)</td>
<td>7.11</td>
</tr>
<tr>
<td>Mo excess (7.4)</td>
<td>nc</td>
</tr>
</tbody>
</table>

nc: no convergence in minimisation.

The calculated energies of the redox processes indicate two main points. First, the high positive values suggest that oxidation is not significant in Bi\(_2\)Mo\(_2\)O\(_9\). Second, the energetically most favourable process is the reduction reaction involving loss of oxygen and reduction of Mo\(^{6+}\) to Mo\(^{4+}\). This result nicely accords with observation as it is
known that $\text{Bi}_2\text{Mo}_2\text{O}_9$ is reduced with the creation of anion vacancies as key catalytic sites [161-163,165,166]. We, therefore, predict that the non-stoichiometry of this catalyst arises from the variable oxidation state of Mo, which allows the reversible addition and removal of oxygens, and enables the oxide to act as an oxygen store in oxidation reactions. It is thought that the gaseous oxygen present as one of the reactants is taken up by the catalyst at the vacant sites, thus making good the anion deficiency created by the sacrificial loss [163]. The cycle repeats itself for as long as the catalyst is active.

7.3 OXYGEN ION MIGRATION

It is well established that solid state diffusion, allowing the flow of oxygen into and through the bulk lattice, is of central importance to the mode of operation of most oxidation catalysts. Indeed, Grasselli [162,163] noted that the reoxidation mechanism of oxygen vacancies in the bulk of the bismuth molybdate catalysts involves a diffusion component. However, limited attention has been focused on oxygen diffusion in these materials. Atomistic modelling can greatly enhance our understanding of ion diffusion, as demonstrated in Chapter 4 for the perovskite-structured oxides, by evaluating activation energies and investigating possible migration pathways. We, therefore, use simulation methods to investigate oxygen ion diffusion in $\text{Bi}_2\text{Mo}_2\text{O}_9$. 
For the complex β phase structure, there are numerous migration routes, so we will concentrate on those involving the most favourable oxygen vacant sites i.e. O (1-3, 11-13). The activation energies for oxygen vacancy migration are reported in table 7.8. These preliminary results reveal activation energies as low as 0.6 eV, which show the existence of discrete low energy pathways within the crystal, and is indicative of high oxygen mobility as suggested by experiment [161-163].

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1) - O(2)</td>
<td>0.90</td>
</tr>
<tr>
<td>O(1) - O(12)</td>
<td>2.09</td>
</tr>
<tr>
<td>O(3) - O(11)</td>
<td>1.95</td>
</tr>
<tr>
<td>O(3) - O(13)</td>
<td>0.63</td>
</tr>
<tr>
<td>O(11) - O(13)</td>
<td>1.53</td>
</tr>
</tbody>
</table>

The lowest energy pathway, for each of the migration jumps, was found by performing a search of the potential energy surface surrounding the mid-point between the two vacant sites. The pathway for each migration jump was highly dependent upon the surrounding environment. Future studies, should attempt to investigate long-range diffusion by performing a more complete search of the potential energy surface for vacancy migration. Nevertheless, the low activation energies suggest that the oxygen...
vacancies consumed in the oxidation reaction will be readily replenished by fast anion
diffusion through the bulk and to the surface.

7.4 OXIDE SURFACES

In the preceding sections we have concentrated on the bulk properties of Bi$_2$Mo$_2$O$_9$. However, in the area of heterogeneous catalysis, understanding the surface properties of the material is of vital importance. To date, limited attention has been paid to the structure and defect chemistry of the surfaces of Bi$_2$Mo$_2$O$_9$, which is partly due to the difficulties concerned with obtaining high-quality experimental data for oxide surfaces at the atomic level. Therefore, we now present preliminary simulation studies of the surface structures of Bi$_2$Mo$_2$O$_9$.

Our approach is to model the low index surfaces (100), (010), (001), (111), (110), (101), and (011). The surface energies are calculated, using the methods described in Chapter 2, and defined as the difference in lattice energy per unit area at the surface compared to the bulk. The energies for both the unrelaxed and energy minimised surfaces are reported in table 7.9.

The results show that, for all surface planes, the fully relaxed surface energies are lower than those for the unrelaxed structures. Considerable relaxation occurs (up to 85% reduction in energy) suggesting that the relaxation of ions in the surface region can significantly increase the stability of that surface. This in itself is an important result, as
deductions of catalytic reactivity based on ideal (unrelaxed) surfaces may be incorrect. The complexity of the Bi$_2$Mo$_2$O$_9$ structure means that it is possible to cleave the crystal to expose a variety of ion types.

Table 7.9. Calculated energies of low index surfaces of Bi$_2$Mo$_2$O$_9$ before relaxation (bulk termination) and after relaxation.

<table>
<thead>
<tr>
<th>Surface plane</th>
<th>Unrelaxed</th>
<th>Relaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>7.74</td>
<td>0.93</td>
</tr>
<tr>
<td>(010)</td>
<td>4.18</td>
<td>1.31</td>
</tr>
<tr>
<td>(001)</td>
<td>8.07</td>
<td>1.32</td>
</tr>
<tr>
<td>(111)</td>
<td>5.91</td>
<td>1.38</td>
</tr>
<tr>
<td>(110)</td>
<td>14.32</td>
<td>2.17</td>
</tr>
<tr>
<td>(101)</td>
<td>2.88</td>
<td>1.10</td>
</tr>
<tr>
<td>(011)</td>
<td>10.89</td>
<td>1.67</td>
</tr>
</tbody>
</table>

However, it is found that for all the surface planes considered, oxygen predominates at the outermost surface in the relaxed structure. Bi and Mo are found in varying ratios according to the surface plane, although the deviation from the bulk ratio is small. Of the surface planes considered, the (100) surface is calculated to be the most stable. Experimental surface energies, which are difficult to measure, are unavailable for Bi$_2$Mo$_2$O$_9$ but the energies presented here are in the range obtained for other oxide materials [61,169].
Using the crystal growth techniques embodied in the Insight II software package [131], it is possible to predict the morphology of single crystal Bi$_2$Mo$_2$O$_9$ based on relaxed surface energies, shown in figure 7.2. Examination of the results show that the (100) surface will dominate the low-temperature crystal morphology in the absence of dopants or surface irregularities, with lesser contribution from the (010), (001) and (101) surfaces. Unfortunately, there are no single-crystal experiments for direct comparison.

Figure 7.2. Morphology of single crystal Bi$_2$Mo$_2$O$_9$, shown in two orientations with key surfaces labelled.

Finally, future work should examine the formation of defects at the surface of the crystal. Preliminary calculations investigating the reduction of Bi$_2$Mo$_2$O$_9$ involving loss of oxygen, suggest that this process is more favourable at the (100) surface than in the bulk.
7.5 CONCLUSIONS

Computer simulation techniques have been used to examine the defect and surface properties of the oxidation catalyst Bi$_2$Mo$_2$O$_9$. The following points have arisen from the results:

1. The complex structure of the β phase is successfully reproduced. Our model is in excellent agreement with available experimental crystal data.

2. The most favourable intrinsic defects are those of the oxygen Frenkel and Bi$_2$O$_3$ Schottky-type, although the formation energies suggest that they will not play a significant role in the catalytic behaviour. It is likely, therefore, that dopant substitution is required to enhance defect concentrations.

3. Reduction involving loss of oxygen and creation of Mo$^{4+}$ is calculated to be the most favourable redox process, which accords well with observation.

4. The low activation energy (0.63eV) for oxygen vacancy migration suggests that the oxygen species consumed in the oxidation process will be replenished by rapid diffusion through the bulk.

5. Surface simulations indicate that lattice relaxation is an important factor. The (100) surface is predicted to be the most stable, and may be the most important for catalytic activity.
INTERATOMIC POTENTIALS

The interatomic potential parameters, used in the oxidation/reduction reactions of LaBO₃, and derived using the shifted electron gas procedure are now reported. In addition, we also list the lattice energies used in the defect reactions.

Table A.1. Interatomic potentials for the LaBO₃ perovskites.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>ρ (Å)</th>
<th>C (eV Å⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺...O⁻</td>
<td>1544.05</td>
<td>0.3447</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr²⁺...O²⁻</td>
<td>1277.44</td>
<td>0.3206</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr⁴⁺...O²⁻</td>
<td>1907.60</td>
<td>0.2911</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr³⁺...O⁻</td>
<td>1763.28</td>
<td>0.2790</td>
<td>0.0</td>
</tr>
<tr>
<td>Mn²⁺...O²⁻</td>
<td>1041.16</td>
<td>0.3379</td>
<td>0.0</td>
</tr>
<tr>
<td>Mn⁴⁺...O²⁻</td>
<td>1345.92</td>
<td>0.3140</td>
<td>0.0</td>
</tr>
<tr>
<td>Mn³⁺...O⁻</td>
<td>1055.31</td>
<td>0.3101</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe²⁺...O²⁻</td>
<td>992.11</td>
<td>0.3441</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe⁴⁺...O²⁻</td>
<td>1195.49</td>
<td>0.3241</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe³⁺...O⁻</td>
<td>1735.25</td>
<td>0.2833</td>
<td>0.0</td>
</tr>
<tr>
<td>Co²⁺...O²⁻</td>
<td>1086.36</td>
<td>0.3250</td>
<td>0.0</td>
</tr>
<tr>
<td>Co⁴⁺...O²⁻</td>
<td>1421.32</td>
<td>0.3012</td>
<td>0.0</td>
</tr>
<tr>
<td>Co³⁺...O⁻</td>
<td>1163.86</td>
<td>0.2902</td>
<td>0.0</td>
</tr>
<tr>
<td>O⁻...O⁻</td>
<td>22764.3</td>
<td>0.1490</td>
<td>43.0</td>
</tr>
</tbody>
</table>
(ii) Shell model\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(Y) (e)</th>
<th>(k) (e(\text{V\AA}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}^{2+})</td>
<td>-0.03</td>
<td>67.0</td>
</tr>
<tr>
<td>(\text{Cr}^{4+})</td>
<td>1.97</td>
<td>67.0</td>
</tr>
<tr>
<td>(\text{Mn}^{2+})</td>
<td>2.0</td>
<td>95.0</td>
</tr>
<tr>
<td>(\text{Mn}^{4+})</td>
<td>4.0</td>
<td>95.0</td>
</tr>
<tr>
<td>(\text{Fe}^{2+})</td>
<td>3.97</td>
<td>304.7</td>
</tr>
<tr>
<td>(\text{Fe}^{4+})</td>
<td>5.97</td>
<td>304.7</td>
</tr>
<tr>
<td>(\text{Co}^{2+})</td>
<td>1.04</td>
<td>196.3</td>
</tr>
<tr>
<td>(\text{Co}^{4+})</td>
<td>3.04</td>
<td>196.3</td>
</tr>
<tr>
<td>(\text{O}^1)</td>
<td>-1.39</td>
<td>42.0</td>
</tr>
</tbody>
</table>

\(^a\)\(Y\) and \(k\) refer to the shell charge and harmonic force constant respectively

Note: Potential Cut off = 12.0\(\text{Å}\); Region I = 250 ions

Table A.2. Calculated lattice energies. (i) perovskite oxides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LaCrO}_3)</td>
<td>-141.76</td>
</tr>
<tr>
<td>(\text{LaMnO}_3)</td>
<td>-139.69</td>
</tr>
<tr>
<td>(\text{LaFeO}_3)</td>
<td>-138.51</td>
</tr>
<tr>
<td>(\text{LaCoO}_3)</td>
<td>-143.08</td>
</tr>
</tbody>
</table>
## Table A.2. Calculated lattice energies. (ii) binary oxides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-155.79</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>-152.05</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>-150.85</td>
</tr>
<tr>
<td>Co$_2$O$_3$</td>
<td>-158.07</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>-127.29</td>
</tr>
</tbody>
</table>
APPENDIX B

SECOND-ELECTRON AFFINITY of OXYGEN

The second-electron affinity of the oxygen atom (EA₂) is often required in modelling the behaviour of materials. Indeed, in Chapter 6 we model the incorporation of protons into perovskite-structured oxides, where EA₂ is used to calculate the difference in proton affinity between O²⁻ and OH⁻. Typically a value of around 8eV is used [156], but recently, Harding and Pyper [155] have shown that the second-electron affinity of oxygen in a crystal is dependent upon both the chemical composition and the structure of the crystal.

We now report our calculations of these electron affinity terms, in which we calculate the difference in energy between an O' and O²⁻ ion embedded in a point-charge array of lattice ions simulating the electrostatic potential of the metal oxide. The calculations were performed at a high level of accuracy: open shell, UHF, with MP2 correlation. The basis set for oxygen was O 8-411G, and the CADPAC [102] code was used for these studies. Calculations were initially performed on an isolated oxygen atom (i.e. no point charge array), although, we note that O²⁻ is unstable in free space and will spontaneously dissociate. We obtain a value of 8.89eV for the second-electron affinity of an isolated oxygen atom, which is in general accord with previous energies calculated using thermochemical cycles [156]. In table B.1 we present the second-electron affinities of oxygen for a series of materials (simulated using the appropriate point charge array), calculated using the UHF methodology and then including MP2 correlation effects.
Table B.1. Calculated second-electron affinities for oxides and oxyhalides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>EA2 (eV)</th>
<th>UHF</th>
<th>+ MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaAlO$_3$</td>
<td>12.20</td>
<td></td>
<td>10.56</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>11.95</td>
<td></td>
<td>10.30$^a$</td>
</tr>
<tr>
<td>BaCeO$_3$</td>
<td>11.41</td>
<td></td>
<td>9.7</td>
</tr>
<tr>
<td>MgO</td>
<td>11.32</td>
<td></td>
<td>9.49</td>
</tr>
<tr>
<td>CaO</td>
<td>10.89</td>
<td></td>
<td>9.02</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>11.25</td>
<td></td>
<td>9.25</td>
</tr>
<tr>
<td>LaOCl</td>
<td>11.01</td>
<td></td>
<td>8.99</td>
</tr>
<tr>
<td>BiOCl</td>
<td>11.20</td>
<td></td>
<td>9.20</td>
</tr>
</tbody>
</table>

$^a$value used in Chapters 4 and 6.

The results clearly show the dependence of the second-electron affinity on the crystal environment. In particular, we note the variation in EA2 with lattice parameter for the three (LaAlO$_3$, LaMnO$_3$, BaCeO$_3$) perovskite-structured oxides. It is important to note that excluding correlation effects results in affinity energies approximately 2eV greater in magnitude.
**Bi₂Mo₂O₉ RESULTS**

The following tables give detailed results of the calculated energies of intrinsic and electronic defects in Bi₂Mo₂O₉, as well as lattice energies used in the defect reactions. In addition, interatomic potential parameters used in the calculation of electronic defects are also reported.

Table C.1. Calculated energies of isolated point defects.

(i) bismuth sites.

<table>
<thead>
<tr>
<th>Ion site</th>
<th>Vacancy</th>
<th>Bi&lt;sup&gt;3+&lt;/sup&gt; → Bi&lt;sup&gt;2+&lt;/sup&gt; (e&lt;sup&gt;−&lt;/e&gt;)</th>
<th>Bi&lt;sup&gt;3+&lt;/sup&gt; → Bi&lt;sup&gt;4+&lt;/sup&gt; (h&lt;sup&gt;+&lt;/h&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi (1)</td>
<td>55.24</td>
<td>3.28</td>
<td>16.79</td>
</tr>
<tr>
<td>Bi (2)</td>
<td>55.56</td>
<td>3.42</td>
<td>17.04</td>
</tr>
<tr>
<td>Bi (3)</td>
<td>52.40</td>
<td>2.48</td>
<td>16.76</td>
</tr>
<tr>
<td>Bi (4)</td>
<td>55.44</td>
<td>3.88</td>
<td>17.11</td>
</tr>
</tbody>
</table>

(ii) molybdenum sites.

<table>
<thead>
<tr>
<th>Ion site</th>
<th>Vacancy</th>
<th>Mo&lt;sup&gt;6+&lt;/sup&gt; → Mo&lt;sup&gt;5+&lt;/sup&gt; (e&lt;sup&gt;−&lt;/e&gt;)</th>
<th>Mo&lt;sup&gt;6+&lt;/sup&gt; → Mo&lt;sup&gt;4+&lt;/sup&gt; (e&lt;sup&gt;−&lt;/e&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo (1)</td>
<td>174.33</td>
<td>14.34</td>
<td>-5.47</td>
</tr>
<tr>
<td>Mo (2)</td>
<td>174.34</td>
<td>15.00</td>
<td>-3.99</td>
</tr>
<tr>
<td>Mo (3)</td>
<td>174.25</td>
<td>14.46</td>
<td>-4.98</td>
</tr>
<tr>
<td>Mo (4)</td>
<td>176.09</td>
<td>15.41</td>
<td>-3.47</td>
</tr>
</tbody>
</table>
(iii) oxygen sites.

<table>
<thead>
<tr>
<th>Ion site</th>
<th>Defect / Energy (eV)</th>
<th>Vacancy</th>
<th>O$^2 \rightarrow$ O' (h*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (1)</td>
<td></td>
<td>16.97</td>
<td>6.91</td>
</tr>
<tr>
<td>O (2)</td>
<td></td>
<td>17.03</td>
<td>7.01</td>
</tr>
<tr>
<td>O (3)</td>
<td></td>
<td>16.84</td>
<td>9.90</td>
</tr>
<tr>
<td>O (4)</td>
<td></td>
<td>18.95</td>
<td>11.50</td>
</tr>
<tr>
<td>O (5)</td>
<td></td>
<td>17.88</td>
<td>10.63</td>
</tr>
<tr>
<td>O (6)</td>
<td></td>
<td>19.82</td>
<td>12.05</td>
</tr>
<tr>
<td>O (7)</td>
<td></td>
<td>18.70</td>
<td>11.74</td>
</tr>
<tr>
<td>O (8)</td>
<td></td>
<td>17.58</td>
<td>12.04</td>
</tr>
<tr>
<td>O (9)</td>
<td></td>
<td>17.60</td>
<td>11.01</td>
</tr>
<tr>
<td>O (10)</td>
<td></td>
<td>18.27</td>
<td>11.31</td>
</tr>
<tr>
<td>O (11)</td>
<td></td>
<td>16.48</td>
<td>10.28</td>
</tr>
<tr>
<td>O (12)</td>
<td></td>
<td>17.35</td>
<td>10.87</td>
</tr>
<tr>
<td>O (13)</td>
<td></td>
<td>16.43</td>
<td>9.47</td>
</tr>
<tr>
<td>O (14)</td>
<td></td>
<td>18.76</td>
<td>10.90</td>
</tr>
<tr>
<td>O (15)</td>
<td></td>
<td>17.85</td>
<td>9.83</td>
</tr>
<tr>
<td>O (16)</td>
<td></td>
<td>17.81</td>
<td>9.88</td>
</tr>
<tr>
<td>O (17)</td>
<td></td>
<td>18.55</td>
<td>11.27</td>
</tr>
<tr>
<td>O (18)</td>
<td></td>
<td>18.34</td>
<td>11.08</td>
</tr>
</tbody>
</table>
### Table C.2. Lattice energies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice energy (eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₂Mo₂O₉</td>
<td>-559.68</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>-339.95</td>
</tr>
<tr>
<td>Bi₂MoO₁₂</td>
<td>-637.03</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>-139.39</td>
</tr>
<tr>
<td>MoO₃</td>
<td>-291.45</td>
</tr>
</tbody>
</table>

*per formula unit.

### Table C.3. Interatomic potentials for Bi₂Mo₂O₉ derived using the shifted electron-gas method.

(i) Short-range

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>ρ (Å)</th>
<th>C (eVÅ⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi³⁺...O⁻</td>
<td>83475.08</td>
<td>0.2043</td>
<td>0.0</td>
</tr>
<tr>
<td>Bi²⁺...O²⁻</td>
<td>36673.39</td>
<td>0.2313</td>
<td>0.0</td>
</tr>
<tr>
<td>Bi⁴⁺...O²⁻</td>
<td>64328.55</td>
<td>0.2142</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo⁶⁺...O⁻</td>
<td>507.59</td>
<td>0.4638</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo⁵⁺...O²⁻</td>
<td>792.45</td>
<td>0.4382</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo⁴⁺...O²⁻</td>
<td>795.51</td>
<td>0.4408</td>
<td>0.0</td>
</tr>
<tr>
<td>O⁻...O⁻</td>
<td>9547.96</td>
<td>0.2192</td>
<td>32.0</td>
</tr>
</tbody>
</table>
(ii) Shell model\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (e)</th>
<th>k (eV Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(^{2+})</td>
<td>-6.51</td>
<td>359.55</td>
</tr>
<tr>
<td>Bi(^{4+})</td>
<td>-4.51</td>
<td>359.55</td>
</tr>
<tr>
<td>Mo(^{5+})</td>
<td>4.89</td>
<td>7.69</td>
</tr>
<tr>
<td>Mo(^{4+})</td>
<td>3.89</td>
<td>7.69</td>
</tr>
<tr>
<td>O(^-)</td>
<td>-1.04</td>
<td>6.3</td>
</tr>
</tbody>
</table>

\(^a\)Y and k refer to the shell charge and harmonic force constant respectively

Note: Potential Cut off = 12.0Å; Region I = 250 ions
REFERENCES

REFERENCES

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