Large throughput analysis of crystal structures for identification of promising li-ion battery materials

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LARGE THROUGHPUT ANALYSIS OF CRYSTAL STRUCTURES FOR IDENTIFICATION OF PROMISING LI-ION BATTERY MATERIALS

A thesis submitted in partial fulfilment of the requirements for the award of the degree

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2014
I, Matthew Sale, declare that this thesis, submitted in partial fulfilment of the requirements for the award of Master of Physics (Engineering)-Research, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Matthew Sale
31 March 2014
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ABSTRACT

It is a popular research pursuit to improve the properties of rechargeable batteries. The motivation for this research is to make rechargeable batteries more suitable for powering electric vehicles as well as increasing the operating time of portable electronics. Cheaply storing large amounts of electricity from renewable energy sources such as solar and wind as well as providing grid electricity buffering for electricity generation would also help offset peak electricity demand[1], [2], [3].

Unfortunately, current battery materials are experiencing a plateau in performance improvements due to the maximum intrinsic capacity and cost of commonly used cathode materials. As a result, further research into improving battery performance will require either a change in battery technology or the discovery of a new cathode material with different or superior properties.

All active battery materials must possess ionic conductivity as the electrochemical reactions which produce electrical energy for rechargeable batteries operate by transferring electrons and mobile ions between two structures of different energies. It is often a relatively straightforward process to modify the electrical and mechanical properties of existing cathode materials using chemical doping, mechanical grinding or nano-structuring in order to optimise their properties. However, it is usually not possible by any type of processing to impart any significant ionic
conductivity to a material which it does not already possess. As a result, this study focuses on searching for new intercalation cathode materials and solid ionic conductors by searching for new materials which have high ionic conductivity.

The Inorganic Crystal Structure Database (ICSD) [4] contains crystal structural details about most currently known inorganic crystalline materials (~166,000) and most of these have never been tested to determine their ionic conductivity. The two main methods available to survey the ionic conductivity of materials are experimental and computational.

Unfortunately, experimental methods are not suitable for surveying very large numbers of different types of materials as this would be very costly and time consuming. Various accurate computational methods are also not suited to large surveys due to the complexity and time consumption of these methods. However, several computational methods still remain suitable for use as a large survey tool.

The Bond Valence Sum Map (BVSM) [5] and Bond Valence Energy Landscape (BVEL) [6] methods were selected to perform a computational survey of a large number of known oxide materials from the ICSD to approximate their ionic conductivity[7].
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<td>Modification of NEB method to search for highest energy transition point</td>
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</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
<td>Database containing large number of known inorganic crystal structures</td>
<td>2.6</td>
</tr>
<tr>
<td>Perl</td>
<td>N/A</td>
<td>Programming Language</td>
<td>5.2.1</td>
</tr>
<tr>
<td>GUI</td>
<td>Graphical User Interface</td>
<td>Program which is operated by using a screen and computer mouse</td>
<td></td>
</tr>
<tr>
<td>3DBVSM APPER</td>
<td>Program developed for this thesis work</td>
<td>Program written to implement BVSM and BVEL methods automatically for large groups of *.cif files</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>Cut-off length</td>
<td>Mean Square Displacement</td>
<td>Maximum included bond radius</td>
<td>4.2.2.2</td>
</tr>
<tr>
<td>MSD</td>
<td>Minimum Field value</td>
<td>Minimum field value inside of infinitely connected isosurface</td>
<td>6.3</td>
</tr>
<tr>
<td>MinField</td>
<td>Minimum Connected isosurface/isovalue</td>
<td>Minimum infinitely connected isosurface/isovalue</td>
<td>6.3</td>
</tr>
<tr>
<td>MinConneected</td>
<td>Fractional Volume</td>
<td>Isosurface volume scaling method</td>
<td>6.5.2.1</td>
</tr>
<tr>
<td>FV</td>
<td>Volume per atom</td>
<td>Isosurface volume scaling method</td>
<td>6.5.2.2</td>
</tr>
<tr>
<td>VA</td>
<td>Volume per total atomic framework volume</td>
<td>Isosurface volume scaling method</td>
<td>6.5.2.3</td>
</tr>
<tr>
<td>VAV</td>
<td>Volume available per mobile ion</td>
<td>Isosurface volume scaling method</td>
<td>6.5.2.4</td>
</tr>
<tr>
<td>FVPMI</td>
<td>Fractional volume per proportion of mobile ion</td>
<td>Isosurface volume scaling method</td>
<td>6.5.2.5</td>
</tr>
</tbody>
</table>
High performance rechargeable batteries are an essential component of many electronic devices in the modern electronic age. Mobile phones, laptops, power tools and many portable electronic devices rely on rechargeable batteries with high energy density, high charge/discharge rates and long cycling lifes. The current leading battery technology suffers from several safety, cost and performance issues which affects the batteries suitability for certain applications. For example, development of batteries with a higher energy to weight ratio, long cycling life and construction from environmentally friendly, cheap, abundant, less toxic and safer materials may enable the financially viable mass manufacturing of electric cars. Rechargeable batteries with excellent cycling energy efficiency, low cost and long cycling lives would be suitable for power distribution applications to offset peak electricity demands and to store electrical energy from intermittent green energy sources such as wind, wave and solar power.

Much research and investment has been put into improving the characteristics of rechargeable batteries as a result of these considerations [1-3]. This study focuses on identifying new battery materials with different and potentially better properties in order to improve the performance of rechargeable batteries.

Chapter 2 presents an overview of rechargeable intercalation battery technology. It commences with a description of intercalation rechargeable
battery operation of the common Li-ion rechargeable battery. It also overviews the various aspects of battery performance and how this relates to the macroscopic and microscopic properties of the individual battery materials. It also details the performance and limitations of currently available and popular battery materials followed by a digression on the ionic conductivity properties of these materials.

Chapter 3 presents a review of some of the most commonly used methods, both experimental and computational, for measuring the ionic conductivity of crystalline materials. It also details the suitability of different methods for use as a large scale survey tool to analyse large numbers of materials.

Chapter 4 presents theory on the Bond Valence Sum Map (BVSM) and Bond Valence Energy Landscape (BVEL) methods which were selected to computationally analyse large numbers of materials to help qualitatively analyse their ionic conductivities. Some example data is also presented in this section illustrating the operation of the methods.

Chapter 5 presents a review of the general operation of the 3DBVSMAPPER program which was written in order to conduct a survey of known crystalline structures from the Inorganic Crystal Structure Database (ICSD). This program implements the Bond Valence Sum Map and Bond Valence Energy Landscape methods described in Chapter 4.
Chapter 6 presents a review of some of the different methods which can be used to analyse the data produced by the 3DBVSMSAPPER program as well as their usefulness.

Chapter 7 presents a review of the data generated by the 3DBVSMSAPPER program when it was executed using oxide crystalline material structures selected from the Inorganic Crystal Structure Database (ICSD). It also presents a review of the usefulness of some of the different methods used to analyse the data.

Chapter 8 presents details of DFT cNEB calculations to determine the activation energy of Diithium Copper(II) Pyrophosphate (Li₂CuP₂O₇), a novel new ionic conductor identified from the previous calculations.

Chapter 9 presents example data from collaborations with other people using the 3DBVSMSAPPER program as well as their supporting evidence.

Chapter 10 presents general conclusions of this thesis study.
CHAPTER 2 RECHARGEABLE INTERCALATION BATTERIES

2.1 Types of batteries

The two general categories of batteries are primary cells and secondary cells. Primary cells are designed to be discharged and then discarded whereas secondary cells are designed to be repeatedly discharged and recharged by the application of external current in order to be re-used. Various mechanisms such as intercalation, alloying and chemical conversion reactions exist to facilitate the motion and accommodation of mobile ions in the battery anode and cathode materials. This study focuses on rechargeable batteries of similar mechanism to rechargeable Li-ion intercalation batteries.

2.2 Li-ion rechargeable batteries

The first commercially successful lithium ion rechargeable battery was created by the Sony Corporation in 1990 [8]. This rechargeable lithium ion insertion battery was constructed from a layered LiCoO$_2$ cobalt oxide cathode, a graphite anode and a liquid electrolyte permeated separator Figure 2.1. While this battery technology was the first generation of commercial success of the Li-ion family of batteries, it still remains one of the best performing types of the family of Li-ion batteries due to its high power to weight ratio.
The general operation of a rechargeable intercalation battery is illustrated in Figure 2.2. The battery is charged by applying an electrical potential or voltage to the battery terminals which causes electrons to transfer from the cathode to the anode. This current oxidises the cathode transition metal atoms and also creates a negative charge at the anode which attracts the mobile ions liberated by oxidation from the cathode. The battery is
discharged by allowing an electron current to flow along the external circuit from the anode to the cathode, which also allows the transport of mobile ions from the anode to the cathode, where the cathode is reduced by these mobile ions.

The electrolyte and separator allows mobile ions to easily travel between the anode and cathode but also acts as an electrical insulator so that the reduction/oxidation chemical reaction at the cathode cannot occur without a current in the external circuit. This ensures that the battery does not self-discharge and that the current must flow via the external circuit to provide electrical energy to a device.

The energy of the battery is mainly stored in the energy required to oxidise the transition metal atoms in the cathode when the mobile ions are removed from it. This energy is provided by the potential energy difference of the voltage applied to the terminals of the battery when charging. The energy of the charged battery is higher than the energy of the discharged battery because the charging process puts the battery materials in a net higher energy configuration. Specifically, the energy of the anode structure which is intercalated with mobile ions is higher than the energy of the cathode structure when it is intercalated with mobile ions.
Cathode: \( \text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^- \)

Anode: \( C + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x C \)

\( \text{Li}^+ + \text{e}^- \leftrightarrow \text{Li}(s) V = -3.04\text{V} \)

\( \text{Co}^{3+} + \text{e}^- \leftrightarrow \text{Co}^{2+} V = +1.82\text{V} \)

Equation (2.1) – Chemical reaction and oxidation potentials of common LiCoO\(_2\) insertion rechargeable battery

As an example, the energy of the LiCoO\(_2\) battery is stored in the redox reaction between lithium and the cobalt transition metal in the framework. This battery is charged and discharged as the cathode is oxidised and reduced between the 2+ and 3+ states when lithium is inserted and removed from it. The chemical reaction and typical reduction potentials of these battery materials for this process is illustrated in Equation (2.1).

These reactions give a theoretical cell potential of 4.86V. However, the typical voltage may be less due to internal material resistances and various non-equilibrium processes such as interface resistances, materials impedances and polarisation of battery materials [3].

2.3 Properties of batteries

Many of the properties of batteries have their origin in the microscopic and atomic-level properties of the battery materials themselves. Also, many desirable properties of rechargeable batteries are universal to all battery applications. Below are listed some of these properties and how they relate
to the macroscopic and atomic properties of the battery materials themselves [3, 10].

2.3.1 High power to weight ratio

In many mobile electronics applications, the battery is a significant proportion of the total weight of the device. Therefore the power to weight ratio is most important in mobile electronics applications in order to reduce the weight of the overall system and therefore improve the total power to weight ratio of the final product. The mass to coulomb ratio of the electrodes and the battery voltage are the two primary determining factors of the energy to weight ratio. This ratio is also affected by the requirement of additional battery materials such as electrical conductivity increasing agents, binding materials, current collectors and packaging.

2.3.2 High power to volume ratio

This property is related to the total density of the battery materials. This property is possibly less important than the power to weight ratio in most mobile applications but is still important for applications which require particularly large capacity batteries in a small space or for very small electronic devices.
2.3.3 High dis/charge rate

The maximum charging and discharging rate is limited by the total internal impedance of the battery. This internal impedance is a result of the sum of the electrical and ionic conductivities of the battery materials themselves. Improving the electrical conductivity of the battery materials is usually easy to achieve through chemical doping of electrodes and the addition of electrically conductive materials to the battery. However, the ionic conductivity of the battery materials is usually quite difficult to improve. This is the main limiting factor of the charge and discharge rate. Although it is possible to improve the ionic conductivity of the battery materials by several orders of magnitude through the use of appropriate doping and nanosizing of the materials, the intrinsic ionic conductivity of the crystal framework presents the main obstacle to reducing the impedance of the battery.

Another alternative to improve the ionic conductivity of the battery material is to increase the temperature of the battery, however, this approach is not very common due to the extra complexity, weight and energy consumption required to maintain the high temperature of the battery. Also, current common battery electrolyte materials are not suitable for high temperature use as they degrade at moderately elevated temperatures, see section 2.4. The discovery of solid electrolyte material with very high ionic conduction at room temperature to replace the current electrolyte in the rechargeable battery would improve the safety of current battery technology and allow the development of high temperature batteries. Therefore, identification of
new materials with high intrinsic ionic conductivity may help to significantly improve the properties of the rechargeable battery.

2.3.4 Long cycling lives

Batteries which can be repeatedly charged and discharged without losing a significant proportion of their capacity are desirable as this increases the useful life span of the battery. Long life batteries are more financially efficient as the battery component does not need to be replaced as often, increasing the effective value of the component. The cycling life of the battery relates to the phase stability of the electrode materials as well as the chemical stability of the battery components when charging and discharging. Build-up of undesirable chemicals on the surfaces of the electrodes from the liquid electrolyte is a common cause of cycling degradation. Stable battery materials are desirable to increase battery life span as irreversible phase transformations of the electrode materials when charging and discharging may make these materials inert to Li-ion insertion, reducing the capacity of the battery. Also, the dimensionality of the ion conduction channels of the bulk battery material has an effect on the cycling life of the battery. The ionic conduction of single channel 1-dimensional ionic conduction battery materials significantly degrades with even a very small amount of blocking by foreign atoms. Without another channel dimension for the mobile ions to travel in, the overall ionic conductivity of the channels may be significantly reduced with even a small number of foreign atoms. Therefore materials with multiple dimensional channels are desirable for battery materials with long cycling life spans.
2.3.5 High and stable voltage profile

A high and stable cell voltage helps to increase the energy density of the rechargeable battery. Also, from an electrical engineering perspective, it is simpler and more efficient to create electrical circuits for batteries which have a stable voltage over their discharge curve.

2.3.6 Cost

Batteries made from very common and cheap materials would lower manufacturing costs and reduce reliance on precious and rare materials. Low energy fabrication methods which do not require complex and specialised procedures would also help to reduce manufacturing costs. High performance batteries may enable new electronic devices to be constructed which may also enable new electronic devices to be constructed.

2.3.7 Toxicity

Batteries made from non-toxic materials would be safer for humans and the environment and would also be easier to recycle at the end of their life-cycle. Battery materials which have been reduced to nano-sized particles may present some toxicity hazard for humans and the environment. Also, the full manufacturing cycle should be considered as the by-products of manufacturing can also be toxic.
2.3.8 Safety

Improvements in battery safety include the development of battery materials which are resistant to self-destructing and catching on fire when exposed to adverse conditions. When heated, the current leading liquid polymer electrolyte material causes the battery to short out internally and therefore explode or catch fire. Also, liquid electrolyte materials have the potential to leak reactive/corrosive chemicals in the event of damage or old age.

2.4 Limited number of common battery materials

At the moment, only a few materials are commonly used as commercial battery anodes and cathodes. Table 2.1 indicates some of the key properties of some popular Lithium battery cathodes and anodes. In most applications, these electrodes are usually combined with a polymer separator and liquid electrolyte which has a very high ionic conductivity and low electron conductivity. Unfortunately, most liquid/polymer electrolytes begin to degrade at the relatively low temperature of 135°C and thus presents a safety hazard with the potential for dangerous self-discharge of the battery when overheated [11].
<table>
<thead>
<tr>
<th>Electrode (Aldrich Product No.)</th>
<th>Potential vs. Li/Li$^+$(V)$^A$</th>
<th>Specific Capacity, (mAh/g)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Positive Electrodes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>3.9</td>
<td>140</td>
<td>Performance</td>
<td>Cost and resource limitations of Co, low capacity</td>
</tr>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$</td>
<td>3.8</td>
<td>180–200</td>
<td>High capacity and voltage, excellent rate performance</td>
<td>Safety, cost and resource limitations of Ni and Co</td>
</tr>
<tr>
<td>LiNi$<em>{1/3}$Mn$</em>{1/3}$Co$_{1/3}$O$_2$</td>
<td>3.8</td>
<td>160–170</td>
<td>High voltage, moderate safety</td>
<td>Cost and resource limitations of Ni and Co</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$ variants</td>
<td>4.1</td>
<td>100–120</td>
<td>Low cost and abundance of Mn, high voltage, moderate safety, excellent rate performance</td>
<td>Limited cycle life, low capacity</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>3.45</td>
<td>170</td>
<td>Excellent safety, cycling, and rate capability, low cost and abundance of Fe, low toxicity</td>
<td>Low voltage and capacity (substituted variants), low energy density</td>
</tr>
<tr>
<td><strong>Negative Electrodes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>0.1</td>
<td>372</td>
<td>Long cycle life, abundant</td>
<td>Relatively low energy density; inefficiencies due to Solid Electrolyte Interface formation</td>
</tr>
<tr>
<td>Li$_4$Ti$_3$O$_12$</td>
<td>1.5</td>
<td>175</td>
<td>&quot;Zero strain&quot; material, good cycling and efficiencies</td>
<td>High voltage, low capacity (low energy density), low ionic conductivity</td>
</tr>
</tbody>
</table>

Table 2.1 – Common battery materials with their advantages and disadvantages, table adapted from original material – [12]
2.5 Improving rechargeable battery performance

Most of the properties of battery materials can be optimised by adjusting the chemical composition of the battery materials as well as performing mechanical processes such as grinding to form nano-sized particles with high surface areas. Much research using these methods has already been performed to optimise the performance of these existing known battery materials. As a result, most recent improvements in performance have been incremental rather than dramatic as battery technology fast approaches the theoretical maximum performance of the given set of popular materials.

A large improvement in rechargeable battery performance will therefore require the use of a new technology or material which has significantly better properties than existing rechargeable batteries. The main limitation in the development of any new battery material is the selection of a material with a high enough ionic conductivity to be useful as a battery material.

The bulk ionic conductivity of a material is a relatively fixed property of the framework of the crystal structure for crystalline materials. The geometry, dimensionality and activation energy of the ion conduction pathways of inorganic solid electrolytes and insertion cathodes are the primary determining factors of the ionic conductivity, charge/discharge rate, internal impedance and cycling lifetime of the battery [13]. As a result, the ionic conductivity of any battery material cannot be dramatically altered by traditional methods such as chemical substitution or mechanical processes.
2.6 Materials with high ionic conductivity

As previously mentioned, ionic conductivity is an essential property of all electrochemically active battery materials. As can be seen in Table 2.1, there are a very limited number of commonly used electrode materials and no known viable room temperature solid electrolyte material. Therefore it is necessary that new materials are found with substantially better properties to enable further improvements in rechargeable battery performance. The focus of this research is to find materials with high ionic conductivity and optionally low weight per unit of mobile ion in order to identify potentially interesting new materials for further detailed research into rechargeable batteries.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Year crystal structure reported</th>
<th>Year reported as a battery component</th>
</tr>
</thead>
</table>

Table 2.2 – Years between discovery and implementation of common battery materials – [22]

In the past, discoveries in battery materials have included identifying existing materials which have high ionic conductivity and are suitable for use in electrodes and electrolytes. As can be seen in Table 2.2, there is often a substantial time gap of 10-35 years between when a structure is first synthesised and measured and when it is identified for use in rechargeable batteries. This large time gap suggests that there may be some existing
crystal structures which have not yet been identified which have favourable properties for use as electrodes or electrolytes.

There are a limited number of databases containing well-formatted lists of crystal structures, see Table 2.3. This study will be focusing on the extensive list of materials contained in the Inorganic Crystal Structure Database (ICSD) [4] which contains more than 16,000 oxides.
<table>
<thead>
<tr>
<th>Name</th>
<th>Long Name</th>
<th>Webpage</th>
<th>Comment</th>
<th>No. of structures (early 2014)</th>
<th>CIF files</th>
<th>Price/Licence</th>
<th>Submission method</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>Crystallography Open Database</td>
<td><a href="http://www.crystallography.net">http://www.crystallography.net</a></td>
<td>-</td>
<td>245,000</td>
<td>Yes</td>
<td>Free - Public Domain</td>
<td>Self-submission</td>
</tr>
<tr>
<td>PCD</td>
<td>Pearson's Crystal Data - Crystal Structure Database for Inorganic Compounds</td>
<td><a href="http://www.crystalimpact.com/pcd/Default.htm">http://www.crystalimpact.com/pcd/Default.htm</a></td>
<td>Similar to ICSD</td>
<td>242,600</td>
<td>Unknown</td>
<td>Proprietary</td>
<td>Unknown</td>
</tr>
</tbody>
</table>
CHAPTER 3       SURVEYING IONIC CONDUCTIVITY

Although the tuning of chemistries and manufacturing methods of existing battery materials is a common research pursuit, the search for new materials with high ionic conductivity is a much more difficult task. Large surveys of the ionic conductivity of different materials using conventional methods can be prohibitively expensive and time consuming. There are various conventional methods which can be used to measure the ionic conductivity of a material in great detail, some of which are described in the following sections.

3.1 Experimental methods

There are many experimental methods which can measure the ionic conductivity of crystalline samples. Some of the more common experimental methods for investigating the ionic conductivity of samples include impedance spectroscopy, Nuclear Magnetic Resonance (NMR) measurements, coin cell testing, x-ray and neutron diffraction methods to measure structure and nuclear density distributions using Rietveld refinement and the Maximum Entropy Method (MEM), as well as electron microscopy and atomic force microscopy. [23]

While these methods are commonly employed in the study of known ionic conductors, most crystalline materials which are fabricated are never analysed for their ionic conductivity after synthesis and structural characterisation. Experimental review papers [24, 25] contain lists of known
ionic conductors, however, these reviews do not help to identify other materials with known crystal structures which may potentially also possess ionic conductivity.

Although these experimental methods produce accurate results, performing a comprehensive survey of the ionic conductivity of all known crystal structures using experimental methods is unfeasible. Experimental methods are often expensive and time consuming because the material must be physically made before any measurements can be conducted. This usually requires specialised and expensive equipment to fabricate the samples and perform the measurements. The help of specialists to operate this equipment is usually also necessary. As a result, the ability of facilities to fabricate large numbers of different types of materials is low.

Also, for a material selected at random, there is a very high probability that the material will not have any significantly measurable ionic conductivity. All of these factors make a comprehensive experimental survey of ionic conductivity of large numbers of materials an unattractive and risky option. As a result, experimental investigation of potential battery materials by individuals is usually limited to single materials or small groups of similar materials.
3.2 Computational methods

Computational methods may allow the scientist to simulate some of the properties of a material without having to first fabricate it [26]. This can eliminate a significant amount of experimental effort by targeting materials for experimental studies which probably already have desirable properties such as ionic conductivity. These methods are also useful to supplement experimental measurements and may offer insights into the chemical processes at an atomic and electron level. Computational methods by their nature are very suitable for large surveys as the calculations can potentially be automated to calculate properties of materials with minimal user intervention per material. Previous computational surveys have included work using computationally expensive DFT as detailed in [27-30].

However, the nature of many simulation methods prohibits this type of use due to various details of the methods themselves. The required properties of a computational method to be used as a survey tool are as follows. The method must be reasonably fast and accurate so that large numbers of materials can be analysed in a reasonable time frame. Also, the method needs to be transferable between different types of materials. This includes the availability of constants, if required by the method, as many different crystal structure types and chemistries will be analysed using the selected method. The method must also be able to cope with partial occupancies as many materials contain these. Finally, the method must be able to be automated as it is impractical to analyse each material individually for very large number of materials [7].
3.2.1 Atomic simulations

Atomistic simulations attempt to determine the properties of a material model by simulating the behaviour of its atoms and electrons. These simulations can involve monitoring the configuration and total energy of an atomistic system as a function of various conditions.

3.2.1.1 Energy/force calculation methods

In order to perform these types of simulations, some method must be selected to determine the interactions between different atoms in the simulation. Some of the most common methods are illustrated below.

3.2.1.1.1 Classical force-field simulations

Classical force-field based types of simulations have traditionally been used to analyse the ionic conduction properties of various materials[31]. These simulations consider the atomic system as a series of point particles which interact via an empirical potential calculated from the positions of the atoms relative to each other and a set of empirical constants. This simplified model does not explicitly model any quantum mechanical effects or interactions except those already described by the empirical potentials.

These types of simulations are usually very quick to calculate because the forces and energies are based on a very simple potential model. This high computational speed allows simulation of large systems with vacancy
distributions and complex molecules and also allows long simulation times. However, the absolute accuracy of the trajectories may be limited as the measured energy values may significantly vary from experimental measurement, depending on the potential in use.

Most importantly, an extensive list of transferable potentials does not currently exist for the inorganic materials which are of interest for this study. Because of this, the automation of this type of calculation is not practical which makes this method of investigation unsuitable for an extensive survey of known materials.

3.2.1.1.2 Density Function Theory (DFT) simulations

Density Function Theory (DFT) simulations calculate the distribution of electron charge density in an atomistic material based on the position of the nucleus’s of the atoms in the material and a set of pseudo-potentials. This method can calculate very accurate energies and forces as well as band structures, theoretical battery potentials and phase diagrams [26].

Although this method can be much more accurate than classical force-field based approaches, the computational resources that this method requires are several orders of magnitude larger. As a result, only small unit cells and short simulation times are practical to simulate with this method.
The transferability of the general pseudo-potentials used in these methods allows the calculation of the properties of most materials without significant user intervention. A comprehensive survey using this method is somewhat unfeasible because of the very long calculation times of this method. However, advances in computer processing power and DFT algorithms have made such an approach more feasible in recent years. A notable example of this is the Materials Genome Project [26] which uses this method to simulate various properties of potential battery materials in an automated fashion using large computing clusters. Also, the Open Quantum Materials Database (OQMD) uses DFT to calculate the thermodynamic and structural properties of a large number of theoretical and experimental materials[32].

3.2.1.2 Atomic motion methods

Although the forces, energies and electron densities of an atomic system theoretically describe most of the properties of a material, extracting information about specific properties requires the use of specific simulation methods. Some of the more common methods for determining ionic conductivity are illustrated below.

3.2.1.2.1 Molecular Dynamics (MD)

Molecular Dynamics (MD) uses the forces calculated from the previously described methods to model the trajectories of individual atoms in a material [33]. This method incorporates the motions of the atoms due to temperature. The atomistic trajectories generated by this method can be analysed to
identify diffusion between atom positions. It can also be used as input for Mean Squared Displacement (MSD) calculations which can be used to calculate the ionic conductivity and activation energy of the material, see 3.2.1.3.1.

3.2.1.2.2 Nudged Elastic Band (NEB)

The Nudged Elastic Band (NEB) method involves using artificial forces to ‘encourage’ an atom to move between two positions in physical space in a material. The change in energy of the system as the atom moves across this barrier is used to measure the activation energy of this transition. This activation energy can then be used to calculate the ionic conductivity of the bulk phase of the material using the Nernst equation – Equation 3.3. This method is implemented by creating a series of intermediate images between the beginning and end points of the transition in question and then relaxing them together while maintaining an appropriate gap between each image [34].

3.2.1.2.3 Climbing image Nudged Elastic Band (cNEB)

The climbing image Nudged Elastic Band (cNEB) method is similar to the NEB method with an additional feature. Once the individual images have converged to the minimum energy barrier positions, the image which has the highest energy is then driven to the local energy maximum in order to find the highest energy point in the given transition. This allows for a more
accurate determination of the activation energy of the barrier with less intermediate images than standard NEB methods [35].

3.2.1.3 Calculation of diffusion coefficient

The diffusion coefficient is related to the activation energy and Mean Squared Displacement (MSD) by the equations described in this section [36].

3.2.1.3.1 Mean Squared Displacement (MSD) ↔ Diffusion coefficient of ionic conductivity

The Mean Squared Displacement (MSD) is calculated from the atomistic trajectories of a simulation by Equation 3.1.

\[
\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} (|r_i(t) - r_i(0)|^2)
\]  

(3.1)

Where \( \langle r^2(t) \rangle \) is the MSD and \( r_i(t) \) is the position of the mobile ion as a function of time. The MSD is then fitted to the relationship described equation (3.2) to calculate the diffusion coefficient for the simulation temperature [36].

\[
\langle r^2(t) \rangle = 6Dt + C
\]  

(3.2)

Where \( \langle r^2(t) \rangle \) is the MSD, \( D \) is the diffusion coefficient at a given temperature, \( t \) is time envelope and \( C \) is a constant offset.
3.2.1.3.2 Diffusion coefficient of ionic conductivity ↔ Activation energy

The activation energy of a mobile ion in a material is a somewhat temperature independent property of the crystal framework. For simple systems where diffusion is primarily due to vacancy hopping, the activation energy of a material is related to the diffusion coefficient by the Nernst equation - Equation 2.3.

\[ D(T) = D_0 e^{-\frac{E_{\text{act}}}{k_B T}} \]  \hspace{1cm} (3.3)

Where \( D(T) \) is the diffusion coefficient at the given temperature, \( D_0 \) is the diffusion coefficient constant, \( E_{\text{act}} \) is the activation energy, \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

This equation can be used to calculate the diffusion coefficient of a material given the ion transport activation energy. The equation can also be used in reverse to calculate the activation energy from a given set of diffusion coefficients at different temperatures from calculations of MSD or from experimental impedance spectroscopy at different temperatures.

3.2.2 Geometric analysis computational methods

There exist a variety of geometric and volumetric methods which can approximate the geometry and location of ion conduction channels of a material. The methods described in this section generally do not incorporate
any lattice dynamics effects so that any paddle-wheel type molecule rotation, structure flexibility or correlated motion effects are not modelled. Most of these methods are suitable for approximating the effect of partial occupancies by a fractional contribution from these atoms.

3.2.2.1 Voronoi tessellation

The Voronoi Tessellation method divides the volume contained in a crystal structure into a series of zones located around the framework atoms. It can be used to identify possible ion conduction pathways and dimensions of bottlenecks in a material. The size of these bottlenecks can be compared to the dimensions of the mobile ions in order to help understand the ionic conduction properties of the material [37, 38].

3.2.2.2 Space filling spheres with pathway percolation

This method involves placing a sphere of pre-determined ionic radius according to atomic species around every atom in a crystal structure and analysing the remaining volume for size and infinite pathway connectivity. Materials with infinitely connected available space therefore may be ionic conductors. This method can be used to conduct a survey of ionic conductivity but would produce extremely crude results [39].
3.2.2.3 Classical/ DFT energy landscape

This method involves plotting the change in total system energy as a function of the position of a mobile test ion using either a classical force-field or DFT based approach. This method has the same positives and negatives as described in their respective sections. Both these methods are not suitable in their current form due to the lack of transferable constants for the classical force-fields and extremely long calculation times for DFT. Using DFT for this method would take an especially long time as it would require the calculation of at least 10,000-100,000 energy values even for small unit cells. This may be suitable for the analysis of a few selected materials but not for a large survey of 1,000’s of materials. DFT code is also generally not compatible with partially occupied atomic sites.

3.2.2.4 Pro-crystal maps

This method involves looking for pathways through a material with low electron densities as mobile ions may find it easier to travel in these areas [40]. The method uses a crude electron density field which is calculated from the summation of a series of pre-determined fixed electron densities centred on each atom. The areas with low electron density are then analysed for size and regions of connectivity. This method has the advantage of an existing universally transferable set of approximate electron densities so therefore can be automatically applied to most materials and is also very fast, making it suitable for use as a general surveying method.
3.2.2.5 DFT charge density maps for static calculations

Although slower, it is possible to perform a similar procedure to the procrystal map method using a calculated DFT electron density instead of an approximated one. This would be significantly slower than the procrystal method, but still well within the reach of modest amounts of computing power. This method may also be suitable for performing a survey and is orders of magnitude faster than the DFT energy landscape method. However, this method is also not compatible with partially occupied atomic sites.

3.2.2.6 Bond Valence Sum Maps

The Bond Valence Sum Map (BVSM) method uses the bond valence sum method to calculate the oxidation state of a mobile ion as a function of position in the unit cell of the material. Regions of space which have a valence which is close to the ideal oxidation state of the mobile ion are considered as likely ion conduction pathways. These pathways can be calculated and then analysed for connectivity and size which may be proportional to the ionic conductivity of the material [5]. This method is very similar to the classical energy landscape method as a Bond Valence Sum is essentially a special form of diatomic potential with units of valence (VU) or oxidation state.

This method is very computationally cheap and therefore is suitable to process very large numbers of materials. There is also a large transferable
database of constants available for this method so that most materials can be analysed. The method is also suitable for use with non-stoichiometric materials and fractional occupancies [41].

3.2.2.7 Bond Valence Energy Landscapes

The Bond Valence Energy Landscape (BVEL) method is similar to the Classical energy landscape method as it employs an empirical potential to calculate an energy landscape. The potential is based on an expansion of the Bond Valence Sum method by [6]. This method has been well developed and includes a comprehensive and transferable list of constants for the analysis of the solid crystalline inorganic materials which are of interest for this study and is also suitable to process very large numbers of materials.

3. 3 Project aim

The aim of this project is to implement the BVSM and BVEL methods to perform a comprehensive survey of all Lithium, Sodium, Potassium, Silver, Copper and Magnesium Oxides in the ICSD in order to identify existing materials which may have high ionic conductivity and better performance for use in battery technology.

This list of materials will then be published and these materials will then be further studied using more detailed computational and experimental methods such as DFT cNEB, classical force-field based MD and neutron based nucleus distribution mapping using the Maximum Entropy Method
(MEM). Also, some of these materials may be suitable for chemical substitution and mechanical nano-sizing to improve their performance.
CHAPTER 4      BOND VALENCE METHODS

The Bond Valence Sum (BVS) family of methods were chosen to perform a survey of a large number of crystalline materials from the ICSD. The BVS methods employed in this project are the Bond Valence Sum Map (BVSM) method and the Bond Valence Energy Landscape (BVEL) methods. These two methods both generate a 3-d scalar field which helps to identify the possible ion conduction pathways. These fields represent the change in oxidation state and energy of an imaginary mobile atom as a function of position. This field is then analysed to qualitatively approximate the ionic conductivity of the specific material and thus identify potential new ionic conductors.

4.1 Overview

The Bond Valence Sum (BVS) methods [5] are based on a simple empirical chemical bonding model calculated from the distances between neighbouring atoms. These methods can be described as a type of two-body potential model with a set of transferable empirical constants which produces a reasonably accurate determination of the oxidation state or energy of an atom in a crystalline structure.

4.1.1 Area of applicability

The BVS method describes interactions for idealised point atoms with a fixed oxidation state and describes a blended ionic and covalent interaction
between oppositely charged ions. “The bond valence model … provides a rational for the classic chemical model of localized bonds, at least for acid-base bonds, that is, those that have a cation at one end and an anion at the other.”, “However, it suffers from one important limitation - for reasons given below, it cannot be applied to bonds that are formed between atoms with the same electronegativity. This unfortunately excludes C-C and C-H bonds and therefore large parts of organic chemistry.” [5]

This makes the method applicable to most inorganic crystalline atomic systems but not suitable to describe biological, molecular chemistry and metallically bonded systems. Also, the BVS method does not model any quantum mechanical interactions and therefore may be of limited use for modelling systems containing hydrogen. However, some work is being conducted into expanding the method to include hydrogen within the BVS framework [5].

4.1.2   Strengths and weaknesses

4.1.2.1   Strengths

The BVS method is well developed and mature and is commonly used for structure validation and the determination of the oxidation state of atoms in materials. The family of BVS methods are all very computationally cheap and thus are suitable for conducting large surveys of materials in a reasonable time frame. The methods are easy to implement as the potentials are very simple. A large and comprehensive list of empirical constants [42,
4.1.2.1 Strengths

is available for the method which are transferable and accurate for materials this study is interested in. The method does not require complicated set-up or user interaction while running.

The method is able to visually identify the likely ion conduction pathways in a material and is natively capable of processing materials with partial occupancies. The method also does not suffer from artefacts due to small supercells which other methods may have difficulty with. These combined strengths make the method very suitable to be implemented as a survey tool to help identify possible new ionic conductors.

4.1.2.2 Weaknesses

The method does not take into account the dynamics of the atoms in the material being tested so that the effects such as distributed vacancies, paddle wheel mechanisms, structure flexibility, and such are not modelled [5]. Also, the results produced by these methods are rather qualitative and must be verified using other, more accurate, methods.

Also, there is no quantitative relationship for BVSM between the volumetric field data and the ionic conductivity of the material, apart from a general trend towards conductors and non-conductors based on the size and geometry of pathways [5]. There is also no interaction potential between same same charged ions in the BVS method. These two previous problems
do not influence the BVEL method as significantly due to its units of energy and the incorporation of a repulsive potential as described below.

4.2 Theory

4.2.1 Pauling’s bond strength

The Bond Valence Sum model is a development of the Pauling bond strength model [5]. In 1929, Pauling proposed the principle of localised charge neutrality for ionic materials. This principle leads to the existence of a local charge compensation effect where adjacent atoms provide the compensating charge to each of their neighbours. This contribution charge can be described by Equation (4.1).

\[ S_p = \frac{V_c}{N_c} \]  

(4.1)

Where \( S_p \) is the ‘bond strength’, ‘charge compensation amount’ or contribution to total oxidation state, \( V_c \) is the valence state or oxidation state of the surrounding atom and \( N_c \) is the number of coordinated atoms.

Pauling’s bond strength model assigned a ‘bond strength’ or ‘charge compensation amount’ to every bond for their local next nearest neighbours in a material. When these bond strengths are added together for any specific atom, the total sum was sufficient to neutralise the charge on that atom. Therefore this local charge or oxidation state can be given by Equation 4.2.
\[ V_a = \sum S_p \]  

(4.2)

Where \( V_a \) is the valence state, also called the charge or oxidation state of the atom and \( S_p \) is the Pauling bond strength. Although this method is fairly crude, it is a first approximation to the bond valence sum method where each neighbour atom provides some proportion of compensating charge to ensure the average charge neutrality of the materials.

### 4.2.2 Bond Valence Sum (BVS)

The Bond Valence Sum (BVS) method is an expansion of the Pauling’s bond strength model which uses a simple empirical formula with two constants per pair of atoms. These added terms help to include the effect of bond-length on total calculated oxidation state. This method can be described as a two-body interatomic potential whose calculated value is oxidation state in units of valence units (VU). The BVS method calculates the oxidation state of an atom as a function of the distances to its neighbouring atoms as well as their oxidation state and species. Development of computers allowed the fitting of large numbers of constants to this model, allowing the refinement of the method. Equation 4.3 shows the formula most commonly used to describe the BVS model.

\[ S = m_j \exp \left( \frac{(R_0 - R)}{b} \right) \]  

(4.3)

Where \( S \) is the bond valence, contribution to oxidation state or Pauling bond strength, \( R \) is the length of the bond in Angstroms, \( R_0 \) is the nominal bond
length in Angstroms and \( b \) is the bond softness constant in Angstroms. \( R_0 \), and \( b \) are both constants which must be determined based on fitting to experimental data. \( m_j \) is the occupancy of the atom and allows for calculations of materials with partially occupied sites.

Although the treatment of partially occupied atomic sites as a fractional atom as indicated in Equation 4.3 is not an actual physical representation of the physical system itself, it is useful in this context as this allows the average treatment of mixed atomic sites without the use of large super-cells and comparison to experimental data where atomic site mixing does not show any observable ordering. The family of BVS methods do not suffer from neighbour image interactions issues as the calculations never require the test ion to be a part of the unit cell and therefore the test atom can never interact with itself.

4.2.2.1 Example Calculation

The oxidation state of an atom is calculated in the BVS model by summing together all of the contributions from neighbouring atoms using Equation 4.2 and 4.3. An example calculation of a bond valence sum for \( \text{Li}_2\text{Co(SiO}_4\text{)} \) is given below for a Li atom position, see Figure 4.1. The values shown in Figure 4.2 are the distances between the selected Lithium atom and the surrounding Oxygen atoms. Other atoms of the same sign oxidation state are excluded from the calculation because the BVS method only describes an interaction between the positively charged Li\(^+\) atom and the negatively
charged O$^2^-$ atoms. Figure 4.2.a. also shows the individually calculated Bond Valence Sum values for each bond, calculated from Equation 4.3, which are also plotted in order of size in Figure 4.2.b. These individual BVS values are summed together using Equation 4.2 to calculate the oxidation state of the test ion.

![Figure 4.1 - Li$_2$Co(SiO$_4$) - Inter-atomic distances (Å) between test Li-ion and next nearest anions. Details: Oxygen-Red, Silicon-Yellow, Lithium-Purple](image)

<table>
<thead>
<tr>
<th>Length (Å)</th>
<th>BVS Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.95</td>
<td>0.22</td>
</tr>
<tr>
<td>1.97</td>
<td>0.21</td>
</tr>
<tr>
<td>2.00</td>
<td>0.20</td>
</tr>
<tr>
<td>2.09</td>
<td>0.17</td>
</tr>
<tr>
<td>2.98</td>
<td>0.03</td>
</tr>
<tr>
<td>3.40</td>
<td>0.01</td>
</tr>
<tr>
<td>3.41</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Sum Total BVS value: ≈ 1*

![Figure 4.2 - a. Tabular and b. graphical representation of individual BVS values. Oxidation state comes to within 10% of expected value of ‘1+’](image)
The final result of the calculated oxidation state of the Li atoms is 0.95 VU, which is 0.05 VU from the ideal oxidation state of 1.00 of the 1+ Li-ion. This difference is called the valence mismatch and is typically within 0.10 VU of the actual value of oxidation state of the test atom but may vary depending on the specific material.

4.2.2.2 Cut-off length

As can be seen in Figure 4.2, most of the contribution to total oxidation state is made by the first few contributing terms. Increasing the number of included bonds at longer distances provides a diminishing contribution to total oxidation state. Therefore extra computing effort does not significantly improve the accuracy of the calculation past a certain maximum bond length or cut-off length. Also, any given set of constants is usually created with a certain cut-off length criteria in mind. For example, a fixed maximum length or number of coordination spheres which should be used in calculations to replicate the same conditions as those used to originally derive these constants.

4.2.3 Selection of calculation constants

Refinement of BVS constants has been the subject of significant amounts of research effort as indicated in [5]. Many individuals and organisations have produced lists of bond valence sum parameters for various materials of varying accuracy and detail. Some sets of constants target specific groups of
materials in detail while others cover a larger range of materials. A large combined list of these constants can be found at [44].

Due to the difficulty in tuning these parameters, the value of $b$ is often set to the value of 0.37 and the value of $R_0$ is then tuned to the experimental data in order to reduce the complexity of the fitting procedure. “The value of $b$ is found to lie between 0.3\text{\AA} and 0.6\text{\AA}$ but because of the limited range of experimental bond lengths its precise value is not easy to determine. For this reason a value of 0.37 \text{\AA} is frequently assumed although recent work discussed in [5] shows that significantly different values should be used for some bond types.” [5].

4.2.3.1 softBV constants

Of substantial interest to this project is the recent work [6, 23, 42, 43] which contains an extensive set of constants for both the BVS/M and BVEL methods. These constants incorporate both a variable value of $b$, which relates to the softness of the bond [45]. This refinement allows more accurate BV calculations for materials with non-standard bond lengths and intermediate atomic positions such as those found in this project. These constants also include the effect of multiple coordination rings of atoms in some cases of 4-8\text{\AA} instead of only the next nearest neighbours. This long cut-off length effectively eliminates the step-effects which would be observed in the BVSM/BVEL field data if only short bond lengths or less coordination rings of atoms were used as described in 5.3.2.4
The refinement of these constants was based on a large amount of structural data from the ICSD of a similar type to the materials of interest to this project as well as experimental activation energies from literature. As a result, the data is reasonably accurate and wide ranging and is also targeted at the group of materials of interest in this project, making a comprehensive survey using both the BVSM and BVEL methods a very feasible and attractive option.

This work relies on the accuracy of these softBV constants which were selected for both the BVSM and BVEL methods as detailed below. An additional term related to bond softness mixing is also specified for this potential set and is further documented in 4.2.5; however, this b-value mixing is not currently implemented 3DBVSMAPPER BVSM code.

4.2.4 Bond Valence Sum Map (BVSM)

The Bond Valence Sum Map (BVSM) method for investigating ionic conductivity is detailed in Chapter 10 of [5] but a simple description follows. The oxidation state of an imaginary test atom is investigated as a function of position by calculating its BVS value at a series of regular points spanning the unit cell. This field of calculated oxidation states is then analysed to identify regions which are close to the ideal oxidation state of the test atom, or alternatively have a low valence mismatch. It is expected that these regions are the more likely positions that a mobile test ion would travel in.
4.2.4.1 Example calculation

Figure 4.3 illustrates two extreme cases of a spinel type material which is a known ionic conductor and a salt type material which is a known insulator. As can be seen, there are regions of connected space of low bond valence mismatch in the spinel which suggests that this material is a potential conductor of lithium, whereas the salt structure shows isolated regions of low BV mismatch which suggests it is not a conductor.

Figure 4.3 – BVSM isosurfaces for (a) LiV$_2$O$_4$ Spinel and (b) LiCl rock salt. (Isovalue: ±0.2VU)
4.2.4.2 Blocking Spheres

As previously mentioned, the standard BVS method only takes into account the atoms of opposite sign charge. The lack of repulsive potential term between same-sign oxidation state atom usually leads to unphysical pathways predicted to pass through the locations of the framework atoms as can be seen in Figure 4.4. The standard BVS method makes no distinction between areas that already contain framework atoms which are probably stationary and areas which contain atoms of the same species as the test ion which may be mobile.

As a result, an additional repulsive term must be added to the calculations to force mobile atoms to avoid the areas which already contain same-charged framework atoms and therefore remove unphysical pathways from the resulting field. It is common to use either coulombic repulsion or a simple blocking sphere which defines an exclusion radius around existing non test ion species framework atoms[5]. While others have used a blocking sphere based on the metallic radius [46], the program written in this project uses simple blocking spheres of fixed radius.

As an example, Figure 4.4 shows BVSM field slices for a known lithium ionic conductor which has 3-dimensional ion conduction pathways as indicated by the lithium atom distribution in the original structure. The BVSM field without blocking spheres predicts several unphysical ionic conduction pathways which pass close to known framework atoms. As can
be seen, the blocking spheres are effective in preventing these unphysical pathways.

Figure 4.4 – BVSM slice through x-y plane at $z = 0.5$ of solid oxide crystalline ionic conductor ‘Hexalithium barium dilanthanum ditantalum oxide’ $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ (ICSD: 163861). Lithium has been removed from figures with slices for clarity. (a) Section of original structure including known Li-ion positions as large purple spheres. (b) Slice through BVSM data with blocking spheres. Red and magenta shaded areas indicated same same and same-opposite oxidation state blocking spheres respectively. The variation in radius of the different circles is due to the distance between the atoms and the field plane as well as the different blocking sphere radii of positive and negative oxidation state framework atoms. (c) Same slice through BVSM data with no blocking spheres. The unphysical ionic conduction pathways are indicated by black circles.
4.2.5 Bond Valence Energy Landscape (BVEL)

The Bond Valence Energy Landscape (BVEL) method is an adaptation of the BVS method to convert valence units (VU) into energy units (eV) using a Morse-type potential \([45]\). This method also incorporates a repulsive potential for same-same charged atoms which removes the necessity of hard blocking spheres and produces smoother field data. The potential for this method is described by Equation 4.4 - Equation 4.8.

\[
\text{BVEL}_{+/−} = \sum_{j=1}^{N} \left[ m_j \times D_0 \times \left( \exp\left( \alpha \left( R_{\text{min}} - d_j \right) \right) - 1 \right)^2 - 1 \right] (4.4)
\]

\[
\text{BVEL}_{+/−,−/−} = \sum_{j=1}^{N} \left[ \text{ConvEv} \times \frac{m_j \times |V_{\text{T}}| |V_j|}{\sqrt{\text{n}_{\text{qT}} \times \text{n}_{\text{qj}}}} \times \left( \text{erfc}\left( \frac{d_j}{\rho} \right) - \text{erfc}\left( \frac{d_{\text{cutoff}}}{\rho} \right) \right) \right] (4.5)
\]

\[
\rho = \rho_f \times (r_{\text{T}} + r_j) (4.6)
\]

Where \( j \) - \( j^{th} \) ion, \( d_j \) - Bond length, \( m_j \) - occupancy, \( N \) - number of counterions, \( D_0, R_{\text{min}} \), and \( \alpha \) – tabulated constants, \( \text{ConvEv} \) - conversion factor from inverse length to energy in eV, \( V_{\text{T}}/V_j \), \( n_{\text{qT}}/n_{\text{qj}} \) - oxidation states and quantum numbers of test ion and \( j^{th} \) neighbour, \( \text{erfc} \) - complementary error function, \( d_{\text{cutoff}} \) - erfc tail cutoff length, \( \rho_f \) - constant equal to 0.74, \( r_{\text{T}} \) and \( r_j \) - tabulated covalent radii.

These equations can be used to produce a 3-dimensional energy landscape similar to a BVSM field or used as a classical force field for atomistic simulations. A large and comprehensive set of constants (from \([42]\)) as
described in 4.2.3 are also provided for this method so that it can also be used to automatically survey a broad range of compounds.

An additional bond softness mixing effect is also included for materials with mixed oppositely charged atoms. It should be noted that the effect of this averaging of b-values only has an effect on materials with multiple different types of negative charged ions. Of these materials, the effect is only significant on materials with negative charged ions with significantly different softness.

As noted in [42], “the effectively used bond valence parameter $b$ ($b = \frac{1}{a}$) will differ from the … tabulated constants … to account for the mutual equalization of bond softness. For each … -ve charged ion … the program calculates a weighted mean … b value … averaging over all … +ve charged ion … types

$$ W = N \cdot abs(V_{an}) \quad (4.7) $$

(… Where $W$ – weighting factor, $N$ – number of anions per unit cell and $V_{an}$ – oxidation state of anion…) and calculates the effective b-value

$$ b_{effective}(cation, anion) = $$

$$ = f \cdot b_{average}(cation) + (1 - f) \cdot b(cation, anion) \quad (4.8) $$
with an empirical factor $f = 2/3$ … This averaging becomes relevant for compounds that contain anions with strongly different softnesses. It should be noted that compounds with containing different types of anions had been excluded from the reference data sets for the determination of softBV parameters (while most compounds in the reference data sets contained different types of cations).”

4.2.5.1 Example calculations

Figure 4.5 illustrates similar behaviour to that described in 4.2.2.1 where an ionic conductor and insulator are presented. Similar to Figure 4.3, there are regions of connected space of low bond valence mismatch in the spinel which suggests that this material is a potential conductor of lithium, whereas the salt structure shows isolated regions of low BV mismatch which suggests it is not a conductor.
Figure 4.5 – BVEL isosurfaces for (a) LiV$_2$O$_4$ Spinel ($\Delta$Isovalue: 0.02eV) and (b) LiCl rock salt. ($\Delta$Isovalue: 0.5eV)
CHAPTER 5 3DBVSMAPPER PROGRAM

5.1 Existing software

Many existing software packages implement various BVS based methods. In VaList [47], BondVal [48] and Rietica [49], BVS is used to validate crystal structures by calculating BVS at existing atom locations. However, these programs do not have the native ability to calculate 3-dimensional BVSM fields. BondStr within the Fullprof Suite [50], Valmap [51] and Jumpiter [52]) all have the ability to calculate 2/3-D BVSM data but are not suitable for automation as they are operated from a GUI and none implement the BVEL method. As a result, it was necessary to write the 3DBVSMAPPER software [53] in order to implement the program features which are required for a large survey of crystalline materials.

5.2 Program description

The 3DBVSMAPPER software was written to automatically generate and analyse 3-dimensional BVSM and BVEL fields for large sets of crystal structures. The built-in fractional volume tools automatically analyse these fields at various pre-defined BV mismatch and energy isovalues with low-valued infinitely connected isosurfaces. The software can calculate BVEL and BVSM fields for both positive and negatively charged test ions and a comprehensive list of constants from [23, 42] is provided with this program as well as the combined constants provided from [44].
5.2.1 Program features

The software is designed to use *.cif (Crystallographic Information File [54]) files in the ICSD format as input, including those with partially occupied sites, and produces *.grd and *.xsd files in Materials Studio Format as well as *.grd files in VESTA [55] compatible format. The program also produces individual and combined *.csv files which contain the measurements of the isosurfaces.

The program is configured by editing the input configuration text files and a simple GUI has also been developed which allows the average user easy access to most important program features. Most of the settings of the program are customisable, such as the test ion species and oxidation state, resolution, folder locations, blocking sphere radii and isosurface isovalue settings.

The software is executed by running the scripts in the Materials Studio [56] environment and the program is currently available to the end user by requesting a copy from the author. Unfortunately the software is not available apart from Materials Studio at the moment. The program is not limited in resolution or size of field, except the limitations imposed by the Materials Studio libraries and available computer memory. Larger unit cells and finer resolutions require more memory and computational time to calculate.
The program was written in the PERL scripting language which is integrated within the Materials Studio materials modelling program from [56]. This software environment was selected to take advantage of the existing atomistic simulation features of Materials Studio which already implement many of the tools required for this program such as an atomistic model and 3-d voxel field analysis tools. It was also selected in order to take advantage of the client/server capabilities in order to utilise the larger computing power available on servers. The choice to develop custom software also allowed customisation of the software to the specific task of large, automated surveys.

The code is stable and although was originally designed to automatically process the specific type of *.cif file found in the ICSD, is generally compatible with most other *.cif files generated by other software. An area of common program improvement is the minor modification of the *.cif file loading algorithm in order to implement compatibility with various details of the different types of *.cif files. The program script is single threaded and does not directly take advantage of parallel processing. However, the automation architecture is designed to process multiple *.cif files in parallel from a single set of input data.

The program has experienced some speed and stability problems due to issues with the Materials Studio scripting libraries which have hindered the speed, maximum resolution and stability of the program. These issues have been mostly resolved with updates to the code. The BVEL code implements
the softness mixing effect documented at [42] while the BVSM code currently does not. This mixing method does not have any effect on the results for most materials tested in this thesis.

5.3 Main calculation program operation

The general operation of the main calculation and analysis part of the program is illustrated in Figure 5.1; however, a more detailed description follows. The program variables described in this section were refined as we deemed fit to produce reasonable results using the Li-O ICSD data set described in Table 7.1. An example of the program and the associated configuration variables is included in the electronic supplementary information.

5.3.1 Load CIF file

When the calculation script is executed, the program first loads the setup files and calculation constants. These files contain information about the test ion species and oxidation state, the resolution of calculation, the location of folders containing the input and output files and the remaining configuration data. Once this is complete, the program proceeds to read the contents of the *.cif input folder and selects a crystal structure which has not yet been calculated. The program uses a shared directory to identify which crystalline materials have been processed.
1. Load CIF file

2. Pre-calculation tasks
   • Removal of low occupancy atoms (< 5%)
   • (BVSM only) Deletion of atoms of same sign oxidation state as test atom which are too close (2Å) to any test atom species
   • (BVSM only) Placement of blocking spheres (2Å) around remaining atoms with same sign oxidation state as test atom
   • Removal of test atom species

3. Calculation of BVSM/BVEL field
   • Generation of a 3D grid of specified resolution over the volume of the unit cell
   • Placement of test ion at a single grid point
   • Calculation of BVSM/ BVEL value for atom at that specific location
   • Repetition of above steps for all grid points
   • Population of field with these calculated values

4. Analysis of BVSM/BVEL field
   • Creation of an isosurface on 3D field which selects regions of low values
   • Removal of non-infinitely connected isosurfaces
   • Measurement of volume and surface area of isosurface over a single unit cell

5. Save Results
   • Save fields in both *.grd and *.xsd formats
   • Save isosurface information about volume and area in *.csv file.

6. Repeat process
   • Repeat to beginning until all *.cif files have been processed

(Separate script) Combine all results together
   • Make a copy of all files in one location
   • Sort individual calculation folders according to errors and warnings
   • Append all volume and area information into a single *.csv file, ready for analysis

Figure 5.1 – Diagram illustrating the general operation of the 3DBVSMapper program.
5.3.2 Pre-calculation tasks

Once a new crystal structure has been loaded, the program proceeds to the pre-calculation screening tasks. As detailed below, these involve selecting calculation constants, removal of some of the atoms in the structure, selection of blocking sphere radii and maximum bond cut-off lengths.

5.3.2.1 Resolution

The resolution was adjusted to a value of 0.25Å for BVSM to give a good compromise between speed and fractional volume accuracy. Later upgrades to the code allowed a finer resolution of 0.2Å for the BVEL calculations.

5.3.2.2 Removal of low occupancy atoms of same sign oxidation state to the test ion

It was found when processing large numbers of crystalline materials from the ICSD that many materials contained atoms of the same sign oxidation state as the test ion with very low occupancy in various locations. Although these atoms had an extremely low occupancy, these atoms created blocking spheres which often blocked the likely ionic conduction pathways. As a result, the program is configured to remove atoms of the same sign oxidation state as the test ion with a very small occupancy prior to calculation. A threshold value of 0.05 produced reasonable results for most materials.
5.3.2.3 Removal of same sign oxidation state atoms which are too close to test ion positions

In some cases, crystalline materials from the ICSD would report atoms to have an unphysically close distance to known test atom positions. Even after the test atom species was removed, an ion conduction pathway could not be

Figure 5.2 – Adapted from histogram of various positive-positive oxidation state interatomic bond lengths for all crystalline materials in ICSD up to 5Å [4].
formed through these regions due to the blocking spheres around these atoms. The short interatomic distances described by these crystal structures were unphysical in that they were much shorter than most reasonable bond lengths found in the ICSD Figure 5.2. The cause of these short interatomic distances may be due to the existence of partially occupied atomic sites, eg, ICSD: 59646, 71221. Also, some crystal structures may have questionable data accuracy or the original samples may not have been a pure single phase.

As a result, we implemented a structure cleaning procedure where any atom of same sign oxidation state as the test ion which was too close to an existing test ion position is removed from the structure. The radius for this process was tuned to 2.00Å. This distance is shorter than observed bond lengths, for example, between Li and Mn, Fe and Co as seen in Figure 5.2. This process is disabled by default in the BVEL program as the repulsive interaction of this method is proportional to the occupancy of the atom, making this process redundant.

5.3.2.4 Maximum bond length or cut-off length

As previously mentioned in 4.2.2.1 and 4.2.3.1, the choice of maximum included bond length or cut-off length is very important to balance the calculation speed and data accuracy of the BVSM and BVEL calculations. A longer cut-off value can improve the accuracy and field data smoothness
by including more atoms in the calculations but requires more calculation time.

Standard BVS calculations usually only consider the first coordination ring of atoms around the test atom by forming bonds to all atoms within a short radii or cut-off length. However, using such a short cut-off length is not suitable for the calculation of BVSM and BVEL field data as this produces large spherical steps around each atom in the field data. These large steps in the field values are an artefact of the short cut-off length and terminate the infinitely connected isosurfaces which should normally represent the ion conduction pathways. As a result, a longer cut-off length than this must be used.

Most importantly, it is important to use the same cut-off length criteria used in the creation of the original calculation constants so that any calculations will reproduce these results. In this study, extensive use was made of the softBV constants [23, 42], therefore the cut-off criteria described in this method was employed in our calculations. This set of constants describes a long cut-off length of 4-8Å, depending on same-opposite sign oxidation state atomic species, which ensures that the BVSM/BVEL field is smooth. For the use of other sets of calculation constants, a fixed cut-off length can be specified in the setup files. For the BVEL method, an additional cut-off length must be specified between the same-same repulsive interaction and is set by default to a long fixed length of 9Å as described by [57] in a private communication.
5.3.2.5 Blocking Spheres

As mentioned in [5], for the BVSM method, some form of repulsive potential must be implemented around same-same oxidation state atoms so that unphysical pathways which would normally pass near to same-sign oxidation state framework atoms are removed. Therefore a fixed length blocking sphere for same-same oxidation state atoms has been implemented in this program. The field values inside of these blocking spheres are set to an arbitrary large value so that isosurfaces avoid these areas. The same-opposite and same-same oxidation state blocking sphere radii were set to 0.75Å and 2.0Å respectively as described below.

Blocking spheres are not necessary in the BVEL method as the specified repulsive potential prevents false pathways around same-same oxidation state framework atoms. In the BVEL method, the blocking spheres are set to very small values in order to avoid calculation errors due to division by zero problems and are set to 0.1 for both settings by default.

5.3.2.5.1 Same-opposite oxidation state blocking spheres

The blocking sphere radii were adjusted to give reasonable results through an iterative process. A small radius of 0.75Å was selected for the same-opposite oxidation state interaction between the mobile ion and the opposite charge oxidation state framework ions. This value is quite conservative as it is less than half the average first coordination ring interatomic distances shown in the Li-O bond lengths ICSD histogram Figure 5.3. Also, the
BVSM equations essentially describe a repulsive term between same-opposite sign oxidation state atoms so that such a blocking sphere is not strictly necessary.

Figure 5.3 – Adapted from histogram of lithium oxygen bond lengths for all crystalline materials in ICSD up to 5Å [4]. As can be seen, the most common Li-O bond length at the first, second and third coordination rings are approximately 2.0, 3.5 and 4.5Å respectively.

5.3.2.5.2 Same same oxidation state blocking spheres

The same same oxidation state atom blocking sphere radius was crudely refined to a conservative value of 2Å which gave good results upon review of a large number of materials. As can be seen in Figure 5.2, this length is shorter than the bond lengths between the same same interatomic distance histograms for several typical atom species. Also, this value is the same length as a typical same opposite bond, for example, the average Li-O bond length as seen in Figure 5.3. It is expected that most same same oxidation state bond lengths will be substantially longer than this due to coulombic repulsion.
This radius was initially set to a smaller value but it was found that many small and incorrect ionic conduction pathways would appear at the edge of these smaller spheres. The radius was therefore increased to ensure that false ionic conduction pathways are removed from the field data so that materials are not incorrectly identified.

Also, the materials being simulated are made from alternating positive and negative oxidation state atoms. As a result, all ion conduction pathways usually pass through an oppositely charged bottleneck. The volume of these bottlenecks is usually fairly small and therefore the change in total fractional volume of the isosurfaces is not as sensitive to blocking sphere radius in these locations (Figure 4.4).

In any case, it is important to visually inspect the BVSM/BVEL fields to identify any possible ionic conduction pathway artefacts which are very small or pass between positively and negatively charged atoms. It is also important to remember that the radii selected for the blocking spheres was arbitrary and any suggested ionic conduction pathway which are surrounded by blocking spheres should be investigated further using more accurate methods.

5.3.2.6 Selection of constants

The program gathers the specific calculation constants required for the calculations from the calculation constants files in this part of the program.
The program is configured by default to use the softBV constants [23, 42] for both BVSM and BVEL methods, see 4.2.3. The program has the ability to select constants from more than one author from the constants file. It is not recommended to mix constants from different authors as the refinement methods vary between authors and different sets of constants may not be compatible with each other. Also, if multiple negative oxidation state atoms are present when testing with a positive oxidation state mobile test atom and the softBV constants are selected, b-value mixing is performed on the constants data as described in 4.2.5. This feature is not currently implemented in the BVSM code.

5.3.2.7 Removal of test ion species atoms

Existing atoms of the test ion species are usually involved in ionic conduction and therefore occupy locations of probably ion conduction pathways. Therefore, all atoms of the same atomic species as the test atom must be removed from the crystal structure so that the program can calculate ion conduction pathways at without blocking spheres (BVSM) or local repulsive energy fields (BVEL) to block these likely channels.

It is also possible to configure the program to remove other likely mobile species. For example, a material may contain a mixture of mobile Na and Li so that it is necessary to remove both of these species of atoms before performing the calculation. The option of removal of other mobile atoms is not currently implemented in the BVSM code.
5.3.3 Calculation of BVSM/BVEL field

The calculation section of the program uses the crystal structure and the data from the pre-calculation task section to calculate the BVSM or BVEL field data. The program first validates the configuration data from the previous section and then generates a 3-dimensional grid of points at the specified field resolution to store the field data. After this, the program sequentially calculates the individual BVSM/BVEL field values at every grid point using an imaginary test atom. Periodic boundary conditions are used to expand the boundaries of the unit cell. This field is then passed to the next section of the program for further analysis.

5.3.4 Analysis of BVSM/BVEL field

The program has routines for automatically analysing the calculated fields to measure the volume and surface area of low-valued infinitely connected isosurfaces, for example see Figure 4.3 and Figure 6.1.

The program implements several schemes (Chapter 6) for selecting the isovalues of the infinitely connected isosurfaces used to measure the BVSM/BVEL fields which are configured in the setup file. The program measures and records the volume and surface area of each isosurface at every measured isovalue. The program is configured by default to select a range of isovalues which are useful for most research purposes. These values include 0.2 BV mismatch and the ‘activation energy’ as described further in Chapter 6. The results of this analysis is then written to the
*_statistics.txt file. The program also reads many of the auxiliary data fields from the original *.cif files which are also written to the *_statistics.txt file to help in the comparison of different crystalline materials.

The program is configured to only include isosurfaces which are low valued and infinitely connected. These isosurfaces are selected so that it is possible for a mobile atom to infinitely travel in at least one direction in areas of low BV mismatch or energy barrier, for example see Figure 4.3 and Figure 6.1.

Isolated areas with low BV mismatch or energy are excluded from the fractional volume and surface area measurements. The program uses a recursive algorithm to correctly identify these infinitely connected areas even if they involve complex pathways looping back and forth through the unit cell boundary.

The field isosurface analysis usually consumes as much computational time as the calculation of the field itself and can be adjusted to minimise computational times. For the BVSM data, the program creates a copy of the original field in the *.xsd file to represents the BV mismatch value using Equation (5.1).

\[ BVMismatch(\bar{x}) = \text{abs}(BV(\bar{x}) - OxState) \]  (5.1)
Where: $BVMismatch(\bar{x})$: Bond Valence Sum Mismatch field value, $BV(\bar{x})$: Original Bond Valence Sum Map field value and $OxState$: oxidation state of the test ion.

The program also measures the fractional volume of the isosurfaces at isovalues below the minimum infinitely connected isovalue inside of this isosurface for both BVEL and BVSM. To achieve this, the program identifies the minimum connected field and separately measures the fractional volume and surface area Figure 6.3 within this field area.

5.3.5 Save Results

As a final step, the program saves all of the data from these calculations into various files and marks the crystal structure as complete. The program outputs the field data in the *.grd and *.xsd file formats compatible with Materials Studio [56] as well as the *.grd format compatible with VESTA [55]. These programs can then be used to visualise the likely ion conduction pathways from both the BVSM and BVEL methods.
5.3.6 Repeat process

This entire process is repeated until all of the crystal structures have been processed. Multiple calculation scripts can be executed in parallel to process multiple *.cif files in parallel to accelerate the calculation progress of large groups of materials. The nature of the parallel architecture of the program is illustrated in Figure 5.4.

5. 4 Summary of program details

Once all calculations have completed, another script is executed which combines and summarises the output of the individual calculation scripts.
This summary script sorts the results of the calculations into folders according to the success or failure of the individual calculation. It also combines the results of the infinitely connected isosurface analysis of the BVSM/BVEL fields into a single file so that different crystal structures can easily be compared with each other. This ‘statistics’ file is in a *.csv format and can be read and processed in Microsoft Excel or other suitable programs.
CHAPTER 6    FIELD DATA ANALYSIS METHODS

In order to use the BVSM and BVEL methods to survey the ionic conductivity of materials, some relationship must be selected to convert the 3-dimensional field data into an approximation of ionic conductivity. Previous works [5, 41, 58, 59] have generally shown a relationship between increasing fractional volume of the infinitely connected low BV mismatch isosurface and ionic conductivity.

This relationship is due to the fact that pathways of infinitely connected low valued BV mismatch or energy are the areas which are physically accessible to mobile atoms, according to the BVSM and BVEL methods, see Figure 4.3 and Figure 6.1. The existence of these areas may correspond to the existence of ionic conductivity in the material and is the first step to approximating the ionic conductivity of the material.

Several different available methods for selecting isovalues as well as their utility using the 3DBVSMAPPER program will be described in this section. Also, the activation energy analysis method will be described as well as some of the scaling methods necessary to compare isosurface volume data between different materials.
Figure 6.1 – Figure illustrating isosurfaces of increasing isovalue. Data calculated from Li$_3$Bi$_2$PdO$_{10}$ (ICSD: 73000). Left: BVSM of isovalue 0.05VU (top), 0.11VU (middle) and 0.17VU (bottom). Right: BVEL of ~Δisovalue 1.15eV (top), 1.775eV (middle) and 2.45eV (bottom). Blue isosurfaces represent infinitely connected areas and brown isosurfaces represent isolated areas. As can be seen, increasing the isovalue progressively includes isolated areas of isosurface which form the steps seen in Figure 6.2. Interestingly, while both BVSM and BVEL fields indicate that the minimum connected isosurface is connected along the B direction, the suggested easiest pathway is different from both methods. The pathway suggested by the BVEL method passes through the centre of the unit cell whereas the BVSM method passes towards the side of this area. At higher isovalues, both methods suggest the same general pathway geometry, with the exception of the centre ion conduction pathway of the BVEL method.
6.1 Infinitely connected isosurfaces

The fields generated by the BVSM and BVEL methods are analysed using isosurfaces of low BV mismatch or energy. This condition selects field areas or pathways which are easily accessible to a mobile ion. These isosurfaces are also required to be infinitely connected in at least one direction so that a mobile ion would be able to travel or conduct through the structure. This condition excludes measurement of field areas which are isolated from the ion conducting pathways, for example, see Figure 6.1.

![Figure 6.1](image)

Figure 6.1 – Example plot of fractional volume of the infinitely connected isosurface at different isovalues. Data calculated from Octalithium dibismuth(V) palladium oxide, Li$_8$Bi$_2$PdO$_{10}$ (ICSD: 73000) (a) BVSM fractional volume vs valence mismatch, (b) BVEL fractional volume vs energy starting at the MinField energy. As can be seen, the BVEL graph clearly shows two steps in the fractional volume data. The first step at 1.5eV is associated with the onset of connectivity and the second at 2.0eV is due to the sudden inclusion of a previously isolated region of field. The BVSM graph also shows some evidence of this two-step behaviour due to the discontinuity in the step at about 0.11VU. See Figure 6.1 for isosurfaces at various isovalues for both BVSM and BVEL.

6.2 Characterisation of volume vs isoalue curves

Some attempts have been made to characterise the general shape of the fractional volume vs. isoalue curves from this data. A typical plot of these
curves is presented in Figure 6.2. As can be seen, the curve is characterised by a step at the point of first infinite connectivity followed by a region of increasing fractional volume with a few possible steps where isolated areas become connected to the infinitely connected isosurface at higher isovalues.

\[ y = a b \sqrt{x} \]  

(6.1)

The large isovalue behaviour of the curve can be approximated by Equation (6.1) or similar. However, characterising the smaller isovalue region using such a simple equation is inadequate due to the numerous discontinuities at low-isovalues. The small isovalue region of data is the region of interest to identify potential ionic conductors and therefore other methods were used to analyse this data.

Importantly, it is observed that increasing the isovalue has an approximately linear effect on fractional volume once an infinitely connected isosurface has been obtained. Apart from a few possible discontinuities, this is observed once the isovalue is larger than the value required to reach the minimum infinitely connected isosurface, or MinConnected isosurface value. Therefore the use of slightly larger isovalues when ranking materials does not significantly shuffle the order of the materials, but only increases the isovalue threshold to include more of them.
Figure 6.3 – Diagram illustrating the method used to determine the global ‘activation energy’ from the BVEL field data. The black curve shows a plot of the 3-dimensional BVEL field values along a line segment in the unit cell. This line passes through a region of field which is inside of the ‘MinConnected’ isosurface, which is the minimum isovalue infinitely connected isosurface. The green line represents the isovalue of the ‘MinConnected’ isosurface which, as can be seen, is at the same energy value as the highest energy peak of the black BVEL line plot. This figure also shows the ‘MinField’ value, which is the lowest field value inside of the ‘MinConnected’ isosurface. The ‘activation energy’ is calculated by measuring the difference between the MinField value and the MinConnected isovalue. Although a lower global field minima field value may exist outside of the ‘MinConnected’ isosurface, only the minima inside of the isosurface is used as the MinField value. A similar method is used for identifying the global minimum BV mismatch for the BVSM field data.

6.3 Minimum BV mismatch or ‘activation energy’ method

This method of analysis calculates the global minimum activation energy (BVEL) or global minimum BV mismatch (BVSM) required for a mobile ion to infinitely travel in the crystal structure in at least one dimension. As illustrated in Figure 6.3, this ‘activation energy’ is calculated by first identifying the minimum isovalue infinitely connected isosurface, or ‘MinConnected’ isosurface. This MinConnected value is the minimum
possible isosurface isovalue which is still infinitely connected in at least one
dimension and therefore represents the lowest possible energy or BV
mismatch isosurface area which still allows infinite travel through the
crystal structure. Next, for BVEL, the lowest energy value within this area is
identified and this is referred to as the MinField value. Although a lower
field minima energy may exist outside of the ‘MinConnected’ isosurface,
only the minima inside of the isosurface is used as the MinField value. For
BVSM, the BV mismatch MinField value is equal to zero by definition.
Finally, the difference between the MinConnected isovalue and the
MinField value is calculated and this value is referred to as the ‘activation
energy’ of the material for a particular species of mobile ion.

The value generated by this method is in units of energy (eV) and BV
mismatch (VU) respectively and cannot be scaled when used to compare
different materials like the required scaling for the volume measurements
described in (6.5.2). While it would be possible to identify the magnitude of
the individual local barriers, this procedure is more complex to automate
and is not as simple to use for the comparison of many materials.

As can be seen in Figure 6.4, for BVEL, the MinField energy is a
reasonably good measure of the energy at the known mobile ion positions
due to the good correlation between these two values. This figure effectively
shows that the mobile atoms are usually found near the calculated energy
minima’s.
Figure 6.4 – BVEL MinField energy (eV) vs minimum energy at mobile ion site energy (eV) for the Li-O ICSD data set described in Table 7.1. Some extreme data points outside the plot area are not shown for clarity. This plot shows the good agreement between the connected field minima and the mobile ion position energy value due to the nearly unity slope of the linear fit. As a result, the minimum connected isosurface field minimum energy value can be used to set the zero energy point for the BVEL field values.

These ‘activation energy’ values can be used to compare materials by ranking them according to how much BV mismatch (BVSM) or energy (BVEL) is required for a mobile ion to overcome the highest barrier inside the minimum infinitely connected isosurface. For BVEL, the measurement method for activation energy is a similar representation of the physical activation energy of the ion diffusion process. Materials can be compared to one another using this value as the Nernst equation (3.2.1.3.2) states that ionic conductivity is inversely proportional to the activation energy. As a result, the activation energy method used with the BVEL field data is one of the primary methods used for comparing materials in this project.
However, the minimum BV mismatch isovalue in the BVSM method is not as useful to compare materials because the infinitely connected isosurface is formed at 0VU mismatch for many materials so that another method must be used to further rank these low valued and interesting materials.

The program uses the fixed isovolume algorithm (6.4) to search for the MinConnected isovalue, within a given tolerance. The values calculated from this method such as the MinConnected isovalue and MinField energy are also used in some of the volume analysis methods described in (6.5.1) when required.

6.4 Fixed isovolume

This analysis method determines the isovalue of a target fractional volume by using an interval searching algorithm. Depending on the convergence criteria, this type of analysis usually takes about 100 times longer per measurement than other analysis methods described in this section as the isosurface must be re-calculated for every isovalue guess. The algorithm is configured to select the maximum fractional volume when it encounters a step in the data, see Figure 6.2. As a result, several fractional volume targets can result in the same isovalue which often makes the data non-linear and therefore not useful when comparing large groups of crystal structures to each other.
6.5 Fixed isovalue methods

The fixed isovalue methods of comparing different materials are based on ranking materials according to their scaled isosurface volume. As previously mentioned, there may be some correlation between ionic conductivity and fractional volume \([5, 41, 58, 59]\).

6.5.1 Isovalue selection methods

In order to perform this type of comparison analysis, some isovalue must be selected. The 3DBVSMMAPPER program implements several schemes for selecting different isovalue at which to measure the volume and surface area of the BVSM and BVEL field infinitely connected isosurfaces. Except for the fixed isovalue method (6.5.1.1), all of these isovalue selection methods apply to only the BVEL field data analysis.

6.5.1.1 Fixed Isovalue

The program measures the fractional volume and surface area of the infinitely connected isosurface at a series of fixed isovalue. This is the main type of measurement for the BVSM field as it measures the fractional volume at different values of BV mismatch. This type of measurement is configured by specifying the start and end isovalue as well as the step interval and an example of this data is presented in Figure 6.2.a. This measurement type is not very useful for the BVEL data as the units of energy of the BVEL data have no fixed zero energy. A modification to this
method to make it more suitable for BVEL field data is described in section 6.5.1.2.

### 6.5.1.2 Relative to minima stepping isovalues

A very good correlation was found between the MinField energy and the minimum energy calculated at the existing mobile ion positions for the Li-O ICSD data set described in Table 7.1 as shown in Figure 6.4. The slope of the linear fit of this data is very close to unity. Therefore the minimum connected field energy gives a good measurement of the energy at existing mobile ion locations.

Using the MinField energy as a zero reference creates the opportunity to compare the fractional volumes of different materials at fixed energy isovalues, similar to the fixed isovalue method for BVSM, see Figure 6.2.b. Therefore, the program is configured to measure isosurfaces at a series of isovalue steps starting at the MinField energy. This is one of the primary ways which the crystal structures can be compared to each other when using the BVEL method.

### 6.5.1.3 Relative to first connected stepping isovalues

This measurement is identical to the previous measurement except that it is started at the MinConnected isovalue. This measurement method has not yet proved to be useful and is disabled by default.
6.5.1.4 Proportional to activation energy stepping isovalue

Another method to analyse the BVEL field is to select isovalue relative to the activation energy. This method is enabled by default but has not yet proved to be useful as it produces a very large variation in selected isovalue, depending on the magnitude of the activation energy.

6.5.2 Isosurface volume scaling methods

Due to the variation in chemistry and unit cell size, the volume measurements of the isosurfaces must be scaled before they can be compared to each other. There are several ways to scale these measurements, as described in this section. Each method incorporates factors to compensate the infinitely connected isosurface volume for some combination of unit cell size, total chemical composition size and total mobile ion concentration size per material as displayed in Table 6.1.

<table>
<thead>
<tr>
<th>Method</th>
<th>Ignores unit cell volume</th>
<th>Includes unit cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not scaled by mobile ion proportion</td>
<td>Volume per atom (VA), Volume per total atomic framework volume (VAV)</td>
<td>Fractional volume (FV)</td>
</tr>
<tr>
<td>Scaled by mobile ion proportion</td>
<td>Volume available per mobile ion (VMI)</td>
<td>Fractional volume per proportion of mobile ion (FVPMI)</td>
</tr>
</tbody>
</table>

Table 6.1 – Matrix illustrating some of the different methods available to scale the volume measurements of the infinitely connected isosurfaces. See (6.5.2.1) – (6.5.2.5) for more details.

All charge equations in this section refer to the oxidation state of the atoms and assume that these charges retain their signs. For example, Li⁺ has a
charge of +1 and O\(^{-2}\) has a charge of -2. This section also assumes that a positively charged mobile ion is the type of mobile ion being analysed. Some methods may require slight adjustment when using negatively charged mobile ions, depending on the stability of the input data. Also, for the formulas in the following section, volume refers to the infinitely connected isosurface volume and any reference to atoms in the framework is to any non-mobile atom species. Also, any counting of atoms or charges refers to the total contained within one unit cell. It may be necessary to multiply by the number of formula units per unit cell if using the original chemical formula as the source of atomistic and charge counts. Also, all sums are scaled by the occupancy of the individual atoms.

6.5.2.1 Fractional volume (FV)

The fractional volume of these infinitely connected isosurfaces is a simple way to measure the magnitude and geometry of the potential ion conducting channels of a material as described in Equation 6.2. Previous studies have shown a relationship between the ionic conductivity and the fractional volume of infinitely connected isosurfaces of low bond valence mismatch [5, 41, 58, 59]. This method does not take into account any information about the chemical composition or the proportion of mobile ions present in the material.

\[
FV = \frac{\text{volume}}{\text{unit cell volume}}
\]  

(6.2)
6.5.2.2 Volume per atom (VA)

One method to compare crystalline materials is to scale the isosurface volume by the total number of atoms in the unit cell as described in Equation (6.3). The total sum of the number of atoms in the unit cell may be a good method to measure the total size of the chemical composition. This method does not account for the unit cell size.

\[
VA = \frac{\text{volume}}{\sum \text{atom count}} \quad (6.3)
\]

6.5.2.3 Volume per total atomic framework volume (VAV)

It is also possible to account for the different typical radii of different atoms by calculating an effective volume occupied by the atoms in the unit cell. This volume can be approximated by the volume of a sphere with the same radius as the ionic radii of the atom, see Equation (6.4). The value produced by this method is unit-less.

\[
VAV = \frac{\text{volume}}{\sum (\text{atom count} \times \frac{\pi}{6} \times \text{ionic radii}^3)} \quad (6.4)
\]

6.5.2.4 Volume available per mobile ion (VMI)

The methods described in this section and the next are designed to compensate the volume measurement for the amount of mobile ion contained in the structure.
One method to scale the isosurface volume is to calculate the isosurface volume available per mobile ion as described by Equation 6.5. This scaling procedure does not account for the unit cell volume and also requires a reasonably accurate count of the total number of mobile ions.

\[
VMI(1) = \frac{\text{volume} \times \text{mobile ion oxidation state}}{\sum \text{mobile ion charge}}
\]  

(6.5)

Materials with a higher ratio of volume to mobile ion may have a higher ionic conductivity. This scaling also equalises results for materials with large numbers of potential pathways vs materials with a few conduction channels. Both of these materials would normally have significantly different fractional volumes but both may still be interesting as ionic conductors due to the existence of infinitely connected ion conduction pathways.

Many crystal structures may report fractional or inaccurate amounts of mobile ion in a crystal structure, or may contain transition metals which allow the mobile ion content to vary. As a result, it may be better to calculate the effective amount of mobile ions present from the remaining charge of the framework atoms as described in Equation (6.6) and (6.7) as all ionically bonded materials must consist of an equal amount of positive and negative charge. This may also present difficulties due to the multiple possible oxidation states of some framework atoms.

\[
\sum \text{mobile ion charge} = -\sum \text{total framework charge}
\]
\[
\text{frac. volume per proportion of mobile ion} = \frac{\sum \text{mobile ion charge}}{\text{mobile ion oxidation state} \times \Sigma \text{atom count}}
\]

\[
= \frac{\sum \text{mobile ion charge}}{\text{mobile ion oxidation state} \times \Sigma \text{atom count}}
\]

\[
=(\Sigma +ve \text{ framework charge} + \Sigma -ve \text{ framework charge})
\]

\[
\text{FVPMI} = \frac{\text{fractional volume}}{\text{proportion of mobile ion}}
\]

\[
= \frac{\text{volume}}{\text{unit cell volume}} \cdot \frac{\sum \text{mobile ion charge}}{\text{mobile ion oxidation state} \times \Sigma \text{atom count}}
\]

As previously mentioned, the mobile ion content described by the original crystal structure can often be unstable or very small. As a result, it may be better to use the effective mobile ion concentration calculated using only the charge neutrality condition of ionic materials and the amount of ±ve framework atoms by using Equation (6.6) which leads to Equation (6.11).
6.5.2.6 Example calculations for LiFePO₄

In this section, LiFePO₄ (ICSD: 56291) will be used as an example to present calculation of the values generated by the different scaling methods. The BVSM results for this material are similar to those presented in Figure 7.4.b. The BVSM data at fixed isovalue of 0.2VU was used to calculate the isosurface volume. The BVEL volume data is also scaled in the same way as what is described in this section. Table 6.2 present various data about the chemistry of the material used in the scaling formulas. Equations (6.12) to (6.18) detail the values used in each formula in 6.5.2. The “#” character in the below equations is used to represent a counting unit for atoms and charge. As can be seen in the equations, the more complicated scaling methods require larger amounts of input data from various forms, making them more complicated to implement and use when scaling large numbers of materials relative to each other.

<table>
<thead>
<tr>
<th>Atom name</th>
<th>Li</th>
<th>Fe</th>
<th>P</th>
<th>O</th>
<th>Sum:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation state</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>Chemical formula count</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Unit cell count</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>16</td>
<td>28</td>
</tr>
<tr>
<td>Total oxidation state count</td>
<td>4</td>
<td>8</td>
<td>20</td>
<td>-32</td>
<td>0</td>
</tr>
<tr>
<td>Coordination No</td>
<td>6</td>
<td>6</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Ionic radii (Å) [60]</td>
<td>0.90</td>
<td>0.92</td>
<td>0.31</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>Sphere volume</td>
<td>3.054</td>
<td>3.262</td>
<td>0.125</td>
<td>7.986</td>
<td></td>
</tr>
<tr>
<td>Total sphere volume</td>
<td>12.215</td>
<td>13.047</td>
<td>0.499</td>
<td>127.783</td>
<td>153.544</td>
</tr>
</tbody>
</table>

Table 6.2 – Table of assorted data for calculation of scaled isosurface volume
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isosurface volume at 0.2VU</td>
<td>31.848 Å³</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>297.25 Å³</td>
</tr>
<tr>
<td>Formula units per unit cell</td>
<td>4</td>
</tr>
<tr>
<td>Total sum mobile ion charge</td>
<td>4</td>
</tr>
<tr>
<td>Total sum framework oxidation state charge</td>
<td>-4</td>
</tr>
</tbody>
</table>

Table 6.2 continued

\[
FV = \frac{\text{volume}}{\text{unit cell volume}} = \frac{31.85\text{Å}^3}{297.25\text{Å}^3} = 0.107 \quad (6.12)
\]

\[
VA = \frac{\text{volume}}{\sum \text{atoms in unit cell}} = \frac{31.85\text{Å}^3}{28\#} = 1.14\frac{\text{Å}^3}{\#} \quad (6.13)
\]

\[
VAV = \frac{\text{volume}}{\sum \left(\text{atom count} \times \frac{4}{3}\pi \times (\text{ionic radii})^3\right)}
\]

\[
= \frac{31.85\text{Å}^3}{\frac{4}{3}\pi \left(4\times(0.90\text{Å})^3\right)_{\text{Li}} + \left(4\times(0.92\text{Å})^3\right)_{\text{Fe}} + \left(4\times(0.31\text{Å})^3\right)_{\text{P}} + \left(16\times(1.24\text{Å})^3\right)_{\text{O}}} = 0.207 \quad (6.14)
\]

\[
VMI(1) = \frac{\text{volume} \times \text{mobile ion oxidation state}}{\sum \text{mobile ion charge}} = \frac{31.85\text{Å}^3 \times (+1)}{4\#} = 7.962\frac{\text{Å}^3}{\#} \quad (6.15)
\]

\[
VMI(2) = \frac{\text{volume} \times \text{mobile ion oxidation state}}{-\sum \text{+ve framework charge} + \sum \text{-ve framework charge}}
\]

\[
= \frac{31.85\text{Å}^3 \times (+1)}{-32\# + 20\# - 32\#} = \frac{31.85\text{Å}^3 \times (+1)}{-4\#} = 7.962\frac{\text{Å}^3}{\#} \quad (6.16)
\]

\[
FVPMI(1) = \frac{\text{volume}}{\text{unit cell volume}} \times \frac{\sum \text{mobile ion charge}}{\sum \text{mobile ion oxidation state} \times \sum \text{atoms in unit cell}}
\]

\[
= \frac{31.85\text{Å}^3}{297.25\text{Å}^3} \times \frac{4\#}{(+1) \times 28\#} = 0.75 \quad (6.17)
\]

\[
FVPMI(2) = \frac{\text{volume}}{\text{unit cell volume}} \times \frac{-\sum \text{+ve framework charge} + \sum \text{-ve framework charge}}{\sum \text{mobile ion oxidation state} \times \sum \text{atoms in unit cell}}
\]

\[
= \frac{31.85\text{Å}^3}{297.25\text{Å}^3} \times \frac{-32\#}{(+1) \times 28\#} = \frac{31.85\text{Å}^3}{297.25\text{Å}^3} \times \frac{-4\#}{(+1) \times 28\#} = 0.75 \quad (6.18)
\]

In comparison, the calculated values of FV, VA, VAV, VMI and FVPMI for a known non ionically conducting material of LiCl are all zero, see Figure
4.3 and Figure 4.5. This is due to the fact that all isosurfaces are isolated from each other and therefore the accessible volume is zero.
CHAPTER 7  SURVEY OF INORGANIC CRYSTAL
STRUCTURE DATABASE (ICSD)

7. 1  Comparison between BVSM/BVEL and other methods

The program was initially tested by comparing the results of BVSM and BVEL calculations to crystal materials with known experimentally and computationally determined ionic conduction pathways. As can be seen in Figure 7.1 - Figure 7.9, there is often an excellent agreement between the general geometry of the ion conducting pathways and the predicted BVSM and BVEL results for a variety of diffusion-based solid crystalline ionic conductors.
7.1.1 Molecular Dynamics Simulations

Figure 7.1 – Na\(^+\) β-alumina. (a) (Na\(_{1+x}\)Al\(_{11}\)O\(_{17+x/2}\) for x≈0.22) Molecular Dynamics simulation of Na-ion distribution at 700K (Adapted with permission from [61]), (b) BVSM field (Isovalue: ±0.15VU) and (c) BVEL field (△Isovalue: 1.3eV) [53] data calculated for (ICSD: 60635) [62].

Figure 7.2 – LiMn\(_2\)O\(_4\). (a) Molecular Dynamics simulation of Li-ion distribution at 300K (Adapted with permission from [63], Elsevier), (b) BVSM field (Isovalue: ±0.15VU) [7] and (c) BVEL field (△Isovalue: 2.1eV) data calculated for (ICSD: 53603) [64].
7.1.2 Other computational methods

Figure 7.3 – TlFe\textsubscript{0.22}Al\textsubscript{0.78}As\textsubscript{2}O\textsubscript{7}. (a) Minimum BV Sum mismatch path along the [001] direction for Tl\textsuperscript{+}, (Adapted with permission from [65]), (b) BVSM field (Isovalue: ±0.3VU) and (c) BVEL field (ΔIsovalue: 0.6eV) [53] data calculated for (ICSD: 245550) [65].

Figure 7.4 – LiFePO\textsubscript{4}. (a) Computer simulation of Li-ion distribution of LiMPO\textsubscript{4} (M = Mn, Fe, Co, and Ni). (Adapted with permission from [66], American Chemical Society), (b) BVSM field (Isovalue: ±0.15VU) [7] and (c) BVEL field (ΔIsovalue: 2.1eV) data calculated for LiFePO\textsubscript{4} (ICSD: 92198) [67].
7.1.3 Neutron Diffraction experiments – Rietveld refinement

Figure 7.5 – La$_3$Li$_5$O$_{12}$Ta$_2$. Lithium ion distribution shown from the diffraction data by a large number of low occupancy atomic sites (purple spheres) overlaid with the (a) BVSM field (Isovalue: ±0.1VU) and (b) BVEL field (ΔIsovalue: 0.8eV) [53] data calculated for (ICSD: 154400) [68]. Shaded area represents area of low BVSM and BVEL field values.

Figure 7.6 – Li$_{1.5}$Fe$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$. Lithium ion distribution shown from the diffraction data by a large number of low occupancy atomic sites (purple spheres) overlaid with the (a) BVSM field ( Isovalue: ±0.17VU) [7] and (b) BVEL field (ΔIsovalue: 3.2eV) data calculated for (ICSD: 55751) [69]. Shaded area represents area of low BVSM and BVEL field values.
7.1.4 Neutron Diffraction experiments utilising the experimental Maximum Entropy Method (MEM)

Figure 7.7 – CuI at 773 K. (a) Experimental Cu-ion distribution determined by Maximum Entropy Method analysis of neutron diffraction data (Adapted with permission from [70]), (b) BVSM field (Isovalue: ±0.1VU) and (c) BVEL field (∆Isovalue: 0.1eV) [53] data calculated for (ICSD: 163859) [70].

Figure 7.8 – (Pr$_{0.9}$La$_{0.1}$)$_2$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_{4+δ}$ at 1288.75K. (a) Experimental oxygen-ion distribution determined by Maximum Entropy Method analysis of neutron diffraction data (Adapted with permission from [71]), (b) BVSM field (Isovalue: ±0.2VU) and (c) BVEL field (∆Isovalue: 3.6eV) [53] data calculated for (ICSD: 248032) [71].
Figure 7.9 – Li$_{0.16}$La$_{0.62}$TiO$_3$. (a) Experimental Li-ion distribution determined by Maximum Entropy Method analysis of neutron diffraction data (reproduced with permission from [72]), similar slice through (b) BVSM field and (c) BVEL field showing variation in oxidation state (VU) and energy (eV) respectively for (ICSD: 152480) [73].

7.2 Calculation of ICSD materials

Next, the program was executed using both BVEL and BVSM methods and the settings described in the previous section on the remaining ~14,000 materials satisfying the criteria described in Table 7.1 from the ICSD. These selection criteria were chosen to target oxide materials which already contained some of the mobile species being tested and also avoided certain toxic chemistries in some cases.

<table>
<thead>
<tr>
<th>Included atomic species</th>
<th>Excluded atomic species</th>
<th>Count of materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li, O</td>
<td>H, Na, K, Rb, Cs, S, Se, F, Cl, Br, I</td>
<td>2806</td>
</tr>
<tr>
<td>Na, O</td>
<td>H, Li, K, Rb, Cs</td>
<td>4069</td>
</tr>
<tr>
<td>K, O</td>
<td>H, Li, Na, Rb, Cs</td>
<td>2505</td>
</tr>
<tr>
<td>Ag, O</td>
<td>H, Li, Na, K, Rb, Cs</td>
<td>602</td>
</tr>
<tr>
<td>Cu, O</td>
<td>H</td>
<td>382</td>
</tr>
<tr>
<td>Mg, O</td>
<td>H, Li, Na, K, Rb, Cs</td>
<td>3665</td>
</tr>
</tbody>
</table>

Table 7.1 – Chemical search criteria used for searching the ICSD
7.3 Selection of data analysis method

In order to further analyse the data, a low isovalue and scaling method must be selected to qualitatively compare the ionic conductivity between different materials. Analysis of the data has shown that it is hard to distinguish between different scaling methods for several reasons.

In order to select a scaling method, it would be useful to have some data which contains the bulk ionic conductivity of a range of materials which we have simulated. Unfortunately, this data is sparse in literature as many individuals perform impedance spectroscopy but do not publish results which distinguish between bulk and grain ionic conductivity. Also, investigation of the ranking data shows that many crystalline materials which are known ionic conductors are found at the top of most scaling methods. Also, crystalline materials which are known ionic conductors are distributed throughout the whole list. As a result, there is currently no clear best isovalue or scaling method.

Another complicating factor is the generally poor accuracy of approximating ionic conductivity using volume. As a result, the intrinsic error associated with the method can be large, especially considering that many materials may have mechanisms which are not modelled by the BV methods that substantially affect the final ionic conductivity (7.6.1). Most scaling methods apart from the fractional volume method also introduce
more error into the data due to the error in the extra input data used for scaling.

While the choice of isovalue can have a large effect on which materials are included in the analysis, the main effect of selecting a different scaling method is to re-order the ranking of the materials which already possess infinitely connected isosurfaces. No choice of scaling method will ever cause a material to be included in the rankings which does not already possess an infinitely connected isosurface at the given isovalue.

Due to the scarcity of new interesting materials in the rankings, it is important to reduce the number of exclusion conditions applied when analysing the data. Materials with a large infinitely connected isosurface may be suitable as high power to weight ratio cathode materials. However, even a small infinitely connected isosurface may belong to an interesting ionic conductor or low power to weight ratio cathode or anode material. The most important feature of an interesting material is the existence of at least a single very low energy barrier pathway which has a high ionic conductivity as this is the key property which makes a material interesting in this study.

As a result, the simplest analysis methods were initially selected to rank the data due to their simplicity and lower intrinsic error. Also, as previously mentioned, previous works have also used these simple methods for analysing the ionic conductivity of different materials [5, 41, 58, 59].
7.4 Results

In addition to identifying materials with infinite pathway networks, the materials were quantitatively ranked according to several simple methods. The BVSM data was ranked according to fractional volume at fixed BV mismatch of 0.2VU. The BVEL data was also ranked according to activation energy as well as fractional volume relative to the MinField energy of 2.0eV. The count of the number of materials with infinitely connected isosurfaces at given isovalues are shown in Table 7.2. Also, these results are reproduced in the electronic supplementary information and histograms of this data are presented in Figure 7.10 and Figure 7.11.

As can be seen, for alkali metal oxides, the proportion of structures featuring infinite network of pathways with low bond-valence mismatch reduces from Li$^+$ to K$^+$ as metal-oxide frameworks become progressively less suitable for transport of bigger cations. However, this trend is not observed in the Ag, Cu and Mg data sets as these atoms are not part of the alkali metal group and therefore have significantly different properties.
<table>
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<th>Cu</th>
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</tr>
</tbody>
</table>

Table 7.2 – The number and percentage of the structures featuring infinite network of low BVS mismatch pathways at 0.00, 0.05, 0.1, 0.2 and 0.4 bond valence mismatch values for BVSM results and 0.5eV, 1eV, 2eV and 4eV for the BVEL results
Figure 7.10 – BVSM histograms of fractional volume of different materials at fixed BV mismatch isoalue of 0.2 VU. Data was obtained from respective data sets as described in Table 7.1. Note: The count axis was limited to the highest count in the non-zero bin as many materials were in the 0.0 fractional volume bin. Also, less than 1% of data points may lie outside the displayed fractional volume range.
Figure 7.11 – BVEL histograms of fractional volume of different materials at fixed offset from MinField energy isovalue of 2.0 eV. Data was obtained from respective data sets as described in Table 7.1. Note: The count axis was limited to the highest count in the non-zero bin as many materials were in the 0.0 fractional volume bin. Also, less than 1% of data points may lie outside the displayed fractional volume range.
7. 5 Comments on BVSM/BVEL data review

Manually investigating the field and structure data from the Li-O crystal material data set indicated in the electronic supplementary information has shown that the BVSM/BVEL methods can help locate and confirm the position and oxidation state of ions in a crystalline material. It has also shown that the method can predict the geometries of ionic conduction pathways and may also predict the correct order of the easiest to hardest ionic conduction pathways.

The distribution of different fractional volumes and activation energies (7.6.1) has also shown that the general absolute accuracy of the method to predict the ionic conductivity of a particular framework may be influenced by the chemistry of the material and can substantially vary even within the same structure type.

7. 6 Common materials

There is a wide variety of different material types in the data sets. Figure 7.12 shows the distribution of different materials according to structure type. As can be seen, the most common types of structure type are Spinel, layered LiCoO₂, materials with isolated 4-coordinated framework atoms and LiFePO₄ materials.
Figure 7.12 – Pie chart showing the distribution of the different framework types from the Li-O ICSD data set as described in Table 7.1

7.6.1 Statistics of spinels

Isolating the data for the spinel materials from the Li-O ICSD data Table 7.1 presents an opportunity to characterise the distribution of values for materials within a similar structure type in order to evaluate the data trends.

An example of the spinel structure type and the associated isosurfaces are presented in Figure 4.3.a. and Figure 4.5.a. As can be seen, this structure has dense 3-dimensional open pathways throughout the whole structure due to the open space around the framework atoms. This structure type is the same as the commonly used spinel Manganese battery cathode. Unlike the LiCoO$_2$ structure whose BVSM/BVEL isosurface volume depends on the
separation of the layers, the unit cell parameters of the spinel material all contract and expand evenly with de/lithiation as well as substitution of the main positively charged framework atom. This effect can be seen in Figure 7.13 as a fairly linear relationship between fractional volume and unit cell length parameter. However, this trend is not as obvious in the BVEL data as can be seen in Figure 7.14 and Figure 7.15.

Also, as this project aims to identify frameworks suitable for chemical substitution which may be ionic conductors, it is worthwhile studying the distribution of fractional volume and activation energy values for this structure type which is often an ionic conductor. As can be seen in the histograms in Figure 7.16 and Figure 7.17, the selected isovalue of activation energy and BV mismatch values used to rank the BV data include most of the materials which possessed any infinitely connected isosurface at any isovalue.

For the BVSM method, approximately 46% (188/404) of all materials did not possess any infinitely connected isosurface lower than 0.75 BV mismatch. This may be due to the existence of blocking spheres in materials which block the ionic conduction channels or the materials may not possess smooth enough BV pathways to satisfy the worst case isovalue criteria of 0.75 BV mismatch used in this data analysis method. This large proportion of materials without any infinitely connected isosurface may be a concern when looking for materials which are isostructural to a potential ionic
conductor. This is especially relevant considering that some structure types may only have very few known members.

Furthermore, the spinel data set was analysed to look at the distribution of fractional volumes at the given isovalue of activation energy (2.0eV) and BV mismatch (0.2VU). As can be seen in Figure 7.18 and Figure 7.19, most spinel materials have a fractional volume less than 0.15 for BVSM and 0.11 for BVEL. Although the data in these plots is not highly distributed, selecting a higher maximum threshold value for the rest of the ICSD data is a good idea as other interesting materials are likely to have a wider variety of ideal fractional volumes due to the different structure types.

Figure 7.13 – Scatter plot of unit cell length parameter vs BVSM fractional volume at 0.2VU BV mismatch for ICSD Li-O Spinels. A few extreme data points as well as all of the materials which did not show any infinitely connected isosurface were removed from this plot prior to the linear extrapolation to the scatter data.
Figure 7.14 – Scatter plot of unit cell length parameter vs BVEL activation energy for ICSD Li-O Spinels. A few extreme data points may have been removed from this plot.

Figure 7.15 – Scatter plot of unit cell length parameter vs BVEL fractional volume at 2.0 eV energy mismatch from MinField energy for ICSD Li-O Spinels. A few extreme data points may have been removed from this plot.
Figure 7.16 – BVSM: Histogram of required BV mismatch value to form an infinitely connected isosurface for the Spinel materials from Li-O ICSD data set. Note: 188/404 ($\approx 46\%$) of spinel materials did not show any connectivity even at the very large BV mismatch of 0.75VU.

Figure 7.17 - BVEL: Histogram of required activation energy value to form an infinitely connected isosurface for the Spinel materials from Li-O ICSD data set. A few extreme data points are not shown.
Figure 7.18 – BVSM: Histogram of fractional volumes of 0.2 VU BV mismatch isosurfaces for the Spinel materials from Li-O ICSD data set. 52% (209/404) of materials are in the zero isosurface volume bin. Count axis has been truncated in order to show more detail.

Figure 7.19 – BVEL: Histogram of fractional volumes of isosurfaces of 2.0 eV from the MinField energy for ICSD Li-O Spinels. 29% (116/404) of materials are in the zero volume isosurface bin. Count axis has been truncated in order to show more detail.
7.6.2 Crystalline materials with isolated polyhedra

Many of the materials which achieve a high fractional volume ranking are materials which contain isolated polyhedra held together by surrounding mobile ions, for example see Figure 7.20. These types of material may have high ionic conductivity and often appear high in the materials rankings due to their large mobile ion content. However, as these materials have no inter-framework bonds between isolated polyhedra, these materials are most likely unstable when cycling and may easily dissolve in the liquid solvent electrolytes found in conventional batteries. As a result, these materials they are probably not suitable for use as conventional battery materials. It may be possible to use this type of material as the solid electrolyte in an all solid state battery if the material was stable with electrochemical cycling. Due to the very large number and variety of these materials this study will not be focusing on these materials.

One possible method to exclude these materials is to further scale the volume results to down weigh materials with a high positive mobile ion to positive framework atom ratio as this is observed in most of these materials. However, this method may also down weigh materials which possess high mobile ion content to framework atoms ratio which may be favourable for use as cathodes. A more reliable method to remove these crystalline materials is to simply identify them either by automated geometry analysis of the bonds between the framework atoms or by manual visual identification.
Figure 7.20 – Crystal structure of $\alpha$ – Li$_3$AlO$_4$ (ICSD: 42697) [74] Showing isolated framework molecules surrounded by potentially mobile ions – Li, Al and O are purple, yellow and red respectively.
CHAPTER 8

DFT CALCULATIONS FOR DIITHIUM COPPER(II) PYROPHOSPHATE

Figure 8.1 – Crystal structure of Diithium Copper(II) Pyrophosphate (Li$_2$CuP$_2$O$_7$). As can be seen, this material consists of 2-D layers of alternating Lithium and framework atoms.

<table>
<thead>
<tr>
<th>Type</th>
<th>Measurement Point</th>
<th>Value</th>
<th>Rank (using methods specified in 7.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BVSM fractional volume</td>
<td>0.2VU</td>
<td>0.19</td>
<td>353/2663</td>
</tr>
<tr>
<td>BVEL fractional volume</td>
<td>2eV from connected field minima</td>
<td>0.23</td>
<td>103/2908</td>
</tr>
<tr>
<td>BVEL activation energy</td>
<td>N/A</td>
<td>0.54eV</td>
<td>247/2908</td>
</tr>
</tbody>
</table>

Table 8.1 – Key BV statistics for Diithium Copper(II) Pyrophosphate (Li$_2$CuP$_2$O$_7$ – ICSD: 160321 – [75])
This material was identified as a potential ionic conductor from the BVSM/BVEL calculations, see Table 8.1. The material consists of 2-D layers of Cu-P-O framework material with Li-ions occupying the interlayer area. The BVSM and BVEL results suggest that there is ionic conductivity along the Li-ion layer, see Figure 8.2. This material was then used to calculate the activation energy barriers for Li-ion conduction using the DFT cNEB method implemented in VASP [76] with the special add on code to calculate climbing image nudged elastic band method (cNEB) [35].

8.1 Review of material

![Figure 8.2](image.png)

Figure 8.2 – a. BVSM field slice and b. BVEL isosurface (ΔIsolvalue: 0.53eV) for structure showing the most likely conduction pathway for the material. The small region between the blocking sphere (red) and the BVS barrier in a. which would allow direct ion transit along the y-direction is an artefact as a larger blocking sphere would prevent this path from occurring. Black dotted lines denote the most likely conduction pathway in both figures.

This material was selected for further DFT study because of several factors. The material appears near the top of the bond valence rankings as indicated in Table 8.1 which suggests it may be a good ionic conductor. These positive results were further verified by visual investigation of the suggested
bond valence ion pathways which did not show any substantial artefacts of incorrect small channels. The Bond Valence method indicates that this material has a zigzag Li-ion ionic conductivity along the B direction as indicated by the dark lines in Figure 8.2.

A short literature review reveals that although many think that this particular material possesses ionic conductivity, no study has been conducted to measure the ionic conductivity and specific mobile ions pathways [77]. This material formed using sodium [78, 79], has shown an experimental ionic conductivity of 0.84-0.97eV, depending on temperature. [80]. The crystal structure of the material appears reasonable and the material has been recently synthesised and measured using X-Ray radiation at ambient conditions from both high temperature synthesis [81] and hydrothermal [75] methods. The material is also stable when relaxed using ab-initio DFT code [82].

The material is part of a class of similar materials with different mobile ions (Li, Na…) and transition metals (Cu, Pd…). Li₂PdP₂O₇, an isostructural material, also showed similar Bond Valence results to the Cu material. However, palladium is a rare and expensive metal; therefore the Cu material was selected for initial DFT calculations. It may also be desirable to investigate the effect of materials with a composition of Li₂PdₓCu¹₋ₓP₂O₇ on ionic conductivity in the future.
This material exhibits the Jahn-Teller effect; where the copper atom bonds have a distorted octahedron bonding arrangement with very long bond lengths between the neighbouring chains as shown in Figure 8.2. The Jahn-Teller effect can help generate ionic conduction by creating voids in the crystal structure due to the distortions caused by the long bond lengths which disrupt the normally close packed crystalline structures found in most other crystalline materials.

This material is not suitable as a cathode material as it has no available transition metal oxidation states, however, it may have some ionic conductivity and be suitable for study as an ionic conductor for use as a solid electrolyte or other application. The material may not be extremely stable when electrochemically cycled or placed in a solvent due to the 2-dimensional layered nature of the material.

The material does not possess any intrinsic mobile ion vacancies which may help improve ionic conductivity. Even low level doping with small amounts of F or S$^{6+}$ may help introduce such vacancies and should significantly increase Li$^+$ mobility. It is expected that, like other solid inorganic oxides, that the electrical conductivity of Diithium Copper(II) Pyrophosphate (Li$_2$CuP$_2$O$_7$) should also be fairly small in stoichiometric form. When synthesised, an isostructural material K$_2$CuP$_2$O$_7$ [83], had a blue colour which suggested that it was an insulator. However, doping may also increase the electronic conductivity which would be an undesirable property for use as a solid electrolyte battery material.
8. 2 Computational Analysis – Classical Molecular Dynamics

Classical forcefield based structure relaxation and molecular dynamics was initially attempted using GULP [84] and the Pedone constants library [85]. Unfortunately, the simulations were not stable as the material appeared to undergo some form of phase transition upon structure relaxation. This instability is most likely due to the Jahn-Teller bonding arrangement which may not be well modelled by the interatomic potential selected. It may be possible to further refine the empirical potentials to compensate for this effect but this will be left for future research.

8. 3 DFT NEB Calculations

The crystal structure was simulated using VASP [76] version 5.2 with the special add on code to implement the climbing image nudged elastic band method (cNEB) [35]. The initial crystal structure was converted into VASP format using customised SHIRAZ program [86] libraries incorporated into customised utility scripts in Materials Studio [56].

```
SYSTEM = Li2CuP2O7_160321_AntiFerro4
! Structure Optimise with Spin

! Electronic Settings...
ISMEAR = 0 ! Gaussian smearing
SIGMA = 0.05
PREC = High
LREAL = Auto
ISYM = 0
```
NELM = 150 ! Max no. of electronic iterations
NELMIN = 5 ! Min no. of electronic iterations
EDIFF = 1.0E-6 ! Electronic Accuracy

VOSKOWN = 1
LORBIT = 11

! Ionic Settings...
IBRION = 2 ! use the conjugate gradient algorithm
ISIF = 3 ! Change all unit cell parameters, volume, ion positions, calculate energies
EDIFFG = -1.0E-4
NSW = 100 ! Ionic steps

! Data distribution and computational settings...
LPLANE = .TRUE.
NPAR = 2
NSIM = 4
LSCALU = .FALSE.

! Magnetic Configuration Settings...
ALGO = Normal
ISPIN = 2
MAGMOM = -1 2*1 -1 1 2*-1 1 88*-1

Figure 8.3 – Example VASP INCAR configuration file showing the selected options

An example INCAR file used to configure VASP for the initial magnetic relaxation of the Anti-ferromagnetic4 configuration is presented in Figure 8.3. A large supercell of 1*2*1 was used with a long energy cut-off of 500eV selected using the high precision setting. The electronic convergence criterion was also set to a fine value of $1.0 \times 10^{-6}$ to ensure the accuracy of the finally converged wave functions. The PAW potentials [87] were selected and the specially compiled single k-point gamma program version
was used. The Gaussian method for determining smearing of orbital partial occupancies was used with a fine value of 0.05. This setting was selected as this material is not metallic and the single k-point calculation is not compatible with the tetrahedron method with Blochl corrections which would be preferable for this type of calculation. The extrapolated sigma energies were used to evaluate all energy values.

The projection operators were evaluated in real space and symmetrisation of the structure was also disabled for the calculations in order to simulate the independent free movement of all atoms. The Vosko Wilk and Nusair [88] correction was also used to enhance the effect of the magnetism when using the PAW potentials as recommended in [89]. No U+J corrections were applied to this system due to the non-convergence of the wave functions using this method and the extra complexity of using this feature.

The conjugate-gradient ionic method was used to relax the crystal structure and the ionic convergence criterion was also set to a high value of 1.0 * 10^{-4} to ensure good ionic relaxation. A minimum of 5 electronic convergence steps was performed for each ionic step in order to continuously improve the structure and forces when the system was well converged. In practice, such a small ionic force convergence criteria was never reached in any of the conjugate-gradient relaxations. As a result, the structures were deemed to be relaxed when a substantial amount of ionic steps have been performed such that the total energy was very stable and no substantial atomic movements were occurring.
Also, for calculations with changing unit cell parameters, the Pulay stress was eliminated by repeating the full structure relaxations until the unit cell parameters and total energy had converged as described in [90]. The Pulay stress is an artefact of changing basis sets due to the changing unit cell parameters upon unit cell relaxation.

8.3.1 Initial structural relaxation and magnetic configuration

Literature indicates [82] that this material is antiferromagnetic along the Cu-P framework primary 1-dimensional chains with spin of 1/2 on the Cu atoms. The known strong magnetic interaction along the Cu-P chains and weak inter chain interaction allows 4 unique magnetic solutions for any given Supercell as shown in Figure 8.4.

The crystal structure was initially relaxed in a series of different magnetic configurations to crudely determine the magnetic behaviour of the system as well as the stability of the simulation. Each selected magnetic configuration was initially relaxed by calculating the non-spin wave functions followed by the spin-wave functions which included the imposed the magnetic structure. This two-step procedure was necessary to stabilise the desired magnetic structure of the initial wave functions.
Figure 8.4 – Possible magnetic configurations of the crystal structure given the strong antiferromagnetic interaction along the chains of framework atoms. The different spin directions on Cu atoms are indicated by the light blue and light brown colours. The magnitude of the spins is \( \frac{1}{2} \). The hidden Cu atoms in the centre of each diagram are blue, blue, brown and brown respectively for Antiferromagnetic 1-4 respectively as can be extrapolated from the visible Cu atoms in the rear centre chain.

Once the magnetic structure had been imposed on the wave functions of the materials, each structure was repeatedly re-relaxed with variable unit cell parameters to cancel the effects of Pulay stress using 100 steps of conjugate-gradient algorithm [90] until the energy difference between the initial and
final images was very small. This minimisation of Pulay stress procedure was then verified by a single energy calculation and measuring the external stress which gives a measure of the Pulay stress. This was found to be quite small in every case. Also, the unit cell parameters and energies of the final selected configurations are presented in Table 8.2.

<table>
<thead>
<tr>
<th>Magnetic Structure</th>
<th>Original</th>
<th>Non-spin</th>
<th>Ferromagnetic</th>
<th>Antiferromagnetic1</th>
<th>Antiferromagnetic2</th>
<th>Antiferromagnetic3</th>
<th>Antiferromagnetic4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repetitions</td>
<td>N/A</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Δenergy (eV)</td>
<td>N/A</td>
<td>1.16</td>
<td>0.12</td>
<td>0.0016</td>
<td>0.0011</td>
<td>0.00047</td>
<td>0</td>
</tr>
<tr>
<td>Force</td>
<td>N/A</td>
<td>0.003792</td>
<td>0.003324</td>
<td>0.002408</td>
<td>0.002588</td>
<td>0.001997</td>
<td>0.001881</td>
</tr>
<tr>
<td>Pulay Stress (kB)</td>
<td>N/A</td>
<td>-0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Unit-cell volume (Å³)</td>
<td>1170.487</td>
<td>1230.077</td>
<td>1232.859</td>
<td>1232.031</td>
<td>1231.973</td>
<td>1232.195</td>
<td>1232.222</td>
</tr>
<tr>
<td>A (Å)</td>
<td>15.336</td>
<td>15.45632</td>
<td>15.50012</td>
<td>15.49275</td>
<td>15.49268</td>
<td>15.49243</td>
<td>15.49213</td>
</tr>
<tr>
<td>B (Å)</td>
<td>9.7466</td>
<td>10.01362</td>
<td>10.01889</td>
<td>10.03059</td>
<td>10.03034</td>
<td>10.02892</td>
<td>10.02956</td>
</tr>
<tr>
<td>C (Å)</td>
<td>8.6259</td>
<td>8.7813</td>
<td>8.81411</td>
<td>8.79627</td>
<td>8.79605</td>
<td>8.79897</td>
<td>8.79875</td>
</tr>
<tr>
<td>α</td>
<td>90</td>
<td>89.9947</td>
<td>90.0001</td>
<td>89.9986</td>
<td>90.0012</td>
<td>90</td>
<td>90.0001</td>
</tr>
<tr>
<td>β</td>
<td>114.795</td>
<td>115.169</td>
<td>115.7497</td>
<td>115.6708</td>
<td>115.67</td>
<td>115.6692</td>
<td>115.669</td>
</tr>
<tr>
<td>Γ</td>
<td>90</td>
<td>90.0057</td>
<td>89.9997</td>
<td>90.0014</td>
<td>89.9996</td>
<td>90</td>
<td>89.9998</td>
</tr>
<tr>
<td>Δvolume</td>
<td>N/A</td>
<td>5.091%</td>
<td>5.329%</td>
<td>5.258%</td>
<td>5.253%</td>
<td>5.272%</td>
<td>5.274%</td>
</tr>
<tr>
<td>Δα</td>
<td>N/A</td>
<td>0.785%</td>
<td>1.070%</td>
<td>1.022%</td>
<td>1.022%</td>
<td>1.020%</td>
<td>1.018%</td>
</tr>
<tr>
<td>Δβ</td>
<td>N/A</td>
<td>2.740%</td>
<td>2.794%</td>
<td>2.914%</td>
<td>2.911%</td>
<td>2.897%</td>
<td>2.903%</td>
</tr>
<tr>
<td>Δc</td>
<td>N/A</td>
<td>1.802%</td>
<td>2.182%</td>
<td>1.975%</td>
<td>1.973%</td>
<td>2.006%</td>
<td>2.004%</td>
</tr>
<tr>
<td>ΔαΔβ</td>
<td>N/A</td>
<td>-0.006%</td>
<td>0.000%</td>
<td>-0.002%</td>
<td>0.001%</td>
<td>0.000%</td>
<td>0.000%</td>
</tr>
<tr>
<td>ΔαΔγ</td>
<td>N/A</td>
<td>0.326%</td>
<td>0.832%</td>
<td>0.763%</td>
<td>0.762%</td>
<td>0.762%</td>
<td>0.761%</td>
</tr>
<tr>
<td>ΔβΔγ</td>
<td>N/A</td>
<td>0.006%</td>
<td>0.000%</td>
<td>0.002%</td>
<td>0.000%</td>
<td>0.000%</td>
<td>0.000%</td>
</tr>
</tbody>
</table>

Table 8.2 – Energy, force, pressure and unit cell parameters of non-spin, ferromagnetic and antiferromagnetic magnetic configurations in order of decreasing energy

The antiferromagnetic nature of the material was confirmed by our calculations as all of the antiferromagnetic configurations had a similar low energy. The strong magnetic interaction along the framework chains was observed in our calculations as all antiferromagnetic configurations had a
similar energy, suggesting that interactions between layers were small. The crudeness of the single k-point calculations and relatively small supercell can only clearly distinguish the first order interaction as the energies of the compared antiferromagnetic calculations are all very similar, probably within the error of the accuracy of these calculations.

Comparing the ferromagnetic and antiferromagnetic energies of these materials shows an energy difference of 0.119859eV, which is a substantial amount compared to the final minimum activation energy barrier calculated in the next sections. The energy difference between different magnetic configurations is usually small compared to the final barrier energy, however, this material may prove to be an exception to this trend. In any case, the comparison of structural energies between different NEB images with the same magnetic configuration may not substantially alter the magnitude of the energy barrier itself.

8.3.2 cNEB calculations

The lowest energy antiferromagnetic configuration structure, Antiferromagnetic4, was selected for activation energy barrier simulation using the cNEB method. Several probably mobile ion pathways were selected for simulation as indicated in Figure 8.5. The end images of these transition pathways with vacancies were relaxed with fixed unit cell parameters using a similar procedure used to relax the initial images except for the use of the Pulay stress elimination method. These end images were used as input for
the cNEB method which extrapolates a fixed number of intermediate images which are then relaxed together in order to simulate the energy profile of the transition pathway.

The cNEB method was executed on these images for 200 steps of conjugate-gradient algorithm which produced well converged final barrier energies as seen in Figure 8.8. Figure 8.6 shows the physical shape of the pathways, Table 8.3 shows the calculated activation energy barriers for the selected transitions and Figure 8.7 shows the energy barrier profiles for the simulated trajectories.

![Diagram of attempted cNEB barriers for mobile Li-ion. Black line shows lowest energy pathway of pathway1 from DFT cNEB calculations. All Lithium positions are symmetrically equivalent so that only these few pathways need to be simulated to evaluate every ionic conductivity energy barrier in the material.]
Figure 8.6 – a.-d. Pathway1-4 respectively of final cNEB trajectories of mobile Li-ion. Black lines denote symmetry equivalent pathways to simulated pathway per image. As can be seen, pathway 1 leads to 1-D conductivity along the B-direction with pathway 3, the next lowest energy barrier, leading to 2-D conductivity.

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pathway1</td>
<td>0.37</td>
</tr>
<tr>
<td>Pathway2</td>
<td>0.74</td>
</tr>
<tr>
<td>Pathway3</td>
<td>0.46</td>
</tr>
<tr>
<td>Pathway4</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 8.3 – Table of final calculated activation energies for the given transitions. These energies were obtained with 200 ionic relaxation steps of the conjugate-gradient algorithm.
Figure 8.7 – Plots of final cNEB energy barriers for Pathway1-4. Note: Due to the use of the cNEB method, these images are not equally spaced in physical space.

Figure 8.8 – Plot of energy convergence of Pathway1 of images of cNEB method using 200 ionic relaxation steps of the conjugate-gradient algorithm. As can be seen, the final energy values are quite stable. Other trajectories exhibit similar behaviour for this material.
This material appears to be a 1-D conductor along the B-axis through the Pathway1 pathway. As can be seen in Table 8.3, the Pathway1 pathway is the lowest energy pathway, with the Pathway3 pathway the next most probable pathway. This matches the BVEL data as seen in Figure 8.2 quite well as this is the same geometry and ordering predicted by the BVEL data. The BVSM data is less clear about the probably pathways from the isosurface data but shows good agreement in the slice data. The 1-D nature of the lowest energy pathway is not as desirable for battery performance as even small amounts of foreign atoms can block the 1-d channels and substantially reduce ionic conductivity. However, the existence of the second low energy pathway of similar energy may negate this problem.

The magnitude of the energy barriers is comparable to the activation energy of the current best known Li-ion conductor of lithium lanthanum titanate (LLTO) with activation energy of 0.37eV as described in [25]. However, the lack of mobile ion vacancies in the normal crystal structure of this material may reduce the experimentally measured ionic conductivity of this material. As previously mentioned, it is likely that vacancies could be introduced in this material through doping with F⁻ and S⁶⁺ would likely improve the ionic conductivity. It may be possible to optimise the channel geometries using chemical substitution to further reduce the activation energy and therefore improve ionic conductivity. Further calculations for the Pd material may also potentially show further improvements in ionic conductivity for this material. Further calculations with different types of mobile ion may also produce interesting results.
8.3.3 Errors in calculation

Unfortunately, the calculations have showed some signs of inconsistency. The total magnetic moment of the system has been shown to depend on the position of the mobile ion in the calculation, suggesting that there may be some interesting electronic interactions occurring between the mobile ion and the framework. The total magnetic moment of all end images was not observed to be the same as required by symmetry. This error has not yet been accounted for and may be due to the small unit cell selected for calculations.

Further investigations, including the use of the U+J corrections, more k-points and a larger unit cell may offer further improvements in the accuracy of these energy barriers and magnetic configuration calculations.

8.4 Conclusion

Dithium Copper(II) Pyrophosphate is a promising candidate for a new 1-D/2-D solid oxide ionic conductor. More computational study and experimental work is required to further study the ionic and electronic properties of this potentially novel ionic conductor.

Added note: Further calculations using a larger supercell of 1x2x2 has corrected the magnetic moment problems with very similar activation energy barrier values. The use of the U+J corrections may offer further improvements in calculated activation energy barrier value.
CHAPTER 9 COLLABORATIONS

The program has been made available to other scientific users and various papers have been published from the data calculated by the 3DBVS Mapper program. A short review of these is included in the following section.

9.1 Studies involving neutrons

The BVSM method was used in [91] to predict Li-ion distributions and likely ion conduction pathways in Li$_{0.18}$Sr$_{0.66}$Ti$_{0.5}$Nb$_{0.5}$O$_3$ (LSTN) perovskite type oxide, a novel ionic conductor with similar ionic conductivity to the Li$_{3x}$La$_{0.66-x}$TiO$_3$ perovskite type oxides. The BVSM data was used to help identify the locations of the Li-ion positions and site disorder from Neutron Data as shown in Figure 9.1 and Figure 9.2.

![Figure 9.1 – BVSM isosurface at mismatch of ±0.1 VU for Li$_{0.18}$Sr$_{0.66}$Ti$_{0.5}$Nb$_{0.5}$O$_3$. Shows possible 3-d ionic conduction network of pathways. a) Semi-transparent view of the direct pathway between unit cell faces, b) Cross-section at height 0.5.](image)
Figure 9.2 - Fourier difference maps before (a) and after (b) including lithium in the $\text{Li}_{0.18}\text{Sr}_{0.66}\text{Ti}_{0.5}\text{Nb}_{0.5}\text{O}_3$ model, converted into 3D visualisation maps in VESTA. An intensity cut-off of 0.25 for (a) and 0.15 for (b) was implemented to remove low intensity noise. Placing lithium at the (0.5 0.5 0) position resulted in large reductions of the scattering difference as shown in (b).

The BVSM method was also used in [92] to provide supporting evidence of the geometry of the ion conduction pathways in the Cu-Se superionic conductors and showed excellent agreement with the analysis of the Quasi-Elastic Neutron Scattering data for these samples as shown in Figure 9.3.

The BVSM method was used in [93] to predict the oxygen ion diffusion pathways and geometries in the oxygen ion conductor $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Nuclear density distributions were measured for this material but unfortunately did not clearly show the diffusion pathways for this known oxygen conducting material at room temperature. The nuclear density and BVSM results are illustrated in Figure 9.4, Figure 9.5 and Figure 9.6.
Figure 9.3 – BVSM isosurface at ±0.2 VU mismatch for Cu ion in Cu-Se superionic conductor illustrating agreement between Quasi-Elastic Neutron Scattering data and BVSM results.

Figure 9.4 – Nuclear density isosurfaces at 0.1 fm Å⁻³ of (a) tetragonal Ce₀.5Zr₀.5O₂ and (b) cubic CeO₂. As can be seen, the ion conduction pathways of the oxygen ions are not revealed in this data.
Figure 9.5 – BVSM Isosurfaces for Ce$_{0.5}$Zr$_{0.5}$O$_2$ oxygen ion conductor with valence mismatch of ±0.1 VU illustrating possible ion conduction pathways.

Figure 9.6 – BVSM slice for Ce$_{0.5}$Zr$_{0.5}$O$_2$ oxygen ion conductor. This diagram illustrates the $<111>_f$ forbidden transition and the agreement between experimental oxygen ion position and BVSM calculated oxygen position.
9. 2 Studies involving DFT

In [94], the BVSM method was used to provide supporting evidence of the geometry of the possible ion conduction pathways of the potential new Sodium cathode Na$_{1.5}$VPO$_{5}$-$\delta$F$_{0.5}$-$\delta$. The BVSM results showed excellent agreement with the DFT NEB results and also accurately predicted the order of the activation energies of the two possible ion pathways as shown in Figure 9.7.

![Figure 9.7 – Left: BVSM slice through ab plane of Na$_{1.5}$VPO$_{5}$-$\delta$F$_{0.5}$-$\delta$, showing likely ion conduction pathways. Right: Crystal structure with ±0.45 VU isosurface in yellow with enlarged figures showing calculated DFT NEB pathways and activation energies.](image)

9. 3 Studies without volumetric experimental validation

In [95], the BVSM method was used to predict the location of the oxide ion conduction channels in the novel oxide ion conductor NdBaInO$_4$ at 1000 °C. The details of the pathway geometries predicted by the BVSM method were not verified using other calculation or experimental methods and are presented in Figure 9.8. However, the oxide ion conduction of this material
was measured using impedance spectroscopy. “The activation energy … for the oxide-ion diffusion were estimated to be 0.95(5) eV below 830 °C and 1.52(4) eV above 830 °C” – adapted from [95].

In [96], the BVSM method was used to predict the location and ordering of the ion conduction channels in the novel pyrophosphate cathode $\beta$ – Na$_2$MnP$_2$O$_7$ which has a very high redox potential of 3.6V against sodium. The predictions of the BVSM method were not verified using other calculation or experimental methods and are presented in Figure 9.9.

Figure 9.8 – “Difference bond valence sum (DBVS) maps for an oxide ion with isovalue at ±0.2 v. u. in NdBaInO$_4$ at 1000 °C viewed along the c-axis (left side) and b-axis (right side). Red arrows show the possible diffusion paths of oxide ions.” – adapted from [95].
Figure 9.9 – BVSM mismatch iso价值 of 0.25, identifying the most suitable Na⁺ diffusion pathway which connects the Na7-Na8-Na7 sites. Obtained from the supplementary information.
CHAPTER 10 CONCLUSIONS:

In conclusion, Bond Valence methods can be used to qualitatively survey the ionic conductivity of large numbers of crystalline materials. In this study, 16,000 solid oxide crystalline materials were processed using Bond Valence methods and the 3DBVSMAPPER program.

A computational method was identified as suitable for qualitatively analysing the ionic conductivity of solid crystalline materials for use as battery materials. This method was then implemented in the 3DBVSMAPPER code, a new program designed to automatically survey large numbers of crystalline materials with little user intervention.

This program was then executed on 16,000 crystalline materials using various known mobile cation species such as Lithium, Sodium, Potassium, Magnesium, Silver and Copper. The results of these calculations were then sorted according to various ranking criteria.

Diithium Copper(II) Pyrophosphate (Li₂CuP₂O₇), an interesting potential new ionic conductor was identified according to the Bond Valence Sum Map and Bond Valence Energy Landscape methods. The ionic conductivity of this material was then further studied using the computational method of cNEB DFT method inside of the VASP program. The activation energy of various possible lithium pathways was explored with this method and the most likely ionic conduction pathways were identified. The main ionic
A conduction pathway was identified to be a zigzag 1-dimensional conductor along the B-axis with an activation energy of 0.37eV. At higher energies, the material appears to be a 2-dimensional conductor along the B-C plane between the framework layers with an activation energy of 0.46eV.

Further computational study is required to correct some of the possible errors in these calculations. However, in spite of this, the low activation energy of the primary ionic conduction pathway makes this material interesting for further study using experimental and computational methods.

The 3DBVSMAPPER program was also distributed to various interested scientific users for their own individual research as a simple GUI was also developed for the program.
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