

Towards an accurate and transferable charge transfer model in polarisable interatomic potentials

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Declaration of authorship

I, Vadim Nemytov, declare that the results and analyses presented in this thesis, as well as the thesis itself, constitute my own original work. Every effort was made to indicate the contributions of other researchers by providing the appropriate references.

Abstract

Understanding the properties of defects, interfaces and other heterogeneities in metal oxides is crucial for enabling new applications. Some properties can be explored in a computer simulation using classical interatomic potentials (IPs) – analytic functions of nuclear positions that provide interatomic forces.

In this thesis I have focused on developing, testing and analysing an ionic IP which combines variable-charge (QEq) and polarisable-ion (PI) models, allowing ions' charges and induced dipole moments to vary in response to their changing environments. We aim to improve the limited transferability to heterogeneous environments of the current state-of-the-art, PI-based, IPs.

For several bulk and heterogeneous systems, past applications of QEq-based IPs showed no improvement over fixed-charge IPs – at variance with common expectations. Two reasons for this have been suggested in our work – in some systems ionic charges are essentially-constant, in other systems the bonding doesn't adhere well to the limit of the QEq model. Using density functional theory and the QEq-PI IP we calculated and analysed the charge distributions and interatomic forces in BaTiO_3 at finite temperature, in a pristine crystal and near neutral O (V_{O}) and Ti (V_{Ti}) vacancies. Ionic charges were found to be essentially-constant in the defect-free BaTiO_3 , but to deviate from their bulk values near the vacancies. The improvement of QEq-PI IP over fixed-charge IP was greater for the system with V_{O} than with V_{Ti} , which was explained by the bonding near V_{O} adhering better to the limit of this model.

For systems with V_{O} the QEq-PI IP demonstrated a marked improvement in accuracy and transferability over the fixed-charge PI IP; this is the first time, to our knowledge, that a clear improvement over PI IPs has been demonstrated.

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Units and conventions used in this thesis

Several conventions are used throughout the thesis, unless explicitly stated otherwise.

Hartree atomic units are used, so e , $\hbar$, m_e and Coulomb's constant k_e are all equal to 1. The Hartree energy unit is designated as E_h .

When discussing simulations of condensed phase systems, the use of periodic boundary conditions is assumed with N_{atm} atoms per simulation cell; in this case the use of the Ewald summation with tin-foil boundary conditions[1, 2] for evaluating electrostatic interactions is implied. For example, for a system of point charges $\{q_i\}$ within a cubic simulation cell of side length L , the Coulomb interaction energy per simulation cell, E , can be written explicitly as follows:

$$E = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{n_x=-\infty}^{n_x=\infty} \sum_{n_y=-\infty}^{n_y=\infty} \sum_{n_z=-\infty}^{n_z=\infty} \sum_{j=1}^{N_{\text{atm}}} ' \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + L[n_x, n_y, n_z]|} \quad (1)$$

where $\mathbf{r}_i$ is the position of point charge i and the apostrophe indicates that for the case $n_x = n_y = n_z = 0$ the term $i = j$ is excluded. However, in this thesis, instead we use the following expression:

$$E = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} \frac{q_i q_j}{r_{ij}} \quad (2)$$

where the Ewald summation is implied; $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two charges i and j .

Summations over the repeated Greek indices are implied in the expressions, e.g. $v^\alpha v^\alpha = \mathbf{v} \cdot \mathbf{v}$ for a vector $\mathbf{v}$.

In expressions that involve electron density, the symbols $\rho(\mathbf{r})$ and $n(\mathbf{r})$ are reserved for the electron *charge* and *number* densities, respectively. For a system of electrons the former integrates to a negative integer and the latter integrates to a positive integer.

Chapter 1

Interatomic potentials for ionic systems

1.1 Introduction

A classical interatomic potential (IP), also referred to as a force field, is an analytic or numeric expression that provides interatomic forces as a function of the set of all atomic positions. Equipped with sufficiently accurate IPs, one can calculate many properties of materials and gain insight into causes of, or trends in, certain materials' properties – this information is supplementary to what can be learned by running an experiment.

The majority of IPs are analytic expressions that represent recognised physical effects, such as Pauli exclusion principle and van der Waals interactions, that are thought to contribute significantly to the energetics and interatomic forces in a given system. Such an expression involves several parameters which are fit to *ab initio* and/or experimental data for the system of interest.

Although such an IP can be of general utility[3], usually IPs are developed and optimised assuming a certain bonding type, e.g. ionic or metallic, and are restricted in applicability to materials whose bonding conforms closely to the chosen approximations. The reason for this can be seen by considering the form of the Hellmann-Feynman[4, 5] force on the atomic nucleus within a system of N_{atm} atoms:

$$\mathbf{F}_i = Z_i \sum_{j \neq i}^{N_{\text{atm}}} Z_j \frac{\mathbf{r}_{ij}}{r_{ij}^3} + Z_i \int \frac{(\mathbf{r}_i - \mathbf{r}) \rho(\mathbf{r})}{|\mathbf{r}_i - \mathbf{r}|^3} d\mathbf{r} \quad (1.1)$$

where $\{Z_i\}$ are the ionic core charges and $\rho(\mathbf{r})$ is the ground state charge density¹ of the electrons; here lower case Roman letters index atoms, $\{\mathbf{r}_i\}$ are the atomic positions,

¹The ground state charge density integrates to a negative integer.

$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$ and $r = |\mathbf{r}|$. The challenge is to approximate the second term on the r.h.s. of Eq. 1.1 as an analytic function of the nuclear positions, however, the charge density profile and its response to changing atomic positions is very different in such diverse materials as metals, covalent insulators, such as diamond, and highly ionic materials such as NaCl. Thus, for example, for NaCl the energetics and interatomic forces are strongly influenced by the long-range Coulomb interactions, while for diamond the influence of distant charges is considerably less.

In this thesis, we are concerned with improving accuracy and transferability of IPs for ionic systems, which can approximate energies and forces of such industrially important materials as metal oxides[6–12]. In the ionic limit, discussed in detail in Chapter 3, the ground state electron charge density $\rho(\mathbf{r})$ is assumed to be a sum of nuclei-centered localised contributions $\{\rho_i(\mathbf{r} - \mathbf{r}_i)\}$, $\rho(\mathbf{r}) = \sum_i^{N_{\text{atm}}} \rho_i(\mathbf{r} - \mathbf{r}_i)$. This implicitly introduces the identity of an ion and its properties, in a sense that within this limit quantities such as ionic charges are defined in terms of $\rho_i(\mathbf{r})$. Consequently, ionic IPs represent the total energy in terms of interactions between ions. For example, many of the ionic IPs are variants of, or are related to, the Born-Mayer expression[13] for the total energy E^{BM} :

$$E^{\text{BM}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} E_{ij}^{\text{BM}}(r_{ij}) \quad (1.2)$$

$$E_{ij}^{\text{BM}}(r_{ij}) = \frac{q_i q_j}{r_{ij}} + B_{ij} e^{-\gamma_{ij}(r_{ij} - \sigma_i - \sigma_j)} - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} \quad (1.3)$$

where $\{q_i\}$ are the ionic charges, usually set to nominal values, $\{B_{ij}, C_{ij}, D_{ij}, \gamma_{ij}, \sigma_i\}$ are the fitting parameters defined per ion or pairwise, based on the chemical species. This expression includes the following: a charge-charge Coulomb interaction, a short-range exponential repulsion term, which is meant to capture Pauli exclusion repulsion and, finally, the dispersion interaction terms meant to capture the van der Waals or London dispersion forces. Born-Mayer model represents the ground state density as a collection of rigid ions, i.e. charges that move together with the nuclei. A limitation of this and other rigid-ion models is that the redistribution of the ground state charge density in response to moving nuclei is not represented – modern state-of-the-art ionic IPs include some model of the response mechanism[14–19].

For a wide range of metal oxides very good ionic IPs exist for describing the homogeneous bulk by suitably modelling the response of the ground state density to changes in atomic positions[7–11, 19–22] – multiple supporting examples from the literature are discussed in Section 1.3.2. Central to this success has been the representation of changes in the ground state density in terms of induced dipole moments which describe how the ions’ densities distort in response to their environment – this approach is detailed

in Section 1.3.1. In particular, significant improvement has been achieved in accuracy and in transferability of ionic IPs between different phases and within a wide range of temperatures and pressures when simulating the material’s interior, referred to as bulk phase.

However, achieving the greater transferability that is required to describe both bulk and atoms in heterogeneous environments, such as surfaces or near defects, poses a greater challenge[23–27]. Changes in the atomic coordination number are often accompanied by dramatic changes in the ground state density relative to the bulk. This, in turn, significantly modifies the interatomic forces. For example, in the presence of a neutral Mg vacancy², O ions nearest to the vacancy site become significantly more positive relative to the bulk[29–33]. Significant changes in the ground state density are also demonstrated in Chapter 7 for test systems involving point vacancies. Within an ionic model, these changes in the ions’ charge densities, $\rho_i(\mathbf{r})$, can be treated as a charge transfer between the bulk and the O ions nearest to the vacancy site and included in an IP by treating ionic charges as variables that respond to the ion’s environment. Modern variable-charge (QEq) models, reviewed in Section 1.4.1, are predominantly either variants of, or related to, the following modification of the electrostatic energy, which was first introduced by W. Mortier *et al.*[34]:

$$\frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \sum_{j \neq i}^{N_{\text{atm}}} \frac{q_j^0}{r_{ij}} \rightarrow \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \left((q_i^0 + \Delta q_i) \underbrace{\sum_{j \neq i}^{N_{\text{atm}}} \frac{q_j^0 + \Delta q_j}{r_{ij}}}_{\phi_i} \right) + \sum_{i=1}^{N_{\text{atm}}} (A_i \Delta q_i + D_i \Delta q_i^2) \quad (1.4)$$

where A_i and D_i are parameters based on atomic species, $\{q_i^0\}$ are the fixed reference ionic charges and $\{\Delta q_i\}$ are the charge-transfer variables; the total energy is minimised subject to charge conservation to obtain a solution. The second term represents the energy cost, or “*self-energy*”, to change the charge of the ion by Δq_i while the first term is the charge multiplied into the on-site electrostatic potential, ϕ_i , due to the lattice comprised of all the other ions. This model can be understood as follows: the electrostatic potential at an ion’s site varies with its changing atomic environment; this acts as a driving force for increasing or decreasing its charge, while the self-energy is a competing term that describes changes to the ion’s internal energy (the sum of kinetic and Coulomb contributions).

Perhaps contrary to intuition, by and large, applications of the variable-charge model to condensed matter systems fail to demonstrate a non-negligible improvement in ac-

²Neutral vacancy refers to $V_{\text{Mg}}^{\times}$ in Kröger-Vink notation[28]. This is elaborated on in Chapter 7.

curacy or transferability – this statement is supported by multiple examples in Section 1.4.2. The literature review in Section 1.4.2 and original work in Chapters 6 and 7 reveal that in applications to bulk phases the results obtained with QEq model are often essentially identical to those of fixed-charge models, while in applications to heterogeneous systems, such as surfaces and point vacancies, the predicted charge distribution and interatomic forces can be in poor agreement with the much more reliable *ab initio* reference data. Additionally, in the literature it is often not demonstrated whether the values of the charge-transfer variables actually make physical sense, i.e. correspond to changes in the underlying ground state density.

This unfavourable and, at times, counter-intuitive behaviour of the QEq-based IPs prompted a debate in the related research community leaving some open questions[23–26, 35, 36]. Firstly, some researchers[24, 35, 36] have questioned the functional form of the QEq model in Eq. 1.4, introducing instead several qualitatively distinct alternative formulations. The diversity of the proposed functional forms stems from the distinct set of underlying assumptions[35–37] that underpin each model. This leads us to a set of related questions: **a)** what is the minimal set of assumptions from which QEq models can be related to a well established theory, such as density function theory (DFT)? **b)** what physical quantities do self-energy parameters A_i and D_i represent? **c)** what can be said of the transferability of these parameters between different atomic environments? **d)** for a given QEq model, are the assumptions that underpin it approximately true in the systems where the model is used?

Some[24] have suggested that in bulk insulators inter-ionic charge transfers are very small and so have a negligible effect on interatomic forces. This leads us to a second set of questions: **i)** do changes in the QEq ionic charges reflect the changes in the underlying ground state density? **ii)** can the observed lack of improvement in representing bulk metal oxides with QEq models be explained by there being very little inter-ionic charge transfer in these systems as ions move? Addressing questions i) and ii) is made difficult by ionic charge being an ill-defined quantity. This makes it difficult to quantify inter-ionic charge transfers in *ab initio* calculations and to compare them to the QEq charge-transfer variables in an ionic IP – our approach is described in Sections 6.1 and 7.1.3.

In Chapter 3 a minimal set of assumptions is proposed that allows one to interpret QEq and related ionic models as approximations to the DFT formulation, addressing questions a), b) and partly c) and d). Different parts of the derivation in Chapter 3 are similar to some of the previous work; our approach also differs from all previous work[36–39] in two aspects. The main difference is that we argue that the QEq self-

energy parameters, A_i and D_i in Eq. 1.4, depend on the nuclear positions in a way that was not previously recognised. Secondly, to a lesser extent, the difference is in the emphasis – we seek to highlight a minimum set of assumptions that underpin the QEq model in Eq. 1.4 and when these assumptions might break down. In particular, it is emphasised that QEq model self-energy parameters may have a limited transferability between the bulk phase and heterogeneous atomic environments and that the quadratic form of the self-energy expression is adequate only to describe relatively small changes in the ground state density that, additionally, adhere to the ionic limit. The analytic form of the QEq model may not be suitable to describe large, change-of-valence, changes in the ion’s charge. Both these aspects have consequences for interpreting the transferability of these parameters and guiding future attempts to represent them analytically.

Importantly, in Chapter 7 the performance of the QEq model is then linked to the breakdown of the limit in which its analytic form can be considered to be approximately valid. Two examples are contrasted in Chapter 7. For a neutral Ti vacancy in BaTiO_3 the changes in the ground state density do *not* adhere to the minimal set of assumptions that underpin the QEq model, while for the O vacancy they do. At the same time, the ability of the QEq model to represent interatomic forces in the former case is markedly poorer, consistent with expectations based on theoretical derivations of Chapter 3. This addresses primarily d) and partly c). Additionally, to the best of my knowledge, the case of the O vacancy serves as the first and only known example where a combined polarisable-ion QEq model offers a marked improvement in transferability relative to the fixed-charge polarisable-ion model. Finally, addressing question i), the charge-transfer variables in this case are shown to have a clear intuitive meaning, representing a local increase or decrease in the charge density.

In Chapter 6 several ionic IPs, including those based on the QEq and polarisable-ion models, as well as on the combination of the two, are applied to a defect-free crystal of BaTiO_3 across a range of temperatures in a comparative study with an aim to address questions i) and ii). In this regime of small perturbations to the ground state density, the analytic form of the QEq model is considered to be adequate. The main points of the study are: inter-ionic QEq charge transfers are small in magnitude, not exceeding $0.05 e$, and are argued to reflect changes in the ground state density; the agreement of the reference *ab initio* interatomic forces with those calculated by an ionic IP are quantified, and based on this measure the effect of the QEq model on the accuracy is shown to be very small or even negligible relative to other fixed-charge ionic IPs; in sharp contrast, the polarisable-ion model dramatically improves accuracy relative to the non-polarisable IP;

charge-transfer variables are shown to have no clear physical interpretation in this regime of weak perturbations to the electrostatic potential; in contrast, induced dipole moments are shown to reflect changes in the ground state density in an intuitive transparent way. This analysis addresses questions i) and ii). At least for the thermally perturbed bulk BaTiO_3 , charge fluctuations in the system can be said to be negligible and the use of the QEq model is not advisable – it improves accuracy negligibly and does not offer any clear physical insight.

Together, the theoretical analysis of the QEq model and the numerical results for BaTiO_3 are consistent with the following view. The widely used analytic form of the QEq model based on Eq. 1.4 serves as a good approximation to describe relatively small changes in the ground state density in an ionic limit. For the small thermal perturbations of ionic positions in a bulk insulating phase, changes in the ground state density that can be interpreted as inter-ionic charge transfer are in some cases so small that although the QEq model is applicable, it has a negligible impact on the accuracy and is not useful. For large perturbations of the electrostatic potential, such as those associated with a change in the local coordination number, the analytic form of the QEq self-energy can become inadequate for describing the corresponding dramatic changes in the ground state density. Thus, the range of systems where QEq models can offer an improved transferability and accuracy is narrower than previously thought. Nevertheless, the system of a neutral O vacancy in BaTiO_3 serves as an important example of a system where the QEq model does offer a marked improvement, widening further the class of materials that ionic IPs can adequately represent.

The remainder of the present chapter is structured as follows. The overarching aim of the thesis is the development of ionic models that are transferable between the bulk and heterogeneous atomic environments. Section 1.2 links transferability to the ability to represent adequately the many-body effects related to the response of the ground state density to perturbations; then discusses how these effects can be represented in an ionic model. Section 1.3 introduces the polarisable-ion (PI) model and demonstrates via numerous examples that it is particularly good at representing the many-body effects, at least in bulk phase, improving accuracy and extending transferability. In particular, a PI IP is used as the base IP in this thesis and the focus is on extending it to additionally contain the QEq model in order to achieve transferability between the bulk and heterogeneous systems. Section 1.4 introduces different QEq models and demonstrates shortcomings of the model that became apparent as a result of past applications. In

particular, it is argued that an improvement in accuracy or transferability due to QEq model has not been demonstrated so far and, additionally, it is generally not established whether charge-transfer variables adequately represent the changes in the underlying ground state density. Section 1.5 introduces the combined charge-transfer PI IP, as implemented previously by J. Sarsam[27], and summarises the broadly-inconclusive early results that J. Sarsam had obtained using this model. Additionally, in Section 1.5 our approach towards reaching the overarching aim of this thesis is discussed in greater detail. This includes extending J. Sarsam’s model to better represent short-range electrostatic interactions, rationalising its functional form theoretically and testing it in order to identify the systems for which transferability is achieved by the model in its present form as well as to point out the model’s current limitations.

While Section 1.5 outlines our research and thesis structure in some detail, we also provide a summary here. The present chapter introduces and motivates the use of the combined charge-transfer PI IP which we further develop, test and analyse in the our work. Additionally, open questions related to the use of this model are presented and our approach to address these questions is described. Chapters 2 and 3 introduce and motivate the functional form of the combined charge-transfer PI IP, as well as highlight the assumptions that underpin it. Chapter 4 introduces theoretical techniques that we subsequently use to quantify and compare changes in the ground state charge density to changes in IP variables such as ionic charges and dipole moments. Chapter 5 introduces computational techniques used in our work for parameterising IPs for the test system BaTiO₃, simulating molecular dynamics and carrying out DFT calculations to generate reference *ab initio* data. In Chapters 6 and 7 the combined charge-transfer PI IP is applied to BaTiO₃, defect-free and with neutral O and Ti vacancies, and analysed in a comparative study with a focus on interpreting the role of the QEq model in representing interatomic forces and the underlying charge density. In Chapter 8, the IPs from the previous two chapters are used to calculate lattice and elastic constants and the phonon spectra of BaTiO₃ in its rhombohedral phase, in order to verify that these IPs indeed represent BaTiO₃, at least with respect to a selected set of properties. Finally, in Chapter 9 we summarise our main findings and suggest possible routes of further research.

1.2 Many-body effects in ionic IPs and polarisability

The overarching aim of the present work is to achieve greater transferability of ionic IPs between different atomic environments. Transferability can be improved by improving

an IP's description of the response of the ground state density to the changing atomic positions, which can be highlighted by considering the Hellmann-Feynman force in Eq. 1.1. The expression is not pairwise-additive and introduces the many-body effect via the dependence of the ground state density on all the positions of the ions. Thus the physical origin of the many-body dependence of forces is the polarisation – in the broad sense of the response of the electronic density. In ionic models it is assumed that, to a good approximation, the total electron charge density $\rho(\mathbf{r})$ is a sum of contributions $\{\rho_i(\mathbf{r})\}$ localised at ionic nuclei. Thus, in the ionic limit, the many-body effects can be represented by modelling the polarisation of each individual ion while retaining an explicitly pairwise-additive functional form³:

$$\mathbf{F}_i = Z_i \sum_{j \neq i} Z_j \frac{\mathbf{r}_{ij}}{r_{ij}^3} + Z_i \sum_j \int d\Delta\mathbf{r} \frac{(\mathbf{r}_{ij} - \Delta\mathbf{r}) \rho_j(\mathbf{r}_j + \Delta\mathbf{r})}{|\mathbf{r}_{ij} - \Delta\mathbf{r}|^3} \quad (1.5)$$

where $\{\mathbf{r}_i\}$ designate ionic positions, $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$ and $\Delta\mathbf{r}$ is the integration dummy variable.

Historically, the polarisation of each ion was initially assumed to be negligible and the early ionic IPs expressed total energy, E , in a pairwise-additive form, $E = \sum_{i=1, j>i}^{N_{\text{atm}}} E_{ij}$. These are still widely used today, the most popular forms are based on either Born-Mayer expression, Eq. 1.2, or Morse-stretch[40] type potential supplemented by a charge-charge Coulomb term:

$$E_{ij}^{\text{MS}}(r_{ij}) = \frac{q_i^0 q_j^0}{r_{ij}} + D_{ij} [e^{\gamma_{ij}(1-r_{ij}/r_{ij}^0)} - 2e^{0.5\gamma_{ij}(1-r_{ij}/r_{ij}^0)}] \quad (1.6)$$

where $\{q_i^0\}$ are the ionic charges, $\{B_{ij}, C_{ij}, D_{ij}, \gamma_{ij}, r_{ij}^0, \sigma_i\}$ are fitting parameters defined per ion or, pairwise, based on the chemical species; depending on the parameter values, Morse term may contain a non-negligible cohesive contribution, in addition to exponential repulsion. However, as demonstrated in Section 1.3.2, including the response of the ionic charge density to its environment in an ionic IP can greatly increase its accuracy and transferability, motivating development of non-pairwise-additive IPs.

Common ways to represent aspects of the charge redistribution in an ionic model include the following three distinct approaches. The first[14–16, 18] is to assign each ion dipole polarisability and to allow its dipole to be induced by the electric field emanating from the other ions' charges and dipole moments⁴. This approach is described in detail

³If the ground state density is represented in nuclei-centered basis set, this expression additionally contains Pulay forces which may or may not vanish. Nevertheless, an IP with a pairwise additive analytic form can be defined that contains many-body effects.

⁴More generally, one can include higher order multipole moment polarisabilities and moments in an analogous way.

in Section 1.3.1 and is contained in the IP being developed in this thesis. The second approach[41–44] represents changes in the size and shape of the ion’s charge density, but in a way that doesn’t couple these degrees of freedom to the electrostatic potential and its gradients. Instead, it represents the steric effect of the short-range interactions amongst nearest neighbour ions⁵. Finally, in the charge-transfer model[34, 45], the ionic charges are allowed to vary, in response to the varying electrostatic potential.

The primary subject of study in this thesis is an IP, initially introduced by J. Sarsam[27], which combines the QEq charge-transfer and the Tangney-Scandolo polarisable-ion models. The latter includes ionic dipole moments but not higher-order multipole moments. The ionic size is assumed constant. Consequently, in Sections 1.3 and 1.4 only the induced-dipole polarisable-ion model and the QEq model are reviewed in detail. Extending the IP by including other models of the response of the ionic density may prove beneficial, but this is outside of the scope of the present work.

Our approach to modelling many-body response reflects our focus on materials whose bonding is reasonably close to the ionic limit. Other approaches to model many-body effects also exist, which, however, are normally used in IPs designed to represent materials with covalent or metallic bonding. A well known example of an explicitly⁶ many-body IP, typically used for metals, is the empirical Finnis-Sinclair potential[46] which introduces a square-root dependence on the atomic coordination number for the cohesive energy E^{coh} , $E^{\text{coh}} = \sum_{i=1}^{N_{\text{atm}}} \sqrt{\sum f_{ij}(r_{ij})}$, where f_{ij} is some short-range pairwise function. This term can be viewed to originate from the Tight-Binding (TB) model applied to d-series metals[47–50]. In the TB model the total cohesive energy can be expressed as a sum of atomic energies $\{E_i\}$ that depend on the local (atomic) densities of states (LDOS), $\{N_i(E)\}$, as follows[48, 50]:

$$E_i = \int_{-\infty}^{E_F} (E - \epsilon_i) N_i(E) dE \quad (1.7)$$

where E_F is the Fermi energy and ϵ_i is a TB parameter for the average orbital energy per electron for the given atomic species. Within TB, an approximate form of E_i in terms of the second moment of the LDOS $N_i(E)$ leads to the analytic form of the Finnis-Sinclair IP. Alternative physical interpretations of this empirical term are also possible[46].

Finnis-Sinclair type IPs are not commonly used for ionic systems except to model metal-oxide/metal interfaces. However, for pure metal oxide systems this form is also

⁵The steric effect itself is, of course, in part the result of an electron-electron repulsion.

⁶The functional form itself is not pairwise-additive.

occasionally invoked, including the use in conjunction with the QEq model[35, 51–53], discussed in Section 1.4.

Polarisable IPs require an additional step to calculate optimal values for the polarisation variables during the simulation, such as ionic dipole moments. Therefore, including many-body effects explicitly is computationally simpler. However, polarisable IPs arguably offer greater insight when interpreting the trends in the physical properties and, as discussed in Section 1.3.2, for many bulk metal oxides have been demonstrated to achieve superior accuracy and transferability.

1.3 Polarisable ion models

1.3.1 Overview of the models

Different ways of representing ionic dipole moment, introduced from the late 1960s onwards, can be viewed as variants on the following three main approaches, the Shell model[14, 15], the distributed-charge model of M. Wilson and P. Madden (WM)[16, 54] and, finally, representation by independent vector-valued variables[18, 19], such as in the Tangney-Scandolo (TS)[19] IP. The latter two models are essentially equivalent in the way they represent the electrostatic energy and are discussed in this section in some detail; all IPs developed and studied in this thesis are based on the TS IP. Beyond comparing the functional forms, further important differences exist at the level of implementation – this consists of choosing how to obtain the solution for the variable ionic dipole moments and how to parameterise the IP. The discussion of the differences in implementation is deferred to Section 1.5, where the approach followed in this thesis is detailed.

As explained in the next few paragraphs, the functional forms in all these models are meant to describe essentially the same physics and differ instead in technical aspects which affect accuracy and the ease with which they can be implemented. A clear way to highlight the physics contained in the PI models is to use the TS model as an example, because it represents electrostatic energy in a way that can be related easily to the exact expression. The Shell and WM models are then related to the TS model to highlight their similarities and differences.

As demonstrated in Chapter 2, for two sufficiently separated ion-centered localised charge densities $\rho_i(\mathbf{r})$ and $\rho_j(\mathbf{r})$ the Coulomb interaction can be approximated in terms

of their charges and dipole moments as follows:

$$\int \frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' \approx \frac{q_i^0 q_j^0}{r_{ij}} + (p_i^\alpha q_j^0 - q_i^0 p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\beta \partial r_{ij}^\alpha} \frac{1}{r_{ij}} \quad (1.8)$$

where q_i^0 is the charge of ion i , p_i^α are the cartesian components of its dipole moment and r_{ij} is the distance between ions i and j ; summation over cartesian components is implied by repeated Greek indices. Supplementing this expression by the energy cost to polarise an ion, which is $\epsilon_i p_i^2$ in the TS model, with ϵ_i as a material and chemical species dependent parameter, dipole moments can be treated as variables with the optimal values being those that minimize the total energy. Assuming periodic boundary conditions for a system of N_{atm} ions, the total electrostatic energy per simulation cell has the following form:

$$E^{\text{ES}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \underbrace{\left(\sum_{j \neq i}^{N_{\text{atm}}} \frac{q_j^0}{r_{ij}} - p_j^\alpha \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} \right)}_{\phi_i} - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} p_i^\alpha \underbrace{\left(\sum_{j \neq i}^{N_{\text{atm}}} -q_j^0 \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} + p_j^\beta \frac{\partial^2}{\partial r_{ij}^\beta \partial r_{ij}^\alpha} \frac{1}{r_{ij}} \right)}_{E_i^\alpha} + \sum_{i=1}^{N_{\text{atm}}} \epsilon_i p_i^2 \quad (1.9)$$

$$\equiv \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \phi_i - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} p_i^\alpha E_i^\alpha + \sum_{i=1}^{N_{\text{atm}}} \epsilon_i p_i^2 \quad (1.10)$$

where the implicitly defined ϕ_i and $\mathbf{E}_i$ are the electrostatic potential and electric field at site i due to the charges and dipole moments of all the other ions in the system; Ewald summation is implied⁷. By setting $\partial E^{\text{ES}}/\partial p_i^\alpha = 0 \ \forall \ i$, it can be shown that the minimum energy E^{ES} is attained for the solution:

$$\mathbf{p}_i = \frac{1}{2\epsilon_i} \mathbf{E}_i \ \forall \ i \quad (1.11)$$

To achieve this relationship between $\mathbf{p}_i$ and $\mathbf{E}_i$, a self-consistent scheme is used since a given dipole moment both changes the electric field, by changing other dipole moments, and is influenced by it. The polarisability, α_i , of ion i can be identified with $\alpha_i = 1/2\epsilon_i$ in this model. Thus the first and most essential aspect common to all the polarisable-ion models is that each ion polarises in response to the long-range electric field emanating from all the other ions in the system.

The second aspect common to most polarisable-ion models can be thought of as a correction to the scheme described above, due to the finite radial extent of ionic charge densities, which causes neighbouring overlapping ions to influence one another's shapes

⁷To be precise, the $\epsilon_i p_i^2$ term represents electrons kinetic energy, in addition to electrostatic interactions.

and sizes:

$$E^{\text{ES}} \rightarrow \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \phi_i - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} p_i^\alpha \left(E_i^\alpha + \underbrace{w_{ij}^{\text{qp}} \sum_{j \neq i}^{\text{n.n.}} q_j^0 \frac{\partial}{\partial r_{ij}^\alpha} \tilde{I}_0(r_{ij})}_{E_i^{\text{SR}\alpha}} \right) + \sum_{i=1}^{N_{\text{atm}}} \epsilon_i p_i^2 \quad (1.12)$$

$$\mathbf{p}_i \rightarrow \frac{1}{2\epsilon_i} (\mathbf{E}_i + \mathbf{E}_i^{\text{SR}}) \quad \forall i \quad (1.13)$$

where n.n. stands for a finite set of close neighbours, $\{w_{ij}^{\text{qp}}\}$ are IP's pairwise defined fitting parameters, $\tilde{I}_0(r_{ij}) \rightarrow 0$ rapidly as r_{ij} exceeds the nearest neighbour distance and $\mathbf{E}_i^{\text{SR}}$ is a short-range correction due to the two effects – the nearest-neighbour repulsion of electron clouds and the overlap of the electron clouds due to the finite size. This term is discussed in detail in Chapter 2; the former effect influences the magnitude and orientation of the dipole moments so as to reduce the electron-electron repulsion at the neighbouring sites and the latter effect dampens the overall magnitude of the interaction and prevents unphysical divergence of the dipole moments of ions in close proximity[54, 55]. One or both⁸ of these effects are included in most implementations of PI models, with varying definitions of $\tilde{I}_0(r_{ij})$. The concept of the short-range correction was first recognised to be important and introduced in the original work on the Shell model in 1958 by Dick and Overhauser[14]. The short-range dipole correction is discussed at length by P. Fowler and P. Madden[56]. The actual choice of the function $\tilde{I}_0(r_{ij})$ used in TS and WM models is somewhat *ad hoc*, it was introduced by M. Wilson and P. Madden[54] and is discussed in Chapter 2.

The WM distributed-charge model preceded the TS model. It represents ionic polarisation essentially in an equivalent way. In the next section it is argued that due to the similarity between the two models, most of the conclusions in the published work in connection to the WM model likely carry over to the TS model. Ignoring the short-range dipole correction, the electrostatic energy in the WM model is given by:

$$E^{\text{ES}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \phi_i + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{\gamma=1}^2 \Delta q_{i\gamma} \phi_{i\gamma} + \sum_{i=1}^{N_{\text{atm}}} \frac{1}{2} k_q \sum_{\gamma=1}^2 \Delta q_{i\gamma}^2 \quad (1.14)$$

where q_i^0 is the (constant) charge of ion i at position $\mathbf{r}_i$, $\Delta q_{i1} = -\Delta q_{i2} \equiv \Delta q_i$ are the two (fictitious) variable charges close to the ion's center at positions $\mathbf{r}_{i1} = \mathbf{r}_i - \mathbf{d}_i/2$ and $\mathbf{r}_{i2} = \mathbf{r}_i + \mathbf{d}_i/2$ for a vector $\mathbf{d}_i$ of fixed length and variable orientation, while ϕ_i ($\phi_{i\gamma}$) is the electrostatic potential at site i ($i\gamma$) due to all the charges excluding those on ion i

⁸Trivially, for $\tilde{I}_0(r_{ij}) = 0$, none of the effects are included.

itself. The solution results in the following relations:

$$\Delta q_i = \frac{1}{2k_q}(\phi_{i1} - \phi_{i2}) \quad (1.15)$$

$$\approx \frac{1}{2k_q} \mathbf{E}_i \cdot \mathbf{d}_i \quad (1.16)$$

$$\mathbf{p}_i = \frac{d_i^2}{2k_q} \mathbf{E}_i \quad (1.17)$$

where $\mathbf{E}_i \equiv -\nabla_i \phi_i$ and $\mathbf{p}_i \equiv \Delta q_i \mathbf{d}_i$. The work by M. Wilson and P. Madden preceded the TS model and introduced the short-range correction in a way that is now common to both models. With the inclusion of the short-range corrections in the WM model the relations in equations 1.14 and 1.17 are modified as follows:

$$E^{\text{ES}} \rightarrow \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \phi_i + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{\gamma=1}^2 \Delta q_{i\gamma} \left(\phi_{i\gamma} + \sum_{j \neq i}^{\text{n.n.}} q_j^0 \frac{\tilde{f}^{\text{SR}}(r_{ij})}{r_{i\gamma j}} \right) + \sum_{i=1}^{N_{\text{atm}}} \frac{1}{2} k_q \sum_{\gamma=1}^2 \Delta q_{i\gamma}^2 \quad (1.18)$$

$$\mathbf{p}_i \rightarrow \frac{d_i^2}{2k_q} (\mathbf{E}_i + \mathbf{E}_i^{\text{SR}}) \quad (1.19)$$

where $\mathbf{E}_i^{\text{SR}} \equiv \tilde{f}^{\text{SR}}(r_{ij}) \mathbf{r}_{ij} / r_{ij}^3$ and $\tilde{f}^{\text{SR}}(r_{ij})$ is a short-range function such that $\tilde{f}^{\text{SR}}(r_{ij}) \rightarrow 0$ rapidly as r_{ij} exceeds nearest neighbour distance. The TS IP was based on the WM model[57] and the $\mathbf{E}_i^{\text{SR}}$ term, discussed in Chapter 2, is identical in both models.

Finally, the original and still popular model that included polarization effects was the Shell model[14, 15]. It represents an ion as a core positive charge and a negatively charged spherical shell, attached to the core by a spring; the position of the shell relative to the parent ion is a variable. The total energy consists of the energy of the extension of springs, the Coulomb interaction energy excluding the interaction of the core with its own shell and the modified Born-Mayer short-range repulsion term $B_{ij} e^{-\gamma_{ij} r_{ij}^{\text{ss}}}$ where r_{ij}^{ss} is the distance between the centres of the spherical electron shells on ions i and j :

$$E^{\text{ES}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} B_{ij} e^{-\gamma_{ij} r_{ij}^{\text{ss}}} + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} Z_i \phi_i + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^s \phi_{i\Delta} + \sum_{i=1}^{N_{\text{atm}}} \frac{1}{2} k_i |\Delta \mathbf{r}_i|^2 \quad (1.20)$$

where Z_i and q_i^s are fixed core and shell charges, respectively, $\Delta \mathbf{r}_i$ is the vector from the ionic core, at $\mathbf{r}_i$, to the centre of the shell and ϕ_i ($\phi_{i\Delta}$) is the electrostatic potential at $\mathbf{r}_i$ ($\mathbf{r}_i + \Delta \mathbf{r}_i$) due to all the charges other than those on the same ion. In TS- and WM-based IPs the electrostatic energy is supplemented by short-range exponential repulsion terms that are independent of the charges and dipole moments, thus not affecting the self-consistent solution. In contrast, in the Shell-model the electrostatic energy includes, at the very least[58], the short-range exponential repulsion which strongly couples repulsion to the dipole moments. This strong coupling, deemed unrealistic by P. Fowler, M. Wilson *et al.*[54, 56], was one of the primary reasons motivating the subsequent WM model.

In Section 1.3.2 the applications of the polarisable-ion IPs are reviewed, highlighting the numerous examples that clearly demonstrate great improvements in accuracy and the ability to represent a wider class of materials.

1.3.2 Applications

Central to interpreting the results obtained with PI IPs is the concept of screening, which is now introduced via a simple example. Consider two non-overlapping ions in vacuum labelled i and j with charges $q_i^0 = 1.0$ and $q_j^0 = -1.0$ at positions $\mathbf{r}_i = [0, 0, 0]$ and $\mathbf{r}_j = [10, 0, 0]$, with $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j = -\mathbf{r}_j = [-10, 0, 0]$. The simplest expression⁹ for the interaction energy that includes dipole moments of each ionic charge density is given by:

$$E_{ij}^{\text{ES}} \approx \frac{q_i^0 q_j^0}{r_{ij}} + (\mathbf{p}_i q_j - q_i \mathbf{p}_j) \cdot \nabla \frac{1}{r_{ij}} \quad (1.21)$$

$$= \frac{1}{2} \frac{q_i^0}{r_{ij}} \left(\underbrace{q_j^0}_{<0} - \underbrace{\mathbf{p}_j \cdot \frac{-\mathbf{r}_{ij}}{r_{ij}^2}}_{<0} \right) + \frac{1}{2} \left(\underbrace{q_i^0}_{>0} + \underbrace{\mathbf{p}_i \cdot \frac{-\mathbf{r}_{ij}}{r_{ij}^2}}_{<0} \right) \frac{q_j^0}{r_{ij}} \quad (1.22)$$

$$= \left(1 - \frac{1}{2} \left(\frac{1}{q_i^0} \mathbf{p}_i - \frac{1}{q_j^0} \mathbf{p}_j \right) \cdot \frac{\mathbf{r}_{ij}}{r_{ij}^2} \right) \frac{q_i^0 q_j^0}{r_{ij}} \quad (1.23)$$

$$\equiv \frac{1}{\epsilon^{\text{eff}}(\mathbf{r}_{ij})} \frac{q_i^0 q_j^0}{r_{ij}} \quad (1.24)$$

where $\epsilon^{\text{eff}}(\mathbf{r}_{ij}) > 1$ is defined implicitly. The above example is a one-dimensional problem and one can easily verify the inequalities. Electron density on the negative ion j shifts towards the positive ion i while density on the ion i moves away from the ion j , both in the direction $[-1, 0, 0]$ giving $\mathbf{p}_i \propto \mathbf{p}_j \propto [1, 0, 0]$ after multiplying the displacement by the negative charge of the electrons. In this simple example the effect of the polarisation can be interpreted as a screening of the ionic charges, effectively lowering them in magnitude $q_i^0 \rightarrow q_i^0 / \sqrt{\epsilon^{\text{eff}}}$ and $q_j^0 \rightarrow q_j^0 / \sqrt{\epsilon^{\text{eff}}}$. In an insulating ionic material one generally expects the same to be true on average, with ionic charges being effectively screened due to the polarisation of the electron density throughout the material. As we shall see in Section 1.4.2, in an ionic model that doesn't represent electron density response explicitly or represents it incompletely, screening between distant charges can be included approximately in an average way by using effective charges, q_i^{eff} , that are smaller in magnitude, $q_i^{\text{eff}} \equiv q_i^0 / \sqrt{\epsilon^{\text{eff}}}$ where $\epsilon^{\text{eff}} > 1$ is a constant and q_i^0 are the nominal ionic charges. Screening in the context of ionic IPs has been discussed at length by J. Sarsam *et al.*[10].

⁹As noted earlier, this approximation is derived in Chapter 2.

All PI models discussed in the previous section exhibit the effect of polarisability to some extent, although the most dramatic improvements over pairwise IPs can be ascribed to the IPs that superseded the Shell model. The Shell model, despite its simplicity, exhibits the physical effect of screening on some properties, apparent, for example, in the lowering of the vibrational frequencies of the longitudinal optical modes in the phonon spectrum calculations[59].

However, the importance of including ionic polarisability in classical IPs was decidedly demonstrated by M. Wilson, P. Madden *et al.*[7, 17, 60, 61], using the WM model described in Section 1.3.1. In a series of papers[7, 17, 60, 61], they clearly showed that a large set of static and dynamical properties, not only of simple ionic systems (Alkali Halides), but of metal oxides with complex structure such as amorphous SiO₂, can be reproduced and interpreted as a result of ionic polarizability. Firstly, using the WM model one is able to reproduce and rationalise the trends in a wide range of experimentally observed crystal structures. Some of these cannot be made stable at all when using the standard pairwise-additive Born-Mayer IP (rigid ion model or RIM) and parameter values within a physically meaningful range.

One representative study demonstrating the effect of inducible dipoles on structure is now outlined. In Ref. 60 it is demonstrated that taking RIM IP and only modifying it to additionally include anion polarisability, based on the WM model, allows one to reproduce all the experimentally observed trends with respect to cation radius in a diverse set of crystal structures of halides MX₂, where M is divalent metal and X ∈ {F, Cl, Br, I}. The cation radius is defined within the IP as the parameter σ_+ that enters the exponential repulsion term, $B_{ij}e^{-\gamma_{ij}(r_{ij}-\sigma_+-\sigma_-)}$, and is related by the authors to the ionic crystal radius, taken from the published chemical data[62]; this chemical data implies an ordered set of metals based on the radius, M ∈ {Mg, Zn, Mn, Ca, Sr, Ba}¹⁰, making it possible to compare the trends in the model and in the experimentally measured structures for these halides. In particular, layered structures, such as MgI₂, involve same-charge anion layers in close proximity and due to the strong Coulomb repulsion are not the lowest energy structures when using RIM. At the same time, anions in this low-symmetry structure are subjected to strong electric field and, as a result, the induced dipole moments significantly lower the electrostatic energy. For a suitably small cation radius this phase is the energy minimum when using the WM model. Therefore the stability of this phase

¹⁰In a condensed phase ionic radius cannot be defined uniquely and it is precisely the types of studies such as in Ref. 60 that promote the view that despite this the notions such as ionic radius or ionic polarisability are useful concepts for understanding trends in the physical properties.

can be related to the anion polarisability.

Similar studies have rationalised the structural trends in terms of the inducible ionic dipole moments[61] or higher multipole moments[63] for several other metal oxides in solid[61] and molten[64] phases.

Instead of rationalising qualitatively structural trends, their work on amorphous SiO_2 had demonstrated a concrete example of a PI IP that reproduces non-trivial structural, dynamical and dielectric properties in very good quantitative agreement with the experiment. As before, experimentally observed properties were rationalised in terms of ionic polarisability[7]. The infrared (IR) spectrum for amorphous SiO_2 is in a qualitative disagreement with the experiment[65–67] when calculated with pairwise-additive IPs, either with an ionic IP[68] or an IP modified to capture covalency by using lower partial charges and an additional cohesive term[7, 69]. This suggests that the missing many-body effects are at the root of the discrepancy with the experiment. The key points of the work in Ref. 7 can be summarised as follows. The experimentally obtained IR spectrum is dominated by two strong absorption peaks at $\sim 465 \text{ cm}^{-1}$ and $\sim 1100 \text{ cm}^{-1}$, thought to be associated with a bending of the Si-O-Si “bond” and an asymmetric stretching of the SiO_4 tetrahedra, respectively¹¹. The RIM model predicts the first peak at a considerably higher frequency, $\sim 800 \text{ cm}^{-1}$, indicating that the energy cost for deviating from the equilibrium Si-O-Si “bond” angle is unrealistically high¹². In the WM-based polarisable ion model, this first peak shifts down to the value of $\sim 463 \text{ cm}^{-1}$, consistent with the view that screening lowers the electrostatic energy associated with this vibrational motion. Furthermore, consistent with the intuition, the analysis showed that the dipole moments correctly represent O^{2-} electron cloud as deforming to point towards the nearest Si^{4+} cations. This means that for the Si-O-Si bond-angle vibration, the O^{2-} electron cloud distorts in an opposite direction to the motion of the ion itself, while for the asymmetric stretching of the SiO_4 tetrahedra the O electron cloud shifts in sync with the anion’s motion. As a result, the fluctuating ionic dipole moments directly contribute to the total calculated polarization fluctuations, lowering and amplifying, respectively, the IR absorption at the $\sim 460 \text{ cm}^{-1}$ and $\sim 1080 \text{ cm}^{-1}$ peaks. Overall, the PI model modifies the interaction energy so as to correctly shift the location of the main peaks in the IR spectrum resulting in an excellent overall agreement with the experiment.

A series of subsequent studies based on the TS PI model each focused on developing an PI IP for one material at a time and testing the accuracy for a range of proper-

¹¹Please see Ref. 7 for a more detailed analysis of the features in the IR spectrum.

¹²If the “bond” angle is imagined to be controlled by a spring, this spring comes out too stiff in the RIM model, resulting in a relatively high frequency of vibration.

ties and transferability over multiple phases. TS IPs were parameterised and tested for metal oxides including SiO₂[8, 19, 70], Al₂O₃[10], BaTiO₃[9], TiO₂[11], MgO[20], simultaneous representation of SiO₂ and TiO₂[12] and a dissociable IP for water[21], overall demonstrating the ability to reproduce well simultaneously several distinct properties and phases. In particular, D. Herzbach *et al.*[70] was able to successfully reproduce the α -quartz to β -quartz phase transition in SiO₂ using the TS IP and demonstrated that the transition is mediated by the oxygen anions’ inducible dipole moments; this transition is not observed in their study when simulated using a pairwise-additive IP. Furthermore, Y. Liang *et al.*[8] demonstrated that, among other things, the TS IP for SiO₂ reproduces the IR spectra for α -quartz, α -cristobalite and β -cristobalite in excellent agreement with experiment. Overall, the results from applications of both the TS and WM PI models to SiO₂ lead us to conclude that the inclusion of inducible dipoles improves the descriptions of crystal structures, dynamical and dielectric properties.

In summary, a series of works on PI IPs demonstrated that including the polarisability of ions in an IP allows one both to reproduce and to physically interpret a wide range of experimentally observed structures and properties in metal oxides. Screening generally has a stabilising effect for lower symmetry structures and results in a more realistic description of the potential energy surface when ions deviate from their equilibrium positions, overall improving the dynamical properties. In addition, inducible dipoles also directly modify dielectric properties.

Several other popular ways of representing the response of the ionic charge density to the environment must be acknowledged. Including higher order multipole moments can be important to fully represent screening in some special cases due to the symmetry of the crystal structure[63, 71, 72].

Compressible ion (CI) models allow the sizes of ions to vary in response to their environments, in order to capture short-range repulsion more realistically[41–44]. However, given the aim of this thesis, the merit of these other approaches is not explored further. The aim of this thesis is to develop, understand, and test the QEq model, when implemented in combination with the inducible-dipole polarisable-ion TS IP.

1.4 Charge transfer models

The QEq model, as applied to condensed matter, is yet to be demonstrated to capture novel physics in a simulation or to enable greater accuracy or transferability. In Section 1.4.2, it is argued that the published applications of the QEq-based IPs to condensed

matter fail to demonstrate convincingly any improvement, ascribable to the use of this model. Additionally, as pointed out in the same section, some studies imply the crucial importance of combining QEq models with an IP that adequately represents screening – otherwise, embedding QEq model in simple pairwise-additive IPs can result in a significantly underestimated electrostatic energy. This primarily stems from the fact that if ionic charges are not set to nominal values and instead are a result of parameterisation, they tend to reduce in magnitude, $q_i \rightarrow q_i/\sqrt{\epsilon_{\text{eff}}}$ ($\epsilon_{\text{eff}} > 1$), as has been discussed in Section 1.3.2 and elsewhere[10]. Most common pairwise-additive ionic IPs simply assign large nominal values to ionic charges and by construction do not have this issue, but charge-transfer IPs do, with the (implicit) ϵ_{eff} generally turning out to be somewhat large.

Furthermore, motivated partly by this lack of success[35], partly due to other known shortcomings[36, 73, 74], several qualitatively distinct QEq models have been introduced, demonstrating an apparent lack of consensus as to the “correct” functional form for capturing charge transfer in ionic systems. In Section 1.4.1 an overview is presented meant to clarify the similarities and the differences of various QEq models as well as to relate them to our approach.

1.4.1 Overview of the models

The QEq model was first proposed by W. Mortier *et al.*[34, 45, 75, 76] and all subsequent QEq-type models are extensions, containing this one as a special case. The electrostatic energy per unit cell is given by:

$$E^{\text{ES}} = \sum_i^{N_{\text{atm}}} (A_i q_i + D_i q_i^2) + \frac{1}{2} \sum_i^{N_{\text{atm}}} q_i \sum_{j \neq i}^{N_{\text{atm}}} \frac{q_j}{r_{ij}} \quad (1.25)$$

where A_i and D_i are parameters which were interpreted in the original work as the electronegativity and atomic hardness of atom i , respectively, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. It is important to emphasize that this self-energy expression – the first term – is derived assuming[34] that the embedded atom is essentially decoupled¹³ from the rest of the system[77], and doing a Taylor expansion of the independent atom’s energy E_{atom} , about the neutral-atom state:

$$E_{\text{atom}} \approx E_{\text{atom}}^0 + \left. \frac{\partial E_{\text{atom}}}{\partial N} \right|_0 \Delta N + \frac{1}{2} \left. \frac{\partial^2 E_{\text{atom}}}{\partial N^2} \right|_0 \Delta N^2 + \dots \quad (1.26)$$

¹³Following J. Perdew *et al.*[77] an atom can be interpreted as an open system in contact with an electron reservoir, with E and N representing the average energy and electron number, respectively, of a statistical ensemble. Electronegativity can then be identified with $-\partial E_{\text{atom}}/\partial N$.

where N is the total number of electrons on the isolated atom and 0 designates the neutral-atom reference state. This approximation, originally derived in the Chemistry community, has been used in the vast majority of QEq-type models applied to condensed matter systems. As discussed in Section 1.5, in our work we also treat A_i and D_i as constants. However, in Chapter 3 a perturbation using, instead, a condensed phase as a reference state is carried out, highlighting that in general the coefficients A_i and D_i are functions of the positions of the atoms in the system, suggesting a limited transferability of these parameters.

Note, the energy expression in Eq. 1.25 completely defines the charges of ions but if one wishes to evaluate forces, e.g. to perform molecular dynamics simulations, then this expression has to be supplemented at the very least with some type of short-range repulsion to prevent atoms collapsing into one another. Ewald-type summation techniques are applied if necessary and the potential at i , $\phi(\mathbf{r}_i) = \partial E^{\text{ES}}/\partial q_i$, is then evaluated. A unique set of charges is obtained by extremising the total energy subject to charge conservation:

$$\frac{\partial}{\partial q_l} \left[E^{\text{ES}} - \chi \left(\sum_i^{N_{\text{atm}}} q_i \right) \right] \equiv 0 \quad \forall l \quad (1.27)$$

$$\Leftrightarrow$$

$$\chi = A_l + D_l q_l + \phi(\mathbf{r}_l) \quad (1.28)$$

Once the solution is obtained, the quantity $\chi_l = \chi$ is the same for all atoms. W. Mortier *et al.* interpret A_i to represent electronegativity of an *isolated* atom, whereas χ – the electronegativity of an *embedded* atom, i.e. embedded in a lattice and hence subjected to electrostatic potential produced by all the other atoms in the system[78]. D_i is referred to as atomic hardness. It is important to emphasize that implicitly this model makes a further assumption, namely, charges are expressed as $q_i = q_i^0 + \Delta q_i$ where the constant reference charge for ion i is implicitly set to zero, $q_i^0 \equiv 0$.

Mortier’s QEq model can be supplemented by different charge-independent terms creating a variety of QEq-based IPs suitable for performing molecular dynamics and other simulations. Different IPs built this way will all give identical set of charges for the same input atomic structure (provided that the A_i and D_i parameters used are the same). In fact, using identical expression for E^{ES} but choosing a different reference charge q_i^0 in practice creates a somewhat different model due to non-equivalent constraints during the parameterisation. As already discussed, the parameters A_i and D_i can be viewed as arising due to a Taylor expansion and in that case the theory behind the model suggests Δq_i to represent small fluctuations about a non-zero reference charge q_i^0 .

Greater difference among QEq-type models is obtained when the terms that depend on charge are modified.

The first such modification was due to A. Rappe and W. Goddard[79].

$$E^{\text{ES}} = \sum_{i=1}^{N_{\text{atm}}} (A_i q_i + D_i q_i^2) + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i \sum_{j \neq i}^{N_{\text{atm}}} q_j I_0^{\text{S}}(r_{ij}) \quad (1.29)$$

where the only type of modification was to represent the finite size of each ion’s electron cloud by replacing a point-charge Coulomb interaction by the interaction between two spherically symmetric ion-centered charge densities, which are defined using Slater-type orbitals, as follows:

$$I_0^{\text{S}}(r_{ij}) \equiv \int \int \frac{\rho_i(\mathbf{r}) \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (1.30)$$

The function $I_0^{\text{S}}(r_{ij})$ and similar forms that include short-range corrections are discussed in detail in Chapter 2. This QEq model was then supplemented by a Morse-stretch short-range term to create an IP called MS-Q[80, 81], which greatly popularised QEq-based IPs.

$$E_{\text{tot}}^{\text{MS-Q}} = E^{\text{MS}} + E^{\text{ES}}; \quad (1.31)$$

$$E^{\text{MS}} = \frac{1}{2} \sum_{i,j \neq i}^{N_{\text{atm}}} E_{ij}^{\text{MS}} \quad (1.32)$$

In fact, although the two papers of Ref. 80 and Ref. 81 are likely to have been a major reason for the uptake of MS-Q model by many other workers in the field, their work was misleading as to the actual way in which their results were obtained. E^{ES} with Slater-type orbitals was used to calculate the set of charges, but these charges were then substituted into a point-charge based MS-Q model to evaluate forces, stress components and energy. This was first pointed out and verified by Daniel Herzbach[82, 83] for the model applied to SiO_2 of Ref. 80 and later confirmed for the work on MgO of Ref. 81 in Chapter 2 by the present author. In 2002 the same team has published a model that they called “Dynamic Charge-Equilibration Morse-stretch”[84] where this inconsistency was resolved, using Slater-type orbitals for finding both the equilibrium charges and the forces on ions. This later work is arguably harder to come across during a literature review and many, perhaps most, workers familiar with MS-Q model are likely unaware of the inconsistency in the work of References 80 and 81. In this thesis, the abbreviation MS-Q is reserved to describe Slater-type QEq model supplemented by Morse-stretch where charges and forces are evaluated *consistently*. To the best of my knowledge, most works except in Ref. 80 and 81, use MS-Q consistently. As a practical note, MS-Q

is correctly implemented in the GULP[85] package, the latter being frequently cited in published works where MS-Q is used¹⁴

A close relative of the QEq scheme discussed so far is a family of *split* charge equilibration (SQEq) models[73, 86, 87] based on a competing approach that proposes using charge transfer variables defined pairwise, instead of on-site ionic charges as in QEq. Thanks to the work of J. Chen *et al.*[88], all the variants of the SQEq-type models are expressible in a unified mathematical framework¹⁵ and can be seen to contain the original QEq as well as the SQEq formalism as special cases:

$$E_{SQEq} = E_{QEq} + \sum_{i=1, j \neq i}^{N_{\text{atm}}} \left(f_D^{\text{bond}}(r_{ij}) \frac{1}{2} D_{ij}^{(s)} \frac{(\Delta q_i - \Delta q_j)^2}{N^2} + f_A^{\text{bond}}(r_{ij}) \Delta A_{ij} \frac{(\Delta q_i - \Delta q_j)}{N} \right) \quad (1.33)$$

where $f_D^{\text{bond}}(r_{ij}) \rightarrow 0$ and $f_A^{\text{bond}}(r_{ij}) \rightarrow 0$ for the nearest neighbours (i.e. “bonded”) and approach 1 for atoms further apart in the most common implementation; ΔA_{ij} and $D_{ij}^{(s)}$ are pairwise defined IP parameters. These extra parameters allow one in principle to inhibit charge transfer over long distances. In practice, there is an upper limit to the energy penalty that can be enforced because cut-off functions introduce forces that reach unphysically large magnitudes if $f_{A/D}^{\text{bond}}(r_{ij})$ isn’t smooth enough or the prefactor is too large.

As demonstrated by R. Nistor and M. Muser[89], and verified in Chapter 8, QEq-type models mimic ideal conductors with respect to the dielectric properties due to the uninhibited long-range charge transfer – this is unphysical for insulators. Nevertheless, SQEq-type models are not studied in this thesis and more generally A_i and D_i are assumed to be constants, and no additional self-energy terms are considered. The focus in the present thesis is to rationalise and identify limitations and the domain of applicability of the combined polarisable-ion charge-transfer models, starting with the simplest case. The analysis and conclusions presented in Chapters 6 and 7 are not expected to be affected by the long-range charge transfer due to relatively small dimensions of the simulation cells used and the symmetry of the systems considered. In Chapter 3 it is indeed demonstrated that the A_i and D_i self-energy parameters are best thought of as functions of atomic positions in general, however finding a suitable analytic expression is a highly non-trivial task and is beyond the scope of the present work.

¹⁴I may add, as verified in February 2017, the LAMMPS implementation of QEq *does not use Ewald summation* to obtain on-site electrostatic potential in an extended system of infinitely many ions.

¹⁵J. Chen showed that split-charge-transfer variables, $\{\bar{q}_{ij}\}$, of SQEq and charge-transfer variables, $\{\Delta q_j\}$, of QEq-type models are linked simply as $\bar{q}_{ij} = (\Delta q_i - \Delta q_j)/N_{\text{atm}}$.

Finally, a substantially distinct QEq-type IP modifies the QEq scheme by including extra charge-dependent term meant to represent energy contribution from covalent effects¹⁶. This model substantially differs from those based on an ionic limit and, hence, is not reviewed at length. It is based on the work of Noguera *et al.*[90, 91] where a Tight-Binding model was originally applied to binary metal oxides, that could be viewed to consist of two sublattices that interact in resemblance to a diatomic molecule. Their model can be said to extend MS-Q in two steps. Firstly, as an intermediate step (SMB-Q model[25, 51]) the anion-cation Morse-stretch short-range interaction is modified to have non-pairwise-additive cohesive energy contribution via the familiar square root dependence on the coordination number:

$$E^{\text{short}} = \sum_{i \in \{O\}} \sum_{j \in \{n.n.C\}} D_{ij}^{\text{short}} e^{-\gamma_{IJ}(r_{ij}/r_0^{IJ}-1)} - \sum_{i \in \{O\}} \sqrt{\sum_{j \in \{n.n.C\}} \tilde{D}_{ij}^{\text{short}} e^{-2\tilde{\gamma}_{IJ}(r_{ij}/r_0^{IJ}-1)}} \quad (1.34)$$

where D_{ij}^{short} , $\tilde{D}_{ij}^{\text{short}}$, γ_{ij} and $\tilde{\gamma}_{ij}$ are adjustable pairwise parameters; $i \in \{O\}$ is the summation over O ions, $j \in \{n.n.C\}$ is the summation over nearest neighbour cations. Here the energy is defined per oxygen ion i and a summation of their nearest neighbour cations j . As a second step, the final model, called SMTB-Q[52] (Second Moment Tight Binding with QEq) further modifies the cohesive term to have a charge dependence:

$$E^{\text{short}} = \sum_{i \in \{O\}} \sum_{j \in \{n.n.C\}} D_{ij}^{\text{short}} e^{-\gamma_{IJ}(r_{ij}/r_0^{IJ}-1)} - \sum_{i \in \{O\}} \sqrt{\sum_{j \in \{n.n.C\}} \tilde{D}_{ij}^{\text{short}} e^{-2\tilde{\gamma}_{IJ}(r_{ij}/r_0^{IJ}-1)} \left(\frac{n}{m}\right) \left(2\frac{m}{n} - q_j\right) \left(2\frac{n_0}{m} - 2 - q_i\right)} \quad (1.35)$$

$$(1.36)$$

where n and m are defined by the stoichiometry of the metal oxide system M_nO_m and n_0 is defined in terms of the notion of atomic orbitals involved in covalent bonding. As with other QEq-type models, the equilibrium charges are obtained by minimising the total energy, $E_{\text{SMTB-Q}}$, with respect to charges subject to charge conservation. The total energy has the following form:

$$E_{\text{SMTB-Q}} = E_{\text{QEq}} + E^{\text{short}} \quad (1.37)$$

The proposed justification for this model can be found in Refs. 35, 51–53 and references therein. However, the theoretical underpinnings are not of general nature and are instead

¹⁶In this context the intended definition of covalency is to be found by reading the work of the authors of this model[90, 91].

based on a very special case of binary metal oxide system, using approximations and concepts of the Tight-Binding model, in way that departs substantially from the ionic limit we assume in our work. Therefore, this approach is not studied in any detail in this thesis.

1.4.2 Applications

At first glance, the QEq model may seem to contain the correct physics and it looks promising for improving the accuracy and transferability of ionic IPs as applied to condensed matter. However, a careful examination of the published results reveals that, in fact, in applications of QEq-based IPs it has not been demonstrated conclusively that the QEq model improves accuracy or transferability of the IP relative to the fixed-charge IP or that it provides a realistic description of charge redistribution.

It is difficult to verify whether QEq charges reflect the changes in the underlying ground state density since an ionic charge in condensed matter is not well defined in quantum mechanics. There are studies[34, 45, 87, 92–94] that specifically compare QEq charge transfer values to the underlying ground state density, using Mulliken[95], Hirshfield[96] and similar definitions of the atomic charges. However, those studies are confined to the applications that by-pass evaluating interatomic forces entirely, and can be said to belong to the chemistry community where molecular charge distribution[45, 97], molecular polarisability[93] and electrostatic potential surface outside a molecule[92, 98, 99] are the quantities of interest. In contrast, an IP is generally parameterised and tested based on its ability to reproduce experimentally measured static and dynamical properties and/or the *ab initio* potential energy surface for a given material. These studies warrant a separate discussion and are reviewed in the next subsection. On the other hand, when QEq model is embedded in an IP that enables calculations of interatomic forces, mechanical, dynamical and other properties, the charge-transfer values are generally not verified to reflect the underlying ground state density.

Secondly, demonstrating accuracy or transferability ideally requires a comparative study, such that any calculations are repeated using at least two IPs, with and without the inclusion of the QEq model. Alternatively, a favourable comparison can be made by calculating the same properties using QEq-based IP as have been previously calculated using fixed-charge IPs, and demonstrating an improved agreement with the experiment. Instead, in most publications that promote the use of QEq-based IPs a comparative study is not carried out and the presented results and analysis fall short of demonstrating any improvement due to the QEq model. Representative work is discussed in detail in this

section to highlight some short-comings of the analysis that are common to most of these publications. On the other hand, those publications that do include a comparative study clearly show that QEq-based IPs do not improve accuracy or transferability relative to the fixed-charge IPs. These comparative publications are put forward at the end of the present section.

Finally, B. Thomas *et al.*[24, 26] demonstrated that when a QEq model is used in conjunction with a simple pairwise additive IP, the predicted ionic charges tend to be very low which dramatically lowers the contribution of Coulomb interactions to the total energy. In part, this can be understood as follows – in a model that allows ionic charges to take arbitrary values, these tend to be small because screening becomes implicitly included, $q_i \rightarrow q_i/\sqrt{\epsilon_{\text{eff}}}$, as already discussed in Section 1.3.2 and elsewhere[10]. As a result, interatomic forces and many calculated properties in such IPs become less sensitive to the average values of ionic charges while the relatively small charge fluctuations predicted by the QEq model have essentially a negligible effect on the forces. This raises the question about the ability of the QEq model to improve the accuracy and transferability. The studies where the negligible effects of QEq charge transfers has been demonstrated are discussed at the end of this section. In particular, we point out that polarisable-ion IPs include some of the screening mechanisms explicitly, in the form of induced dipole moments – as we shall see this leads to larger magnitude of the effective ionic charges in the combined polarisable-ion charge-transfer IP.

Model applications without an evaluation of forces.

As discussed in Section 1.4.1, the QEq model defines only the inter-ionic electrostatic interactions energy and an energy cost for changing an ion’s charge from the reference value. This is sufficient to determine the QEq equilibrium charge distribution but other important effects, such as short-range repulsion due to Pauli exclusion principle, are not included within the model. Therefore, at the very least, a QEq-based IP needs to be supplemented with some sort of short-range repulsion term in order to enable calculations of interatomic forces and structural and dynamical properties. Otherwise, ions would simply collapse into one another during a molecular dynamics simulation, due to cohesive interactions between the oppositely charged nearest neighbour ions. Having said that, a body of work exists[34, 45, 76, 87, 97, 100–105] (Ref-noF) where the QEq model is *not* embedded in an IP that would enable the calculation of forces – instead it is used to calculate the QEq atomic charges[34, 45, 87, 103, 105] and related quantities including electronegativity (Eq. 1.28)[76, 97, 100], electrostatic potential surfaces outside

the molecules[102, 104], Fukui function[101] and molecular dipole moments[104]. The input structures of the molecules or solids considered in these studies are taken from the literature or *ab initio* calculations – one cannot assume that the structures examined would even be stable in a calculation based on a given QEq-based IP. In contrast, IPs are normally parameterised and tested based on their ability to reproduce a combination of experimentally measurable structural and dynamical properties and the *ab initio* potential energy surface¹⁷, i.e. quantities that depend on interatomic forces. Therefore, the studies in Ref-noF are inconclusive regarding the QEq model’s ability to improve the accuracy and transferability in classical IPs.

In this thesis we are also interested in addressing whether charge transfers in a QEq-based IP represent the underlying charge density in a given system. More specifically we wish to test this, subject to IP parameters being *optimised for accuracy* with respect to the calculated properties and/or interatomic forces. Once again, because the interatomic forces in Ref-noF are not evaluated, the link that we wish to explore between the QEq charge transfers and accuracy is absent. What’s more the QEq model parameters are often fit to reproduce reference *ab initio* charges[34, 87, 101–103, 105] based on Mulliken[95], Hirshfield[96] or other definitions. This introduces a bias that is not necessarily physically justified. It must be emphasized, that ionic charges are not well defined in condensed matter and it isn’t clear *a priori* whether for the QEq charge transfers “to reflect the ground state density” in a given system implies an agreement with reference charges based on Mulliken or other commonly used definitions. In particular, in Chapter 6 we find that QEq ionic charges in hot bulk BaTiO₃ *anti-correlate* with DFT charges based on Löwdin[106, 107]¹⁸ and Bader[108] definitions. Yet we argue that the predicted QEq charge distribution is correct in a sense that it reflects changes in the electrostatic potential and captures some of the effects on interatomic forces that can be ascribed to a redistribution of the upper valence band.

For the reasons outlined above, the type of studies in Ref-noF do not warrant a detailed discussion in the present thesis. Nevertheless, a few early works are reviewed in some detail to make an important point regarding physical interpretability of the QEq charge distribution and related variables. In some studies QEq charges or electronegativities are found to correlate with the changes in physical properties, such as optical refractive index[76, 97, 100] and carbon 1s electron binding energy[45]. This indirectly suggests that the QEq variable values in the systems considered are physically mean-

¹⁷Parameterisation via force-matching is implied – see Section 5.3.

¹⁸Löwdin’s definition of atomic charges is also reviewed in Section 4.4.

ingful. However, such conclusions must be analysed with care since, by construction, a correlation with QEq variables is strongly affected by electrostatic potential – this latter quantity tends to depend strongly on ionic positions but may depend only weakly on the QEq predicted charge transfers. To substantiate this point by a form of example and, to a lesser extent, to provide some historical context to the discussion in the present chapter, several early applications of the QEq model are now reviewed.

First we summarise the main findings and conclusions in the first applications of the QEq model[76, 97, 100] that followed the paper[45] that introduced it and subsequently we comment on their results. In a series of three publications K. Van Genechten, L. Uytterhoeven *et al.* applied the QEq model to solids, firstly to SiO₂ polymorphs[76, 100] and subsequently to AlPO₄ polymorphs[97] – they discovered a correlation between the QEq calculated electronegativities and changes in the optical refractive index in those systems. They found that, on one hand, a low atomic volume density leads to a large QEq electronegativity¹⁹(EN) and, on the other hand, the EN exhibits an approximately linear relationship with the optical refractive index. In turn, they suggest a physical explanation for the experimentally observed (positive) correlation between the system’s refractive index and its atomic volume density in terms of the relationship of the former quantity and the QEq electronegativity. A large EN was interpreted to indicate that ionic electron clouds are more compact (more tightly bound) and hence distort (i.e. polarisable) less easily in response to an external oscillating electric field²⁰. A larger EN is then suggested as the reason for the lower refractive index in low density SiO₂ structures. The same trend is observed in AlPO₄ polymorphs[97].

However, firstly, while the notion of a chemical potential and electronegativity can be well defined for an isolated atom[77], for an embedded ion in a condensed phase this notion is less well defined. More importantly, the last term in the definition of EN, $\chi_i \equiv A_i + D_i q_i + \sum_{j \neq i}^{N_{\text{atm}}} q_j / r_{ij}$, is the electrostatic potential at the site of ion i , $\phi_i = \sum_{j \neq i}^{N_{\text{atm}}} q_j / r_{ij}$, which strongly influences the linear relation that they observe (Fig. 3 in Ref. 76). In order to explore the role of QEq variables on the uncovered correlations, I have converted the published values of the charges, χ_i and the QEq parameters in Ref. 76 for SiO₂ polymorphs into ϕ_i at O and Si sites, then tested the relation between the refractive index and a) ϕ_i at O and Si sites, b) ϕ_i at O sites using the same fixed charge,

¹⁹In QEq, the quantity identified with electronegativity takes on the same value for each atom and the system as a whole.

²⁰They use experimentally measured refractive indexes for the incident light of wavelength 589 nm (yellow light)[76].

averaged over all phases²¹ and c) QEq electronegativity χ_i but evaluated using the same fixed charge for each phase. I found a perfect linear agreement with EN when fixed charges are used and a similar, approximately linear, relationship with $-\phi_i$ at O sites using either variable or fixed charges. The former result indicates that charge transfers actually play no role in the uncovered relation. The latter result implies that they may have uncovered a relation of the refractive index with the in-crystal electrostatic potential at O sites, a result that can be obtained with a fixed-charge ionic model. While the interpretation in their work remains plausible, the uncovered correlation of the QEq EN with the refractive index seems to be largely due to changes in the electrostatic potential. The latter quantity is sensitive to changes in nuclear positions but fairly insensitive to small QEq charge transfers predicted in the systems they considered.

In summary, applications of the QEq model that do not involve evaluation of forces are inconclusive regarding the ability of this model to improve accuracy and transferability in QEq-based IPs, or whether the QEq charge transfers reflect changes in the charge density. Moreover, any uncovered correlations of the QEq variables with trends in physical properties need to be analysed with care since, by construction, one ends up correlating trends in the physical properties with the on-site electrostatic potential. The latter, in turn, tends to vary in value strongly to reflect the changing structure of the molecule or a solid, but to be only weakly affected by the small QEq charge transfers. Therefore, in some instances the same trends between physical properties and the electrostatic potential may be obtained using a fixed-charge model.

Simple force fields with QEq

Starting with the 1994 work on TiO₂ and the α -alumina/aluminium interface by F. Streitz and J. Mintmire[109, 110], QEq became embedded in an IP that enabled calculation of forces and, therefore, the use for molecular dynamics and structural relaxations. However, the most commonly used QEq-type potential is based on the later work on SiO₂ by E. Demiralp *et al.*[80] and on MgO by A. Strachan *et al.*[81]. They used the Slater-type QEq model of Rappe and Goddard[79] in conjunction with a Morse potential (Eqs. 1.29 and 1.6 respectively) and specifically emphasised and promoted the improved accuracy and transferability of this new IP. This IP (MS-Q) is the most commonly used QEq-type potential for ionic solids[80, 81, 84, 111–116] and in this section I discuss

²¹I averaged the charge over the QEq values for the five SiO₂ phases for which the experimental refractive index is compared.

Ref. 80 in some detail to demonstrate that there is, in fact, no evidence indicating that QEq improves accuracy or transferability or that changes in ionic charges reflect changes in the underlying ground state density. I briefly discuss several other, representative, studies to emphasize that the lack of evidence in Ref. 80 is not an exception. In most studies[25, 80, 81, 84, 109–117] there is no evidence presented which would convincingly demonstrate that QEq improves accuracy.

In those studies that do compare the accuracy of the QEq-based and fixed-charge IPs, the evidence suggests no improvement and in some tests, such as those based on reproducing experimentally measured lattice constants, occasionally fair slightly *worse* than fixed-charge IPs. These comparative studies are discussed below.

Finally, B. Thomas *et al.*[24, 26] make two relevant points. Firstly, they suggest that in some systems, changes in the ground state density may correspond to small or even negligible inter-ionic charge transfer, questioning the use of charge-transfer models in such cases. Secondly, they highlight an important challenge associated with using a QEq model to represent electrostatic interactions in an ionic IP due to low effective charges, as already discussed. Both points are elaborated on in the present section and connected to the results of this thesis.

In Ref. 80 MS-Q potential is fit to SiO₂ properties, such as density, cohesive energy and elastic moduli, in α -quartz and stishovite phases based on the reference DFT calculations. A comparison to a fixed-charge IP (MS-Q_o) is not made in general, with the sole exception of an NPT simulation of α -quartz to stishovite phase transition; the two models broadly behave very similarly and MS-Q_o agrees with the experiment slightly better. Despite this not being a comparative study, other published work allows us to make comparisons. One test of the transferability of MS-Q, which the authors put forward, is its ability to reproduce density and the lattice constants reasonably well, in NPT simulations, for several different phases. For some of these phases, namely α -cristobalite, coesite and α -quartz, equivalent calculations had already been carried out[19] using a fixed nominal charge pairwise additive potential of van Beest, Kramer and van Santen (BKS)[118]. I have calculated the root-mean-squared difference of the calculated and experimental values, and on this figure of merit alone, the fixed-charge BKS IP is very similar to MS-Q and fares slightly better. Finally, a laborious in-depth comparative study was published by Daniel Herzbach *et al.*[70] using the MS-Q potential of Ref. 80, the BKS IP and a polarisable TS potential applied to SiO₂. The results decisively showed that the MS-Q IP for SiO₂ does *not* improve on the fixed-charge BKS IP qualitatively or quantitatively.

In another work, released in the same year, MS-Q was applied to MgO. The work on MgO[81] is discussed, and some results are reproduced, in Section 2.2.3 of this thesis. In the context of this section, it suffices to say that, as with the work on SiO₂, the IP is essentially not tested, with the only figure of merit being the ability to fit well a highly-correlated reference data set.

Another series of applications of MS-Q warrants a discussion, because the debate[23–26, 117, 119] that it initiated revealed some unexpected behaviour of the QEq model. This is the work on titanium oxides, originally initiated by V. Swamy *et al.*[23, 112, 119]. V. Swamy *et al.* had parameterised MS-Q to reproduce lattice constants of a diverse set of titanium oxide structures of varying stoichiometry – rutile, anatase, brookite, TiO₂-II, Ti₂O₃, monoclinic forms of Ti₃O₅, and elastic constants of rutile[112]. The training data set was meant to enable an IP to be transferable between a wide range of structures, with an apparent emphasis on reproducing equilibrium lattice constants. In a subsequent comparative study[119], lattice constants and bulk moduli were calculated for a set of TiO₂ polymorphs, indicating no improvement relative to a fixed-charge ionic IPs[120]. Applying MS-Q to rutile TiO₂ (110) and (001) surfaces revealed the model to be inadequate – both MS-Q and fixed-charge IP showed surface structures inconsistent with one another as well as with the DFT calculations and with experiment[23]. What’s more, B. Thomas *et al.*[24, 26] repeated the calculations using the same MS-Q for several TiO₂ polymorphs as well as a wide set of Ti_xO_y structures, and found that if, instead, *charges are set to zero without refitting*, the calculated lattice constants agree with the experiment slightly *better*. Similarly, recalculating the reported equilibrium lattice structures using published MS-Q IPs, with and without the electrostatic terms, they found root-mean-squared difference between calculated and experimental values of less than 2% for SiO₂[84, 121], MgO[81] and VPI-5[111]. This clearly shows that in the above mentioned studies the QEq model has a negligible effect on the calculated properties, let alone on improving transferability. What many published works based on QEq[25, 80, 81, 84, 109–115, 117] share in common is the absence of an adequate comparative study or a detailed analysis that would show whether or not calculated properties are improved by MS-Q and whether the improvement is due to a better description of interatomic forces. The latter can be contrasted with the available work on the polarizable-ion model, where certain properties are clearly shown to arise as a result of an ion’s ability to polarize[7, 60, 70], as discussed in Section 1.3.2.

The work of B. Thomas *et al.* also raises two points worth discussing. Firstly, they suggest that in some bulk insulators changes in the ground state density may correspond

to a very small inter-ionic charge transfer, making QEq and similar models not useful for representing such changes. The results and analysis of Chapter 6 are consistent with this view. Secondly, they highlight that in the studies where the QEq model is used in conjunction with a simple pairwise-additive IP with short-range cohesive terms (e.g. Morse-stretch), the ionic charges tend to take on relatively low values, leading, at times, to a negligible contribution of charge fluctuations to the interatomic forces and many calculated properties. This echoes a view expressed earlier in the work by V. Swamy *et al.*[23] who suggest low average charges as the reason for the inability of the MS-Q IP to adequately represent rutile TiO_2 surfaces. It is worth emphasising that the charges turn out low during fitting in order to compensate for the IP’s functional form if it doesn’t describe bonding well. In other words, setting charge magnitudes to higher values manually *disimproves* the accuracy of the IP, in general. Motivated in part by this latter point, in Chapter 2 we extend our combined QEq PI IP to describe short-range electrostatic interactions more realistically. However, the results and analyses of Chapters 3, 6 and 7 strongly suggest that relatively low charges have little or no effect on the ability of the QEq model to improve accuracy and transferability, at least when it is used in conjunction with a polarisable-ion TS IP. Instead, the analyses of Chapters 3 and 7 suggest the following view: polarisable ionic IPs, such as QEqTS, are approximations based on a certain assumed limit and can adequately describe changes in the ground state density in response to a perturbation, *as long as* those changes adhere to this limit. The two Chapters, respectively, introduce the definition of the appropriate limit and provide an example of two related systems that adhere to this limit to varying degrees.

Nevertheless, the issue of relatively low charges in QEq-based IPs is worth keeping in mind and deserves elaboration. Their findings can be largely interpreted in terms of the concept of screening, introduced in Section 1.3.2, and are relevant also to any IP that treats fixed ionic charge values as fitting parameters. As discussed in Section 1.3.2, when a model of electrostatic interactions includes electronic response explicitly, such as in the inducible-dipole model, it is *as though* no response mechanism is included but instead the charges are scaled down in magnitude, $q_i \rightarrow q_i/\sqrt{\epsilon^{\text{eff}}}$ with $\epsilon^{\text{eff}} > 1$. This tends to be the case on average, especially for interacting ions that are far apart. Conversely, in an IP where ionic charge values are treated as fitting parameters²² and other short-range cohesive energy terms are present, the effective charges q_i^{eff} tend to be relatively low because they represent the value of $q_i^{\text{eff}} = q_i/\sqrt{\epsilon^{\text{eff}}}$, approximately capturing part of the screening implicitly. The results in the present work are consistent with this

²²Or, as in the QEq model, are functions of parameters.

interpretation. Parameterising MS-Q and QEqTS IPs to reference data based on a thermally perturbed defect-free bulk BaTiO₃ in Chapter 6, it is found that ionic charges are higher in magnitude in the latter model, e.g. Ti average charges are 2.05 e and 2.65 e respectively. This is consistent with the view that in the TS and QEqTS IPs some of the screening mechanisms are represented explicitly via the inducible dipole moments, therefore ϵ^{eff} is implicitly lower and the effective ionic charges are higher in magnitude. Furthermore, this interpretation is further supported by the results of Chapter 7, where TS and QEqTS IPs are parameterised to a system with a neutral O or Ti vacancy, which corresponds to a sublattice of vacancies due to the use of periodic boundary conditions. Relative to the parameterisation for the bulk system, average charge values in TS IP decrease slightly but in QEqTS IP they noticeably increase, with Ti average charge equal to 3.0 e . This can be similarly interpreted – in a system with a sublattice of vacancies, the increased QEqTS average charge magnitudes are due to the charge transfer variables representing part of the screening explicitly.

1.5 Combined charge transfer and polarisable ion model

The broad aim of the present work is to contribute towards developing classical IPs that are transferable between the bulk and heterogeneous systems in which atoms experience a range of local chemical environments, able to adequately represent a broad class of materials including metal oxides. Our approach towards this goal currently focuses on developing, gaining a greater understanding of, and testing, a combined charge-transfer polarisable-ion model, and the exact steps taken are now rationalised and presented in some detail.

The combined model is an extension of the polarisable-ion TS model. In Sections 1.3.1 and 1.3.2 it was demonstrated that TS and similar fixed-charge polarisable-ion IPs adequately approximate the electronic response to atomic motion in ionic materials, including numerous bulk metal oxides, leading to an improved accuracy, transferability and a greater insight into the origin of, or trends in, some physical properties. The use of the TS IP, in particular, is further rationalised by the following considerations. Firstly, the TS IP accurately represents dynamical and dielectric properties of many bulk metal oxides. In particular this was demonstrated[9] for the test system of choice in the present work – BaTiO₃. Secondly, the TS IP is implemented to be parameterised via force-matching[122] (FM) and the ability to fit forces is a particularly appropriate measure to use in a comparative study meant to quantify and analyse the roles of different

terms in the functional form of an IP. In a FM method, described in Chapter 5, an IP is parameterised to the underlying potential energy surface by fitting to DFT forces, stress components and energy differences. This approach does not bias the IP to reproduce any set of observables or for the charge-transfer and induced dipole variables to mimic changes in the underlying ground state density. As such, FM has the advantage of allowing to explore the qualities of various forms of an IP. In particular, it is generally implied that polarisable-ion and charge-transfer IPs are more accurate, because the self-consistent variables, such as charges and dipole moments, mimic changes in the ground state density – but this link is something we want to test. Thirdly, P. Tangney and J. Sarsam[19, 27] have implemented a series of efficient linear algebra solvers that are able to directly obtain the self-consistent solution for the induced dipole moments and charge transfer, while conserving the appropriate physical quantities during a simulation, such as the total energy in an NVE ensemble. Finally, the TS IP is defined using a relatively small number of terms and free parameters in its functional form, making it relatively easy to isolate the effect of the QEq model on the calculated properties and interatomic forces in a combined QEqTS IP.

The combined QEqTS IP is an extension of the TS IP to include a charge-transfer model. This is motivated by examples such as that of a neutral Mg vacancy in MgO discussed earlier, which strongly suggest that the ground state density within the bulk and near a defect or interface sometimes cannot be represented by an ionic model that assigns the same fixed charge to a species throughout the system. This IP was initially implemented by J. Sarsam[27] in the form:

$$E^{\text{QEqTS}} = \frac{1}{2} \sum_{i,j \neq i}^{N_{\text{atm}}} E_{ij}^{\text{MS}} + \frac{1}{2} \sum_{i,j \neq i}^{N_{\text{atm}}} E_{ij}^{\text{ES}}(\{q_i, \mathbf{p}_i\}) + \sum_{i=1}^{N_{\text{atm}}} (A_i \Delta q_i + D_i \Delta q_i^2 + \epsilon_i p_i^2) \quad (1.38)$$

$$\begin{aligned} E_{ij}^{\text{ES}}(\{q_i, \mathbf{p}_i\}) = & \quad q_i q_j \left(\frac{1}{r_{ij}} \right) \\ & + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\ & - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} \right) \end{aligned} \quad (1.39)$$

which represents electrostatic interactions partly as that of point-particles, as can be seen from the form of the charge-charge and dipole-dipole coupling terms²³; $\{q_i = q_i^0 + \Delta q_i\}$, $\{q_i^0, A_i, D_i, \epsilon_i\}$ and w_{ij}^{qp} are the fitting parameters, E_{ij}^{MS} is the Morse-stretch pairwise

²³This includes the original QEq point-charge model by W. Mortier *et al.*[34, 45] as a special case but does not contain the popular finite-atom implementation of A. Rappe and W. Goddard[79].

term in Eq. 1.6, $\tilde{I}_0(r_{ij})$ is a short-ranged function as explained in Section 1.3.1 and discussed further in Chapter 2, and $\{\Delta q_i, \mathbf{p}_i\}$ are the self-consistent variables for the charge transfer and the induced dipoles, respectively. However, J. Sarsam’s results of applying the QEqTS IP to heterogeneous MgO systems were broadly inconclusive, without a clear way to rationalise her findings. In her work, the QEqTS IP was parameterised to systems that include charged vacancies and interstitials, V_{Mg}^{2-} , V_{O}^{2+} , I_{Mg}^{2+} and I_{O}^{2-} in Kröger-Vink notation[28], as well as a polar[123] MgO (111) surfaces; the ionic IP was essentially unsuccessful in representing the last system since the average charges were unphysically low, less than $0.6e$ in magnitude. In all cases, the QEqTS IP numerically reduced to the TS IP since the charge fluctuations never exceed $0.005e$ – consequently, there is no improvement in accuracy or transferability²⁴. This negligible charge transfer may seem unphysical, but a comparison to interatomic forces and the underlying ground state density near the defects was not carried out. For example, *ab initio* results[124] for V_{O}^{2+} suggest the largest deviation of the ionic charge from its bulk value to be $\sim 0.05e$ based on the density difference contour plots – this is at variance with the QEqTS value of $0.0006e$ but, at the same time, it is overall quite small, indicating that maybe in this system the interatomic forces are dominated by other forms of electron density response, other than inter-ionic charge transfer. The results of the numerous applications of other QEq-based IPs in the literature, presented in Section 1.4.2, can be broadly described as unfavourable, without an immediately clear way to rationalise them. This, together with J. Sarsam’s findings, prompted us to take several steps in the present work.

Firstly, in Chapter 2, J. Sarsam’s model is extended to represent short-range electrostatic interactions more realistically. We use the following form:

$$\begin{aligned}
E_{ij}^{\text{ES}}(\{q_i, \mathbf{p}_i\}) = & \quad q_i q_j \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) \right) \\
& + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\
& - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{pp}} \tilde{I}_0(r_{ij}) \right) \quad (1.40)
\end{aligned}$$

where w_{ij}^{qq} and w_{ij}^{pp} are the fitting parameters. This is motivated by several considerations. For a finite overlap between ionic charge densities, a point-charge representation is inadequate and may lead to relatively low charges during parameterisation, as explained in Chapter 2. As pointed out by V. Swamy *et al.*[23] and B. Thomas *et al.*[24, 26], charge

²⁴Unlike QEq-based IPs, fixed-charge models cannot transfer to distinct stoichiometry while keeping system’s net charge constant unless charges are rescaled manually. Thus, in principle, QEq-based IPs do introduce a level of transferability by construction.

fluctuations predicted by the QEq model would then have a relatively small effect on interatomic forces. Additionally, an extended QEqTS IP includes the widely used MS-Q model as a special case, which allows us to connect our results with those presented in the literature. In Chapters 6 and 7 the use of the extended model improves accuracy somewhat relative to the original model of J. Sarsam but qualitatively the extended model behaves the same.

As a second step, in Chapter 3, some theoretical work is undertaken to relate the QEqTS IP to density functional theory. This allows us to understand and to rationalise physical quantities that the QEq model functional form and parameters represent and to get a better idea about the domain of applicability of this IP in its present form. In particular, the quadratic form and the parameters of the QEq self-energy expression are suggested to have a limited transferability and, additionally, constraints on the ground state density are pointed out. The theoretical work is motivated by the fact that the form of the self-energy in the QEq model assumes small perturbations to individual ions' charge densities, and small changes in their charges. Therefore, when applied to heterogeneous systems, such as a vacancy or a surface, where changes in the ground state are often dramatic and cannot be considered small, the analytic form of the QEq model's self-energy may be inadequate. This is discussed with more rigor in Chapter 3 and a minimal set of necessary assumptions is suggested that allows one to recover the analytic form of the QEq and similar models.

Finally, motivated by these observations about the form of the self-energy, the QEqTS IP is tested in three qualitatively different regimes of perturbations to the ground state density. These three regimes, to put it simply, correspond to small, moderate and strong perturbations. In Chapter 3 the limit in which the QEqTS approximation can be considered valid (QEqTS-limit) is defined more precisely. In a thermally perturbed defect-free bulk BaTiO₃ (Chapter 6) the changes in the ground state density are “small” and adhere to the QEqTS-limit. For this system, the analysis suggests that the QEqTS analytic form is adequate, in principle, but the changes in the ground state density correspond to very small or negligible inter-ionic charge transfer, making the use of the QEq model not useful. Echoing B. Thomas *et al.*[24, 26], the use of a fixed-charge model is advocated instead. In Chapter 7 a neutral O vacancy in BaTiO₃ results in “moderate” changes in the ground state – there is a high lattice electrostatic potential at O sites and once the neutral O atom is taken out, the density near the vacancy site resembles that in the bulk. In the same chapter, a neutral Ti vacancy in BaTiO₃ is demonstrated to result in dramatic changes in the ground state density, such that this does not adhere well to the

QEqTS-limit. The results and analysis of Chapter 7 are consistent with the hypothesis – the QEqTS IP represents interatomic forces and charge density noticeably better in a system where the charge density corresponds to the QEqTS-limit more closely, the system with an O vacancy in this case. Importantly, this comparative study allows us to identify a system, that of a neutral O vacancy, for which the QEqTS IP is markedly more accurate than the benchmark fixed-charge polarisable-ion TS IP. This suggests that there is a class of systems of “moderate” density perturbations, where the analytic form of the QEqTS IP is both adequate and useful, enabling the desired transferability between the bulk and the heterogeneous atomic environment.

The decision to focus on a single material allows us to keep the study computationally tractable. Firstly, the undertaken comparative study requires parameterisation of many distinct IPs. Secondly, relating the ground state density to quantities defined in a classical IP, such as electrostatic potential, ionic charge and induced dipoles, requires non-trivial and computationally demanding post-processing of the *ab initio* reference data.

Choosing to focus on BaTiO₃ is motivated by two considerations. Firstly, a good TS IP had been previously developed and tested[9] for bulk BaTiO₃. Secondly, in a thermally-perturbed bulk phase, its ground state charge density is expected to undergo non-trivial changes that may be representable by inter-ionic charge transfer. This latter point is motivated by the anomalously-large Ti and highly-anisotropic O Born Effective charges[125] (BEC) in this material[126, 127], and can be understood as follows. In an extended system, assuming periodic boundary conditions, the BEC is a measure of the change of polarisation in response to displacing a sublattice of atoms, one atom per primitive unit cell[127]. The change in polarisation, in turn, indicates the change in the centre-of-charge within the unit cell[128]. A rigid ion model corresponds to an isotropic BEC tensor with nominal ionic charge values. Large BEC charges in excess of the nominal values, as found in BaTiO₃, indicate that there is a significant contribution to the shift in the centre-of-charge due to the redistribution of the electron density that accompanies the nuclear motion. Both the charge-transfer and the polarisable-ion models can, in principle, describe electronic contributions to the change in the centre-of-charge. In Chapter 6 the changes in the centre-of-charge of the ground state electron density are quantified and shown to agree very well with an equivalent quantity calculated using the QEqTS or TS IP. However, charge transfer variables are shown to have a negligible contribution.

Finally, in Chapter 8 the lattice constants, elastic constants and phonon spectra

are calculated with every QEqTS IP that is considered in this thesis. The calculated properties are in good agreement with the reference *ab initio* values, lending support to what is otherwise implicitly assumed: all the tested IPs are good approximations of the bonding in BaTiO₃, at least with respect to some of its mechanical and dynamical properties.

Chapter 2

Coulomb interactions of overlapping ions

A major contribution to the energy and forces in ionic IPs comes from the inter-ionic Coulomb interactions, as discussed in Chapter 1. The form of the electrostatic interaction energy used in the combined QEqTS IP was introduced in Section 1.5 in the form:

$$E^{\text{ES}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} E_{ij}^{\text{ES}} \quad (2.1)$$

$$\begin{aligned} E_{ij}^{\text{ES}} = & \quad q_i q_j \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) \right) \\ & + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\ & - \quad p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{pp}} \tilde{I}_0(r_{ij}) \right) \end{aligned} \quad (2.2)$$

where the Ewald summation is implied. In the present chapter, this analytic form is rationalised and discussed in greater detail. The terms proportional to w_{ij}^{qq} and w_{ij}^{pp} constitute novel features of the model, incorporated during the course of the present research. The new extended QEqTS IP offers two advantages. Firstly, as argued in Section 2.2, the electrostatic interactions are now represented more realistically. This leads to small improvements in accuracy. Secondly, for a suitable choice of the parameters w_{ij}^{qq} , w_{ij}^{qp} , w_{ij}^{pp} and the function $\tilde{I}_0(r_{ij})$, the new extended model contains both the TS and the widely used MS-Q IPs as special cases; the latter was not previously included. Thus, the use of the new extended model allows us to connect our findings to those published in the literature.

This chapter is organised as follows. In Section 2.1 we introduce an approximation based on the multipole expansion, which is suitable for describing interactions of

well-separated non-overlapping ions. Multipole expansion corresponds to the above expression with w_{ij}^{qq} , w_{ij}^{qp} and w_{ij}^{pp} parameters set to zero. In Section 2.2.1, the electrostatic interaction energy of overlapping nearest neighbour ions is presented using the distributed-charge model, leading to the general expression 2.1. In this model an ion is represented by several spherically symmetric distributions, each centered close to the ionic nucleus. Two variants of the distributed-charge model are then presented. The original work in Section 2.2.2 demonstrates that the form of the short-range dipole correction introduced by M. Wilson and P. Madden, discussed in Section 1.3.1, is recovered as a special case in the distributed-charge model. This is the first variant. Secondly, in Section 2.2.3 another analytic form of $\tilde{I}_0(r_{ij})$ is introduced, which allows us to contain MS-Q IP as a special case of the QEqTS IP. In Section 2.2.3 a selection of published results[81] of applying MS-Q to MgO are reproduced, confirming the new terms in the QEqTS IP have been implemented correctly. Finally, in Section 2.2.4 numerical results show that the short-range corrections are not sensitive to the exact analytic form of the function $\tilde{I}_0(r_{ij})$. In other words, the two distinct analytic forms of the short-range corrections are numerically equivalent. Given this equivalence, in Section 2.2.4 we recommend the use of an analytic form of the short-range correction that is associated with a lower computational cost when implemented in a computer program.

2.1 An asymptotic limit and the multipole expansion

Consider the Coulomb interaction between two charge densities¹ $\rho_i(\mathbf{r})$ and $\rho_j(\mathbf{r})$ localised at sites $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively.

$$E_{ij}^{\text{ES}} = \int \int \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.3)$$

$$= \int \int \rho_i(\mathbf{r}_i + \Delta\mathbf{r}) \rho_j(\mathbf{r}_j + \Delta\mathbf{r}') \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + \Delta\mathbf{r} - \Delta\mathbf{r}'|} d\Delta\mathbf{r} d\Delta\mathbf{r}' \quad (2.4)$$

where the second line is obtained by a change of variables $\mathbf{r} \rightarrow \mathbf{r}_i + \Delta\mathbf{r}$ and $\mathbf{r}' \rightarrow \mathbf{r}_j + \Delta\mathbf{r}'$; $\Delta\mathbf{r}$ and $\Delta\mathbf{r}'$ are the integration dummy variables. Assuming $|\Delta\mathbf{r} - \Delta\mathbf{r}'| \ll |\mathbf{r}_i - \mathbf{r}_j|$ in the domain of integration where the numerator is non-vanishing, a multipole expansion of the integral can be obtained by carrying out a Taylor expansion of the factor appearing

¹Charge value is contained in the definition of charge densities. For example, if ρ_i represents an anion then it integrates to a negative number.

in the integrand.

$$f(\Delta\mathbf{r}, \Delta\mathbf{r}') \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + \Delta\mathbf{r} - \Delta\mathbf{r}'|} \quad (2.5)$$

$$\begin{aligned} f(\Delta\mathbf{r}, \Delta\mathbf{r}') &= \frac{1}{r_{ij}} + (\Delta r^\alpha - \Delta r'^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} - \Delta r^\alpha \Delta r'^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \frac{1}{r_{ij}} \\ &+ \left[\frac{1}{2} \Delta r^\alpha \Delta r^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \frac{1}{r_{ij}} + \frac{1}{2} \Delta r'^\alpha \Delta r'^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \frac{1}{r_{ij}} \right] + \mathcal{O}\left(\frac{1}{r_{ij}^4}\right) \end{aligned} \quad (2.6)$$

where α and β stand for the cartesian coordinates and the summation over these indices is implied. Substituting the Taylor expansion of $f(\Delta\mathbf{r}, \Delta\mathbf{r}')$ into the integrand for the Coulomb interaction results in a multipole expansion.

The terms in the square brackets lead to monopole-quadrupole coupling once the Coulomb interaction integral is evaluated – we shall omit these terms since we wish to retain only ionic charges and dipole moments in the final IP. Thus, omitting the terms in the square brackets and higher order terms, an approximate expression for the Coulomb interaction is obtained.

$$q_s \equiv \int \rho_s(\mathbf{r}_s + \Delta\mathbf{r}) d\Delta\mathbf{r} \quad (2.7)$$

$$\mathbf{p}_s \equiv \int \Delta\mathbf{r} \rho_s(\mathbf{r}_s + \Delta\mathbf{r}) d\Delta\mathbf{r} \quad (2.8)$$

$$E_{ij}^{\text{ES}} \approx \frac{q_i q_j}{r_{ij}} + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \frac{1}{r_{ij}} \quad (2.9)$$

where $s \in \{i, j\}$.

If we assume that the ground state density for a system of interest adheres to an ionic limit $\rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{atm}}} \rho_i(\mathbf{r})$ and that $|\Delta\mathbf{r} - \Delta\mathbf{r}'| \ll |\mathbf{r}_i - \mathbf{r}_j|$ integration condition is satisfied for all pairs of ions, the total Coulomb interaction energy, E^{ES} can be written as:

$$\begin{aligned} E^{\text{ES}} &\approx \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i \underbrace{\sum_{j \neq i}^{N_{\text{atm}}} \left[\frac{q_j}{r_{ij}} - p_j^\alpha \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} \right]}_{\equiv \phi_i} - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} p_i^\alpha \underbrace{\sum_{j \neq i}^{N_{\text{atm}}} \left[-q_j \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} + p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \frac{1}{r_{ij}} \right]}_{\equiv E_i^\alpha} \\ & \quad (2.10) \end{aligned}$$

$$= \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i \phi_i - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \mathbf{p}_i \cdot \mathbf{E}_i \quad (2.11)$$

where the use of periodic boundary conditions and an Ewald summation is implied; the implicitly defined ϕ_i and $\mathbf{E}_i$ represent the electrostatic potential and electric field, respectively, at the site of ion i due to all the other ions in the system. The sizes of the charge distributions do not enter the final expression in the multipole expansion,

representing interactions as that of point particles. The expressions for ϕ_i and $\mathbf{E}_i$ constitute an asymptotic limit in a sense that the inter-ionic separation to ionic size ratio is assumed to approach infinity.

2.2 Short-range corrections to the asymptotic limit

The asymptotic expression for the electrostatic interaction energy, E^{ES} , becomes invalid for the overlapping ions since $|\Delta\mathbf{r} - \Delta\mathbf{r}'|$ in the integrand 2.4 can no longer be assumed to be less than the inter-ionic separation. This requires modifying the analytic form of the expression E^{ES} for ion pairs that are close relative to their sizes.

For some simple forms of densities $\rho_i(\mathbf{r})$ and $\rho_j(\mathbf{r})$, such as a spherically symmetric Gaussian or a Slater-type orbital, the Coulomb interaction in Eq. 2.4 can be evaluated analytically. These analytic terms reduce to the $1/r_{ij}$ coupling as r_{ij} increases, and so connect to the first term in the multipole expression. More generally, in the absence of the spherical symmetry, obtaining an analytic correction to charge-dipole, dipole-dipole and higher order multipole moment couplings requires making some further assumptions about the densities $\rho_i(\mathbf{r})$ and $\rho_j(\mathbf{r})$. In the present work we follow a common approach, introduced by B. Thole[55], based on the distributed charge model of an ion. In this model an ion is viewed as a set of several superimposed spherically symmetric distributions centered close to the nucleus. The main motivation to use this model is, in B. Thole's own words, *"to retain the interpretation of $t_{ij}^{\alpha\beta}$ [dipole-dipole coupling tensor] as the dipole-dipole interaction where a dipole is thought to be built up from two infinitesimally shifted monopoles, which in our case won't be point charges."*; an equivalent statement applies to the charge-dipole coupling. B. Thole suggested that this physical picture is equivalent to the following relations between the charge-charge, charge-dipole and dipole-dipole² coupling tensors:

$$t_{ij} = I_0(r_{ij}) \quad (2.12)$$

$$t_{ij}^\alpha = \frac{\partial}{\partial r_{ij}^\alpha} I_0(r_{ij}) \quad (2.13)$$

$$t_{ij}^{\alpha\beta} = \frac{\partial}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} I_0(r_{ij}) \quad (2.14)$$

$$E_{ij}^{\text{ES}} = q_i q_j t_{ij} + (p_i^\alpha q_j - q_i p_j^\alpha) t_{ij}^\alpha - p_i^\alpha p_j^\beta t_{ij}^{\alpha\beta} \quad (2.15)$$

where $I_0(r_{ij})$ represents the Coulomb interaction of two spherically symmetric finite charge distributions, with a limiting behaviour $I_0(r_{ij}) \rightarrow \text{const.}$ as $r_{ij} \rightarrow 0$ and $I_0(r_{ij}) \rightarrow$

²This series of relation can be trivially extended to coupling tensors for higher order multipole moments.

$1/r_{ij}$ for r_{ij} sufficiently large. For convenience, we shall later use a short-range correction $\tilde{I}_0(r_{ij})$, implicitly defined as $I_0(r_{ij}) \equiv 1/r_{ij} - \tilde{I}_0(r_{ij})$.

Section 2.2.1 presents an overview of Thole’s distributed-charge model. In this model the problem of evaluating Coulomb interaction of two ions maps to a problem of two interacting spherically symmetric distributions. The latter problem can be solved analytically for certain choices of the spherical densities. In Section 2.2.2 we show that for suitably chosen spherical densities, one recovers an analytic form of the short-range dipole correction introduced by M. Wilson and P. Madden [17] and used in the TS and QEqTS IPs. In Section 2.2.3 we introduce another analytic form of $I_0(r_{ij})$, such that the charge-charge, charge-dipole and dipole-dipole coupling tensors are based on the interaction of Slater-type ions. This extends the QEqTS IP to include MS-Q IP as a special case. In Section 2.2.3 we verify that the new features of the QEqTS IPs have been implemented correctly in our in-house computer code by applying MS-Q IP to reproduce a set of results from a previous publication. Finally, in Section 2.2.4 we argue that the short-range Coulomb interactions are not sensitive to the exact choice of the spherical density used in Thole’s model, as long as physically meaningful range of parameters and interionic distances are considered.

2.2.1 Thole’s distributed charge model of an ion

As we have seen in Section 2.1, carrying out a multipole expansion necessitates introducing fairly restrictive assumptions on the size of the ionic densities relative to the inter-ionic separation, r_{ij} . In contrast, the distributed-charge model allows one to evaluate the Coulomb interaction of two ions without the need to introduce the restrictive assumptions of the multipole expansion. The analytic results based on Thole’s distributed-charge model are provided in detail in Appendix 10.1.1 and here the main aspects of this approach are summarised instead.

Each ionic charge distribution, ρ_i , is assumed to consist of several spherically symmetric normalised distributions g_i (monopoles), each centered close to the nucleus. For example, $\rho_i(\mathbf{r}) = \rho_{1,i}(\mathbf{r}) + \rho_{2,i}(\mathbf{r}) = q_{1,i}g_i(\mathbf{r} - \mathbf{r}_{i,1}) + q_{2,i}g_i(\mathbf{r} - \mathbf{r}_{i,2})$, where $\mathbf{r}_{i,1}$ and $\mathbf{r}_{i,2}$ are the positions of the monopoles and $q_{1,i}$ and $q_{2,i}$ are the respective charges such that they add up to the total ionic charge $q_{1,i} + q_{2,i} = \int \rho_i(\mathbf{r})d\mathbf{r}$. Only two monopoles per ion are considered in the present discussion since this is sufficient to describe ions’ dipole moments, although this approach can be generalised to include multipole moments of an arbitrarily high order.

In order to shed some light on the approximations involved in obtaining the short-

range Coulomb interaction expressions, a concrete set of calculation steps are introduced and summarised³. The two monopoles associated with the same ion are displaced by an infinitesimal distance $\pm\Delta x/2$ from the nucleus along a predefined displacement unit vector; the coordinates of the centers of the monopoles are:

$$\rho_{1,i} \quad \text{at} \quad \mathbf{r}_i - \frac{\Delta x}{2} \underbrace{[\cos \phi_i \sin \theta_i, \sin \phi_i \sin \theta_i, \cos \theta_i]}_{\boldsymbol{\vartheta}_i} \quad (2.16)$$

$$\rho_{2,i} \quad \text{at} \quad \mathbf{r}_i + \frac{\Delta x}{2} \boldsymbol{\vartheta}_i \quad (2.17)$$

where $\mathbf{r}_i$ and $\boldsymbol{\vartheta}_i$ are the position of the ion i and the unit displacement vector specifying the direction of its dipole moment. The Coulomb interaction energy of the two ions with nuclei at positions $\mathbf{r}_i$ and $\mathbf{r}_j$ and distributed charges defined by $\pm\Delta x\boldsymbol{\vartheta}_i/2$ and $\pm\Delta x\boldsymbol{\vartheta}_j/2$, respectively, can be viewed as a function of these variables.

$$E_{ij}^{\text{ES}} \equiv \int \int \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.18)$$

$$\begin{aligned} &= \int \int \frac{\rho_{1,i}(\mathbf{r}_i - \Delta x\boldsymbol{\vartheta}_i/2 + \tilde{\mathbf{r}}) \rho_{1,j}(\mathbf{r}_j - \Delta x\boldsymbol{\vartheta}_j/2 + \tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} - \Delta x(\boldsymbol{\vartheta}_i - \boldsymbol{\vartheta}_j)/2 + \Delta\tilde{\mathbf{r}}|} d\tilde{\mathbf{r}} d\tilde{\mathbf{r}}' \\ &+ \int \int \frac{\rho_{1,i}(\mathbf{r}_i - \Delta x\boldsymbol{\vartheta}_i/2 + \tilde{\mathbf{r}}) \rho_{2,j}(\mathbf{r}_j + \Delta x\boldsymbol{\vartheta}_j/2 + \tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} - \Delta x(\boldsymbol{\vartheta}_i + \boldsymbol{\vartheta}_j)/2 + \Delta\tilde{\mathbf{r}}|} d\tilde{\mathbf{r}} d\tilde{\mathbf{r}}' \\ &+ \int \int \frac{\rho_{2,i}(\mathbf{r}_i + \Delta x\boldsymbol{\vartheta}_i/2 + \tilde{\mathbf{r}}) \rho_{1,j}(\mathbf{r}_j - \Delta x\boldsymbol{\vartheta}_j/2 + \tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} + \Delta x(\boldsymbol{\vartheta}_i + \boldsymbol{\vartheta}_j)/2 + \Delta\tilde{\mathbf{r}}|} d\tilde{\mathbf{r}} d\tilde{\mathbf{r}}' \\ &+ \int \int \frac{\rho_{2,i}(\mathbf{r}_i + \Delta x\boldsymbol{\vartheta}_i/2 + \tilde{\mathbf{r}}) \rho_{2,j}(\mathbf{r}_j + \Delta x\boldsymbol{\vartheta}_j/2 + \tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} + \Delta x(\boldsymbol{\vartheta}_i - \boldsymbol{\vartheta}_j)/2 + \Delta\tilde{\mathbf{r}}|} d\tilde{\mathbf{r}} d\tilde{\mathbf{r}}' \end{aligned} \quad (2.19)$$

$$E_{ij}^{\text{ES}} = E_{ij}^{\text{ES}}(\mathbf{r}_{ij}, \Delta x, \boldsymbol{\vartheta}_i, \boldsymbol{\vartheta}_j) \quad (2.20)$$

where changes of integration variables of the type $\mathbf{r} \rightarrow \mathbf{r}_i - \Delta x\boldsymbol{\vartheta}_i/2 + \tilde{\mathbf{r}}$ were introduced; $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\Delta\tilde{\mathbf{r}} = \tilde{\mathbf{r}} - \tilde{\mathbf{r}}'$. This model allows us to do a Taylor expansion of $E_{ij}^{\text{ES}}(\mathbf{r}_{ij}, \Delta x, \boldsymbol{\vartheta}_i, \boldsymbol{\vartheta}_j)$ in Δx about $\Delta x = 0$ – an approximation contingent only on the condition $\Delta x \ll |\mathbf{r}_{ij}|$, which is satisfied even for two overlapping ions. In contrast to the multipole expansion, we are not approximating the integrand, but the integral itself, for which an assumed analytic solution is generally available.

$$I_0(r_{ij}) = \int \int \frac{g_i(\tilde{\mathbf{r}}) g_j(\tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} + \tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|} d^3\tilde{r} d^3\tilde{r}' \quad (2.21)$$

$$\begin{aligned} \mathbf{p}_i &\equiv \int \rho_i(\mathbf{r})(\mathbf{r} - \mathbf{r}_i) d\mathbf{r} \\ &= \left(q_{1,i} \frac{-\Delta x}{2} + q_{2,i} \frac{\Delta x}{2} \right) \boldsymbol{\vartheta}_i \end{aligned} \quad (2.22)$$

$$E_{ij}^{\text{ES}}(r_{ij}; \Delta x, \boldsymbol{\vartheta}_i, \boldsymbol{\vartheta}_j) = q_i q_j I_0(r_{ij}) + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} I_0(r_{ij}) - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} I_0(r_{ij}) + \dots \quad (2.23)$$

³The calculation steps are not unique, but alternative approaches don't change the main arguments.

For a suitable choice of g_i and g_j , the integral $I_0(r_{ij})$ and its derivatives can be solved for analytically. Note that the two ions can be described by different spherically symmetric functions g_i and g_j . For example, one may choose to represent cation's distributed charges in terms of the Dirac delta function and anions' monopoles in terms of Slater-type orbitals. We shall argue in Section 2.2.4 that Coulomb interactions in the above model are not sensitive to the choice of the spherically symmetric functions $\{g_i\}$.

Finally, we define the short-range correction function as $\tilde{I}_0 \equiv 1/r_{ij} - I_0(r_{ij})$ and introduce extra free fitting parameters w_{ij}^{qq} , w_{ij}^{qp} and w_{ij}^{pp} as follows:

$$\begin{aligned}
E_{ij}^{\text{ES}} = & q_i q_j \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) \right) \\
& + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\
& - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{pp}} \tilde{I}_0(r_{ij}) \right)
\end{aligned} \tag{2.24}$$

Setting $w_{ij}^{\text{qq}} = w_{ij}^{\text{qp}} = w_{ij}^{\text{pp}} = 1$ recovers the original result of Thole's model described above. While the distributed-charge model is internally consistent, when it is used in conjunction with a polarisable IP it implicitly represents additional physical effects that were not considered in the above derivation. Therefore, in the next section we argue that in an ionic polarisable IP w_{ij}^{qq} , w_{ij}^{qp} and w_{ij}^{pp} should be treated as fitting parameters.

2.2.2 Special case: Tang-Toennies damping function

Thole's distributed-charge model simply accounts for the fact that the Coulomb interaction strength of two overlapping finite charge densities is damped relative to an equivalent system of point particles. However, when the E_{ij}^{ES} terms, derived in Section 2.2.1, are used in conjunction with a polarisable-ion IP, its analytic form and parameters represent multiple additional effects that were not considered in Thole's model in Section 2.2.1. For example, the Morse-stretch term also represents some of the overlap effects, hence there is an element of double-counting. Also, in the QEqTS and TS IPs, quadrupole and higher order moments are not part of the model; thus, the charge- and dipole-dependent terms are expected to take on parameter values that allow one partly to compensate for the missing interactions. Finally, in the context of polarisable-ion IPs applied to a condensed matter, it is particularly important to note that the polarisability itself is best thought of as a function of ionic positions. Numerous computational experiments, such as those where a single anion is placed within a lattice of point charges representing the effect of an ionic crystal, demonstrate that the ion's polarisability is best thought

of as environment-dependent[56, 129–133]. For an anion, the nearest neighbour overlap and the confining potential due to the crystal lattice can be thought of as having the effect of compressing the ion. In turn, this affects the polarisability of the ion, in a loose analogy to a conducting sphere, for which the polarisability can be shown to be proportional to its volume[132]. At the same time, in TS, QEqTS IPs and in most common implementations of PI IPs polarisability is represented simply as a constant.

Thus, due to the effects that are not considered in Thole’s model, it is appropriate to treat w_{ij}^{qq} , w_{ij}^{qp} and w_{ij}^{pp} as fitting parameters, allowing them to take on values other than 1. The focus of the present section is to relate the short-range correction, introduced by M. Wilson, P. Madden *et al.*[17, 134, 135] to capture the effect of nearest-neighbour overlap on the induced dipole moments, to the empirical term $w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij})$ in Thole’s model. As discussed in Section 1.3.1, this short-range correction is contained in the TS and QEqTS IPs. This relation is provided at the end of this section and, to the best of our knowledge, constitutes an original result.

The short-range correction has the following effect on the solution for the induced dipoles:

$$f^{\text{TT}}(r_{ij}) \equiv w_{ij}^{\text{qp}} e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \quad (2.25)$$

$$\mathbf{p}_i \rightarrow \mathbf{p}_i - \alpha_i \sum_{j \neq i}^{\text{n.n.}(i)} f^{\text{TT}}(r_{ij}) \frac{q_j \mathbf{r}_{ij}}{r_{ij}^3} \quad (2.26)$$

where the value $\tilde{n} + 1 = 4$ is typically chosen, $\{w_{ij}^{\text{qp}}, \tilde{\zeta}_{ij}\}$ are fitting parameters, defined for each pair of atomic species, and α_i stands for the (constant) isotropic polarisability of the ion. The original choice of the function $f^{\text{TT}}(r_{ij})$ is somewhat *ad hoc* – it is normally referred to as the Tang-Toennies damping function, because it was originally introduced by K. Tang and J. Toennies, who used it to represent dispersion coefficients in an empirical van der Waals energy expression[136]. We now show how this short-range correction emerges from Thole’s distributed-charge model if w_{ij}^{qp} is treated as a fitting parameter.

Let us assume, for the purpose of the present argument, that $w_{ij}^{\text{qq}} = w_{ij}^{\text{pp}} = 0$ but $w_{ij}^{\text{qp}} \neq 0$ in general – in this way, setting $w_{ij}^{\text{qp}} = 0$ the interaction E_{ij}^{ES} reduces to the multipole expansion of Section 2.1⁴ and $w_{ij}^{\text{qp}} \neq 0$ means that we are treating it as a fitting parameter to capture the overlap effects. These parameter values correspond to WM-based IPs⁵, TS IPs and J. Sarsam’s implementation of the QEqTS IP. The

⁴And setting $w_{ij}^{\text{qq}} = w_{ij}^{\text{qp}} = w_{ij}^{\text{pp}} = 1$ corresponds to Thole’s model of Section 2.2.1.

⁵WM-based IPs that exclude quadrupole and higher order multipole moments.

electrostatic interaction energy for a system of ions can be written in a way that isolates the short-range effects on the ionic polarisability and the long-range field due to the lattice:

$$E^{\text{ES}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} E_{ij}^{\text{ES}} \quad (2.27)$$

$$= \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i (\phi_i^{\infty} + \phi_i^{\text{SR}}) - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \mathbf{p}_i \cdot (\mathbf{E}_i^{\infty} + \mathbf{E}_i^{\text{SR}}) \quad (2.28)$$

where

$$E_{ij}^{\text{ES}} = q_i q_j \frac{1}{r_{ij}} + (p_i^{\alpha} q_j - q_i p_j^{\alpha}) \frac{\partial}{\partial r_{ij}^{\alpha}} \frac{1}{r_{ij}} - p_i^{\alpha} p_j^{\beta} \frac{\partial^2}{\partial r_{ij}^{\alpha} \partial r_{ij}^{\beta}} \frac{1}{r_{ij}} \\ - w_{ij}^{\text{qp}} (p_i^{\alpha} q_j - q_i p_j^{\alpha}) \frac{\partial}{\partial r_{ij}^{\alpha}} \tilde{I}_0(r_{ij}) \quad (2.29)$$

$$\phi_i^{\infty} \equiv \sum_{j \neq i}^{\infty} \left[q_j \frac{1}{r_{ij}} - p_j^{\alpha} \frac{\partial}{\partial r_{ij}^{\alpha}} \frac{1}{r_{ij}} \right] \quad (2.30)$$

$$\phi_i^{\text{SR}} \equiv -w_{ij}^{\text{qp}} \sum_{j \neq i}^{\text{n.n.}(i)} -p_j^{\alpha} \frac{\partial}{\partial r_{ij}^{\alpha}} \tilde{I}_0(r_{ij}) \quad (2.31)$$

$$\mathbf{E}_i^{\infty} \equiv \sum_{j \neq i}^{\infty} \left[-q_j \frac{\partial}{\partial r_{ij}^{\alpha}} \frac{1}{r_{ij}} + p_j^{\beta} \frac{\partial^2}{\partial r_{ij}^{\alpha} \partial r_{ij}^{\beta}} \frac{1}{r_{ij}} \right] \quad (2.32)$$

$$\mathbf{E}_i^{\text{SR}} \equiv -w_{ij}^{\text{qp}} \sum_{j \neq i}^{\text{n.n.}(i)} -q_j \frac{\partial}{\partial r_{ij}^{\alpha}} \tilde{I}_0(r_{ij}) \quad (2.33)$$

Here a summation over repeated cartesian coordinates $\{\alpha, \beta\}$ is implied, $\sum_{j \neq i}^{\infty}$ emphasizes the use of the Ewald summation technique and the fact that the potential ϕ_i^{∞} and the electric field $\mathbf{E}_i^{\infty}$ are due to the lattice made up of infinitely many ions⁶, while $\text{n.n.}(i)$ stands for a finite number of nearest and possibly next nearest neighbours of ion i ; $\tilde{I}_0(r_{ij})$ is short-ranged and vanishes quickly with the distance r_{ij} . In a polarisable ionic model, there is an induction energy associated with the energy cost to induce a dipole moment. A common approach, followed in the TS and QEqTS IPs of the present work as well as WM-based PI IPs discussed in Section 1.3.1, is to represent this induction energy with a term quadratic in p_i and a constant prefactor. As we shall see shortly, this is equivalent to assuming a constant isotropic ionic polarisability. In a fixed-charge PI IP

⁶To be more precise, $\mathbf{E}_i^{\infty}$ is the field due to a macroscopic crystal with the tin foil boundary conditions.

the electrostatic energy and the self-consistency equations have the following form:

$$E^{\text{ES}} = \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i (\phi_i^{\infty} + \phi_i^{\text{SR}}) - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \mathbf{p}_i \cdot (\mathbf{E}_i^{\infty} + \mathbf{E}_i^{\text{SR}}) + \sum_{i=1}^{N_{\text{atm}}} \epsilon_i p_i^2 \quad (2.34)$$

$$\frac{\partial E^{\text{ES}}}{\partial p_i^{\alpha}} \equiv 0 \quad \forall p_i^{\alpha} \quad (2.35)$$

$\Rightarrow$

$$\mathbf{p}_i = \frac{1}{2\epsilon_i} \mathbf{E}_i^{\infty} + \frac{1}{2\epsilon_i} \mathbf{E}_i^{\text{SR}} \quad (2.36)$$

$$= \frac{1}{2\epsilon_i} \mathbf{E}_i^{\infty} + \frac{1}{2\epsilon_i} \sum_{j \neq i}^{\text{n.n.}(i)} q_j w_{ij}^{\text{qp}} \frac{\partial}{\partial r_{ij}^{\alpha}} \tilde{I}_0(r_{ij}) \quad (2.37)$$

where the constant $1/2\epsilon_i$ is identified with the ionic polarisability, α_i in equation 2.26. If the IP additionally includes the QEq model, the analytic expression for the induced dipoles is not modified and the solution is affected only numerically⁷. Note, we can equally redefine ϕ_i^{∞} and $\mathbf{E}_i^{\infty}$ by setting $w_{ij}^{\text{qq}} = w_{ij}^{\text{pp}} = 1$ and treating $w_{ij}^{\text{qp}} \neq 1$ as a fitting parameter, without affecting the overall argument – this simply includes *some* of the overlap effects explicitly based on Thole’s model.

The relation between the short-range dipole correction used in TS and WM-based IPs and Thole’s distributed-charge model is the following:

$$f^{\text{TT}}(r_{ij}) \frac{r_{ij}^{\alpha}}{r_{ij}^3} = -w_{ij}^{\text{qp}} \frac{\partial}{\partial r_{ij}^{\alpha}} \tilde{I}_0(\mathbf{r}_{ij}) \quad (2.38)$$

where

$$\tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r}) \equiv \frac{\tilde{\zeta}_{ij}^{\tilde{n}+2}}{4\pi [(\tilde{n}+1)!]} \tilde{r}_1^{\tilde{n}-1} e^{-\tilde{\zeta}_{ij} \tilde{r}_1} \quad (2.39)$$

$$g_i(\mathbf{r}) = \delta(\mathbf{r}) \quad (2.40)$$

$$g_j(\mathbf{r}) = \tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r}) \quad (2.41)$$

$$I_0(\mathbf{r}_{ij}) = \int \frac{g_i(\mathbf{r} - \mathbf{r}_i) g_j(\mathbf{r}' - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.42)$$

Here $\tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r})$ is the Slater-type charge density⁸. An analogous result for $\partial \tilde{I}_0 / \partial r_{ij}^{\alpha}$ has been previously obtained by R. Birge *et al.* as an intermediate step in evaluating a dipole-dipole damping function based on Thole’s distributed-charge model[137]; this and related analytic results can be found in Appendix 10.1.2. Here $I_0(\mathbf{r}_{ij})$ is defined pairwise while $g_i(\mathbf{r})$ and $g_j(\mathbf{r})$ remain implicit and do not actually represent any one ion. Taking BaTiO₃ as an example, one could assume that in the O-Ti interaction the

⁷The equilibrium values of dipoles and QEq charge transfers must be consistent with one another.

⁸For any odd integer $\tilde{n} \geq 1$ one can define an equivalent Slater-type orbital $\chi_{n, \zeta}$ by setting $n = (\tilde{n} + 1)/2$ and $\zeta = \tilde{\zeta}_{ij}/2$ leading to $\tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r}) = |\chi_{n, \zeta}(\mathbf{r})|^2$. The short-range function $I_0(r_{ij})$ is not sensitive to the exact value of n , as demonstrated in Section 2.2.4.

term $I_0(\mathbf{r}_{ij})$ corresponds to the Slater-type and point-like representations of the O and Ti ions, respectively; for O-Ba pair this would imply that Ba is treated as point-like, but then for the Ba-Ti interaction this leads to a contradiction. It may seem more satisfactory to define $I_0(\mathbf{r}_{ij})$ in terms of a pair of Slater-type densities instead, which is defined in terms of the ionic parameters and not pairwise. This is done in Section 2.2.3, however, the analytic expression turns out to be vastly more complicated and requires additional use of random-access-memory when evaluated using a computer algorithm during a molecular dynamics simulation. In Section 2.2.4 we argue that 2.42 is the preferred way to represent short-range overlap effects on the electrostatic interactions.

In the present work, the QEqTS and TS IPs were extended to include w_{ij}^{qq} and w_{ij}^{pp} terms in the expression 2.24 for E_{ij}^{ES} , treating them as parameters. $I_0(\mathbf{r}_{ij})$ was implemented based on $g_i(\mathbf{r}) = \delta(\mathbf{r})$, $g_j(\mathbf{r}) = \tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r})$ which reproduces Tang-Toennies type short-range function as well as based on two Slater-type atoms, described in Section 2.2.3. The latter extension reproduces MS-Q IP as a special case.

2.2.3 Special case: Slater-type ions

In the present section we evaluate Coulomb interaction integral $I_0(r_{ij})$ in equation 2.21 using Slater-type orbitals to represent ions, as in the work by A. Rappe and W. Goddard[79] that led to the widely used MS-Q IP, discussed in Section 1.4.1. In particular, this enables us to reproduce published results obtained using MS-Q IP and so place our findings based on the QEqTS IP into a wider context.

The integral $I_0(r_{ij})$ in terms of normalised Slater-type orbitals has the following form:

$$\chi_{n,i}(\tilde{\mathbf{r}}) \equiv \sqrt{\frac{(2\zeta_i)^{2n+1}}{4\pi(2n)!}} |\tilde{\mathbf{r}} - \mathbf{r}_i|^{n-1} e^{-\zeta_i |\tilde{\mathbf{r}} - \mathbf{r}_i|} \quad (2.43)$$

$$I_0(r_{ij}) = \int \int \frac{\chi_{n,i}^2(\tilde{\mathbf{r}}) \chi_{m,j}^2(\tilde{\mathbf{r}}')}{|\tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|} d^3\tilde{r} d^3\tilde{r}' \quad (2.44)$$

Here, n and m are the principal quantum numbers of the respective Slater type orbitals $\tilde{\chi}$ which are implicitly equal in MS-Q IPs, $n = m$, and in practical implementations of the QEq (e.g. LAMMPS[138]) are often set equal to one, $n = m = 1$. The analytic expression for this integral is surprisingly complicated, as compared to the Tang-Toennies-type damping functions:

$$A_s(x) \equiv e^{-x} \frac{s!}{x^{s+1}} \sum_{p=0}^s \frac{x^p}{p!} \quad (2.45)$$

$$B_s(x) \equiv \sum_{p=0}^{\infty} \frac{1 - (-1)^{s+p+1}}{(s+p+1)p!} (-x)^p$$

$$\approx \sum_{p=0}^{p_{\text{cut}}} \frac{1 - (-1)^{s+p+1}}{(s+p+1)p!} (-x)^p \quad (2.46)$$

$$I_0(r_{ij}) = \frac{1}{r_{ij}} - \left[\frac{e^{-2\zeta_i r_{ij}}}{r_{ij}} \sum_{t=1}^{2n} \frac{t(2\zeta_i r_{ij})^{2n-t}}{2n(2n-t)!} \right.$$

$$+ \frac{\zeta_i(\zeta_i r_{ij})^{2n}}{2m(2n)!} \sum_{t=1}^{2m} \frac{t(\zeta_j r_{ij})^{2m-t}}{(2m-t)!} \sum_{k=0}^{2n-1} \sum_{l=0}^{2m-t} \binom{2n-1}{k} \binom{2m-t}{l} (-1)^l$$

$$\left. B_{k+l}(r_{ij}(\zeta_i - \zeta_j)) A_{2n+2m-k-l-t-1}(r_{ij}(\zeta_i + \zeta_j)) \right] \quad (2.47)$$

where p_{cut} is some positive integer for which the summation converges in the relevant finite range of values of the argument $x = r_{ij}(\zeta_i - \zeta_j)$ and $x = \zeta_i r_{ij}$; for an arbitrarily large argument $p_{\text{cut}} \rightarrow \infty$. In practice it was found that $p_{\text{cut}} \leq 80$ if implemented as is or $p_{\text{cut}} < 15$ once the expression is rearranged in a more suitable form, as in the Appendix Section 10.1.3. The function $B_s(x)$ is introduced to handle a singularity $|\zeta_i - \zeta_j| \rightarrow 0$ due to a mathematical artefact, and follows an approach by D. Herzbach[82]. The details can be found in Appendix 10.1.3.

The function $I_0(r_{ij})$ based on Slater-type ions is plotted in Figure 1 in the work by A. Rappe and W. Goddard[79] – it is reproduced in Figure 2.1. For $n = m$ the actual value of n is irrelevant as long as the size of the Slater-orbitals is fixed. In this plot, the integer n is varied, while adjusting the parameter $\zeta_i = \zeta_j$ such that the size, $R(n, \zeta_i) = R(m, \zeta_j)$, of the orbitals are held constant, defined as:

$$\zeta_i(n) \equiv 0.4913 \frac{2n+1}{2 \times 0.759a_0} \quad (2.48)$$

$$R(n, \zeta_i) \equiv \langle \chi_{n,i} | r | \chi_{n,i} \rangle \quad (2.49)$$

$$= \frac{2n+1}{2\zeta_i} \quad (2.50)$$

$$= \text{constant} \quad (2.51)$$

To reproduce the figure in their work, the values $\zeta_i(n) = \lambda(2n+1)/(2R_{n,i})$ with $\lambda = 0.4913$, $R_{n,i} = 0.759a_0$ as in the original QEq paper by Rappe and Goddard[79]. Here, λ is a fitting parameter introduced in their work, otherwise the internally consistent relation is $\zeta_i = (2n+1)/(2\langle \chi_{n,i} | r | \chi_{n,i} \rangle)$, by definition of the Slater-type orbital. The

factor 14.4 converts the plotted quantity into units of eV/e^2 and $\text{\AA}$ for the y - and x -axes, respectively.

Evaluating $I_0(r_{ij})$ in terms of two Slater-type atoms enables us to contain the MS-Q IP of W. Goddard *et al.*[79, 80] as a special case of QEqTS IP – this is something we verify in the next section.

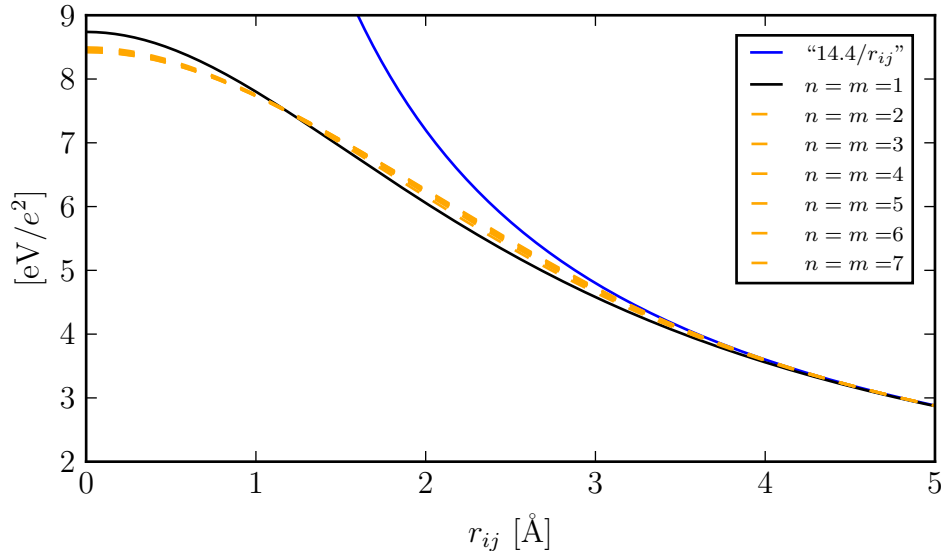


Figure 2.1: A reproduction of Fig. 1 from Ref. 79 of $14.4I_0(r_{ij})$ using two identical STOs centered r_{ij} apart, as in equation 2.43. This is equivalent to $I_0(r_{ij})$ in eV/e^2 units, evaluated at r_{ij} in $\text{\AA}$ units. As $n = m$ is varied, the STO size is kept constant $\langle \chi_{n,i} | r | \chi_{n,i} \rangle = 0.759 a_o$. See text for details.

MS-Q based on Slater-type ions applied to MgO

In order to test the implementation of $I_0(r_{ij})$ in equation 2.43 based on Slater-type ions, we reproduce several calculations from Ref. 81 in which MS-Q IP was applied to MgO – this work is referred to as Ref-MgO and the in-house code that implements IPs is referred to as ASAP. The short-range electrostatic interactions in MS-Q of Ref-MgO are represented using $I_0(r_{ij})$ based on Slater-type ions, the same as introduced in Section 2.2.3 and implemented in ASAP during the course of this PhD.

In their work, MS-Q IP is applied to MgO, with the aim to estimate the phase diagram for a range of P and T values. Molecular dynamics simulations at finite temperature are preceded by a series of static calculations at zero temperature to parameterise and compare the IP to the reference DFT calculations. We focus only on reproducing calculations at zero temperature since this is sufficient to test the implementation of $I_0(r_{ij})$ and carries only a modest associated computational cost. These types of calcula-

tions in their work are carried out for two phases of MgO – the B1 (6-coordinated NaCl) and B2 (8-coordinated CsCl) phases. The latter has lower enthalpy at higher pressures, $P \geq 400$ GPa in their calculations.

Firstly, Table 2.1 compares the equilibrium QEq charges reported in Ref-MgO to those obtained using ASAP, for the B1 and B2 phases at zero temperature and varying pressure. The agreement is to within three significant digits – the variance in the fourth

P [GPa]	QEq charge [e]					
	B1 phase			B2 phase		
	Ref.	ASAP	GULP	Ref.	ASAP	GULP
0	0.7078	0.7076(0.7078)	0.7076	0.7017	0.7016	0.7016
50	0.7141	0.7137	0.7137	0.7092	0.7093	0.7093
100	0.7162	0.7162	0.7162	0.7123	0.7124	0.7124
200	0.7180	0.7184	0.7184	0.7157	0.7155	0.7155
300	0.7193	0.7194	0.7194	0.7169	0.7171	0.7171
400	0.7198	0.7200	0.7200	0.7182	0.7181	0.7181

Table 2.1: QEq charges for MgO in B1 and B2 phases, at different pressures, compared to values in Table IV of Ref. 81 (Ref-MgO). The QEq solution convergence in Ref-MgO is unknown, and in ASAP is set to $10^{-8} e$; $10^{-4} e$ for the value in brackets. GULP QEq solution accuracy is at the level of machine precision (see text).

decimal place is likely down to the differences in numerical implementation of the QEq scheme. A. Rappe and W. Goddard had introduced the QEq model based on the Slater-type ions in 1991 and in 1996 the former author, together with other co-workers[139], presented a combined implementation of the QEq scheme with an Ewald summation suitable for simulations of periodic solids – that scheme is *iterative*, with the QEq solution accuracy determined by the numerical convergence tolerance pre-defined by the user. It seems likely that this scheme is used in Ref-MgO by W. Goddard *et al.* and the numerical tolerance, which isn’t reported, must be on the order of $10^{-4} e$. In our calculations, we have used a numerical iterative scheme at $10^{-8} e$ tolerance, and supplemented the results with those obtained using the open-source GULP package[85], where an equivalent implementation of MS-Q IP is available. The latter package uses a direct matrix inversion which leads to the QEq solution accuracy at the level of the machine

precision. There is a perfect agreement between the ASAP and GULP QEq charges. Finally, the value in the brackets in Table 2.1 is the ASAP result obtained using the convergence threshold of 10^{-4} e, which coincides with the Ref-MgO result, consistent with the view that in their work a relatively low tolerance was used when converging the QEq solution.

Overall, it is safe to conclude that the QEq charges from Ref-MgO are reproduced exactly, implying that the charge-charge coupling $I_0(r_{ij})$ based on Slater-type ions is implemented correctly. The charge-dipole and dipole-dipole couplings cannot be compared to any published work, since our QEqTS IP has no exact counterparts. However, we have used Mathematica software package[140] to complete the necessary tests. Using the analytic form of $I_0(r_{ij})$ as an input Mathematica allows one to evaluate $\partial I_0(r_{ij})/\partial r_{ij}^\alpha$ and similar derivatives both *analytically* and numerically, allowing for an extensive comparison⁹. We can say with confidence that all the variants of the QEq model are implemented correctly in the QEqTS IP. The rigorous tests are emphasized, in part, because in Chapter 6 we present some counter-intuitive results regarding the predicted QEq charge distribution in bulk BaTiO₃ – the possibility of any errors in the implementation can be safely dismissed.

Next, we tried to reproduce several calculated observables using the (consistent) MS-Q IP but were unable to, in agreement with the findings by D. Herzbach[82] for the application of MS-Q to SiO₂ by the same group of researchers in the same year. Recall, as already mentioned in Section 1.4.1, the early applications of the MS-Q IP turned out to have used an inconsistent scheme for finding equilibrium charges and evaluating forces and other properties. The short-range shielding of the electrostatic interactions, in the form of $I_0(r_{ij})$ in equation 2.43, was used when solving for the equilibrium QEq charges, however, subsequent calculations of properties used unshielded $1/r_{ij}$ Coulomb interactions. This was confirmed by D. Herzbach[82] for the early work of W. Goddard *et al.* from 1999 on SiO₂[80] and now in the present thesis for their work on MgO[81] in the same year. A subsequent publication by W. Goddard *et al.*[84] in 2002 confirmed, retrospectively, that the early applications of the MS-Q were inconsistent.

Consistent with the above observations, the only way we were able to reproduce their results on MgO of Ref. 81 is by implementing a similarly inconsistent scheme. For the sake of making comparisons in the present section, the inconsistent scheme was implemented temporarily into the in-house code ASAP. This inconsistent implementation is

⁹Analogous tests that use in part Mathematica and in part comparisons to published work using TS IP were carried out for the Tang-Toennies type of $I_0(r_{ij})$ function and its derivatives (not presented).

referred to as ASAP*.

Firstly, in Figure 2.2 we reproduce the dependence of pressure and energy on the system volume in the cubic (B1) phase at zero temperature – this is representative of the numerous static calculations in their work involving two of the following: pressure, volume, energy and enthalpy. Excellent agreement is observed and similar plots are not shown.

Secondly, in Figure 2.3 we reproduce stress tensor components, energy and enthalpy

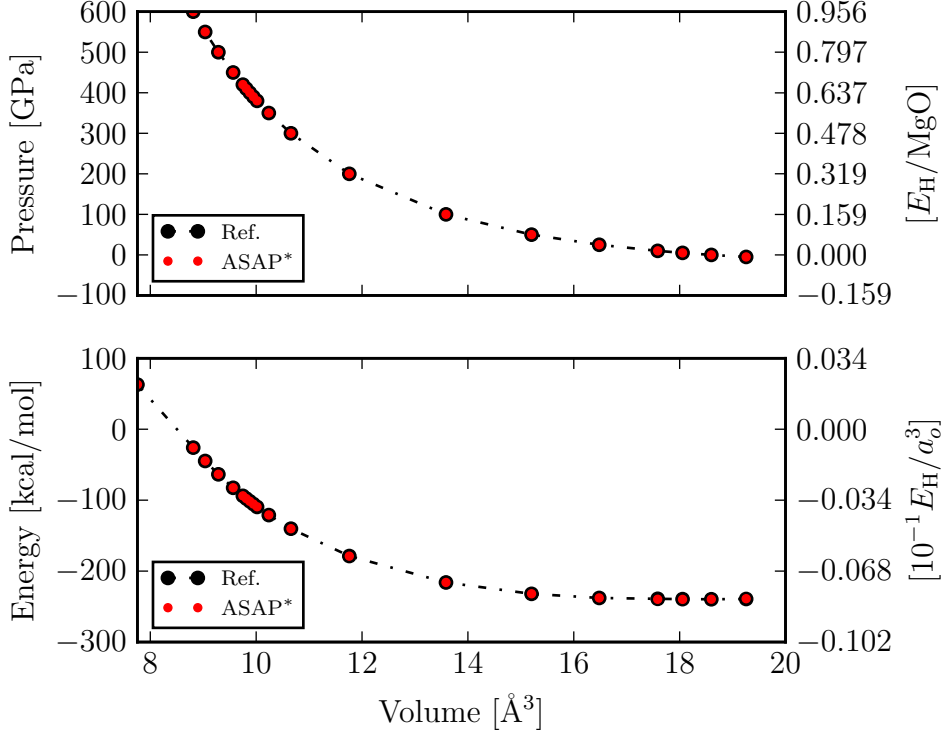


Figure 2.2: Top and bottom panels show pressure and energy, respectively, as a function of volume in the (B1) cubic MgO phase. Black points are taken from Ref. 81, red points are obtained using the ASAP code, modified to evaluate properties without short-range shielding (ASAP*) (see text).

along a Buerger path, to be defined shortly, connecting phases B1 and B2 of MgO. Arguably, the properties along this path are relatively sensitive to the QEq charges since the system is far from equilibrium – hence reproducing this data serves as a good test. The B2 phase has a lower enthalpy at high pressures, $P \geq 400$ GPa in their calculations. A Buerger lattice transformation, also known as the $R\bar{3}m$ mechanism[141, 142]¹⁰, can be defined in terms of the cell parameters: $a = b = c$, $\alpha = \beta = \gamma$ and the order-parameter $0 \leq \lambda \leq 1$ such that $\alpha = \beta = \gamma = 90^\circ + \lambda 19.47^\circ$; B1 and B2 phases correspond to $\lambda = 0$

¹⁰Ref. 142 contains video visualisations by G. Mallia of the B1-B2 transformation mechanisms.

and $\lambda = 1$, respectively. The atomic relaxations are not allowed by symmetry¹¹ while the cell parameters $a = b = c$ are adjusted at each value of λ subject to maintaining a constant pressure, $P = 420$ GPa in Fig. 2.3. There is an excellent agreement, except for the enthalpy calculations, which require some comments. The supplementary material of Ref-MgO contains that subset of the published results which was obtained using DFT; reference results based on MS-Q were obtained directly from the plots using an open-source tool g3data[143]¹². There are two reasons for the discrepancy. Firstly,

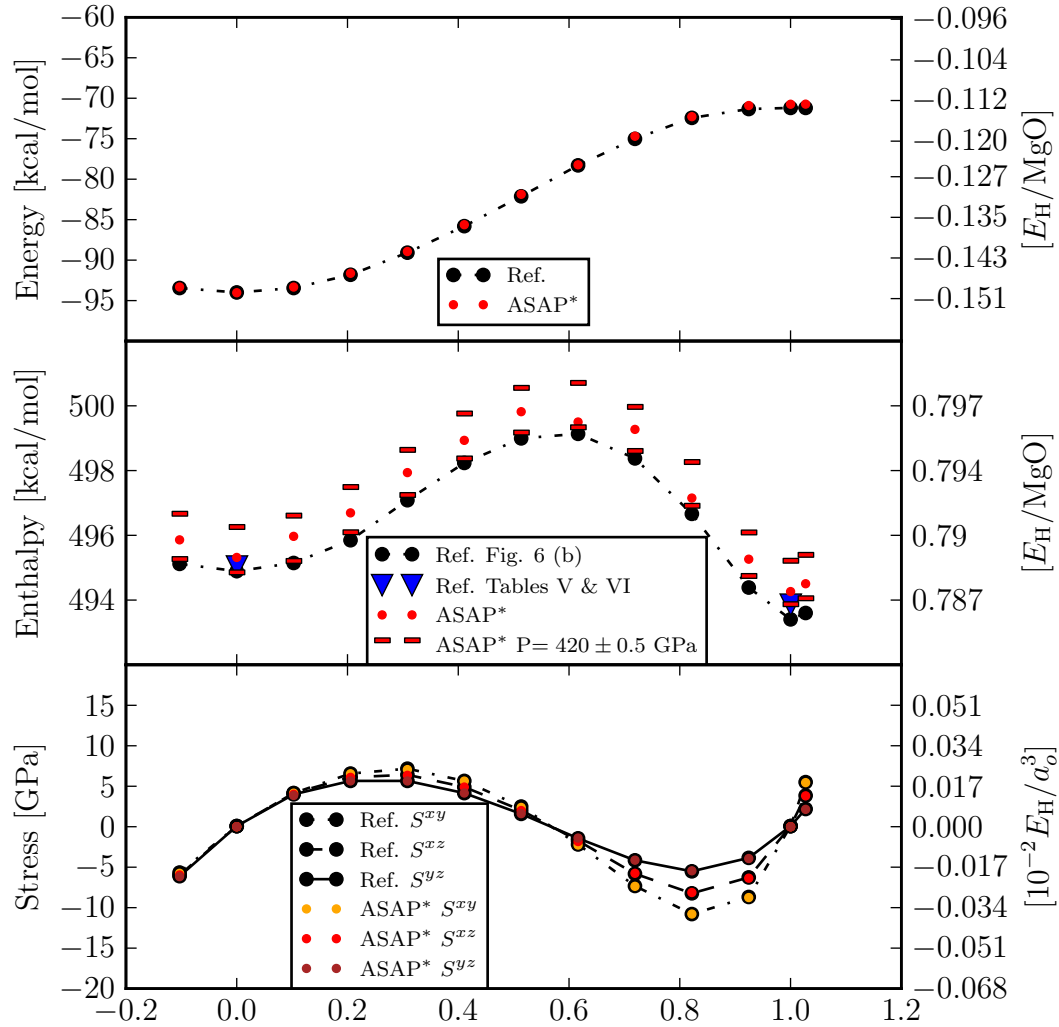


Figure 2.3: Panels top to bottom show energy, enthalpy and stress components, along a Buerger path B1→B2 path parameterised by λ , as described in text. Black and blue markers are the values from the plots and tables, respectively, in Ref. 81. Coloured points are obtained with the ASAP code, modified to evaluate properties without short-range shielding (ASAP*) (see text).

¹¹The coordinates, expressed in terms of the lattice vectors, remain unchanged.

¹²This GUI-type tool takes a graphical image of a plot as an input, calibrates the y - and x -axis and assigns values to data points in response to the user's mouse clicks.

the pressure along the Buerger path does not correspond to 420 GPa exactly – the supplementary data for the DFT calculations along the Buerger path reveals that two points can differ by as much as 0.42 GPa; furthermore the same reference enthalpy data points calculated twice in Ref-MgO reveal a discrepancy of 0.143 [kcal/mol] (blue and black markers at $\lambda \in \{0, 1\}$ in Fig. 2.3). The secondary and likely the primary reason, however, is the non-equivalent way in which Morse-stretch term is truncated at the cut-off distance in MS-Q as implemented in Ref-MgO and ASAP. The actual way in which Morse-stretch term is implemented in a computer code has the following functional form:

$$E_{ij}^{\text{MS}} \rightarrow E_{ij}^{\text{MS}} f^{\text{cut}}(r_{ij}) \quad (2.52)$$

with the analytic form of the $f^{\text{cut}}(r_{ij})$ function chosen so as to impose exactly vanishing $E_{ij}^{\text{MS}} f^{\text{cut}}(r_{ij})$ and its first derivative at $r_{ij} = r_{ij}^{\text{cut}}$; the latter is set by the user to define an ion’s neighbour list. The function $f^{\text{cut}}(r_{ij})$ is not the same in ASAP and in Ref-MgO. This must, in general, lead to slightly different volumes at the same pressure. The red points in Fig. 2.3 correspond to the λ and P values taken from the Ref-MgO supplementary material, while the red bars are included to reveal the degree to which enthalpy values are sensitive to volume. A relatively small change in volume of $0.005 a_o^3$ (per MgO) at $P = 420$ GPa corresponds to changes in pressure and enthalpy of 0.5 GPa and 0.77 kcal/mol, respectively.

Overall, it is safe to conclude that their results are reproduced to within numerical errors that can be rationalised on the basis of slightly different ways in which MS-Q is implemented in Ref-MgO and in ASAP (and ASAP*) and/or the fact that some details and data in Ref-MgO are simply not available and have to be estimated.

2.2.4 Model dependence of the short-range correction

During the course of this PhD work, it was found that the same quality of fit during force-matching was obtained whether one used $I_0(r_{ij})$ expression based on Slater-type ions or Tang-Toennies damping function. The same conclusion was drawn by B. Thole in his numerical tests of using several distinct ways to represent $I_0(r_{ij})$ [55].

What’s more, the charge-charge ($I_0(r_{ij})$) and dipole-dipole ($\partial^2 I_0(r_{ij}) / \partial r_{ij}^\alpha \partial r_{ij}^\beta$) short-range corrections in the extended QEqTS IP were found to result in only a small quantitative improvement in accuracy without changing the behaviour of the QEqTS IP qualitatively relative to the implementation of J. Sarsam. Consequently, an extended comparative study of the extended QEqTS IP *vs.* the one previously implemented by J. Sarsam is not presented.

In the present section we compare the short-range correction based on Tang-Toennies damping function to those based on Slater-type ions. In particular, we show that for a physically meaningful range of parameter values and interionic distances, such as encountered in molecular dynamics simulations, the two attenuation schemes are numerically identical. Therefore, this helps us explain the fact that we observe numerically equivalent QEqTS IPs regardless which of the two short-range correction representations we use. Having said that, the latter approach demands more computer resources in order to be implemented in a simulation software. Therefore, Tang-Toennies damping functions are adopted throughout the rest of the thesis.

In the literature it is uncommon to find the use of attenuation based on two Slater-type orbitals with arbitrary values of n and m . It is thus interesting to see how the charge-charge, charge-dipole and dipole-dipole interactions scale with r_{ij} for different combinations of n and m . First, we fix the average atomic size using the following relation:

$$R_i \equiv \langle \chi_{i,n} | r | \chi_{i,n} \rangle \quad (2.53)$$

$$= (2n + 1)/2\zeta_i \quad (2.54)$$

This way, when n is varied for a given ion's Slater-type orbital representation, the parameter ζ_i can be adjusted so as to maintain a constant ionic size, defined in terms of R_i in equation 2.53. This way we see the effect of varying principal quantum number on the shape of the attenuation function *without* the effect of the atomic size. For the sake of the clarity of visualisations, for a pair of ions i and j , only a small set of representative values for n and m , as well as sizes R_i and R_j , are chosen in the present section – to represent Ti, O and, occasionally, Ba ions in the BaTiO₃. In particular, the principal quantum number associated with Ba, Ti and O are 6, 4 and 2, respectively. We take ion i to represent the cation Ti or Ba while ion j to represent O and vary $\{n, m\}$ and $\{R_i, R_j\}$ accordingly. The ionic sizes are set to the values based on our own estimates, presented in Section 6.4.3, as well as the widely used crystal ionic radii, from the table compiled by R. Shannon[144]; for Ba, Ti and O our own ionic radius estimates are 2.6, 1.4, 2.4 a_o , respectively, while Shannon's values are 2.8, 1.9, 2.4 a_o . Also, Ti distance to its closest three O nearest neighbours in BaTiO₃ is 3.6 a_o on average, while the next shortest nearest neighbour distance, that between Ba and O ions, is 5.4 a_o . Therefore, the Ti-O nearest neighbour overlap is most significant.

The results in Fig. 2.4 keep the cation and anion sizes fixed at the our estimated radii values for Ti and O, while varying n and m . It is clear from the plots that the attenuation

is essentially identical for atoms of fixed sizes, irrespective of the principal quantum number used to represent the Slater-type orbitals. The choice of the principal numbers n and m only becomes relevant close to the vanishing interionic distance, $r_{ij} \rightarrow 0$, which represents two ions collapsed into one another. This is an unphysical situation, at the very least for the thermally perturbed solid phase BaTiO₃ studied in the present work. Next, we look at how the scaling profile changes as the size of an atom varies. The

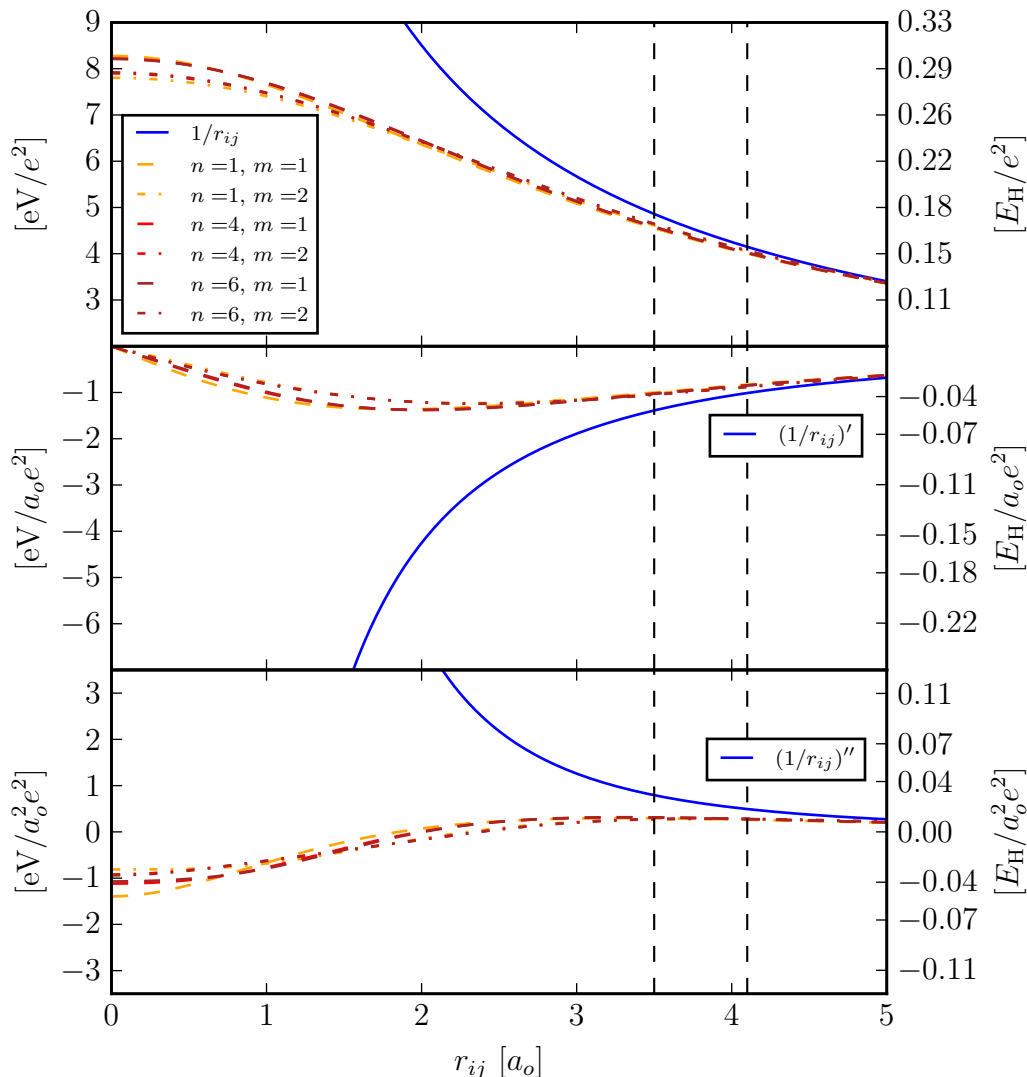


Figure 2.4: Top to bottom panels: dashed lines show derivatives $[\partial/\partial r_{ij}^x]^k I_0$ for $k = 0, 1, 2$ and 3 respectively, with x -axis parallel to $\mathbf{r}_{ij}$ vector connecting ions i and j ; blue – same but applied to $1/r_{ij}$. Ionic sizes, defined as $\langle \chi | r | \chi \rangle$ are held fixed at $1.4 a_o$ and $2.4 a_o$, values representative of Ti and O ions in BaTiO₃ (see text), while n and m are varied. Top to bottom, the panels show charge-charge, charge-dipole, dipole-dipole coupling.

parameters are meant to represent three pairs of interactions, two for Ti and O based on

our estimates of ionic radii as well as Shannon's values and Ba-O interaction based on Shannon's values. The results are presented in Fig. 2.4. As one might expect, changing ionic radius does change the interaction strength in the physically relevant region on the order of nearest neighbour distance. This is to say, the exact values of n and m are not

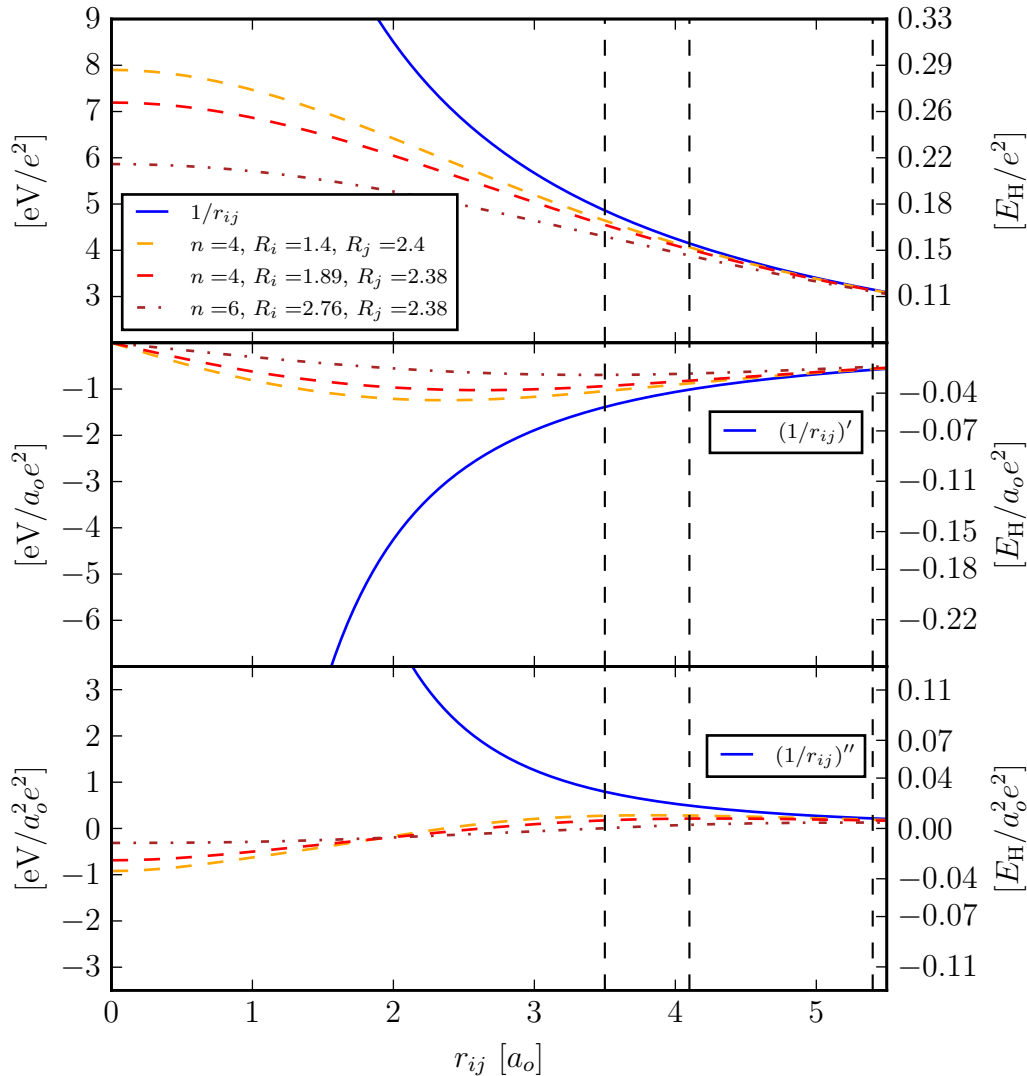


Figure 2.5: Top to bottom panels: dashed lines show derivatives $[\partial/\partial r_{ij}^x]^k I_0$ for $k = 0, 1, 2$ and 3 respectively, with x -axis parallel to $\mathbf{r}_{ij}$ vector connecting ions i and j ; blue – same but applied to $1/r_{ij}$. Ionic sizes, defined as $\langle \chi | r | \chi \rangle$ are held fixed at $1.4 a_o$ and $2.4 a_o$, values representative of Ti and O ions in BaTiO₃ (see text), while n and m are varied. Top to bottom, the panels show charge-charge, charge-dipole, dipole-dipole coupling.

important but the ionic size is.

Finally, Fig. 2.6 contains the same curves as in Fig. 2.5 but is additionally supplemented with $I_0(r_{ij})$ based on Tang-Toennies damping function. The parameter $\tilde{n}$ is

set to $\tilde{n} = 3$, which is that most commonly used value in the literature, and is kept fixed while $\tilde{\zeta}_{ij}$ is deliberately adjusted so that the Tang-Toennies curves coincide in the physically relevant range of values r_{ij} with those based on Slater-type ions.

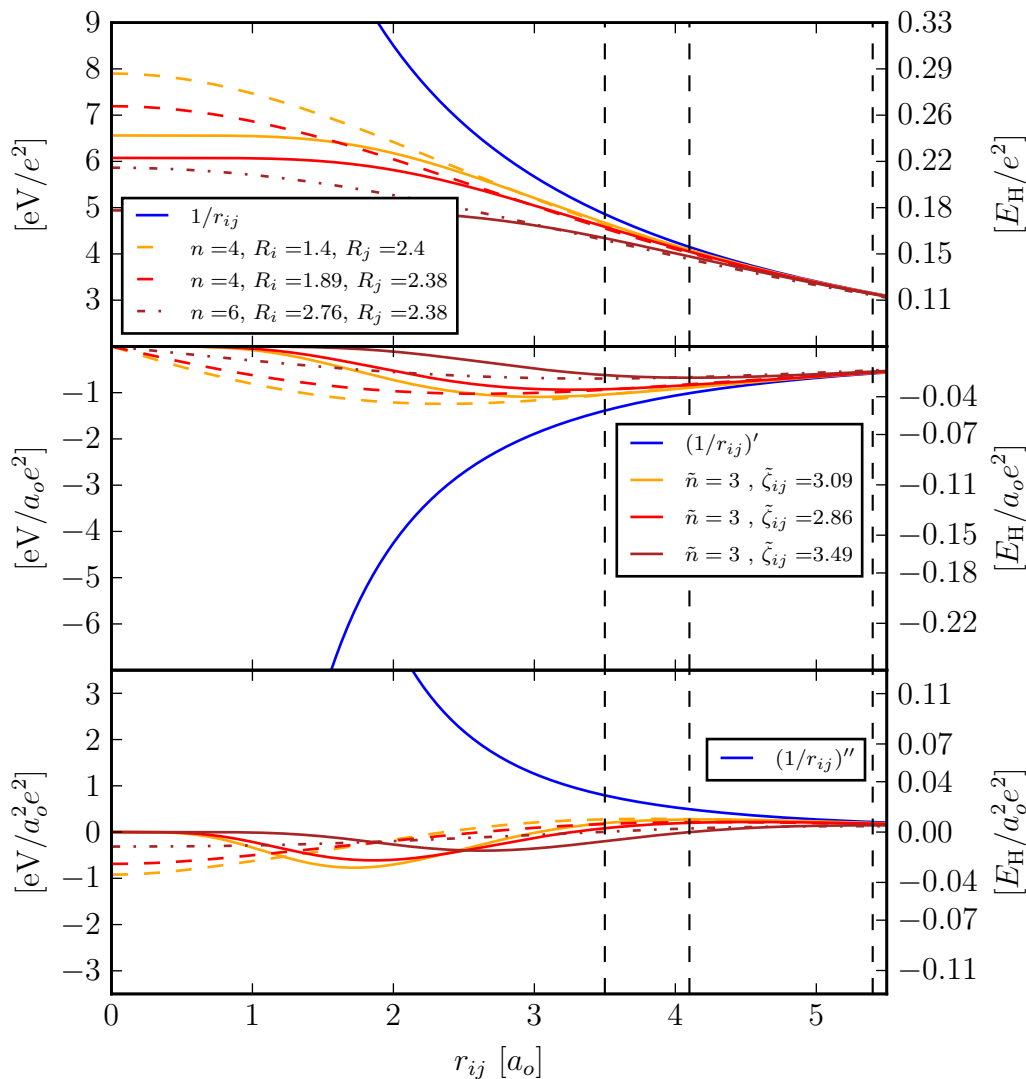


Figure 2.6: The blue and dashed curves are as in Fig. 2.5. Additional solid curves correspond to the Tang-Toennies damping function, with $\tilde{n} = 3$ and the parameter $\tilde{\zeta}_{ij}$ adjusted so as to coincide with the dashed curves of the same color in the physically relevant range of interionic distance.

The figure shows that the Tang-Toennies damping functions deviate substantially from those based on Slater-type ion representations only at relatively short interionic separations, too short to be encountered in a solid phase BaTiO_3 (see Chapter 6) and likely most other solids. This explains why we observe numerically equivalent QEqTS IPs regardless whether the short-range correction $I_0(r_{ij})$ is based on Slater-type ions or a Tang-Toennies damping function. This echoes the findings of B. Thole[55] who tested

several analytic forms of $I_0(r_{ij})$ and reached the same conclusion.

Chapter 3

Density functional theory in the ionic limit

In Chapter 1 we've seen that, in comparison to a simple fixed-charge rigid-ion model, the PI¹ model results in a marked improvement in accuracy and transferability. In contrast, it has not been clearly demonstrated that an improvement can be ascribed to the use of the QEq² model and, what is more, we've seen that the QEq-based IPs sometimes numerically reduce to fixed-charge IPs. In this chapter polarisable ionic IPs, including those based on the PI and QEq models, are derived by starting from the exact DFT expression and applying a series of approximations. It is highlighted that the assumptions underpinning the QEq model may not hold true in systems where large, change-of-valence type, charge transfer takes place.

This chapter is organized as follows. Theoretical underpinnings of polarisable ionic IPs are rationalized in terms of a well-defined ionic limit applied to density functional theory. A preliminary discussion in Section 3.1 provides a review of the DFT. In Section 3.2 approximations that define the ionic limit are made explicit and in Section 3.3 electrostatic interaction energy is approximated in this limit. In Section 3.4 parts of the total energy functional that describe electron kinetic and electron repulsion energy are approximated using a perturbation technique. In Section 3.5, the approximations to DFT of Sections 3.3 and 3.4 are combined and the classical ionic IPs discussed in Chapter 1 are demonstrated to be derivable in this limit.

Finally, in Section 3.6 the results of this chapter are summarised and the domain of applicability of the approximations that underpin polarisable IPs are briefly discussed.

¹Recall, PI – Polarisable ion

²Recall, QEq – charge equilibration.

3.1 Density functional theory for non-degenerate ground states

In their well known paper[145], P. Hohenberg and W. Kohn (HK) have proved two important theorems for a system of electrons in an external single-particle potential $v(\mathbf{r})$.

Firstly, for two distinct electrostatic potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ ³, each with a non-degenerate ground state wavefunction $\psi(\mathbf{r})$ and $\psi'(\mathbf{r})$, the ground state densities cannot be the same – one must have $\rho(\mathbf{r}) \neq \rho'(\mathbf{r})$. Conversely, for a given density $\rho(\mathbf{r})$, *assuming* that an external potential generating this density exists with a non-degenerate ground state, this potential is unique (up to a constant). The assumption that for any density integrating to a positive integer there exists an external electrostatic potential that generates it is referred to as v -representability, while assuming there exists a wavefunction corresponding to $\rho(\mathbf{r})$ – N -representability⁴. Assuming non-degeneracy and v -representability both the external potential and the ground state wavefunction are unique functionals of the density. In turn the ground state energy is itself a unique functional of the density⁵ and has the following form:

$$E[\rho] \equiv F[\rho] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (3.1)$$

where the implicitly defined $F[\rho]$ is a universal functional of the density, independent of $v(\mathbf{r})$ – it evaluates the electron kinetic and repulsion energies. As discussed further below, $F[\rho]$ can be redefined, relaxing the conditions of v -representability and non-degeneracy.

The second theorem demonstrates the variational principle for $E[\rho]$ – the ground state energy is the global minimum with respect to number-conserving variations in the input density; the ground state density is the density that minimises $E[\rho]$. The proof rests on the assumption that for any electron number density integrating to a positive integer there exists at least one many-body wavefunction that generates this density. This assumption, referred to as N -representability, had been shown to hold true by T. Gilbert [146], for reasonably smooth densities.

In this thesis, in Chapters 6, 7 and 8, DFT is used to study systems with a non-degenerate ground state, hence the assumptions of the HK theorems are true at the

³i.e. differing other than by a constant

⁴Note, you might have the latter without the former, i.e. an anti-symmetric wavefunction that is not generated by any single-particle external potential.

⁵Charge density $\rho(r)$ and number density $n(\mathbf{r})$ integrate to the negative and positive integers, respectively. We use charge density in this chapter. External potential is defined conventionally, i.e. $v(\mathbf{r}) = -\sum_{j=1}^{N_{\text{atm}}} Z_j/|\mathbf{r} - \mathbf{r}_j|$ if nuclei are assumed to be point particles, with charges $Z_j > 0$.

ground state itself and possibly for the trial densities close to the solution. Strictly speaking, for a trial density $\rho'(\mathbf{r})$ one may not be certain that it corresponds to a non-degenerate state $\psi'(\mathbf{r})$ of some external potential $v'(\mathbf{r})$ – the HK functional $F[\rho]$ may not be defined at all in this case. This issue had been circumvented by M. Levy in 1979[147] who generalised the definition of $F[\rho]$ to have the following form:

$$F[\rho] = \min_{\psi \rightarrow \rho} \langle \psi | T + U_{ee} | \psi \rangle \quad (3.2)$$

where $F[\rho]$ takes on the value of the lowest energy by evaluating a set of wavefunctions $\{|\psi\rangle\}$ each of which corresponds to the trial density ρ . T. Gilbert has demonstrated N -representability and so there is always at least one wavefunction in this set. Assuming non-degeneracy and v -representability is not required anymore to define $F[\rho]$. The original proof for the variational principle can be adapted to the new definition of $F[\rho]$ and so it still holds.

Levy's definition has since been generalised and DFT itself reinterpreted so as to apply to a wider class of systems[148–152] – beyond those studied in this thesis.

As a matter of mathematical convenience, one may introduce a Lagrange multiplier, μ , and state the variational principle replacing number-conserving variations in $\rho(\mathbf{r})$ by arbitrary variations:

$$\delta[E_v[\rho] - \mu(N[\rho] - N_0)] = 0; \quad (3.3)$$

$$N[\rho] \equiv \int \rho(\mathbf{r}) d\mathbf{r}. \quad (3.4)$$

where N_0 is the total (negative integer) charge of the electrons.

3.2 Density functional theory in different basis sets

In this section, DFT is re-stated with the use of a basis set to represent electron density. The motivation primarily comes from the fact that taking an ionic limit is equivalent to a statement that a localised atom-centered basis set is a good approximation to describe the ground state density. To demonstrate this, an argument is presented in Section 3.2.1.

Periodic boundary conditions are assumed throughout the chapter.

3.2.1 Implicit use of an ionic basis set

Introducing an ionic IP is always based on an assumption that the total ground state density $\rho(\mathbf{r})$ can be re-expressed, to a good approximation, as a sum of localised ionic contributions $\rho(\mathbf{r}) = \sum_{i=1} i^{N_{\text{atm}}} \rho_i(\mathbf{r})$; here N_{atm} is the total number of atoms in the

system. Applying the ionic limit to DFT then necessitates re-expressing the total energy and the variational principle in terms of contributions $\{\rho_i(\mathbf{r})\}$. However, there are infinitely many ways to partition the density and so searching for the ground state in terms of $\{\rho_i(\mathbf{r})\}$ directly is not a well-defined problem since a unique solution does not exist. In contrast, if the density is expressed in terms of some basis set, a unique ground state solution exists in terms of the basis set coefficients.

The above argument provides the first reason to explicitly use a basis set in applying ionic limit approximations to DFT. The second reason is highlighted in Section 3.3, in the context of approximating electrostatic interaction energy. The final approximated expression is a function only of the positions, charges $\{q_i\}$ and dipole moments $\{\mathbf{p}_i\}$ of the ionic density contributions ρ_i . Therefore, while there are many different densities ρ_i that integrate to the same charge q_i and dipole moment $\mathbf{p}_i$, they all result in the exact same energy and interatomic forces, when evaluated using the approximated expression. This statement is equivalent to a statement that the density ρ_i is expressed implicitly by two basis set coefficients only, coefficients q_i and $\mathbf{p}_i$. For the sake of completeness, an explicit construction of one such basis set, with q_i and $\mathbf{p}_i$ as coefficients, is presented in Section 3.2.3. Additionally, the use of the basis set in Section 3.2.3 allows for a clear way to unify many different types of ionic IPs in terms of distinct ways of truncating the same infinite basis set.

Finally, recall that the self-energy expression for the QEq model is based on a quadratic Taylor expansion, $A_i\Delta q_i + D_i\Delta q_i^2$, with constant coefficients A_i and D_i . Explicitly representing the charge density in terms of the nuclei-centered basis set allows one to highlight the dependence of the self-energy coefficients on the ionic positions. In our combined QEqTS IP, we also treat A_i and D_i as constants, but in the present chapter we seek to emphasize that these parameters may have a limited transferability between bulk and heterogeneous atomic environments.

From Section 3.3 onwards, variables such as ionic charges and dipoles, are simply referred to as density-representing coefficients, with the understanding that, if need be, the corresponding energy minimisation principle can be well defined.

3.2.2 DFT in a general infinite basis set

If charge density is expressed in terms of a basis set, $\{y_n(\mathbf{r})\}$ then all functionals in DFT become functions of basis set expansion coefficients, $\{c_n\}$:

$$\rho(\mathbf{r}) \doteq \sum_n c_n y_n(\mathbf{r}) \quad (3.5)$$

$$E_v[\rho] \doteq E_v(\{c_n\}) \quad (3.6)$$

$$N[\rho] \doteq N(\{c_n\}) \quad (3.7)$$

$$= \sum_n c_n \int y_n(\mathbf{r}) d\mathbf{r}. \quad (3.8)$$

where $\doteq$ indicates equality to within some arbitrarily small numerical error due to the use of an arbitrarily large truncated basis set instead of an infinite set. The constrained search variational principle takes on the form:

$$\delta E_v = \int \frac{\delta E}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) d\mathbf{r} \quad (3.9)$$

$$\doteq \sum_n \frac{\partial E}{\partial c_n} dc_n \quad (3.10)$$

$$\frac{\partial E}{\partial c_n} \equiv 0 \quad \forall n; \quad (3.11)$$

$$\sum_n c_n \int y_n(\mathbf{r}) d\mathbf{r} \equiv N_0. \quad (3.12)$$

If, instead, we introduce a Lagrange multiplier, the variational principle takes the form:

$$\delta [E_v - \mu(N(\{c_n\}) - N_0)] = 0 \quad (3.13)$$

$$\frac{\partial E}{\partial c_n} = \begin{cases} \mu & \text{if } \int y_n(\mathbf{r}) d\mathbf{r} \neq 0 \\ 0 & \text{if } \int y_n(\mathbf{r}) d\mathbf{r} = 0 \end{cases} \quad (3.14)$$

Here Lagrange multiplier is connected to coefficients c_n of the basis functions that actually contribute to the total particle number. Some basis functions $y_n(\mathbf{r})$, as we shall see in Section 3.2.3, integrate to zero due to symmetry and do not contribute to the particle number operator.

So far no approximations were made that are specific to an ionic limit. In practice one always invokes some basis set representation in order to seek the ground-state solution. In solid state physics one usually uses plane waves.

3.2.3 Density functional theory in an ion-centered basis set

When seeking an approximate expression for a classical interatomic potential, at some point one has to introduce local polarization effects (dipole moments, higher order multipole moments, size effects, etc.) and/or charge transfer between ions. One can arguably

say that taking an ionic limit is equivalent to a statement that a certain finite, localised, basis set is a good approximation to the complete (infinite) basis set. Furthermore, although the choice of the local basis is not unique, arguably the only sensible option for expressing angular dependence is in terms of (real) spherical Harmonics. These are defined⁶[153]:

$$Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} \begin{cases} P_l^{|m|}(\cos \theta) \sin|m|\phi, & \text{if } m < 0 \\ P_l^m(\cos \theta), & \text{if } m = 0 \\ P_l^m(\cos \theta) \sin m\phi, & \text{if } m > 0 \end{cases} \quad (3.15)$$

where $m \in \{-l, \dots, 0, \dots, l\}$ and $P_l^m(z)$ are the associated Legendre polynomials. Spherical harmonics are orthonormal over the solid angle:

$$\int_0^\pi d\theta \int_0^{2\pi} \sin \theta d\phi Y_l^m(\theta, \phi) Y_{l'}^{m'}(\theta, \phi) = \delta_{ll'} \delta_{mm'} \quad (3.16)$$

If $\rho_i(\mathbf{r})$ satisfies suitable spherical boundary conditions, it is expressible[154] in terms of the spherical Fourier series⁷ which indeed represent the angular dependence via the spherical Harmonics. However, in solid state physics one typically uses periodic boundary conditions defined on a parallelepiped and in this case the plane wave basis set is naturally defined instead, based on Sturm-Liouville theory applied to Helmholtz equation. However, as discussed in Ref. 154, it is possible to reconcile a basis set defined for spherical boundary conditions with the parallelepiped boundary conditions that are actually used in a DFT calculation. Doing so rests on several assumptions: a) ionic density $\rho_i(\mathbf{r})$ approaches zero within some cut-off radius⁸ $r_{\text{cut}}^{(i)}$ on the order of bond length, b) the simulation supercell is sufficiently large with the smallest side length of about three times as large as $\text{Max}_i\{r_{\text{cut}}^{(i)}\}$, c) spheres defined by $r_{\text{cut}}^{(i)}$ are large enough to overlap so that the entire supercell is covered and d) a large, yet finite number of basis functions is actually used. With these conditions met, each $\rho_i(\mathbf{r})$, centered at the ionic position $\mathbf{r}_i$, can be expanded using spherical Fourier series within $|\mathbf{r} - \mathbf{r}_i| \leq r_{\text{cut}}$ and set to zero outside r_{cut} , reconciling it with the conventional boundary conditions. This makes it possible to express charge density in terms of a sum of atom-centered expansions in

⁶Condon-Shortley phase convention is used

⁷Fourier-Bessel series

⁸The zero-boundary conditions are imposed, $\rho_i(\mathbf{r}) = 0$ for $|\mathbf{r}| = 0$ and $|\mathbf{r}| = r_{\text{cut}}$.

spherical Fourier series like so:

$$\rho(\mathbf{r}) \doteq \sum_{i=1}^{N_{\text{atm}}} \rho_i(\mathbf{r}); \quad (3.17)$$

$$\rho_i(\mathbf{r}) \equiv \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^l c_{nlm}^{(i)} y_{nlm}(|\mathbf{r} - \mathbf{r}_i|, \theta, \phi); \quad (3.18)$$

$$y_{nlm}(\tilde{r}, \theta, \phi) = \frac{1}{\sqrt{N_n^{(l)}}} j_l(k_{nl}\tilde{r}) Y_l^m(\theta, \phi) \quad (3.19)$$

where $j_l(z)$ is the spherical Bessel function, k_{nl} is defined via $j_l(k_{nl}r_{\text{cut}}) = 0$, $c_{nlm}^{(i)}$ are the expansion coefficients and $N_n^{(l)}$ is the normalization constant, defined in Ref. 154⁹. Using such a basis set is challenging in practice and one is faced with issues such as basis set superposition errors, overcompleteness and the introduction of Pulay forces. What's important in the context of this chapter's discussion is that the charge density is in principle expressible in terms of this basis set. The goal is to emphasize unavoidable assumptions and approximations that go into deriving a classical interatomic potential – viewed from this angle the use of this basis set does not constitute an approximation.

An approximation that is necessarily made in order to derive a classical ionic IP is to only retain a very small number of basis functions from this infinite set. Common choices are guided by the following considerations:

- whether ionic sizes is variable or fixed
- whether ions can polarise and if so, how many multipole moments to retain
- whether ionic charges are variable or fixed

I now demonstrate how these choices result in different basis set truncations.

Firstly, keeping ionic radial shape fixed corresponds to factorization

$$\rho_i(\mathbf{r}) \equiv \sum_{l=0}^{\infty} \sum_{m=-l}^l \tilde{c}_{lm}^{(i)} Y_l^m(\theta, \phi) f_{lm}(|\mathbf{r} - \mathbf{r}_i|), \quad (3.20)$$

$$f_l^m(|\mathbf{r} - \mathbf{r}_i|) \equiv \sum_{n=0}^{\infty} b_{nlm}^{(i)} \frac{1}{\sqrt{N_n^{(l)}}} j_l(k_{nl}|\mathbf{r} - \mathbf{r}_i|, \theta, \phi) \quad (3.21)$$

where $b_{nlm}^{(i)} \equiv c_{nlm}^{(i)} / \tilde{c}_{lm}^{(i)}$ are now held fixed during energy minimization while $\tilde{c}_{lm}^{(i)}$ are free variables; $\tilde{c}_{lm}^{(i)}$ are implicitly defined as the common factors over n for fixed l and m . In this thesis, all ionic IPs used assume constant ionic sizes.

⁹ $y_{nlm}(\tilde{r}, \theta, \phi)$ is to be identified with $\Psi_{nlm}(r, \theta, \phi)$ in equation (53) of Ref. 154 except that real spherical harmonics are used here.

Secondly, making ions polarisable corresponds to retaining terms $l \geq 1$ and treating $\tilde{c}_{lm}^{(i)}$ as variables. In practice only very few terms are retained, virtually never going beyond $l \leq 2$ and in this thesis polarisable-ion IPs only include terms $l \leq 1$. By enforcing the following normalisation:

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{r_{\text{cut}}} r^2 dr Y_0^0(\theta, \phi) f_0^0(|\mathbf{r} - \mathbf{r}_i|) \equiv 1 \quad (3.22)$$

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{r_{\text{cut}}} r^2 dr Y_1^{-1}(\theta, \phi) f_{1-1}(|\mathbf{r} - \mathbf{r}_i|) \underbrace{|\mathbf{r} - \mathbf{r}_i| \cos \phi \sin \theta}_x \equiv 1 \quad (3.23)$$

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{r_{\text{cut}}} r^2 dr Y_1^1(\theta, \phi) f_{11}(|\mathbf{r} - \mathbf{r}_i|) \underbrace{|\mathbf{r} - \mathbf{r}_i| \sin \phi \sin \theta}_y \equiv 1 \quad (3.24)$$

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{r_{\text{cut}}} r^2 dr Y_1^0(\theta, \phi) f_{10}(|\mathbf{r} - \mathbf{r}_i|) \underbrace{|\mathbf{r} - \mathbf{r}_i| \cos \theta}_z \equiv 1 \quad (3.25)$$

the ionic density takes the form:

$$\begin{aligned} \rho_i(\mathbf{r}) &= q_i Y_0^0(\theta, \phi) f_{00}(|\mathbf{r} - \mathbf{r}_i|) \\ &\quad p_i^x Y_1^{-1}(\theta, \phi) f_{1-1}(|\mathbf{r} - \mathbf{r}_i|) \\ &\quad p_i^y Y_1^1(\theta, \phi) f_{11}(|\mathbf{r} - \mathbf{r}_i|) \\ &\quad p_i^z Y_1^0(\theta, \phi) f_{10}(|\mathbf{r} - \mathbf{r}_i|) \end{aligned} \quad (3.26)$$

where coefficients are relabelled as $\tilde{c}_{00}^{(i)} \rightarrow q_i$, $\tilde{c}_{1-1}^{(i)} \rightarrow p_i^x$, $\tilde{c}_{11}^{(i)} \rightarrow p_i^y$ and $\tilde{c}_{10}^{(i)} \rightarrow p_i^z$. Imposed normalisation and symmetry of the real spherical harmonics ensures that the charge and multipole moments are defined in terms of the expansion coefficients:

$$\int \rho_i(\mathbf{r}) d\mathbf{r} = q_i \quad (3.27)$$

$$\int (\mathbf{r} - \mathbf{r}_i) \rho_i(\mathbf{r}) d\mathbf{r} = \mathbf{p}_i \quad (3.28)$$

where $\mathbf{p}_i = [p_i^x, p_i^y, p_i^z]$.

Lastly, variable charge models treat $\{q_i\}$ coefficients ($l = 0, m = 0$) as variables. In the context of variable charge models it is worth noting the suggestion of R. Parr and L. Bartolotti[155] to factor charge density in terms of shape and particle number,

$$\rho(\mathbf{r}) = N_0 \sigma(\mathbf{r}) \quad (3.29)$$

where N_0 is the (negative integer) total charge of electrons and sigma is the shape function, satisfying the constraints $\int \sigma(\mathbf{r}) d\mathbf{r} = 1$ and $\int \delta \sigma(\mathbf{r}) d\mathbf{r} = 0$ during energy minimization. Given the symmetry of spherical harmonics, q_i coefficients describe the number of electrons while all other coefficients describe the *shape* of the charge density ρ_i . Thus

the above basis set has the following property:

$$\int \rho(\mathbf{r}) d\mathbf{r} = \sum_i q_i; \quad (3.30)$$

$$\delta E_v = \sum_i \frac{\partial E_v}{\partial q_i} dq_i + \sum_i \sum_{\alpha=x,y,z} \frac{\partial E_v}{\partial p_i^\alpha} dp_i^\alpha; \quad (3.31)$$

$$\delta N = \sum_i \frac{\partial N}{\partial q_i} dq_i \quad (3.32)$$

$$= \sum_i dq_i \quad (3.33)$$

which, with the use of a Lagrange multiplier, leads to the following form of the minimization principle:

$$\frac{\partial E_v}{\partial q_i} = \mu \quad \forall \quad i; \quad (3.34)$$

$$\frac{\partial E_v}{\partial p_i^\alpha} = 0 \quad \forall \quad i, \alpha. \quad (3.35)$$

3.3 Ionic limit approximation of the electrostatic interaction energy

Having made sure that the partition of the total density in terms of ionic contributions is well defined, in this section a major part of the electrostatic interaction energy is approximated in this limit.

3.3.1 Unknown part of the DFT functional

It is convenient to isolate a major contribution to the electron-electron repulsion energy from the universal functional $F[\rho]$ as follows:

$$F[\rho] = E_H[\rho] + F_{\text{Txc}}[\rho] \quad (3.36)$$

$$E_H = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (3.37)$$

where E_H is referred to as Hartree energy, F_{Txc} contains the kinetic energy as well as the difference between the true electron-electron repulsion energy and that obtained with a Hartree term. Rewriting the unknown functional in this way allows us to “contain” the error in a somewhat smaller term than before, $F_{\text{Txc}}[\rho] < F[\rho]$, while explicitly evaluating a major contribution via the term E_H .

In the context of developing a polarisable classical IP, E_H can be re-cast rather easily into an analytic form once the density is expressed in terms of localised ionic contributions, as presented in Section 3.3, while F_{Txc} poses a greater challenge.

A perturbative approach to F_{Txc} energy evaluation is presented in Section 3.4.1 which allows us to circumvent this challenge to some extent by modelling *changes* in F_{Txc} energy about a reference state rather than the energy itself.

3.3.2 Electrostatic interaction energy in the ionic limit

The total energy can be written as:

$$E[\rho] = F_{\text{Txc}}[\rho] + E_{\text{H}}[\rho] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + E_{\text{ii}} \quad (3.38)$$

where the last term is the interaction energy between ionic nuclei, respectively. The total charge density ρ is rewritten in terms of atom-centered localised contributions $\{\rho_i^{\text{ref}}\}$ and $\{\Delta\rho_i\}$:

$$\rho(\mathbf{r}) = \sum_i^{N_{\text{atm}}} (\rho_i^{\text{ref}}(\mathbf{r}) + \Delta\rho_i(\mathbf{r})) \quad (3.39)$$

In this thesis $\{\rho_i^{\text{ref}}\}$ are assumed to be spherically symmetric, not carrying any multipole moments, while changes in charge density, $\{\delta\rho_i\}$, can polarize up to a dipole moment.

$$\int \rho_i^{\text{ref}} d\mathbf{r} = q_i^{\text{ref}} \quad (3.40)$$

$$\int (\mathbf{r} - \mathbf{r}_i) \rho_i^{\text{ref}} d\mathbf{r} = 0 \quad (3.41)$$

$$\int \Delta\rho_i d\mathbf{r} = \Delta q_i \quad (3.42)$$

$$\int (\mathbf{r} - \mathbf{r}_i) \Delta\rho_i d\mathbf{r} = \mathbf{p}_i \quad (3.43)$$

so that the total ionic reference and total charge are defined as $q_i^0 \equiv Z_i + q_i^{\text{ref}}$ and $q_i \equiv q_i^0 + \Delta q_i$ respectively, where Z_i is the nuclear charge. Substituting in the ionic representation of density into the expression for $E_{\text{H}} + E_v + E_{\text{ii}}$ the result can be written as a sum of a constant, the on-site interaction term, $E^{\text{ES,self}}$, and an inter-site interaction energy E^{ES} . The constant is omitted because only the energy differences have a physical meaning, and so one obtains:

$$E_{\text{H}} + E_v + E_{\text{ii}} = \text{const.} + E^{\text{ES,self}} + E^{\text{ES}} \quad (3.44)$$

$$E^{\text{ES,self}} = \sum_i \left[Z_i \int \frac{\Delta\rho_i(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' + \frac{1}{2} \int \int \frac{\Delta\rho_i(\mathbf{r})\Delta\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \right] \quad (3.45)$$

$$E^{\text{ES}} = \frac{1}{2} \sum_i \sum_{j \neq i} \int \int \frac{(\rho_i^{\text{rf,ion}}(\mathbf{r}) + \Delta\rho_i(\mathbf{r}))(\rho_j^{\text{rf,ion}}(\mathbf{r}') + \Delta\rho_j(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (3.46)$$

where $\rho_i^{\text{rf,ion}}(\mathbf{r}) \equiv Z_i\delta(\mathbf{r} + \mathbf{r}_i) - \rho_i^{\text{ref}}(\mathbf{r})$. The terms $E^{\text{ES,self}}$ and E^{ES} in equation 3.44 are approximated in a way that allows integration of the electron density to obtain an

expression in terms of a few free parameters and self-consistent variables for charge and dipole moment. The integrand factor $1/|\mathbf{r} - \mathbf{r}'|$ is approximated as a constant in the self-energy expression, giving a simple final form:

$$Z_i \int \frac{\Delta\rho_i(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \approx \text{const.} Z_i \int \Delta\rho_i(\mathbf{r}') d\mathbf{r}' \quad (3.47)$$

$$\frac{1}{2} \int \int \frac{\Delta\rho_i(\mathbf{r})\Delta\rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \approx \frac{1}{2} \text{const.}' \int \int \Delta\rho_i(\mathbf{r})\Delta\rho_i(\mathbf{r}') d\mathbf{r}d\mathbf{r}' \quad (3.48)$$

$$E^{\text{ES,self}} \approx \sum_i a_i^{\text{i-q}} \Delta q_i + \frac{1}{2} d_i^{\text{q-q}} \Delta q_i^2 + \frac{1}{2} d_i^{\text{p-p}} p_i^2 \quad (3.49)$$

where $a_i^{\text{i-q}} > 0$, $d_i^{\text{q-q}} > 0$ and $d_i^{\text{p-p}} > 0$ are constants. The approximation of the inter-ionic ($i \neq j$) interaction energy E^{ES} has been presented in Chapter 2 and has the following form:

$$E^{\text{ES}} \approx \frac{1}{2} \sum_i \sum_{j \neq i} E_{ij}^{\text{ES}} \quad (3.50)$$

$$\begin{aligned} E_{ij}^{\text{ES}} \equiv & q_i q_j \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) \right) \\ & + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\ & - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{pp}} \tilde{I}_0(r_{ij}) \right) \end{aligned} \quad (3.51)$$

3.4 Approximate DFT as a perturbation about a reference state

Explicit dependence of the universal functional on the density is not known exactly. In deriving ionic IPs this limitation is addressed by approximating the total energy as a sum of a reference state and a perturbation about the reference state, introducing perturbation variables that can be considered small. The energy dependence on such “small” variables can then be captured via the Taylor expansion. This brings about a simplified analytic form that depends on empirical parameters, suitable for classical interatomic potentials.

In Section 3.3.1 the total energy functional was re-expressed as a sum of a term that can be evaluated explicitly in terms of the input density and a term that is to be approximated via a perturbation technique. In Section 3.4.1 an $\mathcal{O}(\delta\rho^2)$ approximation to the unknown part of the functional is presented. In Section 3.4.2 the approximated density functional is evaluated for the electron density in the ionic limit. Approximations that represent the energy of the ionic polarisability and charge transfer are highlighted.

Importantly, for some intended applications of charge transfer models, the canonical approximations (Eq. 1.25 and 1.29) may not be valid.

3.4.1 An $\mathcal{O}(\delta\rho^2)$ energy functional approximation

Following the discussion in Section 3.3.1, the energy functional can be expressed in the following form:

$$E[\rho] = F_{\text{Txc}}[\rho] + E_{\text{H}}[\rho] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (3.52)$$

where the last two terms can be evaluated directly in terms of the density. Alternatively, the last two terms can be approximated in terms of coefficients that describe the density, such as the approximation in terms of ionic monopole and dipole moments presented in Section 3.3. The first term cannot be evaluated in terms of the input density explicitly and in this section, instead, small changes in F_{Txc} about a value evaluated at a reference input density are approximated via the Taylor expansion.

The perturbation of F_{Txc} is about a reference state represented by ρ^{ref} or $\{c_n^{(i)\text{ref}}\}$. The reference state is *not* a ground state in general and, furthermore, depends on the nuclear positions. When deriving ionic IPs, ρ^{ref} corresponds to a sum of ion-centered rigid spherical densities, $\rho^{\text{ref}} = \sum_i \rho_i^{\text{ref}}$, and hence is defined in terms of ionic positions – this makes $F_{\text{Txc}}[\rho^{\text{ref}}]$ and its derivatives functions of atomic positions as well. In Section 3.4.2 it is highlighted that the canonical approximation, also adopted in our QEqTS IP, is to assume, instead, that the derivatives of $F_{\text{Txc}}[\rho^{\text{ref}}]$ are independent of atomic positions.

The second order expressions are the following:

$$F_{\text{Txc}}^{(2)}[\rho] \equiv F_{\text{Txc}}[\rho^{\text{ref}}] + \int \left. \frac{\delta F_{\text{Txc}}}{\delta \rho(\mathbf{r})} \right|_{\text{ref}} \Delta \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \left. \frac{\delta^2 F_{\text{Txc}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right|_{\text{ref}} \Delta \rho(\mathbf{r}) \Delta \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (3.53)$$

$$\begin{aligned} F_{\text{Txc}}^{(2)}(\{c_m^{(l)}\}) &\equiv F_{\text{Txc}}(\{c_m^{(l)\text{ref}}\}) + \sum_i \sum_n \left. \frac{\partial F_{\text{Txc}}}{\partial c_n^{(i)}} \right|_{\text{ref}} \Delta c_n^{(i)} + \frac{1}{2} \sum_{i,j} \sum_{n,n'} \left. \frac{\partial^2 F_{\text{Txc}}}{\partial c_n^{(i)} \partial c_{n'}^{(j)}} \right|_{\text{ref}} \Delta c_n^{(i)} \Delta c_{n'}^{(j)} \\ &= F_{\text{Txc}}(\{c_m^{(l)\text{ref}}\}) + \sum_i \sum_n \left[\left. \frac{\partial F_{\text{Txc}}}{\partial c_n^{(i)}} \right|_{\text{ref}} \Delta c_n^{(i)} + \frac{1}{2} \sum_{n'} \left. \frac{\partial^2 F_{\text{Txc}}}{\partial c_n^{(i)} \partial c_{n'}^{(i)}} \right|_{\text{ref}} \Delta c_n^{(i)} \Delta c_{n'}^{(i)} \right] \\ &\quad + \frac{1}{2} \sum_{i,j \neq i} \sum_{n,n'} \left. \frac{\partial^2 F_{\text{Txc}}}{\partial c_n^{(i)} \partial c_{n'}^{(j)}} \right|_{\text{ref}} \Delta c_n^{(i)} \Delta c_{n'}^{(j)} \end{aligned} \quad (3.54)$$

where $\Delta \rho = \rho - \rho^{\text{ref}}$ and $\Delta c_n^{(i)} = c_n^{(i)} - c_n^{(i)\text{ref}}$ and derivatives are evaluated at reference density, represented by ρ^{ref} or $\{c_m^{(l)\text{ref}}\}$. The approximate total energy expression,

including interactions between ionic nuclei, is defined with the use of $F_{\text{Txc}}^{(2)}(\{c_m^{(l)}\})$:

$$E^{(2)}(\{c_m^{(l)}\}) \equiv F_{\text{Txc}}^{(2)}(\{c_m^{(l)}\}) + E_{\text{H}}(\{c_m^{(l)}\}) + E_{\text{v}}(\{c_m^{(l)}\}) + E_{\text{ii}} \quad (3.55)$$

where the last two terms stand for the electron interactions with the nuclei and the interaction between nuclei, previously defined in Section 3.3.2.

As already mentioned, partial derivatives in the above expressions are functions of interatomic displacements $\{\mathbf{r}_{ij}\}$. To highlight this fact, and to simplify notation, it is convenient to introduce functions $\tilde{A}_n^{(i)}(\{\mathbf{r}_{ij}\})$ and $\tilde{D}_{nm}^{(i,j)}(\{\mathbf{r}_{ij}\})$:

$$\tilde{A}_n^{(i)}(\{\mathbf{r}_{ij}\}) \equiv \left. \frac{\partial F_{\text{Txc}}}{\partial c_n^{(i)}} \right|_{\text{ref}} \quad (3.56)$$

$$\tilde{D}_{n,n'}^{(i,j)}(\{\mathbf{r}_{ij}\}) \equiv \left. \frac{\partial^2 F_{\text{Txc}}}{\partial c_n^{(i)} \partial c_{n'}^{(j)}} \right|_{\text{ref}} \quad (3.57)$$

In Section 3.5 the terms $\tilde{A}_n^{(i)}(\{\mathbf{r}_{ij}\})$ and $\tilde{D}_{nm}^{(i,j)}(\{\mathbf{r}_{ij}\})$ are combined with the on-site electrostatic interaction $E^{\text{ES,self}}$ from Section 3.3.2, to obtain the QEq and other self-energy terms that appear in QEqTS and other IPs.

3.4.2 An $\mathcal{O}(\delta\rho^2)$ energy functional in the ionic limit

The classical polarisable IP is obtained via two approximations, the use of a perturbative energy expression as in Sections 3.3 and 3.4.1 as well as the representation of the total charge density in the ionic limit via a few density-representing coefficients, as in Section 3.3. The latter can be seen to correspond, implicitly, to representing the ground state density using an atom-centered truncated basis set, as demonstrated in Section 3.2.3.

The reference density ρ^{ref} and the variable change in density $\Delta\rho$ were rewritten in terms of atom-centered representations in Section 3.3.2, $\rho(\mathbf{r}) = \sum_i^{N_{\text{atm}}} \rho_i^{\text{ref}}(\mathbf{r}) + \Delta\rho_i(\mathbf{r})$. The contributions ρ_i^{ref} are assumed to be spherically symmetric, not carrying any multipole moments and of fixed radial extent; $\Delta\rho_i$, in general, can polarize up to a dipole moment, integrates to a variable number of particles and also has a fixed radial extent.

Substituting in the ionic representation of density into the approximated energy

expression $E^{(2)}$, from Section 3.4.1, we get:

$$\begin{aligned}
E_{\text{tot}} &= F_{\text{Txc}}^{(2)} + E_{\text{H}} + E_v + E_{\text{ii}} \\
&= F_{\text{Txc}} \Big|_{\text{ref}} + \sum_i \left[\frac{\partial F_{\text{Txc}}}{\partial q_i} \Delta q_i + \sum_{\alpha} \frac{\partial F_{\text{Txc}}}{\partial p_i^{\alpha}} p_i^{\alpha} \right. \\
&\quad \left. + \frac{1}{2} \frac{\partial^2 F_{\text{Txc}}}{\partial q_i^2} (\Delta q_i)^2 + \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial F_{\text{Txc}}}{\partial p_i^{\alpha} \partial p_i^{\beta}} p_i^{\alpha} p_i^{\beta} + \sum_{\alpha} \frac{\partial F_{\text{Txc}}}{\partial q_i \partial p_i^{\alpha}} \Delta q_i p_i^{\alpha} \right] \\
&\quad + \sum_{i, j \neq i} \left[\frac{1}{2} \frac{\partial^2 F_{\text{Txc}}}{\partial q_i \partial q_j} \Delta q_i \Delta q_j + \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial F_{\text{Txc}}}{\partial p_i^{\alpha} \partial p_j^{\beta}} p_i^{\alpha} p_j^{\beta} + \frac{1}{2} \sum_{\alpha} \left(\frac{\partial F_{\text{Txc}}}{\partial q_i \partial p_j^{\alpha}} \Delta q_i p_j^{\alpha} \right. \right. \\
&\quad \left. \left. + \frac{\partial F_{\text{Txc}}}{\partial p_i^{\alpha} \partial q_j} p_i^{\alpha} \Delta q_j \right) \right] \\
&\quad + E_{\text{H}} + E_v + E_{\text{ii}} \tag{3.58}
\end{aligned}$$

As already emphasized in Section 3.4.1, the partial derivatives of F_{Txc} depend on interatomic positions, since the reference density itself depends on the atomic configuration.

3.5 Interatomic potential as DFT in the ionic limit

The approximations made so far, allow us finally to recover the familiar classical IPs for ionic systems. In particular, before attempting to use any given ionic IP one can try to estimate the domain of applicability of the model, given the approximations that go into it.

3.5.1 Non-polarisable interatomic potentials

Ionic IPs virtually always contain a short range exponential repulsion term which only depends on interatomic distances. This term is to be identified mainly with $F_{\text{Txc}}[\rho^{\text{ref}}]$ which, recall, depends on interatomic displacements $\{\mathbf{r}_{ij}\}$. In my derivations, the repulsive nuclear energy E_{ii} is contained in the electrostatic term E_{ES} where it is absorbed by the ionic density $\{\rho_i^{rf, ion}\}$ which upon further approximations gets absorbed into a single ionic charge q_i^0 . In reality, of course, nuclear cores are point-like in comparison to the finite extent of the disperse valence electrons and, hence, at very short range distances ($\leq \sim 1a_0$) E_{ii} repulsive term increasingly contributes to the overall repulsion. This effect is also captured in the short-range exponential repulsion. In this thesis, Morse-stretch is used and this additionally includes a cohesive contribution. Morse-stretch term adds cohesive contribution to an ionic model that is otherwise too simplistic to capture electrostatic interactions explicitly with sufficient accuracy.

$$E^{\text{MS}} \sim F_{\text{Txc}}[\rho^{\text{ref}}] \tag{3.59}$$

where the symbol “ $\sim$ ” is used to indicate that a strict equality is not quite appropriate, given that the interactions formally captured in E^{ES} are in practice represented partly by terms such as E^{MS} .

The simplest of ionic IPs, the rigid ion model (RIM), is then identified with the non-self-consistent expression:

$$E^{\text{RIM}'} = \frac{1}{2} \sum_{i,j \neq i}^{N_{\text{atm}}} B_{ij} e^{-\gamma_{ij} r_{ij}} + E^{\text{ES}}(\{q_i \equiv q_i^0, \mathbf{p}_i \equiv \mathbf{0}\}) \quad (3.60)$$

OR

$$E^{\text{RIM}} = E^{\text{MS}} + E^{\text{ES}}(\{q_i \equiv q_i^0, \mathbf{p}_i \equiv \mathbf{0}\}) \quad (3.61)$$

$$E_{ij}^{\text{ES}}(\{q_i \equiv q_i^0, \mathbf{p}_i \equiv \mathbf{0}\}) = q_i^0 q_j^0 \frac{1}{r_{ij}} \quad (3.62)$$

with E^{ES} being evaluated with $w_{ij}^{\text{qq}} = 1.0$ and I_0 based on Diract delta functions (point charges)¹⁰, as defined in Section 3.3. Normally, simple ionic models do not include Morse-stretch term and instead use repulsive term as in $E^{\text{RIM}'}$, possibly with the added dispersion $1/r_{ij}^6$ or $1/r_{ij}^8$ terms due to long-range correlations in the term $F_{\text{Txc}}[\rho^{\text{ref}}]$ – this recovers the Born-Mayer expression introduced in Chapter 1. In this thesis it is convenient to define the simplest fixed-charge ionic model with the use of Morse-stretch, E^{RIM} , in order to have an expression more easily comparable to MS-Q, TS and QEqTS models, all of which use Morse-stretch for short-range interactions.

3.5.2 Polarizable interatomic potentials

Next, I present polarizable IPs studied in this thesis, highlighting the self-energy approximations, which are briefly discussed in Section 3.6.

The $E^{\text{ES,self}}$ term in Section 3.4.2 as well as terms that involve partial derivatives of F_{Txc} , i.e. $\tilde{A}_n^{(i)}(\{\mathbf{r}_{ij}\})$ and $\tilde{D}_{nm}^{(i,j)}(\{\mathbf{r}_{ij}\})$. While on-site electrostatic potential and electrostatic field create the driving force for transferring charge and inducing dipole moments, the self-energy terms represent the corresponding energy cost. Self-energy terms control how “easy” or “difficult” it is to change the ion’s charge from a reference value or to induce a dipole. The canonical approximation of the self-energy terms, also adapted here, is to set most terms to zero and to represent the remaining terms by

¹⁰Or, equivalently, simply by setting $w_{ij}^{\text{qq}} = 0.0$.

constants, as follows:

$$\frac{\partial F_{\text{Txc}}(\{\mathbf{r}_{ij}\})}{\partial q_s} + a_s^{\text{i-q}} \equiv A_s \quad (3.63)$$

$$\frac{\partial F_{\text{Txc}}(\{\mathbf{r}_{ij}\})}{\partial p_s^\alpha} \equiv 0 \quad (3.64)$$

$$\frac{1}{2} \frac{\partial^2 F_{\text{Txc}}(\{\mathbf{r}_{ij}\})}{\partial q_s \partial q_{s'}} + \frac{1}{2} \delta_{ss'} d_s^{\text{q-q}} \equiv \delta_{ss'} D_s \quad (3.65)$$

$$\frac{1}{2} \frac{\partial^2 F_{\text{Txc}}(\{\mathbf{r}_{ij}\})}{\partial p_s^\alpha \partial p_{s'}^\beta} \equiv \delta_{s,s'} \delta_{\alpha\beta} \epsilon_s \quad (3.66)$$

$$\frac{\partial^2 F_{\text{Txc}}(\{\mathbf{r}_{ij}\})}{\partial q_s \partial p_{s'}^\alpha} \equiv 0 \quad (3.67)$$

where A_s , D_s and ϵ_s are constants. This gives the following simple expression for the self-energy:

$$E^{\text{self}} = \sum_{i=1}^{N_{\text{atm}}} \left[A_i \Delta q_i + D_i \Delta q_i^2 + \epsilon_i p_i^2 \right] \quad (3.68)$$

If a polarisable IP only includes charge transfer or else inducible dipoles, then E^{self} excludes the terms ϵ_i or A_i and D_i , respectively.

It is important to emphasize that there is no reason *a priori* to assume that the approximations for the self-energy are adequate for applications to heterogeneous atomic environments, such as near a defect or a surface. In particular, the A_i and D_i (and ϵ_i) parameters may have a limited transferability. Additionally, the quadratic expression, based on the Taylor expansion, assumes that changes in charge density are relatively small – something that may not be the case in a given system of interest. The transferability of the self-energy expression to heterogeneous atomic environments is something that needs to be tested.

Tangney-Scandolo polarisable ion potential

Tangney-Scandolo polarisable-ion potential is obtained as follows:

$$E^{\text{TS}} = E^{\text{MS}} + E^{\text{ES}}(\{q_i \equiv q_i^0, \mathbf{p}_i\}) + \sum_i \epsilon_i p_i^2 \quad (3.69)$$

$$\begin{aligned} E_{ij}^{\text{ES}}(\{q_i \equiv q_i^0, \mathbf{p}_i\}) = & q_i^0 q_j^0 \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) \right) \\ & + (p_i^\alpha q_j^0 - q_i^0 p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\ & - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{pp}} \tilde{I}_0(r_{ij}) \right) \end{aligned} \quad (3.70)$$

where $1/(2\epsilon_i)$ is identified with the ionic polarisability. In all work up to this thesis, E^{ES} was evaluated with $w_{ij}^{\text{qq}} = w_{ij}^{\text{pp}} = 0$ and w_{ij}^{qp} as a fitting parameter; $\frac{\partial}{\partial r_{ij}^\alpha} (-w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}))$

corresponds to the short-range dipole correction following the work M. Wilson and P. Madden, as discussed in Sections 1.3.1 and 2.2.2. In this thesis $w_{ij}^{\text{qq}} = w_{ij}^{\text{pp}} \neq 0$ are also treated as fitting parameters. Furthermore, as demonstrated in Chapter 2, $I_0(r_{ij})$ used in TS IP corresponds to Coulomb interaction of a spherical Slater-type density and Dirac-delta (point-particle) distribution¹¹. This form of $I_0(r_{ij})$ is retained in this thesis based on the combination of the ability to fit reference training set and the computational speed with which it can be evaluated – this is discussed in detail in Chapter 2.

MS-Q charge equilibration potential

The popular MS-Q charge-equilibration model of A. Rappe, W. Goddard *et al.*, introduced in Section 1.4.1, is similarly obtained as:

$$E^{\text{MS-Q}} = E^{\text{MS}} + E^{\text{ES}}(\{q_i, \mathbf{p}_i \equiv \mathbf{0}\}) + \sum_i (A_i \Delta q_i + D_i \Delta q_i^2) \quad (3.71)$$

$$E_{ij}^{\text{ES}}(\{q_i, \mathbf{p}_i \equiv \mathbf{0}\}) = q_i q_j \left(\frac{1}{r_{ij}} - 1.0 \tilde{I}_0(r_{ij}) \right) \quad (3.72)$$

with E^{ES} being evaluated with $w_{ij}^{\text{qq}} = 1.0$ and I_0 based on spherically symmetric Slater-type orbitals, as defined in Section 2.2.3.

QEqTS polarisable potential

Finally, the model that combines charge transfer and the polarisable ion TS model, first implemented by J. Sarsam and then extended by the present author to treat more realistically the effect of finite ionic size on nearest-neighbour electrostatic interactions, has the following form:

$$E^{\text{QEqTS}} = E^{\text{MS}} + E^{\text{ES}}(\{q_i, \mathbf{p}_i\}) + \sum_i (A_i \Delta q_i + D_i \Delta q_i^2 + \epsilon_i p_i^2) \quad (3.73)$$

$$\begin{aligned} E_{ij}^{\text{ES}}(\{q_i, \mathbf{p}_i\}) = & q_i q_j \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) \right) \\ & + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{qp}} \tilde{I}_0(r_{ij}) \right) \\ & - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \left(\frac{1}{r_{ij}} - w_{ij}^{\text{pp}} \tilde{I}_0(r_{ij}) \right) \end{aligned} \quad (3.74)$$

with $\tilde{I}_0$ being identical to those used in TS IP.

¹¹Recall, $\tilde{I}_0(r_{ij}) = 1/r_{ij} - I_0(r_{ij})$.

3.6 Summary

In this section, approximations that were introduced in order to derive polarisable ionic IPs are summarised. It is highlighted that the approximations that underpin the QEq self-energy are likely to break down in some systems for which the model was intended.

There are two types of approximations that underpin polarisable IPs. Firstly, as with all ionic IPs, the total charge density is assumed to be representable as a sum of localised ionic contributions, $\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r})$. As discussed in Section 3.3 and elaborated further in Chapter 2, this allows us to approximate the main contribution to the electrostatic interaction energy via a simple analytic function E^{ES} that depends on ionic charges, dipoles and higher multipole moments.

Polarisable ionic IPs differ from simple fixed-charge rigid-ion IPs qualitatively in that the former require solving self-consistent-field (SCF) type equations to obtain an optimal set of variables that describes charge density, such as charge transfer, ionic size or multipole moments. Such SCF type equations are introduced by approximating the electron kinetic and part of the electron-electron repulsion energy via a perturbation technique described in Section 3.4.1 and by approximating the on-site Hartree energy, in Section 3.3.2. This results in an $\mathcal{O}(\Delta c_n^2)$ expression in SCF variables $\{\Delta c_n\}$ which is used to define the self-energy term in a polarisable IP. In the QEqTS IP $\{\Delta c_n\}$ correspond to inter-ionic charge transfers and induced dipole moments. In general, self-energy parameters A_i and D_i (and ϵ_i) are functions of ionic positions, but in QEqTS IP we approximate them as constants.

The assumptions and approximations that underpin polarisable ionic IPs were highlighted in this chapter, but their domain of applicability was not discussed. An analysis of the QEqTS model is deferred to Chapters 6 and 7 where it is applied to a thermally perturbed, pristine BaTiO₃ crystal, as well as with neutral O and Ti vacancies. In particular, the results of those two chapters are consistent with the view that the ionic limit and the approximated self-energy expression are approximately valid for bulk BaTiO₃ and the system with a neutral Oxygen vacancy. In contrast, for the system with a neutral Ti vacancy the results and analysis suggest that both the ionic limit and the self-energy approximation partly break down.

Chapter 4

Localised representations of the ground state based on the Kohn-Sham equations

In Chapters 6 and 7 IP charge transfer and induced dipole variables are compared to changes in the underlying ground state density. The analysis is facilitated by representing the ground state density of the extended condensed phase in terms of contributions localised at ionic nuclei. The methods used for representing the ground state in terms of localised contributions are based on the Kohn-Sham (KS) equations that map the density of the interacting electrons onto a fictitious system of non-interacting fermions. The KS equations are reviewed in Section 4.1 as a preliminary step. Furthermore, calculations are simplified by imposing periodic boundary conditions – this is introduced in Section 4.2

Maximally localised Wannier functions (MLWFs) are introduced in Section 4.3, primarily to facilitate the discussion in Chapter 6 – an analysis of polarisable IPs applied to bulk BaTiO₃. In Chapter 6 MLWFs are used to introduce well defined measures of similarity between changes in the charge density obtained with DFT calculations and density-describing variables obtained with polarisable QEqTS and TS IPs.

Finally, in Section 4.4 Löwdin population analysis is introduced, which provides one way to define ionic charges. Löwdin charges are occasionally evoked in the analysis of Chapters 6 and 7.

4.1 Kohn-Sham density functional theory

Recall from Section 3.1, the first HK theorem introduces a universal functional $F[\rho]$ that evaluates kinetic and repulsion energies for a system of electrons. However, for a system of *non-interacting* fermions in an external potential v^{eff} the HK functional and the variational principle subject to a constraint $\int \delta n(\mathbf{r}) d\mathbf{r} = 0$ have the following form¹:

$$E[n] = T_s[n] + \int n(\mathbf{r}) v^{\text{eff}}(\mathbf{r}) d\mathbf{r} \quad (4.1)$$

$$\int \left(\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\text{eff}}(\mathbf{r}) \right) \delta n(\mathbf{r}) d\mathbf{r} = 0 \quad (4.2)$$

where $F[\rho]$ has been indentified with the kinetic energy of the non-interacting fermions – $T_s[\rho]$. In this special case the kinetic (and total) energy functional and the ground state density can be evaluated by directly solving the following Schrödinger equation:

$$\left[-\frac{1}{2} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}) \quad (4.3)$$

$$n(\mathbf{r}) = \sum_{n=1}^{N_e} |\psi_n(\mathbf{r})|^2 \quad (4.4)$$

$$T_s[n] = \sum_{n=1}^{N_e} \epsilon_n - \int v^{\text{eff}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (4.5)$$

where N_e is the total number of electrons and the sum is over the N_e lowest energy eigenstates.

In 1965 W. Kohn and L. Sham (KS) demonstrated how to partition the energy functional of the system of *interacting* electrons in a way that isolates the $T_s[n]$ operator allowing one to evaluate it by solving the Schrödinger equation of a fictitious auxiliary system of non-interacting fermions[156]:

$$E[n] = E_H[n] + T_s[n] + E_{\text{xc}}[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \quad (4.6)$$

where $E_H[n]$ is the Hartree term introduced in Section 3.3.1, and $E_{\text{xc}}[n]$ is implicitly defined as $E_{\text{xc}}[n] \equiv F[n(\mathbf{r})] - E_H[n] + T_s[n]$. Good approximations exist for $E_{\text{xc}}[n]$ thus making the evaluation of the unknown universal functional $F[n]$ a tractable problem.

Extremising the energy in equation 4.6 gives an expression equivalent to the one from the example of non-interacting fermions:

$$\int \left(\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \left[v(\mathbf{r}) + \mu_{\text{xc}}(n(\mathbf{r})) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \right) \delta n(\mathbf{r}) d\mathbf{r} = 0 \quad (4.7)$$

where $\mu_{\text{xc}}(n(\mathbf{r})) = \delta E_{\text{xc}} / \delta n(\mathbf{r})$ and the expression in the square brackets defines the KS effective potential, $v^{\text{KS}}(\mathbf{r})$. Identifying $v^{\text{KS}}(\mathbf{r}) = v^{\text{eff}}(\mathbf{r})$ we can proceed as in the example

¹In this chapter $n(\mathbf{r})$ refers to the number density and integrates to a positive integer.

of non-interacting fermions and directly solve the Schrödinger equation:

$$v^{\text{KS}}(\mathbf{r}) \equiv \left[v(\mathbf{r}) + \mu_{\text{xc}}(\rho(\mathbf{r})) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \quad (4.8)$$

$$\left[-\frac{1}{2} \nabla^2 + v^{\text{KS}}(\mathbf{r}) \right] \psi_n^{\text{KS}}(\mathbf{r}) = \epsilon_n^{\text{KS}} \psi_n^{\text{KS}}(\mathbf{r}) \quad (4.9)$$

$$n(\mathbf{r}) = \sum_{n \in \text{occ.}} |\psi_n^{\text{KS}}(\mathbf{r})|^2 \quad (4.10)$$

where the summation is over the occupied, lowest energy states. The effective KS potential defines the Schrödinger equation affecting the solution for the ground state density and at the same time is itself a function of the density. Therefore the set of equations 4.8 – 4.10 has to be solved self-consistently. These equations and the DFT implementations that use them are usually referred to as the KS equations and KS-DFT, respectively. In our work all *ab initio* calculations, presented in Chapters 6, 7, and 8, are based on KS-DFT.

Once the self-consistency is reached, one can evaluate the total energy:

$$E[n] = \underbrace{\left(\sum_{n \in \text{occ.}} \epsilon_n^{\text{KS}} - \int n(\mathbf{r}) \left[v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{\text{xc}}(n(\mathbf{r})) \right] d\mathbf{r} \right)}_{T_s[n]} + \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n] \quad (4.11)$$

$$= \sum_{n \in \text{occ.}} \epsilon_n^{\text{KS}} - \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[n(\mathbf{r})] - \int \mu_{\text{xc}}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad (4.12)$$

Caution must be taken interpreting KS orbitals and energies and derived quantities such as MLWFs introduced in Section 4.2 – neither can they be said to be entirely devoid of physical meaning nor do they have a well-defined nonambiguous interpretation.

4.2 Bloch states

The ground state density for a system of interacting electrons is linked to the MLWFs via an auxiliary KS fictitious system of non-interacting fermions. Before introducing MLWFs, it is best to review how a solution is obtained in practice in standard DFT calculations.

KS equations map the problem of interacting electrons onto a “fictitious” system of non-interacting fermions, which are eigenstates of a one electron Hamiltonian with a local effective potential. The KS potential is uniquely defined (up to a constant) so as to produce non-interacting fermion wavefunctions that reproduce the correct ground state density for the original system of interacting electrons. The eigenfunctions of the

KS one electron Hamiltonian are ϕ_i^{KS} and the ground state density is:

$$n(\mathbf{r}) = \sum_i f_i^{\text{occ.}} |\phi_i^{\text{KS}}(\mathbf{r})|^2 \quad (4.13)$$

where $f_i^{\text{occ.}}$ is the occupation number, which for a band gap insulator is simply 1 or 0.

In condensed matter physics one often studies extended systems, such as bulk material which may include point defects or surfaces. For such extended systems it is common to use periodic boundary conditions (PBCs), which introduces further simplifications. In particular, in Chapters 6 and 7 we carry out molecular dynamics simulations and DFT calculations for the extended BaTiO₃ crystal, which we represent using a simulation cell (a supercell) subject to PBCs. We place the following discussion in the context of the actual DFT calculations in our work, namely for the snapshot configurations taken from a molecular dynamics simulation, subject to PBCs.

Consider a supercell of size $N_1 \times N_2 \times N_3$ under periodic boundary conditions $\mathbf{r} \rightarrow \mathbf{r} + N_i \mathbf{a}_i$, defined via primitive unit cell vectors $\mathbf{a}_1, \mathbf{a}_2$ and $\mathbf{a}_3$. For such a system the one electron KS potential is periodic, $v^{\text{KS}}(\mathbf{r}) = v^{\text{KS}}(\mathbf{r} + \mathbf{R})$, for any lattice vector $\mathbf{R} \in \{n_1 \mathbf{A}_1 + n_2 \mathbf{A}_2 + n_3 \mathbf{A}_3 : n_i \in \mathbb{Z}, \mathbf{A}_i \equiv N_i \mathbf{a}_i\}$. Therefore, KS Hamiltonian commutes with translation operators, $\hat{T}_{\mathbf{R}} \equiv e^{-i\mathbf{R} \cdot \hat{\mathbf{p}}}$, which also commute amongst themselves, $\hat{T}_{\mathbf{R}'} \hat{T}_{\mathbf{R}} = \hat{T}_{\mathbf{R}} \hat{T}_{\mathbf{R}'}$. The eigenvalue equation for the unitary operator $\hat{T}_{\mathbf{R}}$ defines Bloch states² $\{\psi_{\mathbf{k}}\}$ (up to a phase)[157, 158] and eigenvalues that have the following form:

$$\hat{T}_{\mathbf{R}} \psi_{\mathbf{k}} = e^{-i\mathbf{k} \cdot \mathbf{R}} \psi_{\mathbf{k}} \quad (4.14)$$

The form of the eigenvalue introduces crystal momentum wavevectors $\{\mathbf{k}\}$ as good quantum numbers, which label the eigenvalues in Eq. 4.14. Furthermore, imposing Born-von Karman boundary conditions on the wavefunctions, $\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R})$, restricts $\mathbf{k}$ to take on a discrete set of real values:

$$e^{-i\mathbf{k} \cdot \mathbf{R}} = 1 \quad (4.15)$$

$\Rightarrow$

$$\mathbf{k} = m_1 \mathbf{B}_1 + m_2 \mathbf{B}_2 + m_3 \mathbf{B}_3 \quad (4.16)$$

$$= \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 \quad (4.17)$$

where $m_i \in \mathbb{Z}$, $\mathbf{B}_i$ define the reciprocal lattice unit cell commensurate with the supercell, e.g. $\mathbf{B}_1 = 2\pi \mathbf{A}_2 \times \mathbf{A}_3 / (\mathbf{A}_1 \cdot \mathbf{A}_2 \times \mathbf{A}_3)$, and $\mathbf{b}_i$ are the reciprocal lattice vectors for the

²In Chapters 6 and 7 we carry out DFT calculations for snapshot configurations taken from molecular dynamics simulations, subject to PBCs. The translational invariance $v^{\text{KS}}(\mathbf{r}) = v^{\text{KS}}(\mathbf{r} + \mathbf{R})$ is preserved because we impose PBCs, but Bloch's theorem itself does not require PBCs as a prerequisite[157, 158].

primitive unit cell; $\mathbf{B}_i = \mathbf{b}_i/N_i$. This leads to a total of $N_{\mathbf{k}} \equiv N_1 N_2 N_3$ unique eigenvalues in the Eq. 4.14; these are conventionally labelled by $N_{\mathbf{k}}$ unique wavevectors in the first Brillouin zone, since $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}} = e^{i\mathbf{k}\cdot\mathbf{R}}$ for any reciprocal lattice vector³ $\mathbf{G}$. For each allowed value of $\mathbf{k}$ in the Brillouin zone there are, in general, many different Hamiltonian eigenstates with energies $\epsilon_n(\mathbf{k})$. This, in turn, defines the energy bands as functions of $\mathbf{k}$. Solving one electron KS Hamiltonian in terms of Bloch states allows one to rewrite the ground state density as:

$$n(\mathbf{r}) = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}}^{\text{occ.}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 \quad (4.18)$$

where $f_{n,\mathbf{k}}^{\text{occ.}}$ is the occupation number; for a band gap insulator it takes on a value of 1 or 0. These Bloch states form a complete orthonormal set in the one electron Hilbert space.

4.3 Maximally localised Wannier functions

A set of Bloch states can be transformed into a set of orthogonal states localised in position space, called Wannier functions[159–161].

The procedure of obtaining Wannier functions both resembles and differs from the familiar Fourier transform. The similarity is that the transform involves integration (or summation) over reciprocal space to obtain a position space representation. For example, for an isolated single energy band $\epsilon_n(\mathbf{k})$, the Wannier function can be defined, in ket notation, as follows:

$$|W_{\mathbf{R},n}\rangle \equiv \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{n,\mathbf{k}}\rangle \quad (4.19)$$

$$= \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{n,\mathbf{k}}\rangle \quad (4.20)$$

where the summation is appropriate if a discrete uniform $\mathbf{k}$ -mesh is used instead of a continuum⁴; $|W_{\mathbf{R},n}\rangle$ is a Wannier function localised in a supercell⁵ at $\mathbf{R}$ and $|\psi_{n,\mathbf{k}}\rangle$ is a Bloch state. The difference from the Fourier transform is that Wannier functions are not uniquely defined by Eq. 4.19 because Bloch states are only determined up to a phase. Multiplying a set of Bloch states $|\psi_{n,\mathbf{k}}\rangle$ by complex numbers $e^{i\phi_n(\mathbf{k})}$, with a real phase factor satisfying $\phi_n(\mathbf{k} + \mathbf{G}) = \phi_n(\mathbf{k}) + 2\pi m$, $m \in \mathbb{Z}$ for any reciprocal lattice vector $\mathbf{G}$, defines an equally valid set of Bloch states but leads to a distinct set of Wannier functions.

³ $\mathbf{G} = m_1\mathbf{B}_1 + m_2\mathbf{B}_2 + m_3\mathbf{B}_3$, commensurate with the supercell dimensions.

⁴Like in Fourier transforms, the factor $1/N_{\mathbf{k}}$ is a matter of convention

⁵The extended system consists of infinitely many supercells.

Thus, defining Wannier functions uniquely requires imposing some additional constraints – different types of constraints lead to distinct types of Wannier functions. Here I outline the process for obtaining maximally localised Wannier functions (MLWFs), following the review of N. Marzari, D. Vanderbilt *et al.*[162]. As we shall see, the properties of MLWFs make them suitable for carrying out the analysis in Chapter 6, where the QEeqTS IP is applied to bulk BaTiO₃.

The non-uniqueness in the definition of the Bloch states can be seen as a “freedom” to find alternative representations of the states in the single electron KS system and hence the manybody ground state density. N. Marzari, D. Vanderbilt *et al.*, have introduced a generalised unitary transformation that, for an isolated set of N_b possibly entangled bands⁶, maps a set of Bloch states to another set of Bloch states:

$$|\tilde{\psi}_{n\mathbf{k}}\rangle = \sum_{m=1}^{N_b} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}\rangle \quad (4.21)$$

$U_{mn}^{(\mathbf{k})}$ is a unitary transformation matrix, periodic in reciprocal space. A generalisation to metals can be found in Ref. 161. The tranformed Bloch states $|\tilde{\psi}_{n\mathbf{k}}\rangle$ are not energy eigenstates in general, and n does not indicate a band index any more. By introducing this transformation, the most general definition of Wannier functions can be provided, explicitly highlighting non-uniqueness of the transform for an arbitrary set $\{U_{mn}^{(\mathbf{k})}\}$:

$$|W_{\mathbf{R},n}\rangle = \frac{1}{N_k} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^{N_b} U_{mn}^{(\mathbf{k})} |\psi_{m\mathbf{k}}\rangle \quad (4.22)$$

This definition of Wannier functions can be seen as a unitary transformation of a manifold of Bloch states or a “rotation”. This is because for any isolated set of possibly entangled bands, indexed $\{n_1, n_2, \dots, n_{\max}\}$, Wannier functions $\{|W_{\mathbf{R},n_1}\rangle, \dots, |W_{\mathbf{R},n_{\max}}\rangle\}$ defined from this *subspace* of Bloch states $\{|\psi_{n_1,\mathbf{k}}\rangle, \dots, |\psi_{n_{\max},\mathbf{k}}\rangle\}$ span the same subspace:

$$\sum_{n=n_1}^{n_{\max}} \sum_{\mathbf{k}} |\psi_{n,\mathbf{k}}\rangle \langle \psi_{n,\mathbf{k}}| = \sum_{n=n_1}^{n_{\max}} \sum_{\mathbf{R}} |W_{\mathbf{R},n}\rangle \langle W_{\mathbf{R},n}| \quad (4.23)$$

In practice $\{|\psi_{n,\mathbf{k}}\rangle\}$ are taken to be the energy eigenstates of the KS single particle Hamiltonian, available at the end of a standard DFT calculation. Obtaining MLWFs can be seen as a post-processing step that determines a unique set of unitary transformation matrices $\{U_{mn}^{(\mathbf{k})}\}$ such that the sum of quadratic spreads of Wannier functions is minimised, which is defined as follows:

$$\Omega = \sum_n [\langle W_{\mathbf{0},n} | r^2 | W_{\mathbf{0},n} \rangle - \langle W_{\mathbf{0},n} | \mathbf{r} | W_{\mathbf{0},n} \rangle^2] \quad (4.24)$$

⁶a set of bands with a finite energy gap above and below.

Wannier functions so defined are real⁷[163] and form a complete orthonormal basis set in the one electron Hilbert space. It is simple to show that for any given n different Wannier functions are related by a translation $\langle \mathbf{r} - \mathbf{R}' | W_{\mathbf{R},n} \rangle = \langle \mathbf{r} | W_{\mathbf{R}+\mathbf{R}',n} \rangle$. Therefore, minimising Ω determines all Wannier functions.

Evaluation and minimisation of Ω , henceforth referred to as the Wannierization algorithm, is a highly non-trivial process[162] and has been implemented in a software package Wannier90[164]. In a DFT calculation, Wannier90 can be used as a post-processing tool, transforming the subspace of occupied Bloch states in the auxiliary KS one electron system to MLWFs, which in turn allows one to re-express the true ground state density as:

$$n(\mathbf{r}) = \sum_{\mathbf{R}} \sum_n f_n^{\text{occ.}} w_{n,\mathbf{R}}(\mathbf{r}) \quad (4.25)$$

$$w_{n,\mathbf{R}}(\mathbf{r}) \equiv 2 \langle W_{\mathbf{R},n} | \mathbf{r} \rangle \langle \mathbf{r} | W_{\mathbf{R},n} \rangle \quad (4.26)$$

where a factor of 2 is added assuming a spin degeneracy.

Note that, firstly, only the *sum* of spreads is minimised and, secondly, any given MLWF is localised within a supercell rather than at any particular ionic site. Nothing in the definition of the MLWFs implies that each individual MLWF has to be highly localised or centered close to an ionic core. Yet, in Chapter 6 it is empirically found that for a thermally perturbed BaTiO₃, each MLWF is highly localised on an ionic site, thus providing a concrete example of a partition of the ground state density in an ionic limit. Such a partition is not unique, nor has any clear unambiguous physical meaning. However, in Chapter 6 the use of MLWFs facilitates the comparison of charge transfer and induced dipole variables, defined within the QEqTS IP, to changes in the underlying ground state density.

4.4 Löwdin population analysis

This section describes the Löwdin population analysis for assigning ionic charges based on the ground state of a band-gap insulator, obtained using standard KS-DFT with the use of periodic boundary conditions. This reflects that type of system where Löwdin population analysis is invoked in this thesis, in Chapters 6 and 7. The domain of applicability of the Löwdin population analysis is more general, however[106].

For the KS system of non-interacting fermions one can expand single-particle wave-functions, $\psi_n(\mathbf{r})$, in terms of a basis set based on a linear combination of atomic orbitals

⁷For time-reversal invariant systems, up to an overall phase.

(LCAO), as follows:

$$\psi_n(\mathbf{r}) = \sum_{\sigma} c_{\sigma}^{(n)} \phi_{\sigma}(\mathbf{r}) \quad (4.27)$$

where $\{c_{\sigma}^{(n)}\}$ are the expansion coefficients and each $\phi_{\sigma}(\mathbf{r})$ is a normalised localised function centered at the position of one of the nuclei in the system, at $\mathbf{r}_i$. In general, depending on the chemical species, several atomic orbitals are used at each ionic site. Imposing normalisation the one-electron wavefunction⁸ leads to the definition of the overlap integrals[106]:

$$\int \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) d\mathbf{r} \equiv 1 \quad (4.28)$$

$$S_{\nu\sigma} \equiv \int \phi_{\nu}^*(\mathbf{r}) \phi_{\sigma}(\mathbf{r}) d\mathbf{r} \quad (4.29)$$

$\Rightarrow$

$$\sum_{\nu\sigma} c_{\nu}^{(n)*} S_{\nu\sigma} c_{\sigma}^{(n)} = 1 \quad (4.30)$$

When solving the Kohn-Sham equations, one uses a basis set different from the LCAO in general, for example the use of plane waves is common for extended condensed phases systems. Once the set of KS eigenstates $\{\psi_n(\mathbf{r})\}$ is obtained, each can be re-expressed using LCAO. This can be defined in terms of a projection operator:

$$P_{\text{LCAO}} \equiv \sum_{\sigma} |\phi_{\sigma}\rangle \langle \phi_{\sigma}| \quad (4.31)$$

$$|\psi_n\rangle \approx |\psi_n^{\text{LCAO}}\rangle \quad (4.32)$$

$$|\psi_n^{\text{LCAO}}\rangle \equiv P_{\text{LCAO}} |\psi_n\rangle \quad (4.33)$$

In principle a change-of-basis modifies the representation of a vector but not the vector itself, however the approximate sign is used, $|\psi_n\rangle \approx |\psi_n^{\text{LCAO}}\rangle$, to highlight that the LCAO basis set is incomplete in general. For a system of N_e non-interacting fermions in a KS system, a *spilling parameter* can be defined, $0 \leq \mathcal{S} \leq 1$, that measures the extent to which the set of N_e occupied $|\psi_n\rangle$ KS orbitals are successfully projected onto the LCAO basis set:

$$\mathcal{S} \equiv \frac{1}{N_e} \sum_{n \in \text{occ.}} \langle \psi_n | (1 - P_{\text{LCAO}}) | \psi_n \rangle \quad (4.34)$$

A value of $\mathcal{S} = 0$ corresponds to a perfect representation of the ground state KS wavefunction in terms of LCAO basis set, $|\psi_n\rangle = |\psi_n^{\text{LCAO}}\rangle \forall n \in \text{occ.}$. Finally, the charge of

⁸It is assumed to represent two spin-degenerate electrons.

an ion at position $\mathbf{r}_i$ is defined using the Löwdin population analysis as follows[165]:

$$N_i^e \equiv \sum_{n \in \text{occ.}} \sum_{\sigma \in i} [\mathbf{S}^{1/2} \mathbf{P}_{\text{LCAO}} \mathbf{S}^{1/2}]_{\sigma\sigma} \quad (4.35)$$

$$q_i^{\text{Lwdn}} \equiv -N_i^e + Z_i \quad (4.36)$$

where $\sigma \in i$ enumerates atomic orbitals that are centered at $\mathbf{r}_i$, the capital bold symbols, e.g. $\mathbf{S}$, stand for matrix representation of the operators with respect to the LCAO basis; $\mathbf{S}^{1/2}$ is defined such that $\mathbf{S}^{1/2} \mathbf{S}^{1/2} = \mathbf{S}$. Z_i is the charge of the nucleus i consistent with the pseudopotentials used in the DFT calculations in the present work, +10, +12, +6 for Ba, Ti and O respectively; N_i^e represents the fraction of the valence electron density that is associated with ion i . For a charge neutral system, if $\mathcal{S} = 0$, the Löwdin charges satisfy $\sum_i q_i^{\text{Lwdn}} = 0$, otherwise charge conservation is satisfied approximately.

In Chapter 6 Löwdin population analysis is applied to a thermally perturbed defect-free bulk BaTiO_3 and the spilling parameter is found to equal 0.02. This can be loosely interpreted as 98% of the ground state density being successfully represented using the LCAO basis.

Chapter 5

Methods used for atomistic simulations and parameterisation

In Chapters 6, 7 and 8 we compare several different IPs for BaTiO₃ in terms of their ability to reproduce reference *ab initio* interatomic forces, charge densities and selected physical properties. In each of these chapters, relevant computational details are described preceding the subsequent presentation of the results and the analysis. In the present chapter, instead, we describe the computational methods that are common to all three chapters.

This chapter is organised as follows. Molecular dynamics simulations are described in Section 5.1. The reference *ab initio* data is based on DFT calculations – these are discussed in Section 5.2. The force-matching method[122] is presented in Section 5.3. Obtaining an optimal set of parameters for an IP involves a series of steps, including molecular dynamics simulations, DFT calculations, and parameterisation, which are summarised in Section 5.4. Finally, details of crystal structure relaxations are presented in Section 5.5.

5.1 Molecular dynamics simulations

A given IP provides forces $\{\mathbf{F}_i\}$ on all ions. By Newton’s Second Law the force on an ion determines its acceleration, $\mathbf{a}_i$:

$$\mathbf{a}_i = \mathbf{F}_i / m_i \tag{5.1}$$

$$= - \frac{1}{m_i} \frac{\partial E^{\text{tot}}}{\partial \mathbf{r}_i} \tag{5.2}$$

where m_i and $\mathbf{r}_i$ are the ion’s mass and position and E^{tot} is the potential energy of the system. This, in turn, allows us to calculate ionic trajectories in time and to simulate

their dynamics. We use the Verlet algorithm[166, 167], which is based on the use of the Taylor expansion in the time variable.

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2 + \frac{1}{6}\frac{\partial^3\mathbf{r}_i}{\partial\Delta t^3} + \mathcal{O}(\Delta t^4) \quad (5.3)$$

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2 - \frac{1}{6}\frac{\partial^3\mathbf{r}_i}{\partial\Delta t^3} + \mathcal{O}(\Delta t^4) \quad (5.4)$$

$\Rightarrow$

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \mathbf{a}_i(t)\Delta t^2 + \mathcal{O}(\Delta t^4) \quad (5.5)$$

where $\mathbf{r}_i$, $\mathbf{v}_i$ and $\mathbf{a}_i$ are the ion's position, velocity and acceleration, respectively. Ionic positions can be evaluated iteratively at consecutive discrete time steps $n\Delta t$, for an integer n . In the present work we used $\Delta t = 30$ au ≈ 0.73 fs. As described, this is a time-reversible algorithm for simulations in the NVE ensemble, since the volume, the number of ions and the total energy are conserved¹.

We wish to simulate molecular dynamics at a range of temperatures at a constant (zero) pressure, rather than constant volume. The aim is to sample realistic system configurations where ions deviate from their equilibrium positions and hence are subject to a diverse set of non-vanishing forces. We use snapshot configurations taken from classical molecular dynamics as input for DFT calculations to generate reference *ab initio* data for subsequent use in parameterisation and analysis of IPs.

The temperature can be related to ionic velocities via the equipartition theorem, as follows:

$$\frac{3(N_{\text{atm}} - 1)}{2}k_B T = \lim_{\tau \rightarrow \infty} \sum_{i=1}^{N_{\text{atm}}} \frac{1}{2}m_i \langle v_i^2 \rangle_{\tau} \quad (5.6)$$

where τ is a time segment used for averaging and k_B is the Boltzmann's constant. Using the instantaneous velocities in Eq. 5.6, an instantaneous temperature can be defined, $T(t)$, which fluctuates during the course of the simulation. Assuming the Maxwell-Boltzmann velocity distribution, the standard deviation of the $T(t)$, $\sigma_{T(t)}$, is related to the number of ions and the (average) temperature as follows[168]:

$$\sigma_{T(t)} = T \sqrt{\frac{2}{3(N_{\text{atm}} - 1)}} \quad (5.7)$$

which informs us about the physically meaningful range of fluctuations in $T(t)$ that we should observe during a simulation. In our work, we use velocity rescaling to set the desired temperature T . Such a simulation corresponds roughly to an NVT ensemble. This simple algorithm introduces jump discontinuities in the total energy and ionic

¹Energy conservation was numerically verified.

velocities, however, we only use this algorithm to reach the target temperature and subsequently use an NPH ensemble, discussed below.

To control the pressure, we use the Parrinello-Rahman barostat[169], which we now summarise. A matrix $\underline{\mathbf{h}}$ is defined in terms of simulation cell lattice parameters $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ as the matrix columns:

$$\underline{\mathbf{h}} \equiv [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] \quad (5.8)$$

The position and velocity of ion i can be expressed as $\mathbf{r}_i = \underline{\mathbf{h}}\mathbf{s}_i$ and $\mathbf{v}_i = \underline{\mathbf{h}}\dot{\mathbf{s}}_i$, respectively, where $\{\mathbf{s}_i\}$ are expressed in scaled coordinates, i.e. using the lattice vectors $\mathbf{a}_i$ as a basis². The idea behind the Parrinello-Rahman barostat is to extend the system's Lagrangian to include the matrix components of $\underline{\mathbf{h}}$ as extra degrees of freedom, which, in turn, allows the simulation cell shape and volume to change during the course of the simulation. The original and the extended Lagrangians, $\mathcal{L}$ and $\mathcal{L}_{\text{ext}}$ respectively, have the following forms:

$$\mathcal{L} = \sum_{i=1}^{N_{\text{atm}}} \frac{1}{2} m_i \dot{\mathbf{s}}_i^{\top} \underline{\mathbf{h}}^{\top} \underline{\mathbf{h}} \dot{\mathbf{s}}_i - E^{\text{tot}} \quad (5.9)$$

$$\mathcal{L}_{\text{ext}} = \mathcal{L} - p_a V + \frac{1}{2} W_{\text{cell}} \text{Tr } \dot{\underline{\mathbf{h}}}^{\top} \dot{\underline{\mathbf{h}}} \quad (5.10)$$

where E^{tot} and V are the potential energy and the volume of the system, p_a is the desired (applied) pressure and W_{cell} is a parameter with units of mass. The Euler-Lagrange equations can be used to derive equations of motion for the atoms and the matrix $\underline{\mathbf{h}}$. In particular, this leads to the following relationship:

$$W_{\text{cell}} \ddot{\mathbf{h}}_{\alpha\beta} = (\Pi_{\alpha\gamma} - p_a \delta_{\alpha\gamma}) V (\underline{\mathbf{h}}^{\top})_{\gamma\beta}^{-1} \quad (5.11)$$

$$\Pi_{\alpha\gamma} \equiv \frac{1}{V} \left(\sum_{i=1}^{N_{\text{atm}}} m_i v_i^{\alpha} v_i^{\gamma} - \frac{\partial E^{\text{tot}}}{\partial \mathbf{h}_{\alpha\lambda}} \mathbf{h}_{\lambda\gamma}^{\top} \right) \quad (5.12)$$

where the summation over repeated Greek indices is implied. The expression for $\Pi_{\alpha\gamma}$ can be identified with the internal stress and $(1/3)\text{Tr } \underline{\mathbf{\Pi}}$ with the internal pressure[169–172]. The term $W_{\text{cell}} \ddot{\mathbf{h}}_{\alpha\beta}$, which can be seen as an effective force, is proportional to $(\Pi_{\alpha\gamma} - p_a \delta_{\alpha\gamma})$. As this term oscillates about zero during the dynamics, the internal pressure oscillates around the desired value of p_a . The target pressure can be maintained during the simulation, which approximately corresponds to the NPH ensemble.

The parameter W_{cell} determines the relaxation time for the recovery from an imbalance between the applied and the internal pressure, and its value cannot be uniquely prescribed[169]. We set it to the sum of ionic masses within the simulation cell. This

²The dot above a symbol indicates the derivative with respect to time.

ensures the correct scaling of $\mathcal{L}_{\text{ext}}$ with the system size and is approximately the same value as used by J. Fallon in his simulations of BaTiO₃[9].

Simulations of BaTiO₃

The steps taken to equilibrate the system and the desired temperature and pressure are now described.

The target temperature, $T \in \{100 \text{ K}, 200 \text{ K}, 300 \text{ K}, 500 \text{ K}, 1000 \text{ K}\}$ was set using velocity rescaling during a simulation of 10 ps. This was supplemented by simulations in an NVE ensemble for another 10 ps to ensure that the temperature indeed oscillates around the target value and to equilibrate the system.

Once the target temperature was reached, the system was further evolved in time using simultaneously the Parrinello-Rahman barostat at zero pressure and velocity rescaling. The fictitious cell mass parameter was set equal to the sum of ionic masses within the simulation cell. Usually, a 10 ps simulation was sufficient to reach the target values.

Once the pressure and temperature were reached, subsequent simulations were carried out using only the barostat, without controlling the temperature. This approximately corresponds to an NPH ensemble. The system was first equilibrated in an NPH ensemble for 10 ps, verifying the average temperature and pressure are at the target values. Following equilibration, a subsequent NPH simulation was used to extract snapshot configurations for later parameterisation and analysis. In Chapter 6, snapshots 2 ps apart were used to fit IPs and in Chapter 7 the snapshots used were at least 3 ps apart, depending on the IP being parameterised.

5.2 Density functional theory calculations

DFT calculations were carried out using the open source Quantum Espresso software[173].

The BaTiO₃ reference DFT data was obtained using a $3 \times 3 \times 3$ supercell, which corresponds to a total of 135 atoms for a defect-free system. A uniform $4 \times 4 \times 4$ Monkhorst-Pack grid was used in all DFT calculations for this supercell size; convergence tests are presented in Appendix 10.2.

We used the PBEsol exchange-correlation functional, which is optimised for use in solids and at surfaces[174]. This choice was motivated in part by the results of J. Fallon[9] who had previously parameterised a TS IP to the LDA-based DFT reference data for BaTiO₃. The use of LDA leads to an underestimated equilibrium volume in BaTiO₃ relative to experimental value, which in turn leads to a relatively poor description of the

ferroelectric phases[9, 175]. In turn, parameterising IPs to LDA-based reference data can have adverse consequences. A rhombohedral phase is the lowest energy structure for BaTiO₃ at zero temperature and pressure, yet J. Fallon’s TS IP predicts this to be unstable unless a negative external pressure is applied. In the present work, reparameterising J. Fallon’s TS IP to PBEsol-based reference *ab initio* data has resolved this issue – phonon calculations in Chapter 8 demonstrate that the rhombohedral phase is stable.

The choice of pseudopotentials (PPs) was guided by the desire to keep the plane-wave energy cutoff, E_{cut} , relatively low without compromising the accuracy. Since we are parameterising IPs to reference interatomic forces, energy differences and stress components, it is primarily these quantities that we want to be sufficiently converged with respect to DFT parameters, as discussed in Appendix 10.2. The need to keep the energy cut-off relatively low is primarily driven by the analysis in Chapter 6 which is largely based on the use of MLWFs (introduced in Section 4.3). In particular, for an optimal use of the supercomputer available at Imperial College, it takes about 70 hours to converge MLWFs for a $3 \times 3 \times 3$ BaTiO₃ supercell using $E_{\text{cut}} = 60$ Ry. The use of higher values of E_{cut} makes the MLWF-based analysis of Chapter 6 computationally intractable. An Optimised Norm Conserving Vanderbilt PP[176, 177] was used for Ba, while Garrity-Bennett-Rabe-Vanderbilt ultrasoft PPs[178] were used to represent Ti and O core electrons³. The electrons Ba (5s, 5p, 6s), Ti (3s, 3p, 3d, 4s) and O (2s, 2p) were treated explicitly. All PPs were generated using PBEsol exchange-correlation functional. With this choice, forces, energy differences and stress components were sufficiently converged at a relatively low cut-off, $E_{\text{cut}} = 60$ Ry, as demonstrated in Appendix 10.2.

A self-consistent DFT calculation was deemed converged when the total energy difference between successive iterations was within $10^{-10} E_{\text{h}} \approx 3 \times 10^{-9}$ eV.

5.3 Parameterisation based on force-matching

As was mentioned in Section 1.5, we parameterise IPs to *ab initio* data via a version[19, 179] of the force-matching method of F. Ercolessi and J. Adams[122]. We fit IP parameters to reproduce the reference DFT forces, stress components and energy differences,

³Extensive tests of these PPs can be found in the provided references.

by minimising a “cost” function, Γ_{cost} , defined[9] as follows:

$$\Delta F_{\text{r.m.s.}} \equiv \frac{1}{N_c} \sum_{k=1}^{N_c} \frac{\sqrt{\sum_{I=1}^{N_{\text{atm}}} \sum_{\alpha} |F_{\text{IP},kI}^{\alpha} - F_{\text{DFT},kI}^{\alpha}|^2}}{\sqrt{\sum_{I=1}^N \sum_{\alpha} |F_{\text{DFT},kI}^{\alpha}|^2}} \quad (5.13)$$

$$\Delta S_{\text{r.m.s.}} \equiv \frac{1}{N_c} \sum_{k=1}^{N_c} \frac{\sqrt{\sum_{\alpha,\beta \geq \alpha} |\sigma_{\text{IP},k}^{\alpha\beta} - \sigma_{\text{DFT},k}^{\alpha\beta}|^2}}{\sqrt{6B}} \quad (5.14)$$

$$\Delta E_{\text{r.m.s.}} \equiv \frac{\sqrt{\sum_{k,l}^{N_c} [(E_k^{\text{IP}} - E_l^{\text{IP}}) - (E_k^{\text{DFT}} - E_l^{\text{DFT}})]^2}}{\sqrt{\sum_{k,l}^{N_c} (E_k^{\text{DFT}} - E_l^{\text{DFT}})^2}} \quad (5.15)$$

$$\Gamma_{\text{cost}} \equiv w_f \Delta F_{\text{r.m.s.}} + w_s \Delta S_{\text{r.m.s.}} + w_e \Delta E_{\text{r.m.s.}} \quad (5.16)$$

where N_c is the number of reference configurations used in the fit, B is the approximate bulk modulus (taken from literature), $\sigma^{\alpha\beta}$ is the stress tensor, $\alpha, \beta \in \{x, y, z\}$ stand for the cartesian components and the weights w_f , w_s and w_e set the relative importance of reproducing each type of data; subscripts DFT and IP indicate whether a quantity was calculated with DFT or with the IP, respectively.

We prioritise reproducing forces since there is considerably more data available for this quantity. For a $3 \times 3 \times 3$ BaTiO₃ supercell there are 135×3 force components and 6 stress components per configuration and only $N_c - 1$ energy differences for N_c reference configurations. The weights we used in the present work are $w_f = 1.0$, $w_s = 0.1$, $w_e = 0.0001$.

There are several advantages to this approach. In a FM method, we fit IP parameters directly to the underlying potential energy surface. This approach does not bias the IP to reproduce any set of observables; instead one calculates properties and compares to reference experimental or *ab initio* values *a posteriori*. What’s more, one can generate vastly more *ab initio* reference data than the amount of available experimental data, such as bulk modulus and phonon frequencies. The use of a large reference data set reduces the chance of over-fitting and has been found to improve IP transferability (e.g. see Ref. 43). Furthermore, in the present work we are interested in analysing the roles of different terms in the functional form of the polarisable IP and the ability to fit forces is a good measure to quantify an IP’s accuracy and to carry out comparative studies, such as those presented in Chapters 6 and 7.

Finally, in the context of polarisable IPs, it must be highlighted that we do not bias the QEq charge transfer variables or induced dipoles to agree with changes in the DFT charge density during a parameterisation. In Chapters 6 and 7 we investigate the relationships between these IP variables and changes in the DFT charge density. In particular, since the parameters are optimised to reproduce the underlying potential

energy surface, we try to answer the following question: when a fixed-charge IP is extended to include QEq charge transfer, is there an improvement in accuracy and if so, is it *because* the inclusion of these variables provides a more realistic representation of the DFT charge density?

5.4 Iterative parameterisation

When parameterising a new IP the calculation steps described in Sections 5.1, 5.2 and 5.3 are repeated several times, until a convergence is achieved, in a sense to be defined shortly.

Ideally, reference snapshot configurations should contain information about a wide range of bonding environments, in resemblance to those encountered in the real material, BaTiO₃ in our case. Once we obtain such a set of configurations, DFT calculations can be carried out to provide reference data for fitting. Molecular dynamics (MD) simulations at constant temperature and pressure allow us to generate atomic trajectories that are representative of the real material. Ideally, we would simulate dynamics using an *ab initio* method to calculate forces. However, due to a relatively high associated computational cost, only short simulation times are accessible, which can lead to correlated forces in the snapshot configurations. Therefore, instead, we use classical IPs to simulate MD to define snapshot configurations for DFT calculations. To generate the initial set of snapshot configurations, we either use an estimated set of parameters for the IP that we wish to parameterise, or a different IP, taken from the literature. This means, generally, that the initial MD simulation is inferior in accuracy and is less representative of the real material than the subsequent simulations, obtained using an IP with optimised parameters. For this reason, we repeat the steps of generating snapshot configurations, carrying out DFT calculations, and parameterising the IP, several times until a convergence is reached. We now summarise an iterative procedure that was used to generate IPs for BaTiO₃ in Chapters 6 and 7, and make the notion of convergence precise.

Initially the TS IP developed by J. Fallon[9] for bulk BaTiO₃ was used in MD simulations to generate snapshot configurations for the DFT calculations used for parameterisation. Configurations were taken from an NPH ensemble at zero pressure and temperatures $T \in \{100 \text{ K}, 200 \text{ K}, 300 \text{ K}, 500 \text{ K}, 1000 \text{ K}\}$ ⁴, as described in Section 5.1. This allowed us to parameterise the first QEqTS IP. The corresponding cost function value then defined the zeroth iteration value, $\Gamma_{\text{cost}}^{(0)}$.

⁴Configurations from the 1000 K simulation were not used in fitting.

The zeroth iteration QEqTS IP was then used for subsequent molecular dynamics simulations to define new configurations for DFT calculations. DFT calculations then provided a new set of reference data. Reparameterising the QEqTS IP then led to the first iteration of the IP, with a corresponding cost function value $\Gamma_{\text{cost}}^{(1)}$. This step is repeated several times until $\Gamma_{\text{cost}}^{(n)} \approx \Gamma_{\text{cost}}^{(n+1)}$, at which point the parameters from the final $(n+1)^{\text{th}}$ iteration defined the IP that was used in atomistic simulations in Chapters 6, 7 and 8.

In the present work, to keep the study computationally tractable, we deviate from the general protocol outlined above in some minor details. These are described in the computational details sections of Chapters 6 and 7. In all cases, however, configurations were taken from molecular dynamics based on the QEqTS IP. Thus, even when parameterising TS, MS-Q or other IPs, the reference configurations are always based on QEqTS IP simulations.

5.5 Crystal structure relaxation

Chapters 7 and 8 involve calculations of the relaxed crystal structure for BaTiO₃ in its rhombohedral phase.

Calculations based on classical IPs used the steepest descent algorithm to minimise the potential energy with respect to atomic positions and the lattice vectors. The total energy was converged to within $10^{-5} E_{\text{h}} \approx 3 \times 10^{-4}$ eV per atom, force and stress components were converged to within $10^{-5} E_{\text{h}}/a_o \approx 5 \times 10^{-4}$ eV/Å and $10^{-7} E_{\text{h}}/a_o^3 \approx 3 \times 10^{-3}$ GPa, respectively. The configuration used as the initial guess had the symmetry of the rhombohedral phase. Therefore, this phase corresponds to a local energy minimum. We did not test whether for a given IP it also corresponds to a global energy minimum.

Calculations based on DFT used the Quantum Espresso package. Both the nuclear positions and cell vectors were relaxed using the Broyden–Fletcher–Goldfarb–Shanno quasi-Newton algorithm[180]. The total energy was converged to within $10^{-7} E_{\text{h}} \approx 3 \times 10^{-6}$ eV per atom, force and stress components were converged to within $2 \times 10^{-5} E_{\text{h}}/a_o \approx 10^{-3}$ eV/Å and $10^{-7} E_{\text{h}}/a_o^3 \approx 3 \times 10^{-3}$ GPa, respectively. The configuration used as the initial guess had the symmetry of the rhombohedral phase.

Chapter 6

Polarizable charge transfer model applied to bulk BaTiO₃

In Chapter 1 we have motivated extending ionic IPs to include the QEq model by the anticipated improvement in accuracy and transferability, in particular between the bulk and heterogeneous atomic environments. However, a survey of the literature has failed to uncover any conclusive demonstration that QEq brings an improvement, and in particular in applications to bulk phases of fixed-stoichiometry such as SiO₂[80, 82], TiO₂[119] and MgO[27, 81]. What’s more, it is generally not verified whether QEq charge transfer variables reflect changes in the underlying ground state density in these systems.

While previous applications of the QEq-based IPs inform our research, the primary aim of the present thesis is to further develop, understand and test the combined QEqTS IP. Based on a theoretical analysis of Chapter 3, a limit on the changes in the ground state density was defined in which the QEqTS functional form can be considered approximately valid (QEqTS-limit). In particular, it was highlighted that the QEq model is only justified for representing relatively small changes in the ground state density, suggesting that its analytic form and parameters may have a limited transferability across the atomic environments of varying coordination number. This may help us rationalise the behaviour of the QEq model, especially in the applications to heterogeneous systems as demonstrated in Chapter 7. On the other hand, as was suggested in Section 1.4.2, in some systems, such as bulk phases of fixed stoichiometry¹, changes in the ground state may correspond to very small charge transfers, justifying the QEq functional form but

¹It may be that other examples include heterogeneous systems as well, for example V_{Mg}^{2-} and V_{O}^{2+} vacancies in MgO, where estimates based on the electron density difference contour plots[124] suggest that the local charge transfer doesn’t exceed 0.05 e relative to the bulk values.

at the same time making the model itself not useful.

In the present chapter the focus is on a thermally perturbed defect-free bulk BaTiO₃, in the temperature range 100 K – 1000 K. On one hand, in this temperature range different snapshot configurations of BaTiO₃ have very similar atomic structures, thus the perturbations of the ground state density due to the thermal atomic motion can be considered relatively small and the analytic form of the QEq model can be assumed to be valid. On the other hand, as discussed in Section 1.5, anomalous Born effective charges in BaTiO₃ suggest that the changes in the ground state density may nevertheless correspond to non-negligible inter-ionic charge transfers.

The structure of the present chapter is now described and motivated. The idea is to test the QEqTS IP in a system where its functional form is approximately valid. In particular, we wish to test whether the QEq charge transfer variables, $\{\Delta q_i\}$, reflect the changes in the ground state density. An ionic charge and other ionic properties are ill-defined in the condensed phase and in Section 6.1 we describe our approach to quantifying the changes in the ground state density in a way that facilitates a direct comparison with the ionic properties defined in the QEqTS and TS IPs. It is primarily based on the use of MLWFs and, to a lesser extent, Löwdin population analysis, both defined in Chapter 4.

The approach described in Section 6.1 is then used in Sections 6.2, 6.3 and 6.4 to compare the electrostatic potential at ionic sites, induced dipole moments and charge fluctuations, respectively, to analogous quantities defined in terms of the DFT ground state density. Firstly, induced dipole moments $\{\mathbf{p}_i\}$ are demonstrated to represent local polarisation of the ground state density, consistent with the intuitive and intended physical interpretation for these variables. Secondly, the fluctuations in the electrostatic potential are found to be in a good quantitative agreement with the reference *ab initio* values. This is an important result – recall, the QEq model assigns ionic charges based on the electrostatic potential subject to an energy “penalty” for deviations in charges from their reference values. This is to say, QEq-based IP may or may not provide the correct electrostatic potential but it is certainly the premise of the QEq model that given the correct “input” electrostatic potential, the “correct output” ionic charges are supposed to come out. If the electrostatic potential is accurate and the QEq-based IP does not improve the accuracy, then either the functional form of the self-energy is inadequate or the changes in the ground state simply correspond to very small or negligible inter-ionic charge transfers.

The physical interpretation and the effect on interatomic interactions of the QEq

charge transfer variables is discussed at length in Section 6.4. The QEq $\{\Delta q_i\}$ variables do indeed reflect changes in the ground state density, but at the same time do not have a clear physical interpretation. A small but non-negligible amount of charge transfer occurs between ions whose electrons contribute to the upper valence band. The distribution of the QEq charges is consistent with the electrostatic potential – this is presented in Sections 6.2 and 6.4.1. At the same time, contrary to intuition, in general a negative (positive) value of Δq_i does *not* correspond to a higher (lower) ground state density in the vicinity of the nucleus i . A possible alternative physical interpretation of the $\{\Delta q_i\}$ variables is offered in Section 6.4.4.

In Section 6.4.3 the overall effect of the QEq model on the accuracy is shown to be very small, especially when used in conjunction with the TS IP. A root-mean-squared (r.m.s.) agreement with the reference *ab-initio* forces is used as a measure of accuracy, and on this measure alone the QEq model results in an improvement of 2.3% and 0.8% when used in conjunction with the rigid-ion MS-Q_o and polarisable-ion (PI) TS IPs, respectively. In contrast, TS PI model improves accuracy by 41% relative to the MS-Q_o IP.

Finally, Section 6.5 summarises key findings and draws conclusions with regards to the application of the QEq model to the thermally perturbed BaTiO₃. The QEqTS-limit is satisfied in this system and the changes in the electrostatic potential are represented accurately, implying the QEqTS functional form can be taken as a good approximation. The effect of the QEq model on the interatomic forces is very small, a $\leq 2.3\%$ improvement in r.m.s. agreement with the reference calculation, yet the PI model brings about an improvement of 41%. This last point, in particular, means that there are non-negligible changes in the ground state density in this system, yet the QEq model is not a suitable way to represent these changes. In other words, changes in the ground state density correspond to a very small or negligible inter-ionic charge transfer.

6.1 Ionic properties from the ground state density

In Section 6.1.1 the data set used in the parameterisation and testing of the IPs in this chapter is presented. An ionic charge and other ionic properties are not uniquely defined in condensed matter. Yet, the intention of the present chapter is to compare variables in an ionic IP directly to changes in the DFT ground state density. In Sections 6.1.2, 6.1.3 and 6.1.4 our approach towards this goal is outlined and motivated.

6.1.1 Parameterisation details

The general parameterisation protocol was discussed in detail in Chapter 5, and here instead we outline the data set used for fitting and subsequent tests.

Initially the TS IP parameterised for bulk BaTiO₃ in Ref. 9 was used in molecular dynamics simulations to generate configurations for the DFT calculations and the subsequent parameterisation. DFT convergence tests can be found in Appendix 10.2. Once the first QEqTS IP was parameterised it was used for subsequent molecular dynamics simulations to define new configurations for DFT calculations.

After initial velocity rescaling and equilibration, molecular dynamics simulations in the NPH ensemble at zero pressure and temperatures of 100, 200, 300, 500 and 1000 K were used to define reference atomic configurations for DFT calculations. Ten snapshots 1 picosecond apart were used at each temperature. DFT calculations in turn defined the training data of *ab initio* interatomic forces, energy differences and stress components. All IPs presented in this chapter were parameterised to the same data. This procedure was repeated a total of two times before reaching convergence in the quality of the fit. Relatively few iterations were required since the initial molecular dynamics simulation was obtained using the TS IP of Ref. 9 which was highly optimised for bulk BaTiO₃ at this pressure and temperature range. Half of the training data at temperatures 100 – 500 K was used in parameterisation, corresponding to snapshot configurations 2 ps apart. All the data at all temperatures was used in subsequent tests and analysis of this chapter.

In the best-fit QEqTS IP charge fluctuations only take place between Ti ions, and this IP is referred to interchangeably as QEqTS or QEqTS(Ti) IP, depending on the context. In another parameterisation of the combined IP the charge fluctuations additionally occur between O ions, and this latter IP is always referred to as QEqTS(Ti,O). Both IPs are used to facilitate analysis of the role of the QEq charge transfer.

Quantum Espresso package was used for the Löwdin population analysis, defining the reference *ab initio* values for ionic charges. Wannier90 package was used to obtain MLWFs. MLWFs were defined in Chapter 4 and the convergence tests for the algorithm that defines MLWFs can be found in the Appendix 10.3.

Parameter sets for all IPs used in this thesis are presented in the Appendix 10.4.

6.1.2 Maximally Localised Wannier Functions in BaTiO₃

Much of the analysis is based on the results of Wannierization of the ground state density, a procedure introduced in Chapter 4. The BaTiO₃ ground state was calculated in this chapter using the canonical Kohn-Sham DFT, subject to periodic boundary conditions,

so equations 4.25 and 4.26 can be applied to express the charge density in terms of MLWFs:

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \sum_{n \in \text{occ.}} w_{n,\mathbf{R}}(\mathbf{r}) \quad (6.1)$$

$$w_{n,\mathbf{R}_m}(\mathbf{r}) \equiv -2|W_{\mathbf{R},n}(\mathbf{r})|^2 \quad (6.2)$$

where $W_{\mathbf{R},n}(\mathbf{r})$ is a MLWF, a factor of 2 is due to the spin degeneracy and the negative sign designates electron charge. Each function $w_{n,\mathbf{0}}(\mathbf{r})$ is real and localised in the position space somewhere within the supercell at the origin, $\mathbf{R} = \mathbf{0}$; other MLWFs are simply re-centered copies $w_{n,\mathbf{R}}(\mathbf{r}) = w_{n,\mathbf{0}}(\mathbf{r} - \mathbf{R})$.

The main results of Wannierization applied to BaTiO₃ ground state are now discussed to facilitate the subsequent discussion. It was found that in BaTiO₃ at all temperatures in the range 100 – 1000 K, all functions $\{w_{n,\mathbf{0}}(\mathbf{r})\}$ naturally fall into groups of four, with MLWFs in each group centered very close to one nucleus in the system². Therefore, this set can be relabeled $w_{n,\mathbf{0}}(\mathbf{r}) \rightarrow w_{i,s}(\mathbf{r})$ where indices $i \in \{1, \dots, N_{\text{atm}}\}$ and $s \in \{1, 2, 3, 4\}$ enumerate atoms in the (reference) simulation cell and MLWFs within each group of four localised at a given ion i , respectively.

$$\rho^{\text{sc}}(\mathbf{r}) \equiv \sum_{i=1}^{N_{\text{atm}}} \sum_{s=1}^4 w_{i,s}(\mathbf{r}) \quad (6.3)$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}} \rho^{\text{sc}}(\mathbf{r} - \mathbf{R}) \quad (6.4)$$

where $\rho(\mathbf{r})$ is the density defined throughout the infinite extended crystal and $\rho^{\text{sc}}(\mathbf{r})$ is the contribution per supercell. Furthermore, at the end of a well-converged Wannierization algorithm, the quadratic spread of every single MLWF, $\Omega_n \equiv [\langle W_{\mathbf{R},n} | r^2 | W_{\mathbf{R},n} \rangle - \langle W_{\mathbf{R},n} | \mathbf{r} | W_{\mathbf{R},n} \rangle^2]$, was found to be very small, with a lower and upper bounds $0.93 a_o \leq \sqrt{\Omega_n} \leq 2.15 a_o$. Note that this does not have to happen in general since the algorithm minimizes *the sum* of the quadratic spreads of all the MLWFs rather than each spread individually. To place the degree of localisation into context – the average shortest nearest neighbour distance, that between O and Ti ions, is $3.6 a_o$ and the longest, between Ba and O, is $5.4 a_o$. Furthermore, the center-of-charge of each group of four MLWFs is always within $0.1 a_o$ of the position of the nucleus; these and similar properties of MLWFs in a thermally perturbed bulk BaTiO₃ are summarised in Table 6.1. In Table 6.1 $|\bar{\mathbf{r}}_{i,s}|$, $|\bar{\mathbf{r}}_i^{\text{c.o.c.}}|$ and $r_{ij}^{\text{n.n.}}$ stand for the distance from the MLWF to its parent nucleus, the distance from the center-of-charge of the four MLWFs to their parent nucleus and the nearest neighbour distance between nuclei, respectively. It is an empirical fact, that

²Within the supercell at the origin.

$[a_o]$	$\sqrt{\Omega_i}$			$ \bar{\mathbf{r}}_{i,s} $	$ \bar{\mathbf{r}}_i^{\text{c.o.c.}} $	$r_{ij}^{\text{n.n.}}$
	Min.	Ave.	Max.	Ave.	Max.	Ave.
Ba	1.73	1.80	2.07	0.83	0.03	5.44
Ti	0.93	1.00	1.12	0.40	0.03	3.61
O	1.49	1.78	2.13	0.62	0.14	3.61

Table 6.1: The minimum, average and maximum of the quadratic spread of MLWFs centered at Ba, Ti and O is summarised; additionally, the average distance from the MLWF to its parent nucleus ($|\bar{\mathbf{r}}_{i,s}|$), the maximum distance from the center-of-charge of the four MLWFs to their parent nucleus ($|\bar{\mathbf{r}}_i^{\text{c.o.c.}}|$) and the average nearest neighbour distance between nuclei ($r_{ij}^{\text{n.n.}}$) are presented. Units used are a_o .

for this system the (exact) representation of the ground state density in terms of MLWFs resembles an ionic limit, i.e. a sum of ion-centered localised contributions. This fact suggests that, despite a lack of formal justification, it is reasonable to affiliate each of these groups of four MLWFs with a single ion, based on proximity. Throughout this section I interchangeably use expressions such as “MLWFs anchored on O”, “MLWFs centered on Ti”, “O on-site MLWFs” or “Ba’s MLWFs” to refer to a group of four MLWFs affiliated with an ion based on proximity. Each group of four MLWFs corresponds to 8 electrons, and the pseudopotentials used in the DFT calculations correspond to nuclear effective charge of +10, +12 and +6 for Ba, Ti and O, respectively, leading to nominal ionic charges of +2, +4 and −2. Upper valence bands³ corresponds to three MLWFs per O ion⁴.

To be clear, the representation of the ground state and the ions’ density in terms of MLWFs is not unique, nor does it have a clear physical interpretation. Nevertheless, as we shall see in the remainder of this chapter, MLWFs greatly facilitate the comparison of the changes in the IP variables $\{\Delta q_i\}$ and $\{\mathbf{p}_i\}$ to changes in the underlying ground state density.

³Upper valence bands are those separated by finite energy gaps from both the conduction bands and other valence bands, located higher and lower on the energy scale, respectively.

⁴Additionally, a decomposition of the Born effective charges in Cubic BaTiO₃ in terms of MLWFs can be found in Ref. 181.

6.1.3 Electrostatic potential at ionic sites

In the present chapter it is important to verify that the TS and QEqTS IPs represent the changes in the electrostatic potential with sufficient accuracy, since this quantity largely determines charge transfers predicted by the QEq model. Recall from Section 1.4.1, the QEq model simply assigns ionic charges based on the electrostatic potential, subject to the energy “penalty” for deviations in ionic charges from the reference values:

$$E^{\text{ES}} = \sum_{i=1}^{N_{\text{atm}}} (A_i \Delta q_i + D_i \Delta q_i^2) + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} (q_i^0 + \Delta q_i) \phi_i \quad (6.5)$$

$$\frac{\partial E^{\text{ES}}}{\partial \Delta q_i} = 0 \quad \forall i, \text{ such that } \sum_{i=1}^{N_{\text{atm}}} \Delta q_i \equiv 0 \quad (6.6)$$

where ϕ_i is the electrostatic potential at site i . Thus, it is desirable to verify that the electrostatic potential calculated with an IP resembles the same quantity in the reference *ab initio* calculations.

It is not straightforward defining the electrostatic potential based on *ab initio* data in a way that represents an equivalent quantity as in the classical IP. A canonical DFT implementation involves the use of non-local pseudopotentials and an approximate energy density functional which bundles the exchange and correlation effects together. Quantum Espresso and other DFT packages output the sum of the exchange-correlation potential, the Hartree potential and the local part of the pseudopotential, and this sum is often interpreted loosely as the electrostatic potential. However, it is arguably not suitable to use this quantity for a comparative study. Firstly, in Chapter 3 the functional form of the QEqTS and other IPs was related to DFT, and in particular the classical electrostatic potential defined in an IP can be seen *not* to include the exchange-correlation potential. Secondly, a potential in DFT is defined at points in the position space, and one would need to average it over the space occupied by an ion, comprising the nucleus and its “on-site” electrons – the radius and shape of an ion is not well-defined however. Here, instead, we construct an approximate ground state density using MLWFs and evaluate electrostatic potential classically. While the approximation, introduced shortly, is crude for the density itself, we shall argue that the changes in the electrostatic potential are nevertheless captured well. This method is now presented and motivated.

In what follows, the notation for the electrostatic potential distinguishes two cases using a subscript: $\phi_{[i]}$ is the potential calculated excluding the interaction of the nucleus with the on-site electrons; ϕ_i is the potential due to the interaction of the nucleus with all electrons in the system, including its on-site electrons. Using this notation, electrostatic potential in the TS and QEqTS IPs corresponds to $\phi_{[i]}$ while in DFT both definitions

are possible. The exact details of the calculations will be provided in this section as they are presented.

The electron density is approximated by placing spherically symmetric Slater-type orbitals (STOs) at the positions of the centers of the MLWFs, defined as follows:

$$\chi_A(\mathbf{r}) \equiv \sqrt{\frac{(2\zeta)^{2n+1}}{4\pi(2n)!}} |\mathbf{r}|^{n-1} e^{-\zeta_A |\mathbf{r}|} \Big|_{n=2, \zeta_A} \quad (6.7)$$

with $n = 2$ and⁵ $A \in \{\text{Ba}, \text{Ti}, \text{O}\}$ and ζ_A value imposes $\langle \chi_A | (\mathbf{r} - \bar{\mathbf{r}})^2 | \chi_A \rangle = \Omega_{\text{ave}}^A$, the average quadratic spread of the MLWFs associated with ions of type A . Each Slater-type charge density integrates to a charge of -2 . Ionic nuclei are treated as point particles, with nuclear charges, Z_A , determined by the pseudopotentials used in the DFT calculations, $Z_A \in \{Z_{\text{Ba}} = 10, Z_{\text{Ti}} = 12, Z_{\text{O}} = 6\}$. After the approximation to the ground state density is made, the electrostatic potential at a site i is calculated exactly, as follows:

$$\phi_{[i]}^{\text{DFT}} \equiv \sum_{j \neq i}^{N_{\text{atm}}} \frac{Z_j}{r_{ij}} - 2 \sum_{j \neq i}^{N_{\text{atm}}} \sum_{s=1}^4 \int \frac{|\chi_j(\mathbf{r}' - (\mathbf{r}_j + \Delta \mathbf{r}_{s,j}))|^2}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \quad (6.8)$$

$$\begin{aligned} \phi_i^{\text{DFT}} \equiv & \sum_{j \neq i}^{N_{\text{atm}}} \frac{Z_j}{r_{ij}} - 2 \sum_{j \neq i}^{N_{\text{atm}}} \sum_{s=1}^4 \int \frac{|\chi_j(\mathbf{r}' - (\mathbf{r}_j + \Delta \mathbf{r}_{s,j}))|^2}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \\ & - 2 \sum_{s=1}^4 \int \frac{|\chi_i(\mathbf{r}' - (\mathbf{r}_i + \Delta \mathbf{r}_{s,i}))|^2}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \end{aligned} \quad (6.9)$$

where an Ewald summation is implied, $\Delta \mathbf{r}_{s,j}$ are the displacement vectors from ionic core j to MLWF indexed s centered on this ion; Slater orbitals are defined based on the specie of the ion at site j , $\chi_j \in \{\chi_{\text{Ba}}, \chi_{\text{Ti}}, \chi_{\text{O}}\}$.

It is important to emphasize that while the above is a crude approximation of the ground state density, we are interested instead in estimating changes in the electrostatic potential:

$$\delta \phi_{[i]} \equiv \phi_{[i]} - \langle \phi_{[i]} \rangle_A |_{T_o} \quad (6.10)$$

$$\delta \phi_i \equiv \phi_i - \langle \phi_i \rangle_A |_{T_o} \quad (6.11)$$

where the average $\langle \cdot \rangle_A |_{T_o}$ is taken over all ions of type $A \in \{\text{Ba}, \text{Ti}, \text{O}\}$ in all snapshot configurations taken from MD simulations at a temperature T_o or a range of temperatures. The change in the electrostatic potential is approximated better than it may seem at first, since, by definition, the dipole moment of a MLWF relative to its own centre

⁵Recall from Chapter 2, the contribution to the electrostatic potential due to overlap is insensitive to the parameter n for the same size STOs. Without loss of generality we can set $n = 2$.

vanishes. To see this, suppose we evaluate the potential $\phi_{[i]}$ using MLWFs:

$$\phi_{[i]}^{\text{MLWF}} \equiv \sum_{j \neq i}^{N_{\text{atm}}} \frac{Z_j}{r_{ij}} - 2 \sum_{j \neq i}^{N_{\text{atm}}} \sum_{s=1}^4 \int \frac{|w_{j,s}(\mathbf{r}')|^2}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \quad (6.12)$$

$$= \sum_{j \neq i}^{N_{\text{atm}}} \frac{Z_j}{r_{ij}} - 2 \sum_{j \neq i}^{N_{\text{atm}}} \left[\frac{1}{r_{ijs}} - \tilde{I}_0(r_{ijs}) \right] + \mathcal{O} \left(\text{Max} \left[\left\{ \frac{1}{r_{ijs}^3} \right\} \right] \right) \quad (6.13)$$

where $r_{ijs} \equiv \mathbf{r}_i - (\mathbf{r}_j + \Delta \mathbf{r}_{s,j})$ and $\tilde{I}_0(r_{ijs})$ is the short-range contribution due to the overlap, discussed in Chapter 2; $\text{Max} \left[\left\{ 1/r_{ijs}^3 \right\} \right]$ represent the largest quotient due to the shortest distance r_{ijs} in the summation. The error introduced by using spherically symmetric STOs instead of MLWFs is on the order $\mathcal{O}(1/r_{ijs}^3)$, due to the unaccounted contributions from the quadrupole and higher order multipoles. Note that the dipole moments relative to nuclear positions are nevertheless captured since the STOs are placed at positions of MLWF centers and not at the positions of the ionic cores. Furthermore, there are likely to be cancellations of errors when evaluating changes in the potential rather than the potential itself.

It is important to establish that the estimate of $\delta\phi_{[i]}^{\text{DFT}}$ is insensitive to the input parameters within a reasonable range of values. The quadratic spread of the STOs is set to the average values, so the sensitivity to these parameters is tested first. Secondly, the “on-site” electron density is ill-defined, therefore $\delta\phi_i^{\text{DFT}}$ is also calculated to see how much the potential changes if all the electrons are included in the definition of the potential.

The dependence of $\delta\phi_{[i]}^{\text{DFT}}$ on the size of STOs is examined first, presented in the Figure 6.1. For ease of visualization, in this and, occasionally, other figures in this chapter the quantity of interest is shown only for the ions in the snapshot configurations corresponding to the first three time steps, numbered 1, 2 and 3 for Ba and Ti and configuration 1 for O – ions of each type are indexed 1, ..., 81. Given that the STOs used in the calculations are spherically symmetric, the exact size of the orbitals only matters for the nearest neighbour interactions due to the overlap whereas for all other interactions the integral reduces to a simple analytic $1/r_{ij}$ expression by Gauss’s law. Consequently, when evaluating electrostatic potential at a give ionic site, the relevant size parameter to vary is that of its nearest neighbour. Note that for Ba, Ti and O the nearest neighbours are O, O and Ti respectively. It is clear from Figure 6.1 that the exact value of the quadratic spreads assigned to STOs has a negligible effect on the estimated values of the change in the electrostatic potential, $\delta\phi_{[i]}^{\text{DFT}}$. The overall shape of the graph in Figure 6.1 is expected to be correct, since the effect of the neglected MLWFs’ quadrupole and higher order multipole moments can be thought of as a relatively small

corrections, too small to change the location of the peaks and troughs of the potential.

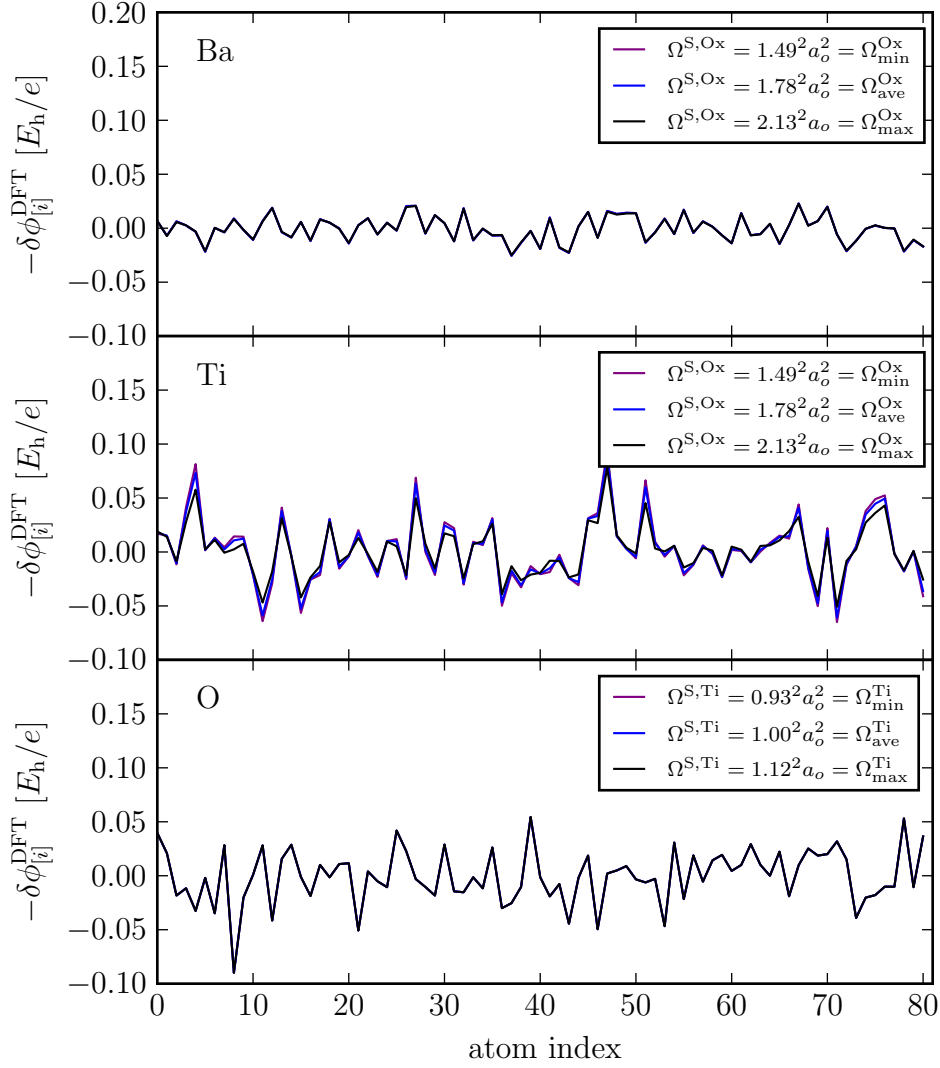


Figure 6.1: Change in the estimated on-site electrostatic potential, $\delta\phi_{[i]}^{\text{DFT}}$, based on treating MLWFs as spherically symmetric STOs, χ_A . The estimate is independent of the exact orbital size, measured as $\Omega^{S,A} \equiv \langle \chi_A | (\mathbf{r} - \bar{\mathbf{r}})^2 | \chi_A \rangle$, plotted in the range of nearest neighbour MLWF quadratic spread values $\Omega_{\min}^A \leq \Omega_{\text{MLWF}}^A \leq \Omega_{\max}^A$ for $A \in \{\text{Ba}, \text{Ti}, \text{O}\}$. Configurations 1 for O, 1, 2 and 3 for Ba, Ti are shown.

Since the size of the nearest neighbours essentially does not affect the calculations of on-site electrostatic potential, one can simply set these to the average values. Next, an estimate that does not exclude the contribution from the on-site electrons is shown in Figure 6.2 for different sizes of the on-site STOs and compared to the potential calculated excluding the on-site electrons' contribution (blue curve). As already mentioned in Section 6.1.2, partition of the ground state density into MLWFs is a well-defined procedure which allows us to affiliate each MLWF with a single ion. This then allows one

to define the on-site and inter-site contributions to the electrostatic potential. However,

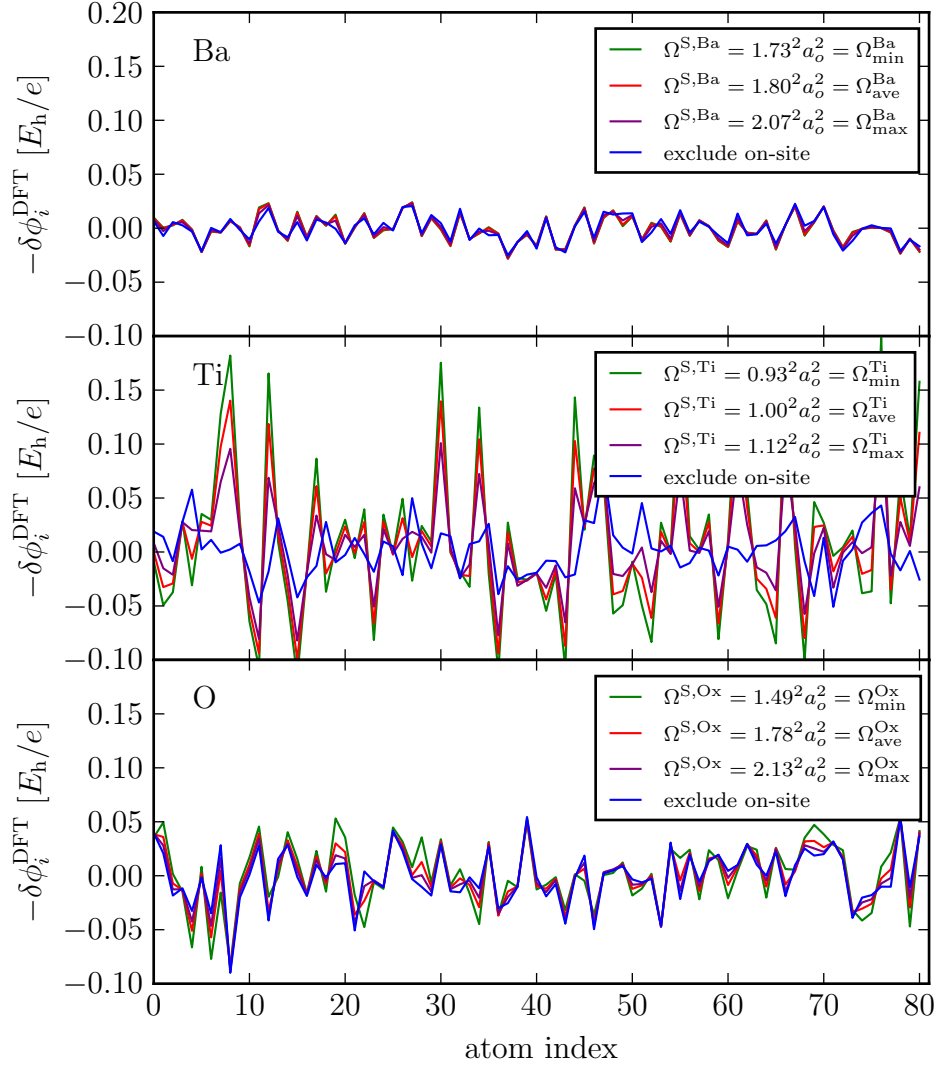


Figure 6.2: Change in the estimated on-site electrostatic potential, $\delta\phi_i^{\text{DFT}}$, based on treating MLWFs as spherically-symmetric STOs, χ_A , including contributions from the on-site electrons. The size of STOs is varied by setting $\Omega^{S,A} \equiv \langle \chi_A | (\mathbf{r} - \mathbf{r})^2 | \chi_A \rangle$ to the size of on-site MLWFs in the range of values for a given chemical specie, $\Omega_{\min}^A \leq \Omega_i^{\text{MLWF}} \leq \Omega_{\max}^A$ for $A \in \{\text{Ba}, \text{Ti}, \text{O}\}$. Configurations 1 for O, 1, 2 and 3 for Ba, Ti are shown.

the physical interpretation of MLWFs is debatable and, Ba and O MLWFs are still fairly delocalised. In particular, upper valence band MLWFs are centered on O sites and have a non-negligible density extending at least as far as the nearest neighbour Ti ions. We can see that for Ba, the change in the local electrostatic potential is not affected at all by the on-site charge density, for oxygen, the on-site electron density makes small quantitative corrections but does not change the order of magnitude of the fluctuations or the

general shape of the potential. On the other hand, for Ti sites we see that the estimated change in the on-site electrostatic potential is considerably larger in magnitude and even disagrees at times in overall shape. However, at the same time there is less ambiguity in defining the Ti on-site electrons. Firstly, MLWFs centered on Ti sites do not correspond to the upper valence band. Secondly, the MLWFs on Ti sites are very small: on average the square root of the quadratic spread is $\sqrt{\Omega} = 1.00 a_o$ for Ti compared to $\sim 1.8 a_o$ for Ba and O. Thus, unlike in the case of MLWFs centered on O sites, associating MLWFs centered at Ti sites with Ti ions is physically motivated.

We can conclude that $\delta\phi_{[i]}^{\text{DFT}}$ is insensitive to the parameters used in the approximation for the Ba and O ions. For Ti ions, $\delta\phi_{[i]}^{\text{DFT}}$ is sensitive to the contribution of the on-site electrons, however there are physical grounds to exclude these contributions when defining the quantity that is equivalent to the potential calculated in the TS and QEqTS IPs.

6.1.4 Ionic dipole moments

It is the intention of the present chapter to physically interpret the charge transfer variables in the QEqTS IP. However, $\{\Delta q_i\}$ vary in concert with the induced dipole variables $\{\mathbf{p}_i\}$ in order to collectively describe the changes in the ground state density. Understanding how the induced dipole variables reflect changes in the density helps in turn with the subsequent analysis of the charge transfer variables. Additionally, there is an intrinsic interest in interpreting physically the $\{\mathbf{p}_i\}$ variables.

We now use MLWFs to define an ionic dipole moment based on the *ab initio* data. Recall that there are four MLWFs per ionic site – these can be enumerated, $s = 1, \dots, 4$, and centered at positions near the parent ion i , which can be labelled $\mathbf{R}_{i,s}^{\text{MLWF}}$. An intuitive definition of ionic dipole moments, $\{\mathbf{P}_i\}$, can be provided in terms of the on-site MLWFs as follows:

$$\mathbf{P}_i \equiv \sum_{s=1}^4 \int (\mathbf{r} - \mathbf{r}_i) w_{i,s}(\mathbf{r}) d\mathbf{r} \quad (6.14)$$

$$= -2 \sum_{s=1}^4 (\mathbf{R}_{i,s}^{\text{MLWF}} - \mathbf{r}_i) \quad (6.15)$$

Alternatively, this can be restated as:

$$\mathbf{P}_i = -8(\mathbf{R}_{i,\text{c.o.c.}}^{\text{MLWF}} - \mathbf{r}_i) \quad (6.16)$$

where $\mathbf{R}_{i,\text{c.o.c.}}^{\text{MLWF}}$ is the center-of-charge of the four MLWFs associated with the ion i . This is simply the displacement vector from the ionic nucleus to the center-of-charge of the

four on-site MLWFs, multiplied by the total charge of the on-site electrons represented by these MLWFs, $-8 e$. This definition is not intended to be “the true” dipole moment of an ion, nevertheless it is an example of well-defined quantity that reflects the changes in the ground state density. Comparing dipoles $\{\mathbf{P}_i\}$ to the IP variables $\{\mathbf{p}_i\}$ informs us about how the latter relate to the local changes in the ground state density. In Section 6.3 it is shown that, remarkably, the two sets of dipole moments shows essentially a perfect correlation.

6.2 Ionic electrostatic potential in relation to the ground state density

As stated in the introduction of the present chapter, we wish to physically interpret QEq charge transfer variables and related them to changes in the ground state density. Furthermore, we’d like to asses whether the QEq model predicts the magnitude and distribution of ionic charge fluctuations that can be considered “correct”. As a preliminary step, in the present section we compare the changes in the electrostatic potential as calculated using the IP to the same quantity estimated using the reference *ab initio* data. By construction, the peaks and troughs in the ionic charge distribution predicted by the QEq model mirror those in the negative of the changes in the electrostatic potential (a positive potential attracts negative charge). Thus, if the latter quantity is in poor resemblance to the reference *ab initio* data, it is reasonable to expect that in turn the QEq charge distribution does not reflect the ground state density.

In Figure 6.3 the MLWF-based electrostatic potential difference is compared to the same quantity in the TS and QEqTS IPs. Negative of the potential is reported throughout the chapter for consistency, since changes in this quantity are expected to correlate positively with the fluctuations in ionic charges, based on electrostatic arguments. The latter two are almost identical and are very close to the reference estimate $\delta\phi_{[i]}^{\text{DFT}}$. The correlation values are listed in Table 6.2, using the correlation function, $C(v, u; \{A\}, \{T_k\})$, and variables defined as:

$$\sum_{T,A,i} \equiv \sum_{T \in \{T_k\}} \sum_{A \in \{A\}} \sum_{i \in A @ T} \quad (6.17)$$

$$C(v, u; \{A\}, \{T_k\}) \equiv \frac{\sum_{T,A,i} (v_i - \langle v \rangle_{A|T}) (u_i - \langle u \rangle_{A|T})}{\sqrt{\left(\sum_{T,A,i} (v_i - \langle v \rangle_{A|T})^2\right) \left(\sum_{T,A,i} (u_i - \langle u \rangle_{A|T})^2\right)}} \quad (6.18)$$

where $\{T_k\} \in \{\{100 \text{ K}\}, \dots, \{1000 \text{ K}\}, \{100, 200, 300, 500, 1000 \text{ K}\}\}$, $\{A\} \in \{\{\text{Ba}\}, \{\text{Ti}\}, \{\text{O}\}, \{\text{Ba}, \text{Ti}, \text{O}\}\}$ and $\sum_{i \in A @ T}$ enumerates ions that correspond to ion type A in all

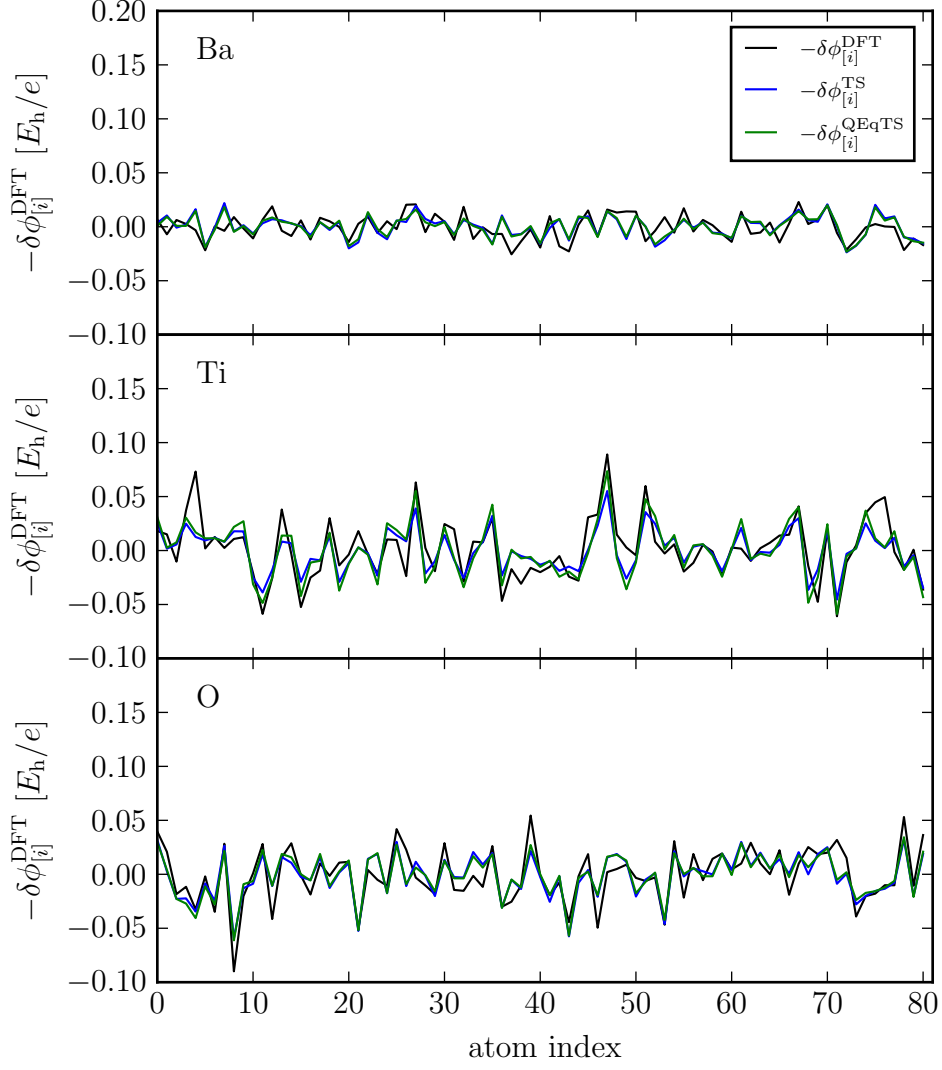


Figure 6.3: Change in the on-site electrostatic potential, based on DFT estimate and from an IP (TS and QEqTS). Configurations 1 for O, 1, 2 and 3 for Ba, Ti are shown.

$-\delta\phi_{[i]}^{\text{DFT}}$ Correlation				
	total	Ba	Ti	O
$-\delta\phi_{[i]}^{\text{TS}}$	0.79	0.62	0.68	0.84
$-\delta\phi_{[i]}^{\text{QEqTS (Ti,O)}}$	0.79	0.68	0.70	0.83
$-\delta\phi_{[i]}^{\text{QEqTS (Ti)}}$	0.80	0.67	0.68	0.85

Table 6.2: Correlation of the estimated change in the electrostatic potential based on DFT calculations with the same quantity calculated with the TS and QEqTS IPs. The estimate in this table is evaluated using average values $\Omega^{\text{S,A}} = \Omega_{\text{ave}}^{\text{A}}$ for $\text{A} \in \{\text{Ba}, \text{Ti}, \text{O}\}$ (see Section 6.1.3). Calculation temperature range is 100K–1000K.

the snapshot configurations taken from an MD simulation at temperature T . In Table 6.2 the set $\{T_k\}$ spans all temperatures, $v_i = \phi_{[i]}^{\text{DFT}}$ and $u_i = \phi_{[i]}^{\text{IP}}$ where IP superscript stands for the TS, QEqTS(Ti) or QEqTS(Ti,O). For example, the “total” correlation in Table 6.2 is based on a summation over all the ions over all the snapshot configurations at all temperatures 100 – 1000 K, while “Ba” correlation is restricted to only consider indices i that correspond to Ba ions in the same set of configurations. A good agreement of the potential fluctuations relative to the reference *ab initio* values is an important result. This shows that the QEq model is used in conjunction with an IP that provides a physically-reasonable description of electrostatics. All that the QEq model does is assign ionic charges based on the on-site electrostatic potentials subject to an energy penalty for deviations in ionic charges from the reference values. The ions’ self-energies are simply modelled with a second order Taylor expansion in charge transfer variables about reference charge states. This is to say, QEq-based IPs may or may not provide the correct electrostatic potential but it is certainly the premise of the QEq model that, given the correct “input” electrostatic potential, the “correct output” ionic charges should come out. It is thus satisfying to verify that the electrostatic potential in the QEqTS and TS IPs is qualitatively correct.

6.3 Induced dipole variables in relation to the ground state density

In Section 6.1.4 we have introduced MLWF-based dipole moments $\{\mathbf{P}_i\}$ with an intuitive definition, the one that effectively tracks the changes in the centre-of-charge of the local electron density. We now compare the TS and QEqTS $\{\mathbf{p}_i\}$ variables to the MLWF-based dipoles in order to give a physical interpretation to the former. Remarkably, this comparison reveals an essentially perfect correlation, summarised in Table 6.3. As a

	$\mathbf{P}_i$ Correlation		
	Ba	Ti	O
$\mathbf{p}_i^{\text{TS}}$	0.98	1.00	0.99
$\mathbf{p}_i^{\text{QEqTS (Ti,O)}}$	0.99	1.00	0.99
$\mathbf{p}_i^{\text{QEqTS (Ti)}}$	0.99	1.00	0.99

Table 6.3: A correlation of MLWF-based on-site dipole moments and dipole moment variables in QEqTS and TS IPs. Calculation temperature range is 100 K – 1000 K.

representative example, Figure 6.4 shows x -component of the dipole moments at 500 K⁶. Among other things, this agreement in fluctuations in $\{\mathbf{P}_i\}$ allows us to interpret QEqTS

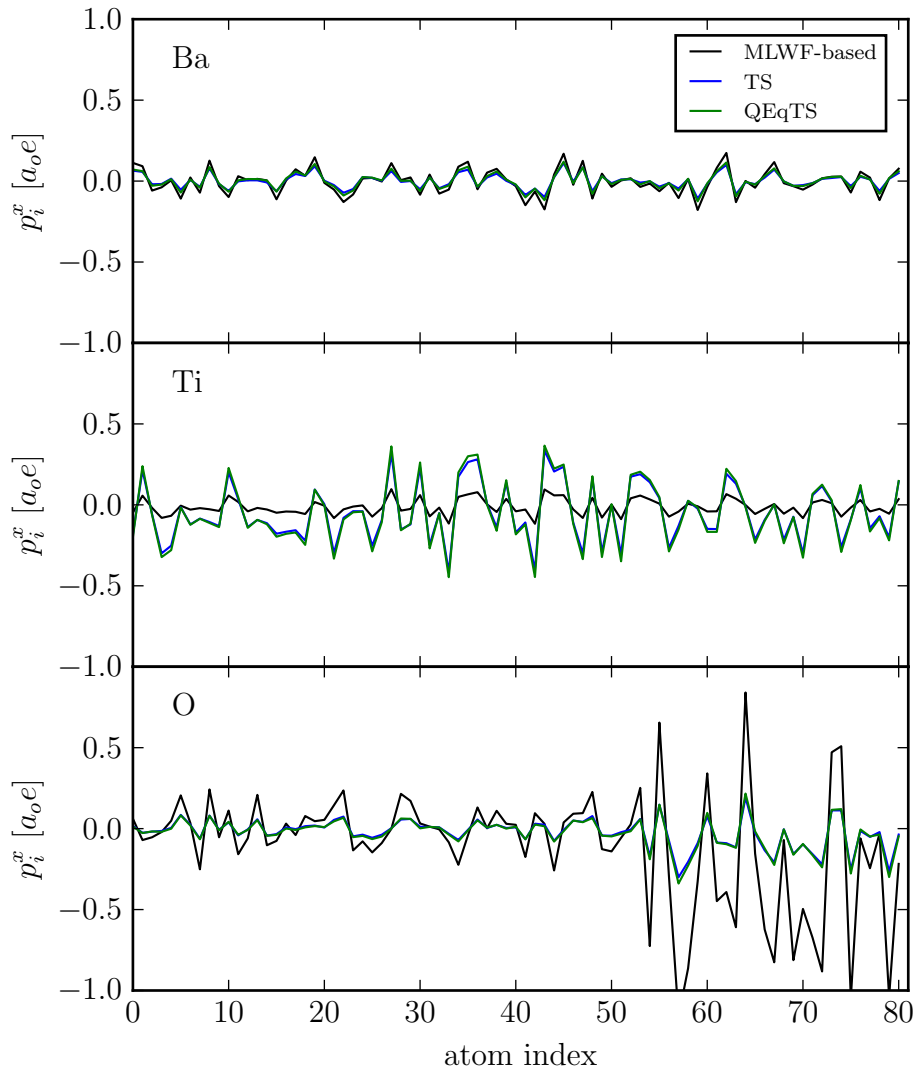


Figure 6.4: x -component of the dipole moment, comparing MLWF-based definition with variables from TS and QEqTS IPs. Change in the on-site electrostatic potential, based on DFT estimate and from an IP (TS and QEqTS). Configurations 1 for O, 1, 2 and 3 for Ba, Ti are shown at 500K.

and TS dipole moment variables $\{\mathbf{p}_i\}$ physically as descriptive of the local electron density at site i ; the magnitude of the dipole $\mathbf{p}_i$ tells us how *far* the local charge density has shifted from the ionic core while the opposite direction of $\mathbf{p}_i$ tells us *where* the electrons have shifted. When designing a polarizable ion IP one certainly intends for the dipole moment variables to represent local changes in electron density in exactly this

⁶For ease of visualisation, only the first 81 indexed atoms are considered, corresponding to configurations 1 for O; 1, 2 and 3 for Ba, Ti.

way; however this observed correlation actually proves that the dipole moment variables indeed have this physical meaning.

Furthermore, for Ba ions the magnitude of the dipole moments practically coincides, $\mathbf{p}_i \approx \mathbf{P}_i \forall i \in \text{Ba}$. For Ti and O ions, IP dipole variables are noticeably larger and smaller in magnitude, respectively, relative to MLWF-based dipoles. These do not have to agree in magnitude. Firstly, as already mentioned earlier, MLWF-based representation of the ground state is not unique and the physical interpretation of MLWFs is debatable; assigning parts of the electron density between Ti and O ions is a somewhat arbitrary step. Secondly, for the sake of the argument, we can assume that IP variables $\{\Delta q_i, \mathbf{p}_i\}$ are coefficients of some unspecified basis set, as explained in Section 3.2. Choosing different basis sets to represent the electron density leads to different coefficient values⁷. In other words, there is similarly no unique representation of the ground state density in terms of the IP variables. Nevertheless, the disagreement in magnitude between the $\{\mathbf{p}_i\}$ and $\{\mathbf{P}_i\}$ dipoles for Ti and O ions invites further analysis. The physical role of the induced dipole variables is revisited in Section 6.4.4 after a preliminary discussion. In Sections 6.4.2 and 6.4.3 the presented data and analysis suggest that the variables $\{\Delta q_i, \mathbf{p}_i\}$ associated with the Ti and O ions act in unison to simultaneously describe the long-range Coulomb interactions on one hand and the short-range Ti-O interaction in conjunction with the Morse-stretch term on the other hand. It is argued, in particular, that Ti and O variables are best thought of as collectively describing the entire electron cloud associated with the TiO_6 structural units, comprised of Ti ions and their six nearest neighbour O ions.

Finally, from Figure 6.4 it is evident that the induced dipole variables have nearly identical values in the TS and QEqTS IPs. This aids the subsequent analysis of the physical interpretation and the role of the QEq charge transfer variables. The QEq model has an implicit and an explicit effect on the interatomic forces and other properties calculated with an IP. The explicit effect is that one makes a substitution of $q_i^0 \rightarrow q_i^0 + \Delta q_i$ in all the calculations. The implicit effect is the fact that, in principle, the QEq equations affect the solution for the induced dipole moments, modify the electrostatic potential and, in general, lead to a different best-fit parameter set. However, we see that in a thermally perturbed defect-free BaTiO_3 the induced dipoles are largely unaffected. Similarly, in Section 6.2 we saw that the electrostatic potential in TS and QEqTS IPs

⁷It may be added that experience shows that distinct parameterisations of a TS (QEqTS) IP, where each corresponds to nearly the best-fit result, all lead to approximately the same $\{\mathbf{p}_i\}$ or $\{\Delta q_i, \mathbf{p}_i\}$ variable values for the same input atomic structure.

is also very similar. This suggests that in this system the QEq model has primarily the explicit effect on the IP-based calculations. The discussion and analysis presented in Section 6.4 is consistent with this view.

6.4 Charge transfer variables in relation to the ground state density

In the present section, in a series of steps, we address the physical interpretation and the role of the QEq charge transfer variables in describing inter-ionic interactions.

The Bader definition of an ionic charge or that based on the Löwdin population analysis do not represent a physical, measurable quantity – in condensed phase an ionic charge cannot be uniquely defined. Having said that, one may expect Löwdin, Bader and similarly-defined ionic charges to reflect correctly local increases and decreases in electron density. It is, therefore, reasonable to expect QEq charge transfers to correlate with the changes in the Löwdin or Bader charges. However, charge fluctuations predicted by the QEq are found to *anti-correlate* with changes in charges based on the Löwdin population analysis or Bader definition; this is likely to be the case if Hirshfeld, Mulliken or other definitions of charges are used instead. Thus, firstly, in Section 6.4.1 we address and rationalise the observed anti-correlation between changes in Bader or Löwdin charges and the QEq charge transfer variables. The concerted changes in the local charge density and electrostatic potential are examined in more detail to reveal that, in fact, this counter-intuitive correlation is correct, in a sense that QEq charges reflect changes in the electrostatic potential.

In Section 6.4.2 the interdependence of the changing atomic environment and the redistribution of the ground state density is examined. TiO_6 units, consisting of Ti ions and their six nearest neighbours, emerge as natural structural components in BaTiO_3 , due to highly correlated changes in $\{\mathbf{p}_i, \Delta q_i\}$ on one hand and the local changes in atomic positions within TiO_6 on the other hand.

In Section 6.4.3 the influence of the QEq variables on forces is examined. On average, interatomic forces are modified by a relatively small amount and the primary positive effect, it is argued, is an improved description of the short-range interactions between the Ti ions and their three nearest neighbour O ions.

Section 6.4.4 considers an alternative physical interpretation of the QEq charge transfer variables. Instead of viewing charge transfers as local increases and decreases in density, an interpretation is considered that views these variables as descriptors of the

electron cloud associated with each TiO_6 unit as a whole. For example, charge transfer variables modify the position of the center-of-charge of each TiO_6 unit, although this contribution is shown to be numerically small.

6.4.1 Local charge density in a model of overlapping ions

It is now demonstrated that a self-consistent ionic model that assigns charges in response to fluctuations in the electrostatic potential will necessarily disagree with the charges based on Löwdin or similar definitions, at least in the regime of small thermal perturbations to ionic positions in a defect-free ionic insulator, such as BaTiO_3 . We also show that, in contrast, the dipole moment variables are consistent with the profile of the electrostatic potential and retain an intuitive physical interpretation.

Before commencing the relevant analysis, it may be added that it was attempted to bias the force-matching algorithm to a parameter set such that QEq charge transfers correlated positively with the changes in Löwdin charges – this resulted in a markedly worse fit and a QEq solution that corresponded to a global energy *maximum* rather than a minimum. The latter point means that in this reparameterised QEqTS IP the regions of the more negative (positive) electrostatic potential attract negative (positive) charge, which constitutes an unphysical model. Furthermore, the Löwdin spilling parameter, which was defined in Section 4.4, is only 0.02 in BaTiO_3 studied in this chapter, which means that the vast majority of the ground state density is projected successfully onto the localised atom-centered basis set in this analysis. The same results were found in parameterisations of the QEqTS IP to bulk rutile TiO_2 (not presented). The possibility of any sign mistakes in the implementation of the QEq model can be discarded due to a multitude of rigorous tests, including those presented in Section 2.2.3.

The analysis proceeds as follows. We introduce a simple system of two ions to illustrate the interdependence of changes in the electrostatic potential on one hand and charge transfer or induced dipole variables on the other hand. Firstly, it will be demonstrated that the QEq model cannot assign charges that are simultaneously consistent with the electrostatic potential and correlate with charges based on Löwdin population analysis or similar definitions. This is not a deficiency of the QEq model, rather this constitutes a clarification of the physical interpretation of the QEq charge transfer variables in the regime of small perturbations. Secondly, induced dipoles are demonstrated to have an intuitive physical interpretation representing a shift in the ion’s centre-of-charge, while taking on values consistent with changes in the electrostatic potential.

Consider two overlapping ions i and j with fixed charges $q_i^0 = +1$ and $q_j^0 = -1$, respectively; atomic units are assumed throughout. The cation is treated as a point-particle with a charge distribution $\rho_i(\mathbf{r}) = q_i^0 \delta(\mathbf{r} - \mathbf{r}_i)$ while the anion j is finite with a distribution $\rho_j(\mathbf{r}) = (q_j^0 - Z_j)g(\mathbf{r} - \mathbf{r}_j) + Z_j \delta(\mathbf{r} - \mathbf{r}_j)$; $Z_j = 0$ is the nuclear charge, set to zero without loss of generality, and $g(\mathbf{r})$ defines the distribution, e.g. a STO or a Gaussian. This model is somewhat representative of the nearest neighbour Ti-O interaction in BaTiO₃, where O ion size and polarisability exceed considerably that of Ti cation, as estimated using MLWFs in Section 6.1.

The first thing to note is that the self-consistent-field variables, like charge transfers and induced dipole moments, both modify the electrostatic potential and are determined by it. However, as will be shown shortly, charge transfer and induced dipole variables introduce a relatively small correction to the electrostatic potential. The total electrostatic potential in the two-ion system, $\phi_{[i]}^{\text{total}}$, can be expressed $\phi_{[i]}^{\text{total}} = \phi_{[i]}^{\text{RIM}} + \phi_{[i]}^{\text{Model}}$, as follows⁸:

$$\begin{aligned} \phi_{[i]}^{\text{RIM}} &\equiv \frac{q_j^0}{r_{ij}} \\ \phi_{[i]}^{\text{Model}} &\equiv \frac{\Delta q_j}{r_{ij}} && \text{when using QEq model} \\ \phi_{[i]}^{\text{Model}} &\equiv \frac{-\mathbf{r}_{ij} \cdot \mathbf{P}_j}{r_{ij}^3} && \text{when using polarisable-ion model} \\ \phi_{[i]}^{\text{Model}} &\equiv \frac{\Delta q_j}{r_{ij}} + \frac{-\mathbf{r}_{ij} \cdot \mathbf{P}_j}{r_{ij}^3} && \text{when using combined model} \end{aligned}$$

The changes in the electrostatic potential, $\delta\phi_{[i]}^{\text{total}}$, are largely determined by changes in the ionic positions, $\delta\phi_{[i]}^{\text{total}} \approx \delta\phi_{[i]}^{\text{RIM}}$, while charge fluctuations or induced dipoles result in changes, $\delta\phi_{[i]}^{\text{Model}}$, that constitute a correction that is smaller in magnitude. This can be demonstrated by the correlation between $\delta\phi_{[i]}^{\text{RIM}}$ and $\delta\phi_{[i]}^{\text{total}}$ for the MS-Q, TS and QEqTS IPs in the thermally perturbed defect-free BaTiO₃. The correlation for MS-Q is 0.98, 0.98 and 0.75 at Ba, Ti and O sites, respectively, at any temperature; for TS and QEqTS it is 0.95, 0.91 and 0.80. It follows that to understand how charge-transfer or induced dipole variables vary in response to changes in the electrostatic potential, it is sufficient to use a rigid-ion $\phi_{[i]}^{\text{RIM}}$ and ignore the self-consistency. For example, when the distance between a cation and an anion is reduced, the QEq model predicts cation charge to be more positive because the on-site electrostatic potential becomes more negative – this conclusion can be reached without regard to the self-consistency and the details of the model used. Accordingly, two models are now introduced to relate QEq charge-

⁸For simplicity, the damping of the interactions due to the overlap is ignored, since it does not affect the argument.

transfer and induced dipole variables to changes in the underlying ground state density in general and Löwdin charges in particular.

As a first example, consider the ion j to be non-polarisable. As the distance between the ions, r_{ij} , decreases, the electrostatic potentials $\phi_{[i]} = -\int d\mathbf{r}g(\mathbf{r} - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}|$ and $\phi_{[j]} = 1/r_{ji}$ at sites i and j , respectively, become more negative and positive. In turn, the predicted QEq charge transfers are $\Delta q_i > 0$ and $\Delta q_j < 0$. In contrast, since more of the charge density j overlaps with site i , the changes in the Löwdin, Bader or similarly defined charges are $\Delta q_i^{\text{Lwdn}} < 0$ and $\Delta q_j^{\text{Lwdn}} > 0$. In a thermally perturbed defect-free BaTiO₃ changes in the electrostatic potential are due to small displacements of atoms away from their equilibrium positions, resembling the situation in this simple example. In this regime of perturbations of the electrostatic potential, the predicted QEq charges should not correlate with those based on the Löwdin population analysis and so cannot be interpreted as representative of local increases and decreases in charge density.

To examine the effect of the ionic polarisability on changes in the local charge density and electrostatic potential, we discuss a second simple example. Consider the same system of two ions but now keep the separation r_{ij} fixed and include instead an inducible dipole moment for the anion j . In the next paragraph, this model is described in greater detail and supplemented with a diagram. In contrast to the first example, we shall see that an induced dipole moment is both consistent with the gradient of the electrostatic potential and retains an intuitive physical interpretation, that of a shift in the center-of-charge of the ionic electron density. To see this, the second example of a polarisable anion is supplemented by an exact calculation of the electrostatic potential.

We define the anion electron distribution in terms of a Slater-type orbital, $\rho_j(\mathbf{r}) = q_j^0 \chi^2(\mathbf{r} - \mathbf{r}_j)$:

$$\chi(\mathbf{x}) \equiv \sqrt{\frac{(2\zeta)^{2n+1}}{4\pi(2n)!}} |\mathbf{x}|^{n-1} e^{-\zeta|\mathbf{x}|} \Big|_{n=2, \zeta=1.54[a_o^{-1}]} \quad (6.19)$$

The chosen n and ζ values impose normalisation, $\langle \chi | \chi \rangle = 1$, and that $\langle \chi | (\mathbf{x} - \bar{\mathbf{x}})^2 | \chi \rangle = \Omega_{\text{ave}}^{\text{O}}$, i.e. equal to the average quadratic spread of O MLWFs in a thermally perturbed BaTiO₃. Next, we define ionic positions and the anion dipole moment $\mathbf{p}_j$; the latter takes on values within a prescribed range:

$$\begin{array}{lll} \mathbf{r}_i = [0, 0, 0], & \mathbf{r}_j = [3.7, 0, 0], & \mathbf{r}_i, \mathbf{r}_j \text{ are held fixed} \\ \Delta \mathbf{x}_j^e \equiv \Delta d \hat{\mathbf{r}}_{ji} & \hat{\mathbf{r}}_{ji} = \mathbf{r}_{ji}/|\mathbf{r}_{ji}| & -0.7 \leq \Delta d \leq 0.0 \\ \mathbf{r}_j^e \equiv \mathbf{r}_j + \Delta \mathbf{x}_j^e, & \mathbf{p}_j \equiv \Delta \mathbf{x}_j^e (q_j^0 - \underbrace{Z_j}_{=0}) & 0.0 \leq |\mathbf{p}_j| \leq 0.7 \end{array}$$

where $\mathbf{r}_{ji} \equiv \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}_j^e$ points to the center-of-charge of the anion electron distribution, i.e. $\rho_j(\mathbf{r}) \rightarrow q_j^0 g(\mathbf{r} - \mathbf{r}_j^e)$. This system is depicted in Figure 6.5 in the top and bottom panels for the unpolarised $\Delta\mathbf{x}_j^e \equiv 0.0\hat{\mathbf{r}}_{ji}$ and polarised $\Delta\mathbf{x}_j^e \equiv -0.7\hat{\mathbf{r}}_{ji}$ anion, respectively.

The equations summarise a system where an electron cloud at site j is initially centered at $\mathbf{r}_j^e = \mathbf{r}_j = [3.7, 0.0, 0.0]$ and then it shifts towards the site i with the final value of $\mathbf{r}_j^e = [3.0, 0.0, 0.0]$. The nucleus of the ion j is held fixed at all times at $\mathbf{r}_j$ and the shift in the electron cloud is interpreted as an induced dipole of the anion. The dipole is defined analogously to the way MLWF-based dipoles $\{\mathbf{P}_i\}$ were defined in Eq. 6.14 and is justified given the perfect correlation with the IP variables $\{\mathbf{p}_i\}$. The values chosen are representative of the nearest neighbour Ti-O interaction in BaTiO₃ where interatomic distance between Ti and its three closest O ions falls in the range 3.4 – 3.8 a_o and the magnitude of the O dipole moments $\{\mathbf{P}_i\}$, defined in terms of MLWFs, varies in the range $\sim 0.1 - 0.8 ea_o$, corresponding to an electron cloud distorted towards the closest Ti cation (see Section 6.4.2). Thus, the sites at $\mathbf{r}_i$ and $\mathbf{r}_j$ can be thought of as representative of the Ti ion and O ions, respectively.

A measure of the local charge based on a volume partition is defined – these charges are expected to increase (decrease) whenever Löwdin, Bader or similarly defined charges increase (decrease) in this example.

A plane perpendicular to $\mathbf{r}_{ji}$ halfway between the two ionic nuclei partitions the space in two, defining the ionic charges in terms of the volume associated with each ion:

$$q_i^{\text{vol}}(\Delta\mathbf{x}_j^e) \equiv - \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{0.5|\mathbf{r}_{ji}|} dz' |\chi(\mathbf{r}' - (\mathbf{r}_j + \Delta\mathbf{x}_j^e))|^2, \quad \hat{\mathbf{z}} \parallel \mathbf{r}_{ji} \quad (6.20)$$

$$q_j^{\text{vol}}(\Delta\mathbf{x}_j^e) \equiv - \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{0.5|\mathbf{r}_{ji}|}^{\infty} dz' |\chi(\mathbf{r}' - (\mathbf{r}_j + \Delta\mathbf{x}_j^e))|^2, \quad \hat{\mathbf{z}} \parallel \mathbf{r}_{ji} \quad (6.21)$$

where $\hat{\mathbf{z}} \parallel \mathbf{r}_{ji}$ designates that the z -axis in the integrand is along the vector $\mathbf{r}_{ji}$.

Finally, the change in the electrostatic potential at site i is calculated exactly as well as approximately in terms of the dipole moment $\mathbf{p}_j$ and in terms of the volume-based definition of anion's charge, q_j^{vol} , as follows:

$$\delta\phi_{[i]}^{\text{vol}} \equiv \frac{q_j^{\text{vol}}(\Delta\mathbf{x}_j^e)}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{q_j^{\text{vol}}(\mathbf{0})}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (6.22)$$

$$\delta\phi_{[i]}^{\text{exact}} \equiv \int \frac{-|\chi(\mathbf{r}' - (\mathbf{r}_j + \Delta\mathbf{x}_j^e))|^2}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' - \int \frac{-|\chi(\mathbf{r}' - \mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \quad (6.23)$$

$$\delta\phi_{[i]}^{\text{p}} \equiv \frac{\mathbf{p}_j \cdot (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3} \quad (6.24)$$

The middle panel of Figure 6.5 shows, as expected, that the change in the ionic charge q_i^{vol} , based on a definition similar to Löwdin population analysis, is inconsistent with the change in electrostatic potential. At the same time, it shows that approximating

the changes in the exact electrostatic potential, $\delta\phi_{[i]}^{\text{exact}}$, in terms of an induced dipole moment, $\delta\phi_{[i]}^{\text{p}}$, results in a qualitatively and, in this simple example, quantitatively good agreement. The induced dipoles adequately reflect changes in the electrostatic potential

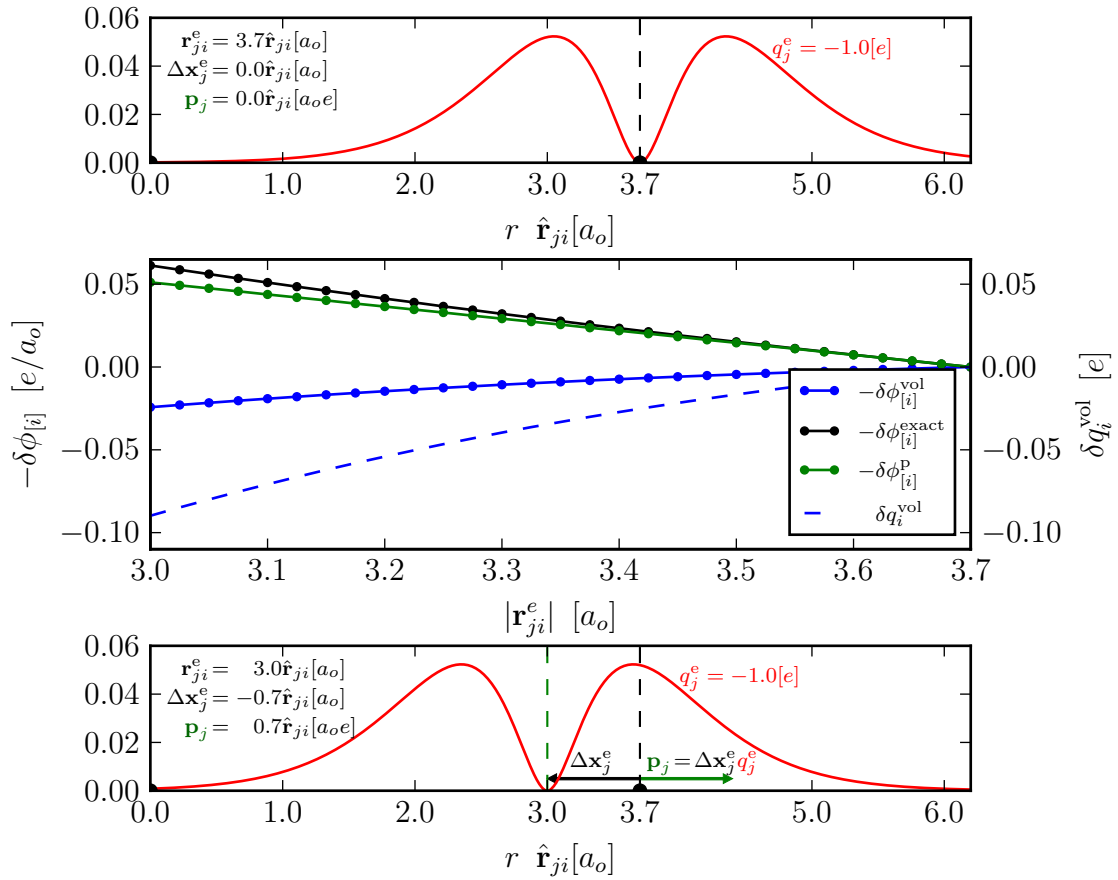


Figure 6.5: Change in the electrostatic potential is shown based on the exact calculation using Slater-type charge density, as well as based on an approximation using a dipole moment and volume-based charge q_j^{vol} , as defined in text.

and at the same time represent changes in the anion charge density in a physically intuitive way.

Finally, for completeness, electrostatic potential changes are calculated based on the definition of ionic charges similar to Löwdin population analysis, $\delta\phi_{[i]}^{\text{vol}}$. By construction, $\delta\phi_{[i]}^{\text{vol}}$ is consistent with changes in q_i^{vol} but this approximation turns out to be in qualitative disagreement with the exact result.

The conclusions can now be summarised considering the regime of small fluctuations in electrostatic potential such as those in the thermally perturbed defect-free BaTiO₃. A QEq-based IP cannot both reproduce accurately changes in the electrostatic potential and predict charge fluctuations in agreement with the charges based on the Löwdin

population analysis or similar definitions. Instead, an alternative physical interpretation of QEq charge transfer variables is considered in Section 6.1.4. In contrast, induced dipole moments reflect the changes in the electrostatic potential and have an intuitive physical interpretation, that of a shift in the center-of-charge of the ionic electron density.

6.4.2 Charge transfer in response to changes in ionic positions

In Section 6.4.1 we saw that QEq charge transfer variables cannot be interpreted to represent local increases or decreases in the ground state charge density. In the present

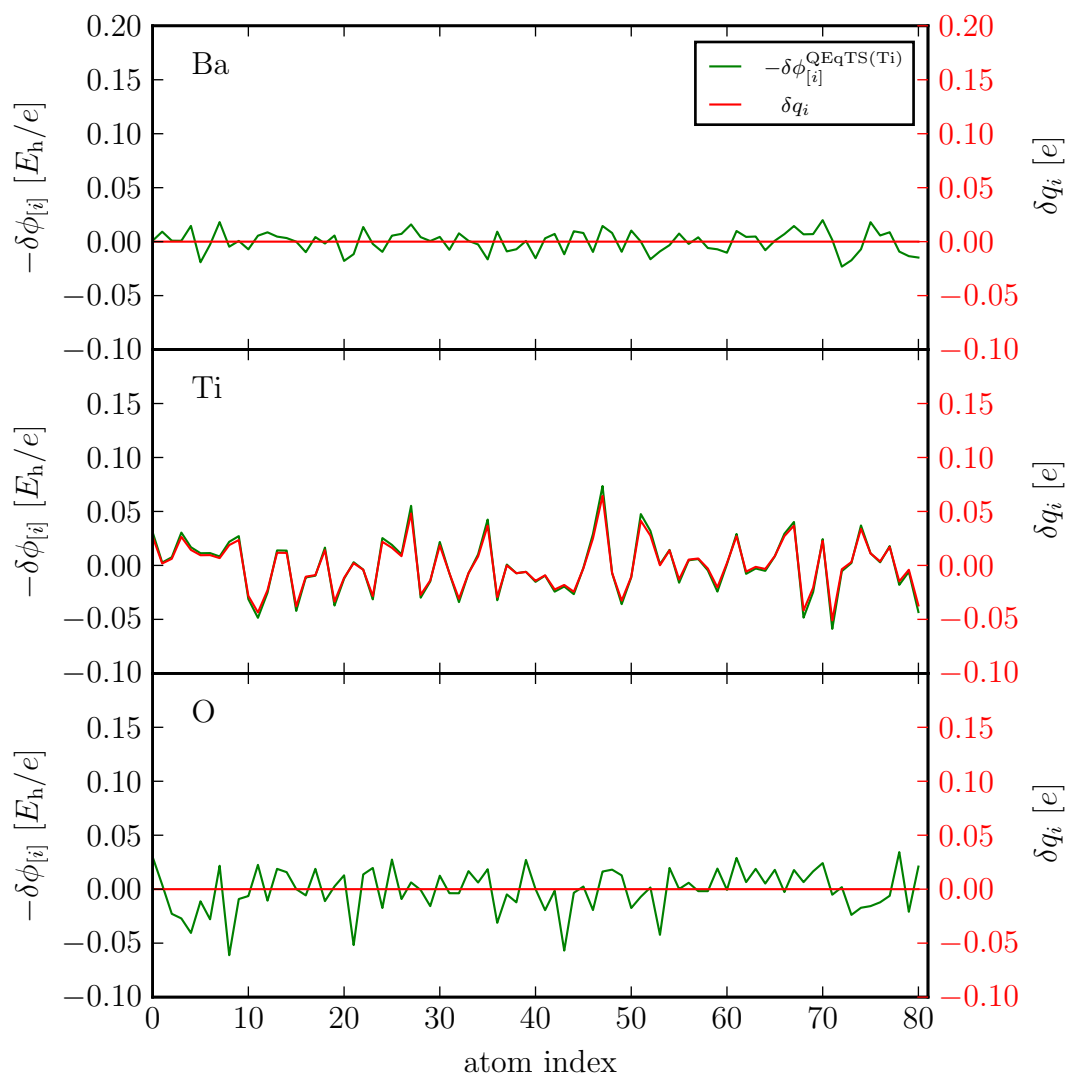


Figure 6.6: Change in the negative of on-site electrostatic potential *vs.* change in charges, calculated using QEqTS(Ti) IP. Configurations 1 for O and 1, 2 and 3 for Ba and Ti are shown, at 500 K.

section, firstly, we relate changes in the ground state density to changes in the positions of ionic nuclei and, secondly, we correlate QEq charge transfer variables to changes in

the ground state density. In particular, in the TiO_6 units, consisting of the Ti ions and their six nearest neighbours, the motion of the Ti ion can be thought to be in sync with the local electron density redistribution. As Ti ion moves into one of the eight corners of the reference cubic cell, it effectively modulates the polarisation of the local Ti and O ions' density.

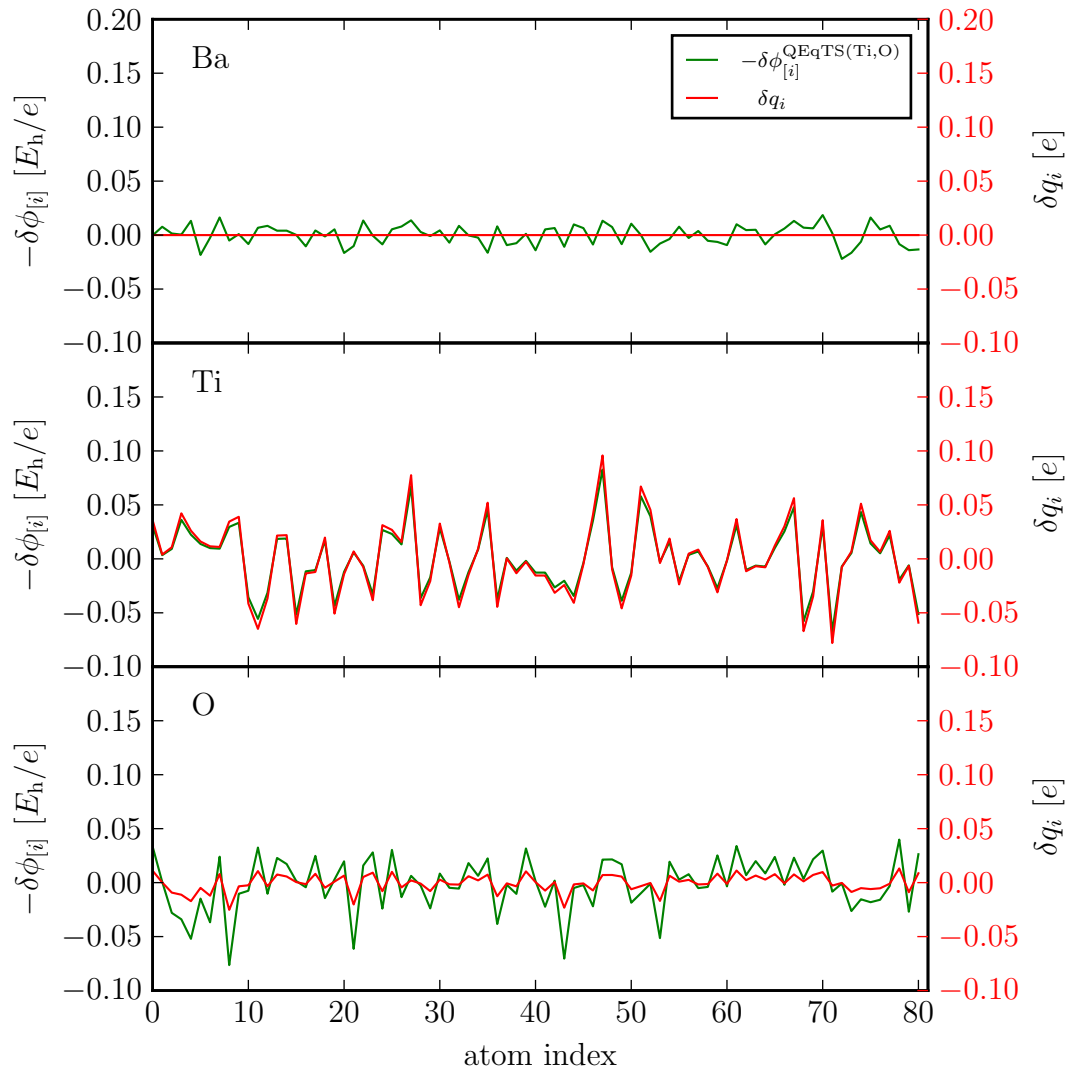


Figure 6.7: Change in the negative of on-site electrostatic potential *vs.* change in charge, calculated using QEqTS(Ti,O) IP. Configurations 1 for O, 1, 2 and 3 for Ba, Ti are shown, at 500 K.

Figures 6.6 and 6.7 show charge fluctuations in the QEqTS(Ti) and QEqTS(Ti,O) IPs, respectively. The correlation of the changes in the ionic charges and the negative of the electrostatic potential is built into the model to a large extent – as long as the best fit QEq parameters give a solution that is a global *minimum* this correlation must be observed.

QEqTS(Ti) and QEqTS(Ti,O) IPs predict non-zero charge transfers between Ti ions and none between Ba ions; additionally the latter IP corresponds to non-zero charge transfers between O ions. The absence of charge fluctuations between Ba ions can be rationalised as follows – the upper valence band in BaTiO₃ corresponds primarily to O sites and, to a lesser extent, Ti sites due to nearest-neighbour overlaps, as discussed in Section 6.1.2. Therefore, Ba ions’ electrons correspond to lower valence bands that

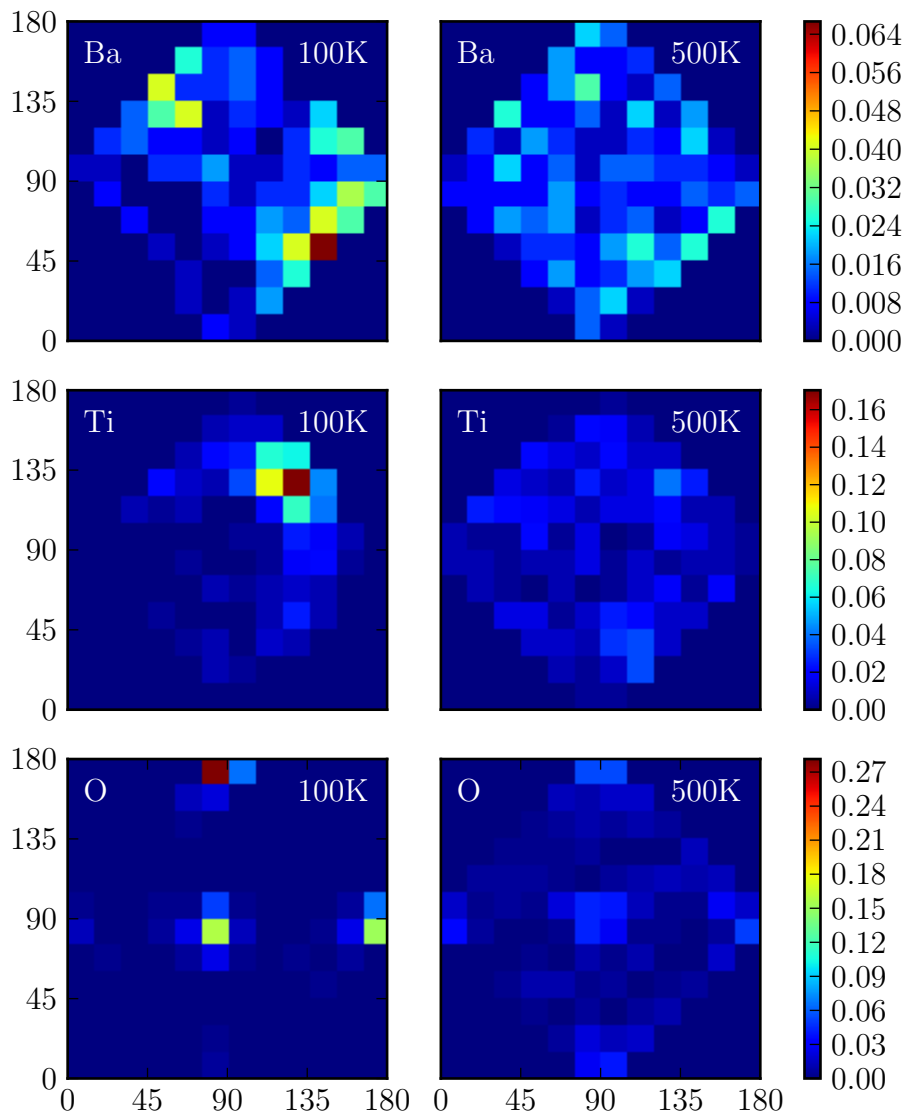


Figure 6.8: QEqTS IP dipole moment normalised distribution of orientation angles, at 100 K and 500 K, from a 10 picosecond NPH simulation. Vertical and horizontal axes indicate angle with the z - and x -axis, respectively.

are relatively chemically inert. Additionally, the fluctuations in the electrostatic potential at Ba sites are noticeably smaller in magnitude relative to O and Ti sites. The absence of charge fluctuations for O ions in the best-fit QEqTS IP is rationalised in

Section 6.4.3, when the effect on forces is considered. It will be argued in Section 6.4.3 that the QEq charge transfers simultaneously improve and disimprove the description of the interatomic pairwise interactions for different ion pairs. During force-matching the balance of the positive and negative effects on the accuracy results in a suppression of charge transfers between O ions.

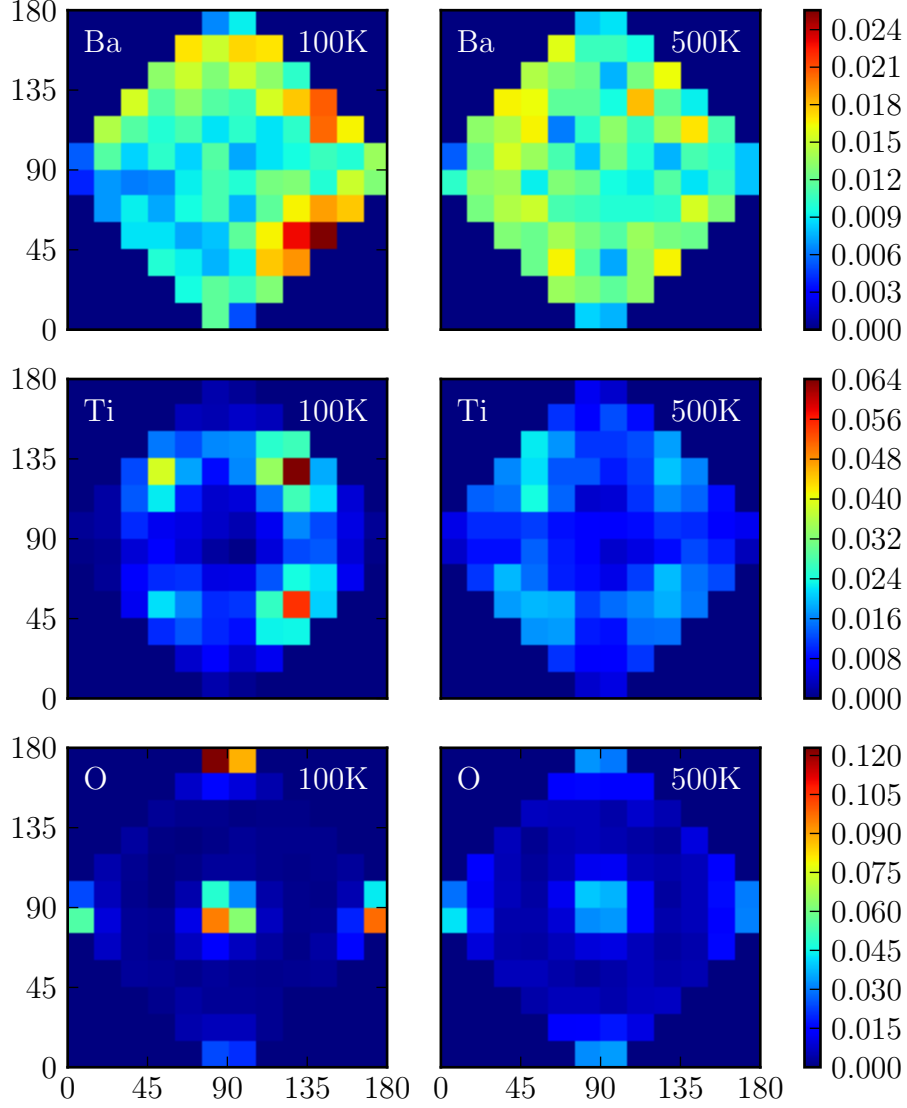


Figure 6.9: QEqTS IP dipole moment normalised distribution of orientation angles, at 100 K and 500 K, from a 100 picosecond NpH simulation. Vertical and horizontal axes indicate angle with the z - and x -axis, respectively.

Changes in the MLWF-based dipole moments, $\{\mathbf{P}_i\}$, provide information on the ground state charge density response to changing positions of ionic nuclei; recall from Section 6.1.4, $\mathbf{P}_i/(-8.0)$ is the position of the center-of-charge of the electron cloud of the ion i , defined in terms of the four MLWFs anchored on this ion.

Given the nearly perfect correlation between $\{\mathbf{P}_i\}$ and the IP variables $\{\mathbf{p}_i\}$, the latter contain qualitatively the same information. Figures 6.8 and 6.9 show the average of the QEqTS(Ti) dipole moments over 10 and 100 picoseconds, respectively, for Ba, Ti and O at 100 K and 500 K. In order to interpret the histogram, note that in BaTiO₃ Ti has 6

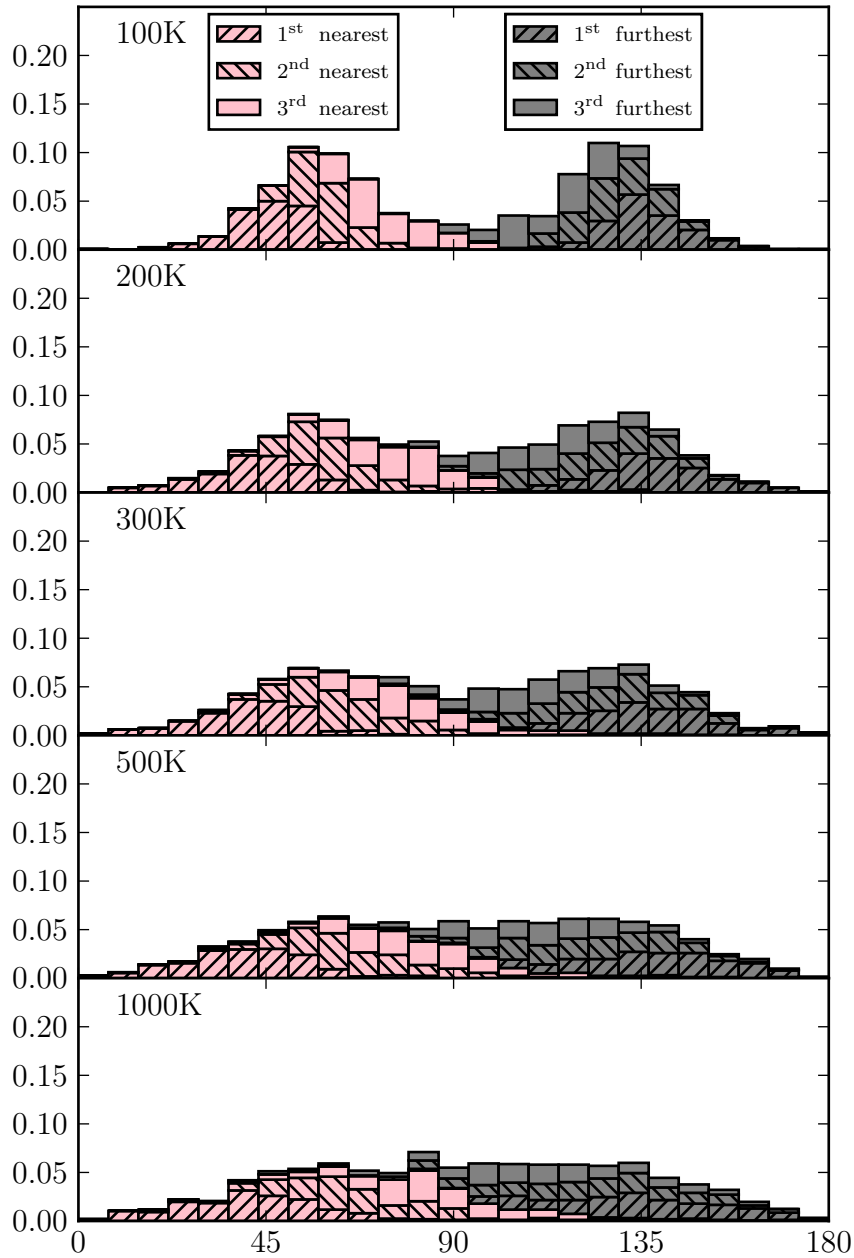


Figure 6.10: Normalised histogram of Ti dipole moment angles relative to nearest neighbour O ions, defined in text. The Ti dipole moment points in-between the three nearest O ion (pink) at about 45° to each neighbour at lower temperatures.

nearest neighbours while O ions have two Ti nearest neighbours, forming approximately a straight Ti-O-Ti line; in the simulation cell used in this study the Ti-O-Ti nearest neighbour units are aligned along either x -, y - or z -axis.

At 100 K it is clear that the system maintains approximately constant ionic polarization over the span of 10 picoseconds in a NPH simulation; the average Ti dipole moment is approximately conserved pointing into one corner of the simulation cell. O ions are polarised along x -, y - or z -axis. O induced dipoles are aligned with the average Ti dipole moment in a sense that $\mathbf{p}_i^{\text{O}} \cdot \langle \mathbf{p}^{\text{Ti}} \rangle > 0$ for most O ions i , implying there may be an interdependence of the Ti and O average induced dipole moments at 100 K.

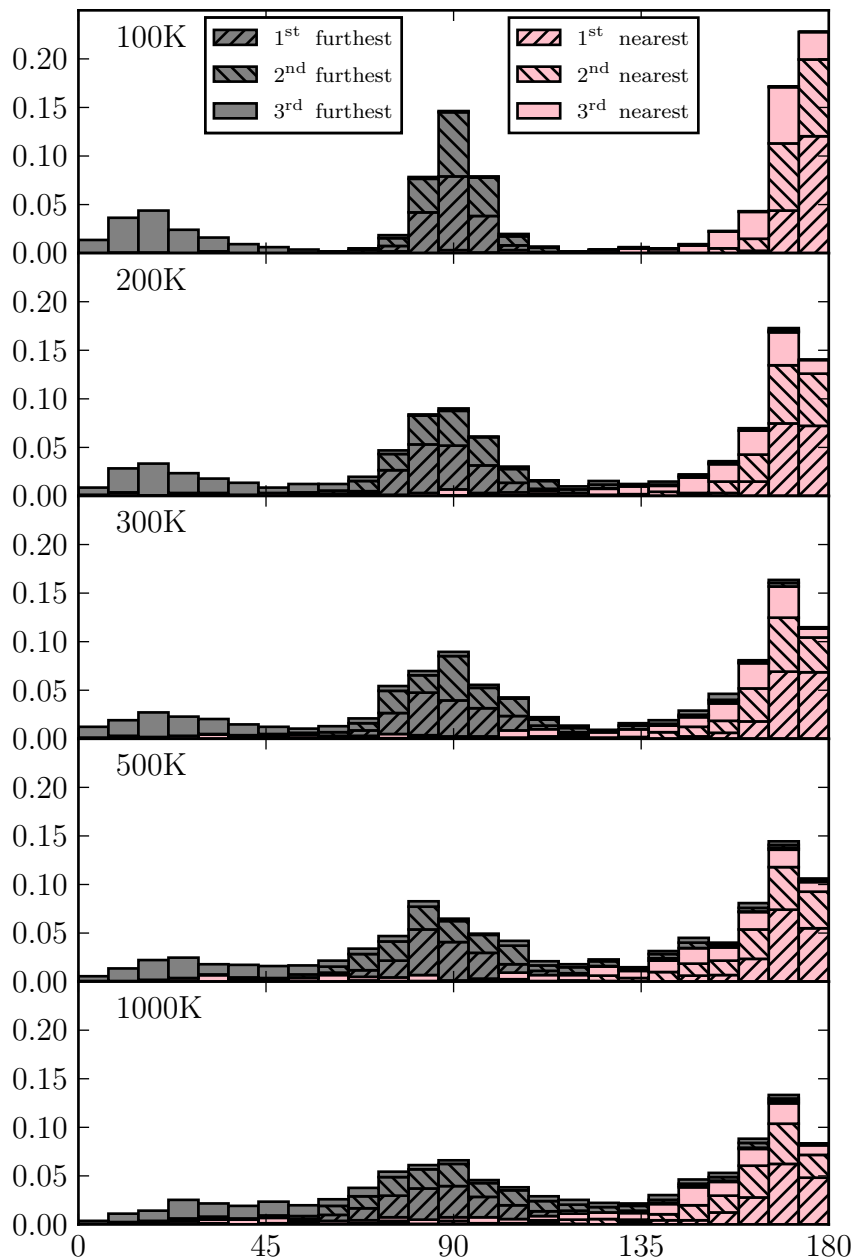


Figure 6.11: Normalised histogram of O dipole moment angles θ relative to nearest neighbour Ti ions, defined in text. For the three nearest O ions (pink) the dipole moments clearly point away from Ti at all temperatures.

It is clear from Figure 6.9, which displays dipole moments averaged over a 100 ps

NPH simulation, that at 100 K the Ti dipole moment occasionally “flips” to point into a different corner of the simulation cell. This suggests considering instead whether there is an interdependence of the Ti and O dipole moments at any one instance in time.

Figure 6.11 demonstrates the interdependence of the local atomic structure of the TiO_6 subunits and the O induced dipole moments; Figure 6.10 shows a similar information for the Ti dipole moments. In Figure 6.11, six histograms are defined and superimposed based on an ordered set of six nearest neighbours of every Ti ion, from the closest to the furthest O neighbour. For every Ti ion i six angles are defined via $\cos \theta_{ij} \propto \mathbf{p}_j^{\text{O}} \cdot (\mathbf{r}_{i\text{Ti}} - \mathbf{r}_{j\text{O}})$ where $j \in \{1, \dots, 6\}$ enumerates six nearest neighbour O ions from the closest to the furthest O. Thus, for example, we see that at 100 K for every Ti ion the dipole moment of its closest O neighbour is approximately at $\sim 180^\circ$, i.e. it points away from Ti; this implies that the electrons associated with the O anion move towards the Ti ion. The superimposed histograms in Figure 6.10 are defined similarly but reflect the orientation of the induced dipole moment of the Ti ion itself – for each Ti ion the six angles are defined as $\cos \theta_{ij} \propto \mathbf{p}_i^{\text{Ti}} \cdot (\mathbf{r}_{j\text{O}} - \mathbf{r}_{i\text{Ti}})$ where index j , $j \in \{1, 2, 3, 4, 5, 6\}$, enumerates O nearest neighbours.

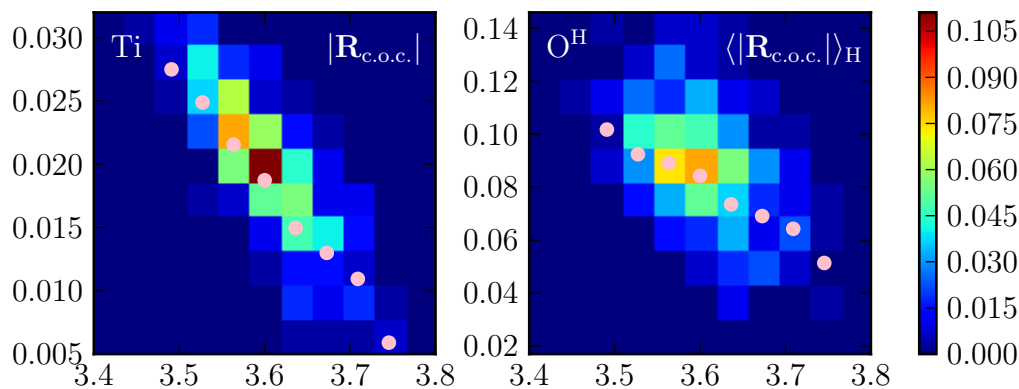


Figure 6.12: Distance to the centre-of-charge on Ti ions (left) and averaged over three closest O ions (right). Units are in a_o . Pink dots mark the mean position of each column. Histogram based on MLWFs’ centers, for configurations taken from the 300 K NPH 10 ps MD run, 1 ps apart.

It is clear that the Ti and O dipole moments are highly correlated with the structure of the TiO_6 units. At all temperatures, the dipole moments of the three closest O ions always point *away* from the closest Ti ion, even at 1000 K. In contrast, Ti dipole moments point *towards* the closest three O ions, at lower temperature the direction is at about 45° (the midpoint between the three Oxygens) while at higher temperatures this direction peak is less pronounced in the histogram. Of the six nearest neighbours of Ti,

the induced dipoles of the furthest three O do not exhibit such a strong correlation in the TiO_6 unit. Therefore, grouping closest three and furthest three nearest neighbour O ions into “Head”(H) and “Tail”(T) sets, respectively, the subunit TiO_3^{H} emerges naturally as a building block of the BaTiO_3 because the electronic degrees of freedom are locked together for these four ions.

The following qualitative picture emerges. As TiO_6 units get thermally deformed, Ti ion moves into one of the eight corners of the reference cubic cell at any one moment in time and the on-site electrons polarize approximately in that same direction; the three nearest O ions then polarize away from this Ti ion. Given the perfect correlation between the MLWF-based $\mathbf{P}_i$ and the IP dipole moment variables $\mathbf{p}_i$, we can interpret the observed correlations of dipole moments within the TiO_3^{H} unit in terms of charge redistribution among these nearest neighbours. Electron clouds on O_3^{H} move towards the Ti ions while electrons on the Ti ion move away from O_3^{H} .

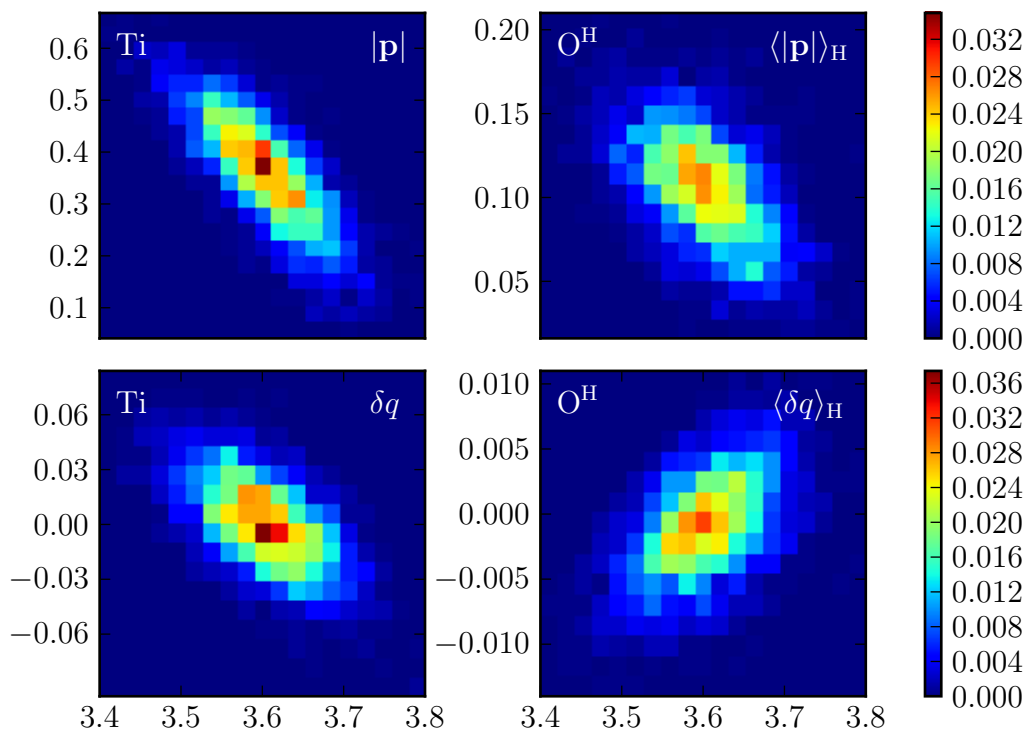


Figure 6.13: Dipole moment magnitude (top) and change in charge (bottom) on Ti ions (left) and averaged over three closest O ions (right). Histogram is from the 300 K NPH 100 ps MD simulation, configurations taken 1 ps apart.

The shorter is the distance between the Ti and O_3^{H} ions the more O_3^{H} electron cloud moves towards the Ti ion and the more Ti “on-site” electrons move away from the O_3^{H} ions. The degree of this shift can be quantified by considering the distance from the

ionic nucleus to the center-of-charge of the four on-site MLWFs, $|\mathbf{R}_{\text{c.o.c. } i}|$, defined as:

$$\mathbf{R}_{\text{c.o.c. } i} \equiv \frac{\sum_{s=1}^4 (\mathbf{R}_{i,s}^{\text{MLWF}} - \mathbf{r}_i)(-2.0)}{\sum_{s=1}^4 (-2.0)} \quad (6.25)$$

where $\mathbf{R}_{i,s}^{\text{MLWF}}$ is the position of the MLWF center indexed s anchored on the ion i . This is demonstrated in the histograms of Figure 6.12. The horizontal axis shows the distance between the Ti nucleus and the O_3^{H} nuclei, averaged over the three O ions, i.e. this is the average interatomic distance within the TiO_3^{H} unit. The vertical axis stands for $|\mathbf{R}_{\text{c.o.c. } i}|$ for the Ti ions (left subfigure) and for O_3^{H} , averaged over the three O ions (right subfigure). Eight electrons on Ti ion move away from O while eight electrons on O ions move towards Ti.

Figure 6.13 shows that both the Ti and O $\{\mathbf{p}_i, \Delta q_i\}$ variables are highly correlated among themselves as well as with the interatomic distance within the TiO_3^{H} unit. The histograms in Figure 6.13 use QEqTS(Ti,O) IP because it enables charge transfers between O ions and so its use offers greater insight; QEqTS(Ti) exhibits the same trends except O charge is numerically constant.

Correlation		
T [K]	$\delta\phi_{[i]}$ and $\delta\phi_{[i]}^{\text{H}}$	$\delta\phi_{[i]}$ and $\delta\phi_{[i]}^{\text{T}}$
100	0.47	-0.10
200	0.47	-0.04
300	0.47	0.00
500	0.52	0.04
1000	0.56	0.06
All T	0.50	-0.01

Table 6.4: Correlation of change in QEqTS(Ti) potential $\phi_{[i]}$ at Ti sites i and that due to three closest and furthest nearest neighbours, $\phi_{[i]}^{\text{H}}$ and $\phi_{[i]}^{\text{T}}$, respectively. Calculation is based on 100 time steps from 100 ps NPH simulation.

The QEq model is a global charge equilibration scheme in the sense that charges are based on electrostatic the potential due to all pther ions in the system. The reason QEq charge fluctuations correlate with the local structural changes of TiO_3^{H} is that the electrostatic potential at Ti sites is largely determined by these three oxygens, as demonstrated in Table 6.4. Table 6.4 presents the correlation of the total electrostatic potential at Ti sites i , $\phi_{[i]}$, with the contribution only due to the three closest and

furthest nearest neighbour O ions, $\phi_{[i]}^H$ and $\phi_{[i]}^T$, respectively. Notice the contrast, the contribution due to the three furthest of the six nearest neighbours, $\phi_{[i]}^T$, is essentially uncorrelated with $\phi_{[i]}$ while $\phi_{[i]}^H$ shows a significant correlation of ~ 0.5 .

6.4.3 Effect of charge transfer variables on interatomic interactions

It is difficult to isolate the effect of charge transfer in the QEqTS IP on the interatomic interactions. Firstly, the net force on an ion is a sum over infinitely many pairwise interactions with all the ions in the system. Secondly, the analytic form of the IP is a sum of several terms, some of which are charge-independent. Finally, observed charge fluctuations are relatively small, not exceeding $\leq 0.05 e$ for Ti ions, and even smaller for O ions, so even the charge-dependent terms are only slightly affected. Nevertheless, the analysis of Sections 6.4.1 and 6.4.2 allows us to construct a plausible argument, addressing the role of the QEq charge-transfer variables in representing interatomic interactions in the thermally perturbed bulk BaTiO₃.

The ability to reproduce *ab initio* forces is used as a measure of accuracy, allowing us to compare several distinct analytic forms of the ionic IPs. Additionally, this shows the average effect of the QEq model on representing forces. The results for the attained accuracy when applying a set of distinct IPs to bulk BaTiO₃ are summarised in Table 6.5. Table 6.6 additionally compares two different parameterisations of QEqTS IPs –

IP	$\Delta F_{\text{r.m.s.}} \%$			
	total	Ba	Ti	O
MS-Q _o	56.23 (41.25)	51.44 (43.89)	66.58 (52.25)	44.80 (27.71)
MS-Q	53.95 (38.97)	33.96 (26.41)	56.95 (42.62)	56.06 (38.97)
TS	14.98 (0.00)	7.55 (0.00)	14.33 (0.00)	17.09 (0.00)
QEqTS	14.14 (-0.84)	8.88 (1.33)	14.22 (-0.11)	15.45 (-1.64)

Table 6.5: Quality of force-matching for each IP, for temperatures 100 K – 1000 K. Half of configurations at temperatures 100 K – 500 K and all configurations at 1000 K were not included in the fit.

in IPs designated by QEqTS(Ti) and QEqTS(Ti,O) charge transfer takes place on Ti ions only, and both the Ti and O ions, respectively. Although the latter IP results in a slightly poorer overall fit, it is used to facilitate the analysis of the effect of the QEq model on the interatomic interactions. Any reference to QEqTS parameterisation

implies QEqTS(Ti) unless explicitly stated otherwise.

IP	$\Delta F_{\text{r.m.s.}} \%$			
	total	Ba	Ti	O
TS	14.98 (0.00)	7.55 (0.00)	14.33 (0.00)	17.09 (0.00)
QEqTS (Ti,O)	14.25 (-0.73)	9.90 (2.35)	14.70 (0.37)	15.19 (-1.90)
QEqTS (Ti)	14.14 (-0.84)	8.88 (1.33)	14.22 (-0.11)	15.45 (-1.64)

Table 6.6: Quality of force-matching for each IP, for temperatures 100 K – 1000 K. Half of configurations at temperatures 100 K – 500 K and all configurations at 1000 K were not included in the fit.

The information presented in Tables 6.5 and 6.6 is to be interpreted as follows. Firstly, the QEq model improves the accuracy of forces only by a small amount, $\sim 0.8\%$ and 2.3% if used in conjunction with the polarisable-ion TS and rigid-ion MS-Q_o IPs, respectively. This is to be contrasted with a dramatic improvement of 41% when a rigid-ion IP is extended to include a polarisable-ion model. Secondly, supplementing the TS IP with the QEq model has the primary effect of improving forces on the O ions, while disimproving forces on the Ba ions and having approximately no effect on the Ti ions, with changes for any one specie on the order of $\sim 1 - 2\%$.

A plausible explanation of the observed effect on forces is presented shortly, but first it is convenient to separate the long-range and short-range contributions. An expression for the forces can be written as:

$$E_{ij} = E_{ij}^{\text{MS}}(\{r_{ij}\}) + E_{ij}^{\text{ES}}(\{r_{ij}; \Delta q_i^{\text{scf}}, \mathbf{p}_i^{\text{scf}}\}) \quad (6.26)$$

$$\mathbf{F}_s = -\frac{1}{2} \nabla_s \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} E_{ij}(\{r_{ij}\}) \quad (6.27)$$

$$= \sum_{j \neq s}^{N_{\text{atm}}} -\nabla_s E_{sj}(\{r_{sj}\}) \quad (6.28)$$

$$\equiv \underbrace{\sum_{j \in \text{n.n.}(s)} -\nabla_s E_{sj}(\{r_{sj}\})}_{\equiv \mathbf{F}_s^{\text{short}}} + \underbrace{\sum_{j \notin \text{n.n.}(s)}^{\infty} -\nabla_s E_{sj}(\{r_{sj}\})}_{\equiv \mathbf{F}_s^{\text{long}}} \quad (6.29)$$

$$= \mathbf{F}_s^{\text{short}} + \mathbf{F}_s^{\text{long}} \quad (6.30)$$

Here, the summation that defines $\mathbf{F}_s^{\text{short}}$ is over the nearest and next neighbours of ion s , while the term $\mathbf{F}_s^{\text{long}}$ involves the summation over the remaining infinitely many ions; the symbol ∞ is included explicitly to emphasize the otherwise implied Ewald summation.

The definition of $\mathbf{F}_s^{\text{short}}$ is somewhat arbitrary, and it may be appropriate to include more or less neighbours. Morse-stretch and other short-range terms vanish for large interionic distances r_{ij} , and so $\mathbf{F}_s^{\text{long}}$ is approximated by the multipole expansion:

$$\mathbf{F}_s^{\text{long}} \approx \sum_{j \notin \text{n.n.}(s)}^{\infty} -\nabla_s \left[q_s q_j \frac{1}{r_{sj}} + (p_s^\alpha q_j - q_s p_j^\alpha) \frac{\partial}{\partial r_{sj}^\alpha} \frac{1}{r_{sj}} - p_s^\alpha p_j^\beta \frac{\partial^2}{\partial r_{sj}^\alpha \partial r_{sj}^\beta} \frac{1}{r_{sj}} \right] \quad (6.31)$$

The first part of the argument is that the QEqTS IP can be assumed to leave the long-range forces approximately unchanged. Firstly, in Figure 6.4 it was demonstrated that the $\{\mathbf{p}_i\}$ variables in QEqTS and TS IPs are essentially identical. Secondly, $\mathbf{F}_s^{\text{long}}$ requires the summation over infinitely many ions and, due to the charge conservation within each simulation cell, the charge fluctuations are approximately homogeneously distributed in space. Therefore, charge fluctuations are expected to leave the magnitude and the direction of the force $\mathbf{F}_s^{\text{long}}$ approximately unchanged relative to the fixed-charge TS IP.

The second part of the argument is based on the analysis of Section 6.4.2 and the correlation in Figure 6.13 in particular, which demonstrates that $\{\Delta q_i\}$ variables, along with $\{\mathbf{p}_i\}$, clearly modulate short-range cohesive interaction between the Ti ion and its three closest O neighbours, in conjunction with the Morse-stretch term.

The final part of the argument is based on the anti-correlation of the QEq charge transfer variables with the changes in the ionic charges based on the Löwdin population analysis or Bader charges, discussed in Section 6.4.1. If there is relatively more charge density near ion i , in general the variable Δq_i will *not* reflect this by assuming a negative value. In fact, the observed anti-correlation means Δq_i will usually be positive in such a case. This means that the $q_i q_j / r_{ij}$ term incurs an error, which is significant for the interaction of Ti and its next nearest neighbour Ba ions. In the QEqTS(Ti,O) IP, charge fluctuations take place among O ions as well, so this issue seems to be exacerbated, disimproving the representation of the Ti-O_3^{T} and the next-nearest neighbour Ba-O interactions.

The proposed net effect on the short-range interactions is schematically represented in Figure 6.14. The symbol $\times$ designates the center-of-charge of the four on-site MLWFs. Consistently with Figure 6.12, for the Ti and O ions these are set to their limiting values of 0.005 and 0.04 a_o in the top panel and 0.03 and 0.14 a_o in the bottom panel, respectively. The Ti-O_3^{H} nearest neighbour distance between the nuclei is set to 3.5 and 3.7 a_o in the top and bottom panels, respectively, consistent with the range observed in BaTiO_3 . The solid and dashed circles in the diagram are centered at the center-of-charge of the ion's four MLWFs and at the ionic nuclei, respectively. The dashed circle has the

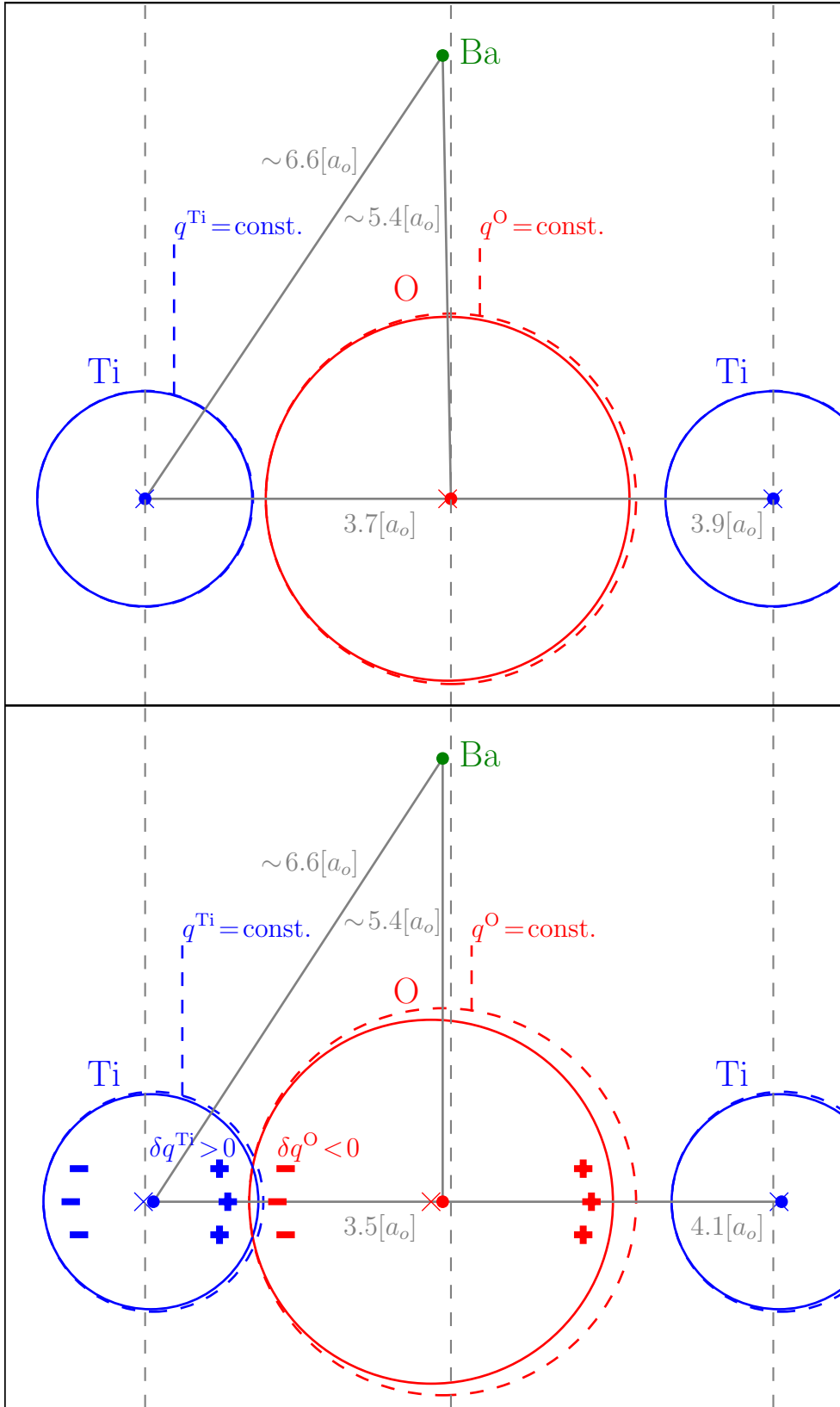


Figure 6.14: The $\times$ symbol indicates MLWFs' center-of-charge and the solid circle the size of the on-site electron cloud, as described in text. The dashed circles are centered at ionic nuclei, represented by solid dots, with the radius just large enough to enclose the solid circle. Dashed circles represent charge density of constant charge.

smallest radius that is large enough to encompass the solid circle – it represents an ion of constant charge. The radius of the solid circle, representing the on-site electron cloud, is set to $\langle \sqrt{\Omega_i} \rangle_A + \langle |\bar{\mathbf{r}}_i, s| \rangle_{s,A}$ for $A \in \{\text{Ti}, \text{O}\}$ and $s \in \{1, 2, 3, 4\}$, i.e. the sum of the average of the square root of the quadratic spread and the average distance from the nucleus to any one on-site MLWF. This is meant to be representative of the size of the ionic electron cloud. The inclusion of the $\langle |\bar{\mathbf{r}}_i, s| \rangle_A$ term is motivated by the fact that while the center-of-charge of MLWFs is never further than 0.03 and 0.14 a_o away from the parent Ti and O nuclei, respectively, the distance to any one on-site MLWF is more significant, on average 0.40 and 0.62 a_o ; the four on-site MLWFs tend to move in the opposite directions relative to one another, contributing to the overall ionic size.

Figure 6.14 is to be interpreted as follows. As the distance between the Ti ion and its closest three O ions (represented by a single ion O) is reduced, the cohesive interaction is amplified by the Δq_i^{Ti} or Δq_i^{Ti} and Δq_i^{O} variables in the QEqTS(Ti) or QEqTS(Ti,O)) IPs, respectively. Charge transfer variables $\{\Delta q_i\}$ offer the additional degrees of freedom for describing the non-trivial dependence of the interatomic interaction on Ti-O distance between the Ti ions and its three nearest neighbours. In conjunction with the Morse and other terms this leads to an improved description of Ti-O_3^{H} interactions. However, the $q_i q_j / r_{ij}$ term for the Ti ion and the three furthest nearest neighbour O ions as well as with the next nearest neighbour Ba ions, incurs an error. In particular, during force-matching parameters correspond to charge fluctuations that balance the improvement in the cohesive interaction Ti-O_3^{H} and the disimproved representation of the mid-range Coulomb interaction Ti-O_3^{T} , Ti-Ba and O-Ba. For this reason charge fluctuations on O ions are suppressed in the best-fit parameterisation.

Recall from Table 6.5, extending the TS IP to include the QEq model modifies the accuracy of the forces on the Ba, Ti and O ions on the order of $\sim 1 - 2\%$. The magnitude of the charge-charge pairwise force contribution, $q_i q_j / r_{ij}^2$, is proportional to charges. Substituting the charge fluctuations of $\sim 0.05 e$, as observed for Ti ions, these terms are modified by $(q^{Ti} \pm \Delta q^{Ti}) / q^{Ti} \sim \pm 2\%$, using the TS and the average QEqTS value of Ti charges, $\langle q_i^{\text{Ti}} \rangle = 2.6 e$. This estimate is consistent with the observed changes in Table 6.5.

6.4.4 Charge transfer variables representing TiO_6 center-of-charge

In Section 6.4.1 it was argued that charge transfers in a QEq model applied to a thermally perturbed defect-free bulk BaTiO_3 do not represent local increases and decreases in electron density. In Section 6.4.2 the variables $\{\Delta q_i, \mathbf{p}_i\}$ were shown to be strongly

correlated with the atomic positions within the TiO_6 structural units, and in Section 6.4.3 this was linked to the description of the short-range Ti-O_3^{H} interactions. In the present section we consider a physical interpretation of the Ti (Ti and O) charge transfer variables in the QEqTS(Ti) (QEqTS(Ti,O)) IP as being descriptive of the electron cloud associated simultaneously with the Ti ion and its nearest neighbour O ions. In particular, we shall consider changes in the center-of-charge of the TiO_6 units, as represented in the TS and QEqTS IPs and compare this to an equivalent quantity defined using MLWFs. The QEq model is shown to marginally improve the agreement. Furthermore, the analysis of the present section allows us to rationalise the disagreement in magnitude of the $\{\mathbf{p}_i\}$ and $\{\mathbf{P}_i\}$ dipoles for the Ti and O ions, discussed in Section 6.3.

Consider a MLWF-based definition of the center-of-charge of the TiO_6 unit, $\mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6}$, relative to the position of the Ti ionic core:

$$\begin{aligned} \mathbf{P}_i^{\text{TiO}_6} &\equiv \sum_{s=1}^4 (\mathbf{R}_{i,s}^{\text{MLWF}} - \mathbf{r}_i^{\text{Ti}})(-2.0[e]) \\ &+ \frac{1}{2} \sum_{j=1}^6 \left[(\mathbf{r}_j^{\text{O}} - \mathbf{r}_i^{\text{Ti}})Z_{\text{O}} + \sum_{s=1}^4 (\mathbf{R}_{j,s}^{\text{MLWF}} - \mathbf{r}_i^{\text{Ti}})(-2.0[e]) \right] \end{aligned} \quad (6.32)$$

$$= \mathbf{P}_i^{\text{Ti}} + \frac{1}{2} \sum_{j=1}^6 \mathbf{P}_i^{\text{O}} + \frac{1}{2} \sum_{j=1}^6 \mathbf{r}_{ji}^{\text{O,Ti}} Q^{\text{O}} \quad (6.33)$$

$$\mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6} \equiv \mathbf{P}_i^{\text{TiO}_6} / (-2) \quad (6.34)$$

where $\mathbf{r}_i^{\text{A}}$ and $\mathbf{R}_{i,s}^{\text{MLWF}}$ are the positions of the nucleus i for $\text{A} \in \{\text{Ti}, \text{O}\}$ and MLWF centers associated with the ion i , $\mathbf{r}_{ji}^{\text{O,Ti}} \equiv \mathbf{r}_j^{\text{O}} - \mathbf{r}_i^{\text{Ti}}$, $\mathbf{P}_i$ are the MLWF-based dipole moments and the constant $Q^{\text{O}} \equiv -2.0$ is the oxygen MLWF-based ionic charge; site i refers to the Ti ion and the sum over j enumerates six nearest neighbour O ions with a factor $1/2$ included to avoid double counting since one O has two Ti neighbours.

One can clearly define an analogous quantity in TS and QEqTS IPs, in order to test if it agrees with the MLWF-based center-of-charge.

$$\mathbf{p}_i^{\text{TiO}_6} \equiv \mathbf{p}_i^{\text{Ti}} + \frac{1}{2} \sum_{j=1}^6 \mathbf{p}_i^{\text{O}} + \frac{1}{2} \sum_{j=1}^6 \mathbf{r}_{ji}^{\text{O,Ti}} q_j^{\text{O}} \quad (6.35)$$

$$\mathbf{r}_{\text{c.o.c. } i}^{\text{TiO}_6} \equiv \frac{\mathbf{P}_i^{\text{TiO}_6}}{q_i^{\text{Ti}} + \frac{1}{2} \sum_{j=1}^6 q_j^{\text{O}}} \quad (6.36)$$

In particular, notice that the denominator in the definition of $\mathbf{r}_{\text{c.o.c. } i}^{\text{TiO}_6}$ is not constant in the QEqTS IP due to charge fluctuations. Comparing $\mathbf{r}_{\text{c.o.c. } i}^{\text{TiO}_6}$ and $\mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6}$ can inform us about the physical interpretation of the $\{\Delta q_i, \mathbf{p}_i\}$ variables associated with Ti and O ions. However, the center-of-charge defined above depends on the displacements, r_{ji} , and this strongly affects any uncovered correlations. Therefore, we additionally define a

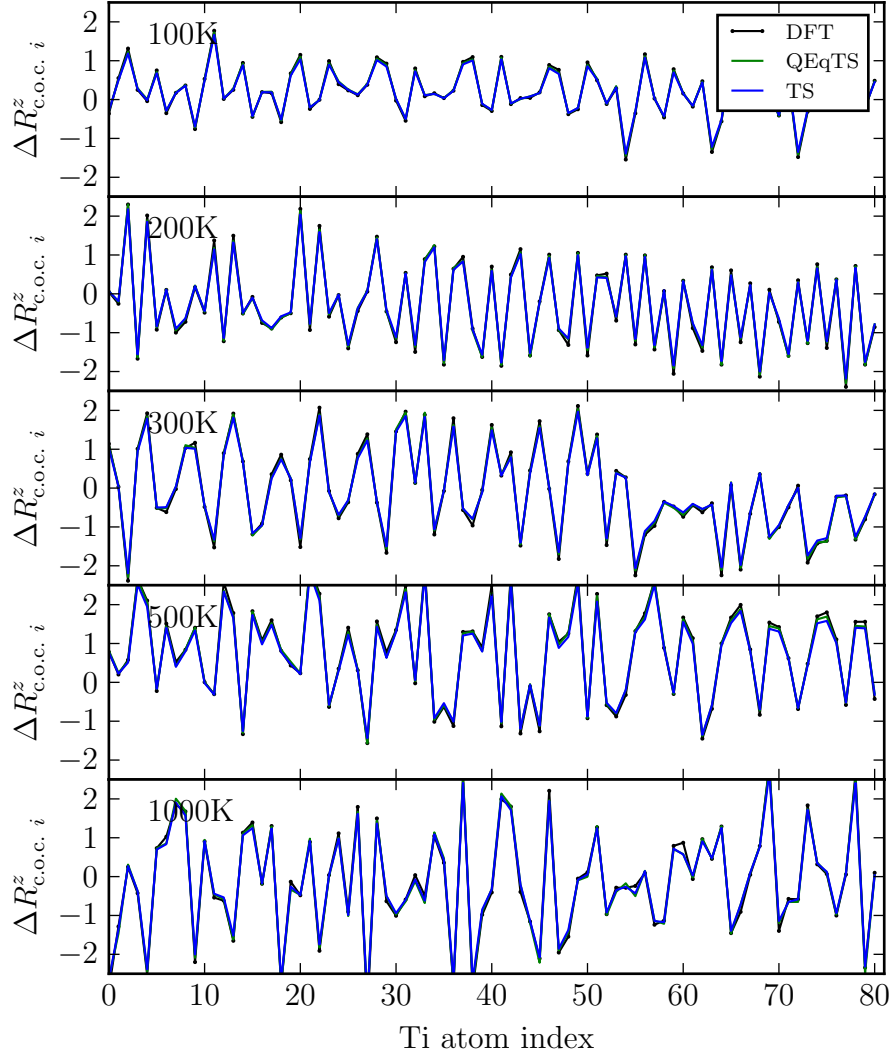


Figure 6.15: z -component of changes of the center-of-charge of the TiO_6 units, $\Delta \mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6}$ and $\Delta \mathbf{r}_{\text{c.o.c. } i}^{\text{TiO}_6}$, defined in text. Results using MLWF-based definition are compared to those defined in terms of QEqTS(Ti) and TS IP variables. Configurations 1, 2 and 3 are shown.

related quantity that is independent of the ionic positions.

$$\tilde{\mathbf{P}}_i^{\text{TiO}_6} \equiv \mathbf{P}_i^{\text{Ti}} + \frac{1}{2} \sum_{j=1}^6 \mathbf{P}_i^{\text{O}} \quad (6.37)$$

$$\tilde{\mathbf{p}}_i^{\text{TiO}_6} \equiv \mathbf{p}_i^{\text{Ti}} + \frac{1}{2} \sum_{j=1}^6 \mathbf{p}_i^{\text{O}} \quad (6.38)$$

Next, for any given Ti ion site i we define changes in these quantities in time, between

the snapshot configurations in the NPH simulation:

$$\Delta \mathbf{M}_i(n) \equiv \mathbf{M}_i(t_{\text{ref}} + n\Delta t) - \mathbf{M}_i(t_{\text{ref}}) \quad \text{if } \mathbf{M}_i \neq \tilde{\mathbf{p}}_i^{\text{TiO}_6} \Big|_{\text{QEqTS}} \quad (6.39)$$

$$\begin{aligned} \Delta \tilde{\mathbf{p}}_i^{\text{TiO}_6} \Big|_{\text{QEqTS}} &\equiv \Delta \mathbf{p}_i^{\text{Ti}} + \frac{1}{2} \sum_{j=1}^6 \Delta \mathbf{p}_i^{\text{O}} \\ &+ \frac{1}{2} \sum_{j=1}^6 (\mathbf{r}_{ji}^{\text{O,Ti}} \Delta q_j^{\text{O}} + \Delta \mathbf{r}_{ji}^{\text{O,Ti}} \Delta q_j^{\text{O}}) \quad \text{if } \mathbf{M}_i = \tilde{\mathbf{p}}_i^{\text{TiO}_6} \Big|_{\text{QEqTS}} \end{aligned} \quad (6.40)$$

where n is a positive integer, Δt is the time step used in the NPH simulations, $\mathbf{M}$ refers to a vector or a scalar quantity of interest, e.g. $\tilde{\mathbf{p}}_i^{\text{TiO}_6}$ or $\mathbf{p}_i^{\text{O}}$, and t_{ref} is the simulation time corresponding to the last (10th) snapshot configuration at a given temperature, used as a reference.

Recall, the definitions of $\Delta \tilde{\mathbf{P}}_i^{\text{TiO}_6}$ as well as $\Delta \tilde{\mathbf{p}}_i^{\text{TiO}_6}$ evaluated using TS and QEqTS IPs exclude the terms of type $\Delta \mathbf{r}_{ji}^{\text{O,Ti}} q_j^{\text{O}}$ in order to avoid biasing the correlation. However, in the definition of $\Delta \tilde{\mathbf{p}}_i^{\text{TiO}_6}$, when evaluated using QEqTS(Ti,O), we additionally include extra terms due to varying charges, of the type $\mathbf{r}_{ji}^{\text{O,Ti}} \Delta q_j^{\text{O}}$ and $\Delta \mathbf{r}_{ji}^{\text{O,Ti}} \Delta q_j^{\text{O}}$, which do not vanish for this IP. This allows us to bring forward the effect of charge fluctuations on the TiO₆ center-of-charge.

Changes in the center-of-charge, $\Delta \mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6}$, are compared to changes in an equivalent quantity calculated using the TS IP, as well as QEqTS(Ti) and QEqTS(Ti,O) IPs in Figures 6.15 and 6.16, respectively. Both QEqTS IPs represent the center-of-charge slightly better relative to the TS IP. However, the improvement is marginal and the center-of-charge calculated using the TS IP already shows an excellent agreement. Next, changes in the TiO₆ dipole-like MLWF-based quantity $\tilde{\mathbf{P}}_i^{\text{TiO}_6}$, $\Delta \tilde{\mathbf{P}}_i^{\text{TiO}_6}$, are compared to changes in an equivalent quantity calculated using the TS IP, as well as QEqTS(Ti) and QEqTS(Ti,O) IPs in Figures 6.17 and 6.18, respectively. There is an overall small improvement in the agreement when using QEqTS IPs.

You may recall from Section 6.3 that for Ti and O ions the TS and QEqTS dipoles noticeably disagree in magnitude with those defined in terms of MLWFs. In comparison, the quantity $\Delta \tilde{\mathbf{P}}_i^{\text{TiO}_6}$ agrees in magnitude with $\Delta \tilde{\mathbf{p}}_i^{\text{TiO}_6}$ considerably better, when the latter is calculated with any of the TS or QEqTS IPs.

A good agreement of $\Delta \mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6}$ with the equivalent quantity calculated using the TS or QEqTS IPs implies that the long-range interactions are likely described well in the TS and QEqTS models. To see this, recall from Section 2.1 that the asymptotic expression for electrostatic interactions in TS and QEqTS IPs is based on the multipole expansions with respect to ionic nuclei. However, this representation of the asymptotic electric field is not unique. One can also represent the asymptotic electric field emanating from

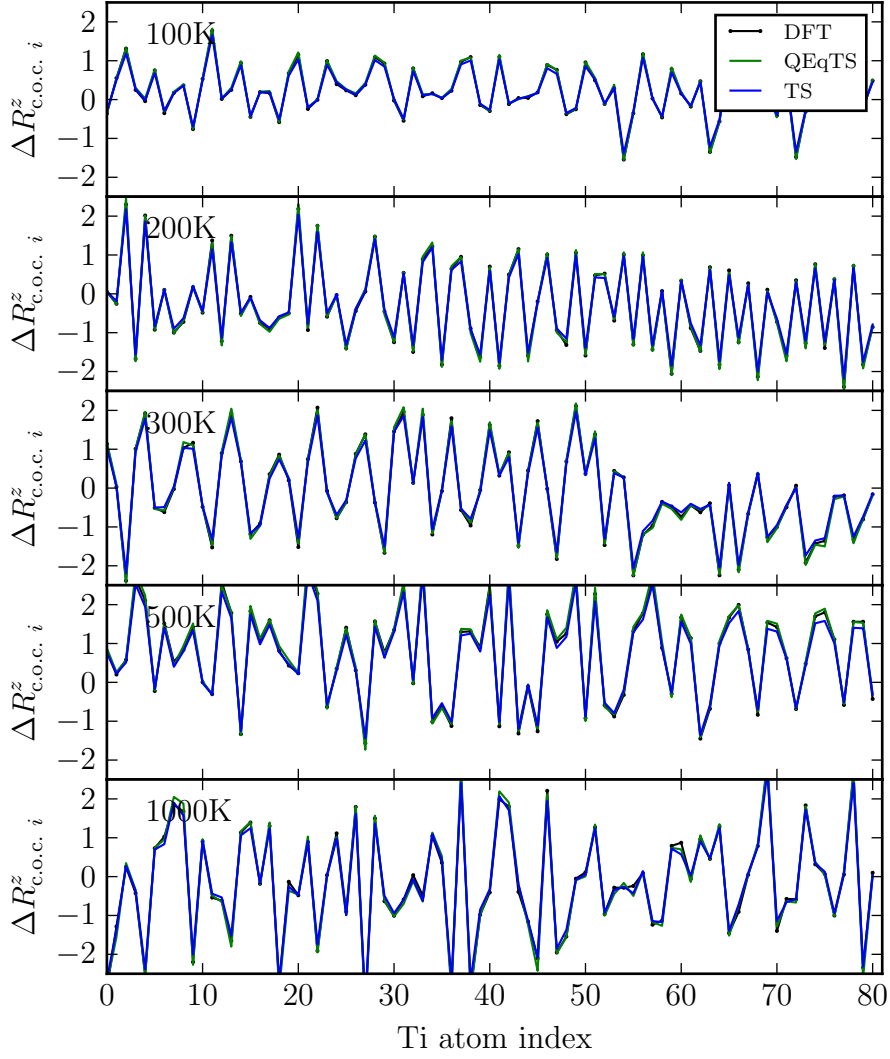


Figure 6.16: z -component of changes of the center-of-charge of TiO_6 units, $\Delta \mathbf{R}_{\text{c.o.c. } i}^{\text{TiO}_6}$ and $\Delta \mathbf{r}_{\text{c.o.c. } i}^{\text{TiO}_6}$, defined in text. Results using MLWF-based definition are compared to those defined in terms of QEqTS(Ti,O) and TS IP variables. Configurations 1, 2 and 3 are shown.

the charge distribution affiliated with a given TiO_6 unit by carrying out a multipole expansion about its center-of-charge. Ions, that are sufficiently far away from a given TiO_6 unit, are subjected to this asymptotic electric field, without the “knowledge” of the exact charge distribution that acts as the source of the field. Thus, the Ti and O $\{\mathbf{p}_i\}$ variables may collectively describe the electron cloud affiliated with both the Ti and O ionic sites, rather than the electron cloud of each ion individually. At short range, these variables can be interpreted to provide the degrees of freedom to describe the nearest neighbour interactions in conjunction with the Morse stretch and other short-range terms. At long range, these variables can be viewed as descriptive of the TiO_6 electron cloud as a whole, representing the asymptotic electric field emanating from this

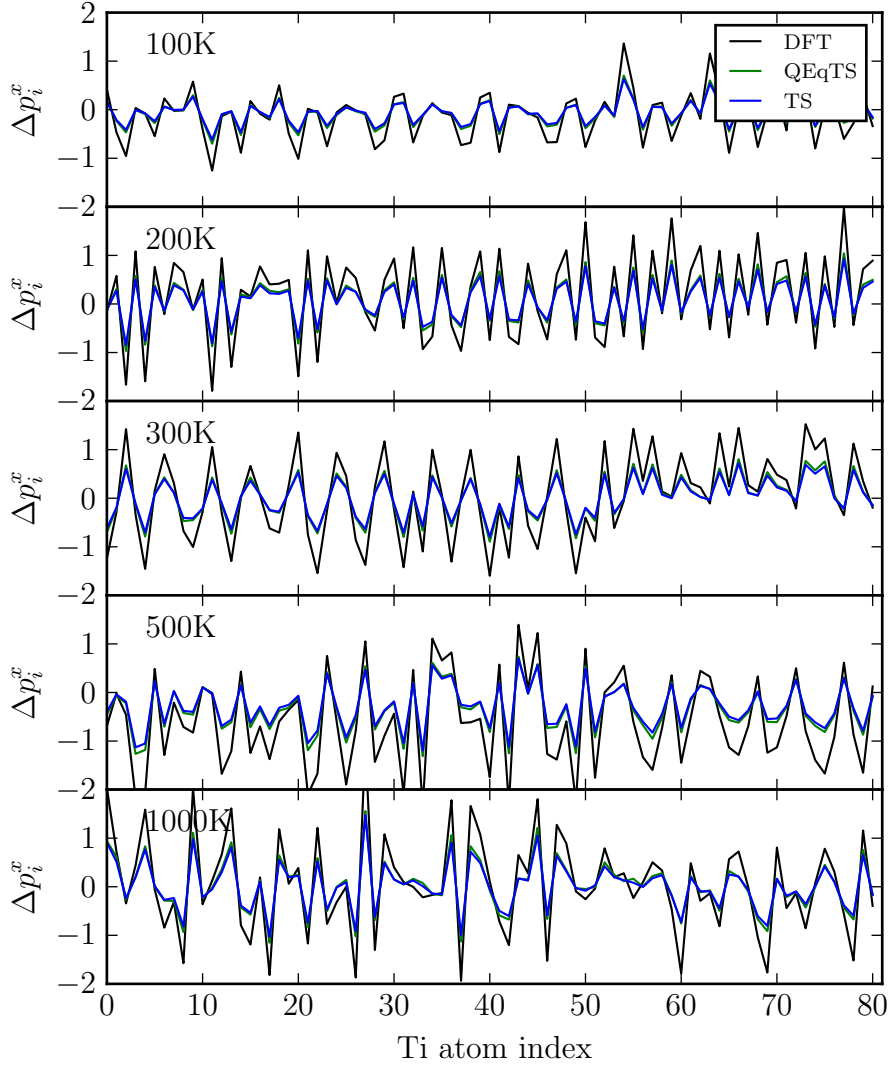


Figure 6.17: x -component of changes of the TiO_6 dipole-like quantities, $\Delta\tilde{\mathbf{P}}_i^{\text{TiO}_6}$ and $\Delta\tilde{\mathbf{p}}_i^{\text{TiO}_6}$, defined in text. Results using MLWF-based definition are compared to those defined in terms of QEqTS(Ti) and TS IP variables. Configurations 1, 2 and 3 are shown.

structural unit. When TS IP is extended to include the QEq model, the same argument is applicable for the variables $\{\Delta q_i\}$.

6.5 Summary

In the present chapter we have analysed the ability of the QEq model to represent changes in the underlying ground state density as well as its effect on the interatomic interactions. We chose a thermally perturbed bulk BaTiO_3 as the test system where the QEqTS-limit is assumed to be satisfied and the changes in the electrostatic potential are represented with a reasonable accuracy, implying that the QEqTS functional form can

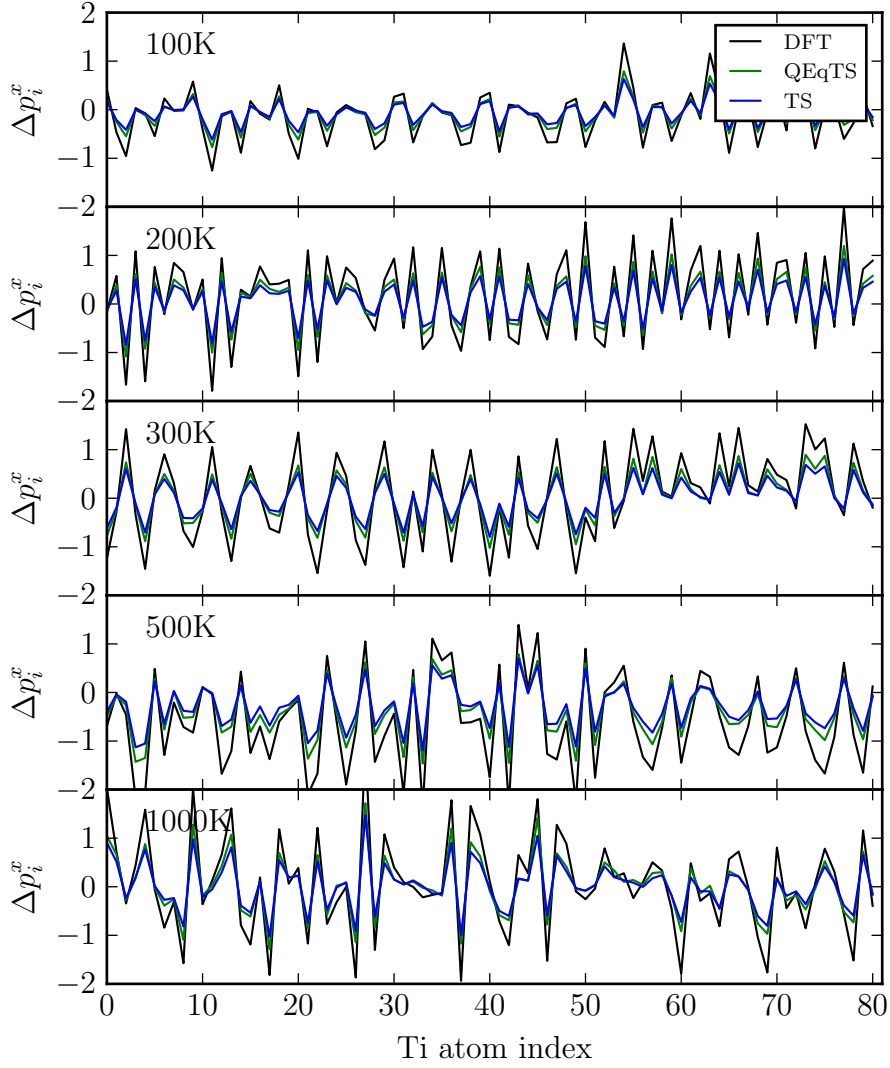


Figure 6.18: x -component of changes in the dipole-like quantities, $\Delta\tilde{\mathbf{P}}_i^{\text{TiO}_6}$ and $\Delta\tilde{\mathbf{p}}_i^{\text{TiO}_6}$, defined in text. Results using MLWF-based definition are compared to those defined in terms of QEqTS(Ti,O) and TS IP variables. Configurations 1, 2 and 3 are shown. Configurations 1, 2 and 3 are shown.

be taken as a good approximation.

Although in the regime of thermal perturbations to ionic positions the changes in the ground state are relatively small, they are not negligible in a sense that an ionic IP must capture many-body effects due to electron density response in order to achieve good accuracy. In particular, we saw that the use of the polarisable-ion model brings a marked improvement in accuracy, a 41% improvement in the r.m.s. agreement with the reference *ab initio* forces. In contrast, the QEq model results in only a small improvement in accuracy, on the order of $\sim 1 - 2\%$ using the same figure of merit. Changes in the ground state in this system are not represented well by the inter-ionic charge transfers.

In other words, changes in the ground state density correspond to very small or negligible inter-ionic charge transfer.

Finally, charge transfer variables were shown to reflect changes in the underlying ground state density but, at the same time, to have an unclear physical interpretation. Firstly, there are several indicators that $\{\Delta q_i\}$ variables reflect the ground state density. The upper valence band corresponds to the electron density primarily at O sites and, to a lesser extent, on Ti sites. This suggests that the density near these ionic sites ought to undergo a relatively large redistribution during the thermal motion of ionic cores. This conclusion is consistent with the anomalous Ti and O Born effective charges in BaTiO_3 , as discussed in Section 1.5. Indeed, as expected on physical grounds, the QEqTS model predicts charge fluctuations on the Ti ions or both the Ti and O ions, in the two similar parameterisations of the QEqTS IP presented in this chapter. Furthermore, the analysis revealed concerted changes in the local electron density on one hand and the positions of the nuclei on the other hand, associated with the Ti and its closest three neighbour O ions. The variables $\{\Delta q_i\}$ were then shown to correlate with these concerted changes, in a way that modulates cohesion of the nearest neighbours. Secondly, for the system studied in this chapter, the physical interpretation of QEq charge transfers isn't clear, primarily because $\{\Delta q_i\}$ anti-correlate with Löwdin and Bader charges. Thus, in general, a negative value of Δq_i does not correspond to a locally higher electron density. In Section 6.4.4 we suggested that possibly the Ti and O variables $\{\Delta q_i\}$, along with $\{\mathbf{p}_i\}$, collectively describe the electron cloud simultaneously associated with both Ti and O ions for a given TiO_6 unit, rather than each ionic cloud individually. For the long-range interactions, this can adequately represent an asymptotic electric field due to the electron cloud associated with TiO_6 units, while for the short-range interactions these variables act as degrees-of-freedom in conjunction with the Morse stretch and other short-range terms.

In conclusion, if the objective is to develop an accurate IP for bulk BaTiO_3 whose functional form lends itself to a clear physical interpretation, then, in the opinion of the present author, the QEq model should not be used and the fixed-charge TS IP should be used instead. In Chapter 7 we shall see that the QEq model offers a marked improvement in representing interatomic forces and changes in the ground state density in the vicinity of a neutral O vacancy. Thus, if, on the other hand, a QEqTS IP is applied to describe simultaneously bulk and heterogeneous phases of BaTiO_3 , then the use of the combined this QEq-based IP is advisable. In particular, in this latter case, any possible observations of the anti-correlation of QEq charge transfers with the changes

in Löwdin or Bader charges in the bulk phase should not cause concern; as explained in Section 6.4.1, this is the expected and internally consistent behaviour of the QEq model.

Chapter 7

Polarizable charge transfer model applied to BaTiO₃ point vacancies

The behaviour of the QEqTS model when applied to the defect-free, thermally perturbed bulk BaTiO₃ was analysed in Chapter 6, with a focus on physically interpreting QEq charge transfer variables. In this chapter QEqTS is applied to heterogeneous systems and the aim, instead, is to link the relative ability of the QEqTS model to describe a given system to the degree to which the ground state density in that system deviates from the assumed limit. The assumed limit is the one in which the QEqTS model was shown to be derivable in Chapter 3. Two concrete examples are studied, a neutral O vacancy and a neutral Ti vacancy in BaTiO₃. The ground state density is compared and contrasted amongst the two systems as well as relative to the defect-free bulk.

For one of the systems, namely the neutral O vacancy in BaTiO₃, QEqTS model shows a dramatic improvement in reproducing *ab initio* forces relative to the TS IP. Furthermore, order-of-magnitude calculations suggest that QEq charge transfer variables in this case take on the (arguably) intended physical meaning of representing increase or decrease in the local charge density. To the best of our knowledge, this is currently the only known such example and so constitutes a discovery of a valuable “test-bench” system, suitable for future development of the QEqTS model and polarisable IPs in general. Thus, the secondary aim of this chapter is simply to showcase this example in order to promote further research along this route.

This chapter is structured as follows. Section 7.1 defines the systems studied, computational methods, as well as the analysis methods used in the remainder of the chapter. In Section 7.2 changes in the ground state density induced by the vacancy are shown to deviate from the limit in which QEqTS was derived in Chapter 3. Furthermore, changes

in the density caused by introducing an O vacancy are qualitatively distinct from those caused by a Ti vacancy. At the same time, the ability of the QEqTS model to reproduce *ab initio* forces is markedly different for these two types of system. The likely link between the limit breakdown in a given system and the ability to model it with the QEqTS IP are discussed in Section 7.3. Additionally, order-of-magnitude calculations are made to compare QEqTS charge transfer variables to ground state density in the reference system. Finally, Section 7.4 summarises key points and main conclusions of the chapter.

7.1 Calculation summary

In this section the systems studied are defined and the details pertaining to data analysis and visualisation are outlined, in order to facilitate the discussion that follows.

7.1.1 Systems studied

Two BaTiO₃ systems were considered, one with a neutral O vacancy and one with a neutral Ti vacancy – $V_O^\times$ and $V_{Ti}^\times$ in Kröger-Vink notation[28], respectively. In DFT calculations $3 \times 3 \times 3$ charge neutral supercells were set up by “taking out” a single neutral O or Ti atom, resulting in stoichiometries Ba₂₇Ti₂₇O₈₀ or Ba₂₇Ti₂₆O₈₁, respectively. DFT computational details can be found in Section 5.2. It must be mentioned that the true ground state of these systems is likely to be ferromagnetic, as has been found theoretically for O and Ti vacancies[182, 183]¹ using spin-polarised DFT[156, 184], as well as experimentally for the former[185]. However, using spin-polarised DFT in this study would create inappropriate reference training data for fitting ionic IPs, since capturing spin degrees of freedom is beyond the scope of the models studied in this thesis. Thus, strictly speaking, we are not modelling O and Ti vacancies *per se*, but their representation within the DFT spin-degenerate model.

The vacancies considered in this chapter are conventionally referred to as neutral (e.g. Ref. [182, 183]), which means that the net charge remains the same relative to the defect-free system. Yet in the context of ionic IPs some elaboration is appropriate. As a concrete example, consider the neutral O vacancy in BaTiO₃. The nominal charge of the anion is -2 and the same charge may be affiliated with the site of the neutral vacancy – however, this charge is delocalised over several bond lengths in general. An ionic IP implicitly assumes a different length scale – recall the total charge density $\rho(\mathbf{r})$

¹In Ref. [183] LDA exchange-correlation functional is used but in addition LDA+U calculations are carried out verifying that the ferromagnetic spin-polarised ground state is retained for a wide range of values of U; $0.0\text{eV} \leq U \leq 6.0\text{eV}$.

is expressed as a sum of atom-centered localised contributions $\rho_i(\mathbf{r})$, with each $\rho_i(\mathbf{r})$ localised on the length scale of a single bond length. However, as will be shown in Section 7.2, on this length scale there is a net charge of about $-1.0e$ concentrated in the O vacancy region. To be clear, in this chapter any net charge in connection to the vacancy refers to the vacancy *region* on the scale of a single bond length.

7.1.2 Parameterisation of interatomic potentials

When it comes to representing systems containing vacancies with an IP, some care must be taken in regards to charge conservation. IPs that include charge transfer, such as QEqTS, by construction automatically impose charge neutrality for any stoichiometry. Thus, the QEqTS IP can describe simultaneously defect-free system, as well as those with point vacancies, with a single set of parameters, in each case imposing charge neutrality (or any desired net charge). In contrast, fixed-charge IPs, such as polarisable-ion TS model, need to be refit for each new stoichiometry. At the very least, one has to refit or change manually the fixed charges in order to ensure the system’s charge neutrality. Consequently, some comparisons among the IPs in this chapter necessitate TS to be reparameterised to each stoichiometry.

The procedure for parameterising IPs via force-matching was discussed in Chapter 5, however in this chapter we deviate from that protocol somewhat. Recall, parameterisation involves repeating several times the procedure of a) extracting input supercell vectors and atomic positions to DFT from classical molecular dynamics, b) performing DFT calculations and c) re-fitting the IP. Due to the large number of IPs parameterised in this section the study remained computationally tractable by following these steps only once. The QEqTS(Ti) IP from Chapter 6 was used to perform molecular dynamics at 100 K, 200 K, 300 K and 500 K in NPH ensemble for the systems with an O and a Ti vacancy. These were then used to define the input atomic positions and the supercell vectors for the DFT calculations. All reported IPs in this chapter were then fit to the *ab initio* reference data set. In practice, this means that a slightly better fit is achievable if the procedure is repeated several more times. Qualitatively, the main conclusions of this chapter are unlikely to be affected.

For IPs fit only to systems with an O vacancy or only with a Ti vacancy, a total of 24 configurations were used in each case, comprising of 6 “snapshots” taken 3 picoseconds apart from a NPH simulation at 100 K, 200 K, 300 K and 500 K. For the IP fit simultaneously to systems with both types of vacancy and to the defect-free system a total of 32 configurations were used, with 3 snapshots 6 ps apart at each temperature

for each system with the O and the Ti vacancy and 2 samples 5 ps apart for the defect-free system. Test results used to report root-mean-squared agreement with the *ab initio* forces used, at each temperature, 21 configurations for the system with an O vacancy, 12 configurations for the system with a Ti vacancy and 10 configurations for the defect-free system; all configurations are 1 ps apart. A single exception is the test result cited for the defect-free system in Table 7.4 which also includes 10 configurations at 1000 K, to retain continuity with the results presented in Chapter 6, Table 6.5.

7.1.3 Data analysis and visualisation

One of the aims of this chapter is to expose the fact that introducing a point vacancy induces the kind of changes in the ground state density that deviate from the limit in which QEqTS model is derivable from DFT.

The deviation from the limit is demonstrated by examining directly the difference in the ground state density of the system with the vacancy relative to the reference defect-free system, presented in a series of contour plots. Unlike the atomic charge, this is a well defined quantity.

When examining density contour plots and density difference contour plots, it is difficult to get a sense of the magnitude of charge in a given neighbourhood of interest, such as near a vacancy or an ion. Therefore, contour plots are supplemented by estimated charges in a given neighbourhood of interest. Ionic charge or the charge in the vacancy region is not a well defined quantity in a condensed matter system, yet frequently one makes estimates using conventional methods such as Löwdin population analysis (as in Chapter 6), Mulliken, Bader or Hirshfeld definitions of the atomic charge. In this chapter, instead, charge density or charge density difference is integrated inside a sphere centered at a given neighbourhood of interest; the data so obtained is supplemented by Löwdin population analysis where appropriate.

The details pertaining to contour plots as well as the method of estimating charges are rationalised and discussed in the following two subsections, respectively.

Changes in the ground state density relative to a defect-free reference

In Chapter 6 charge transfer in a defect-free thermally perturbed BaTiO₃ was analysed. Here, instead, we are interested in the charge transfer induced by a vacancy. Therefore, although IPs are parameterised using reference structures taken from a finite temperature molecular dynamics simulation, the analysis is based on $T = 0$ K systems in order to isolate the effect of the vacancy on charge transfer.

To obtain meaningful well-defined ground state density difference plots, supercell vectors of the systems being compared must be the same and the atomic coordinates coincide whenever possible. The relaxed cell vectors and atomic positions are distinct for each of the systems, with an O vacancy, a Ti vacancy and the defect-free system. In this chapter, the relaxed atomic configuration of a defect-free system is used in all $T = 0$ K contour plots, with the appropriate atom missing in the case of the vacancy. The parameters of the relaxed BaTiO₃ are summarised in Table 7.1, which correspond to the rhombohedral phase². The O and Ti vacancies were introduced in the central unit cell of

Rhombohedral (R3m)	This work	Exp.[186]
a [a_o]	7.538	7.566
α [deg]	89.877	89.839
Δx_{Ti}	-0.0107	-0.0128
Δx_{O}	0.0114	0.0109
Δz_{O}	0.0174	0.0193
Ba	(0, 0, 0)	
Ti	$(\frac{1}{2} + \Delta x_{\text{Ti}}, \frac{1}{2} + \Delta x_{\text{Ti}}, \frac{1}{2} + \Delta x_{\text{Ti}})$	
O	$(\frac{1}{2} + \Delta x_{\text{O}}, \frac{1}{2} + \Delta x_{\text{O}}, \Delta z_{\text{O}})$	
O	$(\frac{1}{2} + \Delta x_{\text{O}}, \Delta z_{\text{O}}, \frac{1}{2} + \Delta x_{\text{O}})$	
O	$(\Delta z_{\text{O}}, \frac{1}{2} + \Delta x_{\text{O}}, \frac{1}{2} + \Delta x_{\text{O}})$	
$\tilde{\mathbf{a}}_1$	(u, p, p)	
$\tilde{\mathbf{a}}_2$	(p, u, p)	
$\tilde{\mathbf{a}}_3$	(p, p, u)	
$c = \cos(\alpha), u = \sqrt{\frac{1+2c}{3}} + 2\sqrt{2\frac{1-c}{6}}, p = \sqrt{\frac{1+2c}{3}} - \sqrt{2\frac{1-c}{6}}$		

Table 7.1: Upper set of rows: lattice constants obtained with DFT in this work and the experimental values at $T = 15$ K; middle: atomic coordinates; bottom: the primitive unit cell definition used in this chapter. $\tilde{\mathbf{a}}_i$ are the primitive unit cell vectors and the $3 \times 3 \times 3$ supercell actually used corresponds to supercel vectors $\mathbf{a}_i = 3\tilde{\mathbf{a}}_i$.

a $3 \times 3 \times 3$ supercell, with the “taken out” O atom coordinates $(\frac{1}{2} + \Delta x_{\text{O}}, \frac{1}{2} + \Delta x_{\text{O}}, \Delta z_{\text{O}})$, without loss of generality. This means that the planes $s_1\mathbf{a}_1 + s_3\mathbf{a}_3$ and $s_2\mathbf{a}_2 + s_3\mathbf{a}_3$ ($s_i \in \mathbb{R}$)

²A practical note: the unit cell definition used here corresponds to `ibrav = -5` in the Quantum Espresso DFT package.

are approximately parallel to the Ti-O-Ti bond of the oxygen vacancy and its two nearest neighbours, while $s_1\mathbf{a}_1 + s_2\mathbf{a}_2$ is approximately perpendicular. Contour plots for the density difference in the perpendicular plane do not show any appreciable change in the density for the case of O vacancy. All other $s_i\mathbf{a}_i + s_j\mathbf{a}_j$ type planes contain equivalent information and therefore, without the loss of generality, the planes $s_1^*\mathbf{a}_1 + s_2\mathbf{a}_2 + s_3\mathbf{a}_3$ were chosen for the contour plots, where $0 \leq s_2, s_3 \leq 1$ and (s_1^*, s_2^*, s_3^*) corresponds either to the coordinates of the O vacancy or that of the Ti vacancy depending on which system is being visualised. This ensures that the plane intersects the vacancy site and approximately the sites of its nearest neighbours – the regions where the most substantial changes in the ground state density can be observed.

Finally, with regards to data visualisation, all contour plots in this chapter use the same scale for the color bar and the same set of contour levels.

Order-of-magnitude estimates of charge using ground state density

Arguably the intended physical meaning of the QEq model charge transfer variables is that of representing an increase or a decrease in the local charge density in the ionic limit. Thus, although ground state density difference plots provide exact information on charge transfer in a system, it is desirable to obtain quantities directly comparable to charge transfer in an ionic model.

Conventional approaches of calculating atomic charges, such as based on Löwdin, Bader, or other definitions, are mostly side-stepped in this chapter in favour of a more simple definition. To estimate an ionic charge transfer due to a vacancy or the amount of charge concentrated in the vacancy region, an order-of-magnitude calculation is made by integrating charge density within a sphere centered at a given nucleus of an ion³. This method is more transparent in that one can test whether the calculated charge is sensitive to the ionic size parameter by simply varying it and recalculating the values. Another advantage of this method is that it is trivially applicable directly to density *difference* or the ground state density in the vacancy region. In contrast, conventional methods are not designed to work in these situations – for example Bader charge algorithm gives divergent values if applied to density difference directly, while Löwdin population analysis projects ground state wavefunction onto ion-centered basis set and so is not well adapted for vacancy region charge calculation. In particular, working directly with the density difference is advantageous in the case of an O vacancy. The density difference is highly localised on ionic nuclei in this case, much more than the ground state of either

³For the vacancy, centering is on the nucleus of the atom that was taken out.

of the systems being compared – meaning charge transfer adheres to the ionic limit well and can be associated with individual ions with little ambiguity.

To estimate the radius of a sphere representing a volume associated with an ion, results of the MLWF-based analysis of Chapter 6 can be used. Recall, for the MLWF centered near Ti and O nuclei, the average quadratic spreads, $\langle(\mathbf{r} - \bar{\mathbf{r}})^2\rangle$, are $1.00^2 a_o^2$ and $1.78^2 a_o^2$, while the average displacements from the “parent” nucleus, $\Delta\bar{\mathbf{r}}$, are $0.40 a_o$ and $0.62 a_o$, respectively (Table 6.1). At the same time, there are four MLWFs per ion and their centre of charge is always within $0.025 a_o$ and $0.1 a_o$ for the Ti and O ions, respectively (Figure 6.12), meaning that the four MLWFs on a given ion tend to be off-set in opposite directions on average. Thus, assuming each centre of charge approximately concides with the nucleus, one can estimate the ionic radius as the sum $\langle|\mathbf{r} - \bar{\mathbf{r}}|\rangle + \Delta\bar{\mathbf{r}}$. However the quantity $\langle|\mathbf{r} - \bar{\mathbf{r}}|\rangle$ isn’t available, so instead this is approximated. I define $\langle|\mathbf{r} - \bar{\mathbf{r}}|\rangle$ in terms of a spherically symmetric Slater type density that has identical second moment to the desired value, here $1.00^2 a_o^2$ and $1.78^2 a_o^2$ for Ti and O ions. The result of this estimate is that if Ti and O ions are modelled as spherical localised Slater-type charge densities, then the radii are approximately $1.31 a_o$ and $2.24 a_o$ respectively. The same estimate for Ba ion gives the radius of $2.47 a_o$.

Another way to estimate ionic radii is simply to vary the values until reasonable ionic charges are obtained. The reasonable ionic charges in the context of the present chapter are those that resemble the values in TS and QEqTS models, $\sim 2.84 e$ and $\sim -1.3 e$ for Ti and O, respectively. The aim is to estimate the charge transfer that QEqTS model ought to reproduce given the magnitude of charges that it assigns to ions. Recall, as discussed in Chapter 2, the values for ionic charges assigned in a given ionic IP, call them $\{q_i^{\text{eff}}\}$, are expected to implicitly include some of the effects of the screening in an average way, $q_i^{\text{eff}} = q_i / \sqrt{\epsilon_{\text{eff}}}$ where $\epsilon_{\text{eff}} \geq 1$. Hence, effective ionic charges in TS and QEqTS IPs can be interpreted as providing lower bounds in magnitude on the ionic charges actually represented in these models, $q_i = q_i^{\text{eff}} \sqrt{\epsilon_{\text{eff}}} \geq q_i^{\text{eff}}$, giving an estimate $q^{\text{Ti}} \geq 2.84 e$ and $q^{\text{O}} \leq -1.3 e$.

Table 7.2 summarises estimated ionic charges based on the integration of the density within ion-centered spheres. A set of ionic radii estimated based on MLWF second moments is supplemented by radii based on average interatomic distance of $3.6 a_o$ between Ti and its closest O neighbours (Fig. 6.12) – $1.8 a_o$, $2.7 a_o$ and $3.6 a_o$ correspond to $1/2$, $3/4$ and full bond length. The purpose of this table is to estimate reasonable ionic radii for the Ti and O ions in order to later use these radii for estimating charge transfer induced by a vacancy. Varying ionic size of Ba ion essentially does not affect the ionic

charges of Ti and O ions and so it is simply set to the estimated value from the MLWF quadratic spreads.

$(r_{\text{cut}}^{\text{A}} [a_o])$			Charge [e]			
Ba	Ti	O	q^{Ba}	q^{Ti}	q^{O}	$q^{\text{btwn}}/\text{BaTiO}_3$
(2.47)	(1.31)	(2.24)	2.95	5.10	-0.76	-5.78
(2.47)	(1.31)	(2.70)	2.95	5.10	-1.79	-2.69
(2.47)	(1.31)	(3.60)	2.95	5.10	-2.75	-0.04
(2.47)	(1.80)	(2.24)	2.95	3.13	-0.67	-4.06
(2.47)	(1.80)	(2.70)	2.95	3.13	-1.41	-1.87
(2.47)	(1.80)	(3.60)	2.95	3.13	-2.06	-0.04
(2.47)	(2.24)	(2.24)	2.95	2.31	-0.59	-3.49
(2.47)	(2.24)	(2.70)	2.95	2.31	-1.18	-1.73
(2.47)	(2.24)	(3.60)	2.95	2.31	-1.78	-0.04
<i>Charges from Löwdin population analysis</i>						
			0.44	1.67	-0.65	-0.15
<i>Charges based on MLWF centers' proximity</i>						
			2	4	-2	0

Table 7.2: Integrated charge density, within a sphere of radius $r_{\text{cut}}^{\text{A}}$ centered at each ion $\text{A} \in \{\text{Ba}, \text{Ti}, \text{O}\}$. Density is available on a set of grid points in position space; each value is assigned to the closest ion if there is at least one such ion within $r_{\text{cut}}^{\text{A}}$ – else to q^{btwn} which represents charge in the space between the ions.

Table 7.2 primarily demonstrates that O ion ought to be considered relatively large, in the range $2.70 a_o \leq r_{\text{cut}}^{\text{O}} < 3.60 a_o$, if the size is to be consistent with the value of $-1.3 e$ assigned to oxygen by the QEqTS IP. Similarly, Ti charge in an IP is $\sim 2.84 e$ and this value is consistent with a relatively small Ti ion, $r_{\text{cut}}^{\text{Ti}} \leq 1.80 a_o$.

Löwdin charges are approximately half in magnitude as those assigned to Ti and O ions in the QEqTS model. In particular, nominal anion charge of $-2 e$ can only be associated with O ion if it is considered relatively large, overlapping with the nearest neighbour Ti ions.

7.2 Deviation of the ground state density from the limit of the QEqTS model.

In this section, it is demonstrated that introducing a vacancy into BaTiO₃ system breaks the limit in which QEqTS was derived. Firstly, it is appropriate to recall what that limit is.

As discussed in Chapter 3, QEqTS model is derivable under two principle assumptions, a) ground state density $\rho(\mathbf{r})$ is representable as a sum of the reference density $\rho^0(\mathbf{r})$ and a *small* deviation from this reference $\Delta\rho(\mathbf{r})$, b) ionic limit holds, meaning the density is representable in terms of atom-centered localised contributions $\rho_i^0(\mathbf{r})$ and $\Delta\rho_i(\mathbf{r})$ such that $\rho^0(\mathbf{r}) = \sum_i \rho_i^0(\mathbf{r})$ and $\Delta\rho(\mathbf{r}) = \sum_i \Delta\rho_i(\mathbf{r})$. The former assumption justified a simple quadratic form for the QEq self-energy obtained using the Taylor expansion. The latter justified expressing Coulomb interaction energy in a pairwise-additive form in terms of coefficients q_i^0 , $\mathbf{p}_i$ and Δq_i representing ionic densities $\rho_i^0(\mathbf{r})$ and $\Delta\rho_i(\mathbf{r})$.

By looking at the charge density contour plots and making some order-of-magnitude estimates of charge transfer, the above limits are shown to be violated in three different ways. Firstly, there is a non-negligible amount of charge concentrated in the vacancy region itself – clearly violating the assumption that the density is composed of ion-centered contributions. Secondly, some charge is present in the inter-ionic region, not close to any one ionic center. This violates the ionic limit for the change in density, $\Delta\rho(\mathbf{r})$. Finally, charge transfer can be very large, on the order of 0.5 e per ion and so the form of the QEq self-energy is put into question. These aspects of the ground state density are discussed in Section 7.2.1 and 7.2.2.

Interestingly, densities in the system with the O vacancy and with the Ti vacancy deviate from the QEqTS-limit in distinct ways and at the same time the ability of the QEqTS IP to reproduce forces in each system is markedly different. The system with an O vacancy only breaks the limit in that there is an appreciable charge concentration in the vacancy region. The system with a Ti vacancy, in contrast, exhibits negligible charge concentration in the vacancy region, but involves large charge transfer, much of which is not localised on the ionic sites.

7.2.1 Charge concentration in the vacancy region

Firstly, we take a look at the charge concentration in the vacancy region. Figure 7.1 is a contour plot in the $\mathbf{a}_2, \mathbf{a}_3$ plane intersecting the vacancy and its nearest neighbours, where $\{\mathbf{a}_i\}$ are the supercell vectors. As discussed in Section 7.1.3, the perpendicular

plane that doesn't contain nearest neighbours exhibits essentially no charge transfer and so is not shown; all other $s_i \mathbf{a}_i + s_j \mathbf{a}_j$ type planes contain equivalent information. A non-negligible charge concentration in the region of the vacancy is clearly visible. For the reference, density is above $0.010 e/a_o^3$ in the inter-atomic region of the perfect bulk. In comparison, the density drops to below $0.005 e/a_o^3$ in the Ti vacancy region, and stays above $0.015 e/a_o^3$ in the O vacancy region.

To get a better idea of the amount of charge concentrated in the vacancy region, an order-of-magnitude estimate is made by integrating charge density within a sphere centered at the vacancy site, as described in detail in Section 7.1.3. If we use the estimated average ionic radii, extracted from the MLWF-based analysis of Chapter 6, the net charge is $-0.04 e$ and $-0.88 e$ for the Ti and O vacancy regions, respectively. Alternatively, using the estimated upper bound and lower bound on Ti and O ionic sizes of $1.80 a_o$ and $2.7 a_o$, respectively, gives the net charge of $-0.19 e$ and $-1.31 e$. Estimates of the charge concentrated in the vacancy region can be found in Table 7.6 for a range of ionic cut-off radii. No matter what set of ionic radii is used in estimating the charge in the vacancy region, it is clear that there is substantially more charge concentrated in the O vacancy, on the order of $-0.8 e - -2.0 e$ compared to $-0.0 e - -0.2 e$ for the Ti vacancy.

The estimated values are clearly very sensitive to the ambiguous notion of an ionic radius. This estimate ought to be supplemented with the known fact that O^{2-} ion is not stable as a free radical, meaning in particular that in $BaTiO_3$ there is a sufficiently strong contribution to the electrostatic potential at O sites due to the lattice to localise one “extra” electron. Designating the O vacancy region as $\tilde{V}_O^{1-}$, the O^{2-} ion in $BaTiO_3$ can be thought of as a combination $O^{1-} + \tilde{V}_O^{1-}$, i.e. one electron is trapped due to the high oxygen electronegativity relative to other atomic species and one extra electron is localised at the O site due to strong lattice electrostatic potential. Once the neutral O atom is taken out, a single electron, represented by $\tilde{V}_O^{1-}$, remains in the vacancy region. On the other hand, Ti atom acts as an electron donor in $BaTiO_3$, with O sites being the acceptor sites. Removing a Ti atom leaves fewer electrons to be donated to other ions and so there is no reason to expect any appreciable charge concentration in the the Ti vacancy region.

The vacancy region cannot be well defined, yet the reasonable conclusion seems to be that there is only very small or even negligible charge concentration in the Ti vacancy region, while there is a substantial charge concentration in the O vacancy region on the order $\sim -1e$. The ground state density in the latter case deviates from the ionic limit

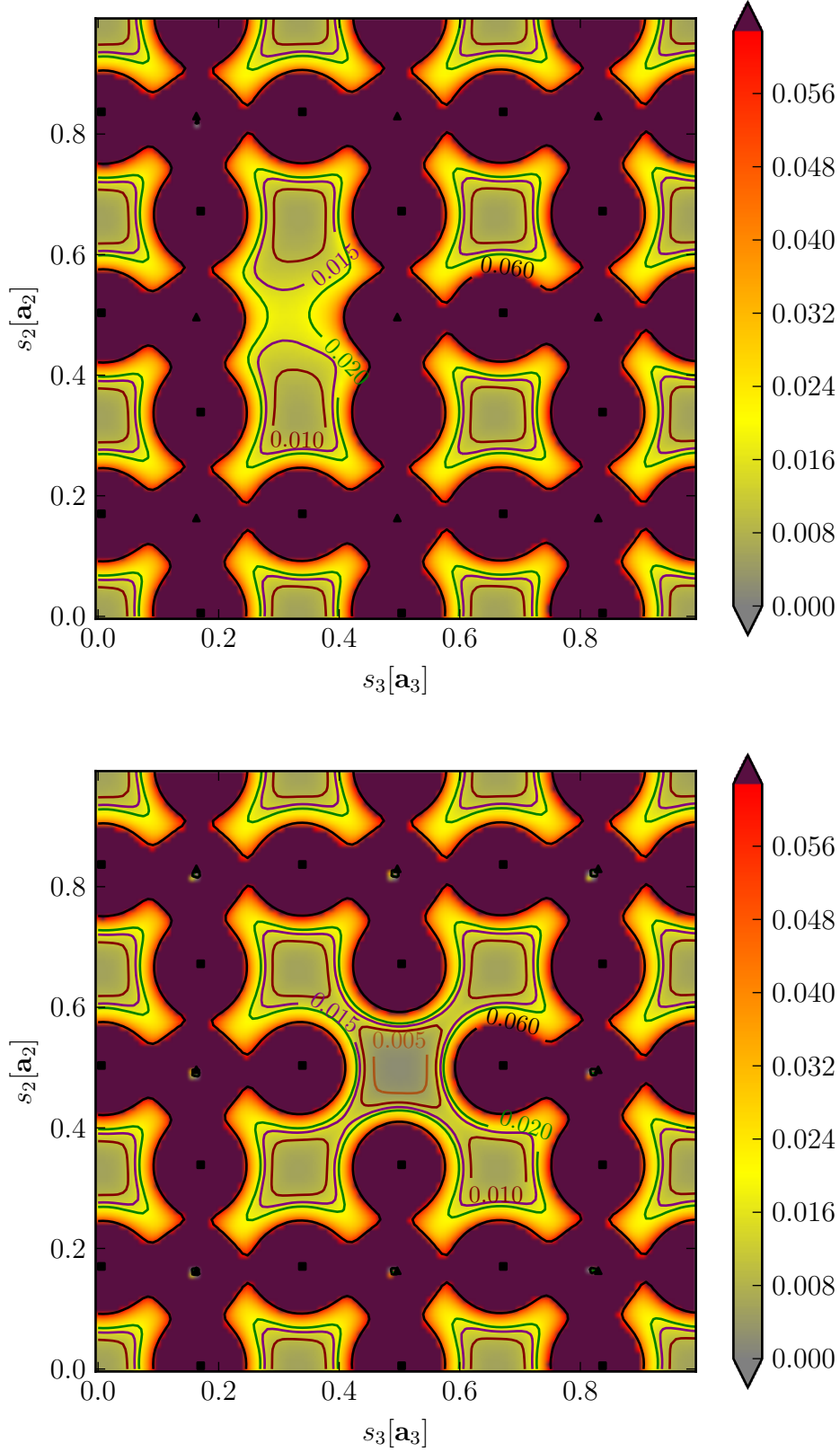


Figure 7.1: Electron number density, in e/a_o^3 , of the systems with a neutral vacancy V_O (top) and a neutral V_{Ti} (bottom), in the plane $s_1^*\mathbf{a}_1 + s_2\mathbf{a}_2 + s_3\mathbf{a}_3$. s_1^* is held fixed and $[s_1^*, s_2^*, s_3^*]$ are the coordinates $[s_1^*, s_2^*, s_3^*]$ of the missing atom. The colorbar is the same as those in Figure 7.2. Squares and triangles – O and Ti ions' $[s_2, s_3]$ coordinates.

at the O vacancy site.

7.2.2 Charge transfer on ions near the vacancy

A non-ambiguous way to define and visualise charge transfer induced by a vacancy is to consider charge density difference plots. These are available in 3D, but 2D contour plots are more suitable for visualisation. Having examined these plots in various planes, only a representative plot is shown that exhibits non-negligible charge transfer.

Figure 7.2 shows the change in the ground state density relative to a relaxed defect-free system in the rhombohedral phase. The plane crosses the vacancy site and its nearest neighbours. The contour plot in the plane perpendicular to O nearest neighbours does not exhibit any appreciable charge transfer and is not shown.

It is clear from the figure that charge transfer is markedly different for the systems with the O and Ti vacancies. In the first case, charge transfer is localised on ionic sites, mostly on Ti sites. In the latter case significant difference in the ground state density is visible in the inter-ionic regions. Firstly, O ions nearest to the Ti vacancy become less negatively charged ($\Delta\rho(\mathbf{r}) \leq -0.010e/a_o^3$ and $\Delta\rho(\mathbf{r}) \leq -0.040e/a_o^3$ blue regions in the figure), but this charge transfer cannot be well described by ion-centered localised contributions $\{\Delta\rho_i\}$. Secondly, there is a small increase in electron density inbetween the O ions and its only remaining nearest neighbour Ti ions ($\Delta\rho(\mathbf{r}) \geq 0.005e/a_o^3$ yellow cloud in the figure). One could say that when a Ti vacancy is introduced, interaction between the O ion nearest to the vacancy and its only remaining Ti close neighbour acquire a greater covalent character. Another way to interpret change in the charge density introduced by the Ti vacancy is to say that some Ti and O ions become larger relative to the bulk. In either case, charge transfer deviates from the assumed limit in the fixed-size ionic models studied in this thesis.

Although contour plots help us visualise clearly the extent of localisation in density difference, it is harder to appreciate the magnitude of the corresponding charge transfer. Therefore, an order-of-magnitude estimate for charge transfer on each ion is presented in Table 7.3, using integration within ion-centered spheres as discussed in Section 7.1.3. It was argued in Section 7.1.3 that the reasonable ionic radius for O ion is in the range $2.7 a_o \leq r_{\text{cut}}^{\text{O}} \leq 3.6 a_o$, however in this range the results are qualitatively the same and so charge transfer using the latter value is not presented. Instead, a very small radius of $r_{\text{cut}}^{\text{O}} = 2.24 a_o$ is included in the table to demonstrate that charge transfer on ions nearest to Ti vacancy is very large, an order of magnitude larger than that near the O vacancy – a conclusion that is qualitatively independent of the ionic sizes used in the estimate.

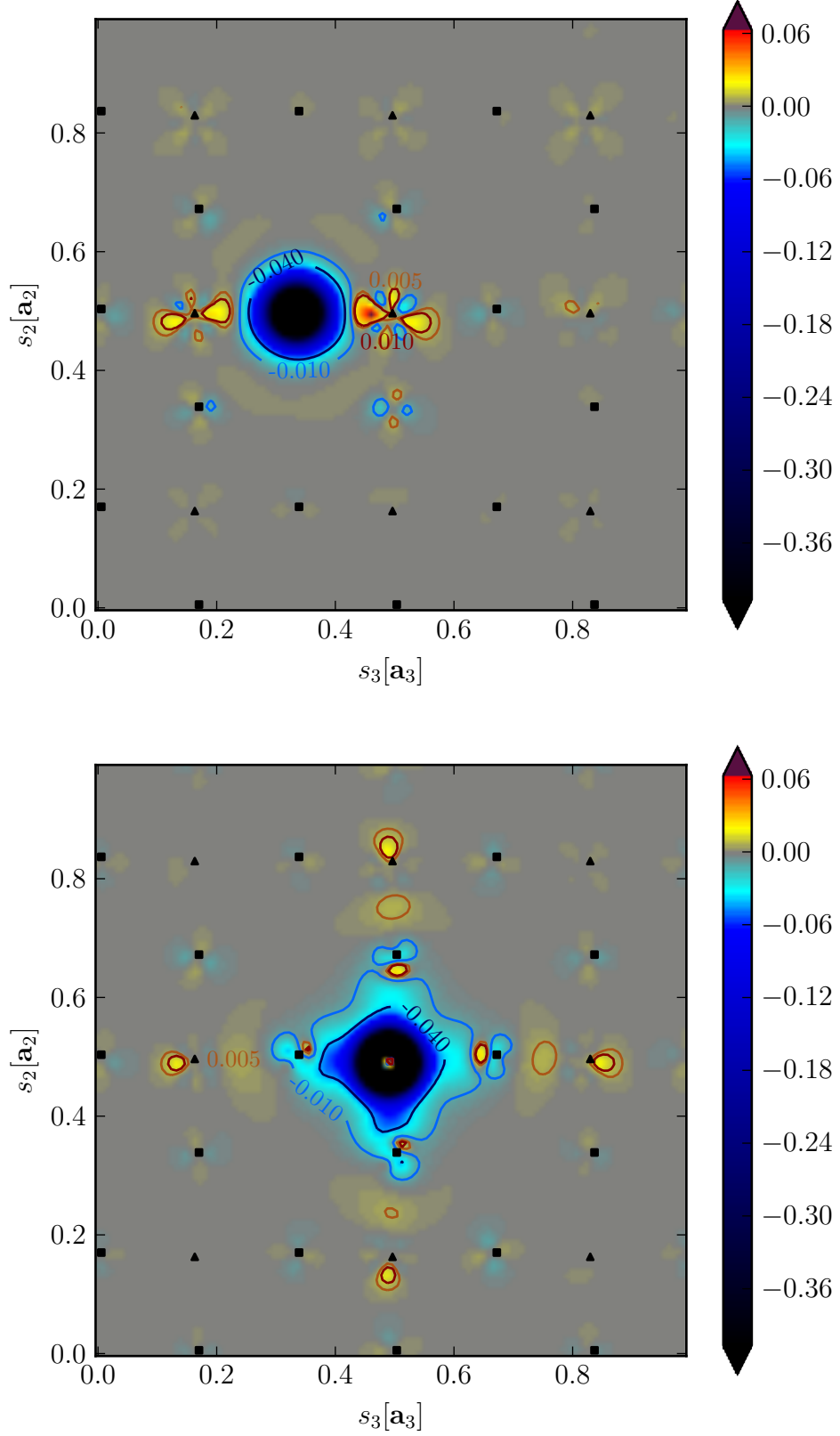


Figure 7.2: Electron number density difference $n^V(\mathbf{r}) - n(\mathbf{r})$ where $n^V(\mathbf{r})$ and $n(\mathbf{r})$ are the densities in the system with the vacancy and in the bulk, respectively. The Figure details and the colorbar scale are the same as in Fig. 7.1.

Charge transfer [e]	Δq^{Ba}	Δq^{Ti}	Δq^{O}	Δq_V^{NN}	Δq^{btwn}
	Min – Max	Min – Max	Min – Max	Min – Max	
$(r_{\text{cut}}^{\text{A}} [a_o])$	(2.47)	(1.31)	(2.24)		
O vacancy	0.00 – 0.00	–0.01 – 0.00	0.00 – 0.01	–0.02 – –0.02	0.16
Ti vacancy	0.01 – 0.01	–0.01 – 0.00	0.00 – 0.01	0.25 – 0.48	2.61
$(r_{\text{cut}}^{\text{A}} [a_o])$	(2.47)	(1.31)	(2.70)		
O vacancy	0.00 – 0.00	–0.01 – 0.00	0.00 – 0.01	–0.02 – –0.02	–0.02
Ti vacancy	0.00 – 0.01	–0.01 – 0.00	0.00 – 0.01	0.45 – 0.78	1.07
$(r_{\text{cut}}^{\text{A}} [a_o])$	(2.47)	(1.80)	(2.24)		
O vacancy	0.00 – 0.00	–0.01 – 0.00	0.00 – 0.01	–0.03 – –0.02	0.19
Ti vacancy	0.00 – 0.01	–0.02 – 0.00	0.00 – 0.01	0.25 – 0.41	1.04
$(r_{\text{cut}}^{\text{A}} [a_o])$	(2.47)	(1.80)	(2.70)		
O vacancy	0.00 – 0.00	–0.01 – 0.00	0.00 – 0.01	–0.03 – –0.02	0.00
Ti vacancy	0.00 – 0.01	–0.02 – 0.00	0.00 – 0.02	0.36 – 0.52	0.30
<i>Difference of Löwdin charges in a system with a vacancy and the defect-free system</i>					
O vacancy	–0.10 – 0.00	–0.01 – 0.00	0.00 – 0.01	–0.08 – –0.07	–
Ti vacancy	0.00 – 0.02	–0.03 – 0.00	0.00 – 0.01	0.19 – 0.23	–

Table 7.3: Bottom two rows: difference of Löwdin charges based on density in each system. Other rows: charge density difference is integrated within a sphere of radius $r_{\text{cut}}^{\text{A}}$ centered at each ion $\text{A} \in \{\text{Ba}, \text{Ti}, \text{O}\}$. Density difference is available on a set of grid points in position space; each value is assigned to the closest ion if there is at least one such ion within $r_{\text{cut}}^{\text{A}}$ – else to Δq^{btwn} which represents charge in the space between the ions. Δq_V^{NN} stands for the charge on the ions nearest to the vacancy.

The values highlighted in red indicate possible deviation from the limit in which QEqTS model is derivable. The QEq self-energy form, based on the Taylor expansion in “small” charge transfer variable, may become inadequate for large charge transfer, such as that near the Ti vacancy.

The degree of delocalisation of charge transfer can also be estimated, although this is highly sensitive to $r_{\text{cut}}^{\text{A}}$ values for the system with the Ti vacancy. Density difference is provided on a grid of points in position space and each value is assigned based on

proximity to a single ion subject to radial cut-off; values on the grid points outside the cut-off of any ions are assigned instead to the space inbetween the ions. The value Δq^{btwn} in Table 7.3 is the integrated charge of the density difference inbetween the ions – very large value indicates that $\Delta\rho(\mathbf{r})$ cannot be well represented in the ionic limit. In the case of the O vacancy, Δq^{btwn} is small no matter what cut-off radii are used, confirming that the ionic limit is adequate. In contrast, for the system with the Ti vacancy, this value is highly sensitive to the ionic radius, falling in the range $0.0e \geq \Delta q^{\text{btwn}} \geq -2.61e$. Thus, it seems likely that the representation of charge transfer $\Delta\rho(\mathbf{r})$ in the system with a Ti vacancy conforms less well to the ionic limit of the fixed-size QEqTS model.

7.3 QEqTS model’s ability to represent forces and charge transfer of point vacancies.

In Section 7.2 we have seen that the ground state density deviates from the assumed limit in the QEqTS IP in a distinct way for each type of vacancy. At the same time the ability to reproduce *ab initio* forces by the QEqTS model is markedly different for the two systems, as summarised in Table 7.4. It seems highly plausible that successes and failures of the model are linked to the extent to which the ground state density can be described as a small perturbation about a reference density, in the ionic limit.

$\Delta F_{\text{r.m.s.}}[\%]$	Total	Ba	Ti	O	V_{O}^{NN}	$V_{\text{Ti}}^{\text{NN}}$
<i>fit, test using only system with O vacancy</i>						
TS	21.25	14.32	20.56	22.32	31.84	–
QEqTS	15.72	12.87	16.88	15.57	17.54	–
<i>fit, test using only system with Ti vacancy</i>						
TS	21.20	17.30	23.44	21.78	–	27.31
QEqTS	18.76	15.99	20.54	17.07	–	25.54
<i>fit, test using only defect-free system</i>						
TS	14.98	7.55	14.33	17.09	(14.33)	(17.09)
QEqTS	14.14	8.88	14.22	15.45	(14.22)	(15.45)

Table 7.4: Test results, based on the ability to reproduce *ab initio* forces, for TS and QEqTS IPs parameterised using one type of system at a time. V_{A}^{NN} designate the ions nearest to the A vacancy, $\text{A} \in \{\text{O}, \text{Ti}\}$.

Table 7.4 highlights in red relatively large disagreements in *ab initio* forces and those obtained with the QEqTS model. As discussed in Section 7.1.2, the TS IP is a fixed-charge model and therefore has to be reparameterised for each new stoichiometry. The results for the reparameterised TS model are included to provide a reference and to get a sense to what extent the improvement is due to charge transfer. The bottom two rows of the table restate the results from fitting to defect-free bulk BaTiO₃, from Chapter 6 Table 6.5⁴. The quantities in brackets serve as an aid to the eye, to compare the fit in the same column for the same specie once a vacancy is introduced in place of the nearest neighbour.

Firstly, for the system with the O vacancy, the most dramatic improvement in accuracy, 31.84% $\rightarrow$ 17.54%, is for the Ti ions nearest to the O vacancy (designated by V_O^{NN}). Forces on the atoms further away from the vacancy are also in good agreement, on the order $\sim$ 16% or less. It is not shown here, but if QEqTS model is fit simultaneously⁵ to the defect-free system and the system with the O vacancy, the results are essentially unchanged.

Next, we can see that the ability of QEqTS IP to fit forces in the system with a Ti vacancy are markedly poorer. In particular, the forces on the O ions nearest to the vacancy are essentially not improved at all, 27.31% $\rightarrow$ 25.54% (designated by V_{Ti}^{NN}). Furthermore, forces on Ti ions in the system are also not well represented, possibly due to somewhat unphysical ionic charges assigned to O ions, as can be seen in Table 7.6.

Table 7.5 contains very similar information to that in Table 7.4 but emphasises non-transferability of the QEqTS model between the systems with a Ti and an O vacancy. In this case, QEqTS is fit simultaneously to systems with O and Ti vacancies, as well as to defect-free systems. As can be seen, this IP no longer describes forces on Ti ions nearest to the O vacancy accurately. As has already been mentioned, one can fit simultaneously defect-free bulk and the system with an O vacancy extremely well. Thus, the lack of transferability should be ascribed to the inability of the QEqTS IP to model both the defect-free environment and that near a Ti vacancy. The dramatic changes in the ground state induced by the Ti vacancy, demonstrated in Section 7.2.2, are likely too severe to be representable by the QEqTS IP which is instead applicable to model small perturbative

⁴In both this chapter and 6, IPs are fit to systems at 100 K, 200 K, 300 K and 500 K. However, test results include a system at 1000 K only in Chapter 6.

⁵A system with the vacancy in principle contains atomic environments that resemble defect-free bulk, sufficiently far from the vacancy. However, reference *ab initio* calculations are restricted to a relatively-modest size of the supercell, hence it is sensible to explicitly fit to defect-free reference data in order to test transferability between atomic environment in the bulk and that near the vacancy.

changes in ionic limit.

$\Delta F_{\text{r.m.s.}}[\%]$	Total	Ba	Ti	O	V_{O}^{NN}	$V_{\text{Ti}}^{\text{NN}}$
O vacancy	17.94	17.26	19.00	16.97	23.31	–
Ti vacancy	21.67	16.84	23.94	19.68	–	30.97
defect-free	19.08	15.37	23.16	17.02	(23.16)	(17.02)

Table 7.5: The QEqTS IP parameterised simultaneously to the system with the O vacancy, with the Ti vacancy and to the defect-free system. Each row presents test results when applying this IP to a specific system.

The upper four panels in Table 7.6 summarise the estimated charge in the vacancy region and ionic charge transfer based on the ground state density, the second lowest panel includes charge transfer based on Löwdin population analysis and in the lowest panel charge transfer variables from the QEqTS model are presented. The lower panel values are obtained using the QEqTS IPs parameterised to one type of the system at a time, i.e. same IPs as reported in Table 7.4. Values in red highlight charge transfer variables in QEqTS model that are likely unphysically large or small in magnitude. The last two columns are meant to imply that QEqTS model assigns charge transfer to vacancy nearest neighbours so as to reflect *both* the ionic charges and the charge in the vacancy region. Simple order-of-magnitude estimates suggest that the QEqTS fit to systems with the Ti vacancy likely assigns unphysical charges to some Ti and O ions. In particular, charge transfer of 0.13 on Ti ions seems to be an order-of-magnitude larger than is physically reasonable, when comparing either to QEqTS model fit to other systems or to estimates based on DFT ground state density. Comparing QEqTS charge transfer on vacancy nearest neighbours to the same values estimated from DFT results, one can certainly conclude that the sign is correct – Ti ions and O ions nearest to the vacancy become less positive and less negative, respectively. If we compare the magnitude then charge transfer on Ti and O nearest neighbours seem too large and too small in magnitude, respectively. Alternatively, if $\{\Delta q\}$ QEqTS variables are interpreted also to represent charge concentrated in the vacancy region (last two columns), values from the DFT results agree better with those from the IP. In particular, $-0.31 e \leq \Delta q_{\text{V}_\text{O}}^{\text{NN}} \leq -0.20 e$ for Ti ions nearest to O vacancy are now of the same order-of-magnitude as $\sim -0.4 e - \sim -0.7 e$ estimated based on the ground state for this system.

A more thorough analysis comparing $\{\Delta q_i\}$ and $\{\mathbf{p}_i\}$ to the changes in the ground state density of the reference system are outside of the scope of this chapter. However,

Charge [e]	$ \Delta q^{\text{Ti}} $	$ \Delta q^{\text{O}} $	Δq_V^{NN}	q_V	$\Delta q_{V_{\text{Ti}}}^{\text{NN}} + \frac{1}{6}q_{V_{\text{Ti}}}$	$\Delta q_{V_{\text{O}}}^{\text{NN}} + \frac{1}{2}q_{V_{\text{O}}}$
DFT	Max	Max	Min – Max		Min – Max	Min – Max
$(r_{\text{cut}}^{\text{A}} [a_o])$	(1.31)	(2.24)				
O vacancy	0.01	0.01	−0.02 – −0.02	−0.88	–	−0.45 – −0.45
Ti vacancy	0.01	0.01	0.25 – 0.48	−0.04	0.24 – 0.47	–
$(r_{\text{cut}}^{\text{A}} [a_o])$	(1.31)	(2.70)				
O vacancy	0.01	0.01	−0.02 – −0.02	−1.69	–	−0.86 – −0.86
Ti vacancy	0.01	0.01	0.45 – 0.78	−0.19	0.42 – 0.75	–
$(r_{\text{cut}}^{\text{A}} [a_o])$	(1.80)	(2.24)				
O vacancy	0.01	0.01	−0.03 – −0.02	−0.79	–	−0.42 – −0.41
Ti vacancy	0.02	0.01	0.25 – 0.41	−0.19	0.22 – 0.38	–
$(r_{\text{cut}}^{\text{A}} [a_o])$	(1.80)	(2.70)				
O vacancy	0.01	0.01	−0.03 – −0.02	−1.31	–	−0.68 – −0.67
Ti vacancy	0.02	0.02	0.36 – 0.52	−0.19	0.33 – 0.49	–
<i>Difference of Löwdin charges</i>					$\Delta q_{V_{\text{Ti}}}^{\text{NN}}$	$\Delta q_{V_{\text{O}}}^{\text{NN}}$
O vacancy	0.01	0.01	−0.08 – −0.07	–	–	−0.08 – −0.07
Ti vacancy	0.03	0.01	0.19 – 0.23	–	0.19 – 0.23	–
QEqTS					$\Delta q_{V_{\text{Ti}}}^{\text{NN}}$	$\Delta q_{V_{\text{O}}}^{\text{NN}}$
O vacancy	0.04	0.01	−0.31 – −0.20	–	–	−0.31 – −0.20
Ti vacancy	0.13	0.01	0.07 – 0.11	–	0.07 – 0.11	–

Table 7.6: Integrated charge density difference, within a sphere of radius $r_{\text{cut}}^{\text{A}}$ centered at each ion $\text{A} \in \{\text{Ba}, \text{Ti}, \text{O}\}$ or a vacancy. Density difference is available on a set of grid points in position space; each value is assigned to the closest ion if there is at least one such ion within $r_{\text{cut}}^{\text{A}}$. Δq_V^{NN} stands for the charge on the ions nearest to the vacancy. The last two columns imply that QEqTS Δq variables also represent the charge in the vacancy region.

based on simple estimates alone, it seems likely that Δq_i QEqTS variables represent local increase or decrease in charge density – this is arguably the intended physical meaning for these variables. This ought to be contrasted with the analysis of charge transfer in

thermally perturbed bulk BaTiO₃ in Chapter 6, where the variables were shown *not* to be interpretable as local increase or decrease in charge density.

In particular, it seems safe to conclude that not only QEqTS offers a marked improvement in transferability between the bulk environment and that near an O vacancy, but that the density-representing variables $\{\Delta q_i\}$ likely take on physically meaningful values. It is very interesting to take up a more in-depth analysis of QEqTS applied to this system. Neutral O vacancy in BaTiO₃ may be an example that helps define a class of systems where QEqTS model in its current form is both applicable and of practical use. Furthermore, this result can be placed in the context of the ongoing PhD work on phase transitions in photoexcited BaTiO₃ by Fangyuan Gu[187]. In her work F. Gu had reparameterised the QEqTS IPs from Chapter 6 to *ab initio* reference data based on photoexcited state of bulk BaTiO₃. In contrast to results of Chapter 6, applying QEqTS to photoexcited BaTiO₃ offers a marked increase in accuracy relative to the TS IP, on the order of $\sim 4 - 5\%$. In the context of computer simulations of phase transitions, this difference in accuracy is significant enough to prefer to use QEqTS IP instead of the fixed-charge TS model, or at least supplement it⁶.

7.4 Discussion

On a superficial level the two systems, one with the O and one with the Ti vacancy, are equivalent and one might falsely expect the QEqTS model to be equally applicable in both cases. From the point of view of an ionic model, in each case an ion is missing and the remaining ions are meant to redistribute their charges in response to changes in the electrostatic potential. In practice, QEqTS demonstrates accuracy and transferability in reproducing interatomic interactions simultaneously in bulk and near an O vacancy yet is essentially unable to capture interactions near the Ti vacancy. Going beyond the superficial level, it is demonstrated in Section 7.2 that the ground state in the two systems is qualitatively distinct.

The system with the O vacancy exhibits non-negligible charge concentration in the vacancy region on the order $\sim -1 e$ and – perhaps because of this – the ground state density surrounding the vacancy that differs only very little from that in a defect-free reference system. The excellent ability of QEqTS to reproduce *ab initio* forces in this

⁶It is demonstrated in Chapter 8 that the QEqTS IP exhibits unphysical long-range charge transfer, resulting in a vanishing longitudinal optical/transverse optical splitting. Depending on the aim and details of a given atomistic simulation, care must be taken in choosing an appropriate IP to use since the fixed-charge TS model might give more physically sensible results.

system, as well as the interpretation of QEqTS charge transfer variables as representative of charge in the vacancy region, together suggest that a) overall the ground state density in this system adheres to the ionic limit and can be viewed as a small perturbation about the density in the defect-free BaTiO_3 , thus justifying the functional form of the QEqTS model, and b) despite the fact that the non-negligible charge concentration in the vacancy region partly violates the ionic limit, the issue is largely mitigated by using charge transfer variables of the vacancy nearest neighbours to additionally represent the charge in the vacancy region.

The system with the Ti vacancy exhibits significant changes in the ground state density, particularly in the region encompassing O ions nearest to the vacancy. Estimates of charge transfer on the vacancy nearest neighbours give values that are an order-of-magnitude larger than the equivalent values for the O vacancy. Furthermore, change in ground state density deviates from the ionic limit. The overall inability of the QEqTS to improve representation of forces in this system and seemingly unphysical values for charge transfer variables indicate that the system is beyond the scope of the model. Ground state density in a system with Ti vacancy cannot be viewed as a small perturbation around the density in the defect-free reference system. In particular, QEq self-energy may well be inadequate to describe significant changes in the charge density taking place in this system.

Chapter 8

Phonon spectrum of a charge-transfer model

In Chapters 6 and 7 charge transfer in the QEqTS IP was physically interpreted in two different regimes of perturbations to the electrostatic potential. In Chapter 6 we saw that, in a thermally-perturbed defect-free bulk BaTiO_3 , charge transfer variables $\{\Delta q_i\}$ do not represent local increases or decreases in the charge density. They may possibly be interpreted as representative of higher-order multipole moments of the TiO_6 sub-units or, alternatively, perhaps these variables have no simple physical meaning and only provide additional degrees of freedom that enable an improved “mathematical” fit to the short-range forces between Ti and O nearest neighbours. In contrast, in Chapter 7, charge transfer variables near the O and Ti vacancies were interpreted as local increases or decreases in charge density. These two qualitatively-different interpretations of $\{\Delta q_i\}$ in the bulk environment and near a vacancy provide original insight into the physics that the QEqTS model represents. To complete this discussion, in this chapter charge transfer over macroscopic distances in the presence of long wavelength lattice waves is demonstrated and physically interpreted. It is highlighted that the QEq-based IPs, such as QEqTS, have metallic screening built into them due to a combination of the charge equilibration scheme being global, in a sense that charge transfer over arbitrary distances can take place in the process of energy minimisation¹, and the simple quadratic form of the self-energy. Unlike the results of Chapters 6 and 7, long-range charge transfer in response to a long-wavelength (varying) electrostatic potential is a well-known feature of the QEq model[89, 188]. Thus, firstly, the aim of the present chapter is simply to highlight the long-range charge transfer and to relate it to the observed metallic

¹Recall, equilibrium charges are obtained in the QEq model by minimising the total energy with respect to charge transfer variables, subject to charge conservation.

screening.

The secondary aim of this chapter is to verify that the IPs presented in this thesis accurately represent BaTiO_3 , or at least its elastic and vibrational properties in the low temperature rhombohedral phase. In Chapters 6 and 7 the ability to reproduce reference *ab initio* forces was used as an unbiased measure of the IP's quality, which allowed a comparative study of different functional forms of the ionic IPs and an analysis of the relevance and physical meaning of the charge transfer variables. In this chapter it is highlighted instead that all TS and QEqTS IPs presented in the thesis are very accurate. In particular, the QEqTS IP parameterised to the system with an O vacancy is likely to be the best currently-available classical IP for BaTiO_3 in terms of its accuracy and transferability between the pristine bulk and the environment near a vacancy.

The chapter is organised as follows. Computational details of calculating the selected properties are described in Section 8.1. Verifying the mechanical stability of the low temperature rhombohedral phase of BaTiO_3 is the subject of Section 8.2. In Section 8.3 charge transfer over macroscopic distances, and the unphysical metallic screening in QEq-based IPs, is demonstrated by focusing on the vanishing longitudinal optical/transverse optical (LO/TO) splitting near the Γ point in the phonon spectrum. The origin of metallic screening in QEq-based IPs is then discussed.

8.1 Computational details

Properties calculated with DFT using the PBEsol exchange-correlation (xc) functional, as described in Chapter 5, constitute the reference values. Since IPs are parameterised to DFT reference data, any properties calculated with classical IPs are meant to agree with the experiment or other *ab initio* calculations only to the extent that the reference DFT calculations agree.

Furthermore, ultrasoft Garrity-Bennett-Rabe-Vanderbilt LDA pseudopotentials from Vanderbilt's group[178] were used to supplement property calculations. All other DFT parameters, such as the energy cutoff value, were kept the same as before. This highlights that different methods, each of which is considered *ab initio* and is expected to be quite accurate, actually only agree among themselves to within a certain error, depending on the type of xc functional used. The error in DFT calculations associated with the approximate xc functional can be estimated from the spread of values calculated with different xc approximations. The idea is that if the results obtained with an IP agree with the reference DFT calculations at least as well as the *ab initio* results obtained

using a different exchange-correlation functional then the IP is deemed fairly accurate.

8.1.1 Elastic constants

The second-order elastic constants were obtained using the energy-strain relationship with the aid of an open-source program ElaStic[189]². At $T = 0$ K BaTiO₃ is in the rhombohedral phase, which corresponds to the space group 160 (R3m)[191]. For this space group there are six independent elastic constants – in Voigt notation these are C_{11} , C_{12} , C_{13} , C_{14} , C_{33} and C_{44} [192]. These were obtained by applying six types of strain, summarised in Table 8.1 using superscript enumeration identical to that defined in Ref. 189. For each strain tensor $\boldsymbol{\eta}^{(i)}$, the strain was applied to the relaxed structure

$\boldsymbol{\eta}^{(i)}$	η_1	η_2	η_3	η_4	η_5	η_6
$\boldsymbol{\eta}^{(1)}$	η	η	η	0	0	0
$\boldsymbol{\eta}^{(2)}$	η	0	0	0	0	0
$\boldsymbol{\eta}^{(4)}$	0	0	η	0	0	0
$\boldsymbol{\eta}^{(5)}$	0	0	0	2η	0	0
$\boldsymbol{\eta}^{(8)}$	η	η	0	0	0	0
$\boldsymbol{\eta}^{(10)}$	η	0	0	2η	0	0

Table 8.1: Strain tensors, in Voigt notation, used when calculating the elastic constants in the rhombohedral phase. The i^{th} tensor is represented as vector $\boldsymbol{\eta}^{(i)} = [\eta_1, \eta_2, \eta_3, \eta_4, \eta_5, \eta_6]$. The superscript i , defined as in Ref 189, has no special meaning.

at a set of strain values $\eta = \eta(j)$ defined as $\eta(j) = -\eta_{\text{max}} + 2(j-1)\eta_{\text{max}}/(j_{\text{max}}-1)$ where j_{max} is a positive odd integer and $\eta_{\text{max}} > 0$ is a parameter defining the maximum applied strain. This definition ensures that the points $\eta = -\eta_{\text{max}}$, $\eta = 0$ and $\eta = \eta_{\text{max}}$ are included. This set of calculations allows one to obtain the second order derivatives of the energy with respect to strain tensors $\boldsymbol{\eta}^{(i)}$, which in turn define six coupled linear equations that can be solved to obtain the elastic constants.

Second-order derivatives were obtained by fitting a polynomial to the energy-strain curve. The parameters η_{max} and j_{max} were varied to test how sensitive the results are to these parameters and to the order of the polynomial used in fitting. Sensitivity was probed in the following way. Firstly, it was verified that fitting the polynomial only to

²This package itself uses an auxiliary program SGROUP[190] to identify the space group and symmetry operations of a crystal structure.

a low-strain subset of energy-strain points, defined by $\eta(j) \leq \tilde{\eta}_{\max} < \eta_{\max}$, would still generate approximately the same derivatives. Ideally, one ought to see a plateau in the values of the second order derivative of energy with respect to strain, obtained using different values of $\tilde{\eta}_{\max}$. With only one exception, for all classical IP-based calculations as well as DFT calculations, it was found that with $\eta_{\max} = 0.01$, $j_{\max} = 17$ and using a quadratic polynomial fit, the test results are fulfilled in a sense that the calculated energy derivatives and elastic constants are approximately independent of the $\tilde{\eta}_{\max}$ value. The one exception was the calculations using the QEqTS potential parameterised only to the system with a Ti vacancy – it was found that at $\eta_{\max} = 0.01$ the quadratic polynomial fit is highly sensitive to $\tilde{\eta}_{\max}$, whereas fourth and sixth order polynomials were not. Thus, a fourth order polynomial was used to obtain elastic constants for this IP.

8.1.2 Phonon calculations

The phonon spectra for the classical IPs were calculated via the “frozen-phonon” method using the Phonopy open-source package[193]. In this method the force constants matrix is evaluated using a direct method – by perturbing a single atom within a large supercell and calculating the resulting forces on all other atoms. The phonon frequencies at all lattice wave vectors calculated using the direct method are non-interpolated, as explained in the next paragraph. As such, the non-analytic correction is never invoked.

The path sampled in the Brillouin zone was chosen to pass through those high symmetry points that are present in both the rhombohedral and the cubic phases. All other high symmetry points are nearly coincident with this set because the rhombohedral unit cell is nearly identical to the cubic cell and hence evaluating phonon frequencies at those points is not very useful for our purposes. Exact non-interpolated phonon frequencies along the chosen path were obtained by choosing lattice wave vectors $\mathbf{q}$ commensurate with the supercell dimensions used in the force constants calculations. For example, for the path $\Gamma - K$, where $K = [1/2, 0, 0]$ in the basis of the reciprocal lattice vectors, $\mathbf{q}$ points were selected via $[m/n, 0, 0]$ setting the integer m is in the range $0 \leq m \leq n/2$ for a $n \times n \times n$ supercell.

The phonon spectrum along the same path and at the same points $\mathbf{q}$ in the reciprocal space was calculated using density functional perturbation theory[194], for comparison.

8.2 Stability of the rhombohedral phase

In this section it is demonstrated that all parameterised and presented TS and QEqTS IPs accurately describe the rhombohedral phase of bulk BaTiO₃, at least with respect to the properties listed below. This result is non-trivial and should be placed in the context of the work by J. Fallon[9] who developed a TS IP for bulk BaTiO₃ as part of his investigation into the atomic structure and dynamics of its ferroelectric phases. J. Fallon used *ab initio* data obtained using the LDA exchange correlation functional and found that the resultant IP represents a material that is *not* stable in the rhombohedral phase at $T = 0$ K, unless an external negative pressure of ~ 8.5 GPa is applied. In this thesis, phase transitions are generally not examined – the work along this route is currently being undertaken by F. Gu[187] using the QEqTS IP of Chapter 6, reparameterised for photoexcited states.

	DFT		TS	QEqTS			Exp.[186]
(R3m)	LDA	PBEsol		fit: bulk	fit: V _O	fit: V _{Ti}	
a [a_o]	7.475	7.538	7.538	7.539	7.526	7.520	7.566
α [deg]	89.932	89.877	89.710	89.721	89.738	89.915	89.839
Δx_{Ti}	−0.0092	−0.0107	−0.0113	−0.0109	−0.0090	−0.0048	−0.0128
Δx_{O}	0.0089	0.0114	0.0110	0.0106	0.0109	0.0066	0.0109
Δz_{O}	0.0135	0.0174	0.0168	0.0164	0.0160	0.0094	0.0193

Table 8.2: Lattice constants of BaTiO₃ in the rhombohedral phase, obtained with DFT and the classical IPs of this work. The last column shows experimental values at $T = 15$ K. Δx_{Ti} , Δx_{O} and Δz_{O} are in scaled coordinates, as defined as in Table 7.1. The three QEqTS columns are for the IPs fit to the pristine bulk, to a supercell containing a neutral O, and Ti, vacancies.

We focus on reproducing a set of observables advocated for verifying a given IP by M. Finnis[195] in his classic textbook “Interatomic forces in condensed matter” – this includes lattice constants, elastic constants and the phonon spectrum. Lattice constants trivially allow one to verify whether the relaxed system is in the same phase as is found in nature and/or reference *ab initio* calculations. Elastic constants are related to the second order derivatives of the energy with respect to strain and thus probe how well the internal stress is captured by the IP, at least near equilibrium. The phonon spectrum serves as

a reliable test for whether a given phase is thermodynamically stable. Furthermore, the phonon spectrum is particularly challenging to reproduce with a classical IP since it involves phonon modes of wavelengths that considerably exceed the dimensions of the supercells used during the parameterisation – hence it probes the ability of the IP to describe long-range correlations that were not present in the training data set. In particular, long wavelength lattice waves probe the way a polarisable IP captures screening, an effect that generally lowers the frequencies of the longitudinal optical modes relative to fixed-charge non-polarisable models[54, 59].

	Elastic constants [GPa]					
	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₃₃	C ₄₄
DFT (PBEsol)	267	82	44	45	252	42
TS	277	80	34	38	199	40
QEqTS	280	85	41	37	213	43
QEqTS fit: V _O	288	76	38	41	218	29
QEqTS fit: V _{Ti}	306	83	48	31	221	46
DFT (LDA)	307	96	59	42	298	58

Table 8.3: Elastic constants calculated using QEqTS and TS IPs as well as DFT. The latter calculation is repeated using the LDA exchange correlation functional. There are no experimental values available, to the best of our knowledge.

Recall that all of the IPs were parameterised using reference data obtained with the PBEsol exchange correlation functional. In this section, additionally, LDA results are included in order to get the sense for what kind of error is “acceptable”. The idea is that if the results from an IP agree with the reference DFT calculations at least as well as *ab initio* results obtained by using a different xc functional then the IP can be considered to be within the xc-related uncertainty in the calculated elastic constants.

Firstly, Table 8.2 shows the minimum energy relaxed structure. It is clear that all the TS and QEqTS IPs find a stable rhombohedral phase that closely resembles to the reference structure³. At the same time, it must be noted that the QEqTS IP of Chapter

³Phonon calculations in the cubic phase, using the TS and QEqTS IPs of Chapter 6, showed it to be thermodynamically unstable, in good agreement with the reference *ab initio* calculation. This data is not shown. I have not tested whether the rhombohedral phase corresponds to a *global* energy minimum.

7 parameterised only to a system with a Ti vacancy differs from other IPs in that it predicts a structure that is closer to the cubic phase. For example, Δx_{Ti} , Δx_{O} and Δz_{O} are about half of the magnitude they should be based on the reference PBEsol calculations. Lattice constants calculated with all other IPs are in excellent agreement with the reference PBEsol calculations – noticeably better than those calculated with the LDA.

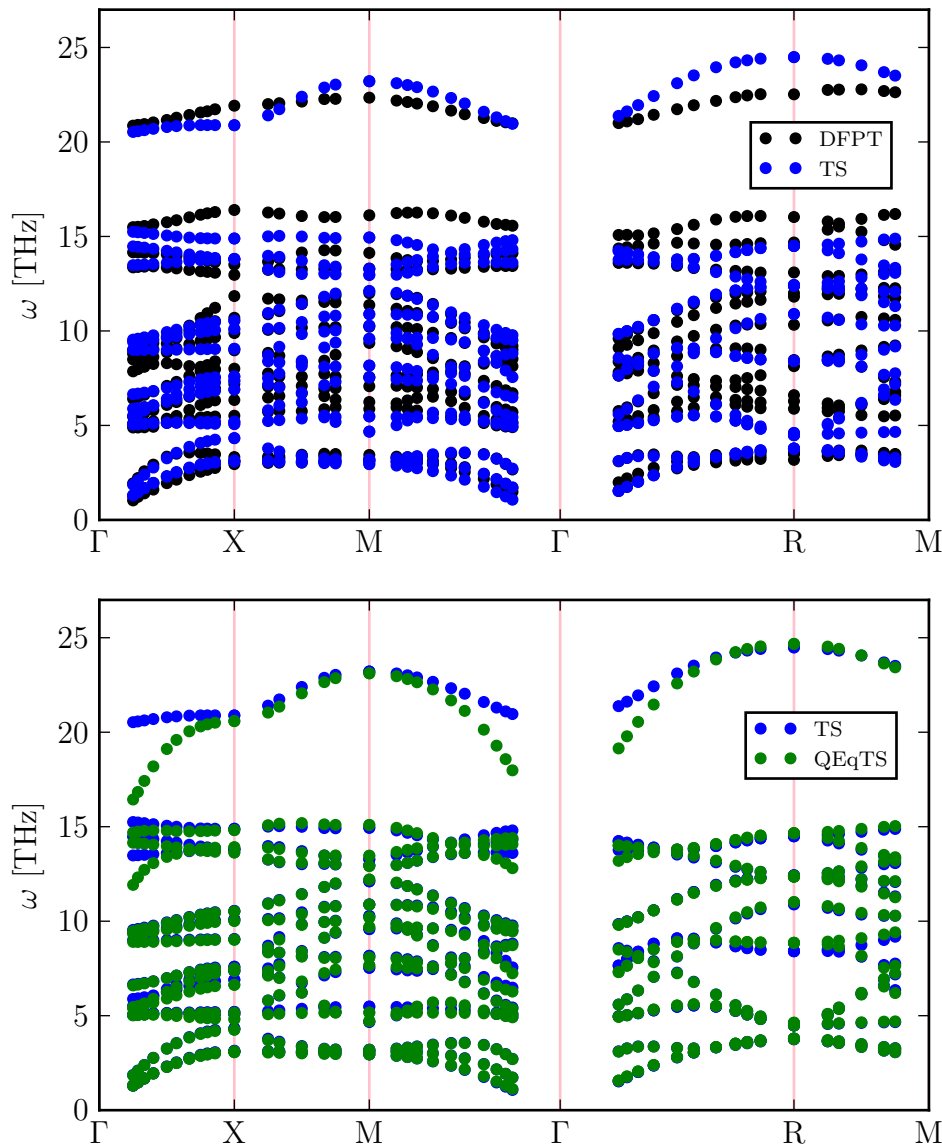


Figure 8.1: Phonons calculated for the BaTiO_3 in its rhombohedral phase using $n \times n \times n$ supercells with $n \in \{5, 6, 7, 8\}$, using TS (blue) and QEqTS (green) IPs. The black points are from a DFPT calculation at the same set of wave vectors. The expected LO/TO splitting near Γ point is clearly apparent in both the *ab initio* calculations and those based on the TS IP but it vanishes in calculations based on the QEqTS IP.

Next, Table 8.3 compares elastic constants obtained with QEqTS and TS IPs to the

reference values obtained with DFT. As before, DFT calculations were also repeated with the LDA xc functional, to get a rough estimate of the xc error.

It is clear that all IPs result in elastic constants in a very good agreement with the reference calculation. TS and QEqTS IPs that were parameterised to defect-free bulk show excellent agreement, in particular, $C_{13} \approx C_{14} \approx C_{44}$ are well captured⁴. Again, LDA calculations show that the error in elastic constants obtained with any of the IPs is well within the error one may encounter when repeating the *ab initio* calculation with a different exchange-correlation functional.

It is convenient to introduce the following notation: QEqTS(fit: V_O) and QEqTS(fit: V_{Ti}) for the QEqTS IPs parameterised in Chapter 7 to configurations of the system with a neutral O vacancy, and a neutral Ti vacancy, respectively. Next, a series of phonon calculations are presented – for ease of visualisation TS is compared with DFPT results in Figure 8.1 (top) and then QEqTS⁵, QEqTS(fit: V_O) and QEqTS(fit: V_{Ti}) are compared to TS since all the IPs produce nearly identical spectra and differences are easier to notice. These phonon calculations serve a dual purpose. Firstly, as can be seen in Figures 8.1 and 8.2, it is demonstrated that all TS and QEqTS IPs result in a stable rhombohedral phase, because none of the frequencies are imaginary. The QEqTS results differ appreciably from those obtained with the TS IP only near the Γ point, where the LO/TO splitting is seen to vanish, clearly indicating metallic screening. It is argued in Section 8.3 that this is due to the long-range charge transfer inherent in the model.

Figure 8.2 shows the phonon spectrum obtained using QEqTS IPs which were parameterised to the system with the O vacancy (top) and the Ti vacancy (bottom). The top phonon branch is overall lowered by both IPs relative to TS (and DFPT) and the LO/TO splitting vanishes more rapidly. This indicates that when fitting interatomic forces near the vacancy, the energy cost of charge transfer is lowered. Otherwise, the QEqTS IP parameterised using the O vacancy agrees well with the TS IP, which is consistent with the conclusion of Chapter 7 that it is transferable between the pristine bulk crystal and near an O vacancy. The QEqTS IP fit to the Ti vacancy noticeably disagrees with the reference TS IP (and DFPT) at ~ 14 THz near the M point and the path Γ -R-M, highlighting the somewhat reduced transferability of the model between the defect-free environment and that near the Ti vacancy – consistent with the discussion in Chapter 7.

⁴We were unable to find experimental values for the elastic constants of $BaTiO_3$ in its rhombohedral phase. Such experiments were probably not carried out, since other, recent, *ab initio* calculations of $BaTiO_3$ elastic constants do not include experimental values only for this phase[196, 197].

⁵The IP denoted by QEqTS(Ti) in Chapter 6 is used.

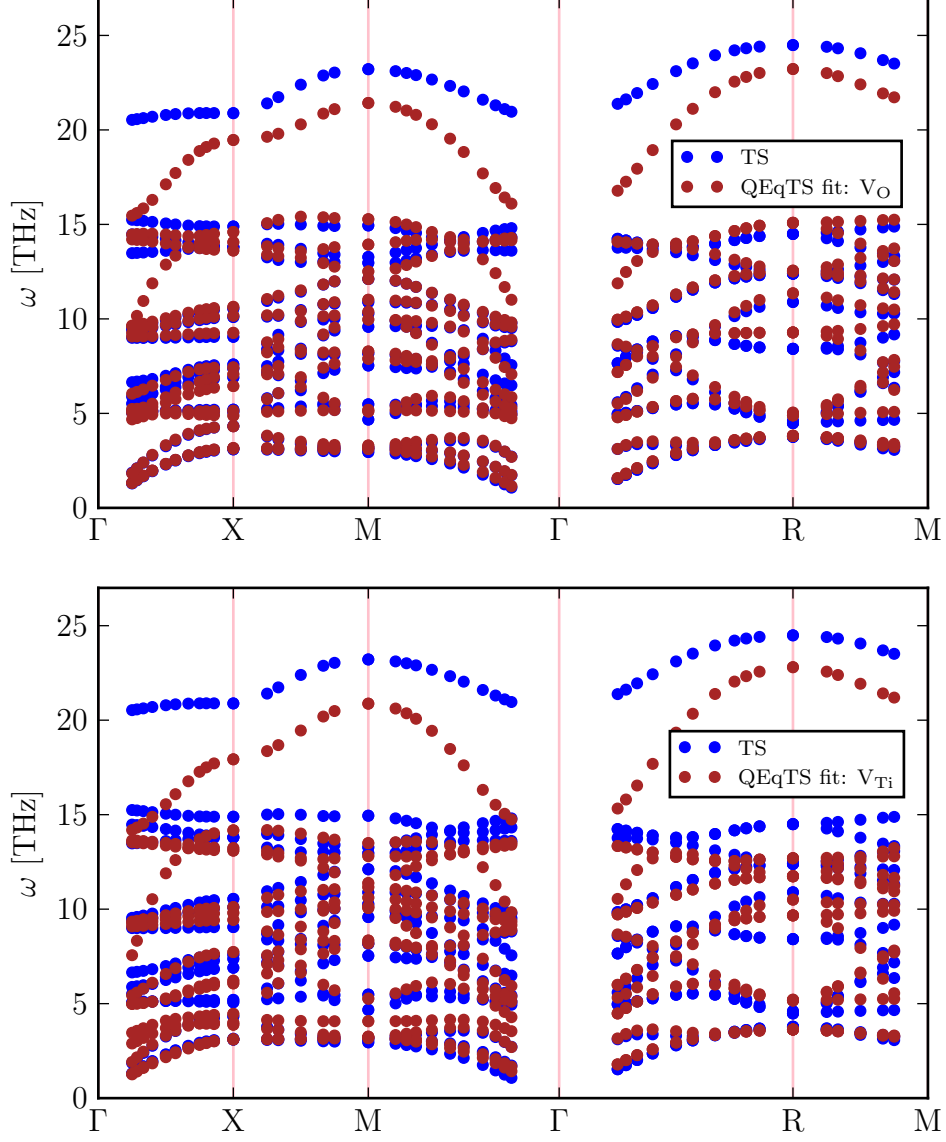


Figure 8.2: Phonons calculated for BaTiO₃ in its rhombohedral phase using $n \times n \times n$ supercells with $n \in \{5, 6, 7, 8\}$. Interatomic forces were obtained using TS (blue) and QEqTS (brown) IPs – parameterised to the systems with a neutral O vacancy and a neutral Ti vacancy, in the top and bottom subfigures, respectively.

8.3 Screening due to long-range charge transfer

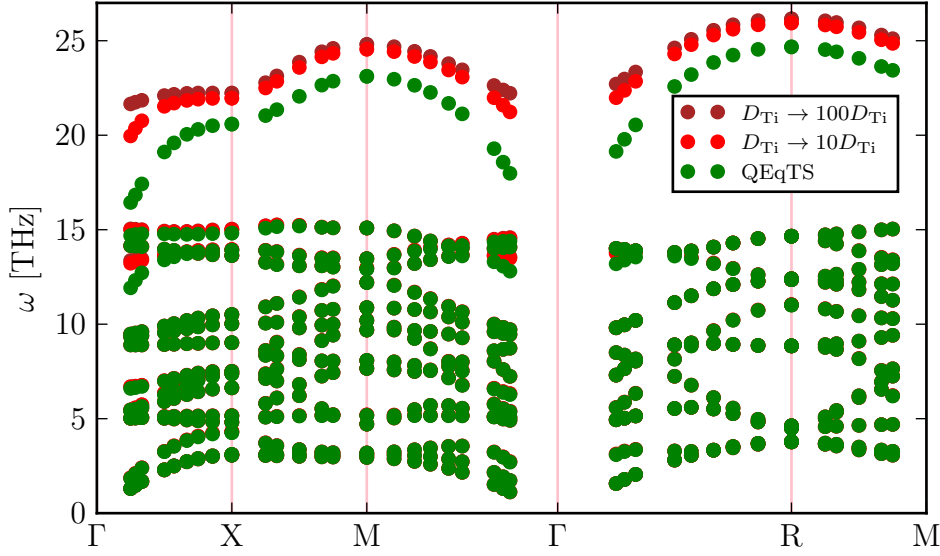


Figure 8.3: Phonons calculated for the BaTiO₃ in its rhombohedral phase using $n \times n \times n$ supercells with $n \in \{5, 6, 7, 8\}$. Interatomic forces were obtained using QEqTS (green), as well as the same IP with QEq self-energy modified as $D_{\text{Ti}} \rightarrow 10D_{\text{Ti}}$ (red) and $D_{\text{Ti}} \rightarrow 100D_{\text{Ti}}$ (brown).

Recall that the QEq self-energy is the simple quadratic expression $A_i \Delta q_i + D_i \Delta q_i^2$ where $A_i \in \{A_{\text{Ba}}, A_{\text{Ti}}, A_{\text{O}}\}$ and $D_i \in \{D_{\text{Ba}}, D_{\text{Ti}}, D_{\text{O}}\}$. Also, recall that the QEqTS(Ti) IP of Chapter 6, used in phonon calculations in Figure 8.3, only allows for significant charge transfer to take place between Ti ions. Thus, suppressing charge transfer between Ti ions suppresses *all* charge transfer. Figure 8.3 shows the effect of making charge transfer more costly by rescaling $D_{\text{Ti}} \rightarrow 10D_{\text{Ti}}$ and $D_{\text{Ti}} \rightarrow 100D_{\text{Ti}}$ which trivially confirms the origin of the metallic screening as due to charge transfer.

The qualitatively-different screening in the TS and QEqTS IPs can be understood in two steps. As a preliminary step, the physics behind the LO/TO splitting itself is outlined. It is presented in detail elsewhere[125]. For two point charges at positions $\mathbf{r}_i + \Delta \mathbf{r}_i$ and $\mathbf{r}_j + \Delta \mathbf{r}_j$ such that $\text{Max}(|\Delta \mathbf{r}_i|, |\Delta \mathbf{r}_j|) \ll |\mathbf{r}_{ij}|$, with (fixed) charges q_i^0 and q_j^0 the electrostatic interaction energy can be written exactly and approximately as:

$$E_{ij}^{\text{ES}} = \frac{q_i^0 q_j^0}{|\mathbf{r}_{ij} + \Delta \mathbf{r}_{ij}|} \quad (8.1)$$

$$\approx \frac{q_i^0 q_j^0}{r_{ij}} + (\tilde{\mathbf{P}}_i q_j - q_i \tilde{\mathbf{P}}_j) \cdot \frac{-\mathbf{r}_{ij}}{r_{ij}^3} \quad (8.2)$$

where $\Delta \mathbf{r}_{ij} \equiv \Delta \mathbf{r}_i - \Delta \mathbf{r}_j$ and $\tilde{\mathbf{P}}_i \equiv q_i^0 \Delta \mathbf{r}_i$ is *not* an induced dipole moment, but an approximate representation in which $\mathbf{r}_i$ is a reference equilibrium position for the point

charge located at $\mathbf{r}_i + \Delta\mathbf{r}_i$. For an ideal ionic material, consisting of non-polarisable, non-overlapping, fixed-charge ions at equilibrium positions $\{\mathbf{r}_i\}$ and a lattice wave that causes small displacements $\{\Delta\mathbf{r}_i\}$, an approximation to the total electrostatic energy is given by:

$$E^{\text{ES}} \approx \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} \frac{q_i^0 q_j^0}{r_{ij}} + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \underbrace{\left(\sum_{j \neq i}^{N_{\text{atm}}} \frac{\tilde{\mathbf{P}}_j \cdot \mathbf{r}_{ij}}{r_{ij}^3} \right)}_{\tilde{\phi}_i} - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \tilde{\mathbf{P}}_i \cdot \underbrace{\left(\sum_{j \neq i}^{N_{\text{atm}}} q_j^0 \frac{\mathbf{r}_{ij}}{r_{ij}^3} \right)}_{\tilde{\mathbf{E}}_i^\alpha} \quad (8.3)$$

$$\equiv \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \sum_{j \neq i}^{N_{\text{atm}}} \frac{q_i^0 q_j^0}{r_{ij}} + \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} q_i^0 \tilde{\phi}_i - \frac{1}{2} \sum_{i=1}^{N_{\text{atm}}} \tilde{\mathbf{P}}_i \cdot \tilde{\mathbf{E}}_i \quad (8.4)$$

where the implicitly defined $\tilde{\phi}_i$ and $\tilde{\mathbf{E}}_i$ allow us to interpret the effect of a lattice wave on the electrostatic energy as being due to a perturbing electrostatic potential and electric field, respectively. Due to the dot product of the type $\tilde{\mathbf{P}}_i \cdot \mathbf{r}_{ij} \propto \Delta\mathbf{r}_i \cdot \mathbf{r}_{ij}$, the summation that defines $\tilde{\phi}_i$ and $\tilde{\mathbf{E}}_i$ vanishes for a purely transverse wave but not for a longitudinal wave. This causes the LO/TO splitting; a phonon mode far from the Γ point is, in general, a mixture of transverse and longitudinal vibrations, so the cancellation is partial in that case. For a LO mode, $\tilde{\mathbf{E}}_i$ opposes the motion of ion i , thereby increasing the frequency of vibration.

In a polarisable-ion IP, such as the TS IP, induced dipoles $\{\mathbf{p}_i\}$ introduce screening, as discussed in Section 1.3.2, which, on average, has the effect $q_i^0 \Delta\mathbf{r}_i \rightarrow q_i^0 \Delta\mathbf{r}_i / \epsilon^{\text{eff}}$ with $\epsilon^{\text{eff}} > 1$ and therefore $\tilde{\mathbf{P}}_i \rightarrow \tilde{\mathbf{P}}_i / \epsilon^{\text{eff}}$, which lowers the frequency of the LO modes.

The metallic screening, evident in the phonon calculation using QEqTS IP, can be rationalised in analogy to a parallel plate capacitor. The perturbing potential due to a lattice wave $\tilde{\phi}_i$ has the form[194] $\tilde{\phi}_i = v(\mathbf{r}_i) e^{i\mathbf{q} \cdot \mathbf{r}_i}$, where $v(\mathbf{r}_i)$ has the periodicity of the *primitive* unit cell and $e^{i\mathbf{q} \cdot \mathbf{r}_i}$ is the envelope function with periodicity defined by the lattice wave⁶. As the wavelength approaches macroscopic lengthscales ($\mathbf{q} \rightarrow 0$) the divergence of $\tilde{\mathbf{E}}_i$ becomes small and the field locally resembles a spatially-constant externally applied field. In the QEq model charge transfer over arbitrarily long distances is allowed. Hence, opposite excess charge, relative to the bulk value, accumulates in the troughs and crests of the periodic potential defined by the wavevector $\mathbf{q}$. This sets up the field, in analogy to the field in the interior of a parallel plate capacitor, which opposes the electric field $\tilde{\mathbf{E}}_i$ and cancels it completely as $\mathbf{q} \rightarrow 0$. Similarly, in a perfect conductor, which is finite in extent⁷, an externally applied electric field is completely cancelled out in the interior due to the excess charge accumulation at the system boundaries (surfaces).

⁶In a computer simulation subject to the periodic boundary conditions only lattice waves commensurate with the supercell exist.

⁷It is assumed the conductor is much larger than the skin depth of the material.

Chapter 9

Conclusions and future work

In the present chapter we, firstly, summarise the main points of the present thesis and, secondly, suggest future work that can grow out of our research.

9.1 Summary and conclusions

In Chapter 1 we have introduced and motivated the focus of the present work on developing, testing and analysing the QEqTS IP, which combines the PI and QEq models. The overarching aim is to improve the transferability relative to the TS IP and, therefore, to extend the range of systems that can be simulated accurately. In Chapter 7 we have demonstrated an example of a neutral O vacancy in BaTiO₃, where the QEqTS IP was shown to markedly improve the accuracy and transferability relative to the TS IP. A comparison between the charge transfer variables and the DFT ground state density revealed that $\{\Delta q_i\}$ mimic the DFT density in and near the vacancy region. Thus, the improvement in accuracy and transferability can be ascribed to a better representation of the ground state density in a polarisable IP. To the best of our knowledge, this is the first demonstration of its kind.

In Section 1.4.2 we have shown, based on examples taken from the literature, that in some systems QEq-based IPs do *not* improve accuracy or transferability relative to the fixed-charge IPs. What's more, in the examples considered, it was highlighted that the $\{\Delta q_i\}$ are generally very small and have a negligible effect on interatomic forces or calculated properties. These results are consistent with J. Sarsam's work, where QEqTS IP was applied to charged MgO vacancies and interstitials, among other systems, and QEq charge transfers were found to be negligible[27]. Her model numerically reduced to the TS IP for the parameter values that best fit DFT reference data and, consequently, offered no improvement in accuracy or transferability. We have pointed out an existing

hypothesis that, at least in some systems, changes in the charge density correspond to very small or even negligible inter-ionic charge transfers, making the QEq model not useful for representing such changes. In turn, in Chapter 6 we have applied a series of IPs to hot defect-free bulk BaTiO₃ and demonstrated that the effect of the QEq model can indeed be rationalised by the fact that changes in the underlying charge density correspond to very small inter-ionic charge transfers. Using root-mean-squared agreement with the reference *ab initio* forces as a measure of accuracy, we have shown in Chapter 6 that the QEq model improves accuracy only by 2% and 1% relative to the fixed-charge rigid-ion and TS IPs, respectively. In contrast, the TS IP improves accuracy by 41% relative to the rigid-ion IP, indicating that the charge density does undergo non-negligible changes, but that the QEq model isn't suitable for representing these changes. Additionally, an analysis relating TS induced dipole variables to changes in the ground state density revealed these to be descriptive of the local polarisation in a physically intuitive and transparent way. This further supports the view that the PI model improves accuracy *because* the changes in the charge density are represented better.

In Chapters 3 and 7 we tried to answer the question of why the QEq-based IP might have a limited ability to represent systems that exhibit substantial charge redistribution, such as BaTiO₃ with a neutral Ti vacancy. Firstly, it was highlighted that the QEq self-energy terms may have a limited transferability between environments of different atomic coordination. Secondly, we argued that the QEqTS functional form is justified only to the extent that the underlying charge density adheres closely to an ionic limit and when the amount of charge exchanged between ions is relatively small (QEqTS-limit). We then identified two examples, BaTiO₃ with neutral O or Ti vacancies, where the ground state density adheres to these conditions to varying degrees. Consistent with the theoretical analysis, we saw that the less the density corresponds to the QEqTS-limit the less accurate is the QEqTS IP in reproducing the *ab initio* forces and charge density.

Finally, we pointed out in Section 1.4.2 that, although QEq charge transfers are assumed to represent changes in the underlying charge density, this is generally not demonstrated. In particular, we parameterised QEq-based IPs to the DFT potential energy surface, without biasing induced dipole or charge-transfer variables to any particular set of values. In Chapter 6, applying QEqTS to hot defect-free BaTiO₃ we found an arguably counter-intuitive result: Ionic charges predicted by the QEq model tend to be *more* (less) negative when locally the underlying charge density is *less* (more) negative. We used a simple ionic model to demonstrate that this is indeed the cor-

rect QEq solution, in the sense that it correctly reflects changes in the electrostatic potential due to thermal motion of ions. Furthermore, although these variables do not have a clear physical interpretation, they do capture the *effects* of the charge density redistribution on the interatomic forces. We argued that QEq variables modulated the cohesive interaction between the Ti ions and their nearest three O neighbours, reflecting the redistribution of charge density in the upper valence band. Therefore, in general, the observed anti-correlation of the QEq charges with those based on Löwdin or similar definitions should not cause concern. On the other hand, if an IP is developed solely for the use in a defect-free bulk phase, then, in the opinion of the present author, it is best to use a fixed-charge IP – QEq variables result in only a very small improvement in accuracy and, arguably, do not provide more physical insight.

9.2 Future work

We have seen that the changes in the charge density in the hot bulk BaTiO₃ and near the neutral O and Ti vacancies correspond to, to put it simply, negligible, moderate and significant interionic charge transfers, respectively. Consequently, this helped us rationalise why the QEq model improves accuracy in some systems but not others. However, it is desirable to generalise and find a simple set of rules, if possible, that allow one to *anticipate* the effect of the QEq model on accuracy and transferability for a given system, *before* actually applying a QEq-based IP. Such simple rules could be based on considering whether the system is closed-shell or open-shell; for a neutral vacancy whether the “missing” atom is an electron acceptor or a donor, etc. It may seem, at first sight, that the main difference between the bulk system of Chapter 6 and those with a vacancy in Chapter 7 is the fact that the latter have a reduced coordination number which dramatically modifies the local electrostatic potential. However, the former and the latter correspond to closed-shell and open-shell systems, respectively – this distinction may be of greater relevance. In particular, J. Sarsam had applied the QEqTS IP to a series of charged vacancies and interstitials in MgO and found that the QEqTS predicted negligible charge transfers and numerically reduced to the TS IP. However, all the systems she had considered are closed-shell. The estimates based on the available electron density difference plots for V_{Mg}^{2-} and V_{O}^{2+} [124], for example, indicate that the ionic charges near the vacancy are essentially the same as in the bulk. On the other hand, F. Gu [187], a PhD student at Imperial College London, found that applying QEqTS to photoexcited bulk BaTiO₃ offers a marked increase in accuracy relative to TS IP, on the order of

$\sim 4 - 5\%$, from $\sim 16\%$ to $\sim 11 - 12\%$. In her work, the ionic positions are subjected to the same thermal perturbations as those considered in Chapter 6. Therefore, her results suggest that the cause for the inhibited inter-ionic charge transfers, observed in Chapter 6, is the insulating property[198, 199] of the ground state density itself rather than the relatively weak perturbation of the electrostatic potential. Thus, it would be interesting to carry out a similar analysis to that presented in Chapters 6 and 7 but applied to the photoexcited bulk BaTiO_3 as well as to charged vacancies V_{Ba}^{2-} , V_{Ti}^{4-} and V_{O}^{2+} .

It is interesting to use the QEqTS IP in applications, both to address some open scientific questions and as a further test of this model. In particular, the QEqTS IP was shown to adequately represent BaTiO_3 both in the pristine bulk and near a neutral O vacancy – this potentially enables a computer simulation of systems with varying V_{O} concentrations. For example, the O vacancy concentration in BaTiO_{3-x} thin films has been shown to markedly influence its structure and other properties – affecting crystallographic orientation, stability of the tetragonal phase and resulting in an abnormal lattice expansion[200–202]. Thus, firstly, it would be interesting to see if we can reproduce some or all of the observed trends¹. Secondly, in an experimental setting there are numerous competing factors that can influence the observed trends, such as stress resulting from the substrate misfit strain and the presence of other point defects, such as interstitials[200, 202]. In this sense, a computer simulation serves as a complementary study, since some of these factors can be isolated or explicitly controlled. It is worth noting that the experimentally considered system dimensions and the vacancy concentration are accessible in a simulation. T. Zhao *et al.*[200, 201] examined films of thickness in the range 10 – 400 nm ($193 - 7559 a_o$) and vacancy concentration in the range defined by $\sim 0.07 \leq x \leq 0.48$ – this can be represented in a simulation supercell consisting of several thousand atoms. Molecular dynamics simulations and other calculations for this number of atoms can be carried out on a regular desktop computer. Finally, it may be added that, by construction, fixed-charge IPs, especially those that use partial ionic charges, are unable to represent neutral point defects since the charge neutrality cannot be imposed for an arbitrary stoichiometry. Thus, fixed-charge IPs are limited in their ability to study the effects of the neutral vacancy concentration on properties not only due to the relatively poor accuracy, but also due to the inability to impose charge neutrality.

¹Parameterisation of QEqTS and TS IPs to bulk and surfaces simultaneously has not been presented in this thesis, but experience suggests this can be modelled with acceptable accuracy for BaTiO_3 , as long as bulk properties are the main interest of the study. Also, insight can be gained from bulk simulations.

Another potential utility of the QEqTS IP is to aid exploring the trends in structural, vibrational and other properties for perovskites in chemical spaces defined by $A_xB_{1-x}TiO_3$, $PbA_xB_{1-x}O_3$ and similar formulas, where A and B represent cations. For example, this can aid the search for a lead-free material with similar or even superior electromechanical properties to materials based on $PbTiO_3$ [203–205]. D. Corradini *et al.* had parameterised the TS IP simultaneously to SiO_2 and TiO_2 systems, with preliminary results suggesting good accuracy[12]. Similarly, during the course of the present research we have observed good accuracy when fitting QEqTS or TS simultaneously to bulk $BaTiO_3$ and $PbTiO_3$. This is primarily due to the transferability of the TS IP while the QEq model offers a relatively small additional improvement, consistent with the analysis of Chapter 6. Nevertheless, QEqTS allows the A and B cation average charges to be different. Thus, something to explore is whether the QEqTS IP proves to be more accurate and transferable when simultaneously representing two or more perovskite materials in bulk phase.

In Chapter 7, using examples of the neutral O and Ti vacancies, we have suggested that the QEqTS IP functional form is too simple to accurately represent forces in some heterogeneous systems. It is interesting, therefore, to explore ways to modify the QEqTS and/or TS IPs in a way that would allow us to improve its accuracy by modelling density response and its effect on forces more realistically. In particular, during the course of the present work we have implemented an additional force term proportional to an ion’s induced dipole moment, $\mathbf{F}_i^{\text{self}} = c_i \mathbf{p}_i$ for an ion i , where c_i is a parameter and $\mathbf{p}_i$ is the induced dipole moment. The idea is that the ion’s on-site electron cloud “pulls” on the parent nucleus, in analogy to a mass on a spring. The energy of, and the force due to, the mass on a spring are $(1/2)k\Delta x^2$ and $-k\Delta \mathbf{x}$, respectively, where k is the spring constant and Δx is the deviation from the equilibrium spring length. In Chapter 6 a MLWF-based analysis has revealed that the TS dipole variables can be thought to be proportional to the displacement of the ionic on-site electron cloud from the nucleus. The dipole induction energy is $\epsilon_i p_i^2$ in TS and similar PI IPs, and so in analogy to the mass on a spring a “self-force” term $\mathbf{F}_i^{\text{self}}$ would appear to be missing. With the addition of this *ad hoc* term, reparameterising the QEqTS IP to bulk $BaTiO_3$ showed a small improvement in accuracy, on the order of 0.4%². It would be interesting to explore the role of this term in heterogeneous systems such as those with point vacancies or surfaces.

In Chapter 3 we have demonstrated that in general the QEq and PI model self-energy

²The same measure of accuracy is implied as used in Chapter 6.

terms are functions of ionic positions. It is interesting to investigate whether the QEq parameters A_i and D_i are transferable or if they should be replaced with functions of positions, $A_i(\{r_{ij}\})$ and $D_i(\{r_{ij}\})$. In the latter case, finding the appropriate functional form can be the subject of further study.

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Chapter 10

Appendix

10.1 Short-range Coulomb interactions

Some of the analytic results in connection to the evaluation of short-range Coulomb interactions involve lengthy non-trivial derivations. These can be found in the present section.

10.1.1 Derivation of the Thole-type relations

Recall, in Thole's distributed-charge model, the charge-charge, charge-dipole and dipole-dipole coupling tensors satisfy the following relation:

$$t_{ij} = I_0(r_{ij}) \quad (10.1)$$

$$t_{ij}^\alpha = \frac{\partial}{\partial r_{ij}^\alpha} I_0(r_{ij}) \quad (10.2)$$

$$t_{ij}^{\alpha\beta} = \frac{\partial}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} I_0(r_{ij}) \quad (10.3)$$

$$E_{ij}^{\text{ES}} = q_i q_j t_{ij} + (p_i^\alpha q_j - q_i p_j^\alpha) t_{ij}^\alpha - p_i^\alpha p_j^\beta t_{ij}^{\alpha\beta} \quad (10.4)$$

where the summation over the cartesian indices $\{\alpha, \beta\}$ is implied, $I_0(r_{ij})$ represents the Coulomb interaction of two spherically symmetric finite charge distributions, with a limiting behaviour $I_0(r_{ij}) \rightarrow \text{const.}$ as $r_{ij} \rightarrow 0$ and $I_0(r_{ij}) \rightarrow 1/r_{ij}$ for r_{ij} sufficiently large.

These relations are introduced, quote: “to retain the interpretation of $t_{ij}^{\alpha\beta}$ as the dipole-dipole interaction where a dipole is thought to be built up from two infinitesimally shifted monopoles, which in our case won't be point charges” [55]. The equivalence of this physical picture to the above mathematical relations 10.1–10.3 is not obvious. These relations are now explicitly derived for a simple case of *two* distributed charges per ion

Assume two charge distributions ρ_i and ρ_j , each consisting of two spherically symmetric distributions (monopoles), i.e. $\rho_i = \rho_{1,i} + \rho_{2,i}$ and $\rho_j = \rho_{1,j} + \rho_{2,j}$. The two monopoles associated with the same ion are displaced by an infinitesimal distance $\pm\Delta x/2$ from the nucleus along a predefined displacement unit vector; the coordinates of the centers of the monopoles are:

$$\rho_{1,i} \quad \text{at} \quad \mathbf{r}_i - \frac{\Delta x}{2} \underbrace{[\cos \phi_i \sin \theta_i, \sin \phi_i \sin \theta_i, \cos \theta_i]}_{\boldsymbol{\vartheta}_i} \quad (10.5)$$

$$\rho_{2,i} \quad \text{at} \quad \mathbf{r}_i + \frac{\Delta x}{2} \boldsymbol{\vartheta}_i \quad (10.6)$$

$$\rho_{1,j} \quad \text{at} \quad \mathbf{r}_j - \frac{\Delta x}{2} \boldsymbol{\vartheta}_j \quad (10.7)$$

$$\rho_{2,j} \quad \text{at} \quad \mathbf{r}_j + \frac{\Delta x}{2} \boldsymbol{\vartheta}_j \quad (10.8)$$

where ($s \in \{i, j\}$) $\mathbf{r}_s$ and $\boldsymbol{\vartheta}_s$ are the position of the ion s and the unit displacement vector specifying the direction of its dipole moment. Two monopoles on a given site are represented by the same spherically symmetric normalized distribution g_i , centered at different points in space and multiplied by distinct charge factors, e.g. $\rho_{1,i}(\mathbf{r}) = q_{1,i}g_i(\mathbf{r} - (\mathbf{r}_i - \Delta x\boldsymbol{\vartheta}_i/2))$. However, g_i and g_j can be different for the two different ions, e.g. a Gaussian on site i and a Slater-type orbital on site j . The scalar Δx is fixed and is the same for both distributions ρ_i and ρ_j while the direction and magnitude of the dipole moment is controlled by the unit rotation vectors and charges, e.g. dipole at $\mathbf{r}_i$ via $\boldsymbol{\vartheta}_i$, $q_{1,i}$ and $q_{2,i}$. The total charge of an ion is held fixed, $q_{1,i} + q_{2,i} = q_i \equiv \text{const.}$. This type of construction has been used previously[16, 54] and reflects the desired interpretation of a dipole moment as being composed of two infinitesimally displaced monopoles, for example:

$$\mathbf{p}_i = \int \rho_i(\mathbf{r})(\mathbf{r} - \mathbf{r}_i)d\mathbf{r} \quad (10.9)$$

$$= \int \rho_{1,i}(\mathbf{r}_i + \tilde{\mathbf{r}})\tilde{\mathbf{r}}d\tilde{\mathbf{r}} + \int \rho_{2,i}(\mathbf{r}_i + \tilde{\mathbf{r}})\tilde{\mathbf{r}}d\tilde{\mathbf{r}} \quad (10.10)$$

$$= q_{1,i} \int g_i(\tilde{\mathbf{r}} + \Delta x\boldsymbol{\vartheta}_i/2)\tilde{\mathbf{r}}d\tilde{\mathbf{r}} + q_{2,i} \int g_i(\tilde{\mathbf{r}} - \Delta x\boldsymbol{\vartheta}_i/2)\tilde{\mathbf{r}}d\tilde{\mathbf{r}} \quad (10.11)$$

$$= \left(q_{1,i} \frac{-\Delta x}{2} + q_{2,i} \frac{\Delta x}{2} \right) \boldsymbol{\vartheta}_i \quad (10.12)$$

It remains to show that the relations 10.1–10.3 follow from this model – and hence are equivalent to the statement quoted above. The Coulomb interaction energy of charge

distributions ρ_i with ρ_j , for $i \neq j$ is:

$$I(r_{ij}) \equiv \int \int \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (10.13)$$

$$\begin{aligned} &= \int \int \rho_{1,i}(\mathbf{r}) \rho_{1,j}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \int \rho_{1,i}(\mathbf{r}) \rho_{2,j}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &+ \int \int \rho_{2,i}(\mathbf{r}) \rho_{1,j}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \int \rho_{2,i}(\mathbf{r}) \rho_{2,j}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \end{aligned} \quad (10.14)$$

$$\equiv I_{11}(r_{ij}) + I_{12}(r_{ij}) + I_{21}(r_{ij}) + I_{22}(r_{ij}) \quad (10.15)$$

respectively. The evaluation of each integral $I_{st}(r_{ij})$, $s, t \in \{1, 2\}$, proceeds along the same steps, so here we only evaluate explicitly $I_{11}(r_{ij})$:

$$I_{11} = \int \int \frac{\rho_{1,i}(\mathbf{r}) \rho_{1,j}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (10.16)$$

$$= \int \int \frac{\rho_{1,i}(\mathbf{r}_i + \tilde{\mathbf{r}}) \rho_{1,j}(\mathbf{r}_j + \tilde{\mathbf{r}}')}{|\mathbf{r}_i - \mathbf{r}_j + \tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|} d\tilde{\mathbf{r}} d\tilde{\mathbf{r}}' \quad (10.17)$$

$$= q_{1,i} q_{1,j} \int \int \frac{g_i(\tilde{\mathbf{r}}) g_j(\tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} + \Delta\tilde{\mathbf{r}} - (\Delta x/2) \Delta\boldsymbol{\vartheta}_{ij}|} d\tilde{\mathbf{r}} d\tilde{\mathbf{r}}' \quad (10.18)$$

$$I_{11} = I_{11}(\mathbf{r}_{ij}, \Delta x, \Delta\boldsymbol{\vartheta}_{ij}) \quad (10.19)$$

where a change of variables $\mathbf{r} \rightarrow \mathbf{r}_i - (\Delta x/2) \boldsymbol{\vartheta}_i + \tilde{\mathbf{r}}$ and $\mathbf{r}' \rightarrow \mathbf{r}_j - (\Delta x/2) \boldsymbol{\vartheta}_j + \tilde{\mathbf{r}}'$ was made; $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\Delta\tilde{\mathbf{r}} = \tilde{\mathbf{r}} - \tilde{\mathbf{r}}'$ and $\Delta\boldsymbol{\vartheta}_{ij} = \boldsymbol{\vartheta}_i - \boldsymbol{\vartheta}_j$. Notice that the integral I_{11} is a function of $\mathbf{r}_{ij}$, Δx and $\Delta\boldsymbol{\vartheta}_{ij}$ while $\Delta\tilde{\mathbf{r}}$ is a dummy integration variable. We can therefore make a Taylor expansion of I_{11} with respect to Δx about the value $\Delta x = 0$. This approximation is valid for $\Delta x \ll r_{ij}$ and does *not* require the two ions to be non-overlapping, in contrast to the multipole expansion.

Viewing I_{11} as a function of the scalar Δx while keeping $\mathbf{r}_{ij}$ and $\Delta\boldsymbol{\vartheta}_{ij}$ fixed, the Taylor expansion takes the following form:

$$I_{11}(\Delta x) = I_{11}(0) + \Delta x \left. \frac{dI_{11}}{d\Delta x} \right|_{\Delta x=0} + \frac{1}{2} (\Delta x)^2 \left. \frac{d^2 I_{11}}{d\Delta x^2} \right|_{\Delta x=0} + \dots \quad (10.20)$$

$$\left. \frac{dI_{11}}{d\Delta x} \right|_{\Delta x=0} = q_{1,i} q_{1,j} \underbrace{(-(1/2) \Delta\boldsymbol{\vartheta}_{ij}) \cdot \nabla_{\mathbf{r}_{ij}} \int \int \frac{g_i(\tilde{\mathbf{r}}) g_j(\tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} + \Delta\tilde{\mathbf{r}}|} d^3\tilde{r} d^3\tilde{r}'}_{I_0} \quad (10.21)$$

where the chain rule was used to convert the derivative with respect to Δx into a derivative with respect to vector components of $\mathbf{r}_{ij} - (\Delta x/2) \Delta\boldsymbol{\vartheta}$; the final expression of the integral is the same regardless whether $\Delta x = 0$ is set before or after taking the derivative.

Similarly, taking the first derivative of I_{12} , I_{21} and I_{22} gives:

$$\Delta x \frac{d}{d\Delta x} \underbrace{(I_{11} + I_{12} + I_{21} + I_{22})}_{I(r_{ij}) \text{ in eq. 10.13}} \Big|_{\Delta x=0} = \left[\underbrace{\left(-\frac{\Delta x \boldsymbol{\vartheta}_i}{2} q_{1,i} + \frac{\Delta x \boldsymbol{\vartheta}_i}{2} q_{2,i} \right)}_{\mathbf{p}_i} q_{1,j} - \underbrace{\left(-\frac{\Delta x \boldsymbol{\vartheta}_j}{2} q_{1,j} + \frac{\Delta x \boldsymbol{\vartheta}_j}{2} q_{2,j} \right)}_{\mathbf{p}_j} q_{1,i} - \underbrace{\left(-\frac{\Delta x \boldsymbol{\vartheta}_j}{2} q_{1,j} + \frac{\Delta x \boldsymbol{\vartheta}_j}{2} q_{2,j} \right)}_{\mathbf{p}_j} q_{2,j} + \underbrace{\left(-\frac{\Delta x \boldsymbol{\vartheta}_i}{2} q_{1,i} + \frac{\Delta x \boldsymbol{\vartheta}_i}{2} q_{2,i} \right)}_{\mathbf{p}_i} q_{2,j} \right] \cdot \nabla I_0 \quad (10.22)$$

$$= \left[(q_{1,j} + q_{2,j}) \mathbf{p}_i - (q_{1,i} + q_{2,i}) \mathbf{p}_j \right] \cdot \nabla I_0 \quad (10.23)$$

$$= (\mathbf{p}_i q_j - q_i \mathbf{p}_j) \cdot \nabla I_0 \quad (10.24)$$

Carrying out algebraic manipulations for the zeroth and second order terms proceeds along the same lines and gives charge-charge and dipole-dipole interaction terms.

In the distributed-charge model, the integral in equation 10.13 is viewed as a function of interionic distance r_{ij} and the small local displacement Δx which introduces the multipole moments of each ion; the latter allows us to carry out a Taylor expansion about $\Delta x = 0$, resulting in the final form:

$$I_0 = \int \int \frac{g_i(\tilde{\mathbf{r}}) g_j(\tilde{\mathbf{r}}')}{|\mathbf{r}_{ij} + \tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|} d^3 \tilde{r} d^3 \tilde{r}' \quad (10.25)$$

$$I(r_{ij}; \Delta x, \boldsymbol{\vartheta}_i, \boldsymbol{\vartheta}_j) = q_i q_j I_0 + (p_i^\alpha q_j - q_i p_j^\alpha) \frac{\partial}{\partial r_{ij}^\alpha} I_0 - p_i^\alpha p_j^\beta \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} I_0 + \dots \quad (10.26)$$

This is exactly the Thole-type mathematical relations we sought to verify. This expression only depends on $\Delta x/r_{ij}$ being small, which is satisfied for the overlapping ions.

10.1.2 Tang-Toennies damping function from the Slater-type charge density

In Section 2.2.2 we related Tang-Toennies function to the following integral:

$$\tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r}) \equiv \frac{\tilde{\zeta}_{ij}^{\tilde{n}+2}}{4\pi [(\tilde{n}+1)!]} \tilde{r}_1^{\tilde{n}-1} e^{-\tilde{\zeta}_{ij} \tilde{r}_1} \quad (10.27)$$

$$g_i(\mathbf{r}) = \delta(\mathbf{r}) \quad (10.28)$$

$$g_j(\mathbf{r}) = \tilde{\chi}_{\tilde{n}, \tilde{\zeta}_{ij}}(\mathbf{r}) \quad (10.29)$$

$$I_0(\mathbf{r}_{ij}) = \int \frac{g_i(\mathbf{r} - \mathbf{r}_i) g_j(\mathbf{r}' - \mathbf{r}_j)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (10.30)$$

$$f^{\text{TT}}(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}^3} = -w_{ij}^{\text{qp}} \frac{\partial}{\partial r_{ij}^\alpha} \tilde{I}_0(\mathbf{r}_{ij}) \quad (10.31)$$

In the present appendix section we evaluate $I_0(\mathbf{r}_{ij})$. Before evaluating this integral using the Slater-type density, a general result is presented. Consider a spherically symmetric charge distribution ρ located at the origin interacting with a delta function charge distribution located $\mathbf{r}$ away where, without loss of generality (w.l.o.g.), $\mathbf{r}$ is aligned with the z-axis of the reference coordinate system¹.

$$I_0(r) = \int \int \frac{\rho(\tilde{\mathbf{r}}_1) \delta(\tilde{\mathbf{r}}_2 - \mathbf{r})}{|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} d^3 \tilde{r}_1 d^3 \tilde{r}_2 \quad (10.32)$$

$$= \int \frac{\rho(\tilde{\mathbf{r}}_1)}{|\tilde{\mathbf{r}}_1 - \mathbf{r}|} d^3 \tilde{r}_1 \quad (10.33)$$

$$= \int \frac{\rho(\tilde{\mathbf{r}}_1)}{\sqrt{\tilde{\mathbf{r}}_1 \cdot \tilde{\mathbf{r}}_1 + \mathbf{r} \cdot \mathbf{r} - 2\tilde{\mathbf{r}}_1 \cdot \mathbf{r}}} d^3 \tilde{r}_1 \quad (10.34)$$

¹The variable $\mathbf{r}$ is used to make equations more legible, but later this is identified with $\mathbf{r}_{ij}$

Next, we switch to a spherical coordinate system, where $r = |\mathbf{r}|$, ϕ is the angle from the z -axis (traversing 0 to π) and θ is the angle in the x - y plane.

$$I_0(r) = \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{\rho(\tilde{\mathbf{r}}_1)}{\sqrt{\tilde{r}_1^2 + r^2 - 2\tilde{r}_1 r \cos \phi}} \tilde{r}_1^2 \sin \phi d\tilde{r}_1 d\phi d\theta \quad (10.35)$$

$$= 2\pi \int_0^\pi \int_0^\infty \frac{\rho(\tilde{\mathbf{r}}_1)}{\sqrt{2\tilde{r}_1 r}} \frac{1}{\sqrt{\frac{\tilde{r}_1^2 + r^2}{2\tilde{r}_1 r} - \cos \phi}} \tilde{r}_1^2 \sin \phi d\tilde{r}_1 d\phi \quad (10.36)$$

$$= 2\pi \int_0^\infty \frac{\rho(\tilde{\mathbf{r}}_1) \tilde{r}_1^2}{\sqrt{2\tilde{r}_1 r}} \int_{-1}^1 \frac{1}{\sqrt{\frac{\tilde{r}_1^2 + r^2}{2\tilde{r}_1 r} - w}} dw d\tilde{r}_1 \quad (10.37)$$

$$= 2\pi \int_0^\infty \frac{\rho(\mathbf{u}_1) u_1^2}{\sqrt{2u_1 r}} \left[-2\sqrt{\frac{u_1^2 + r^2}{2u_1 r}} - w \right]_{-1}^1 du_1 \quad (10.38)$$

$$= 4\pi \int_0^\infty \frac{\rho(\tilde{\mathbf{r}}_1) \tilde{r}_1^2}{2\tilde{r}_1 r} \left[-\sqrt{(\tilde{r}_1^2 + r^2 - 2\tilde{r}_1 r)} + \sqrt{(\tilde{r}_1^2 + r^2 + 2\tilde{r}_1 r)} \right] d\tilde{r}_1 \quad (10.39)$$

$$= 4\pi \int_0^\infty \frac{\rho(\tilde{\mathbf{r}}_1) \tilde{r}_1^2}{2\tilde{r}_1 r} \left[-\underbrace{\sqrt{(\tilde{r}_1 - r)^2}}_{\geq 0} + \underbrace{\sqrt{(\tilde{r}_1 + r)^2}}_{\geq 0} \right] d\tilde{r}_1 \quad (10.40)$$

$$= 4\pi \left[\int_0^{\tilde{r}} \frac{\rho(\tilde{\mathbf{r}}_1) \tilde{r}_1^2}{2\tilde{r}_1 r} [-(r - \tilde{r}_1) + (\tilde{r}_1 + r)] d\tilde{r}_1 \right. \\ \left. + \int_r^\infty \frac{\rho(\tilde{\mathbf{r}}_1) \tilde{r}_1^2}{2\tilde{r}_1 r} [-(\tilde{r}_1 - r) + (\tilde{r}_1 + r)] d\tilde{r}_1 \right] \quad (10.41)$$

$$= 4\pi \left[\frac{1}{r} \int_0^r \rho(\tilde{r}_1) \tilde{r}_1^2 d\tilde{r}_1 + \int_r^\infty \rho(\tilde{r}_1) \tilde{r}_1 d\tilde{r}_1 \right] \quad (10.42)$$

We can also write a general result for the derivative of $I_0(r)$:

$$\frac{dI_0}{dr} = 4\pi \left[-\frac{1}{r^2} \int_0^r \rho(\tilde{r}) \tilde{r}^2 d\tilde{r} + \frac{1}{r} \rho(r) r^2 - \rho(r) r \right] \quad (10.43)$$

$$= -\frac{1}{r^2} \int_0^r 4\pi \rho(\tilde{r}) \tilde{r}^2 d\tilde{r} \quad (10.44)$$

The last expression is identical to the result in equation (25) in the paper by B. Thole on the distributed-charge model[55].

It is now convenient to substitute the Slater-type charge density expression for $\rho(\mathbf{r})$. Introducing the shorthand notation for the normalisation constant be $\eta_{\tilde{n}} \equiv \tilde{\zeta}_{ij}^{\tilde{n}+2} / (4\pi [(\tilde{n} + 1)!])$ and identifying $r = r_{ij}$, the integral $I_0(r_{ij})$ is cast into the following

form:

$$I_0(r_{ij}) = 4\pi\eta_{\tilde{n}} \left[\frac{1}{r_{ij}} \int_0^{r_{ij}} \tilde{r}_1^{\tilde{n}+1} e^{-\tilde{\zeta}_{ij}\tilde{r}_1} d\tilde{r}_1 + \int_{r_{ij}}^{\infty} \tilde{r}_1^{\tilde{n}} e^{-\tilde{\zeta}_{ij}\tilde{r}_1} d\tilde{r}_1 \right] \quad (10.45)$$

$$= 4\pi\eta_{\tilde{n}} \left[\frac{1}{\tilde{\zeta}_{ij}^{\tilde{n}+2} r_{ij}^2} \int_0^{\tilde{\zeta}_{ij} r_{ij}} w^{\tilde{n}+1} e^{-w} dw + \frac{1}{\tilde{\zeta}_{ij}^{\tilde{n}+1}} \int_{\tilde{\zeta}_{ij} r_{ij}}^{\infty} \tilde{w}^{\tilde{n}} e^{-\tilde{w}} d\tilde{w} \right] \quad (10.46)$$

$$= 4\pi\eta_{\tilde{n}} \left[\frac{1}{\tilde{\zeta}_{ij}^{\tilde{n}+2} r_{ij}^2} \left[\gamma(\tilde{n}+2, \tilde{\zeta}_{ij} r_{ij}) \right] + \frac{1}{\tilde{\zeta}_{ij}^{\tilde{n}+1}} \left[\Gamma(\tilde{n}+1, \tilde{\zeta}_{ij} r_{ij}) \right] \right] \quad (10.47)$$

$$= 4\pi\eta_{\tilde{n}} \left[(\tilde{n}+1)! \left(1 - e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right) + \frac{1}{\tilde{\zeta}_{ij}^{\tilde{n}+1}} \tilde{n}! e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right] \quad (10.48)$$

$$= \left[\frac{1}{r_{ij}} \left(1 - e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right) + \frac{\tilde{\zeta}_{ij}}{\tilde{n}+1} e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right] \quad (10.49)$$

and the derivative:

$$\frac{dI_0}{dr_{ij}} = -\frac{1}{r_{ij}} \int_0^{r_{ij}} 4\pi\eta_{\tilde{n}} \tilde{r}_1^{\tilde{n}+1} e^{-\tilde{\zeta}_{ij}\tilde{r}_1} d\tilde{r}_1 \quad (10.50)$$

$$= -\frac{4\pi\eta_{\tilde{n}}}{\tilde{\zeta}_{ij}^{\tilde{n}+2} r_{ij}^2} \int_0^{\tilde{\zeta}_{ij} r_{ij}} \tilde{r}^{\tilde{n}+1} e^{-\tilde{r}} d\tilde{r} \quad (10.51)$$

$$= -\frac{4\pi\eta_{\tilde{n}}}{\tilde{\zeta}_{ij}^{\tilde{n}+2} r_{ij}^2} \left[\gamma(\tilde{n}+2, u) \right]_{u=0}^{u=\tilde{\zeta}_{ij} r_{ij}} \quad (10.52)$$

$$= -\frac{4\pi\eta_{\tilde{n}}}{\tilde{\zeta}_{ij}^{\tilde{n}+2} r_{ij}^2} (\tilde{n}+1)! \left(1 - e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right) \quad (10.53)$$

$$= -\frac{1}{r_{ij}^2} \left(1 - e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right) \quad (10.54)$$

$$\frac{\partial I_0}{\partial r_{ij}^\alpha} = -\frac{r_{ij}^\alpha}{r_{ij}^3} \left(1 - e^{-\tilde{\zeta}_{ij} r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij} r_{ij})^k}{k!} \right) \quad (10.55)$$

where $\Gamma(n, x) = (n-1)!e^{-x} \sum_{k=0}^{n-1} (x^k/k!)$ and $\gamma(n, x) = (n-1)! [1 - e^{-x} \sum_{k=0}^{n-1} (x^k/k!)]$ are, respectively, the upper and lower Incomplete Gamma Functions[206]. An analogous expression for dI_0/dr_{ij} has been previously obtained by R. Birge *et al.* as an intermediate step in evaluating a dipole-dipole damping function based on Thole's distributed-charge model[137]. One can now trivially relate $\tilde{I}_0$ and w_{ij}^{qp} of Section 2.2.2 to the Tang-Toennies damping function $f^{\text{TT}}(r_{ij})$.

Carrying out similar algebraic manipulations we obtain $\partial^2 I_0 / \partial r_{ij}^\alpha \partial r_{ij}^\beta$. The relevant

expressions have the following forms:

$$I_0(r_{ij}) = \frac{1}{r_{ij}} - \left[e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} - \frac{\tilde{\zeta}_{ij}}{\tilde{n}+1} e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} \right] \quad (10.56)$$

$$\frac{\partial I_0(r_{ij})}{\partial r_{ij}^\alpha} = \frac{\partial}{\partial r_{ij}^\alpha} \frac{1}{r_{ij}} - \left[\frac{-\mathbf{r}_{ij}}{r^3} e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} \right] \quad (10.57)$$

$$\frac{\partial^2 I_0(r_{ij})}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} = \frac{\partial^2}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} \frac{1}{r} - \left[\frac{e^{-\tilde{\zeta}_{ij}r_{ij}} (\tilde{\zeta}_{ij}r_{ij})^{\tilde{n}+2}}{(\tilde{n}+1)! r_{ij}^5} r_{ij}^\alpha r_{ij}^\beta + \frac{3r_{ij}^\alpha r_{ij}^\beta - \delta_{\alpha\beta} r_{ij}^2}{r_{ij}^5} e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} \right] \quad (10.58)$$

and the corresponding correction terms:

$$w_{ij}^{\text{qq}} \tilde{I}_0(r_{ij}) = w_{ij}^{\text{qq}} \left[e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} - \frac{\tilde{\zeta}_{ij}}{\tilde{n}+1} e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} \right] \quad (10.59)$$

$$w_{ij}^{\text{qp}} \frac{\partial \tilde{I}_0(r_{ij})}{\partial r_{ij}^\alpha} = w_{ij}^{\text{qp}} \left[\frac{-\mathbf{r}_{ij}}{r^3} e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} \right] \quad (10.60)$$

$$w_{ij}^{\text{pp}} \frac{\partial^2 \tilde{I}_0(r_{ij})}{\partial r_{ij}^\alpha \partial r_{ij}^\beta} = w_{ij}^{\text{pp}} \left[\frac{e^{-\tilde{\zeta}_{ij}r_{ij}} (\tilde{\zeta}_{ij}r_{ij})^{\tilde{n}+2}}{(\tilde{n}+1)! r_{ij}^5} r_{ij}^\alpha r_{ij}^\beta + \frac{3r_{ij}^\alpha r_{ij}^\beta - \delta_{\alpha\beta} r_{ij}^2}{r_{ij}^5} e^{-\tilde{\zeta}_{ij}r_{ij}} \sum_{k=0}^{\tilde{n}+1} \frac{(\tilde{\zeta}_{ij}r_{ij})^k}{k!} \right] \quad (10.61)$$

10.1.3 Coulomb interaction of two Slater-type ions.

A common convention for writing a Slater-type orbital, also used by Rappe and Goddard[79], with wavefunction $\chi_{n,A}$, normalization N_n and the average radial extent R_A is:

$$\chi_{n,A}(\tilde{\mathbf{r}}) = N_n |\tilde{\mathbf{r}} - \mathbf{r}_A|^{n-1} e^{-\zeta_A |\tilde{\mathbf{r}} - \mathbf{r}_A|}; \quad (10.62)$$

$$N_n = \sqrt{\frac{(2\zeta_A)^{2n+1}}{4\pi(2n)!}}; \quad (10.63)$$

$$R_A \equiv \langle \tilde{r} \rangle = \frac{2n+1}{2\zeta_A} \quad (10.64)$$

The Coulomb interaction of a Slater-type atom A of principal quantum number n at the origin and atom B (m) centered at $\mathbf{r}$ is:

$$I_0(r_{ij}) = N_n^2 N_m^2 \int \int \frac{|\tilde{\mathbf{r}}_1|^{2n-2} e^{-2\zeta_A |\tilde{\mathbf{r}}_1|} |\tilde{\mathbf{r}}_2 - \mathbf{r}|^{2m-2} e^{-2\zeta_B |\tilde{\mathbf{r}}_2 - \mathbf{r}|}}{|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} d^3 \tilde{r}_1 d^3 \tilde{r}_2 \quad (10.65)$$

$$= N_n^2 \int |\tilde{\mathbf{r}}_1|^{2n-2} e^{-2\zeta_A |\tilde{\mathbf{r}}_1|} \underbrace{\left(N_m^2 \int \frac{|\tilde{\mathbf{r}}_2 - \mathbf{r}|^{2m-2} e^{-2\zeta_B |\tilde{\mathbf{r}}_2 - \mathbf{r}|}}{|\tilde{\mathbf{r}}_1 - \tilde{\mathbf{r}}_2|} d^3 \tilde{r}_2 \right)}_{\equiv I} d^3 \tilde{r}_1 \quad (10.66)$$

where I is the electrostatic potential due to charge density B centered at $\mathbf{r}$. Let $\mathbf{r}_2 \equiv \tilde{\mathbf{r}}_2 - \mathbf{r}$, $\mathbf{d} \equiv \tilde{\mathbf{r}}_1 - \mathbf{r}$, so

$$(N_m^2)^{-1}I = \int \frac{|\mathbf{r}_2|^{2m-2} e^{-2\zeta_B |\mathbf{r}_2|}}{|\mathbf{d} - \mathbf{r}_2|} d^3 r_2 \quad (10.67)$$

$$= \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{r_2^{2m} e^{-2\zeta_B r_2}}{\sqrt{d^2 + r_2^2 - 2dr_2 \cos \phi}} \sin \phi d\theta d\phi dr_2 \quad (10.68)$$

$$= 2\pi \left[\int_0^d \frac{r_2^{2m} e^{-2\zeta_B r_2}}{dr_2} (-(d - r_2) + (d + r_2)) dr_2 \right. \\ \left. + \int_d^\infty \frac{r_2^{2m} e^{-2\zeta_B r_2}}{dr_2} (-(r_2 - d) + (d + r_2)) dr_2 \right] \quad (10.69)$$

$$= 4\pi \left[\frac{1}{d} \int_0^d r_2^{2m} e^{-2\zeta_B r_2} dr_2 + \int_d^\infty r_2^{2m-1} e^{-2\zeta_B r_2} dr_2 \right] \quad (10.70)$$

where the z -axis defining the spherical coordinates is taken along $\mathbf{d}$; angle ϕ is measured from the z -axis.

A similar integral has been evaluated in Section 10.1.2 expression 10.35. However, we proceed by evaluating this integral differently, following a spatial integral transform as outlined, e.g. by J. Rico[207]:

$$V(r) = 4\pi \left[\frac{1}{r} \int_0^r dr' r'^2 f(r') + \int_r^\infty dr' r' f(r') \right] \quad (10.71)$$

$$= \frac{4\pi}{r} \int_0^r dr' \bar{f}(r'); \quad (10.72)$$

$$\bar{f}(r') = \int_{r'}^\infty dt f(t) t \quad (10.73)$$

The final analytic expression for $I_0(r_{ij})$ can come in a number of different forms – this spatial transform will allow casting the final expression in a form identical to that used by D. Herzbach[82], thus allowing for comparison.

Setting $f(t) = t^{2m-2}e^{-2\zeta_B t}$ we obtain a more symmetric expression for I :

$$\bar{f}(r_2) = \int_{r_2}^{\infty} dt f(t) t \quad (10.74)$$

$$= \underbrace{\int_{r_2}^{\infty} t^{2m-1} e^{-2\zeta_B t}}_{\Gamma(2m, 2\zeta_B r_2)/(2\zeta_B)^{2m}} \quad (10.75)$$

$$= \frac{(2m-1)!}{(2\zeta_B)^{2m}} e^{-2\zeta_B r_2} \sum_{k=0}^{2m-1} \frac{(2\zeta_B r_2)^k}{k!}; \quad (10.76)$$

$$(N_m^2)^{-1} I = \frac{4\pi}{d} \frac{(2m-1)!}{(2\zeta_B)^{2m}} \sum_{k=0}^{2m-1} \frac{1}{k!} \underbrace{\int_0^d (2\zeta_B r_2)^k e^{-2\zeta_B r_2} dr_2}_{\gamma(k+1, 2\zeta_B d)/2\zeta_B} \quad (10.77)$$

$$= \frac{4\pi}{d} \frac{(2m-1)!}{(2\zeta_B)^{2m+1}} \sum_{k=0}^{2m-1} \frac{k!}{k!} \left(1 - e^{-2\zeta_B d} \sum_{j=0}^k \frac{(2\zeta_B d)^j}{j!} \right) \quad (10.78)$$

$$= \frac{4\pi}{d} \frac{(2m)!}{(2\zeta_B)^{2m+1}} \left[1 - e^{-2\zeta_B d} \sum_{j=1}^{2m} \frac{j(2\zeta_B d)^{2m-j}}{2m(2m-j)!} \right]; \quad (10.79)$$

$$I = \frac{1}{d} \left[1 - e^{-2\zeta_B d} \sum_{j=1}^{2m} \frac{j(2\zeta_B d)^{2m-j}}{2m(2m-j)!} \right] \quad (10.80)$$

Substituting this result back into an expression for $I_0(r_{ij})$ we get:

$$\begin{aligned} I_0(r_{ij}) = N_n^2 & \left[\underbrace{\int \frac{|\tilde{\mathbf{r}}_1|^{2n-2} e^{-2\zeta_A |\tilde{\mathbf{r}}_1|}}{|\tilde{\mathbf{r}}_1 - \mathbf{r}|} d^3 \tilde{r}_1}_{\mathcal{J}_0} \right. \\ & \left. - \sum_{j=1}^{2m} \frac{j(2\zeta_B)^{2m-j}}{2m(2m-j)!} \underbrace{\int \frac{|\tilde{\mathbf{r}}_1|^{2n-2} |\tilde{\mathbf{r}}_1 - \mathbf{r}|^{2m-j} e^{-2\zeta_A |\tilde{\mathbf{r}}_1|} e^{-2\zeta_B |\tilde{\mathbf{r}}_1 - \mathbf{r}|}}{|\tilde{\mathbf{r}}_1 - \mathbf{r}|} d^3 \tilde{r}_1}_{\mathcal{J}_j} \right] \end{aligned} \quad (10.81)$$

where it remains to evaluate $\mathcal{J}_0$ and $\mathcal{J}_j$. Now we switch to a coordinate system referred to as elliptic[208]² or elliptical[209, 210]:

$$|\tilde{\mathbf{r}}_1| = \frac{1}{2} r(\mu + \nu); \quad (10.82)$$

$$|\tilde{\mathbf{r}}_1 - \mathbf{r}| = \frac{1}{2} r(\mu - \nu); \quad (10.83)$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\tilde{x}_1 d\tilde{y}_1 d\tilde{z}_1 = \left(\frac{r}{2}\right)^3 \int_0^{2\pi} \int_{-1}^1 \int_1^{\infty} (\mu^2 - \nu^2) d\mu d\nu d\theta \quad (10.84)$$

The final analytic form of the expression, again, is not unique. Here we proceed so as to

²See, for instance, section G_{XI} in Ref. 208.

reproduce the results of D. Herzbach.

$$\mathcal{J}_0 = 2\pi \left(\frac{r}{2}\right)^3 \int_{-1}^1 \int_1^\infty \left(\frac{r}{2}\right)^{2n-3} (\mu + \nu)^{2n-1} e^{-\zeta_A r(\mu+\nu)} d\mu d\nu \quad (10.85)$$

$$= 2\pi \left(\frac{r}{2}\right)^{2n} \sum_{j=0}^{2n-1} \binom{2n-1}{j} \underbrace{\left(\int_1^\infty \mu^{2n-1-j} e^{-\zeta_A r \mu} d\mu\right)}_{A_{2n-1-j}(\zeta_A r)} \underbrace{\left(\int_{-1}^1 \nu^j e^{-\zeta_A r \nu} d\nu\right)}_{B_j(\zeta_A r)} \quad (10.86)$$

and

$$\begin{aligned} \mathcal{J}_j = 2\pi \left(\frac{r}{2}\right)^{2n+2m-j} \sum_{k=0}^{2n-1} \sum_{l=0}^{2m-j} \binom{2n-1}{k} \binom{2m-j}{l} (-1)^l \\ \underbrace{\left(\int_{-1}^1 \nu^{k+l} e^{-r\nu(\zeta_A - \zeta_B)} d\nu\right)}_{B_{k+l}(r(\zeta_A - \zeta_B))} \underbrace{\left(\int_1^\infty \mu^{2n+2m-k-l-j-1} e^{-r\mu(\zeta_A + \zeta_B)} d\mu\right)}_{A_{2n+2m-k-l-j-1}(r(\zeta_A + \zeta_B))} \end{aligned} \quad (10.87)$$

The auxiliary function $B_j(x)$ is the main reason for evaluating this Coulomb integral in real space. No matter what method is used to evaluate the integral, the final analytic expression is singular with negative powers of x resulting in a highly numerically unstable result as $r \rightarrow 0$ or $\zeta_A \rightarrow \zeta_B$. As a result, the final exact analytic expression is simply not usable for any practical implementation. When evaluated in real space, the singularity is conveniently isolated in the term $B_j(x)$ which can be handled by replacing the exponential in the integrand by a truncated series representation[82]:

$$B_s(x) \approx \sum_{p=0}^{p_{\text{cut}}} \frac{1 - (-1)^{s+p+1}}{(s+p+1)p!} (-x)^p \quad (10.88)$$

where p_{cut} is some positive integer for which the summation converges in the relevant finite range of the argument $x = r(\zeta_A - \zeta_B)$ and $x = \zeta_A r$; for an arbitrarily large argument $p_{\text{cut}} \rightarrow \infty$. In practice I found that $p_{\text{cut}} < 60 - 80$ if implemented as is but $p_{\text{cut}} < 15$ once the expression is rearranged as in subSection 10.1.3.

The auxiliary function $A_s(x)$ is

$$A_s(x) = e^{-x} \frac{s!}{x^{s+1}} \sum_{p=0}^s \frac{x^p}{p!} \quad (10.89)$$

Analytic form suitable for implementation in a computer code.

When implementing a finite-size effect on Coulomb interaction of charged ions, in practice, one wishes to have a scaling function $\tilde{I}_0(r_{ij})$ such that:

$$I_0(r_{ij}) = \frac{1}{r} + (-1) \cdot \tilde{I}_0(r_{ij}); \quad (10.90)$$

For this reason, $N_n^2 \mathcal{J}_0$ can be rewritten as:

$$N_n^2 \mathcal{J}_0 = \frac{1}{r} - \left[\frac{e^{-2\zeta_A r}}{r} \sum_{k=0}^{2n} \frac{(2\zeta_A r)^k}{k!} - \frac{\zeta_A e^{-2\zeta_A r}}{n} \sum_{k=0}^{2n-1} \frac{(2\zeta_A r)^k}{k!} \right] \quad (10.91)$$

$$= \frac{1}{r} - \frac{e^{-2\zeta_A r}}{r} \sum_{j=1}^{2n} \frac{j(2\zeta_A r)^{2n-j}}{2n(2n-j)!} \quad (10.92)$$

casting the expression for $\phi_{n,m}^{SS}$ into the following form:

$$I_0(r_{ij}) = \frac{1}{r} - \left[\frac{e^{-2\zeta_A r}}{r} \sum_{j=1}^{2n} \frac{j(2\zeta_A r)^{2n-j}}{2n(2n-j)!} + N_n^2 \sum_{j=1}^{2m} \frac{j(2\zeta_B)^{2m-j}}{2m(2m-j)!} \mathcal{J}_j \right] \quad (10.93)$$

$$= \frac{1}{r} - \left[\frac{e^{-2\zeta_A r}}{r} \sum_{j=1}^{2n} \frac{j(2\zeta_A r)^{2n-j}}{2n(2n-j)!} + \frac{\zeta_A (\zeta_A r)^{2n}}{2m(2n)!} \sum_{j=1}^{2m} \frac{j(\zeta_B r)^{2m-j}}{(2m-j)!} \sum_{k=0}^{2n-1} \sum_{l=0}^{2m-j} \binom{2n-1}{k} \binom{2m-j}{l} (-1)^l \right. \\ \left. B_{k+l}(r(\zeta_A - \zeta_B)) A_{2n+2m-k-l-j-1}(r(\zeta_A + \zeta_B)) \right] \quad (10.94)$$

where $\tilde{I}_0(r_{ij})$ is implicitly defined by the expression in the big square brackets. Next, we'll be needing the first and second mixed derivatives for the scaling of charge-dipole and dipole-dipole Coulomb interactions following Thole-type construction. What's more, obtaining forces and stress-components due to dipole-dipole interaction requires a third order mixed derivative of $\tilde{I}_0(r_{ij})$. Writing $\tilde{I}_0(r_{ij})$ as:

$$\tilde{I}_0(r_{ij}, \lambda) = \left[\frac{e^{-2\zeta_A r}}{r} \sum_{j=1}^{2n} \frac{j(2\zeta_A r)^{2n-j}}{2n(2n-j)!} + \lambda N_n^2 \sum_{j=1}^{2m} \frac{j(2\zeta_B)^{2m-j}}{2m(2m-j)!} \mathcal{J}_j \right] \quad (10.95)$$

$$\equiv \left[\frac{e^{-2\zeta_A r}}{r} \sum_{j=1}^{2n} \frac{j(2\zeta_A r)^{2n-j}}{2n(2n-j)!} + \lambda \tilde{\phi} \right] \quad (10.96)$$

we see that for $\lambda = 0$ we recover the Birge-type scaling that represents a Slater-type orbital at the origin interacting with a Dirac-delta point particle a distance r away. Thus $\tilde{I}_0(r_{ij}, \lambda = 0)$ expression is already available from Section 10.1.2 and what we need are the mixed partial derivatives of the implicitly defined $\tilde{\phi}$. Recall:

$$\frac{\partial}{\partial r^\alpha} \tilde{\phi}(r) = \frac{r^\alpha}{r} \frac{d\tilde{\phi}}{dr} \quad (10.97)$$

hence we construct the desired mixed derivatives in terms of the single derivatives d/dr :

$$\frac{\partial \tilde{\phi}}{\partial r^\alpha} = \frac{r^\alpha}{r} \frac{d\tilde{\phi}}{dr} \quad (10.98)$$

$$\frac{\partial^2 \tilde{\phi}}{\partial r^\alpha \partial r^\beta} = \frac{\delta^{\alpha\beta}}{r} \frac{d\tilde{\phi}}{dr} - \frac{r^\alpha r^\beta}{r^3} \left(\frac{d\tilde{\phi}}{dr} - r \frac{d^2 \tilde{\phi}}{dr^2} \right) \quad (10.99)$$

$$\begin{aligned} \frac{\partial^3 \tilde{\phi}}{\partial r^\alpha \partial r^\beta \partial r^\gamma} = & - \frac{(\delta^{\alpha\beta} r^\gamma + \delta^{\beta\gamma} r^\alpha + \delta^{\gamma\alpha} r^\beta)}{r^3} \left(\frac{d\tilde{\phi}}{dr} - r \frac{d^2 \tilde{\phi}}{dr^2} \right) \\ & + \frac{r^\alpha r^\beta r^\gamma}{r^5} \left[3 \left(\frac{d\tilde{\phi}}{dr} - r \frac{d^2 \tilde{\phi}}{dr^2} \right) + r^2 \frac{d^3 \tilde{\phi}}{dr^3} \right] \end{aligned} \quad (10.100)$$

This can then be evaluated, in practice, if $\tilde{\phi}$ is written as a product of a polynomial with monotonically increasing power of r and an exponential:

$$\tilde{\phi} \equiv C_0^{(n,m)} e^{-(\zeta_A + \zeta_B)r} P(r); \quad (10.101)$$

$$\frac{d\tilde{\phi}}{dr} = C_0^{(n,m)} e^{-(\zeta_A + \zeta_B)r} [-(\zeta_A + \zeta_B)P + P'] \quad (10.102)$$

$$\frac{d^2 \tilde{\phi}}{dr^2} = C_0^{(n,m)} e^{-(\zeta_A + \zeta_B)r} [(\zeta_A + \zeta_B)^2 P - 2(\zeta_A + \zeta_B)P' + P''] \quad (10.103)$$

$$\frac{d^3 \tilde{\phi}}{dr^3} = C_0^{(n,m)} e^{-(\zeta_A + \zeta_B)r} [-(\zeta_A + \zeta_B)^3 P + 3(\zeta_A + \zeta_B)^2 P' - 3(\zeta_A + \zeta_B)P'' + P'''] \quad (10.104)$$

The polynomial $P(r)$ can be obtained by rearranging the expression to “pull out” the r outside of the nested inner summations.

$$C_0^{(n,m)} \equiv \frac{\zeta_A^{2n+1}}{2m(2n)!(\zeta_A + \zeta_B)^{2m+2n}}; \quad (10.105)$$

$$\tilde{C}_p \equiv \frac{(\zeta_A + \zeta_B)^p}{p!}, \quad (10.106)$$

$$C_{p'}^{(k,l)} \equiv \frac{1 - (-1)^{k+l+p'+1}}{(k+l+p'+1)p'!} [-(\zeta_A - \zeta_B)]^{p'}; \quad (10.107)$$

$$G_p^{(k,l;j)} \equiv \sum_{p'=\underline{p}'}^{\bar{p}'} \tilde{C}_{p-p'} C_{p'}^{(k,l)} \quad (10.108)$$

with $\underline{p}'(p, k, l, j) \equiv \text{Max}[0, p - (2n + 2m - k - l - j - 1)]$ and $\bar{p}'(p) \equiv \text{Min}[p, p'_{\text{cut}}]$;

$$D_l^{(k,j)} \equiv \binom{2m-j}{l} (-1)^l (\zeta_A + \zeta_B)^l (2n + 2m - k - l - j - 1)! \quad (10.109)$$

$$T_s^{(k,j)} \equiv \sum_{l=0}^{\bar{l}} D_l^{(k,j)} G_{s-l}^{(k,l;j)} \quad (10.110)$$

with $\bar{l}(s, j) = \text{Min}[s, 2m - j]$;

$$O_k \equiv \binom{2n-1}{k} (\zeta_A + \zeta_B)^k; \quad (10.111)$$

$$V_q^{(j)} \equiv \sum_{k=0}^{\bar{k}} O_k T_{q-k}^{(k,j)} \quad (10.112)$$

with $\bar{k}(q) = \text{Min}[q, 2n - 1]$;

$$B_j \equiv \frac{j \zeta_B^{2m-j} (\zeta_A + \zeta_B)^j}{(2m-j)!} \quad (10.113)$$

$$W_q \equiv \sum_{j=1}^{\bar{j}} B_j V_q^{(j)} \quad (10.114)$$

with $\bar{j}(q) = \text{Min}[2m, 2m + 2n + p'_{cut} - 1 - q]$. This gives the final expression:

$$P(r) = \sum_{q=0}^{\bar{q}} r^q W_q \quad (10.115)$$

$$= \sum_{q=0}^{\bar{q}} r^q \left(\sum_{j=1}^{\bar{j}(q)} B_j V_q^{(j)} \right) \quad (10.116)$$

$$= \sum_{q=0}^{\bar{q}} r^q \left(\sum_{j=1}^{\bar{j}(q)} \frac{j \zeta_B^{2m-j} (\zeta_A + \zeta_B)^j}{(2m-j)!} \left[\sum_{k=0}^{\bar{k}(q)} O_k T_{q-k}^{(k,j)} \right] \right) \quad (10.117)$$

$$= \sum_{q=0}^{\bar{q}} r^q \left(\sum_{j=1}^{\bar{j}(q)} \frac{j \zeta_B^{2m-j} (\zeta_A + \zeta_B)^j}{(2m-j)!} \left[\sum_{k=0}^{\bar{k}(q)} \binom{2n-1}{k} (\zeta_A + \zeta_B)^k \left\{ \sum_{l=0}^{\bar{l}(q-k,j)} D_l^{(k,j)} G_{q-k-l}^{(k,l;j)} \right\} \right] \right) \quad (10.118)$$

$$= \sum_{q=0}^{\bar{q}} r^q \left(\sum_{j=1}^{\bar{j}(q)} \frac{j \zeta_B^{2m-j} (\zeta_A + \zeta_B)^j}{(2m-j)!} \left[\sum_{k=0}^{\bar{k}(q)} \binom{2n-1}{k} (\zeta_A + \zeta_B)^k \left\{ \sum_{l=0}^{\bar{l}(q-k,j)} \left(\binom{2m-j}{l} (-1)^l (\zeta_A + \zeta_B)^l (2n + 2m - k - l - j - 1)! \sum_{\substack{\bar{p}'(q-k-l) \\ p'=\underline{p}'(q-k-l,k,l,j)}} \tilde{C}_{q-k-l-p'} C_{p'}^{(k,l)} \right) \right\} \right] \right) \quad (10.119)$$

$$= \sum_{q=0}^{\bar{q}} r^q \left(\sum_{j=1}^{\bar{j}(q)} \frac{j \zeta_B^{2m-j} (\zeta_A + \zeta_B)^j}{(2m-j)!} \left[\sum_{k=0}^{\bar{k}(q)} \binom{2n-1}{k} (\zeta_A + \zeta_B)^k \left\{ \sum_{l=0}^{\bar{l}(q-k)} \left(\binom{2m-j}{l} (-1)^l (\zeta_A + \zeta_B)^l (2n + 2m - k - l - j - 1)! \sum_{\substack{\bar{p}'(q-k-l) \\ p'=\underline{p}'(j)}} \frac{(\zeta_A + \zeta_B)^{q-k-l-p'}}{(q-k-l-p')!} \frac{1 - (-1)^{k+l+p'+1}}{(k+l+p'+1)p'!} [-(\zeta_A - \zeta_B)]^{p'} \right) \right\} \right] \right) \quad (10.120)$$

with $\bar{q} = 2n + 2m + p'_{cut} - 2$, which defines the degree of the polynomial. For $n, m \leq 4$ I found that $p'_{cut} \leq 10$ ensures convergence; thus in practice one can expect a polynomial of order ~ 20 or less. Higher n and m require increasing p'_{cut} . Note that $\underline{p}'(q-k-l, k, l, j) \equiv \underline{p}''(j) = \text{Max}[0, q - (2n + 2m - j - 1)]$.

10.2 DFT convergence tests

First, convergence tests with respect to cutoff energy are presented in figure 10.1. Three bulk BaTiO₃ configurations were taken from NPH simulation at 300 K and -0.8 GPa to reflect the actual data used in parametrisation of classical IPs and to have non-negligible stress components. Only representative results are plotted in the figure 10.1 in the left column, using configurations $I = 1$ and $J = 2$ in the top subfigure, configuration $I = 1$ and single Ba, Ti and O atom in the middle subfigure and configuration $I = 1$ in the bottom subfigure. In the right column subfigures, quantities representative of the cost function used in parameterisation are plotted. For the energy, forces and stress tensor, measures of error $\Delta_{\text{rms}}(E)$, $\Delta_{\text{rms}}(F)$ and $\Delta_{\text{rms}}(S)$, respectively, were calculated as follows:

$$\Delta_{\text{rms}}(E) \equiv \frac{\sqrt{\sum_I \sum_{J \neq I} ((E_I - E_J) - (E_I^{\text{ref}} - E_J^{\text{ref}}))^2}}{\sqrt{\sum_I \sum_{J \neq I} ((E_I^{\text{ref}} - E_J^{\text{ref}}))^2}} \quad (10.121)$$

$$\Delta_{\text{rms}}(F) \equiv \frac{\sqrt{\sum_I \sum_{i=1}^N \sum_{\alpha} (F_{I,i}^{\alpha} - F_{I,i}^{\alpha,\text{ref}})^2}}{\sqrt{\sum_I \sum_{i=1}^N \sum_{\alpha} (F_{I,i}^{\alpha,\text{ref}})^2}} \quad (10.122)$$

$$\Delta_{\text{rms}}(S) \equiv \frac{\sqrt{\sum_I \sum_{\alpha, \beta \geq \alpha} (S_I^{\alpha\beta} - S_I^{\alpha\beta,\text{ref}})^2}}{\sqrt{\sum_I \sum_{\alpha, \beta \geq \alpha} (S_I^{\alpha\beta,\text{ref}})^2}} \quad (10.123)$$

where I is the atomic configuration index, i enumerates atoms and $\alpha, \beta \in \{x, y, z\}$. Next, an equivalent set of plots is presented, but now the reciprocal space grid density is being varied. A uniform $n \times n \times n$ Monkhorst-Pack grid was used in all DFT calculations, and results are presented at each positive integer n . Figure 10.2 is analogous to figure 10.1, with quantities plotted in the subfigures on the left and right defined in the same way.

The results indicate that at $E_{\text{cut}} = 60\text{Ry}$, the error in energy differences, forces and stress tensor are within 0.001%, 0.1% and 0.1% respectively. These errors are acceptable with respect to the error in the overall fit quality of classical potentials – the cost function is mostly determined by the fit to forces and the best fit obtained³ agrees with the reference data only within an error of $\sim 14.0\%$. The smallest difference in the fit amongst different potentials⁴ is on the order of 0.7% – this is still large enough so as not to get ascribed to numerical noise.

Following the convergence tests, the cut-off energy was set to $E_{\text{cut}} = 60\text{Ry}$ since the most relevant quantity, an error in forces, approaches precision of 1meV and 0.1% error.

³The best fit is obtained when QEqTS IP is applied to bulk BaTiO₃ in Chapter 6.

⁴The smallest difference in the fit is that of QEqTS and TS IPs applied to bulk BaTiO₃ in Chapter 6.

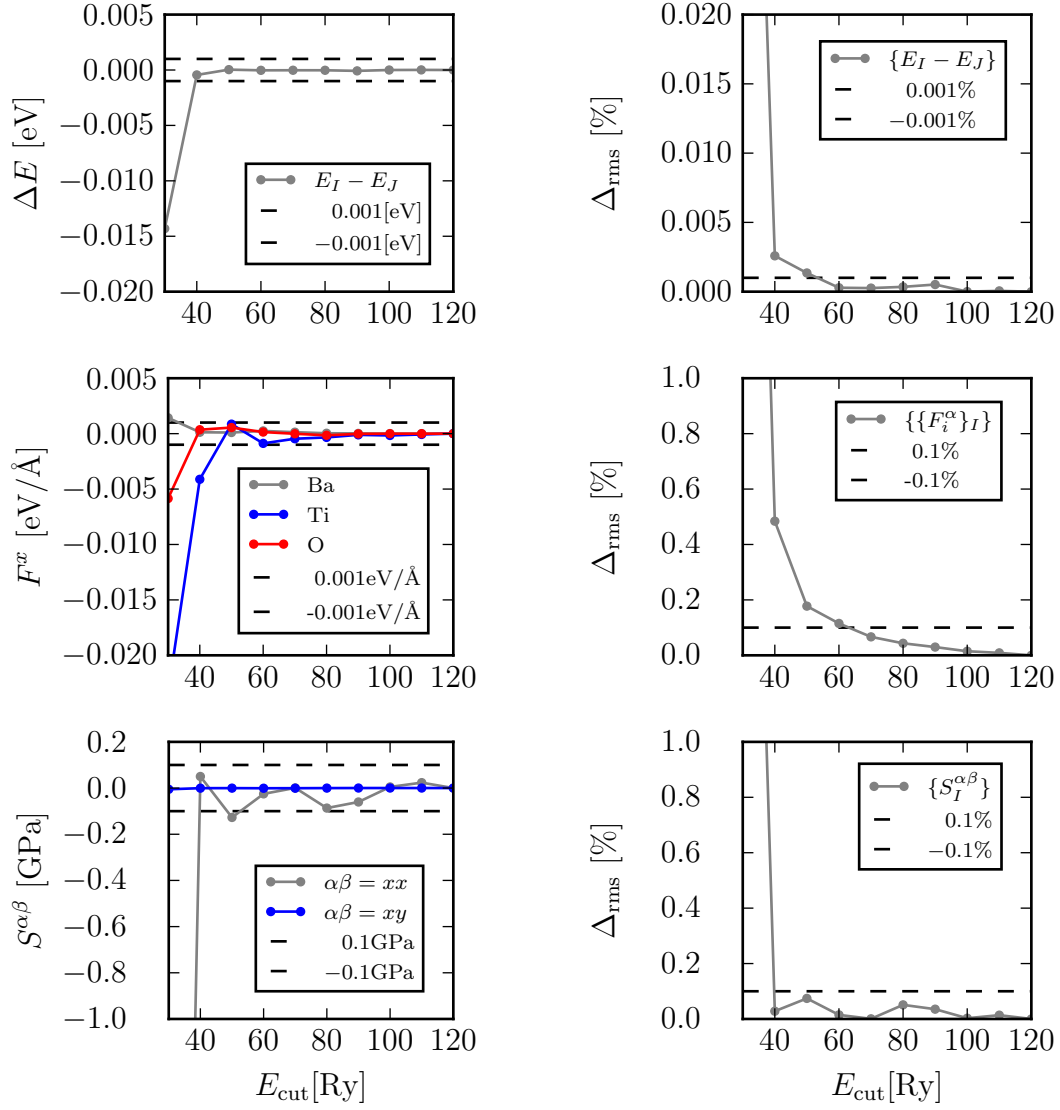


Figure 10.1: Convergence with respect to energy cut-off parameter, E_{cut} . Top to bottom, left: energy difference, force on selected atom, stress components, respectively, relative to values at $E_{\text{cut}} = 120$ Ry; right: error in energy differences, forces and stress tensor as defined in equation 10.121. 40 atom $2 \times 2 \times 2$ supercell and $6 \times 6 \times 6$ Monkhorst-Pack grid were used, configurations taken from NPT simulation at $T = 300$ K and $P = -0.8$ GPa.

Monkhorst-Pack grid density was set to $6 \times 6 \times 6$. The $6 \times 6 \times 6$ grid in the convergence tests corresponds to $4 \times 4 \times 4$ grid for a $3 \times 3 \times 3$ supercell that was actually used when generating reference data for parameterisation and analysis.

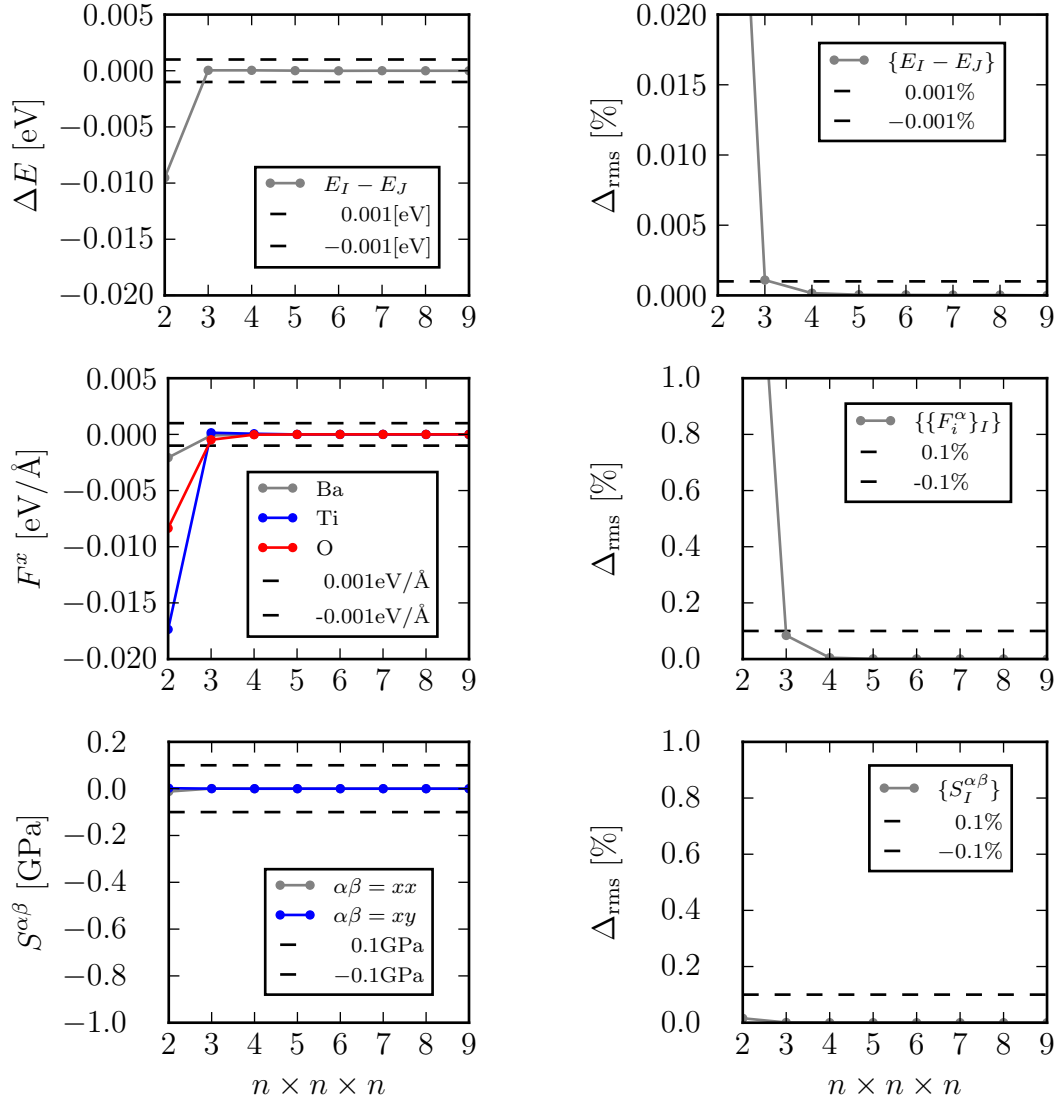


Figure 10.2: Convergence with respect to reciprocal space $n \times n \times n$ Monkhorst-Pack grid density. Top to bottom, left: energy difference, force component for the selected atom, stress components, respectively, relative to values at $n = 9$; right: error in energy differences, forces and stress tensor as defined in equation 10.121. 40 atom $2 \times 2 \times 2$ supercell was used, configurations were taken from NPH simulation at $T = 300$ K and $P = -0.8$ GPa.

10.3 Wannierization convergence tests

In Section 6 Maximally Localised Wannier Functions are used to facilitate the analysis of QEqTS model applied thermally perturbed bulk BaTiO_3 . MLWF-based quantities used in analysis include dipole moments, defined in Eq. 6.14 which depend on the centers of the MLWFs. Another quantity used in the analysis is the centre-of-charge of TiO_6 units, but this quantity is defined in terms of dipole moments and hence does not

need to be checked for convergence separately. Figure 10.3 shows the convergence *vs.* reciprocal space mesh used, defined via Monkhorst-Pack grid $n \times n \times n$. Convergence is very rapid in general. The spike at $n = 7$ corresponds to Wannierization algorithm being stuck in a local minimum where several MLWF quadratic spreads grow exceeding several tens of Å. This can in principle be fixed by varying the step parameter used in the search algorithm, but in fact it is a sign of overly high density of the grid. The test is based on a $2 \times 2 \times 2$ system at 300 K while final calculations used in analysis are $3 \times 3 \times 3$, with k-mesh of $4 \times 4 \times 4$. So k-mesh of $6 \times 6 \times 6$ in $2 \times 2 \times 2$ system maps onto k-mesh of $4 \times 4 \times 4$ in $3 \times 3 \times 3$ system. It is clear that this mesh density is sufficiently high. Figure 10.4 compares the same quantity, but taken from $3 \times 3 \times 3$

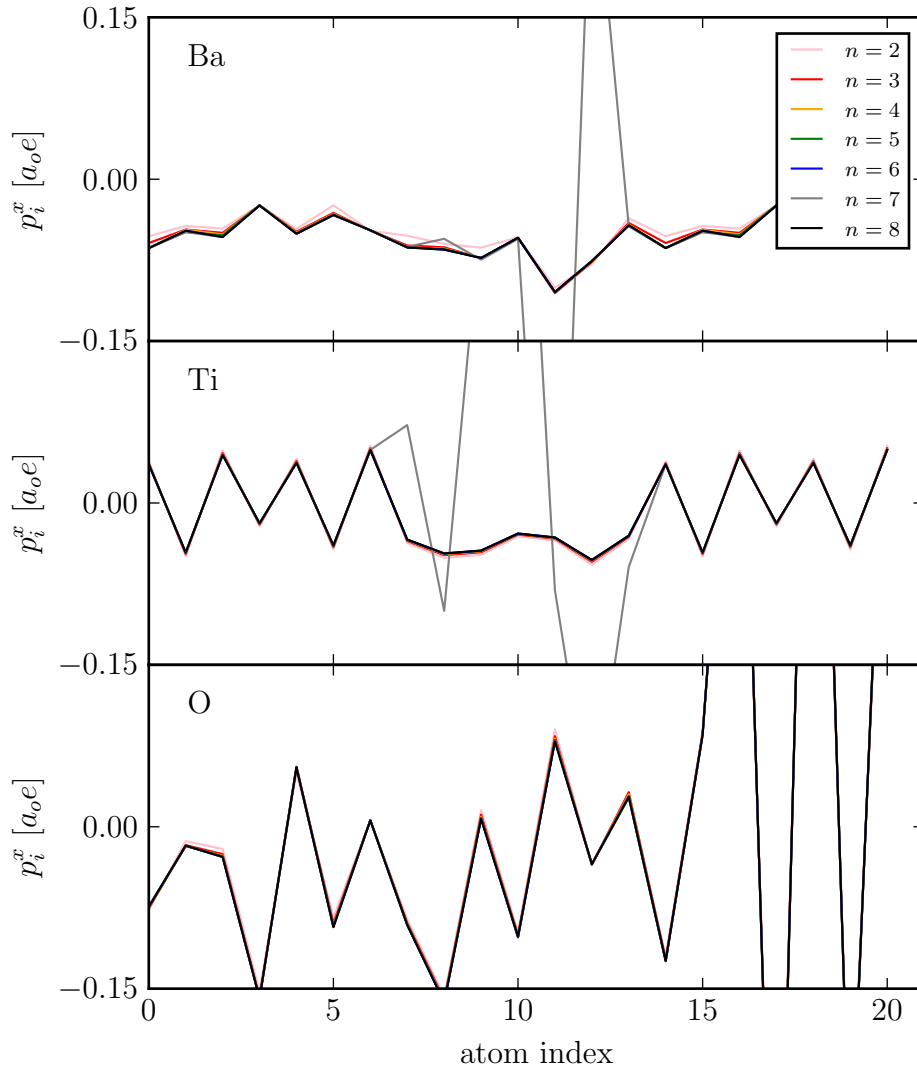


Figure 10.3: Convergence tests with respect to k-mesh density, using a $2 \times 2 \times 2$ BaTiO₃ supercell (see text).

system and k-mesh $4 \times 4 \times 4$ and $5 \times 5 \times 5$; structures used for comparison are 1, 2 and

10 ps snapshot configurations taken from a NPH simulation at 300 K and zero pressure. Again, clearly k-mesh $4 \times 4 \times 4$ is sufficiently dense. Finally, Wannierization algorithm

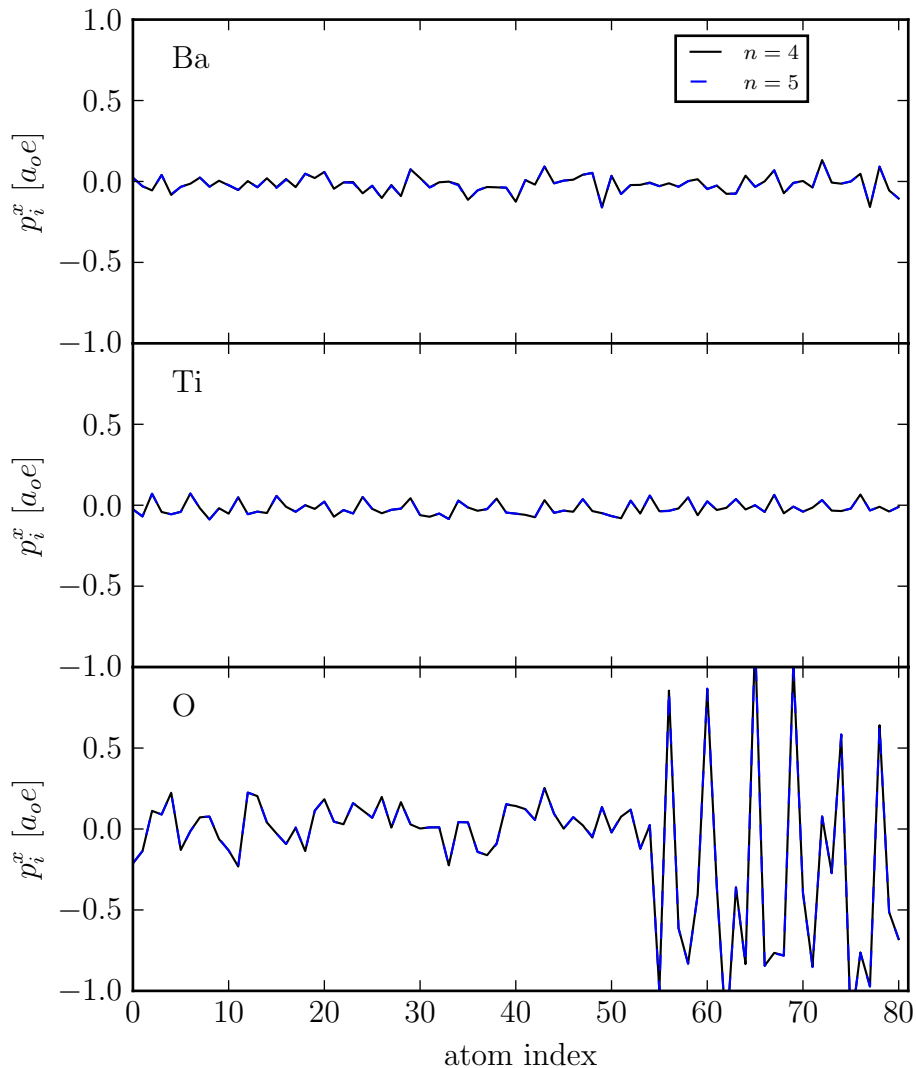


Figure 10.4: Convergence tests with respect to k-mesh density, using a $3 \times 3 \times 3$ BaTiO₃ supercell (see text).

does not converge in general and in practice it is manually terminated after a finite number of steps. Figure 10.5 shows the convergence of dipole moments *vs.* iteration number *i*. It is clear from the figure that terminating Wannierization after 200 steps the results obtained are sufficiently converged. The calculations in Chapter 6 are based on $3 \times 3 \times 3$ systems with k-mesh $4 \times 4 \times 4$ and Wannierization terminated after 1000 steps.

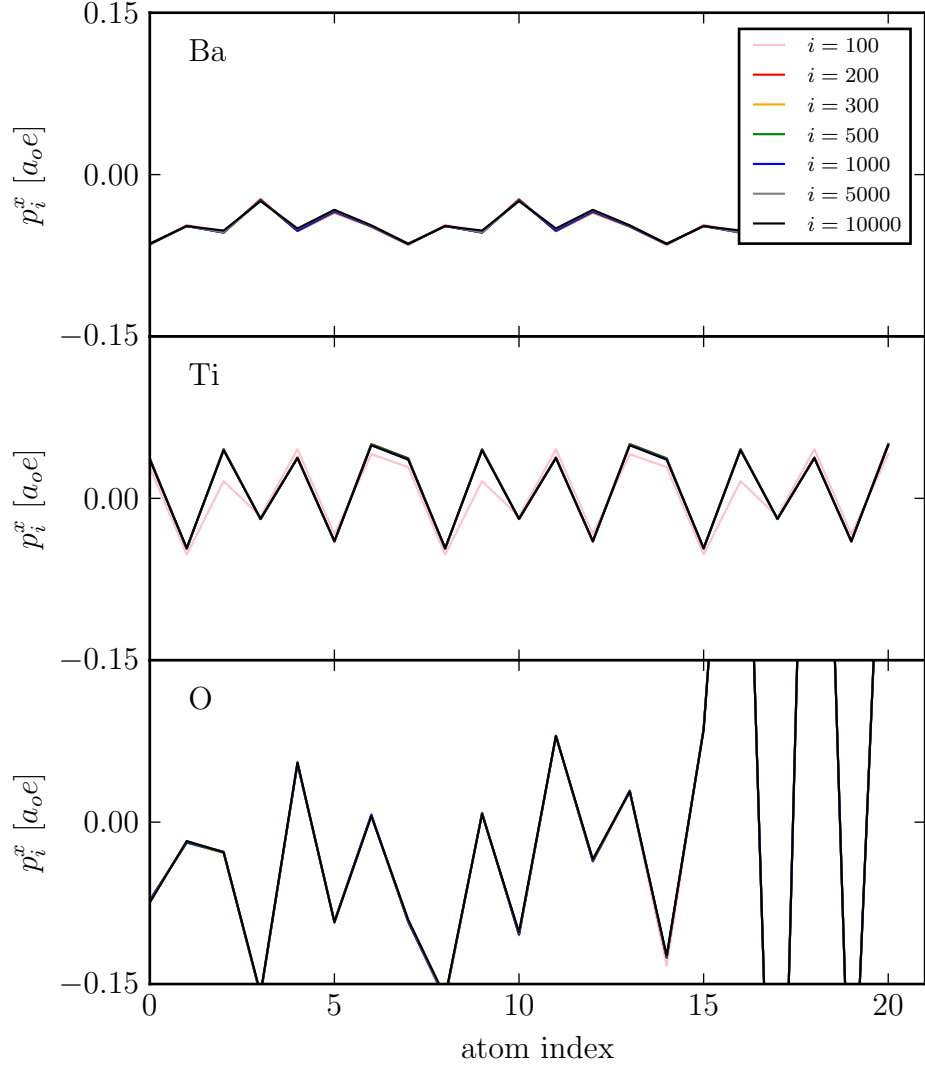


Figure 10.5: Convergence tests with respect to number of iterative steps during Wannierization (see text).

10.4 Interatomic potential parameter sets

Parameters are in atomic units. The parameter ϵ_i for the dipole induction energy, $\epsilon_i p_i^2$, is expressed in terms of polarisability $\alpha_i = 1/(2\epsilon_i)$. The parameters w_{ij}^{qq} , w_{ij}^{qp} and w_{ij}^{pp} are expressed as $w_{\text{qq}}c_{ij}$, $w_{\text{qp}}c_{ij}$ and $w_{\text{pp}}c_{ij}$, respectively. Parameter values of 0 indicate that during parameterisation a value of zero was numerically approached, i.e. the ability to reproduce *ab initio* data was independent of those particular parameters.

[a.u.]	$w_{\text{qq}} = -0.28678047$	$w_{\text{qp}} = 0.89290873$	$w_{\text{pp}} = 0.58327476$
	O	Ti	Ba
A_i	1.4781178918×10^7	1.0654713573×10^5	$5.1274280051 \times 10^{10}$
D_i	1.7392984917×10^8	$5.6433155657 \times 10^{-1}$	$9.9589996105 \times 10^{14}$
q_i^0	-1.265110	2.530218	1.265110
α_i	3.708333	7.279149	8.390608
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.3121455930×10^0	4.3483577921×10^0	0
c_{ij}	2.0002302924×10^0	$-3.8656000345 \times 10^1$	0
r_{ij}^0	1.3260517031×10^1	4.9113653624×10^0	5.3510541903×10^0
γ_{ij}	1.8751405177×10^1	1.0652870209×10^1	8.8824972483×10^0
D_{ij}	$1.4996398739 \times 10^{-7}$	$3.9562967096 \times 10^{-3}$	$1.3097658575 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	1.4288073624×10^0	0
c_{ij}	0	$-2.0089429803 \times 10^0$	0
r_{ij}^0	1.0144933551×10^1	1.4222692220×10^1	1.2290512274×10^1
γ_{ij}	2.0786436909×10^1	8.1759576709×10^0	6.9747710696×10^0
D_{ij}	$-1.4207535212 \times 10^{-5}$	$2.6897796120 \times 10^{-4}$	$1.0845409487 \times 10^{-3}$

Table 10.1: Parameter set for the QEqTS IP introduced in Chapter 6, also referred to as QEqTS(Ti).

Morse term and short-range electrostatic terms⁵ were evaluated between pairs of ions within a cut-off distance. This cut-off distance was set to 20.0 a_o . Cut-off distances for

⁵Recall, the terms $\tilde{I}_0(r_{ij})$, $\partial\tilde{I}_0(r_{ij})/\partial r_{ij}^\alpha$ and $\partial^2\tilde{I}_0(r_{ij})/\partial r_{ij}^\alpha\partial r_{ij}^\beta$ discussed in Chapter 2.

the Ewald summation in the real and reciprocal space were set to $25.0 a_o$ and $1.1 a_o^{-1}$, respectively, optimised for speed following convergence tests. The Ewald exponent was set to $4.5 a_o$. All IPs used the same cut-off distances.

[a.u.]	$w_{\text{qq}} = -0.58990495$	$w_{\text{qp}} = 0.96754862$	$w_{\text{pp}} = 0.75790534$
	O	Ti	Ba
A_i	$-4.8023399466 \times 10^4$	$-4.8022284991 \times 10^4$	$5.1274280051 \times 10^{10}$
D_i	1.5164437249×10^0	$4.2873692908 \times 10^{-1}$	$9.9589996105 \times 10^{14}$
q_i^0	-1.206128	2.585940	1.264981
α_i	4.015831	7.810669	10.099937
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.3804821187×10^0	3.6536285915×10^0	0
c_{ij}	1.8959350087×10^0	$-8.8931599894 \times 10^0$	0
r_{ij}^0	1.4582461941×10^1	5.0042514066×10^0	5.2467090034×10^0
γ_{ij}	1.8364281657×10^1	1.0879768864×10^1	7.4427337828×10^0
D_{ij}	$1.5047586448 \times 10^{-7}$	$3.7135304448 \times 10^{-3}$	$2.3984214336 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	1.8324462614×10^0	0
c_{ij}	0	$-7.0780289746 \times 10^0$	0
r_{ij}^0	6.8670621073×10^0	1.6964731546×10^1	1.2747195138×10^1
γ_{ij}	4.3405864289×10^1	6.7248527267×10^0	6.8114496062×10^0
D_{ij}	$7.2393652844 \times 10^{-3}$	$5.8585064210 \times 10^{-4}$	$1.1268516920 \times 10^{-3}$

Table 10.2: Parameter set for the QEqTS(Ti,O) IP introduced in Chapter 6.

During parameterisation, the solution for the QEq charge transfers and induced dipole moments were obtained exactly by direct matrix inversion, i.e. to within a machine precision. During all other calculations, these variables were converged iteratively[27] using threshold value of 10^{-5} and 10^{-6} , in atomic units, for the induced dipoles and charge transfers, respectively. This means the iterative method would stop once the biggest difference for any one charge transfer variable or dipole moment between steps was within these thresholds.

[a.u.]	$w_{\text{qq}} = -0.88757697$	$w_{\text{qp}} = 1.01037129$	$w_{\text{pp}} = 0.06189529$
	O	Ti	Ba
q_i^0	-1.243181	2.504274	1.225268
α_i	3.889429	7.185920	7.357326
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.3382568076×10^0	4.1714922168×10^0	0
c_{ij}	1.6441848456×10^0	$-4.3096253531 \times 10^0$	0
r_{ij}^0	1.3181499130×10^1	4.8493125693×10^0	5.3168826258×10^0
γ_{ij}	1.9209722403×10^1	1.0589777916×10^1	9.0131793034×10^0
D_{ij}	$1.5145499999 \times 10^{-7}$	$3.9992363842 \times 10^{-3}$	$1.2303824785 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	1.3624808843×10^0	0
c_{ij}	0	$-1.6412769408 \times 10^0$	0
r_{ij}^0	9.7148951520×10^0	1.4385768730×10^1	1.2534511366×10^1
γ_{ij}	2.6852613678×10^1	7.8601271880×10^0	7.5873423557×10^0
D_{ij}	$-6.4145935978 \times 10^{-7}$	$2.2492872645 \times 10^{-4}$	$7.0908865036 \times 10^{-4}$

Table 10.3: Parameter set for the TS IP introduced in Chapter 6.

[a.u.]	$w_{\text{qq}} = -0.83761974$		
	O	Ti	Ba
A_i	1.4781178918×10^7	4.5752668835×10^7	$5.1274280051 \times 10^{10}$
D_i	1.7392984917×10^8	$8.0440897000 \times 10^{-1}$	$9.9589996105 \times 10^{14}$
q_i^0	-1.058876	2.489657	1.254676
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	$4.4742780332 \times 10^{-1}$	4.7108824656×10^0	0
c_{ij}	$1.9483864459 \times 10^{-1}$	6.6127349728×10^2	0
r_{ij}^0	1.1237211302×10^1	8.2065002722×10^0	5.3854648012×10^0
γ_{ij}	2.0262366438×10^1	4.5034551664×10^0	1.0967984524×10^1
D_{ij}	$1.5145500000 \times 10^{-7}$	$6.6437151328 \times 10^{-3}$	$6.1919825408 \times 10^{-3}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	0	0
c_{ij}	0	0	0
r_{ij}^0	5.3373808822×10^0	4.1671876534×10^0	1.1156001964×10^1
γ_{ij}	1.6819982876×10^1	4.1639926132×10^0	2.9139220909×10^0
D_{ij}	$-2.7001496489 \times 10^{-1}$	$-1.5478558605 \times 10^{-1}$	$3.3320798432 \times 10^{-2}$

Table 10.4: Parameter set for the MS-Q IP introduced in Chapter 6.

[a.u.]	$w_{\text{qq}} = 0.0$		
	O	Ti	Ba
q_i^0	-0.82600503	1.35797000217	0.73046448608
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	0	0	0
c_{ij}	0	0	0
r_{ij}^0	9.7122661×10^0	3.8787704×10^0	4.8898340×10^0
γ_{ij}	2.2767346×10^1	2.1259991×10^1	1.0788105×10^1
D_{ij}	1.5145500×10^{-7}	5.8964447×10^{-4}	1.8439772×10^{-2}
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	0	0
c_{ij}	0	0	0
r_{ij}^0	7.1788024×10^0	1	1.4479793×10^1
γ_{ij}	8.2618084×10^1	0	4.2958398×10^0
D_{ij}	$-7.1214108 \times 10^{-3}$	0	1.7755572×10^{-2}

Table 10.5: Parameter set for the MS-Q_o IP introduced in Chapter 6.

[a.u.]	$w_{\text{qq}} = -0.37698280$	$w_{\text{qp}} = 0.74092896$	$w_{\text{pp}} = 0.49337958$
	O	Ti	Ba
A_i	$-4.8023456002 \times 10^4$	$-4.8022323232 \times 10^4$	$5.1274280051 \times 10^{10}$
D_i	1.2409027826×10^0	$3.2163506976 \times 10^{-1}$	$9.9589996105 \times 10^{14}$
q_i^0	-1.233167	2.585248	1.264644
α_i	3.809648	7.090146	9.438829
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.2388003350×10^0	3.6605882896×10^0	0
c_{ij}	1.6324581991×10^0	$-9.6572628893 \times 10^0$	0
r_{ij}^0	1.4446747707×10^1	5.0535667090×10^0	5.3779672974×10^0
γ_{ij}	1.8211613872×10^1	1.0997275091×10^1	8.1744845628×10^0
D_{ij}	$1.5047586448 \times 10^{-7}$	$3.7383930097 \times 10^{-3}$	$1.5825059260 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	1.5655826990×10^4	0
c_{ij}	0	1.5636916515×10^4	0
r_{ij}^0	6.6879225993×10^0	1.6904490823×10^1	1.3667441237×10^1
γ_{ij}	4.0320609267×10^1	8.0933263759×10^0	5.2438196725×10^0
D_{ij}	$1.5289162873 \times 10^{-2}$	$2.0521506491 \times 10^{-4}$	$4.1069936113 \times 10^{-3}$

Table 10.6: Parameter set for the QEqTS(fit: V_{O}) IP introduced in Chapter 7 and used in Chapter 8.

[a.u.]	$w_{\text{qq}} = 0.19826698$	$w_{\text{qp}} = 1.00751865$	$w_{\text{pp}} = 0.76915725$
	O	Ti	Ba
A_i	$-4.8023618419 \times 10^4$	$-4.8022315345 \times 10^4$	$5.1274280051 \times 10^{10}$
D_i	$5.7233583232 \times 10^{-1}$	$3.3256147670 \times 10^{-1}$	$9.9589996105 \times 10^{14}$
q_i^0	-1.186462	2.584900	1.264474
α_i	3.855768	7.475611	13.729817
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.0181555089×10^0	3.5628818306×10^0	0
c_{ij}	1.0003170479×10^0	$-6.2488704112 \times 10^0$	0
r_{ij}^0	1.3455133522×10^1	4.9569565479×10^0	5.4775958405×10^0
γ_{ij}	1.7517641872×10^1	1.1090292180×10^1	8.1549672436×10^0
D_{ij}	$1.5047586448 \times 10^{-7}$	$3.6285945435 \times 10^{-3}$	$1.3778977551 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	2.2190086676×10^4	0
c_{ij}	0	2.2181176201×10^4	0
r_{ij}^0	5.7676221649×10^0	9.4881875776×10^0	1.6760582634×10^1
γ_{ij}	1.6676372860×10^1	5.9457458810×10^0	4.1624694296×10^0
D_{ij}	$3.9581892607 \times 10^{-2}$	$1.9423027483 \times 10^{-3}$	$6.6471399044 \times 10^{-3}$

Table 10.7:]

Parameter set for the QEqTS(fit: V_{Ti}) IP introduced in Chapter 7 and used in Chapter 8.

[a.u.]	$w_{\text{qq}} = -1.17369307$	$w_{\text{qp}} = 0.95355338$	$w_{\text{pp}} = -0.44108174$
	O	Ti	Ba
q_i^0	-1.189198	2.680045	0.843505
α_i	2.710280	7.607900	16.705325
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.6934496424×10^0	5.7542802193×10^0	0
c_{ij}	5.5220263393×10^0	$-2.5817990288 \times 10^3$	0
r_{ij}^0	1.3927429173×10^1	4.8767749767×10^0	5.2209180562×10^0
γ_{ij}	1.9293146058×10^1	1.0546285856×10^1	9.6582188169×10^0
D_{ij}	$1.5145499999 \times 10^{-7}$	$4.0662348583 \times 10^{-3}$	$1.2440707936 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	1.6530787828×10^4	0
c_{ij}	0	$-6.0917707958 \times 10^0$	0
r_{ij}^0	1.4019048093×10^1	5.6306716486×10^0	1.3183487939×10^1
γ_{ij}	1.9811855330×10^1	5.2825966186×10^0	1.0082621836×10^1
D_{ij}	$-6.0371090738 \times 10^{-7}$	$-2.1007201621 \times 10^{-4}$	$1.4069731553 \times 10^{-4}$

Table 10.8: Parameter set for the TS IP parameterised to a system with a neutral O vacancy in Chapter 7.

[a.u.]	$w_{\text{qq}} = 0.75210690$	$w_{\text{qp}} = 1.43214714$	$w_{\text{pp}} = 0.52799139$
	O	Ti	Ba
q_i^0	-1.114497	2.379098	1.052509
α_i	3.217609	10.182830	22.664189
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.8503618846×10^0	3.4092815392×10^0	0
c_{ij}	5.8446867809×10^0	$-4.6128342265 \times 10^0$	0
r_{ij}^0	1.0879610534×10^1	4.6844251484×10^0	5.2913238157×10^0
γ_{ij}	1.9410000124×10^1	1.0383551874×10^1	9.3348837449×10^0
D_{ij}	$1.3357449031 \times 10^{-7}$	$4.0553820365 \times 10^{-3}$	$1.2246327805 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	1.5412162108×10^0	0
c_{ij}	0	$-9.3408336712 \times 10^{-1}$	0
r_{ij}^0	5.9255206800×10^0	7.7637156459×10^0	2.1067853380×10^1
γ_{ij}	1.2872660843×10^0	4.9775683200×10^0	1.6482470964×10^1
D_{ij}	$-3.0313493710 \times 10^{-2}$	$1.2091256426 \times 10^{-2}$	$1.7408783171 \times 10^{-7}$

Table 10.9: Parameter set for the TS IP parameterised to a system with a neutral Ti vacancy in Chapter 7.

[a.u.]	$w_{\text{qq}} = -0.32166090$	$w_{\text{qp}} = 1.05442891$	$w_{\text{pp}} = 0.58651361$
	O	Ti	Ba
A_i	$-4.8023519981 \times 10^4$	$-4.8022285024 \times 10^4$	$5.1274280051 \times 10^{10}$
D_i	$7.7539377559 \times 10^{-1}$	$3.8184247026 \times 10^{-1}$	$9.9589996105 \times 10^{14}$
q_i^0	-1.147617	2.585248	1.264644
α_i	4.002439	7.814888	10.285406
	O-O	O-Ti	O-Ba
$\tilde{\zeta}_{ij}$	1.3490105618×10^0	3.5802158341×10^0	0
c_{ij}	1.5424269088×10^0	$-7.6707736650 \times 10^0$	0
r_{ij}^0	1.4237150636×10^1	4.9683341822×10^0	5.2385465461×10^0
γ_{ij}	1.8115547459×10^1	1.1020201157×10^1	7.5946300957×10^0
D_{ij}	$1.5047586448 \times 10^{-7}$	$3.6624314873 \times 10^{-3}$	$2.3020786010 \times 10^{-2}$
	Ti-Ti	Ti-Ba	Ba-Ba
$\tilde{\zeta}_{ij}$	0	8.9849810224×10^3	0
c_{ij}	0	8.9760705471×10^3	0
r_{ij}^0	6.1163090758×10^0	1.3429190960×10^1	1.7692200676×10^1
γ_{ij}	2.0983083188×10^1	7.8008537954×10^0	5.6555443964×10^0
D_{ij}	$1.9904632505 \times 10^{-2}$	$4.0526322336 \times 10^{-4}$	$2.0191341939 \times 10^{-3}$

Table 10.10: Parameter set for the QEqTS IP parameterised simultaneously to the system with the O vacancy, with the Ti vacancy and to the defect-free system in Chapter 7.