TROISIEME CYCLE DE LA PHYSIQUE en Suisse Romande

Microscopic Properties of Ferroelectric Oxides from First-Principles : Selected Topics

(Preliminary version)

Philippe GHOSEZ

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Introduction

The crystals having a spontaneous polarization are called pyroelectrics and the direction of the polarization is the polar axis. Ferroelectrics are pyroelectrics which possess a spontaneous polarization which can be reversed by applying a suitable electric field. The process is known as switching and is accompanied by hysteresis in the field-polarization curve. The value of the spontaneous polarization is easily determined from the switching loop.

Pyroelectricity has been know since ancient time because of the ability of such materials to attract objects when they are heated. During the eighteenth century, many experiments where carried out in an attempt to characterize the pyroelectric effect in a quantitative manner for instance by Gaugain [1] in 1856. At the opposite, ferroelectricity was discovered less than hundreed years ago. It was first identified in 1920 by Valasek [2] who observed that the polarization of Rochelle salt can be reversed by the application of an external electric field. The principal reason that ferroelectrics were discovered so much later is because the formation of domains of differently oriented polarization within virgin single crystals leads to a lack of any net polarization and a very poor pyroelectric response.

From the very beginning, ferroelectricity aroused joined scientific and industrial interests. With the passing years, distinct families of ferroelectric crystals were identified. A tremendous lot of experimental data were accumulated and different theories were proposed to explain its origin.

Since decades, ferroelectric materials are used in various technological applications [3, 4, 5, 6], not only according to their intrinsic ferroelectric behavior but also because they present unusual properties such as high dielectric, piezoelectric, non-linear optical and pyroelectric constants. During the recent years, different ferroelectric oxides systems have particularly attracted the attention for applications. A new class of ferroelectric relaxors has been discovered which presents an anomalously high piezoelectric response and could therefore tremendously improve the efficiency of piezoelectric transducers [7, 8]. Lithium niobate, already used for frequency doubling in some lasers, has been identified as a promizing candidate for holographic data storage [9, 10]. Finally, and without being exhaustive, in the research for "high K" dielectrics to replace the amorphous SiO₂ layer in electronic devices, as well as for the development of MEMS¹ and ferroelectric data storage

¹MEMS is an acronym for Micro Electro Mechanical Systems which are miniature multifunctional systems consisting of sensors, actuators and electronics

systems, thin films of ABO_3 ferroelectric oxides that can be grown on silicon [11, 12] are expected to play a major role in the near future [13].

In spite of many years of constant interest for this class of compounds, the origin of ferroelectricity and related phenomena was for long unclear [14, 6] and some questions still remain open today. As a single example, let us cite the debate concerning the evolution of ferroelectricity with thickness in thin films and small particles. During the last decade, some important advances in the microscopic understanding of ferroelectricity in oxides have been achieved in the framework of first-principles simulations. These developments are the subject of the present course. In this introductory Chapter, they will be put back in the context of a brief history of ferroelectricity focusing on the ABO₃ compounds.

The family of ABO₃ compounds

The first series of isomorphous ferroelectric crystals was produced in Zürich, during the thirties. It concerned a family of phosphates and arsenates. The most popular of these compounds is potassium dihydrogen phosphate (KH_2PO_4), usually abbreviated as KDP. At that time, it was commonly thought that the existence of a hydrogen bond was a necessary, if not sufficient, condition for the polar instability to occur. Consequently, there was only very little motivation for looking for ferroelectricity in materials such as oxides which did not contain hydrogen.

The ferroelectric properties of barium titanate (BaTiO₃) were discovered incidentally, in 1945, when searching for new dielectrics to replace mica [14]. Rapidly, it became by far the most extensively studied ferroelectric material. On cooling, it undergoes a sequence of three successive structural transitions from a paraelectric cubic phase to ferroelectric structures of tetragonal, orthorhombic and rhombohedral symmetry. It was the first ferroelectric without hydrogen bonds, the first with a non-polar paraelectric phase, the first with more than one ferroelectric state. In addition, its *prototype* crystal structure was cubic perovskite ² with only five atoms per unit cell. It was therefore offering to physicists an opportunity to study the onset of ferroelectricity from a very simple structure.

The sudden interest for $BaTiO_3$ broadened gradually to different oxides of the ABO₃ family [14]. A ferroelectric activity was discovered in KNbO₃ presenting the same sequence of phase transitions as $BaTiO_3$, or in PbTiO₃ that remains stable at low temperature in tetragonal symmetry. Ferroelectricity was also observed in LiNbO₃ and LiTaO₃, which do not have the perovskite structure ³ but still are ABO₃ lattices with oxygen octahedra.

The great fascination for the family of ABO₃ compounds is that, in addition to ferroelectric potentialities, it also readily undergoes non-polar structural phase transitions, associated with different tilts of the oxygen octahedra. Moreover, the observed transitions are not necessarily ferrodistortive (involving a Γ type displacement of the atoms of the prototype phase) but may be antiferrodistortive (displacement associated to a non-zero phonon wavevector within the Brillouin zone). The most frequently observed case consists in a cell doubling transition, associated to a Brillouin zone boundary type displacement

²Barium titanate crystallizes also in a more complex hexagonal structure

³They crystallize in a trigonal structure related to but slightly different from the ilmenite.

like in $SrTiO_3$ (non-polar distortion) or $PbZrO_3$ (antiferroelectrics). Sometimes, like in $NaNbO_3$, instabilities of different characters are present and produce a chain of transitions of different natures: ferroelectric, anti-ferroelectric, non-polar.

Empirical and semi-empirical models

Due to the simplicity of the ABO_3 perovskite structure, it was quite natural to expect theoretical progress at the *microscopic* level in the understanding of ferroelectricity. A first important step was performed in 1950 by Slater [15] who suggested that the ferroelectric instability of BaTiO₃ should be caused by long-range dipolar forces which, via the Lorentz local effective field, tend to destabilize the high symmetry configuration favored by local forces. It was the starting point for a "displacive" explanation of the phase transition, as opposed to the more conventional order-disorder description⁴. The concept of "rattling" Ti ion was introduced in models considering motion of the Ti atom in the rigid framework of the rest of the lattice. It was a first neat picture, however questionable as all the atoms were actually displaced after the ferroelectric transition has occurred. A new breakthrough arrived in 1959, when Cochran [17]⁵ realized that the theory describing the displacive lattice instability should be cast within the framework of lattice dynamics, when considering one of the lattice modes as the basic variable. His theory was exhibited in the framework of a shell-model approach. The concept of soft-mode was introduced. The competition between short-range and Coulomb forces highlighted by Slater reappeared coherently in this context as the origin of the softening of a particular transverse optic mode. Later, the ideas of Cochran were generalized in the framework of microscopic effective Hamiltonians [14] and the soft-mode became a central quantity in the description of different structural instabilities.

Independently, we note that theory had also progressed rapidly at the macroscopic level when focusing on thermodynamic concepts. An interesting description of $BaTiO_3$ was, for instance, already reported by Devonshire [19] in 1949, from an expression of the free energy in powers of polarization and strain. While the microscopic description of Cochran was essentially concerned by the atomic displacements, one of the major contribution of the thermodynamic approach was probably to emphasize the crucial role of the macroscopic strain. Coupling between the soft-mode and the strain, neglected in many of the microscopic models, appeared recently as a major ingredient for a correct description of the successive phase transitions in ABO₃ compounds [20, 21].

Since the sixties, the emphasis has been placed dominantly on the lattice dynamical description of the ferroelectricity. There was an explosion of experimental activity using techniques allowing to measure frequency and temperature dependent properties of the soft-mode. A new step in the microscopic understanding of the ferroelectricity in ABO_3 compounds arose from the fit of these experimental data within a shell-model approach.

⁴The order-disorder description makes reference to a multi-well energy surface, yielding macroscopically non-polar but microscopically polar paraelectric phase. In the displacive model, the paraelectric phase is also microscopically non-polar [16].

⁵A similar approach was taken independently by Anderson [18].

In 1976, Migoni, Bilz and Bäuerle [22] suggested that the ferroelectric instability should originate in a non-linear and anisotropic polarizability of the oxygen atoms. This gave rise to the "polarizability-model" [23, 24] that was widely used to describe the dynamics of ABO₃ compounds. The unusual polarizability of the oxygen atom was discussed [22, 25, 23] and is still sometimes referred to as the origin of the ferroelectricity [26]. In particular, it was already suggested by Bilz *et al.* [22] that the anisotropy of the oxygen pstates and transition metal d-states [22, 23]. As we will see later, this intuition was correct and these hybridizations play a major role in the ferroelectric instability. However, within their semi-empirical approach, it was not possible to understand the *mechanisms* of interplay between the electronic and dynamical properties.

At the same time, but in a different context, Comes, Lambert and Guinier [27] reported diffuse X-ray scattering for crystals of BaTiO₃ and KNbO₃, in three sets of planes normal to the cubic axis. This feature was associated to a *static* linear disorder, explained in terms of what is now usually referred to as the "8-sites model". This model is another meaningful picture currently invoked to visualize the mechanism of the phase transition. It was however contested by Hüller [28] who preferred to favor a *dynamical* explanation for the linear disorder. Independently of the debate on the static or dynamical nature of the disorder, the existence of chain correlations became well accepted, although its microscopic origin remained unclear [29].

At the end of the seventies, different interesting features had therefore been identified as playing an important role in the ferroelectricity of ABO_3 compounds. Different models were available, well suited for a qualitative description of the ferroelectric instability within a specific context. Nevertheless, accumulating the experimental data, it appeared gradually that the ferroelectric transition was more complex than previously expected: for instance, it was observed that the phase transition is not purely displacive in the sense defined by Cochran, but has also an order-disorder character around the transition temperature ⁶. Unfortunately, the theoretical models available at that time had their limitations and were not accurate enough to describe and investigate all the subtle features of the phase transition.

A first-principles approach

A new opportunity for addressing the remaining open questions concerning ferroelectricity was given beginning of the nineties when ABO_3 compounds became accessible to firstprinciples calculations performed within the Density Functional Theory (DFT) [30, 31]. Indeed, such a technique does not restrict to the description of the electronic properties of materials but is also particularly suited to investigate their structural properties. Earlier DFT calculations on ABO_3 compounds were reported by Weyrich [32, 33] during the eighties. The renewal of interest in these materials during the last decade is a consequence

⁶The appearance of the order-disorder character originates in the evolution of the thermal energy with respect to the height of the multi-well energy barrier [16].

of different theoretical advances combined with a gigantic jump of the computational power.

A first crucial advance concerns the emergence of the modern theory of polarization, pioneered by Resta [34], King-Smith and Vanderbilt [35, 36]. Until 1992, the macroscopic electronic polarization was indeed not directly accessible for periodic systems with continuous electronic distributions. This was a major impediment to a systematic study of ferroelectric materials for which the polarization appears as the fundamental quantity. Since 1992, the electronic contribution to the polarization can be conveniently obtained as a Berry phase of the electronic wavefunctions and is easily computed in the framework of DFT.

A second ingredient is the effective Hamiltonian approach to structural phase transitions, developed by Rabe and Joannopoulos [37, 38, 39], in which the parameters of the Hamiltonian are determined from the results of first-principles calculations. Such an approach, first applied to GeTe [37], was then generalized by Rabe and Waghmare [40, 41, 21] for general phonon-related phase transitions, opening the door to a systematic firstprinciples study of the family of ABO₃ compounds. In this specific context, the density functional perturbation theory (DFPT) [42, 43], appeared as an important complementary tool for an efficient determination of the parameters associated to the model Hamiltonians.

Since 1992, an impressive number of first-principles calculations have been performed yielding a similarly impressive number of interesting results that will be reintroduced all along this course. A spectacular achievement concerns a correct description of the sequence of phase transitions for various pure and mixed ABO₃ compounds like BaTiO₃ [20, 44, 45], SrTiO₃ [46, 47], PbTiO₃ [48, 21, 49], PbZrO₃ [21, 50], KNbO₃ [51], CaTiO₃ [52] or NaNbO₃ [52].

Starting from the "first principles", such kind of calculations was also a new opportunity to connect, within a rigorous approach, the macroscopic properties of ABO_3 compounds to their intimate microscopic features. It allowed to clarify the interplay between the electronic and dynamical properties and to understand better the mechanism of the ferroelectric instability [53]. It gave some insight on the origin of the unusually high piezoelectric response of relaxor compounds [8]. Going further, the approach seems now appropriate for an *ab initio* design of perovskite alloys with predetermined properties [54].

The present course

In this course, we propose a microscopic description of some selected properties of ABO_3 ferroelectric materials, as it emerges in the framework of first-principles calculations within the density functional formalism. We try to present a coherent overview starting from the basics and going to the most recent advances. However, we have no pretension to make an exhaustive summary of all the recent achievements in the field. Instead, we concentrate on two prototype materials: barium titanate (BaTiO₃) and lithium niobate (LiNbO₃). We proceed step by step, mainly focusing on the results we have obtained since we started working on these compounds in 1992.

Because the opportunity of this course was kindly offered to us by the 3^e Cycle de

la Physique en Suisse Romande on the initiative of Prof. Jean-Marc Triscone and Dr. Thomas Tybell, this manuscript is essentially devoted to experimentalists. So, even if the results presented here arise from computer simulations, we mainly bypass the technical details of the calculations in order to concentrate on the physics of the materials.

Nowadays, the best reference concerning the principles and applications of ferroelectric compounds is the famous book of Lines and Glass [14]. Readers interested in the density functional formalism can find a good introduction in the review of Payne *et al.* [55]. Additional references are also mentionned at the end of each Chapter, directly related to what has been discussed. Some more informations can also be found in our PhD thesis from which this manuscript is partly inspired (http://www.ulg.ac.be/phythema).

The course is made up of 5 Chapters and is organized as follows. In Chapter 1, we briefly introduce and describe the density functional theory, which will be used in the next Chapters. In Chapter 2, we report a brief description of the structural and electronic properties of both prototype materials. In Chapter 3, we introduce a key concept in the understanding of ferroelectricity : the Born effective charges. It will be seen that these charges are anomalously large in ABO_3 compounds. This feature will be explained in terms of transfers of charge induced by dynamic changes of orbital hybridizations. In Chapter 4, we briefly comment on the electron localization in ferroelectric compounds, and discuss how these results are compatible with the explanation of anomalous effective charges. In Chapter 5, we discuss the dielectric and dynamical properties of ABO_3 compounds, themselves directly associated to the ferroelectric instability. Our purpose will be to identify how these properties are directly associated to the electronic features. The balance between dipolar and short-range forces will be quantified. The origin of the transition will be assigned to giant dipolar forces induced by the anomalously large Born effective charges. Full phonon dispersion curves will be obtained in the paraelectric phase. The notion of chain-structure correlation will be discussed. The transferability of force constants from one ABO₃ compound to another will be pointed out as well as the implication on the dynamics of mixed compounds.

Note that two more Chapters are expected to be introduced in a forthcoming version of this course. The first one will be devoted to the concept of effective Hamiltonian and its use to describe the evolution of the dielectric, piezoelectric and pyroelectric properties of ABO_3 compounds with temperature. The second is intended to make a brief review of recent advances concerning the understanding of the behavior of ferroelectric ultrathin films.

Chapter 1

Basics of the density functional theory

1.1 Introduction

Within this Chapter, we propose a brief summary of the planewave-pseudopotential density functional formalism within which most of the calculations reported all along the next Chapters have been performed. We will not be exhaustive nor too technical. Our goal is to introduce general concepts and define some widely used acronyms in order to provide to the non expert reader a basic knowledge allowing him to understand and critically read theoretical papers making use of the density functional formalism. In this way, we will not discuss practical implementation.

Prediction of the electronic and geometric structures of solids requires calculations of the quantum mechanical total energy of the system and subsequent minimization of that energy with respect to the electronic and nuclear coordinates (variational principle). This consists of a complex quantum mechanical many-body problem associated to interacting electrons and nuclei. It is unaffordable in practice, and some approximations are required to face it.

First, because of the large difference in mass between the electrons and nuclei and the fact that the forces on the particles are the same, both in nature (electrostatic) and amplitude, the electrons respond essentially instantaneously to the motion of the nuclei. Thus, the nuclei can be treated adiabatically, leading to a separation of electronic and nuclear coordinates in the many-body wave functions (Born-Oppenheimer approximation). This reduces the many-body problem to the solution of the dynamics of the electrons in some frozen-in configuration of the nuclei whose positions \mathbf{R}_{κ} are considered as parameters.

Even with this simplification, the problem remains formidable due to the electronelectron interaction. However, Density Functional Theory (DFT) developed by Hohenberg and Kohn [30] and Kohn and Sham [31] provided some hope of a simple method for describing the effects of electron-electron interactions. Hohenberg and Kohn proved that the total energy of an electron gas is a unique functional of the electronic density. This means that instead of seeking directly for the complex many-body wave function of the systems, we can adopt an intrinsically different point of view and consider the electronic density as the fundamental quantity of the problem. The minimum value of the total energy functional is the ground-state energy and the density yielding this minimum value is the exact ground-state density. The theorem of Hohenberg and Kohn demonstrated the *existence* of such a functional but did NOT provide its *form*. Kohn and Sham then showed how it is possible to map the many-body problem onto another system of non-interacting particles moving in an external potential, with the *same* exact ground-state electronic density. In practice, the electronic density can be obtained from one-body wave functions, self-consistent solution of a set of one-particle equations describing the behavior of an electron in an effective potential. Again, the form of this potential is *a priori* unknown but, as it will be discussed, can be efficiently approximated.

1.2 Kohn-Sham energy functional

Within this one-particle framework, the Kohn-Sham total energy functional for a set of doubly occupied states ${}^1 \psi_i$ can be written :

$$E_{e+i}[\mathbf{R}_{\kappa},\psi_{i}] = \sum_{i}^{occ} \left\langle \psi_{i} \left| -\frac{1}{2} \nabla^{2} \right| \psi_{i} \right\rangle + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_{1}) n(\mathbf{r}_{2})}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} d\mathbf{r}_{1} d\mathbf{r}_{2} + E_{xc}[n] + E_{ion}[\mathbf{R}_{\kappa}]$$
(1.1)

where the successive terms represents, respectively, the electronic kinetic energy, the interaction between the electrons and the static electron-ion potential v_{ext} , the electronelectron Coulomb repulsion, the exchange-correlation energy, $E_{xc}[n]$ (this term contains all the electron-electron interactions that go beyond the Coulomb term), and the Coulomb energy associated with the interaction among the nuclei $E_{ion}[\mathbf{R}_{\kappa}]$. The electronic density, $n(\mathbf{r})$, is given by

$$n(\mathbf{r}) = \sum_{i}^{occ} \psi_i^*(\mathbf{r}).\psi_i(\mathbf{r})$$
(1.2)

For a given set of atomic positions \mathbf{R}_{κ} , the ground-state is obtained by minimizing Eq. (1.1) under the following orthonormalization constraints :

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

This provides the total energy of the system and the associated electronic density.

In practice, the minimization of Eq. (1.1) is equivalent to solve self-consistently the

¹Along the rest of the chapter we will assume spin-degeneracy

following set of Kohn-Sham equations :

$$\begin{bmatrix} -\frac{1}{2}\nabla^2 + v_s \end{bmatrix} |\psi_i\rangle = \epsilon_i |\psi_i\rangle$$

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$n(\mathbf{r}) = \sum_i^{occ} \psi_i^*(\mathbf{r}) \cdot \psi_i(\mathbf{r})$$
(1.3)

where the derivative of the exchange-correlation energy with respect to the density is usually referred to as the exchange-correlation potential $v_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r})$.

The Kohn-Sham equations represent a mapping of the interacting many-electron system onto a system of noninteracting fictitious particles moving in an effective potential due to the ions and all the other electrons. If the exchange-correlation energy functional were known exactly, taking the functional derivative with respect to the density would provide an exchange-correlation potential that included the effects of exchange and correlation exactly. In practice, however, the form of $E_{xc}[n]$ is unknown.

1.3 Usual approximate functionals

The exchange-correlation energy, $E_{xc}[n]$, is expected to be a universal functional of the density everywhere. However, Hohenberg and Kohn theorem [30] provides some motivation for using approximate methods to describe the exchange-correlation energy as a function of the electron density.

The first, and most widely used approach in this sense is the Local Density Approximation (LDA) [31]. It assumes (i) that the exchange-correlation energy per particle at point \mathbf{r} , $\epsilon_{xc}(\mathbf{r})$, only depends on the density at this point and (ii) that it is equal to the exchange-correlation energy per particle of a homogeneous electron gas of density $n(\mathbf{r})$ in a neutralizing background:

$$E_{xc}[n] = \int n(\mathbf{r}) \cdot \epsilon_{xc}^{LDA}(\mathbf{r}) \ d\mathbf{r}$$
(1.4)

with

$$\epsilon_{xc}^{LDA}(\mathbf{r}) = \epsilon_{xc}^{hom}[n(\mathbf{r})] \tag{1.5}$$

The form of $\epsilon_{xc}^{hom}[n]$ used in the calculation may be borrowed from various sources. The *exchange* part can be obtained analytically from the Hartree-Fock technique. It can be shown that it scales like :

$$\epsilon_x^{hom}[n] = -\frac{3}{4\pi} (3\pi^2)^{1/3} \ n^{1/3} \tag{1.6}$$

For the *correlation* part, one may rely on accurate values obtained by Ceperley-Alder [56] from Monte-Carlo simulations of the energy of the homogeneous electron gas. In the

next Chapters, we use a polynomial parametrization of the previous data as proposed by Teter [57]. Other approximations (Wigner, X-alpha, Gunnarson-Lundqvist, Perdew-Zunger, Perdew-Wang ...) are also referred to as local density approximations. They rely on the same exchange part but consider slightly different treatments of the correlation term.

The LDA is probably one of the crudest approximation that we may do. It has however the advantage of the simplicity. Moreover, it already allows to describe structural and dynamical properties of materials with surprising accuracy [58, 59]² : calculated bond lengths and bond angles reproduce the experiment within a few percents; phonon frequencies are usually obtained within 5-10 %. Well known exceptions are however the cohesive energy and the dielectric susceptibility.

Different techniques were proposed that are going beyond the LDA. A first alternative, but connected approach, is to build a "semi-local" functional that does not only depend on the density at \mathbf{r} but also on its gradient, or on higher order gradient expansion. Different forms have been proposed that are summarized under the label of Generalized Gradient Approximations (GGA). They are based on a functional of the type [60, 61]:

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r}) \cdot \epsilon_{xc}^{GGA}[n(\mathbf{r}); |\nabla n(\mathbf{r})|; \nabla^2 n(\mathbf{r})] dr$$
(1.7)

This kind of approximation improves the computed value of the cohesive energy. It can also improve the description of bond lengths and lattice parameters even if the gradient correction usually overcorrects the LDA [62, 63] yielding longer values than the experimental ones. Finally, the correction has a rather limited effect on the dielectric constant [62]. The GGA remains a quasi-local approximation that cannot include any long-range density dependency of $E_{\rm xc}[n]$.

Different other functionals also exist like the average density approximation (ADA) [64] or the weighted density approximation (WDA) [64]. It was argued that WDA should be intrinsically unable to improve LDA results [65]. For ABO₃ compounds, it seems however that this last technique is an interesting alternative to the LDA [66].

Without being exhaustive, let us finally mention that another interesting scheme consists in a mixing of Hartree-Fock and local density functionals as justified from the adiabatic connection formula [67]. This method is quite popular in quantum chemistry but is not widely used by the community of physicists.

1.4 The periodic solid

1.4.1 Periodic boundary conditions

All along this course, we will be interested in periodic systems, built from a basic unit cell that is periodically repeated in the three directions of space. In this context, the atomic

²The LDA exchange-correlation hole integrates to -1. This simple feature should be a first intuitive argument to explain its success.

position $\mathbf{R}_{a,\kappa}$ of atom κ within unit cell a can be conveniently dissociated as:

$$\mathbf{R}_{a,\kappa} = \mathbf{R}_a + r_\kappa \tag{1.8}$$

where \mathbf{R}_a is a lattice vector and r_{κ} is the vector position of the atom within the unit cell.

A macroscopic solid would basically consists in the limit of a finite system of increasing size. Since long, however, physicists do usually prefer to investigate solids from infinite truly periodic systems defined by imposing Born-von Karman periodic boundary conditions [68]. The approximation seems reasonable and was widely used because it presents numerous conceptual and practical advantages. It leads to what we will refer to as a "periodic-DFT", in which the energy appears as a functional of the *periodic* part of the density.

1.4.2 Bloch functions

In infinite periodic solids obtained by imposing periodic boundary conditions, the electronic wavefunctions have the Bloch form and can be written as the product of a planewave function of wave vector \vec{k} , by a cell periodic function $u_{n\mathbf{k}}(\mathbf{r})$:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$
(1.9)

where N is the number of unit cells repeated in the Born-von Karman periodic box, and Ω_0 is the volume of the basic unit cell. A normalization factor has been introduced, such that the normalization condition imposed to $\psi_{n\mathbf{k}}$ now writes in terms of $u_{n\mathbf{k}}$:

$$\langle u_{m\mathbf{k}}|u_{n\mathbf{k}}\rangle = \delta_{mn} \tag{1.10}$$

when the scalar product of *periodic* functions is defined as:

$$\langle f|g\rangle = \frac{1}{\Omega_0} \int_{\Omega_0} f^*(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}.$$
 (1.11)

In our infinite solid, \mathbf{k} may have any value. Basically, the Bloch theorem has reduced the problem of calculating an infinite number of electronic wavefunctions to the determination of a finite number of electronic states but at an infinite number of \mathbf{k} points. Similarly to the fact that each electron of the solid must be taken into account, the occupied states at each \mathbf{k} point contribute to the electronic density and to the potential in the bulk solid. However, as a consequence of the periodicity in real space, the \mathbf{k} -space is also periodic [68] so that, in practice, the only \mathbf{k} -vectors to be considered are those which are within the first Brillouin zone (BZ). From our conventions, the electronic density reads in terms of the periodic functions :

$$n(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_{BZ} \sum_{m}^{occ} s \; u_{m\mathbf{k}}^*(\mathbf{r}) \; u_{m\mathbf{k}}(\mathbf{r}) \; d\mathbf{k}.$$
(1.12)

where s is the occupation number of states in the valence band (in spin-degenerate systems s = 2).

1.4.3 Brillouin zone sampling

The use of Bloch functions has to be associated with *integration* over the Brillouin zone and would *a priori* require to compute different quantities at a large number of **k**-points. Fortunately, the electronic wavefunction at **k** points that are close to each other are almost identical so that it is possible to represent the electronic wavefunction over a region of **k** space by that at a single **k** point. Consequently, integrations over the entire Brillouin zone can be conveniently replaced by sums on a limited number of **k** points.

Efficient sampling methods have been proposed by different authors [69, 70, 71] to obtain accurately the density, the electronic potential and the contribution to the total energy from the knowledge of the electronic states on a very restricted set of "special" **k**-points. The study of ABO₃ compounds typically required a $6 \times 6 \times 6$ mesh of special **k**-points. This is relatively dense in comparison with what is usually needed for other typical insulators. In contrast, for metals, larger meshes are required in order to define precisely the Fermi surface.

We note that the error induced by the \mathbf{k} -point sampling is not the consequence of any physical approximation but consists in a computational error. Its magnitude must be checked and can always be reduced by increasing the size of the \mathbf{k} -point mesh.

1.5 A plane-wave pseudopotential approach

1.5.1 Plane-wave basis set

The Bloch theorem relates the electronic wavefunction $\psi_{n\mathbf{k}}$ to a periodic function $u_{n\mathbf{k}}$, that satisfies:

$$u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) \tag{1.13}$$

for any vector **R** satisfying the lattice periodicity. As a consequence, $u_{n\mathbf{k}}$ can be conveniently expanded in terms of a plane-wave basis set.

Typically, the Fourier transform of a periodic function is indeed identically zero except on the reciprocal vector **G** defined as $\mathbf{G}.\mathbf{R} = m.2\pi$, where *m* is an integer. The function is therefore related to its Fourier transform by the following relationships:

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}}$$
(1.14)

$$u_{n\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega_0} \int_{\Omega_0} u_{n\mathbf{k}}(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} d^3 \mathbf{r}$$
(1.15)

In this context, the global electronic wavefunction can also be written as a sum of planewaves:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i (\mathbf{k}+\mathbf{G}).\mathbf{r}}$$
(1.16)

From a mathematical viewpoint, the sum appearing in the previous equation is an infinite one. However, in practical calculations this sum must be restricted to a limited number of **G** vectors. The conventional choice is to consider only plane-waves that have a kinetic energy smaller than a chosen cutoff energy: $\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2 \leq E_{cut}$.

The plane-wave basis seems only very poorly suited to expand the electronic wavefunctions because a very large cutoff is *a priori* needed to describe the tightly bound core orbitals or to follow the rapid oscillations of the valence wavefunctions in the core region due to the strong ionic potential. In practice, a plane-wave basis set will only become tractable when considering simultaneously the pseudopotential approximation that will be described in the next Section. For all electron calculations, other expansions of the electronic wavefunction must be preferred (LAPW, LMTO...).

The truncation of the infinite basis set at a *finite* cutoff energy introduces a second computational error. Similarly to what was discussed for the \mathbf{k} -point sampling, the amplitude of such an error can always be reduced by increasing the value of the cutoff energy.

The plane-waves basis has the computational advantage to be associated to convenient Fast Fourier Transform (FFT). Also, it will be particularly suitable for the calculation of the response to external perturbations. However, one difficulty arises in practical calculations at a finite cutoff due to the incompleteness of the basis set. Change in size of the unit cell will modify abruptly the number \mathbf{G} vectors inside the cutoff sphere, and consequently, the number of plane-wave included in the basis set. As the total energy is monotonically decreasing with the number of plane-waves, this phenomenon will be associated to discontinuous jumps in the total energy. The values of the energy for different unit cells, obtained at a fixed cutoff, are associated to slightly different basis sets and cannot be directly compared: they require to include a correction factor usually referred to as a "Pulay correction" [72, 73].

1.5.2 Pseudopotentials

Two major impediments have been identified to the use of a plane-wave basis set. They were associated to the difficulty (i) of describing the tightly bounded core states and (ii) of following the rapid oscillations of the valence bands orbitals inside the core region. We now briefly explain how the first-problem may be avoided within the frozen-core approximation. The second requires the use of pseudopotentials.

The frozen-core approximation is based on the following observations. In many situations, the physical and chemical properties of solids are essentially dependent on the valence electrons. On the other hand, it is expected that the core electrons that do not directly participate to the chemical bonding are only slightly affected by modifications of the atomic environment. It may therefore reasonably be expected that the configuration of the core electrons within the solid is equivalent to that of the isolated atoms. In term of the density, the frozen-core approximation corresponds to assume that:

$$n(\mathbf{r}) = n_c^{atom}(\mathbf{r}) + n_v(\mathbf{r}) \tag{1.17}$$

where $n_c^{atom}(\mathbf{r})$ represents the atomic frozen-core charge density and $n_v(\mathbf{r})$ represents the valence charge density. Within this approximation, the problem of treating the core electrons is considered as being solved (i.e. it has been solved at the atomic level), while the study restricts to the investigation of the behaviour of the valence electrons within the ionic potential, partly screened by the core electrons.

We note that the segregation between core and valence electrons so introduced is not necessarily similar to that usually considered by chemists, being in fact arbitrary. In practice, electrons from deep energy levels can always be treated as valence electrons and the partitioning must be performed in order to validate the frozen-core approximation. For instance, in our study of BaTiO₃, the 5s, 5p and 6s levels of barium, the 3s, 3p and 3d levels of titanium, and the 2s and 2p levels of oxygen have been treated as valence states. For LiNbO₃, niobium 4s, 4p, 4d and 5s electrons, lithium 1s and 2s electrons as well as oxygen 2s, 2p electrons were considered as valence states.

The second problem, associated to the oscillation of the valence wave functions inside the core region is solved from the pseudopotential approximation. The latter basically consists in a mathematical transformation in which the ionic potential screened by the core electrons is replaced by another fictitious potential such that the valence wavefunctions remain unchanged beyond a given spatial cutoff distance but are replaced by smoothly varying pseudo-functions inside the core region. The pseudopotential, generated for isolated atoms, is built in such a way that the eigenenergies of the pseudo-problem remain that of the real system. It is then expected that such a potential is *transferable* to the solid or, in other words, that the similarity between the real and pseudo-problem remains valid whatever the modifications of the ionic environment within which the frozen core approximation remains valid.

At the beginning, the pseudopotential approach was relatively empirical. Now, it has become a well-controlled approximation. The potentials are generated from first-principles atomic calculations [59]. Their construction is submitted to a series of constraints that ensure their transferability from one chemical environment to another: norm conservation [74, 75], extended norm conservation [76], chemical hardness conservation [77, 78]. In this context, the pseudopotential is usually not a local potential anymore but has the more general form of a non-local operator, commonly of a separable type [79, 80]. Recently, some progresses were also made for the design of ultra-soft pseudopotentials requiring a minimum number of plane-waves to expand the wave function [81, 82]. A good overview of the pseudopotential concept may be found in the review of Pickett [59].

In our calculations on $BaTiO_3$, we adopted extended norm-conserving, highly transferable pseudopotential, as proposed by M. Teter [78, 57]. For the oxygen, in order to increase the transferability, we included a chemical hardness correction [78]. For LiNbO₃, we used usual Troullier-Martins pseudopotentials.

1.6 Merging of DFT and perturbation theory

Different quantities such as the interatomic force constants, the elastic constants, the dielectric tensor, the Born effective charges, Raman intensities, phonon-phonon coupling (...) are related to various derivatives of the total energy of the system with respect to given perturbations (atomic displacement, macroscopic strain, electric field). As such, they can be access using a perturbative approach.

For the ground-state, we have seen that it is equivalent to minimize a variational expression of the energy or to solve the set of KS equations in order to get the ground-state wave functions, density and energy. Merging these DFT approaches with perturbation theory provides two different ways to determined the changes of density and energy induced by a given perturbation.

In a previous section, we have presented two different alternatives to get the Kohn-Sham total energy of the ground state and associated ground-state density: (i) a minimization of the energy functional, imposing some orthonormalization constraints on the wave functions, and (ii) the self-consistent solution of the one-particle Kohn-Sham equations.

Merging these DFT approaches with perturbation theory provides two different ways to get the changes of wavefunction, density and energy induced by a given perturbation. The formulae that yield to this response are quite complex, and beyond the scope of these notes. They will be not discussed here ³. We will simply mention that the change of the eigenstates at linear order respect the perturbation can be obtained by: (*i*) the minimization of a variational expression for the second derivative of the electronic part of the total energy [43, 85], orthonormalizing the first-order changes in wavefunctions respect the ground-state eigenstates (the variational approach), or (*ii*) solving self-consistently a set of first-order Sternheimer equations [42, 86, 60] that comes from the expansion of the set of Eq. refKS equations to first-order (Sternheimer approach).

In principle this perturbative approach can be set up to any order. In practice, calculations are usually limited to the computation of the first-order change in the wave-functions allowing to access, thanks to the (2n+1) theorem [87]⁴, successive derivatives of the energy (and related quantities) up to the third order.

1.7 Accessible quantities and usual accuracy

The density functional theory within the usual LDA or GGA approximations allows to compute various physical properties with more or less accuracy. The basic quantities directly accessible within DFT are the ground-state total energy of the system and the associated total electronic density.

 $^{^{3}}$ The reader interested can find further technical details in Ref. [[83, 84]] and references therein.

⁴This theorem says that the knowledge of the change in the wave functions up to n-order is sufficient to know the change in the energy up to (2n+1)-order.

The total energy allows to access to cohesive, surface and interface energies. As previously mentionned, within the LDA, the cohesive energy is usually badly described being typically overstimated by 15-20 %. This is due to the fact that this approach is not suitable enough to deal with isolated atoms, where the charge density is a rapidly varying function of the position. Consequently the atomic energies, ingredients to calculate the cohesion energies, are not well reproduced. The values of the cohesion energies are improved within the GGA aproximation. Nevertheless the error in energy differences between different structures is much smaller than that in absolute-energy.

Relaxing the atomic degrees of freedom, it is also possible to perform structural optimisations and to determine cell shape, bond lengths and bond angles with an accuracy usually of the order of a few percent (experimental values of the lattice parameters are usually understimated within LDA by 1-2 %). These optimizations are easily performed thanks to the calculation of the stress tensor and the atomic forces that are associated to first derivatives of the energy with respect to the atomic positions or a macroscopic strain and are therefore directly accessible from the ground-state wave functions thanks to the Hellmann-Feynman theorem [88, 89].

Electronic density plots can be performed. Moreover, Kohn-Sham band structure are also usually produce. Let us emphasize that it concerns the dispersion curves of the *fictitious* Kohn-Sham particles that have no guarantee to be equivalent to those of the *real* interacting electrons of the system (the only guarantee is that both real and fictitious systems produce the same total density in "exact" DFT). In practice, it is observed that the valence bands are relatively well described in DFT while the bandgap is usually largely underestimated. This does not mean that the theory is wrong but that excited properties such as the bandgap are beyond the scope of DFT which is a ground-state theory.

Using pertubation theory, various quantities related to successive derivatives of the energy are also accessible. The case of the Born effective charges and interatomic force constants will be illustrated in the next Chapters. The second derivative, the accuracy is usually around 5 % with the experimental, except for the optical dielectric constant which is often overestimated by 20 % in the case of ABO₃ compounds ⁵

1.8 Conclusions

To conclude, density functional theory has become a standard for the investigation of the properties of solids and molecules. It allows to access various physical quantities with an accuracy usually of few percents. Nowadays, it is considered as a powerfull tool to complement experimental investigations. It allows to perform "computational experiments" wherever the required parameters are unreachable, or the design of new materials with some given desired properties before the real synthesis in the Labs. In the next Chapters, we will illustrate, through selected examples, how it was useful to clarify the behavior of ABO₃ compounds.

⁵This feature has been related to the lack of polarization dependence of usual local functional [90].

1.9 References

Good review of the first-principles density functional theory method are for instance :

- ◇ R. O. Jones and O. Gunnarsson, , Rev. Mod. Phys. 61, 698 (1989).
- M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Iterative minimization technique for ab initio total energy calculations : molecular dynamics and conjugate gradients, Rev. Mod. Phys. 64, 1045 (1992).

Chapter 2

Ground-state properties

2.1 Generalities

In spite of their apparent similarities, ABO_3 ferroelectric oxides crystallize in various forms. At high temperature, they cease to be ferroelectric and they have a highly symmetric reference paraelectric structure. When the temperature is lowered, they undergo one or more phase transitions to ferroelectric states of lower symmetry.

A very important group of ferroelectrics is that known as the *perovskites* (from the mineral perovskite $CaTiO_3$). The ideal perovskite corresponds to a simple cubic unit cell with space group $Pm\overline{3}m$ and 5 atoms located as illustrated in Fig. 2.1 : if the A atom is taken at the corner of the cube, the B atom is at the center and there is an oxygen at the center of each face ; alternatively, if the B atom is taken at the corner, the A atom appears at the center and O atoms are located at the mid-point of each edge.



Figure 2.1: Two different views of the unit cell of the ABO_3 ideal cubic perovskite structure. The B atom (grilled pattern) is at the center of an octahedra composed of oxygen atoms (white pattern). The A atom (dashed pattern) has 12 oxygen first neighbors.

As it appears more clearly in Fig. 2.2, in the perovskite structure, the B atom is at the center of 6 oxygens first neighbors, arranged at the corners of a regular octahedron. The octahedra are linked at their corners into a 3-dimensional framework, enclosing large



Figure 2.2: Another view of the ABO₃ ideal cubic perovskite structure.

holes which are occupied by A atoms. Each A atom has 12 equidistant O atoms. Each O atom is adjacent to 2 B-type and 4 A-type atoms.

The first simple perovskite identified as being ferroelectric is $BaTiO_3$. As $KNbO_3$, it undergoes a sequence of three ferroelectric phase transitions from cubic to slightly distorted structures successively of tetragonal, orthorhombic and rhombohedral symmetry. Some other ferroelectric perovskites that were discovered later (like $PbTiO_3$) only have one phase transition to a tetragonal ground-state.

A few substances are also referred to as multiple-cell perovskites. Their ground-state can be obtained as a distortion of the perfect perovskite but result in a more complex unit cell containing more than one formula unit. Although it is not impossible for such a multiple cell to possess polar symmetry, it is physically less probable, and none of these structures have been shown to be ferroelectric. Some of them are anti-ferroelectric such as PbZrO₃.

Alternatively to the perovskite family, some ferroelectric oxides, such as $LiNbO_3$, have a trigonal paraelectric structure. It consists in a rhombohedral unit cell of $R\overline{3}c$ symmetry with two formula units per unit cell. The positions of the 10 atoms in the rhombohedral primitive unit cell are shown on Figure 2.3. The threefold axis is formed by a chain of equidistant A and B atoms. Each B atom is located at the center of an octahedron formed by 6 oxygen atoms.

As for the perovskites, the trigonal structure is composed of oxygen octahedra containing the B atom and surrounded by the A atoms. However, in this case, both A and B atoms only have 6 oxygens first neighbors.



Figure 2.3: Primitive unit cell of the $R\overline{3}c$ trigonal structure of LiNbO₃. Projections (a) perpendicular and (b) parallel to the three fold axis.

 $LiTaO_3$ has a structure similar to $LiNbO_3$. Both of them undergo a single ferroelectric phase transition when the temperature is lowered. Their ground-state has a structure of R3c symmetry that will be described later.

An empirical criterium for the stability of the perfect perovskite-type structure was put forward by Goldschmidt (1926), based on the rules he had previously derived for ionic binary compounds. His model is based on the concept of ionic radius and the following rules : (i) a cation will be surrounded by as many anions as can touch it, but no more; (ii) all the anions must touch the cations and the anion-cation distance is obtained as the sum of their ionic radii.

The perovskite structure is fully determined by the size of the oxygen octahedra containing the B atoms, while the A atoms must fit the holes between the octahedra. Following the rules of Goldschmidt, this condition provides an ideal relation between ionic radii :

$$r_A + r_O = \sqrt{2}(r_B + r_O).$$
 (2.1)

In practice, this cannot always be exactly satisfied and the deviation can be measured through a tolerance factor t defined as follows :

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}.$$
 (2.2)

Goldschmidt has shown that the perovskite structure is formed when the above condition is satisfied ($t \approx 1$). When t > 1, the structure is imposed by the A–O distance and the B atom is to small for the oxygen octahedron so that the structure will evolve to a small polar distortion as in BaTiO₃. At the opposite, when t < 1, the A atom is small in comparison to the hole between the oxygen octahedra : the A atom cannot afford bonding with 12 neighboring O atoms and the compound will evolve to a structure with only 6 neighbors for the A atom as in $LiNbO_3$.

The lattice constants and atomic positions of the ABO₃ compounds can be experimentally determined and numerous data are available. A structural optimization is also easily performed within density functional theory (DFT). As discussed in Chapter , it basically consists in determining the atomic configuration which minimizes the total energy of the system (or its electric enthalpy for the polar phases). The calculation is based on the computation of three quantities directly accessible from the ground-state electronic wavefunctions : the total energy and its first-order changes with respect to atomic displacements (the forces) and to macroscopic strains (the stress tensor).

In the remaining part of this section, we focus on the structure and electronic properties of two prototype compounds : $BaTiO_3$ and $LiNbO_3$. We describe the results we have obtained with the ABINIT package ¹, a standard code for plane-wave/pseudopotential DFT calculations. Structural relaxations have been performed within the local density approximation (LDA) except when it is explicitly mentionned. Technical details are reported in Ref. [91] for $BaTiO_3$ and Ref. [92] for $LiNbO_3$.

2.2 Crystal structure

2.2.1 Barium titanate

As previously stated, barium titanate cristallizes at high temperature in a paraelectric cubic perovskite structure ($Pm\overline{3}m$). When the temperature is lowered, it undergoes a sequence of 3 ferroelectric phase transitions (Fig. 2.4).

Around 130°C, its structure transforms from cubic to tetragonal (P4mm). This phase remains stable until about 5°C, where there is a second transformation to a phase of orthorhombic symmetry (Pmm2). The last transition arises around -90° C. The low temperature ferroelectric phase is rhombohedral (P3m1). Each transition is accompanied by small atomic displacements and a macroscopic strain. In the successive ferroelectric phases, the polar axis is aligned respectively along the <100>, <110> and <111> directions corresponding to the direction of the atomic displacements with respect to their position in the reference cubic structure.

Paraelectric phase

In the cubic phase of $BaTiO_3$, the positions of the atoms in the unit cell are imposed by symmetry. Choosing the barium atom as reference, the atomic positions are (in reduced coordinates):

Ba :
$$(0.0, 0.0, 0.0)$$

Ti : $(0.5, 0.5, 0.5)$

¹ABINIT is a powerful DFT code developped in collaboration by different groups all over the world. It is a free package accessible at the URL : http://www.abinit.org.



Figure 2.4: The 4 phases of $BaTiO_3$

```
\begin{array}{rrrr} O_1 & : & (0.5, 0.5, 0.0) \\ O_2 & : & (0.5, 0.0, 0.5) \\ O_3 & : & (0.0, 0.5, 0.5) \end{array}
```

During a structural optimization performed from first-principles, the only degree of freedom that must be relaxed is therefore the lattice parameter a_o . Its equilibrium value can be determined as the one which minimizes the total energy. Equivalently, it can be obtained as the value for which the hydrostatic pressure on the material is zero².

The results of our calculations are presented in Figure 2.5. We deduce for the equilibrium lattice parameter a value of 3.943 Å. This result is similar to that reported from other previous LDA calculations ($a_o=3.94$ Å from Ref. [93], $a_o=3.95$ Å from Ref. [94]). It only slightly underestimates the experimental lattice constant of 4.00 Å. We note that a better agreement can be obtained within a "weighted density approximation" (WDA) [66, 95]. The bulk modulus, deduced from the curvature of the energy around its minimum, is valued at 189 GPa, in close agreement with another value of 188 GPa, deduced from results reported by King-Smith and Vanderbilt [96].

For the cubic phase, the cohesive energy has also been obtained as the difference between the energy per unit cell of the solid and the energy of the respective free atoms. At the experimental volume, we estimated $E_{\rm coh}$ at -38.23 eV/cell. A previous value equal to -31.16 eV/cell was reported by Weyrich and Siems [97, 32]. The better agreement of their result with the experimental value of -31.57 eV/cell is probably accidental, since

²Within the plane-wave technique we have used, the second approach requires an additional "Pulay correction" [73] in order to compensate for the incompleteness of the finite basis set



Figure 2.5: Determination of the optimized lattice constant of cubic $BaTiO_3$.

Weyrich and Siems determined the free atom energies from non-spin-polarized LDA. In our case, the spin-polarized correction decreased the value of $E_{\rm coh}$ by 5.17 eV/cell.

Let us mention that the small underestimate of the lattice constant and the overestimate of the cohesive energy we have reported above are typical of the LDA and similar to what is also achieved on other ABO_3 compounds.

Ferroelectric phases

In the ferroelectric phases, the specification of the unit cell requires more than one parameter. Moreover, the ionic positions are not fully determined by symmetry, but must be relaxed simultaneously. The tetragonal, orthorhombic and rhombohedral structures contain respectively 5, 6 and 5 atomic degrees of freedom.

A full structural optimization requires to relax together all these different degrees of freedom. However, as it was pointed out by many authors [93, 98, 94, 99], the ferroelectric instability of ABO_3 compounds is strongly sensitive to the volume. In this context, the volume underestimation within the LDA, albeit small, appears problematic. We attempted a full relaxation of the rhombohedral phase. However, in the final optimized structure, the ferroelectric instability had nearly disappeared: due to the underestimate of the lattice constant, the shift of the atoms from their centrosymmetric position became anomalously small.

It was observed that the correct simulation of different properties of ABO₃ compounds (like the phase transition temperature [20]) requires to work at the experimental lattice constants rather than at the LDA optimized one. As they are accurately obtained from Xray diffraction data [100], in the following calculations, we chose to adopt the *experimental* lattice parameters. We note that results obtained by Singh [66] raise the hope that problems associated to the LDA underestimate of the optimized volume are solved when using a weighted density approximation (WDA).

In our computations, all the atomic positions have been relaxed concurrently until

Phase	Atom	Position
Tetragonal	Ba	$(0.0,\ 0.0,\ 0.0)$
	Ti	$(0.5, 0.5, 0.5 + \Delta_{T-Ti})$
	O_1	$(0.5, 0.5, 0.0 + \Delta_{T-O1})$
	O_2	$(0.5, 0.0, 0.5{+}\Delta_{T-O2})$
	O_3	$(0.0, 0.5, 0.5{+}\Delta_{T-O2})$
Orthorhombic	Ba	(0.0, 0.0, 0.0)
	Ti	$(0.5, 0.5 + \Delta_{O-Ti}, 0.5 + \Delta_{O-Ti})$
	O_1	$(0.5, 0.5 + \Delta_{O-O1}, 0.0 + \Delta_{O-O2})$
	O_2	$(0.5, 0.0 + \Delta_{O-O2}, 0.5 + \Delta_{O-O1})$
	O_3	$(0.0, 0.5 + \Delta_{O-O3}, 0.5 + \Delta_{O-O3})$
Rhombohedral	Ba	$(0.0,\ 0.0,\ 0.0)$
	Ti	$(0.5 + \Delta_{R-Ti}, 0.5 + \Delta_{R-Ti}, 0.5 + \Delta_{R-Ti})$
	O_1	$(0.5 + \Delta_{R-O1}, 0.5 + \Delta_{R-O1}, 0.0 + \Delta_{R-O2})$
	O_2	$(0.5 + \Delta_{R-O1}, 0.0 + \Delta_{R-O2}, 0.5 + \Delta_{R-O1})$
	O_3	$(0.0+\Delta_{R-O2}, 0.5+\Delta_{R-O1}, 0.5+\Delta_{R-O1})$

Table 2.1: Notation of atomic positions (in reduced coordinates) in the three ferroelectric phases of $BaTiO_3$, used in Tables 2.2–2.3–2.4.

the residual forces on the atoms are smaller than 10^{-5} Hartree/bohr. Similar theoretical optimizations of atomic positions were reported previously for the tetragonal and rhombohedral symmetry [94], but keeping the lattice parameters of the cubic phase. In the present work, we perform the structural optimization at the experimental lattice parameters corresponding to each phase. Moreover, for the tetragonal and rhombohedral symmetry, we also investigate the influence of the macroscopic strain, associated to the phase transitions. Our calculations have been performed on a $6 \times 6 \times 6$ mesh of special **k**-points, that was checked by different authors to be sufficiently accurate [94, 101].

The notations adopted for the atomic positions in reduced coordinates are reported for the different phases in Table 2.1. The Ba atom has been chosen as the reference and remains localized at (0,0,0). In each phase, the Ti atom is slightly displaced from its central position, along the polar axis. Due to the symmetry, only two oxygen atoms are equivalent in the tetragonal (O₂ and O₃) and orthorhombic (O₁ and O₂) structures. In the rhombohedral phase, all the oxygen are equivalent, as in the cubic phase. Results of the optimization are reported in Table 2.2, Table 2.3, and Table 2.4.

In the orthorhombic structure (Table 2.3) our atomic positions compare well with the experiment. We probably slightly overestimate the Ti atom shift. However, there is a large spread in the experimental Ti displacements, reported by Kwei *et al.* [100], so that part of the observed discrepancy should be attributed to the experimental uncertainty.

For the rhombohedral phase (Table 2.4), our results are close to those of King-Smith and Vanderbilt [94]. The difference observed for Δ_{R-O1} could be due to the better accu-

a_0	c_0	Δ_{T-Ti}	Δ_{T-O1}	Δ_{T-O2}	Reference
3.994	4.036	0.0143	-0.0307	-0.0186	Present
3.986	4.026	0.015	-0.023	-0.014	Ref. [102]
3.994	4.036	0.0215	-0.0233	-0.0100	Ref. [100]
_	_	0.014	-0.0249	-0.0156	Ref. [103]
_	—	0.0135	-0.0250	-0.0150	Ref. [104]
_	—	0.0135	-0.0243	-0.0153	Ref. [105]
4.00	4.00	0.0129	-0.0248	-0.0157	Present
4.00	4.00	0.0138	-0.0253	-0.0143	Ref. [94]

Table 2.2: Lattice parameters (Å) and atomic displacements (see Table 2.1) in the tetragonal phase of BaTiO₃.

Table 2.3: Lattice parameters (Å) and atomic displacements (see Table 2.1) in the orthorhombic phase of BaTiO₃.

	Present	Ref. [100]	Ref. [100]	Ref. [102]
a_0	3.984	3.984	3.981	3.990
b_0	5.674	5.674	5.671	5.669
c_0	5.692	5.692	5.690	5.682
Δ_{O-Ti}	0.0127	0.0079	0.0143	0.010
Δ_{O-O1}	-0.0230	-0.0233	-0.0228	-0.016
Δ_{O-O2}	-0.0162	-0.0146	-0.0106	-0.010
Δ_{O-O3}	-0.0144	-0.0145	-0.0110	-0.010

Table 2.4: Lattice parameters (\mathring{A}) and atomic displacements (see Table 2.1) in the rhombohedral phase of BaTiO₃.

a_0	α	Δ_{R-Ti}	Δ_{R-O1}	Δ_{R-O2}	Reference
4.001	89.87°	-0.011	0.0133	0.0192	Present
4.001	89.87°	-0.013	0.011	0.018	Ref. [105]
4.004	89.87°	-0.011	0.011	0.018	Ref. [106]
4.003	89.84°	-0.013	0.011	0.019	Ref. [100]
4.00	90.00°	-0.011	0.0129	0.0191	Present
4.00	90.00°	-0.012	0.0105	0.0195	Ref. [94]

racy imposed in our calculation ³. In addition, it is observed that the macroscopic strain, small for this phase, has no influence on the atomic positions.

On the contrary, for the tetragonal distortion (Table 2.2), we observe that the elongation of the c axis favors a larger displacement of the Ti and O atoms. This result confirms the important role of the macroscopic strain in the stabilization of the tetragonal structure [98, 107]. Keeping the lattice parameters of the cubic phase, our displacements are close to those deduced by King-Smith and Vanderbilt, and in good agreement with experimental data. However, considering the experimental tetragonal unit cell, we overestimate the atomic displacements of Ti and O atoms. Similarly to the underestimation of the lattice constant, this feature should be assigned to the LDA, which usually shortens the bond lengths. This problem might be more stringent for the tetragonal structure for which the Ti displacements are along a rather covalent bond.

2.2.2 Lithium niobate

Contrary to barium titanate, LiNbO₃ crystallizes at high temperature in a paraelectric structure of trigonal symmetry (R $\overline{3}$ c). When the temperature is lowered, it undergoes at 1480 K a phase transition to a ferroelectric ground state of R₃c symmetry. The ferroelectric phase corresponds to a small distortion of the paraelectric state. Both phases are rhombohedral with 10 atoms in the unit cell. Their geometry can be described using the primitive (rhombohedral) unit cell as mentionned previously in this Chapter. Alternatively, we can also consider a non-primitive hexagonal unit cell. This is the most usual choice in the litterature which is therefore also adopted in the following part of this Section. In the discussion of our results, the symbols *a* and *c* correspond to the lengths of the basis vectors of the hexagonal unit cell and the atomic positions are given in hexagonal coordinates.

Paraelectric phase

The paraelectric phase belongs to the space group $R\overline{3}c$. The positions of the 10 atoms in the primitive rhombohedral unit cell were illustrated in Fig. 2.3. This unit cell is defined by 3 vectors **a**', **b**' and **c**' of length *a*' and forming angle α '. Here, instead, we will consider an hexagonal unit cell, build from the vectors **a**, **b** and **c** and related to the primitive one as sketched on Fig. 2.6. The **c** vector is aligned along the three fold axis. The **a** and **b** axis are perpendicular to it , have both the same length and define and angle of 120°.

In Fig. 2.7, we show the atomic positions in the hexagonal unit cell. As in Fig. 2.3, we have chosen views in directions perpendicular and parallel to the three fold axis. In Fig. 2.8 we show another view in a direction perpendicular to the **b** and **c** vectors in which LiNbO_3 appears composed of alternative planes of atoms. One is composed of Nb

³Contrary to us, King-Smith and Vanderbilt only relaxed the atomic positions until forces are less than 10^{-3} Hartree/Bohr. This criterion seems not sufficient to guarantee a well converged result, since the forces computed at the experimental atomic positions are already of the order of 10^{-3} Hartree/Bohr.



Figure 2.6: Hexagonal and rhombohedral unit cell of LiNbO₃



Figure 2.7: Atomic positions in the hexagonal unit cell of $LiNbO_3$. Views in directions perpendicular and parallel to the three fold axis.

atoms while the other one is contains both Li and O atoms. Two successive planes are separated by a distance c/12.



Figure 2.8: Atomic positions in the hexagonal unit cell of $LiNbO_3$. View in a direction perpendicular to **b** and **c** vectors.

In summary, from Fig. 2.3, $LiNbO_3$ can be viewed as Nb-Li chains along the three-fold axis, with each Nb at the center of an oxygen octahedra. Alternatively, from Fig. 2.8, it can also be considered as alternating planes along the three-fold axis : the first one is composed of Nb atoms while the other one contains both Li and O atoms.

In Table 2.5, we define the parameters that determine the atomic positions by reporting the hexagonal coordinates of five atoms of the rhombohedral unit cell. The coordinates of the other atoms can easily be obtained by using the symmetry operations of the space groups $R\overline{3}c$ and R3c.

In the paraelectric phase, the positions of the niobium and lithium atoms are fixed by symmetry while the positions of the oxygen atoms are determined by the internal parameter x. The results of our structural optimizations are summarized in Table 2.6. They are compared to the results obtained by Parlinski *et al.* [108] and Caciuc *et al.* [109] as well as to the experimental values deduced from neutron diffraction on a powder [110]. The calculations have been performed with two different exchange-correlation functionals. The GGA gives the closest agreement with the experiment whereas our LDA results present errors similar to those of the previous DFT calculations (also performed within the LDA). .

Phase	Atom			Position		
Paraelectric	Nb_1	(0,	0,	0)
	Li_1	(0,	0,	$\frac{1}{4}$)
	O_1	($-\frac{1}{3}$,	$-\frac{1}{3} + x$,	$\frac{7}{12}$)
	O_2	($\frac{1}{3}-x,$	-x,	$\frac{7}{12}$)
	O_3	(x,	$\frac{1}{3}$,	$\frac{7}{12}$)
Ferroelectric	Nb_1	(0,	0,	0)
	Li_1	(0,	0,	$\frac{1}{4} + z$)
	O_1	($-\frac{1}{3}-u$,	$-\frac{1}{3}+v$,	$\frac{7}{12} - w$)
	O_2	($\frac{1}{3} - v$,	-u - v,	$\frac{7}{12} - w$)
	O_3	(u + v,	$\frac{1}{3} + u$,	$\frac{7}{12} - w$)

Table 2.5: Atomic positions (in hexagonal coordinates) in the two phases of litihium niobate

Table 2.6: Lattice constants and atomic position parameter x (see Table 2.5) in the paraelectric phase of lithium niobate.

	a(A)	$c(\text{\AA})$	x
Exp. [110]	5.289	13.848	0.060
Calc. (LDA) [109]	5.138	13.499	0.049
Calc. (LDA) [108]	5.097	13.708	0.036
Present (LDA)	5.125	13.548	0.042
Present (GGA)	5.255	13.791	0.048

Ferroelectric phase

The ferroelectric phase belongs to the space group R3c. It corresponds to a small distortion of the paraelectric phase as illustrated in Fig. 2.9 where the arrows indicate the atomic displacements at the phase transition.



Figure 2.9: Atomic displacements during the ferroelectric phase transition of $LiNbO_3$.

During the structural optimizations, we held the niobium Nb₁ atom fixed at the origin. The coordinates of the lithium and oxygen atoms are reported in the lower part of Table 2.5. Our results for the ferroelectric phase are summarized on Table 2.7. As for the paraelectric phase, our values are close to those of Parlinski *et al.* [108]. Again, we tried to improve the accuracy of the calculation using the GGA. However, this does not yield a significative improvement: looking for example at the value of the parameter a, we observe that the GGA tends to overcorrect the errors of the LDA, a fact already observed in this kind of calculations [111, 112].

Comparing Table 2.6 and 2.7, we see that our values for the lattice parameters are in better agreement with the experiment for the ferroelectric than for the paraelectric phase. A possible explanation is that within our calculation is artificially performed at 0 K and we thus neglected the effects of the thermal expansion. As the paraelectric phase of lithium niobate is only stable above 1480 K, these effects are more important for this phase than for the ferroelectric one and the calculated parameters tend to be smaller than the measured ones.

2.3 Chemical bond and electronic structure

ABO₃ compounds are usually classified as ionic materials. As such, barium titanate is sometimes consider in simple models as a $Ba^{2+}Ti^{4+}O_3^{-2}$ crystal. If this picture is essentially true, we must emphasize that on top of their main ionic character, the ABO₃

	$a(\mathrm{\AA})$	c(A)	z	u	v	w
Exp. [110]	5.151	13.876	0.0329	0.00947	0.0383	0.0192
Calc. (LDA) [108]	5.086	13.723	0.0350	0.01497	0.0247	0.0186
Present (LDA)	5.067	13.721	0.0337	0.01250	0.0302	0.0183
Present (GGA)	5.200	13.873	0.0318	0.00973	0.0382	0.0199

Table 2.7: Lattice constants and atomic position parameters (see notations of Table 2.5) in the ferroelectric phase of lithium niobate.

compounds also present some covalent features. In the next Chapters, we will see that it is precisely this small covalent interaction and the mixed ionic-covalent nature of their bonding which is at the origin of their interesting properties.

A first empirical indication of the partial covalent character of their bonding arises from the inspection of the lattice constants. On the basis of tabulated values for the ionic radii (corrected by the appropriate coordination corrections proposed by Pearson) it is possible to deduce a lattice constant of 4.16 Å for $BaTiO_3$. This result significantly overestimates the experimental value around 4.00 Å, therefore suggesting that the bond length has been shortened by partial covalent interactions and that the bonding is not purely ionic.

A better and more complete insight on the electronic properties of ABO_3 compounds can be obtained from the inspection of their electronic band structure. In what follows, we discuss the Kohn-Sham electronic band structures of $BaTiO_3$ and $LiNbO_3$ as they were computed for the different optimized structures.

2.3.1 Barium titanate

In Figure 2.10, we show the electronic band structure of the cubic phase of $BaTiO_3$. Its shape corresponds to that expected for a rather ionic material. It is globally composed of well separated sets of bands, located in the same energy regions than the different orbitals of the isolated atoms. Each of these sets of bands has a marked dominant character and is labeled by the name of the atomic orbital that mainly composes this energy state in the solid.

The position of the different energy levels can be compared to the experimental data [113]. The results presented in Table 2.8 show a good agreement with the experimental findings, despite a systematic underestimation of the energy separation from the valence edge, a well-known characteristics of the LDA.

As previously mentionned, in spite of its mainly ionic character, $BaTiO_3$ has also some covalent features. First, there is a well-known hybridization between O 2p and Ti 3d orbitals. The four electrons of the Ti 3d orbitals are not completely transferred to the oxygen atoms, but remain partly delocalized on Ti. This clearly appears from

Band	Ref. [113]	(Cubic	Ron	nbohedral
Ti 3d		R	+4.23	R	+4.49
			+2.98		+3.39
		Γ	+1.72	Γ	+2.29
O 2p	0.0	R	0.00	R	0.00
			-2.27		-2.21
	-5.5	Γ	-4.54	Γ	-4.42
Ba 5p		Λ	-9.41	Х	-9.40
	-12.2		-10.02		-10.02
		R	-10.63	R	-10.61
O 2s		Х	-15.56	Х	-15.52
	-18.8		-16.20		-16.15
		Х	-16.84	Х	-16.78
Ba 5s		R	-24.46	R	-24.45
	-27.0		-24.60		-24.59
		Γ	-24.73	Γ	-24.72
Ti 3p		М	-32.47	Γ	-32.22
	-34.4		-32.50		-32.25
		Х	-32.53	Х	-32.28
Ti 3s		R	-55.89	R	-55.60
			-55.89		-55.60
		Γ	-55.89	Γ	-55.60

Table 2.8: Top, middle and bottom values (eV) of the different electronic bands of cubic and rhombohedral $BaTiO_3$.


Figure 2.10: (a) Brillouin zone of cubic BaTiO₃. (b) Kohn-Sham electronic band structure of cubic BaTiO₃ along different high symmetry lines of the Brillouin zone.

the inspection of the static ionic charges, obtained by integrating the electronic density around each atom : the Ti charge is not of +4 but rather 2.50–3.00 [93, 114, 115].

In terms of band theory, the incomplete transfer of Ti 3d electrons to the oxygen ions means that there is some admixture of Ti 3d character to the O 2p bands. This feature was already clearly identified from the overlap integrals in early LCAO band structure calculations on ABO₃ compounds [116, 117]. It was often considered as an essential feature to explain the ferroelectricity in these materials [22]. It was confirmed by recent experiments [113] and was also clearly illustrated from DFT by the analysis of partial density of states (DOS) [97, 98, 107].

Less spectacular, the hybridization between Ba 5p and O 2p orbitals is sometimes controversial. In simple models, Ba is indeed usually considered as ionic in BaTiO₃. The interaction of Ba with other atoms was however detected in LCAO calculations [118], and even in DFT from partial DOS [97, 98]. It was discussed by Pertosa and Michel-Calendini [118] who have shown that it has only small consequences on the band structure. However, it might have a more significant influence on other properties. For instance, it was suggested that its presence should enhance the Ti-O interaction [119]. More recently, it was also invoked to explain the origin of some non-negligible contributions to the Born effective charges [120], as it will be discussed in the next Chapter.

The computed bandgap is indirect $(R \to \Gamma)$ in cubic BaTiO₃ and equal to 1.72 eV. The direct gap at Γ is of 1.84 eV. However, these values cannot be compared to the experiment

due to the DFT bandgap misfit ⁴.

Due to a different reason, the identification of the *experimental* value of the bandgap was also for long under discussion. In ABO₃ perovskite materials, the interband absorption edge displays Urbach-rule behaviour [121]: the absorption coefficient increases exponentially with increasing photon energy, so that no uniquely defined bandgap can be extracted from absorption measurements. A realistic value of 3.2 eV was nevertheless estimated by Wemple [121] in the cubic phase. It was attributed to the direct gap at the Γ point [122].

Going now from cubic the rhombohedral structure (Figure 2.11), significant changes in the bands are observed, especially when considering the small atomic displacements and macroscopic strains involved in the phase transition. First, the energy gap increases from 1.72 eV to 2.29 eV. This evolution is consistent with an intensification of the O 2p – Ti 3d hybridization, as expected when going from the cubic to a ferroelectric phase [33]. Such a trend in the hybridization was confirmed from partial DOS for rhombohedral KNbO₃ and KTaO₃ [99]. As for BaTiO₃, it was accompanied in that compounds by a small reduction of the O 2p bandwidth. Moreover, we observe a small but significant *chemical shift* of the Ti 3s (0.25 eV) and Ti 3p (0.29 eV) bands with respect to the Ba and O levels. This feature corroborates a modification of the electronic environment of the Ti atom in the rhombohedral structure.

The reinforcement of the covalent character is not a particular feature of the rhombohedral phase. A modification of the O 2p - B d hybridizations have been observed in the tetragonal structure of different ABO₃ compounds [33, 98]. For indication, in our calculation, the indirect gap between A and Γ becomes equal to 2.27 eV in the tetragonal phase. A similar evolution is expected when going from the cubic to the orthorhombic phase.

2.3.2 Lithium niobate

In Figure 2.12, we report the Kohn-Sham band structure of the paraelectric phase of lithium niobate obtained within the LDA. The notations of the high symmetry points between which we have drawn the band structure correspond to those chosen in Ref. [[123]]. As for BaTiO₃, we observe the presence of well separated groups of bands. Each of these groups has a marked dominant character and has been labeled by the name of the atomic orbital that mainly composes this energy state in the solid.

As previously discussed by Inbar and Cohen [124, 125], the chemical bonding in lithium niobate has also a mixed covalent-ionic character. The Nb 4d and O 2p atomic orbitals strongly interact to form the valence and conduction bands near the Fermi level while the Li atoms completely loose their 2s electrons. In other words, the bonding between niobium and oxygen atoms has a non-negligible covalent character while the bonding with the lithium atoms is essentially ionic.

⁴The bandgap problem is a well-known feature of the DFT [58]. Let us recall that this discrepancy only concerns the excitation energies; it does not influence the accuracy obtained on the ground-state properties, that should be obtained correctly within DFT.



Figure 2.11: Comparison of the Kohn-Sham electronic band structure of cubic and rhombohedral $BaTiO_3$ along different high symmetry lines of the Brillouin zone.



Figure 2.12: (a) Brillouin zone of the paraelectric phase of $LiNbO_3$. (b) Kohn-Sham electronic band structure in the paraelectric phase of $LiNbO_3$ calculated within the LDA.

The transition to the ferroelectric state mainly affects the bands in the region close to the Fermi level. In LDA, the indirect bandgap E_g increases from 2.60 to 3.48 eV and the spread of the O 2p bands reduces from 5.06 to 4.71 eV (Fig. 2.13). In GGA, we obtained similar values for E_g (2.51 and 3.50 eV) while the O 2p group is narrower than in LDA in both the paraelectric (4.80 eV) and the ferroelectric phase (4.48 eV). We note that, in spite of the well known DFT bandgap problem [58], the values of the E_g in the ferroelectric phase only slightly underestimate the experimental value of 3.78 eV [126]. For the deeper bands the spread remains unaffected at the transition while the position with respect to the top of the valence band is slightly shifted to higher energies. We conclude that the only significant effect of the phase transition on the electronic properties is to modify the hybridizations between O 2p and Nb 4d orbitals.



Figure 2.13: Kohn-Sham electronic band structure in the paraelectric (lines) and ferroelectric (dots) phases of LiNbO_3 calculated within the LDA.

2.4 Conclusions

To summarize, most ABO_3 compounds cristallizes in the perovskite structure but some of them, for which the tolerance factor of Goldschmidt is significantly smaller than 1, adopt a trigonal symmetry. In all cases, the ferroelectric phase corresponds to a slight polar distortion of the paraelectric reference structure.

The bonding in this class of compound is essentially ionic. However, it also exhibits some covalent features. These essentially consist in a non-negligible hybridization between B-metal d levels and oxygen 2p orbitals. At the phase transitions, there is an increase of the bandgap and a narrowing of the O 2p and metal d bands.

2.5 References

A extensive review of the properties of ferroelectric compounds is given in :

 M. E Lines and A. M. Glass, Principles and applications of Ferroelectrics and related materials, Ed. by W. Marshall and D. H. Wilkinson, Clarendon Press, Oxford (1977).

The results presented in this Chapter have been discussed in the following references:

- ◇ Ph. Ghosez, X. Gonze and J.-P. Michenaud, Structural and electronic properties of barium titanate from first-principles, Ferroelectrics 220, 1-15 (1999).
- ◊ M. Veithen and Ph. Ghosez, First-Principles study of the dielectric and dynamical properties of lithium niobate, Phys. Rev. B, in press (to appear in 2002).

Chapter 3

Static and dynamical ionic charges

3.1 Introduction

For a long time, there has been a continuing interest in the definition of atomic charges in solid state physics as well as in chemistry [127, 128, 129, 130]. This interest lies essentially in the fact that the concept of atomic charge naturally arises in a large diversity of frameworks and is frequently helpful for a simple description of solids and molecules. The variety of contexts in which the charge is involved (IR spectrum analysis, XPS chemical shifts analysis, theory of ionic conductivity of oxides, determination of electrostatic potential, definition of oxidation states...) underlines its central role but also reveals a concomitant problem: inspired by various models or by the description of various physical phenomena, many different definitions have been proposed that, unfortunately, are not equivalent [130].

Following a distinction already made by Cochran [127], it seems possible to classify the different concepts into static and dynamical charges. The *static* charge is an intuitive concept, usually based on a partitioning of the ground-state electronic density into contributions attributed to the different atoms. It is an ill-defined quantity that depends on the convention artificially chosen to affect a given electron to a particular ion [127, 128]. On the other hand, the *dynamical* charge is directly related to the change of polarization (or dipole moment, for molecules) created by an atomic displacement. This change of polarization is a quantity that can be experimentally measured, at least in principles, giving the dynamical charge a well-defined character.

In order to clarify the concept of atomic charge, it was important to compare on practical examples the numerical results obtained from its different definitions. Recent studies of the statistical correlation between various atomic charges using a principal component analysis have suggested that the different definitions are not independent but correspond to different scales driven by a unique underlying physical factor [130]. If this assertion seems plausible as far as static charges are concerned, we will argue that the dynamical charge should not reduce to the same physical factor but should also depend on an additional parameter: the rate of transfer of charge, influenced by the bonding with the other atoms of the system and additionally, for large systems, by the condition imposed on the macroscopic electric field.

The Born effective charge tensor $Z^{*(T)}$ – alias transverse charge –, that is at the center of the present Chapter, is a dynamical quantity introduced by Born [131] in 1933. In solid state physics, it is since a long time considered as a fundamental quantity because it monitors the long-range Coulomb interaction responsible of the splitting between transverse and longitudinal optic phonon modes [131]. During the seventies, the Born effective charges were already investigated and discussed within empirical approaches (see for example Harrison [132]). More recently, they became accessible to first-principles calculations [42, 43, 35], and accurate values have been reported for a large variety of materials.

For the case of ABO₃ compounds, old experimental data [133] and empirical studies [132] had suggested that the amplitude of the Born effective charges should deviate substantially from the amplitude of the static atomic charge. Surprisingly, this result remained in the dark until first-principles calculations confirmed that the components of $Z^{*(T)}$ are anomalously large in these oxides [134, 135, 136]. It was observed that the components of $Z^{*(T)}$ can reach twice that of the nominal ionic charges. This result reopened the discussion on the physics of the Born effective charges and different recent studies tried to clarify the microscopic processes monitoring the amplitude of $Z^{*(T)}$.

In this Chapter, we first clarify the relationship between various atomic charges. We then present results concerning $BaTiO_3$ and $SrTiO_3$ in order to illustrate how a careful analysis of the Born effective charges can teach us interesting physics concerning these compounds. It reveals the mixed ionic and covalent character of the bond [137, 138]. It allows to visualize the mechanism of polarization as electronic currents produced by dynamical changes of orbital hybridizations [132, 138]. It also clarifies the origin of the giant destabilizing dipole-dipole interaction producing the ferroelectric instability of these materials [53].

In Section II and III, we contrast the concepts of static and dynamical charges and we reintroduce the Born effective charge that is at the center of the present discussion. In Section IV, we compare various results obtained within different frameworks for the paraelectric phase of BaTiO₃, SrTiO₃ and LiNbO₃. We also discuss the origin of the large anomalous contributions in terms of local electronic polarizability and dynamical changes of orbital hybridization. A decomposition of the role played by the different bands is reported in Section V. Section VI is devoted to the evolution of the Born effective charges in the three ferroelectric phases of BaTiO₃ as well as in the cubic phase under hydrostatic pressure. This points out the role of the anisotropy of the atomic environment on the amplitude of $Z^{*(T)}$. Finally, in Section VII, we report the evolution of the effective charges all along the path of atomic displacements from the cubic to the rhombohedral phase and we estimate the spontaneous polarization of the three ferroelectric phases of BaTiO₃.

	Z_{Ba}	Z_{Ti}	Z_0	Reference
Nominal	+2	+4	-2	
Empirical models	+2.00	+0.19	-0.73	Ref. [132]
	+1.40	+2.20	-1.20	Ref. [139]
	+2.00	+1.88	-1.29	Ref. [140]
	+1.86	+3.18	-1.68	Ref. [141]
	+1.48	+1.86	-1.11	Ref. [142]
	+2.00	+1.86	-1.29	Ref. [143]
First-principles calculations	+2.00	+2.89	-1.63	Ref. [93]
	+2.12	+2.43	-1.52	Ref. [114]
	+1.39	+2.79	-1.39	Ref. [115]

Table 3.1: Static charges of $BaTiO_3$ in the cubic structure.

3.2 The concept of static charge

Intuitively, the atomic charge may first appear as a static concept. The charge associated to an isolated atom is a well-defined quantity. The purpose of defining static atomic charges is therefore to extend this notion to molecules and solids. For these cases, the challenge basically consists to replace the delocalized electronic density by localized point charges associated to each atom. This could a priori be performed from electronic density maps obtained experimentally or theoretically. However, as already mentioned by Mulliken [128] in 1935, "there are some difficulties of giving exact definition without arbitrariness for any atomic property". During the seventies, Cochran [127] similarly emphasized that the partition of the electronic distribution into atomic charges can only be done unambiguously when "boundary can be drawn between the ions so as to pass through regions in which the electron density is small compared with the reciprocal of the volume inclosed". This is never the case in practice, and especially when there is appreciable covalent bonding. For most of the solids and molecules, there is consequently no absolute criterion to define the static atomic charge and a large variety of distinct definitions have been proposed that are not necessarily quantitatively equivalent (see for instance Ref. [129, 130]).

As an illustration, different approaches have been considered in order to evaluate the amplitude of the static atomic charges of barium titanate. Some results are summarized in Table 3.1, where different atomic charges are reported in comparison with the nominal charges expected in a purely ionic material (+2 for Ba, +4 for Ti, -2 for O). Some of them were obtained from empirical models; others were deduced from first-principles. The static atomic charges of Ref. [132] were deduced by Harrison within his bond orbital model using universal parameters and neglecting the interactions with the Ba atom. The atomic charges reported by Hewat [139] were approximated from a model initially designed by Cowley [144] for SrTiO₃. The charges reported by Khatib *et al.* [141] have been obtained

in a shell-model context. In two references, Turik and Khasabov [142, 143] estimated the charges from the Madelung constant thanks to a fit of the crystal energy with shell-model parameters. Michel-Calendini *et al.* [140] proposed charges from a population analysis of the X α electronic distribution of a TiO₆ cluster, assuming a charge of +2 on Ba. Cohen and Krakauer [93] deduced the atomic charges from a fit of the DFT-LDA electronic distribution by that of overlapping spherical ions (generated according to the potential induced breathing model) for different ionic configurations. Xu *et al.* [114] reported values deduced from a Mulliken population analysis of a self-consistent OLCAO calculation ¹. In another reference [115], Xu *et al.* proposed different values by integrating the electronic charges in spheres centered on the ions, and partitioning rather arbitrarily the remaining charge outside the spheres following a method proposed in Ref. [145, 146].

The results of Table 3.1 are not quantitatively identical and illustrate that there is no formal equivalence between the different procedures used to define the atomic charge. However, in agreement with an analysis reported by Meister and Schwartz [130] for the case of molecules, we observe that the values of Table 3.1 have some common features, suggesting that the different charges are not independent but should correspond to different scales driven by a common factor.

In particular, all the calculations reveal that the charge transfer from Ti to O is not complete. If $BaTiO_3$ was a purely ionic crystal, the 3d and 4s electrons of Ti would be entirely transferred to the oxygen atoms, yielding a charge of +4 on titanium. However, due for instance to the partial hybridization between O 2p and Ti 3d states [119, 113, 117, 147, 148, 97, 98], these electrons remain partly delocalized on the Ti atom so that the static charges on the Ti and O atoms are smaller than they would be in a purely ionic material. This delocalization is illustrated in Figure 3.1, where we have plotted the partial electronic density associated to the O 2p bands. For the Ba atom, the situation is not so clear than for titanium but most of the studies suggest similarly that the 6s electrons are not fully transferred to the oxygen.

From the previous examples, it is clear that, strictly speaking, the static charge does not give a quantitative information. In the study of mixed ionic-covalent compounds, it remains however a useful concept to discuss qualitatively the transfer of charges from one atom to the other. As a general rule, the partial covalence reduces the amplitude of the static charge. Comparison of a specific static charge in the different phases of a given material or in different compounds can therefore give a relevant information on the evolution of the chemical bond [115].

3.3 The concept of dynamical charge

As emphasized by Harrison [132], "whenever an ambiguity arises about the definition of a concept such as the atomic charge, it can be removed by discussing only quantities that

¹We note the unphysical charge on Ba. It is the result of a negative Mulliken population and reflects the inadequacy of the Mulliken population analysis which assumes an equal share of overlap between each pair of atoms.



Figure 3.1: Ti-O plane cut in the partial electronic density coming from the O 2p bands in the cubic phase of barium titanate.

can be experimentally determined, at least in principles". If there are some ambiguities to determine the charge to be associated to a given atom, the charge carried by this atom when it is displaced is directly accessible from the induced change of polarization (or dipole moment for molecules). As it is now discussed, the dynamical charges are defined by the change of polarization induced by an atomic displacement; from the viewpoint of Harrison, they appear therefore as more fondamental quantities.

3.3.1 Role of the macroscopic electric field

In molecules, the change of dipole moment in direction β (p_{β}) linearly induced by a small displacement of atom κ in direction α ($\tau_{\kappa,\alpha}$) is uniquely defined. The proportionality coefficient between the dipole moment and the atomic displacement has the dimensionality of a charge and is usually referred to as the *atomic polar tensor* (APT) :

$$Z^*_{\kappa,\alpha\beta} = \frac{\partial p_\beta}{\partial \tau_{\kappa,\alpha}} \tag{3.1}$$

This concept was introduced by Biarge, Herranz and Morcillo [149, 150, 151] for the interpretation of infra-red intensities measurements. Later, Cioslowski [152, 153] introduced a scalar charge in connection with this tensor : it is the generalized atomic polar tensor (GAPT) defined as one-third of the trace of the atomic polar tensor.

In periodic systems, equivalent atoms appear in the different unit cells and the definition of the charge can be generalized. A dynamical charge tensor is conventionally defined as the coefficient of proportionality at the linear order between the *macroscopic polarization* per unit cell created in direction β and a rigid displacement of the *sublattice* of atoms κ in direction α , times the unit cell volume Ω_0 :

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}}$$
(3.2)

We note that $\Omega_0 \mathcal{P}$ can be interpreted as a dipole moment per unit cell. As one κ atom is displaced in each unit cell, in the linear regime, this definition is equivalent to Eq. (3.1) : it corresponds to the change of dipole moment induced by an isolated atomic displacement. However, contrary to the case of molecules, in macroscopic systems, the previous quantity is not uniquely defined. Indeed, the change of polarization is also dependent on the boundary conditions fixing the macroscopic electric field \mathcal{E} throughout the sample. Basically, we can write :

$$Z_{\kappa,\alpha\beta}^{*} = \Omega_{0} \left. \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0} + \Omega_{0} \left. \sum_{j} \frac{\partial \mathcal{P}_{\beta}}{\partial \mathcal{E}_{j}} \cdot \frac{\partial \mathcal{E}_{j}}{\partial \tau_{\kappa,\alpha}} \right.$$
(3.3)

As the electrostatics imposes a relationship between macroscopic polarization, electric and displacement fields :

$$\mathcal{D}_{\alpha} = \mathcal{E}_{\alpha} + 4\pi \mathcal{P}_{\alpha} = \sum_{j} \epsilon_{\alpha,j}^{\infty} \mathcal{E}_{j}$$
(3.4)

we can deduce the following equivalent expression :

$$Z_{\kappa,\alpha\beta}^{*} = \Omega_{0} \left. \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0} + \Omega_{0} \left. \sum_{j} \frac{(\epsilon_{\beta,j}^{\infty} - \delta_{\beta,j})}{4\pi} \cdot \frac{\partial \mathcal{E}_{j}}{\partial \tau_{\kappa,\alpha}} \right.$$
(3.5)

Depending on the condition imposed on the macroscopic electric field, different concepts have historically been introduced ².

The Born effective charge [131] – alias transverse charge, $Z^{*(T)}$ – refers to the change of polarization that would be observed under the condition of zero macroscopic electric field, so that the second term appearing in the previous equation vanishes :

$$Z_{\kappa,\alpha\beta}^{*(T)} = \Omega_0 \left. \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0}$$
(3.6)

The *Callen charge* [155] – alias longitudinal charge, $Z^{*(L)}$ – is defined from the change of polarization under the condition of zero macroscopic displacement field :

$$Z_{\kappa,\alpha\beta}^{*(L)} = \Omega_0 \left. \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{D}=0}.$$
(3.7)

²Besides the different definitions of dynamical charges reported in this Chapter, let us note that another related charge is sometimes also introduced, which is defined as $Z^{*(T)}/\sqrt{\epsilon^{\infty}}$. This charge can reveal useful in the study of $A^N B^{8-N}$ compounds in the sense that it is directly accessible from LO-TO splitting data without any hypothesis on the amplitude of the dielectric constant. In more complex materials, as ABO₃ compounds, the extraction of the charges from the splitting is not straightforward but requires to introduce some hypothesis. This has been made by Gervais *et al.* [154] who estimated the amplitude of $Z^{*(T)}/\sqrt{\epsilon^{\infty}}$ in BaTiO₃.

Introducing in Eq. (3.5) the relationship between field \mathcal{E} and polarization \mathcal{P} , deduced from Eq. (3.4) under the condition of vanishing displacement field, Born and Callen charges can be related to each other thanks to the knowledge of the optical dielectric tensor ϵ^{∞} :

$$Z_{\kappa,\alpha\beta}^{*(L)} = Z_{\kappa,\alpha\beta}^{*(T)} - \sum_{j} \frac{(\epsilon_{\beta,j}^{\infty} - \delta_{\beta,j})}{4\pi} \cdot 4\pi \underbrace{\Omega_{0} \left. \frac{\partial \mathcal{P}_{j}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{D}=0}}_{Z_{\kappa,\alphaj}^{*(L)}}$$
(3.8)

so that finally [156]:

$$Z_{\kappa,\alpha\beta}^{*(T)} = \sum_{j} \epsilon_{\beta j}^{\infty} \ Z_{\kappa,\alpha j}^{*(L)}$$
(3.9)

For the case of isotropic materials, we recover the well known equality : $Z_{\kappa}^{*(T)} = \epsilon^{\infty} Z_{\kappa}^{*(L)}$. Even if they are both related to the change of polarization induced by an atomic displacement, Born and Callen charges appear as two distinct quantities and will be significantly different in materials where ϵ^{∞} is different from unity.

Basically, an infinite number of charges could be defined corresponding to different boundary conditions, relating \mathcal{P} and \mathcal{E} . One of them is the *Szigeti charge* [157, 158] – $Z^{*(S)}$ –, defined as the change of polarization under the condition of vanishing local field, \mathcal{E}_{loc} , at the atomic site:

$$Z_{\kappa,\alpha\beta}^{*(S)} = \Omega_0 \left. \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}_{loc}=0}$$
(3.10)

The concept of local field will be discussed in Chapter 5. Let us already mention that, contrary to Born and Callen charges, $Z^{*(S)}$ was sometimes considered as a model-dependent concept in the sense that the local field is not observable as the macroscopic field but require some assumptions to be estimated. In the particular case of an isotropic material, the condition of vanishing local field can be written as follows:

$$\mathcal{E}_{loc} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P} = 0 \tag{3.11}$$

Introducing this condition in Eq. (3.5):

$$Z_{\kappa}^{*(S)} = Z_{\kappa}^{*(T)} - \frac{(\epsilon^{\infty} - 1)}{4\pi} \cdot \frac{4\pi}{3} \underbrace{\Omega_{0} \left. \frac{\partial \mathcal{P}}{\partial \tau_{\kappa}} \right|_{\mathcal{E}_{loc}=0}}_{Z_{\kappa}^{*(S)}}$$
(3.12)

so that we find :

$$Z_{\kappa}^{*(T)} = \frac{(\epsilon^{\infty} + 2)}{3} Z_{\kappa}^{*(S)}$$
(3.13)

In calculations of the dynamical properties of crystals, the contribution from the longrange Coulombic interaction to the atomic forces is usually restricted to dipolar forces and is included through a term : $F_{\kappa}^{d} = Z_{\kappa}^{*(T)} \mathcal{E}$. From Eq. (3.13), it can be checked that this force can be alternatively written in terms of local quantities : $F_{\kappa}^{d} = Z_{\kappa}^{*(S)} \mathcal{E}_{loc}$. In shell-model calculations, this second formulation is usually preferred. Indeed, from its definition, $Z^{*(S)}$ only includes the effects of charge redistribution resulting from shortrange interactions and it is therefore conveniently assimilated to the static charge [17, 140].

From the previous discussion, it appears that the amplitude of the dynamical charge in macroscopic bodies is sensitive to the condition imposed on the macroscopic electric field. Considering finite clusters of increasing size, we deduce that the amplitude of the dynamical charge, reducing to the APT for a microscopic body, will tend to a different value when the macroscopic limit is taken, depending from the *shape* of the cluster. We investigate now this observation in more details, and provide a unified treatment of dynamical charges in periodic solids and clusters, sufficiently large for the macroscopic quantities $(\mathcal{E}, \mathcal{P}, \epsilon^{\infty}, ...)$ to be defined.

Following the well-known practice for the study of dielectric bodies [159], we consider that the cluster has a macroscopic ellipsoïdal shape. In this case, the macroscopic field within the cluster present the practical advantage to be homogeneous. In absence of any applied external field, it reduces to the depolarizing field related to the macroscopic polarization thanks to the depolarization coefficients n_{α} [159]. If we assume in what follows that the principal axes of the ellipsoïd are aligned with the axes of coordinates, we have the following relationship :

$$\mathcal{E}_{\alpha} = -4\pi n_{\alpha} \mathcal{P}_{\alpha} \tag{3.14}$$

where the geometry imposes : $\sum_{i} n_i = 1$. Following the same procedure as previously, the dynamical charge $Z^{*(E)}$ of a given atom κ in an ellipsoïd of volume Ω can be written as :

$$Z_{\kappa,\alpha\beta}^{*(E)} = \Omega \left. \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0} + \Omega \left. \sum_{j} \frac{(\epsilon_{\beta,j}^{\infty} - \delta_{\beta,j})}{4\pi} \cdot \frac{\partial \mathcal{E}_{j}}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}_{j}=-4\pi n_{j}\mathcal{P}_{j}}$$
(3.15)

$$= Z_{\kappa,\alpha\beta}^{*(T)} - \sum_{j} \frac{(\epsilon_{\beta,j}^{\infty} - \delta_{\beta,j})}{4\pi} \cdot 4\pi n_{j} \Omega \frac{\partial \mathcal{P}_{j}}{\partial \tau_{\kappa,\alpha}} \Big|_{\mathcal{E}_{j} = -4\pi n_{j} \mathcal{P}_{j}}$$
(3.16)

and we have the general relationship :

$$Z_{\kappa,\alpha\beta}^{*(T)} = \sum_{j} [(\epsilon_{\beta j}^{\infty} - \delta_{\beta j})n_j + \delta_{\beta j}] \ Z_{\kappa,\alpha j}^{*(E)}$$
(3.17)

In this expression, the presence of the depolarization coefficients emphasizes the influence of the shape of the cluster on the amplitude of $Z^{*(E)}$. The above-mentioned sum rule on the depolarization coefficients forbid to impose the condition of zero electric or displacement fields simultaneously in the three directions. However, we have the following three interesting cases. First, we consider an extremely oblate ellipsoïdal (slab-like) cluster and take the macroscopic limit. Along the z direction perpendicular to the surface, $n_z \to 1$, while, along the two other directions, $n_x = n_y \to 0$. The dynamical charge for the ellipsoïd is therefore related to the Born effective charge through the following expression:

$$\begin{pmatrix} Z_{\kappa,\alpha x}^{*(T)} \\ Z_{\kappa,\alpha y}^{*(T)} \\ Z_{\kappa,\alpha z}^{*(T)} \end{pmatrix} = \begin{pmatrix} 1 & 0 & \epsilon_{xz}^{\infty} \\ 0 & 1 & \epsilon_{yz}^{\infty} \\ 0 & 0 & \epsilon_{zz}^{\infty} \end{pmatrix} \begin{pmatrix} Z_{\kappa,\alpha x}^{*(E)} \\ Z_{\kappa,\alpha y}^{*(E)} \\ Z_{\kappa,\alpha z}^{*(E)} \end{pmatrix}$$
(3.18)

For uniaxial systems with no off-diagonal terms in the dielectric tensor, we note that the cluster charge along the direction perpendicular to the slab becomes identified with the Callen charge, while that in the slab plane reduces to the Born effective charge. We will come back to this discussion in Chapter 7, devoted to thin films.

Differently, for an extremely prolate ellipsoïdal (needle-like) cluster aligned along the z direction (for which $n_z \to 0$ and $n_x = n_y \to 1/2$), we have the following relationship:

$$\begin{pmatrix} Z_{\kappa,\alpha x}^{*(T)} \\ Z_{\kappa,\alpha y}^{*(T)} \\ Z_{\kappa,\alpha z}^{*(T)} \end{pmatrix} = \begin{pmatrix} \frac{1}{2} (\epsilon_{xx}^{\infty} + 1) & \frac{1}{2} \epsilon_{xy}^{\infty} & 0 \\ \frac{1}{2} \epsilon_{yx}^{\infty} & \frac{1}{2} (\epsilon_{yy}^{\infty} + 1) & 0 \\ \frac{1}{2} \epsilon_{zx}^{\infty} & \frac{1}{2} \epsilon_{zy}^{\infty} & 1 \end{pmatrix} \begin{pmatrix} Z_{\kappa,\alpha x}^{*(E)} \\ Z_{\kappa,\alpha y}^{*(E)} \\ Z_{\kappa,\alpha z}^{*(E)} \end{pmatrix}$$
(3.19)

Here also, the charge along the z direction will reduce to the Born charge in uniaxial systems.

Finally, for a spherical cluster, the symmetry imposes $n_1 = n_2 = n_3 = 1/3$, so that $\mathcal{E}_{\alpha} = -4\pi \mathcal{P}/3$. For the case of an isotropic material, we recover therefore the condition of vanishing local field and $Z_{\kappa}^{(E)}$ becomes equivalent to $Z_{\kappa}^{(S)}$. Therefore, we obtain the interesting result that in isotropic compounds, the Szigeti charge appears as a well-defined quantity and is simply the dynamical charge observed in a spherical cluster.

To summarize, the concept of dynamical charge in macroscopic systems is not uniquely defined : it depends on the relationship between \mathcal{E} and \mathcal{P} . In each case, the charge was however expressed in terms of two basic concepts, $Z^{*(T)}$ and ϵ^{∞} . In this Section, we focused on the term that includes the dielectric constant, and that describes the part of the electronic charge redistribution induced by the presence of a macroscopic field. In the next Section, we will discuss the physical processes responsible of the amplitude of $Z^{*(T)}$.

3.3.2 Dynamical changes of orbital hybridizations

During the seventies, a large variety of semi-empirical models were proposed to investigate the underlying physical processes driving the amplitude of dynamical charges. Without being exhaustive, let us mention the interesting treatments of Lucovsky, Martin and Burnstein [160] who decomposed $Z^{*(T)}$ in a local and a non-local contribution, of Lucovsky and White [161] discussing $Z^{*(T)}$ in connection with resonant bonding properties, or the bond charge model of Hübner [162]. The most popular and sophisticated of these approaches remains however that of Harrison [132, 163, 164, 165] within his bond orbital model (BOM). A similar theory was developed independently by Lannoo and Decarpigny [166]. The BOM basically consists in a simplified tight-binding model, where the Hamiltonian is limited to the on-site and nearest-neighbour terms. The on-site elements are identified to free atom terms value, while the interatomic elements are taken as universal constants times a particular distance dependence. Among other things, these parameters determine the transfer of charge between the interacting atoms. As noted by Dick and Overhauser [167], the charge redistribution produced by the sensitivity of the overlap integrals on the atomic positions is at the origin of an "exchange charge polarization". Similarly, in the Harrison model, the dependence of the parameter on the bond length are at the origin of dynamical transfer of charges and monitors the amplitude of $Z^{*(T)}$ that can become anomalously large as it is illustrated in the following examples.

Let us first consider a diatomic molecule XY, composed of two open shell atoms, where Y has the largest electronegativity. The interatomic distance is u and the dipole moment p(u). These observables allow us to identify a convenient static charge $Z(u) = \frac{p(u)}{u}$, while the dynamical charge is defined as :

$$Z^{*}(u) = \frac{\partial p(u)}{\partial u}$$

= $\frac{\partial}{\partial u} (u \cdot Z(u))$
= $Z(u) + u \frac{\partial Z(u)}{\partial u}$ (3.20)

In the last expression, Z^* appears composed of two terms. The first one is simply the static charge. The second corresponds to an additional *dynamical* contribution: it originates in the transfer of charge produced by the modification of the interatomic distance. Within the BOM, this last contribution is associated to off-site orbital hybridization changes and is deduced from the universal dependence of the orbital interaction parameters on the bond length. We deduce that the difference between Z(u) and $Z^*(u)$ will be large if Z(u)changes rapidly with u. It can even be non-negligible when $\partial Z(u)/\partial u$ is small, when the charge is transferred on a large distance u.

Moreover, this simple model naturally predicts anomalous amplitude of the dynamical charges, i.e. a value of $Z^*(u)$ not only larger than the static charge Z(u) but even larger than the "nominal" ionic charge. As the distance between X and Y is modified from 0 to some \overline{u} , the distance corresponding to a *complete* transfer of electrons from X to Y, the dipole moment evolves continuously from p(0) = 0 (since there is no dipole for that case) to $p(\overline{u})$. Interestingly,

$$\int_0^{\overline{u}} Z^*(u) \, du = [p(\overline{u}) - p(0)] = \overline{u} \, Z(\overline{u}) \tag{3.21}$$

so that:

$$\frac{1}{\overline{u}} \int_0^{\overline{u}} Z^*(u) du = Z(\overline{u}) \tag{3.22}$$

From the last relationship the mean value of $Z^*(u)$ from 0 to \overline{u} is equal to $Z(\overline{u})$ (the "nominal" ionic charge). Consequently, if Z(u) changes with $u, Z^*(u)$ must be larger

than $Z(\overline{u})$ for some u between $[0,\overline{u}]$. The difference between $Z^*(u)$ and the nominal charge $Z(\overline{u})$ is usually referred to as the *anomalous* contribution ³.

Switching now from a molecule to a linear chain ...-Y-X-Y-..., and displacing coherently the X atoms by du, shortened and elongated bonds will alternate all along the chain. For Harrison [132], the interaction parameters will be modified such that "the covalent energy increases in the shorted bond, making it less polar by transferring electron to the positive atom". Inversely, electronic charge will be transferred to the negative atom in the elongated bond. These transfers of charge will propagate all along the chain, so that even if the net charge on the atom is not modified, a *current* of electrons will be associated to the atomic displacement. The direction of this electronic current is opposite to that of the displacement of positive atoms, so that it reinforces the change of polarization associated to this displacement and may generate an anomalously large dynamical charge. In our example, we have implicitely considered a truly periodic system under the condition of zero macroscopic electric field so that the associated dynamical charge is $Z^{*(T)}$. Under other conditions, the amplitude of the transfers of charge would be additionally influenced by the presence of the field as discussed in the previous Section. We note that, contrary to what was observed for the static charge, consequences of the covalence effects are to increase the amplitude of $Z^{*(T)}$.

The previous model can finally be extended to three dimensional solids. For this case, however, the calculation of the dynamical contribution may become questionable when the identification of the charge transfers is restricted to some specific bonds [168]. As it will be discussed in Sections 3.5 and 3.6 the Harrison model remains however a meaningful picture of practical interest to interpret more accurate results.

Up to now, we focused on a "delocalized" model within which the electronic charge redistribution induced by an atomic displacement is visualized by transfer of charge induced by off-site changes of hybridization. In the past, various shell-models have however also been developed to investigate the dynamical properties of crystals. In these calculations, an accurate description of $Z^{*(T)}$ was mandatory in order to reproduce correctly the splitting between longitudinal and transverse optic modes in the vicinity of the Γ point. Contrary to the BOM, the shell-model is "local" and treats the charges within the Clausius-Mosotti limit. The previous discussion in terms of a static and dynamical contribution to $Z^{*(T)}$ remains valid. However, the dynamical contribution results there simply from the relative displacement of the shell charge as a whole with respect to the atom. It is attributed to the polarizability of the electrons in the local field at the atomic site. In the language of the BOM, such a displacement of the electronic cloud can be understood in terms of on-site changes of hybridizations. This approach contrasts with the model developped by Harrison but can also yield plausible Born effective charge amplitudes [120].

It must be emphasized that it is not possible to discriminate *a priori* between localized and delocalized models. Within the recent theory of polarization, it has been clarified that

³Nominal and static charges may differ widely due to covalency effects. As the static charge is ill defined, one usually prefers to define the anomalous contribution in reference to the nominal charge. The difference between Born effective charge and static charge is sometimes referred to as the dynamical contribution.



Figure 3.2: Schematic representation of the two basic mechanisms that can explain the displacement of the Wannier center of a band under atomic displacement : (a) local polarizability, (b) interatomic transfers of charge.

for the purpose of understanding polarization problems, "the true quantum mechanical electronic system can be considered as an effective classical system of quantized point charges, located at the centers of gravity associated with the occupied Wannier functions in each unit cell" [36]. Consequently, the correct description of the Born effective charges does not require to reproduce correctly all the features of the valence charge distribution but *only* the displacement of its Wannier center (see Ref. [169]). As schematized in Fig. 3.2, antagonist models can reproduce a similar displacement of the Wannier center. In real materials, both local polarizability and transfers of charge do probably contribute to the charge reorganisation. It will be emphasized later, in this Chapter and in Chapter 4, how first-principles investigations can help to identify the dominant mechanism.

In conclusion, this Section has shown that Z^* is related to the static charge (see Eq. 3.20) but does not restrict to it: Z^* may also include an additional, important, dynamical contribution. Whatever the mechanism of the charge redistribution (localized or delocalized), the amplitude of the dynamical contribution cannot be estimated from the inspection of the electronic density alone. So, we partly disagree with Meister and Schwarz [130] who suggested that all the charges *including* the GAPT are driven by the same underlying parameter. In what follows, based on first-principles calculations, we illustrate on different examples that $Z^{*(T)}$ may become anomalously large and independent of the amplitude of the static charge Z. Moreover, two atoms with similar Z can also exhibit strongly different $Z^{*(T)}$.

3.4 A first-principles approach

In the previous Section, the Born effective charge tensor $Z^*_{\kappa,\alpha\beta}$ was defined as the coefficient of proportionality relating the change in macroscopic polarization to a collective nuclear displacement :

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa\alpha}} \right|_{\mathcal{E}=0}.$$
(3.23)

This standard definition of Z^* , Eq. (3.23), emphasizes the response with respect to the collective nuclear displacement. However, a thermodynamical equality relates the macroscopic polarization to the derivative of the electric enthalpy \tilde{E} with respect to a homogeneous electric field. Similarly, another relationship connects the forces on the nuclei to the derivative of the electric enthalpy with respect to atomic displacements. Combining these expressions, Z^* can be alternatively formulated, either as a mixed second-order derivative of the electric enthalpy,

$$Z^*_{\kappa,\alpha\beta} = -\frac{\partial^2 E}{\partial \mathcal{E}_\beta \partial \tau_{\kappa\alpha}},\tag{3.24}$$

or as the derivative of the force felt by a nucleus κ with respect to an homogeneous effective electric field \mathcal{E}_{β} , at zero atomic displacements :

$$Z_{\kappa,\alpha\beta}^* = \left. \frac{\partial F_{\kappa,\alpha}}{\partial \mathcal{E}_{\beta}} \right|_{\tau_{\kappa\alpha}=0}.$$
(3.25)

The three previous definitions – Eqs. (3.23), (3.24), and (3.25) – are formally equivalent. However, each of them can provide a different method the compute the effective charges.

A brief review of the most commonly used first-principles approaches for computing the Born effective charges has been reported in Ref. ([169]). Going beyond semi-empirical approaches, *ab initio* techniques allow accurate prediction of $Z^{*(T)}$ in materials where its amplitude is not necessarily directly accessible from the experiment. Going further, the first-principles approaches are also offering a new opportunity to clarify the microscopic mechanism modulating the amplitude of $Z^{*(T)}$ without any preliminary hypothesis. As it will be illustrated in the following sections, it reveals particularly useful to understand the origin of anomalously large $Z^{*(T)}$ in ABO₃ compounds.

The results presented here have been obtained in the framework of the density functional formalism as described in Chapter 1. The exchange-correlation energy has been evaluated within the local density approximation, using a Padé parametrization [57] of Ceperley-Alder homogeneous electron gas data [56]. Integrals over the Brillouin-zone were replaced by a sum on a mesh of $6 \times 6 \times 6$ special **k**-points [71, 170] (10 points in the irreducible Brillouin zone). The "all electron" potentials were replaced by the same ab initio, separable, extended norm-conserving pseudopotentials as in Ref. [135]. The wavefunctions were expanded in plane waves up to a kinetic energy cutoff of 35 Hartree (about 4100 plane waves).

As a second derivative of the total energy, the Born effective charges have been deduced from linear response calculations [42], using a variational formulation [43, 83, 84]

		$Z_{Ba}^{*(T)}$	$Z_{Ti}^{*(T)}$	$Z_{O_{\perp}}^{*(T)}$	$Z_{O_{\parallel}}^{*(T)}$	Reference
Nominal		+2	+4	-2	-2	
Experiment		+2.9	+6.7	-2.4	-4.8	Ref. [133]
Models	(Shell model)	+1.63	+7.51	-2.71	-3.72	Ref. [120]
	(SCAD model)	+2.9	+7.3	-2.2	-5.8	Ref. [174]
First-principles	(Linear response)	+2.77	+7.25	-2.15	-5.71	Present
	(Berry phase)	+2.75	+7.16	-2.11	-5.69	Ref. [136]

Table 3.2: Born effective charges of $BaTiO_3$ in the cubic structure.

to the density functional perturbation theory. The decomposition of individual contributions from separate groups of occupied bands has been performed following the scheme described in Ref. [169]. The parameters used for the calculations guarantee a convergency better than 0.5% on $Z^{*(T)}$ as well as on each of its band-by-band contributions.

3.5 The paraelectric phase of ABO₃ compounds

3.5.1 Perovskite compounds

The Born effective charge tensors of perovskite ABO₃ compounds have been at the center of numerous investigations [134, 135, 136, 137, 138, 120, 171, 172, 101, 173]. In the cubic phase, they are fully characterized by a set of four independent numbers. The charge tensor of the A and B atoms is isotropic owing to the local spherical symmetry at the atomic site. For oxygen, the local environment is tetragonal and two independent elements O_{\parallel} and O_{\perp} must be considered, referring respectively to the change of polarization induced by an atomic displacement parallel and perpendicular to the B-O bond. In Table 3.2, we summarize the results obtained within different approaches for the cubic phase of BaTiO₃.

The first reliable estimation of $Z^{*(T)}$ in BaTiO₃ is probably due to Axe [133], from empirical fitting to experimental mode oscillator strengths ⁴. In ABO₃ compounds, $Z^{*(T)}$ cannot be determined unambiguously from the experiment. However, within some realistic hypothesis, Axe identified the independent elements of the effective charges of BaTiO₃ and already pointed out their two essential features. First, the oxygen charge tensor is highly anisotropic. Second, the charges on Ti and O_{||} contain a large *anomalous* contribution (i.e. an additional charge with respect to the nominal ionic value of +2 for Ba, +4 for Ti and -2 for O).

Both these characteristics are confirmed by the first-principles calculations. Our ab

⁴Let us mention that an early investigation of the Born effective charges of BaTiO₃ was performed by Last in 1957 [175], but without identifying any anomaly. Another discussion was reported in Ref. [176] but without separating the respective values of $Z^{*(T)}$.

ABO_3	$Z_A^{*(T)}$	$Z_B^{*(T)}$	$Z_{O\parallel}^{*(T)}$	$Z_{O\perp}^{*(T)}$	Reference
nominal	2	4	-2	-2	
$CaTiO_3$	2.58	7.08	-5.65	-2.00	Ref. [136]
$ m SrTiO_3$	2.56	7.26	-5.73	-2.15	$\mathbf{Present}$
	2.54	7.12	-5.66	-2.00	Ref. [136]
	2.55	7.56	-5.92	-2.12	Ref. [173]
	2.4	7.0	-5.8	-1.8	Ref. [133]
BaTiO_3	2.77	7.25	-5.71	-2.15	Present
	2.75	7.16	-5.69	-2.11	Ref. [136]
BaZrO_3	2.73	6.03	-4.74	-2.01	Ref. [136]
$PbTiO_3$	3.90	7.06	-5.83	-2.56	Ref. [136]
PbZrO_3	3.92	5.85	-4.81	-2.48	Ref. [136]
nominal	1	5	-2	-2	
NaNbO_3	1.13	9.11	-7.01	-1.61	Ref. [136]
KNbO_3	0.82	9.13	-6.58	-1.68	Ref. [134]
	1.14	9.23	-7.01	-1.68	Ref. [136]
	1.14	9.37	-6.86	-1.65	Ref. [172]
nominal	-	6	-2	-2	
WO_3	-	12.51	-9.13	-1.69	Ref. [177]

Table 3.3: Born effective charges of various ABO₃ compounds in their cubic structure.

initio results, computed from linear response, are also in excellent agreement with those of Zhong *et al.* [136], obtained from finite differences of polarization. The charge neutrality sum rule, reflecting the numerical accuracy of our calculation, is fulfilled to within 0.02. We note that the values of $Z^{*(T)}$ are also qualitatively reproduced from a shell-model calculation [120] and accurately predicted within the SCAD model [174].

The anomalous amplitude of the dynamical charge, reported in this Section, is not a specific feature of BaTiO₃. Similar computations of $Z^{*(T)}$ were performed on different perovskite ABO₃ compounds and they all reproduce the same characteristics than in BaTiO₃. A non exhaustive list of these results is reported in Table 3.3. We observe that the choice of the A atom has a rather limited influence on $Z_B^{*(T)}$ and $Z_{O\parallel}^{*(T)}$, which appear closely related to the B atom. While the nominal ionic charge of Ti and Zr is +4 in these compounds, the Born effective charge is between +7.08 and +7.56 for Ti, and approximately equal to +6.03 for Zr. For Nb, the ionic charge is +5, while the Born effective charge is between +9.11 and +9.37. Extending the investigations to WO₃ in the reference cubic phase (defect perovskite structure), the ionic charge on W is equal to +6, while the Born effective charge reaches the much larger value of +12.51. For the class of perovskite ABO₃ compounds, it can be checked that $Z_B^{*(T)}$ evolves quasi linearly with the nominal charge of the B atom [177].

For materials containing Pb, the previous considerations remain valid but there are

additional anomalies concerning $Z_A^{*(T)}$ and $Z_{O\perp}^{*(T)}$. This feature is due to the more covalent bonding of lead with oxygen that was illustrated in Ref. [98, 107]. In what follows, we will not be concerned with these lead compounds.

3.5.2 Lithium niobate

We also calculated the Born effective charge tensors in LiNbO₃. Table 3.4 summarizes the results for Li₁, Nb₁ and the three O₁, O₂, O₃ oxygen atoms. Due to the low symmetry, the full tensors must be considered. At the last line, we mention the eigenvalues of the symmetric part of Z_O^* that are identical for all the oxygens. The labels of the atoms correspond to those defined in Chapter 2. The tensors are reported in cartesian coordinates with z along the trigonal axis.

Table 3.4: Born effective charges (in atomic units) of Nb₁, Li₁, O₁, O₂ and O₃ in the two phases of lithium niobate. The last line gives the eigenvalues of the symmetric part of Z_O^* (identical for all the oxygens).

	parae	electric	phase	ferroe	ferroelectric phase		
Li ₁	1.15	0	0	1.19	-0.25	0	
	0	1.15	0	0.25	1.19	0	
	0	0	1.11	0	0	1.02	
Nb.	8 28	2.07	0	7 39	1 65	0	
1,01	-2.07	8.28	0	-1.65	7 3 2	0	
	2.01	0.20	0.17	1.00	1.02	6.04	
	0	0	9.17	0	0	0.94	
O_1	-1.80	0	0	-1.62	0.31	-0.17	
	0	-4.48	2.46	0.23	-4.06	1.79	
	0	2.32	-3.43	-0.13	1.85	-2.66	
\cap	0.01	1 10	0.10	0.00	1 1 5	1 40	
O_2	-3.81	-1.10	-2.13	-3.22	-1.15	-1.46	
	-1.16	-2.47	-1.23	-1.23	-2.46	-1.04	
	-2.01	-1.16	-3.43	-1.53	-1.04	-2.66	
\bigcirc	3 8 1	1 16	9 13	3 68	0.06	1 63	
\bigcirc_3	-0.01	1.10 9.47	2.10 1.02	-0.00	2.00	1.00	
	1.10	-2.47	-1.20 0.40	0.00	-2.00	-0.75	
	2.01	-1.10	-3.43	1.07	-0.81	-2.00	
O (eig.)	-6.40	-1.51	-1.80	-5.33	-1.41	-1.60	

Analysing the charges reported in Table 3.4, we observe that Z_{Li}^* is nearly isotropic and that the diagonal elements have a value close to the nominal charge of the lithium atom (+1). At the opposite, the amplitude of Z_{Nb}^* is highly anomalous in the sense that it is significantly larger than the nominal charge expected in a purely ionic crystal (+5). The niobium charge is slightly anisotropic with a significantly different value along the trigonal axis. For the oxygen atoms, the anisotropy is much stronger. This feature appears clearly form the inspection of the tensor eigenvalues. The highest eigenvalue is strongly anomalous (-6.4 for the paraelectric phase, to be compare to the nominal charge of -2) and the inspection of the associated eigenvector reveals that it is the charge associated to an oxygen displacement (nearly) along the Nb–O bond. In contrast, the two other eigenvalues (associated to oxygen displacement in the plane perpendicular to the Nb–O bond) are smaller than -2.

Most of our observations on LiNbO₃ are comparable to what has been reported for related perovskite compounds like KNbO₃ [101, 136] or NaNbO₃ [136]. For instance, the Nb charge in the paraelectric phase for a displacement along the Nb–O bond is respectively equal to 8.75, 9.11 and 9.23 in LiNbO₃, NaNbO₃ [136] and KNbO₃ [136] while the Li, Na and K charges are equal respectively to 1.11, 1.13 and 1.14.

3.5.3 Origin of the anomalous contributions

The approximate reciprocity between O_{\parallel} and B anomalous contributions suggests that they should originate in a global transfer of charge between B and O atoms as described in Section 3.3.2. In Ref. [132], Harrison had in fact already suggested the existence of giant Born effective charges in perovskite materials. Being unaware of the earlier results of Axe, he had however no experimental evidence to corroborate his semi-empirical calculations.

In Ref. [90], we report results obtained within the Harrison model (it follows the method described for KCl in Ref. [132], p. 334.). For SrTiO₃, from the universal tightbinding parameters of Harrison, we get a value of -8.18 for $Z_{O||}^{*(T)}$, making plausible the giant anomalous effective charges only by focusing on the dynamical changes of hybridization between occupied O 2s–O 2p states and the unoccupied metal d states. In BaTiO₃, the hybridization between O 2p and Ti 3d orbitals is a well known feature, confirmed by various sources (experiments [119, 113], LCAO calculations [117, 147, 148] and DFT results [97, 98]). In this context, it was therefore realistic to focus on O 2p - B d hybridization changes to explain intuitively large anomalous contributions [136].

At the opposite, it may therefore appear surprising that model calculations which do not explicitly include transfers of charges are able to predict correctly the amplitude of the Born effective charges. For instance, in Table I, we observe that the values of $Z^{*(T)}$ are qualitatively reproduced by a shell-model calculation [120]. A similar agreement between *ab initio* and shell model results was highlighted for KNbO₃ [178]. In both cases, the calculation was performed within the "polarizability model" introduced by Bilz *et al.* [23], which includes an anisotropic and non-linear polarizability of the O atoms. In the same spirit, at the level of the SCAD model, the Born effective charges are accurately reproduced while there is no explicit transfer of electrons between the different atomic sites. As discussed in Section 3.3, antagonist models can be invoked to explain the origin of anomalous contributions as soon as they globally reproduce a similar displacement of the Wannier center of the valence charge distribution. What appears as a macroscopic current along the Ti–O chain within the BOM shows itself as an unusual polarizability of the oxygen atoms within the shell model.

It was not possible to discriminate unambiguously between localized and delocalized model until Posternak *et al.* [138] proposed a convincing proof of the crucial role of "off-site" hybridizations. Based on first-principles calculations, they demonstrated for KNbO₃ that the anomalous contribution to the charge of Nb and O_{||} disappears if the hybridization between O 2p and Nb 4d orbitals is artificially suppressed. In a similar spirit, the inspection of the Wannier functions of BaTiO₃ and the analysis of their deformation under an atomic displacement reported by Marzari and Vanderbilt [179] confirm the predominant role played by the Ti 3d orbitals and the explanation introduced by Harrison. In Chapter 4, we will see that the evolution of the electron localization tensor at the phase transition is also in favor of off-site hybridization.

In the next Section, we propose a band-by-band decomposition of the Born effective charges [137, 120]. This technique appears as a tool of paramount importance to clarify the microscopic origin of anomalous contributions. Identifying the dynamical transfer of charges without any preliminary hypothesis on the orbitals that interact, it will allow to generalize the basic mechanism that was proposed by Harrison.

3.6 Identification of dynamical changes of hybridization

In ABO₃ compounds, the electronic band structure is composed of well separated sets of bands. The hybridizations between the orbitals of the different atoms are relatively small and each band can be identified by the name of the main atomic orbital which contributes to this energy level in the solid. The Born effective charge is defined by the change of polarization associated to a specific atomic displacement. Our purpose will be to identify the contribution of each well separated set of bands to this change of polarization [137, 120].

3.6.1 Reference configuration

In Ref. [169], we have described how band-by-band contributions to $Z^{*(T)}$ can be separated from each others. Moreover, it has been demonstrated that the contribution to $Z_{\kappa,\alpha\beta}^{*(T)}$ from a single occupied band n can be interpreted as a change of polarization $\Omega_o \Delta \mathcal{P}_{\beta} =$ $-2.\Omega_o \Delta d_{\beta}$ where Δd_{β} is the displacement in direction β of the Wannier center of band n, induced by the unitary displacement of the sublattice of atoms κ in direction α .

In order to understand the origin of the displacement of the Wannier center of each band, it is helpful to define a *reference* configuration that corresponds to what we would expect in a purely ionic material. In such fictitious material, each band would be composed of a single non-hybridized orbital and the Wannier center of each band would be centered on a given atom. In absence of any hybridization, when displacing a given sublattice of atoms κ , the Wannier center of the bands centered on the moving atoms would remain centered on it, while the position of the center of gravity of the other bands would remain unaffected. The contributions of these two kinds of bands to $Z_{\kappa}^{*(T)}$ would therefore be -2and 0 electrons, respectively.

In the real material, the *anomalous* contribution of a particular band m to a given atom κ is defined as the additional part with respect to the reference value expected in absence of any hybridization: it reflects how the Wannier center of band m is displaced relatively to the atoms when the sublattice κ moves ⁵. Considering each band as a combination of atomic orbitals, such a displacement of the Wannier center of a band with respect to its reference position *must* be attributed to hybridization effects: it is associated to the admixture of a new orbital character to the band. When the orbitals which interact are located on different atoms ("off-site" hybridization), the dynamical changes of hybridization can be visualized as transfers of charge. If the interacting orbitals are on the same atom ("on-site" hybridization), the mechanism much looks like a polarizability.

Rigorously, our band-by-band decomposition is performed within DFT and formally only concerns the Kohn-Sham particles. It seems however that the results are rather independent of the one-particle scheme [180] used for the calculation so that the results presented here should give a good insight on the physics of the ABO₃ compounds.

3.6.2 BaTiO₃

Let us first apply the band-by-band decomposition to barium titanate. The band structure of BaTiO₃ has been discussed in Chapter 2 (Fig. 2.10). Results of the decomposition of $Z^{*(T)}$ in the theoretical cubic structure of BaTiO₃ are reported in Table 3.5. The first line (Z_{κ}) brings together the charge of the nucleus and core electrons included in the pseudopotential. The other contributions come from the different valence electron levels. The sum of the band-by-band contributions on one atom is equal to its global effective charge while the sum of the contributions to a particular band from the different atoms is equal to -2 (within the accuracy of the calculation), the occupancy of this band.

Focusing first on the titanium charge, we observe that the Ti 3s contribution (-2.03) is close to -2, confirming that the Ti 3s electrons follow the Ti atom when moving, independently from the change of its surrounding. At the opposite, it is shown that the giant anomalous charge of titanium essentially comes from the O 2p bands (+2.86). It corresponds to a displacement of the Wannier center of the O 2p bands in opposite direction to the displacement of the Ti atom. This observation is in perfect agreement with the Harrison model: it can be understood by dynamical changes of hybridization between O 2p and Ti 3d orbitals, producing a transfer of electron from O to Ti when the Ti-O distance shortens. This explanation was confirmed recently from the inspection of the O 2p Wannier functions [179]. Beyond the previous observations, we note however

⁵Depending from the structure and from the interactions, the initial position of the electron Wannier center is not necessarily on an atom. However, in the cubic perovskite structure, symmetry imposes to the Wannier centers to be located on an atom so that the anomalous contribution exactly describes the displacement from such a centered position.

Band	$Z_{Ba}^{(T)}$	$Z_{Ti}^{(T)}$	$Z_{O_{\perp}}^{(T)}$	$Z_{O_{\parallel}}^{(T)}$	Total
Z_{κ}	+10.00	+12.00	+6.00	+6.00	+40
Ti 3s	0 + 0.01	-2 - 0.03	0 + 0.00	0 + 0.02	-2.00
Ti 3p	0 + 0.02	-6 - 0.22	0 - 0.02	0 + 0.21	-6.03
Ba 5s	-2 - 0.11	0 + 0.05	0 + 0.02	0 + 0.01	-2.01
O 2s	0 + 0.73	0 + 0.23	-2 - 0.23	-2 - 2.51	-6.01
Ba 5p	-6 - 1.38	0 + 0.36	0 + 0.58	0 - 0.13	-5.99
O 2p	0 + 1.50	0 + 2.86	-6 - 0.50	-6 - 3.31	-17.95
Total	+2.77	+7.25	-2.15	-5.71	+0.01

Table 3.5: Band by band decomposition of $Z^{*(T)}$ in the optimized cubic phase of BaTiO₃. The contributions have been separated into a reference value and an anomalous charge (see text).

that there are also small anomalous charges from the Ti 3p, O 2s and Ba 5p bands. These contributions are not negligible. The positive anomalous charges correspond to a displacement of the center of the Wannier function of the O and Ba bands in the direction of the closest Ti when this atom has moved. Some of these features go beyond the Harrison model, within which anomalous contributions to $Z_{Ti}^{*(T)}$ in Table 3.5 would be restricted to the O 2p and O 2s bands. They suggest other kind of hybridization changes, that will be now more explicitly investigated.

Focusing on barium, the global anomalous effective charge (+0.77) is small compared to that of Ti and this feature was first attributed to its more ionic character [136]. This ionicity is inherent to the Harrison model [132] and was confirmed in some ab initio studies [98, 107]. Surprisingly, our decomposition reveals however that the anomalous charges of the O 2s (+0.73) and O 2p (+1.50) bands are not small at all. They are nevertheless roughly compensated by another Ba 5s (+0.11) and Ba 5p (+1.38) anomalous contributions. This result suggests that there are dynamical changes of hybridization between Ba and O orbitals as it was the case between O and Ti, except that the mechanism is here restricted to occupied states. This basically corresponds to a unitary transform within the subspace of the occupied states which is unable to displace the global Wannier center of the valence charge. Our result so supports the hybridization of Ba orbitals, in agreement with experiment [119, 113], LCAO calculations [147, 148] and DFT [97] computations. Similar compensating contributions were recently observed in ZnO which has conventional Born effective charges [180] and in a series of alkaline-earth oxides [181].

We note that a confusion sometimes appears that should be removed: the *amplitude* of the anomalous contributions to $Z^{*(T)}$ is not related to the amplitude of the hybridizations but to the *rate of change* of these hybridizations under atomic displacements. It is clear that, in BaTiO₃, the Ba 5p contribution to the O 2p bands is smaller than the contribution from the Ti 3d orbitals [97, 98]. However, the high sensitivity of this relatively weak



Figure 3.3: Kohn-Sham electronic band structure of $SrTiO_3$.

covalent character under atomic positions is sufficient to produce large band by band anomalous contributions to $Z^{*(T)}$. From that point of view, the Born effective charge appears therefore as a sensitive tool to identify the presence of even small hybridizations.

Finally, concerning the oxygen, even if O_{\parallel} and O_{\perp} are defined respectively for a displacement of O in the Ti and Ba direction, it seems only qualitative to associate $Z_{O_{\parallel}}^{*(T)}$ with $Z_{Ti}^{*(T)}$ and $Z_{O_{\perp}}^{*(T)}$ with $Z_{Ba}^{*(T)}$ as suggested in Ref. [136]. The O 2p anomalous contributions to Ti and O_{\parallel} do not exactly compensate. Moreover, O 2p contribution to $Z_{Ba}^{*(T)}$ does not come from O_{\perp} only but has equivalent contributions from O_{\parallel} . This seems to confirm the idea of Bennetto and Vanderbilt [168] that in 3D materials, transfers of charges are not necessarily restricted to a particular bond, but is a rather complex mechanism that must be treated as a whole.

To summarize, our study has clarified the mixed ionic-covalent character of BaTiO₃: it clearly establishes that the covalent character is not restricted to the Ti-O bond but also partly concerns the Ba atom. Moreover, it leads to a more general issue. It illustrates that the presence of a large anomalous charge requires a modification of the interactions between occupied and unoccupied electronic states. The contributions originating from the change of the interactions between two occupied states correspond to unitary transforms within the subspace of the valence charge : they compensate, and do not modify the global value of $Z^{*(T)}$.

3.6.3 $SrTiO_3$

The same analysis is now performed on $SrTiO_3$. Its band structure (Fig. 3.3) is very similar to that of $BaTiO_3$, except that the Ti 3p and Sr 4s bands are energetically very close to each others. Consequently, they strongly mix and it should be relatively meaningless to separate their respective contributions. The Sr 4p and O 2s states are in the same energy region but can be separated, contrary to what was observed in a study of SrO [181].

Band	$Z_{Sr}^{(T)}$	$Z_{Ti}^{(T)}$	$Z_{O_{\perp}}^{(T)}$	$Z_{O_{\parallel}}^{(T)}$	Total
Z_{κ}	+10.00	+12.00	+6.00	+6.00	+40
Ti 3s	0 + 0.01	-2 - 0.03	0 + 0.00	0 + 0.03	-1.99
Sr 4s Ti 3p	-2+0.02	-6 - 0.18	0 - 0.03	0 + 0.23	-7.99
O 2s	0 + 3.08	0 + 0.02	-2 - 1.31	-2 - 0.48	-6.00
Sr 4p	-6 - 3.11	0 + 0.37	0 + 1.42	0 - 0.10	-6.00
O 2p	0 + 0.56	0 + 3.08	-6 - 0.12	-6 - 3.41	-18.01
Total	+2.56	+7.26	-2.15	-5.73	+0.01

Table 3.6: Band by band decomposition of $Z^{*(T)}$ in the experimental cubic phase of $SrTiO_3$. The contributions have been separated into a reference value and an anomalous charge (see text).

The result of the decomposition is very similar (Table 3.6) to that reported for BaTiO₃. There is still a giant contribution to $Z_{Ti}^{*(T)}$ from the O 2p bands. On the other hand, while the Ba 5p bands were approximately centered between O 2s and O 2p bands in BaTiO₃, the Sr 4p electrons are closer to the O 2s bands and mainly hybridize with them in SrTiO₃. This phenomenon produces large but compensating contributions from Sr 4p and O 2s bands to $Z_{Sr}^{*(T)}$. Such an evolution is in agreement with the picture that anomalous contributions originate from off-site orbital hybridization changes.

3.6.4 $LiNbO_3$

In spite of its different structure, the amplitude of the effective charges in LiNbO₃ can be explained following the same line of thought as for perovskite compounds. The Li atom is close to a fully ionized configuration and only carries its nominal charge. At the opposite, there is a partly covalent interaction between Nb and O which is responsible for their *anomalous* effective charges and for the strong anisotropy of the oxygen tensor. During an atomic displacement, the parameters that determine the covalent interactions between the Nb 4d and O 2p atomic orbitals (the hopping integrals) vary. This variation produces a dynamical charge transfer between the niobium and the oxygen atoms which is at the origin of the anomalous part of Z_{Nb}^* and Z_O^* .

The essential role played by the O 2p bands can be emphasized from the analysis of the contribution of the different isolated sets of bands (as identified in Figure 2.10) to the global niobium charge. The results of the decomposition for the Nb charge are summarized in Table 3.7. The full tensor is considered. The first line (Z_{core}) brings together the nucleus and core electrons contributions. The last line corresponds to the total charge. The second column refers to the isotropic nominal value that would be expected in a purely ionic compound.

Bands	Nominal	parae	electric j	phase	ferro	electric	phase
Z_{core}	13.00	13.00	0	0	13.00	0	0
		0	13.00	0	0	13.00	0
		0	0	13.00	0	0	13.00
Nb 4s	-2.00	-2.04	0.03	0.00	-2.06	0.02	0.00
		-0.03	-2.04	0.00	-0.02	-2.06	0.00
		0.00	0.00	-2.02	0.00	0.00	-2.04
т. ч	0.00	0.01	0.01	0.00	0.01	0.00	0.00
L1 1S	0.00	0.01	-0.01	0.00	0.01	-0.00	0.00
		0.01	0.01	0.00	0.00	0.01	0.00
		0.00	0.00	0.00	0.00	0.00	0.00
Nh 4n	-6.00	-6 42	-0.06	0.00	-6.49	-0.05	0.00
100 IP	0.00	0.12	-6.42	0.00	0.15	-6.49	0.00
		0.00	0.42	6.37	0.00	0.45	635
		0.00	0.00	-0.01	0.00	0.00	-0.00
O 2s	0.00	0.57	0.09	0.00	0.60	0.10	0.00
		-0.09	0.57	0.00	-0.10	0.60	0.00
		0.00	0.00	0.58	0.00	0.00	0.50
O 2p	0.00	3.14	1.89	0.00	2.25	1.45	0.00
		-1.89	3.14	0.00	-1.45	2.25	0.00
		0.00	0.00	3.89	0.00	0.00	1.71
Total	5.00	8.26	2.07	0.00	7.30	1.62	0.00
		-2.07	8.26	0.00	-1.62	7.30	0.00
		0.00	0.00	9.08	0.00	0.00	6.83

Table 3.7: Band by band decomposition of the Born effective charge of the niobium atom (LDA calculation).

Focusing first on the deep Nb 4s and Li 1s levels, we do not identify any significant anomalous contribution, in agreement with the fact that these electrons do not participate to the bonding. To the contrary, the anomalous O 2p contribution is very large and mainly responsible for the total anomalous charge. This can be explained by dynamical changes of the Nb 4d orbital contribution to the O 2p bands producing a dynamical transfer of electrons from O to Nb when the Nb–O distance shortens. We note finally small and compensating anomalous contributions at the level of the Nb 4p and O 2s bands : they reveal the existence of hybridizations between these levels.

3.6.5 Other examples

From the two previous results that concern ferroelectric materials, it might be suggested that not only the dynamical hybridization of the valence bands with unoccupied d-states but also the particular structure of ABO₃ compounds plays a major role in determining $Z^{*(T)}$. For instance, the anomalous charge could partly originate in the local fields at the atomic sites, known to be anomalously large at least in this cubic perovskite structure [15]

It is interesting to observe that anomalous charges are not restricted to ferroelectric solids but were also detected in a series of alkaline-earth oxides of rocksalt structure (CaO, SrO, BaO) [182, 181] or even Al₂Ru [183, 184], all examples where the unoccupied d-states seem to play a major role. Interestingly, two materials belonging to the same structure can present completely different charges. This was illustrated for the case of TiO₂ rutile and SiO₂ stishovite [185, 186]: while relatively conventional charges were observed on Si (+4.15) and O (-2.46) along the Si-O bond in stishovite, giant effective charges, similar to those of BaTiO₃, were obtained on Ti (+7.33) and O (-4.98) along the Ti-O bond in rutile. Similarly, no anomalous charge was reported for MgO ($Z_O^{*(T)} = -2.07$), presenting the same rocksalt structure than BaO ($Z_O^{*(T)} = -2.80$) [181]. In the same spirit, the same atom in different environments can present similar dynamical charge, as illustrated for $Z_{Ti}^{*(T)}$ in BaTiO₃ and TiO₂ [186], or for $Z_{Zr}^{*(T)}$ in BaZrO₃ [136] and ZrO₂ [187]. Also, in the family of ABO₃ compounds, giant effective charges are observed on Ti in CaTiO₃ ($Z_{Ti}^{*(T)} = 7.08$, [136]) but not on Si in CaSiO₃ ($Z_{Si}^{*(T)} = 4.00$, [188]).

We observe that the presence of partly hybridized d-states seems the only common feature between the materials presenting giant anomalous effective charges, listed up to date. This feature finds a basic justification within the BOM of Harrison: the interaction parameters involving d-states are indeed much more sensitive to the interatomic distance than those involving, for example, s and p orbitals [132]: They will therefore be associated to larger dynamical transfers of charge and will generate higher $Z^{*(T)}$.

3.7 Sensitivity of $Z^{*(T)}$ to structural features

In the litterature, calculations of $Z^{*(T)}$ essentially focused on the cubic phase of ABO₃ compounds [134, 135, 136, 137, 138, 120, 171, 172]. On the basis of an early study of KNbO₃ [134], it was concluded that the Born effective charges are independent of the

Table 3.8: Born effective charges in the three ferroelectric phases of BaTiO₃. Tensors are reported in cartesian coordinates, with the z-axis along the ferroelectric direction. For Ba and Ti, the tensors are diagonal and only the principal elements are mentioned. For O, full tensors are reported. The eigenvalues of the symmetric part of $Z^{*(T)}$ are mentioned in brackets; the eigenvector associated to the highest eigenvalue approximately points in the Ti direction. In the cubic phase, we had: $Z_{Ti}^{*(T)} = 7.29$, $Z_{Ba}^{*(T)} = 2.74$, $Z_{O\parallel}^{*(T)} = -5.75$ and $Z_{O\parallel}^{*(T)} = -2.13$.

	Tetragon	al	Or	thorhom	bic	Rho	ombohedral	
$Z_{Ba}^{*(T)}$	(+2.72+2.72	+2.83)	(+2.72	+2.81	+2.77)	(+2.79	+2.79 +2.74)
$Z_{Ti}^{\ast(T)}$	(+6.94+6.94	+5.81)	(+6.80	+6.43	+5.59)	(+6.54	+6.54 +5.61)
$Z_{O1}^{\ast(T)}$	$\left(\begin{array}{rrr} -1.99 & 0 \\ 0 & -1.99 \\ 0 & 0 \end{array}\right)$	$\begin{pmatrix} 0\\ 0\\ -4.73 \end{pmatrix}$	$\left(\begin{array}{c} -2.04\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -3.63 \\ +1.57 \end{array}$	$\begin{pmatrix} 0\\ +1.38\\ -3.17 \end{pmatrix}$	$\left(\begin{array}{c} -2.54 \\ -0.99 \\ +0.72 \end{array}\right)$	$\begin{array}{rrr} -0.99 & +0.63 \\ -3.68 & +1.09 \\ +1.25 & -2.78 \end{array}$)
	[-1.99 -1.99]	-4.73]	[-1.91	-2.04	-4.89]	[-1.97]	-1.98 -5.05]
$Z_{O2}^{*(T)}$	$\left(\begin{array}{rrr} -2.14 & 0 \\ 0 & -5.53 \\ 0 & 0 \end{array}\right)$	$egin{array}{c} 0 \\ 0 \\ -1.95 \end{array} ight)$	$\left(\begin{array}{c} -2.04\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -3.63 \\ +1.57 \end{array}$	$\begin{pmatrix} 0\\ +1.38\\ -3.17 \end{pmatrix}$	$\left(\begin{array}{c} -2.54 \\ +0.99 \\ +0.72 \end{array}\right)$	$\begin{array}{rrr} +0.99 & +0.63 \\ -3.68 & -1.09 \\ -1.25 & -2.78 \end{array}$)
	[-1.95 -2.14]	-5.53]	[-1.91	-2.04	-4.89]	[-1.97]	-1.98 - 5.05]
$Z_{O3}^{*(T)}$	$\left(\begin{array}{rrr} -5.53 & 0 \\ 0 & -2.14 \\ 0 & 0 \end{array}\right)$	$\begin{pmatrix} 0\\ 0\\ -1.95 \end{pmatrix}$	$\left(\begin{array}{c} -5.44\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -1.97 \\ 0 \end{array}$	$\begin{pmatrix} 0\\ 0\\ -2.01 \end{pmatrix}$	$\left(\begin{array}{c} -4.25\\ 0\\ -1.44\end{array}\right)$	$\begin{array}{ccc} 0 & -1.26 \\ -1.97 & 0 \\ 0 & -2.78 \end{array}$)
	[-1.95 -2.14]	-5.53]	[-1.97]	-2.01	-5.44]	[-1.97]	-1.98 - 5.05]

ionic ferroelectric displacements (i.e. they remain similar in the different phases). Another investigation in the tetragonal phase of KNbO₃ and PbTiO₃ [136], seemed to confirm that $Z^{*(T)}$ are quite insensitive to structural details.

These results were surprising if we remember that anomalous contributions to $Z^{*(T)}$ are closely related to orbital hybridizations, these in turn, well known to be strongly affected by the phase transitions [98, 107]. We will see in this Section that, contrary to what was first expected, Born effective charges in BaTiO₃ are strongly dependent of the structural features.

We first investigate the sensitivity of the Born effective charges to the ferroelectric atomic displacements [120]. For that purpose, we compute $Z^{*(T)}$ in the three ferroelectric phases at the experimental unit cell parameters, with relaxed atomic positions as reported in Chapter 2. Table 3.8 summarizes the results for a cartesian set of axis where the z-

Figure 3.4: Born effective charge of Ti atoms in the direction of the shortest Ti-O bond length (d_{min}) as a function of this interatomic distance, for the cubic (square), tetragonal (lozenge), orthorhombic (circle) and rhombohedral (triangle) phases.

axis points in the ferroelectric direction. The Ba and Ti charge tensors are diagonal in each phase for this particular choice. In the case of O, we note the presence of a small asymmetric contribution for the lowest symmetry phases. The eigenvalues of the symmetric part of the tensor are also reported. In each phase, the eigenvector associated to the highest eigenvalue of O approximately points in the Ti-O direction and allows to identify the highest contribution as O_{\parallel} . The other eigenvalues can be referred to as O_{\perp} , by analogy with the cubic phase.

Although the charges of Ba and O_{\perp} remain globally unchanged in the 4 phases, strong modifications are observed for Ti and O_{\parallel} : for example, changing the Ti position by 0.076Å (2% of the unit cell length) when going from the cubic to the rhombohedral phase, reduces the *anomalous* part of $Z_{Ti}^{*(T)}$ by more than 50% along the ferroelectric axis (Table 3.8). Equivalent evolutions are observed in the other ferroelectric phases. Similar changes were detected in KNbO₃ [101] as well as in LiNbO₃ (see Table 3.4) in spite of its different structure.

In the isotropic cubic structure, Harrison had explained the large value of $Z^{*(T)}$ in terms of the Ti-O bond length. For the anisotropic ferroelectric phases, it should be intuitively expected that the shortest Ti-O distance d_{min} in the structure will dominate the bonding properties. It is therefore tempting to transpose the Harrison model to understand the evolution of $Z^{*(T)}$ in terms of the distance d_{min} . In Fig. 3.4, the amplitude of $Z_{Ti}^{*(T)}$ in the direction of the shortest Ti-O bond length of each phase is plotted with respect to d_{min} . A similar graph can be obtained for O. For the different phases, at the experimental lattice parameters, we observe that the anomalous parts evolve quasi linearly with d_{min} .

Independently from the previous calculations, we also investigated the evolution of $Z^{*(T)}$ under isotropic pressure (Table 3.9). In contrast with the changes observed with

Table 3.9: Evolution of the Born effective charges of $BaTiO_3$ under isotropic pressure in the cubic phase.

a_o (Å)	$Z_{Ba}^{*(T)}$	$Z_{Ti}^{*(T)}$	$Z_{O_{\perp}}^{*(T)}$	$Z_{O_{\parallel}}^{*(T)}$
3.67	+2.95	+7.23	-2.28	-5.61
3.94	+2.77	+7.25	-2.15	-5.71
4.00	+2.74	+7.29	-2.13	-5.75
4.40	+2.60	+7.78	-2.03	-6.31

respect to the atomic displacements, the charge appears essentially insensitive to isotropic compression. In particular, in the compressed cubic cell at 3.67 Å where the Ti-O distance is the same as the shortest Ti-O bond length in the tetragonal structure ⁶, $Z_{Ti}^{*(T)}$ remains very close to its value at the optimized volume. This new element clearly invalidates the expected dependence from $Z^{*(T)}$ to d_{min} .

The fundamental difference between the cubic and tetragonal structures lies in the fact that in the cubic phase every Ti-O distance is equal to the others, while in the tetragonal phase, along the ferroelectric axis, a short Ti-O bond length (d_{min}) is followed by a larger one (d_{max}) which breaks the Ti-O chain in this direction. In order to verify that it is not this large Ti-O distance which, alternatively to d_{min} , is sufficient to inhibit the giant current associated to the anomalous charges, we also performed a calculation in an expanded cubic phase where $a_o = 2.d_{max}$: we observe however that the Ti charge is even larger than in the optimized cubic phase.

We conclude from the previous investigations that the amplitude of $Z^{*(T)}$ in $BaTiO_3$ is not dependent on a particular interatomic distance (d_{\min}, d_{\max}) but is more critically affected by the anisotropy of the Ti environment along the Ti–O chains. In agreement with this picture, Wang et al. [101] reported recently an insensitivity of $Z^{*(T)}$ to a tetragonal macroscopic strain in KNbO₃. Also, the charges reported by Bellaiche et al. [189] in mixed a compound as PZT, where the ionic environment becomes anisotropic, seem to confirm our results.

A band by band decomposition of $Z_{Ti}^{*(T)}$ (Table 3.10) points out that the difference between the cubic and tetragonal phases is essentially localized at the level of the O 2p bands (+1.48 instead of +2.86) while the other contributions remain very similar. This suggests an intuitive explanation. In the cubic phase the O 2p electrons are widely delocalized and dynamical transfers of charge can propagate along the Ti-O chain as suggested by Harrison. In the tetragonal phase, the Ti-O chain behaves as a sequence of Ti-O dimers for which the electrons are less polarizable. This smaller polarizability is confirmed by a similar reduction of the optical dielectric constant along the ferroelectric

 $^{^{6}}$ In the tetragonal phase, shortened and elongated Ti–O bonds alternate along the ferroelectric axis. The shortened bond corresponds to an interatomic distance of 3.67 Å in our optimized tetragonal structure.

Band	$Z_{Ti}^{*(T)}$	$Z_{Ti}^{*(T)}$	$Z_{Ti}^{*(T)}$	$Z_{Ti}^{*(T)}$
	(cubic - 3.67 Å)	(cubic - 3.94 Å)	(tetragonal - exp)	(cubic - 4.40 Å)
Z_{κ}	+12.00	+12.00	+12.00	+12.00
$Ti \ 3s$	-2 - 0.07	-2 - 0.03	-2 - 0.05	-2 + 0.01
Ti 3p	-6 - 0.43	-6 - 0.22	-6 - 0.26	-6 - 0.07
$\operatorname{Ba}5\mathrm{s}$	0 + 0.09	0 + 0.05	0 + 0.05	0 + 0.02
O 2s	0 + 0.27	0 + 0.23	0 + 0.25	0 + 0.19
Ba 5p	0 + 0.64	0 + 0.36	0 + 0.34	0 + 0.13
O 2p	0 + 2.73	0 + 2.86	0 + 1.48	0 + 3.50
Total	+7.23	+7.25	+5.81	+7.78

Table 3.10: Band by band decomposition of $Z_{Ti}^{*(T)}$ in different structure of BaTiO₃. The contributions have been separated into a reference value and an anomalous charge (see text).

direction. This analysis seems plausible from the Wannier function analysis reported by Marzari and Vanderbilt [179].

We note that a behavior similar to the perovskite is observed in $LiNbO_3$, even if the explanation is not so straightforward due to its more complex structure : In Table 3.7, the reduction of the Nb charge at the phase transition originates in a neat decrease of the O 2p contribution.

Finally, let us mention that if the evolution of $Z^{*(T)}$ is relatively weak under isotropic pressure, it would be wrong to consider that the dynamical properties of BaTiO₃ are insensitive to the volume: small changes are observed that are of the same order of magnitude than for other compounds like SiC [190, 191]. The direction of the evolution is however different. Moreover, the evolution of the different charges is even not identical: while the absolute value of $Z_{Ba}^{*(T)}$ and $Z_{O\perp}^{*(T)}$ decreases with increasing volume, the inverse behaviour is observed for $Z_{Ti}^{*(T)}$ and $Z_{O\parallel}^{*(T)}$.

Here also, the band by band decomposition (Table 3.11) reveals some hidden features. In the compressed cubic phase, the anomalous part of the Ba 5p, Ba 5s and Ti 3p bands are 50% larger than in the optimized cubic cell. This suggests an evolution of the interactions between occupied orbitals that is coherent with the modification of the interatomic short-range forces observed independently [53]. At the opposite, in our expanded cubic phase, most of the anomalous contributions to $Z_{Ba}^{*(T)}$ and $Z_{Ti}^{*(T)}$ have disappeared in agreement with the picture of a more ionic material. The O 2p contribution, is the only one that remains surprisingly large. Comparing to the value obtained for the cubic phase at the experimental volume, its evolution was even more important than the linear dependence upon the bond length, expected from the Harrison model.

Band	$Z_{Ba}^{*(T)}$	$Z_{Ba}^{*(T)}$
	(cubic - 3.94 Å)	(cubic - 4.40 Å)
Z_{κ}	+10.00	+10.00
$Ti \ 3s$	0 + 0.01	0 - 0.01
Ti 3p	0 + 0.01	0 + 0.01
$\operatorname{Ba}5\mathrm{s}$	-2 - 0.11	-2 + 0.00
O 2s	0 + 0.73	0 + 0.37
Ba 5p	-6 - 1.38	-6 - 0.44
O 2p	0 + 1.50	0 + 0.66
Total	+2.77	+2.59

Table 3.11: Band by band decomposition of $Z_{Ba}^{*(T)}$ in the optimized cubic phase of BaTiO₃ and in an expanded cubic structure. The contributions have been separated into a reference value and an anomalous charge (see text).

3.8 Spontaneous polarization

The spontaneous polarization (P_s) of the ferroelectric phases can be determined by integrating the change of polarization along the path of atomic displacement from the paraelectric cubic phase (taken as reference) to the considered ferroelectric structure. If the effective charges were roughly constant, this integration should be approximated by:

$$P_{s,\alpha} = \frac{1}{\Omega_o} \sum_{\kappa,\beta} Z_{\kappa,\alpha\beta}^{*(T)} \,\delta\tau_{\kappa,\beta} \tag{3.26}$$

However, we have seen, in the previous Section, that the Born effective charges are strongly affected by the atomic displacements. It is therefore important to investigate their evolution all along the path of atomic displacements from one structure to the other.

We performed the calculation for a transformation from the cubic to the rhombohedral structure. The rhombohedral macroscopic strain is very small and was neglected ⁷: our calculation was performed by displacing the atoms to their theoretically optimized position in rhombohedral symmetry, when keeping the cubic lattice parameters. The result is reported in Figure 3.5, for $Z_{Ti}^{*(T)}$ along the ferroelectric direction. A similar curve can be obtained for $Z_{O\parallel}^{*(T)}$. We observe that the evolution of $Z^{*(T)}$ is approximately quadratic close to the cubic phase. However, it becomes rapidly linear, and remains linear for displacements even larger than those associated to the ferroelectric distortion.

⁷The Born effective charges obtained for the rhombohedral structure when neglecting the strain (i. e. when keeping a cubic unit cell) are the following: $Z_{Ba,11}^{*(T)} = +2.79$, $Z_{Ba,33}^{*(T)} = +2.79$, $Z_{Ti,11}^{*(T)} = +6.54$, $Z_{Ti,33}^{*(T)} = +5.61$, $Z_{O,\perp}^{*(T)} = -1.97$, $Z_{O,\parallel}^{*(T)} = -5.05$. These values must be compared to those reported in Table 3.8, where the rhombohedral strain was taken into accounts. It can be checked that the effect of this strain is negligible.



Figure 3.5: Evolution of the amplitude of $Z_{T_i}^{*(T)}$ in the < 111 > direction all along the path of atomic displacements from the cubic ($\lambda = 0$) to the rhombohedral ($\lambda = 1$) phase. The distortion of the cubic cell has been neglected.

Expecting a similar evolution of the dynamical charges for the tetragonal and orthorhombic displacements, an estimation of the spontaneous polarization in the ferroelectric phases can be found when using Eq. (3.26) with a mean effective charge determined from its value in both phases. Using a mean charge estimated from the values in the paraand ferro-electric phases, we obtain the spontaneous polarizations presented in Table 3.12.

Our results are only in relative agreement with the experiment [192, 139] and suggest different comments. Firstly, we would like to mention that part of the discrepancy must be assigned to the theoretical overestimation of the computed ferroelectric displacements, discussed in Chapter 2 : when using the experimental displacements of Ref. [105], we recover a better estimation of P_s as in Ref. [136]. The dispersion of X-rays diffraction data makes however difficult the exact identification of the ferroelectric displacements. Secondly, another part of the error could be due to the lack of polarization dependence of the LDA [193]. Finally, we note that there is also some uncertainty on the experimental value of P_s .

3.9 Conclusions

In this Chapter, we first analyzed the links between different definitions of atomic charge. We have shown that, contrary to the static definitions, dynamical effective charges also depend on the electronic charge reorganisation induced by an atomic displacement. The amplitude of this dynamical contribution is monitored not only by the bonding with the other atoms but also, for large systems, by the condition imposed on the macroscopic electric field. A unified treatment of the concept of dynamical charge in molecules,
Table 3.12: Spontaneous polarization in the three ferroelectric phases of BaTiO₃ in $\mu C/cm^2$. The results were deduced from Eq. (3.26) when using either $Z^{*(T)}$ from the cubic phase (Cubic) or a mean charge (Mean) defined as $(Z_{mean}^{*(T)} = 0.68 \times Z_{cubic}^{*(T)} + 0.32 \times Z_{ferro}^{*(T)})$. Results are reported for the experimental (Exp) and theoretical (Theo) atomic ferroelectric displacements.

$Z^{*(T)}$	Positions	Tetragonal	Orthorhombic	Rhombohedral	Reference
_	_	26.3	30.7	33.5	Exp. [192]
Cubic	Exp	30	26	44	Ref. [136]
Cubic	Theo	36.35	42.78	43.30	Present
Mean	Theo	34.02	39.68	40.17	Present
Mean	Exp	28.64	36.11	—	Present

large clusters, and truly periodic systems has been presented, in which the Born effective charge and the optical dielectric constant appear as the two fundamental quantities. The microscopic origin of the dynamical contribution has been discussed in terms of local polarizability and delocalized transfers of electrons.

Based on various first-principles results, we have then emphasized that the Born effective charges are anomalously large in the family of ABO₃ compounds: their amplitude can reach more than twice that of the nominal ionic charges. This feature was explained in terms of interatomic transfers of charge, produced by "off-site" dynamical changes of hybridization. For BaTiO₃ and SrTiO₃, we have brought to light complex dynamical changes of hybridization, concerning not only Ti and O but also Ba and Sr orbitals. The hybridizations restricted to occupied states generate however compensating anomalous contributions so that, finally, the total value of $Z^{*(T)}$ is essentially affected by dynamical changes of hybridization between O 2p and Ti 3d orbitals.

As a more general issue, it appears that the existence of partial hybridizations between occupied and unoccupied states is an important feature for candidate to large anomalous Born effective charges. Moreover, the dynamical transfers of charge are expected to be larger when such a hybridization involve d states, for which the interactions parameters with other orbitals are particularly sensitive to the interatomic distance.

Investigating the evolution of $Z^{*(T)}$ to the structural features, we have shown that they are strongly affected by the ferroelectric atomic displacements and much less sensitive to isotropic pressure. The results have clarified that the amplitude of $Z^{*(T)}$ is not monitored by a particular interatomic distance but is dependent on the anisotropy of the Ti environment along the Ti-O chains.

Finally, the effective charges were used to estimate the spontaneous polarization in the ferroelectric phases of $BaTiO_3$. For that purpose, their evolution was investigated all along the path of atomic displacements from the cubic to the rhombohedral structure and reveal a highly non-linear character.

All along this Chapter, we only focused on the *microscopic* mechanisms that govern

the amplitude of the Born effective charges. In Chapter 5, it will be emphasized that the anomalously large Born effective charges produce a giant LO-TO splitting in ABO_3 compounds, specially for the ferroelectric phonon mode [136, 53]. Moreover, it will be demonstrated that this feature is associated to the existence of an anomalously large destabilizing dipole-dipole interaction, sufficient to compensate the stabilizing short-range forces and induce the ferroelectric instability [53]. In materials where polar modes play a major role, the Born effective charge appears therefore also as a "key concept" to relate the electronic and structural properties.

In the next Chapters we will simplify the notations : Z^* (without additional subscript) will refer to the Born effective charge except when it is explicitly mentionned.

3.10 References

The results presented in this Chapter have been discussed in the following papers:

- Ph. Ghosez, X. Gonze and J.-P. Michenaud, First-principles calculations of dielectric and effective charge tensors in barium titanate, Ferroelectrics 153, 91 (1994).
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- M. Veithen and Ph. Ghosez, First-principles study of the dielectric and dynamical properties of lithium niobate, Phys. Rev. B, in press (to appear in 2002).

Chapter 4

Electron localization

4.1 Introduction

From a pure phenomenological point of view, our understanding of the electronic properties of crystalline solids is quite clear: the inner electrons are chemically innert and localized on the nucleus while the outer ones are responsible for the cohesion between atoms. In insulators, they are confined to a particular bond while they are free to move through the whole system in metals.

At the opposite, in a microscopic description based on quantum mechanics, the electronic wavefunctions have the Bloch form and are delocalized on the whole crystal. This picture is valid for the inner electrons as well as the outer ones, for insulators and metals. In order to describe the properties of these systems we have to refer to their excitation spectrum and to the fermionic nature of the particles.

These two approaches allow to understand a huge number of physical phenomena but it does not seem trivial to make a connection between them. In particular, it appears difficult to define a "center of gravity" for the electronic wavefunctions as well as their degree of localization because of the extended nature of the Bloch functions. In confined systems like molecules, these properties are simply related to the expectation values of the position operator and its square. But in crystalline solids the operators x and x^2 are incompatible with the usually adopted Born von Karman boundary conditions and cannot be used. Even a description based on locallized Wannier functions [194] (WF) does not solve this problem because of their nonuniqueness.

During the last decade, the modern theory of polarization [35, 36, 34] and the apperance of many body phase operators [195, 196] allowed these difficulties to be overcome. While the former theory identifies the center of the electronic distribution to a Berry phase of the Bloch functions, the latter one leads to a unified treatment of polarization and localization. It shows that electron localization is a property of the many-body ground-state wavefunction, an idea already emphasized by W. Kohn in 1964 [197]. It also permits one to define a characteristic localization length [198] that is finite in insulators and diverges in metals. In order to describe anisotropic media, this length has been generalized to a localization tensor [199, 200] that is the basic quantity we are dealing with in this Chapter. In this Chapter, we will investigate the degree of electron localization in lithium niobate (LiNbO₃). Similar results have been obtained on various oxides including BaO and BaTiO₃ as well as PbO and PbTiO₃. In the next section we will summarize the formalism of the localization tensor and show how it can be decomposed into contributions coming from the different groups of bands forming the energy spectrum of a solid. These techniques will then be applied to study the degree of electron localization in the two phases of LiNbO₃. In the discussion we will make a comparison with the evolution of the Born effective charges and the electronic structure of this compound.

4.2 Background and Formalism

4.2.1 Localization tensor

Our electronic structure calculations are performed in the framework of density functional theory (DFT). In an infinite crystal on which we impose periodic Born von Karman boundary conditions the one particle orbitals are of the Bloch form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}). \tag{4.1}$$

Their choice is not unique. An equivalent set of wavefunctions can be obtained from a unitary (gauge) transformation [85]

$$\left|u_{n\mathbf{k}}'\right\rangle = \sum_{m=1}^{N} U_{nm,\mathbf{k}} \left|u_{m\mathbf{k}}\right\rangle \tag{4.2}$$

where N is the number of doubly occupied bands. For the ground-state the most natural choice is the so called "diagonal gauge" where the Hamiltonian is diagonal

$$\langle u_{m\mathbf{k}}|H_{\mathbf{k}}|u_{n\mathbf{k}}\rangle = \varepsilon_{n\mathbf{k}}\delta_{nm} \tag{4.3}$$

and where its matrix elemets are the Kohn-Sham eigenenergies.

In an insulating crystal, the localization tensor can be computed from the Bloch functions and their first derivatives with respect to their wavevector [199, 200]

$$\langle r_{\alpha}r_{\beta}\rangle_{c} = \frac{V_{c}}{N(2\pi)^{3}} \int_{BZ} d\mathbf{k} \left\{ \sum_{n=1}^{N} \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \right| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle - \sum_{n,n'=1}^{N} \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \right| u_{n'\mathbf{k}} \left\rangle \left\langle u_{n'\mathbf{k}} \right| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle \right\}$$

$$(4.4)$$

where V_c is the volume of the primitive unit cell in real space and α , β are two cartesian directions. The derivatives $\left|\frac{\partial u_{nk}}{\partial k_{\alpha}}\right\rangle$ are computed from a linear response approach to DFT [83]. As for the ground-state wavefunctions we have a gauge freedom. The calculations are most easily performed within the so called parallel gauge (subscript 'p') where the first order wavefunctions are orthogonal to the subspace of occupied states

$$\left\langle u_{n\mathbf{k}} \left| \frac{\partial u_{m\mathbf{k}}}{\partial k_{\alpha}} \right|_{p} \right\rangle = 0 \qquad \text{m,n} = 1, \dots, \text{N}.$$
 (4.5)

4.2.2 Band by band decomposition

As stated above, the localization tensor is related to a kind of second moment of the electronic wavefunctions. From standard statistics, it is known that when we take the sum of two scalar random variables their variances do not simply add but there is a supplementary term that enters the sum: their covariance. It indicates how these two variables are related and it is zero if they are independent. In this case the total two dimensional probability density function can be written as the product of two scalar functions, each beeing associated to one variable only. Based on this argument, we propose a decomposition of the localization tensor on the different groups of bands composing the energy spectrum of a solid: Suppose that the band structure is formed of N_g isolated groups that contain n_i bands. The localization tensor of a particular group is defined as

$$\langle r_{\alpha}r_{\beta}\rangle_{c}(i) = \frac{V_{c}}{n_{i}(2\pi)^{3}} \int_{BZ} d\mathbf{k} \left\{ \sum_{n \in i} \left\langle \frac{\partial u_{n}\mathbf{k}}{\partial k_{\alpha}} \middle| \frac{\partial u_{n}\mathbf{k}}{\partial k_{\beta}} \right\rangle - \sum_{n,n' \in i} \left\langle \frac{\partial u_{n}\mathbf{k}}{\partial k_{\alpha}} \middle| u_{n'}\mathbf{k} \right\rangle \left\langle u_{n'}\mathbf{k} \middle| \frac{\partial u_{n}\mathbf{k}}{\partial k_{\beta}} \right\rangle \right\}$$

$$\tag{4.6}$$

where the sums have to be taken over the bands of group *i*. The covariance of two groups i and j ($i \neq j$) is given by the relation

$$\langle r_{\alpha}r_{\beta}\rangle_{c}(i,j) = \frac{-V_{c}}{n_{i}n_{j}(2\pi)^{3}} \int_{BZ} d\mathbf{k} \sum_{n \in i} \sum_{n' \in j} \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \middle| u_{n'\mathbf{k}} \right\rangle \left\langle u_{n'\mathbf{k}} \left| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle.$$
(4.7)

Its origin comes from the fact that the total, many-body wavefunction is a Slater determinant of the one-particle orbitals and not simply their product. Using these definitions, the total tensor, associated to the whole set of occupied bands, can be written as

$$\langle r_{\alpha}r_{\beta}\rangle_{c} = \frac{1}{N}\sum_{i=1}^{N_{g}} n_{i} \left\{ \langle r_{\alpha}r_{\beta}\rangle_{c}(i) + \sum_{j\neq i}^{N_{g}} n_{j}\langle r_{\alpha}r_{\beta}\rangle_{c}(i,j) \right\}.$$
(4.8)

This global quantity is independent of the gauge chosen to calculate the ground-state and first-order wavefunctions. On the contrary, the above defined decomposition is only meaningful if there is no admixture between the wavefunctions associated to different groups of bands. That means that the Hamiltonian matrix and its first-order perturbation expansion $H_{\mathbf{k}}^{(1)}$ have to be diagonal. This is the case of the ground state wavefunctions calculated within the diagonal gauge (4.3) but not of their derivatives obtained within the parallel gauge (4.5). In order to give a physical sense to the different terms in Eq. (4.8) we have to apply a gauge transformation to the set of first-order wavefunctions that diagonalizes $H_{\mathbf{k}}^{(1)}$ [169].

4.3 Results and discussions

4.3.1 Technical details

As in the previous Chapter, our results are obtained thanks to the ABINIT package. For bulk $LiNbO_3$, the wavefunctions were expanded in plane waves up to a kinetic-energy

cutoff of 45 Hartrees and the Brillouin zone was sampled using a $6 \times 6 \times 6$ Monkhorst-Pack mesh of special k-points. All calculations are performed at the optimized lattice constants and atomic positions as they are reported in Chapter 2.

We also computed the localization tensor for the isolated atoms Nb, Li and O by placing each atom at the origin of a periodic supercell of 20 Bohrs. As this theory only applies to systems where the highest occupied state is separated from the lowest unoccupied level by a finite gap, we did not perform the calculations on the neutral atoms with partial filling of the atomic orbitals. We used instead the ionic configurations Li⁺ and Nb⁵⁺. For the oxygen atom, the most natural choice was the O²⁻ ion. Unfortunately, such a system is difficult to describe in the LDA so that we fixed the occupation of the states $2p_x$, $2p_y$ and $2p_z$ to 4/3 in order to get accurate values for the O 2s state.

4.3.2 Band by band decomposition of the localization tensor

The electronic properties of lithium niobate have been presented in Chapter 2. Its band structure is composed of well separated groups of bands (Fig. 2.12). In Table 4.1, we summarize the band by band decomposition of the localization tensor in the two phases. As the dielectric tensor in uniaxial crystals, this quantity is diagonal when it is expressed in the principal axes. Its eigenvalues $\langle r_{\perp}r_{\perp}\rangle_c$ (two times degenerate) and $\langle r_{\parallel}r_{\parallel}\rangle_c$ refer to cartesian directions perpendicular and parallel to the optical axis. The first five lines give the variance $\langle r_{\alpha}r_{\beta}\rangle(i)$ (see Eq. (4.6)) for each of the five groups of bands shown in Fig. 2.12. They are compared to the localization tensors of the corresponding atomic states calculated on isolated atoms. The last three lines give the total variance

$$\frac{1}{N}\sum_{i=1}^{N_g} n_i \langle r_\alpha r_\beta \rangle(i),$$

the total covariance

$$\frac{-1}{N}\sum_{i=1}^{N_g} n_i \sum_{j=1}^{N_g} n_j \langle r_\alpha r_\beta \rangle(i,j)$$

and the localization tensor calculated on the whole set of valence bands from Eq. (4.8). We see that the bands Nb 4s, Li 1s and O 2s present a degree of localization similar to the associated atomic orbitals in the two phases. The Nb 4p electrons are more delocalized in the crystal but these values are also quite unaffected by the phase transition. The only appreciable variation concerns the element $\langle r_{\parallel}r_{\parallel}\rangle_c$ of the O 2p group which decreases of about 6.4 %.

As it was shown earlier [199, 200], the localization tensor is related to the spread of the so called "maximally localized WF" [179]. Another quantity related to these WF is the spontaneous polarization [35, 36, 34] which depends on the displacement of the WF centers during the phase transition. LiNbO₃ exhibits a particularly large spontaneous polarization. Experimentally [201, 202], a value of 0.71 C/m² has been measured while we obtained a value of 0.80 C/m² from a Berry phase calculation. By combining this

Table 4.1: Band by band decomposition of the localization tensor $(Bohr^2)$ in the two phases of lithium niobate and for the inner orbitals of the Nb, Li and O atoms. The elements $\langle r_{\perp}r_{\perp}\rangle_c$ and $\langle r_{\parallel}r_{\parallel}\rangle_c$ refer to two cartesian directions perpendicular and parallel to the threefold axis. The tensors calculated on the isolated atoms are isotropic and defined by their eigenvalues $\langle r^2 \rangle_c$.

Bands	Atom	Paraelectric phase		Ferroelect	ric phase
	$\langle r^2 \rangle_c$	$\langle r_{\perp}r_{\perp}\rangle_c$	$\langle r_{\parallel}r_{\parallel} angle_{c}$	$\langle r_{\perp}r_{\perp}\rangle_c$	$\langle r_{ }r_{ } angle_{c}$
Nb 4s	0.479	0.514	0.514	0.516	0.514
Li 1s	0.158	0.167	0.164	0.166	0.165
Nb 4p	0.576	0.721	0.719	0.728	0.714
O 2s	0.892	0.879	0.870	0.893	0.848
O 2p		1.488	1.515	1.483	1.418
Tot. variance		1.110	1.123	1.111	1.066
Tot. covariance		-0.388	-0.384	-0.395	-0.377
Tot. tensor		0.722	0.738	0.716	0.689

result with the localization tensors in Table 4.1 we see that the WF centers are strongly affected by the phase transition while their spread remains quite constant. We also have performed calculations on other ABO_3 compounds where we obtain similar results: the localization tensor varies only slightly during the phase transitions.

It is interesting to compare the values in Table 4.1 to the band by band decomposition of the Born effective charge of the Nb atoms reported in Chapter 3. In Table 4.2 we recall the eigenvalues of the symmetric part of Z_{Nb}^* .

For the Nb 4s and Li 1s bands, Z_{Nb}^* is nearly equal to its nominal value. This and the fact that the localization tensors for these two groups are close to the atomic ones allow us to conclude that the corresponding atomic orbitals are inert and do not contribute to the chemical bonds in LiNbO₃.

For the Nb 4p and O 2s bands, we observe small *anomalous* contributions indicating non negligible interactions of the original atomic states. This is coherent with the localization tensor of the Nb 4p bands which is larger than for the isolated Nb⁵⁺ ion. For the O 2s bands however we do not observe any sizeable delocalization.

The largest anomalous contributions come from the O 2p bands. During the transition to the ferroelectric state, their contributions to $Z_{Nb\perp}^*$ and $Z_{Nb\parallel}^*$ present an important decrease of 28 % and 56 %. This and the observation concerning the evolution of E_g made in Chapter 2 suggest a strong variation of the Nb 4d - O 2p hybridization during the phase transition. In spite of these important changes, the localization tensor of the O 2p bands varies only slightly (6.4 %) suggesting that the second moment of the electronic distribution is less sensitive to the details of the covalent interaction than Z^* and E_g . It is interesting to note that not only E_g varies during the phase transition but also the spread of the O 2p bands. This latter quantity presents a change (6.9 %) that is similar to what

Table 4.2: Band by band decomposition of Z_{Nb}^* in the two phases of lithium niobate. Reported are the eigenvalues (in atomic units of charge) of the symmetric parts of the tensors. The elemets $Z_{Nb\perp}^*$ and $Z_{Nb\parallel}^*$ refer to two catesian directions perpendicular and parallel to the threefold axis.

Bands	Paraelectric phase		ctric phase	Ferroel	ectric phase
	Nominal	$Z^*_{Nb\perp}$	$Z^*_{Nb\parallel}$	$Z^*_{Nb\perp}$	$Z^*_{Nb\parallel}$
Z_{core}	13.00	13.00	13.00	13.00	13.00
Nb 4s	-2.00	-2.04	-2.02	-2.06	-2.04
Li 1s	0.00	0.01	0.00	0.01	0.00
Nb 4p	-6.00	-6.42	-6.37	-6.49	-6.35
O 2s	0.00	0.57	0.58	0.60	0.50
O 2p	0.00	3.14	3.89	2.25	1.71
Tot.	5.00	8.26	9.08	7.30	6.83

we observe for the localization tensor of the O 2p group.

4.3.3 Charge transfer versus local polarizability

The relative insensitivity of the localization tensor to the phase transition contrasts with the evolution of the Born effective charges and, at first sight, may appear surprising. However, as it is now discussed, it is compatible with the simple Harrison model introduced in the previous Chapter. Let us emphasize that results similar to those reported above have been obtained for cubic perovskites such as $BaTiO_3$ so that they are not related to the specific structure of lithium niobate.

As illustrated in Fig. 4.1, the Born effective charges are related to the unusually high slope of the polarization in the graph of \mathcal{P} versus ferroelectric atomic displacements. The decrease of Z^* from the paraelectric to the ferroelectric phase originates in the non-linear behavior of \mathcal{P} in this graph and in particular to the decrease of the slope. Along the same path of displacements, and contrary to \mathcal{P} , the localization length is only slightly varying and tends to decrease.

To clarify these evolutions we can discuss a simple one-dimensional model . For simplicity, let us consider a Ti–O chain of atoms intended to mimick what happens in BaTiO₃. The atoms are at a distance *a* from each others. In Fig. 4.2, we report a schematic view of electronic density associated to the O 2p Wannier function. We can investigate separately the behavior expected from the two extreme cases of (a) charge transfer and (b) local polarizability introduced in the previous Chapter to explain the origin of anomalous effective charges

Whithin the Harrison model (panel a), this density is centered on an oxygen atom but, due to small hybridizations with Ti 3d orbitals, is also slightly delocalized on the two neighbouring Ti atoms. When the oxygen atom is displaced by a quantity $\Delta \tau$,



Figure 4.1: Schematic evolution of (a) the macroscopic polarization and (b) the localization length along the path of displacements from the paraelectric to the ferroelectric phase. The Born effective charges are proportional to the slope of P in panel (a).

the central part of the density follows the atom while, due to changes of O 2p – Ti 3d hybridizations, there is a charge transfer of electrons from one Ti atom to the other which is responsible for a large displacement $\Delta < x > > \Delta \tau$ of the center of gravity of the Wannier function and the anomalous value of the Born effective charge. However, during the oxygen displacement, the second moment of the central part of the density remains unaffected. Moreover, the electrons delocalized on the Ti atoms are transfered from one side of the unit cell to the other but, roughly speaking, remain at a distance *a* of the O atom so that, for those electrons, the second moment remains essentially unaffected. More correctly, a small reduction proportional to the atomic displacement is expected because most of the electrons on the Ti atoms are now at a distance $a - \Delta \tau$ from the oxygen.

Alternatively, within a *shell model* (panel b), the electronic charge is expected to be located on the oxygen. During an atomic displacement, there is no transfer of charge but the anomalous value of Z^* originates in the unusual polarizability of the oxygen atom. This means that the electronic charge is globally displaced by a quantity $\Delta < x > > \Delta \tau$. This however would produce an increase of the second moment of the electronic density.

The results of the previous Section are more compatible with the first explanation and appear therefore as an additional proof of the validity of Harrison's model. We note that this model predicts an highly asymmetric charge density in the ferroeloectric phase and therefore suggests that the third moment of the density is annalously high.

4.4 Conclusions

In this Chapter, we briefly summarized the formalism of the localization tensor and shown how this quantity can be decomposed into contributions coming from the different groups of bands composing the energy spectrum of a solid. This formalism has then been applied to investigate the degree of electron localization in the two phases of $LiNbO_3$. Our results were compared to the electronic structure and the Born effective charges of this compound.

We observed that the deepest levels Nb 4s and Li 1s are chemically innert while the atomic states Nb 4p and O 2s present weak covalent interactions that generate small



Figure 4.2: Schematic view of the electronic density associated to the O 2p Wannier function along a one dimensional Ti–O chain berore (full line) and after (dashed line) the oxygen atom is displaced in case of (a) charge transfer and (b) local polarizability. When the atom is displaced by $\Delta \tau$, the center of gravity of the Wannier function is displaced by $\Delta < x >$.

anomalous effective charges and that delocalize the Nb 4p electrons. The O 2p bands are the only group that presents an appreciable change of electron localization during the phase transition. This variation is small compared to what we observed for E_g and Z_{Nb}^* but of the same order of magnitude as the variation of the spread of these bands. These results suggest that the localization tensor is less sensitive to the details of the electronic structure of a compound than are for example the Born effective charges. This insensitivity is compatible with the Harrison model in which the electrons of the O 2p bands are partly delocalized on the Ti atoms.

4.5 References

A good review of the concepts of Berry phase and geometric quantum distance is given in the following course :

 R. Resta, Berry's Phase and Geometric Quantum Distance : macroscopic polarization and electron localization, Troisième Cycle de la Physique en Suisse Romande (année académique 1999-2000). A electronic version of this course is accessible at the URL : http://www-dft.ts.infn.it/~resta/publ/notes2000.ps.gz.

The results presented in this Chapter are discussed in:

 M. Veithen, X. Gonze and Ph. Ghosez, *Electron localization in lithium niobate*, In "Fundamental Physics of Ferroelectrics", AIP CP , ed. R. E. Cohen (AIP, Melville, 2002), in press.

CHAPTER 4 : ELECTRON LOCALIZATION

♦ M. Veithen, X. Gonze and Ph. Ghosez, unpublished.

Chapter 5

Lattice dynamics

5.1 Introduction

BaTiO₃ is well known to exhibit a ferroelectric instability and since long there have been considerable efforts to understand the microscopic origin of its successive phase transitions [14]. Among all these works, the most gratifying explanation is probably due to Cochran [17] who realized that the problem could be interestingly recast in the framework of lattice dynamics ¹. Within a shell-model approach, he associated the ferroelectric transition with the softening of a transverse optic phonon, originating in the near cancellation of Coulomb and short-range interactions. The destabilizing role of dipolar forces had been previously pointed out by Slater [15], but it appeared more coherently within the shell-model. In spite of the qualitative character of Cochran's investigations, the delicate balance between short-range repulsions and long-range destabilizing electrostatic forces is still now usually referred to as the origin of the ferroelectricity [93, 98, 44].

Cochran, when introducing the concept of "soft mode", was the first who associated the ferroelectric instability to the lattice dynamics. Consequently to his work, the lattice dynamics of ABO₃ compounds has been subject to various investigations. A large number of experiments have been performed in order to confirm the existence of a soft ferroelectric mode in BaTiO₃ (and other ABO₃ compounds. They include infra-red [203, 204, 205, 206] and Raman [207, 208, 209, 210, 211, 212, 213, 214] measurements of the Γ phonon modes as well as various neutron diffraction data [215, 216, 217, 218, 219, 220]. These experiments focused on the temperature behaviour of the soft phonon and were mainly concerned by the low frequency modes.

Simultaneously, theoretical phonon dispersion curves of $BaTiO_3$ were deduced from a fit of the experimental data using different shell models. Let us mention the pseudo-ionic model developed by Gnininvi and Bouillot [221] or the rigid-shell model used by Jannot *et al.* [220]. These models were however not particularly suited to describe the ABO₃ crystals. During the seventies, Migoni, Bilz and Bäuerle [22] pointed out that the behaviour of the ferroelectric soft mode in the oxidic perovskites originates from an unusual anisotropic

¹A similar approach was taken independently by Anderson [18].

polarizability of the oxygen that, in turn, may be connected to hybridization between O 2p and B d states. A more sophisticated "polarizability model" [23, 24] was then introduced in order to include the specific physical features of ABO₃ compounds. The application of this model to BaTiO₃ was reported by Khatib *et al.* [141]. In their work, they obtained a full phonon band structure and investigated the temperature behaviour of the ferroelectric soft mode. However, their interesting results still remained at a semi-empirical level.

Since a few years, theoretical advances have enabled one to determine the phonon frequencies of solids from first principles. The phonon frequencies at the Γ point have been computed for various ABO₃ compounds using frozen phonon or linear response techniques. Going further, *ab initio* phonon dispersion curves are now available for numerous compounds (KNbO₃ [222], SrTiO₃ [173], BaTiO₃ [223], PbTiO₃ [91], PbZrO₃ [91], LiNbO₃).

In this Chapter, we will first reintroduce some basics concerning the lattice dynamics of ionic crystals. We shall then summarize results concerning different ABO₃ compounds, paying a particular attention to the case of BaTiO₃. We will report on the phonon frequencies at the Γ point in the cubic and rhombohedral structure. The phonon dispersion curves will then be deduced in the cubic phase and the interatomic force constants analysed. Finally, the behavior of BaTiO₃ will be compared to that of other perovskite compounds and the lattice dynamics of mixed compounds will be discussed. These results will allow to address some fundamental questions concerning the ferroelectric instability.

First, the different quantities involved in the Cochran model are directly accessible from our first-principles calculations. This will enable us to investigate the concomitant role played by Coulomb and short-range interactions in a more general context, going beyond Cochran's results [53]. In this framework, we will be able to highlight the connection between the electronic and dynamical properties.

Second, the analysis of the phonon dispersion curves will suggest that the appearance of the ferroelectric instability requires some specific correlations of the atomic displacements. This feature will be investigated with the help of the interatomic force constants. Our results will be contrasted with some experimental evidences. They will be discussed in connection with the existing "8-sites" model [27, 224] and the model of Hüller [28].

Third, the lattice dynamics and structural instabilities of the perovskite ABO_3 compounds can be very different in spite of their identical structure at high temperature. From the inspection of the interatomic force constants, we will point out that all these compounds are very similar and that their different behavior originates in small differences of only few key quantities.

5.2 The dynamical equation

In Chapter 1, we have reported atomic positions for the ions. Implicitely, we have considered that the position \mathbf{R}^a_{κ} of atom κ in unit cell a is fixed and given by :

$$\mathbf{R}^{a}_{\kappa} = (\mathbf{R}^{a} + \mathbf{R}_{\kappa}) \tag{5.1}$$

where \mathbf{R}^a is the vector defining the position of unit cell *a* and \mathbf{R}_{κ} gives the position of the atom within the unit cell. In fact, these \mathbf{R}^a_{κ} are mean positions around which the atoms can oscillate.

In the present Chapter, we consider that the instantaneous position $\mathbf{R}^{a}_{\kappa}(t)$ of atom κ in unit cell *a* may be of a small deviation $\boldsymbol{\tau}^{a}_{\kappa}(t)$ around the mean position :

$$\mathbf{R}^{a}_{\kappa}(t) = (\mathbf{R}^{a} + \mathbf{R}_{\kappa}) + \boldsymbol{\tau}^{a}_{\kappa}(t).$$
 (5.2)

The movement of the ions will be treated thanks to classical equations of motions. We shall consider ionic displacements that are small compared with the interionic spacing, so that it remains possible to work in the *harmonic* approximation. Moreover, we shall remain in the *adiabatic* approximation, in which it is considered that the electrons are in their ground-state for any instantaneous ionic configuration.

In the harmonic approximation, the total energy of a periodic crystal with small lattice distortions from the equilibrium positions can be expressed as

$$E_{\rm e+i}^{\rm harm}(\{\boldsymbol{R}_{\boldsymbol{\kappa}}^{\boldsymbol{a}}\}) = E_{\rm e+i}^{(0)} + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left(\frac{\partial^2 E_{\rm e+i}}{\partial \tau_{\kappa\alpha}^a \partial \tau_{\kappa'\beta}^b}\right) \tau_{\kappa\alpha}^a \tau_{\kappa'\beta}^b$$
(5.3)

where $\tau_{\kappa\alpha}^{a}$ is the displacement along direction α of the atom κ in the cell a (with vector \mathbf{R}^{a}), from its equilibrium position $\mathbf{R}^{a} + \mathbf{R}_{\kappa}$. The classical equations of motion for the ions are then:

$$M_{\kappa} \frac{\partial^2 \tau_{\kappa\alpha}^a}{\partial t^2} = -\frac{\partial E_{e+i}^{harm}}{\partial \tau_{\kappa\alpha}^a} = -\sum_{b\kappa'\beta} \left(\frac{\partial^2 E_{e+i}}{\partial \tau_{a\kappa\alpha} \partial \tau_{b\kappa'\beta}}\right) \tau_{b\kappa'\beta}$$
(5.4)

We have 3 equations of motions of this type (one for each direction) for *each* atom in the crystal. We seek a general solution of the form:

$$\tau^a_{\kappa\alpha}(t) = \eta^a_m(\kappa\alpha)e^{-i\omega_m t} \tag{5.5}$$

Due to the lattice periodicity, the matrix of the second derivative of the energy appearing in Eq. (5.3) is invariant against a rigid body translation of the crystal by a lattice translation vector. Coherently with this property, we can propose a more explicit solution of the form:

$$\tau^{a}_{\kappa\alpha}(t) = \eta_{m\mathbf{q}}(\kappa\alpha) \ e^{i\mathbf{q}.\mathbf{R}_{a}} \ e^{-i\omega_{m}t}$$
(5.6)

for which the vibrations of the ions have been classified according to a wave vector \mathbf{q} . This approach is strictly equivalent to that taken for the electrons through the Bloch theorem. For an infinite solid, it will allow to replace the problem of solving a infinite set of coupled equations (Eq. 5.4) by another problem of $3 \times N_{at}$ equations (where N_{at} is the number of atoms per basic unit cell) to be solved for an infinite number of wave vector \mathbf{q} . For a finite solid composed of N unit cells, only \mathbf{q} -vectors compatible with Born-von Karman boundary conditions must be considered. In practice, we will see later that the full dispersion curves can be deduced from calculations on a very small set of \mathbf{q} -vectors.

A few definitions are now introduced. The matrix of the interatomic force constants (IFCs) in real space is defined as

$$C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E_{e+i}}{\partial \tau^a_{\kappa\alpha} \partial \tau^b_{\kappa'\beta}}\right),\tag{5.7}$$

while its discrete Fourier transform takes the following form:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \frac{1}{N} \sum_{ab} C_{\kappa\alpha,\kappa'\beta}(a,b) e^{-i\mathbf{q}\cdot(\mathbf{R}_a - \mathbf{R}_b)} \\
= \sum_{b} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b} ,$$
(5.8)

where N is the number of cells of the crystal in the Born-von Karman approach. This last quantity is connected to the dynamical matrix $\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$ by

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) / (M_{\kappa}M_{\kappa'})^{1/2} .$$
(5.9)

From these definitions, the movement of the ions can be described in terms of the following dynamical equation:

$$\sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})\eta_{m\mathbf{q}}(\kappa'\beta) = M_{\kappa}\omega_{m\mathbf{q}}^2\eta_{m\mathbf{q}}(\kappa\alpha) .$$
(5.10)

Equivalently, the normal modes of vibrations are solution of the following eigenvalue problem:

$$\sum_{\kappa'\beta} \tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})\gamma_{m\mathbf{q}}(\kappa'\beta) = \omega_{m\mathbf{q}}^2\gamma_{m\mathbf{q}}(\kappa\alpha) .$$
(5.11)

The square root of the eigenvalues of the previous equations $\omega_{m\mathbf{q}}$ are the phonon frequencies at wave vector \mathbf{q} , while $\gamma_{m\mathbf{q}}$ are their associated phonon eigenvectors. The $\eta_{m\mathbf{q}}$ are usually referred to as the phonon eigendisplacements. They are normalized such that $\langle \eta | M | \eta \rangle = 1$, where $M = M_{\kappa} \delta_{\kappa\kappa'}$ is the mass matrix. Phonon eigenvectors and eigendisplacements are therefore related by: $\gamma = \sqrt{M}.\eta$.

Let us emphasize that ω^2 are the eigenvalues of the dynamical matrix and are therefore directly related to the second derivatives of the energy with respect to the atomic positions. When the reference crystalline phase of interest is stable and the associated mean position of the atoms corresponds to a minimum of energy, the curvature of the energy surface around this minimum is always positive as well therefore as ω^2 and the phonon frequencies. At the opposite, when the reference ionic configuration is unstable and related to a more stable phase through a double-well energy profile for a given pattern of ionic displacements, the curvature of the energy at the origin, along this path of displacements, will be negative. This yields a negative ω^2 and an *imaginary* phonon frequency ².

 $^{^{2}}$ This imaginary frequency is associated, within the harmonic approximation, to atomic displacements increasing exponentially with time. In practice, this does not happen and the ions are stabilized in another structure by the anharmonicities.

Within the harmonic approximation, an imaginary phonon frequency corresponds therefore to a crystal instability and the associated phonon eigendisplacement pattern provides the path of displacements along with the energy is decreasing. In this context, the computation of the phonons appears therefore as an interesting tool to identify and characterize structural instabilities. In this study, it will reveal of paradigm importance.

5.3 First-principles calculations

From the dynamical equation, the basic ingredient to be known to compute the phonon frequencies is the *dynamical matrix*. To determine this matrix, different theoretical approaches can be considered.

In semi-empirical shell-models (like the model of Cochran [17] discussed later in this Chapter or the polarizability model of Bilz [23]), the crystal is described in terms of atoms composed of an ionic core and an electronic shell, each of these having their own charge and being connected to each others and neighboring atoms by springs. The interactions to be considered are chosen *a priori* and unambiguously define the form of the dynamical matrix. However, each pair interaction is described with one or more parameters that need to be adjusted to reproduce the correct dispersion curves. Consequently, the method is helpful to understand the shape of the dispersion curves from a microscopic simple model but is not predictive.

Using a first-principles approach, it is possible to compute the total energy of a crystal as a function of the atomic positions and therefore to determine the phonon band structure *a priori* with an accuracy usually around 5 % with the experimental data. The dynamical matrix is constructed by computing directly the change of the total (electronic and ionic) energy under atomic displacements. This can be done using a so-called *frozen phonon* technique : finite atomic displacements are frozen in the structure and the second derivative of the energy is extracted (either from the curvature of the energy or from finite differences of the atomic forces). The approach is straightforward at the Brillouin zone center. For non- Γ phonons, a supercell must be considered compatible with the **q**-vector of interest.

Alternatively, the second derivative of the energy can also be determined using perturbation theory as discussed in Chapter 1. This method requires some additional implementation efforts ³ but presents the advantage that it allows to keep the simplicity of a single cell calculation whatever the **q**-vector which is considered and that can even be incommensurate with the crystal lattice.

All the results reported here have been obtained using a variational formulation [83, 84] of the density functional perturbation theory [42].

 $^{^{3}}$ It is relatively straightforward for plane-wave codes but it not so easy with ultra-soft pseudopotentials or using LAPW techniques

5.4 Ionic crystals

5.4.1 Introduction

The *chemical* interactions between atoms in a crystal are expected to produce relatively short-range forces. However, in ionic compounds, there is an additional Coulomb interaction between charged species which has a long-range character.

Let us consider for simplicity a lattice of point charges Z_{κ} in vacuum, the force between a given pair of atoms is derivable from a two-body potential which depends only on the magnitude of the separation $d = ||R_{\kappa}^{a} - R_{\kappa'}^{b}||$ between the atoms :

$$V^{C}(d) = \frac{Z_{\kappa} Z_{\kappa'}}{d}.$$
(5.12)

It can be checked that this gives rise to interatomic force constants of the form [225]:

$$C^{DD}_{\kappa\alpha,\kappa'\beta}(a,b) = Z_{\kappa}Z_{\kappa'}(\frac{\delta_{\alpha\beta}}{d^3} - 3\frac{d_{\alpha}d_{\beta}}{d^5})$$
(5.13)

This demonstrates that the interatomic force constants associated to the Coulomb interaction exhibit a long-range $1/d^3$ behavior. This distance dependence is typical of a dipole-dipole interaction (as emphasized in the DD superscript used all along this Chapter) and may appear surprizing because we are dealing with point charges. Physically, it can be viewed as arising from the fact that when a given charge Z^{κ} is displaced by a distance τ , the difference of charge configuration after and before displacement corresponds to a dipole made of charges $\pm Z_{\kappa}$ at a distance tau. When two atoms are displaced, two such dipoles are induced so that the Coulomb interatomic force constants take the form of a dipole-dipole interaction. We will see in Section 5.6.2 that, in a real solid, we keep a very similar expression. However, the charge to be considered in Eq. (5.13) is the Born effective charge tensor and the screening must be included through an additional $1/\epsilon_{\infty}$ factor.

In practical calculations, the long-range character of the Coulomb interaction can be correctly treated by summing interactions up to infinite distances thanks to the use of Ewald summation techniques [226] and should appear has a rather technical point. However, a good understanding of the Coulomb interaction is helpful to clarify the specific behavior of ionic crystals and some of the theoretical investigations on ferroelectric perovskite that are reported later in this Chapter.

In this Section, we first recall the definition of some basic concepts such as the macroscopic electric field, the depolarizing field, the local field and we establish the relationships between them ⁴. We also make the connection between macroscopic quantities (obeying to the equations of the electrostatics) and microscopic concepts (useful to describe the local behavior of the atoms). We recall the origin of the splitting between longitudinal and transverse optical mode in the long-wavelength limit and deduce an expression for the static dielectric tensor.

 $^{^{4}}$ A good review of these concepts (from which this Section is mainly inspired) is given in the book of Ashcroft and Mermin [68].

5.4.2 Macroscopic and microscopic electric fields

When viewed at the atomic scale, the charge density $n(\mathbf{r})$ of any insulator is a rapidly varying function of position, reflecting the microscopic atomic structure of the crystal. On the same atomic scale, the electrostatic potential $v(\mathbf{r})$ and the electric field $\mathcal{E}^{micro}(\mathbf{r}) = -\nabla v(\mathbf{r})$ also have strong and rapid variations since they are related to $n(\mathbf{r})$ by

$$\nabla \mathcal{E}^{micro}(\mathbf{r}) = 4\pi \ n(\mathbf{r}). \tag{5.14}$$

On the other hand, in conventional electromagnetic theory of insulators, the charge density $n^{macro}(\mathbf{r})$, potential $\phi(\mathbf{r})$, electric field $\mathcal{E}(\mathbf{r})$ and electric displacement field $\mathcal{D}(\mathbf{r})$ show no such rapid variations. In the case of an insulator bearing no excess charge, the Maxwell equations yield :

$$\nabla \mathcal{D}(\mathbf{r}) = 0, \tag{5.15}$$

in addition with

$$\mathcal{D}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) + 4\pi \mathcal{P}(\mathbf{r}). \tag{5.16}$$

This implies that the macroscopic electric field satisfies :

$$\nabla \mathcal{E}(\mathbf{r}) = -4\pi \ \nabla \mathcal{P}(\mathbf{r}). \tag{5.17}$$

where $\mathcal{P}(\mathbf{r})$ is the macroscopic polarization.

As first derived by Lorentz, microscopic and macroscopic quantities can be related to each others. The macroscopic electric field $\mathcal{E}(\mathbf{r})$ is defined to be an average of $\mathcal{E}^{micro}(\mathbf{r})$ over a region about \mathbf{r} of characteristic size r_0 that is small at the macroscopic scale, but large compare to characteristic atomic dimensions:

$$\mathcal{E}(\mathbf{r}) = \int d\mathbf{r}' \, \mathcal{E}^{micro}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}'), \qquad (5.18)$$

where f is a slowly varying pair function, normalized to 1 and which vanishes for $r > r_0$. Beyond these assumptions, the theory is independent of the properties of the weight function f. This implies that

$$\nabla \mathcal{E}(\mathbf{r}) = \int d\mathbf{r}' \, \nabla \mathcal{E}^{micro}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}') = 4\pi \int d\mathbf{r}' \, n(\mathbf{r} - \mathbf{r}') f(\mathbf{r}'), \qquad (5.19)$$

and also that

$$\nabla \mathcal{P}(\mathbf{r}) = -\int d\mathbf{r}' \ n(\mathbf{r} - \mathbf{r}') f(\mathbf{r}').$$
 (5.20)

In conclusions, macroscopic and microscopic quantities are directly related to each others. Consequently, the relationships imposed by Maxwell equations translate into equivalent constraints at the microscopic level.

5.4.3 Macroscopic field within a dielectric

Contrary to what happens for a metal, the electric field inside an insulator is not necessarily zero because charge cannot flow freely in it. As a first step, it is important to define what we call the macroscopic field.

Let us assume that an insulator is placed in an external electric field \mathcal{E}_{app} . The field polarizes the material and the *macroscopic* field, \mathcal{E} , within the sample is different from \mathcal{E}_{app} . It will be the sum of the external applied field \mathcal{E}_{app} with the so-called depolarizing field \mathcal{E}_{dep} :

$$\mathcal{E} = \mathcal{E}_{app} + \mathcal{E}_{dep} \tag{5.21}$$

where \mathcal{E}_{dep} is the field associated to the macroscopic polarization \mathcal{P} (i.e. the field produced by the induced dipoles within the sample in a Clausius Mosotti model).

From the electrostatic, it is well known that the macroscopic field induced by a uniform polarization is equivalent to the field induced, in the vacuum, by a charge density $\sigma = \hat{\mathbf{n}}.\mathcal{P}$ at the surface of the sample (here, $\hat{\mathbf{n}}$ is a unitary vector perpendicular to the surface and pointing outside). It follows that for a thin platelet sample in a perpendicular external field, the depolarizing field perpendicular to the surface simply writes :

$$\mathcal{E}_{dep,\perp} = -4\pi |\sigma| = -4\pi \mathcal{P}_{\perp} \tag{5.22}$$

Similarly, for an ellipsoid with its principal axis along the cartesian coordinates, it can be checked that an homogeneous external field will induced an homogeneous polarization and that the associated depolarizing field writes [227] :

$$\mathcal{E}_{x,dep} = -n_x \mathcal{P}_x, \ \mathcal{E}_{y,dep} = -n_y \mathcal{P}_y, \ \mathcal{E}_{z,dep} = -n_z \mathcal{P}_z;$$
(5.23)

where the n_i 's are called the *depolarizing factors*. They depend on the *shape* of the ellispoid. They are positive, inversely proportional to the length of the principal axis of the ellipsoid and satisfy $n_x + n_y + n_z = 1$. In the case of a sphere : $n_i = 4\pi/3$. In the case of a platelet, we recover : $n_{\perp} = 4\pi$ and $n_{\parallel} = 0$. In the case of a needle, we get $n_{\perp} = 2\pi$ and $n_{\parallel} = 0$.

The measurable electric field inside a dielectric, which is also the field appearing in Maxwell equations is the *total* macroscopic field \mathcal{E} . It is therefore the sum of the (eventual) applied field \mathcal{E}_{app} with an additional depolarizing field $\mathcal{E}_{dep,i} = -n_i \mathcal{P}_i$, the amplitude of which depends of the macroscopic *shape* of the sample. It can be non-zero even in absence of external field when the polarization is non-vanishing as it can happen when atoms are displaced in an ionic crystal.

5.4.4 Local electric field

Since each ion in a solid as microscopic dimensions, its displacement and distortion from equilibrium position will be dependent of the force due to the *microscopic* field at the position of the ion (diminished by the contribution to the field from the ion itself). This field is frequently called the *local* field, \mathcal{E}_{loc} .

It is important to realize that the *local* electric field at an atomic site can be different from the macroscopic electric field. As an example, let us consider a macroscopic simple cubic cristal of spherical shape, composed of well separated polarizable atoms at each site and in an external field oriented along z. The macroscopic field within the sample simply writes :

$$\mathcal{E} = \mathcal{E}_{z,app} - \frac{4\pi}{3} \mathcal{P}_z \tag{5.24}$$

The local field at the center of the crystal is defined as the sum of (i) the applied field and (ii) the field produced by the dipoles $\mathbf{p} = p_z \hat{\mathbf{z}}$ induced on each atom by the external field :

$$\mathcal{E}_{loc} = \mathcal{E}_{z,app} + \mathcal{E}_{z,dip}. \tag{5.25}$$

 $\mathcal{E}_{z,dip}$ is obtained from a sum on the different sites :

$$\mathcal{E}_{z,dip} = \sum_{i} \frac{3(\mathbf{p}.\mathbf{r}_{i})z_{i} - \mathbf{r}_{i}^{2}p_{z}}{r_{i}^{5}}$$
(5.26)

$$= p_z \sum_{i} \frac{3z_i^2 - (x_i^2 + y_i^2 + z_i^2)}{r_i^5}$$
(5.27)

$$= p_z \sum_{i} \frac{2z_i^2}{r_i^5} - \sum_{i} \frac{x_i^2}{r_i^5} - \sum_{i} \frac{y_i^2}{r_i^5}$$
(5.28)

Because, the 3 directions x, y, z are equivalent by symmetry in this simple example, $\mathcal{E}_{z,dip}$ sums up to zero so that the local field is simply $\mathcal{E} = \mathcal{E}_{z,app}$. It differs from the macroscopic field.

As the local field appears as a useful concept, we can try to obtain its expression at a given site of a crystal non necessary of cubic symmetry. We will consider that the solid has the shape of an ellipsoid. The local field is the sum of the applied field induced by external sources and the field produced by all the induced dipoles inside the sample. The latter can be decomposed in three terms if we consider our sample as composed of two regions:

- 1. a *near* spherical region composed of all the atoms within a small fictive sphere centered on the site of interest;
- 2. a *far* region composed of the part of the crystal outside from the sphere and assimilated to a continuum.

We write :

$$\mathcal{E}_{loc} = \mathcal{E}_{app} + \mathcal{E}_{dep} + \mathcal{E}_{Lorentz} + \mathcal{E}_{int} \tag{5.29}$$

where:

- 1. \mathcal{E}_{app} is the usual applied external field;
- 2. \mathcal{E}_{dep} is depolarizing field induced by the surface charge density $\sigma = \hat{\mathbf{n}}.\mathcal{P}$ at the surface of the ellipsoid ;
- 3. $\mathcal{E}_{Lorentz}$ is the Lorentz field induced at the surface of the internal sphere by the polarization in the far region ;
- 4. \mathcal{E}_{int} is the internal field, produced by the individual dipoles within the internal sphere.

The sum of the internal and depolarization field correspond to the macroscopic field \mathcal{E} . Moreover, the Lorentz field is the electric field produced by the charge density $\sigma = \hat{\mathbf{n}}.\mathcal{P}$ appearing at the surface of the internal sphere and, as such, it simply writes

$$\mathcal{E}_{Lorentz} = \frac{4\pi}{3} \mathcal{P}.$$
 (5.30)

In general, the local field therefore writes (independently of the symmetry of the crystal) :

$$\mathcal{E}_{loc} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P} + \mathcal{E}_{int} \tag{5.31}$$

If we now assume a crystal of *cubic symmetry*, the internal field induced by the dipoles within the internal sphere will be zero (as demonstrated above in this Section) so that we finally obtain the well-known **Lorentz relation** :

$$\mathcal{E}_{loc} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P} \tag{5.32}$$

This result is widely used in the theory of dielectrics. It is very important to remember the assumptions underlying it, particularly that of cubic symmetry about every atomic site. We note that for a crystal of spherical shape, the Lorentz field compensate exactly the depolarizing field so that $\mathcal{E}_{loc} = \mathcal{E}_{app}$, as obtained in the simple example at the beginning of this Section.

Let us emphasize that \mathcal{E}_{loc} is the total microscopic field at the atomic site. In addition to the eventual external field, it summarizes the field produced by all the individual dipole all over the material (generated by the external field and/or atomic displacements). To compute the force on an atom it is therefore equivalent to sum individual Coulomb interactions or to treat them globally through the local field they generate at a given atomic site. As it will be illustrated later, this latter approach is sometimes preferred in shell-models.

5.4.5 Dielectric constant and local polarizability

The dielectric constant ϵ of a dielectric medium is a macroscopic quantity defined from the macroscopic field as :

$$\epsilon = \frac{\mathcal{E} + 4\pi\mathcal{P}}{\mathcal{E}} = 1 + 4\pi\chi \tag{5.33}$$

and the susceptibility χ is defined as

$$\chi = \frac{\epsilon - 1}{4\pi} \tag{5.34}$$

These macroscopic concepts can be related to microscopic quantities. The polarizability α_i of an atom *i* is the quantity which relates the induced dipole moment to the local electric field on the atom :

$$p_i = \alpha_i \, \mathcal{E}^i_{loc}. \tag{5.35}$$

The local field is

$$\mathcal{E}_{loc}^{i} = \frac{\epsilon + 2}{3} \mathcal{P} \tag{5.36}$$

and the polarization is the dipole moment per unit volume :

$$\mathcal{P} = \frac{1}{\Omega_0} \sum_i p_i. \tag{5.37}$$

Combining the last three expressions we get the well-known Clausius - Mossotti relation :

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3\Omega_0} \sum_i \alpha_i \tag{5.38}$$

where Ω_0 is the volume of the unit cell and the sum over *i* extends to atoms within the unit cell. This relationship connects the local atomic polarizability to the macroscopic dielectric constant. We notice that it is based on the Lorentz relation to relate macroscopic and local fields. It makes therefore implicitly the assumption of cubic symmetry.

Theories treating the Coulomb interaction through the local field will make use of local quantities such as the local polarizability and the Szigeti charge. Theories working with the macroscopic electric field will consider instead the macroscopic dielectric constant and the Born effective charges.

5.4.6 Long-wavelength optical modes in ionic crystals

In ionic crystals, long-wavelength longitudinal and transverse optical modes exhibit different frequencies. This particular feature is a direct consequence of the conditions imposed by the Maxwell equations on the macroscopic field in both cases.

In a long-wavelength ($\mathbf{q} \approx 0$) optical mode, the oppositely charged ions in each unit cell undergo oppositively directed displacements, giving rise to a non-vanishing polarization density \mathcal{P} . Associated with this polarization, there will in general be macroscopic electric and displacement fields related by :

$$\mathcal{D} = \epsilon \ \mathcal{E} = \mathcal{E} + 4\pi \mathcal{P} \tag{5.39}$$

In the absence of free charge, we have :

$$\nabla \mathcal{D} = 0. \tag{5.40}$$

Furthermore, \mathcal{E}^{micro} , and consequently \mathcal{E} are the gradient of a potential ⁵:

$$\nabla \times \mathcal{E} = \nabla \times -\nabla \phi = 0. \tag{5.41}$$

In a cubic crystal, $\mathcal{D}, \mathcal{E}, \mathcal{P}$ are parallel to each others. If they have the spacial dependence,

$$\mathcal{D} = Re(\mathcal{D}_0 e^{i\mathbf{q}.\mathbf{r}}); \quad \mathcal{E} = Re(\mathcal{E}_0 e^{i\mathbf{q}.\mathbf{r}}); \quad \mathcal{P} = Re(\mathcal{P}_0 e^{i\mathbf{q}.\mathbf{r}}); \quad (5.42)$$

then, Eq. (5.40) reduces to $\mathbf{q}.\mathcal{D}_0 = 0$, or

$$\mathcal{D} = 0 \text{ or } \mathcal{D}, \, \mathcal{E}, \, \mathcal{P} \perp \mathbf{q} \tag{5.43}$$

while, Eq. (5.41) reduces to $\mathbf{q} \times \mathcal{E}_0 = 0$, or

$$\mathcal{E} = 0 \text{ or } \mathcal{D}, \mathcal{E}, \mathcal{P} \parallel \mathbf{q}$$
 (5.44)

In a longitudinal optical (LO) mode, \mathcal{P} is parallel to \mathbf{q} so that \mathcal{D} must vanish and

$$\mathcal{E} = -4\pi \mathcal{P} \ (\epsilon = 0) \tag{5.45}$$

In a transverse optical (TO) mode, \mathcal{P} is perpendicular to \mathbf{q} so that \mathcal{E} must vanish and

$$\mathcal{E} = 0 \ (\epsilon = \infty) \tag{5.46}$$

It can now be understood why longitudinal and transverse frequencies differ in the long-wavelength limit. This is in fact because the atoms experiences different electrostatic restoring forces. If we evaluate the local field, we obtain for a LO mode :

$$\mathcal{E}_{loc}^{LO} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P} = -\frac{8\pi}{3}\mathcal{P}$$
(5.47)

while for a TO mode :

$$\mathcal{E}_{loc}^{TO} = \frac{4\pi}{3} \mathcal{P} \tag{5.48}$$

In longitudinal modes, the local field acts to reduce the polarization; it therefore produces an additional restoring force which produces a stiffening of the mode. At the opposite, in TO modes, the local field acts to support the polarization and produces therefore a softening.

⁵This is not strictly through since the right side of the Maxwell equation $\nabla \times \mathcal{E} = -(1/c)\partial \mathcal{B}/\partial t$ needs not to be negligible. However, a rigorous electrodynamic treatment leads to conclusions very similar to what is reported here.

5.4.7 The LO-TO splitting

From the previous discussion, we expect the frequencies of the zone-center LO modes to differ from those of TO modes due to the different condition on the macroscopic electric field. This field is related to the polarization field associated to phonon modes with a polar pattern of displacement and only such polar (IR active) modes will be splitted.

In order to get better insight on the LO-TO splitting, the interatomic force constant matrix can be conveniently separated into two parts 6 :

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\to 0) = \tilde{C}^{\mathrm{TO}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=0) + \Delta\tilde{C}^{\mathrm{LO}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\to 0)$$
(5.49)

The first term $\tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{TO}}(\mathbf{q}=0)$ is the IFC matrix, obtained as a sum of the electronic and ionic contributions previously reported, *but* from which the interaction with the macroscopic electric field has been excluded. The second contribution $\Delta \tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{LO}}(\mathbf{q}\to 0)$ is an additional term that treats correctly the interaction with the eventual macroscopic electric field. The amplitude of this term depends explicitly of the direction taken to approach the Γ point.

Separating the contribution involving the macroscopic electric field from the other contributions, the driving force induced on atom 0κ in a surrounding of displaced atoms may be written as ⁷:

$$F_{0\kappa,\alpha} = -\sum_{b,\kappa',\beta} C^{TO}_{\kappa\alpha,\kappa'\beta}(0,b) \ \tau^b_{\kappa',\beta} + \sum_{\beta'} Z^*_{\kappa,\beta'\alpha} \ . \ \mathcal{E}_{\beta'}$$
(5.50)

so that the equation of motion for the ions becomes:

$$M_{\kappa} \frac{\partial^2 \Delta \tau^a_{\kappa\alpha}}{\partial t^2} = \left[-\sum_{b,\kappa',\beta} C^{TO}_{\kappa\alpha,\kappa'\beta}(0,b) \ \tau^b_{\kappa',\beta} + \sum_{\beta'} Z^*_{\kappa,\beta'\alpha} \ . \ \mathcal{E}_{\beta'} \right]$$
(5.51)

The amplitude of electric field \mathcal{E}_{β} must now be determined. It can be deduced from conditions on the electric field and displacement field derived from Maxwell's equations. The change of electric field associated to the appearance of a phonon is directed along $\hat{\mathbf{q}} = (q_x, q_y, q_z)$: $\mathcal{E}_{\beta} = |\mathcal{E}| \cdot q_{\beta}$. The induced displacement field is given by :

$$\mathcal{D}_{\alpha} = \mathcal{E}_{\alpha} + 4\pi \mathcal{P}_{\alpha} \tag{5.52}$$

The macroscopic polarization is related to atomic displacements and macroscopic electric field through:

$$\mathcal{P}_{\alpha} = \sum_{b,\kappa',\beta} \frac{\partial \mathcal{P}_{\alpha}}{\partial \tau^{b}_{\kappa',\beta}} |_{\mathcal{E}=0} \tau^{b}_{\kappa',\beta} + \sum_{\beta} \frac{\partial \mathcal{P}_{\alpha}}{\partial \mathcal{E}_{\beta}} |_{\tau=0} |\mathcal{E}| q_{\beta}$$
(5.53)

$$= \frac{1}{\Omega_0} \sum_{b,\kappa',\beta} Z^*_{\kappa',\beta\alpha} \tau^b_{\kappa',\beta} + \sum_{\beta} \chi^{\infty}_{\alpha\beta} |\mathcal{E}| q_{\beta}$$
(5.54)

⁶Matematically, a divergence problem arises at $\mathbf{q} = 0$ so that this decomposition is also performed in the calculations to compute LO modes at the Γ point.

⁷An alternative expression $(Z_{\kappa,\beta'\alpha}^{*(S)}, \mathcal{E}_{loc,\beta'})$ can be used for the interaction with the electric field. As highlighted in Chapter 3, both are strictly equivalent

so that

$$\mathcal{D}_{\alpha} = \frac{4\pi}{\Omega_0} \sum_{b,\kappa',\beta} Z^*_{\kappa',\beta\alpha} \tau^b_{\kappa',\beta} + |\mathcal{E}| \sum_{\beta} \epsilon^{\infty}_{\alpha\beta} q_{\beta}$$
(5.55)

Along direction \mathbf{q} , the component of the displacement field must be preserved so that we have the condition: $\mathbf{q}.\mathcal{D} = 0$. From $q_{\alpha}.D_{\alpha} = 0$, we deduce:

$$|\mathcal{E}| = -\frac{4\pi}{\Omega_0} \frac{\sum_{b,\kappa'} \sum_{\alpha'\beta} \tau^b_{\kappa',\beta} Z^*_{\kappa',\beta\alpha'} q_{\alpha'}}{\sum_{\alpha'\beta'} q_{\alpha'} \epsilon^{\infty}_{\alpha'\beta'} q_{\beta'}}.$$
(5.56)

From this equation, it appears that the macroscopic electric field associated to the phonon (\mathcal{E}) is connected to the polarization field induced by the atomic displacement $(Z^*.\Delta\tau)$ thanks to the dielectric constant (ϵ_{∞}) . Introducing this result in equation (5.51) we get:

$$M_{\kappa} \frac{\partial^{2} \tau_{\kappa\alpha}^{a}}{\partial t^{2}} = -\sum_{b,\kappa',\beta} \Delta \tau_{\kappa',\beta}^{b} [C_{\kappa\alpha,\kappa'\beta}^{TO}(0,b) + \frac{4\pi}{\Omega_{0}} \frac{\sum_{\beta'} (Z_{\kappa,\beta'\alpha}^{*} q_{\beta'}) \sum_{\alpha'} (Z_{\kappa',\alpha'\beta}^{*} q_{\alpha'})}{\sum_{\alpha'\beta'} q_{\alpha'} \epsilon_{\alpha'\beta'}^{\infty} q_{\beta'}}].$$
(5.57)

so that the additional contribution to the IFC matrix for the LO modes can finally be written as: $\sum (Z^*) = (Z^*)$

$$\Delta \tilde{C}^{\rm LO}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\to 0) = \frac{4\pi}{\Omega_0} \frac{\sum_{\beta'} \left(Z^*_{\kappa,\beta'\alpha} q_{\beta'}\right) \sum_{\alpha'} \left(Z^*_{\kappa',\alpha'\beta} q_{\alpha'}\right)}{\sum_{\alpha'\beta'} q_{\alpha'}\epsilon^{\infty}_{\alpha'\beta'} q_{\beta'}}.$$
(5.58)

It is this term that is added in order to compute the LO-TO splitting in the limit of the Γ point. Note that for LO modes, the full dynamical matrix including this $\Delta \tilde{C}_{\kappa\alpha,\kappa'\beta}^{\text{LO}}(\mathbf{q} \to 0)$ must be diagonalized. When there are more than one polar modes, this additional term can mix them up so that LO and TO eigenvectors are not necessarily identical.

5.4.8 Static dielectric constant

When a insulator is placed in a static homogeneous electric field (such as that existing between the plates of a capacitor), the field will polarize the material and many important consequences of the resulting internal distortions can be deduced if one knows the static dielectric tensor, $\epsilon_{\alpha\beta}^0$, of the material. The calculation of $\epsilon_{\alpha\beta}^0$ is therefore an important aim of any microscopic theory of insulators.

The dielectric constant is directly related to the suceptibility :

$$\epsilon^{0}_{\alpha\beta} = 1 + 4\pi \chi^{0}_{\alpha\beta}$$
$$= 1 + 4\pi \frac{\partial \mathcal{P}_{\alpha}}{\partial \mathcal{E}_{\beta}}$$
(5.59)

(5.60)

If the electric field is static (or sufficiently slowly varying), the ions can relax so that the change of polarization is the sum of ionic and electronic contributions :

$$\epsilon^{0}_{\alpha\beta} = 1 + 4\pi \left(\frac{\partial \mathcal{P}_{\alpha}}{\partial \mathcal{E}_{\beta}}\Big|_{\tau=0} + \sum_{\kappa,\beta'} \frac{\partial \mathcal{P}_{\alpha}}{\partial \tau_{\kappa\beta'}}\Big|_{\mathcal{E}=0} \frac{\partial \tau_{\kappa\beta'}}{\partial \mathcal{E}_{\beta}}\right)$$
$$= \epsilon^{\infty}_{\alpha\beta} + \frac{4\pi}{\Omega_{0}} \sum_{\kappa,\beta'} Z^{*}_{\kappa,\beta'\alpha} \frac{\partial \tau_{\kappa\beta'}}{\partial \mathcal{E}_{\beta}}$$
(5.61)

The only unknown in the previous equation is the derivative of the atomic positions with respect to the field. This can be worked out since the ions will relax until the force they feel becomes equal to zero. This condition can be imposed on Eq. (5.50):

$$-\sum_{b,\kappa',\beta} C^{TO}_{\kappa\alpha,\kappa'\beta}(0,b) \ \tau^b_{\kappa',\beta} + \sum_{\beta'} Z^*_{\kappa,\beta'\alpha} \ . \ \mathcal{E}_{\beta'} = 0$$
(5.62)

In order to get a familiar expression for the dielectric constant, we can choose to express the atomic displacements in terms of the TO modes eigenvectors which define a complete basis ($\tau^a_{\kappa,\alpha} \to \tau_i \eta^{TOi}_{\kappa,\alpha}$). This provides the following equivalent condition :

$$-\omega_{TOi}^2 \tau_i + \sum_{\kappa,\alpha} \sum_{\beta} Z_{\kappa,\alpha\beta}^* \eta_{\kappa,\alpha}^{TOi} \mathcal{E}_{\beta} = 0$$
(5.63)

or

$$\tau_i = \frac{1}{\omega_{TOi}^2} \sum_{\kappa,\alpha} \sum_{\beta} Z^*_{\kappa,\alpha\beta} \ \eta^{TOi}_{\kappa,\alpha} \ \mathcal{E}_{\beta}$$
(5.64)

Introducing this in Eq. (5.61), we finally get :

$$\epsilon_{\alpha\beta}^{0} = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_{0}} \sum_{i} \left(\sum_{\kappa,\beta'} Z_{\kappa,\beta'\alpha}^{*} \eta_{\kappa,\beta'}^{TOi} \right) \frac{1}{\omega_{i}^{2}} \left(\sum_{\kappa,\alpha'} Z_{\kappa,\alpha'\beta}^{*} \eta_{\kappa,\alpha'}^{TOi} \right)$$
$$= \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_{0}} \sum_{i} \frac{S_{i,\alpha\beta}}{\omega_{TOi}^{2}}$$
(5.65)

where we have defined the mode oscillator strength as

$$S_{i,\alpha\beta} = \left(\sum_{\kappa,\gamma} Z^*_{\kappa,\gamma\alpha} \eta^{TOi}_{\kappa,\gamma}\right)^* \left(\sum_{\kappa,\gamma} Z^*_{\kappa,\gamma\beta} \eta^{TOi}_{\kappa,\gamma}\right).$$
(5.66)

This quantity requires the knowledge of the Born effective charges and phonon eigenvectors, two quantities directly accessible from our calculations.

In order to exhibit a large dielectric constant, the material must have modes combining large oscillator strength (favored by large Z^*) and small frequencies (soft modes). We will see that these two conditions are not necessarly independent since, as it will be illustrated later, large Z^* produce a strong destabilizing Coulomb interaction producing a softening of the phonon frequencies.

Mode	Exp.[203]	$a_o = 3.67 \text{\AA}$	$a_o=3.94\text{\AA}$	$a_o = 4.00 \text{\AA}$	Ref. [136]
$F_{1u}(TO1)$	soft	214	113i	219i	178i
$F_{1u}(LO1)$	180	250	180	159	173
$F_{1u}(TO2)$	182	296	184	166	177
$F_{1u}(LO2)$	465	513	460	447	453
$F_{1u}(TO3)$	482	737	481	453	468
$F_{1u}(LO3)$	710	1004	744	696	738
F_{2u}	306^{a}	308	288	281	_

Table 5.1: Phonon frequencies (cm^{-1}) at the Γ point for cubic BaTiO₃. The LO-TO splitting has been computed with the help of the scissors corrected dielectric constant.

^a This value has been measured in the tetragonal phase.

5.5 BaTiO₃ phonon modes at the Γ point

As a first step, we investigate the lattice dynamics of barium titanate at the Γ point in its cubic and rhombohedral structures. We consider cubic phases at the experimental and theoretically optimized volumes corresponding to a lattice parameter a_o equal respectively to 4.00 and 3.94 Å. We will also study a compressed cubic phase with $a_o=3.67$ Å. For the rhombohedral phase, we adopt the experimental unit cell parameters and relaxed atomic positions, as described in Chapter 1.

There are 12 optic phonons in BaTiO₃. In the cubic phase, at the Γ point, we have three modes of F_{1u} symmetry and a silent mode of F_{2u} symmetry, each of them triply degenerated. Going to the rhombohedral phase, each triply degenerated F_{1u} mode (resp. F_{2u}) gives rise to a mode of A_1 (resp. A_2) symmetry and a doubly degenerated mode of E symmetry.

5.5.1 Cubic phase

Our phonon frequencies in the cubic phase, as well as experimental and other theoretical results, are reported in Table 5.1. Our values are in good agreement with the experiment [203] and another calculation by Zhong *et al.*[136]. In particular, we identify the instability ⁸ of the TO1 mode that corresponds to the vibration of Ti and Ba against the O atoms. The phonon frequencies change by a noticeable amount when going from the experimental to the optimized volume. This behavior is different to the one previously observed for other physical quantities like Z_{κ}^* . This sensitivity is particularly large for the soft TO1 mode : Its instability even disappears in our compressed cubic phase.

The eigendisplacements associated with the $F_{1u}(TO)$ modes are described in Table 5.2.

 $^{^{8}\}mathrm{An}$ instability is associated to a negative curvature of the energy hypersurface which yields an imaginary phonon frequency.

Table 5.2: Phonon eigendisplacement patterns for the $F_{1u}(TO)$ mode of the cubic phase of BaTiO₃. In comparison with results of Cohen and Krakauer (CK), we report values at the experimental (V_{exp}) and optimized (V_{opt}) volume, as well as for a compressed (V_{comp}) cubic phase. Eigendisplacements η are normalized such that $\langle \eta^{TO} | M | \eta^{LO} \rangle = 1$, with Min atomic mass units.

Mode	Volume	Ba	Ti	01	O2	O3
$F_{1u}(TO1)$	V_{exp}	-0.002	-0.096	0.158	0.071	0.071
	V_{opt}	-0.002	-0.098	0.137	0.087	0.087
	V_{comp}	-0.028	0.121	0.026	-0.074	-0.074
	Ref. [107]	-0.006	-0.091	0.144	0.091	0.091
$F_{1u}(TO2)$	Vexp	-0.055	0.080	0.068	0.081	0.081
	V_{opt}	-0.055	0.082	0.071	0.077	0.077
	V_{comp}	-0.047	0.017	0.085	0.133	0.133
	Ref. [107]	-0.054	0.088	0.053	0.075	0.075
$F_{1u}(TO3)$	Vexp	-0.002	0.032	0.170	-0.124	-0.124
	V_{opt}	-0.001	0.018	0.186	-0.116	-0.116
	V_{comp}	0.002	-0.040	0.224	-0.061	-0.061
	Ref. [107]	-0.003	0.022	0.186	-0.115	-0.115

They are in agreement with those obtained by Cohen and Krakauer [107] from a frozen phonon calculation. These eigenvectors remains relatively similar at the experimental and optimized volume. By contrast, there is a mixing between the three $F_{1u}(TO)$ modes in the compressed cubic phase so that not a single one corresponds to the unstable mode of the optimized cubic cell (see also Table 5.3).

The correlation between the LO and TO modes can be measured by the overlap matrix between their respective eigenvectors. A priori, the eigendisplacements of the LO modes (η^{LO}) do not necessarily corresponds to those of the TO modes (η^{TO}) , because of the long-range Coulomb interaction. The overlap matrix reported in Table 5.3 ($\langle \eta^{TO} | M | \eta^{LO} \rangle$, where M is such that $M = M_{\kappa} \delta_{\kappa\kappa'}$ and M_{κ} is the mass of atom κ) establishes however that the mixing is very small: we observe a one-to-one correspondence. Interestingly, the softest TO mode, $F_{1u}(TO1)$, is associated with the hardest LO mode, $F_{1u}(LO3)$, suggesting a giant LO-TO splitting [136]. The same kind of results has been reported for KNbO₃ [136, 101], even if the overlap between LO and TO modes was not so large for that compound.

The amplitude of the LO-TO splitting lies essentially in the value of the mode effective charges. This quantity is defined as

$$Z_{TO}^* = \left\| \frac{\sum_{\kappa,\beta} Z_{\kappa,\alpha\beta}^* \eta_{\kappa,\beta}^{TO}}{\langle \eta^{TO} | \eta^{TO} \rangle} \right\|.$$
(5.67)

			Vont	
		$F_{1u}(TO1)$	$F_{1u}(TO2)$	$F_{1u}(TO3)$
	$F_{1u}(LO1)$	0.17	-0.99	0.01
V_{opt}	$F_{1u}(LO2)$	-0.36	-0.07	-0.93
	$F_{1u}(LO3)$	0.92	-0.16	0.37
	$F_{1u}(TO1)$	0.71	-0.54	0.46
V_{comp}	$F_{1u}(TO2)$	-0.49	-0.84	-0.22
-	$F_{1u}(TO3)$	-0.51	0.07	0.86

Table 5.3: Overlap matrix elements between the eigenvectors of the $F_{1u}(TO)$ modes of the optimized cubic phase and those respectively of the associated $F_{1u}(LO)$ mode and of the $F_{1u}(TO)$ mode of the compressed cubic phase.

Table 5.4: Mode effective charge and respective partial contribution due to each atom for the $F_{1u}(TO)$ modes of the optimized cubic phase.

Mode	Partial contribution due to					Mode charge
	Ba	Ti	O∥	O_{\perp}	O_{\perp}	\mathbf{Z}^*_{TO}
$F_{1u}(TO1)$	0.03	3.42	3.77	0.90	0.90	9.02
$F_{1u}(TO2)$	0.92	-3.66	2.48	1.02	1.02	1.79
$F_{1u}(TO3)$	-0.01	-0.53	4.28	-1.01	-1.01	1.74

The mode charges are reported in Table 5.4 where we identify the respective contribution due to each atom. We observe that the very large Z_{TO1}^* , responsible of the strong Coulomb interaction of this mode, originates essentially from the large Born effective charges on Ti and O_{\parallel} , that combine according to the specific pattern of eigendisplacement associated to this mode. In comparison, for the TO2 mode, Ti and O contributions remain large but cancel out so that the global charge is smaller.

As a consequence of the observed similarity between eigenvectors, we can predict fictitious LO frequencies on the basis of the Born effective charges, by the simple approximate formula ⁹

$$\omega_{LO}^{2}(\mathbf{q} \to 0) = \omega_{TO}^{2} + \frac{4\pi}{\Omega_{0}} \frac{\left(\sum_{\alpha} q_{\alpha} \left(\sum_{\kappa,\beta} Z_{\kappa,\alpha\beta}^{*} \eta_{\kappa,\beta}^{TO}\right)\right)^{2}}{\sum_{\alpha\beta} q_{\alpha} \epsilon_{\alpha\beta}^{\infty} q_{\beta}}$$
(5.68)

⁹This equation allows to compute the splitting within the hypothesis that the eigenvector was not modified by the interaction with the macroscopic electric field. Note that the additional contribution on the right hand is always positive. It should also be conveniently expressed in terms of the mode oscillator strengths introduced later.

Mode		Mode	
$A_1(TO1)$	168	E(TO1)	161
$A_1(LO1)$	180	E(LO1)	173
$A_1(TO2)$	265	E(TO2)	205
$A_1(LO2)$	462	E(LO2)	438
$A_1(TO3)$	505	E(TO3)	461
$A_1(LO3)$	702	E(LO3)	725
A_2	274	E	293

Table 5.5: Phonon frequencies (cm^{-1}) at the Γ point for rhombohedral BaTiO₃.

where Ω_0 is the volume of the unit cell, α and β indices denote the space direction and κ labels the atom within the unit cell. We find values respectively of 701, 214 and 508 cm⁻¹, in close agreement with real LO frequencies (180, 460 and 744 cm⁻¹). This result emphasizes again the giant LO-TO splitting of the unstable mode (113*i* \rightarrow 701 cm⁻¹) in comparison to that of the two other modes (184 \rightarrow 214 cm⁻¹, 481 \rightarrow 508 cm⁻¹). This unusual splitting is associated to a particularly strong Coulomb interaction that will be discussed later.

5.5.2 Rhombohedral phase

The phonon frequencies of the rhombohedral phase are reported in Table 5.5. The only other result we found is experimental [211] and localizes the phonon frequencies in three regions (100-300 cm⁻¹, 480-580 cm⁻¹, and 680-750 cm⁻¹), in qualitative agreement with our values.

There is no unstable mode in the rhombohedral structure. If we compare the eigenvectors to those of the cubic phase, we observe that they are very similar in both cases. This is illustrated for the A_1 mode in Table 5.6. Similar overlaps are obtained for the E modes. They point out that $A_1(TO2)$ and E(TO2) originate from the hardening of the soft mode.

If we compute the overlap matrix between LO and TO modes (Table 5.6), we observe that the mixing produced by the Coulomb interaction is larger than in the cubic phase. Moreover, the ferroelectric $A_1(TO2)$ mode is the most closely associated with the $A_1(LO3)$ mode.

In this phase, the mode effective charges of the A_1 (resp. E) modes are respectively of 2.79 (4.48), 6.99 (8.41) and 2.33 (1.99). The TO2 modes, originating from the soft TO1 mode of the cubic phase, continue to couple strongly with the electric field but the smaller Born effective charges makes their mode effective charge smaller. This is particularly true for the A_1 modes polarized along the ferroelectric direction.

All the computed phonons are stable in the rhombohedral phase, and we can obtain

	$A_1(TO1)$	$A_1(TO2)$	$A_1(TO3)$
$A_1(LO1)$	0.96	0.29	0.02
$A_1(LO2)$	-0.15	0.56	-0.81
$A_1(LO3)$	0.25	-0.77	-0.58
$F_{1u}(TO1)$	0.13	-0.97	0.19
$F_{1u}(TO2)$	-0.99	-0.13	-0.01
$F_{1u}(TO3)$	-0.02	-0.18	-0.98

Table 5.6: Overlap matrix elements between the eigenvectors of the $A_1(TO)$ modes of the rhombohedral phase and those respectively of the associated $A_1(LO)$ modes and of the $F_{1u}(TO)$ mode of the optimized cubic phase.

the low frequency (infra-red) dielectric tensor by adding to ϵ_{∞} the ionic contribution (evaluated here in the harmonic approximation, without damping). The expression is the generalization of that we have obtained in the static case :

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_{TOi} \frac{S_{i,\alpha\beta}}{\omega_{TOi}^2 - \omega^2}$$
(5.69)

The value of the dielectric constant along some direction $\hat{\mathbf{q}} = (q_x, q_y, q_z)$ is evaluated from:

$$\epsilon_{\hat{\mathbf{q}}}(\omega) = \sum_{\alpha\beta} q_{\alpha} \epsilon_{\alpha\beta}(\omega) q_{\beta} \tag{5.70}$$

We obtain for the static dielectric constant ($\omega = 0$) a value of 33.09 along the ferroelectric axis and of 68.89 perpendicularly to it. In both directions, the main ionic contribution comes from the TO2 modes (73% and 62% respectively). This is another manifestation of the large effective charge of this mode. The large anisotropy of the static dielectric tensor is associated with the smaller value of Z^* and ϵ_{∞} along the ferroelectric direction.

The determination of the low frequency dielectric constant is sometimes associated to a measurement of the reflectivity $R(\omega)$ of optical waves normal to the surface, with their electric field along an optical axis of the crystal $\hat{\mathbf{q}}$, and defined as:

$$R(\omega) = \left|\frac{\epsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) - 1}{\epsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) + 1}\right|^2$$
(5.71)

The result is presented in Fig. 5.1 10 for $\hat{\mathbf{q}}$ aligned along the ferroelectric direction. Unfortunately, no experimental data can be compared to our theoretical results.

¹⁰The saturation to one observed for the curve of Fig. 5.1 is due to the absence of damping.



Figure 5.1: Infrared reflectivity of rhombohedral BaTiO₃, with $\hat{\mathbf{q}}$ along the ferroelectric direction.

5.6 Origin of the ferroelectric instability

In the previous Section we have reported first-principles results concerning the Γ phonons of BaTiO₃. We have characterized the unstable mode in the experimental cubic phase. It seems now important to investigate the microscopic origin of the structural instability and the reason of its disappearance in the rhombohedral phase or in our compressed cubic structure.

5.6.1 The model of Cochran

During the sixties, Cochran [17] investigated the dynamics of ABO₃ compounds within a shell model approach and he related the ferroelectric transition to the softening of a transverse optic phonon at the Γ point. In his model, the interatomic forces are separated into two parts: the short range forces and the long range Coulomb (dipole-dipole) interaction. In this framework, he was able to isolate the contribution of each kind of force on the frequency of the transverse modes and to identify the structural instability with the possible cancellation of the two terms. This competition between forces, first suggested by Slater [15], is still now usually invoked to explain the microscopic origin of the ferroelectricity [93, 98, 44].

The polarizable ion model of Cochran is a simple application of the lattice shell-model. For simplicity, it will be described here in the simple case of a one-dimensional lattice. It can be easily generalize for three dimensional systems.

Linear atomic chain

Let us consider the atomic chain of Fig. 5.2. Each unit cell of lattice parameter a contains two atoms : one cation of mass m_+ and static charge +Z and one anion of mass m_- and static charge -Z. The anion consists of a spherical electronic shell of negligible mass ¹¹ and charge -Y coupled to an ion core of charge +X and mass m_- . The charge neutrality imposes the relation X - Y = -Z. The cation is connected to the anion-shell by a spring of force constant f. The anion core and shell are connected through a spring of force constant k. For the j-th cell, the relative displacements of the cation, anion-core and ion-shell are respectively $u_+(j)$, $u_-(j)$ and v(j).



Figure 5.2: Shell-model of Cochran with a polarizable anion : the case of a linear diatomic chain.

Microscopic approach

Equations of motion

When the atoms are displaced from their equilibrium positions they experience forces due to (i) the short-range interactions with the neighboring atoms described by coreshell springs and (ii) a long-range Coulomb interaction. As usual within a shell-model approach, the latter is described by the product of the core or shell charge by the local field induced by all the other atoms. The resulting equations of motion for cores and shell are :

$$m_{+}\ddot{u}_{+}(j) = f[v(j) + v(j+1) - 2u_{+}(j)] + Z\mathcal{E}_{loc}$$

$$m_{-}\ddot{u}_{-}(j) = k[v(j) - u_{-}(j)] + X\mathcal{E}_{loc}$$

$$0 = f[u_{+}(j) + u_{+}(j-1) - 2v(j)] + k[u_{-}(j) - v(j)] - Y\mathcal{E}_{loc}$$
(5.72)

¹¹This assumption is equivalent to the adiabatic approximation

For a periodic chain, the displacements, solutions of these equations, have the general form :

$$u_{+}(j) = U_{+}e^{i[q.(ja)-\omega t]}; \ u_{-}(j) = U_{-}e^{i[q.(ja)-\omega t]}; \ v(j) = Ve^{i[q.(ja)-\omega t]}.$$
(5.73)

In what follows we will focus only on Γ modes such that q = 0. Introducing, for this specific case, the displacements in the equations of motion, we get:

$$m_{+}\omega^{2}U_{+} = F(U+W) - Z\mathcal{E}_{loc}$$

$$m_{-}\omega^{2}U_{-} = kW - X\mathcal{E}_{loc}$$

$$0 = F(U+W) + kW - Y\mathcal{E}_{loc}$$
(5.74)

where we have defined F = 2f, $U = U_+ - U_-$ and $W = U_- - V$. The last equation yields relative core-shell displacement

$$W = -\frac{FU - Y\mathcal{E}_{loc}}{k + F} \tag{5.75}$$

so that only the displacements of the two ion cores must be explicitly considered. We obtain therefore two equations describing the movement of the two ions:

$$m_+\omega^2 U_+ = \Phi U - Z_S^* \mathcal{E}_{loc} \tag{5.76}$$

$$m_{-}\omega^{2}U_{-} = -\Phi U + Z_{S}^{*}\mathcal{E}_{loc}$$
(5.77)

We have introduced a global effective force constant between both ions

$$\Phi = \frac{Fk}{F+k} \tag{5.78}$$

including both short-range interactions and intra-ionic forces, and the Szigeti charge ¹²

$$Z_S^* = Z - \frac{F}{F+k}Y \tag{5.79}$$

which is an effective dynamical charge including the static charge and the effect resulting from core-shell deformations.

The energy of the ionic chain is invariant under translation so that only the relative displacement U of both type of ions is important. Introducing the reduced mass $\mu = m_+m_-/(m_++m_-)$, we finally obtain the following equation of motion for relative anion-cation displacements:

$$\mu\omega^2 U = \Phi U - Z_S^* \mathcal{E}_{loc} \tag{5.80}$$

¹²The dynamical charge appearing here is the charge experienced in the local electric field. From the discussion of Chapter 2, it corresponds therefore to the Szigeti charge. This will appear more clearly from Eq. (5.82) where it is shown that it corresponds to $\partial \mathcal{P} / \partial U$ in zero local field.

To solve this equations and identify the frequencies ω still requires to identify the relationship between the local field and the atomic displacements.

Local field, atomic polarizability and Szigeti charge

From Eq. [5.48]-[5.47], the local field is directly related to the macroscopic polarization :

$$\mathcal{E}_{loc} = \frac{4\pi}{3} \gamma \mathcal{P} \tag{5.81}$$

with $\gamma = 1$ for transverse modes and to -2 for longitudinal modes. The polarization can be decomposed into ionic and electronic contributions :

$$\mathcal{P} = \mathcal{P}_{i} + \mathcal{P}_{e}$$

$$= \frac{1}{\Omega} [ZU - YW]$$

$$= \frac{1}{\Omega} [ZU + Y \frac{FU - Y\mathcal{E}_{loc}}{k + F}]$$

$$= \frac{1}{\Omega} [(Z + \frac{F}{k + F}Y)U + \frac{Y^{2}}{k + F}\mathcal{E}_{loc}]$$

$$= \frac{1}{\Omega} Z_{S}^{*}U + \frac{1}{\Omega} \frac{(Y)^{2}}{(k + F)}\mathcal{E}_{loc} \qquad (5.82)$$

This allows to write the total polarization as the sum of two terms :

$$\mathcal{P} = \frac{1}{\Omega} Z_S^* U + \frac{1}{\Omega} \alpha_e \mathcal{E}_{loc}$$
(5.83)

where we have introduced the electronic polarizability :

$$\alpha_e = \frac{Y^2}{k+F} \tag{5.84}$$

Introducing this result in Eq. 5.81, we get a relationship between the local field and the atomic displacements :

$$\mathcal{E}_{loc} = \frac{4\pi\gamma}{3\Omega} \frac{Z_S^*}{(1 - \frac{4\pi\gamma\alpha_e}{3\Omega})} U$$
(5.85)

This allows to write the polarization in terms of the Szigeti charge and the ionic polarizability :

$$\mathcal{P} = \frac{1}{\Omega} \frac{Z_S^*}{\left(1 - \frac{4\pi\gamma\alpha_e}{3\Omega}\right)} U \tag{5.86}$$

Transverse and longitudinal frequencies

Introducing the expression of \mathcal{E}_{loc} in the equation of motion, we obtain :

$$\mu\omega^2 = \Phi - \frac{(Z_S^*)^2}{\left(\frac{3\Omega}{4\pi\gamma} - \alpha_e\right)}$$
(5.87)

This yields the following frequencies:

$$\omega_{TO}^2 = \frac{1}{\mu} \left[\Phi - \frac{4\pi}{3\Omega} \frac{(Z_S^*)^2}{(1 - \frac{4\pi\alpha_e}{3\Omega})} \right]$$
(5.88)

$$\omega_{LO}^2 = \frac{1}{\mu} \left[\Phi + \frac{8\pi}{3\Omega} \frac{(Z_S^*)^2}{(1 + \frac{8\pi\alpha_e}{3\Omega})} \right]$$
(5.89)

Transverse and longitudinal frequencies are not identical due to the different condition on the electric field. Both frequencies result from contributions from short-range and Coulomb forces.

Macroscopic approach

Macroscopic field, dielectric constant, Born effective charge

Instead of working in terms of local quantities (local field, polarizability, Szigeti charge), we can reformulate the previous relations in terms of macroscopic concepts : macroscopic field, dielectric constant, Born effective charges.

In the Lorentz approximation, the macroscopic field is related to the local field through

$$\mathcal{E}_{loc} = \mathcal{E} + \frac{4\pi}{3}\mathcal{P} \tag{5.90}$$

so that the polarization takes the form :

$$\mathcal{P} = \frac{1}{\Omega} \frac{Z_S^* U + \alpha_e \mathcal{E}}{(1 - \frac{4\pi\alpha_e}{3\Omega})}$$
(5.91)

The electronic contribution to the dielectric constant is related to the change of polarization in an electric field and corresponds to :

$$\epsilon_{\infty} = 1 + 4\pi \frac{\partial \mathcal{P}}{\partial \mathcal{E}}|_{U=0}$$

= $1 + \frac{4\pi\alpha_e}{\Omega} (\frac{1}{1 - \frac{4\pi\alpha_e}{3\Omega}})$ (5.92)

The Born effective charge corresponds to the polarization induced by an atomic displacement in zero-field and is therefore equal to

$$Z_T^* = \Omega \frac{\partial \mathcal{P}}{\partial U}|_{\mathcal{E}=0}$$

= $\frac{Z_S^*}{(1 - \frac{4\pi\alpha_e}{3\Omega})}$
= $\frac{\epsilon_{\infty} + 2}{3} Z_S^*$ (5.93)
where we recover the usual relationship between Born and Szigeti charges.

In terms of these macroscopic quantities, the polarization therefore writes :

$$\mathcal{P} = \frac{1}{\Omega} Z_T^* U + \frac{\epsilon_\infty - 1}{4\pi} \mathcal{E}$$
(5.94)

Introducing this relation in Eq. 5.81, we get the relationship between the local field and macroscopic quantities :

$$\mathcal{E}_{loc} = \frac{4\pi}{3\Omega} Z_T^* U + \frac{\epsilon_\infty + 2}{3} \mathcal{E}$$
(5.95)

Transverse and longitudinal frequencies

Using the previous relationships, the equations of motion become :

$$\mu\omega^2 = (\Phi + \frac{4\pi}{\Omega} \frac{Z_T^{*2}}{\epsilon_\infty + 2})U + Z_T^* \mathcal{E}$$
(5.96)

The transverse and longitudinal modes correspond respectively to the condition $\mathcal{E} = 0$ and $\mathcal{E} = -4\pi \mathcal{P}$. This yields the following frequencies:

$$\omega_{TO}^2 = \frac{1}{\mu} \left[\left(\Phi - \frac{4\pi}{\Omega} \frac{Z_T^{*2}}{(\epsilon_\infty + 2)} \right) \right]$$
(5.97)

$$\omega_{LO}^2 = \frac{1}{\mu} \left[\left(\Phi - \frac{4\pi}{\Omega} \frac{Z_T^{*2}}{(\epsilon_\infty + 2)} \right) + \frac{4\pi}{\Omega} \frac{Z_T^{*2}}{\epsilon_\infty} \right]$$
(5.98)

These equations are strictly equivalent to those deduced from the microscopic approach. We observe that we recover the usual expression for the LO-TO splitting in terms of the Born effective charges and the optical dielectric constant.

Structural instability

The previous model gives some insight on the origin of the instability of the ferroelectric mode. As first highlighted by Cochran, the TO frequency results from the compensation between two contributions. The first one arises from what we will refer to as the short-range forces. It is positive which means that it tends to stabilize the crystal. The second comes from the long range Coulombic interaction and, consequently to the opposite charge of both kind of ions, it is negative so that it is destabilizing.

An instability, characterized by an imaginary frequency, takes place when the Coulombic interaction is sufficiently large to compensate the short-range forces. Historically, the approach was carried out using the microscopic approach and it was usually assumed that the instability occurs from unusual divergence of the electronic polarizability. From the macroscopic expression, we see this can alternatively be explained from unusually high Born effective charges. From the results of Chapter 2 and as it will be rediscuss in the following of this Chapter, the second interpretation is more appropriate.

5.6.2 First-principles approach

In spite of its meaningful character, the approach of Cochran is only qualitative. The parameters to be included in the shell-model are not known *a priori*. Moreover, the Coulombic energy is obtained through questionable approximations. In particular, the Coulomb interaction is estimated within a Lorentz field approach assuming a local spherical symmetry at each atomic site, while it was shown by Slater [15], before Cochran's study, that the local symmetry is far from spherical in $BaTiO_3$. In his work, Slater computed the Lorentz field explicitly by summing dipole-dipole interactions following Luttinger and Tisza [228].

In what follows, we will propose a model to separate the Coulomb interaction from the remaining short-range forces within our first-principles approach. This model will allow to quantify the role played by both kind of forces in the ferroelectric instability of $BaTiO_3$.

When an atom is displaced in $BaTiO_3$, a dipole is created so that the specific displacement pattern associated to a given phonon generates a lattice of dipoles. Our purpose is to compute the resulting dipole-dipole interaction by summing the different contributions instead of approximating them through the local field as in the previous shell-model.

The conventional dipole-dipole energy between two dipoles $\vec{p_1}$ and $\vec{p_2}$ in vacuum, separated by the vector \vec{d} is given by [229]:

$$E_{\rm e+i}^{DD} = \frac{1}{4\pi\epsilon_0} \frac{(\vec{p}_1.\vec{p}_2) \ d^2 - 3 \ (\vec{p}_1.\vec{d}) \ (\vec{p}_2.\vec{d})}{d^5} \tag{5.99}$$

with ϵ_0 being the vacuum permittivity, so that, in atomic units, $\frac{1}{4\pi\epsilon_0}$ is equal to 1.

In solids, the dipole created by an atomic displacement $\tau_{0\kappa,\alpha}$ is $p_{\beta} = \sum_{\beta} Z^*_{\kappa,\beta\alpha} \cdot \tau_{0\kappa,\alpha}$, while the polarizability of the medium is to be described by the dielectric permittivity tensor $\epsilon^{\infty}_{\alpha\beta}$. For the case where ϵ_{∞} and Z^* tensors are isotropic, the contribution to the interatomic force constant of the dipole-dipole interaction created by the displacement of atoms 0κ and $j\kappa'$, separated by $\vec{d} = (\vec{R}_j + \vec{\tau}_{\kappa'} - \vec{\tau}_{\kappa})$ is [230]:

$$C^{DD}_{\kappa\alpha,\kappa'\beta}(0,j) = \frac{\delta^2 E^{DD}_{e+i}}{\delta\tau_{0\kappa,\alpha}\delta\tau_{j\kappa',\beta}} = \frac{Z^*_{\kappa}Z^*_{\kappa'}}{\epsilon_{\infty}} (\frac{\delta_{\alpha\beta}}{d^3} - 3\frac{d_{\alpha}d_{\beta}}{d^5})$$
(5.100)

The generalization of this formula was proposed for the case of anisotropic Z_{κ}^* and ϵ_{∞} tensors [231]:

$$C^{DD}_{\kappa\alpha,\kappa'\beta}(0,j) = \sum_{\alpha'\beta'} Z^*_{\kappa,\alpha\alpha'} Z^*_{\kappa',\beta\beta'} (\det \epsilon_{\infty})^{-\frac{1}{2}} \left(\frac{(\epsilon_{\infty}^{-1})_{\alpha'\beta'}}{D^3} - 3\frac{\Delta_{\alpha'}\Delta_{\beta'}}{D^5} \right)$$
(5.101)

where $\Delta_{\alpha} = \sum_{\beta} (\epsilon_{\infty}^{-1})_{\alpha\beta} d_{\beta}$, and $D = \sqrt{\vec{\Delta}.\vec{d}}$. The previous result has been obtained in real space. The corresponding dipole-dipole contribution to the dynamical matrix in reciprocal space, \tilde{C}^{DD} , can be obtained using Ewald summation technique [231].

Table 5.7: Partial DD and SR contributions (see text) to the TO mode frequency squared (cm^{-2}) for the cubic phase at the optimized volume. Values in brackets where obtained with the scissors corrected value of ϵ_{∞} .

	$F_{1u}(TO1)$	$F_{1u}(TO2)$	$F_{1u}(TO3)$	F_{2u}
ω_{DD}^2	-625897	7232	-130549	109745
	(-745610)	(8615)	-155518)	130736)
ω_{SR}^2	613107	26538	361998	-26951
	(732820)	(25155)	(386967)	(-47942)
ω^2	-12790	33770	231449	82794

Note that, in this formulation, the macroscopic ϵ_{∞} is used to parametrize the dipoledipole interactions down to nearest neighbors; no correction for the **q**-dependence of ϵ_{∞} and Z^* is included. This procedure seems however the natural generalization of the previous computation of the Lorentz field by Luttinger and Tisza [228]. It will be used to generalize Cochran's results on the basis of our first-principles approach [53].

The dynamical matrix \tilde{C} was obtained explicitly from our *ab initio* calculations. Using the above-mentioned analytic form, we can now isolate the model dipole-dipole (DD)contribution ¹³ from the remaining short-range (SR) part ¹⁴ of this dynamical matrix in a way similar to the one of Cochran [17]: $\tilde{C} = \tilde{C}_{DD} + \tilde{C}_{SR}$. The partial contributions to ω^2 are then evaluated as follows:

$$\underbrace{\langle \eta | \tilde{C} | \eta \rangle}_{\omega^2} = \underbrace{\langle \eta | \tilde{C}_{DD} | \eta \rangle}_{\omega^2_{DD}} + \underbrace{\langle \eta | \tilde{C}_{SR} | \eta \rangle}_{\omega^2_{SR}}$$
(5.102)

where η is an eigenvector of the full dynamical matrix \tilde{C} . Finally, \tilde{C}_{DD} and \tilde{C}_{SR} can also be modified independently in order to investigate their respective influence on the instable mode.

5.6.3 Cubic phase

We first compute the decomposition for the cubic phase at the optimized volume. In Table 5.7, we report the values of ω_{DD}^2 and ω_{SR}^2 for the TO modes. We observe that the *small* instability of the $F_{1u}(TO1)$ mode originates from the compensation of two very *large* numbers: The DD interaction greatly destabilizes the crystal and is only

¹³The dipole-dipole interaction cannot be properly separated from other interactions at short distances. We chose to work with a model interaction that is mathematically unambiguous. All the deviations with respect to this model interaction (that will probably appear at short distances) will be included in the SR part.

 $^{^{14}{\}rm The}~SR$ part also contains higher Coulomb terms like dipole-octupole and octupole-octupole interactions.

partly compensated by the SR contribution. This result confirms, in the framework of a more accurate approach, the idea suggested by Cochran, and usually referred to as the origin of the ferroelectric instability. Interestingly, the close compensation exists for the unstable mode *only*. The giant destabilizing DD interaction of this mode is inherent to its anomalously large mode effective charge that was discussed previously.

It is now possible to investigate the sensitivity of this compensation. In the cubic phase, it was shown that the large values of Z_{Ti}^* and $Z_{O_{\parallel}}^*$ (responsible of the strong Coulomb interaction) are mainly produced by a dynamic transfer of charge along the Ti-O bond [120]. Postulating \tilde{C}_{SR} to be fixed, we can fictitiously reduce this transfer of charge by decreasing simultaneously Z_{Ti}^* and $Z_{O_{\parallel}}^*$, and monitor the $F_{1u}(TO1)$ mode frequency changes ¹⁵. Figure 5.3 shows that $\omega^2(TO1)$ evolves approximately linearly with



Figure 5.3: Evolution of the $F_{1u}(TO1)$ mode frequency squared and of its partial SR and DD contributions with respect to the dynamic transfer of charge along the Ti-O bond (quantified here by the evolution of Z_{Ti}^* , see text), in the optimized cubic phase. The open circles correspond to the evolution when taking into account the modification of eigenvector produced by the change of \tilde{C}_{DD} , while the crosses show the result obtained when keeping the initial eigenvector of the unstable mode in the optimized cubic phase. A zoom around zero frequency is shown in the inset.

the transfer of charge and that a change corresponding to a reduction of the order of 1% of

¹⁵When changing Z^* and/or ϵ_{∞} , \tilde{C}_{DD} is replaced by \tilde{C}'_{DD} and the modified full dynamical matrix $(\tilde{C}' = \tilde{C}'_{DD} + \tilde{C}_{SR})$ has new eigenvectors η' . The matrix elements giving ω^2 , ω^2_{DD} and ω^2_{SR} are calculated using η' . Results are however also presented when keeping the eigenvector of the initial full dynamical matrix, in order to investigate the role of the change of eigenvector from η to η' . As η is not an eigenvector of \tilde{C}' , for that case a fictitious total frequency is obtained as $\bar{\omega}^2 = \langle \eta | \tilde{C}'_{DD} | \eta \rangle + \langle \eta | \tilde{C}_{SR} | \eta \rangle$.

 Z_{Ti}^* is enough to suppress the instability. Of course, this situation is artificial and in a real material any modification of Z_{κ}^* would be associated with a change of the SR forces. This result however highlights the very <u>delicate</u> nature of the compensation existing between dipole-dipole and short range interactions.

Interestingly, if we plot the evolution of partial SR and DD contributions with the transfer of charge described by the evolution of Z_{Ti}^* (see Fig. 5.3), we observe that ω_{SR}^2 is also modified: because \tilde{C}_{SR} was kept constant, this is due to the change of the eigenvector η induced by the modification of \tilde{C}_{DD} . This change of η is however not crucial and a similar evolution of ω^2 is observed if we keep the eigenvector of the original optimized structure.

We checked that all these conclusions are independent of the use of the scissor correction for ϵ_{∞} . From now on, we report only results obtained without scissors correction.

5.6.4 Rhombohedral phase

The eigenvector of the $A_1(TO2)$ modes of the rhombohedral structure remains very close to that of the unstable $F_{1u}(TO1)$ mode of the cubic phase (see Table 5.6). Surprisingly the displacement of the Ti atom against the O cage has now become stable. It was found that the Z_{κ}^* are smaller in this ferroelectric phase, suggesting a smaller DD interaction, but this could be partly compensated by a concomitant reduction of ϵ_{∞} . For the $A_1(TO2)$ mode coming from the soft mode, ω_{DD}^2 (-286267 cm⁻²) is counterbalanced by a slightly larger SR contribution (356373 cm⁻²). The values differ widely from those of the cubic phase: The SR forces give less stabilization (so a priori increasing the instability) but this is compensated by a larger reduction of the DD contribution.

If we fictively modify C_{DD} and replace Z_{κ}^* and ϵ_{∞} of the ferroelectric structure by their value in the cubic phase ¹⁶, we modify the frequency of the $A_1(TO2)$ mode from 265 to 266*i* cm⁻¹: We obtain an instability even *larger* than in the cubic phase. From this point of view, the reduction of Z_{κ}^* in the rhombohedral phase appears as a crucial element to the stabilization of the $A_1(TO2)$ mode.

Introducing Z_{κ}^* and ϵ_{∞} of the cubic phase, we also have strongly modified ω_{DD}^2 and ω_{SR}^2 that become respectively equal to -871017 and 800371 cm⁻². The drastic change of ω_{SR}^2 results only from the change of eigenvector η (\tilde{C}_{SR} was not modified) and points out the anisotropy of the SR forces (the overlap between the new and original eigenvector is equal to 0.86). If we had kept the eigenvector unchanged, we would still have observed a small instability (74*i* cm⁻¹) for the $A_1(TO2)$ mode. This means that the inclusion of the effective charges of the cubic phase is already sufficient to destabilize the crystal, but at the same time produces a change of eigenvector enlarging the instability.

5.6.5 Compressed cubic phase

No more instability is present in the compressed cubic phase, although the global values of Z_{κ}^* do not differ significantly from those obtained at the optimized volume[120]. Moreover, the reduction of volume even increases the destabilizing effect of the DD interaction by

¹⁶See previous footnote.

20%: calling η_{TO1}^{opt} the eigenvector of the soft TO1 mode of the optimized phase and \tilde{C}_{DD}^{opt} (resp. \tilde{C}_{DD}^{comp}) the dipole-dipole part of the dynamical matrix of the optimized (resp. compressed) cubic phase, we obtain:

$$<\eta_{TO1}^{opt}|\tilde{C}_{DD}^{opt}|\eta_{TO1}^{opt}> = -625897 \text{cm}^{-2},$$
(5.103)

while

$$<\eta_{TO1}^{opt}|\tilde{C}_{DD}^{comp}|\eta_{TO1}^{opt}> = -775203 \text{ cm}^{-2}.$$
 (5.104)

In fact, for this compressed cubic phase, the modifications of the SR forces alone are enough to produce a mixing of modes so that no single mode can still be identified with the unstable one observed at the optimized volume (see Table III). Consequently, none of the mode of this compressed cubic phase develops the giant DD or SR contributions that are a particular feature of the displacement pattern associated to the ferroelectric mode.

If we replace A_{SR} by its value at the optimized volume we recover a very large instability (437*i* cm⁻¹). The disappearance of the unstable mode under pressure seems therefore essentially connected to a modification of the SR forces in contrast to its stabilization in the rhombohedral phase which is associated with a reduction of Z_{κ}^{*} .

5.6.6 From electronic to dynamical properties

Since it was introduced by Cochran during the sixties, the soft-mode picture is considered as a key concept to explain the ferroelectric phase transition in ABO_3 compounds. Moreover, the competing role of the short-range and Coulomb interactions, invoked to justify qualitatively the appearance of an instability, is still usually considered as the microscopic origin of the ferroelectric instability.

In this Chapter, we have proposed a model to quantify from our first-principles results the respective role played by both kind of forces. We have justified on a more rigorous basis the gratifying explanation of Cochran. Doing that, we were going even further in the microscopic understanding of the ferroelectric instability. The giant dipole-dipole interaction, able to compensate the stabilizing short-range forces is connected to the large anomalous effective charges in turn explained by dynamic changes of orbital hybridization between O 2p and Ti 3d states.

Cohen and Krakauer [93] recently discussed the importance of the O 2p – Ti 3d hybridization on the ferroelectric instability of BaTiO₃: they suggested that this hybridization should reduce the short-range forces. If their argument remains pertinent, our study has emphasized that dynamic change of hybridization will also greatly enhance the destabilizing role of the Coulomb interaction. It is our choice to attribute the ferroelectric instability to this latter unexpected feature. Hybridizations are indeed not a specific character of ABO₃ compounds but are also common to a large variety of other materials. The peculiarity of the hybridization in BaTiO₃ (and related compounds) stays in the fact that it concerns occupied and unoccupied orbitals and is able to generate giant Born effective charges as discussed in Chapter 5.

Our results are closely related to the unusual non-linear anisotropic polarizability of the oxygen reported by Migoni, Bilz and Bäuerle [22], and that is still usually considered as the origin of the ferroelectricity in ABO₃ compounds [232, 25, 23, 24, 141, 26, 233]. In particular, our work confirms the important role plays by the hybridization between the 2p-states of oxygen and the d-states of the B atom. In our approach, however, the mechanisms of polarization have been clarified: they have been reformulated in terms of dynamic transfer of charge and the interplay between electronic and dynamic properties has been presented within a coherent approach. In our description, the Born effective charge was introduced as a key concept for the understanding of the ferroelectric instability.

Interestingly, we have shown that the balance of force is *delicate* and strongly sensitive to small changes like tiny modification of the Born effective charges. The reduction of Z^* is sufficient to suppress the instability in the rhombohedral phase while a modification of the short-range forces is likely at the origin of the stabilization of the ferroelectric mode under isotropic pressure.

The previous results are not specific to $BaTiO_3$. A similar balance of forces was identified in $SrTiO_3$ and $LiNbO_3$. WO_3 , that undergoes a sequence of ferroelectric phase transitions, also presents large anomalous Born effective charges [177]. The competition between short range and Coulomb forces should be a characteristic of ABO_3 perovskites and related materials. Due to the delicate nature of the balance of forces, it is however not surprising to observe that closely related materials do not necessarily present the same ferroelectric instability, that remains a vagary of Nature ¹⁷.

5.7 Irreductible representation at different high symmetry q-points

Up to know, we focused on the Γ phonons and this already allowed to address some interesting questions. The formalism previously reported does however not restrict to this specific case and the dynamical matrix can be obtained everywhere within the Brillouin zone. In this Section we report results obtained at different high symmetry points.

As some of the properties of the normal modes of vibrations are a direct consequence of the specific symmetry of the crystal (degeneracies of different frequencies, separation into longitudinal and transverse vibrations), a careful analysis of the symmetry may reveal useful for classifying the different phonon modes. As mentioned in Chapter 2, the structure of most ABO₃ compounds is cubic perovskite and its space group is $Pm\bar{3}m$. The determination of the irreducible representations at high symmetry **q** points and along high symmetry lines of the Brillouin zone has been reported by Cowley [144]. The notations are summarized in Table 5.8⁻¹⁸. This Table gives us a first information on the phonon mode degeneracy that are expected at the different **q** points. Simultaneously, the symmetry of the different normal mode of vibration imposes constraints on the associated

 $^{^{17}}$ We note also that the arguments presented here are only part of a more complex problem: for instance, the macroscopic strain also plays a major role in the phase transition.

 $^{^{18}\}mathrm{At}$ the Γ point, these notations differ from that used in the previous Section.

Table 5.8: Irreducible representations at high symmetry \mathbf{q} points and along high symmetry lines of the Brillouin zone as reported by Cowley for the cubic phase of ABO₃ perovskite materials.

\mathbf{q} vector	little group	irreducible representation
(0,0,0)	m3m	$4\Gamma_{15} + \Gamma_{25}$
(0,0,q)	4mm	$4\Delta_1 + \Delta_2 + 5\Delta_5$
$(0, 0, \frac{1}{2})$	4/mmm	$2X_1 + 2X_{2'} + X_3 + 3X_5 + 2X_{5'}$
(q,q,0)	mm	$5\Sigma_1 + \Sigma_2 + 5\Sigma_3 + 4\Sigma_4$
$(\frac{1}{2}, \frac{1}{2}, 0)$	4/mmm	$M_1 + M_2 + M_{2'} + M_3$
		$+2M_{3'}+M_4+M_5+3M_{5'}$
(q,q,q)	3m	$4\Lambda_1 + \Lambda_2 + 5\Lambda_3$
$\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$	m3m	$R_{2'} + R_{12'} + R_{25} + R_{25'} + 2R_{15}$

atomic displacement pattern that were also identified by Cowley in Ref. [144]. The combination of the informations given by the degeneracy and by the phonon eigenvectors allow to label unambiguously the different phonon modes. As an example, results obtained in the cubic phase of BaTiO₃ at the experimental volume are reported in Table 5.9. This classification and the identification of the phonon modes at high symmetry q-points will appear particularly useful in Chapter 6 when constructing an effective Hamiltonian for ABO₃ perovskite compounds.

5.8 Interpolation of phonon dispersion curves

As illustrated in the previous Section, the dynamical matrix can be *a priori* calculated everywhere within the Brillouin zone. However, for computational reasons, calculations are usually restricted to a small set of wavevectors. A mathematical interpolation technique must therefore be used to deduce the full phonon dispersion curves. Moreover, a numerical integration is required to determine the interatomic force constants (IFCs) by inverting Eq. (5.8). Both these problems will be addressed simultaneously [230, 231, 84].

If the dynamical matrix was known everywhere in the Brillouin zone, the IFCs could be built as:

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \int_{\mathrm{BZ}} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_b} d\mathbf{q}$$
(5.105)

When the dynamical matrix is known only on a regular grid S of $(l \times m \times n)$ points in the Brillouin zone, the use of a discrete Fourier transform, that will generate approximate IFCs in a large box made of $(l \times m \times n)$ periodic cells, is tempting. Outside of this box,

Table 5.9: Computed phonon frequencies (cm^{-1}) of cubic BaTiO₃ $(a_o=4 \text{ Å})$ at Γ (0,0,0), X (.5, 0,0), M (.5, .5, 0) R (.5, .5, .5) and at a few points along the Γ -R direction: $\Lambda_{\frac{1}{8}}$ (.125, .125, .125), $\Lambda_{\frac{1}{4}}$ (.25, .25, .25) and $\Lambda_{\frac{3}{8}}$ (.375, .375, .375). The computation of the splitting at the Γ was performed without scissor correction.

\overline{q}	label	frequency	label	frequency
Γ	Γ_{15} (TO)	219 i	Γ_{25}	281
	Γ_{15} (A)	0	Γ_{15} (LO)	445
	$\Gamma_{15} (LO)$	159	Γ_{15} (TO)	453
	Γ_{15} (TO)	166	$\Gamma_{15} (LO)$	631
Х	X_5	189 i	X_3	322
	$X_{5'}$	104	$X_{5'}$	330
	$X_{2'}$	146	X_5	421
	X_5	194	\mathbf{X}_{1}	517
	X_1	260	$X_{2'}$	627
Μ	$M_{3'}$	167 i	M_5	344
	$M_{2'}$	103	M_2	354
	$M_{5'}$	104	$\mathrm{M}_{5'}$	435
	M_3	208	M_1	456
	$M_{5'}$	270	${ m M}_4$	683
	$M_{3'}$	333		
\mathbf{R}	R_{15}	128	$ m R_{25'}$	386
	R_{25}	182	R_{15}	414
	$R_{12'}$	314	$R_{2'}$	717
$\Lambda_{\frac{1}{8}}$	Λ_3	$137 \ i$	Λ_2	272
0	Λ_3	70	Λ_3	310
	Λ_1	103	Λ_3	447
	Λ_1	180	Λ_1	461
	Λ_3	184	Λ_1	645
$\Lambda_{\frac{1}{4}}$	$\overline{\Lambda_3}$	96	$\overline{\Lambda_1}$	277
4	Λ_1	105	Λ_3	358
	Λ_3	190	Λ_3	428
	Λ_3	221	Λ_1	467
	Λ_2	244	Λ_1	679
$\Lambda_{\frac{3}{2}}$	Λ_1	115	Λ_1	354
0	Λ_3	121	Λ_3	381
	Λ_3	204	Λ_3	414
	Λ_2	205	Λ_1	440
	Λ_3	290	Λ_1	708

the IFCs are supposed to vanish:

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}\in S} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_{b}} \quad \text{if } \mathbf{R}_{b} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa}' \in \text{box}$$
(5.106)
$$= 0 \qquad \qquad \text{if } \mathbf{R}_{b} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa}' \notin \text{box}$$

The vanishing of the IFCs beyond some distance is intrinsic to the discrete Fourier transform technique. If the integrand in Eq. (5.105) was infinitely differentiable, then the IFCs should decrease exponentially fast, and this condition would not be a practical limitation. However, for insulators with non-vanishing effective charges, close to $\mathbf{q} = \mathbf{0}$, the behavior of the dynamical matrices is strongly non-analytical: it depends on the direction along which $\mathbf{q} = \mathbf{0}$ is attained.

In the real space, this non-analytical behavior (due to the Coulomb interaction) corresponds to long-range IFCs, with an average $1/d^3$ decay (d being the distance between atoms), corresponding to dipole-dipole interactions. Even if the Born effective charge vanishes (this may be imposed by symmetry constraints, in elemental crystals), the atomic displacement will create a quadrupole or an octupole (the latter cannot be forbidden by symmetry reasons), with corresponding quadrupole-quadrupole $1/d^5$ decay, or octupoleoctupole $1/d^7$ decay.

The non-analyticity corresponding to the dipole-dipole interaction is the strongest. The idea that is proposed is to subtract this term from the other contributions and to treat it explicitly.

In this context a short range dynamical matrix is introduced:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}^{\mathrm{SR}}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \tilde{C}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}^{\mathrm{DD}}(\mathbf{q}).$$
(5.107)

It is expected that these forces are sufficiently short range so that their inverse Fourier transform can be approximated with good accuracy by:

The total interatomic force constants in real space, are then obtained as:

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = C_{\kappa\alpha,\kappa'\beta}^{\mathrm{SR}}(0,b) + C_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}^{\mathrm{DD}}(0,b)$$
(5.109)

The dipole-dipole part to be added to the short-range part is computed explicitly: it is given by Eq. (5.101), discussed in Section 7.5. Its Fourier transform had been previously subtracted in Eq. (5.107). This contribution of the dipole-dipole interaction in reciprocal space may be evaluated using Ewald summation technique as described in Ref. [231].

This technique does not only allow to get the IFCs, but it also permits an easy interpolation of the dynamical matrix across the full Brillouin zone, with

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \sum_{\mathbf{d}_b \in \text{box}} C^{\text{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b} + \tilde{C}^{\text{DD}}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}).$$
(5.110)

To summarize, the full phonon dispersion curves can in practice be determine from the knowledge of the dynamical matrix on a relatively restricted mesh of q-points, even for ionic compounds and in spite of the long-range character of the Coulomb interaction. The interpolation technique basically consists in a double discrete Fourier transform on the short-range part of the dynamical matrix while the long-range dipole-dipole interaction is treated separately. The convergence of the results so obtained must be checked when using \mathbf{q} point meshes of increasing size until a sufficient accuracy has been reached.

5.9 The phonon dispersion curves of $BaTiO_3$

The previous interpolation technique can now be applied to $BaTiO_3$. Our calculations are performed at the experimental lattice parameter of 4.00 Å. This choice facilitates the comparison with the experimental data. Some indications on the volume dependence of the phonon frequencies can be found in Section 7.4, where the frequencies of the Γ phonons at different lattice constants have been compared.

5.9.1 Technical remarks

Prior to the presentation of the results, it is necessary to mention a few technical points.



Figure 5.4: Convergence achieved on the calculated phonon dispersion curves of cubic $BaTiO_3$ along the Γ -R line. The open symbols correspond to q-points included in the M1 (circle) and M2 (circle+square) meshes used to extrapolate the curves (M1: dotted lines; M2: full lines). The filled symbols are associated to points not included in the mesh: they illustrate that a satisfactory convergence is obtained with the M2 mesh.

First, the computation of well converged phonon frequencies required to include plane waves up to a 45 Ha energy cutoff and a 6X6X6 mesh of special k-points. This cutoff energy is higher from that needed for the Born effective charges and the dielectric tensor (35 Ha). For coherency, these latter quantities were recalculated. In this Chapter, we use: $Z_{Ba}^* = +2.74$, $Z_{Ti}^* = +7.32$, $Z_{O\perp}^* = -2.14$, $Z_{O\parallel}^* = -5.78$, and $\epsilon_{\infty} = 6.75$.

A second point concerns the dielectric constant. The computed optical dielectric constant (6.75) largely overestimates the experimental value (5.40) [234], as usual within the LDA. A scissor corrected value can be used at the Γ point where the long-range part of the dynamical matrix is computed separately. For small but finite **q** vector, the LDA is similarly flawed but the interaction with the slowly oscillating field is treated self-consistently with the other terms. There is therefore no direct scheme to include the scissor correction in those cases. Our results are reported without scissor correction but it was checked that the problem related the dielectric tensor has no dramatic consequences on the phonon frequencies. It was observed that the discrepancy essentially affects the position of the highest longitudinal optic mode: when replacing the theoretical dielectric constant by the experimental value, its frequency at the Γ point changes from 631 to 696 cm⁻¹. At the opposite, the frequencies of the two other longitudinal modes at the Γ point are affected by less than 2 cm⁻¹. Our LDA results should therefore remain accurate except for the highest LO phonon branch.

Finally, it is always necessary to investigate the error induced by the use of a discrete Fourier transform in the determination of the IFC's, and the interpolation of the dispersion curves. An insight into the convergence reached on the phonon band structure is reported in Fig. 5.4. The frequencies deduced from the dynamical matrix at q = (.125, .125, .125)and q = (.375, .375, .375) are compared to those extrapolated from two different meshes of q-points: the first mesh (M1) includes Γ (.0, .0, .0), X (.5, .0, .0), M (.5, .5, .0) and R (.5, .5, .5) points; the second mesh (M2) is the cubic mesh M1 to which the A (.25, .25, .25) point was added. It is observed that we obtain a very good convergence with the M2 mesh. It is this mesh that was used to obtain the results presented in the next Sections.

5.9.2 Phonon band structure

The calculated phonon dispersion curves [223] are plotted along high symmetry directions in Fig. 5.5. The Γ -X, Γ -M and Γ -R lines are along the <100>, <110> and <111> directions, respectively. The unstable modes associated to a negative curvature of the energy hypersurface have imaginary phonon frequencies.

Our result can be compared to the experimental data [203, 215, 216, 217, 218, 219, 220]. However, a difficulty arises from the fact that all the experimentally observed vibrational excitations have a real frequency while the computed unstable modes are obtained with an imaginary frequency. As the soft mode can be clearly identified by its symmetry, the associated experimental frequencies were removed from the comparison, for clarity. In the low-frequency region, the presence of this additional soft mode may have slightly modified the frequency of the other modes. In spite of these difficulties we observe a good correspondence between our theoretical frequencies and the experimental data, specially



Figure 5.5: Calculated phonon dispersion curves of cubic BaTiO₃ at the experimental lattice constant. The theoretical result shows a reasonable agreement with the experimental data: (•) Ref. [3], (•) Ref. [6], (+) Ref. [7], (\Box) Ref. [8], (×) Ref. [9], (∇) Ref. [10], (\triangle) Ref. [11].

for the acoustic modes for which a large variety of data are available.

The ferroelectric phase transitions are driven by the unstable phonon modes. We are therefore mainly concerned by the analysis of these specific phonons within the Brillouin zone (see Fig. 5.6). Two transverse optic modes are unstable at the Γ point: they correspond to a displacement of the Ti atom against the oxygen cage. The associated displacement eigenvector is equal to $[\delta(Ba) = -0.002, \delta(Ti) = -0.096, \delta(O_1) = +0.158,$ $\delta(O_2) = \delta(O_3) = +0.071$]¹⁹. These two modes remain unstable all along the Γ -X line, with very little dispersion ²⁰. One of them stabilizes along the Γ -M and X-M lines. Examination of the eigenvectors reveals that the unstable mode at the M (.5, .5, .0) point is polarized along the z-direction: its displacement eigenvector is equal to $[\delta(Ti_z) = -0.130,$ $\delta(O_{1,z}) = +0.106$]. Both of the unstable modes become stable when deviating from the three Γ -X-M planes to the R-point.

These features were also observed for KNbO₃ [222] and point out a marked 2D character of the instability in the Brillouin zone. This behaviour is more easily visualized in Fig. 5.7 where we show the frequency isosurface of the lowest unstable phonon branch corresponding to $\omega = 0$. The region of instability, $\omega^2(\mathbf{q}) < 0$, lies between three pairs of

¹⁹The eigendisplacement vector η was normalized such that $\langle \eta | M | \eta \rangle = 1$, where M is such that $M = M_{\kappa} \delta_{\kappa,\kappa'}$ and M_{κ} is the mass of atom κ in atomic mass units.

²⁰At the X point, one of the unstable mode is polarized along the z-axis and has an eigenvector equal to $[\delta(\text{Ti}_z) = -0.117, \delta(O_{1z}) = +0.133, \delta(O_{2z}) = = +0.062]$; the other is polarized along the y direction.



Figure 5.6: Analysis of the unstable phonon mode within the Brillouin zone.



Figure 5.7: Zero-frequency isosurface of the lowest unstable phonon branch over the Brillouin zone. Γ is located at the center of the cube. The mode is unstable in the region between the nearly flat surfaces.

flat surfaces, that are parallel to the faces of the Brillouin zone cube. In other words, the unstable modes are contained in three perpendicular interpenetrating slab-like regions of finite thickness containing the Γ point.

As highlighted by Yu and Krakauer [222], this behaviour corresponds to chain instabilities in real space. At the M-point, we have seen that there is a single unstable mode polarized along the z-axis and dominated by the Ti_z and O1_z displacements. At this wave vector ($q_z = 0$), the Ti and O₁ atoms will be coherently displaced all along an *infinite* <001> chain. Going now from M to the R-point, the coherency of the displacement will gradually disappear and a *finite* length of correlation will be reached for which the phonon becomes stable. The finite thickness of the slab region of instability therefore corresponds to a minimum correlation length of the displacement required to observe an unstable phonon mode. From Fig. 5.7, the length of the shortest unstable chain can be estimated to 4 $a_{cell} = 16$ Å²¹. We note finally, the small dispersion of the unstable mode in the Γ -X-M plane: it suggests a small correlation of the displacements between the different Ti–O chains.

5.9.3 The interatomic force constants

In cubic $BaTiO_3$, we will see that the single displacement of a particular atom never leads to an instability: When one atom is displaced, a force is induced and brings it

²¹The length of the shortest unstable chain is slightly different from that reported for KNbO₃. Changes in material properties could explain this difference although part of it could be due to the different k-point and q-point convergence achieved in Ref. [222]: as observed in Fig. 5.4, the use of a finer mesh of q-points could still slightly decrease the size of the zone of instability of BaTiO₃.

Atom	Total force	DD force	SR force
Ti(0)	+0.15215	-0.27543	+0.42758
$O_{\parallel}(1)$	+0.00937	+0.23247	-0.22310
$Ti_{\parallel}(2)$	-0.06721	-0.03680	-0.03041
$O_{\parallel}(3)$	+0.01560	+0.00861	+0.00699
$T\dot{i}_{\parallel}(4)$	-0.00589	-0.00460	-0.00129
$O_{\perp}(1)$	-0.02114	-0.04298	+0.02184
$Ti_{\perp}(2)$	+0.00751	+0.01840	-0.01089

Table 5.10: Longitudinal (||) and transverse (\perp) interatomic force constants (Ha/Bohr²) with respect to a reference Ti atom (Ti(0)) along the Ti-O chain of cubic BaTiO₃.

back in its initial position (the self-force on Ba, Ti and O is positive ²²). However, its atomic displacement simultaneously induces forces on the other atoms. It is only the additional displacement of some other atoms in this force field that can lower the total energy and produce an instability. The amplitude and the range of the interatomic force constants (IFC) associated to this mechanism can be analysed [223] in order to clarify the chain instability pointed out in the previous Section. Moreover, the specific role of the dipole-dipole interaction (DD) can be separated from that of the short-range forces (SR).

Our convention is that the IFC matrix $C_{\kappa\alpha,\kappa'\beta}(a,b)$ which relates the force $F^a_{\kappa\alpha}$ on atom κ in cell a and the displacement $\tau^b_{\kappa'\beta}$ of atom κ' in cell b is defined through the following expression: $F^a_{\kappa\alpha} = -C_{\kappa\alpha,\kappa'\beta}(a,b).\tau^b_{\kappa'\beta}$. The total IFC is decomposed into a dipole-dipole part (DD) and a short-range part (SR), following Refs. [231, 90]. Such a decomposition is somewhat arbitrary but is useful for understanding the microscopic origin of the trends among different compounds.

Let us first investigate the IFC with respect to a reference Ti atom along a Ti-O chain (Table 5.10). As previously mentioned, we note that the self-force on the Ti atom is large and positive $(+0.15215 \text{ Ha/Bohr}^2)$. We observe also that the longitudinal IFC with the first neighbour O atom is surprisingly small $(+0.00937 \text{ Ha/Bohr}^2)$; moreover, it is positive. The analysis of the DD and SR contributions points out that these characteristics are the result of a destabilizing DD interaction, sufficiently large to compensate the SR forces. It is this close compensation which allows the displacement of Ti against the O atoms. Another insight on this balance of forces was already reported previously in this Chapter (see also Ref. [53, 235]). Consequently to the very small total IFC, the Ti and O displacements might be relatively decoupled.

At the opposite, the DD forces induced on the next Ti atom are negative: they will combine with the SR forces in order to produce sizable coupling $(-0.06721 \text{ Ha/Bohr}^2)$.

²²The self-force are the following (Ha/Bohr²): Ba \rightarrow 0.08065, Ti \rightarrow 0.15215, O_{||} \rightarrow 0.12741, O_{\perp} \rightarrow 0.06807.

$\operatorname{coordinate}$	distance	IFC	DD part	SR part
(.5, .5, .5)	0.0000	+0.15215	-0.27543	+0.42758
(5, .5, .5)	7.5589	-0.06721	-0.03680	-0.03041
(5,5, .5)	10.6899	-0.01114	-0.01301	+0.00187
(5,5,5)	13.0924	-0.00643	-0.00780	+0.00065
(-1.5, .5, .5)	15.1178	-0.00589	-0.00460	-0.00129

Table 5.11: Ti-Ti longitudinal interatomic force constants $(Ha/Bohr^2)$ with respect to a reference Ti atom at (.5, .5, .5).

Table 5.12: O–O longitudinal interatomic force constants $(Ha/Bohr^2)$ with respect to a reference O atom at (.5, .5, .0).

$\operatorname{coordinate}$	$\operatorname{distance}$	IFC	DD part	SR part
(.5, .5, .0)	0.0000	+0.12741	-0.35322	+0.48062
(.5, .0, .5)	5.3450	-0.02838	-0.03367	+0.00529
(5, .5, .0)	7.5589	-0.00190	-0.00314	+0.00124
(.5, .5, -1.0)	7.5589	-0.03212	-0.02295	-0.00918
(5, .0, .5)	9.2577	-0.00183	-0.00289	+0.00106
(5,5, .0)	10.6899	-0.00290	-0.00111	-0.00179
(5, .5, -1)	10.6899	-0.00415	-0.00340	-0.00078
(.5, -1,5)	11.9517	-0.00254	-0.00246	-0.00008
(5,5, -1)	13.0924	-0.00113	-0.00129	+0.00016

This mechanism is at the origin of the chain correlation of the Ti atomic displacements. By contrast, the *transverse* force on the first Ti neighbour is very small and confirms the small correlation of the displacements from chain to chain.

The decay of the Ti–Ti and O–O longitudinal IFC with the interatomic distance can also be investigated. The results are reported in Table 5.11 and 5.12. It is seen that the longitudinal IFC are anisotropic: they propagate essentially along the Ti–O chain. This appears clearly for the SR part. For O, the DD contribution is also highly anisotropic due to the anisotropy of the Born effective charges. The anisotropy of the IFC is inherent to the chain correlation.

5.9.4 The chain-structure instability

The presence of *chain-structure instabilities* in $BaTiO_3$, is since long under discussion. Historically, the debate was initiated during the late sixties by Comes, Lambert and Guinier [27, 224] who reported diffuse X-rays scattering for crystals of $BaTiO_3$ and $KNbO_3$ in three set of planes normal to the cubic axis. When a scattering is observed outside the directions of diffraction, it must provide from a defect in the crystal periodicity. Clearly, the pattern observed by Comes *et al.* was the fingerprint of a linear disorder in real space. The subsequent controvert was on the static or dynamic nature of this linear disorder.

Interestingly, diffuse X-ray scattering is not a particular feature of ABO₃ compounds: similar features had been reported (even before Comes) by Honjo *et al.* [236], for a large variety of materials (Si, Al, LiF, NaCl...). In most cases, the origin of the disorder was identified in the thermal oscillations. For ABO₃ compounds, it was therefore tempting to make the connection with Cochran's soft-mode theory of the ferroelectricity. Hüller [28] favored this approach and explained the results in terms of *dynamical correlations* from an empirical model with a low frequency TO branch with flat dispersion along < 100 >directions.

Differently, Comes *et al.* [27, 224] preferred to invoke a *static disorder* to explain their results and they proposed what is now usually referred to as the 8-sites model ²³. In this model, it is suggested that the equilibrium position of the Ti (Nb) atom is not at the center of the cubic unit cell but is slightly displaced along one of the <111> directions. It may therefore occupy 8 equivalent positions. In this context, the diffuse scattering is explained by a strong correlation of the Ti positions along <100> chains. As an additional argument to their model, they suggested that the correlation should propagate through the subsequent displacement of the O atoms in an opposite direction to the Ti atoms.

The controversy between the static and dynamic explanation of the linear disorder is still now under debate. Some recent experiments argue in favor of the 8-sites model [239] while other authors prefer to refer to Hüller's explanation [240]. As already mentioned by Comes *et al.* [224], this discussion is not central as both approaches involve the same underlying concept of correlation. The crucial question instead concerns the *existence* and the *mechanisms* of correlation between the atomic displacements. Are atomic correlations really present? What is their microscopic origin? These questions were still recently emphasized by Maglione and Jannot [29] who introduced the concept of "relaxator ferroelectrics", that is based explicitly on the existence of these chain structure correlations.

In complement to the experiments, the chain-structure correlation was recently investigated from first-principles. Early computations, as those reported in Chapter 3, have pointed out the existence of energy wells for Γ soft-mode distortions that are deeper for rhombohedral than for tetragonal types of displacements. This seemed to be a step toward the 8-sites model. However, it only concerned the cooperative displacement of Ba, Ti and O atoms, correlated in all the different unit cells. Consequently, it did not contain

 $^{^{23}}$ The 8-sites model is different from the model reported by Mason and Matthias [237]. It remains also a reference in spite of the existence of more complicated but questionable models like in Ref. [238].



Figure 5.8: Lowest eigenvalue of the restricted force constant matrix associated to atomic displacements along a finite Ti-O chain of increasing size.

any information on the form of the energy surface around a single-atom displacement and the requirement (or not) of a correlation to produce an instability.

In Section 7.8 we have seen that the form of the dispersion curves support the idea of chain-correlation. In the previous Section, we have clearly shown that $BaTiO_3$ is not unstable with respect to the displacement of a single atom. In this Section, we will quantify with the help of a simple model the correlation of the atomic displacements, required to observe an instability.

Let us consider that we have a bulk cubic crystal with the atoms frozen at their equilibrium position τ_{κ_0} . Then, we allow displacements of Ti and O atoms belonging to a [100] single Ti–O chain of finite but increasing size. The total energy of this system will be given by:

$$E(\{\tau_{\kappa}\}) = E(0) + \sum_{a,\kappa} \sum_{b,\kappa'} C_{\kappa 1,\kappa 1}(a,b) \tau^{a}_{\kappa 1} \tau^{b}_{\kappa' 1}$$

where C is the interatomic force constant matrix and the sum on a, κ and b, κ' is restricted to the Ti and O atoms that are allowed to move. With the help of this equation, we can track the appearance of an instability in terms of the length of the chain of displaced atoms. An instability will correspond to a specific displacement pattern that lowers the total energy of the system: it will be associated to a negative eigenvalue of the restricted force constant matrix.

In Fig. 5.8, we report the evolution of the lowest eigenvalue of the force constant matrix with respect to the length of the chain of moving atoms. Displacing only a single atom, the force induced on the Ti is larger than that on the O atom. With 3 atoms, we observe, at the opposite, that the Ti-terminated chain (Ti-O-Ti) is more stable than the O-terminated one (O-Ti-O): it points out the important role of the Ti-Ti interaction. The difference between Ti and O terminated chains will disappear progressively with the chain length. It is seen that an instability takes place for a chain longer than 10 atoms

(5 unit cells). This is in close agreement with the correlation length estimated in the previous Section. It suggests that the behaviour of $BaTiO_3$ is already well reproduced when considering the present isolated Ti–O chain of displacements. It confirms also that the correlation between the different chains may play a minor role.

Going further, it seems interesting to check the role of the small coupling between Ti and O displacements. Freezing all the O atoms in such a way that only the Ti atoms are allowed to move along the chain, we can repeat the previous calculations. For this case, however, we do not observe any instability even for an infinite chain of correlated Ti displacements. This result aims to prove that the relatively weak coupling between Ti and O displacements still remains an important feature in the appearance of the structural instability.

Our calculations, performed within the harmonic approximation at zero temperature does not allow to discriminate between the 8-sites and Hüller models. It has however confirmed the existence of chains of correlation in BaTiO₃. It has also revealed the crucial role of the coupling between O and Ti displacements, that was hypothetically suggested by Comes *et al.* [224] to explain the correlation. Going beyond the result presented here, Krakauer *et al.* have recently clarified the *dynamic* nature of the chain-structure correlation in KNbO₃ from their first-principles results [51].

5.10 Comparative study of the lattice dynamics of various perovskite ABO₃ compounds

5.10.1 Phonon band structure

In this section, we compare the phonon dispersion relations of BaTiO₃, PbTiO₃ and PbZrO₃, providing a global view of the quadratic-order energy surface around the cubic perovskite structure in these different compounds. The calculated phonon dispersion curves along the high symmetry lines of the simple cubic Brillouin zone are shown in Fig. 5.9. In each case we worked at the experimental lattice constant (4.00 Åfor BaTiO₃, 3.97 Åfor PbTiO₃ and 4.12 Åfor PbZrO₃. The unstable modes have imaginary frequencies. Their dispersion is shown below the zero-frequency line. The *character* of these modes also has significant implications for the properties of the system. This character has been depicted in Fig. 5.9 by assigning a color to each eigenvalue, determined by the percentage of each atomic character in the normalized eigenvector of the dynamical matrix (red for A atom, green for B atom and blue for O atoms) 24 .

Barium titanate and potassium niobate both undergo a transition sequence with decreasing temperature through ferroelectric tetragonal, orthorhombic and rhombohedral (ground state) structures, all related to the cubic perovskite structure by the freezing-in of a polar mode at Γ . The main features of the phonon dispersion of BaTiO₃ discussed in

 $^{^{24}}$ For example, a normalized mode with A displacement 0.7, B displacement 0.5, and O displacements 0.5, 0.1, and 0.0 (in generalized coordinates) would be colored via the command "0.49 0.25 0.26 setrgb-color" in the Adobe Systems Inc. PostScriptTM language.



Figure 5.9: Calculated phonon dispersion relations of $BaTiO_3$, $PbTiO_3$ and $PbZrO_3$ along various high-symmetry lines in the simple cubic Brillouin zone. A color has been assigned to each point based on the contribution of each kind of atom to the associated dynamical matrix eigenvector (red for the A atom, green for the B atom, and blue for the oxygens). Symmetry labels follow the convention of Cowley, with the A atom at the origin.

Table 5.13: Normalized dynamical matrix eigenvector for the unstable ferroelectric mode at Γ (z-polarization). The corresponding eigendisplacement in real space can be obtained by dividing each value by the appropriate mass factor $\sqrt{M_{ion}}$.

ABO ₃	А	В	O_x	O_y	O_z
$BaTiO_3$	+0.0178	+0.6631	-0.2842	-0.2842	-0.6311
$PbTiO_3$	+0.2314	+0.4024	-0.4792	-0.4792	-0.5704
PbZrO_3	+0.5033	-0.1786	-0.5738	-0.5738	-0.2374

the previous Section are very similar to those of KNbO₃ [222]. As a brief summary, the most unstable mode is at Γ , and this mode, dominated by the Ti displacement against the oxygens (Table 5.13), is the one that freezes in to give the ferroelectric phases. However, the instability is not restricted to the Γ point. Branches of Ti-dominated unstable modes extend over much of the Brillouin zone. The flat dispersions of the unstable transverse optic mode towards X and M, combined with its rapid stiffening towards R, confine the instability to three quasi-two-dimensional "slabs" of reciprocal space intersecting at Γ . This is the fingerprint of a "chain-like" unstable localized distortion for the Ti displacements in real space [222, 241]. Except for these modes, all the other phonons are stable in BaTiO₃, which makes the behavior of the unstable branches relatively easy to understand.

Lead titanate has a single transition to a low-temperature ferroelectric tetragonal structure, related to the cubic perovskite structure by the freezing-in of a polar mode at Γ . The phonon dispersion of PbTiO₃ shows similar features to that of BaTiO₃, with some important differences. As in $BaTiO_3$, the most unstable mode is at Γ , consistent with the observed ground state structure. However, the eigenvector is no longer strongly dominated by the displacement of the Ti against the oxygen along the Ti–O chains, but contains a significant component of the Pb moving against the O atoms in the Pb–O planes (see Table 5.13). Unstable Ti-dominated modes, similar to those in $BaTiO_3$, can be identified in the vicinity of the M–X line ($M_{3'}$, X_5 modes). However, Pb now plays an active role in the character of the majority of the unstable branches, notably those terminating at $M_{5'}$ and $X_{5'}$. Also, the Pb-dominated branch emanating from the ferroelectric Γ mode towards R has a much weaker dispersion than the corresponding, Ti-dominated, branch in BaTiO₃. In consequence, the unstable localized ferroelectric distortion in real space is nearly isotropic, in contrast to the pronounced anisotropy in $BaTiO_3$. Finally, there is an antiferrodistortive instability at the R-point (R_{25} mode). As similarly observed in $SrTiO_3$ [173], this instability is confined to quasi-one-dimensional "tubes" of reciprocal space running along the edges of the simple cubic Brillouin zone (R_{25} and M_3 modes and the branch connecting them). The branches emanating from this region stabilize rapidly away from the Brillouin zone edge towards, in particular, Γ_{25} and X_3 . In real space, this instability appears as a cooperative rotation of oxygen octahedra, with strong correlations in the plane perpendicular to the axis of rotation, and little correlation between rotations in different planes. The lack of interplane correlation, arising from



Figure 5.10: Schematic three-dimensional view of the atoms labeled in Table 5.14.

the flatness of the $R_{25}-M_3$ branch, suggests the absence of coupling between the oxygen motion in different planes. This will be discussed further in the next section.

The ground state of PbZrO₃ is an antiferroelectric with 8 formula units per unit cell, obtained by freezing in a set of coupled modes, most importantly modes at R and $\Sigma(\frac{1}{4}\frac{1}{4}0)[242]$. The phonon dispersion correspondingly shows even more pronounced and complex instabilities than for PbTiO₃. Overall, the unstable branches are dominated by Pb and O displacements, with no significant Zr character. There is still a polar instability at the Γ point but the eigenvector (see Table 5.13) is clearly dominated by the displacement of lead against the oxygens while the Zr atom now moves with these oxygens. In fact, the modes where the Zr is displaced against the oxygens ($\Gamma_{\rm LO}$ at 160 cm⁻¹, M_{3'}, X₅ modes) are now all stable. The octahedral rotation branch is again remarkably flat and is significantly more unstable at R₂₅ and M₃ than in PbTiO₃. The antiferrodistortive instability retains some one-dimensional character but spreads into a larger region of reciprocal space : the Γ_{25} and X₃ transverse oxygen motions, related to the R₂₅ mode, are still stable but with a relatively low frequency. We note finally that the stiffest longitudinal and tranverse oxygen branches have been shifted to higher energy relative to the titanates.

5.10.2 Interatomic force constants

In the previous section, comparisons between the three compounds were made by analyzing phonon dispersion relations along high-symmetry lines in reciprocal space. As previously illustrated for $BaTiO_3$, highly instructive picture of the quadratic-order structural energetics of the system is provided by direct examination of the real-space interatomic force constants (IFC).

Our convention are the same as those defined for $BaTiO_3$ in Section 5.9.3. For convenience, the atoms are labeled according to Table 5.14, as illustrated in Fig. 5.10. The interatomic force constants are reported either in cartesian coordinates or in terms of

Table 5.14: Label assigned to various atoms in terms of their position in reduced coordinates.

A_0	(0.0, 0.0, 0.0)	B_0	(0.5, 0.5, 0.5)	O_1	(0.5, 0.5, 0.0)
A_1	(0.0, 0.0, 1.0)	B_1	(1.5, 0.5, 0.5)	O_2	$(\ 0.5,\ 0.0,\ 0.5)$
				O_3	(-0.5, 0.5, 0.0)
				O_4	(0.5, 0.5, -1.0)
				O_5	(-0.5, 0.0, 0.5)

Table 5.15: Self-force constant $(Ha/Bohr^2)$ on the different atoms in the unit cell.

Atom	Direction	BaTiO_3	$PbTiO_3$	$PbZrO_3$
A ₀	x=y=z	+0.0806	+0.0247	+0.0129
B_{0}	x=y=z	+0.1522	+0.1393	+0.2302
O_1	x=y	+0.0681	+0.0451	+0.0166
	Z	+0.1274	+0.1518	+0.2758

their longitudinal (||) and transverse (\perp) contributions along the line connecting the two atoms. The results for BaTiO₃, PbTiO₃ and PbZrO₃ are presented in Tables 5.15, 5.16 and 5.17.

First, we examine the "self-force constant," which specifies the force on a single isolated atom at a unit displacement from its crystalline position, all the other atoms remaining fixed. The values are given in Table 5.15. The self-force constants are positive for all atoms in the three compounds, so that all three are stable against isolated atomic displacements. Therefore, it is only the cooperative motion of different atoms that can decrease the energy of the crystal and generate an instability, such as is observed in the phonon dispersion relations presented in the previous Section. The analysis of the IFCs will help us to identify the energetically favorable coupling in the displacements and elucidate the origin of the unstable phonon branches.

Next, we discuss the ferroelectric instability at Γ , and the phonon branches which emanate from it. In barium titanate, it was found that the unstable eigenvector is dominated by Ti displacement along the Ti–O–Ti chain. If we consider the simple case where only Ti atoms are allowed to displace, we find that the destabilizing contribution from the Ti₀–Ti₁ || interaction itself is nearly enough to compensate the Ti self-force constant (Table 5.16). In addition, the fact that the Ti₀–Ti₁ \perp interaction is comparatively small can account directly for the characteristic flat dispersion along Γ -X and Γ -M and the strong stiffening along Γ -R, associated with the chain-like nature of the instability. For the true eigenvector, another important, though relatively small, destabilizing contribution comes from the cooperative displacement of the O₁ atoms against the titaniums along the Ti–O

Table 5.16: Selected longitudinal (||), transverse (\perp) and cartesian ($\alpha\beta$) interatomic force constants (Ha/Bohr²) between different pairs of atoms. The dipole-dipole (DD) and remaining short-range (SR) contribution, have been separated following the scheme described in Ref. [241].

			$BaTiO_3$			$PbTiO_3$			$PbZrO_3$	
Atom		Total	DD	\mathbf{SR}	Total	DD	\mathbf{SR}	Total	DD	\mathbf{SR}
B ₀ -O ₁	()	+0.0094	+0.2325	-0.2231	-0.0012	+0.1865	-0.1877	-0.0687	+0.1380	-0.2067
	(\perp)	-0.0211	-0.0430	+0.0218	-0.0178	-0.0417	+0.0239	-0.0100	-0.0358	+0.0258
$B_0 - B_1$		-0.0672	-0.0368	-0.0304	-0.0615	-0.0285	-0.0330	-0.0499	-0.0211	-0.0288
	(上)	+0.0075	+0.0184	-0.0109	+0.0065	+0.0142	-0.0077	+0.0054	+0.0105	-0.0052
$B_0 - O_4$	(II)	+0.0156	+0.0086	+0.0070	+0.0135	+0.0069	+0.0066	+0.0106	+0.0051	+0.0055
	(上)	+0.0009	-0.0016	+0.0007	+0.0015	-0.0015	+0.0006	+0.0012	-0.0013	+0.0002
$B_0 - A_0$	(II)	-0.0286	-0.0212	-0.0074	-0.0277	-0.0241	-0.0036	-0.0271	-0.0216	-0.0054
	(上)	+0.0134	+0.0106	+0.0028	+0.0157	+0.0121	+0.0036	+0.0145	+0.0108	+0.0037
	(xx)	-0.0006	+0.0000	-0.0006	+0.0012	+0.0000	+0.0012	+0.0007	+0.0000	+0.0007
$A_0 - O_1$	()	-0.0004	+0.0114	-0.0118	+0.0108	+0.0162	-0.0054	+0.0139	+0.0169	-0.0030
	(zz)	-0.0108	-0.0154	+0.0045	-0.0110	-0.0181	+0.0071	-0.0103	-0.0163	+0.0060
$A_0 - A_1$	()	-0.0112	-0.0052	-0.0060	-0.0108	-0.0086	-0.0022	-0.0094	-0.0093	-0.0001
	(±)	+0.0038	+0.0025	+0.0012	+0.0054	+0.0043	+0.0011	+0.0056	+0.0047	+0.0009

Table 5.17: Interatomic force constant matrix in cartesian coordinates $(Ha/Bohr^2)$ between various pairs of oxygen atoms. Lines and columns of the matrix correspond respectively to x, y and z displacements for the first and second atom mentioned in the first column of the Table.

Atoms	${ m BaTiO}_3$		$PbTiO_3$	$PbZrO_3$
0 ₁ -0 ₂	$\left(\begin{array}{ccc} +0.0037 & 0.0000 \\ 0.0000 & -0.0087 \\ 0.0000 & +0.0274 \end{array}\right)$	$ \begin{pmatrix} 0.0000 \\ +0.0119 \\ -0.0087 \end{pmatrix} \left(\begin{array}{c} +0.0035 \\ 0.0000 \\ 0.0000 \end{array} \right)$	$ \left. \begin{array}{ccc} 0.0000 & 0.0000 \\ -0.0091 & +0.0123 \\ +0.0271 & -0.0091 \end{array} \right) \\$	$\left(\begin{array}{cccc} +0.0038 & 0.0000 & 0.0000 \\ 0.0000 & -0.0065 & +0.0110 \\ 0.0000 & +0.0229 & -0.0065 \end{array}\right)$
O ₁ -O ₃	$\left(\begin{array}{ccc} -0.0019 & 0.0000 \\ 0.0000 & +0.0017 \\ 0.0000 & 0.0000 \end{array}\right)$	$ \begin{pmatrix} 0.0000 \\ 0.0000 \\ +0.0091 \end{pmatrix} \qquad \begin{pmatrix} -0.0012 \\ 0.0000 \\ 0.0000 \end{pmatrix} $	$\left(\begin{array}{ccc} 0.0000 & 0.0000 \\ + 0.0022 & 0.0000 \\ 0.0000 & + 0.0079 \end{array}\right)$	$\left(\begin{array}{cccc} -0.0012 & 0.0000 & 0.0000 \\ 0.0000 & +0.0021 & 0.0000 \\ 0.0000 & 0.0000 & +0.0055 \end{array}\right)$
0 ₁ -0 ₄	$\left(\begin{array}{ccc} -0.0003 & 0.0000 \\ 0.0000 & -0.0003 \\ 0.0000 & 0.0000 \end{array}\right)$	$\left(\begin{array}{c} 0.0000\\ 0.0000\\ -0.0321 \end{array}\right) \qquad \left(\begin{array}{c} +0.0003\\ 0.0000\\ 0.0000 \end{array}\right)$	$ \left. \begin{array}{ccc} 0.0000 & 0.0000 \\ + 0.0003 & 0.0000 \\ 0.0000 & - 0.0326 \end{array} \right) \\$	$\left(\begin{array}{cccc} -0.0010 & 0.0000 & 0.0000 \\ 0.0000 & -0.0010 & 0.0000 \\ 0.0000 & 0.0000 & -0.0362 \end{array}\right)$
0 ₁ -0 ₅	$\left(\begin{array}{rrr} -0.0006 & -0.0013 \\ -0.0007 & +0.0013 \\ +0.0013 & +0.0025 \end{array}\right)$	$ \begin{array}{c} +0.0007 \\ +0.0007 \\ +0.0013 \end{array} \right) \qquad \left(\begin{array}{c} -0.0010 \\ -0.0010 \\ +0.0013 \end{array} \right)$	$\left. \begin{array}{ccc} - \ 0.0013 & + \ 0.0010 \\ + \ 0.0012 & + \ 0.0011 \\ + \ 0.0022 & + \ 0.0012 \end{array} \right)$	$\left(\begin{array}{rrrr} -0.0010 & -0.0013 & +0.0010 \\ -0.0010 & +0.0011 & +0.0010 \\ +0.0013 & +0.0018 & +0.0011 \end{array}\right)$

chains. This, together with the total contribution of the rest of the IFCs, is responsible for the actual instability of the ferroelectric Ti-dominated branches in $BaTiO_3$.

For lead titanate, the energetics of the Ti-only displacements, dominated by the Ti self-force constant and the $Ti_0-Ti_1 \parallel$ and \perp interactions, are remarkably similar to those in BaTiO₃ (Table 5.16). However, in PbTiO₃ there is also an important destabilization associated with pure Pb displacements²⁵. This can be fully attributed to the large difference in the Ba and Pb self-force constants, while the $A_0-A_1 \parallel$ and \perp interactions are very similar in the two compounds. Also, the $A_0-B_0 \parallel$ and \perp cation interactions are of the same order of magnitude as in $BaTiO_3$ and combine to give a surprisingly small xxcoupling. At Γ , symmetry considerations permit the mixing of Ti–O and Pb–O displacements and in the phonon branches which emanate from it, thus accounting for the nature of the ferroelectric eigenvector. However, at X, M and R symmetry labels distinguish the Ti-dominated $(X_5, M_{3'} \text{ and } R_{25'})$ and Pb-dominated $(X_{5'}, M_{2'} \text{ and } R_{15})$ modes, which can be readily identified in the calculated phonon dispersion. Also, the Pb_0-Pb_1 coupling is much smaller in magnitude than the Ti_0-Ti_1 coupling, which accounts for the relatively weak dispersion of the Pb-dominated branch from Γ to R. In the true eigenvectors, these instabilities are further reinforced by displacements of the oxygens. While the longitudinal IFC between Ba_0 and O_1 was very small in $BaTiO_3$, there is a significant destabilizing interaction between Pb_0 and O_1 in $PbTiO_3$, which further promotes the involvement of Pb in the unstable phonon branches. We note that the Ti_0-O_1 longitudinal interaction is repulsive in $PbTiO_3$, but it is even smaller in amplitude than in $BaTiO_3$ and its stabilizing effect is compensated by the transverse coupling between Pb and O_1 .

In lead zirconate, the unstable eigenvector at Γ is strongly dominated by Pb–O motion, with little involvement of Zr. This can be understood by comparing, in Table 5.16, the energetics of Zr-only displacements with those of Ti-only displacements in PbTiO₃ and BaTiO₃: the Zr self-force constant is significantly larger and the Zr₀–Zr₁ || and \perp interactions are smaller, so that Zr cannot move as easily as Ti. Also, the Zr₀–O₁ || interaction is now significantly repulsive, explaining why the Zr atom does not move against the oxygens, but with them. As for the titanates, we note finally that the Zr atoms are mainly coupled along the B–O chains, so that the characteristic dispersion of the B-atom modes is preserved, only at higher frequencies. On the other hand, the Pb self-force constant is much smaller, the Pb₀–Pb₁ || and \perp interactions are only slightly smaller, and the destabilizing coupling between lead and oxygen is similar to that in PbTiO₃, accounting for the involvement of Pb in the instability.

Finally, we discuss the antiferrodistortive instability identified with the R_{25} and M_3 modes and the branch along R–M connecting them. There is a marked variation in the frequency of the R_{25} mode in the three compounds, ranging from the lack of any instability in BaTiO₃, to PbTiO₃ with an unstable R_{25} mode that nonetheless does not contribute to the ground state, and finally to PbZrO₃ in which the R_{25} mode is even more unstable and contributes significantly to the observed ground state [242]. The eigenvector of this mode is completely determined by symmetry and corresponds to a

²⁵Specifically, the Pb diagonal element of the full force constant matrix at Γ (-0.0018 Ha/Bohr²) shows that uniform Pb displacement is unstable. This is not the case for Ba in BaTiO₃.

coupled rotation of the corner-connected oxygen octahedra. Its frequency depends only on the oxygen IFCs, predominantly the self-force constant and the off-diagonal coupling between nearest neighbor oxygen atoms. In fact, the latter (for example, $O_{1y}-O_{2z}$ in Table 5.17) is remarkably similar in all three compounds. The trend is therefore associated with the rapid decrease in the transverse O self-force constant from BaTiO₃ to PbTiO₃ to PbZrO₃ and the resulting compensation of the contribution from the self-force constant by the destabilizing contribution from the off-diagonal coupling.

The self-force constant can be written as a sum over interatomic force constants, according to the requirement of translational invariance: $C_{\kappa\alpha,kappa\beta}(a,a) = -\sum_{b,\kappa'}' C_{\kappa\alpha,\kappa'\beta}(a,b)$. It is therefore of interest to identify which interatomic force constants are responsible for the trend in the transverse oxygen self-force constant. The suggestion that the trend is due to covalency-induced changes in the Pb–O interactions can be directly investigated through a "computer experiment." Everything else being equal, we artificially replace the IFC between A₀ and O₁ atoms in BaTiO₃ by its value in PbTiO₃, consequently modifying the self-force constant on A and O atoms. For this hypothetical material, the A-atom dominated modes are shifted to lower frequencies while the frequency of the R₂₅ mode is lowered to 40*i* cm⁻¹. If we introduce the stronger A₀–O₁ interaction of PbZrO₃, we obtain an even larger R₂₅ instability of 103*i* cm⁻¹.

The previous simulation demonstrates the crucial role played by the lead-oxygen interaction in generating the AFD instability. However, this change alone is not sufficient to reproduce the flatness of the $R_{25}-M_3$ branch, as the corresponding frequencies of the M_3 mode in the two hypothetical cases above are 92 cm⁻¹ and 25*i* cm⁻¹, respectively. Naively, the absence of dispersion of the antiferrodistortive mode along that line would be interpreted as the absence of coupling between the oxygens in the different planes. However, as can be seen in Table 5.17, the *yy* transverse coupling between O_1 and O_3 is far from negligible, and acts to amplify the AFD instability at R with respect to M. In the lead compounds, however, this is compensated by another *yz* coupling, between O_1 and O_5 . The latter is significantly smaller in BaTiO₃ (by 35 %). If we consider a third hypothetical compound in which this coupling in BaTiO₃ is additionally changed to its value in PbTiO₃, we recover a flat behavior along the R–M line. In the lead perovskites, the flatness of this band appears therefore as a consequence of a compensation between different interplane interactions, and cannot be attributed to complete independence of oxygen motions in the different planes.

5.10.3 Transfer of the interatomic force constants

At first, we observed marked differences between the phonon dispersion relations and eigenvectors in the three related compounds. Through the real-space analysis in the previous section, we have seen that these differences arise from changes in a few key interatomic force constants.

First, we remark that B–O interactions depend strongly on the B atom, being similar in PbTiO₃ and BaTiO₃, and quite different in PbZrO₃. In fact, the SR force contribution to the Zr_0-O_1 interaction and Ti_0-O_1 are very similar, so that the difference arises from

the dipolar contribution. In $PbZrO_3$, this contribution is reduced in consequence of the lower values of the Born effective charges (see Chapter 3). This trend provides another example of the *very* delicate nature of the compensation between SR and DD forces, previously pointed out for BaTiO₃.

Next, we remark that A–O interactions depend strongly on the A atom, being similar in PbTiO₃ and PbZrO₃, and quite different in BaTiO₃. This change originates in the covalent character of the bonding between Pb and O, which results both in smaller A–O SR coupling and a larger Born effective charge for Pb. Even though the impact of the latter on destabilizing the DD interaction is partly compensated by the increased ϵ_{∞} , the net effect is to promote the Pb–O instability.

As discussed above, the self-force constant can be written as a sum over interatomic force constants. It can be easily verified that the trends in the self-force constants observed in Table 5.15 are primarily associated with the trends in A–O and B–O interactions.

The rest of the IFCs given in Table 5.16 are actually remarkably similar. For example, A–B interactions are apparently insensitive to the identity of A (Ba, Pb) or B (Ti, Zr). This is true also for A–A, B–B and most O–O interactions. The small differences observed can at least in part be attributed to differences in the lattice constants and in ϵ_{∞} for the three compounds.

The similarities in IFC's among compounds with related compositions offer an intriguing opportunity for the modelling of the lattice dynamics of solid solutions. In the simplest case, the lattice dynamics of ordered supercells of compounds such as PZT or BST could be obtained by using the appropriate A–O and B–O couplings from the pure compounds and averaged values for the A–B, A–A, B–B and O–O interactions. These ideas have been successfully tested by Bungaro and Rabe [243] for PZT and by Ghosez *et al.* [244] for BST.

5.11 Phonons in LiNbO₃

The investigation of the lattice dynamics of ferroelectric oxides was not restricted to perovskite compounds. The phonon dispersion curves of $LiNbO_3$ in its two phases have also been reported [].

As for BaTiO₃, a particular attention has been recently paid at the Γ phonons [245]. This allowed to clarify some ambiguities concerning the assignation of the different modes modes. Moreover, it has been showed that the eigenvector of the unstable ferroelectric mode has an overlap of 99% with the pattern of atomic displacement at the phase transition. Also, following the same approach as for BaTiO₃, it has been demonstrated that the instability results from the near cancellation between SR and DD forces, the latter being sufficiently large to destabilize the crystal. Again, this illustrate that the ferroelectric behavior of the ferroelectric compounds is not related to the perovskite structure but to the giant Born effective charges associated to the mixed ionic-covalent character of their bonding.

5.12 Conclusions

In this Chapter, we have described the computation of the phonon frequencies within a variational formulation of the density functional perturbation theory and we have presented a useful scheme for the interpolation of the phonon dispersion curves. These formalisms have then been applied to various ABO_3 compounds. Our results allowed to address two fundamental aspects of the ferroelectric instability.

First, in agreement with the idea of Cochran, it was demonstrated (for $BaTiO_3$, $SrTiO_3$, $LiNbO_3$) that the ferroelectric instability originates in the compensation of the stabilizing short-range forces by a large destabilizing Coulomb interaction. In this context, the Born effective charge appeared as a meaningful concept to understand the origin of anomalous dipolar forces in connection with the electronic properties. The delicate nature of the balance of forces has been emphasized.

Second, it was observed that the displacement of a single atom is never unstable in the different ABO_3 compounds which where investigated. In $BaTiO_3$, the appearance of an instability requires a correlation of the atomic displacements along a Ti-O chain of minimum 10 atoms. Our calculations also confirm the experimental evidence of linear disorder in $BaTiO_3$.

It is interesting to realize that these two aspects of the phase transition are not independent from each others: the amplitude of the interatomic force constants responsible of the chain structure instability are indeed a direct consequence of the balance between the short range forces and the Coulomb interaction.

Finally it is worth noticing that in spite of significantly different dispersion curves different ABO_3 compounds have very similar interatomic force constants : the differences originate in the modification of few key interactions. This observation is particularly useful to understand and predict the dynamics of mixed compounds.

5.13 References

The results presented in this Chapter have been partly discussed in the following papers:

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