

# UNIVERSITE CATHOLIQUE DE LOUVAIN

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# First-principles study of the dielectric and dynamical properties of barium titanate

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# Contents

1.1 Introd 1.2 The I 1.3 The I 1.3.1 1.3.2	duction
1.2 The I 1.3 The r 1.3.1 1.3.2	Born-Oppenheimer approximation
1.3 The 1 1.3.1 1.3.2	nany-body electron problem
1.3.1 1.3.2	The variational principle
1.3.2	
199	Expectation values
1.3.3	The exchange-correlation hole
1.3.4	Variational electronic energy
1.4 Slater	r determinants
1.5 The I	Hartree-Fock approximation
1.6 The c	lensity functional theory
1.6.1	Hohenberg and Kohn theorem
1.6.2	The Kohn-Sham equations
1.6.3	A Kohn-Sham variational formulation
1.6.4	The exchange-correlation energy
1.7 The (	Green's function approach
1.8 The I	OFT bandgap problem
1.8.1	Kohn-Sham eigenenergies
1.8.2	Bandgap problem
1.9 Concl	lusions
1.10 Refer	ences
1.9 Concl 1.10 Refer	lusions

## CONTENTS

		2.3.1 Periodic boundary conditions
		2.3.2 Bloch functions
		2.3.3 Brillouin zone sampling 45
	2.4	A plane-wave pseudopotential approach
		2.4.1 Plane-wave basis set
		2.4.2 Pseudopotentials
	2.5	Total crystal energy
		2.5.1 The macroscopic limit
		2.5.2 The electronic energy
		2.5.3 The ion-ion energy
		2.5.4 Crystal energy
	2.6	Structural optimization
	2.7	Conclusions
	2.8	References
3	Gro	ound-state properties of BaTiO <sub>3</sub> 57
	3.1	Introduction
	3.2	Structural optimization
		3.2.1 Cubic phase
		3.2.2 Ferroelectric phases
	3.3	Electronic properties
	3.4	The ferroelectric instability
	3.5	$Conclusions \dots \dots$
4	АТ	Density Functional Perturbation Theory 73
-	41	Introduction 73
	4.2	Perturbations and physical properties 75
	1.2	4.2.1 The electric enthalpy 75
		4.2.2 Derivatives of the electric enthalpy 78
		4.2.3 Summary 80
	43	Basics of perturbation theory 80
	1.0	4.3.1 The Sternheimer approach 81
		4.3.2 The variational approach 85
	44	Merging of DFT and perturbation theory 87
	1.1	4.4.1 The Sternheimer approach 88
		4.4.2 The variational formulation 89
	45	Incommensurate perturbations 90
	1.0	4.5.1 Energy expansion 90
		4.5.2 Factorization of the phase 91
	46	The phonon-type perturbation 02
	1.0	4.6.1 Change of external notential
		4.6.9 Variational expression 03
		10.2 Faranonal expression in the transmission of 90

	4.7 The ele	ectric field perturbation	. 94
	4.7.1	Change of external potential	. 94
	4.7.2	Variational expressions	. 95
	4.8 The ca	se of mixed perturbations	. 97
	4.9 Conclu	sions	. 99
	4.10 Referen	nces	. 100
5	The Born	effective charges	101
	5.1 Introdu	action	. 101
	5.2 The co	ncept of static charge	. 103
	5.3 The co	ncept of dynamic charge	. 106
	5.3.1	Definition	. 106
	5.3.2	Dynamic transfer of charge	. 107
	5.4 A first-	principles formulation	. 110
	5.4.1	Introduction	. 110
	5.4.2	The perturbative approach	. 112
	5.4.3	The Berry phase approach	. 114
	5.4.4	Band by band decomposition	. 115
	5.4.5	Choice of the gauge	. 118
	5.4.6	Technical details	. 119
	5.5 The cu	bic phase of ABO <sub>3</sub> compounds	. 119
	5.5.1	Various results	. 119
	5.5.2	The Harrison model	. 121
	5.6 The ba	Ind-by-band decomposition	. 123
	5.6.1	A reference configuration	. 124
	5.6.2	BaTiO <sub>3</sub>	. 124
	5.6.3	$SrTiO_3$	. 127
	5.6.4	Other examples	. 128
	5.7 Sensiti	vity to structural features	. 130
	5.8 Sponta	neous polarization	. 135
	5.9 Role of	the Born effective charge in the lattice dynamics .	. 137
	5.10 Conclu	sions	. 138
	5.11 Referen	1ces	. 138
6	The optica	l dielectric tensor	141
	6.1 Introdu		. 141
	6.2 The lin	lear response formalism	. 142
	6.3 The "s	cissors" correction	. 143
	6.4 The ca	se of BaTiO <sub>3</sub>	. 144
	6.5 Conclu	sions	. 147
	6.6 Referen	nces	. 147
	5.0 10010101		

7	$\mathbf{Pho}$	onons 14	9
	7.1	Introduction	9
	7.2	The dynamical equation	1
	7.3	The linear response approach	3
		7.3.1 The electronic contribution	3
		7.3.2 The ion-ion contribution	4
		7.3.3 The $\mathbf{q} \rightarrow 0$ case	5
		7.3.4 The acoustic sum rule	6
	7.4	BaTiO <sub>3</sub> phonon modes at the $\Gamma$ point $\ldots \ldots \ldots \ldots \ldots 15$	$\overline{7}$
		7.4.1 Cubic phase	8
		7.4.2 Rhombohedral phase	<b>1</b>
	7.5	Origin of the ferroelectric instability	<b>4</b>
		7.5.1 Cochran's model	<b>4</b>
		7.5.2 Short-range and dipole-dipole interactions 16	<b>5</b>
		7.5.3 Cubic phase	6
		7.5.4 Rhombohedral phase	8
		7.5.5 Compressed cubic phase	9
		7.5.6 From electronic to dynamical properties 17	0
	7.6	$BaTiO_3$ phonons at different high symmetry q-points 17	1
	7.7	Interpolation of phonon dispersion curves	<b>2</b>
	7.8	The phonon dispersion curves of $BaTiO_3$	<b>5</b>
		7.8.1 Technical remarks	5
		7.8.2 Results and discussion	7
	7.9	The interatomic force constants	1
	7.10	The chain-structure instability 18	<b>2</b>
	7.11	Conclusions	6
	7.12	References	7
8	Den	nsity-polarization functional theory 18	9
	8.1	Introduction	9
	8.2	The Hohenberg and Kohn theorem	0
		8.2.1 Problematics $\dots \dots \dots$	0
		8.2.2 Perturbative analog to HK theorem 19	2
		8.2.3 Periodic systems 19	3
		8.2.4 Hohenberg-Kohn functional	3
	8.3	Exchange-correlation electric fields	<b>5</b>
		8.3.1 Kohn-Sham equation	5
		8.3.2 Sternheimer equation 19	6
	8.4	Illustration for a model semiconductor 19	$\overline{7}$
	8.5	Spontaneous polarization of polar solids	9
		8.5.1 Problematics	9
		8.5.2 Kohn-Sham treatment of polar solids	1

		8.5.3 Model calculation	204
		8.5.4 Conclusions and practical issues	206
	8.6	The exchange-correlation kernel	206
		8.6.1 Problematics	207
		8.6.2 The exact long-wavelength behaviour	208
		8.6.3 The one-dimensional model semiconductor	209
		8.6.4 Within LDA and GGA's	210
		8.6.5 The metal-insulator paradox	212
	8.7	The dielectric constant	212
		8.7.1 The exact dielectric response	213
		8.7.2 Exact DFT and "LDA+scissors" approach	215
	8.8	Origin of the Polarization dependence	217
		8.8.1 The exchange-correlation hole	217
		8.8.2 Polarization dependence of the exchange energy	217
	8.9	Conclusions	219
	8.10	References	219
Co	onclu	sions	221
A	Tecl	nnical details	225
A	Tecl A.1	nnical details Pseudopotentials	<b>225</b> 225
Α	Tecl A.1 A.2	nnical details Pseudopotentials	<b>225</b> 225 226
A	Tecl A.1 A.2	nnical details       :         Pseudopotentials       :         Convergence study       :         A.2.1       Ground-state properties	<b>225</b> 225 226 226
Α	Tecl A.1 A.2	nnical details       :         Pseudopotentials       :         Convergence study       :         A.2.1       Ground-state properties         A.2.2       Response functions	<b>225</b> 225 226 226 227
Α	<b>Tecl</b> A.1 A.2 A.3	nnical details:Pseudopotentials:Convergence study:A.2.1 Ground-state properties:A.2.2 Response functions:Structural optimization:	<b>225</b> 225 226 226 227 227
АВ	Tecl A.1 A.2 A.3 The	mical details       Seudopotentials       Se	<ul> <li>225</li> <li>225</li> <li>226</li> <li>226</li> <li>227</li> <li>227</li> <li>227</li> <li>231</li> </ul>
A	<b>Tecl</b> A.1 A.2 A.3 <b>The</b> B.1	mical details       :         Pseudopotentials       :         Convergence study       :         A.2.1 Ground-state properties       :         A.2.2 Response functions       :         Structural optimization       :         atomic charges       :         The static atomic charges       :	<ul> <li>225</li> <li>225</li> <li>226</li> <li>227</li> <li>227</li> <li>227</li> <li>231</li> </ul>
A B	Tecl A.1 A.2 A.3 The B.1 B.2	nical details       :         Pseudopotentials       :         Convergence study       :         A.2.1 Ground-state properties       :         A.2.2 Response functions       :         Structural optimization       :         atomic charges       :         The static atomic charges       :         The Harrison model       :	<ul> <li><b>225</b></li> <li>226</li> <li>226</li> <li>227</li> <li>227</li> <li><b>231</b></li> <li>232</li> </ul>
A B	<b>Tecl</b> A.1 A.2 A.3 <b>The</b> B.1 B.2	mical details       Seudopotentials       Se	<ul> <li>225</li> <li>225</li> <li>226</li> <li>227</li> <li>227</li> <li>227</li> <li>231</li> <li>232</li> <li>233</li> </ul>
A B	Tecl A.1 A.2 A.3 The B.1 B.2	mical details       Seudopotentials       Se	<ul> <li><b>225</b></li> <li>225</li> <li>226</li> <li>227</li> <li>227</li> <li><b>231</b></li> <li>232</li> <li>233</li> <li>233</li> </ul>
A B	<b>Tecl</b> A.1 A.2 A.3 <b>The</b> B.1 B.2 <b>Pho</b>	mical details       Seudopotentials       Se	<ul> <li><b>225</b></li> <li>226</li> <li>227</li> <li>227</li> <li><b>231</b></li> <li>232</li> <li>233</li> <li>233</li> <li><b>235</b></li> </ul>
A B C	<b>Tecl</b> A.1 A.2 A.3 <b>The</b> B.1 B.2 <b>Pho</b> C.1	mical details       Seudopotentials       Se	<ul> <li><b>225</b></li> <li>225</li> <li>226</li> <li>227</li> <li>227</li> <li><b>231</b></li> <li>232</li> <li>233</li> <li>233</li> <li><b>235</b></li> <li>235</li> </ul>
A B C	<b>Tecl</b> A.1 A.2 A.3 <b>The</b> B.1 B.2 <b>Pho</b> C.1 C.2	mical detailsSeudopotentialsPseudopotentialsConvergence studyA.2.1Ground-state propertiesA.2.2Response functionsStructural optimizationStructural optimizationatomic chargesStructural optimizationThe static atomic chargesStructural optimizationB.2.1Effective static chargeB.2.2Born effective chargenonsSrTiO <sub>3</sub>	<ul> <li>225</li> <li>225</li> <li>226</li> <li>227</li> <li>227</li> <li>231</li> <li>232</li> <li>233</li> <li>233</li> <li>235</li> <li>240</li> </ul>

CONTENTS

# Introduction

#### Brief history of the ferroelectricity

Ferroelectricity was discovered in 1920 by Valasek [281] who observed that the polarization of Rochelle salt can be reversed by the application of an external electric field. From the very beginning, the 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 the phenomenon. Ferroelectric materials are now currently used in various technological applications [138, 103, 119, 274]. However, in spite of many years of interest, there still remain many academic questions concerning the fundamental nature of the ferroelectricity [171, 274] and some of its related properties [171, 78]. Some of these questions are at the origin of the present study. They will be reintroduced within a partial history of the ferroelectricity, focusing on the ABO<sub>3</sub> compounds.

The first series of isomorphous ferroelectric crystals was produced in Zurich, 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 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  $(BaTiO_3)$  were found incidentally, in 1945, when searching for new dielectrics to replace mica [171]. 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 *pro*-

*totype* crystal structure was cubic perovskite 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 ABO<sub>3</sub> family [171]. A ferroelectric activity was discovered in KNbO<sub>3</sub> presenting the same sequence of phase transitions than  $BaTiO_3$ , or in PbTiO<sub>3</sub> that remains stable at low temperature in tetragonal symmetry. Ferroelectricity was also observed in LiNbO<sub>3</sub> and LiTaO<sub>3</sub>, which do not have the perovskite structure but still are ABO<sub>3</sub> lattices with oxygen octahedra (illmenite structure).

The great fascination for the ABO<sub>3</sub> perovskite structure 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  $\Gamma$  type displacement of the atoms of the prototype phase) but may be antiferrodistortive (displacement associated to a non-zero vector within the Brillouin zone). The most frequently observed case consists in a cell doubling transition, associated to a Brillouin zone boundary type displacement like in SrTiO<sub>3</sub> (non-polar distortion) or PbZrO<sub>3</sub> (antiferroelectrics). Sometimes, like in NaNbO<sub>3</sub>, instabilities of different characters are present and produce a chain of transitions of different natures: ferroelectric, anti-ferroelectric, non-polar.

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 [272] who suggested that the ferroelectric instability of BaTiO<sub>3</sub> 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 description<sup>1</sup>. 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 [39]<sup>2</sup> realized that the theory describing the displacive lattice instability should be cast within the framework of lattice dynamics, when considering one of the lattice mode as the basic variable. His theory was exhibited in the framework

<sup>&</sup>lt;sup>1</sup>The 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 [81].

<sup>&</sup>lt;sup>2</sup>A similar approach was taken independently by Anderson [3].

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 [171] 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<sub>3</sub> was, for instance, already reported by Devonshire [57] 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 ABO<sub>3</sub> compounds [314, 289].

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<sub>3</sub> compounds arose from the fit of these experimental data within a shell-model approach. In 1976, Migoni, Bilz and Bäuerle [196] 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" [18, 25] that was widely used to describe the dynamics of ABO<sub>3</sub> compounds. The unusual polarizability of the oxygen atom was discussed [196, 24, 18] and is still now usually referred as the origin of the ferroelectricity [26]. In particular, it was already suggested by Bilz et al. [196] that the anisotropy of the oxygen polarizability should be induced by the dynamical hybridization between oxygen p-states and transition metal d-states [196, 18]. 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 [46] reported diffuse X-ray scattering for crystals of BaTiO<sub>3</sub> and KNbO<sub>3</sub>, 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 mean-

ingful picture currently invoked to visualize the mechanism of the phase transition. It was however contested by Hüller [125] 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 [180].

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 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 <sup>3</sup>. 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 the ferroelectricity was given recently when ABO<sub>3</sub> compounds became accessible to first-principles calculations performed within the Density Functional Theory (DFT) [121, 147]. 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<sub>3</sub> compounds were reported by Weyrich [298, 299] during the eighties. The recent renewal of interest in these materials is a consequence of different theoretical advances combined with a gigantic jump of computational power during the last few years.

A first crucial advance concerns the emergence of the modern theory of polarization, pioneered by Resta [243] and King-Smith and Vanderbilt [142, 283]. Until recently, 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. Now, the electronic contribution to the polarization can be conveniently obtained from a Berry phase of the electronic wavefunctions and is easily computed in the framework of DFT.

<sup>&</sup>lt;sup>3</sup>The 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 [81].

A second ingredient is the effective Hamiltonian approach to structural phase transitions, developed by Rabe and Joannopoulos [227, 228, 229], in which the parameters of the Hamiltonian are determined from the results of first-principles calculations. Such an approach, first applied to GeTe [227], was then generalized by Rabe and Waghmare [230, 232, 289] for general phonon-related phase transitions, opening the door to a systematic firstprinciples study of the ABO<sub>3</sub> family compounds. In this specific context, the recent density functional perturbation theory (DFPT) [11, 91] 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 work. The most spectacular achievement probably concerns a correct description of the sequence of phase transitions for various ABO<sub>3</sub> compounds like BaTiO<sub>3</sub> [314, 315, 211], SrTiO<sub>3</sub> [316, 317], PbTiO<sub>3</sub> [233, 289, 235], PbZrO<sub>3</sub> [289, 290], KNbO<sub>3</sub> [148], CaTiO<sub>3</sub> [284] or NaNbO<sub>3</sub> [284].

Starting from the "first-principles", such kind of calculations was also a clear opportunity to connect, within a rigorous approach, the macroscopic properties of  $ABO_3$  compounds to their intimate microscopic features.

#### The present work

In this context, our purpose will be to clarify the interplay between the electronic and dynamical properties of BaTiO<sub>3</sub>. In a discussion where the Born effective charge appears as a central concept, we will see that the ferroelectric instability is driven by anomalously large Coulomb forces, themselves induced by dynamic changes of orbital hybridizations. Going further, we will describe how these features lead naturally to the notion of chain-structure instability. Independently, we will also address fundamental questions concerning the theory within which the results have been obtained.

This work is organized as follows. In Chapters 1, we reinvestigate the fundamentals of the density functional theory introduced by Hohenberg, Kohn and Sham during the sixties. We will pay a particular attention to the electronic exchange-correlation effects. In Chapter 2, we briefly describe a "periodic-density" functional theory as it is usually implemented within the local density approximation (LDA) for the description of crystalline solids. In Chapter 3, we report some basic results concerning the electronic and structural properties of BaTiO<sub>3</sub>. We also reintroduce the problematics of the phase transition in the context of our first-principle approach. In particular, it will be checked if DFT-LDA calculations have the required

accuracy to investigate the ferroelectric instability. In Chapter 4, we formulate different quantities of interest as derivatives of the crystal energy. We then describe the computation of these properties within a perturbative treatment of the density functional theory. A particular emphasis will be placed on the connection between the Sternheimer approach and the variational formulation. General equations will be obtained for the investigation of the response of the system to electric field and atomic displacement perturbations. In Chapter 5, we discuss the concept of Born effective charge. We first point out that it is a quantity distinct from the conventional static charge, in the sense that it contains a dynamic contribution. It will be seen that the Born effective charges are anomalously large in ABO<sub>3</sub> compounds. This feature will be described in terms of transfers of charge induced by dynamic changes of orbital hybridizations. In Chapter 6, we mention results concerning the optical dielectric constant. This will be the opportunity to recall a well-known failure of DFT-LDA calculations. In Chapter 7, we discuss the dynamical properties of BaTiO<sub>3</sub>, 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 cubic phase. The notion of chain-structure correlation will be discussed. In Chapter 8, we come back to a more fundamental point of view, questioning the validity of using a periodic-density functional theory for the investigation of successive derivatives of the crystal energy with respect to a macroscopic electric field and for the study of polar insulators. This will lead to the introduction of a density-polarization functional theory (DPFT). It will be argued however that periodic-DFT remains a coherent approach within the LDA. Finally, we propose a summary of the main results obtained within this work.

All along this manuscript, results concerning barium titanate alternate with a discussion of the theory within which the calculations have been performed. Readers only concerned by the physics of the ABO<sub>3</sub> compounds should focus on Chapters 3-5-6-7. People more interested by the fundamental aspects of the theory should concentrate on Chapters 1-2-4-8.

# Chapter 1

# Ground-state theory

# 1.1 Introduction

The description of macroscopic solids from first-principles is based on the determination of the quantum mechanical ground-state associated to their constituting electrons and nuclei. In this Chapter, we first reintroduce this general many-particles problem, defining some of the notations that will be used all along this work. We then address its resolution.

A first natural simplification arises from the large difference in mass between electrons and nuclei, allowing the separate treatment of their dynamics using the so-called Born-Oppenheimer approximation. Considering the ionic core positions as fixed parameters, we then pay a particular attention to the many-electrons problem.

We show that, as an alternative to the direct resolution of a Schrödinger equation, the quantum-mechanical ground-state of the electrons can be determined from the minimization of a functional of the electronic energy. This electronic energy is, a priori, a functional of the many-body electronic wavefunction. Thanks to the Hohenberg and Kohn theorem [121], it will be reformulated as a functional of the electronic density. Within the Kohn and Sham construction [147], it will also appear as a functional of one-body wavefunctions associated to fictitious non-interacting particles.

It it this last, convenient, Kohn-Sham formulation that will then be used all along this work. It will be emphasized that the Kohn-Sham electrons are only fictitious particles, result of a mathematical construction. They give however access to correct ground-state electronic energy and density.

Most of the reviews that were at the origin of the present Chapter are mentioned in Section 1.10.

## 1.2 The Born-Oppenheimer approximation

The ground-state of a system of  $N_i$  nuclei and  $N_e$  electrons in interaction is determined from the following time independent Schrödinger equation:

$$H(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, \mathbf{R}) = E \Phi(\mathbf{r}, \mathbf{R})$$
(1.1)

where the Hamiltonian can be written as:

$$H(\mathbf{r}, \mathbf{R}) = T_i(\mathbf{R}) + U_{ii}(\mathbf{R}) + T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{ie}(\mathbf{r}, \mathbf{R})$$
(1.2)

 $T_i(\mathbf{R})$  and  $U_{ii}(\mathbf{R})$  are the kinetic energy operator and the potential energy operator for nuclei.  $T_e(\mathbf{r})$  and  $U_{ee}(\mathbf{r})$  are the kinetic energy operator and the potential energy operator for electrons.  $U_{ie}(\mathbf{r}, \mathbf{R})$  is the interaction operator between electrons and nuclei. The notation  $\mathbf{R}$  is a short-hand for the position of all nuclei  $(R_{\kappa\alpha}, \text{ for } \alpha = 1, 2, 3 \text{ and } \kappa = 1, ..., N_i)$ , while  $\mathbf{r}$ denotes the position of all electrons  $(r_{j\alpha}, \text{ for } \alpha = 1, 2, 3 \text{ and } j = 1, ..., N_e)$ .

The different terms appearing in the previous Hamiltonian have the following more explicit form  $^{1}$ :

$$T_i(\mathbf{R}) = -\sum_{\kappa} \frac{1}{2M_{\kappa}} \nabla^2_{\mathbf{R}_{\kappa}}$$
(1.3)

$$U_{ii}(\mathbf{R}) = + \sum_{\kappa < \kappa'} \frac{Z_{\kappa} Z_{\kappa'}}{|\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa'}|}$$
(1.4)

$$T_e(\mathbf{r}) = -\sum_i \frac{1}{2} \nabla_{\mathbf{r}_i}^2 \qquad (1.5)$$

$$U_{ee}(\mathbf{r}) = +\sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(1.6)

$$U_{ie}(\mathbf{r}, \mathbf{R}) = -\sum_{i,\kappa} \frac{Z_{\kappa}}{|\mathbf{r}_i - \mathbf{R}_{\kappa}|}$$
(1.7)

Taking into account the large nuclei masses appearing in the kinetic energy operator for nuclei,  $T_N(\mathbf{R})$  can be dissociated from the other terms in the Hamiltonian and considered as a perturbation :

$$H(\mathbf{r}, \mathbf{R}) = H_{e+i}(\mathbf{r}, \mathbf{R}) + T_i(\mathbf{R})$$
(1.8)

with

$$H_{e+i}(\mathbf{r}, \mathbf{R}) = T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{ie}(\mathbf{r}, \mathbf{R}) + U_{ii}(\mathbf{R})$$
(1.9)

<sup>&</sup>lt;sup>1</sup>All along this work, we make use of atomic units (i.e.  $m_{e^-} = |e^-| = 1$ ).

The unperturbed Hamiltonian  $H_{e+i}$  does not include differential operators with respect to nuclear positions. Consequently, the nuclear positions can be considered as classical variables and no more as quantum ones. The problem has been reduced to the search of the solution of the electronic system where positions of nuclei are parameters of the Hamiltonian. The corresponding physical intuition is illustrated by the instantaneous and adiabatic adaptation of the electrons to the positions of the nuclei. It is the Born-Oppenheimer approximation.

The eigenfunctions of the Hamiltonian  $H_{e+i}$  verify the following Schrödinger equation for a given set of nuclear positions :

$$H_{e+i}(\mathbf{r}, \mathbf{R}) \varphi(\mathbf{r}, \mathbf{R}) = E_{e+i}(\mathbf{R}) \varphi(\mathbf{r}, \mathbf{R})$$
(1.10)

The energy  $E_{e+i}$  is usually referred to as the Born-Oppenheimer energy of the system.

As the nuclear positions are fixed parameters in the previous equation, the ion-ion interacting term is fully determined and  $H_{e+i}$  can still be decomposed:

$$H_{e+i}(\mathbf{r}, \mathbf{R}) = H_{el}(\mathbf{r}, \mathbf{R}) + U_{ii}(\mathbf{R})$$
(1.11)

where the electronic part of the Hamiltonian is defined as:

$$H_{el}(\mathbf{r}, \mathbf{R}) = T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{ie}(\mathbf{r}, \mathbf{R})$$
(1.12)

Similarly, the ground-state energy of the system  $E_{e+i}$  can be split into two parts:

$$E_{e+i}(\mathbf{R}) = E_{el}(\mathbf{R}) + E_{ii}(\mathbf{R}) \tag{1.13}$$

where  $E_{ii}(\mathbf{R})$  is the potential energy of the ions, and  $E_{el}(\mathbf{R})$  is the energy of the electrons in presence of the ions.  $E_{ii}(\mathbf{R})$  is formally equivalent to the operator  $U_{ii}(\mathbf{R})$  that reduces to a scalar.  $E_{el}(\mathbf{R})$  is made of three contributions:

$$E_{el}(\mathbf{R}) = K_e(\mathbf{R}) + E_{ee}(\mathbf{R}) + E_{ie}(\mathbf{R})$$
(1.14)

where  $K_e$  is the kinetic energy of the electrons,  $E_{ee}$  is the electron-electron interaction energy and  $E_{ie}$  is the electron-ion energy.  $E_{ii}(\mathbf{R})$  is fixed for a given set of atomic position so that the only remaining unknown of the problem is  $E_{el}(\mathbf{R})$ . From now and all along this Chapter, we will be only concerned by the calculation of this electronic contribution to the Born-Oppenheimer energy.

Reference to the atomic positions are usually omitted in what follows. They remain however implicit, and will be reintroduced when necessary.

## 1.3 The many-body electron problem

The many-body electron problem that we would like to address can now be reformulated as follows. We must solve the following Schrödinger equation:

$$H_{el}(\mathbf{r}) \varphi(\mathbf{r}) = E_{el} \varphi(\mathbf{r}) \tag{1.15}$$

The many-body wavefunction, solution of this equation, will be chosen in order to satisfy the following normalization condition :

$$\int |\varphi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N = 1.$$
(1.16)

Moreover, it must be antisymmetric under exchange of any two electrons: for any pair of i and j particles,

$$\varphi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = -\varphi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N)$$
(1.17)

We note that there is a phase freedom associated to the resolution of such a set of equations: if  $\varphi$  is a solution,

$$\varphi'(\mathbf{r}) = e^{i\lambda} \varphi(\mathbf{r}) \tag{1.18}$$

is another solution, for any  $\lambda$ , real. This indeterminacy of the phase corresponds to what is called a "gauge" freedom. In practice, the phase can be defined by fixing arbitrarily the gauge.

### 1.3.1 The variational principle

Instead of addressing directly the resolution of Eq. (1.15), a usual and convenient approach for solving this problem consists in the variational method. It assumes that  $H_{el}$  has a lowest eigenvalue  $E_{el}$  and it states that the expectation value of an operator cannot be smaller than its lowest eigenvalue: for any normalized antisymmetric wavefunction,  $\varphi$ ,

$$E_{el} \leq E_{el}[\varphi] = \langle \varphi | H_{el} | \varphi \rangle, \qquad (1.19)$$

The ground-state wavefunction  $\varphi_o$  is a stationary point of the energy functional  $E_{el}[\varphi]$ : if

$$|\varphi\rangle = |\varphi_o\rangle + |\delta\varphi\rangle, \qquad (1.20)$$

then

$$E_{el}[\varphi] = E_{el} + \mathcal{O}[(\delta\varphi)^2] \tag{1.21}$$

The ground-state electronic energy may therefore be obtained from a minimization of a functional of the many-body wavefunction:

$$E_{el} = \min_{\varphi} E_{el}[\varphi] = \min_{\varphi} \langle \varphi | H_{el} | \varphi \rangle$$
(1.22)

within the subspace of wavefunctions that satisfy Eq. (1.16)–(1.17). The ground-state electronic wavefunction is that which minimizes  $E_{el}[\varphi]$ .

It is straightforward to demonstrate that the search of the previous energy minimum is equivalent to solve Eq. (1.15). Using the Euler-Lagrange multiplier technique to minimize  $E_{el}[\varphi]$  under the constraints that the wave-function is normalized, we get:

$$\frac{\delta\left(\langle\varphi|H_{el}|\varphi\rangle - \lambda(\langle\varphi|\varphi\rangle - 1)\right)}{\delta\varphi^*} = 0$$
(1.23)

so that, we recover the Schrödinger equation:

$$H_{el} \varphi - \lambda \varphi = 0 \tag{1.24}$$

where the Euler-Lagrange multiplier identifies with the electronic energy. The search of the solution of the previous Schrödinger equation is therefore strictly equivalent to the minimization of a variational expression of the electronic energy within the subspace of normalized and antisymmetric wavefunctions  $\varphi$ .

#### 1.3.2 Expectation values

In the framework of the variational approach, to the determination of the total electronic energy,  $E_{el}[\varphi]$ , requires the estimate of the following expectation values:

$$K_e[\varphi] = \langle \varphi | T_e | \varphi \rangle = \sum_i \langle \varphi | \left( -\frac{1}{2} \nabla_{\mathbf{r}_i}^2 \right) | \varphi \rangle \qquad (1.25)$$

$$E_{ie}[\varphi] = \langle \varphi | U_{ie} | \varphi \rangle = \sum_{i} \langle \varphi | v(\mathbf{r}_{i}) | \varphi \rangle$$
(1.26)

$$E_{ee}[\varphi] = \langle \varphi | U_{ee} | \varphi \rangle = \sum_{i < j} \langle \varphi | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \varphi \rangle.$$
(1.27)

The operators constituting the Hamiltonian are rather simple: they are sum of identical operators acting separately either on a single particle or on pairs of particles. Convenient expressions can be obtained when introducing the first- and second-order density matrices. The kinetic and electron-ion energy are defined through a one-body operator. When introducing the first-order density matrix,

$$\gamma_{\varphi}(\mathbf{r}_{1'};\mathbf{r}_{1}) = N \int \varphi^{*}(\mathbf{r}_{1'},\mathbf{r}_{2},...,\mathbf{r}_{N}) \varphi(\mathbf{r}_{1},\mathbf{r}_{2},...,\mathbf{r}_{N}), \ d\mathbf{r}_{2}...d\mathbf{r}_{N} \quad (1.28)$$

we can write:

$$\langle \varphi | T_e | \varphi \rangle = \int \delta(\mathbf{r}_{1'} - \mathbf{r}_1) \left( -\frac{1}{2} \nabla_{\mathbf{r}_1}^2 \right) \gamma_{\varphi}(\mathbf{r}_{1'}; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_{1'} \quad (1.29)$$

$$\langle \varphi | U_{ie} | \varphi \rangle = \int v(\mathbf{r}) \ \gamma_{\varphi}(\mathbf{r}; \mathbf{r}) \ d\mathbf{r} = \int v(\mathbf{r}) \ n_{\varphi}(\mathbf{r}) \ d\mathbf{r}$$
(1.30)

We note that the electron-ion energy can already be estimated from the density  $n_{\varphi}(\mathbf{r})$ , the diagonal part of  $\gamma_{\varphi}(\mathbf{r};\mathbf{r}')$ . At the opposite, the determination of the kinetic energy explicitly requires the knowledge of the off-diagonal terms of  $\gamma_{\varphi}(\mathbf{r};\mathbf{r}')$ .

The electron-electron interaction is associated to a two-body operator. When introducing the second-order density matrix:

$$\gamma_{\varphi}(\mathbf{r}_{1'};\mathbf{r}_{2'};\mathbf{r}_{1};\mathbf{r}_{2}) = \frac{N(N-1)}{2} \int \varphi^{*}(\mathbf{r}_{1'},\mathbf{r}_{2'},\mathbf{r}_{3},...,\mathbf{r}_{N})$$
$$\varphi(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},...,\mathbf{r}_{N})d\mathbf{r}_{3}...d\mathbf{r}_{N} \qquad (1.31)$$

it can be written as:

$$\begin{aligned} \langle \varphi | U_{ee} | \varphi \rangle &= \int \delta(\mathbf{r}_{1'} - \mathbf{r}_1) \, \delta(\mathbf{r}_{2'} - \mathbf{r}_2) \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \gamma_{\varphi}(\mathbf{r}_{1'}, \mathbf{r}_{2'}; \mathbf{r}_1, \mathbf{r}_2) \\ &= \int \frac{d\mathbf{r}_{1'} d\mathbf{r}_{2'} d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \gamma_{\varphi}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, n_{\varphi}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$
(1.32)

A two-particles density has been introduced:

$$n_{\varphi}(\mathbf{r}_{1},\mathbf{r}_{2}) = \frac{N(N-1)}{2} \int \varphi^{*}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},...,\mathbf{r}_{N}) \varphi(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},...,\mathbf{r}_{N}) d\mathbf{r}_{1}d\mathbf{r}_{2}d\mathbf{r}_{3}...d\mathbf{r}_{N}.$$
(1.33)

It gives the probability of finding a pair of electrons, one at the point  $\mathbf{r}_1$ , and the second at the point  $\mathbf{r}_2$ .

The first and second order density appearing in the previous equations are always positive. Moreover, they integrate respectively to the number

of electron and to the number of pair of electron. They are related to each other through:

$$n_{\varphi}(\mathbf{r}_1) = \frac{2}{(N-1)} \int n_{\varphi}(\mathbf{r}_1, \mathbf{r}_2) \, d\mathbf{r}_2 \tag{1.34}$$

All these relationships will enable us to rewrite the expectation value of the electron-electron operator.

#### 1.3.3 The exchange-correlation hole

The conditional probability of finding an electron in  $\mathbf{r}_2$ , if we know that there is already another one in  $\mathbf{r}_1$  is not equal to  $n_{\varphi}(\mathbf{r}_2)$  but must be written as:

$$P_{\varphi}(\mathbf{r}_{2}|\mathbf{r}_{1}) = \frac{n_{\varphi}(\mathbf{r}_{1},\mathbf{r}_{2}) + n_{\varphi}(\mathbf{r}_{1},\mathbf{r}_{2})}{n_{\varphi}(\mathbf{r}_{1})} = 2 \frac{n_{\varphi}(\mathbf{r}_{1},\mathbf{r}_{2})}{n_{\varphi}(\mathbf{r}_{1})}$$
(1.35)

The "exchange-correlation hole" is defined as the deficit of electron in  $\mathbf{r}_2$  due to the presence of another electron in  $\mathbf{r}_1$ :

$$n_{\varphi}^{xc}(\mathbf{r}_2|\mathbf{r}_1) = P_{\varphi}(\mathbf{r}_2|\mathbf{r}_1) - n_{\varphi}(\mathbf{r}_2).$$
(1.36)

Its name originates from the property that it corresponds exactly to a deficit of one electron when integrated over the all space:

$$\int n_{\varphi}^{xc}(\mathbf{r}_2|\mathbf{r}_1)d\mathbf{r}_2 = -1 \tag{1.37}$$

The exchange-correlation hole is associated to a *conditional* probability. It is not a purely quantum phenomenon and the same concept already exists for classical particles without interaction (Fermi-Amaldi). The shape and spreading of  $n_{\varphi}^{xc}(\mathbf{r}_1|\mathbf{r}_2)$  are however strongly affected by the quantum nature of the particles and by their interaction.

From the previous definitions,  $E_{ee}[\varphi]$  can be decomposed as:

$$\langle \varphi | U_{ee} | \varphi \rangle = E_H[\varphi] + E_{xc}[\varphi]$$
(1.38)

where

$$E_H[\varphi] = \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) n_{\varphi}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$
(1.39)

$$E_{xc}[\varphi] = \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) n_{\varphi}^{xc}(\mathbf{r}_2 | \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$
(1.40)

The first term,  $E_H[\varphi]$ , is called the Hartree energy and corresponds to the electron-electron energy that we would have if the presence of one electron in  $\mathbf{r}_2$  was independent of the presence of another one in  $\mathbf{r}_1$ . The second,  $E_{xc}[\varphi]$ , will be referred to as the exchange-correlation energy of the many-body system <sup>2</sup> and includes the deviations from  $E_H$  associated to the existence of the exchange-correlation hole. Due to the isotropic nature of the Coulomb interaction, we note that the exchange-correlation energy depends only on the *spherical average* of the exchange-correlation hole [105]. The distinction between exchange and correlation effects will appear naturally in the next Section.

### 1.3.4 Variational electronic energy

Making use of the variational principle, the resolution of Eq. (1.15) was recast into a minimization procedure (Eq. 1.22). From the previous definitions, the expectation value of the electronic energy takes form of a functional of the many-body wavefunction:

$$\begin{aligned} \langle \varphi | H_e | \varphi \rangle &= \int \delta(\mathbf{r}_{1'} - \mathbf{r}_1) \left( -\frac{1}{2} \nabla_{\mathbf{r}_1}^2 \right) \gamma_{\varphi}(\mathbf{r}_{1'}; \mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_{1'} \\ &+ \int v(\mathbf{r}) n_{\varphi}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) n_{\varphi}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) n_{\varphi}^{xc}(\mathbf{r}_2 | \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$
(1.41)

Identifying the ground-state requires to minimize this expression under conditions of normalization (Eq. 1.16) and exchange (Eq. 1.17) of the manybody electronic wavefunction.

## **1.4 Slater determinants**

The many-body electronic wavefunction, giving the amplitude of probability to find  $N_e$  particles for every point of a three-dimensional space, is a very complex object, so that the minimization of Eq. (1.41) would be prohibitively difficult. Fortunately, a good insight in the properties of many-particle systems can already be obtained from the study of effective non-interacting particles models. In these models, the interacting electron problem is replaced by a non-interacting system of particles in which the

 $<sup>{}^{2}</sup>E_{xc}[\varphi]$  is a quantity distinct from the DFT exchange-correlation energy,  $E_{xc}[n]$ , that will be introduced later.

external field is replaced by an effective external field which incorporates to some extent the interparticle interactions.

When the fictitious electrons are non-interacting, the different variables can be separated in the wavefunction that basically takes the form of a "Hartree product" :

$$\varphi_H(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \psi_1(\mathbf{r}_1) \cdot \psi_2(\mathbf{r}_2) \cdot \dots \cdot \psi_N(\mathbf{r}_N)$$
(1.42)

The normalization of the one-body wavefunctions is defined in a manner consistent with Eq. (1.16):

$$\int |\psi_j(\mathbf{r})|^2 \, d\mathbf{r} = 1 \tag{1.43}$$

In order to define a properly antisymmetrized wavefunction, the antisymmetrizer operator  $\mathcal{A}_N$  is simply acted upon the Hartree product. The resulting many-body wavefunction can be obtained from an expansion in terms of "Slater determinants":

$$\varphi_{S}(\mathbf{r}_{1}, \mathbf{r}_{2}, ..., \mathbf{r}_{N}) = \sqrt{N!} \mathcal{A}_{N}[\psi_{1}(\mathbf{r}_{1}) \cdot \psi_{2}(\mathbf{r}_{2}) \cdots \psi_{N}(\mathbf{r}_{N})]$$

$$= (1/\sqrt{N!}) det \begin{bmatrix} \psi_{1}(\mathbf{r}_{1}) & \psi_{1}(\mathbf{r}_{2}) & \cdots & \psi_{1}(\mathbf{r}_{N}) \\ \psi_{2}(\mathbf{r}_{1}) & \psi_{2}(\mathbf{r}_{2}) & \cdots & \psi_{2}(\mathbf{r}_{N}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{N}(\mathbf{r}_{1}) & \psi_{N}(\mathbf{r}_{2}) & \cdots & \psi_{N}(\mathbf{r}_{N}) \end{bmatrix}$$

$$(1.44)$$

A Slater determinant is invariant under any unitary transform of the onebody wavefunctions. These can therefore be chosen to be orthonormalized,

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \tag{1.45}$$

and the Slater determinant describes the Hilbert space spanned by the one-body wavefunctions  $\psi_i(\mathbf{r})$ .

The decomposition of the electron-electron interaction energy in terms of Hartree, exchange and correlation contributions acquires more sense in the context of this Section. The complexity of a *Hartree product* is much smaller than the one of a full many-body wavefunction. The amplitude of finding one of the particles at one point, using a Hartree product, does not depend on where the other particles are located any more : there is no inter-particle dependency and, within the limit of large systems, the electron-electron energy associated to such a wavefunction restricts to the Hartree contribution. In the case of the *Slater determinant*, the probability of finding a particle at some point depends on the location of the other particles, but only due to the antisymmetry requirement applied to otherwise independent particles. Modification of  $E_{ee}$  due to that type of dependency will be referred to as "exchange" effects. The *additional* modification of the electron-electron energy brought out by the extra dimensionalities of the unrestricted antisymmetric wavefunction with respect to a Slater determinant will be referred to as "correlation" effects. Exchange and correlation energies are both negative. For real systems, we have typically the following order of magnitude:

$$T_e, E_H \approx 10.|E_x| \approx 100.|E_c| \tag{1.46}$$

Different techniques have been proposed to recast the many-body problem into one-electron schemes. Each of them includes the exchange-correlation effects to some extent. Some of these methods will now be discussed.

## 1.5 The Hartree-Fock approximation

The Hartree-Fock method basically consists in solving the Schrödinger equation in the space of Slater determinants. The approximation results in the fact that the method totally neglects the electron correlation. It has however the advantage to include exactly the exchange effects as previously defined.

For the Slater determinant of Eq. (1.44), we get (see, for instance, Ref. [149]):

$$n_{\varphi_s}(\mathbf{r}_1) = \sum_{i=1}^N \psi_i^*(\mathbf{r}_1) . \psi_i(\mathbf{r}_1)$$
(1.47)

$$\gamma_{\varphi_s}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^N \psi_i^*(\mathbf{r}_1) . \psi_i(\mathbf{r}_2)$$
(1.48)

$$n_{\varphi_s}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} [n_{\varphi}(\mathbf{r}_1) \ n_{\varphi}(\mathbf{r}_2) - \gamma_{\varphi}(\mathbf{r}_1, \mathbf{r}_2) \gamma_{\varphi}(\mathbf{r}_2, \mathbf{r}_1)] \quad (1.49)$$

The exchange hole can be obtained from :

$$n_{\varphi_s}^x(\mathbf{r}_2|\mathbf{r}_1) = \frac{-\gamma_{\varphi_s}(\mathbf{r}_1, \mathbf{r}_2)\gamma_{\varphi_s}(\mathbf{r}_2, \mathbf{r}_1)}{n_{\varphi_s}(\mathbf{r}_1)}$$
(1.50)

Finding the ground-state expectation value of the Hartree-Fock Hamiltonian simply requires the minimization of Eq. (1.41) in which the previous explicit formulation of  $n_{\varphi_s}$ ,  $n_{\varphi_s}^x$  and  $n_{\varphi_s}^x$  has been introduced. Compared to the many-body case, the problem has been greatly simplified because  $E_{el}$ appears now as a functional of orthonormalized *one-body* wavefunctions  $\psi_i$ . It can be checked that the minimization procedure is strictly equivalent to solve a set of coupled one-body Schrödinger-like equations <sup>3</sup>. More informations on this technique can be found in Ref. [149]. In what follows we only point out some interesting results concerning the exchange energy, obtained exactly at the Hartree-Fock level.

First, it can be checked that the "only"-exchange hole already integrates to -1. Moreover, it has been shown that it integrates to -1 over a microscopic region of space: in insulators, it goes to -1 exponentially in the interatomic distance [238]. Consequently to this result, we deduce that the correlation (neglected here) will only modify the *shape* of the exchange hole: the correlation hole integrates to 0. However, it has not be proved that it integrates to zero locally and it was recently suggested that it should be partly delocalized at the surface of the materials [245]. This will be more explicitly discussed in Chapter 8. For an homogeneous electron gas, it can be checked that the exchange energy takes the form:

$$E_x^{hom} = -\frac{3}{4\pi} (3\pi^2)^{\frac{1}{3}} \int n^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r}_1$$
(1.51)

This result will be used later.

## 1.6 The density functional theory

As in the Hartree-Fock method, the *density functional theory* (DFT) reduces the many-body electron problem to a series of coupled single particle equations. In contrast, the formalism of the DFT is *exact* and the final effective potential is *local*.

Instead of seeking directly the many-body wavefunction of the system as in the previous methods, DFT adopts an intrinsically different point of view: it considers the electronic density as the fundamental quantity of the problem. So, it basically reduces the problem from  $3 \times N_e$  to 3 spatial variables. The first aim of the present section will be to explain how the many-body problem can be recast into another one involving only the electron density, while density matrices were *a priori* needed to evaluate the expectation value of the Hamiltonian [121]. Going further, we will show how this density can be deduced from a non-interacting fictitious particle system [147].

<sup>&</sup>lt;sup>3</sup>The exchange potential appearing in this equation is non-local and has the form of an integral operator.

### 1.6.1 Hohenberg and Kohn theorem

The theoretical foundation of DFT has been laid by Hohenberg and Kohn (HK) in 1964 [121]. Their result is formulated in the following context. Suppose a set of Hamiltonians that have all identical kinetic  $T_e$  and electronelectron  $U_{ee}$  operators, but differ by their "external potential"  $v_{\text{ext}}(\mathbf{r})$ , a general one-body local potential :

$$H_{el,v} = T_e + U_{ee} + v_{\text{ext}}(\mathbf{r}).$$
(1.52)

The theorem states that :

The ground-state density  $n(\mathbf{r})$  of the many-electron system determines uniquely the external potential  $v_{\text{ext}}(\mathbf{r})$ , modulo a constant.

The proof is relatively straightforward and is reported in Ref. [121], for a system consisting of an arbitrarily large but finite number of electrons. It will be re-investigated more carefully in Chapter 8, for the case of infinite periodic solids.

Since the density uniquely defines the external potential <sup>4</sup>, that in turn determines unambiguously the Hamiltonian  $H_v$ , all the quantities that can *a priori* be deduced when  $H_v$  is fixed (wavefunctions, kinetic energy, electron-electron interaction energy,...), can be *de facto* written as a functional of the density.

Using this fundamental result and the variational principle, the whole search for the ground-state of the many-body problem can now be reformulated in terms of the density as the fundamental variable leading the total energy to be expressed as follows :

$$E_{el,v} = \min_{\varphi} \left\{ \langle \varphi | H_v | \varphi \rangle \right\} = \min_{n} \left\{ \min_{\varphi \to n} \left\{ \langle \varphi | H_v | \varphi \rangle \right\} \right\}$$
$$= \min_{n} \left\{ \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r} + \min_{\varphi \to n} \left\{ \langle \varphi | T_e + U_{ee} | \varphi \rangle \right\} \right\}$$
$$= \min_{n} \left\{ \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r} + F[n] \right\}$$
(1.53)

We have introduced F[n], the Hohenberg and Kohn functional <sup>5</sup>, defined as:

$$F[n] = \min_{\varphi \to n} \left\{ \langle \varphi | T_e + U_{ee} | \varphi \rangle \right\}$$
(1.54)

 $<sup>^4\,{\</sup>rm The}$  shift in the potential may be fixed through a simple condition, i.e. the external potential goes to zero at infinite distance.

 $<sup>^{5}</sup>$ This functional, only defined by HK for *v*-representable densities, has been extended by Levy to *N*-representable densities [169].

Within DFT, the search of the ground-state therefore basically consists in minimizing the following functional of the electronic density  $^6$ :

$$E_{el,v}[n] = \int v_{\text{ext}}(\mathbf{r}) \ n(\mathbf{r}) \ d\mathbf{r} + F[n]$$
(1.55)

under the constraint that the density integrates to the correct number of electrons  $N_e$ . Although it has been proved that the functional F[n] exists, its exact form remains unfortunately elusive.

#### 1.6.2 The Kohn-Sham equations

A scheme that breaks the Hohenberg and Kohn functional into convenient parts allowing practical implementation was proposed by Kohn and Sham (KS) [147]. Their technique lies on an assumption with respect to the HK formalism and can be reformulated as follows.

We start by introducing a system of *non-interacting* particles moving in an external potential  $v_s$ . The Hamiltonian is  $H_s = T_e + v_s(\mathbf{r})$  ( $U_{ee} = 0$ ) and the density is  $n(\mathbf{r})$ . The ground-state of that system is described by a wavefunction  $\varphi_s$  obtained as a Slater determinant of orbitals  $\psi_i$  which satisfy the equations:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \qquad (1.56)$$

while the electronic density is:

$$n(\mathbf{r}) = \sum_{i}^{occ} |\psi_i(\mathbf{r})|^2.$$
(1.57)

Applying the HK theorem to this non-interacting system, we conclude that there is at most one external potential,  $v_s$  (within a constant), that generates the density n. For a given density, all the properties of the system are determined and, in particular,  $T_s[n]$  and  $E_s[n]$  correspond to:

$$T_s[n] = \sum_{i}^{occ} -\frac{1}{2} \int \psi_i^*(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi_i(\mathbf{r}) d\mathbf{r}$$
(1.58)

$$E_{el,s}[n] = T_s[n] + \int v_s(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$
(1.59)

<sup>&</sup>lt;sup>6</sup>This result contrasts with Eq. (1.41), where  $E_{el}$  was obtained as a functional of the wavefunction  $\varphi$ .

The functional  $T_s[n]$  is the Kohn-Sham kinetic energy. It is also the HK functional F[n] for the case where  $U_{ee} = 0$ . It satisfies:

$$T_s[n] = \min_{\varphi \to n} \left\{ \langle \varphi | T_{e^-} | \varphi \rangle \right\}$$
(1.60)

The ground-state density of the previous system, constrained to be normalized to  $N_e$ , is also solution of the following Euler-Lagrange equations:

$$0 = \frac{\delta}{\delta n(\mathbf{r})} (E_s[n] - \mu_s [\int n(\mathbf{r}) d\mathbf{r} - N_e])$$
(1.61)

$$= \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) - \mu_s \tag{1.62}$$

Up to now for the non-interacting system.

Let us now go back to the real *interacting* system for which the energy functional writes:

$$E_{el,v}[n] = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n]$$
(1.63)

and let us define the exchange-correlation energy functional as:

$$E_{xc}[n] = F[n] - \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) n_{\varphi}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - T_s[n]$$
(1.64)

As  $T_s[n]$  is only defined for the ground-state densities of non-interacting systems, doing that we have implicitly assumed that for any ground state density, n, of an interacting system, there exists a non-interacting system with the same ground-state density n. Within this assumption, the Euler-Lagrange equation of the interacting system is given by:

$$0 = \frac{\delta}{\delta n(\mathbf{r})} (E_v[n] - \mu[\int n(\mathbf{r}) d\mathbf{r} - N])$$
(1.65)

$$= \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) - \mu \qquad (1.66)$$

where the exchange-correlation potential is defined as

$$v_{\rm xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})},\tag{1.67}$$

and the Hartree potential corresponds to:

$$v_{\rm H}(\mathbf{r}) = \int \frac{n_{\varphi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \qquad (1.68)$$

Comparing Eq. (1.62) to Eq. (1.66), we deduce that the non-interacting system will give the same density as the interacting one under the constraint that

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}).$$
(1.69)

Following the previous procedure, the real many-body electron problem has been mapped onto another independent-particle system, with the *same* exact ground state electronic density. In practice, this density can therefore be obtained from one-body wavefunctions solution of the following set of equations (Eq. 1.56-1.57-1.69) to be solved self-consistently:

$$\begin{bmatrix} -\frac{1}{2}\nabla^2 + v_s \end{bmatrix} |\psi_i\rangle = \epsilon_i |\psi_i\rangle$$
$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$
(1.70)
$$n(\mathbf{r}) = \sum_i^{occ} \psi_i^*(\mathbf{r}) \cdot \psi_i(\mathbf{r})$$

under conditions of orthonormalization of the one-body wavefunctions:

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

However, the ground-state electronic energy Eq. (1.55) is not equal to the sum of the fictitious independent particles eigenenergies that overcounts the effects of the electron-electron interactions. It can be deduced from the ground state self-consistent density as [147]:

$$E_{el} = \sum_{i}^{occ} \epsilon_{i} - \frac{1}{2} \int \frac{n(\mathbf{r}_{1}) n(\mathbf{r}_{2})}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} d\mathbf{r}_{1} d\mathbf{r}_{2} + E_{xc}[n] - \int \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} n(\mathbf{r}) d\mathbf{r}$$
(1.71)

We note that the form of the exchange-correlation potential to be used is unknown, as that of  $E_{\rm xc}[n]$ . In practical applications,  $E_{\rm xc}[n]$  must be approximated. In the next Chapter, we will describe some of the usual approximations, the most popular of them being the local density approximation (LDA).

#### 1.6.3 A Kohn-Sham variational formulation

Instead of solving the previous set of coupled one-body Schrödinger equations, the ground-state electronic energy can also be obtained from the variational principle. Making use of Eq. (1.55)-(1.58)-(1.64), the variational expression of the electronic energy may be written as a functional of *one-body wavefunctions*:

$$E_{el}[\psi_i] = \sum_{i}^{occ} \left\langle \psi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \right\rangle + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[n]$$
(1.72)

to be minimized under the following orthonormalization constraints :

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

It is interesting to establish the connection between the previous minimization procedure and the search of the solution of the Kohn-Sham (KS) equations. The Euler-Lagrange equation associated to the previous constrained minimization, can be written:

$$0 = \frac{\delta}{\delta \psi_i^*(\mathbf{r})} \left( T_s[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_H[n] + E_{\text{xc}}[n] - \sum_{i,j} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}) \right)$$
(1.73)

or equivalently:

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}\right)|\psi_i\rangle = \sum_j \Lambda_{ij}|\psi_j\rangle \qquad (1.74)$$

where  $v_{\rm H}$  and  $v_{\rm xc}$  are the potentials that were previously defined. Following this procedure, we recover something similar to the set of KS equations, that however have been mixed together. Such a freedom is inherent to the *set* of constraints related to any independent-electrons scheme <sup>7</sup>. It is associated to a "gauge freedom" much wider to than the one obtained by simply changing the phase of each KS orbital [96]. It corresponds to the fact that the electronic density and total energy are invariant under any unitary transform within the subspace of the occupied one-body wavefunctions.

In practice, we can fix the gauge [96] so that :

$$\Lambda_{ij} = \delta_{ij}\epsilon_i \tag{1.75}$$

in which case Eq. (1.74) takes the form of a KS equation and the  $\psi_i$  become identified with the KS orbitals. The KS eigenenergies are therefore obtained as the eigenvalues of the Euler-Lagrange parameter matrix,

$$\Lambda_{ij} = \langle \psi_i | H | \psi_j \rangle. \tag{1.76}$$

<sup>&</sup>lt;sup>7</sup>A similar freedom appears within the Hartree-Fock method

#### **1.6.4** The exchange-correlation energy

From the construction outlined in the previous Section, it appears that the exchange-correlation energy  $E_{xc}[n]$  of the Kohn-Sham formalism is not equivalent to that of the many-electron interacting system  $E_{xc}[\varphi_n]$  obtained from the exchange-correlation hole. The difference originates in a transfer of part of the many-body kinetic energy to the exchange-correlation term within the KS formalism. If  $\varphi_n$  is the electronic wavefunction of the interacting system of density n, and  $\varphi_s$  those of the associated non-interacting system minimizing the expectation value of  $H_s$ , it follows from the variational principle that

$$\langle \varphi_n | H_s | \varphi_n \rangle \geq \langle \varphi_s | H_s | \varphi_s \rangle$$
 (1.77)

$$\langle \varphi_n | T_e | \varphi_n \rangle + \int n(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \geq T_s[n] + \int n(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \quad (1.78)$$

so that

$$T_e[\varphi_n] \ge T_s[n] \tag{1.79}$$

In the context of the Kohn-Sham formalism, we can therefore define the exchange-correlation part of the kinetic energy as:

$$T_{xc}[n] = T_e[\varphi_n] - T_s[n] \ge 0 \tag{1.80}$$

and the Kohn-Sham exchange correlation energy takes the form:

$$E_{xc}[n] = T_{xc}[n] + \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) n_{\varphi}^{xc}(\mathbf{r}_2 | \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$
(1.81)

The additional kinetic contribution makes the exchange-correlation density functional even more complex than it was first a priori expected. An interesting exact relationship is however satisfied by  $E_{xc}[n]$ , known as the "adiabatic connection formula" [158, 105]. This result can be obtained as follows. Let us consider the following family of Hamiltonian with different electron-electron interaction governed by a single parameter  $\lambda$  varying from 0 to 1:

$$H_{el}(\lambda) = T_e + \lambda \ U_{ee} + v_\lambda \tag{1.82}$$

For  $\lambda = 1$ , we have the fully interacting system with  $v_{\lambda} = v_{\text{ext}}$  and the ground state density n. The electronic energy is:

$$E_{el}(1) = T_s[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_H[n] + E_{xc}[n]$$
(1.83)

For  $0 < \lambda < 1$ , we define  $v_{\lambda}$  in such a way that the density *n* remains unchanged. For  $\lambda = 0$ , we have  $v_{\lambda} = v_s$ , the Kohn-Sham potential associated to the density *n*. The energy is given by:

$$E_{el}(0) = T_s[n] + \int v_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$
(1.84)

From the two previous relations we deduce:

$$E_{el}(1) - E_{el}(0) = E_{H}[n] + E_{xc}[n] + \int [v_{\text{ext}}(\mathbf{r}) - v_{s}(\mathbf{r})]n(\mathbf{r})d\mathbf{r} \quad (1.85)$$

Independently, this difference can also be obtained as:

$$E_{el}(1) - E_{el}(0) = \int_0^1 \frac{dE_{el}(\lambda)}{d\lambda} d\lambda \qquad (1.86)$$

If we denote  $\varphi_{\lambda}$ , the ground state associated to the coupling constant  $\lambda$ , using the Hellmann-Feynmann theorem we obtain:

$$\frac{dE_{el}(\lambda)}{d\lambda} = \langle \varphi_{\lambda} | \frac{dH_{el}(\lambda)}{d\lambda} | \varphi_{\lambda} \rangle$$

$$= \langle \varphi_{\lambda} | U_{ee} | \varphi_{\lambda} \rangle + \frac{d}{d\lambda} \int v_{\lambda}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}.$$
(1.87)

Therefore:

$$\int_{0}^{1} \frac{dE_{el}(\lambda)}{d\lambda} d\lambda = \int_{0}^{1} \langle \varphi_{\lambda} | U_{ee} | \varphi_{\lambda} \rangle d\lambda + \int [v_{ext}(\mathbf{r}) - v_{s}(\mathbf{r})] n(\mathbf{r}) d\mathbf{r} = E_{H}[n] + \frac{1}{2} \int \frac{n(\mathbf{r}_{1}) \int_{0}^{1} n_{\varphi_{\lambda}}^{xc}(\mathbf{r}_{2} | \mathbf{r}_{1}) d\lambda}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} d\mathbf{r}_{1} d\mathbf{r}_{2} + \int [v_{ext}(\mathbf{r}) - v_{s}(\mathbf{r})] n(\mathbf{r}) d\mathbf{r}$$
(1.88)

Comparing Eq. (1.85) to Eq. (1.88), we finally deduce:

$$E_{xc}[n] = \frac{1}{2} \int \frac{n_{\varphi}(\mathbf{r}_1) \bar{n}^{xc}(\mathbf{r}_2 | \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \qquad (1.89)$$

where

$$\bar{n}^{xc}(r_2|r_1) = \int_0^1 n^{xc}_{\varphi_\lambda}(r_2|r_1) d\lambda$$
(1.90)



Figure 1.1: The Kohn-Sham exchange-correlation energy,  $E_{\rm xc}[n]$ , is obtained as the exchange-correlation energy of the truly interacting system,  $E_{\rm xc}[\varphi]$ , modified from a positive quantity equal to the transfer of kinetic energy  $(T_{xc}[n])$  all along the path of integration of the coupling constant  $\lambda$ .

This approach literally "connects" the non-interacting KS system to the fully interacting real system through a continuum of partly interacting systems (with interaction strength  $\lambda e^2$ ), which have all the same density. The exchange-correlation hole of DFT,  $\bar{n}_{\rm xc}$  is not the exchange-correlation hole at  $\lambda = 1$ , but is the average of the correlation function for  $\lambda$  ranging from 0 to 1. The integration over  $\lambda$  generates the kinetic part of  $E_{\rm xc}[n]$ .

Another insight on this result is provided in Fig. 1.1. In absence of correlation ( $\lambda = 0$ ), the only remaining electron interaction energy originates in the exchange effects. It is convenient to define the exchange energy of the system from Eq. (1.50) as within the Hartree-Fock method but on the basis of the Kohn-Sham wavefunctions [248]. The correlation energy appearing at  $\lambda = 1$  may be identified as the additional quantity with respect to the exchange contribution calculated at  $\lambda = 0$ . The Kohn-Sham exchange-correlation term  $E_{xc}[n]$  differs from the exchange-correlation energy at  $\lambda = 1$  (equal to  $E_{xc}[\varphi]$ ) from a positive quantity equal to  $T_{xc}[n]$ , and corresponding to the transfer of kinetic energy all along the path of

integration of the coupling constant  $\lambda$ .

# 1.7 The Green's function approach

Up to now, we have focused on the determination of the ground-state of the system. We should also be interested in its optical properties that involve the identification of excitation energies. In particular, the energy gap must be defined from the energies of the quasi-particles of the system.

Within many-body theory, it can be shown that the quasi-particle energies are solution of the following Dyson equation [130]:

$$\begin{bmatrix} -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) \end{bmatrix} \Psi_i(\mathbf{r}) + \int \Sigma_{xc}(\mathbf{r}, \mathbf{r}'; E_i) \Psi_i(\mathbf{r}') d\mathbf{r}' = E_i \Psi_i(\mathbf{r}) \qquad (1.91)$$

where the operator  $\Sigma_{xc}$  is called the exchange-correlation self-energy operator: it is linear, non-local, non-hermitian and energy-dependent. This is another reformulation of the many-body problem through one-body Schrödinger like equations. It is also an alternate approach giving access to the correct ground state electronic density. A good review on the basics of this method is proposed in Ref. [130].

The complexity of  $\Sigma_{xc}$  has been the main reason for the difficulty of firstprinciples calculations of quasi-particle energies. Nevertheless, some realistic calculations have been reported within the GW approximation [130]<sup>8</sup>. Some recent results obtained within this approximation have shown that the  $\Sigma_{xc}$  operators of various semiconductors have some common features and can be schematized through a relatively simple expression [83]. From this analysis, it was suggested that the non-locality of  $\Sigma_{xc}$  is essential in determining the quasi-particle energy gap, while the energy dependence more greatly alter the dispersion of the individual bands (see also Appendix D).

## 1.8 The DFT bandgap problem

### 1.8.1 Kohn-Sham eigenenergies

There is a formal resemblance of the Dyson equation giving the quasiparticle energies, to the Schrödinger equation for the effective one electron

<sup>&</sup>lt;sup>8</sup>This approximation is so called because it restricts to the first term of an expansion of  $\Sigma$  in terms of the screened Coulomb interaction W and the one-particle Green's function G.

eigenvalues of DFT. This has suggested that there might be a connection between the quasi-particle energies  $E_i$  and the eigenvalues  $\epsilon_i$  for the fictitious, non-interacting particles of the Kohn-Sham system.

It can be shown that the ionization energy of a system (the work function for a metal) is given correctly by the energy of the highest occupied Kohn-Sham orbital [2]. No further exact relationship is however known for the other KS eigenenergies.

In spite of any formal evidence, in practice [83], it is observed that the DFT and quasi-particles wavefunctions are nearly identical. Similarly, the valence energy bands are usually well reproduced within DFT. At the opposite, it is well known that the fundamental energy gap of semiconductors is usually much larger than its DFT estimate from the N-particle system.

### 1.8.2 Bandgap problem

Let us now investigate more carefully the origin of the bandgap problem [89] as it was explained by Sham and Schüter [257, 258] and Perdew and Levy [214]. The band structure in a semiconductor can be rigorously defined as the energies of one-particle excitations, which are in turn related to the difference between total energies of states differing by one electron. The fundamental bandgap is defined by:

$$E_g = \epsilon_c - \epsilon_v \tag{1.92}$$

where lowest conduction band and higher valence band are related to quasiparticle energies:

$$\epsilon_c = E_{N+1} - E_N$$
,  $\epsilon_v = E_N - E_{N-1}$  (1.93)

Making use of Janak's theorem [132], it can be shown that within DFT we must write [258]:

$$\epsilon_c = \epsilon_{N+1}(N+1) \quad , \quad \epsilon_v = \epsilon_N(N) \tag{1.94}$$

where  $\epsilon_M(P)$  is the M-eigenenergy of the P-electron system. The energy gap is therefore related to the Kohn-Sham eigenenergies as:

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N) \tag{1.95}$$

and may differ from the bandgap of the N-particle system:

€

$$_{g} = \epsilon_{N+1}(N) - \epsilon_{N}(N) \tag{1.96}$$

We write the deviation as:

$$E_g = \epsilon_g + \Delta_{xc} \tag{1.97}$$
The appearance of a gap  $\epsilon_g$  in the KS eigenenergy spectrum is related to the existence of a discontinuity in the kinetic energy functional derivative [258]. Similarly, the contribution  $\Delta_{xc}$  originates from a discontinuity in the exchange-correlation potential upon addition of an electron to the system [214, 257, 258]. Such a discontinuity may be large and is typically of the same order of magnitude than  $\epsilon_g$ . The inclusion of such a discontinuity is intrinsic to the optimized effective potential (OEP) method [69]. It is however not reproduced within the usual local implementation of the DFT (LDA, GGA). These approximations seems however to describe correctly  $\epsilon_g$  in comparison to what would be expected in exact DFT [82]. From the distinction between  $E_g$  and  $\epsilon_g$ , it was suggested that an insulator might be described as a metal in exact DFT [84]. This surprising feature will be rediscussed in Chapter 8.

#### **1.9 Conclusions**

In this Chapter, we gave a brief overview of the approximations required to identify the ground-state of a system of electrons and ions in interaction. Making use of the adiabatic approximation to separate the dynamics of the electrons from that of the ions, we focused on the many-body electron problem. We have shown that, as an alternative to the direct resolution of a Schrödinger equation, the quantum-mechanical ground-state can be conveniently determined from the minimization of a functional of the electronic energy. Different approaches have then been explored.

The electronic energy was first formulated as a functional of the manybody wavefunction (Eq. 1.41). As a second step, the Hohenberg-Kohn theorem allowed to reformulate the problem in terms of a more convenient density functional (Eq. 1.55). Finally, within the Kohn-Sham approach, the energy became accessible from a functional of one-body wavefunctions (Eq. 1.72) associated to non-interacting particles.

The Kohn-Sham formulation of the many-body problem is a very convenient approach, giving access to the correct ground-state electronic energy and electron density. It was however emphasized that the Kohn-Sham independent electrons are fictitious particles that cannot be formally connected to the quasi-particle of the system.

From now, we will focus on the Kohn-Sham formalism that will be used all along this work.

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40

## Chapter 2

## A periodic-DFT

#### 2.1 Introduction

Starting from the general results obtained in the previous Chapter, we are now investigating more carefully how the density functional formalism can be adapted for the case of periodic solids when considering functionals of the periodic part of the density. First, we will present some usual approximations of the exchange-correlation density functional. Then, we will pay a particular attention to the *technical* approximations that are currently introduced in practical calculations. We will describe how the electronic wavefunctions can be conveniently expanded from a finite plane-wave basis set, when making use of pseudopotentials. Our discussion will contain some specific informations concerning  $BaTiO_3$ . Finally, explicit expressions will be proposed for the different terms of the electronic energy functional.

The electronic problem being solved, we will show how the total *crystal energy* can be obtained as a sum of the electronic and ionic energies. Structural optimization will then naturally arise within the scope of our theory: it will basically consist in a minimization of the total energy in terms of the ionic degrees of freedom considered up to now as parameters. We will briefly describe how this structural optimization may be facilitated thanks to the Hellmann-Feynmann theorem.

Good reviews concerning the concepts presented in this Chapter are mentioned in the last Section.

41

#### 2.2 The local density approximation

The formalism of the density functional theory is a priori exact. However, as it was pointed out in the previous Chapter, the form of the universal exchange-correlation energy functional to be used is unknown and, in practice, it must be approximated. The estimate of  $E_{\rm xc}[n]$  is the only uncontrolled approximation introduced in practical calculations and is a source of systematic errors. In this Section, we present some common approximations: in particular, we describe the local density approximation that will be used all along this work.

From the Hohenberg and Kohn theorem [121], the exchange-correlation energy is expected to be a universal functional of the density *everywhere*. The local density approximation (LDA) [147] assumes (i) that the exchangecorrelation 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:

$$E_{xc}[n] = \int n(\mathbf{r}) \cdot \epsilon_{xc}^{LDA}(\mathbf{r}) d\mathbf{r}$$
(2.1)

with

$$\epsilon_{xc}^{LDA}(\mathbf{r}) = \epsilon_{xc}^{hom}[n(\mathbf{r})] \tag{2.2}$$

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. We have seen that it scales like (Eq. 1.51):

$$\epsilon_x^{hom}[n] = -\frac{3}{4\pi} (3\pi^2)^{1/3} n^{1/3}$$
(2.3)

For the *correlation* part, one may rely on accurate values obtained by Ceperley-Alder [29] from Monte-Carlo simulations of the energy of the homogeneous electron gas. In our study, we used a polynomial parametrization of the previous data as proposed by Teter [280]. Other approximations (Wigner, X-alpha, Gunnarson-Lundqvist...) 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 [136, 218]<sup>1</sup> : calculated bond lengths and bond angles

<sup>&</sup>lt;sup>1</sup>The LDA exchange-correlation hole intergates to -1. This simple feature should be a first intuitive argument to explain its success.

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 **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 [50, 140]:

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r}) \cdot \epsilon_{xc}^{GGA}[n(\mathbf{r}); |\nabla n(\mathbf{r})|; \nabla^2 n(\mathbf{r})] dr$$
(2.4)

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 result [51, 87]. Finally, the correction has a rather limited effect on the dielectric constant [51]. The GGA remains a quasi-local approximation that cannot include any long-range density dependency of  $E_{\rm xc}[n]$ . We will see in Chapter 8 that this should explain why it cannot significantly improve the description of the dielectric susceptibility [74].

Different other functionals also exist like the average density approximation (ADA) [106] or the weighted density approximation (WDA) [106]. It was recently argued that WDA should be intrinsically unable to improve LDA results [31]. For ABO<sub>3</sub> compounds, it seems however that this last technique is an interesting alternative to the LDA (see Chapter 4) [269].

Without being exhaustive, let us finally mention that another interesting scheme consists in a mixing of Hartree-Fock and and local density functionals justified from the adiabatic connection formula [13].

#### 2.3 The periodic solid

#### 2.3.1 Periodic boundary conditions

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

$$\mathbf{R}_{a,\kappa} = \mathbf{R}_a + \tau_\kappa \tag{2.5}$$

where  $\mathbf{R}_a$  is a lattice vector and  $\tau_{\kappa}$  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 [4]. The approximation seems reasonable and was widely used because it presents numerous conceptual and practical advantages. In the context of this Chapter, 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.

However, for such infinite solid, the surface (and the associated surface charge) has artificially disappeared. We will see later that, within the particular context of Kohn-Sham calculations, imposing periodic boundary conditions is not necessarily equivalent to considering a finite solid of increasing size (Chapter 8).

In this Chapter we describe the results obtained within a "periodic-DFT". It will be argued later that it constitutes a *coherent* procedure within the LDA (or even within other semi-local approximations like the GGA's) that remains a standard for DFT calculations.

#### 2.3.2 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 plane-wave by a cell periodic function:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$
(2.6)

where N is the number of unit cells repeated in the Born-von Karman periodic box, and  $\Omega_0$  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  $u_{n\mathbf{k}}$ :

$$\langle u_{m\mathbf{k}} | u_{n\mathbf{k}} \rangle = \delta_{mn} \tag{2.7}$$

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

$$\langle f|g\rangle = \frac{1}{\Omega_0} \int_{\Omega_0} f^*(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}.$$
 (2.8)

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 [4] so that, in practice, the only  $\mathbf{k}$ -vectors to be considered are those which are within the Brillouin zone (BZ). From our conventions, the electronic density reads in terms of the periodic functions :

$$n(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_{BZ} \sum_{m}^{occ} s \ u_{m\mathbf{k}}^*(\mathbf{r}) \ u_{m\mathbf{k}}(\mathbf{r}) \ d\mathbf{k}.$$
 (2.9)

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

#### 2.3.3 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 [30, 63, 197] 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. In our calculations we made use of the technique developed by Monkhorst and Pack [197, 198]. As it is discussed in Appendix A, our study of BaTiO<sub>3</sub> 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.

#### 2.4 A plane-wave pseudopotential approach

#### 2.4.1 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:

$$u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) \tag{2.10}$$

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:

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i \mathbf{G} \cdot \mathbf{r}}$$
(2.11)

$$u_{n\mathbf{k}}(\mathbf{G}) = \frac{1}{\Omega_0} \int_{\Omega_0} u_{n\mathbf{k}}(\mathbf{r}) \ e^{-i \ \mathbf{G} \cdot \mathbf{r}} \ d^3\mathbf{r}$$
(2.12)

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

$$\psi_{n\mathbf{k}}(\mathbf{r}) = (N\Omega_0)^{-1/2} \sum_{\mathbf{G}} u_{n\mathbf{k}}(\mathbf{G}) e^{i (\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$$
(2.13)

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. Also, it will be particularly suitable for the calculation of the response to external perturbations (Chapter 4). 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" [67, 247].

#### 2.4.2 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 firstproblem 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:

$$n(\mathbf{r}) = n_c^{atom}(\mathbf{r}) + n_v(\mathbf{r}) \tag{2.14}$$

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. 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 BaTiO<sub>3</sub>, 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 (see Appendix A).

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 [218]. Their construction is submitted to a series of constraints that ensure their transferability from one chemical environment to another: norm conservation [7, 107], extended norm conservation [263], chemical hardness conservation [65, 279]. 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 [90, 145]. 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 [236, 282]. A good overview of the pseudopotential concept may be found in the review of Pickett [218]. A summary of the most recent trends is reported in Ref. [32].

In our calculations on  $BaTiO_3$ , we adopted extended norm-conserving, highly transferable pseudopotential, as proposed by M. Teter [279, 280]. For the oxygen, in order to increase the transferability, we included a chemical hardness correction [279]. More information concerning these pseudopotentials can be found in Appendix A.

Within the pseudopotential approach, the external potential appearing in the DFT consists in the pseudopotentials from all atoms inside each repeated cell with lattice vector  $\mathbf{R}_a$ :

$$v_{\text{ext}}(\mathbf{r}, \mathbf{r}') = \sum_{a\kappa} v_{\kappa} \left( \mathbf{r} - \boldsymbol{\tau}_{\kappa} - \mathbf{R}_{a}, \mathbf{r}' - \boldsymbol{\tau}_{\kappa} - \mathbf{R}_{a} \right)$$
(2.15)

Each atom contribution is made of a local and a non-local contribution:

$$v_{\kappa}(\mathbf{r}, \mathbf{r}') = v_{\kappa}^{\text{loc}}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + v_{\kappa}^{\text{sep}}(\mathbf{r}, \mathbf{r}').$$
(2.16)

The local part is long-range, with asymptotic behavior  $-Z_{\kappa}/r$ , where  $Z_{\kappa}$  is the charge of the (pseudo)ion. Usually, the non-local part is of a separable

type [145]:

$$v_{\kappa}^{\text{sep}}(\mathbf{r},\mathbf{r}') = \sum_{\mu} e_{\mu\kappa} \zeta_{\mu\kappa}(\mathbf{r}) \zeta_{\mu\kappa}^{*}(\mathbf{r}')$$
(2.17)

where only a few separable terms, labeled by  $\mu$ , are present. The functions  $\zeta_{\mu\kappa}$  are short-range, and should not overlap for adjacent atoms.

A major contribution to transferability in pseudopotentials came from Louie, Froyen and Cohen [175], who realized that the deletion of the electron density of the core states removed by the pseudopotential construction results in a non-linear error in the exchange-correlation potential in the LDA. By restoring the core density  $n_{core}$ , they were able to show that atoms would respond correctly over a wider range of conditions (core correction). The pseudo-core density from each atom can be build at the same time as the pseudopotential. The total core density is made of non-overlapping contributions from each atom:

$$n_{c}(\mathbf{r}) = \sum_{a\kappa} n_{c,\kappa} \left( \mathbf{r} - \boldsymbol{\tau}_{\kappa} - \mathbf{R}_{a} \right).$$
(2.18)

This contribution is known, as soon as the ionic positions have been assigned.

#### 2.5 Total crystal energy

The total energy of a crystal is defined as the energy difference between the condensed system and a system where all the electrons and ions constituents are separated by infinite distances. Within the Born-Oppenheimer approximation, this energy corresponds to  $E_{e+i}(\mathbf{R})$ . This crystal energy can be dissociated into two terms:

$$E_{e+i}(\mathbf{R}) = E_{el}(\mathbf{R}) + E_{ii}(\mathbf{R}) \tag{2.19}$$

The first term, associated to  $H_e$ , involves the electrons placed in the potential of the ions  $(E_{el} = T_e + E_{ee} + E_{ie})$ . The second is due to the ion-ion interaction  $(E_{ii})$ , and is fully determined when the atomic positions are fixed. We can now investigate the more explicit form of these two terms for a periodic solid, when the many-body electron problem is treated within the density functional formalism, a plane-wave pseudopotential approach and the local density approximation.

#### 2.5.1 The macroscopic limit

In Section 2.3, we have introduced the notion of infinite periodic solid obtained by imposing Born-von Karman periodic boundary conditions. As highlighted by Makov and Payne [182], we must however be careful when switching from finite to infinite solid. In particular, we must be sure of the convergence of the electrostatic energy, obtained by summing contributions from the different unit cells. Two cases of convergent sums are possible. (i) The sum is *absolutely* convergent, in which case the potential energy will have converged for large systems and extending the sum to infinity will not affect the result. In this case, the surface terms make a negligible contribution. (ii) The sum is only *conditionally* convergent and depends on the order of summation. By that they mean that the surface charge has a non-negligible contribution that must be taken into account to obtain a convergent result.

From the expression of the electrostatic energy, only zero- and firstmoment of a multipole expansion of the charge may give a sizable contribution to the energy at large distance. Consequently, the electrostatic energy will be absolutely convergent only if the lowest non-zero multipole is a quadrupole.

The zero-order term corresponds to a charge and would produce a divergence. However, it is zero in a *charge neutral system*. The first moment corresponds to the dipolar terms and is never present for Bravais lattices with inversion symmetry. For polar solids however, Makov and Payne [182] have shown that, due to this term, the electrostatic energy is only conditionally convergent: it remains undetermined until the surface contribution has been explicitly defined. In practice this requires to impose an additional boundary condition. Calculations can be performed under the condition of *zero macroscopic electric field*, in which case it can be shown that there will be no contribution from the surface <sup>2</sup>. Strictly speaking, the energy considered in that case is an electric enthalpy.

In the framework of this Chapter, the surface contributions are induced by the  $\mathbf{G} = 0$  terms and the previous convergence problem is associated to the  $\mathbf{G} = 0$  divergence of  $E_{ee}$ ,  $E_{ie}$  and  $E_{ii}$ . For a neutral system under the condition of zero macroscopic electric field, there is no surface contribution to be included (i.e. the different divergences must cancel out) so that , in practice, the  $\mathbf{G} = 0$  contributions can be omitted in each of these three terms <sup>3</sup>.

We note that, when considering pseudopotential, the Coulombic behaviour of the ionic potential has been modified and a residual charge contribution appears. As such a component is constant in real space, it is of no importance for the generation of the wavefunctions and the density (only the mean of the potential is affected) and it is usually included in the

<sup>&</sup>lt;sup>2</sup>This will appear more clearly in the framework of Chapter 4.

 $<sup>^{3}</sup>A$  "prime" will be typically added to quantities from which the  $\mathbf{G=0}$  term has been removed.

ion-ion term.

#### 2.5.2 The electronic energy

In terms of our periodic Bloch functions, the KS equations associated to the valence electrons, placed in pseudopotential associated to the ions and core electrons may be written in compact form, as:

$$H_{\mathbf{k},\mathbf{k}}|u_{m,\mathbf{k}}\rangle = \epsilon_{m,\mathbf{k}} |u_{m,\mathbf{k}}\rangle. \qquad (2.20)$$

where

$$H_{\mathbf{k},\mathbf{k}} = T_{\mathbf{k},\mathbf{k}} + v_{\text{ext},\mathbf{k},\mathbf{k}} + v_{\text{H}} + v_{\text{xc}}^{LDA}.$$
 (2.21)

The associated variational expression of the electronic energy is:

$$E_{\rm el}[u] = \frac{\Omega_0}{(2\pi)^3} \int_{\rm BZ} \sum_m^{\rm occ} s \langle u_{m\mathbf{k}} | T_{\mathbf{k},\mathbf{k}} + v_{\rm ext,\mathbf{k},\mathbf{k}} | u_{m\mathbf{k}} \rangle d\mathbf{k} + E_{\rm H}[u] + E_{\rm xc}^{LDA}[u].$$
(2.22)

Because of their different mathematical formulation, the different terms of the previous equation may be more conveniently treated either in real or in reciprocal space, while transformations of the wavefunctions from one space to the other are carried out by means of fast Fourier transforms. Let us now go through a brief description the different terms. The valence charge density is obtained from Eq. (2.9).

**The kinetic energy** is computed in reciprocal space where its operator is diagonal:

$$T_{\mathbf{k},\mathbf{k}}(\mathbf{G},\mathbf{G}') = \frac{(\mathbf{k}+\mathbf{G})^2}{2} \,\delta_{\mathbf{G}\mathbf{G}'} \tag{2.23}$$

The external potential is a non-local operator within our pseudopotential approach and has been separated into local and non-local parts. The Coulomb divergence associated to the local term must be removed by subtracting the G=0 contribution. The local potential in real space is obtained from the following Fourier components:

$$v'_{\rm loc}(\mathbf{G}) = \begin{cases} \frac{1}{\Omega_0} \sum_{\kappa} e^{-i\mathbf{G}\cdot\boldsymbol{\tau}_{\kappa}} v^{loc}_{\kappa}(\mathbf{G}) & \text{when } \mathbf{G} \neq 0\\ 0 & \text{when } \mathbf{G} = 0 \end{cases}$$
(2.24)

This operator is naturally applied in real space since it is diagonal in that representation. The separable part keeps the same form as in the previous Section. A separable potential could be treated efficiently either in real space or in reciprocal space. In our case, it is treated in reciprocal space so that finally:

$$E_{ie}[u] = \frac{\Omega_{0}}{(2\pi)^{3}} \int_{BZ} \sum_{m}^{occ} s \langle u_{m\mathbf{k}} | v_{sep,\mathbf{k},\mathbf{k}} | u_{m\mathbf{k}} \rangle d\mathbf{k} + \int_{\Omega_{0}} n(\mathbf{r}) v_{loc}^{'}(\mathbf{r}) d\mathbf{r}$$
(2.25)

The Hartree potential is conveniently defined in reciprocal space. Subtracting, the  $\mathbf{G} = 0$  divergence,

$$v'_{\mathbf{H}}(\mathbf{G}) = \begin{cases} 4\pi \frac{n(\mathbf{G})}{|\mathbf{G}|^2} & \text{when} \mathbf{G} \neq 0\\ 0 & \text{when} \mathbf{G} = 0 \end{cases}$$
(2.26)

The Hartree energy can be written as:

$$E'_{\rm H}[u] = 2\pi\Omega_0 \sum_{\mathbf{G}\neq 0} \frac{|n(\mathbf{G})|^2}{|\mathbf{G}|^2}$$
 (2.27)

The exchange correlation energy is obtained, within the LDA, as an integral of the density  $n(\mathbf{r})$  times the mean exchange-correlation energy per particle  $\epsilon_{xc}^{LDA}(\mathbf{r})$  of the homogeneous electron gas of density  $n(\mathbf{r})$ . However, when combined with pseudopotentials, this simple definition has to be modified, in order to take into account that only valence states are used to build the density : the contribution of the core electrons  $(n_c)$  should be included, because of the non-linear character of the exchange-correlation energy functional [175]. The functional then reads

$$E_{\rm xc}[u] = \int_{\Omega_0} \left( n(\mathbf{r}) + n_c(\mathbf{r}) \right) \cdot \epsilon_{\rm xc}^{LDA}[n(\mathbf{r}) + n_c(\mathbf{r})] \, d\mathbf{r} \qquad (2.28)$$

where the pseudocore density  $n_c$  is made of non-overlapping contributions, built at the same time as the pseudopotential (Eq. 2.18).

To summarize, the global Hamiltonian for the electrons has been recast as:

$$H_{\mathbf{k},\mathbf{k}} = T_{\mathbf{k},\mathbf{k}} + \left(v_{\text{sep},\mathbf{k},\mathbf{k}} + v'_{\text{loc}}\right) + v'_{\text{H}} + v_{\text{xc}}$$
(2.29)

and the associated total electronic energy functional can be written as:

$$E_{\rm el}[u] = \frac{\Omega_0}{(2\pi)^3} \int_{\rm BZ} \sum_m^{\rm occ} s \langle u_{m\mathbf{k}} | T_{\mathbf{k},\mathbf{k}} + v_{\rm sep,\mathbf{k},\mathbf{k}} | u_{m\mathbf{k}} \rangle d\mathbf{k}$$

$$+ \int_{\Omega_0} n(\mathbf{r}) v'_{\text{loc}}(\mathbf{r}) d\mathbf{r} + 2\pi \Omega_0 \sum_{\mathbf{G} \neq 0} \frac{|n(\mathbf{G})|^2}{|\mathbf{G}|^2} + \int_{\Omega_0} \left( n(\mathbf{r}) + n_c(\mathbf{r}) \right) \cdot \epsilon_{\text{xc}}^{LDA} [n(\mathbf{r}) + n_c(\mathbf{r})] d\mathbf{r}. \quad (2.30)$$

In practical calculations, the integrations over the BZ are replaced by sums on a mesh of special **k**-points, and the periodic functions  $\{u\}$  are expanded in a sum of plane-waves that have a kinetic energy smaller than a given cutoff.

The ground-state electronic energy is obtained by minimizing the previous energy functional with respect to the  $\{u\}$  degrees of freedom under the orthonormalization condition given by Eq. (2.7). The valence density is computed from Eq. (2.9).

Different computational techniques are available to perform such a minimization. In our calculations, the minimization was performed thanks to a band by band preconditioned conjugate gradient algorithm as described in Ref. [212, 278].

#### 2.5.3 The ion-ion energy

In our system where the position of the ions are considered as fixed parameters, the ion-ion energy reduces to a well defined quantity. Within our pseudopotential approach, the ion-ion energy may be separated into two terms:

$$E_{ii}(\mathbf{R}) = E_{Ew}(\mathbf{R}) + E_{Res}. \qquad (2.31)$$

 $E_{Ew}$  is the bare Coulomb ion-ion electrostatics energy as recast when using Ewald summation technique, and from which the **G=0** term has been removed from the reciprocal space summation:

$$E_{\rm Ew}(\mathbf{R}) = \frac{1}{2} \sum_{\kappa\kappa'} Z_{\kappa} Z_{\kappa}' \left( \sum_{\mathbf{G}\neq\mathbf{0}} \frac{4\pi}{\Omega_0 G^2} e^{i\mathbf{G}\cdot(\boldsymbol{\tau}_{\kappa}-\boldsymbol{\tau}_{\kappa'})} \exp(-\frac{G^2}{4\Lambda^2}) - \sum_{a} \Lambda e^{i\mathbf{q}\cdot\mathbf{R}_a} H(\Lambda d_{a,\kappa\kappa'}) - \frac{2}{\sqrt{\pi}} \Lambda \delta_{\kappa\kappa'} - \frac{\pi}{\Omega_0 \Lambda^2} \right)$$
(2.32)

 $E_{Res}$  comes from the non-cancellation of the different Coulomb terms at  $\mathbf{G} = \mathbf{0}$  when using pseudopotentials:

$$E_{\text{Res}} = \frac{1}{2} \sum_{\kappa \kappa'} \frac{Z_{\kappa} C_{\kappa'}}{\Omega_0}$$
(2.33)

where  $C_{\kappa}$  describes the deviation from the purely Coulombic behaviour of the local part of the pseudopotential of atom  $\kappa$ :

$$C_{\kappa} = \int \left( v_{\kappa}^{\text{loc}}(\mathbf{r}) + \frac{Z_{\kappa}}{r} \right) \, d\mathbf{r} \tag{2.34}$$

#### 2.5.4 Crystal energy

The previous results may finally be synthesized as follows. The Born-Oppenheimer total energy of a neutral crystal, under the condition of zero macroscopic electric field is calculated as:

$$E_{e+i}(\mathbf{R}) = \min_{u} E_{el}(\mathbf{R}, [u]) + E_{Ew}(\mathbf{R}) + E_{Res}.$$
(2.35)

The electronic energy is implicitly dependent on the atomic positions that are reintroduced in the notations. It is determined through a minimization procedure within our DFT approach (Eq. 2.30). The electrostatic energy of the ions is obtained from Ewald summation technique (Eq. 2.32). The pseudopotentials require the inclusion of a constant residual electrostatic energy contribution (Eq. 2.33).

#### 2.6 Structural optimization

In the previous Section, we have obtained an explicit expression for the crystal energy in terms of the atomic positions considered as parameters. Such a result therefore opens the door to structural optimizations by searching the energy minimum within the parameter space of the atomic positions  $(3 \times N_{at}$  degrees of freedom). In periodic solids, the problem can be recast into the determination of the unit cell lattice parameters and of the atomic positions within this basic unit cell.

Interestingly, the Hellmann-Feynman theorem [64, 115] (see Chapter 4) teaches us that not only the total crystal energy, but also its first-order derivatives with respect to atomic displacements are directly accessible from the ground-state wavefunctions. Calculation of these energy derivatives will be of appreciable help to perform efficient structural optimizations. In periodic solids, such derivatives are indeed associated to well known physical quantities. The force on atom  $\kappa$  in direction  $\alpha$  is related to the first-oder change of the total energy with respect displacement of atom  $\kappa$  in direction  $\alpha$ :

$$F_{\kappa\alpha} = \frac{dE_{e+i}}{d\tau_{\kappa\alpha}} \tag{2.36}$$

Similarly, the stress tensor  $\sigma_{\alpha\beta}$  is related to the first-order derivative of the crystal energy with respect to a macroscopic strain  $\varepsilon_{\alpha\beta}$ :

$$\sigma_{\alpha\beta} = \frac{dE_{e+i}}{d\varepsilon_{\alpha\beta}} \tag{2.37}$$

The forces are accurately described within our plane-wave approach. The stress tensor however always requires an additional Pulay correction [247] in order to compensate for the incompleteness of the finite basis set.

In practice, efficient structural optimizations are performed from a finite number of ground-state calculations for different atomic configurations expected to be close to the optimal configuration. The ground-state ionic positions are determined from the energy minimum reached thanks to the informations on crystal energy, stresses and atomic forces obtained at each calculation.

#### 2.7 Conclusions

In this Chapter, we have detailed a practical method for total energy calculations based on the density functional formalism. This method was taking advantage of the translational symmetry of periodic solids. It also required some technical approximations. Equations were obtained in the framework of a plane-wave pseudopotential approach and within the local density approximation.

Since a few years, this kind of techniques is currently applied, in complement to experiments, to investigate the ground-state properties of different class of materials. In most cases, it yields very accurate results. However, it does also require substantial amounts of computational time.

The equations developed in this Chapter will now be used to investigate the ground-state properties of barium titanate. In particular, it will be checked if, in spite of the approximations that have been introduced, DFT-LDA calculations have sufficient accuracy to describe correctly the essential features of the BaTiO<sub>3</sub> total energy surface.

#### 2.8 References

In addition to references explicitly mentioned in the text, this Chapter was essentially drawn from the following reviews:

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- Gonze X., First-principles responses of solids to atomic displacements and atomic electric fields: implementation of a conjugate gradient algorithm, Phys. Rev. B 55, 10337 (1997).

## Chapter 3

# Ground-state properties of $BaTiO_3$

#### 3.1 Introduction

Barium titanate crystallizes in two distinct polymorphic forms. One is the well known and most extensively investigated perovskite structure. The other is a hexagonal phase first observed by Megaw [193, 288] in 1946<sup>1</sup>. Each polymorph undergoes its own sequence of phase transition. Both of them are ferroelectric [307], but exhibit different ferroelectric properties. All along this work, we will be only concerned with the perovskite structure.

The perovskite form is stable at high temperature in a simple cubic lattice containing five atoms per unit cell. This cubic phase is paraelectric and is the reference *prototype*<sup>2</sup> structure. Its space group symmetry is Pm3m. The experimental lattice parameter  $a_o$  is equal to 4.00 Å.

As the temperature is lowered,  $BaTiO_3$  undergoes a sequence of three ferroelectric phase transitions (see Fig. 3.1). Around 130°C, it transforms from cubic to tetragonal structure (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  $-90^{\circ}$ 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

 $<sup>^1\</sup>mathrm{The}$  hexagonal structure of  $\mathrm{BaTiO}_3$  was then characterized by Burbank and Evans [21].

<sup>&</sup>lt;sup>2</sup>This name is usually given to the highest symmetry phase, in terms of which the ferroelectric phase(s) can be described by small perturbational structural changes.



Figure 3.1: The four phases of  $BaTiO_3$ . In the cubic phase, the Ba atom is located at the corner of the cell, the Ti atom at the center and the O atoms in the middle of the faces.

along the <100>, <110> and <111> directions.

In this Chapter, we report results concerning the *ab initio* structural optimization of the four phases. We also describe the electronic properties of the cubic and rhombohedral structures. We finally reintroduce the problematics of the ferroelectric instability in the context of first-principles calculations. Technical details concerning the calculations are reported in Appendix A.

#### 3.2 Structural optimization

The structural optimization is easily performed within the density functional formalism presented in the previous Chapter. It 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).



Figure 3.2: Determination of the optimized lattice constant of cubic BaTiO<sub>3</sub>.

#### 3.2.1 Cubic phase

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

The only degree of freedom that must be relaxed is therefore the lattice parameter  $a_o$ . Its equilibrium value can be determined *ab initio* 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 zero. Within a plane-wave approach, such calculations require an additional "Pulay correction" [247].

The results of our calculation are presented in Fig. 3.2. 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. [41],  $a_o=3.95$  Å from Ref. [141]). It only slightly underestimates the experimental lattice constant of 4.00 Å. We note that a better agreement was recently reported within a "weighted density approximation" (WDA) [269, 270]. The Bulk modulus, deduced from the curvature of the energy curve around the minimum, is estimated to 197 GPa.

For this cubic phase, we also calculated the cohesive energy 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 estimate  $E_{\rm coh}$  to -38.23 eV/cell. A previous value equal to -31.16 eV/cell was reported by Weyrich and Siems [296, 298], in better agreement with the experimental value of -31.57 eV/cell. In their calculation, 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. The value that we report is only indicative. An accurate prediction of the cohesive energy usually requires to go beyond the LDA.

#### 3.2.2 Ferroelectric phases

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

A full structural optimization would require to relax together all the different degrees of freedom. However, as it was pointed out by many authors [41, 43, 141, 224], the ferroelectric instability of ABO<sub>3</sub> compounds is strongly sensitive to the volume. In this context, the volume underestimation of the LDA, even if small, appears problematic<sup>3</sup>. It was observed that the correct simulation of different properties of ABO<sub>3</sub> compounds (like the phase transition temperature [314]) requires to work at the experimental lattice constants. As they are accurately obtained from X-ray diffraction data [153], we chose to keep the experimental lattice parameters, without optimization. The results obtained by Singh [269, 270] suggest that the use of a WDA should be a promising way to eliminate these experimental parameters from the calculation in the future.

Contrary to the lattice parameters, all the atomic positions have been relaxed together until the residual forces on the atoms are smaller than  $10^{-5}$ 

<sup>&</sup>lt;sup>3</sup>We attempted a full relaxation of the rhombohedral structure. However, in the optimized structure that we obtained, the ferroelectric instability had quasi completely disappeared: the associated microscopic strains became anomalously small.

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 3.1: Atomic positions (in reduced coordinates) in the three ferroelectric phase of  $BaTiO_3$ .

Hartree/Bohr. Similar theoretical optimization of atomic positions were reported previously for the tetragonal and rhombohedral symmetry [141], 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 calculation have been performed on a  $6 \times 6 \times 6$  mesh of special k-points, that was verified by different authors to be sufficiently accurate [141, 292].

The atomic positions in reduced coordinates are reported for the different phases in Table 3.1. 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  $(O_2 \text{ and } O_3)$  and orthorhombic  $(O_1 \text{ and } O_2)$  structures. In the rhombohedral phase, all the oxygen are equivalent, as in the cubic phase. Results of the optimization are reported in Table 3.2, Table 3.3, and Table 3.4.

In the orthorhombic structure (Table 3.3) our atomic positions com-

<i>a</i> <sub>0</sub>	$c_0$	$\Delta_{T-Ti}$	$\Delta_{T-O1}$	$\Delta_{T-O2}$	Reference
3.994	4.036	0.0143	-0.0307	-0.0186	$\mathbf{Present}$
4.00	4.00	0.0129	-0.0248	-0.0157	$\mathbf{Present}$
4.00	4.00	0.0138	-0.0253	-0.0143	Ref. [141]
3.986	4.026	0.015	-0.023	-0.014	Ref. [260]
-	-	0.014	-0.0249	-0.0156	Ref. [68]
-	-	0.0135	-0.0250	-0.0150	Ref. [108]
-	-	0.0135	-0.0243	-0.0153	Ref. [117]
3.994	4.036	0.0215	-0.0233	-0.0100	Ref. [153]

Table 3.2: Lattice parameters (Å) and atomic displacements (see Table 3.1) in the tetragonal phase of BaTiO<sub>3</sub>.

Table 3.3: Lattice parameters  $(\mathring{A})$  and atomic displacements (see Table 3.1) in the orthorhombic phase of BaTiO<sub>3</sub>.

	$\mathbf{Present}$	Ref. [153]	Ref. [153]	Ref. [260]
$a_0$	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
$\Delta_{O-Ti}$	0.0127	0.0079	0.0143	0.010
$\Delta_{O-O1}$	-0.0230	-0.0233	0.0228	-0.016
$\Delta_{O-O2}$	-0.0162	-0.0146	0.0106	-0.010
$\Delta_{O-O3}$	-0.0144	-0.0145	-0.0110	-0.010

$a_0$	$\alpha$	$\Delta_{R-Ti}$	$\Delta_{R-O1}$	$\Delta_{R-O2}$	Reference
4.001	89.87°	-0.011	0.0133	0.0192	$\mathbf{Present}$
4.00	90.00°	-0.011	0.0129	0.0191	$\mathbf{Present}$
4.00	90.00°	-0.012	0.0105	0.0195	Ref. [141]
4.001	89.87°	-0.013	0.011	0.018	Ref. [117]
4.004	$89.87^{\circ}$	-0.011	0.011	0.018	Ref. [259]
4.003	$89.84^{\circ}$	-0.013	0.011	0.019	Ref. [153]

Table 3.4: Lattice parameters (Å) and atomic displacements (see Table 3.1) in the rhombohedral phase of BaTiO<sub>3</sub>.

pare well with the experiment. We probably slightly overestimate the Ti atom shift. However, there is a large dispersion on the experimental Ti displacements, reported by Kwei et al. [153], so that part of the observed discrepancy should come from the experiment.

For the rhombohedral phase (Table 3.4), our results are close to those of King-Smith and Vanderbilt [141]. The difference observed for  $\Delta_{R-O1}$ should be due to the better accuracy reached in our calculation <sup>4</sup>. 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 3.2), we observe that the elongation of the c axis favors a larger displacement of Ti and O. This result confirms the important role of the macroscopic strain in the stabilization of the tetragonal structure [43, 44]. Keeping the lattice parameters of the cubic phase, our displacements are in good agreement with those deduced by King-Smith et Vanderbilt as well as with experimental data. Unfortunately, considering the experimental tetragonal unit cell, we overestimate the atomic displacements of Ti and O. 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 relatively covalent bond.

Globally the results presented here are in satisfactory agreement with the experiment [117, 153]. In particular, they are sufficiently accurate to

<sup>&</sup>lt;sup>4</sup>Contrary 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.

pursue further investigations. However, it must be noted that a better precision is usually achieved in other materials. The relative inaccuracy originates in the fact that the potential well in which the atoms move is very flat in BaTiO<sub>3</sub>. In this context, it was observed that the exchangecorrelation part constitutes the major contribution to the lowering of the total energy in the ferroelectric phases. It is therefore not surprising that our result is more strongly sensitive than in other compounds to the approximate description of this term within the LDA. The problem is briefly discussed in Appendix A.3.

#### **3.3** Electronic properties

The Kohn-Sham electronic band structures can be easily computed for the different phases. Their analysis reveals some interesting features of  $BaTiO_3$  that will have some relevance to the understanding of the different results presented in the next Chapters. We pause therefore to investigate them in some details.

We show in Fig. 3.3 the electronic energy band structure of the cubic phase. Its form corresponds to that expected for a rather ionic material. The band structure 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 as a marked dominant character and is commonly 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 [124]. The results presented in Table 3.5 show a good agreement with the experimental findings, despite a systematic underestimation of the energy separation from the valence edge as a well-known consequence of the LDA.

In spite of its main ionic character,  $BaTiO_3$  has also some covalent features. We will see later that this *mixed* ionic-covalent character is at the origin of some of its interesting properties.

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. In terms of band theory, this 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 ABO<sub>3</sub> compounds [137, 190]. It was often considered as an essential feature to explain the ferroelectricity in these materials [196]. It was confirmed by recent experiments [124] and was also clearly illustrated from DFT by the







Figure 3.3: (a) Brillouin zone of cubic  $BaTiO_3$ . (b) Kohn-Sham electronic band structure of cubic  $BaTiO_3$  along different high symmetry lines of the Brillouin zone.

Band	Ref. [124]	Cubic		Ron	Rombohedral	
Ti 3d		R	4.23	R	4.49	
			2.98		3.39	
		Γ	1.72	Γ	2.29	
O 2p	0	R	0	R	0	
			-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	$\mathbf{R}$	-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	
		Г	-24.73	$\Gamma$	-24.72	
Ti 3p		Μ	-32.47	Г	-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 3.5: Top, center and bottom values (eV) of the different electronic bands of cubic and rhombohedral  $BaTiO_3$ .

analysis of partial density of states (DOS) [296, 43, 44].

Less spectacular, and sometimes controversial, is the hybridization between Ba 5p and O 2p orbitals. In simple models, Ba is indeed usually considered as a perfect ion in BaTiO<sub>3</sub>. The interaction of Ba with other atoms was however detected in LCAO calculations [216], and even in DFT from partial DOS [296, 43]. It was discussed by Pertosa and Michel-Calendini [216] who have shown that it has only small consequences on the band structure. However, it might have a more important influence on other properties. For instance, it was suggested that its presence should enhance the Ti-O interaction [205]. In Chapter 5, it will be invoked to explain the origin of some non-negligible contributions to the Born effective charges. This further study will even reveal some additional small hybridizations at the level of O 2s and Ba 5s semi-core states.

The computed bandgap is indirect  $(R \rightarrow \Gamma)$  and equal to 1.72 eV. The direct gap at  $\Gamma$  is of 1.84 eV. However, these values cannot be compared to the experiment due to the well-known DFT bandgap misfit <sup>5</sup>.

Due to a different reason, the identification of the experimental value of the bandgap was also for long under discussion. In ABO<sub>3</sub> perovskite materials, the interband absorption edge displays Urbach-rule behaviour [295]: the absorption coefficient increases exponentially with increasing photon energy, so that no uniquely defined bandgap can be extracted from absorption measurements. A realistic value around 3.2 eV was nevertheless estimated by Wemple [295] in the cubic phase. It was attributed to the direct gap at the  $\Gamma$  point [28].

Going now from cubic the rhombohedral structure (Fig. 3.4), significant changes in the bands are observed, especially when considering the small atomic displacements 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 [299]. Such a trend in the hybridization was confirmed from partial DOS for rhombohedral KNbO<sub>3</sub> and KTaO<sub>3</sub> [224]. As for BaTiO<sub>3</sub>, it was accompanied by a small reduction of the O 2p bandwidth. Moreover, while the position of the Ba bands remain unaffected, we observe a small but significant chemical shift of the Ti 3s (0.25 eV) and Ti 3p (0.29 eV) levels. This feature corroborates a modification of the electronic environment of the Ti atom in the rhombohedral structure.

<sup>&</sup>lt;sup>5</sup>The bandgap problem is a well-known feature of the DFT that was discussed in Chapter 1. In spite of its spectacular character, this discrepancy only concerns the excitation energies; it does not influence the accuracy obtained on the ground-state properties discussed in the next Chapters, and that should be obtained correctly within DFT.



Figure 3.4: Comparison of the Kohn-Sham electronic band structure of cubic and rhombohedral  $BaTiO_3$  along different high symmetry lines of the Brillouin zone.

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 ABO<sub>3</sub> compounds [299, 43] <sup>6</sup>. A similar evolution is expected when going from the cubic to the orthorhombic phase.

#### 3.4 The ferroelectric instability

As the structural and electronic properties previously discussed, the problematics of the ferroelectric structural instability of  $BaTiO_3$  is also within the scope of DFT. In this Chapter, we would like to adopt the simple approach that was considered in pioneer *ab initio* calculations on  $ABO_3$ compounds. In this context, we shall reintroduce some of the open questions that have motivated this thesis and which were briefly mentioned in the Introduction. It will give us a first flavor of the discussions that will arise in the next Chapters.

For computational reasons, the full investigation of the energy surface of a macroscopic solid in term of the entire parameter space defined by the atoms ( $3 \times N_{\text{atom}}$  variables) cannot be addressed directly from firstprinciples. Fortunately, the ferroelectric phase transitions only involve small transformations. The idea is therefore to capture the essential physics of the material by focusing only on some pertinent cross-sections of the potential energy surface around a reference position defined by the prototype cubic structure.

Since Cochran, the phase transition is usually visualized by the softening of a given phonon in the cubic structure. It is therefore quite natural to expect that a first insight on the phenomenon should be given by freezing, in this cubic structure, the atomic displacement pattern associated to the ferroelectric phonon mode. The earlier computations of this type were reported by Weyrich [299] on BaTiO<sub>3</sub> and SrTiO<sub>3</sub>. More recently, Cohen and Krakauer followed the same approach to understand the origin of the ferroelectricity in BaTiO<sub>3</sub> [41, 42] and to investigate the reasons of the different sequence of phase transitions in BaTiO<sub>3</sub> and PbTiO<sub>3</sub> [43, 44]. Calculations of this type are now numerous and have been reported independently for different ABO<sub>3</sub> compounds like BaTiO<sub>3</sub> [143], KNbO<sub>3</sub> [267, 224], KTaO<sub>3</sub> [224, 268], LiNbO<sub>3</sub> [129], or even BaBiO<sub>3</sub> [151, 191].

The major output of this kind of investigation is an energy diagram, similar to that plotted in Fig. 3.5 for the case of  $BaTiO_3$ . Freezing, in the cubic structure, a specific atomic displacement pattern along different

<sup>&</sup>lt;sup>6</sup>For indication, in our calculation, the indirect gap between A and  $\Gamma$  becomes equal to 2.27 eV in the tetragonal phase.



Figure 3.5: Calculated energy as a function of the amplitude of the softmode distortion  $\lambda.\eta$ , frozen in the experimental cubic phase of BaTiO<sub>3</sub>, where  $\eta = [\delta(Ba) = -0.002, \delta(Ti) = -0.096, \delta(O_1) = +0.158, \delta(O_2) = \delta(O_3) = +0.071]$ . The different curves are associated to atomic displacements frozen along the < 100 >, < 110 > and < 111 > directions, and correspond respectively to a tetragonal, orthorhombic and rhombohedral distortion.

directions points out the existence of double-wells in the potential energy surface. It so demonstrates that the prototype cubic phase, with the atoms at their high symmetry positions, is not the lowest energy configuration but is in fact an unstable structure. Moreover, neglecting the eventual coupling with the macroscopic strain, it already suggests that the rhombohedral phase will be the most stable, the tetragonal and orthorhombic structures appearing only as saddle points of the potential energy surface.

The small amplitude of the energy differences involved in Fig. 3.5 underlines the requirement of high quality calculations. It partly explains the limited success of different empirical approaches developed since the sixties. It seems now commonly accepted that the relief of the BaTiO<sub>3</sub> energy surface is not steep enough to be described by approximate methods. As an example, a pair potential calculation reported by Edwardson [62] looks globally similar to the *ab initio* results in ABO<sub>3</sub> compounds. However, it predicts that the displacement of the B atom alone is already unstable, while we will see, later in this work, that it is not the case. It is the lack of accuracy of previous simpler approaches that has motivated the use of computationally more intensive first-principles methods.

The results presented in Fig. 3.5 were a first crucial test: they demonstrate the ability of DFT calculations, performed within the LDA, to reproduce the ferroelectric instability of  $BaTiO_3$ . Similarly, in Ref. [143], calculations have been reported that correctly predict the low temperature phase of various ABO<sub>3</sub> compounds. The door is therefore open to further more sophisticated investigations.

The challenges concerning  $BaTiO_3$  are numerous. In what follows, we would like to address more specifically two family of questions that naturally arise from the analysis of Fig. 3.5.

The first kind of problem concerns the understanding of the *microscopic* mechanisms responsible of the ferroelectric instability and refer to the relationship that should exist between the electronic and dynamical properties. How is it possible to relate the structural instability, associated to the existence of the double well of Fig. 3.5, and the electronic properties previously described in this Chapter $\Gamma$  What is the origin of the energy lowering associated to the ferroelectric displacement pattern $\Gamma$  These questions will be first re-introduced in Chapter 5. They will then be more extensively discussed in Chapter 7.

A second interesting family of problems concerns the range of the ferroelectric instability. The double well presented in Fig. 3.5 was indeed associated to a specific pattern of atomic displacements that were correlated in the different unit cell. Is the crystal unstable with respect to a single, isolated, atomic displacement or at the opposite does the appearance of the instability require a collective movement of all the atoms at a macroscopic scale  $\Gamma$  In other words, what is the kind of correlation in the atomic displacements that is really required to produce the transition  $\Gamma$ This problem will be discussed in Chapter 7.

To address the previous questions will require to investigate more carefully the form of potential energy surface. Up to now, the energy was parametrized in terms of the atomic positions. As long-wavelength atomic displacement may induce macroscopic electric fields, we will need to introduce such a field as a new parameter of the theory. Questions also concern the tools that will be used to characterize efficiently the potential energy surface in our parameter space. The "frozen-phonon" approach that was used in this Section should be generalized to some extent. In what follows, we prefer however to work within the *perturbative* approach that is described in the next Section.

#### 3.5 Conclusions

72

In this Chapter, we have proposed an overview of the ground-state properties of barium titanate. First, we have reported the optimized structural parameters associated to its 4 phases. Then, we have discussed its electronic properties. BaTiO<sub>3</sub> was identified as a relatively ionic material that exhibits however some covalent features, well summarized by the interactions between O 2p and Ti 3d orbitals. It was observed that the structural transition from the cubic to the rhombohedral phase is accompanied by non-negligible modifications of the orbital hybridizations. We would like to stress that the mixed ionic-covalent character of the bonding, illustrated here for  $BaTiO_3$ , is an essential feature of the family of perovskite ABO<sub>3</sub> compounds. We will see later how it is related to some of their interesting properties. Finally we have exhibited the ability of DFT-LDA calculations to reproduce the ferroelectric instability of  $BaTiO_3$ . Some of the challenges for DFT are now in the investigation of the potential energy surface in the vicinity of the cubic phase. Such a study will be facilitated within the perturbative approach described in the next Chapter.

### Chapter 4

# A Density Functional Perturbation Theory

#### 4.1 Introduction

Up to know, we focused on the description of the ground-state properties of periodic solids within the density functional formalism. Postulating that this problem has been solved, we will now be interested in the efficient prediction of various responses of this periodic system to small external perturbations. In our work, we will restrict our investigations to the response to small atomic displacements and to applied macroscopic electric fields. However, the same line of thought is also usually applied for the response to a macroscopic strain [12, 53] or even to the transmutation of an atom from one chemical species to another (the "alchemical" perturbation [54, 55]).

Our interest in perturbative responses of the system to different orders lies essentially in the fact that many interesting quantities are directly related to successive derivatives of the total energy with respect to different perturbations. This was already illustrated in Chapter 1, where the forces and the stress tensors were connected to a first-derivative of the total energy. In this Chapter, we will pay a particular attention to the formulation of the dielectric tensor, Born effective charges or the dynamical matrix in terms of second derivatives of the total energy. We will then address specifically the determination of these quantities within DFT.

There are basically two techniques to determine the successive derivatives of the total energy with respect to different perturbations. The first one is direct: it consists in freezing the change of external potential asso-

73
ciated to a small but finite perturbation in the unperturbed system and to compute the successive derivatives from finite differences. This approach has been widely used to investigate the response to atomic displacements and to build the dynamical matrix, giving access to the phonon frequencies. The practical advantage of this method is that it only requires ground-state calculations. One of its drawbacks is that it is impossible to handle perturbations incommensurate with the periodic lattice or potentials linear in space, corresponding to homogeneous electric fields <sup>1</sup>. Moreover, the response to perturbations of increasing wavelength requires supercells of increasing size with concomitant evolution of the computational time.

The alternative approach consists in investigating the response to an infinitesimal perturbation within perturbation theory. Incommensurability is not a problem for this kind of techniques any more. The early attempt in this direction was based on the computation of the inverse dielectric matrix (IDM) [217, 255, 256]. However, the whole spectrum of the valence- and conduction-band wavefunctions was required in this kind of calculations. The inversion of a large dielectric matrix was computationally intensive. Moreover, the response to atomic displacements was not accessible in the case where the electron-ion interaction is represented by a nonlocal pseudopotential. More recently, Baroni, Giannozzi and Testa [11] avoided all these problems thanks to an interesting merging of DFT and perturbation theory. A different algorithm, based on a variational principle, was proposed by Gonze, Allan and Teter [91], providing more accurate expressions for the energy derivatives and giving even access to non-linear responses thanks to the (2n+1) theorem [88]. These techniques will be referred to as Density Functional Perturbation Theory (DFPT).

In this Chapter, we first investigate carefully how different quantities of interest can be formulated in terms of derivatives of the microscopic total energy. In Section 4.3, we recall some basics of perturbation theory. In Section 4.4, we introduce these results in the framework of DFT in order to build a DFPT. In Section 4.5, we reformulate the equations for the case of periodic solids and incommensurate perturbations. Sections 4.6 and 4.7 are devoted to the calculation of the first-order changes of the wavefunctions in the specific case of atomic displacement and electric field perturbations. Finally, in Section 4.8, we discuss briefly how to compute a general mixed second derivative of the energy. The specific calculation of the Born effective charges, dielectric tensor and interatomic force constants will be addressed in the next three Chapters.

<sup>&</sup>lt;sup>1</sup>A technique, making use of Wannier functions, has been proposed recently by Nunes and Vanderbilt [208] to investigate the response of a periodic system to a finite field. It is a promising approach even if it was still only applied to model systems.

# 4.2 Perturbations and physical properties

Our first-principles calculations are based on a microscopic expression of the total energy:  $E_{e+i}$ . On the other hand, some interesting quantities, like the polarization or the dielectric tensor, are introduced in electrostatics within a macroscopic context. In this Section, we would like to clarify the connection between such macroscopic concepts and our microscopic formulation of  $E_{e+i}$ .

As the quantity of interest in electrostatics is not the applied field but the total screened electric field, we will need to introduce a new quantity [50]: the electric enthalpy. As a first step, we will relate this electric enthalpy to  $E_{e+i}$ . In a second part, we will show that interesting quantities are directly related to successive derivatives of the electric enthalpy: we will be able to formulate them in term of  $E_{e+i}$ .

## 4.2.1 The electric enthalpy

In the previous Chapters, we have considered a closed form of the total energy as a function of the atomic positions. This total energy was obtained from a microscopic expression of the energy of the electrons and of the ions:

$$E_{e+i}(R_{\kappa}) = \min_{\varphi} E_{e+i}(R_{\kappa}, [\varphi])$$
(4.1)

Now, we would like to introduce the macroscopic electric field as a new independent parameter of the theory. In solids, due to the intimate structure of the medium, electric fields are submitted to microscopic fluctuations at the atomic scale. By macroscopic field, we refer to the electric field appearing within the electrostatics [157]: it is a mean quantity that average out the microscopic fluctuations and basically corresponds to the  $\mathbf{G} = \mathbf{0}$  Fourier component of the fluctuating field. Isolating this macroscopic field, our purpose will be to extract out the associated macroscopic contribution to the total energy in order to stay with a remaining part for which the thermodynamic limit is well defined.

In presence of a macroscopic, external, applied electric field,  $\mathcal{E}_{app}$ , the total energy of the system is that of the electron and the ions in presence of the field *plus* the own electrostatic energy associated to the applied field:

$$E_{e+i}(R_{\kappa}, \mathcal{E}_{app}) = \frac{1}{8\pi} \int |\mathcal{E}_{app}(\mathbf{r})|^2 d\mathbf{r} + \min_{\varphi} E_{e+i}(R_{\kappa}, \mathcal{E}_{app}, [\varphi])$$
(4.2)

Within the solid, the applied electric field induces a macroscopic polarization field  $\mathcal{P}$ , associated to another depolarizing field  $\mathcal{E}_{dep}$ . In what follows, we will consider our solid as the macroscopic limit of an ellipsoïd. For that case, it can indeed be shown [157] that the different fields  $(\mathcal{E}_{app}, \mathcal{P}, \mathcal{E}_{dep})$  are homogeneous within the solid, a situation presenting some evident practical advantages. Also for that case, the depolarizing field within the solid simply writes :

$$\mathcal{E}_{\mathrm{dep},i} = -4\pi n_i \mathcal{P}_i \tag{4.3}$$

where  $n_i$  are well defined form factors [157], that summarize the dependency of  $\mathcal{E}_{dep}$  on the shape of the material.

The part of the electrostatic energy due to the macroscopic fields,  $E_{\text{mac}}$ , can now be written in terms of the total electric field,  $\mathcal{E}$ :

$$E_{\text{mac}}(\mathcal{E}_{\text{app}}, \mathcal{P}) = \frac{1}{8\pi} \int |\mathcal{E}(\mathbf{r})|^2 d\mathbf{r}$$
$$= \frac{1}{8\pi} \int |\mathcal{E}_{\text{app}}(\mathbf{r}) + \mathcal{E}_{\text{dep}}(\mathbf{r})|^2 d\mathbf{r} \qquad (4.4)$$

For an ellipsoïd, it is equal to [92]:

$$E_{\rm mac}(\mathcal{E}_{\rm app},\mathcal{P}) = \frac{1}{8\pi} \int |\mathcal{E}_{\rm app}(\mathbf{r})|^2 d\mathbf{r} - V \mathcal{E}_{\rm app} \mathcal{P} + \frac{4\pi}{2} V \sum_{i=1}^3 n_i \mathcal{P}_i^2 \quad (4.5)$$

where V is the volume of the macroscopic solid. The first term is the own energy of the applied field. The second and third terms are due to the interaction of this field with the material: in Eq. (4.2), they were included in  $E_{e+i}(R_{\kappa}, \mathcal{E}_{app}, [\varphi])$ . Interestingly, we have now a relationship between the external field  $\mathcal{E}_{app}$  and the macroscopic polarization  $\mathcal{P}$  in which the only coupling term has a very simple form. This suggests that, combined with Eq. (4.5), functions of  $\mathcal{E}_{app}$  should alternatively be written as functions of  $\mathcal{P}$ .

In this context, let us introduce:

$$E_{e+i}(R_{\kappa}, \mathcal{E}_{app}, \mathcal{P}) = \min_{\varphi \to \mathcal{P}} E_{e+i}(R_{\kappa}, \mathcal{E}_{app}, [\varphi])$$
(4.6)

such that:

$$\min_{\varphi} E_{e+i}(R_{\kappa}, \mathcal{E}_{app}, [\varphi]) = \min_{\mathcal{P}} E_{e+i}(R_{\kappa}, \mathcal{E}_{app}, \mathcal{P})$$
(4.7)

We can now define a new function from which the contribution due to the macroscopic fields has been removed:

$$\tilde{E}_{e+i}(R_{\kappa},\mathcal{P}) = E_{e+i}(R_{\kappa},\mathcal{E}_{app},\mathcal{P}) - \left(-V\mathcal{E}_{app}\mathcal{P} + \frac{4\pi}{2}V\sum_{i=1}^{3}n_{i}\mathcal{P}_{i}^{2}\right) \quad (4.8)$$

This function is independent of  $\mathcal{E}_{app}$ . It is also independent of the *shape* of the material  $(n_i)$ .  $\tilde{E}_{e+i}$  is a quantity for which the thermodynamic limit is well defined. Moreover, from its definition, we still have the following connection:

$$\tilde{E}_{e+i}(R_{\kappa}, \mathcal{P}) = \min_{\varphi \to \mathcal{P}} \tilde{E}_{e+i}(R_{\kappa}, [\varphi])$$
(4.9)

where  $\tilde{E}_{e+i}$  corresponds in fact to the crystal energy  $E_{e+i}$  from which the macroscopic contributions, involving the polarization have been removed <sup>2</sup>. From Eqs. (4.5)-(4.8)-(4.9), the total energy now finally writes:

$$E_{e+i}(R_{\kappa}, \mathcal{E}_{app}) = \min_{\mathcal{P}} \left[ E_{mac}(\mathcal{E}_{app}, \mathcal{P}) + \min_{\varphi \to \mathcal{P}} \tilde{E}_{e+i}(R_{\kappa}, [\varphi]) \right]$$
(4.10)

This expression is interesting in the sense that all the macroscopic quantities have been isolated from the other energy contributions. The last term has no dependence on  $\mathcal{E}_{app}$  as well as on the shape of the material any more. The only remaining problem is that the electrostatic energy is formulated in terms of the applied field and the macroscopic polarization, while one usually prefers to consider expressions involving the observable total homogeneous electric field inside the body, on which conditions can be easily imposed.

For that purpose, instead of minimizing the total energy  $E_{e+i}$ , one usually prefer to work with the electric enthalpy,  $F_{e+i}$ , defined as:

$$F_{e+i}(R_{\kappa},\mathcal{E}) = E_{e+i}^{in}(R_{\kappa},\mathcal{E}_{app}) - \frac{1}{4\pi} \int \mathcal{E}(\mathbf{r}).\mathcal{D}(\mathbf{r})d\mathbf{r}$$
(4.11)

where  $E_{e+i}^{in}$  is the part of the energy *inside* the body <sup>3</sup> and the displacement field is equal to:

$$\mathcal{D}(\mathbf{r}) = \mathcal{E}(\mathbf{r}) + 4\pi \mathcal{P}(\mathbf{r}) \tag{4.12}$$

From the previous definitions, the electric enthalpy corresponds to:

$$F_{e+i}(R_{\kappa}, \mathcal{E}) = \min_{\mathcal{P}} \left[ \frac{-V}{8\pi} |\mathcal{E}|^2 - V \mathcal{E} \mathcal{P} + \min_{\varphi \to \mathcal{P}} \tilde{E}_{e+i}(R_{\kappa}, [\varphi]) \right] (4.13)$$
$$= \frac{-V}{8\pi} |\mathcal{E}|^2 + \min_{\mathcal{P}} \left[ -V \mathcal{E} \mathcal{P} + \min_{\varphi \to \mathcal{P}} \tilde{E}_{e+i}(R_{\kappa}, [\varphi]) \right] (4.14)$$

 $<sup>\</sup>frac{8\pi}{\varphi \to \varphi} = \frac{8\pi}{\varphi \to \varphi} = \frac{1}{\varphi \to \varphi}$ 

with the  $\mathbf{G} = 0$  term of the electrostatic energy  $(E_{ii} + E_{ie} + E_H)$ , that must be omitted. <sup>3</sup>It corresponds to Eq. (4.10) but in which  $E_{\text{mac}}$  restricts to its contribution inside the body in Eq. (4.4).

The electric enthalpy appears therefore as composed of two terms. The first one is the proper electrostatic energy of the effective field inside the body. The remaining part concerns the crystal energy within this field, and contain a macroscopic contribution  $-V\mathcal{EP}$ . Under the condition of zero macroscopic electric field, we obtain the final expression:

$$F_{e+i}(R_{\kappa}, \mathcal{E} = 0) = \min_{\varphi} [\min_{\varphi \to \mathcal{P}} \tilde{E}_{e+i}(R_{\kappa}, [\varphi])]$$
$$= \min_{\varphi} \tilde{E}_{e+i}(R_{\kappa}, [\varphi])$$
(4.15)

Under the condition of zero macroscopic electric field, the electric enthalpy  $F_{e+i}$  of the system corresponds therefore to the minimum of  $\tilde{E}_{e+i}$ . It is the quantity that has been considered in Chapter 2.

# 4.2.2 Derivatives of the electric enthalpy

The Taylor expansion of the electric enthalpy up to second order, as a function of the atomic positions and macroscopic electric field  $^4$ , can be written as [50]:

$$F_{e+i}(R_{\kappa}, \mathcal{E}) = F_{e+i}(R_{\kappa_o}, 0)$$
  
$$-V \sum_{\alpha} \mathcal{P}_{\alpha}(R_{\kappa_o}, 0) \mathcal{E}_{\beta} - \sum_{\alpha} \sum_{\kappa} F_{\kappa,\alpha}(R_{\kappa_o}, 0) \Delta \tau_{\kappa,\alpha}$$
  
$$-\frac{V}{8\pi} \sum_{\alpha\beta} \epsilon_{\alpha\beta}^{\infty} \mathcal{E}_{\alpha} \mathcal{E}_{\beta} - \sum_{\alpha\beta} \sum_{\kappa} Z_{\kappa,\alpha\beta}^{*} \Delta \tau_{\kappa,\alpha} \mathcal{E}_{\beta}$$
  
$$+\frac{1}{2} \sum_{\alpha\beta} \sum_{\kappa\kappa'} C_{\alpha\beta}(\kappa, \kappa') \Delta \tau_{\kappa,\alpha} \Delta \tau_{\kappa',\beta} + \dots \qquad (4.16)$$

The electric field  $\mathcal{E}$  is the total (screened) electric field inside the solid and  $\Delta \tau_{\kappa,\alpha} = (R_{\kappa} - R_{\kappa o})_{\alpha}$ . Our purpose is now to identify the coefficients appearing in this expression  $(\epsilon^{\infty}_{\alpha\beta}, C_{\alpha\beta}(\kappa, \kappa'), Z^*_{\kappa,\alpha\beta})$  with the well known physical quantities to which they refer.

#### The dielectric tensor

Within the electrostatics, the macroscopic displacement field,  $\mathcal{D}$ , the macroscopic polarization,  $\mathcal{P}$ , and the macroscopic electric field,  $\mathcal{E}$ , are related to each others within the following expression:

$$\mathcal{D}_{\alpha} = \mathcal{E}_{\alpha} + 4\pi \mathcal{P}_{\alpha} \tag{4.17}$$

 $<sup>^{4}\,\</sup>mathrm{This}$  expression can be generalized in order to include the strains as a third set of variables

and the dielectric tensor of insulators is introduced as:

$$\epsilon_{\alpha\beta} = \frac{\partial \mathcal{D}_{\alpha}}{\partial \mathcal{E}_{\beta}} = \delta_{\alpha\beta} + \frac{\partial \mathcal{P}_{\alpha}}{\partial \mathcal{E}_{\beta}}$$
(4.18)

From Eq. (4.13), we deduce that:

$$\frac{\partial F_{e+i}}{\partial \mathcal{E}_{\alpha}} = \frac{-V}{4\pi} \mathcal{E}_{\alpha} - V \mathcal{P}_{\alpha} = \frac{-V}{4\pi} \mathcal{D}_{\alpha}$$
(4.19)

so that

$$\epsilon_{\alpha\beta} = \frac{-4\pi}{V} \frac{\partial^2 F_{e+i}}{\partial \mathcal{E}_{\alpha} \partial \mathcal{E}_{\beta}}.$$
(4.20)

This identifies the coefficient appearing in Eq. (4.16) with the dielectric tensor introduced in electrostatics. Using now Eq. (4.14), we can make the connection with  $\tilde{E}_{e+i}$ :

$$\frac{\partial^2 F_{e+i}}{\partial \mathcal{E}_{\alpha} \partial \mathcal{E}_{\beta}} = \frac{-V}{4\pi} \delta_{\alpha\beta} + \frac{\partial^2 \tilde{E}_{e+i}}{\partial \mathcal{E}_{\alpha} \partial \mathcal{E}_{\beta}}, \qquad (4.21)$$

so that finally  $^5$  :

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} - \frac{4\pi}{V} \frac{\partial^2 \tilde{E}_{e+i}}{\partial \mathcal{E}_{\alpha} \partial \mathcal{E}_{\beta}}.$$
(4.22)

#### The Born effective charge tensor

The Born effective charge is defined as the change of polarization induced by an atomic displacement:

$$Z^*_{\kappa,\alpha\beta} = V \frac{\partial \mathcal{P}_{\beta}}{\partial \tau_{\kappa,\alpha}} \tag{4.23}$$

From Eq. 4.19, it writes:

$$Z^*_{\kappa,\alpha\beta} = -\frac{\partial F_{e+i}}{\partial \mathcal{E}_{\beta} \partial \tau_{\kappa,\alpha}}$$
(4.24)

or equivalently:

$$Z^*_{\kappa,\alpha\beta} = -\frac{\partial E_{e+i}}{\partial \mathcal{E}_{\beta} \partial \tau_{\kappa,\alpha}}$$
(4.25)

<sup>&</sup>lt;sup>5</sup>In the following,  $\tilde{E}_{e+i}$  will be usually considered as an energy per unit cell so that V will have to be replaced by  $\Omega_o$ , the unit cell volume.

#### The harmonic force constants

The interatomic force constants are defined as:

$$C_{\alpha\beta}(\kappa,\kappa') = \frac{\partial F_{\kappa,\alpha}}{\partial \tau_{\kappa',\beta}}.$$
(4.26)

and they correspond to second derivatives of the electric enthalpy as appearing in Eq. 4.16. In absence of macroscopic electric field,  $\tilde{E}_{e+i}$  is equivalent to  $E_{e+i}$  so that we simply obtain:

$$C_{\alpha\beta}(\kappa,\kappa') = \frac{\partial^2 E_{e+i}}{\partial \tau_{\kappa,\alpha} \partial \tau_{\kappa',\beta}}$$
(4.27)

## 4.2.3 Summary

In this Section, we have reintroduced the concept of electric enthalpy and we have shown how it can be connected to the crystal energy. The different quantities, that will be discussed in the next Chapters, have been formulated as second derivatives of the electric enthalpy. Alternatively, they are also directly related to second derivatives of the crystal energy as defined in Chapter 2. We will now be interested in the explicit formulation of such second derivatives.

# 4.3 Basics of perturbation theory

In Chapters 1 and 2, we have addressed the determination of the ground state of periodic solids within density functional theory. In Chapter 3, this formalism has been applied to barium titanate. From now, we postulate that the ground-state problem has been solved, and that all the associated ground state quantities are known (energy, wavefunctions, density,...). Starting from that assumption, we consider that a small external perturbating potential, characterized by the parameter  $\lambda$ , is applied to the system. The new problem is described by the family of Schrödinger equations:

$$H(\lambda) |\varphi(\lambda)\rangle = E(\lambda) |\varphi(\lambda)\rangle \tag{4.28}$$

Within perturbation theory, the external potential  $v_{\text{ext}}$  is expanded in terms of the parameter  $\lambda$ , and is supposed to be known to all orders:

$$v_{\rm ext}(\lambda) = v_{\rm ext}^{(0)} + \lambda v_{\rm ext}^{(1)} + \lambda^2 v_{\rm ext}^{(2)} + \dots$$
(4.29)

Similarly, the other physical quantities (energy, electronic density, electronic wavefunctions...) are expanded in terms of  $\lambda$ :

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \dots$$
(4.30)

In this general context, our purpose is to describe how we can determine the successive derivatives of the total energy, directly connected to interesting quantities, by solving the expansion of Eq. (4.28) up to different orders.

In this Section, we recall some basic results of perturbation theory. For the sake of clarity, they will be exhibited for a system of independent electrons, described by a set of one-body Schrödinger equations. Two different perturbative approaches will be considered: the first one makes use of a Sternheimer equation (see for instance Ref. [181]), the second is based on a variational principle (see for instance Ref. [95]). In the next Section, both will be generalized in the context of DFT.

Interestingly, we already note that, for case of one-state wavefunction, the  $\lambda$ -expansion is not unique. One has indeed complete freedom for the phase factor of  $\varphi(\lambda)$ , in the sense that :

$$\tilde{\varphi}(\lambda) = e^{if(\lambda)} \varphi(\lambda) \tag{4.31}$$

is also solution of Eq. (4.28), whatever would be the *real* function  $f(\lambda)$ , called the "gauge". In what follows, we will pay a particular attention to this phase freedom, that becomes even more pronounced in independent electrons schemes when several states are occupied, because one-body occupied wavefunctions can form linear combinations as previously discussed for the ground-state (Chapter 1).

## 4.3.1 The Sternheimer approach

As previously mentioned, for the purpose of the illustration, we consider here a system composed of independent electrons that is described by a set of one-body Schrödinger equations:

$$[H(\lambda) - \epsilon_{\alpha}(\lambda)] |\psi_{\alpha}(\lambda)\rangle = 0, \qquad (4.32)$$

and submitted to orthonormalization conditions of the wavefunctions:

$$\langle \psi_{\alpha}(\lambda) | \psi_{\beta}(\lambda) \rangle = \delta_{\alpha\beta}, \quad \forall \alpha, \beta \in \{ \text{occ} \}.$$
(4.33)

The different quantities appearing in the previous equations are now expanded in powers of  $\lambda$ .

#### Single-band case

Let us start with the even more simple case of a *single* one-body Schrödinger equation. At the first-order of perturbation, the problem writes as a Sternheimer equation, submitted to a normalization condition:

$$(H - \epsilon_{\alpha})^{(0)} |\psi_{\alpha}^{(1)}\rangle = -(H - \epsilon_{\alpha})^{(1)} |\psi_{\alpha}^{(0)}\rangle, \qquad (4.34)$$

$$\langle \psi_{\alpha}^{(1)} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | \psi_{\alpha}^{(1)} \rangle = 0$$
(4.35)

Without loss of generality, the first-order wavefunctions may be expanded in terms of the complete set formed by the ground-state wavefunctions, supposed to be known:

$$\psi_{\alpha}^{(1)} = c_{\alpha\alpha}^{(1)}\psi_{\alpha}^{(0)} + \sum_{\beta \neq \alpha} c_{\alpha\beta}^{(1)}\psi_{\beta}^{(0)}$$
(4.36)

Our problem therefore basically consists in determining the coefficients  $c_{\alpha\beta}^{(1)}$  that satisfy Eqs. (4.34)-(4.35).

Projecting first the Sternheimer equation in the subspace spanned by  $\langle \psi_{\alpha}^{(0)} \rangle$ , we recover the Hellmann-Feynman theorem:

$$E^{(1)} = \langle \psi_{\alpha}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle \tag{4.37}$$

Applying the same technique to second order (or differentiating the previous equation), we obtain similarly:

$$E^{(2)} = \langle \psi_{\alpha}^{(0)} | H^{(2)} | \psi_{\alpha}^{(0)} \rangle + \frac{1}{2} [\langle \psi_{\alpha}^{(0)} | H^{(1)} | \psi_{\alpha}^{(1)} \rangle + \langle \psi_{\alpha}^{(1)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle]$$
(4.38)

Continuation of the process leading to Eqs. (4.37)-(4.38) points out a (n+1) rule: the knowledge of the wavefunctions up to order n is sufficient to compute the energy derivative up to order n+1. In particular, we have obtained a general expression for the second derivative of the total energy, involving only the zero- and first-order of the wavefunctions. Up to now, however, we did not obtain any information on the first-order wavefunctions, involved in the last expression.

Projecting now the Sternheimer equation on the subspace perpendicular to  $\langle \psi_{\alpha}^{(0)} |$ , we get:

$$P_{-\alpha}(H - \epsilon_{\alpha})^{(0)} P_{-\alpha} |\psi_{\alpha}^{(1)}\rangle = -P_{-\alpha} H^{(1)} |\psi_{\alpha}^{(0)}\rangle, \qquad (4.39)$$

In this equation,  $P_{-\alpha}|\psi_{\alpha}^{(1)}\rangle$  is the only unknown. As  $(H - \epsilon_{\alpha})^{(0)}$  is nonsingular within the subspace perpendicular to  $\langle \psi_{\alpha}^{(0)}|$ , the contribution to  $\langle \psi_{\alpha}^{(1)}|$  within this subspace can be isolated:

$$P_{-\alpha}|\psi_{\alpha}^{(1)}\rangle = \sum_{\beta \neq \alpha} \frac{\langle \psi_{\beta}^{(0)}|H^{(1)}|\psi_{\alpha}^{(0)}\rangle}{(\epsilon_{\alpha} - \epsilon_{\beta})}|\psi_{\beta}^{(0)}\rangle$$
(4.40)

The only remaining unknown is  $c_{\alpha\alpha}^{(1)}$ .

The normalization condition Eq. (4.35), imposes for the *real* part of  $c_{\alpha\alpha}^{(1)}$  to be zero. However, the projection of the equation in the subspace spanned

by  $\langle \psi_{\alpha}^{(0)} |$  did not give us any additional information. This corresponds to the fact that it remains a phase freedom associated to the resolution of Eq. (4.34), that can only be suppressed by imposing the gauge. The "parallel transport" gauge is defined by imposing to the imaginary part of  $c_{\alpha\alpha}^{(1)}$  to be zero. Within this gauge, the normalization condition Eq. (4.35) must be replaced by:

$$\langle \psi_{\alpha}^{(0)} | \psi_{\alpha}^{(1)} \rangle = 0 \tag{4.41}$$

To summarize, within the "parallel transport" gauge, the problem to be solved has been replaced by:

$$P_{-\alpha}(H - \epsilon_{\alpha})^{(0)} P_{-\alpha} |\psi_{\alpha}^{(1)}\rangle = -P_{-\alpha} H^{(1)} |\psi_{\alpha}^{(0)}\rangle, \qquad (4.42)$$

$$\langle \psi_{\alpha}^{(0)} | \psi_{\alpha}^{(1)} \rangle = 0 \tag{4.43}$$

The first-order wavefunctions are equal to:

$$\psi_{\alpha}^{(1)} = \sum_{\beta \neq \alpha} \frac{\langle \psi_{\beta}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle}{(\epsilon_{\alpha} - \epsilon_{\beta})} \psi_{\beta}^{(0)}, \qquad (4.44)$$

and the second energy derivative writes:

$$E^{(2)} = \langle \psi_{\alpha}^{(0)} | H^{(2)} | \psi_{\alpha}^{(0)} \rangle + \sum_{\beta \neq \alpha} \frac{\langle \psi_{\alpha}^{(0)} | H^{(1)} | \psi_{\beta}^{(0)} \rangle \langle \psi_{\beta}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle}{(\epsilon_{\alpha} - \epsilon_{\beta})}$$
(4.45)

Up to now, for a single band problem.

#### Many-band case

As we had seen for the ground state, for the case where there is more than one occupied band, the phase freedom is more pronounced due to the invariance of total energy and density under any unitary transform within the space of the occupied wavefunctions. For the many-band case, starting from Eq. (4.32)-(4.33), we obtain at the first order of perturbation a set of one-body Sternheimer equations submitted to orthonormalization conditions of the occupied wavefunctions:

$$(H - \epsilon_{\alpha})^{(0)} |\psi_{\alpha}^{(1)}\rangle = -(H - \epsilon_{\alpha})^{(1)} |\psi_{\alpha}^{(0)}\rangle$$

$$(4.46)$$

$$\langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle + \langle \psi_{\alpha}^{(1)} | \psi_{\beta}^{(0)} \rangle = 0, \quad \forall \alpha, \beta \in \{\text{occ}\}.$$
(4.47)

Expanding the first-order wavefunctions, in terms of the complete set of ground-state wavefunctions, we can identify two different sub-spaces, corresponding respectively to the occupied ({occ}) and unoccupied ({emp}) bands:

$$\psi_{\alpha}^{(1)} = \sum_{\beta}^{\{\text{occ}\}} c_{\alpha\beta}^{(1)} \psi_{\beta}^{(0)} + \sum_{\gamma}^{\{\text{emp}\}} c_{\alpha\gamma}^{(1)} \psi_{\gamma}^{(0)}$$
(4.48)

Projecting the Sternheimer equations on the subspace spanned by  $|\psi_{\alpha}^{(0)}\rangle$ , we recover the Hellmann-Feynmann theorem and do not get any information on  $c_{\alpha\alpha}^{(1)}$ . Projecting on the subspace of the other occupied bands, we obtain:

$$c_{\alpha\beta}^{(1)} = \frac{\langle \psi_{\beta}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle}{\epsilon_{\beta} - \epsilon_{\alpha}}.$$
(4.49)

The orthonormalization conditions put however an additional requirement within the subspace of the occupied bands: it imposes for the real part of  $c_{\alpha\beta}^{(1)}$  to be zero. The previous coefficients are therefore purely imaginary so that the contribution to  $|\psi_{\alpha}^{(1)}\rangle$  from the subspace of the occupied bands will not affect the total energy or the density. We can always find a unitary transform that aligns  $P_v |\psi_{\alpha}^{(1)}\rangle$  with  $\psi_{\alpha}^{(0)}$ . For this particular choice, the contribution originating from the subspace of the occupied bands is summarized in  $c_{\alpha\alpha}^{(1)}$ . Due to the phase indeterminacy associated to this coefficient in the resolution of Eq. (4.46), we can arbitrarily impose to its imaginary part to be zero. This condition defines the "parallel transport" gauge [96]. To work within this gauge corresponds therefore to replace the normalization condition by:

$$\langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle = 0, \quad \forall \alpha, \beta \in \{ \text{occ} \}.$$

$$(4.50)$$

in which case  $c_{\alpha\beta}^{(1)} = 0$  for any  $(\alpha, \beta)$  within the subspace of the occupied bands.

Within the "parallel transport" gauge, the problem only consists in identifying the projection of the first-order wavefunction within subspace of the conduction bands. The set of Eqs. (4.46)-(4.47), has been replaced by:

$$P_{c}(H - \epsilon_{\alpha})^{(0)} P_{c} |\psi_{\alpha}^{(1)}\rangle = -P_{c} H^{(1)} |\psi_{\alpha}^{(0)}\rangle$$
(4.51)

$$\forall \alpha, \beta \in \{val\} : \langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle = 0 \tag{4.52}$$

Similarly to the single band case, we obtain:

$$\psi_{\alpha}^{(1)} = \sum_{\beta}^{\{\text{emp}\}} \frac{\langle \psi_{\beta}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle}{(\epsilon_{\alpha} - \epsilon_{\beta})} \psi_{\beta}^{(0)}, \qquad (4.53)$$

and the second energy derivative writes:

$$E^{(2)} = \sum_{\alpha} \left( \langle \psi_{\alpha}^{(0)} | H^{(2)} | \psi_{\alpha}^{(0)} \rangle + \sum_{\beta}^{\{\text{emp}\}} \frac{\langle \psi_{\alpha}^{(0)} | H^{(1)} | \psi_{\beta}^{(0)} \rangle \langle \psi_{\beta}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle}{(\epsilon_{\alpha} - \epsilon_{\beta})} \right). \quad (4.54)$$

The previous set of equations gives the correct density and energy expansion. However, the unitary transform performed within the subspace of the occupied bands has mixed the different first-oder Sternheimer equations, so that the  $\psi_{\alpha}^{(1)}$  obtained within this gauge do still not satisfy any of the single Eq. (4.46). In other words, if  $\psi_{\alpha}^{(0)}$  is associated to a single orbital of the unperturbed problem,  $\psi_{\alpha}^{(1)}$  does not describe the first-order change of this single orbital but also contains contributions from other orbitals. As it will be discussed in Chapter 7, for the purpose of identifying band by band contributions all along a path of  $\lambda$ , the valence band contribution (Eq. 4.49) must be added. This corresponds to work within what is referred to as the "diagonal" gauge [96].

## 4.3.2 The variational approach

For the ground-state, we had seen in Chapter 1 that, as an alternative to the direct resolution of the Schrödinger equation, it was also possible to directly minimize the total energy with respect to the ground-state wave functions. Similarly, in perturbation, an alternative to the direct resolution of a Sternheimer equation consists in minimizing a variational expression of successive energy derivatives. This approach, based on an early work of Sinagolu [266] who generalized the minimum Hylleraas principle [128] at different orders of perturbation, was recently reinvestigated by Gonze [95].

#### Variational theorems

When perturbation theory is applied to a quantity for which a variational theorem holds (as it is the case for the ground-state total energy), two major variational perturbation theorems can be derived:

(i) A variational principle can be exhibited for the even order of perturbation. It states that:

$$E^{(2n)} = \min_{\varphi^{(n)}} \left\{ \tilde{E}_{(\lambda)} \left[ \sum_{i=0}^{n-1} \lambda^{i} \varphi_{0}^{(i)} + \lambda^{n} \varphi^{(n)} \right] \right\}^{(2n)}$$
(4.55)

This theorem establishes, for example, that the first-order wavefunctions can be derived from a minimization of a variational expression of  $E^{(2)}$ . Moreover, it teaches that the error on the second derivative, evaluated from approximate trial wavefunctions, is quadratic in the error on the wave function and smaller than that inherent to any other non-variational expression.

(ii) Going beyond the (n + 1) rule previously mentioned, a (2n + 1) theorem can be demonstrated:

$$E^{(2n+1)} = \left\{ \tilde{E}_{(\lambda)} [\sum_{i=0}^{n} \lambda^{i} \varphi_{0}^{i}] \right\}^{(2n+1)}$$
(4.56)

It states that the energy up to order (2n + 1) can be expressed through an expression which requires only the knowledge of the wavefunctions up to order n.

These theorems have been demonstrated in Ref. [95]. They hold for constrained as well as for unconstrained functionals. It can nevertheless be shown that, for our purpose, the use of a constrained functional (i.e. making use of orthonormalization conditions) yields simpler expressions [95].

#### Independent-electrons problem

For the independent-electrons problem, previously discussed, the search of the ground-state can be formulated through the minimization of a variational expression:

$$E^{(0)} = \min_{\psi_{\alpha}^{(0)}} \Big\{ \sum_{\alpha}^{occ} \langle \psi_{\alpha}^{(0)} | H^{(0)} | \psi_{\alpha}^{(0)} \rangle \Big\},$$
(4.57)

under the constraint that:

$$\langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(0)} \rangle = \delta_{\alpha\beta}, \ \forall \alpha, \beta \in \{ \text{occ} \}.$$
(4.58)

The variational approach to perturbation theory is based on the expansion of the previous equations. The second derivative of the energy and the first-order wavefunctions can be determined simultaneously through the minimization of the following variational expression:

$$E^{(2)} = \min_{\psi_{\alpha}^{(1)}} \left\{ \sum_{\alpha} [\langle \psi_{\alpha}^{(1)} | (H - \epsilon_{\alpha})^{(0)} | \psi_{\alpha}^{(1)} \rangle + \langle \psi_{\alpha}^{(0)} | H^{(2)} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | H^{(1)} | \psi_{\alpha}^{(1)} \rangle + \langle \psi_{\alpha}^{(1)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle] \right\},$$
(4.59)

under the constraints:

$$\langle \psi_{\alpha}^{(1)} | \psi_{\beta}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle = 0, \quad \forall \alpha, \beta \in \{ \text{occ} \}.$$

$$(4.60)$$

It is interesting to investigate the connection between this minimization procedure and the resolution of a Sternheimer equation. The Euler-Lagrange equation associated to the minimization under constraint of the previous expression can be obtained as the expansion of the Euler-Lagrange equation obtained for the ground-state. It writes:

$$(H - \epsilon_{\alpha})^{(0)} |\psi_{\alpha}^{(1)}\rangle = -H^{(1)} |\psi_{\alpha}^{(0)}\rangle - \sum_{\beta}^{occ} \Lambda_{\alpha\beta}^{(1)} |\psi_{\beta}^{(0)}\rangle.$$
(4.61)

The projection of this equation on the subspace of the conduction unperturbed wavefunction allows to recover a first-order Sternheimer equation:

$$P_c(H - \epsilon_{\alpha})^{(0)} P_c |\psi_{\alpha}^{(1)}\rangle = -P_c H^{(1)} |\psi_{\alpha}^{(0)}\rangle$$
(4.62)

This demonstrates that the minimization of a variational expression of  $E^{(2)}$  under the more drastic constraints:

$$\langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle = 0, \ \forall \alpha, \beta \in \{ \text{occ} \}$$

$$(4.63)$$

is formally equivalent to solve a first-order Sternheimer equation within the "parallel transport" gauge. Both approaches can therefore be used without distinction.

# 4.4 Merging of DFT and perturbation theory

The two previous methods of addressing perturbation theory can now be introduced in density functional theory. Each of them will give rise to a self-consistent algorithm allowing an efficient determination of the firstorder wavefunctions. Interestingly, these techniques still do not require the explicit knowledge of the whole spectrum of unoccupied wavefunctions of the unperturbed system, as it was the case with the IDM technique.

# 4.4.1 The Sternheimer approach

In Chapter 1, we had presented a set of Kohn-Sham (KS) equations to be solved self-consistently for determining the KS ground state wave functions. Similarly, in perturbation theory, Baroni *et al.* [11, 12, 50] proposed to solve self-consistently a set of first-order Sternheimer equations in order to get the first-order wavefunctions.

The new set of equations can be trivially obtained by expanding the set of Eq. (1.70) to first-order. As it was previously discussed, within the "parallel transport" gauge we are only interested by the projection of the Sternheimer equation on the conduction bands, while the normalization condition has been modified. This yields the following system, to be solved self-consistently:

$$\begin{cases} P_{c} \left[ -\frac{1}{2} \nabla^{2} + v_{s}^{(0)} - \epsilon_{\alpha}^{(0)} \right] P_{c} |\psi_{\alpha}^{(1)}\rangle = P_{c} v_{s}^{(1)} |\psi_{\alpha}^{(0)}\rangle \\ v_{s}^{(1)}(\mathbf{r}) = v_{\text{ext}}^{(1)}(\mathbf{r}) + \int \frac{n^{(1)}(\mathbf{r}_{1})}{|\mathbf{r}_{1} - \mathbf{r}|} d\mathbf{r}_{1} \\ + \int K_{\text{xc}}(\mathbf{r}, \mathbf{r}_{1}) n^{(1)}(\mathbf{r}_{1}) d\mathbf{r}_{1} + v_{\text{Hxc0}}^{(1)}(\mathbf{r}), \\ n^{(1)}(\mathbf{r}) = \sum_{\alpha=1}^{occ} [\psi_{\alpha}^{(0)*}(\mathbf{r}) \cdot \psi_{\alpha}^{(1)}(\mathbf{r}) + \psi_{\alpha}^{(1)*}(\mathbf{r}) \cdot \psi_{\alpha}^{(0)}(\mathbf{r})] \end{cases}$$
(4.64)

under the constraints:

$$\langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle = 0, \quad \forall \alpha, \beta \in \{ \text{occ} \}.$$

$$(4.65)$$

Following the notations introduced for the ground-state, we now define:

$$v_{\rm H}^{(1)}(\mathbf{r}) = \int \frac{n^{(1)}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1$$
 (4.66)

$$v_{\rm xc}^{(1)}(\mathbf{r}) = \int K_{\rm xc}(\mathbf{r}, \mathbf{r}_1) n^{(1)}(\mathbf{r}_1) \, d\mathbf{r}_1$$
 (4.67)

Two new quantities have been introduced:

$$v_{\rm Hxc0}^{(1)}(\mathbf{r}) = \frac{d}{d\lambda} \frac{\delta E_{\rm H}[n^{(0)}]}{\delta n(\mathbf{r})} |_{n^{(0)}(\mathbf{r})} + \frac{d}{d\lambda} \frac{\delta E_{\rm xc}[n^{(0)}]}{\delta n(\mathbf{r})} |_{n^{(0)}(\mathbf{r})} \quad (4.68)$$

$$K_{\rm xc}(\mathbf{r},\mathbf{r}') = \frac{\delta E_{\rm xc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}|_{n^{(0)}(\mathbf{r})}$$
(4.69)

 $v_{\text{Hxc0}}^{(1)}(\mathbf{r})$  summarizes the  $\lambda$ -dependence of  $v_{\text{H}}^{(0)}$  and  $v_{\text{xc}}^{(0)}$ . The Hartree part will always be zero within the present work where we investigate only the response to atomic displacements and applied macroscopic electric field.

It may however be non-zero in some cases, like in the response to a macroscopic strain [12]. There will be an exchange-correlation contribution, for instance, when investigating the response to an atomic displacement in presence of non-linear core corrections.

 $K_{\rm xc}(\mathbf{r}, \mathbf{r}')$  is usually referred to as the exchange-correlation kernel. Within the LDA it reduces to a local operator:

$$K_{\rm xc}^{LDA}(\mathbf{r},\mathbf{r}') = \frac{d\epsilon_{\rm xc}^{LDA}}{dn}|_{\mathbf{r}} \cdot \delta(\mathbf{r}-\mathbf{r}').$$
(4.70)

In Chapter 8, we will discuss some consequences of this approximation and investigate more carefully what would be the form of this kernel within "exact" DFT [74].

## 4.4.2 The variational formulation

Similarly, the variational formulation can be applied to the density functional theory [91, 96]. We obtain that  $E_{\rm el}^{(2)}$  is the minimum of the following expression:

$$E^{(2)}[\psi^{(0)};\psi^{(1)}] = \sum_{\alpha}^{\circcc} [\langle \psi_{\alpha}^{(1)} | H^{(0)} - \epsilon_{\alpha}^{(0)} | \psi_{\alpha}^{(1)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{(2)} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{\text{ext}}^{(1)} | \psi_{\alpha}^{(1)} \rangle + \langle \psi_{\alpha}^{(1)} | v_{\text{ext}}^{(1)} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{\text{Hxc0}}^{(1)} | \psi_{\alpha}^{(1)} \rangle + \langle \psi_{\alpha}^{(1)} | v_{\text{Hxc0}}^{(1)} | \psi_{\alpha}^{(0)} \rangle] + \frac{1}{2} \iint K_{\text{xc}}(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \iint \frac{n^{(1)}(\mathbf{r}) n^{(1)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \frac{d^2 E_{\text{Hxc}}}{d\lambda^2} \Big|_{n^{(0)}} (4.71)$$

where the first-order changes in wavefunctions,  $\psi_{\alpha}^{(1)},$  are varied under the constraints

$$\langle \psi_{\alpha}^{(0)} | \psi_{\beta}^{(1)} \rangle = 0, \quad \forall \alpha, \beta \in \{ \text{occ} \}.$$

$$(4.72)$$

As in Section 4.3.2, it can be checked that the minimization of Eq. (4.71) under the set of constraints Eq. (4.72) is equivalent to solve a set of Sternheimer equations within the parallel transport gauge (Eq. 4.64-4.65).

The practical minimization of the previous expression can be performed in a similar spirit to that mentioned for the ground state in Chapter 2. A band-by-band conjugate-gradient algorithm, inspired from that used for the ground-state problem, but adapted to the minimization of  $E^{(2)}$ , is detailed in Ref. [100].

# 4.5 Incommensurate perturbations

As mentioned in the Introduction, one of the practical advantages of perturbation theory is that it allows to treat perturbations, characterized by a wavevector  $\mathbf{q}$  that is incommensurate with the unperturbed periodic lattice. We will now briefly describe how to deal with such perturbations (see Ref. [100]). We will show that, independently of  $\mathbf{q}$ , the perturbed problem can always be formulated in a way that presents the periodicity of the unperturbed system.

# 4.5.1 Energy expansion

The periodic ground-state potential operator is invariant upon translations by a vector  $\mathbf{R}_a$  of the real space lattice <sup>6</sup>:

$$v_{\text{ext}}^{(0)}(\mathbf{r} + \mathbf{R}_a, \mathbf{r}' + \mathbf{R}_a) = v_{\text{ext}}^{(0)}(\mathbf{r}, \mathbf{r}')$$
(4.73)

The *perturbing potential* operator, characterized by a wavevector  $\mathbf{q}$ , is now such that,

$$v_{\text{ext},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a,\mathbf{r}'+\mathbf{R}_a) = e^{i\mathbf{q}\cdot\mathbf{R}_a} v_{\text{ext},\mathbf{q}}^{(1)}(\mathbf{r},\mathbf{r}').$$
(4.74)

When  $2\mathbf{q}$  is not a vector of the reciprocal lattice, such a perturbing potential is non-hermitian and should be used together with its hermitian conjugate counterpart. At the level of the linear response, there is basically no consequence of working separately with the potential and its hermitian conjugate, since the response to their sum is simply the sum of the response to each perturbation separately. However, as we are also interested in the variational property of the second-order change in energy, we cannot afford a non-hermitian external potential.

The problem is solved by considering a complex parameter  $\lambda$ , and the following specific expansion:

$$v_{\text{ext}}(\lambda) = v_{\text{ext}}^{(0)} + (\lambda v_{\text{ext},\mathbf{q}}^{(1)} + \lambda^* v_{\text{ext},-\mathbf{q}}^{(1)})$$

$$+ (\lambda^2 v_{\text{ext},\mathbf{q},\mathbf{q}}^{(2)} + 2\lambda \lambda^* v_{\text{ext},\mathbf{q},-\mathbf{q}}^{(2)} + \lambda^{*2} v_{\text{ext},-\mathbf{q},-\mathbf{q}}^{(2)})$$
(4.75)

where one has imposed that  $v_{\text{ext},\mathbf{q},-\mathbf{q}}^{(2)}$  is hermitian and equal to  $v_{\text{ext},-\mathbf{q},\mathbf{q}}^{(2)}$ <sup>7</sup>. A similar expansion applies now to the energy:

$$E(\lambda) = E^{(0)} + (\lambda E_{\mathbf{q}}^{(1)} + \lambda^* E_{-\mathbf{q}}^{(1)}) + (\lambda^2 E_{\mathbf{q},\mathbf{q}}^{(2)} + 2\lambda \lambda^* E_{\mathbf{q},-\mathbf{q}}^{(2)} + \lambda^{*2} E_{-\mathbf{q},-\mathbf{q}}^{(2)})$$
(4.76)

 $<sup>^{6}</sup>$  We introduce a linear operator in order to be able to treat non-local pseudopotentials.

<sup>&</sup>lt;sup>7</sup>This is always possible since  $v_{\text{ext}}(\lambda)$  and  $v_{\text{ext}}^{(0)}$  are hermitian and the other terms are two by two hermitian conjugate from each others.

#### 4.5. INCOMMENSURATE PERTURBATIONS

Applying a translation to the first-order wavefunctions and densities, one observes the following behaviors :

$$\psi_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}+\mathbf{R}_a) = e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_a} \,\psi_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) \tag{4.77}$$

and

$$n_{\mathbf{q}}^{(1)}(\mathbf{r} + \mathbf{R}_a) = e^{i\mathbf{q}\cdot\mathbf{R}_a} n_{\mathbf{q}}^{(1)}(\mathbf{r})$$
(4.78)

Due to the requirement of invariance of the total energy under translation of the whole system, one derives, when  $\mathbf{q}$  and  $\mathbf{2q}$  are not vectors of the reciprocal lattice, that

$$E_{\mathbf{q}}^{(1)} = E_{-\mathbf{q}}^{(1)} = E_{\mathbf{q},\mathbf{q}}^{(2)} = E_{-\mathbf{q},-\mathbf{q}}^{(2)} = 0, \qquad (4.79)$$

so that we finally obtain:

$$E(\lambda) = E^{(0)} + 2\lambda\lambda^* E^{(2)}_{\mathbf{q},-\mathbf{q}}$$
(4.80)

 $E_{\mathbf{q},-\mathbf{q}}^{(2)}$  is therefore the only non-zero second-order quantity in the  $\lambda$ expansion of the energy Eq. (4.76). As  $v_{\mathrm{ext},\mathbf{q},-\mathbf{q}}^{(2)}$  is hermitian,  $E_{\mathbf{q},-\mathbf{q}}^{(2)}$  is a
real quantity. It is variational with respect to changes in the first-order
wavefunctions. It is this quantity that must be minimized for the case of
incommensurate perturbations.

From now, we will only be concerned by  $E_{\mathbf{a},-\mathbf{a}}^{(2)}$ .

## 4.5.2 Factorization of the phase

Due to the lattice periodicity of the solid, we have seen in Chapter 2 that the ground state wavefunctions have the Bloch form and can be written as a periodic function only affected by a phase factor. We now show that in the previous expression of the second derivative of the energy to be minimized, the phase factor associated to an incommensurate perturbation can be factorized out and re-introduced in the phase factor of the Bloch function, so that the problem finally keeps the periodicity of the unperturbed system <sup>8</sup>.

Inspired by Eqs. (4.77) and (4.78), one defines the *periodic* functions

$$u_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) = (N\Omega_0)^{1/2} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}} \psi_{m,\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r})$$
(4.81)

and

$$\bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}) = e^{-i\mathbf{q}\cdot\mathbf{r}} n_{\mathbf{q}}^{(1)}(\mathbf{r}), \qquad (4.82)$$

<sup>&</sup>lt;sup>8</sup>The factorization of the phase is associated to the basic idea that, within the parallel transport gauge, a perturbation of wave vector  $\mathbf{q}$  only couples valence states at  $\mathbf{k}$  to conduction states at  $\mathbf{k+q}$ .

The second derivative of the energy Eq. (4.71) now becomes:

$$E_{\mathrm{el},-\mathbf{q},\mathbf{q}}^{(2)}[u^{(0)};u^{(1)}] = \frac{\Omega_{0}}{(2\pi)^{3}} \int_{\mathrm{BZ}} \sum_{m}^{\mathrm{occ}} s\left( \langle u_{m\mathbf{k},\mathbf{q}}^{(1)} | H_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k},\mathbf{q}}^{(1)} \rangle \right. \\ \left. + \langle u_{m\mathbf{k},\mathbf{q}}^{(1)} | v_{\mathrm{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}^{(1)} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}+\mathbf{q}}^{(1)} | u_{m\mathbf{k},\mathbf{q}}^{(1)} \rangle \right. \\ \left. + \langle u_{m\mathbf{k},\mathbf{q}}^{(1)} | v_{\mathrm{Hxc}0,\mathbf{k}+\mathbf{q},\mathbf{k}}^{(1)} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{Hxc}0,\mathbf{k},\mathbf{k}+\mathbf{q}}^{(1)} | u_{m\mathbf{k},\mathbf{q}}^{(1)} \rangle \right. \\ \left. + \langle u_{m\mathbf{k},\mathbf{q}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}}^{(2)} | u_{m\mathbf{k}}^{(0)} \rangle \right] d\mathbf{k} \\ \left. + \frac{1}{2} \int \int_{\Omega_{0}} K_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') \bar{n}_{\mathbf{q}}^{(1)*}(\mathbf{r}) \bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}') e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}' \\ \left. + \frac{1}{2} \int \int_{\Omega_{0}} \frac{\bar{n}_{\mathbf{q}}^{(1)*}(\mathbf{r}) \bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \frac{d^{2} E_{\mathrm{Hxc}}}{d\lambda d\lambda^{*}} \right|_{n^{(0)}}$$
(4.83)

It satisfies a minimum principle with respect to variations of the first-order wavefunctions  $u_{n,\mathbf{k},\mathbf{q}}^{(1)}$  under constraints

$$\langle u_{m,\mathbf{k}+\mathbf{q}}^{(0)}|u_{n,\mathbf{k},\mathbf{q}}^{(1)}\rangle = 0, \ \forall m,n \in \{\text{occ}\}.$$
(4.84)

while the first-order change in density is given by

$$\bar{n}_{\mathbf{q}}^{(1)}(\mathbf{r}) = \frac{2}{(2\pi)^3} \int_{\mathrm{BZ}} \sum_{m}^{\mathrm{occ}} s \, u_{m\mathbf{k}}^{(0)*}(\mathbf{r}) u_{m\mathbf{k},\mathbf{q}}^{(1)}(\mathbf{r}) d\mathbf{k}.$$
(4.85)

At this stage, we have all the ingredients for the determination of the first-order wavefunctions through a minimization of a variational expression of  $E^{(2)}$ , for the case of periodic solids and perturbations of arbitrary wavelength. We will now investigate the more explicit form of these equations for the specific case where the perturbation is associated to an atomic displacement or to a macroscopic external electric field (see also [101]). The equations will be written within the LDA. The different terms will be formulated in real or reciprocal space, depending of how they are computed in practice. The notations will also be slightly modified in such a way that the superscript referring to the order of the perturbation will be identified by the name of the perturbation itself (double superscripts correspond to second order).

# 4.6 The phonon-type perturbation

# 4.6.1 Change of external potential

In this Section, we will consider the perturbation created by the displacements of atoms in sublattice  $\kappa$ , along the  $\alpha$  axis, multiplied by the infinitesimal  $\lambda$  (eventually, a complex quantity), multiplied by a phase determined by the cell to which they belong: the  $\alpha$  component of their vector position is changed from  $\tau_{\kappa,\alpha} + R_{a,\alpha}$  to  $\tau_{\kappa,\alpha} + R_{a,\alpha} + \lambda e^{i\mathbf{q}\cdot\mathbf{R}_a}$ . Atoms in the other sublattices are not displaced <sup>9</sup>. For reasons given in Chapter 7, we consider  $\mathbf{q}$  wavevectors that are not equal to  $\mathbf{0}$ .

For the atomic displacement previously described, the first-order change in the external potential operator is

$$v_{\text{ext},\mathbf{q}}^{\tau_{\kappa,\alpha}}(\mathbf{r},\mathbf{r}') = \sum_{a} e^{i\mathbf{q}\cdot\mathbf{R}_{a}} \frac{\partial}{\partial\tau_{\kappa,\alpha}} v_{\kappa}\left(\mathbf{r}-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_{a},\mathbf{r}'-\boldsymbol{\tau}_{\kappa}-\mathbf{R}_{a}\right) \qquad (4.86)$$

while the second-order change writes:

$$v_{\text{ext},-\mathbf{q},\mathbf{q}}^{\tau_{\kappa,\alpha}^{*}\tau_{\kappa,\alpha}}(\mathbf{r},\mathbf{r}') = \sum_{a} \frac{1}{2} \frac{\partial^{2}}{\partial \tau_{\kappa,\alpha}^{2}} v_{\kappa} (\mathbf{r} - \boldsymbol{\tau}_{\kappa} - \mathbf{R}_{a}, \mathbf{r}' - \boldsymbol{\tau}_{\kappa} - \mathbf{R}_{a})$$
(4.87)

More explicit expressions associated to these changes of the external potential will not be detailed here but are reported in Ref. [100]. In presence of non-linear core correction, the exchange-correlation potential will also be influenced by the atomic displacement at the first and second order.

## 4.6.2 Variational expression

Having obtained the first- and second- derivatives of the potentials, we are able to write the variational expression of the associated second-order electronic energy:

$$\begin{split} E_{\mathrm{el}}^{\tau_{\kappa\alpha}^{\star}\tau_{\kappa\alpha}}\left[u^{(0)};u^{(1)}\right] = \\ & \frac{\Omega_{0}}{(2\pi)^{3}} \int_{\mathrm{BZ}} \sum_{m}^{\mathrm{occ}} s\left( \langle u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} | H_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} \rangle \right. \\ & \left. + \langle u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} | v_{\mathrm{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}+\mathbf{q}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} \rangle \\ & \left. + \langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle \right) d\mathbf{k} \end{split}$$

<sup>&</sup>lt;sup>9</sup>All these collective displacements can be generated from  $\mathbf{q}$  wavevectors restricted inside the Brillouin zone, the only ones that will be considered.

$$+ \frac{1}{2} \int_{\Omega_{0}} \left( [\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^{*} [\bar{v}_{\mathbf{x}c0,\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})] + [\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})] [\bar{v}_{\mathbf{x}c0,\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^{*} \right) d\mathbf{r}$$

$$+ \frac{1}{2} \int_{\Omega_{0}} K_{\mathbf{x}c}^{LDA}(\mathbf{r},\mathbf{r}) |\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})|^{2} d\mathbf{r} + 2\pi\Omega_{0} \sum_{\mathbf{G}} \frac{|\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{G})|^{2}}{|\mathbf{q}+\mathbf{G}|^{2}}$$

$$+ \frac{1}{2} \frac{d^{2} E_{\mathbf{x}c}}{d\lambda d\lambda^{*}} \Big|_{n^{(0)}}$$

$$(4.88)$$

As we have supposed  $\mathbf{q}$  to be non-zero, there is no divergence for  $\mathbf{G} = 0$  in the Hartree term and in the local part of  $\bar{v}_{\text{ext},\mathbf{q}}^{\tau_{\kappa\alpha}}$ . The case  $\mathbf{q} = 0$  will be discussed in Chapter 7.

The minimization of the previous expressions allows to determine the first-order wavefunctions  $u^{\tau_{\kappa\alpha}}$ . Within the "parallel transport" gauge, this expression is minimized under the constraints that:

$$\langle u_{m\mathbf{k}+\mathbf{q}}^{(0)} | u_{n\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} \rangle = 0, \ \forall m, n \in \{\text{occ}\}.$$
(4.89)

The minimization of the previous expression is equivalent to solve the following first-order Sternheimer equation:

$$P_{c,\mathbf{k}+\mathbf{q}} \left( H_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}^{(0)} - \epsilon_{m,\mathbf{k}}^{(0)} \right) P_{c,\mathbf{k}+\mathbf{q}} \left| u_{m,\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}} \right\rangle \\ = -P_{c,\mathbf{k}+\mathbf{q}} \left( v_{\text{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}^{\tau_{\kappa\alpha}} + \bar{v}_{\mathrm{H},\mathbf{q}}^{\tau_{\kappa\alpha}} + \bar{v}_{\text{xc},\mathbf{q}}^{\tau_{\kappa\alpha}} + \bar{v}_{\text{xc}0,\mathbf{q}}^{\tau_{\kappa\alpha}} \right) \left| u_{m,\mathbf{k}}^{(0)} \right\rangle$$
(4.90)

where

$$\bar{v}_{\mathbf{H},\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{G}) = 4\pi \, \frac{\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{G})}{|\mathbf{G}+\mathbf{q}|^2} \tag{4.91}$$

$$\bar{v}_{\mathrm{xc},\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r}) = K_{\mathrm{xc}}^{LDA}(\mathbf{r},\mathbf{r}) \,\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})$$
(4.92)

# 4.7 The electric field perturbation

# 4.7.1 Change of external potential

Similarly to what was done in the previous Section, we now would like to deal with the response to an homogeneous static electric field. However, in this case, the problem is more tricky because the change of external potential is linear in space and breaks the periodicity of the crystalline lattice: for a macroscopic field along direction  $\alpha$ , it writes

$$\Delta v_{\rm ext}(\mathbf{r}) = \mathcal{E}_{\rm app} \, r_{\alpha}. \tag{4.93}$$

The long-wave method is commonly used to deal with this problem. Within this approach, the previous linear potential is obtained as the limit

94

for  $q_{\alpha}$  tending to 0 of

$$\Delta v_{\text{ext}}(\mathbf{r}) = \lim_{q_{\alpha} \to 0} \mathcal{E}_{\text{app}} \frac{2 \sin(q_{\alpha} r_{\alpha})}{q_{\alpha}}$$
$$= \lim_{q_{\alpha} \to 0} \mathcal{E}_{\text{app}} \left( \frac{e^{i(q_{\alpha} \cdot r_{\alpha})}}{iq_{\alpha}} - \frac{e^{-i(q_{\alpha} \cdot r_{\alpha})}}{iq_{\alpha}} \right)$$
(4.94)

A second complication also arises in case of macroscopic electric fields from the fact that the central quantity that must be considered is not the applied field but the total screened field  $\mathcal{E}$ . In this context, it was shown in Section 4.2 that the electronic contribution to the dielectric tensor is connected to a second derivative of  $\tilde{E}_{el}$  with respect to  $\mathcal{E}$ . It is therefore this quantity that we need to compute. Basically, it will appear as a conventional expression of  $E_{el}^{(2)}$ , but in which: (i) the field appearing in the electron-ion term is the total screened field  $\mathcal{E}$ , (ii) the  $\mathbf{G} = 0$  to the Hartree term has been omitted.

The first- and second-order change of potential associated to the screened field have a form similar to those of the applied field and can now be written as:

$$v_{\rm scr}^{\mathcal{E}_{\alpha}}(\mathbf{r}) = \lim_{q_{\alpha} \to 0} \left( \frac{e^{iq_{\alpha} \cdot r_{\alpha}}}{iq_{\alpha}} - \frac{e^{-iq_{\alpha} \cdot r_{\alpha}}}{iq_{\alpha}} \right)$$
(4.95)

$$\mathcal{E}^{\mathcal{E}^*_{\alpha}\mathcal{E}_{\alpha}}_{\text{scr}}(\mathbf{r}) = 0 \qquad (4.96)$$

There is no non linear core correction for this case.

We will see that the determination of the first-order change of the wave function with respect to an electric field proceeds in two steps. Indeed, another unknown appears in the expression to be minimized: the firstorder change of the wavefunction with respect to their wave-vector. This quantity can be obtained by another independent minimization procedure.

## 4.7.2 Variational expressions

#### Derivative of the wavefunctions with respect to an electric field

Introducing the change of potential associated the macroscopic electric field in the general expression of the second-order energy and using the fact that in the limit of  $q_{\alpha} \rightarrow 0^{-10}$ :

$$\langle \psi_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | \frac{e^{iq_{\alpha}\cdot r_{\alpha}}}{iq_{\alpha}} | \psi_{m\mathbf{k}}^{(0)} \rangle \quad = \quad \frac{-i}{q_{\alpha}} \langle u_{m\,\mathbf{k}+q_{\alpha}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle$$

 $<sup>^{10}\</sup>rm We$  are also explicitly using the fact that, within the parallel transport gauge,  $\langle u^{\mathcal{E}_\alpha}_{m{\bf k}} | u^{(0)}_{m{\bf k}} \rangle = 0$ 

$$\begin{aligned} \langle \psi_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | \frac{e^{iq_{\alpha} \cdot r_{\alpha}}}{iq_{\alpha}} | \psi_{m\mathbf{k}}^{(0)} \rangle &= \frac{-i}{q_{\alpha}} [ \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle + q_{\alpha} \langle \frac{du_{m\mathbf{k}}^{\mathcal{E}_{\alpha}}}{dk_{\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle ] \\ &= \frac{-i}{q_{\alpha}} [ q_{\alpha} (\frac{d}{dk_{\alpha}} \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle - \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | \frac{d}{dk_{\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle ) ] \\ &= i \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | \frac{d}{dk_{\alpha}} | u_{m\mathbf{k}}^{(0)} \rangle \end{aligned}$$
(4.97)

the second energy derivative can be written as:

$$\tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\alpha}}[u^{(0)}; u^{\mathcal{E}_{\alpha}}] = \frac{\Omega_{0}}{(2\pi)^{3}} \int_{BZ} \sum_{m}^{occ} s\left( \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} \rangle + \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k}}^{k_{\alpha}} \rangle + \langle iu_{m\mathbf{k}}^{k_{\alpha}} | u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} \rangle \right) d\mathbf{k} + \frac{1}{2} \int_{\Omega_{0}} K_{xc}^{LDA}(\mathbf{r}, \mathbf{r}) | n^{\mathcal{E}_{\alpha}}(\mathbf{r}) |^{2} + 2\pi\Omega_{0} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{|n^{\mathcal{E}_{\alpha}}(\mathbf{G})|^{2}}{|\mathbf{G}|^{2}}.$$
(4.98)

where  $u_{m{\bf k}}^{k_{\alpha}}=du_{m{\bf k}}^{(0)}/dk_{\alpha}$ . Within the parallel transport gauge, it is minimized under the constraints

$$\langle u_{m,\mathbf{k}}^{(0)} | u_{n\mathbf{k}}^{\mathcal{E}_{\alpha}} \rangle = 0, \ \forall m, n \in \{\text{occ}\}.$$

$$(4.99)$$

The Sternheimer equation associated to this problem writes:

$$P_{c,\mathbf{k}+\mathbf{q}} \left( H_{\mathbf{k}+\mathbf{q},\mathbf{k}+\mathbf{q}}^{(0)} - \epsilon_{m,\mathbf{k}}^{(0)} \right) P_{c,\mathbf{k}+\mathbf{q}} \left| u_{m,\mathbf{k},\mathbf{q}}^{\mathcal{E}_{\alpha}} \right\rangle \\ = -P_{c,\mathbf{k}+\mathbf{q}} \left( i \frac{\partial}{\partial k_{\alpha}} + v_{\mathbf{H}}^{'\mathcal{E}_{\alpha}} + v_{\mathbf{x}c}^{\mathcal{E}_{\alpha}} \right) \left| u_{m,\mathbf{k}}^{(0)} \right\rangle (4.100)$$

with

$$v_{\mathbf{H}}^{\prime \mathcal{E}_{\alpha}}(\mathbf{q}) = \begin{cases} 4\pi \frac{n^{\mathcal{E}_{\alpha}}(\mathbf{G})}{|\mathbf{G}|^{2}} & \text{when } \mathbf{G} \neq 0\\ 0 & \text{when } \mathbf{G} = 0 \end{cases}$$
(4.101)

$$v_{\rm xc}^{\mathcal{E}_{\alpha}}(\mathbf{r}) = K_{\rm xc}^{LDA}(\mathbf{r}, \mathbf{r}) n^{\mathcal{E}_{\alpha}}(\mathbf{r})$$
(4.102)

## Derivative of the wavefunctions with respect to their wavevector

Unfortunately, the expression to be minimized in order to obtain the first-order wavefunctions with respect to the electric field perturbation, contains other unknowns:  $u_{m\mathbf{k}}^{k_{\alpha}}$ . In the parallel-transport gauge, these first-order

changes of the wavefunctions can be determined from a previous independent minimization of

$$E_{m,\mathbf{k}}^{k_{\alpha}k_{\alpha}}[u^{(0)};u^{k_{\alpha}}] = \langle u_{m\mathbf{k}}^{k_{\alpha}}|H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)}|u_{m\mathbf{k}}^{k_{\alpha}}\rangle + \langle u_{m\mathbf{k}}^{k_{\alpha}}|T_{\mathbf{k},\mathbf{k}}^{k_{\alpha}} - v_{\mathrm{ext},\mathbf{k},\mathbf{k}}^{k_{\alpha}}|u_{m\mathbf{k}}^{(0)}\rangle + \langle u_{m\mathbf{k}}^{(0)}|T_{\mathbf{k},\mathbf{k}}^{k_{\alpha}} - v_{\mathrm{sep},\mathbf{k},\mathbf{k}}^{k_{\alpha}}|u_{m\mathbf{k}}^{k_{\alpha}}\rangle (4.103)$$

with the constraints

$$\forall m, n \in \{val\} : \langle u_{m\mathbf{k}}^{(0)} | u_{n\mathbf{k}}^{k_{\alpha}} \rangle = 0.$$

$$(4.104)$$

 $T_{\mathbf{k},\mathbf{k}}^{k_{\alpha}}$  and  $v_{\mathrm{sep},\mathbf{k},\mathbf{k}}^{k_{\alpha}}$  are the first derivative of kinetic energy operator and external potential. Their explicit expression is reported in Ref. [100].

The Sternheimer equation associated with the minimization procedure Eq. (4.103) is

$$P_{c,\mathbf{k}}(H^{(0)}_{\mathbf{k},\mathbf{k}} - \epsilon^{(0)}_{m,\mathbf{k}})P_{c,\mathbf{k}} | u^{k_{\alpha}}_{m,\mathbf{k}} \rangle = -P_{c,\mathbf{k}}(T^{k_{\alpha}}_{\mathbf{k},\mathbf{k}} + v^{k_{\alpha}}_{\mathrm{sep},\mathbf{k},\mathbf{k}}) | u^{(0)}_{m,\mathbf{k}} \rangle.$$
(4.105)

# 4.8 The case of mixed perturbations

At this stage, we have described how the first-order electronic wavefunctions can be obtained from the minimization of a variational expression of  $E^{(2)}$ . Explicit expressions have been obtained for the specific case of electric field and atomic displacement perturbations.

Before closing this Chapter, we would like now to describe briefly how these first-order wavefunctions can be used to determined a general mixed energy derivatives [100, 101]. This concerns explicitly the mixed derivative with respect to electric field and atomic displacement perturbations but also the second derivative with respect to the same perturbation for two different directions of space. In the next three Chapters the basic results presented in this Section will be applied to the determination of the Born effective charge tensors, the optical dielectric tensor and the dynamical matrices.

When two or more Hermitian perturbations are considered simultaneously, the Taylor-like expansion Eq. (4.29) can be generalized as follows <sup>11</sup>:

$$v_{\text{ext}}(\boldsymbol{\lambda}) = v_{\text{ext}}^{(0)} + \sum_{j_1} \lambda_{j_1} v_{\text{ext}}^{j_1} + \sum_{j_1 j_2} \lambda_{j_1} \lambda_{j_2} v_{\text{ext}}^{j_1 j_2} + \cdots$$
(4.106)

For this case, it can be shown [101] that the mixed derivative

$$E_{\rm el}^{j_1 j_2} = \frac{1}{2} \frac{\partial^2 E}{\partial \lambda_{j_1} \partial \lambda_{j_2}} \tag{4.107}$$

<sup>&</sup>lt;sup>11</sup> The indices  $j_1$  and  $j_2$  are not exponents, but label the different perturbations.

is obtained from

$$E_{\rm el}^{j_1 j_2} = \frac{1}{2} \left( \bar{E}_{\rm el}^{j_1 j_2} + \bar{E}_{\rm el}^{j_2 j_1} \right), \qquad (4.108)$$

with

$$\begin{split} \bar{E}_{el}^{j_{1}j_{2}}\{\psi^{(0)};\psi^{j_{1}},\psi^{j_{2}}\} &= \sum_{\alpha} \left[ \langle \psi_{\alpha}^{j_{1}} | H^{(0)} - \epsilon_{\alpha}^{(0)} | \psi_{\alpha}^{j_{2}} \rangle + \langle \psi_{\alpha}^{(0)} | v_{ext}^{j_{1}j_{2}} | \psi_{\alpha}^{(0)} \rangle \right. \\ &+ \left( \langle \psi_{\alpha}^{j_{1}} | v_{ext}^{j_{2}} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{ext}^{j_{1}} | \psi_{\alpha}^{j_{2}} \rangle \right) \\ &+ \left( \langle \psi_{\alpha}^{j_{1}} | v_{Hxc0}^{j_{2}} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{Hxc0}^{j_{1}} | \psi_{\alpha}^{j_{2}} \rangle \right) \right] \\ &+ \frac{1}{2} \iint_{\Omega_{0}} \frac{n^{j_{1}}(\mathbf{r}) n^{j_{2}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &+ \frac{1}{2} \iint_{\Omega_{0}} K_{xc}^{LDA}(\mathbf{r}, \mathbf{r}) n^{j_{1}}(\mathbf{r}) n^{j_{2}}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &+ \frac{1}{2} \frac{d^{2} E_{Hxc}}{d\lambda_{j_{1}} d\lambda_{j_{2}}} \bigg|_{n^{(0)}} \end{split}$$
(4.109)

The last equation appears as the natural generalization of Eq. (4.71) for the case of a mixed second energy derivative. In particular, it reduces to Eq. (4.71) when  $j_1 = j_2$ . Interestingly, Eq. (4.71) was a variational expression: supposing that the first-order wavefunctions and densities are not exact, the error on  $E_{\rm el}^{(2)}$  was quadratic in the error on the first-order quantities. For the case of a mixed perturbation, we only have a stationary statement: Eqs. (4.108) and (4.109) give an estimation of  $E_{\rm el}^{j_1j_2}$  that has an error proportional to the product of errors made on the first-order quantities associated to the first and second perturbation. If these errors are small, their product will be much smaller. However, the sign of the error is undetermined, unlike for the variational expressions.

The following expressions do not have this interesting properties: their error is of the order of the errors made on the first-order wavefunctions or densities, and not of their mutual product. However, they present an alternative practical advantage: they allow to evaluate  $E_{\rm el}^{j_1j_2}$  from the knowledge of the derivatives of wavefunctions with respect to only one perturbation:

$$E_{\rm el}^{j_1 j_2} = \frac{1}{2} \sum_{\alpha}^{\rm occ} \left( \langle \psi_{\alpha}^{j_1} | v_{\rm ext}^{j_2} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{\rm ext}^{j_2} | \psi_{\alpha}^{j_1} \rangle + \langle \psi_{\alpha}^{j_1} | v_{\rm Hxc0}^{j_2} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | v_{\rm Hxc0}^{j_2} | \psi_{\alpha}^{j_1} \rangle \right) + E_{\rm non-var}^{j_1 j_2}$$

$$(4.110)$$

98

where

$$E_{\rm non-var}^{j_1 j_2} = \sum_{\alpha}^{\rm occ} \langle \psi_{\alpha}^{(0)} | v_{\rm ext}^{j_1 j_2} | \psi_{\alpha}^{(0)} \rangle + \frac{1}{2} \left. \frac{d^2 E_{\rm Hxc}}{d\lambda_{j_1} d\lambda_{j_2}} \right|_{n^{(0)}}$$
(4.111)

The time-reversal symmetry allows to simplify further these expressions. For example,

$$E_{\rm el}^{j_1 j_2} = \sum_{\alpha}^{\rm occ} \langle \psi_{\alpha}^{j_2} | v_{\rm ext}^{j_1} + v_{\rm Hxc0}^{j_1} | \psi_{\alpha}^{(0)} \rangle + E_{\rm non-var}^{j_1 j_2}$$
(4.112)

These results are generalizations of the so-called "interchange theorem" [52]. This theorem will be demonstrated for the specific case of the Born effective charges in Chapter 5. It will also be exploited in Chapters 6 and 7.

# 4.9 Conclusions

In this Chapter, we first paid a particular attention to the formulation of the dielectric tensor, Born effective charges and dynamical matrices in terms of second derivatives of the total energy as obtained in Chapter 2. We then investigated how such second derivatives of the total energy can be efficiently computed within the density functional formalism.

Starting from basic results of perturbation theory, we have formulated a variational approach to density functional perturbation theory. We have then more specifically addressed the response of the system to macroscopic electric fields and atomic displacements. For each case, we have reported how the first-order wavefunctions can be computed from a minimization of a variational expression of  $E^{(2)}$ . We finally described how these first-order wavefunctions can be used to determine a general mixed second-derivative of the energy.

From now, we will make the assumption that the first-order wavefunctions are known and we will detail how they can be used to compute different interesting quantities. The next three Chapters, will address successively the case of the Born effective charges, dielectric tensor and dynamical matrices.

The present formalism will be applied to  $BaTiO_3$ . Continuing the discussion initiated in Chapter 3, from now we will be more essentially concerned by the physics of this material.

# 4.10 References

In addition to references explicitly mentioned in the text, this Chapter was essentially drawn from the following reviews:

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100

# Chapter 5

# The Born effective charges

# 5.1 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 [40, 202, 300, 194]. This interest lies essentially in the fact that such a concept is helpful for a simple description of solids and molecules.

The large diversity of frameworks in which a concept of atomic charge naturally arises (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. However, it 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 [194]. It seems globally possible to separate the different concepts into static and dynamic charges <sup>1</sup>.

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 however an ill-defined quantity that depends on the convention chosen to affect a given electron to a particular ion [40, 202]. On the other hand, the dynamic 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 well-defined quantity that can be experimentally measured, at least in principles. Recent studies of the statistical correlation between different definitions of atomic charges

<sup>&</sup>lt;sup>1</sup>Equivalently, Cochran made in Ref. [40] the distinction between what he called respectively the ionic charge and the lattice dynamical charge.

using a principal component analysis shown that these are not independent but correspond to different scales driven by a unique underlying physical factor [194]. We will argue that the dynamic charge should not reduce to one physical factor, as the static charges 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.

The Born effective charge  $Z^*$  (alias transverse charge, alias dynamic effective charge) <sup>2</sup>, was introduced by Born [19] 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 phonons [19]. During the seventies, the Born effective charges were already investigated and discussed within empirical approaches (see for example Harrison [113]). Now, it is possible to compute them accurately from first-principles [11, 91, 142] and it seems interesting to rediscuss them in this new context.

In our study of  $BaTiO_3$ , the investigation of  $Z^*$  acquires a more fundamental motivation. Recently, it was indeed emphasized that  $Z^*$  are anomalously large in various ABO<sub>3</sub> compounds [242, 70, 313]. It was observed that their values can reach twice that of the nominal ionic charges. This surprising feature gave rise to many questions and engendered a wide curiosity.

In this Chapter, we would like to summarize our 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 [71, 221]. It allows to visualize the mechanism of polarization as electronic currents produced by dynamic changes of orbital hybridizations [113, 221]. It also clarifies the origin of the giant destabilizing dipole-dipole interaction producing the ferroelectric instability of these materials [73].

In Section 5.2 and 5.3, we make a brief overview of the concept of atomic charge. We emphasize the fundamental differences between static and dynamic charges and we reintroduce the Born effective charge that is at the center of the present discussion.

In Section 5.4, we describe how the Born effective charge can be computed within the density functional formalism, establishing the connection between the linear response and Berry phase approaches. We also pay a particular attention to the significance of this charge in terms of Wannier functions.

In Section 5.5, we report various results obtained within different frame-

<sup>&</sup>lt;sup>2</sup>A similar concept was introduced by chemists for molecules and is referred to as the "atomic polar tensor" [16, 199, 200].

work for the cubic phase of  $BaTiO_3$  and  $SrTiO_3$ . We discuss the origin of the large anomalous contributions in terms of dynamic changes of orbital hybridization. A decomposition of the role played by the different bands is reported in Section 5.6.

Section 5.7 is devoted to the evolution of the Born effective charges in the three ferroelectric phases of  $BaTiO_3$  as well as in the cubic phase under isostatic pressure. This points out the role of the anisotropy of the atomic environment on the amplitude of  $Z^*$ . We also report (Section 5.8) 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 phase of  $BaTiO_3$ .

Finally, in Section 5.9, we emphasize the role of the Born effective charge on the lattice dynamics making the connection between the microscopic consideration previously discussed and the ferroelectric phase transition. This role of  $Z^*$  in the ferroelectric instability will be more intensively discussed in Chapter 7.

# 5.2 The concept of static charge

Intuitively, the atomic charge first appears as a static concept. The charge of an isolated atom is a well defined quantity. The purpose of defining atomic charges was 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 [202] in 1935, "there are some difficulties of giving exact definition without arbitrariness for any atomic property". During the seventies, Cochran [40] 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. A large variety of different definitions have been proposed, which we briefly overview (see also Appendix B.1).

A first group of procedures makes use of the basis functions that are used to represent the wavefunctions. The oldest of these methods is the Mulliken population analysis [203], unfortunately well known to be strongly dependent on the choice of the basis functions. An improvement of this technique, that eliminates most of its drawbacks, was proposed by Weinhold *et al.* [237] who introduced the concept of natural atomic orbitals.

Alternate approaches are based directly on the charge density distribution. These methods are usually preferred because they represent the first term of a multicenter multipole expansion and reproduce the dipole moments and the electrostatic potentials in a satisfactory manner. In a first kind of definitions, like that of Hirshfeld [120], the charge is separated into *overlapping* contributions. Another family of methods splits the electronic density between *non-overlapping* regions on the basis of topological arguments [48, 265], as first suggested by Bader [8, 9]. A different approach, also based on the electronic density, was proposed recently by Lee *et al.* [165] and consists in a fit of the electrostatic potential based on a variational principle.

All the previous methods are related to the electronic density and are probably the most commonly used. Differently, some atomic charges were also introduced in connection with other quantities, experimentally measured and related to an atomic charge via a simplified model. Some of these charges can be considered as static. As a unique example, let us mention the atomic charges deduced from the chemical shifts of core ionization energies in XPS or ESCA measurements [194].

Finally, and without being exhaustive, it is important to mention that natural definitions also arise in the framework of semi-empirical approaches. For example, in the bond orbital model of Harrison [113], the electronic interactions are modelized through a few parameters that monitor the charge transfer between the ions and allow to identify an effective static charge (see Appendix B.2).

Although all these procedures address in principle the same universal concept, each of them yields in practice a different quantitative result. This was, for example, emphasized by Wiberg and Rablen [300] or Meister and Schwarz [194] in the case of molecules. It was argued however that if the different definitions are not equivalent, the corresponding charges are not independent but correspond to different scale underlying a common unique physical reality.

This is illustrated for BaTiO<sub>3</sub> in Table 5.1 where different atomic charges are reported in comparison with those expected in a purely ionic material (+2 for Ba, +4 for Ti, -2 for O). The atomic charge of Ref. [113] were deduced by Harrison from his universal parameters <sup>3</sup>. The atomic charges reported by Hewat (Ref. [116]) were approximated from a model of Cowley [49] for SrTiO<sub>3</sub>. Michel-Calendini *et al.* (Ref. [195]) proposed

<sup>&</sup>lt;sup>3</sup>These charges were deduced from the universal parameters of Harrison as described in Section 19-E of Ref. [113]. More realistic charges should be obtained by applying the same idea to optimized tight-binding parameters, like those of Mattheiss [190].

$Z_{Ba}$	$Z_{Ti}$	$Z_0$	Reference
+2	+4	-2	Nominal
+2.00	+0.19	-0.73	Ref. [113]
+1.40	+2.20	-1.20	Ref. [195]
+2.00	+1.88	-1.29	Ref. [116]
+2.00	+2.89	-1.63	Ref. [41]
+2.12	+2.43	-1.52	Ref. [303]
+1.39	+2.79	-1.39	Ref. [305]

Table 5.1: Static charges of  $BaTiO_3$  in the cubic structure.

charges from a population analysis of the electronic distribution of a  $\text{TiO}_6$ cluster, assuming a charge of +2 on Ba. Cohen and Krakauer (Ref. [41]) deduced the atomic charges from a fit of the "ab initio" electronic distribution by that of overlapping spherical ions (generated according to the potential induced breathing model) for different ionic configurations. Xu *et al.* (Ref. [303]) reported values deduced from a Mulliken population analysis of a self-consistent OLCAO calculation. In another reference [305], Xu *et al.* proposed another 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. [34, 304].

These results were obtained on the basis of schemes, sometimes different from those previously reported, so emphasizing again the diversity of the methods. There is no formal equivalence between the different definitions and the results are not quantitatively identical. The values of Table 5.1 have however some common features. In particular, they all reveal that, due to covalency effects between Ti and O atoms, the charge transfer from Ti to O is not complete (see Chapter 3). Consequently, the static charges are smaller than they would be in a purely ionic material <sup>4</sup>. For the Ba atom, the situation is unfortunately not so clear than for Ti and O: even for the more sophisticated models, its charge oscillates from +2 assuming a purely ionic character, to +1.39 involving some covalency with the other atoms. In spite of the dispersion of the results, we note that the choice of a given definition should remain useful to identify some trends or basic phenomena, like evolutions from one phase to the other [305].

The main purpose of this Section was to recall that, in spite of what

<sup>&</sup>lt;sup>4</sup>We will see later that, at the opposite to what is observed here on the static charge, covalency effects usually increase the amplitude the Born effective charges.

is sometimes expected, the static atomic charges are no observables in the strict sense: they are only deduced from observable quantities on the basis of a particular model. In consequence, we must be careful when discussing them. They remain only meaningful within the particular framework of the model from which they were designed.

# 5.3 The concept of dynamic charge

Following Harrison [113], "whenever an ambiguity arises about the definition of a concept such as the atomic charge, it can be removed by discussing only quantities that can be experimentally determined at least in principles". The effective charge, already discussed in solid state physics by Born [19] in 1933, is related to a change of polarization and satisfies this requirement. In this work, we will refer to it as the Born effective charge but it is also known as the transverse charge or the dynamic effective charge.

## 5.3.1 Definition

For periodic solids, the Born effective charge of atom  $\kappa$  is a tensor defined as the coefficient of proportionality at the linear order and under the condition of zero macroscopic electric field, between the macroscopic polarization per unit cell created in direction  $\beta$  and a cooperative displacement of atoms  $\kappa$ in direction  $\alpha$ :

$$Z^*_{\kappa,\alpha\beta} = \Omega_0 \left. \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa,\alpha}} \right|_{\mathcal{E}=0}$$
(5.1)

where  $\Omega_0$  is the unit cell volume.

The Born effective charge is a dynamic concept in the sense that it concerns the response to an atomic displacement. From its definition,  $Z^*$  is a fundamental quantity in lattice dynamics: it governs, with the optical dielectric constant  $\epsilon_{\infty}$ , the strength of the Coulomb interaction responsible of the splitting between longitudinal (LO) and transverse (TO) optic modes [19, 27] (see Chapter 7). For crystals, like binary  $A^N B^{8-N}$  compounds, in which LO and TO mode eigenvectors are identical and imposed by symmetry, infra-red measurement of the splitting allows accurate determination of  $|Z^*|^2/\epsilon_{\infty}$ : so, it offers an unambiguous way to extract the amplitude of  $Z^*$  (its sign remains undefined) from the experiment <sup>5</sup>. For more complex materials like ABO<sub>3</sub> compounds, LO and TO eigenvectors are not necessarily equivalent and the extraction of  $Z^*$  from the experimental data is not straightforward.

 $<sup>^5</sup>$  The presence of  $\epsilon_\infty$  is sometimes source of uncertainty, when it cannot be determined accurately.

When investigating the lattice dynamics of solids, different other dynamic charges were introduced that are related to  $Z^*$ . In his shell-model [38, 39], Cochran considers an effective charge, equivalent to the charge  $e_*^*$  introduced by Szigeti [276], and that includes only the effects of charge redistribution resulting from short-range interaction <sup>6</sup>. This concept is model dependent and relates to  $Z^*$  through an assumption on the form of the Lorentz effective field associated to the transverse optic modes [23, 81]. In the particular case of a local spherical symmetry we have:  $Z^* = [(\epsilon_{\infty} + 2)/3] e_s^*$ . For the longitudinal phonons, a longitudinal effective charge  $Z_L^*$  was introduced by Callen [27], that can be expressed in terms of the Szigeti charge and the effective electric field associated to these modes [81]. In the particular case of a local spherical symmetry, we have:  $Z_L^* = [(\epsilon_{\infty} + 2)/3\epsilon_{\infty}] e_s^*$ . The LO modes differ from the TO ones due to the additional interaction with the longitudinal electric field <sup>7</sup>. This yields the general relationship:  $Z_L^* = Z^* / \epsilon_{\infty}$ . Note finally that, similarly to what was done with respect to an atomic displacement, in piezoelectric materials, the change of polarization induced by a macroscopic strain was expressed in terms of a piezoelectric charge that can also be related to  $Z^*$  [184, 112].

For the case of molecules, in order to interpret the infra-red intensities, Biarge, Herranz and Morcillo [16, 199, 200] introduced a quantity similar to  $Z^*$  that they called the "atomic polar tensor" and that is defined as the change of the total dipole moment of the molecule with respect to an atomic displacement. From this tensor, Cioslowski [36, 37] later introduced a scalar charge (the generalized atomic polar tensor, GAPT) defined as onethird of the trace of the polar tensor. This charge is sometimes compared to different static charges. Anticipating what will be discuss in the next Sections, we would like to stress that such a comparison is misleading: the GAPT contains a different physics that the static charges and is reliant on dynamic transfer of charges that are not included in any static charge.

## 5.3.2 Dynamic transfer of charge

During the seventies, a large variety of semi-empirical models were proposed to investigate the underlying physical processes driving the values of  $Z^*$ . Without being exhaustive, let us mention the interesting works of Lucovsky, Martin and Burnstein [176] who decomposed  $Z^*$  in a local and

 $<sup>{}^{6}</sup>e_{s}^{*}$  is sometimes assimilated to a static charge and its value deduced from a Mulliken analysis or another definition [195]. There is however no formal justification of this procedure. The Szigeti charge remains indeed a dynamical concept, connected to  $Z^{*}$ through a simplified model.

<sup>&</sup>lt;sup>7</sup>Boundary conditions impose a different requirement on the macroscopic electric field for TO ( $\mathcal{E} = 0$ ) and LO ( $\mathcal{E} = -4\pi\mathcal{P}$ ) modes.

a non-local contribution, of Lucovsky and White [177] discussing  $Z^*$  in connection with resonant bonding properties, or the bond charge model of Hübner [123]. The most popular and sophisticated of this kind of approaches remains however that of Harrison [113, 110, 111, 112] within his bond orbital model (BOM). Similar results were obtained independently by Lannoo and Decarpigny [159].

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 it was interestingly pointed out by Dick and Overhauser [58], 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 monitors the amplitude of  $Z^*$  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. The dipole moment p(u) is related to the static charge  $Z(u) = \frac{p(u)}{u}$  and allows to define the dynamic charge:

$$Z^{*}(u) = \frac{\partial p(u)}{\partial u}$$
  
=  $\frac{\partial}{\partial u} (u \cdot Z(u))$   
=  $Z(u) + u \frac{\partial Z(u)}{\partial u}$  (5.2)

In the last expression,  $Z^*$  appears composed of two terms. The first one is simply the static charge. The second corresponds to an additional dynamic contribution: it originates in the transfer of charge produced by the modification of the interatomic distance. Within the BOM, this last contribution is deduced from the universal dependence of the interaction parameters on the bond length (see Appendix B.2). The difference between Z(u) and  $Z^*(u)$  will be large if Z(u) changes rapidly with u. It can even be nonnegligible when  $\partial p(u)/\partial u$  is small, if the charge is transferred on a large distance u.

This simple model already allows to predict *anomalous* contributions (i.e. a value 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,

$$\int_{0}^{\overline{u}} Z^{*}(u) \ du = [p(\overline{u}) - p(0)] = \overline{u} \ Z(\overline{u})$$
(5.3)

$$\Rightarrow \frac{1}{\overline{u}} \int_0^{\overline{u}} Z^*(u) du = Z(\overline{u})$$
(5.4)

The last relationship points out that the mean value of  $Z^*(u)$  from 0 to  $\overline{u}$  is equal to  $Z(\overline{u})$ . Consequently, if Z(u) changes with  $u, Z^*(u)$  must be greater than  $Z(\overline{u})$  (the "nominal" static charge corresponding to a complete transfer of electrons from X to Y) 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<sup>8</sup>.

Considering now 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 [113], 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 generate an anomalously large  $Z^*$ .

The previous model can finally be extended to three dimensional solids. For this case, however, the calculation of the dynamic contribution may become questionable when the identification of the charge transfer is restricted to some specific bonds [15]. As it will be discussed in Section 5.5, the Harrison model remains however a meaningful picture of practical interest to interpret more accurate results.

In conclusion, this Section has shown that  $Z^*$  is related to the static charge (see Eq. 5.2) but does not restrict to it:  $Z^*$  may also include an additional contribution due to dynamic transfers of charge. We so partly disagree with Meister and Schwarz [194] who suggested that all the charges *including* the GAPT are driven by the same underlying parameter. We will illustrate on different examples that  $Z^*$  may become anomalously large and

<sup>&</sup>lt;sup>8</sup>Nominal 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.
independent of the amplitude of Z. Two atoms with the same Z can also exhibit strongly different  $Z^*$ .

# 5.4 A first-principles formulation

#### 5.4.1 Introduction

Simultaneously to the development of the semi-empirical approaches previously discussed, steps were made toward a first-principles determination of  $Z^*$ . Here also, we propose a brief overview of the different avenues which have been explored.

As mentioned previously, the Born effective charge tensor  $Z^*_{\kappa,\alpha\beta}$  of atom  $\kappa$  is defined as the coefficient of proportionality relating, at linear order and under the condition of zero electric field, the macroscopic polarization per unit cell created along the direction  $\beta$ , and the displacement along the direction  $\alpha$  of the atoms belonging to the sublattice  $\kappa$ . As the polarization is already an energy first-derivative, this coefficient can be connected to the mixed second-order derivative of the total energy with respect to atomic displacements and macroscopic electric field. It equivalently describes the linear relation between the force induced on atom  $\kappa$  and the macroscopic electric field  $\mathcal{E}_{\beta}$ :

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \frac{\partial \mathcal{P}_\beta}{\partial \tau_{\kappa\alpha} (\mathbf{q} = \mathbf{0})} = -\frac{\partial^2 E_{tot}}{\partial \mathcal{E}_\beta \partial \tau_{\kappa\alpha} (\mathbf{q} = \mathbf{0})} = \frac{\partial F_{\kappa,\alpha}}{\partial \mathcal{E}_\beta}.$$
 (5.5)

Without loss of generality, the Born effective charge can be decomposed into two contributions:

$$Z^*_{\kappa,\alpha\beta} = Z_\kappa \delta_{\alpha\beta} + \Delta Z_{\kappa,\alpha\beta}, \qquad (5.6)$$

where  $Z_{\kappa}$  is the charge of the (pseudo-)ion  $\kappa$ , and  $\Delta Z_{\kappa,\alpha\beta}$  is the contribution due to the electronic screening. The first term can be trivially identified. Historically, the computation of the second contribution was addressed following different schemes.

A first general method is to work within a perturbative approach. During the early seventies, a linear response formalism was developed that was making use of the inverse dielectric function  $\epsilon^{-1}$  and an expression was proposed for  $Z^*$  [255, 217, 256]. Computations based on this formalism were, for example, reported by Resta and Baldereschi [239, 10]. However, one important drawback of this procedure is that the charge neutrality, which imposes constraints on the off-diagonal elements of  $\epsilon^{-1}$ , is difficult to control and to guarantee [287]. Consequently, Vogl [287] proposed a method that circumvenced the inversion of the dielectric function by using directly the self-consistent potential induced by a long-wavelength lattice displacement. Unfortunately, at that time, there was no way to determine accurately this potential: it had to be approximated and this formulation was only applied to simplified models [172, 173]. The solution was only reported much later by Baroni, Giannozzi and Testa [11] who proposed, within DFT<sup>9</sup>, to compute the total effective potential by solving a self-consistent first-order Sternheimer equation. It was the first "ab initio" powerful and systematic approach, yielding accurate calculation of  $Z^*$ . A variational formulation of this theory was then reported by Gonze, Allan and Teter [91], offering a different algorithm for the calculation of the first-order wavefunctions and a new stationary expression for  $Z^*$ . The "Sternheimer" and "variational" formalisms were first implemented within DFT (usually within the LDA, but also within the GGA), using plane-wave and different kind of pseudopotentials. LMTO [249] and LAPW [308] versions of this approach have also been proposed recently.

As an alternative to the perturbative approach, another procedure should be to determine  $Z^*$  from finite difference of the macroscopic polarization between the undistorted crystal and a distorted crystal with "frozenin" q=0 atomic displacements, in the limit of small displacements. In what was in fact the earliest first-principles computation of  $Z^*$ , Bennett and Maradudin [14] attempted to deduce  $Z^*$  using this technique but as pointed out by Martin [185], on the basis of an incorrect expression, yielding boundary-sensitive results. The basic problem was that the change of polarization was assimilated to the change of the unit cell dipole, which is ill-defined for periodic charge distributions. A re-formulation of this approach was proposed by Littlewood [174] <sup>10</sup>. More recently, Resta [241] interestingly addressed the change of polarization as an integrated macroscopic current. This yielded King-Smith and Vanderbilt [142] to identify in the change of polarization a geometric quantum phase, and to propose a new scheme, useful for a practical calculation of the polarization [243]. This opened the door to an alternative, convenient way to deduce  $Z^*$ . It is usually referred to as the Berry phase approach.

Finally, let us mention that  $Z^*$  was also calculated, on a few occasions, from finite difference of the force induced on an atom by an internal macro-scopic field using a supercell technique [150, 240] <sup>11</sup>.

<sup>&</sup>lt;sup>9</sup>Such an approach was described in Chapter 4 and is usually referred to as the density functional perturbation theory [77].

 $<sup>^{10}\,{\</sup>rm He}$  did not really address the problem of the polarization but switched to a derivative of the polarization so going back to the linear response formalism.

<sup>&</sup>lt;sup>11</sup>Within this supercell approach, the longitudinal charge is accessible from independent quantities. The determination of  $Z^*$  and  $Z_L^*$  offered a possibility to estimate  $\epsilon_{\infty}$ .

In conclusion, we observe that each of the definitions underlying Eq. 5.5 is at the origin of a practical scheme to determine  $Z^*$ . In the next Sections, we report how  $\Delta Z_{\kappa,\alpha\beta}$  can be computed within DFT from the two most widely used techniques: the linear response formalism and the Berry phase approach. These methods are usually implemented when imposing Bornvon Karman periodic boundary conditions to the system. We will see in Chapter 8 that, within exact DFT, the imposition of such periodic conditions is *conceptually* incorrect to investigate the response to a homogeneous electric field [94], or to compute the polarization [100]. However, it is a perfectly *coherent* procedure of practical interest within the *local density approximation* in which the DFT is usually implemented. The theoretical values of  $Z^*$  obtained within these approximations are typically within a few percents around the experimental data.

#### 5.4.2 The perturbative approach

A first approach to compute  $\Delta Z_{\kappa,\alpha\beta}$  consists to address it in the framework of the density functional perturbation theory, as a mixed second derivative of the electronic energy. Following the formalism introduced in Chapter 4,  $\Delta Z_{\kappa,\alpha\beta}$  can be formulated in terms of a stationary expression, involving the first-order derivative of the wavefunctions with respect to a  $\mathbf{q} = \mathbf{0}$  collective displacement  $(|u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}\rangle)$ , and the first-order derivatives of the wavefunctions with respect to an electric field  $(|u_{m\mathbf{k}}^{\mathcal{E}_{\beta}}\rangle)$  and to their wavevector  $(|u_{m\mathbf{k}}^{\mathcal{E}_{\beta}}\rangle = -i\frac{d}{d\mathbf{k}}|u_{m\mathbf{k}}^{(0)}\rangle)$ :

$$\Delta Z_{\kappa,\alpha\beta} = 2 \left[ \frac{\Omega_0}{(2\pi)^3} \int_{\mathrm{BZ}} \sum_{m}^{\mathrm{occ}} s \left( \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\mathcal{E}_{\beta}} \rangle \right. \\ \left. + \langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} | i u_{m\mathbf{k}}^{\kappa_{\beta}} \rangle + \langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}}^{\tau_{\kappa\alpha}} | u_{m\mathbf{k}}^{\mathcal{E}_{\beta}} \rangle \right) d\mathbf{k} \\ \left. + \frac{1}{2} \int_{\Omega_0} [v_{\mathrm{xc0},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})] [\bar{n}^{\mathcal{E}_{\beta}}(\mathbf{r})]^* d\mathbf{r} \\ \left. + \frac{1}{2} \int_{\Omega_0} K_{\mathrm{xc}}^{LDA}(\mathbf{r},\mathbf{r}) [n_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{r})]^* n^{\mathcal{E}_{\beta}}(\mathbf{r}) d\mathbf{r} \\ \left. + 2\pi\Omega_0 \sum_{\mathbf{G}\neq 0} \frac{[n_{\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}}(\mathbf{G})]^* n^{\mathcal{E}_{\beta}}(\mathbf{G})}{|\mathbf{G}|^2} \right]$$
(5.7)

The first-order wavefunctions needed to evaluate this expression were determined by direct minimization of a variational expression of the second derivative of the total energy as previously discussed in Chapter 4.

#### 5.4. A FIRST-PRINCIPLES FORMULATION

Introducing alternatively in Eq. (5.7), the first-order Sternheimer equation associated to the atomic displacement and electric field perturbation :

$$P_c(H^{(0)} - \epsilon_{m\mathbf{k}}^{(0)}) P_c | u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa,\alpha}} \rangle = -P_c H^{\tau_{\kappa,\alpha}} | u_{m\mathbf{k},\mathbf{0}}^{(0)} \rangle$$
(5.8)

$$P_c(H^{(0)} - \epsilon_{m\mathbf{k}}^{(0)}) P_c | u_{m\mathbf{k},\mathbf{0}}^{\mathcal{E}_\beta} \rangle = -P_c H^{\mathcal{E}_\beta} | u_{m\mathbf{k},\mathbf{0}}^{(0)} \rangle$$
(5.9)

and the explicit form of the first-order Hamiltonian associated to these perturbations <sup>12</sup>:

$$H^{\tau_{\kappa,\alpha}} = v_{\text{ext},\mathbf{k},\mathbf{k}}^{\prime\,\tau_{\kappa,\alpha}} + v_{\text{H}}^{\prime\,\tau_{\kappa,\alpha}} + v_{\text{xc}}^{\tau_{\kappa,\alpha}} \tag{5.10}$$

$$H^{\mathcal{E}_{\beta}} = -i\frac{d}{dk_{\beta}} + v'_{\mathrm{H}}^{\mathcal{E}_{\beta}} + v_{\mathrm{xc}}^{\mathcal{E}_{\beta}}$$
(5.11)

we obtain two alternative non-stationary expressions:

$$\Delta Z_{\kappa,\alpha\beta} = -2\frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_m^{occ} s \left\langle u_{m\mathbf{k},\mathbf{q}=\mathbf{0}}^{\tau_{\kappa\alpha}} \right| - i\frac{d}{dk_\beta} |u_{m\mathbf{k}}^{(0)}\rangle d\mathbf{k} \quad (5.12)$$

$$\Delta Z_{\kappa,\alpha\beta} = 2 \left[ \frac{\Omega_0}{(2\pi)^3} \int_{BZ} \sum_{m}^{occ} s \ \langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}}^{\prime\tau_{\kappa\alpha}} | u_{m\mathbf{k}}^{\mathcal{E}_{\beta}} \rangle d\mathbf{k} + \frac{1}{2} \int_{\Omega_0} [v_{\mathrm{xc0},\mathbf{q=0}}^{\tau_{\kappa\alpha}} (\mathbf{r})] [\bar{n}^{\mathcal{E}_{\beta}} (\mathbf{r})]^* d\mathbf{r} \right]$$
(5.13)

Eq.(5.7) was formulating  $Z^*$  as a second derivative of the electronic energy. Alternatively, the two last expressions address it respectively as the derivative of the macroscopic polarization with respect to an atomic displacement (Eq. 5.12) and as the derivative of the force on the atoms  $\kappa$ with respect to an electric field (Eq. 5.13)<sup>13</sup>.

Numerically, the results of Eq. (5.12) and (5.13) are *a priori* less accurate than that of Eq. (5.7) for which we have a stationary statement [100]. Interestingly, however, the last two expressions only require the knowledge of the first-order wavefunctions associated to *one* of the perturbation as soon as one knows the change of potential associated to the other. For example, the only computation of the first-order wavefunction derivative with respect to the electric field perturbation and to their wavevector already allows to deduce the full set of effective charges from Eq. (5.13).

The translational invariance of the crystal imposes that a charge neutrality is fulfilled at the level of  $Z^*$  through the following expression [255, 217]:

 $<sup>^{12}</sup>$  Notations have been introduced in Chapter 4. The "prime" indicates that the G=0 term has been omitted.

<sup>&</sup>lt;sup>13</sup>Eq. (5.13) was originally proposed by Baroni *et al.* [11, 77] to compute  $Z^*$ .

 $\sum_{\kappa} Z^*_{\kappa,\alpha\beta} = 0$ . This condition is guaranteed in the present approach but it will only be satisfied numerically in the convergence limit. We observe that the violation of the charge neutrality is usually of the same order of magnitude than the numerical error on each separate charge.

#### 5.4.3 The Berry phase approach

As previously mentioned, an alternative approach to the determination of the Born effective charges is to determine them from finite difference of the macroscopic polarization  $\Delta \mathcal{P}$ . Starting from the equilibrium positions of the atoms and considering a small but finite  $\mathbf{q=0}$  collective displacement  $\Delta \tau_{\kappa,\alpha}$  in direction  $\alpha$  of the atoms belonging to the sublattice  $\kappa$ , we can parametrize the associated change in the potential by a parameter  $\lambda$ arranged to vary from 0 (initial state) to 1 (final state). If the material remains an insulator for all the  $\lambda$  in the range 0 - 1, then we have:

$$\Delta Z_{\kappa,\alpha\beta} = \Omega_o \lim_{\Delta\tau_{\kappa,\alpha}\to 0} \frac{\Delta\mathcal{P}_{\beta}}{\Delta\tau_{\kappa,\alpha}} = \Omega_o \lim_{\Delta\tau_{\kappa,\alpha}\to 0} \frac{\int_0^1 \left(\partial\mathcal{P}_{\beta}/\partial\lambda\right)d\lambda}{\Delta\tau_{\kappa,\alpha}}$$
(5.14)

Since the Born effective charge are defined in a null electric field, periodic boundary conditions can be used at any  $\lambda$  so that the Kohn-Sham orbitals have the Bloch form. Within any periodic gauge in which the Bloch functions satisfy

$$u_{n,\mathbf{k}}^{(\lambda)}(\mathbf{r}) = e^{i\mathbf{G}\cdot\mathbf{r}} \ u_{n,\mathbf{k}+\mathbf{G}}^{(\lambda)}(\mathbf{r}), \qquad (5.15)$$

King-Smith and Vanderbilt [142] have shown that:

$$\Delta \mathcal{P}_{\beta} = \mathcal{P}_{\beta}^{(1)} - \mathcal{P}_{\beta}^{(0)} \tag{5.16}$$

where

$$\mathcal{P}_{\beta}^{(\lambda)} = -\frac{1}{8\pi^3} i \sum_{m}^{occ} s \int_{BZ} \langle u_{m\mathbf{k}}^{(\lambda)} | \frac{d}{d\mathbf{k}_{\beta}} | u_{m\mathbf{k}}^{(\lambda)} \rangle d\mathbf{k}$$
(5.17)

Taken independently, the matrix elements of the previous equation are illdefined for periodic Bloch function. However, the *integral* of the right-hand side is a well-defined quantity, which has the form of a Berry phase of band m as discussed by Zak [311]. Associated to the fact that a phase is only defined modulo  $2\pi$ , Eq. (5.16) only provides the change of polarization modulo a "quantum" (in 3 dimensional solids, the quantum is  $(s.R_a/\Omega_0)$ , where  $R_a$  is a vector of the reciprocal lattice). In practice,  $\Delta \tau_{\kappa,\alpha}$  may be chosen sufficiently small for the change of polarization being unambiguously defined.

Direct evaluation of Eq. (5.17) is not trivial in numerical calculations because the wavefunctions are only computed at a finite number of point in

the Brillouin zone, without any phase relationship between the eigenvectors. An elegant scheme that circumvences this problem was reported in Ref. [142].

This method was successfully applied to ABO<sub>3</sub> compounds [242, 313], giving equivalent results than those obtained independently by perturbative techniques [70, 231]. A similar accuracy was reported for alkaline-earth oxides [251, 223].

#### 5.4.4 Band by band decomposition

As similarly first reported by Zak in the general context of a Berry phase, Vanderbilt and King-Smith [283] emphasized that the polarization acquires a particular meaning when expressed in terms of localized Wannier functions. In this Section, we will first recall this important result. Then we will show how it can be extended to the Born effective charges, providing physical significance to its band-by-band contributions. Following that we will also demonstrate the equivalence between the linear response formulation and the Berry phase approach.

The Bloch functions  $u_{n\mathbf{k}}(\mathbf{r})$  are related to the Wannier functions  $W_n(\mathbf{r})$  through the following band by band transformation:

$$u_{n\mathbf{k}}^{(\lambda)}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i\mathbf{k}.(\mathbf{r}-\mathbf{R})} W_n^{(\lambda)}(\mathbf{r}-\mathbf{R})$$
(5.18)

$$W_n^{(\lambda)}(\mathbf{r}) = \frac{\sqrt{N} \,\Omega_o}{(2\pi)^3} \int_{BZ} e^{i\mathbf{k}\cdot\mathbf{r}} \,u_{n\mathbf{k}}^{(\lambda)}(\mathbf{r}) \,d\mathbf{k}$$
(5.19)

From this definition, we deduce that:

$$\frac{d}{d\mathbf{k}_{\beta}}u_{n\mathbf{k}}^{(\lambda)}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{R} \left[-i(r_{\beta} - R_{\beta})\right] e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} W_{n}^{(\lambda)}(\mathbf{r}-\mathbf{R}) \quad (5.20)$$

where **R** runs over all real space lattice vectors. Introducing this result in the equation providing  $P_{\beta}$  (Eq. 5.17), we obtain:

$$\mathcal{P}_{\beta}^{(\lambda)} = \frac{s}{\Omega_o} \sum_{m}^{occ} \int r_{\beta} . |W_m^{(\lambda)}(\mathbf{r})|^2 \, d\mathbf{r}$$
(5.21)

For unmixed Bloch functions corresponding to well separated bands, we will have unmixed Wannier functions such that we can isolate  $P_{n,\beta}$ , the contribution of band n to the  $\beta$  component of the polarization,  $P_{\beta}$ :

$$\mathcal{P}_{n,\beta}^{(\lambda)} = \frac{s}{\Omega_o} \int r_\beta . |W_n^{(\lambda)}(\mathbf{r})|^2 d\mathbf{r}$$
(5.22)

From this equation, the polarization due to the electrons of band n is simply deduced for the position of the center of gravity of the density associated to  $W_n$ <sup>14</sup>. The two last equations are therefore conceptually meaningful: they indicate that, for the purpose of determining the polarization, the true quantum mechanical electronic system can be considered as an effective classical system of quantized point charges, located at the Wannier center associated with the occupied bands in each unit cell.

If we now consider the atomic displacement perturbation  $\tau_{\kappa,\alpha}$  parametrized by our parameter  $\lambda$ , the Born effective charge corresponds to:

$$Z_{\kappa,\alpha\beta}^{*} = \Omega_{o} \frac{\partial \mathcal{P}_{\beta}^{(\lambda)}}{\partial \lambda} |_{\lambda=0} = \Omega_{o} \frac{\partial \mathcal{P}_{\beta}^{(0)}}{\partial \tau_{\kappa,\alpha}}$$
(5.23)

In terms of Wannier function,  $Z^*$  can be written as:

$$Z_{\kappa,\alpha\beta}^* = s \sum_{m}^{occ} \int r_{\beta} [(\frac{\partial W_m^{(0)}(\mathbf{r})}{\partial \tau_{\kappa,\alpha}})^* W_m^{(0)}(\mathbf{r}) + (W_m^{(0)}(\mathbf{r}))^* \frac{\partial W_m^{(0)}(\mathbf{r})}{\partial \tau_{\kappa,\alpha}}] d\mathbf{r} (5.24)$$

In this expression, the contributions of the different bands can also be separated from each others, so that the contribution of band n to  $Z^*_{\kappa,\alpha\beta}$  corresponds to:

$$[Z_{\kappa,\alpha\beta}^*]_n = \int r_\beta [(\frac{\partial W_n^{(0)}(\mathbf{r})}{\partial \tau_{\kappa,\alpha}})^* \ W_n^{(0)}(\mathbf{r}) + (W_n^{(0)}(\mathbf{r}))^* \ \frac{\partial W_n^{(0)}(\mathbf{r})}{\partial \tau_{\kappa,\alpha}}] d\mathbf{r} \quad (5.25)$$

As for the polarization, this contribution has a simple physical meaning. In response to an atomic displacement, the electronic distribution is modified and the Wannier center of the different bands is displaced. The last equation identifies the contribution to the Born effective charge due to band n as the change of polarization corresponding to the displacement of a point charge s on a distance equal to the displacement of the Wannier center of this band.

Starting now from the Bloch function expression of the polarization (Eq. [5.17]), the previous equation can be equivalently written as:

$$Z^*_{\kappa,\alpha\beta} = -\frac{\Omega_o}{(2\pi)^3} i \sum_m^{occ} s \int_{BZ} [\langle \frac{\partial u^{(0)}_{m\mathbf{k}}}{\partial \tau_{\kappa,\alpha}} | \frac{\partial u^{(0)}_{m\mathbf{k}}}{\partial k_\beta} \rangle + \langle u^{(0)}_{m\mathbf{k}} | \frac{\partial}{\partial k_\beta} | \frac{\partial u^{(0)}_{m\mathbf{k}}}{\partial \tau_{\kappa,\alpha}} \rangle] d\mathbf{k}$$
(5.26)

where

$$\int_{BZ} \langle u_{n\mathbf{k}}^{(0)} | \frac{\partial}{\partial k_{\beta}} | \frac{\partial u_{n\mathbf{k}}^{(0)}}{\partial \tau_{\kappa,\alpha}} \rangle d\mathbf{k} = \\
\int_{BZ} [\frac{\partial}{\partial k_{\beta}} \langle u_{n\mathbf{k}}^{(0)} | \frac{\partial u_{n\mathbf{k}}^{(0)}}{\partial \tau_{\kappa,\alpha}} \rangle - \langle \frac{\partial u_{n\mathbf{k}}^{(0)}}{\partial k_{\beta}} | \frac{\partial u_{n\mathbf{k}}^{(0)}}{\partial \tau_{\kappa,\alpha}} \rangle] d\mathbf{k} \quad (5.27)$$

 $<sup>^{14}\,{\</sup>rm Contrary}$  to that of Bloch functions, the center of gravity of localized Wannier functions is well defined.

The first term of the right hand is the gradient of a periodic quantity integrated over the Brillouin zone. Within our periodic gauge (see Eq. 5.15), its contribution will be zero so that, using also the time reversal symmetry, we arrive at the final expression:

$$Z^*_{\kappa,\alpha\beta} = -2\frac{\Omega_o}{(2\pi)^3} i \sum_{n}^{occ} s \int_{BZ} \langle \frac{\partial u^{(0)}_{n\mathbf{k}}}{\partial \tau_{\kappa,\alpha}} | \frac{\partial u^{(0)}_{n\mathbf{k}}}{\partial k_\beta} \rangle d\mathbf{k}$$
(5.28)

First, we observe that, starting from the Berry phase formulation, we have recovered the expression obtained by linear response (Eq. 5.12): this demonstrates the equivalence of both the approaches. Moreover, the contributions of the different band can still be separated from each others:

$$[Z_{\kappa,\alpha\beta}^*]_n = -2\frac{\Omega_o}{(2\pi)^3} \ i \ s \int_{BZ} \langle \frac{\partial u_{n\mathbf{k}}^{(0)}}{\partial \tau_{\kappa,\alpha}} | \frac{\partial u_{n\mathbf{k}}^{(0)}}{\partial k_\beta} \rangle \tag{5.29}$$

As Bloch and Wannier functions were related through a band-by-band transformation, the contribution from band m to  $Z^*_{\kappa,\alpha\beta}$  in Eq. (5.29) keeps the same physical meaning as in Eq. (5.25): it is related to the displacement of the Wannier center of band m induced by the displacements of the atoms belonging to the sublattice  $\kappa$ . This physical interpretation will be particularly useful to identify the underlying mechanisms monitoring the amplitude of  $Z^*$ .

We note finally that the different expressions of  $Z^*$  do not yield equivalent band-by-band contributions. In particular, the band by band decomposition of Eq. (5.13) is not equivalent to the previous expression: it does not allow to separate the contributions of the different bands into the same meaningful quantities. Introducing Eq. (5.12) in Eq. (5.13) and using compact notations, the respective contributions of a particular band m are related by the following expression:

$$\begin{bmatrix} \langle u_{m\mathbf{k}}^{(0)} | v_{\text{ext},\mathbf{k},\mathbf{k}}^{\prime\tau_{\kappa\alpha}} | u_{m\mathbf{k}}^{\mathcal{E}_{\beta}} \rangle + \frac{1}{2} \int_{\Omega_{0}} [v_{\text{xc0},\mathbf{q=0}}^{\tau_{\kappa\alpha}}(\mathbf{r})] [\bar{n}_{m\mathbf{k}}^{\mathcal{E}_{\beta}}(\mathbf{r})]^{*} d\mathbf{r} \end{bmatrix} = \\ \langle u_{m\mathbf{k},\mathbf{q=0}}^{\tau_{\kappa,\alpha}} | -i\frac{d}{dk_{\beta}} | u_{m\mathbf{k}}^{(0)} \rangle \\ - \frac{1}{2} \int_{\Omega_{0}} \frac{dv_{\text{Hxc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [\bar{n}_{\mathbf{q=0}}^{\prime\tau_{\kappa\alpha}}(\mathbf{r})]^{*} \bar{n}_{m\mathbf{k}}^{\mathcal{E}_{\beta}}(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int_{\Omega_{0}} \frac{dv_{\text{Hxc}}}{dn} \Big|_{n^{(0)}(\mathbf{r})} [\bar{n}_{m\mathbf{k},\mathbf{q=0}}^{\prime\tau_{\kappa\alpha}}(\mathbf{r})]^{*} \bar{n}^{\mathcal{E}_{\beta}}(\mathbf{r}) d\mathbf{r}$$
(5.30)

The last two terms on the right hand, related to the local fields effects, do not compensate: they will only cancel out during the summation on the different bands in order to yield the correct global effective charge.

#### 5.4.5 Choice of the gauge

For the ground-state, we have seen in Chapter 1 that the Lagrange multiplier method applied to the minimization of the Hohenberg and Kohn fonctional under orthonormalization conditions on the wavefunctions, allows one to recover the usual Kohn-Sham equation modulo a unitary transform within the space of the occupied orbitals [96] ( $\alpha = n, \mathbf{k}$ ):

$$H^{(0)}|\psi_{\alpha}^{(0)}\rangle = \sum_{\beta}^{occ} \Lambda_{\alpha,\beta}^{(0)} |\psi_{\beta}^{(0)}\rangle$$
(5.31)

The freedom associated to the unitary transform (gauge freedom) is inherent to the invariance of the total energy and density under any mixing between the occupied wavefunctions. For the ground-state, there is no reason not to choose the wavefunctions such that

$$\Lambda^{(0)}_{\alpha,\beta} = \delta_{\alpha\beta} \ \epsilon^{(0)}_{\alpha} \tag{5.32}$$

in which case  $\epsilon_{\alpha}^{(0)}$  correspond to the eigenenergies of a conventional Kohn-Sham equation.

For the first-order wavefunctions, that satisfy the following Lagrange equation (obtained as perturbative expansion of Eq. 5.31),

$$(H^{(0)} - \epsilon_{\alpha}^{(0)}) |\psi_{\alpha}^{(1)}\rangle = -H^{(1)} |\psi_{\alpha}^{(0)}\rangle - \sum_{\beta}^{occ} \Lambda_{\alpha,\beta}^{(1)} |\psi_{\beta}^{(0)}\rangle, \qquad (5.33)$$

we have seen in Chapter 4 that practical implementations are usually performed within the "parallel transport gauge" that corresponds to project the first-order change in valence wavefunction in a subspace orthogonal to all the valence bands. For this particular choice, however,  $\Lambda^{(1)}_{\alpha,\beta}$  is not diagonal [96].

It can be shown that our formulations of the Born effective charge, Eqs. (5.7-5.12-5.13), are "gauge" invariant as it is also the case for the Berry phase formulation of the polarization [243]. This gauge invariance does however not apply to the band-by band contribution. It is therefore important to determine the specific choice of the gauge for which our bandby-band decomposition becomes physically meaningful.

Let us consider the Schrödinger equation defined for a continuous path of atomic displacement  $\lambda$ :

$$H(\lambda) \ \psi_{\alpha}(\lambda) = \Lambda(\lambda) \ \psi_{\alpha}(\lambda) \tag{5.34}$$

 $\epsilon$ 

The electronic energy *bands* are defined at any  $\lambda$  by the solution which diagonalizes  $\Lambda(\lambda)$ . To identify the evolution of a particular band along the path of  $\lambda$ , requires to work in a gauge which diagonalizes  $\Lambda(\lambda)$  at any  $\lambda$ . Within a perturbative approach where

$$\Lambda(\lambda) = \Lambda^{(0)} + \lambda \Lambda^{(1)} + \lambda^2 \Lambda^{(2)} + \dots, \qquad (5.35)$$

the previous requirement imposes to diagonalize  $\Lambda$  at any order. The decomposition of  $Z^*$  into its band-by-band contribution must therefore be performed in what we refer to as the diagonal gauge [96].

The first-order wavefunctions in the diagonal gauge  $(\phi_{\alpha}^{(1)})$  can be deduced from those in the parallel transport gauge  $(\psi_{\alpha}^{(1)})$  by adding the contribution spanned within the subspace of the valence bands as obtained in Section 4.3:

$$\phi_{\alpha}^{(1)} = \psi_{\alpha}^{(1)} - \sum_{\beta \neq \alpha} \frac{\epsilon_{\alpha\beta}^{(1)}}{(\epsilon_{\alpha}^{(0)} - \epsilon_{\beta}^{(0)})} \psi_{\beta}^{(0)}$$
(5.36)

where

$$^{(1)}_{\alpha\beta} = \langle \psi_{\beta}^{(0)} | H^{(1)} | \psi_{\alpha}^{(0)} \rangle$$
 (5.37)

Note that this transformation can present some problems when the denominator vanishes: this happens when the valence energies are degenerated. The problem can be technically bypassed by keeping a parallel transport gauge within the space of degenerated wavefunctions. Practically, this means that we will only be able to separate the contributions of well separated set of bands.

#### 5.4.6 Technical details

Our calculations have been performed within the perturbative approach. Integrals over the Brillouin-zone were replaced by a sum on a mesh of  $6 \times 6 \times 6$  special k-points [197, 198] (10 points in the irreducible Brillouin zone). The wavefunctions were expanded in plane waves up to a cutoff of 35 Hartree (about 4100 plane waves). These parameters guarantee a convergency to within 0.5% on  $Z^*$  as well as on its band by band contributions (see also Appendix A).

# 5.5 The cubic phase of ABO<sub>3</sub> compounds

#### 5.5.1 Various results

The Born effective charge tensors of  $ABO_3$  compounds have been widely investigated [242, 70, 313, 71, 72, 221, 231, 309, 292, 160]. In the cubic

	Ions	Ref. $[6]^{a}$	Shell $Model^b$	$\mathbf{Present}$	Ref. $[313]^c$
$Z^*_{Ba}$	+2	+2.9	+1.63	+2.77	+2.75
$Z_{Ti}^*$	+4	+6.7	+7.51	+7.25	+7.16
$Z_{O_{-}}^{*}$	-2	-2.4	-2.71	-2.15	-2.11
$Z_{O_{\parallel}}^{*}$	-2	-4.8	-3.72	-5.71	-5.69

Table 5.2: Born effective charges of  $BaTiO_3$  in the cubic structure.

<sup>a</sup> Extrapolated from the experiment.

<sup>b</sup> Calculated from the parameters of Ref. [139].

<sup>c</sup> Computed within the Berry phase approach.

phase, they are fully characterized by a set of four independent numbers. The charge on A and B atoms is isotropic owing to the local spherical symmetry at their atomic site. For oxygen, two independent elements  $O_{\parallel}$  and  $O_{-}$  must be considered, referring respectively to an atomic displacement parallel and perpendicular to the B-O bond. In Table 5.2, we summarize the results obtained within different approaches for the cubic phase of  $BaTiO_3$ .

The first real estimation of  $Z^*$  in ABO<sub>3</sub> compounds is probably due to Axe [6], from empirical fitting to experimental mode oscillator strengths <sup>15</sup>. As already mentioned in Section 5.3,  $Z^*$  cannot be determined unambiguously from the experiment in ABO<sub>3</sub> crystals. However, within some realistic hypothesis, Axe identified the independent elements of  $Z^*$  and already pointed out that two surprising features characterize the effective charges of BaTiO<sub>3</sub>. First, the oxygen charge tensor is highly anisotropic. Moreover, the charges on Ti and O<sub>||</sub> 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 initio results, computed by linear response, are also in excellent agreement with those of Zhong *et al.* [313], obtained from finite differences of polarization. Note that the charge neutrality, reflecting the numerical accuracy of our calculation, is fulfilled to within 0.02.

The values of  $Z^*$  are also qualitatively reproduced in a shell model calculation, performed from the parameters proposed by Khatib *et al* [139].

<sup>&</sup>lt;sup>15</sup>As an anecdote, let us mention that an early investigation of the Born effective charges of  $BaTiO_3$  was performed by Last in 1957 [161], but without identifying any anomaly. Another discussion was reported in Ref. [152] but without separating the respective values of  $Z^*$ .

A similar agreement between *ab initio* and shell model calculations was obtained for KNbO<sub>3</sub> [275]. During the seventies, Migoni, Bilz and Bäuerle pointed out what they called "an unusual anisotropic and non linear polarizability of the O atom". A *polarizability* model, able to reproduce this feature, was then introduced to investigate the lattice dynamics of ABO<sub>3</sub> compounds [196, 24]. The results mentioned here where obtained within this framework. They illustrate that such a model includes (even implicitly) the mechanism responsible of anomalous  $Z^*$  in ABO<sub>3</sub> compounds. However, it does not allow a meaningful description in terms of dynamic transfer of charges, as it will be discussed later in this Chapter.

Similar computations of  $Z^*$  were performed on different ABO<sub>3</sub> compounds and they reproduce the same characteristics than in BaTiO<sub>3</sub>. A non exhaustive list of these results is reported in Table 5.3.

For materials with the pair of A and B elements chosen either in the IIa and IVb columns, or in the Ia and Vb columns, we observe that the choice of the A atom has a rather limited influence on  $Z_B^*$  and  $Z_{O\parallel}^*$ , 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. Going now to W, the ionic charge increases to +6, while the Born effective charge reaches the much larger value of +12.51. For this class of compounds, we observe interestingly that  $Z_B^*$  evolves quasi linearly with  $\overline{Z}_B$ , the nominal charge of the B atom.

For materials containing Pb, the previous considerations remain valid but there are additional anomalies concerning  $Z_A^*$  and  $Z_{O-}^*$ . This feature is due to the more covalent bonding of lead with oxygen that was illustrated in Ref. [43, 44]. In what follows, we will not be particularly interested by these compounds.

#### 5.5.2 The Harrison model

In the previous Section, we have identified large anomalous contributions to the Born effective charges of various  $ABO_3$  compounds. It seems now interesting to investigate their origin.

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 5.3.2. In Ref. [113], Harrison had in fact already suggested such 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.

Table 5.3: Born effective charges of various  $ABO_3$  compounds in the cubic structure. The Born effective charge of the B atom is compared to its nominal charge  $\bar{Z}_B$ . The theoretical lattice parameter  $a_o$  is also mentioned.

$ABO_3$	$a_o$	$Z_A^*$	$Z_B^*$	$Z_{O\parallel}^*$	$Z_{O-}^*$	$Z_B^*/Z_B$	Reference
nominal		2	4	-2	-2		
$CaTiO_3$	7.19	2.58	7.08	-5.65	-2.00	1.77	Ref. [313]
$\rm SrTiO_3$	7.30	2.56	7.26	-5.73	-2.15	1.82	$\mathbf{Present}$
		2.54	7.12	-5.66	-2.00	1.78	Ref. [313]
		2.55	7.56	-5.92	-2.12	1.89	Ref. [160]
		2.4	7.0	-5.8	-1.8	1.75	Ref. [6]
${ m BaTiO}_3$	7.45	2.77	7.25	-5.71	-2.15	1.81	$\mathbf{Present}$
		2.75	7.16	-5.69	-2.11	1.79	Ref. [313]
$\mathrm{BaZrO}_3$	7.85	2.73	6.03	-4.74	-2.01	1.51	Ref. [313]
$PbTiO_3$	7.35	3.90	7.06	-5.83	-2.56	1.77	Ref. [313]
$PbZrO_3$	7.77	3.92	5.85	-4.81	-2.48	1.46	Ref. [313]
nominal		1	5	-2	-2		
$\mathrm{NaNbO}_3$	7.40	1.13	9.11	-7.01	-1.61	1.82	Ref. [313]
$\mathrm{KNbO}_3$	7.47	0.82	9.13	-6.58	-1.68	1.83	Ref. [242]
		1.14	9.23	-7.01	-1.68	1.85	Ref. [313]
		1.14	9.37	-6.86	-1.65	1.87	Ref. [309]
nominal		-	6	-2	-2		
WO <sub>3</sub>	7.05	-	12.51	-9.13	-1.69	2.09	Ref. [56]

Results obtained within the model of Harrison are reported in Appendix B.2<sup>16</sup>. They can be summarized as follows. Within the bond orbital model, ABO<sub>3</sub> compounds are described as mixed ionic-covalent crystals. It is assumed that the A atom is fully ionized so that it has no other role than to provide electrons to the system. In contrast, it is considered that there is some covalency between B and O atoms, described by including O 2s, O 2p and B d orbitals interacting through matrix elements  $V_{spd\sigma}$  and  $V_{pd\pi}$  (see Appendix B.2). Due to these orbital interactions, the transfer of electrons from the B atom to oxygen is not complete: for the particular case of SrTiO<sub>3</sub>, from the parameters of Mattheiss [190], we obtain a static effective charge on O equal to -0.97 (instead of -2). The estimation of the Born effective charge now requires to add to the previous static charge, the dynamic contribution induced by the evolution of the interactions parameters with the bond length as explained in Section 5.3.2. For SrTiO<sub>3</sub>, following the idea of Harrison, we get a value of -8.18 for  $Z_{O\parallel}^*$ .

So, the Harrison model make plausible the giant anomalous effective charges by focusing only on the dynamic changes of hybridization between occupied O 2s-O 2p states and the unoccupied metal d states. In BaTiO<sub>3</sub>, the hybridization between these orbitals is a well known feature, confirmed by experiments [205, 124], LCAO calculations [190, 219, 220] and DFT results [296, 43]. In this context, it seemed therefore realistic to restrict to O 2p -B d hybridization changes to explain intuitively large anomalous contributions [313].

Posternak *et al.* [221] went beyond this credible assumption. For KNbO<sub>3</sub>, they demonstrated that the anomalous contribution to the charge of Nb and  $O_{\parallel}$  disappears if the hybridization between O 2p and Nb 4d orbitals is artificially suppressed. It was a convincing proof of the crucial role of the hybridizations.

In what follows, we will propose a band-by-band decomposition of the Born effective charges [71, 72]. This technique will appear 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.

# 5.6 The band-by-band decomposition

In ABO<sub>3</sub> compounds, the electronic band structure is composed of relatively well separated sets of bands (see Chapter 3). The hybridizations between the orbitals of the different atoms are relatively small and each band can

<sup>&</sup>lt;sup>16</sup> It follows the method described by Harrison for KCl in Ref. [113], p. 334.

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 here to identify the contribution of each well separated set of bands to this change of polarization [71, 72].

#### 5.6.1 A reference configuration

In order to assign a physical meaning to our decomposition, we define a reference configuration, in which the contribution to the effective charge of a given atom is -2 for each band associated to its own orbitals and 0 for the other bands. In this particular configuration, the center of the Wannier function associated to each given set of bands is centered on an atom and remains centered on it: in other words, those centered on the moving atom will remain centered on it, while the position of the center of gravity of the other bands will remain unaffected. This reference case corresponds to what would be observed in a purely ionic material where each band is composed of a single non-hybridized orbital.

In this context, the *anomalous* contribution of a particular band m to a given atom  $\kappa$  is defined as the additional part with respect to our reference value and reflects how the center of the Wannier function of band m is displaced from its centered position when atoms  $\kappa$  move. For a single isolated band, this anomalous contribution corresponds to a meaningful quantity: it is equal to  $(-2 \ \Delta d)$ , where  $\Delta d$  is the displacement of the Wannier center of this band.

In the reference configuration, each band had a well defined single orbital character. The 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. It can be visualized as a transfer of charge.

#### **5.6.2 BaTiO**<sub>3</sub>

The band structure of BaTiO<sub>3</sub> is presented in Fig. 5.1. Results of the decomposition <sup>17</sup> of  $Z^*$  in the theoretical cubic structure of BaTiO<sub>3</sub> are reported in Table 5.4. The first line  $(Z_{\kappa})$  brings together the charge of the nucleus and of the core electrons included in the pseudopotential. The other contributions come from the valence electron levels. The sum of the band by band contributions on one atom is equal to its global effective

<sup>&</sup>lt;sup>17</sup>Rigorously, our band by band decomposition was performed within DFT and only concerns the Kohn-Sham electrons. It seems however that the results are rather independent of the one-particle scheme [189] used for the calculation.



Figure 5.1: Kohn-Sham electronic band structure of BaTiO<sub>3</sub>.

charge while the sum of the contribution to a particular band from the different atoms is equal to -2 (within the accuracy of the calculation), the occupancy of this band.

For titanium, the Ti 3s contribution is close to -2, confirming that these electrons follow the Ti atom when it moves, independently from the change of its surrounding. This result a *posteriori* justifies the inclusion of deeper electronic levels as part of the ionic pseudopotentials. At the opposite, it is shown that the giant anomalous charge of titanium essentially comes from the O 2p bands. 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 dynamic 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. Beyond this model, we note however 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<sup>18</sup>. They suggest other kind of hybridization changes, that will be now more explicitly investigated.

 $<sup>^{18}</sup>$  Within the Harrison model, anomalous contributions to  $Z^*_{Ti}$  in Table 5.4 would restrict to the O 2p and O 2s bands.

Dond	7*	7*	7*	7*	Total
Dalid	$^{Z}Ba$	$z_{Ti}$	<sup>2</sup> 0-	$Z_{O_{\parallel}}$	Total
$Z_{\kappa}$	+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 5.4: Band by band decomposition of  $Z^*$  in the optimized cubic phase of BaTiO<sub>3</sub>. The contributions have been separated into a reference value and an anomalous charge (see text).

For barium, the global anomalous effective charge (+0.77) is small and this feature was sometimes attributed to its more ionic character [313]. This ionicity is inherent to the Harrison model [113] and was confirmed in some ab initio studies [43, 44]. 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 dynamic 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. Our result so supports the hybridization of Ba orbitals, in agreement with various independent results discussed in Chapter 3 (experiment [205, 124], LCAO calculations [219, 220], DFT [296] computations). Similar compensating contributions were recently observed in BaO [223], pointing out the existence of O 2p – O 2s interactions.

We note that a confusion sometimes appears that should be removed: the *amplitude* of the anomalous contributions to  $Z^*$  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 BaTiO<sub>3</sub>, the Ba 5p contribution to the O 2p bands is smaller than the contribution from the Ti 3d orbitals [296, 43]. However, the high sensitivity of this relatively weak covalent character under atomic positions is sufficient to produce large band by band anomalous contributions to  $Z^*$ . 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  $O_{-}$  are defined respectively for a displacement of O in the Ti and Ba direction, it seems only qualitative to associate  $Z_{O_{\parallel}}^{*}$  with  $Z_{Ti}^{*}$  and  $Z_{O_{-}}^{*}$  with  $Z_{Ba}^{*}$  as suggested in Ref. [313]. The O 2p anomalous contributions to Ti and  $O_{\parallel}$  do not exactly compensate. Moreover, O 2p contribution to  $Z_{Ba}^{*}$  does not come from  $O_{-}$  only but has equivalent contributions from  $O_{\parallel}$ . This seems to confirm the idea of Bennetto and Vanderbilt [15] 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 BaTiO<sub>3</sub>: 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 indeed that the presence of a large anomalous charge requires a modification of the interactions between occupied and unoccupied electronic state, while the contributions originating from the change of the interactions between two occupied states compensate, and do not modify the global value of  $Z^*$ .

A similar compensation of different anomalous contributions was observed recently in ZnO which has conventional Born effective charges [189] and in a series of alkaline-earth oxides [223].

#### **5.6.3** SrTiO<sub>3</sub>

The same analysis was performed on  $\mathrm{SrTiO}_3$ . Its band structure (Fig. 5.2) is very similar than for  $\mathrm{BaTiO}_3$ , except that the Ti 3p and Sr 4s 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 also in the same energy region but can be separated, contrary to what was observed independently for SrO [223].

The result of the decomposition is strongly similar (Table 5.5) to that reported for BaTiO<sub>3</sub>. There is still a giant contribution to  $Z_{Ti}^*$  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 BaTiO<sub>3</sub>, the Sr 4p electrons are closer to the O 2s bands and mainly hybridize with them in SrTiO<sub>3</sub>. This phenomenon produces large but compensating contributions from Sr 4p and O 2s bands to  $Z_{Sr}^*$ . Such an evolution is in agreement with the picture that anomalous contributions originate in the orbital hybridization changes.



Figure 5.2: Kohn-Sham electronic band structure of SrTiO<sub>3</sub>.

#### 5.6.4 Other examples

From the two previous results that concern two very similar materials, it should be suggested that not only the dynamic hybridization of the valence bands with unoccupied d-states but also the particular cubic perovskite structure of ABO<sub>3</sub> compounds plays a major role in determining  $Z^*$ . In particular, the displacement of the center of gravity of a band that was understood by a transfer of charge could also alternatively be visualized by displacement of the electronic cloud as a whole due to the local field at the atomic site that is known to be large in this structure [272]<sup>19</sup>.

The role of the hybridization seems however of paramount importance. It was demonstrated by Posternak *et al.* [221] (see also Ref. [244]). Moreover, as a complementary argument, it is interesting to observe that anomalous charges are not restricted to perovskite solids but were also detected in a series of alkaline-earth oxides of rocksalt structure (CaO, SrO, BaO) [222, 223] or even Al<sub>2</sub>Ru [209, 234], 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 TiO<sub>2</sub> rutile and SiO<sub>2</sub> stishovite [163, 164]: 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 BaTiO<sub>3</sub>, were obtained on Ti (+7.33) and O (-4.98) along the Ti-O bond in

<sup>&</sup>lt;sup>19</sup>This picture is that which more naturally arise from the shell-model approach.

0 + 0.56

+2.56

O 2p

Total

Band	$Z^*_{Sr}$	$Z_{Ti}^*$	$Z_{O_{-}}^{*}$	$Z_{O_{\parallel}}^{*}$	Total
$Z_{\kappa}$	+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
$\left. \begin{array}{c} \mathrm{Sr} \ \mathrm{4s} \\ \mathrm{Ti} \ \mathrm{3p} \end{array} \right\}$	-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

6 - 0.12

2.15

6 - 3.41

-5.73

0 + 3.08

+7.26

Table 5.5: Band by band decomposition of  $Z^*$  in the experimental cubic phase of  $SrTiO_3$ . The contributions have been separated into a reference value and an anomalous charge (see text).

rutile. Similarly, no anomalous charge was reported for MgO  $(Z_O^* = -2.07)$ , presenting the same rocksalt structure than BaO  $(Z_O^* = -2.80)$  [223]. In the family of ABO<sub>3</sub> compounds, giant effective charges are observed on Ti in CaTiO<sub>3</sub>  $(Z_{Ti}^* = 7.08, [313])$  but not on Si in CaSiO<sub>3</sub>  $(Z_{Si}^* = 4.00, [273])$ .

In conclusion, we point out that the presence of partly hybridized dstates seems the only common feature between the materials presenting giant anomalous effective charges, listed up to date. This feature should find 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 [113]. They will therefore be associated to larger dynamic transfer of charge and will generate higher  $Z^*$ .

Anecdotally, let us finally mention that very surprising features were predicted by Resta and Sorella [244] in strongly correlated mixed covalent/ionic materials, from the study of one-dimensional two-band Hubbard model: they include a divergence of the Born effective charge around the transition from band to Mott insulators. Even if this phenomenon do not concern ABO<sub>3</sub> compounds, it suggests that Born effective charges should play an important role in highly correlated systems.

-18.01

+0.01

Table 5.6: Eigenvalues of the Born effective charge tensors of Ba and Ti in the three ferroelectric phases of BaTiO<sub>3</sub>. The z-axis points along the ferroelectric direction. In the cubic phase, we had:  $Z_{Ti}^* = 7.29$  and  $Z_{Ba}^* = 2.74$ .

phase	$Z_{Ti,xx}^*$	$Z^*_{Ti,yy}$	$\mathbf{Z}^*_{Ti,zz}$	$\mathbf{Z}^*_{Ba,xx}$	$Z^*_{Ba,yy}$	$\mathbf{Z}^*_{Ba,zz}$
tetragonal	6.94	6.94	5.81	2.72	2.72	2.83
$\operatorname{orthorhombic}$	6.80	6.43	5.59	2.72	2.81	2.77
$\mathbf{r}$ hombohedral	6.54	6.54	5.61	2.79	2.79	2.74

#### 5.7 Sensitivity to structural features

In the literature, calculations of  $Z^*$  essentially focused on the cubic phase of ABO<sub>3</sub> compounds [242, 70, 313, 71, 72, 221, 231, 309]. On the basis of an early study of KNbO<sub>3</sub> [242], it was concluded that the Born effective charges are independent of the ionic ferroelectric displacements (i.e. they remain similar in the different phases). Another investigation in the tetragonal phase of KNbO<sub>3</sub> and PbTiO<sub>3</sub> [313], seemed to confirm that  $Z^*$ are quite insensitive to structural details. These results were surprising if we remember that anomalous contributions to  $Z^*$  are closely related to orbital hybridizations, these in turn, well known to be strongly affected by the phase transitions [43, 44]. We will see in this Section that, contrary to what was first expected,  $Z^*$  in BaTiO<sub>3</sub> are strongly dependent of the structural features.

We first investigate the sensitivity of the Born effective charges to the ferroelectric atomic displacements [72]. For that purpose, we compute  $Z^*$  in the three ferroelectric phases at the experimental unit cell parameters, with relaxed atomic positions (see Chapter 3). Tables 5.6 and 5.7 summarize the results for a cartesian set of axis where the z-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  $O_{-}$ , by analogy with the cubic phase.

Although the charges of Ba and  $O_{-}$  remain globally unchanged in the 4 phases, strong modifications are observed for Ti and  $O_{\parallel}$ : for example, changing the Ti position by 0.076 Å (2% of the unit cell length) when going

Table 5.7: Born effective charge tensor of the O atoms in the three ferroelectric phases of BaTiO<sub>3</sub>. Tensors are reported in cartesian coordinates, with the z-axis along the ferroelectric direction. The eigenvalues of the symmetric part of Z<sup>\*</sup> are mentioned in brackets; the eigenvector associated to the highest eigenvalue approximately points in the Ti direction. In the cubic phase, we had:  $Z_{O\parallel}^* = -5.75$  and  $Z_{O-}^* = -2.13$ .

-	T	. 1		0	1 1	1 •	DI	1 1	1 1
	Te	tragonal		Ort	thorhom	bic	Rhe	ombohec	iral
O <sub>1</sub>	$\left(\begin{array}{c} -1.99\\ 0\\ 0\end{array}\right)$	$0 \\ -1.99 \\ 0$	$\begin{pmatrix} 0\\ 0\\ -4.73 \end{pmatrix}$	$\left(\begin{array}{c} -2.04\\ 0\\ 0\end{array}\right)$	$0 \\ -3.63 \\ 1.57$	$\begin{pmatrix} 0\\ 1.38\\ -3.17 \end{pmatrix}$	$\left(\begin{array}{c} -2.54 \\ -0.99 \\ 0.72 \end{array}\right)$	$-0.99 \\ -3.68 \\ 1.25$	$\begin{pmatrix} 0.63 \\ 1.09 \\ -2.78 \end{pmatrix}$
	[ -1.99	-1.99	-4.73 ]	[ -1.91	-2.04	-4.89]	[ -1.97	-1.98	-5.05 ]
$O_2$	$\left(\begin{array}{c} -2.14\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -5.53 \\ 0 \end{array}$	$\begin{pmatrix} 0\\ 0\\ -1.95 \end{pmatrix}$	$\left(\begin{array}{c} -2.04\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -3.63 \\ 1.57 \end{array}$	$\begin{pmatrix} 0\\ 1.38\\ -3.17 \end{pmatrix}$	$\left(\begin{array}{c} -2.54\\ 0.99\\ 0.72\end{array}\right)$	$\begin{array}{c} 0.99 \\ -3.68 \\ -1.25 \end{array}$	$\begin{pmatrix} 0.63 \\ -1.09 \\ -2.78 \end{pmatrix}$
	[ -1.95	-2.14	-5.53 ]	[ -1.91	-2.04	-4.89]	[ -1.97	-1.98	-5.05 ]
$O_3$	$\left(\begin{array}{c} -5.53\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -2.14 \\ 0 \end{array}$	$\begin{pmatrix} 0\\ 0\\ -1.95 \end{pmatrix}$	$\left(\begin{array}{c} -5.44\\ 0\\ 0\end{array}\right)$	$\begin{array}{c} 0 \\ -1.97 \\ 0 \end{array}$	$\begin{pmatrix} 0\\ 0\\ -2.01 \end{pmatrix}$	$\left(\begin{array}{c} -4.25\\ 0\\ -1.44\end{array}\right)$	$\begin{array}{c} 0 \\ -1.97 \\ 0 \end{array}$	$\begin{pmatrix} -1.26 \\ 0 \\ -2.78 \end{pmatrix}$
	[ -1.95	-2.14	-5.53 ]	[ -1.97	-2.01	-5.44 ]	[ -1.97	-1.98	-5.05 ]



Figure 5.3: Born effective charge of Ti (opened symbols) and O (filled symbols) in the direction of the shortest Ti-O bond length  $d_{min}$  with respect to this interatomic distance for the cubic (square), tetragonal (lozenge), orthorhombic (circle) and rhombohedral (triangle) phases.

from the cubic to the rhombohedral phase, reduces the anomalous part of  $Z_{Ti}^*$  by more than 50% along the ferroelectric axis (Table 5.6). Equivalent evolutions are observed in the other ferroelectric phases. Similar dramatic changes were detected recently in KNbO<sub>3</sub> [292].

In the isotropic cubic structure, Harrison had explained the large value of  $Z^*$  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  $Z^*$  in terms of the distance  $d_{min}$ . The amplitude of  $Z_{Ti}^*$  and  $Z_O^*$  in the direction of the shortest Ti-O bond length of each phase is plotted in Fig. 5.3 with respect to  $d_{min}$ . 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  $Z^*$  under isotropic pressure (Table 5.8). In contrast with the changes observed with 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 that the shortest Ti-O bond length in the tetragonal structure  $^{20}$ ,  $Z_{Ti}^*$  remains

<sup>&</sup>lt;sup>20</sup>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 Åin our optimized tetragonal structure.

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

Table 5.8: Evolution of the Born effective charges of  $BaTiO_3$  under isotropic pressure in the cubic phase.

very close to its value at the optimized volume. This new element clearly invalidates the expected dependence from  $Z^*$  to  $d_{min}$  and invites us to go further in our investigations.

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  $Z^*$ in BaTiO<sub>3</sub> is not dependent on a particular interatomic distance  $(d_{min}, d_{max})$  but is critically affected by the anisotropy of the Ti environment along the Ti-O chains<sup>21</sup>.

A band by band decomposition of  $Z_{Ti}^*$  (Table 5.9) 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 dynamic transfer 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 dimere for which the electrons are less polarizable. This smaller polarizability will be confirmed in the next Chapter where we will report a similar reduction of the optical dielectric constant along the ferroelectric direction.

 $<sup>^{21}</sup>$ In agreement with this picture, Wang *et al.* [292] reported recently an insensitivity of  $Z^*$  to a tetragonal macroscopic strain in KNbO<sub>3</sub>.

	cubic	cubic	tetragonal	cubic
Band	$a_{o} = 3.67$ Å	$a_{o} = 3.94 \text{ \AA}$	(exp)	$a_o = 4.40 \text{ Å}$
$Z_{\kappa}$	+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
Ba $5s$	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 5.9: Band by band decomposition of  $Z_{Ti}^*$  in different structure of BaTiO<sub>3</sub>. The contributions have been separated into a reference value and an anomalous charge (see text).

Finally, let us mention that if the evolution of  $Z^*$  is relatively weak under isotropic pressure, it would be wrong to consider that the dynamic properties of BaTiO<sub>3</sub> are insensitive to the volume: small changes are observed that are of the same order of magnitude than for other compounds like SiC [291, 293]. The direction of the evolution is however different. Moreover, the evolution of the different charges is even not identical: while the absolute value of  $Z_{Ba}^*$  and  $Z_{O-}^*$  decreases with increasing volume, the inverse behaviour is observed for  $Z_{Ti}^*$  and  $Z_{O\parallel}^*$ .

Here also, the band by band decomposition (Table 5.10) 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 evolution of the interatomic short-range forces observed independently [73]. At the opposite, in our expanded cubic phase, most of the anomalous contributions to  $Z_{Ba}^*$  and  $Z_{Ti}^*$  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.

Table 5.10: Band by band decomposition of  $Z_{Ba}^*$  in the optimized cubic phase of BaTiO<sub>3</sub> and in an expanded cubic structure. The contributions have been separated into a reference value and an anomalous charge (see text).

	cubic	cubic
Band	$a_{o} = 3.94 \text{ Å}$	$a_{o} = 4.40$ Å
$Z_{\kappa}$	+10.00	+10.00
Ti 3s	0 + 0.01	0 -0.01
Ti 3p	0 + 0.01	0 + 0.01
Ba~5s	-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

### 5.8 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:

$$P_{s,\alpha} = \frac{1}{\Omega_o} \sum_{\kappa,\beta} Z^*_{\kappa,\alpha\beta} d\tau_{\kappa,\beta}$$
(5.38)

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: our calculation was performed by displacing the atoms to their theoretically optimized position in rhombohedral symmetry, when keeping the cubic lattice parameters <sup>22</sup>. The result is reported in Fig. 5.4 for  $Z_{Ti}^*$  along the ferroelectric direction. A similar curve should

 $<sup>^{22}\,\</sup>mathrm{The}\,\,\mathrm{Born}$  effective charges obtained for the rhombohedral structure when neglecting



Figure 5.4: Evolution of the amplitude of  $Z_{T_i}^*$  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.

be obtained for  $Z^*_{O\parallel}$ . We observe that the evolution of  $Z^*$  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.

Expecting a similar evolution of the dynamic charges for the tetragonal and orthorhombic displacements, an estimation of the spontaneous polarization in the ferroelectric phases can be found when using Eq. (5.38) with a mean effective charge determined from its value in both phases. Chosing  $Z^*_{mean} = 0.68 \times Z^*_{cubic} + 0.32 \times Z^*_{ferro}$ , we obtain the spontaneous polarizations presented in Table [5.11].

Our results are only in relative agreement with the experiment [301, 116] and suggest different comments. Firstly, we would like to mention that part of the discrepancy must be assigned to the overestimation of the computed ferroelectric displacements, that was discussed in Chapter 3: when using the experimental displacements of Ref. [117], we recover a better estimation of  $P_s$  as in Ref. [313]. The dispersion of X-rays diffraction data makes

the strain (i. e. when keeping a cubic unit cell) are the following:  $Z^*_{Ba,11} = +2.79$ ,  $Z^*_{Ba,33} = +2.79$ ,  $Z^*_{Ti,11} = +6.54$ ,  $Z^*_{Ti,33} = +5.61$ ,  $Z^*_{O,-} = -1.97$ ,  $Z^*_{O,\parallel} = -5.05$ . These values must be compared to those reported in Tables 5.6–5.7, where the rhombohedral strain was taken into accounts. It can be checked that effect of this strain is negligible.

Table 5.11: Spontaneous polarization in the three ferroelectric phases of BaTiO<sub>3</sub> in  $\mu$ C/cm<sup>2</sup>. The results were deduced from Eq. (5.38) when using the Z<sup>\*</sup> of the cubic phase (Cubic) or a mean charge (Mean) estimated from the values an the para- and ferro-electric phases (see text). Estimations are reported from the experimental and theoretical atomic ferroelectric displacements.

	Exp. [301]	Ref. [313]	$\mathbf{Present}$	Present	Present
$Z^*$		Cubic	Cubic	Mean	Mean
$\operatorname{positions}$		$\operatorname{Exp}$	Opt	Opt	Exp
Tetragonal	26.3	30	36.35	34.02	28.64
Orthorhombic	30.7	26	42.78	39.68	36.11
Rhombohedral	33.5	44	43.30	40.17	-

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 as discussed in Chapter 8 [94]. Finally, we note that there is also some uncertainty on the experimental value of  $P_s$ .

# 5.9 Role of the Born effective charge in the lattice dynamics

In this Chapter, we focused on the *microscopic* mechanisms that govern the amplitude of the Born effective charges and this analysis brought to light some interesting physics concerning  $ABO_3$  compounds.  $Z^*$  however also monitors the amplitude of the long range Coulomb part of the interatomic forces and its knowledge is a prerequisite to any lattice dynamics study.

In Chapter 8, we will emphasize that the anomalously large Born effective charges produce a giant LO-TO splitting in ABO<sub>3</sub> compounds, specially for the ferroelectric phonon mode [313, 73]. We will demonstrate that this feature is associated to the existence of an anomalously large destabilizing dipole-dipole interaction, sufficient to compensate the stabilizing short-range force and induce the ferroelectric instability. Anticipating what will be discussed later, we note that, in this context, the Born effective charge will appear as the key concept to relate the electronic and structural properties.

#### 5.10 Conclusions

In this Chapter, we have illustrated that the Born effective charge is a dynamic concept: it differs from the conventional static charges by a contribution originating in dynamic transfer of charge. We have reported how the Born effective charges can be obtained within an ab initio framework. We have highlighted their significance in terms of Wannier functions.

Summarizing various recent results, we have shown that the Born effective charges are anomalously large in the family of ABO<sub>3</sub> compounds: their amplitude can reach more than twice the nominal ionic charge. This surprising feature was explained in terms of transfers of charge, produced by dynamic changes of hybridization. For BaTiO<sub>3</sub> and SrTiO<sub>3</sub>, we have brought to light complex dynamic 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 the total value of  $Z^*$  is finally essentially affected by dynamic changes of hybridization between O 2p and Ti 3d orbitals.

As a more general issue, we suggest 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 dynamic transfers of charge are expected to be larger when such hybridization involve d states, for which the interactions parameters with other orbitals are particularly sensitive to the interatomic distance.

Investigating the evolution of  $Z^*$  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  $Z^*$  is not monitored by a particular interatomic distance but is affected by 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 displacement from the cubic to the rhombohedral structure.

In Chapter 7, we will show that the anomalous effective charge are at the origin of a giant dipole-dipole interaction able to induce the ferroelectric instability.

#### 5.11 References

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

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140

# Chapter 6

# The optical dielectric tensor

# 6.1 Introduction

The dielectric tensor is a macroscopic concept, introduced in electrostatics to relate, in the linear regime, the electric field to the displacement field. From the definition of the displacement field, it is directly related to the dielectric susceptibility and globally describes the screening of a macroscopic electric field in a polarizable medium. It appears therefore as a fundamental quantity that characterizes this medium.

In solids, both the electrons and the ions may polarize under the action of a macroscopic electric field. In the present Chapter, we will be only concerned in the contribution to the dielectric tensor due to the electronic polarization. We will see later that the identification of this electronic part is mandatory to describe correctly the long range Coulomb part of the interatomic force constants in polar materials.

Experimentally, the electronic contribution to the dielectric tensor can be isolated and measured for frequencies of the applied field sufficiently high to get rid of the ionic contributions, but not high enough for causing direct electronic excitations. It is usually referred to as the high frequency or optical dielectric response and it is noted  $\epsilon_{\alpha\beta}^{\infty}$ . In our theoretical approach where the ions can be artificially clamped, the same quantity can be deduced when computing the electronic response to a static field. In a next Chapter, we will take care of the supplementary contributions from the ionic displacements and we will indicate how to deduce the static dielectric response  $\epsilon_{\alpha\beta}^{\circ}$ .

141

The optical dielectric tensor can be formulated in terms of a second derivative of the electronic energy. We will first report how it can be computed within the variational approach to the density functional perturbation theory. This formalism, implemented within the local density approximation, will then be applied to  $BaTiO_3$ .

As a ground-state property, the dielectric response should be *a priori* correctly reproduced within the density functional formalism [51]. However, for BaTiO<sub>3</sub>, we will observe that the computed value largely overestimates the experiment. Similar discrepancies (more than 10%) are usual in a large variety of materials and exceed the error reported for other properties, computed within the same local density approximation. We recently addressed the origin of this problem [94]: it will be discussed in Chapter 8.

Anticipating on this further discussion, we would like to stress that the formalism presented in this Chapter is coherent within the local density approximation that still remains a standard for DFT calculations. We note also that the more sophisticated generalized gradient approximations have no specific reason to improve directly the result.

# 6.2 The linear response formalism

Within the electrostatics, the macroscopic displacement field  $\mathcal{D}$ , the macroscopic electric field  $\mathcal{E}$  and the macroscopic polarization  $\mathcal{P}$  are related through the following expression:

$$\mathcal{D}_{\alpha} = \mathcal{E}_{\alpha} + 4\pi \mathcal{P}_{\alpha} \tag{6.1}$$

while the dielectric tensor is introduced as

$$\epsilon_{\alpha\beta} = \frac{\partial \mathcal{D}_{\alpha}}{\partial \mathcal{E}_{\beta}} \bigg|_{\mathcal{E}=0}$$
(6.2)

In Chapter 4, we have seen that the electronic contribution to the macroscopic dielectric tensor can be formulated in terms of a second partial derivative of the electric enthalpy with respect to the macroscopic electric field  $\mathcal{E}$ . In this context, following the notations introduced in Section 4.2, we can write:

$$\epsilon_{\alpha\beta}^{\infty} = \delta_{\alpha\beta} - \frac{4\pi}{\Omega} \frac{\partial \tilde{E}_{e+i}}{\partial \mathcal{E}_{\alpha} \partial \mathcal{E}_{\beta}}$$
$$= \delta_{\alpha\beta} - \frac{4\pi}{\Omega} 2.\tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\beta}}$$
(6.3)

Within the formalism of Chapter 4,  $\tilde{E}_{el}^{\mathcal{E}^*_{\alpha}\mathcal{E}_{\beta}}$  can be formulated in terms of a stationary expression, involving the first-order wavefunctions with respect

142

to the electric field  $(|u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}}\rangle)$  and  $|u_{m\mathbf{k}}^{\mathcal{E}_{\beta}}\rangle)$  and to their wave-vector  $(|u_{m\mathbf{k}}^{k_{\alpha}}\rangle)$  and  $|u_{m\mathbf{k}}^{k_{\beta}}\rangle)$ :

$$\begin{split} \tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\beta}}\left\{u^{(0)}; u^{\mathcal{E}_{\alpha}}, u^{\mathcal{E}_{\beta}}\right\} &= \frac{\Omega_{0}}{(2\pi)^{3}} \int_{\mathrm{BZ}} \sum_{m}^{\mathrm{occ}} s\left(\langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\mathcal{E}_{\beta}} \rangle \right. \\ &+ \left\langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | i u_{m\mathbf{k}}^{k_{\beta}} \rangle + \left\langle i u_{m\mathbf{k}}^{k_{\alpha}} | u_{m\mathbf{k}}^{\mathcal{E}_{\beta}} \rangle \right) d\mathbf{k} \\ &+ \frac{1}{2} \int_{\Omega_{0}} K_{\mathrm{xc}}^{LDA}(\mathbf{r}, \mathbf{r}) \left[ n^{\mathcal{E}_{\alpha}}(\mathbf{r}) \right]^{*} n^{\mathcal{E}_{\beta}}(\mathbf{r}) d\mathbf{r} \\ &+ 2\pi\Omega_{0} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{[n^{\mathcal{E}_{\alpha}}(\mathbf{G})]^{*} n^{\mathcal{E}_{\beta}}(\mathbf{G})}{|\mathbf{G}|^{2}}. \end{split}$$
(6.4)

Making use of the interchange theorem, one can also deduce a much simpler non-stationary formula:

$$\tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\beta}}\left\{u^{(0)}; u^{\mathcal{E}_{\alpha}}\right\} = \frac{\Omega_{0}}{(2\pi)^{3}} \int_{BZ} \sum_{m}^{\circ cc} s \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | i u_{m\mathbf{k}}^{k_{\beta}} \rangle d\mathbf{k}$$
(6.5)

In this last expression,  $\tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\beta}}$  appears more explicitly related to the change of macroscopic polarization in direction  $\beta$  induced by a macroscopic electric field  $\mathcal{E}_{\alpha}$ . Here, the knowledge of  $u^{\mathcal{E}_{\alpha}}$ , the first-order derivative of the wavefunctions with respect to an electric field along direction  $\alpha$ , allows us to compute the elements of the dielectric permittivity tensor  $\epsilon_{\alpha\beta}$ , for  $\beta = 1, 2$  or 3, provided that the derivative of the unperturbed wavefunction with respect to their wavevector along  $\beta$  is also known. This expression is particularly useful to determine the full dielectric tensor with minimal computational effort.

# 6.3 The "scissors" correction

Because the agreement between the LDA dielectric permittivity tensor and the experiment was not satisfactory, Levine and Allan have introduced a *scissors operator* correction to the LDA [166, 167]. This correction has been shown to lead to an improved agreement between theory and experiment for many semiconductors. Some cases of negative results have however also been reported, specially for wide bandgap semiconductors. The reasons of the partial failure of LDA, and the role that plays the *scissors* correction in this context, will be discussed in Chapter 8.

Independently from the justification of the correction, the modifications of the equations needed to incorporate a *scissors* operator, are rather simple and can be addressed here. It is well known that the DFT bandgap may not be assimilated to the quasi-particle bandgap, experimentally measured. The correction that was proposed basically consists in adjusting the DFT bandgap to the experimental value. Supposing that the gap between the valence and conduction states must be artificially increased from  $E_g^{\text{LDA}}$  to  $E_g^{\text{LDA}} + \Delta_{SCI}$ , then Eq. (6.4) is slightly modified and becomes

$$\tilde{E}_{SCI}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\beta}}\left\{u^{(0)}; u^{SCI,\mathcal{E}_{\alpha}}, u^{SCI,\mathcal{E}_{\beta}}\right\} = \frac{\Omega_{0}}{(2\pi)^{3}} \int_{BZ} \sum_{m}^{\circcc} s\left(\left\langle u_{m\mathbf{k}}^{SCI,\mathcal{E}_{\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} + \Delta_{SCI} | u_{m\mathbf{k}}^{SCI,\mathcal{E}_{\beta}} \right\rangle + \left\langle u_{m\mathbf{k}}^{SCI,\mathcal{E}_{\alpha}} | i u_{m\mathbf{k}}^{k_{\beta}} \right\rangle + \left\langle i u_{m\mathbf{k}}^{k_{\alpha}} | u_{m\mathbf{k}}^{SCI,\mathcal{E}_{\beta}} \right\rangle\right) d\mathbf{k} + \frac{1}{2} \int_{\Omega_{0}} K_{xc}^{LDA}(\mathbf{r},\mathbf{r}) \left[ n_{SCI}^{\mathcal{E}_{\alpha}}(\mathbf{r}) \right]^{*} n_{SCI}^{\mathcal{E}_{\beta}}(\mathbf{r}) d\mathbf{r} + 2\pi\Omega_{0} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{[n_{SCI}^{\mathcal{E}_{\alpha}}(\mathbf{G})]^{*} n_{SCI}^{\mathcal{E}_{\beta}}(\mathbf{G})}{|\mathbf{G}|^{2}}.$$
(6.6)

The equation of Chapter 4 to be minimized in order to obtain  $u_{m\mathbf{k}}^{\text{SCI},\mathcal{E}_{\alpha}}$  must be replaced by Eq. (6.6) where  $\beta = \alpha$ . The associated Euler-Lagrange equation is <sup>1</sup>:

$$P_{c,\mathbf{k}} \left( H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m,\mathbf{k}}^{(0)} + \Delta_{SCI} \right) P_{c,\mathbf{k}} \left| u_{m,\mathbf{k}}^{\mathrm{SCI},\mathcal{E}_{\alpha}} \right\rangle \\ = -P_{c,\mathbf{k}} \left( i \frac{\partial}{\partial k_{\alpha}} + v_{\mathrm{H}}^{'\mathrm{SCI},\mathcal{E}_{\alpha}} + v_{\mathrm{xc}}^{\mathrm{SCI},\mathcal{E}_{\alpha}} \right) \left| u_{m,\mathbf{k}}^{(0)} \right\rangle.$$
(6.7)

Because of the positive-definiteness of the term governed by  $\Delta_{SCI}$  in the quadratic form underlying  $\tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\alpha}}$ , it is straightforward that if  $\Delta_{SCI}$  is positive, the dielectric permittivity constant along any direction is *always* smaller with the additional *scissors* correction than in the local density approximation.

# 6.4 The case of BaTiO<sub>3</sub>

The previous formalism is now applied to  $BaTiO_3$ . Theoretical results are reported for its four phases and compared to the experimental data. In our calculations, plane-waves were expanded up to a 35Ha cutoff and integrals

<sup>&</sup>lt;sup>1</sup>The notations have been defined in Chapter 4. As usual, the "prime" indicates that the G=0 contribution has been omitted.

Table 6.1: Optical dielectric constant in the cubic phase of BaTiO<sub>3</sub> obtained within the local density approximation (LDA) or with an additional scissors correction  $(LDA + \Delta_{SCI})$ .

$\operatorname{Method}$	$a_o = 3.67$ Å	a <sub>o</sub> =3.94 Å	$a_o = 4.00$ Å	$a_o = 4.40$ Å
LDA	6.60	6.66	6.73	7.75
$LDA + \Delta_{SCI}$	5.71	5.60	5.61	—
Exp. [22]	—	—	5.40	—

over the Brillouin zone were replaced by sums on a  $6 \times 6 \times 6$  mesh of special k-points (see Appendix A). These parameters guarantee a convergence better than 2%.

In the cubic structure, the dielectric tensor reduces to a scalar. Our results are reported in Table6.1. Within the LDA, the values obtained at the experimental  $(a_o=4.00 \text{ Å})$  and theoretical  $(a_o=3.94 \text{ Å})$  lattice constant are respectively equal to 6.73 and 6.66<sup>2</sup>. In comparison, the dielectric constant can be estimated from the experiment, by extrapolating to zero frequency, using a one oscillator Sellmeyer equation [59], refractive index measurements at different wavelengths. The data of Burns and Dacol [22] yield a value of 5.38.

Our computations at both volume greatly overestimate the macroscopic experimental constant. This could be partly due to the fact that our calculations prefigure a solid at 0 K while the experiment was done at 150° C. Nevertheless, as it was mentioned in the Introduction, it is likely to be assigned to the LDA. It can be corrected in first approximation by using the previously described scissor correction proposed by Levine and Allan [166]. When including in the calculation a k-independent scissors shift  $\Delta_{SCI} = 1.36$  eV, that adjusts the LDA bandgap at the  $\Gamma$  point (1.84 eV) to its experimental value of 3.2 eV [295], we find  $\epsilon_{\infty}^{SCI} = 5.60$  at the experimental volume. The discrepancy has then been reduced to less than 5 %.

In our compressed cubic phase, with  $a_o=3.67$  Å, we obtain a value of 6.60 ( $\epsilon_{\infty}^{SCI} = 5.71$ )<sup>3</sup>. Surprinsigly, this result remains very close to that

 $<sup>^{2}</sup>$ The Hartree and exchange-correlations terms of Eq. (6.4) are sometimes referred to as the "local fields effects". These terms lower the value of the dielectric constant by about 4%.

<sup>&</sup>lt;sup>3</sup>We note the different correction induced by the same scissor shift at different vol-
Table 6.2: Eigenvalues of the Born effective charge tensors in the three ferroelectric phases of  $BaTiO_3$ , obtained within the local density approximation (LDA) or with an additional scissors correction (LDA+ $\Delta_{SCI}$ ). For each phase, the eigenvector of  $\epsilon_{zz}^{\infty}$  points along the ferroelectric direction.

Phase	Method	$\epsilon_{xx}^{\infty}$	$\epsilon_{yy}^{\infty}$	$\epsilon_{zz}^{\infty}$
Tetragonal	LDA	6.47	6.47	5.74
	$LDA + \Delta_{SCI}$	5.44	5.44	4.97
	Exp. [264]	5.19	5.19	5.05
Orthorhombic	LDA	6.35	6.07	5.64
	$LDA + \Delta_{SCI}$	5.36	5.20	4.89
Rhombohedral	LDA	6.16	6.16	5.69
	$LDA + \Delta_{SCI}$	5.26	5.26	4.91

obtained at the experimental volume. It reveals a relative insensitivity to isotropic compression already observed for the Born effective charges. At the large lattice constant of 4.40 Å, the dielectric constant has increased coherently with a reduction of the indirect gap between  $\Gamma$  and R from 1.74 eV to 1.16 eV.

In the three axial ferroelectric phases, the dielectric tensor does not reduce to a scalar any more and independent elements must be considered. The tensor diagonalizes when the z-axis is taken along the ferroelectric direction. The eigenvalues of the dielectric tensor are reported in Table 6.2. The values with scissor correction were deduced with the same shift,  $\Delta_{SCI} = 1.36$  eV, than for the cubic phase <sup>4</sup>.

We observe that the permittivity is globally smaller than in the cubic phase. This is specially true along the ferroelectric direction were the value are respectively equal to 5.74 ( $\epsilon_{\infty}^{SCI} = 4.97$ ), 5.64 ( $\epsilon_{\infty}^{SCI} = 4.89$ ) and 5.69 ( $\epsilon_{\infty}^{SCI} = 4.91$ ) for the tetragonal, orthorhombic and rhombohedral phases respectively. This evolution contrasts with the insensitivity under isotropic pressure observed in the cubic phase: here also, it is a behaviour similar to that reported for the Born effective charges in the previous Chapter.

Experimentally, a reduction of the refractive index n ( $\epsilon_{\infty} = n^2$ ) was

umes. This was already observed by Levine and Allan [167]. In our compressed phase, the gap is direct at  $\Gamma$  and equal to 1.87 eV.

<sup>&</sup>lt;sup>4</sup>This hypothesis is questionable. In the tetragonal phase it corrects the indirect gap between  $\Gamma$  and A from 2.27 to 3.63 eV, a value that seems slightly larger than that observed experimentally for this phase [295].

observed coherently with our results when going from the cubic to the ferroelectric tetragonal phase [162]. The experimental data [162, 264, 294, 135] also agree with a more important reduction of the dielectric tensor in the direction of the ferroelectric axis.

A simple explanation can be suggested to explain the evolutions of  $\epsilon_{\infty}$ . A band by band analysis reveals that the dielectric response of BaTiO<sub>3</sub> originates essentially in the polarizability of the electrons of the O 2p bands. These bands are mainly composed of O 2p orbitals partly hybridized with Ti 3d orbitals (see Chapter 3). In the cubic phase, all the Ti-O distances are equivalent and the O 2p electrons are widely delocalized. In the ferroelectric phases, the Ti atom is displaced with respect to its centrosymmetry position and it was shown that the O 2p - Ti 3d orbitals hybridization is modified. The asymmetry slightly breaks some bonds, the O 2p electrons are more localized. This should explain that their polarizability is smaller.

# 6.5 Conclusions

In this Chapter, we have reformulated the dielectric tensor introduced in electrostatics in terms of quantities accessible within a first-principles approach. We have described how the electronic contribution to this tensor can be computed within the variational approach to the density functional perturbation theory. We also briefly discussed the implementation of a *scissors* correction.

The optical dielectric tensor has been computed for the four phases of  $BaTiO_3$ . Its knowledge will be useful to treat correctly the long-range part of the interatomic force constants in the next Chapter. We observe that the dielectric tensor has some common features with the Born effective charges: it is relatively insensitive to isotropic compression but becomes highly anisotropic in the ferroelectric phases. In particular, the polarizability of the electrons is always smaller along the ferroelectric direction.

### 6.6 References

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

- Ghosez Ph., X. Gonze and J.-P. Michenaud, A microscopic study of barium titanate, Ferroelectrics 164, 113 (1995).
- ◊ Ghosez Ph., X. Gonze and J.-P. Michenaud, Coulomb interaction and ferroelectric instability of BaTiO<sub>3</sub>, Europhys. Lett. **33**, 713 (1996).

 Ghosez Ph., X. Gonze and J.-P. Michenaud, Lattice dynamics and ferroelectric instability of barium titanate, Ferroelectrics 194, 39 (1997).

# Chapter 7

# Phonons

# 7.1 Introduction

BaTiO<sub>3</sub> 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 [171]. Among all these works, the most gratifying explanation is probably due to Cochran [39] who realized that the problem could be interestingly recast in the framework of lattice dynamics<sup>1</sup>. 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 [272], but it appeared more coherently within the shell-model. In spite of the qualitative character of Cochran's investigations, the delicate balance between shortrange repulsions and long-range destabilizing electrostatic forces is still now usually referred to as the origin of the ferroelectricity [41, 43, 315].

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 ABO<sub>3</sub> 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 BaTiO<sub>3</sub>. They include infra-red [178, 253, 254, 201] and Raman [215, 250, 133, 80, 154, 60, 204, 66] measurements of the  $\Gamma$  phonon modes as well as various neutron diffraction data [261, 306, 262, 109, 20, 134]. These experiments focused on the temperature behaviour of the soft phonon and were mainly concerned by the low frequency modes.

149

<sup>&</sup>lt;sup>1</sup>A similar approach was taken independently by Anderson [3].

Simultaneously, theoretical phonon dispersion curves of BaTiO<sub>3</sub> 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 [79] or the rigid-shell model used by Jannot *et al.* [134]. These models were however not particularly suited to describe the ABO<sub>3</sub> crystals. During the seventies, Migoni, Bilz and Bäuerle [196] pointed out that the behaviour of the ferroelectric soft mode in the oxidic perovskites originates from an unusual anisotropic polarizability of the oxygen that, in turn, may be connected to hybridization between O 2p and B d states. A more sophisticated "polarizability model" [18, 25] was then introduced in order to include the specific physical features of ABO<sub>3</sub> compounds. The application of this model to BaTiO<sub>3</sub> was reported by Khatib *et al.* [139]. 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  $\Gamma$  point have been computed for various ABO<sub>3</sub> compounds using frozen phonon or linear response techniques. Recently, *ab initio* phonon dispersion curves have been reported and analyzed for KNbO<sub>3</sub> [310] and SrTiO<sub>3</sub> [160]. We performed a similar study on BaTiO<sub>3</sub> [76]<sup>2</sup>.

In this Chapter, we will first describe how the phonon frequencies can be obtained within a first-principles approach. We shall then summarize various results concerning BaTiO<sub>3</sub>. We will report on the phonon frequencies at the  $\Gamma$  point in the cubic and rhombohedral structure. The phonon dispersion curves will then be deduced in the cubic phase. Interestingly, these results will appear very useful to address some open 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 [73]. In this framework, we will be able to clarify 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 a chain-structure correlation 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

<sup>&</sup>lt;sup>2</sup>Partial results are also available concerning the dispersion curves of  $PbTiO_3$  [235] and  $PbZrO_3$  [290].

with the existing "8-sites" model [46, 47] and the model of Hüller [125].

# 7.2 The dynamical equation

In Chapter 1, the movement of the ions was separated from that of the electrons. Up to now, we were essentially interested in the quantum mechanical description of the electrons and we have made the hypothesis that the ions sit without moving at sites  $\mathbf{R}$  of a Bravais lattice. In this chapter, we will relax this artificial assumption and describe the dynamics of the ions. We shall assume that the mean equilibrium position of each ion remains a Bravais lattice site, but that its instantaneous position may oscillate around this site. Their movement 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

$$E_{e+i}^{harm}(\{\Delta\boldsymbol{\tau}\}) = E_{e+i}^{(0)} + \sum_{a\kappa\alpha} \sum_{b\kappa'\beta} \frac{1}{2} \left(\frac{\partial^2 E_{e+i}}{\partial \tau^a_{\kappa\alpha} \partial \tau^b_{\kappa'\beta}}\right) \Delta \tau^a_{\kappa\alpha} \Delta \tau^b_{\kappa'\beta}$$
(7.1)

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

$$M_{\kappa\alpha} \frac{\partial^2 \Delta \tau^a_{\kappa\alpha}}{\partial t^2} = -\frac{\partial E_{e+i}^{\text{harm}}}{\partial \tau^a_{\kappa\alpha}}$$
(7.2)

for which we seek a general solution of the form:

$$\Delta \tau^a_{\kappa\alpha}(t) = \eta^a_m(\kappa\alpha) e^{-i\omega_m t} \tag{7.3}$$

Due to the lattice periodicity, the matrix of the second derivative of the energy appearing in Eq. (7.1) 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:

$$\Delta \tau^a_{\kappa\,\alpha}(t) = \eta_{m\mathbf{q}}(\kappa\alpha) \ e^{i\mathbf{q}\cdot\mathbf{R}_a} \ e^{-i\omega_m t} \tag{7.4}$$

for which the vibrations of the ions have been classified according to a wave vector. 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. 7.2) 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 vectors **q**. In practice, calculations will be restricted to a finite set of **q**-vectors.

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

$$C_{\kappa\alpha,\kappa'\beta}(a,b) = \left(\frac{\partial^2 E_{e+i}}{\partial \tau^a_{\kappa\alpha} \partial \tau^b_{\kappa'\beta}}\right),\tag{7.5}$$

while its Fourier transform takes the following form:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \frac{1}{N} \sum_{ab} C_{\kappa\alpha,\kappa'\beta}(a,b) e^{-i\mathbf{q}\cdot(\mathbf{R}_a - \mathbf{R}_b)} \\
= \sum_{b} C_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b} ,$$
(7.6)

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

$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) / (M_{\kappa}M_{\kappa'})^{1/2} .$$
(7.7)

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

$$\sum_{\kappa'\beta} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})\eta_{m\mathbf{q}}(\kappa'\beta) = M_{\kappa}\omega_{m\mathbf{q}}^2\eta_{m\mathbf{q}}(\kappa\alpha) .$$
(7.8)

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

$$\sum_{\kappa'\beta} \tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) \gamma_{m\mathbf{q}}(\kappa'\beta) = \omega_{m\mathbf{q}}^2 \gamma_{m\mathbf{q}}(\kappa\alpha) .$$
(7.9)

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:  $\gamma = \sqrt{M}.\eta$ .

# 7.3 The linear response approach

The basic ingredient required to compute the phonons is the interatomic force constant matrix  $\tilde{C}$ . From Eq. (7.5) it appears as a second-order derivative of the total energy with respect to collective atomic displacements of the type described in Chapter 4:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = 2E_{\mathrm{e}+\mathrm{i},-\mathbf{q},\mathbf{q}}^{\tau_{\kappa\alpha}^{*}\tau_{\kappa'\beta}} .$$
(7.10)

 $E_{e+i}$  is made of a contribution from the electron system and a contribution from the electrostatic energy between ions. Similarly, the  $\tilde{C}$  matrix can be split into two parts:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\mathrm{el},\kappa\alpha,\kappa'\beta}(\mathbf{q}) + \tilde{C}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q})$$
(7.11)

Each of these contributions will be computed separately.

### 7.3.1 The electronic contribution

The electronic contribution has a conventional form within density functional perturbation theory. Following the formalism introduced in Chapter 4,  $E_{e|,-\mathbf{q},\mathbf{q}}^{\tau_{\kappa\alpha}\tau_{\kappa'\beta}}$  can be formulated in terms of a stationary expression, involving the first-derivative of the wavefunctions with respect to an atomic displacement ( $|u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa\alpha}}\rangle$ ):

$$\begin{split} E_{\rm el}^{\tau_{\kappa\alpha}^{\star}\tau_{\kappa'\beta}} \{ u^{(0)}; u_{\rm q}^{\tau_{\kappa\alpha}}, u_{\rm q}^{\tau_{\kappa'\beta}} \} &= \\ & \frac{\Omega_{0}}{(2\pi)^{3}} \int_{\rm BZ} \sum_{m}^{\rm occ} s\left( \langle u_{m{\bf k},{\bf q}}^{\tau_{\kappa\alpha}} | H_{{\bf k}+{\bf q},{\bf k}+{\bf q}}^{(0)} - \epsilon_{m{\bf k}}^{(0)} | u_{m{\bf k},{\bf q}}^{\tau_{\kappa'\beta}} \rangle \right. \\ & \left. + \langle u_{m{\bf k},{\bf q}}^{\tau_{\kappa\alpha}} | v_{\rm ext,{\bf k}+{\bf q},{\bf k}}^{\tau_{\kappa'\beta}} | u_{m{\bf k}}^{(0)} \rangle + \langle u_{m{\bf k}}^{(0)} | v_{\rm ext,{\bf k},{\bf k}+{\bf q}}^{\tau_{\kappa'\beta}} \rangle \right. \\ & \left. + \langle u_{m{\bf k}}^{(0)} | v_{\rm ext,{\bf k}+{\bf q},{\bf k}}^{\tau_{\kappa'\beta}} | u_{m{\bf k}}^{(0)} \rangle \right) d{\bf k} \right. \\ & \left. + \frac{1}{2} \int_{\Omega_{0}} \left( \left[ \bar{n}_{{\bf q}}^{\tau_{\kappa\alpha}}({\bf r}) \right]^{*} \left[ \bar{v}_{{\rm xc0},{\bf q}}^{\tau_{\kappa'\beta}}({\bf r}) \right] + \left[ \bar{n}_{{\bf q}}^{\tau_{\kappa'\beta}}({\bf r}) \right] \left[ \bar{v}_{{\rm xc0},{\bf q}}^{\tau_{\kappa\alpha}}({\bf r}) \right]^{*} \right) d{\bf r} \\ & \left. + \frac{1}{2} \int_{\Omega_{0}} K_{{\rm xc}}^{LDA}({\bf r},{\bf r}) \left[ \bar{n}_{{\bf q}}^{\tau_{\kappa'}\beta}({\bf r}) \right]^{*} \bar{n}_{{\bf q}}^{\tau_{\kappa'\beta}}({\bf r}) d{\bf r} \right. \\ & \left. + \frac{1}{2} \frac{d^{2}E_{{\rm xc}}}{d\tau_{\kappa\alpha,{\rm r}-{\bf q}}d\tau_{\kappa\beta,{\bf q}}} \right|_{n^{(0)}} \end{split}$$

$$(7.12)$$

Using the interchange theorem, we obtain the following non-stationary expression:

$$E_{\mathrm{el},-\mathbf{q},\mathbf{q}}^{\tau_{\kappa\alpha}^{\star}\tau_{\kappa'\beta}}\left\{u^{(0)};u_{\mathbf{q}}^{\tau_{\kappa\alpha}}\right\} = \frac{\Omega_{0}}{(2\pi)^{3}} \int_{\mathrm{BZ}} \sum_{m}^{\mathrm{occ}} s\left(\left\langle u_{m\mathbf{k},\mathbf{q}}^{\tau_{\kappa'}} | v_{\mathrm{ext},\mathbf{k}+\mathbf{q},\mathbf{k}}^{\tau_{\kappa'}} | u_{m\mathbf{k}}^{(0)}\right\rangle + \left\langle u_{m\mathbf{k}}^{(0)} | v_{\mathrm{ext},\mathbf{k},\mathbf{k}}^{\tau_{\kappa'}\beta} | u_{m\mathbf{k}}^{(0)}\right\rangle\right) d\mathbf{k} + \frac{1}{2} \int_{\Omega_{0}} \left[\bar{n}_{\mathbf{q}}^{\tau_{\kappa\alpha}}(\mathbf{r})\right]^{*} \bar{v}_{\mathrm{xc0},\mathbf{q}}^{\tau_{\kappa'\beta}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \left. \frac{d^{2}E_{\mathrm{xc}}}{d\tau_{\kappa\alpha,-\mathbf{q}}d\tau_{\kappa\beta,\mathbf{q}}} \right|_{n^{(0)}}$$
(7.13)

From this last equation, a whole column of the dynamical matrix  $\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$  can be obtained from the knowledge of the first-order wavefunctions with respect to only one perturbation.

## 7.3.2 The ion-ion contribution

The ion-ion contribution to the unperturbed *total energy* per unit cell was obtained in Chapter 2 following the Ewald summation method. In a similar spirit, the contribution of the second derivative of the ion-ion energy to the matrix  $\tilde{C}_{\rm Ew}(\mathbf{q})$  can be computed following Ref. [183]:

$$\tilde{C}_{\mathrm{Ew},\kappa\,\alpha,\kappa'\beta}(\mathbf{q}) = \bar{C}_{\mathrm{Ew},\kappa\,\alpha,\kappa'\beta}(\mathbf{q}) - \delta_{\kappa\kappa'} \sum_{\kappa''} \bar{C}_{\mathrm{Ew},\kappa\,\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}).$$
(7.14)

The first term,  $\bar{C}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q})$ , can be formulated through the following expression:

$$\bar{C}_{\mathrm{Ew},\kappa\,\alpha,\kappa'\beta}(\mathbf{q}) = Z_{\kappa}Z_{\kappa'}\left(\sum_{\mathbf{K}=\mathbf{G}+\mathbf{q}}\frac{4\pi}{\Omega_{0}}\frac{K_{\alpha'}K_{\beta'}}{K^{2}}e^{i\,\mathbf{K}\cdot(\boldsymbol{\tau}_{\kappa}-\boldsymbol{\tau}_{\kappa'})}\exp(-\frac{K^{2}}{4\Lambda^{2}})\right)$$
$$-\sum_{a}\Lambda^{3}\,e^{i\,\mathbf{q}\cdot\mathbf{R}_{a}}\,H_{\alpha'\beta'}^{\mathrm{iso}}(\Lambda\mathbf{d}_{a,\kappa\kappa'}) - \frac{4}{3\sqrt{\pi}}\Lambda^{3}\,\delta_{\kappa\kappa'}\right)(7.15)$$

with

$$H_{\alpha\beta}^{\rm iso}(\mathbf{x}) = \frac{x_{\alpha}x_{\beta}}{x^2} \left(\frac{3}{x^3}\operatorname{erfc}(x) + \frac{2}{\sqrt{\pi}}e^{-x^2}\left(\frac{3}{x^2} + 2\right)\right) -\delta_{\alpha\beta}\left(\frac{\operatorname{erfc}(x)}{x^3} + \frac{2}{\sqrt{\pi}}\frac{e^{-x^2}}{x^2}\right).$$
(7.16)

The second term  $\bar{C}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0})$  is obtained from the same expression at  $\mathbf{q}=\mathbf{0}$  and from which the  $\mathbf{G}=\mathbf{0}$  term has been removed.

154

### 7.3.3 The $q \rightarrow 0$ case

Mathematically, a divergence problem arises at  $\mathbf{q}=0$  in the previous equations for the Hartree term and the electron-ion term of the electronic contribution, Eq. (7.12), and for the first term of the ion contribution, Eq. (7.15)<sup>3</sup>. Physically, this problem originates in the fact that a macroscopic electric field, parallel to the direction of the wavevector, can be associated to a phonon type displacement in the limit of  $\mathbf{q} \to 0$ . In solids with non-zero Born effective charges, a dipole is created when an atom is displaced and this dipole may interact with the macroscopic field associated to the phonon. The modes that have a polarization perpendicular to  $\mathbf{q}$  will not be concerned by this interaction: they are referred to as transverse modes. By contrast, for the longitudinal modes, the limit of  $\mathbf{q} \to 0$  must be taken carefully in order to reproduce the correct behaviour along different directions.

In this framework, the interatomic force constant matrix can be separated into two parts:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\to 0) = \tilde{C}^{\mathrm{an}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=0) + \tilde{C}^{\mathrm{nan}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}\to 0)$$
(7.17)

The analytical term  $\tilde{C}_{\kappa\alpha,\kappa'\beta}^{an}(\mathbf{q}=0)$  is a "bare" IFC matrix, obtained as a sum of the electronic and ionic contributions previously reported, *but* from which the  $\mathbf{G} = 0$  term has been excluded in the Hartree term and the external potential of Eq. (7.12) and in the first term of Eq. (7.15). The non-analytical contribution  $\tilde{C}_{\kappa\alpha,\kappa'\beta}^{nan}(\mathbf{q}\to 0)$  is an additional term that treats correctly the additional interaction with the macroscopic electric field. It is at the origin of the splitting between longitudinal and transverse optic modes. The contribution of this second term can be investigated in real space.

Separating the contribution involving the macroscopic electric field from the other contributions (in the same spirit that it was done in Chapter 4), the driving force induced on atom  $0\kappa$  in a surrounding of displaced atoms may be written as:

$$F_{0\kappa,\alpha} = -\sum_{b,\kappa',\beta} C_{\kappa\alpha,\kappa'\beta}(0,b) \ \Delta \tau^{b}_{\kappa',\beta} + \sum_{\beta'} Z^{*}_{\kappa,\beta'\alpha} \ . \ \mathcal{E}_{\beta'}$$
(7.18)

so that the equation of motion for the ions becomes:

~ **?** .

$$M_{\kappa\alpha} \frac{\partial^2 \Delta \tau^a_{\kappa\alpha}}{\partial t^2} = \left[ -\sum_{b,\kappa',\beta} C_{\kappa\alpha,\kappa'\beta}(0,b) \ \Delta \tau^b_{\kappa',\beta} + \sum_{\beta'} Z^*_{\kappa,\beta'\alpha} \cdot \mathcal{E}_{\beta'} \right]$$
(7.19)

<sup>&</sup>lt;sup>3</sup>The problem is similar to that discussed in Section 2.5 where we have seen that the energy of a neutral solid may still contain a macroscopic contribution from the dipolar terms. Here the contribution at  $\mathbf{G} = 0$  arises from the macroscopic polarization induced by a long-wavelength phonon in any solid that has non-zero  $Z^*$ .

The amplitude of electric field  $\mathcal{E}_{\beta}$  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 :

$$\mathcal{D}_{\alpha} = \frac{4\pi}{\Omega_0} \sum_{b,\kappa',\beta} Z^*_{\kappa',\beta\alpha} \Delta \tau^b_{\kappa',\beta} + |\mathcal{E}| \sum_{\beta} \epsilon^{\infty}_{\alpha\beta} q_{\beta}$$
(7.20)

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:

$$|\mathcal{E}| = -\frac{4\pi}{\Omega_0} \frac{\sum_{b,\kappa'} \sum_{\alpha'\beta} \Delta \tau^b_{\kappa',\beta} Z^*_{\kappa',\beta\alpha'} q_{\alpha'}}{\sum_{\alpha'\beta'} q_{\alpha'} \epsilon^\infty_{\alpha'\beta'} q_{\beta'}}.$$
 (7.21)

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 ( $\epsilon_{\infty}$ ). Introducing this result in equation (7.19) we get:

$$M_{\kappa\alpha} \frac{\partial^2 \Delta \tau^a_{\kappa\alpha}}{\partial t^2} = -\sum_{b,\kappa',\beta} \Delta \tau^b_{\kappa',\beta} [C_{\kappa\alpha,\kappa'\beta}(0,b) + \frac{4\pi}{\Omega_0} \frac{\sum_{\beta'} (Z^*_{\kappa,\beta'\alpha} q_{\beta'}) \sum_{\alpha'} (Z^*_{\kappa',\alpha'\beta} q_{\alpha'})}{\sum_{\alpha'\beta'} q_{\alpha'} \epsilon^{\infty}_{\alpha'\beta'} q_{\beta'}}].$$
(7.22)

so that the non-analytic contribution to the IFC matrix can finally be written as:

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}^{\mathrm{nan}}(\mathbf{q}\to 0) = \frac{4\pi}{\Omega_0} \, \frac{\sum_{\beta'} \, (Z_{\kappa,\beta'\alpha}^* \, q_{\beta'}) \sum_{\alpha'} \, (Z_{\kappa',\alpha'\beta}^* \, q_{\alpha'})}{\sum_{\alpha'\beta'} q_{\alpha'} \epsilon_{\alpha'\beta'}^{\infty} q_{\beta'}}. \tag{7.23}$$

It is this term that is added in order to compute the LO-TO splitting in the limit of the  $\Gamma$  point <sup>4</sup>.

### 7.3.4 The acoustic sum rule

The total energy of a crystal is submitted to some constraints. In particular, it must remain invariant under homogeneous translations. The dynamical matrix at the zone center should therefore admit the homogeneous

156

<sup>&</sup>lt;sup>4</sup>This non-analytical contribution may alternatively be obtained by treating correctly the long-wavelength part of the Hartree, electron-ion and ion-ion terms in the response to a phonon type perturbation in the limit of  $\mathbf{q} \rightarrow 0$  [102].

translations of the solid as eigenvectors, with zero eigenfrequency. This invariance under translation imposes a requirement on the force-constant matrix, known as the "acoustic sum rule":

$$\sum_{\kappa'} \tilde{C}_{\kappa\alpha,\kappa'\beta} \left( \mathbf{q} = \mathbf{0} \right) = 0.$$
(7.24)

However, in the implementation of the present formalism, this relation is slightly broken because of the presence of the exchange-correlation grid in real space, on which the exchange-correlation potential and energies are evaluated: if all the atoms are translated by a given vector, while the exchange-correlation grid is unchanged, the energies will slightly change, and induce the breaking of the sum rule 5.

The acoustic sum rule can be restored by the following simple operation:

$$\tilde{C}^{\text{New}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}=\mathbf{0}) - \delta_{\kappa\kappa'}\sum_{\kappa''}\tilde{C}_{\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0}). \quad (7.25)$$

By this operation, the eigenfrequencies at  $\mathbf{q} = \mathbf{0}$  will change, and will no more be the limit of the eigenfrequencies obtained by making  $\mathbf{q} \to \mathbf{0}$ , unless the other dynamical matrices, for  $\mathbf{q} \neq \mathbf{0}$ , are also corrected. The generalization of the correction for  $\mathbf{q} \neq \mathbf{0}$  is the following:

$$\tilde{C}^{\text{New}}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \delta_{\kappa\kappa'} \sum_{\kappa''} \tilde{C}_{\kappa\alpha,\kappa''\beta}(\mathbf{q}=\mathbf{0}).$$
(7.26)

In our computations on  $BaTiO_3$ , the violation of the acoustic sum rule was relatively large. The origin of the problem has been investigated and the validity of the correction presented here has been questioned. The discussion is reported in Appendix C.1. All the results presented in this Chapter have been corrected with the help of Eq. (7.26).

# 7.4 BaTiO<sub>3</sub> phonon modes at the $\Gamma$ point

As a first step, we investigate the lattice dynamics of barium titanate at the  $\Gamma$  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 3. Technical details, concerning our calculations are reported in Appendix A.

<sup>&</sup>lt;sup>5</sup>All the other terms can be implemented in a translation-invariant way.

Table 7.1: Phonon frequencies  $(cm^{-1})$  at the  $\Gamma$  point for cubic BaTiO<sub>3</sub>. The LO-TO splitting has been computed with the help of the scissors corrected dielectric constant.

Mode	Exp.[178]	$a_{o} = 3.67 \text{\AA}$	$a_{o} = 3.94 \text{\AA}$	$a_o = 4.00 \text{\AA}$	Ref. [313]
$F_{1u}(TO1)$	$\operatorname{soft}$	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	_

<sup>a</sup> This value has been measured in the tetragonal phase.

There are 12 optic phonons in BaTiO<sub>3</sub>. In the cubic phase, at the  $\Gamma$  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.

### 7.4.1 Cubic phase

Our phonon frequencies in the cubic phase, as well as experimental and other theoretical results, are reported in Table 7.1. Our values are in good agreement with the experiment [178]. In particular, we reproduce the instability <sup>6</sup> 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  $Z_{\kappa}^*$  or  $\epsilon_{\infty}$ . 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 7.2. They are in agreement with those obtained by Cohen and Krakauer [44] from a frozen phonon calculation. These eigenvectors remains relatively similar at the experimental and optimized volume. By

<sup>&</sup>lt;sup>6</sup>An instability is associated to a negative curvature of the energy hypersurface which yields an imaginary phonon frequency.

Table 7.2: Phonon eigendisplacement patterns for the  $F_{1u}(TO)$  mode of the cubic phase of BaTiO<sub>3</sub>. 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  $\eta$  are normalized such that  $\langle \eta^{TO} | M | \eta^{LO} \rangle = 1$ , with M in 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. [44]	-0.006	-0.091	0.144	0.091	0.091
$F_{1u}(TO2)$	$V_{exp}$	-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. [44]	-0.054	0.088	0.053	0.075	0.075
$F_{1u}(TO3)$	$V_{exp}$	-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. [44]	-0.003	0.022	0.186	-0.115	-0.115

Table 7.3: 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.

			Vopt	
		$F_{1u}(TO1)$	$F_{1u}(TO2)$	$F_{1u}(TO3)$
	$F_{1u}(LO1)$	0.17	-0.99	0.01
Vopt	$F_{1u}(LO2)$	-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

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 7.3).

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  $(\eta^{LO})$  do not necessarily corresponds to those of the TO modes  $(\eta^{TO})$ , because of the long-range Coulomb interaction. The overlap matrix reported in Table 7.3 ( $\langle \eta^{TO} | M | \eta^{LO} \rangle$ , where M is such that  $M = M_{\kappa} \delta_{\kappa\kappa'}$  and  $M_{\kappa}$  is the mass of atom  $\kappa$ ) 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 [313]. The same kind of results has been reported for KNbO<sub>3</sub> [313, 292], 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

$$Z_{TO}^{*} = \left\| \frac{\sum_{\kappa,\beta} Z_{\kappa,\alpha\beta}^{*} \eta_{\kappa,\beta}^{TO}}{\langle \eta^{TO} | \eta^{TO} \rangle} \right\|.$$
(7.27)

The mode charges are reported in Table 7.4 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

Table 7.4: Mode effective charge and respective partial contribution due to each atom for the  $F_{1u}(TO)$  modes of the optimized cubic phase.

Mode	Pa	rtial co	Mode charge			
	Ba	Ti	Οl	O_	О_	$Z_{TO}^*$
$F_{1u}(TO1)$	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

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  $^7$ 

$$\omega_{LO}^{2}(\mathbf{q} \to 0) = \omega_{TO}^{2} + \frac{4\pi}{\Omega_{0}} \frac{\left(\sum_{\alpha} q_{\alpha} \left(\sum_{\kappa,\beta} Z_{\kappa,\alpha\beta}^{*} \eta_{\kappa,\beta}^{TO}\right)\right)^{2}}{\sum_{\alpha\beta} q_{\alpha} \epsilon_{\alpha\beta}^{\infty} q_{\beta}}$$
(7.28)

where  $\Omega_0$  is the volume of the unit cell,  $\alpha$  and  $\beta$  indices denote the space direction and  $\kappa$  labels the atom within the unit cell. We find values respectively of 701, 214 and 508 cm<sup>-1</sup>, in close agreement with real LO frequencies (180, 460 and 744 cm<sup>-1</sup>). This result emphasizes again the giant LO-TO splitting of the unstable mode (113*i*  $\rightarrow$  701 cm<sup>-1</sup>) in comparison to that of the two other modes (184  $\rightarrow$  214 cm<sup>-1</sup>, 481  $\rightarrow$  508 cm<sup>-1</sup>). This unusual splitting is associated to a particularly strong Coulomb interaction that will be discussed later.

### 7.4.2 Rhombohedral phase

The phonon frequencies of the rhombohedral phase are reported in Table 7.5. No previous theoretical data were published for this phase. The only previous relevant result is experimental [154] and localizes the phonon frequencies in three regions (100-300 cm<sup>-1</sup>, 480-580 cm<sup>-1</sup>, and 680-750 cm<sup>-1</sup>), in qualitative agreement with our values.

<sup>&</sup>lt;sup>7</sup>This 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 7.5: Phonon frequencies  $(cm^{-1})$  at the  $\Gamma$  point for rhombohedral  $BaTiO_3$ .

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 7.6. 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 7.6), 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 the low frequency dielectric tensor by adding to  $\epsilon_{\infty}$  the ionic contribution (evaluated here in the harmonic approximation, without damping):

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_{TOi} \frac{S_{i,\alpha\beta}}{\omega_i^2 - \omega^2}$$
(7.29)

where the first sum is performed on the different TO phonon modes and  $S_{i,\alpha\beta}$  is the mode oscillator strength tensor defined as:

$$S_{i,\alpha\beta} = \left(\sum_{\kappa,\gamma} Z^*_{\kappa,\alpha\gamma} \eta^{TOi}_{\kappa,\gamma}\right)^* \left(\sum_{\kappa,\gamma} Z^*_{\kappa,\beta\gamma} \eta^{TOi}_{\kappa,\gamma}\right).$$
(7.30)

Table 7.6: 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.

	$A_1(TO1)$	$A_1(TO2)$	$A_1(TO3)$
$A_1(LO1)$	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

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

$$\epsilon_{\hat{\mathbf{q}}}(\omega) = \sum_{\alpha\beta} q_{\alpha} \epsilon_{\alpha\beta}(\omega) q_{\beta} \tag{7.31}$$

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  $\epsilon_{\infty}$  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:

$$R(\omega) = \left|\frac{\epsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) - 1}{\epsilon_{\hat{\mathbf{q}}}^{1/2}(\omega) + 1}\right|^2$$
(7.32)

The result is presented in Fig. 7.1 <sup>8</sup> for  $\hat{\mathbf{q}}$  aligned along the ferroelectric direction. Unfortunately, no experimental data can be compared to our theoretical results.

 $<sup>^{8}\,\</sup>mathrm{The}$  saturation to one observed for the curve of Fig. 7.1 is due to the absence of damping.



Figure 7.1: Infrared reflectivity of rhombohedral BaTiO<sub>3</sub>, with  $\hat{\mathbf{q}}$  along the ferroelectric direction.

# 7.5 Origin of the ferroelectric instability

In the previous Section we have reported first-principles results concerning the  $\Gamma$  phonons of BaTiO<sub>3</sub>. 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.

### 7.5.1 Cochran's model

During the sixties, Cochran [39] investigated the dynamics of ABO<sub>3</sub> compounds within a shell model approach and he related the ferroelectric transition to the softening of a transverse optic phonon at the  $\Gamma$  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 [272], is still now usually invoked to explain the microscopic origin of the ferroelectricity [41, 43, 315].

In spite of its meaningful character, the model of Cochran is only qualitative and it is obtained through questionable approximations. In particular, the dipole-dipole interaction is estimated within a Lorentz field approach assuming a local spherical symmetry at each atomic site, while it was shown by Slater [272], 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 [179].

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

#### 7.5.2 Short-range and dipole-dipole interactions

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 from our first principles data.

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 [155]:

$$E_{e+i}^{DD} = \frac{1}{4\pi\epsilon_0} \frac{(\vec{p}_1 \cdot \vec{p}_2) \ d^2 - 3 \ (\vec{p}_1 \cdot \vec{d}) \ (\vec{p}_2 \cdot \vec{d})}{d^5}$$
(7.33)

with  $\epsilon_0$  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  $\delta \tau_{0\kappa,\alpha}$  is  $p_{\beta} = \sum_{\beta} Z^*_{\kappa,\beta\alpha} \cdot \delta \tau_{0\kappa,\alpha}$ , while the polarizability of the medium is to be described by the dielectric permittivity tensor  $\epsilon^{\infty}_{\alpha\beta}$ . For the case where  $\epsilon_{\infty}$  and  $Z^*$  tensors are isotropic, the contribution to the interatomic force constant of the dipole-dipole interaction created by the displacement of atoms  $0\kappa$  and  $j\kappa'$ , separated by  $\vec{d} = (\vec{R}_j + \vec{\tau}_{\kappa'} - \vec{\tau}_{\kappa})$  is [77]:

$$C^{DD}_{\kappa\alpha,\kappa'\beta}(0,j) = \frac{\delta^2 E^{DD}_{e+1}}{\delta\tau_{0\kappa,\alpha}\delta\tau_{j\kappa',\beta}} = \frac{Z^*_{\kappa}Z^*_{\kappa'}}{\epsilon_{\infty}} (\frac{\delta_{\alpha\beta}}{d^3} - 3\frac{d_{\alpha}d_{\beta}}{d^5})$$
(7.34)

Recently, the generalization of this formula was proposed for the case of anisotropic  $Z_{\kappa}^*$  and  $\epsilon_{\infty}$  tensors [93]:

$$C^{DD}_{\kappa\alpha,\kappa'\beta}(0,j) = \sum_{\alpha'\beta'} Z^*_{\kappa,\alpha\alpha'} Z^*_{\kappa',\beta\beta'} (\det \epsilon_{\infty})^{-\frac{1}{2}} \left( \frac{(\epsilon_{\infty}^{-1})_{\alpha'\beta'}}{D^3} - 3\frac{\Delta_{\alpha'}\Delta_{\beta'}}{D^5} \right)$$
(7.35)

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 [93].

Note that, in this formulation, the macroscopic  $\epsilon_{\infty}$  is used to parametrize the dipole-dipole interactions down to nearest neighbors; no correction for the **q**-dependence of  $\epsilon_{\infty}$  and  $Z^*$  is included. This procedure seems however the natural generalization of the previous computation of the Lorentz field by Luttinger and Tisza [179]. It will be used to generalize Cochran's results on the basis of our first-principles approach [73].

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 <sup>9</sup> from the remaining short-range (SR) part <sup>10</sup> of this dynamical matrix in a way similar to the one of Cochran [39]:  $\tilde{C} = \tilde{C}_{DD} + \tilde{C}_{SR}$ . The partial contributions to  $\omega^2$  are then evaluated as follows:

$$\underbrace{\langle \eta | \tilde{C} | \eta \rangle}_{\omega^2} = \underbrace{\langle \eta | \tilde{C}_{DD} | \eta \rangle}_{\omega^2_{DD}} + \underbrace{\langle \eta | \tilde{C}_{SR} | \eta \rangle}_{\omega^2_{SR}}$$
(7.36)

where  $\eta$  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.

### 7.5.3 Cubic phase

We first compute the decomposition for the cubic phase at the optimized volume. In Table 7.7, we report the values of  $\omega_{DD}^2$  and  $\omega_{SR}^2$  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 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  $Z_{O_{\parallel}}^*$ 

<sup>&</sup>lt;sup>9</sup>The 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.

 $<sup>^{10}\,{\</sup>rm The}\,SR$  part also contains higher Coulomb terms like dipole-octupole and octupole-octupole interactions.

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

Table 7.7: Partial DD and SR contributions (see text) to the TO mode frequency squared (cm<sup>-2</sup>) for the cubic phase at the optimized volume. Values in brackets where obtained with the scissors corrected value of  $\epsilon_{\infty}$ .

(responsible of the strong Coulomb interaction) are mainly produced by a dynamic transfer of charge along the Ti-O bond [72]. 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 <sup>11</sup>. Figure 7.2 shows that  $\omega^2(TO1)$  evolves approximately linearly with the transfer of charge and that a change corresponding to a reduction of the order of 1% of  $Z_{Ti}^*$  is enough to suppress the instability. Of course, this situation is artificial and in a real material any modification of  $Z_{\kappa}^*$  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. 7.2), we observe that  $\omega_{SR}^2$  is also modified: because  $\tilde{C}_{SR}$  was kept constant, this is due to the change of the eigenvector  $\eta$  induced by the modification of  $\tilde{C}_{DD}$ . This change of  $\eta$  is however not crucial and a similar evolution of  $\omega^2$  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  $\epsilon_{\infty}$ . From now on, we report only results obtained without scissors correction.

<sup>&</sup>lt;sup>11</sup>When changing  $Z^*$  and/or  $\epsilon_{\infty}$ ,  $\tilde{C}_{DD}$  is replaced by  $\tilde{C}'_{DD}$  and the modified full dynamical matrix ( $\tilde{C}' = \tilde{C}'_{DD} + \tilde{C}_{SR}$ ) has new eigenvectors  $\eta'$ . The matrix elements giving  $\omega^2$ ,  $\omega^2_{DD}$  and  $\omega^2_{SR}$  are calculated using  $\eta'$ . 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  $\eta$  to  $\eta'$ . As  $\eta$  is not an eigenvector of  $\tilde{C}'$ , for that case a fictitious total frequency is obtained as  $\bar{\omega}^2 = \langle \eta | \tilde{C}'_{DD} | \eta \rangle + \langle \eta | \tilde{C}_{SR} | \eta \rangle$ .



Figure 7.2: 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.

## 7.5.4 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 7.6). Surprisingly the displacement of the Ti atom against the O cage has now become stable. It was found that the  $Z_{\kappa}^*$  are smaller in this ferroelectric phase, suggesting a smaller DD interaction, but this could be partly compensated by a concomitant reduction of  $\epsilon_{\infty}$ . For the  $A_1(TO2)$ mode coming from the soft mode,  $\omega_{DD}^2$  (-286267 cm<sup>-2</sup>) is counterbalanced by a slightly larger SR contribution (356373 cm<sup>-2</sup>). 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  $\tilde{C}_{DD}$  and replace  $Z_{\kappa}^{*}$  and  $\epsilon_{\infty}$  of the ferroelectric structure by their value in the cubic phase  $^{12}$ , we modify the frequency of the  $A_1(TO2)$  mode from 265 to 266*i* cm<sup>-1</sup>: We obtain an instability even larger than in the cubic phase. From this point of view, the reduction of  $Z_{\kappa}^{*}$  in the rhombohedral phase appears as a crucial element to the stabilization of the  $A_1(TO2)$  mode.

Introducing  $Z_{\kappa}^{*}$  and  $\epsilon_{\infty}$  of the cubic phase, we also have strongly modified  $\omega_{DD}^{2}$  and  $\omega_{SR}^{2}$  that become respectively equal to -871017 and 800371 cm<sup>-2</sup>. The drastic change of  $\omega_{SR}^{2}$  results only from the change of eigenvector  $\eta$  ( $\tilde{C}_{SR}$  was not modified) and points out the anisotropy of the SRforces (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 (74i cm<sup>-1</sup>) 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.

### 7.5.5 Compressed cubic phase

No more instability is present in the compressed cubic phase, although the global values of  $Z_{\kappa}^{*}$  do not differ significantly from those obtained at the optimized volume[72]. Moreover, the reduction of volume even increases the destabilizing effect of the DD interaction by 20%: calling  $\eta_{TO1}^{opt}$  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:

$$<\eta_{TO1}^{opt}|\tilde{C}_{DD}^{opt}|\eta_{TO1}^{opt}> = -625897 \,\mathrm{cm}^{-2},$$
(7.37)

while

$$<\eta_{TO1}^{opt}|\tilde{C}_{DD}^{comp}|\eta_{TO1}^{opt}> = -775203 \text{cm}^{-2}.$$
 (7.38)

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<sup>-1</sup>). The disappearance of the unstable mode

<sup>&</sup>lt;sup>12</sup>See previous footnote.

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  $Z_{\kappa}^*$ .

### 7.5.6 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<sub>3</sub> 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 firstprinciples 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 [41] recently discussed the importance of the O 2p - Ti 3d hybridization on the ferroelectric instability of BaTiO<sub>3</sub>: 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 ABO<sub>3</sub> compounds but are also common to a large variety of other materials. The peculiarity of the hybridization in BaTiO<sub>3</sub> (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 [196], and that is still usually considered as the origin of the ferroelectricity in  $ABO_3$ compounds [17, 24, 18, 25, 139, 26, 252]. 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  $SrTiO_3$  (see Appendix C.2). WO<sub>3</sub>, that undergoes a sequence of ferroelectric phase transitions, also presents large anomalous Born effective charges [56]. The competition between short range and Coulomb forces should be a characteristic of ABO<sub>3</sub> 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 <sup>13</sup>.

# 7.6 BaTiO<sub>3</sub> phonons at different high symmetry q-points

Up to know, we focused on the  $\Gamma$  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 3, the structure of BaTiO<sub>3</sub> is cubic perovskite and its space group is Pm3m. 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 [49], as summarized in Table 7.8<sup>-14</sup>. 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 atomic displacement pattern that were

 $<sup>^{13}</sup>$  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.

<sup>&</sup>lt;sup>14</sup>At the  $\Gamma$  point, these notations differ from that used in the previous Section.

-		
${f q}$ 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	$M_1 + M_2 + M_{2'} + M_3$
		$+2M_{3'}+M_4+M_5+3M_{5'}$
$(q, \overline{q}, q)$	$\frac{3}{m}$	$4\Lambda_1 + \Lambda_2 + 5\Lambda_3$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	m3m	$R_{2'} + R_{12'} + R_{25} + R_{25'} + 2R_{15}$

Table 7.8: Irreducible representations at high symmetry  $\mathbf{q}$  points and along high symmetry lines of the Brillouin zone as reported by Cowley [49] for the cubic phase of ABO<sub>3</sub> perovskite materials.

also identified by Cowley in Ref. [49]. The combination of the informations given by the degeneracy and by the phonon eigenvectors allowed us to label unambiguously the different phonon modes.

Results obtained in the cubic phase of  $BaTiO_3$  at the experimental volume are reported in Table 7.9. A comparison of these results with the experimental data will be reported later (Section 7.8).

# 7.7 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. (7.6). Both these problems will be addressed simultaneously [77, 93, 101].

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

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{(2\pi)^3}{\Omega_0} \int_{\mathrm{BZ}} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_b} d\mathbf{q}$$
(7.39)

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

Table 7.9: Computed phonon frequencies  $(cm^{-1})$  of cubic BaTiO<sub>3</sub>  $(a_o=4$  Å) at  $\Gamma$  (0,0,0), X (.5, 0,0), M (.5, .5, 0) R (.5, .5, .5) and at a few points along the  $\Gamma$ -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  $\Gamma$  was performed without scissor correction.

$\overline{q}$	label	frequency	label	frequency
Γ	$\Gamma_{15}$ (TO)	219i	$\Gamma_{25}$	281
	$\Gamma_{15}$ (A)	0	$\Gamma_{15}$ (LO)	445
	$\Gamma_{15}$ (LO)	159	$\Gamma_{15}$ (TO)	453
	$\Gamma_{15}$ (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
	$\mathbf{X}_{1}$	260	$X_{2'}$	627
Μ	${ m M}_{3'}$	167 i	${ m M}_5$	344
	${ m M}_{2^{\prime}}$	103	$M_2$	354
	${ m M}_{5'}$	104	${ m M}_{5'}$	435
	$M_3$	208	$M_1$	456
	${ m M}_{5'}$	270	${ m M}_4$	683
	${ m M}_{3^\prime}$	333		
$\mathbf{R}$	$R_{15}$	128	$\mathrm{R}_{25'}$	386
	$R_{25}$	182	$R_{15}$	414
	$R_{12}$	314	$R_{2'}$	717
$\Lambda_{\frac{1}{8}}$	$\Lambda_3$	137~i	$\Lambda_2$	272
0	$\Lambda_3$	70	$\Lambda_3$	310
	$\Lambda_1$	103	$\Lambda_3$	447
	$\Lambda_1$	180	$\Lambda_1$	461
	$\Lambda_3$	184	$\Lambda_1$	645
$\Lambda_{\frac{1}{4}}$	$\Lambda_3$	96	$\Lambda_1$	277
-	$\Lambda_1$	105	$\Lambda_3$	358
	$\Lambda_3$	190	$\Lambda_3$	428
	$\Lambda_3$	221	$\Lambda_1$	467
	$\Lambda_2$	244	$\Lambda_1$	679
$\Lambda_{\frac{3}{8}}$	$\Lambda_1$	115	$\Lambda_1$	354
0	$\Lambda_3$	121	$\Lambda_3$	381
	$\Lambda_3$	204	$\Lambda_3$	414
	$\Lambda_2$	205	$\Lambda_1$	440
	$\Lambda_3$	290	$\Lambda_1$	708

will generate approximate IFCs in a large box made of  $(l \times m \times n)$  periodic cells, is tempting. Outside of this box, the IFCs are supposed to vanish:

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}\in S} \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_{b}} \quad \text{if } \mathbf{R}_{b} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa}' \in \text{box}$$
$$= 0 \qquad \qquad \text{if } \mathbf{R}_{b} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa}' \notin \text{box}$$
(7.40)

The vanishing of the IFCs beyond some distance is intrinsic to the discrete Fourier transform technique. If the integrand in Eq. (7.39) 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 corresponds to longrange 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 octupole-octupole  $1/d^7$ 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:

$$\tilde{C}^{SR}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) - \tilde{C}^{DD}_{\mathrm{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}).$$
(7.41)

It is expected that these forces are sufficiently short range so that their inverse Fourier transform can be approximated with good accuracy by:

$$C_{\kappa\alpha,\kappa'\beta}^{\mathrm{SR}}(0,b) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}\in S} \tilde{C}_{\kappa\alpha,\kappa'\beta}^{\mathrm{SR}}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_{b}} \quad \text{if } \mathbf{R}_{b} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa}' \in \text{box}$$
$$= 0 \qquad \qquad \text{if } \mathbf{R}_{b} + \boldsymbol{\tau}_{\kappa} - \boldsymbol{\tau}_{\kappa}' \notin \text{box.}$$
$$(7.42)$$

The total interatomic force constants in real space, are then obtained as:

$$C_{\kappa\alpha,\kappa'\beta}(0,b) = C_{\kappa\alpha,\kappa'\beta}^{SR}(0,b) + C_{Ew,\kappa\alpha,\kappa'\beta}^{DD}(0,b)$$
(7.43)

The dipole-dipole part to be added to the short-range part is computed explicitly: it is given by Eq. (7.35), discussed in Section 7.5. Its Fourier transform had been previously subtracted in Eq. (7.41). This contribution

of the dipole-dipole interaction in reciprocal space may be evaluated using Ewald summation technique as described in Ref. [93].

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

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \sum_{\mathbf{d}_b \in \text{box}} C^{\text{SR}}_{\kappa\alpha,\kappa'\beta}(0,b) e^{i\mathbf{q}\cdot\mathbf{R}_b} + \tilde{C}^{\text{DD}}_{\text{Ew},\kappa\alpha,\kappa'\beta}(\mathbf{q}). \quad (7.44)$$

To summarize, 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 was 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.

As mentioned previously, due to the presence of exchange-correlation grid in real space, the dynamical matrix at  $\mathbf{q} = \mathbf{0}$  does not satisfy exactly the acoustic-sum rule. In terms of the IFCs, this sum rule can be written as:

$$\sum_{\kappa'b} C_{\kappa\alpha,\kappa'\beta}(a,b) = 0.$$
(7.45)

It was shown that the acoustic sum rule can be reimposed at the level of the dynamical matrix by a wave-independent, site diagonal correction. Equivalently, the correction can be performed in real space, on the "on site" interatomic force constant as follows:

$$C^{\text{New}}_{\kappa\,\alpha,\kappa\,\beta}(a,a) = -\sum_{(\kappa^{\prime\prime},b)\neq(\kappa,a)} C_{\kappa\,\alpha,\kappa^{\prime\prime}\beta}(a,b).$$
(7.46)

Note that other correction schemes are also possible. This one seems however the most appropriate in our case.

# 7.8 The phonon dispersion curves of BaTiO<sub>3</sub>

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  $\Gamma$  phonons at different lattice constants have been compared.

### 7.8.1 Technical remarks

Prior to the presentation of the results, it is necessary to mention a few technical points.



Figure 7.3: Convergence achieved on the calculated phonon dispersion curves of cubic BaTiO<sub>3</sub> along the  $\Gamma$ -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:  $Z_{Ba}^* = +2.74$ ,  $Z_{Ti}^* = +7.32$ ,  $Z_{O-}^* = -2.14$ ,  $Z_{O\parallel}^* = -5.78$ , and  $\epsilon_{\infty} = 6.75$ .

A second point concerns the dielectric constant. As previously reported, our computed optical dielectric constant (6.75) largely overestimates the experimental value (5.40) [22], as usual within the LDA. A scissor corrected value can be used at the  $\Gamma$  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  $\Gamma$ point changes from 631 to 696 cm<sup>-1</sup>. At the opposite, the frequencies of the two other longitudinal modes at the  $\Gamma$  point are affected by less than 2 cm<sup>-1</sup>. 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. 7.3. The frequencies deduced from the dynamical matrix at q = (.125, .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  $\Gamma$  (.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  $\Lambda$  (.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.

#### 7.8.2 Results and discussion

The calculated phonon dispersion curves [76] are plotted along high symmetry directions in Fig. 7.4. The  $\Gamma$ -X,  $\Gamma$ -M and  $\Gamma$ -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 [178, 261, 306, 262, 109, 20, 134]. 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 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. 7.5). Two transverse optic



Figure 7.4: Calculated phonon dispersion curves of cubic  $BaTiO_3$  at the experimental lattice constant. The theoretical result shows a reasonable agreement with the experimental data: (•) Ref. [3], (o) Ref. [6], (+) Ref. [7], ( $\Box$ ) Ref. [8], (×) Ref. [9], ( $\nabla$ ) Ref. [10], ( $\Delta$ ) Ref. [11].

modes are unstable at the  $\Gamma$  point: they correspond to a displacement of the Ti atom against the oxygen cage. The associated displacement eigenvector is equal to  $[\delta(Ba) = -0.002, \delta(Ti) = -0.096, \delta(O_1) = +0.158, \delta(O_2) = \delta(O_3) = +0.071]^{15}$ . These two modes remain unstable all along the  $\Gamma$ -X line, with very little dispersion <sup>16</sup>. One of them stabilizes along the  $\Gamma$ -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  $\Gamma$ -X-M planes to the R-point.

These features were also observed for KNbO<sub>3</sub> [310] and point out a

<sup>&</sup>lt;sup>15</sup> The eigendisplacement vector  $\eta$  was normalized such that  $\langle \eta | M | \eta \rangle = 1$ , where M is such that  $M = M_{\kappa} \ \delta_{\kappa,\kappa'}$  and  $M_{\kappa}$  is the mass of atom  $\kappa$  in atomic mass units.

<sup>&</sup>lt;sup>16</sup> At the X point, one of the unstable mode is polarized along the z-axis and has an eigenvector equal to  $[\delta(\text{Ti}_z) = -0.117, \delta(\text{O}_{1z}) = +0.133, \delta(\text{O}_{2z}) = +0.062]$ ; the other is polarized along the y direction.



Figure 7.5: Analysis of the unstable phonon mode within the Brillouin zone.



Figure 7.6: Zero-frequency isosurface of the lowest unstable phonon branch over the Brillouin zone.  $\Gamma$  is located at the center of the cube. The mode is unstable in the region between the nearly flat surfaces.

marked 2D character of the instability in the Brillouin zone. This behaviour is more easily visualized in Fig. 7.6 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 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 slablike regions of finite thickness containing the  $\Gamma$  point.

As highlighted by Yu and Krakauer [310], 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<sub>z</sub> and O1<sub>z</sub> displacements. At this wave vector  $(q_z = 0)$ , the Ti and O<sub>1</sub> 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. 7.6, the length of the shortest unstable chain can be estimated to 4  $a_{cell} = 16$  Å<sup>17</sup>. We

<sup>&</sup>lt;sup>17</sup> The length of the shortest unstable chain is slightly different from that reported for KNbO<sub>3</sub>. 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. [310]: as observed in Fig. 7.3, the use of a finer mesh of q-points could still slightly decrease the

note finally, the small dispersion of the unstable mode in the  $\Gamma$ -X-M plane: it suggests a small correlation of the displacements between the different Ti-O chains.

# 7.9 The interatomic force constants

In cubic BaTiO<sub>3</sub>, 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 back in its initial position (the self-force on Ba, Ti and O is positive <sup>18</sup>). 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 [76] 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 conventions on the interatomic force constants  $C_{\alpha,\beta}(\kappa,\kappa')$  are such that the force  $F_{\alpha}(\kappa)$ induced on atom  $\kappa$  by the displacement  $\Delta \tau_{\beta}(\kappa')$  of atom  $\kappa'$  is given by:  $F_{\alpha}(\kappa) = -C_{\alpha,\beta}(\kappa,\kappa') \cdot \Delta \tau_{\beta}(\kappa')$ .

Let us first investigate the IFC with respect to a reference Ti atom along a Ti-O chain (Table 7.10). As previously mentioned, we note that the selfforce 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. [73, 75]). 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  $(-0.06721 \text{ Ha/Bohr}^2)$ . 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.

size of the zone of instability of BaTiO<sub>3</sub>.

 $<sup>^{18}</sup>$  The self-force are the following (Ha/Bohr²): Ba  $\rightarrow$  0.08065, Ti  $\rightarrow$  0.15215, O\_{\parallel}  $\rightarrow$  0.12741, O\_  $\rightarrow$  0.06807.
Atom	Total force	DD force	SR force
Ti(0)	+0.15215	-0.27543	+0.42758
$O_{\parallel}(1)$	+0.00937	+0.23247	-0.22310
$T\ddot{i}_{\parallel}(2)$	-0.06721	-0.03680	-0.03041
$O_{\parallel}(3)$	+0.01560	+0.00861	+0.00699
$T\ddot{i}_{\parallel}(4)$	-0.00589	-0.00460	-0.00129
$O_{-}(1)$	-0.02114	-0.04298	+0.02184
$Ti_{-}(2)$	+0.00751	+0.01840	-0.01089

Table 7.10: Longitudinal (||) and transverse (-) interatomic force constants  $(Ha/Bohr^2)$  with respect to a reference Ti atom (Ti(0)) along the Ti-O chain of cubic BaTiO<sub>3</sub>.

Table 7.11: Ti-Ti longitudinal interatomic force constants  $(Ha/Bohr^2)$  with respect to a reference Ti atom at (.5, .5, .5).

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

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 7.11 and 7.12. 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.

# 7.10 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

coordinate	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

Table 7.12: O-O longitudinal interatomic force constants (Ha/Bohr<sup>2</sup>) with respect to a reference O atom at (.5, .5, .0).

Comes, Lambert and Guinier [46, 47] 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  $ABO_3$  compounds: similar features had been reported (even before Comes) by Honjo *et al.* [122], 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 ABO<sub>3</sub> compounds, it was therefore tempting to make the connection with Cochran's soft-mode theory of the ferroelectricity. Hüller [125] 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.* [46, 47] preferred to invoke a *static disorder* to explain their results and they proposed what is now usually referred to as the 8-sites model <sup>19</sup>. 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

<sup>&</sup>lt;sup>19</sup> The 8-sites model is different from the model reported by Mason and Matthias [188]. It remains also a reference in spite of the existence of more complicated but questionable models like in Ref. [131].

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 [61] while other authors prefer to refer to Hüller's explanation [277]. As already mentioned by Comes *et al.* [47], 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  $\Gamma$  What is their microscopic origin  $\Gamma$  These questions were still recently emphasized by Maglione and Jannot [180] 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  $\Gamma$ 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 any information on the form of the energy surface around a singleatom 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  $\tau_{\kappa_0}$ . 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:

$$E(\tau_{\kappa}) = E(\tau_{\kappa_0}) + \sum_{\kappa,\kappa'} C_{1,1}(\kappa,\kappa') \Delta \tau_{\kappa} \Delta \tau_{\kappa'}$$

where C is the interatomic force constant matrix and the sum on  $\kappa$  and  $\kappa'$  is restricted to the Ti and O atoms that are allowed to move. With the help



Figure 7.7: Lowest eigenvalue of the restricted force constant matrix associated to atomic displacements along a finite Ti-O chain of increasing size.

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. 7.7, 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<sub>3</sub> 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 BaTiO<sub>3</sub>. It has also revealed the crucial role of the coupling between O and Ti displacements, that was hypothetically suggested by Comes *et al.* [47] 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 KNbO<sub>3</sub> from their first-principles results [148].

# 7.11 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  $BaTiO_3$ . Our results allowed to address two fundamental aspects of the ferroelectric instability.

First, in agreement with the idea of Cochran, it was demonstrated 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. The origin of the stabilization of the ferroelectric mode under isotropic pressure and in the rhombohedral phase has been discussed.

Second, it was observed that the displacement of a single atom is never unstable in cubic  $BaTiO_3$ . The appearance of an instability requires a correlation of the atomic displacements along a Ti-O chain of minimum 10 atoms. Our calculations confirm the experimental evidence of linear disorder in  $BaTiO_3$ .

It is finally 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.

# 7.12 References

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

- ◊ Ph. Ghosez, X. Gonze and J.-P. Michenaud, Coulomb interaction and ferroelectric instability of BaTiO<sub>3</sub>, Europhys. Lett. **33**, 713 (1996).
- Ph. Ghosez, X. Gonze and J.-P. Michenaud, Role of the Coulomb interaction on the ferroelectric instability of barium titanate, Ferroelectrics 186, 73 (1996).
- ◊ Ph. Ghosez, X. Gonze and J.-P. Michenaud, Lattice Dynamics and ferroelectric instability of barium titanate, Ferroelectrics 194, 39 (1997).
- ◊ Ph. Ghosez, X. Gonze and J.-P. Michenaud, Ab initio phonon dispersion curves and interatomic force constants of barium titanate, to appear in Ferroelectrics.

CHAPTER 7. PHONONS

# Chapter 8

# Density-polarization functional theory

# 8.1 Introduction

All along this work, we made use of the density functional formalism as it is currently implemented for practical applications. Strictly speaking, it is a *periodic-density* functional theory applied to infinite periodic systems, themselves obtained by imposing Born-von Karman boundary conditions. As illustrated for the specific case of  $BaTiO_3$ , this approach yields very accurate prediction of the ground-state properties of periodic solids. Some exceptions were however pointed out: they concern the DFT bandgap (Chapter 1), the cohesive energy (Chapter 3) and the dielectric constant (Chapter 6). The first failure is well understood in terms of a functional discontinuity in the Kohn-Sham exchange-correlation potential [214, 257], while the second is usually attributed to the LDA. The third failure is more tricky in that it is not easy to see whether it comes from the LDA or from some more fundamental feature of DFT. This problem has been an unceasing source of discussion since several years [167, 51, 192]. It was also the starting point of the reflection that led to the results presented in this Chapter [94, 97, 98, 99].

The idea of a density-polarization functional theory [94] arises from two previous major advancements. The first is the modern theory of the polarization, pioneered by Resta [243] and King-Smith and Vanderbilt [142, 283]. For a long time, the macroscopic polarization of insulators was only accessible from their surface charge [156] and was a well-defined concept only for finite clusters. The recent breakthrough was to reveal that the macroscopic

189

polarization of insulators is intrinsically a *bulk* quantity, making it welldefined even for infinite periodic systems obtained by imposing Born-von Karman (BvK) periodic boundary conditions. However, it was formulated as a Berry phase [311] of the many-body wavefunction [210]: it appeared therefore as a quantity completely independent of the periodic part of the charge density [243]. The second interesting result is the ultra non-local dependence of the exchange-correlation energy on the density pointed out by Godby and Sham [86]. The infinite range of the exchange-correlation energy functional is known since a long time [2]. However, Godby and Sham interestingly reintroduced this feature in the context of semiconductors: they highlighted [86] that the exact exchange-correlation energy functional should present an ultra non-local dependence on the density accumulated at semiconductor interfaces. As the macroscopic polarization is directly connected to a surface charge, this long-range dependency was implicitly suggesting that the exchange-correlation energy should be dependent on the polarization.

In this Chapter, we go back to the more fundamental point of view adopted in Chapter 1, 2 and 4, in order to scrutinize whether some unexpected feature should arise in DFT when switching from finite to infinite systems. We start by reinvestigating the Hohenberg-Kohn (HK) [121] theorem for the specific case of infinite periodic solids: restoring the freedom of homogeneous electric fields, we show that the HK functional is not only dependent on the periodic density but also on another independent quantity, the macroscopic polarization. Repercussions will then be investigated on the Kohn-Sham (KS) [147] construction leading to the notion of exchange-correlation electric fields. Consequences of this new theory will be investigated on different ground-state properties, and in particular on the macroscopic dielectric constant. Our process will occasionally clarify a well-known paradox of DFT. It has also aroused criticisms that will be explicitly addressed. The origin of the polarization dependence in terms of microscopic concepts will be finally discussed.

# 8.2 The Hohenberg and Kohn theorem

#### 8.2.1 Problematics

In Chapter 1, we have seen that the knowledge of the density  $n(\mathbf{r})$  of the ground-state of a system with Hamiltonian  $H_v = T_e + U_{ee} + v_{ext}(\mathbf{r})$  uniquely determines the local potential  $v_{ext}(\mathbf{r})$  up to a constant (HK theorem [121]). It was then deduced that the total energy of the interacting system may be written as a functional of the electronic density  $n(\mathbf{r})$ . In Chapter 2,

macroscopic solids were replaced by infinite periodic systems defined by imposing BvK periodic boundary conditions. The HK theorem, initially demonstrated for an arbitrary large but finite number of electrons was then implicitly generalized to infinite periodic systems. We now show that we must be careful when imposing periodic boundary conditions.

The starting point of our processes is the observation that the straightforward application of an homogeneous electric field (linear potential), to a system with a periodic potential does not allow for a ground-state solution [208]: indeed, a translation against the direction of the field by a whole number of lattice constants would always lower the electronic energy. The impossibility of a ground-state in the presence of a finite electric field renders *invalid* the original proof [121] of density functional theory for this case.

In order to investigate consequences of switching from finite to infinite solids, we will now restore the freedom of linear changes of potential by working within perturbation theory. We start with an infinite solid characterized by a periodic external potential  $v_{\text{ext}}(\mathbf{r})$  and a periodic density  $n(\mathbf{r})$ . We then consider a general infinitesimal change of potential, treated within a long-wavelength approach. The change of potential corresponding to an infinitesimal electric field  $\delta \mathcal{E}$  is (equations are written in one dimension for brevity)

$$\delta v_{\mathcal{E}}(r) = \lim_{q \to 0} \delta \mathcal{E} \cdot \frac{\sin(qr)}{q} = \lim_{q \to 0} \frac{\delta \mathcal{E}}{2iq} (e^{iqr} - e^{-iqr}).$$
(8.1)

We also allow for changes of potential that are periodic in space, with the same periodicity as the unperturbed system:  $\delta v_G(r) = \delta v(G) \cdot e^{iGr}$  with  $\delta v(G) = (\delta v(-G))^*$  where G is a non-zero vector of the reciprocal lattice. These changes of potential are obtained, in the long-wave method, from the Fourier components of the potential:

$$\delta v_G(r) = \lim_{q \to 0} \{ \delta v(G+q) e^{i(G+q)r} + \delta v(G-q) e^{i(G-q)r} \}$$
(8.2)

such that  $\frac{\delta v(G)}{2} = \delta v(G\!+\!q) = \delta v(G\!-\!q)$  .

In response to these perturbations, at finite q, the system will develop changes in density described similarly by  $\delta n(G \pm q)$ . The long-wave part of this change in density, for  $q \rightarrow 0$ , will be [217, 185, 240]

$$\delta n_{\mathcal{P}}(r) = -\lim_{q \to 0} q \cdot \delta \mathcal{P} \, \sin(qr), \qquad (8.3)$$

where  $\delta \mathcal{P}$  is the change of polarization for q = 0.

The elaboration of a density functional theory for these perturbations must answer the following question: what quantities do we need in order to determine  $\delta \mathcal{E}$  and the set of  $\delta v(G)$  uniquely?

# 8.2.2 Perturbative analog to HK theorem

Keeping in mind that we must stay within perturbation theory and treat only infinitesimal electric fields, we now provide a perturbative analog of the first Hohenberg-Kohn theorem[121]:

the knowledge of the change in density everywhere uniquely determines the change in potential.

The following demonstration stays strictly within perturbation theory  $^{1}$ .

We consider the Hylleraas minimum principle [128, 118]: a trial change in wavefunction  $\delta \varphi_t$  gives an upper bound on the second-order change in energy

$$\delta^2 E \le \langle \delta \varphi_t | H - E | \delta \varphi_t \rangle + (\langle \delta \varphi_t | \delta v | \varphi \rangle + (c.c.)).$$
(8.4)

This principle is valid under the constraint  $\langle \delta \varphi_t | \varphi \rangle + \langle \varphi | \delta \varphi_t \rangle = 0$ . The minimum is reached *only* for the  $\delta \varphi$  that is the response of the quantum-mechanical system to the change of potential  $\delta v$ . When this change of potential is a one-body local operator, Eq.(8.4) becomes

$$\delta^{2}E \leq \langle \delta\varphi_{t} | H - E | \delta\varphi_{t} \rangle + \int \delta v(r) \delta n_{t}(r) dr, \qquad (8.5)$$

where the change in density  $\delta n_t(r)$  is easily derived from the knowledge of the unperturbed wavefunction and the trial change in wavefunction. Now consider two changes in potentials  $\delta v_1(r)$  and  $\delta v_2(r)$  such that  $\delta v_1(r) \neq$  $\delta v_2(r)$  + constant. The Hylleraas minimum principle applied to the perturbation  $\delta v_1(r)$  gives

$$\langle \delta \varphi_1 | H - E | \delta \varphi_1 \rangle + \int \delta v_1(r) \delta n_1(r) dr < \langle \delta \varphi_2 | H - E | \delta \varphi_2 \rangle + \int \delta v_1(r) \delta n_2(r) dr,$$
 (8.6)

while for the perturbation  $\delta v_2(r)$ , a similar inequality, where 1 and 2 are interchanged, is obtained. Summing these two inequalities leads to

$$0 < \int (\delta v_1(r) - \delta v_2(r)) (\delta n_2(r) - \delta n_1(r)) dr.$$
(8.7)

<sup>&</sup>lt;sup>1</sup>This theorem could be proved by taking the infinitesimal limit of *finite* differences of the first Hohenberg-Kohn theorem[121], but this approach cannot be followed for electric fields, since *only* infinitesimal electric fields are allowed.

Setting  $\delta n_1(r) = \delta n_2(r)$  would lead to a contradiction, showing that two different changes in potential must induce two different changes in density. Thus, the knowledge of  $\delta n(r)$  everywhere uniquely defines the  $\delta v(r)$  that induced it.

#### 8.2.3 Periodic systems

The same line of argument can now be used in the case of perturbations of periodic systems with finite wavevector q, as previously defined. All quantities have to be normalized to the unit cell volume. This normalization, and a Fourier transform, applied to the term  $\int \delta v(r) \delta n(r) dr$  in Eq.(8.5), changes it into  $\Omega_0 \sum_G \{\delta v^*(G+q) \delta n(G+q) + \delta v^*(G-q) \delta n(G-q)\}$ . The limit  $q \to 0$  is now taken, for two different perturbations described by  $\{\delta \mathcal{E}_1, \delta v_1(G)\}$  and  $\{\delta \mathcal{E}_2, \delta v_2(G)\}$ . The G = 0 term is isolated, and the long-wave values from Eq.(8.1) and (8.3) are used, leading to the following extension of Eq.(8.7):

$$0 < \frac{\Omega_0}{2} \left\{ \left( \delta \mathcal{E}_1 - \delta \mathcal{E}_2 \right) \left( \delta \mathcal{P}_1 - \delta \mathcal{P}_2 \right) + \sum_{G \neq 0} \left( \delta v_1^*(G) - \delta v_2^*(G) \right) \left( \delta n_2(G) - \delta n_1(G) \right) \right\}.$$

$$\tag{8.8}$$

If we now suppose  $\delta \mathcal{P}_1 = \delta \mathcal{P}_2$  and  $\delta n_1(G) = \delta n_2(G)$ , the expected contradiction is obtained. From this result we conclude that:

the change in potential **and** electric field can be deduced from the knowledge of the change in density **and** polarization that were induced by them.

Note that the knowledge of the change of polarization is crucial, since it is the quantity *conjugate* to the change of electric field in Eq.(8.8) : if  $\delta \mathcal{P}_1$ was allowed to be different from  $\delta \mathcal{P}_2$ , Eq.(8.8) could be satisfied for some  $\delta \mathcal{E}_1 \neq \delta \mathcal{E}_2$ . The dependence on polarization is a remnant of the ultra-nonlocal dependence on the long-wave part of the change in density.

#### 8.2.4 Hohenberg-Kohn functional

Because a truly periodic system has no ground-state when placed in a finite electric field, the previous result was obtained strictly within perturbation theory. However, as reported recently by Martin and Ortiz (MO) [187], it can also be generalized for the case of finite fields when allowing for metastable solutions of finite lifetime. Following the recurrence procedure introduced by Nenciu [206], MO reinvestigated the HK theorem. They obtained a relationship similar to Eq. 8.8, that can be written following our notation as:

$$0 < \frac{\Omega_0}{2} \left\{ \left( \mathcal{E}_1 - \mathcal{E}_2 \right) \left( \mathcal{P}_1 - \mathcal{P}_2 \right) + \sum_{G \neq 0} \left( v_1^*(G) - v_2^*(G) \right) \left( n_2(G) - n_1(G) \right) \right\}.$$
(8.9)

This result demonstrates that the periodic density and macroscopic polarization completely determine all properties of a system when macroscopic electric fields are allowed. Following the same line of thought as in Chapter 1, we now deduce from Eq. (8.9) that the HK functional F[n], must be written, for the case of periodic solids when macroscopic field are allowed, as a functional of the periodic density and of the polarization:

$$F[n(\mathbf{G}), \mathcal{P}]. \tag{8.10}$$

As the procedure of Nenciu [206] is not convergent but only asymptotic, we note that this functional is only defined for polarization  $\mathcal{P}$  in an infinitesimal region around the polarization  $\mathcal{P}^0$  observed under the condition of zero macroscopic electric field.

Focusing on the subclass of systems submitted to this condition of zero macroscopic electric field, we observe that the term explicitly involving the polarization is absent in Eq. 8.9. In this case, the original proof of HK applies and the properties of the system are uniquely determined by the periodic density alone. Within this class of problems, the periodic density determines the external potential:  $n(\mathbf{G}) \rightarrow v_{\text{ext}}(\mathbf{G})$ . In turn, the external potential determines the many-body wavefunction and therefore the macroscopic polarization, i.e.,  $v_{\text{ext}}(\mathbf{G}) \rightarrow \varphi \rightarrow \mathcal{P}$ . We note that deducing  $\varphi$  from  $n(\mathbf{G})$ , we have implicitly assumed knowledge of the specific form of the electron-electron interaction. It is only the additional knowledge of the polarization from the periodic density.

As the macroscopic polarization  $\mathcal{P}^0$  of the many-body system under the condition of zero macroscopic electric field is uniquely defined from the set of  $n(\mathbf{G})$ , writing  $\mathcal{P} = \mathcal{P}^0 + \delta \mathcal{P}$ , we have the freedom of considering alternatively:

$$F[n(\mathbf{G}), \mathcal{P}] \leftrightarrow F[n(\mathbf{G}), \delta \mathcal{P}]$$
 (8.11)

The latter functional has been introduced recently by MO [187]. However, in our work, we prefer to consider the first one. Indeed, if both can be equivalently considered at the level of the HK theorem, we will see later that the explicit knowledge of the absolute value of the polarization may remain crucial within the Kohn-Sham construction (Section 8.5).

194

## 8.3 Exchange-correlation electric fields

In Chapter 1, we have seen that the KS formulation to DFT makes one additional hypothesis with respect to the HK theorem: it postulates that any many-body interacting system can be mapped onto another system of fictitious non-interacting particles. Keeping in mind that we are doing the same hypothesis, we would like now to investigate the consequences of the polarization dependence of the HK functional on the KS construction.

Following the same line of thought as in Chapter 1, for periodic solids where the HK functional is of the form  $F[n(\mathbf{G}), \mathcal{P}]$ , we introduce a fictitious independent-particles system to which we impose to reproduce the correct periodic density and polarization. The kinetic energy associated to the non-interacting particles is defined as  $T_s[n(\mathbf{G}), \mathcal{P}]$ . Without worrying about the domain of definition of  $T_s[n(\mathbf{G}), \mathcal{P}]^{-2}$ , we also define a KS exchangecorrelation energy functional as:

$$E_{\rm xc}[n(\mathbf{G}), \mathcal{P}] = F[n(\mathbf{G}), \mathcal{P}] - T_s[n(\mathbf{G}); \mathcal{P}] - \frac{\Omega_0}{2} \sum_{\mathbf{G} \neq 0} v_{\rm H}(\mathbf{G}) n^*(\mathbf{G})$$
(8.12)

We now demonstrate that the polarization dependence of the exchangecorrelation energy leads to the existence of new "exchange-correlation electric fields". For that purpose, we scrutinize the formulation of the exchangecorrelation terms appearing in the KS equation and its first-order analog (usually called a self-consistent Sternheimer equation). We will make use of the King-Smith-Vanderbilt [142] formula (KSV) for the macroscopic polarization, establishing that within any periodic gauge:

$$\mathcal{P} = -\frac{2i}{(2\pi)^3} \int \sum_{n=1}^{\infty} \langle u_{n,\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n,\mathbf{k}} \rangle d\mathbf{k}.$$
(8.13)

We will also keep in mind the following link between the operator "**r**" and the derivative with respect to the wave vector  $(``\nabla_{\mathbf{k}}")$ :

$$P_c \mathbf{r} | u_{n,\mathbf{k}} \rangle = i P_c \nabla_{\mathbf{k}} | u_{n,\mathbf{k}} \rangle \tag{8.14}$$

#### 8.3.1 Kohn-Sham equation

Let us start with the KS equation. Within the variational formulation of the Kohn-Sham formalism (Eq. 1.72), the exchange-correlation potential

<sup>&</sup>lt;sup>2</sup>The KS construction is possible only when F and  $T_s$  are defined on overlapping domains of  $\mathcal{P}$ . It is not necessary the case for polar solids, yielding the pathology described in Section 8.5.

appeared within a Euler-Lagrange equation. Following the procedure of Section 1.7.3, we now write :

$$\frac{E_{\rm xc}[n,\mathcal{P}]}{\delta u_{n\mathbf{k}}^*(\mathbf{r})} = \int \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta u_{n,\mathbf{k}}^*(\mathbf{r})} d\mathbf{r}' + \frac{\delta E_{\rm xc}}{\delta \mathcal{P}} \frac{\delta \mathcal{P}}{\delta u_{n,\mathbf{k}}^*(\mathbf{r})}$$
(8.15)

so that, using KSV, the term  $v_{\rm xc}|u_{n,\mathbf{k}}\rangle$ , appearing in the KS equation, must be replaced in the context of this Section by:

$$v_{\rm xc}|u_{n,\mathbf{k}}\rangle - \frac{i}{(2\pi)^3} \frac{\delta E_{\rm xc}}{\delta \mathcal{P}} \nabla_{\mathbf{k}}|u_{n,\mathbf{k}}\rangle \tag{8.16}$$

From Eq. (8.14), the additional term appears as a potential linear in space. It corresponds to an exchange-correlation electric field:

$$\mathcal{E}_{\rm xc} = \frac{\delta E_{\rm xc}}{\delta \mathcal{P}} \tag{8.17}$$

We stress that this additional field is not a "real" electric field to which the electrons of the system are submitted and that will enter in the total macroscopic field introduced in Chapter 4. It is a "fictitious" field that only affects the KS particles of the system. Even if unphysical, it appears as a crucial part of the only effective KS potential able to generate the correct polarization. We will discuss more carefully in Section 8.5 some consequences of the existence of this field on the correct DFT description of polar solids. In Section 8.8, the microscopic origin of this field will be briefly discussed.

#### 8.3.2 Sternheimer equation

Similarly, within the linear response formalism introduced in Chapter 4, different terms of the first-order KS potential will be influenced by the polarization-dependence of the exchange-correlation energy. Starting now from the definitions introduced in Section 4.4.1, the term  $P_c v_{\rm xc}^{(1)} |u_{n,\mathbf{k}}^{(0)}\rangle >$  (Eq. 4.67) appearing in the first-order Sternheimer equation (Eq. 4.64) now is written :

$$P_{c}v_{\rm xc}^{(1)}|u_{n,\mathbf{k}}^{(0)}\rangle - \frac{i}{(2\pi)^{3}} \mathcal{E}_{\rm xc}^{(1)}P_{c}\nabla_{\mathbf{k}}|u_{n,\mathbf{k}}^{(0)}\rangle$$
(8.18)

where

$$\mathcal{E}_{\mathrm{xc}}^{(1)} = \frac{\delta E_{\mathrm{xc}}[n(\mathbf{G}), \mathcal{P}]}{\delta \mathcal{P} \delta \mathcal{P}} |_{n^{(0)}} \mathcal{P}^{(1)} + \sum_{\mathbf{G} \neq 0} \frac{\delta E_{\mathrm{xc}}[n(\mathbf{G}), \mathcal{P}]}{\delta n(\mathbf{G}) \delta \mathcal{P}} |_{n^{(0)}} n(\mathbf{G})^{(1)} (8.19)$$

Similarly,  $P_c v_{xc0}^{(1)} | u_{n,\mathbf{k}}^{(0)} > \text{now}, a \text{ priori becomes:}$ 

$$P_{c}v_{\rm xc0}^{(1)}|u_{n,\mathbf{k}}^{(0)}\rangle - \frac{i}{(2\pi)^{3}}\mathcal{E}_{\rm xc0}^{(1)}P_{c}\nabla_{\mathbf{k}}|u_{n,\mathbf{k}}^{(0)}\rangle$$
(8.20)

where

$$\mathcal{E}_{\mathrm{xc0}}^{(1)} = \frac{d}{d\lambda} \frac{\delta E_{\mathrm{xc}}[n(\mathbf{G}), \mathcal{P}]}{\delta \mathcal{P}}|_{n^{(0)}}$$
(8.21)

The second term of both Eq. (8.18) and (8.20) were missing in periodic DFT. In Section 8.6 and 8.7, we will investigate consequences of  $\mathcal{E}_{xc}^{(1)}$  on the exchange-correlation kernel and on the computation of the dielectric constant.  $\mathcal{E}_{xc0}^{(1)}$  is zero when investigating the response to an applied macroscopic electric field. However, the second term of Eq. (8.20) should have a contribution in the specific case of a functional explicitly dependent on both  $\mathcal{P}$  and  $\lambda$ .

#### 8.4 Illustration for a model semiconductor

At this stage, we have reinvestigated the HK theorem and the KS construction for the specific case of truly periodic systems. We have emphasized that, for this case, it is necessary to consider functionals of the periodic density and of the macroscopic polarization. We now exhibit two main features of our theory: (i) the knowledge of the density change alone is not sufficient to deduce the periodic potential change and electric field change ; (ii) a non-zero polarization induces a KS exchange-correlation electric field.

The system that we will consider is the model one-dimensional non-polar semiconductor used by Godby and Sham in Ref. [86] (see also Appendix D). In this model, the periodic solid plus electric field is treated by the long-wave method in a supercell consisting of N basic unit cells of length a. The external potential plus the Hartree potential  $v_{\text{ext}}(x) + v_{\text{H}}(x)$  is taken to be the sum of two different contributions:  $V_0 \cos(\frac{2\pi x}{a}) + \lambda \sin(\frac{2\pi x}{Na})$ . The first term has the periodicity of one unit cell, while the second, with the periodicity of the supercell, corresponds to a slowly varying potential of amplitude  $\lambda$ . For an infinitely long supercell, the second term mimics the action of an electric field. A self-energy operator, intended to mimic the relevant many-body effects, is taken to be the non-local potential:  $\Sigma(x, x', \omega) = \frac{f(x)+f(x')}{2}g(|x - x'|)$  where  $f(x) = -F_0[1 - \cos(2\pi x/a)]$  is a negative function with the periodicity of one unit cell and g(y) is a normalized gaussian of width w = 2 a.u. We keep the same set of non critical parameters as in Ref. [86].

197



Figure 8.1: The unit cell of our model one-dimensional semiconductor, where the slowly varying applied potential  $\Delta(v_{\text{ext}} + v_{\text{H}})$ , that changes the interacting electron density by  $\Delta n$ , is the most linear. Both  $\Delta v_{s,1}$  and  $\Delta v_{s,2}$ , used in the non-interacting Kohn-Sham equations, yield the same  $\Delta n$ .  $\Delta v_{s,2}$  is a periodic potential with no linear slope, while  $\Delta v_{s,1}$ , whose linear part is  $\Delta v_{s,1}^{\text{linear}}$ , reproduces not only  $\Delta n$  but also the change of polarization due to  $\Delta(v_{\text{ext}} + v_{\text{H}})$ . This illustrates the need for polarizationdependence in  $E_{xc}$ . For clarity, the potential curves have been aligned so that they all start from zero.

First, the many-body problem is solved by direct diagonalization of the equations containing the self-energy operator, using a plane-wave basis set and a Brillouin zone sampling at the  $\Gamma$  point only. From this result, we construct an *exact* density functional theory by determining the local potential  $v_{s,1}(x)$  which, when filled with non-interacting electrons (no self-energy operator), reproduces the same electron density as in the many-body case (see Fig. 4 of Ref. [86]). Standard iterative non-linear optimization techniques are used for that purpose. Independently, we also extract the (polarized) density of the single unit cell  $\pm \frac{1}{2}a$  where the slowly varying potential is most linear and, again using optimization techniques, we reproduce this density with another potential,  $v_{s,2}(x)$ , having period a. In this case, to retain the sampling of the Brillouin zone at the  $\Gamma$  point, we repeat the density periodically in the supercell. The only problem in reproducing the "target" density comes from the slight non-linearity of the slowly varying potential, and disappears progressively for larger supercells. Fig. 8.1 presents the results obtained with a 80*a* supercell and  $\lambda = 0.95$  eV, for which the r.m.s. difference between the target and computed density is 4 parts per thousand.

Our results contrast with a naïve application of DFT theorems. Constructing a DFT theory for a model system with a linear potential,  $\Delta(v_{\text{ext}} + v_{\text{H}})$ , superimposed on a periodic potential, we have therefore obtained *two* different KS effective potentials  $\Delta v_{s,1}$  and  $\Delta v_{s,2}$  yielding the same correct periodic density. However,  $\Delta v_{s,2}$  is not able to reproduce the polarization (0.037 electrons), associated with the long-wavelength charge density. We observe that  $\Delta(v_{\text{ext}} + v_{\text{H}})$  and the linear component  $\Delta v_{s,1}^{\text{linear}}$  of the Kohn-Sham potential  $\Delta v_{s,1}$  differ by 15%, owing to the existence of the exchange-correlation electric field. As it will be clarified later, the size of the effect seems closely related to the DFT bandgap misfit. As the bandgap problem is a well known feature of DFT, a similar sizable effect is expected for real materials.

Our purpose is now to examine more carefully what would be the consequence of the polarization dependence on different specific ground-state properties.

# 8.5 Spontaneous polarization of polar solids

The first quantity that we would like to address is the spontaneous polarization of polar crystals. Since the emergence of the modern theory of the polarization, the spontaneous polarization is indeed usually deduced from DFT calculations performed within the KS formalism, when imposing periodic boundary conditions. In this Section we show that the exact KS treatment of polar crystals (i) with the usual BvK boundary conditions, or (ii) from the macroscopic limit of large clusters, can give different macroscopic polarizations. Only (ii) is correct.

#### 8.5.1 Problematics

The correct definition of a macroscopic crystal is clearly as the limit of a finite crystal of increasing size. Fig. ??-a shows schematically the total electrostatic potential  $v_{elec} = v_{\rm H} + v_{\rm ie} + v_{\rm appl}$  in such a finite crystal, where  $v_{\rm H}$  is the electrostatic potential due to the ground-state electron density,  $v_{ie}$  is the potential due to the nuclei, and  $v_{\rm appl}$  is an applied potential, created by an external short-circuited capacitor, that maintains equality of the electrostatic potential on the two sides <sup>3</sup>. In this context, the external potential is now  $v_{\rm ext} = v_{ie} + v_{\rm appl}$ . The total electrostatic potential in

<sup>&</sup>lt;sup>3</sup>For the simplicity of the argument, we imagine that the capacitor is a classical device, in which case the analysis of electrostatics performed in Ref. [245] applies.



Figure 8.2: (a) The local electrostatic potential (external plus Hartree) of a polar insulator, and the corresponding ground-state density. In the bulk region the potential is periodic. Short-circuited capacitor plates are also present. (b) The periodic effective potential that, when used in Kohn-Sham equations, is able to reproduce the density of the polar insulator within the bulk region. The macroscopic polarization is not correct. (c) The effective potential that, when used in Kohn-Sham equations, is able to reproduce the density shown in (a), in all the regions of space. The macroscopic polarization is correct (in contrast to (b)).

the bulk region is periodic and, crucially for a non-zero polarization, noncentrosymmetric. The potential just outside the surface is fixed by the electrostatic potential of the capacitor plates. The corresponding groundstate electron density is also shown. In the bulk region, it is periodic, with the same periodicity as the local potential <sup>4</sup>. Close to the surface, the density deviates from perfect periodicity, although this effect decreases exponentially with the distance from the surface [146].

The macroscopic polarization of such a finite solid is directly linked to the total surface charge [156, 283]. Alternatively, within the modern theory of the polarization, it can also be *a priori* determined, up to a quantum, from a Berry phase of the correlated many-body wavefunction of the *bulk* [283, 243, 142, 210, 244]. In practice, this polarization is currently obtained from a Berry phase of the one-body KS wavefunction associated to a truly periodic system built from the periodic part of the finite cluster.

Vanderbilt and King-Smith argued [283] that the Berry phase of the occupied KS wavefunctions possesses an exact physical meaning since the surface charge must be exactly reproduced within DFT [283]. We now show the justification of Vanderbilt and King-Smith apply to exact DFT only when considering *finite* solids, and not when applying BvK periodic boundary conditions.

#### 8.5.2 Kohn-Sham treatment of polar solids

The crucial point when switching from finite to infinite solids is to take the macroscopic limit correctly. For that purpose, we will first examine the construction of an exact KS theory for the case of finite polar solids. We will then examine what is the correct limit of this theory for the case of infinite systems.

Let us start with the finite polar solid of Fig. (??-a). When constructing a KS theory for such system, we must find the local potential that is able to reproduce the density everywhere: in the bulk, but also in the surface region resulting in the correct polarization. Considering first only the periodic density of the bulk region, the HK theorem applied to the KS system demonstrates that there is a unique periodic effective potential  $v_s$  that reproduces the particular periodic density (Fig. ??-b). However, from Eq. (8.8) it appears clearly that, once an additional electric field is allowed, there exists an infinite family of KS potentials that gives the same bulk density but different surface charge. Once the surface charge is defined, the KS electric field is determined. Nothing imposes however that it *must* be zero.

 $<sup>^{4}\</sup>mathrm{In}$  this work, we do not consider symmetry breaking effects like charge- or spindensity waves

As recalled previously, the KS construction makes one additional hypothesis with respect to the HK formalism: it postulates that any manybody system can be mapped by another system of fictitious non-interacting particles. At this stage, it would be an *additional* and more stringent hypothesis to postulate that the subset of interacting many-body systems under the condition of zero macroscopic electric field can always be mapped within the *subset* of non-interacting systems submitted to the condition of zero macroscopic effective field. The HK theorem imposes that there is *at most* one non-interacting system that reproduces the correct density everywhere, without imposing any restriction on the associated effective potential. Our point is that there is not necessary a correspondence between the subsets of systems under the condition of zero electric field, defined for different electron-electron interactions.

A priori, the effective KS potential associated to a polar solid may therefore contain a linear contribution and has the form represented in Fig. (??-c). Imposing additional condition of zero macroscopic electric field would constraint the KS polarization to an arbitrary value  $\mathcal{P}_s^0$  that is not necessarily that of the many-body system  $\mathcal{P}^0$ .

This situation is illustrated differently in Fig. (8.3-a), where we have plotted the polarization of the many-body and Kohn-Sham system in terms of the electric field to which the electrons and KS particles are submitted in each representation <sup>5</sup>. For a finite insulator of length L, the polarization remains only well defined within a range of fields ( $\mathcal{E}$ ) such that the associated change of potential ( $\mathcal{E}.L$ ) is smaller than the gap. Beyond this point the system becomes metallic and the polarization is no more related with the bulk wavefunctions. The graph makes use of the fact that the many-body and KS systems have different polarizability (the slope  $d\mathcal{E}/d\mathcal{P}$ at the origin is different in both cases) and different bandgap (the switch from insulator to metal arrives for a different strength of the electric field). It corresponds to a usual case where the bandgap is underestimated within the KS description.

Fig. (8.3-a) illustrates a general situation where the KS system must develop an exchange-correlation electric field in order to yield the correct polarization  $\mathcal{P}^0$ . Interestingly, it also points out that a problem naturally arises in the KS system when taking the macroscopic limit, from the fact that an arbitrarily large system cannot sustain a finite electric field. As the cluster is made larger, a point will indeed be reached where the variation in potential from one side of the cluster to the other, due to the homogeneous exchange-correlation electric field, reaches the DFT bandgap of the material. Beyond this point, the KS electronic system is *metallic* and the

<sup>&</sup>lt;sup>5</sup>Non-linear effects are ignored.



Figure 8.3: Field-polarization curves (non-linear effects are ignored) for the many-body (MB) and Kohn-Sham (KS) systems associated to finite clusters of increasing size (see text). The graph makes use of the fact that the MB and KS systems have different polarizability and different bandgap.

band edges will "pin" the effective potential. As the cluster is made still larger, charge will flow freely from one face to the other in order to maintain the correct macroscopic polarization. This is illustrated in Fig. (8.3-b). The magnitude of the homogeneous electric field will now change with the size of the cluster : in the limit of large cluster size, the effective homogeneous electric field required to reproduce the correct polarization will becomes infinitesimally small, although crucially non-zero. Replacing now our arbitrary large cluster by an infinite system, obtained by imposing BvK boundary conditions, the infinitesimal electric field is forbidden and the calculation provides the incorrect value  $\mathcal{P}_s^0$  for the polarization. It is therefore a specific case for which the truly periodic solid is not strictly equivalent to a finite solid of increasing size.

The existence of an exchange-correlation electric field, in the absence of a real macroscopic electric field, may appear surprising. However, the negation of that result would be equivalent to state that  $\mathcal{P}_s^0 = \mathcal{P}^0$ . In terms of Fig. (8.3-a), this situation would correspond to the fact that the many-body and KS curves cross at  $\mathcal{E} = 0$ . If it is not a priori excluded, it is only a particular case of the most general situation presented in the foregoing. Up to now, there is no argument establishing why this specific situation should be preferred.

To clarify unambiguously the debate would basically require to compare the polarization computed from a real many-body wavefunction to that of the KS system. It would necessitate a realistic many-body wavefunctions, unfortunately unavailable. Differently, at the level of our model, the phenomenon is already observed.

#### 8.5.3 Model calculation

For the purpose of this Section, our one-dimensional model semiconductor has been slightly modified in order to mimic a polarized solid. In this new model the electrostatic potential is periodic and asymmetric:  $v_{\rm elec}(x) = V_c \cos \frac{2\pi x}{a} + V_s \sin \frac{4\pi x}{a}$ . The non-local self-energy operator, intended to mimic the relevant many-body effects, has the same non-local form as in the first calculation.

As for the previous illustration, the Schrödinger equation containing the self-energy operator is first solved by direct diagonalization using a planewave basis set. The density is deduced from the sum of the squares of the eigenfunctions. From this result, using standard iterative optimization techniques, we then construct an *exact* density-functional theory by determining the local potential  $v_s(x)$  which, when filled with *non-interacting* electrons (no self-energy operator), reproduces the same electron density as in the self-energy calculation. Fig. 8.4 presents the function  $v_{\text{elec}}(x)$ , as



Figure 8.4: The electrostatic potential  $v_{\text{elec}}(x)$ , the electron density n(x) and the Kohn-Sham effective potential  $v_s(x)$  of the model one-dimensional semiconductor are shown when periodic boundary conditions are imposed. The Kohn-Sham electrons correctly reproduce the electron density, but not the macroscopic polarization.

well as the density n(x), and the effective potential  $v_s(x)$ , for the following set of parameters :  $a_0 = 4$  a.u.,  $V_c = V_s = 2.72$  eV,  $F_o = -4.08$  eV, w = 2 a.u.

Using the Berry-phase approach [243, 142], we are now able to compute the polarization <sup>6</sup>. In the self-energy calculation, the polarization is 22.68  $10^{-3}$  electrons with respect to the centrosymmetric system with  $V_s = 0$ , while that calculated from the Berry phase of the Kohn-Sham wavefunctions is 21.99  $10^{-3}$  electrons. The two polarizations differ by 3%, well outside the calculational error bar.

It is important to understand correctly the previous result. Considering an hypothetical system for which the model calculation including the self-energy operator is considered as *exact*, and constructing a KS theory for that system, our calculation has demonstrated that nothing in the KS construction has imposed to the polarization to be correctly reproduce.

Similarly, nothing guarantees that the polarization  $\mathcal{P}_s^0$  of a the KS system associated to a polar solid must be equivalent to  $\mathcal{P}^0$ .

<sup>&</sup>lt;sup>6</sup>The standard Berry phase analysis is applicable to our system, showing the exact polarization to be proportional to the Berry phase of the eigenfunctions of the non-local Hamiltonian. This is distinct from the Berry phase of the Kohn-Sham wavefunctions.

#### 8.5.4 Conclusions and practical issues

In summary, from the foregoing, we suggest that, for a polar insulator, when BvK periodic boundary conditions are used, the polarizations calculated from the Berry phase of the KS wavefunctions and from the Berry phase of the correlated wavefunction may differ, because the DFT effective potential is prevented from acquiring a linear part. When a large cluster is used for the KS calculation, a homogeneous effective exchange-correlation "electric field" develops in order to correctly reproduce the polarization. The KS system becomes metallic.

We note that approximate density-functionals such as the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA), that do not retain any long-wavelength dependence in the density, always fail to yield an exchange-correlation electric field. Within these approximations, using BvK boundary conditions or finite clusters incorrectly provide the *same* value of the polarization. Moreover, any improvement to these functionals which retains a dependence only on the periodic density will be similarly flawed.

Paradoxically, the lack of polarization dependence of the usual approximate functional can be viewed as a "practical advantage": the computation of the polarization under BvK conditions (from a Berry phase of the KS wavefunctions) is indeed intrinsically easier than from the limit of large clusters and constitutes a *consistent* procedure within these approximations. This justifies the calculations performed in the previous Chapters.

# 8.6 The exchange-correlation kernel

As introduced in Section 8.3, not only the ground-state properties of polar crystals but also the response function of any solid to perturbation inducing a macroscopic polarization will be affected by the polarization dependence of the exchange-correlation energy. This involves quantities that can be formulated as a derivative of the total energy with respect to an electric field. It also concerns the response to atomic displacement pattern accompanied by a macroscopic field, as for the case of long-wavelength phonons. In each case, the polarization dependence of the exchange-correlation energy is summarized in the long-wavelength behaviour of the exchange-correlation kernel <sup>7</sup>. In this Section, we will be only concerned by the response of non-polar solids.

<sup>&</sup>lt;sup>7</sup>As mentioned in Section 8.3, a contribution should also appears from  $v_{xc0}^{(1)}$ . In what follows, we will neglect this contribution.

#### 8.6.1 Problematics

The exchange-correlation kernel naturally appeared in Chapter 4 when investigating the response of the KS system to an external perturbation. It was defined as the second derivative of the exchange-correlation energy with respect to the density or, alternatively, as a first derivative of the exchange correlation potential:

$$K_{\rm xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} = \frac{\delta v_{\rm xc}(\mathbf{r})}{\delta n(\mathbf{r}')}.$$
(8.22)

This quantity was then involved in the different responses that were investigated in Chapters 5, 6 and 7. From the variational expression of the second derivative, it appears clearly that a correct description of  $K_{\rm xc}$  is mandatory to obtain the right answer.

Alternatively to the formalism introduced in Chapter 4, the response of solids to an external perturbation is also currently addressed in terms of the *polarizability matrix* that, for instance, can be directly related to the dielectric constant. In order to make the link with this different approach, a few definitions will now be introduced.

The polarizability matrix  $\chi$  is the basic quantity characterizing the response of the electronic system to an external perturbation. It is defined as:

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \, \delta v_{\text{ext}}(\mathbf{r}') \, d\mathbf{r}'$$
(8.23)

For the KS system an independent-particle polarizability  $\chi_o$  may also be introduced, relating the change of density to that of the effective KS potential:

$$\delta n(\mathbf{r}) = \int \chi_o(\mathbf{r}, \mathbf{r}') \ \delta v_s(\mathbf{r}') \ d\mathbf{r}' \tag{8.24}$$

From the relationship between external and KS potential ( $v_s = v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}$ ), both polarizability are related to each other by the following relationship (making use of matrix notations):

$$\chi_o^{-1} = \chi^{-1} + V_C + K_{\rm xc} \tag{8.25}$$

where  $V_C$  is the conventional Coulomb potential (i.e. the "kernel" of the Hartree potential). As reported by Adler and Wiser [1, 302],  $\chi_o$  can be directly computed from the KS electronic wavefunctions. From Eq. (8.25), we conclude that  $K_{\rm xc}$  plays a major role when deducing  $\chi$  from  $\chi_o$ .

We now demonstrate that the polarization dependence of  $E_{\rm xc}$  imposes a requirement on the form of  $K_{\rm xc}$  that is however not satisfied by the usual local approximations (LDA, GGA). In Section 8.7, we will discuss the consequence of this fact on the different definitions of the dielectric constant.

#### 8.6.2 The exact long-wavelength behaviour

Let us first investigate the long-wavelength behaviour of the exchangecorrelation kernel of insulators. For that purpose, we adopt a perturbative approach and the same long-wavelength technique than in Section 8.2. The change of external potential  $\delta v_{\text{ext}}$  produced by an infinitesimal homogeneous electric field  $\delta \mathcal{E}_{\text{ext}}$  is (written in one-dimension for brevity):

$$\delta v_{\text{ext}}(r) = \lim_{q \to 0} \frac{\delta \mathcal{E}_{\text{ext}}}{2iq} \left( e^{iqr} - e^{-iqr} \right)$$
(8.26)

In response to this perturbation, the system will develop a change of density  $\delta n$ . Due to the Umklapp process, it may contain contributions at different (q+G) vectors (where G belongs to the reciprocal lattice). Within linear response, the long-wave part of  $\delta n$  takes the form:

$$\delta n(r) = -\lim_{q \to 0} \frac{q}{2i} \, \delta \mathcal{P} \, \left( e^{iqr} - e^{-iqr} \right) \tag{8.27}$$

where  $\delta \mathcal{P}$  is the change of polarization for q = 0.

The self-consistent screening potential will also generally contain longwave and more rapidly varying terms. Its long-wave part will be composed of an Hartree contribution, corresponding to the screening of the applied field due to the Coulomb interaction. Moreover, as previously discussed, the polarization dependence of  $E_{\rm xc}$  will manifest through an additional exchange-correlation electric field  $\delta \mathcal{E}_{\rm xc}$  so that for  $q \to 0$ :

$$\delta v_{\rm scr}(q) = \delta v_{\rm H}(q) + \delta v_{\rm xc}(q) = \frac{4\pi}{q^2} + \frac{\delta \mathcal{E}_{\rm xc}}{2iq}$$
(8.28)

From Eq. [8.22], the exchange-correlation kernel is defined as  $\delta v_{\rm xc} = K_{\rm xc}\delta n$ . Isolating the long-wave term from the other contributions, following notations of Ref. [127] we obtain (*G* here stands for all non-zero vectors of the reciprocal lattice) :

$$\begin{pmatrix} \frac{1}{q} \frac{\delta \mathcal{E}_{\mathrm{xc}}}{2i} \\ \delta V_{\mathrm{xc},G} \end{pmatrix} = \begin{pmatrix} \frac{1}{q^2} K_{\mathrm{xc},00} & \frac{1}{q} K_{\mathrm{xc},0G'} \\ \frac{1}{q} K_{\mathrm{xc},G0} & K_{\mathrm{xc},GG'} \end{pmatrix} \begin{pmatrix} -q \frac{\delta \mathcal{P}}{2i} \\ \delta n_G \end{pmatrix}$$

In order for the exchange-correlation field to be finite when a finite change of polarization takes place, the head of the exact exchange-correlation kernel must exhibit a  $\mathcal{O}(1/q^2)$  divergence in the limit of  $q \to 0$  (i.e.  $K_{\mathrm{xc},00}$  is finite). For the same reasons, the wings of  $K_{\mathrm{xc}}$  present a  $\mathcal{O}(1/q)$  divergence (i.e.  $K_{\mathrm{xc},0G}$  is finite). Both these divergences are a direct consequence of the polarization-dependence of  $E_{\mathrm{xc}}$ , that materializes as an additional effective electric field <sup>8</sup>.

#### 8.6.3 The one-dimensional model semiconductor

The previous result can interestingly be illustrated in the case of our model one-dimensional semiconductor for which the exchange-correlation kernel can be computed exactly (within the model). As a reminder, in our model, the sum of the external and Hartree potential is taken to be:  $v_{\text{ext}}(x) + v_{\text{H}}(x) = V_o \cos(2\pi x/a)$ , where *a* is the unit cell length. The non-local self-energy operator, intended to mimic many-body effects keep the same form than in Section 8.4.

As for the previous illustrations, the Schrödinger equation containing the self-energy operator is first solved by direct diagonalization using a plane-wave basis set and a supercell technique. The "exact" density is deduced from the sum of the square of the occupied eigenfunctions. Using non-linear optimization technique, an exact DFT is then constructed by determining the local potential  $V_{\text{eff}}$ , which, when filled with non-interacting electrons, reproduce the density obtained when including the self-energy operator. As in Section 8.4, we adopt the non-critical parameters of Ref. [86],

In order to compute the polarizability  $\chi$  of the system one must take into account that the total potential is made of the external potential and the Hartree potential (plus the constant non-local self-energy operator). As a consequence, the computation of responses to changes in the total potential, using the wavefunctions obtained with the self-energy operator and a sum-over-states technique [1], gives a matrix  $\tilde{\chi}_o$ , connected to the polarizability matrix  $\chi$  by (compare with Eq. (8.25))

$$\tilde{\chi}_o^{-1} = \chi^{-1} + V_{\rm C} \tag{8.29}$$

From our KS wavefunctions, that reproduce the same density, it is also possible to compute the KS independent-particle polarizability,  $\chi_o$ , using a similar technique. For that case, the relationship between  $\chi$  and  $\chi_o$  is given by Eq. (8.25). As the polarizability must be correctly reproduced within DFT,  $\chi$  is identical in Eq. (8.25) and Eq. (8.29) so that we obtain the following relationship, that allows  $K_{\rm xc}$  to be determined :

$$K_{\rm xc} = \chi_o^{-1} - \tilde{\chi}_o^{-1} \tag{8.30}$$

 $<sup>^{8}</sup>$  This behaviour was already apparent from the long-wavelength behaviour of the first and second terms of Eq. (8.19).



Figure 8.5: The diagonal part of the exchange-correlation kernel for the one-dimensional model semiconductor. The result was obtained for a 80 unit-cell supercell (320 a.u.). The  $\mathcal{O}(1/q^2)$  character of the  $K_{\rm xc}$  divergence is exhibited in the inset by the non-zero intercept of  $q^2.K_{\rm xc}(q,q)$ .

In Fig. 8.5 we have plotted the diagonal part of the computed  $K_{\rm xc}$ . The calculation was performed on a 80-unit-cell, which guarantees a convergence better than 0.7%. We observe a divergence in the limit of  $q \rightarrow 0$ . The inset points out its  $\mathcal{O}(1/q^2)$  character.

We note that, for our model, the divergence of  $K_{\rm xc}$  is *independent* of long-range correlation effects <sup>9</sup>. Inclusion of these effects would simply affect the coefficient of the  $K_{\rm xc}(q, q)$  divergence <sup>10</sup>.

#### 8.6.4 Within LDA and GGA's

The previous divergence of the exchange-correlation kernel appears as a direct consequence of the polarization-dependence of  $E_{xc}$ . We now show that the correct behaviour is not reproduced within the usual LDA and GGA.

<sup>&</sup>lt;sup>9</sup>In Ref. [192], it was pointed out that the XCLF correction to the Green's function approach diverges like  $\mathcal{O}(1/q^2)$ . However, even without this additional effect, a  $\mathcal{O}(1/q^2)$  divergence is observed in the present model calculation.

<sup>&</sup>lt;sup>10</sup> The success of the scissor-correction (that roughly adjusts the DFT dielectric constant to its Green's function RPA value) seems however to prove that this additional correction should be small.

Within the LDA,

$$K_{\rm xc}(\mathbf{r},\mathbf{r}') = \left. \frac{\delta v_{\rm xc}^{\rm LDA}}{\delta n} \right|_{\mathbf{r}} \cdot \delta(\mathbf{r}-\mathbf{r}').$$
(8.31)

The Fourier transform of this kernel, diagonal in real space, is such that  $K_{\rm xc}(\mathbf{q}, \mathbf{q})$  is independent of  $\mathbf{q}$  [127] and does not satisfy the previous condition.

For generalized gradient approximations, the situation is similar. In general the gradient-corrected exchange-correlation energy has the form

$$E_{xc}[n] = \int \epsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r}, \qquad (8.32)$$

with the corresponding potential :

$$V_{xc}(\mathbf{r}) = \left. \frac{\partial e_{xc}}{\partial n} \right|_{\mathbf{r}} - \nabla \cdot \left. \frac{\partial e_{xc}}{\partial \nabla n} \right|_{\mathbf{r}}$$
(8.33)

The relationship between the long wavelength exchange-correlation potential and the long wavelength density is therefore given by :

$$K_{xc}(\mathbf{q}, \mathbf{q}) = \frac{1}{\Omega} \begin{bmatrix} \int_{\Omega} \frac{\partial^{2} e_{xc}}{\partial n^{2}} \Big|_{\mathbf{r}} d\mathbf{r} \\ -2i \sum_{\alpha} q_{\alpha} & \int_{\Omega} \frac{\partial^{2} e_{xc}}{(\partial n)(\partial(\partial_{\alpha} n))} \Big|_{\mathbf{r}} d\mathbf{r} \\ -\sum_{\alpha\beta} q_{\alpha} q_{\beta} & \int_{\Omega} \frac{\partial^{2} e_{xc}}{(\partial(\partial_{\alpha} n))(\partial(\partial_{\beta} n))} \Big|_{\mathbf{r}} d\mathbf{r} \end{bmatrix}$$
(8.34)

The first term of the right member of this equation is similar to the one appearing in the LDA. Eq. (8.34) makes clear that the gradient correction produces terms with extra powers of q, but not the required  $\mathcal{O}(1/q^2)$  divergence. Contrary to what was expected by Mazin and Cohen [192], the GGA has therefore no apparent ability to improve upon the LDA behaviour in this respect.

At the opposite, within the exact-exchange OEP method [99], it will be demonstrated later (Section 8.8) that the exchange-energy exhibits a polarization dependence that physically originates in a polarization of the exchange hole in the exchange-correlation field. Within this method, the exchange kernel will therefore present the above-mentioned divergence.

#### 8.6.5 The metal-insulator paradox

We are now mentioning an interesting analogy. In connection with the KS bandgap problem, it was shown by Godby and Needs [84], within certain approximations, that the ground state of a periodic insulator is sometimes described as metallic in the KS approach to DFT. This is particularly striking in that the long-wavelength behaviour of the polarizability matrix  $\chi$  for an insulator is qualitatively different from that of a metal, while  $\chi$  is a ground state quantity and should be correctly obtained within DFT. In order for  $\chi$  to be correctly reproduced from  $\chi_o$ , they deduced that  $K_{\rm xc}$  must exhibit some *a priori* unexpected features. We now argue that a  $\mathcal{O}(1/q^2)$  divergence is required.

Indeed [217], the KS independent-particle polarizability of a DFT metallic ground-state behaves like  $\lim_{q\to 0} \chi_o(q,q) = \gamma$ , while for a cubic insulator, one has  $\lim_{q\to 0} \chi_o(q,q) = \alpha q^{2-11}$ . The head of the polarizability matrix  $\chi(q,q)$  for a metal (interacting electrons, not KS electrons) behaves exactly as  $-\frac{q^2}{4\pi}$  in the long-wavelength limit, which corresponds to complete screening of the Coulomb potential, while for cubic insulators, it is  $-\frac{q^2}{4\pi}\beta$ , where  $\beta$ is a positive constant smaller than one, describing the incomplete screening.

Using now Eq. (8.25), and neglecting the local fields effects, one easily sees that in order to have altogether no divergence in  $\chi_o^{-1}(q,q)$  (metallic Kohn-Sham ground state), and divergences in  $\chi^{-1}(q,q)$  and  $V_{\rm C}$  with different coefficients (incomplete screening of the insulating system), one must have

$$\frac{1}{\gamma} = -\frac{4\pi}{\beta q^2} + \frac{4\pi}{q^2} + K_{\rm xc}(q,q), \qquad (8.35)$$

requiring a  $\mathcal{O}(1/q^2)$  divergence in  $K_{\rm xc}(q,q)$ . We note that generalization to the case where local fields are included is trivial and simply leads to an additional  $\mathcal{O}(1/q)$  divergence in  $K_{\rm xc}(q,q+G)$ .

In the framework of this Section, a divergence appears in  $K_{\rm xc}$  in order to compensate the incorrect screening of the KS system. We will see later (Section 8.7.2) that the same mechanism must similarly appear as soon as the bandgap is incorrectly described within DFT.

# 8.7 The dielectric constant

The failure of DFT-LDA calculations to reproduce the experimental dielectric constant is well-known. As illustrated in Chapter 6 for  $BaTiO_3$ , the error goes well beyond that usually observed for other properties within the

 $<sup>^{11}\</sup>gamma$  and  $\alpha$  are some non-zero constants.

LDA. Consequently to this unpleasant feature, Levine and Allan [166, 167] proposed a simple "LDA+ scissors correction" approach to the dielectric response, in which a constant shift  $\Delta$  is imposed on the conduction bands with respect to the valence bands, to reproduce the correct bandgap. The dielectric tensor in this approximation has been found to be within a few percent of the experimental data for more than a dozen semiconductors and insulators [166, 167, 168, 33]. But, as emphasized by Dal Corso, Baroni, and Resta [51], there is no immediate justification within DFT of this successful procedure. Differently, the latter authors correctly pointed out that the dielectric response is a ground-state property that must be correctly described within DFT. Any improvement in the direction of the true functional should therefore improve the result. Consequently, they computed the dielectric constant of Si within GGA, but only with limited success.

In this Section, we clarify the mechanism by which DFT succeeds in reproducing the correct dielectric response. This is closely related to the previously discussed  $\mathcal{O}(1/q^2)$  behaviour of the exchange-correlation kernel and it allows to clarify why the GGA correction has a rather limited success. We also briefly mention how the *scissor* correction appears as an approximate way of bypassing the polarization dependence of the exchange-correlation energy.

#### 8.7.1 The exact dielectric response

Within the electrostatics, the optical dielectric constant can be obtained as [144]:

$$\epsilon_{\infty} = 1 + 4\pi \frac{\partial \mathcal{P}}{\partial \mathcal{E}} \tag{8.36}$$

where  $\mathcal{P}$  is the macroscopic electronic polarization and  $\mathcal{E}$  is the macroscopic electric field. Within DFT, a complication arrives due to the exchangecorrelation term. Consequently, different approximations were proposed that depend (i) whether  $\mathcal{P}$  was computed when including the exchangecorrelation correction, (ii) whether  $\mathcal{E}$  if the field felt by a test charge or by the Kohn-Sham electrons.

For periodic solids, Umklapp processes are allowed by the particular k-space topology. In order to include the associated local fields effects in the computation of  $\epsilon_{\infty}$ , Adler and Wiser [1, 302] introduced a formalism involving the inverse dielectric matrix, defined as

$$\epsilon^{-1}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') = \frac{\delta v_{\text{eff}}(\mathbf{q} + \mathbf{G}')}{\delta v_{\text{ext}}(\mathbf{q} + \mathbf{G})}$$
(8.37)

The connection with the dielectric constant is given by:

$$\epsilon_{\infty} = \frac{1}{\epsilon^{-1}(\mathbf{q}, \mathbf{q})} \tag{8.38}$$

The demonstration was reported at the RPA level. The next step was therefore to include correctly the correction induced by the exchange and correlation effects [271].

In the *test-charge* formulation, the effective potential appearing in Eq. [8.37] is chosen as that experienced by a hypothetical classic charge and reduces to  $\delta v_{\text{eff}} = \delta v_{\text{ext}} + \delta v_{\text{H}}$ . The Hartree potential is however considered as that produced by the response of the quantum system so that  $\delta v_{\text{H}} = V_C \ \delta n$ , where  $\delta n = \chi_o [\delta v_{\text{ext}} + \delta v_{\text{H}} + \delta v_{\text{xc}}]$ . Within these hypothesis (in one dimension),

$$\frac{1}{\epsilon_{TC}^{-1}(q,q)} = 1 - \frac{\delta v_{\rm H}(q)}{\delta v_{\rm ext}(q) + \delta v_{\rm H}(q)}$$
(8.39)

$$= 1 - \frac{4\pi}{q^2} \frac{\delta n(q)}{\delta v_{\text{ext}}(q) + \delta v_{\text{H}}(q)}$$
(8.40)

Making use of the relationship that exist in the long-wave approach between field and potential and between charge and polarization, we recover Eq. [8.36] where  $\delta \mathcal{P}$  was obtained when including the exchange-correlation corrections and  $\delta \mathcal{E}$  is the applied field only screened by the Coulomb interaction.

In the *electron* formulation, the effective potential appearing in Eq. [8.37] is replaced by that felt by the Kohn-Sham electrons and that is equal to  $\delta v_{\text{eff}} = \delta v_{\text{ext}} + \delta v_{\text{H}} + \delta v_{\text{xc}}$ . The Hartree potential is obtained as in the previous formulation. The dielectric constant so becomes equal to:

$$\frac{1}{\epsilon_{e^-}^{-1}(q,q)} = 1 - \frac{\delta v_{\rm H}(q) + \delta v_{\rm xc}(q)}{\delta v_{\rm ext}(q) + \delta v_{\rm H}(q) + \delta v_{\rm xc}(q)}$$
(8.41)

$$= 1 - \frac{4\pi}{q^2} \frac{(1 + K_{\rm xc,00}/4\pi) \,\delta n(q)}{\delta v_{\rm ext}(q) + \delta v_{\rm H}(q) + \delta v_{\rm xc}(q)}$$
(8.42)

We now examine the interplay between these formulas and the new insights previously given in this Chapter. A first interesting point is that, in absence of polarization dependence ( $\delta v_{xc}(q) = 0$ ), Eq. [8.41] reduces to Eq. [8.39]. Within the LDA or the GGA,  $\epsilon_{e^-}$  and  $\epsilon_{TC}$  are therefore identical. Going beyond these approximation, we observe that the electron definition does not reduce to the electrostatics one when including the exchange-correlation contribution in the macroscopic field, but also consider a modified Coulomb interaction.

#### 8.7. THE DIELECTRIC CONSTANT

This distinction being made, it is now possible to analyze the direct effect of the divergences of head and wings of  $K_{\rm xc}$  on both definitions of the dielectric matrix. Following Singhal and Callaway [271], we use the equality  $\delta n = \chi_o [\delta v_{\rm ext} + \delta v_{\rm H} + \delta v_{\rm xc}]$  to find the form of the dielectric matrices in terms of  $\chi_o$ ,  $V_C$  and  $K_{\rm xc}$ . This yields [271]:

$$\epsilon_{TC} = 1 - V_C \chi_o \left[ 1 - K_{\rm xc} \chi_o \right]^{-1}, \tag{8.43}$$

$$\epsilon_e = 1 - [V_C + K_{\rm xc}]\chi_o. \tag{8.44}$$

As the head and wings of  $\chi_o$  behaves like  $\mathcal{O}(q^2)$  and  $\mathcal{O}(q)$  in the limit of  $q \to 0$  [127], the presence of  $\mathcal{O}(1/q^2)$  and  $\mathcal{O}(1/q)$  divergences for the head and wings of  $K_{\rm xc}$  will induce a finite contribution to all the elements of the matrix  $K_{\rm xc}\chi_o$  which, in turn, will affect all the elements of both dielectric matrices. Consequently, it appears clearly that, when using approximate functionals that do not reproduce the correct  $K_{\rm xc}$  divergence, the head of the dielectric matrix and therefore the macroscopic constant will be wrong from a *finite* amount.

Similarly, consequences of the divergence of  $K_{\rm xc}$  on the value of the *test-charge* dielectric constant can be highlighted from our variational approach to the density functional perturbation theory. Going back to Chapter 6, the element  $\epsilon_{\alpha\beta}$  of the dielectric tensor can be obtained from  $\tilde{E}_{el}^{\mathcal{E}^*_{\alpha}\mathcal{E}_{\beta}}$ , in which the exchange-correlation contribution appears as (see Eq. 6.4):

$$\frac{1}{2} \int_{\Omega_o} K_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}') \ [n^{\mathcal{E}_\alpha}(\mathbf{r})]^* \ n^{\mathcal{E}_\beta}(\mathbf{r}') \ d\mathbf{r} \ d\mathbf{r}'.$$
(8.45)

As  $n^{\mathcal{E}_{\beta}}(q)$  behaves like  $\mathcal{O}(q)$  in the limit of  $q \to 0$ , we deduce that the (q,q)and (q,q+G) terms will contribute from a finite amount to  $\tilde{E}_{el}^{\mathcal{E}_{\alpha}^{*}\mathcal{E}_{\beta}}$  when the  $K_{\mathrm{xc}}$  matrix exhibits the correct long-wavelength behaviour.

Interestingly, we note that, within our variational approach, the previous discussion can be trivially extended to the case of another quantity. In particular, it is straightforward to demonstrate from the expressions proposed in Chapters 5 and 7, that the Born effective charges and dynamical matrix in the limit of  $\mathbf{q} \rightarrow 0$  are affected by a finite correction when including the correct divergence of the exchange-correlation kernel.

#### 8.7.2 Exact DFT and "LDA+scissors" approach

We are now ready for understanding more clearly the *mechanism* by which DFT succeeds to reproduce the correct dielectric response. Indeed, this mechanism appears transparent from our model calculation.

As highlighted by Adler and Wiser [1, 302], the independent particle polarizability matrix is directly accessible from the independent-particle wavefunctions. Its long-wavelength part is obtained in the limit of  $\mathbf{q} \to 0$  as (v and c indices run on the valence and conduction bands respectively) [127]:

$$\chi_{o}(\mathbf{q}, \mathbf{q}) = \frac{4}{\Omega} \sum_{c, v, \mathbf{k}} |\mathbf{q}|^{2} \frac{\langle u_{v, \mathbf{k}} | r | u_{c, \mathbf{k}} \rangle \langle u_{c, \mathbf{k}} | r | u_{v, \mathbf{k}} \rangle}{(\epsilon_{v, \mathbf{k}} - \epsilon_{c, \mathbf{k}})}$$
(8.46)

In our model, the previous expression was used to compute  $\chi_o$  and  $\tilde{\chi}_o$ . We know that both calculations must *in fine* lead to the correct answer  $\chi$ . However,  $\chi_o$  and  $\tilde{\chi}_o$  have different long-wavelength behaviours. The matrix elements appearing in Eq. (8.46) may differ in both computations. Moreover, the DFT bandgap problem will induce an incorrect screening in the KS system: usually, the DFT bandgap underestimates the quasiparticle bandgap so that  $\chi_o(q,q) > \tilde{\chi}_o(q,q)$ . From Eq. (8.30), we observe that

the  $\mathcal{O}(1/q^2)$  divergence of  $K_{\mathrm{xc}}(\mathbf{q}, \mathbf{q})$  appears for compensating the different  $\mathcal{O}(q^2)$  behaviours between  $\chi_o(q, q)$  and  $\tilde{\chi}_o(q, q)$  in order to yield finally the right answer  $\chi$ .

The scissors correction naturally arises in this specific context. Within the LDA, we have shown that  $K_{\rm xc}$  does not exhibit the correct behaviour. Assuming that the LDA and quasi-particle wavefunctions are nearly identical, the difference between  $\chi_o$  and  $\tilde{\chi}_o$  appears essentially connected to the DFT bandgap problem. The scissor operator introduced by Levine and Allan [166, 167], appears therefore as a crude tool that roughly eliminates the difference between  $\chi_o$  and  $\tilde{\chi}_o$ : it so artificially compensates the absence of divergence of the LDA approximate  $K_{\rm xc}$ .

A similar approach was taken independently by Aulbur, Jönnsson and Wilkins [5] who estimated for real materials the amplitude of  $K_{\rm xc,00}$ . Remarkably, they observed that the experimental dielectric constant can be reproduced correctly if the coefficient  $K_{\rm xc,00}$  is chosen approximately constant for common semiconductors. More generally, they found that  $K_{\rm xc,00}$ scales roughly linearly with average bond length in the material. Going beyond the basic arguments presented in this Section, they also extensively investigated the pertinence of the *scissors* correction. Moreover, their discussion was not restricted to the dielectric susceptibility but also concerned non-linear optical responses.

## 8.8 Origin of the Polarization dependence

#### 8.8.1 The exchange-correlation hole

Up to now, we essentially discussed consequences of the dependence on polarization of the exchange-correlation energy. Independently, another interesting issue directly concerns the microscopic origin of this polarization dependence. The debate was initiated a few months ago by R. Resta [245] who reintroduced in the discussion the concept of exchange-correlation hole, described in Chapter 1. From his study, he proposed that, in order to observe a polarization dependence, the many-body wavefunction of insulators should display some kinds of long-range correlation. More explicitly, the exchange-correlation hole around each electron would not necessarily integrate to -1 within a microscopic range but should be partly delocalized at the surface of the material. As the exchange hole integrates to -1 over a microscopic distance, this phenomenon would be a purely correlation effect. In response to this intriguing assertion, Vanderbilt and Langreth [285] as well as Martin and Ortiz [186] pointed out arguments suggesting that  $n_{\omega}^{xc}(\mathbf{r}_2|\mathbf{r}_1)$  should have a decay like  $1/(\mathbf{r}_1-\mathbf{r}_2)^{-3}$ . In response Resta [246] emphasized that such arguments are restricted to perturbation theory, so keeping open the debate on the localization of the exchange-correlation hole.

Independently, Martin and Ortiz [186] also argued that the polarization dependence of the KS exchange-correlation energy should find its origin in the polarizability of a localized exchange-correlation hole within the field induced by the polarization charges. From this point of view, it seems clear that a polarization dependence discussed in this Chapter do not require any long-range correlation. As a proof, we now show that the DFT exchange energy (without correlation) already exhibits dependence on the polarization although the exchange hole integrates to -1 in the bulk [99].

#### 8.8.2 Polarization dependence of the exchange energy

From what was previously discussed, it is clear that a O(1/q) divergence in the long-wave part  $(\mathbf{q} \to \mathbf{0})$  of the exchange potential  $v_x(\mathbf{q}) = \frac{\delta E_x}{\delta n^*(\mathbf{q})}$  (corresponding to an homogeneous exchange electric field) is a necessary and sufficient condition for the exchange energy to depend on the polarization. As mentioned in Chapter 1, the exchange energy

$$E_x = -\frac{1}{4} \iint \frac{\gamma(\mathbf{r}, \mathbf{r}') \ \gamma(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \ d\mathbf{r} \ d\mathbf{r}', \qquad (8.47)$$
can be computed from the first-order density matrix obtained from Kohn-Sham (KS) wavefunctions [248, 170]:

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_{i}^{occ} \psi_i^*(\mathbf{r}) \ \psi_i(\mathbf{r}'). \tag{8.48}$$

A tractable scheme for computing the exchange potential was recently proposed by Görling and Levy [104], with the components of the KS potential taken as *independent* variables. In our case, using the chain rule,

$$v_{x}(\mathbf{q}) = \sum_{\mathbf{G}} \frac{\delta E_{x}}{\delta v_{s}(\mathbf{q} + \mathbf{G})} \frac{\delta v_{s}(\mathbf{q} + \mathbf{G})}{\delta n^{*}(\mathbf{q})}$$
$$= \sum_{\mathbf{G}} \chi_{0}^{-1}(\mathbf{q}, \mathbf{q} + \mathbf{G}) \frac{\delta E_{x}}{\delta v_{s}(\mathbf{q} + \mathbf{G})}, \qquad (8.49)$$

where  $\chi_0$  is the independent-particle polarizability of the KS electronic system. The important physics is contained in the  $\mathbf{G} = \mathbf{0}$  component (while other reciprocal-lattice vectors describe local fields).

Thanks to the  $O(1/q^2)$  divergence of  $\chi_0^{-1}$  in the long-wavelength limit, one requires a contribution of order q from  $\delta E_x/\delta v_s(\mathbf{q})$  for the O(1/q) divergence of  $v_x(\mathbf{q})$  to arise.

From Eq. (8.47), one finds

$$\frac{\delta E_x}{\delta v_s(\mathbf{q})} = -\frac{1}{2} \iint \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{\delta \gamma(\mathbf{r}', \mathbf{r})}{\delta v_s(\mathbf{q})} d\mathbf{r} d\mathbf{r}'.$$
(8.50)

The long-wave change in the KS potential can be written [94] as  $\delta v_s(\mathbf{q}) = \delta \mathcal{E}/2iq$  (where  $\delta \mathcal{E}$  is the KS effective electric field), so that:

$$\frac{\delta\gamma(\mathbf{r}',\mathbf{r})}{\delta v_s(\mathbf{q})} = 2iq \quad \frac{\delta\gamma(\mathbf{r}',\mathbf{r})}{\delta\mathcal{E}}.$$
(8.51)

The final step in the proof comes from the fact that the density matrix built from KS wavefunctions indeed depends on the long-wave change in the KS potential or, equivalently, that the exchange hole polarizes [187] when placed in a KS effective electric field. This is easily seen in the following example. Consider a 3D periodic array of widely spaced helium atoms, with its corresponding KS potential and associated KS wavefunctions. The exchange hole, for an electron close to one helium atom, is equal to minus half the density surrounding this helium atom, and integrates to -1. If an independent KS electric field is now applied, the density around each atom, and hence also the exchange hole, will polarize. The dependence of the DFT exchange energy on polarization is thus demonstrated. This result establishes that the polarization dependence of the exchangecorrelation energy do not requires any long-range correlation effects as suggested by Resta [245]. However, it does not invalidate the existence of such correlation effects that would in turn induce additional dependence on the polarization.

#### 8.9 Conclusions

In this Chapter, we have introduced a new density-functional perturbation theory as the correct generalization of the density functional formalism for the case of infinite periodic systems. We have seen that correct handling of the macroscopic polarization is mandatory when investigating the response of insulators to homogeneous electric fields, and can prevent the correct KS description of polar solids when using BvK boundary condition.

The dependence on polarization of the KS exchange-correlation energy manifests as a fictitious exchange-correlation electric field to which are submitted the KS particles of the system. This exchange-correlation field induces a divergence in the long-wavelength part of the exchange-correlation kernel. The optical dielectric tensor, Born effective charges and dynamical matrix associated to phonon of long-wavelength computed within local or semi-local approximations (LDA, GGA), that are not able to reproduce that behaviour, will be wrong from a finite amount.

Physically, the polarization dependence of the exchange-correlation energy has been associated to a polarizability of the exchange-correlation hole within the KS exchange-correlation electric field.

#### 8.10 References

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

- Gonze X., Ph. Ghosez and R. W. Godby, Density-polarization functional theory of the response of a periodic insulating solid to an electric field, Phys. Rev. Lett. 74, 4035 (1995).
- Gonze X., Ph. Ghosez and R. W. Godby, Density-functional theory of polar insulators, Phys. Rev. Lett. 78, 294 (1997).
- Gonze X., Ph. Ghosez and R. W. Godby, Polarization dependence of the exchange energy, Phys. Rev. Lett. 78, 2029 (1997).

# Conclusions

First-principles calculations performed within the density functional formalism are now currently used, as a complement to the experiment, for the investigation of the properties of crystalline solids. In this work, we applied such a technique to the study of ferroelectric barium titanate. Some of our results directly concern the physics of the material. Another part of our work questions the fundamentals of the theory within which our calculations have been performed. Our main results can be summarized as follows.

Concerning first barium titanate, we paid a particular attention to the interplay between the electronic and dynamical properties, with the intention of clarifying the microscopic origin of the instability associated to the ferroelectric distortion. In our discussion (see flowchart *verso*), the Born effective charge appeared as a central quantity: its amplitude, on one hand intimately related to the electronic properties, was also on the other hand monitoring the destabilizing long-range dipolar forces generating the polar instability.

As a first step, anomalously large Born effective charges were identified in  $BaTiO_3$  on titanium and on oxygen for atomic displacements along the Ti–O direction (Table 5.2). It was highlighted that the Born effective charge is a dynamical concept and that its amplitude cannot be deduced from the inspection of the electronic density alone. Following the model of Harrison, the anomalous charges were associated to macroscopic electronic currents. They were understood in terms of transfers of charge induced by dynamic changes of orbital hybridizations. From a band-by-band decomposition (Section 5.6), we emphasized that the existence of partial hybridizations between occupied and unoccupied states is an essential feature for anomalous contributions to appear. In contrast, hybridizations restricted to occupied states generate compensating anomalous contributions, not affecting the global value of the Born effective charges. The anomalously



Figure 8.6: Flowchart summarizing the connection between the O 2p-Ti 3d hybridizations and the chain-structure ferroelectric instability of barium titanate.

large amplitude of the Born effective charges on titanium and on oxygen was attributed to dynamic changes of hybridization between O 2p and Ti 3d orbitals. It was shown that the amplitude of these anomalous charges is strongly sensitive to the anisotropy of the interatomic distances along the Ti-O chain (Fig. 5.3).

As a second step we investigated the consequences of the anomalously large Born effective charges on the lattice dynamics. Following the original idea of Cochran, we separated the respective contribution of the dipolar and short-range forces to the frequency of the transverse modes at the  $\Gamma$  point. It was shown that the instability of the ferroelectric mode is induced by the compensation of stabilizing short-range forces by a larger destabilizing dipole-dipole interaction (Fig. 7.2). The driving force of the transition appeared as the anomalously large Born effective charges, that couple together for the specific displacement pattern associated with the ferroelectric mode, in order to generate a giant dipolar interaction. From that viewpoint, the ferroelectric instability was also coherently related to the dynamic changes of hybridizations between O 2p and Ti 3d orbitals, responsible of the unusual amplitude of the Born effective charges.

It was pointed out that the balance of force, leading to the ferroelectric instability, is very delicate. Disappearance of the unstable mode in the rhombohedral phase was attributed to a reduction of the Born effective charges in this phase while its stabilization under isotropic pressure was more likely connected to a modification of the short-range forces.

Going further, we reported full phonon dispersion curves for the cubic phase of barium titanate (Fig. 7.4). The observed pronounced twodimensional character of the ferroelectric instability in the Brillouin zone (Fig. 7.6) was associated to a chain-structure instability in real space. In agreement with this picture, it was observed that both short-range and dipolar parts of the the interatomic force constants are highly anisotropic: they are associated to a much stronger correlation of the atomic displacements along the Ti–O chains. It was pointed out that a single atomic displacement is never unstable but that a cooperative displacement of a dozen of atoms along a single isolated Ti–O chain is enough to induce the ferroelectric instability (Fig. 7.7). As a consequence of the large dipolar forces, the coupling between the displacements of a Ti atom and its first oxygen neighbour is destabilizing. This destabilizing coupling, even if small, appeared as an essential feature to reproduce the structural instability.

Throughout this work, a particular emphasis has also been placed on the formalism within which our calculations have been performed. In this context, we investigated the correct generalization of the density functional formalism for the case of truly periodic insulators. We highlighted that correct handling of the polarization is mandatory when investigating the response of insulators to homogeneous electric fields, and can prevent the correct Kohn-Sham description of polar insulators when using periodic boundary conditions. The crucial role of the polarization originates in an ultra non-local dependence on the density. It led to the introduction of a new density-polarization functional theory for the case of infinite periodic systems.

It was shown that the polarization dependence of the exchange-correlation energy shows itself in an additional fictitious electric field to which are submitted the Kohn-Sham particles of the system (Fig. 8.1). It also induces a divergence in the long wavelength part of the exact exchange-correlation kernel (Fig. 8.5). These behaviours are not reproduced within the usual local density approximation (LDA) and generalized gradient approximation (GGA). We demonstrated that the absence of divergence in the exchangecorrelation kernel associated to these approximate functionals affects the amplitude of the computed optical dielectric constant by a finite amount. A similar consequence is expected for the Born effective charges and the frequencies of long-wavelength longitudinal phonons.

## Appendix A

## Technical details

In this appendix, we report some technical details concerning our firstprinciples study of barium titanate.

The calculations have been performed in the general framework of the density functional formalism. The exchange-correlation energy has been evaluated within the local density approximation, using a polynomial parametrization [280] of Ceperley-Alder [29] homogeneous electron gas data. Our results have been obtained in the context of a plane-wave pseudopotential approach. Integrations over the Brillouin zone were replaced by sums on a mesh of special **k**-points [197, 198].

In a first Section, we describe the pseudopotentials that have been used in our calculations. In a second part we briefly discuss the convergence of the results in terms of the Brillouin zone sampling and the kinetic energy cutoff, used to defined the plane-wave basis set. In a third Section, we investigate the role of the exchange-correlation energy on the ferroelectric instability.

#### A.1 Pseudopotentials

In our study of  $BaTiO_3$ , the ionic-core electrons potentials were replaced by ab initio, separable, extended norm conserving pseudopotentials, as proposed by M. Teter [279]. For the oxygen atom, in order to increase the transferability, an additional condition of "chemical hardness" conservation has been imposed.

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. The reference configuration and core radii of the pseudopotentials are reported

		Ba	Ti	0
Reference		$5s^2 \ 5p^6 \ 6s^0$	$3s^2 \ 3p^6 \ 3d^2 \ 4s^0$	$2s^2 \ 2p^4$
Core radius (a.u.)	s	1.7	1.25	1.65
	p	1.7	1.25	1.65
	d	1.7	1.65	-

Table A.1: Reference configuration and core radii of the pseudopotentials that we have used in our study of  $BaTiO_3$ .

in Table A.1. The local and non-local part of the pseudopotentials as well as the radial part of the pseudo-wavefunctions are plotted in Ref. [55]. We note that due to the description of the Ti 3s semi-core level as a valence state, the Ti pseudopotential is relatively hard and imposes to work at a relatively high cutoff energy (35-45 Ha).

#### A.2 Convergence study

Typically, the plane-wave energy cutoff and the mesh of  $\mathbf{k}$ -points to be used in order to obtain well converged results are dependent from one property to the other. The convergence problems are now briefly discussed.

#### A.2.1 Ground-state properties

In Chapter 3, a convergence better than 10 meV has been obtained on the electronic band structure when using a  $4 \times 4 \times 4$  mesh of special **k**-points and a 45 Ha cutoff (about 6200 plane-waves included in the basis set).

Although the lattice constant in the cubic phase was fairly insensitive to the quality of the Brillouin zone integration, the optimization of the atomic positions in the ferroelectric phases required a denser mesh of special **k**-points. A convergence of the order of 0.001 (see Table A.2) has been obtained on the atomic positions (in reduced coordinates) in the rhombohedral phase when using a  $6 \times 6 \times 6$  mesh of special **k**-points and a 35 Ha cutoff (about 4100 plane-waves). A similar convergence is expected for the other ferroelectric phases.

Table A.2: Convergence of the atomic positions with **k**-point set and energy cutoff (Hartree) for a rhombohedral distortion in the cubic unit cell of BaTiO<sub>3</sub>. Notations have been defined in Chapter 3.

$\mathbf{k}$ -point mesh	$E_{cut}$	$\Delta_{R-Ti}$	$\Delta_{R-O1}$	$\Delta_{R-O2}$
$2 \times 2 \times 2$	35	-0.0000	0.0000	0.0000
$4 \times 4 \times 4$	35	-0.0104	0.0121	0.0181
	45	-0.0104	0.0120	0.0183
$6 \times 6 \times 6$	35	-0.0110	0.0133	0.0192

#### A.2.2 Response functions

The Born effective charges and the dielectric tensors presented in Chapter 5 and 6 were obtained with a  $6 \times 6 \times 6$  mesh of special **k**-points and a 35 Ha cutoff. These parameters guarantee a convergence better than 0.5% on  $Z^*$  as well as on each of its band by band contributions. A similar accuracy is obtained on  $\epsilon_{\infty}$ .

Well converged phonon frequencies also required a  $6 \times 6 \times 6$  mesh of special k-points (this mesh was verified by different authors to give sufficient accuracy [141, 292]). The phonon frequencies at the  $\Gamma$  point were already well converged (up to the order of 1 cm<sup>-1</sup>) at a 35 Ha cutoff. Similarly, the phonon eigenvectors were fully converged at this specific cutoff energy. However, in order to minimize convergence errors on further associated quantities (like the interatomic force constants), all our calculations in the cubic phase presented in Chapter 7 have been performed at a higher 45 Ha cutoff energy. The Born effective charges and dielectric tensor, required to evaluate the long-range Coulomb interaction were coherently recomputed at this higher cutoff energy. We note that the results concerning the  $\Gamma$ point of the rhombohedral structure were obtained at a 35 Ha cutoff, at which the structural optimization had been previously performed and for which Born effective charges and dielectric tensors were already available.

#### A.3 Structural optimization

In Chapter 3, we reported results concerning the structural optimization of  $BaTiO_3$  in its four different phases. As mentioned in that Chapter, the theoretical results are in satisfactory agreement with the experiment. However, the error is larger than that usually observed within the LDA for



Figure A.1: The cohesive energy ( $\bullet \equiv E_{coh}$ ) of cubic BaTiO<sub>3</sub> and its kinetic ( $\triangle \equiv E_{kin}$ ), electrostatic ( $\square \equiv E_{elec}$ ) and exchange-correlation ( $\diamond \equiv E_{xc}$ ) contributions as a function of the lattice parameter. As shown in the inset, when neglecting the exchange-correlation contribution ( $\blacksquare \equiv E_{kin} + E_{elec}$ ), the optimum lattice parameter is shifted from 3.94 to around 4.9 Å.

other materials. This is not a particular feature of our calculations but it was similarly observed by different groups studying the family of  $ABO_3$ compounds: it was intuitively attributed to the approximate description of the exchange-correlation energy within the LDA. In order to investigate the role of the exchange-correlation energy in the identification of the optimized structures, we decomposed the total crystal energy into its kinetic, electrostatic and exchange-correlation contributions.

A first result, reported in Fig. A.1, concerns the evolution of the cohesive energy of cubic  $BaTiO_3$  in terms of the lattice parameter. In the same spirit, in Fig. A.2, we examine the contribution of the exchange-correlation energy to the lowering of the total energy along a path of atomic displacements from the cubic to the rhombohedral structure (the macroscopic strain has been neglected).

In both cases, it is observed that the well, from which the equilibrium structural parameter is deduced, is very flat. This provides from the near



Figure A.2: Kinetic ( $\Delta \equiv E_{kin}$ ), electrostatic ( $\Box \equiv E_{elec}$ ) and exchangecorrelation ( $\diamond \equiv E_{xc}$ ) contributions to the lowering of the crystal energy ( $\bullet \equiv E_{tot}$ ) along a path of atomic displacements from the cubic ( $\lambda = 0$ ) to the rhombohedral ( $\lambda = 1$ ) structure. As shown in the inset, when neglecting the exchange-correlation contribution ( $\blacksquare \equiv E_{kin} + E_{elec}$ ), the ferroelectric instability disappears.

compensation between large but antagonist kinetic and electrostatic contributions. At the scale of the well depth, the small exchange-correlation energy appears as a major contribution to the lowering of the crystal energy, necessary to reproduce the correct structure (see the insets of Fig. A.1–A.2).

From these graphs, it appears clearly that the exchange-correlation energy plays an important role in the description of  $BaTiO_3$ . Therefore, it should not be surprising if the results were more strongly sensitive than for other compounds to the approximate description of this term within the LDA. It is expected that the amplitude of the calculated optimized parameters should be particularly sensitive to distinct handling of the exchange-correlation effects from one approximation to the other (LDA, GGA, WDA). Recently, it was observed that the lattice parameter of the cubic phase obtained within the WDA [270] is in better agreement with the experiment than that computed within the LDA.

## Appendix B

## The atomic charges

#### **B.1** The static atomic charges

In this Appendix, we give a few additional informations concerning some of the static atomic charges that were briefly discussed in Chapter 5.

**Mulliken population analysis** [203]: this method makes use of the basis functions that are used to represent the wavefunctions (it basically consists in an analysis of the density matrix: see for instance Ref. [194]). Although widely used, this charge has long been recognized as strongly dependent on the basis set. It can also yield unphysical negative value for the population of some orbitals. Finally, it seems sometimes to give an unreasonable physical picture in materials having significant ionic character. An interesting improvement of this method that circumvents most of its drawback, was proposed by Weinhold *et al.* [237] who introduced the concept of natural atomic orbitals.

**Hirshfeld method** [120]: this method separates the charge density into overlapping contributions. The charge density at each point of space is separated between the constituent atoms in the same proportions as they contribute to the charge density to that point in a hypothetical compound, constructed by the superposition of the spherically symmetrized charge density distributions of the isolated atoms. Note that various alternative methods for fitting overlapping atomic densities have been proposed (see Ref. [194]).

**Bader method** [8]: this method splits the electronic density between non-overlapping regions on the basis of topological arguments [48, 265]. Critical points are first identified that correspond to minimum charge density along the bond between the different atoms. From these points, paths

for which the charge density decreases most rapidly are then developed in direction perpendicular to the bond. The sets of these paths define zero-flux surfaces separating the atoms. This method is very elegant but it suffers from some problems. There is a possibility of empty loges, portions of space that do not belong to any particular atom. Moreover, since a high density on a particular atom repels the zero-flux surface, the Bader charge value usually exaggerate the atomic charges. In spite of these inconvenients, this charge is sometimes considered as the best choice [300].

**ESPD** charge of Lee et al. [165]: this method is based on a fit, through a variational principle, of the electrostatic potential energy from spherical atom model potentials. This technique is a generalization from commonly employed methods that derive atomic charges from least-squares fitting of the electrostatic potential at a given set of points and that are usually dependent from the choice of these fitting points. The new method of Lee *et al.* depends only on the electron density and does not require fitting points.

Harrison charges [113]: a static effective charge concept appears naturally within the tight-binding model of Harrison. This charge differ from the bare ionic charge expected in a purely ionic compound by a static transfer of electrons between the atoms, determined from the orbital interaction parameters. It is the additional bond-length dependence of these parameters that is at the origin of the dynamic contribution to the Born effective charge.

#### **B.2** The Harrison model

In this Section, we briefly describe the bond orbital model proposed by Harrison for the case of  $ABO_3$  compounds [113]. In particular, we pay a particular attention to the definition and the calculation of static and dynamic charges within this model. Values are reported for  $SrTiO_3$ .

The bond orbital model of Harrison consists in a simplified tight-binding model, where the Hamiltonian is limited to the on-site and nearest neighbour terms. Moreover, for ABO<sub>3</sub> compounds, it is assumed that the A atom has no other function than to provide electrons to the system, and is fully ionized. The only considered interactions involve B and O atom orbitals.

The model includes O 2s, O 2p and B d orbitals, interacting through  $V_{sd,\sigma}$ ,  $V_{pd,\sigma}$  and  $V_{pd,\pi}$  parameters. The matrix elements  $V_{sd,\sigma}$  and  $V_{pd,\sigma}$  are nearly identical. It is therefore suggested to construct two sp hybrids on the oxygen,  $(|s > \pm|p >)/\sqrt{2}$ , that each will have a large matrix element  $(V_{hd,\sigma}^+ = [V_{sd,\sigma} + V_{pd,\sigma}]/\sqrt{2})$  coupling one hybrid to the d state on one side

and a negligible matrix element  $(V_{hd,\sigma}^- = [V_{sd,\sigma} - V_{pd,\sigma}]/\sqrt{2})$  coupling that hybrid to the *d* state on the other.

#### **B.2.1** Effective static charge

In absence of interactions, the static charges of  $SrTiO_3$  should be of +2 on Sr, +4 on Ti and -2 on O. Due to the Ti-O orbital interactions, the transfer of electrons from Ti to O is not complete and the effective static charge on O becomes:

$$Z_O = -2 + T_\sigma + T_\pi \tag{B.1}$$

where

$$T_{\sigma} = 4 \left( \frac{V_{hd,\sigma}^{+}}{[\epsilon_d - (\epsilon_s + \epsilon_p)/2]} \right)^2$$
(B.2)

("4" because there are 2 hybrids composed of 2 electrons that each interacts mainly with one Ti neighbour) and

$$T_{\pi} = 8 \left( \frac{V_{pd,\pi}^+}{[\epsilon_d - \epsilon_p)]} \right)^2 \tag{B.3}$$

("8" because there are 4 electrons that are each partly delocalized on the 2 Ti neighbours).

For SrTiO<sub>3</sub>, from the parameters of Matheiss,  $T_{\sigma} = 0.35$  and  $T_{\pi} = 0.68$  so that  $Z_O = 0.96$ .

#### B.2.2 Born effective charge

The calculation of the Born effective charge now requires to make use of the dependence of the matrix elements V upon the bond length d. From the Harrison table, the previous matrix elements have all the same interatomic dependence:

$$V = Kd^{-7/2} \tag{B.4}$$

$$\delta V = -\frac{7}{2}V\frac{\delta d}{d} \tag{B.5}$$

so that

$$(V + \delta V)^2 = V^2 + 2 V \,\delta V + \mathcal{O}(2)$$
 (B.6)

$$= V^{2} + 2 \left(\frac{-7}{2}\right) V^{2} \frac{\delta d}{d} + \mathcal{O}(2)$$
 (B.7)

When displacing the O atom along the Ti-O direction, there will be an additional transfer of electron from O to the nearest Ti that is equal to

$$\delta T_{\sigma} = 2\left[2\left(\frac{-7}{2}\right)\left(\frac{V_{hd,\sigma}}{\epsilon_d - \epsilon_h}\right)^2\right]\frac{\delta d}{d}$$
(B.8)

$$\delta T_{\pi} = 4 \left[ 2 \left( \frac{-7}{2} \right) \left( \frac{V_{pd,\pi}}{\epsilon_d - \epsilon_p} \right)^2 \right] \frac{\delta d}{d}$$
(B.9)

On the other hand, there will be the same transfer of charge from the other neighbour Ti atom to O, so that the previous electrons are globally transferred on a distance 2d. The change of polarization associated to this transfer of charge is:

$$\delta P_{\sigma} = -28 \left(\frac{V_{hd,\sigma}}{\epsilon_d - \epsilon_h}\right)^2 \delta d \tag{B.10}$$

$$\delta P_{\pi} = -56 \left(\frac{V_{pd,\pi}}{\epsilon_d - \epsilon_p}\right)^2 \delta d \tag{B.11}$$

The associated dynamic contribution to the Born effective charge is  $(\delta P/\delta d)$ :

$$\delta Z_{\sigma}^{*} = -28\left(\frac{V_{hd,\sigma}}{\epsilon_{d} - \epsilon_{h}}\right)^{2}$$
(B.12)

$$\delta Z_{\pi}^{*} = -56(\frac{V_{pd,\pi}}{\epsilon_d - \epsilon_p})^2 \tag{B.13}$$

The effective charge on the O atom for a displacement along the Ti-O direction is therefore:

$$Z_{O\parallel}^* = Z_O + \delta Z_{\sigma}^* + \delta Z_{\pi}^* \tag{B.14}$$

For SrTiO3, from the parameters of Matheiss,  $\delta Z^*_{\sigma} = -2.45$  and  $\delta Z^*_{\pi} = -4.76$  so that  $Z^*_{O\parallel} = -8.18$ .

# Appendix C

# Phonons

#### C.1 The acoustic sum rule

As mentioned in Chapter 7, the total energy of a crystal must remain invariant under homogeneous translations, so that the dynamical matrix at  $\Gamma$  should admit homogeneous translations as eigenvectors with zero eigenfrequencies. This condition imposes a requirement on the elements of the dynamical matrix well known as the "acoustic sum rule" (ASR). This rule is however not exactly satisfied in practical calculations due to technical approximations that slightly break the translational invariance of the total energy. In this Section, we first reinvestigate the origin of the problem. We then discuss how it can be efficiently eliminated for the case of BaTiO<sub>3</sub>.

The different contributions to the total energy (see Chapter 2) are evaluated in a translational invariant way, except the exchange-correlation part for which the integration in real space over the unit cell is approximated by a sum on a finite grid of points:

$$E_{\rm xc}[n] = \int_{\Omega_o} \epsilon_{xc}^{LDA}[n(\mathbf{r})] \cdot n(\mathbf{r}) \, d\mathbf{r} \qquad (C.1)$$

$$\approx \sum_{i} \epsilon_{xc}^{LDA}[n(\mathbf{r}_{i})] \cdot n(\mathbf{r}_{i})$$
(C.2)

The exchange-correlation energy so obtained is not independent on the position of the atoms with respect to the grid so that small oscillations of the energy are observed when the atoms are homogeneously shifted.

This is illustrated in Fig. C.1-a for the case of  $BaTiO_3$ , for which we used a grid composed of  $48 \times 48 \times 48$  points. It is seen that the total energy



Figure C.1: (a) Evolution of the total energy of BaTiO<sub>3</sub> under homogeneous translation of the crystal. (b) Kinetic, electrostatic and exchangecorrelation contributions to the change of total energy for  $\delta x = 0.5 \times (a_o/48)$  in (a).

of the crystal is not invariant under translation but oscillates at a frequency directly related to the space between points of the grid. In Fig. C.1-b it is highlighted that this oscillation is induced by the exchange-correlation term while the other contributions compensates.

It should be argued that the amplitude of the oscillations is very small compared to the total energy of the crystal (-133.137 Ha/cell). However, the wavelength of the oscillations is also very small so that the curvature of the energy at the origin is not negligible. When identifying the elements of the dynamical matrix (i.e., the second energy derivatives of the energy with respect to a specific atomic displacement), this unphysical curvature will produce an erroneous contribution.

For instance, the dynamical matrix of BaTiO<sub>3</sub> at the  $\Gamma$  point, obtained by linear response, does not satisfy the ASR and the associated eigenfrequencies of the transverse modes are equal respectively to: 156 *i*, 101, 263 and 524 cm<sup>-1</sup>. No one of these modes is associated to a perfect translation of the crystal; no one has zero frequency. From the curvature of the energy at the origin in Fig. C.1, we can estimate the fictitious frequency of the translational mode to 121 cm<sup>-1</sup>. The frequency of the same translational mode, calculated from the dynamical matrix obtained by linear response is equal to 122 cm<sup>-1</sup>. This result clearly identifies the ASR problem with the break of translational invariance induced by our technique of calculation of the exchange-correlation energy.

The ASR imposes a requirement on a specific collective displacement of the different atoms. In order to correct efficiently the different elements of the dynamical matrix (eventually also at other wavevectors than  $\Gamma$ ) it is important to quantify the contribution from each atom to the break of the sum rule. For that purpose, we now consider different cubic unit cells, identical in volume to that of BaTiO<sub>3</sub>, but composed of a single atom of Ba, Ti and O respectively. For each of them, we then study the evolution of the total energy under translation. The result is reported in Fig. C.2. We observe that (i) for Ba and Ti atoms, the translational invariance is well preserved, (ii) the evolution of the energy in BaTiO<sub>3</sub> (Fig. C.1) is reproduced in good approximation as three times the evolution of the energy associated to the displacement of a single isolated O atom. This points out that our ASR problem is associated to the oxygen atom only and is not dependent on the environment in which this atom is placed.

The predominant role plays by the oxygen is confirmed from the inspection of the dynamical submatrix, associated to displacements along



Figure C.2: Evolution of the total energy under homogeneous translation for hypothetical single cubic crystals of Ba, Ti and O, in comparison with the evolution observed in  $BaTiO_3$  (see text).

the x-axis <sup>1</sup>:

$$\tilde{C}_{\kappa_{1,\kappa'1}} = \begin{pmatrix} +3.374 & -1.996 & -0.306 & -0.306 & -0.766 \\ -1.996 & -0.177 & -0.511 & -0.511 & +3.297 \\ -0.306 & -0.511 & +5.569 & +0.343 & -2.603 \\ -0.306 & -0.511 & +0.343 & +5.569 & -2.603 \\ -0.766 & +3.297 & -2.603 & -2.603 & +5.157 \end{pmatrix}$$
(C.3)

for which it can be checked that the sum of the elements of a row are roughly zero for the first two rows associated to Ba and Ti, but significantly nonzero for the three last rows associated to oxygen.

We note that the problem mentioned here for the oxygen is significantly larger than that typically observed in other calculations. It is in fact directly related to the specific "chemical hardness conserving" pseudopotential that was used in our calculation. Interestingly, using another oxygen pseudopo-

 $<sup>{}^1\</sup>tilde{C}_{\kappa 1,\kappa'1} = \partial^2 E_{e+i}/\partial \tau_{\kappa,1}\partial \tau_{\kappa',1}$ , where atoms  $\kappa,\kappa'$  are labeled as follows: Ba, Ti, O1, O2 and O3 (following notations of Chapter 3).



Figure C.3: Phonon frequencies  $(cm^{-1})$  at the  $\Gamma$  point in the experimental cubic phase of BaTiO<sub>3</sub>. We report frequencies of transverse ( $\bullet$ ), longitudinal ( $\circ$ ) and "silent" ( $\bullet$ ) modes before (ASR=0) and after (ASR=1) the ASR correction, in comparison with the experimental (EXP) data. Imaginary frequencies appear as negative frequencies in this graph.

tential, the amplitude of the problem was significantly smaller, and of the same order of magnitude than for Ba and Ti.

As the ASR problem, inherent to our study of BaTiO<sub>3</sub>, is intrinsic to the oxygen atom and is roughly independent on its environment (i.e. presence and cooperative displacement of other atoms within the cell), the ASR can be coherently restored by correcting only the *diagonal* elements of the dynamical matrix following Eq. (7.25). The effect of this correction is illustrated in Fig. C.3 for the case of BaTiO<sub>3</sub>. Moreover, the error induced by the oxygen atom being in first approximation independent from the presence and displacement of other atoms within the cell, it will be *a fortiori* independent on the displacement of the atoms in adjacent cells: it should therefore be independent on the wavevector so that the correction can be generalized at each wavevector following Eq. (7.26).

In this Section we have emphasized that ASR problems may occur because of the presence of a finite grid in real space on which the exchange-

Table C.1: Phonon frequencies  $(cm^{-1})$  at the  $\Gamma$  point in the experimental cubic phase of SrTiO<sub>3</sub>. The LO-TO splitting was computed from the theoretical Z<sup>\*</sup> and  $\epsilon_{\infty}$  (see text). Values in brackets were deduced with the experimental dielectric constant  $\epsilon_{\infty} = 5.18$ .

Mode	Present	Ref. [313]	Experiment
$F_{1u}(\mathrm{TO1})$	87~i	41 i	-
$F_{1u}(\text{LO1})$	140(141)	158	171
$F_{1u}(\mathrm{TO2})$	149	165	175
$F_{1u}(\mathrm{LO2})$	443 (451)	454	474
$F_{1u}(\mathrm{TO3})$	519	546	545
$F_{1u}(\mathrm{LO3})$	746(811)	829	795
$F_{2u}$	223	-	-

correlation energy is evaluated. The problem was particularly stringent in our study of  $BaTiO_3$ . The bad feature was directly related to the specific oxygen pseudopotential that was used in our calculation. Furtunately, a coherent procedure has been found to eliminate the problem. From our experience, it is suggested that invariance under translation should be an additional criterion to be checked when generating atomic pseudopotentials for the study of the dynamical properties of solids.

#### C.2 SrTiO<sub>3</sub>

In the same spirit than for BaTiO<sub>3</sub>, the phonon frequencies at the  $\Gamma$  point have been obtained for the cubic phase of SrTiO<sub>3</sub>. Computations have been performed on a  $6 \times 6 \times 6$  mesh of special **k**-points and at a 45 Ha cutoff. The results are presented in Table C.1 and are associated to a cubic phase at the experimental lattice parameter of 7.38 bohr<sup>2</sup>. The LO-TO splitting was deduced from the Born effective charges reported in Chapter 5 and from the theoretical optical dielectric constant  $\epsilon_{\infty} = 6.33$ .

We note the existence of an unstable mode at the  $\Gamma$  point that is associated to the ferroelectric displacement of the titanium atom against the oxygen cage. Similarly to what was discussed for BaTiO<sub>3</sub>, we have observed that the small instability ( $\omega^2 = -7537 \text{ cm}^{-2}$ ) associated to the ferroelectric polar distortion comes from the near cancellation between destabilizing

<sup>&</sup>lt;sup>2</sup>The LDA optimized lattice constant is of 7.27 bohr [55].

dipolar forces ( $\omega_{DD}^2 = -369265 \text{ cm}^{-2}$ ) and stabilizing short-range forces ( $\omega_{SR}^2 = +361728 \text{ cm}^{-2}$ ). In spite of its small ferroelectric instability, SrTiO<sub>3</sub> is however never

In spite of its small ferroelectric instability,  $SrTiO_3$  is however never ferroelectric: it undergoes an anti-ferrodistortive transition induced by another more unstable phonon at the *R*-point, which is associated to a tilt of the oxygen octahedra.

APPENDIX C. PHONONS

### Appendix D

# One-dimensional model semiconductor

It was shown in Chapter 1 that, within Kohn-Sham (KS) formulation of the density functional theory, the interacting electron problem is mapped onto another system of non-interacting particles [147] within an effective potential  $v_s = v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}$ , where  $v_{\text{ext}}$  is the external potential,  $v_{\text{H}}$  is the Hartree potential and  $v_{\text{xc}}$  is the exchange-correlation potential. This fictitious system satisfies the KS equation:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \ \psi_i(\mathbf{r}) \tag{D.1}$$

Stricto sensu, the eigenvalues and eigenfunctions of the KS equations are unphysical quantities, that appear only for a mathematical reason. However, the formalism guarantees that the KS particles reproduce correctly the total ground-state electron density of the real system as far as the exact form of the exchange-correlation potential is known. As discussed in Chapter 2, this potential is however unknown and, in practice, it must be approximated.

In Chapter 1, we also mentioned that, within many-body theory (MBT), the proper procedure to obtain the one-particles excitations of a system is to solve a Schrodinger-like equation containing a non-local energy-dependent self-energy operator  $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$  [114]:

$$\left[-\frac{1}{2}\nabla^{2}+v_{\mathrm{ext}}(\mathbf{r})+v_{\mathrm{H}}(\mathbf{r})\right]\Psi_{i}(\mathbf{r})+\int\Sigma(\mathbf{r},\mathbf{r}',\omega)\Psi_{i}(\mathbf{r}')\,d^{3}\mathbf{r}'=E_{i}\Psi_{i}(\mathbf{r}).$$
 (D.2)

The eigenfunctions  $\Psi_i$  are usually called the Dyson amplitudes and  $E_i$  correspond to the quasi-particle energies. This is another independent-

particles approach of the many-body problem. It gives the exact groundstate charge density as far as the exact self-energy operator is known.

In practical computations,  $\Sigma$  is usually calculated in the so-called GW approximation [114, 126, 83] using the one-particle Green's function (G) and the screened Coulomb interaction (W). Godby, Schlüter and Sham [83] showed that, within this approximation, the self-energy operator  $\Sigma$  of four classic semiconductors (Si, GaAs, AlAs, diamond) can be approximated by the following simple functional form:

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) \approx \frac{1}{2} [f(\mathbf{r}) + f(\mathbf{r}')] g(|\mathbf{r} - \mathbf{r}'|) h(\omega)$$
(D.3)

They observed that the non-locality (g) is essential in determining the correct bandgap which is only slightly affected by the energy dependence (h).

For our one-dimensional semiconductor, we chose a similar model selfenergy operator, but neglecting the energy dependence  $^{1}$ . We define our model semiconductor as being *exactly* described by this simplified selfenergy operator. Following the procedure describe below, we will then build a KS theory and investigate the behaviour of the associated exchangecorrelation potential, exact within the model. The results must be understood as follows. At a formal level, the DFT theorems are general and can be applied to any system, so in particular, to our model. Our results, considered as exact within the model, will allow to point out formal limits of the KS construction. For instance, quantities that are not correctly reproduced from the KS system within the model have no guarantee to be correctly reproduced in the exact KS representation of a real manybody system. At a more speculative level, it can also be expected that consequences directly related to the non-locality of  $\Sigma$  should be similarly present in real many-body systems, for which the non-locality appears as a fundamental feature.

Our model consists in the same one-dimensional semiconductor as first used by Godby and Sham in Ref. [86]. This solid is treated numerically in a supercell consisting of N basic unit cells of length a. We consider that the exact description of our system is given by Eq. D.2 where the external plus Hartree potential is taken to be:

$$v_{\text{ext}}(x) + v_{\text{H}}(x) = V_c \cos(2\pi x/a) + V_s \sin(4\pi x/a) + \lambda \cos(2\pi x/Na)$$
 (D.4)

<sup>&</sup>lt;sup>1</sup>When neglecting the energy dependence of the self-energy operator, the Dyson amplitudes become orthogonal and can be squared and summed to obtain the electron density. For this particular case, the macroscopic polarization can also be deduced from a Berry phase of the Dyson amplitudes.

where  $V_c$  is the amplitude of the main part of the potential.  $V_s$  is the amplitude of an optional potential required to mimic an asymmetric polar solid. The parameter  $\lambda$  is the amplitude of another optional slowly varying potential intended for reproducing the action of an electric field. In the limit of an infinitely long supercell  $(N \to \infty)$ , this term will reproduce the action of an homogeneous electric field. The self-energy operator is taken to be

$$\Sigma(x, x', \omega) = \frac{1}{2} [f(x) + f(x')]g(|x - x'|)$$
(D.5)

where  $f(\mathbf{r}) = -F_0[1-\cos(2\pi x/a)]$  is a negative function with the periodicity of one unit cell and  $g(y) = \pi^{-1/2} w^{-1} exp[-(y/w)^2]$  is a normalized gaussian of width w. Note that our model self-energy operator  $\Sigma$ , although nonlocal, does not have any non-locality on the scale of the supercell and is the same in two cells whose electron density is the same. This is a physically reasonable in the absence of long-range Coulomb effects.

In this particular framework, and for each particular choice of the parameters of the model, we can first solve the many-body problem by direct diagonalization of the equations containing the self-energy operator (Eq. D.2), using a plane-wave basis set and a supercell technique. The associated many-body ground-state density is deduced from the sum of the squares of the eigenfunctions of the occupied states.

Then, using nonlinear optimization techniques, an *exact* density fonctional theory can be constructed by determining the local potential  $v_s$  which when filled with non-interacting electrons (Eq. D.1) reproduces the same density as in the many-body case. The exact exchange-correlation potential is deduced has  $v_{\rm xc} = v_s - (v_{\rm ext} + v_{\rm H})$ .

Independently of the two optional potentials, our model is characterized by the lattice constant a and three additional parameters:  $V_c$  for the local potential of Eq. (D.2);  $F_0$  and w for the self-energy operator. In this work, we usually considered the same set of non-critical parameters than already used by Godby and Sham [86]: a = 4 a.u.,  $V_c = 0.0$  eV,  $F_0 = -4.08$ eV, w = 2 a.u.. They were chosen to be reasonably representative of a real semiconductor. With these parameters, the bandbap is of 2.2 eV in the nonlocal calculation and of 1.89 eV in the DFT case. A plot of the electronic density and associated effective potential are reported in Ref. [86]. Both the optional potentials ( $V_s$  and  $\lambda$  parameters) can now be alternatively turned on in order to create a non-zero macroscopic polarization.

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