

First-principles study of the nonlinear responses of insulators to electric fields: applications to ferroelectric oxides

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par

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CONTENTS

Introduction

Since their discovery in 1920, ferroelectrics have attracted joined scientific and industrial interest. Within this class of materials, the ABO_3 compounds are probably the most intensively studied. Their simple structure combined with their wide range of applicability in technological devices, make them attractive to both theoretical and experimental studies [1–4].

During the last decade, several theoretical advances combined with a gigantic jump of computational power lead to an intensive study of ferroelectric oxides from firstprinciples density functional theory (DFT) [5,6] and greatly improved our understanding of these materials. These techniques have been applied successfully to a large number of systems and provided insightful information on their electronic and structural properties as well as on their responses to perturbations such as electric fields, atomic displacements and strains.

A first crucial advance concerns the emergence of the *modern theory of polarization* [7–9]. Until the early 1990s, the formulation of a proper quantum mechanical approach for the calculation of the electronic polarization in periodic solids had remained a tricky and challenging problem. The modern theory of polarization offered an elegant solution to this problem by associating the polarization of continuous periodic charge densities to a Berry phase of the Bloch functions. The modern theory of polarization was also at the origin of the theory of electron localization [10–14] and of the recently proposed finite electric field techniques [15, 16].

A second advance is the first-principles effective Hamiltonian approach [17,18] for ferroelectrics. This formalism makes it possible to study the structural phase transitions of ferroelectrics and the temperature dependence of their dielectric and piezoelectric properties [19,20] that are inaccessible from standard DFT techniques. In this formalism, the soft mode is considered as the driving mechanism of the phase transition. The Hamiltonian is constructed from a Taylor expansion of the energy around the paraelectric phase. All parameters that appear in this expansion are determined from DFT total energy and linear response calculations. Since its development in 1994, this formalism has been applied successfully to numerous ABO_3 ferroelectrics and ferroelectric alloys [21–27].

A third advance is the development of a technique to compute *maximally localized Wannier functions* [28–31]. These Wannier functions provide an insightful picture of the nature of the chemical bonds in solids that is missing in the Bloch picture of extended orbitals. Moreover, maximally localized Wannier functions provide a physically appealing interpretation of the modern theory of polarization and of the theory of electron localization. They can also be used as basis functions in order-N methods [32] or for the construction of model Hamiltonians allowing to study the transport properties of nanostructures [33].

Finally, the development of *density functional perturbation theory* [34–38] made accessible from first-principles an increasing number of important physical properties such as phonon frequencies, infrared intensities, dielectric, piezoelectric and elastic constants

Nowadays, the increasing capabilities of first-principles techniques to predict with a good accuracy properties of complex materials meet the requirements of experimentalists for helpful theoretical data. These techniques can guide the experimental work and help to interpret the experimental results since they allow to relate the measured properties to the microscopic structure of the materials. In the recent studies on ferroelectrics, we have to distinguish whether the experiments are performed on bulk crystals or on nanostructures in which case finite size effects influence the properties of the materials.

During the last decade, bulk ferroelectric oxides have been intensively studied because of their unusual dielectric and piezoelectric responses. For example, solid solutions of PbTiO₃ and PbZrO₃ (PZT) are widely used in piezoelectric applications because of their excellent electromechanical properties [2]. In addition, a new generation of mixed relaxor and ferroelectric ABO₃-type crystals such as Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) or Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PZN-PT) have been found to exhibit ultrahigh piezoelectric coefficients that may revolutionize applications in medical imaging, telecommunications and ultrasonic devices. Theoretical studies showed that the large piezoelectric responses of these materials are driven by polarization rotation induced by an external electric field [39]. Moreover, they emphasized that atomic order strongly affects the properties of these materials so that properly oriented compounds can be used to tune their electromechanical responses [25, 40].

More recently, nano-sized ferroelectrics have attracted a lot of interest. Especially the properties of thin ferroelectric films and their compatibility with current siliconbased technologies have been intensively studied by both theorists and experimentalists [41-44]. In addition, there is presently an increasing interest in other ferroelectric nanostructures such as nanowires and nanoparticles [45, 46]. In these structures, the properties of the materials are modified by effects that are usually negligible at the bulk level. For example, in case of epitaxial films, the lattice mismatch between the substrate and the ferroelectric may affect the structure and other properties of the materials so that strain engineering offers new possibilities to tune the properties of nanoscaled ferroelectrics [47, 48]. Moreover, ferroelectricity is a collective phenomenon driven by long-range electrostatic interactions. It is therefore believed that ferroelectricity is altered in nanoscaled structures. Recent theoretical studies revealed the existence of a critical thickness for ferroelectricicty in thin ferroelectric films between conducting electrodes due to the imperfect screening of the depolarizing field [49]. It has also become possible to make heterostructures in which single crystalline perovskite-oxide films of thicknesses down to 1 to 2 lattice constants can be epitaxially matched at atomically sharp interfaces [41, 50]. The properties of these structures can be tuned by varying the superlattice period and the constituents. Moreover, it is possible to combine ferroelectrics with other functional materials such as ferromagnetic materials or superconductors to obtain materials with new multifunctional properties.

Multiferroics [51] form another class of multifunctional materials. These compounds have coupled electric, magnetic and structural order parameters that result in simultaneous ferroelectricity, ferromagnetism and ferroelasticity. They present opportunities for potential applications in information storage or the emerging field of spintronics. There has been recent research interest in a number of prototypical magnetic ferroelectrics, including YMnO₃ [52], TbMn₂O₅ [53] and BiFeO₃ [54].

In spite of the large activity in the field of ferroelectric oxides and of the exceptional optical properties of these compounds, only few first-principles studies of their nonlinear optical properties have been performed [15,55,56]. The purpose of the present work was to develop theoretical methods to study the nonlinear responses of insulators to electric fields in order to determine nonlinear optical properties of ferroelectrics. In this manuscript, we will focus on bulk crystals and study both the amplitude of these properties at 0 K as obtained from standard first-principles techniques and on their temperature dependence in the framework of an effective Hamiltonian approach. We will pay a particular attention to the contribution of the soft mode to nonlinear optical properties such as the electro-optic coefficients.

The nonlinear response of insulators to electric fields is interesting for both fundamental and practical reasons. On the one hand, the response of insulators to electric fields is a difficult problem that has only become tractable recently. On the other hand, these nonlinearities determine many interesting properties such as the nonlinear optical susceptibilities or the electro-optic coefficients that are currently used in various device applications. In contrast to the linear response formalism that is nowadays routinely applied to various systems (see for example Ref. [34]), the applications of the nonlinear response formalism in condensed matter physics have focused on rather simple cases [56–63].

Our work has been done in the framework of the ABINIT project [64]. ABINIT is a plane wave, pseudopotential density functional theory code. It has been developed as an international collaboration between several universities in Europe, North America and Asia. We implemented the formalism developed in this work in the ABINIT code so that it is freely accessible and can now systematically be applied to study the nonlinear responses of insulators to electric fields.

This thesis is organized as follows. Chapter 1 serves as a general introduction in which we summarize the physical and theoretical background of our work. We first discuss the basic aspects of three ferroelectric oxides and of the nonlinear response properties that will be studied in the following Chapters. We then reintroduce several theoretical concepts such as density functional theory and the modern theory of polarization. In Chapter 2, we introduce a physical quantity that makes it possible to quantify the degree of electron localization in insulating crystals and we show, how this quantity can be decomposed into contributions of individual groups of bands. We then apply this formalism to selected oxides and we study the change of electron localization at the phase transitions of $BaTiO_3$ and $LiNbO_3$.

In Chapter 3, we develop a formalism to study the nonlinear responses of insulators to electric fields. This formalism uses either density functional perturbation theory or finite electric field techniques. In particular, we discuss the computation of nonlinear optical susceptibilities, Raman scattering efficiencies and the electro-optic coefficients.

In Chapter 4, we apply the techniques developed in Chapter 3 to selected ferroelectrics and semiconductors. We first compare the performance of density functional perturbation theory to the performance of the finite electric field technique. We then discuss the Raman spectrum and electro-optic coefficients of various ferroelectrics.

In Chapter 5, we develop an effective Hamiltonian approach to study the temperature dependence of the electro-optic coefficients and refractive indexes of ferroelectrics and we apply it to $BaTiO_3$ in its tetragonal phase.

Finally, we provide a summary of our main results and some perspectives.

Chapter 1

Background

1.1 Introduction

The physical properties of macroscopic solids can nowadays be predicted accurately from first-principles density functional theory (DFT). This method makes it possible to study the ground-state of complex systems such as ferroelectric oxides as well as their linear and nonlinear responses to external perturbations. The aim of this work is to develop several methods to determine the nonlinear responses of insulators to electric fields in order to study nonlinear optical properties of ferroelectrics. This introductory Chapter is intended to prepare the ground for this work.

Ferroelectric oxides are an important class of multifunctional materials characterized by unusual dielectric, piezoelectric and optical properties. In Sec. 1.2, we describe the basic aspects of these materials and we characterize the structure and phase transitions of three compounds: barium titanate (BaTiO₃), lead titanate (PbTiO₃) and lithium niobate (LiNbO₃).

In Sec. 1.3, we introduce several nonlinear optical properties. We reinvestigate the definition of the nonlinear optical susceptibilities, the electro-optic coefficients and the elasto-optic coefficients and we summarize some applications of these properties in technological devices. We also discuss the physical mechanisms that determine the amplitude and frequency dependence of the nonlinear coupling coefficients.

The rest of this Chapter is devoted to the description of the theoretical framework of this work. We summarize the basic formalism of density functional theory (Sec. 1.4.1), density functional perturbation theory (DFPT) (Sec. 1.4.2), the modern theory of polarization (Sec. 1.4.3) and Wannier functions (Sec. 1.4.4). In Sec. 1.4.5, we introduce the electric field perturbation in extended solids and in Sec. 1.4.6, we show, how the response properties of insulators are related to derivatives of their energy.

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1.2 Ferroelectric oxides: an important class of multifunctional materials

A crystal is said to be ferroelectric when (i) it has two or more orientational states in the absence of an electric field and (ii) it can be shifted from one to another state by an electric field [1]. Each of these orientational states is characterized by a zerofield spontaneous polarization, \mathcal{P}^s , and two states only differ in the direction (and amplitude) of \mathcal{P}^s . The dependence of the polarization on the electric field can be represented by an hysteresis loop such as the one shown in Figure 1.1.

Figure 1.1: Hysteresis loop of a ferroelectric.



A ferroelectric may have several phases: in most cases a prototype paraelectric phase stable at high temperature and one or more ferroelectric phases stable at lower temperature. The paraelectric phase is characterized by a high degree of symmetry and a vanishing spontaneous polarization. As the temperature is lowered below a critical temperature, T_c , the crystal undergoes a transition to a ferroelectric phase characterized by a polar distortion of the unit cell and the appearance of a spontaneous polarization.

Ferroelectricity was discovered in 1920 by Valasek who observed that the polarization of Rochelle Salt can be reversed by the application of an external electric field. Since then, ferroelectricity has been observed in many different systems [1,2] such as hydrogen bonded crystals (f.ex. $\rm KH_2PO_4$ (KDP)), narrow gap semiconductors (f. ex. GeTe) or polymers. In this section, we focus on (partially) ionic crystals with the general formula ABO₃. We consider two structures: the perovskite structure of $\rm BaTiO_3$ and $\rm PbTiO_3$ and the trigonal structure of $\rm LiNbO_3$.

1.2.1 Crystal structure

The ABO_3 compounds can crystallize in various structures. The simplest is the perovskite structure of barium titanate (BaTiO₃) or lead titanate (PbTiO₃) shown in Figure 1.2. Above T_c , the symmetry of these materials is cubic (Pm $\overline{3}$ m) with 5 atoms per unit cell. As the temperature is lowered, BaTiO₃ undergoes a sequence of three ferroelectric phase transitions. Around 403 K, it transforms to a tetragonal structure (P4mm) with a spontaneous polarization along the $\langle 100 \rangle$ direction [Figure 1.2 (b)]. This phase is stable until about 278 K where there is a transformation to a phase of orthorhombic symmetry (Pmm2) with \mathcal{P}^s along the cubic $\langle 110 \rangle$ direction. The last phase transition arises around 183 K. The low temperature structure of BaTiO₃ is rhombohedral (P3m1) and the polarization of this phase is aligned along the cubic $\langle 111 \rangle$ direction. In contrast to BaTiO₃, PbTiO₃ undergoes a single phase transition around 763 K to a tetragonal P4mm phase as shown in Figure 1.2 (b).

Figure 1.2: Primitive unit cell of $BaTiO_3$ and $PbTiO_3$ in the paraelectric phase (a) and atomic displacements at the transition to the tetragonal phase (b).



In Chapter 4, we study the nonlinear optical properties of the tetragonal phase of $BaTiO_3$ and $PbTiO_3$. Following Ref. [65], these calculations have been performed at the experimental lattice parameters. In contrast, the atomic positions have been relaxed until the residual forces on the atoms are smaller than 10^{-5} hartree/bohr. The atomic positions in reduced coordinates are reported in Table 1.1 and the results of the optimizations are reported in Table 1.2.

Another structure adopted by ABO₃ compounds is the trigonal structure of LiNbO₃¹ shown in Figure 1.3. Above T_c , LiNbO₃ is in a centrosymmetric R3c phase with 10 atoms per cell (Figure 1.3 (a)). Around 1480 K, it undergoes a ferroelectric phase transition to a structure of R3c symmetry as shown in Figure 1.3 (b). The calculations of the nonlinear optical properties of the ferroelectric phase of LiNbO₃ presented in Chapter 4 have been performed at the theoretical lattice constants and atomic positions. In Table 1.3, we define the parameters that determine the atomic positions in the ferroelectric phase by reporting the hexagonal coordinates of five atoms of the

¹See Ref. [68] for a more detailed discussion of the structure of $LiNbO_3$.

Atom	Position		
Ba/Pb	(0, 0, 0)		
Ti	$\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \delta_{Ti}\right)$		
O_1	$(\frac{1}{2}, \frac{1}{2}, 0 + \delta_{O_1})$		
O_2	$(\frac{1}{2}, 0, \frac{1}{2} + \delta_{O_2})$		
O_3	$(0, \frac{1}{2}, \frac{1}{2} + \delta_{O_2})$		

Table 1.1: Atomic positions (in reduce coordinates) in the tetragonal phase of $\rm BaTiO_3$ and $\rm PbTiO_3.$

Table 1.2: Lattice constants and atomic position parameters (see notations of Table 1.1) in the tetragonal phase of $BaTiO_3$ and $PbTiO_3$.

	Ba'	TiO ₃	$PbTiO_3$		
	$\mathbf{Present}$	Exp. [66]	Present	Exp. [67]	
a (Å)		3.994		3.904	
c (Å)		4.036		4.152	
δ_{Ti}	0.0136	0.0215	-0.0478	-0.040	
δ_{O_1}	-0.0273	-0.0233	-0.1205	-0.112	
δ_{O_2}	-0.0167	-0.0100	-0.1278	-0.112	

Figure 1.3: Primitive unit cell of $LiNbO_3$ in the paraelectric phase (a) and atomic displacements during the phase transition (b).



rhombohedral unit cell. The coordinates of the other atoms can easily be obtained by using the symmetry operations of the space groups R3c. The results of the structural optimizations are summarized in Table 1.4 (see also Ref. [69]).

To discuss the electro-optic (EO) tensor of LiNbO₃ in Chapter 4, we have to define a set of mutually orthogonal x, y and z axes. In this work, we follow the I. R. E. Piezoelectric standards [70]. The x axis is taken orthogonal to a mirror plane of the crystal, and the z axis parallel to the threefold symmetry c axis. The positive end of the y axis is the end that becomes electrically negative, due to the piezoelectric effect, when the crystal is compressed along the y axis. Similarly, the positive end of the zaxis becomes negatively charged under compression along z.

1.2.2 Ferroelectric instabilities

The ferroelectric phase transition in $BaTiO_3$, $PbTiO_3$ and $LiNbO_3$ can be associated to an unstable zone-center phonon mode in the paraelectric phase. If the atoms are displaced from their high symmetry positions of Figures 1.2 (a) or 1.3 (a) along the eigenvector of a stable phonon mode the energy increases and the atoms feel a force that tends to bring them back to their equilibrium positions. In contrast, if the atoms are displaced along the eigenvector of an unstable mode, the energy decreases. The potential energy projected along the soft-mode eigenvector has the shape of a double

	D:+:
Atom	Position
Nb_1	(0,0,0)
Li_1	$(0, 0, \frac{1}{4} + z)$
O_1	$\left(-\frac{1}{3}-u,-\frac{1}{3}+v,\frac{7}{12}-w\right)$
O_2	$(rac{1}{3}-v,-u-v,rac{7}{12}-w)$
O_3	$(u+v, \frac{1}{3}+u, \frac{7}{12}-w)$

Table 1.3: Atomic positions (in hexagonal coordinates) in the ferroelectric phase of $LiNbO_3$.

Table 1.4: Lattice constants and atomic position parameters (see notations of Table 1.3) in the ferroelectric phase of $LiNbO_3$.

	a (Å)	c (Å)	z	u	v	w
Exp. [71]	5.151	13.876	0.0329	0.00947	0.0383	0.0192
$\mathbf{Present}$	5.067	13.721	0.0337	0.01250	0.0302	0.0183

well with a negative curvature at the origin 2 . In the harmonic approximation, this negative curvature corresponds to an imaginary phonon frequency.

The origin of the instabilities in BaTiO₃ and LiNbO₃ has been explained from a model based on a seminal idea of Cochran [72]. The interatomic forces in a crystal can be decomposed into short-range forces (covalent interactions and repulsions between ionic cores) and long-range Coulomb (dipole-dipole) interactions. A structural instability can appear from the cancellation of both contributions. As discussed in Refs. [65, 69], the covalent interactions between O 2p and Ti/Nb d atomic orbitals are responsible for the giant Born effective charges in BaTiO₃ and LiNbO₃. These effective charges couple together for the specific displacement pattern associated with the soft mode, in order to generate a giant dipolar interaction that leads to the ferroelectric instability.

As an illustration, we show in Figure 1.4 the phonon dispersion curves of $LiNbO_3$ computed for a structure in which all atoms occupy the high symmetry positions of Figure 1.3 (a) (see also Ref. [73]). The corresponding dispersion curves of $BaTiO_3$ and $PbTiO_3$ can be found in Ref. [74]. At the Γ -point, $LiNbO_3$ has three unstable

²Strictly speaking, the number of equivalent minima of the multi-well potential depends on the number of equivalent directions for the spontaneous polarization. For example, there are only two equivalent minima in case of $LiNbO_3$ where the polarization can only have two directions. In contrast, in BaTiO₃, there are 6, 12 and 8 equivalent minima that correspond respectively to the equivalent directions of the polarization in the tetragonal, orthorhombic and rhombohedral phases.



Figure 1.4: Phonon band structure in the paraelectric phase of $LiNbO_3$.

modes. The eigenvector of the transverse A_{2u} mode has an overlap of 0.99 with the vector representing the atomic displacements at the phase transition shown in Figure 1.3 (b) [69].

The soft mode is not only responsible for the phase transition of ferroelectrics. It is also the origin of their unusual dielectric properties. This can be understood as follows: as mentioned above, the soft mode in the paraelectric phase is highly polar ³. In the ferroelectric phase it transforms into a highly polar (usually stable) mode of low frequency that can strongly interact with an electric field and generate a huge dielectric response.

In Chapter 4, we study the EO coefficients of the three materials discussed above in order to elucidate the contribution of the soft mode to these quantities.

1.2.3 Multifunctional materials

Ferroelectric oxides combine many interesting properties such as high dielectric, piezoelectric and pyroelectric constants and nonlinear optical coefficients (see f. ex. Refs.

 $^{^{3}}$ Roughly speaking, we can say that the polarity or mode effective charge of the soft mode is at the origin of the spontaneous polarization in the ferroelectric phase.

[1, 75, 76]). Some examples of their applicability in technological devices are summarized in Figure 1.5. Their high dielectric constants make ferroelectrics attractive for capacitors as they can be used in dynamic random access memories (DRAMs) or as gate oxides for metal-oxide-silicon field-effect transistors (MOSFETs). Their high piezoelectric coefficients are exploited in applications where mechanical energy has to be converted into electrical energy (transducers) and vice versa (actuators). Such devices are currently used in medical imaging, for the generation of sonar or ultrasonic waves or to displace the tips of atomic force microscopes and scanning tunneling microscopes. The temperature dependence of the spontaneous polarization of ferroelectrics is used to build pyroelectric detectors of infrared radiation and the possibility to switch the polarization by an electric field is potentially interesting to build nonvolatile ferroelectric random access memories. Finally, ferroelectric oxides have good nonlinear optical properties as will be discussed in Sec. 1.3.

Figure 1.5: Summary of the most important properties of ferroelectric oxides and their applications in technological devices.



1.3 Nonlinear optical properties

In this Section, we present different nonlinear optical properties and we discuss the physical mechanisms, which are at their origin. To simplify, we only discuss the basic aspects of the nonlinear response properties. In particular, we neglect any anisotropy in the response of the crystals and we suppose that the relation between the response and the applied perturbation is given by a scalar equation.

1.3.1 Nonlinear optical susceptibilities

The dielectric polarization, \mathcal{P} , induced by a macroscopic electric field, \mathcal{E} , is given by the relation

$$\mathcal{P} = \chi(\mathcal{E})\mathcal{E},\tag{1.1}$$

where $\chi(\mathcal{E})$ is the dielectric susceptibility. For weak electric fields, the electric field dependence of $\chi(\mathcal{E})$ can be neglected to a good approximation and the relation between \mathcal{P} and \mathcal{E} is linear. For strong electric fields, this linear relation is no more valid and we can write \mathcal{P} as a power series of the electric field

$$\mathcal{P} = \chi^{(1)}\mathcal{E} + \chi^{(2)}\mathcal{E}\mathcal{E} + \chi^{(3)}\mathcal{E}\mathcal{E}\mathcal{E} + \dots, \qquad (1.2)$$

where $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are respectively the linear optical susceptibility and the second- and third-order nonlinear optical susceptibilities.

In the present work, we are mainly interested in the second-order nonlinear optical susceptibilities. These quantities vanish in systems with a center of inversion such as the ferroelectric oxides discussed in Sec. 1.2 in their paraelectric phase. In order to illustrate how $\chi^{(2)}$ affects the optical properties of a crystal, let us consider an electric field of frequency ω :

$$\mathcal{E} = \mathcal{E}_0 \cos(\omega t). \tag{1.3}$$

The second-order nonlinear polarization, \mathcal{P}^{NL} , induced by this field has a frequency dependence of 2ω :

$$\mathcal{P}^{NL} = \chi^{(2)} \mathcal{E}_0^2 \cos^2(\omega t) = \frac{1}{2} \chi^{(2)} \mathcal{E}_0^2 [1 + \cos(2\omega t)].$$
(1.4)

 \mathcal{P}^{NL} can act as a source of radiation and generate an electromagnetic wave of frequency 2ω . This phenomenon is called *second-harmonic generation*. It is notably applied for the frequency doubling of laser [77].

Another second-order nonlinear phenomenon is the *optical parametric process* [78]. It describes the breakdown of a pump photon into a signal and an idler photon. Energy conservation requires that the sum of the frequencies of the signal and idler photon equals the frequency of the pump photon. This phenomenon is notably used in parametric oscillators, which are sources of coherent radiation that are continuously tunable over a wide range of frequencies.

Ferroelectric oxides are particularly interesting for this kind of applications. On the one hand, their nonlinear optical susceptibilities are unusually high. On the other hand, they can be quasi phase matched by periodically inverting their spontaneous polarization, which allows to obtain high conversion efficiencies in the second-harmonic generation process [79].

1.3.2 Electro-optic coefficients

The optical properties of a crystal can be described by its index ellipsoid. Applying an electric field, this index ellipsoid can be distorted, which allows to influence the Figure 1.6: EO modulator build from an epitaxial film of $BaTiO_3$ (BTO) grown on a MgO substrate. From Petraru *et al.* [84].



propagation of a light wave inside the crystal. In noncentrosymmetric systems, this change is given by a linear relation

$$\Delta\left(\frac{1}{n^2}\right) = r\mathcal{E},\tag{1.5}$$

where r is the linear electro-optic (EO) coefficient.

This effect is important for several technological applications. For example, photorefractive materials used for holographic applications [80, 81] are required to exhibit large EO coefficients in addition to other properties such as good photoconductivity and low dark conductivity [78]. This effect is also exploited to build EO modulators [78, 82, 83] that are used in integrated optics and fiber-optic communications systems to modulate the amplitude of a light wave in a wave guide. Recently, there has been an increasing interest to build EO modulators from thin ferroelectric films. Figure 1.6 shows an intensity modulator build from a thin film of BaTiO₃ epitaxially grown on a MgO substrate [84]. This device uses a Mach-Zehnder interferometer to modulate the intensity of a light wave in a wave guide. By varying the potential applied to the central electrode while keeping constant the potential of the two outer electrodes, it is possible to induce a phase shift between the light waves in the two branches and to modulate the output of the interferometer.

1.3.3 Elasto-optic coefficients

The elasto-optic effect describes changes in the refractive index of a compound induced by a strain, η . It is defined by a similar relation as the EO effect

$$\Delta\left(\frac{1}{n^2}\right) = \pi\eta,\tag{1.6}$$

where π is the elasto-optic coefficient of the medium. In contrast to the EO coefficients and nonlinear optical susceptibilities, which vanish in centrosymmetric crystals, the elasto-optic coefficients are nonzero in all crystals as well as amorphous solids.

This effect is interesting for several reasons. First, as we will see in Sec. 3.3.4, it determines the piezoelectric contribution to the EO coefficients. Second, this effect is used for applications such as acousto-optic modulators or deflectors where an acoustic wave interacts with an electromagnetic wave to change its direction or intensity [78]. Third, in microelectronics, there is an increasing use of UV laser sources in precision optical applications such as lithography. These energetic beams induce a local densification of the SiO₂ optical lenses, which causes an increase of the absolute value of the refractive index and a loss of resolution due to birefringence [85,86].

1.3.4 Frequency dependence

The amplitude of the nonlinear coefficients discussed above depends on several physical mechanisms. Each mechanism has a characteristic response time and its contribution to these coefficients depends on the frequencies of the electric fields involved in the process. In this work, we distinguish between (i) pure *electronic* contributions, (ii) *ionic* contributions due to electric field induced atomic displacements and (iii) *piezo-electric* contributions due to homogeneous deformations of the crystal⁴. Moreover, for specific frequencies, the nonlinear coupling coefficients can present a resonance, due to electronic excitations, excitations of phonon modes or mechanical resonances of the whole crystal⁵.

In the discussion that follows, we suppose that the frequencies of the electric fields are always far away from any resonance. In this case, we can distinguish three characteristic regions⁶:

- Optical frequencies, i.e. frequencies higher than the frequencies of the optical phonons but lower than the fundamental absorption gap. In this case, only the electrons contribute to the linear and nonlinear susceptibilities while the atomic positions and the unit cell shape are clamped to their equilibrium values.
- Frequencies higher than the highest mechanical resonance of the crystal but lower than the frequencies of the optical phonons (typically between 10² and 10⁶ MHz). In this case, the atoms in the unit cell are able to respond to the electric field while the shape of the cell remains fixed. The linear and nonlinear susceptibilities are the sum of the electronic and ionic contributions.
- Frequencies lower than the frequency of the first mechanical resonance of the

⁴In this work, we consider only intrinsic contributions to the nonlinear coefficients. We do not take into account extrinsic effects that may eventually influence the nonlinear response of ferroelectrics to electric fields such as the reorientation of ferroelectric domains.

 $^{^{5}}$ These mechanical resonances usually depend on the shape and dimension of the crystal.

⁶In addition, the linear and nonlinear susceptibilities present a frequency dependence inside each region. This dependence is usually quite weak and will be neglected in this work.



Figure 1.7: Schematic illustration of the dependence of the EO coefficients on the frequency of the modulating electric field. From Wemple *et al.* [87].

sample (for example static electric fields). In this case, the electrons, the ions and the strain contribute to the linear and nonlinear susceptibilities.

The discussion presented above is general an applies to most phenomena related to the response of insulators to electric fields. We now particularize it to the specific case of the EO coefficients. Figure 1.7 shows the typical dependence of the EO coefficients on the frequency of the modulating field. For high-frequency fields, the ions can be considered to be clamped to their equilibrium positions. As a consequence, the EO coefficients are determined by pure electronic processes. For frequencies higher than the mechanical resonance frequencies but lower than the frequencies of the optical phonons, the ions are able to respond to the electric field. This is the region of the socalled *clamped* (strain-free) EO coefficients that are the sum of the electronic and ionic contributions. Finally, for low frequencies, the shape of the unit cell is modified by the electric field. This is the region of the so-called *unclamped* (stress-free) EO coefficients that are the sum of the electronic, ionic and piezoelectric contributions. In Sec. 3.3.4, we will give explicit expressions of the three contributions to the EO coefficients.

1.4 Theoretical Background

In this section, we summarize the formalisms that are the basis of the theoretical developments and calculations of this work. We first reinvestigate the basic aspects of density functional theory and density functional perturbation theory that make it possible to compute most of the ground-state and response properties of solids and molecules with an accuracy of a few percent. We then summarize the formalism of the modern theory of polarization, the theory of Wannier functions and the electric field perturbation in extended systems. Finally, we show how the response properties of solids are related to derivatives of their energy. We focus on periodic systems described within Born- von Karman boundary conditions.

1.4.1 Density functional theory

From a quantum mechanical point of view, a solid (or a molecule) can be described as a system of electrons and nuclei in interaction. The ground-state of this system can, in principle, be determined by solving the corresponding many-body Schrödinger equation. Unfortunately, the direct solution of this equation is not possible except for a few simple systems. In order to study the properties of complex systems from first-principles we have to make some approximations and simplifications.

A first simplification is obtained from the Born and Oppenheimer approximation that allows to decouple the dynamics of electrons and nuclei and to study properties of the electrons in some frozen in configuration of the nuclei. To determine the electronic ground-state we use the Kohn-Sham density functional theory (DFT) [5,6,32,88,89]. This technique allows one, in principle, to map exactly the problem of a strongly interacting electron gas onto that of independent particles moving in an effective potential $v(\mathbf{r})$. The ground-state energy of this system can be derived by minimizing the following expression with respect to the (single-particle) Kohn-Sham orbitals $\psi_{\alpha}(\mathbf{r})$

$$E[\psi_{\alpha}] = \sum_{\alpha}^{occ} \langle \psi_{\alpha} | T + v_{ext} | \psi_{\alpha} \rangle + E_{Hxc}[n].$$
(1.7)

The sum in Eq. (1.7) runs over all occupied states. T is the kinetic energy operator, $v_{ext}(\mathbf{r})$ the (nuclear) potential external to the electronic system, $E_{Hxc}[n]$ the sum of the Hartree $(E_H[n])$ and exchange-correlation $(E_{xc}[n])$ energy functionals and $n(\mathbf{r})$ the ground-state density

$$n(\mathbf{r}) = \sum_{\alpha}^{occ} |\psi_{\alpha}(\mathbf{r})|^2.$$
(1.8)

The occupied Kohn-Sham orbitals are subject to the orthonormalization constraints

$$\langle \psi_{\alpha} | \psi_{\beta} \rangle = \delta_{\alpha\beta}. \tag{1.9}$$

The minimization of Eq. (1.7) under the constraints (1.9) can be achieved using the Lagrange multiplier method. The problem turns into the minimization of

$$F[\psi_{\alpha}] = E[\psi_{\alpha}] - \sum_{\alpha,\beta}^{occ} \Lambda_{\beta\alpha}(\langle \psi_{\alpha} | \psi_{\beta} \rangle - \delta_{\alpha\beta}), \qquad (1.10)$$

where $\Lambda_{\beta\alpha}$ are the Lagrange multipliers. The corresponding Euler-Lagrange equation is

$$H|\psi_{\alpha}\rangle = \sum_{\beta} \Lambda_{\beta\,\alpha} |\psi_{\beta}\rangle, \qquad (1.11)$$

where the Hamiltonian

$$H = T + v = T + v_{ext} + v_{Hxc} (1.12)$$

has to be determined self-consistently since it depends on the Hartree and exchangecorrelation potential $v_{Hxc}(\mathbf{r})$ that is a functional of the ground-state density

$$v_{Hxc}(\mathbf{r}) = \frac{\delta E_{Hxc}[n]}{\delta n(\mathbf{r})}.$$
(1.13)

The Lagrange multipliers $\Lambda_{\beta\alpha}$ are the matrix elements of the Hamiltonian between the corresponding wave functions

$$\Lambda_{\beta\alpha} = \langle \psi_{\beta} | H | \psi_{\alpha} \rangle. \tag{1.14}$$

The solution of Eq. (1.11) is not unique. In fact, we can always apply a unitary transformation U to the wave functions of the occupied states

$$|\psi_{\alpha}\rangle \longrightarrow \sum_{\beta}^{occ} U_{\beta\alpha} |\psi_{\beta}\rangle \tag{1.15}$$

without affecting the energy or the density. Such a transformation is called a *gauge* transformation. Since the Hamiltonian is a hermitian operator, it is possible to work in the so-called diagonal gauge where the Lagrange multiplier matrix (1.14) is diagonal

$$\langle \psi_{\beta} | H | \psi_{\alpha} \rangle = \varepsilon_{\beta} \delta_{\beta\alpha}. \tag{1.16}$$

In this work, we consider periodic crystals where the wave functions $\psi_{\alpha}(\mathbf{r})$ are Bloch functions characterized by their wave vector \mathbf{k} and a band-index n

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \tag{1.17}$$

with $u_{\mathbf{r}\mathbf{k}}(\mathbf{r})$ a periodic function that has the same periodicity as the crystal lattice.

The self-consistent solution of Eq. (1.11) allows to determine the exact ground-state energy and charge density. Unfortunately, the expression of the exchange-correlation energy functional is not known and we have to use an approximation for this term. In this work, we consider two kinds of approximations: the local density approximation (LDA) and the generalized gradient approximation (GGA).

1.4.2 Density functional perturbation theory

Having defined the DFT equations in Sec. 1.4.1, we investigate in the present section the response of a quantum mechanical system to a perturbation of the external potential. As will be shown in Sec. 1.4.6, many interesting properties of a solid can be characterized by the derivatives of its energy or thermodynamic potentials. In this section, we focus to the response to infinitesimal perturbations. In this context, the energy derivatives are obtained from perturbation theory.

Let us expand all perturbed quantities, X, in terms of a small parameter, λ , around their unperturbed values, $X^{(0)}$:

$$X(\lambda) = X^{(0)} + X^{(1)}\lambda + X^{(2)}\lambda^2 + X^{(3)}\lambda^3...,$$
(1.18)

where

$$X^{(n)} = \frac{1}{n!} \frac{d^n X}{d\lambda^n} \bigg|_{\lambda=0}.$$
 (1.19)

X can be one of the quantities E, $\psi_{\alpha}(\mathbf{r})$, $n(\mathbf{r})$, H, $\Lambda_{\beta\alpha}$, $v_{Hxc}(\mathbf{r})$ or $v_{ext}(\mathbf{r})$. Because E satisfies a variational principle, it is possible to derive two major theorems [35,36]:

1. A variational principle can be established for the even order perturbations. It states that

$$E^{(2n)} = \min_{\psi_{\alpha}^{(n)}} \left\{ E_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^{i} \psi_{\alpha}^{(i)} \right] \right\}^{(2n)}.$$
 (1.20)

This theorem establishes that the n^{th} -order derivatives of the wave functions can be obtained by minimizing the functional expression of $E^{(2n)}$ with respect to $\psi_{\alpha}^{(n)}$. For example, in this work we deal with the first-order derivatives of the wave functions that are computed by minimizing the variational expression of the second-order energy derivatives $E^{(2)}$.

2. A 2n + 1 theorem can be demonstrated for the odd order perturbations:

$$E^{(2n+1)} = \left\{ E_{(\lambda)} \left[\sum_{i=0}^{n} \lambda^{i} \psi_{\alpha}^{(i)} \right] \right\}^{(2n+1)}.$$
 (1.21)

It states that the derivatives of the energy up to the order 2n+1 can be computed from the derivatives of the wave functions up to the order n. For example, in this work, we focus on third-order energy derivatives that are computed from the ground-state and first-order derivatives of the wave functions.

More explicit expressions of even and odd order energy derivatives can be found in Refs. [35, 36]. In Chapter 3, we particularize Eq. (1.21) to the case of third-order energy derivatives with respect to at least two electric fields.

1.4.3 The modern theory of polarization

In Sec. 1.2, we defined a ferroelectric as a material which exhibits a spontaneous polarization, \mathcal{P}^s , that can be switched by an electric field. In this section, we give a rigorous definition of \mathcal{P}^s and we show how this quantity can be computed in practice.

Let us consider first a finite piece of matter of volume V. The polarization of this system can be computed as the dipole moment per unit volume

$$\boldsymbol{\mathcal{P}} = \frac{1}{V} \left[e \sum_{\kappa} Z_{\kappa} \mathbf{R}_{\kappa} - e \int_{V} d\mathbf{r} \, \mathbf{r} n(\mathbf{r}) \right], \qquad (1.22)$$

where Z_{κ} and \mathbf{R}_{κ} are the atomic number and position, e the absolute value of the electronic charge and $n(\mathbf{r})$ the electronic charge density defined in Eq. (1.8). Although such a dipole moment is in principle well defined, it is not a bulk property since it depends upon truncation and shape of the sample. In contrast, the variations of \mathcal{P} are measured as bulk properties in several circumstances. In fact, most macroscopic properties such as the dielectric tensor, the piezoelectric tensor or the nonlinear optical susceptibilities are just derivatives of \mathcal{P} with respect to suitably chosen perturbations. Moreover, the spontaneous polarization of a ferroelectric – measured via hysteresis cycles (see Figure 1.1) – is usually obtained as the difference, $\Delta \mathcal{P}$, between two states of the crystal.

In infinite solids, described in the framework of periodic Born- von Karman boundary conditions, Eq. (1.22) can no more be used to compute the polarization as a dipole moment per unit volume. In fact, the position operator, \mathbf{r} , is not compatible with Born- von Karman boundary conditions. Consider a supercell of size $L_i = M_i a_i$ (i = 1, 2, 3) where \mathbf{a}_i is a lattice vector. The Hilbert space of a single-particle wave function $\psi(\mathbf{r})$ is defined by the condition $\psi(\mathbf{r}) = \psi(\mathbf{r} + M_i \mathbf{a}_i)$. An operator maps a function of this Hilbert space into a function belonging to the same space. The position operator \mathbf{r} is therefore not a legitimate operator when periodic boundary conditions are adopted since $\mathbf{r}\psi(\mathbf{r})$ is not a periodic function when $\psi(\mathbf{r})$ is such.

For crystalline dielectrics, the problem of the polarization was solved by King-Smith, Vanderbilt and Resta in Refs. [7–9]: \mathcal{P} is a manifestation of a Berry phase [90], i.e. it is an observable which cannot be cast as the expectation value of any operator, being instead a gauge invariant phase of the wave functions.

In the discussions that follow, we consider an insulating crystal with N doubly occupied bands separated from the unoccupied bands by a finite gap E_g . Let us consider a continuous adiabatic transformation of the crystalline potential connecting two states of the crystal. We parameterize this transformation by a variable λ and we note λ_1 and λ_2 its values in the initial and final states. The change in polarization induced by this transformation can be expressed as

$$\Delta \boldsymbol{\mathcal{P}} = \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial \boldsymbol{\mathcal{P}}}{\partial \lambda} = \boldsymbol{\mathcal{P}}(\lambda_2) - \boldsymbol{\mathcal{P}}(\lambda_1).$$
(1.23)

The polarization $\mathcal{P}(\lambda)$ can be decomposed as the sum of a bare ionic and an electronic polarization

$$\boldsymbol{\mathcal{P}}(\lambda) = \boldsymbol{\mathcal{P}}_{ion}(\lambda) + \boldsymbol{\mathcal{P}}_{el}(\lambda). \tag{1.24}$$

The ionic polarization can be computed through an expression similar to the first term

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of the right hand side of Eq. (1.22)

$$\boldsymbol{\mathcal{P}}_{ion}(\lambda) = \frac{e}{\Omega_0} \sum_{\kappa}^{cell} Z_{\kappa} \mathbf{R}_{\kappa}$$
(1.25)

where the sum runs over all atoms in the unit cell. The electronic polarization can be computed as a Berry phase of the occupied bands [7]

$$\boldsymbol{\mathcal{P}}_{el}(\lambda) = -\frac{2ie}{(2\pi)^3} \sum_{n=1}^{N} \int_{BZ} d\mathbf{k} \langle u_{n\mathbf{k}} | \boldsymbol{\nabla}_k | u_{n\mathbf{k}} \rangle$$
(1.26)

where BZ is the Brillouin zone, $u_{n\mathbf{k}}(\mathbf{r})$ is the periodic part of the Bloch functions and the factor of 2 accounts for spin degeneracy. The Bloch functions are chosen to satisfy the periodic gauge condition

$$e^{i\mathbf{G}\cdot\mathbf{r}}u_{n\mathbf{k}+\mathbf{G}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) \tag{1.27}$$

where **G** is a reciprocal lattice vector. With this choice of gauge, the polarization changes given by Eq. (1.23) are given to within a factor $(e/\Omega_0)\mathbf{R}$ where **R** is a lattice vector. Using Eq. (1.23), the spontaneous polarization of a ferroelectric, \mathcal{P}^s , can be defined as the change in polarization, $\Delta \mathcal{P}$, when the crystal is transformed from the high-symmetric paraelectric structure to a ferroelectric one.

In order to use Eq. (1.26) in practical calculations, the integration over the BZ, as well as the differentiation with respect to \mathbf{k} , have to be performed on a discrete mesh of $M_k = M_1 \times M_2 \times M_3$ **k**-points. The standard approach is to build strings of **k**-points parallel to a vector of the reciprocal space \mathbf{G}_i . The projection of the polarization along that direction can then be computed as the sum of the string-averaged electronic Berry phase, φ_{el} , and the ionic phase, φ_{ion} ,

$$\mathcal{P}(\lambda) \cdot \mathbf{G}_{i} = \frac{e}{\Omega_{0}} (\varphi_{el}^{(i)} + \varphi_{ion}^{(i)})$$
(1.28)

with

$$\varphi_{el}^{(i)} = \frac{2}{M_{\perp}^{(i)}} \sum_{l=1}^{M_{\perp}^{(i)}} \Im \ln \prod_{j=0}^{M_i-1} \det[S(\mathbf{k}_j^{(i)}, \mathbf{k}_{j+1}^{(i)})]$$
(1.29)

$$\varphi_{ion}^{(i)} = 2\pi \sum_{\kappa}^{cen} Z_{\kappa} R_{\kappa i}$$
(1.30)

In these expressions, $M_{\perp}^{(1)} = M_2 \times M_3$ is the number of strings along \mathbf{G}_1 , each containing M_1 points⁷ $\mathbf{k}_j^{(1)} = \mathbf{k}_{\perp}^{(l)} + j \mathbf{G}_1 / M_1$, S the overlap matrix between Bloch functions

$$S_{n,m}(\mathbf{k},\mathbf{k}') = \langle u_{n\mathbf{k}} | u_{m\mathbf{k}'} \rangle.$$
(1.31)

and $R_{\kappa i}$ the reduced coordinates of atom κ in the unit cell.

 $^{^{7}}M_{\perp}^{(2)}$ and $M_{\perp}^{(3)}$ are given by similar expressions.

1.4.4 Wannier functions

Wannier functions $W_n(\mathbf{r}-\mathbf{R}) \ (=\langle \mathbf{r} | \mathbf{R} n \rangle)$ are orthonormal functions that span the same space as the Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$ of a band or group of bands [91, 92]. They are characterized by two quantum numbers: a band index, n, and a lattice vector, \mathbf{R} . Wannier functions are an interesting tool in the study of the electronic structure and dielectric properties of materials. They are the solid state equivalent of "localized molecular orbitals" [10, 12, 93] and thus provide an insightful picture of the nature of the chemical bonding, otherwise missing from the Bloch picture of extended orbitals. Moreover, Wannier functions are used as a very accurate minimal basis in "order-N" methods [32], the construction of effective Hamiltonians for the study of transport properties of nanostructures [33], strongly correlated electrons [94] and other systems.

Wannier functions are Fourier transforms of the Bloch eigenstates

$$W_n(\mathbf{r} - \mathbf{R}) = \frac{\Omega_0}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R})} u_{n\mathbf{k}}(\mathbf{r}).$$
(1.32)

They allow an interesting interpretation of the Berry phase formalism presented in Sec. 1.4.3. Inserting Eq. (1.32) into Eq. (1.26), we obtain

$$\boldsymbol{\mathcal{P}}_{el}(\lambda) = \frac{-2e}{\Omega_0} \sum_{n=1}^N \int d\mathbf{r} \ \mathbf{r} \ |W_n(\mathbf{r})|^2.$$
(1.33)

Physically, Eqs.(1.23) and (1.33) state that the change in polarization of the solid is proportional to the displacement of the center of charge of the Wannier functions of the occupied bands induced by the adiabatic change in the Hamiltonian.

One of the most serious drawbacks of the Wannier representation is that the functions are not uniquely defined but that they can vary strongly in shape and range. This is a consequence of the phase indeterminacy of the Bloch orbitals at every wave vector **k**. In addition, Bloch orbitals belonging to an isolated group of bands, \mathcal{G}_i , (i.e., a set of bands that are connected between themselves by degeneracies, but separated from others by energy gaps) can undergo arbitrary unitary (gauge) transformations between themselves at every **k**

$$u_{n\mathbf{k}}(\mathbf{r}) \rightarrow \sum_{m \in \mathcal{G}_i} U_{mn}^{(\mathbf{k})} u_{m\mathbf{k}}(\mathbf{r}).$$
 (1.34)

Marzari and Vanderbilt developed a method to construct Wannier functions that are maximally localized around their centers [28, 30, 31]. For each group of bands, \mathcal{G}_i , they proposed to minimize the spread functional

$$\Omega = \sum_{n \in \mathcal{G}_i} \left[\langle \mathbf{0}n | r^2 | \mathbf{0}n \rangle - \langle \mathbf{0}n | \mathbf{r} | \mathbf{0}n \rangle^2 \right] = \sum_{n \in \mathcal{G}_i} \left[\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2 \right]$$
(1.35)

with respect to the unitary transformations $U_{mn}^{(\mathbf{k})}$. Eq. (1.35) can be decomposed into two terms,

$$\Omega = \Omega_I + \Omega \tag{1.36}$$

where

$$\Omega_{I} = \sum_{n \in \mathcal{G}_{i}} \left[\langle r^{2} \rangle_{n} - \sum_{m \in \mathcal{G}_{i}} \sum_{\mathbf{R}} |\langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle|^{2} \right]$$
(1.37)

 and

$$\widetilde{\Omega} = \sum_{n \in \mathcal{G}_i} \sum_{m \in \mathcal{G}_i} \sum_{\mathbf{R}} \ell \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2.$$
(1.38)

The prime in Eq. (1.38) indicates that the terms $\mathbf{R}m = \mathbf{0}n$ have to be omitted. It can be shown that Ω_I and $\widetilde{\Omega}$ are positive definite. Moreover, Ω_I is also gauge-invariant, i.e. it is invariant under any unitary transformation (1.34) among the Bloch orbitals. The minimization of Eq. (1.35) therefore corresponds to the minimization of $\widetilde{\Omega}$ and Ω_I corresponds to a lower bound of the spread functional Ω .

In a one-dimensional crystal this lower bound can be realized by choosing an adequate phase factor for the Bloch functions. In fact, the Wannier functions can be chosen to be eigenfunctions of the position operator projected onto the group of bands under consideration, PxP. In this case, it is straightforward to show that $\tilde{\Omega}$ vanishes so that $\Omega = \Omega_I$ [28]. In a three-dimensional crystal, it is no more possible to diagonalize PxP, PyP and PzP simultaneously. As a consequence, $\tilde{\Omega} > 0$ and Ω will always be larger than Ω_I . The problem is therefore to find a set of Wannier functions that makes the best possible compromise in the attempt to diagonalize all three operators simultaneously ⁸.

1.4.5 The electric field perturbation in extended systems

In this section, we discuss the main difficulties related to the electric field perturbation in extended systems and show, how they can be overcome in practice. In the scalarpotential gauge, the interaction between the electrons and a homogeneous electric field, \mathcal{E} , is described by the potential $V(\mathbf{r}) = e\mathcal{E} \cdot \mathbf{r}$, where e is the absolute value of the electronic charge. Although this potential is widely used to study the response of confined systems such as molecules to electric fields, its application to extended systems such as solids is not straightforward. The main difficulty is the nature of the scalar potential which, is *non-periodic* and *unbound from below*.

The non-periodicity of $V(\mathbf{r})$ is related to the position operator \mathbf{r} . As it is discussed in Sec. 1.4.3 this operator is not compatible with periodic boundary conditions so that it cannot be applied in a straightforward way in extended solids.

The unboundness of the scalar potential can be explained as follows. Figure 1.8 shows the electronic bands of an insulating crystal in the presence of an electric field. As can be seen, the field "bends" the energy bands so that the potential energy of the electrons is lower on the right side of the figure than on the left side. It is therefore

⁸Another approach consists in the minimization of the spread of the Wannier functions in one given direction as realized for the so-called hermaphrodite orbitals introduced in Ref. [12]: these particular functions are localized (Wannier-like) in a given direction and delocalized (Bloch-like) in the two others.

Figure 1.8: Potential energy of an electron, e^- , in an electric field, \mathcal{E} . E_g is the energy of the band gap at zero electric field.



possible to lower the energy of the system by transferring charge from the valence bands (E_v) in one region to the conduction bands (E_c) in a distant region. Because of this interband (Zener) tunneling, an infinite crystal in an electric field has no true ground-state.

However, for sufficiently small fields, the tunneling current through the band gap can be neglected and the system is well described by a set of electric field dependent Wannier functions. As shown by Nunes and Vanderbilt [95], these Wannier functions minimize the energy functional

$$\mathcal{F}[W_n; \mathcal{E}] = E[W_n] - \Omega_0 \mathcal{E} \cdot \mathcal{P}$$
(1.39)

where E is the Kohn-Sham energy under zero field and \mathcal{P} the macroscopic polarization that can be computed from the Wannier function centers (Eq. (1.33), see also Ref. [96]). It is important to note that these Wannier functions do not correspond to the true ground-state of the system but rather to a long lived metastable state.

In practical applications, it is not mandatory to evaluate the functional Eq. (1.39) in a Wannier basis. It can equivalently be expressed using Bloch functions $u_{n\mathbf{k}}(\mathbf{r})$ related to $W_n(\mathbf{r})$ by Eq. (1.32). In this case, the polarization can be computed as a Berry phase of the occupied bands using Eq. (1.28). This approach is discussed more in detail in Chapter 4.

1.4.6 Energy derivatives and multifunctional properties

The linear and nonlinear responses of insulators to selected perturbations can be characterized by the derivatives of its energy and other thermodynamic potentials. In this

\mathcal{F}	1^{st} -order derivatives	2^{nd} -order derivatives		
		$\frac{\partial}{\partial \tau}$	$\frac{\partial}{\partial \eta}$	<u> </u>
$\frac{\partial}{\partial \tau}$	f	C	γ	Z^*
$\frac{\overline{\partial}}{\partial n}$	σ	γ	c^0	e^0
$\frac{\overline{\partial}'}{\partial \mathcal{E}}$	\mathcal{P}^{s}	Z^*	e^0	ε

Table 1.5: Physical quantities related (within a factor of normalization) to first- and second-order derivatives of \mathcal{F} .

work, we consider three kinds of perturbations: atomic displacements, $\tau_{\kappa\alpha}$ (the index κ labels an atom and α a Cartesian direction), macroscopic strains, $\eta_{\mu\nu}$, and homogeneous electric fields, \mathcal{E} . The corresponding thermodynamic potential is the energy functional, \mathcal{F} , defined in Eq. (1.39). To simplify the notations, we represent the three perturbations by a single parameter, λ , defined as

$$\boldsymbol{\lambda} = (\boldsymbol{\tau}, \boldsymbol{\eta}, \boldsymbol{\mathcal{E}}). \tag{1.40}$$

The functional, $\mathcal{F},$ can be expressed as a Taylor series around the zero-field equilibrium structure

$$\mathcal{F}(\boldsymbol{\lambda}) = \mathcal{F}(0) + \sum_{i} \left. \frac{\partial \mathcal{F}}{\partial \lambda_{i}} \right|_{0} \lambda_{i} + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^{2} \mathcal{F}}{\partial \lambda_{i} \partial \lambda_{j}} \right|_{0} \lambda_{i} \lambda_{j} + \frac{1}{6} \sum_{i,j,k} \left. \frac{\partial^{3} \mathcal{F}}{\partial \lambda_{i} \partial \lambda_{j} \partial \lambda_{k}} \right|_{0} \lambda_{i} \lambda_{j} \lambda_{k} + \dots$$
(1.41)

The derivatives of \mathcal{F} in Eq. (1.41) have a well defined physical meaning. As can be seen in Table 1.5, the first-order derivatives are related to the forces on the atoms, f, the stress-tensor, σ and the spontaneous polarization, \mathcal{P}^s . The second-order derivatives characterize the linear response of the solid. They are related to the interatomic force constants, C, the optical dielectric constants, ε , the rigid-atom elastic constants, c^0 , the Born effective charges, Z^* , the rigid-atom piezoelectric constants, e^0 and the internal strain coupling parameters, γ . Finally, the third-order derivatives of \mathcal{F} characterize the nonlinear response of the solid. In this work, we do not consider the whole set of third-order derivatives. We will focus on third-order derivatives of \mathcal{F} with respect to three electric fields and third-order derivatives of \mathcal{F} with respect to two electric fields and one atomic displacement that are related to the nonlinear optical susceptibilities, $\chi^{(2)}$ and the first-order derivatives of the linear optical susceptibilities with respect to atomic displacements, $\frac{\partial \chi^{(1)}}{\partial \tau}$.

1.5 Conclusions

In this Chapter, we first discussed the structure and phase transitions of three ferroelectric oxides: $BaTiO_3$, $PbTiO_3$ and $LiNbO_3$. We then defined the nonlinear optical susceptibilities, the EO coefficients and the elasto-optic coefficients of insulators and we showed that we can distinguish three contributions to the EO coefficients: an electronic contribution, an ionic contribution and a piezoelectric contribution.

To define the theoretical framework of this work, we summarized the main aspects of density functional theory, density functional perturbation theory, the modern theory of polarization, Wannier functions, the electric field perturbation in extended systems and we showed, how linear and nonlinear response properties of insulators are related to their energy derivatives.

1.6 References

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

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Chapter 2

The electron localization tensor

2.1 Introduction

Our qualitative understanding of electron localization in solids is often based on approximate pictures. The core electrons are tightly bound and localized around the nuclei. In insulators, the valence electrons are confined to the chemical bonds (covalent crystals) or to particular atomic sites (ionic crystals) while they are "free to move" and delocalized in metals. In order to quantify the degree of electron localization, this simple description is no more sufficient and we have to adopt a rigorous formalism based on quantum mechanics. However, in this context, even a qualitative description of electron localization is not clear. In periodic solids, described within Born- von Karman periodic boundary conditions, the electronic wave functions are Bloch functions. As a consequence, core and valence electrons appear as delocalized over the whole crystal since the Bloch functions are periodic over the Born- von Karman supercell.

Alternatively, we can choose a Wannier representation of the electronic groundstate. Wannier functions are localized orbitals that can be computed from a unitary transformation of the Bloch functions. But even in the Wannier representation, a rigorous quantification of electron localization is not straightforward. As discussed in Sec. 1.4.4, the Wannier functions are not unique so that their spatial extension cannot directly be used to quantify the degree of electron localization.

The basics of a quantitative characterization of electron localization were formulated by Kohn in 1964 [97]. Recently, this problematic was renewed thanks to the development of the modern theory of polarization [7–9]. Polarization and localization are manifestations of the same phenomenon and they can be studied from essentially the same formalism. Following Resta and Sorella, we define in Sec. 2.2 a characteristic electron localization length that is finite in insulators and diverges in metals. In order to describe anisotropic media, this concept is further generalized to a localization tensor. We also discuss the physical meaning and drawbacks of the definition of the electron localization tensor. In Sec. 2.3, we propose a decomposition of the localization tensor into contributions originating from isolated sets of bands composing the energy spectrum of a solid. Using a simple model, we then illustrate the role of the covalent interactions on the different terms of the decomposition. We also make a connection between the localization tensor and the Born effective charges and we discuss the relation between pseudopotential and all-electron calculations. In Sec. 2.4, we give the technical details underlying our first-principles calculations. In Secs. 2.5 and 2.6, we present the results obtained on three ferroelectric oxides (BaTiO₃, PbTiO₃ and LiNbO₃) as well as on two binary oxides (BaO and α -PbO). We investigate the variations of electron localization during the phase transitions of BaTiO₃ and LiNbO₃ and show that the evolution is compatible with the electronic structure of these compounds.

2.2 The electron localization tensor

2.2.1 Definition

Let us consider first a one-dimensional system of side a and a large Born- von Karman cell of side L = Ma. The localization length is defined through the expectation value of the many-body phase operator [98, 99]

$$z = \left\langle \Psi \left| e^{(2i\pi/L) \sum_{i=1}^{N_e} x_i} \right| \Psi \right\rangle$$
(2.1)

where N_e is the number of electrons and Ψ the many-body wave function defined as a Slater determinant of the one-particle orbitals. The phase of z corresponds to the ground-state expectation value of the position operator, intrinsically connected to the macroscopic polarization, while its modulus provides an unambiguous definition of a localization length

$$\langle x^2 \rangle_c = -\frac{1}{N_e} \left(\frac{L}{2\pi}\right)^2 \ln|z|^2.$$
 (2.2)

If the system is insulating with $N (= N_e/2M)$ doubly occupied bands, z can be computed from the overlap matrices between Bloch functions defined in Eq. (1.31)

$$\sqrt{z} = \prod_{j=0}^{M-1} \det S(k_j, k_{j+1}).$$
(2.3)

In the limit $M \to \infty$, Eq. (2.2) can be expressed as an integral over the BZ

$$\langle x^2 \rangle_c = \frac{a}{N2\pi} \int_{BZ} dk \sum_{n=1}^N \left\{ \left\langle \frac{\partial u_{nk}}{\partial k} \middle| \frac{\partial u_{nk}}{\partial k} \right\rangle - \sum_{n'=1}^N \left\langle \frac{\partial u_{nk}}{\partial k} \middle| u_{n'k} \right\rangle \left\langle u_{n'k} \middle| \frac{\partial u_{nk}}{\partial k} \right\rangle \right\}. \tag{2.4}$$
Eq. (2.4) can be generalized to three-dimensional crystals [12] where the localization length takes the form of a second-order tensor, the so-called localization tensor

$$\langle r_{\alpha}r_{\beta}\rangle_{c} = \frac{\Omega_{0}}{N(2\pi)^{3}} \int_{BZ} d\mathbf{k} \sum_{n=1}^{N} \left\{ \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle - \sum_{n'=1}^{N} \left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \middle| u_{n'\mathbf{k}} \right\rangle \left\langle u_{n'\mathbf{k}} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle \right\}.$$

$$(2.5)$$

2.2.2 Physical interpretations

The localization tensor in Eq. (2.5) may look like an abstract mathematical concept. In this section, we see that it has a well-defined physical meaning and that it can be related to various physical quantities.

Maximally localized Wannier functions

First, the diagonal elements of the localization tensor give a lower bound of the average spread of the Wannier functions build from the Bloch orbitals of all occupied bands. Indeed, it is straightforward to show [12,13,28] that these elements are related to Ω_I defined in Eq. (1.37) by

$$\Omega_I = N \sum_{\alpha=1}^3 \langle r_\alpha r_\alpha \rangle_c.$$
(2.6)

Geometric quantum distance and quantum metric

Second, let us consider a general quantum mechanical Hamiltonian that has a parametric dependence $H(\boldsymbol{\xi})|\psi(\boldsymbol{\xi})\rangle = E(\boldsymbol{\xi})|\psi(\boldsymbol{\xi})\rangle$. For example, $H(\boldsymbol{\xi})$ could be identified to the electronic Hamiltonian of a molecule or a solid in the Born and Oppenheimer approximation and $\boldsymbol{\xi}$ to the nuclear coordinates or $|\psi(\boldsymbol{\xi})\rangle$ could be identified to the cell-periodic part of the Bloch functions and $\boldsymbol{\xi}$ to their wave vector. The geometric distance D_{12} between two eigenstates $|\psi(\boldsymbol{\xi}_1)\rangle$ and $|\psi(\boldsymbol{\xi}_2)\rangle$ can be defined as [10]

$$D_{12}^2 = 1 - |\langle \psi(\boldsymbol{\xi}_1) | \psi(\boldsymbol{\xi}_2) \rangle|^2.$$
(2.7)

For an infinitesimal separation $d\boldsymbol{\xi}$ between the two states, we can write

$$D^{2}_{\boldsymbol{\xi},\boldsymbol{\xi}+d\boldsymbol{\xi}} = 1 - |\langle \psi(\boldsymbol{\xi}) | \psi(\boldsymbol{\xi}+d\boldsymbol{\xi}) \rangle|^{2} = \sum_{\alpha,\beta} g_{\alpha\beta}(\boldsymbol{\xi}) d\boldsymbol{\xi}_{\alpha} d\boldsymbol{\xi}_{\beta}$$
(2.8)

where $g_{\alpha\beta}(\boldsymbol{\xi})$ is the metric tensor

$$g_{\alpha\beta}(\boldsymbol{\xi}) = \Re \left\langle \left. \frac{\partial \psi(\boldsymbol{\xi})}{\partial \xi_{\alpha}} \right| \left. \frac{\partial \psi(\boldsymbol{\xi})}{\partial \xi_{\beta}} \right\rangle - \left\langle \left. \frac{\partial \psi(\boldsymbol{\xi})}{\partial \xi_{\alpha}} \right| \psi(\boldsymbol{\xi}) \right\rangle \left\langle \psi(\boldsymbol{\xi}) \left| \frac{\partial \psi(\boldsymbol{\xi})}{\partial \xi_{\beta}} \right\rangle.$$
(2.9)

The form of the metric tensor is similar to the argument of the integral in Eq. (2.5). If we identify ψ to the cell periodic part of the Bloch functions and $\boldsymbol{\xi}$ to their wave vector, \mathbf{k} , we can define a metric to determine the "quantum distance" along a given path in \mathbf{k} -space. Generalizing Eq. (2.9) to a system composed of N doubly occupied bands, we obtain [28]

$$g_{\alpha\beta}(\mathbf{k}) = \sum_{n=1}^{N} \left\{ \left\langle \left. \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \right| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle - \sum_{n'=1}^{N} \left\langle \left. \frac{\partial u_{n\mathbf{k}}}{\partial k_{\alpha}} \right| u_{n'\mathbf{k}} \right\rangle \left\langle u_{n'\mathbf{k}} \left| \frac{\partial u_{n\mathbf{k}}}{\partial k_{\beta}} \right\rangle \right\}.$$
 (2.10)

The elements of the localization tensor are the BZ average of the metric tensor $g_{\alpha\beta}$ [13,28]

$$\langle r_{\alpha}r_{\beta}\rangle_c = \frac{\Omega_0}{N(2\pi)^3} \int_{BZ} d\mathbf{k} g_{\alpha\beta}(\mathbf{k}).$$
 (2.11)

Fluctuations of the polarization and optical conductivity

Finally, let us consider an extended solid subjected to periodic boundary conditions over a large supercell containing M unit cells. The Cartesian components of the polarization undergo quantum fluctuations related to the elements of the localization tensor. In the thermodynamic limit we can write [13]

$$\langle r_{\alpha}r_{\beta}\rangle_{c} = \lim_{M \to \infty} \frac{\Omega_{0}^{2}M}{e^{2}} \langle \Delta \mathcal{P}_{\alpha}^{el} \Delta \mathcal{P}_{\beta}^{el} \rangle.$$
(2.12)

This equation is particularly interesting since it shows that the localization tensor is more than a mathematical concept. It is a measurable quantity. Using the fluctuationdissipation theorem [100] we obtain the following relation between the localization tensor and the optical conductivity (imaginary part of the electronic dielectric tensor)

$$\int_{0}^{\infty} \varepsilon_{\alpha\beta}^{\prime\prime}(\omega) \, d\omega = \frac{8\pi^2 e^2 N}{\hbar\Omega_0} \left\langle r_{\alpha} r_{\beta} \right\rangle_c.$$
(2.13)

Relation to the optical gap

In a cubic crystal, we can use the sum rule for oscillator strengths [101] together with Eq. (2.13) to obtain the following relation between the localization tensor and the band gap E_q

$$\langle r_{\alpha}^2 \rangle_c \le \frac{\hbar^2}{2m_e E_g},\tag{2.14}$$

where m_e is the electronic mass. This inequality shows that the polarization fluctuations are controlled by the optical gap, lending support to the intuitive notion that the larger the gap, the more localized the electrons.

2.2.3 Drawbacks

The localization tensor as it is defined in Eq. (2.5) is a *global* quantity that characterizes the occupied Kohn-Sham manifold as a *whole* (all **k**-points and all bands). This statement calls for two comments. First, applications of DFT to solids often make use of the frozen-core and pseudopotential approximations, while Eq.(2.5) requires an all-electron calculation. Second, the behavior of core and valence electrons is treated globally while both kinds of electrons are expected to exhibit strongly different localization properties interesting to identify independently.

As it has been discussed in the preceding sections, the localization tensor gives a lower bound for the spread of maximally localized Wannier functions as defined by Marzari and Vanderbilt. In order to get some insight into the physics of the chemical bonds in molecules and solids, such Wannier functions are usually constructed considering only a restricted number of electronic bands close to the Fermi level. The spread of the resulting Wannier functions is strongly dependent on the electronic states included in the minimization process. In this context, it seems interesting to try to identify the intrinsic localization of the electrons in a specific set of bands and to understand how this quantity is affected when including other bands. This would allow to solve the problem associated to the use of pseudopotentials and to characterize separately the behavior of core and valence electrons.

2.3 Band-by-band decomposition of the localization tensor

2.3.1 Formalism

Contrary to the polarization and the Born effective charges, for which band-by-band decompositions have been previously reported [102–105], the localization tensor [Eq. (2.5)] involves scalar products between Bloch functions of different bands, making the identification of the contribution of isolated sets of bands less straightforward. In order to explain this fact, we have to remember that the localization tensor is related to the second moment of Wannier functions while the Born effective charges and the spontaneous polarization are linked to their first moment. From standard statistics, it is well known that first and second moments do not add the same way: when considering two random variables x_1 and x_2 , the mean value of the sum $x_1 + x_2$ is simply the sum of the mean values while the variance of the sum is the sum of the variances *plus* an additional term, the covariance.

These considerations can be transposed in the simple context of a confined model system made of two orthonormalized states $\psi_1(x)$ and $\psi_2(x)$. The total many-body wave function $\Psi(x_1, x_2)$ is a Slater determinant constructed on the one-particle orbitals. The center of mass is given by the expectation value of the position operator

(2.15)

 $X = \sum_{i=1,2} x_i$ $\overline{X} = \langle \Psi | X | \Psi \rangle = \sum_{i=1,2} \langle \psi_i | x | \psi_i \rangle$

while the total spread (two times the localization tensor) is related to X^2 ,

$$\sigma^{2} = \langle \Psi | X^{2} | \Psi \rangle - \langle \Psi | X | \Psi \rangle^{2}$$

=
$$\sum_{i=1,2} [\langle \psi_{i} | x^{2} | \psi_{i} \rangle - \langle \psi_{i} | x | \psi_{i} \rangle^{2}] - 2 \langle \psi_{1} | x | \psi_{2} \rangle \langle \psi_{2} | x | \psi_{1} \rangle.$$
(2.16)

We see that the first moments of the one-particle orbitals add to form the total dipole of the many-body wave function. In contrast, the total spread is not equal to the sum of the individual spreads of ψ_1 and ψ_2 but involves also matrix elements of the oneparticle position operator x between ψ_1 and ψ_2 . The additional term would be absent if the many-body wave function was a simple product of the one-particle orbitals. It arises from the anti-symmetry requirement. In analogy with the language of statistics, we will name it the *covariance*.

Based on the previous arguments, we can now define a band-by-band decomposition of Eq. (2.5). Suppose that the band structure is formed of N_g groups labeled \mathcal{G}_i , each of them composed of n_i bands $(i = 1, ..., N_g)$. The variance of a particular group \mathcal{G}_i is defined as

$$\langle r_{\alpha} r_{\beta} \rangle_{c}(\mathcal{G}_{i}) = \frac{\Omega_{0}}{n_{i}(2\pi)^{3}} \int_{BZ} d\mathbf{k} \left\{ \sum_{n \in \mathcal{G}_{i}} \left\langle \frac{\partial u_{n} \mathbf{k}}{\partial k_{\alpha}} \middle| \frac{\partial u_{n} \mathbf{k}}{\partial k_{\beta}} \right\rangle - \sum_{n, n' \in \mathcal{G}_{i}} \left\langle \frac{\partial u_{n} \mathbf{k}}{\partial k_{\alpha}} \middle| u_{n'} \mathbf{k} \right\rangle \left\langle u_{n'} \mathbf{k} \left| \frac{\partial u_{n} \mathbf{k}}{\partial k_{\beta}} \right\rangle \right\}$$
(2.17)

where the sums have to be taken over the bands of group \mathcal{G}_i . The covariance of two groups \mathcal{G}_i and \mathcal{G}_j $(i \neq j)$ is given by the following relationship:

$$\langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{i},\mathcal{G}_{j}) = \frac{-\Omega_{0}}{n_{i}n_{j}(2\pi)^{3}} \int_{BZ} d\mathbf{k} \sum_{n \in \mathcal{G}_{i}} \sum_{n' \in \mathcal{G}_{j}} \left\langle \frac{\partial u_{n}\mathbf{k}}{\partial k_{\alpha}} \middle| u_{n'}\mathbf{k} \right\rangle \left\langle u_{n'}\mathbf{k} \left| \frac{\partial u_{n}\mathbf{k}}{\partial k_{\beta}} \right\rangle.$$
(2.18)

Using these definitions, the total tensor, associated to the whole set of occupied bands, can be written as

$$\langle r_{\alpha}r_{\beta}\rangle_{c} = \frac{1}{N}\sum_{i=1}^{N_{g}} n_{i} \left\{ \langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{i}) + \sum_{j\neq i}^{N_{g}} n_{j}\langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{i},\mathcal{G}_{j}) \right\}.$$
 (2.19)

The variance $\langle r_{\alpha}r_{\beta}\rangle_c(\mathcal{G}_i)$ is intrinsic to an isolated set of bands. As discussed in section 2.2.2, it is related to the quantity Ω_I introduced by Marzari and Vanderbilt through Eq. (2.6). $\langle r_{\alpha}r_{\alpha}\rangle_c(\mathcal{G}_i)$ is thus the lower bound of the *average* spread [Eq.

(1.35)] $\frac{1}{n_i} \sum_{n \in \mathcal{G}_i} [\langle r_{\alpha}^2 \rangle_n - \langle r_{\alpha} \rangle_n^2]$ where the sum is taken over all Wannier-like functions in the unit cell belonging to group \mathcal{G}_i . This lower bound is reached for Wannier functions that are maximally localized in direction α . The variance therefore gives some insight on the localization of the electrons within a specific set of bands taken independently. This localization is affected by the hybridizations between atomic orbitals giving rise to the formation of the considered electronic bands within the solid so that the variance can act as a probe to characterize these hybridizations.

The covariance is no more related to an isolated set of bands. It teaches us how the construction of Wannier functions including other bands can improve the localization. As discussed in Ref. [28], the definition of groups of bands in a solid is not unique and sometimes there is a doubt about which bands have to be considered together. If we consider two sets of bands \mathcal{G}_i and \mathcal{G}_j as one single group, its total variance is the sum of the individual variances and covariances, that have to be rescaled by the number of bands in each group

$$\langle r_{\alpha}r_{\beta}\rangle_{c} = \frac{1}{n_{i}+n_{j}} \left\{ n_{i} \left[\langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{i}) + n_{j} \langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{i},\mathcal{G}_{j}) \right] + n_{j} \left[\langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{j}) + n_{i} \langle r_{\alpha}r_{\beta}\rangle_{c}(\mathcal{G}_{j},\mathcal{G}_{i}) \right] \right\}.$$

$$(2.20)$$

Until now, we considered separately the two Cartesian directions α and β . Stronger results can be obtained when diagonal elements of the localization tensor are considered, or when this localization tensor is diagonalized, and the eigenvalues are considered. Different inequalities can be derived. In particular, from Eq. (2.18), it appears that the covariances for $\alpha = \beta$ are always *negative*. This means that the diagonal elements of the full tensor are always smaller than those obtained by the sum of the diagonal variances. In other words, it is always possible to obtain more strongly localized orbitals by constructing Wannier functions considering more than one group of bands. As a consequence the covariance appears as a tool to identify which bands have to be considered together in the construction of Wannier functions in order to improve their localization.

In appendix A, we give an interpretation of the variance and covariance in terms of the optical conductivity. It illustrates from a different viewpoint the influence of the fermionic nature of the electrons on the localization tensor: the appearance of the covariance in Eq. (2.19) is a direct consequence of the Pauli principle.

2.3.2 Simple model

In this section we will investigate a one-dimensional model system. This will help us to understand the role of the covalent interactions on the electron localization length and related quantities such as the Born effective charges. We will deal with a confined system for which the localization tensor can be computed from matrix elements of the position operator and its square as described in Refs. [10, 12].

Let us consider a diatomic molecule XY. In order to describe the chemical bonds of this model system we adopt a tight-binding scheme [106] defined by the hopping integral, t, and the on-site terms Δ and $-\Delta$. We will call a the interatomic distance and ψ_X , ψ_Y the s-like atomic orbitals that are used as basis functions. The Hamiltonian can be rescaled by Δ (A=t/ Δ) in order to become a one parameter Hamiltonian defined by

$$H = \begin{pmatrix} -1 & A \\ A & 1 \end{pmatrix}.$$
(2.21)

We further assume that ψ_X is centered at the origin, ψ_Y in *a* and that these two functions do not overlap at any *x*

$$\psi_X(x)\psi_Y(x-a) = 0. \tag{2.22}$$

The eigenfunctions of the Hamiltonian correspond to

$$\phi_{1,2}(x) = u_{1,2}\psi_X(x) + v_{1,2}\psi_Y(x-a)$$
(2.23)

where the coefficients $u_{1,2}$ and $v_{1,2}$ can be expressed in terms of the bond polarity [106] $\alpha_p \ (\alpha_p = \frac{1}{\sqrt{1+A^2}})$:

$$u_{1} = \sqrt{\frac{1+\alpha_{p}}{2}}, \quad v_{1} = \sqrt{\frac{1-\alpha_{p}}{2}} u_{2} = \sqrt{\frac{1-\alpha_{p}}{2}}, \quad v_{2} = -\sqrt{\frac{1+\alpha_{p}}{2}}.$$
(2.24)

In order to see the meaning of the different terms appearing in the band-by-band decomposition of the localization tensor and the Born effective charges let us first consider the molecular orbitals independently.

The variance of state ϕ_1 can be computed from the coefficients u_1 and v_1 . It writes

$$\langle x^2 \rangle_c(1) = \sigma_X^2 \frac{1 + \alpha_p}{2} + \sigma_Y^2 \frac{1 - \alpha_p}{2} + \frac{a^2 A^2}{4(1 + A^2)}$$
(2.25)

where σ_X^2 and σ_Y^2 are the second central moments of ψ_X and ψ_Y . The variance of ϕ_2 is given by a similar expression. This quantity is composed of three positive terms that summarize the mechanisms that are able to delocalize the electrons with respect to the atomic orbitals. On one hand, the electronic cloud on a particular atom is not a delta-Dirac function but presents a degree of delocalization related to σ_X^2 and σ_Y^2 (first and second term). When the state ϕ_1 is made entirely of ψ_X , that is, when α_p equals one, the localization length is correctly equal to σ_X^2 (first term). Incorporating more ψ_Y changes the localization length in proportion of α_p (the balance between first and second terms). On the other hand, the electrons can occupy two sites X and Y that are separated by a distance a (third term). This term scales as a^2 . Even a small covalent interaction is thus able to induce an important delocalization if it acts on a sufficiently large distance.

The Born effective charge of atom X is defined as the derivative of the dipole moment p with respect to a. This dipole moment is the sum of the nuclear and static electronic charges multiplied by the interatomic distance. The contribution coming from the electrons occupying state ϕ_1 is equal to

$$p_1 = -2eu_1^2 a = -e(1+\alpha_p)a \tag{2.26}$$

where e is the module of the electronic charge. The derivative of Eq. (2.26) with respect to a gives the contribution of these electrons to the total effective charge

$$Z_{X,1}^{*} = \frac{\partial p_{1}}{\partial a} = -e(1+\alpha_{p}) + ea\frac{A}{(1+A^{2})^{3/2}}\frac{\partial A}{\partial a}.$$
 (2.27)

The first term is the (static) effective atomic charge [106] of atom X while the second term represents an additional dynamical contribution due to a transfer on electrons between X and Y during a relative atomic displacement. The contribution of the electrons occupying state ϕ_2 is given by a similar expression

$$Z_{X,2}^* = \frac{\partial p_2}{\partial a} = -e(1-\alpha_p) - ea\frac{A}{(1+A^2)^{3/2}}\frac{\partial A}{\partial a}.$$
(2.28)

This simple model illustrates how both the variance of the localization tensor and the Born effective charges depend on the covalent interactions defined by the parameter A. The variance is a *static* quantity depending on the amplitude of the covalent interactions only while the Born effective charges are *dynamical* quantities that also depend on the variations of these interactions during a relative atomic displacement.

If we now consider the states ϕ_1 and ϕ_2 as a single group we have to add their variances and covariances to get the whole localization tensor. The covariance reduces to

$$\langle x^2 \rangle_c(1,2) = \frac{-a^2 A^2}{4(1+A^2)}.$$
 (2.29)

By adding this covariance to the variance in Eq. (2.25), we remove in some sense the delocalization induced by the covalent interactions. The total localization tensor becomes independent of the hopping A and the interatomic distance a. It reduces to the mean spread of the atomic orbitals ψ_X and ψ_Y :

$$\langle x^2 \rangle_c = \frac{\sigma_X^2 + \sigma_Y^2}{2}.$$
 (2.30)

Eq. (2.30) defines the mean spread of the Wannier function constructed as linear combinations of ϕ_1 and ϕ_2 that minimize the spread functional Ω (see Eq. (1.35)). As shown in Ref. [28] (see also Sec. 1.4.4), these orbitals diagonalize the position operator \hat{x} projected on the subspace of occupied states. They are thus equal to the atomic orbitals since the hypothesis of zero overlap (Eq. (2.22)) implies $\langle \psi_X | \hat{x} | \psi_Y \rangle = 0$.

The total Born effective charge of atom X can be obtained by adding the nuclear charge $Z_{core}^* = 2e$ to the terms (2.27) and (2.28). It is easy to check that for this model Z_X^* is equal to zero. This result can be interpreted in two ways. The point of view usually adopted is to say that the two molecular orbitals are of the opposite polarity so that the total dipole of the molecule vanishes. Based on the results of the preceding paragraph, we can also affirm that each maximally localized Wannier function is confined on a single atom so that no interatomic charge transfer can take place.

This result suggests that the variance gives more information about the localization of electrons of particular chemical bonds than the total localization tensor. It also illustrates the observation of Ghosez *et al.* [102,103] that anomalous effective charges mainly come from hybridizations between occupied and unoccupied states. In fact, the different chemical bonds generate opposite effects so that a net charge transfer is possible only if some of them are unoccupied.

In summary, we have illustrated the mechanisms that govern the variance of the localization tensor and the Born effective charges in the particular case of a one dimensional model system. The observations made in this section give us an intuitive understanding of how delocalized electrons can generate anomalous effective charges. Hybridizations between occupied states generate opposite effects that tend to cancel out when they are summed. Because of the simplicity of the above adopted picture, we have however to be careful when we apply this model to real materials. First, we considered only hybridizations between two types of atomic orbitals, while the chemical bonds in real systems generally result from more complicated interactions. In particular, we neglected on-site hybridizations that are also able to generate anomalous effective charges but that induce a stronger localization on the electronic cloud. Second, the hypothesis of zero overlap (2.22) is not always fulfilled so that maximally localized Wannier functions constructed on the whole set of occupied states generally not reduce to the atomic orbitals. Nevertheless, this simple model will allow us to interpret some results in Secs. 2.5 and 2.6.

2.3.3 Pseudopotentials

As mentioned in Sec. 2.2.3, there is a fundamental problem in the computation of the total localization tensor when pseudopotentials are used. This is due to the fact that the localization tensor is related to the bands of the system as a whole : first, there is no cancellation between the core electrons and the nuclear charge, as it is the case in the computation of the total polarization; second, the localization tensor is a kind of mean over all bands, that combines strongly localized (core) states, and weakly localized (valence) states. This is clearly seen in Eq.(2.5), where the number of bands explicitly appears both in the denominator of the prefactor and in the two summations. The band-by-band decomposition allows us to overcome this problem partly, by focusing only on the variances of isolated groups of bands. Thanks to Eq. (2.20) it is also possible to get some insight into the physics of the all-electron localization tensor when pseudopotentials are used. In this section, we focus on the diagonal elements of the electron localization tensor $\alpha = \beta$ (of course, any direction can be chosen as α).

In an all-electron calculation, let us consider separately two sets of bands: core bands (labeled as 'co'), and valence bands (labeled as 'va'). The total localization tensor can be obtained from the localization tensors of each group of bands, combined with the covariance between the two groups of bands:

$$\langle r_{\alpha}r_{\alpha}\rangle_{c} = \frac{1}{n_{co} + n_{va}} \left\{ n_{co} \langle r_{\alpha}r_{\alpha}\rangle_{c}(co) + n_{va} \langle r_{\alpha}r_{\alpha}\rangle_{c}(va) + 2n_{co}n_{va} \langle r_{\alpha}r_{\alpha}\rangle_{c}(co, va) \right\}.$$
(2.31)

Both variances $\langle r_{\alpha}r_{\alpha}\rangle_c(co)$ and $\langle r_{\alpha}r_{\alpha}\rangle_c(va)$ are positive quantities. The covariance times the product of the number of bands $n_{co}n_{va}\langle r_{\alpha}r_{\alpha}\rangle_c(co, va)$, a negative quantity, must always be smaller in magnitude than each of the related variances multiplied by the corresponding number of bands. This translates to bounds on the diagonal elements of the total localization tensor:

$$\frac{|n_{va}\langle r_{\alpha}r_{\alpha}\rangle_{c}(va) - n_{co}\langle r_{\alpha}r_{\alpha}\rangle_{c}(co)|}{n_{co} + n_{va}} \leq \langle r_{\alpha}r_{\alpha}\rangle_{c} \leq \frac{n_{va}\langle r_{\alpha}r_{\alpha}\rangle_{c}(va) + n_{co}\langle r_{\alpha}r_{\alpha}\rangle_{c}(co)}{n_{co} + n_{va}}.$$
(2.32)

In the frozen-core approximation, $\langle r_{\alpha}r_{\alpha}\rangle_c(co)$ can be obtained from separate allelectron calculations for each atom of the system. The localization tensor of the valence bands is (likely) computed accurately in the pseudopotential approximation : the spread of the Wannier functions should be quite similar if estimated from all-electron valence wave functions or from pseudo-wave functions.

2.4 Method and implementation

In the remaining part of this Chapter, we apply the previous formalism to various oxides. The electronic wave functions are obtained within DFT [5, 6] and the local density approximation (LDA) thanks to the ABINIT [64] package. At variance with a previous work on semiconductors [12], the first derivatives of the wave functions with respect to their wave vector are not computed from finite differences but from a linear-response approach [37] within the parallel-transport gauge. The wave functions are further transformed to the diagonal gauge [105]. In all compounds, the groundstate and first-order wave functions are expanded in plane waves up to a kinetic-energy cutoff of 45 Hartree. We use a $8 \times 8 \times 8$ mesh of special **k**-points [107] for BaO, α -PbO, $BaTiO_3$ and $PbTiO_3$ and $a 6 \times 6 \times 6$ mesh of special k-points for $LiNbO_3$. With these parameters, the convergence of the localization tensor for the investigated compounds is better than 10^{-3} Bohr². In BaO, α -PbO, BaTiO₃ and PbTiO₃, the ionic-core electron potentials of the atoms are replaced by ab initio, separable, extended norm-conserving pseudopotentials, as proposed by M. Teter [108]. Ba 5s, 5p and 6s electrons, Pb 6s, 5d and 6p electrons, Ti 3s, 3p and 3d electrons, O 2s and 2p electrons are considered as valence states. In $LiNbO_3$, we use the same norm-conserving pseudopotentials as in Ref. [69]. Nb 4s, 4p, 4d and 5s electrons, Li 1s and 2s electrons as well as O 2s and 2p electrons are considered as valence states. Besides calculating the localization tensor on bulk-materials, we also computed it on the isolated atomic systems Ba^{2+} , Pb^{2+} , Li^+ , Nb^{5+} and O by placing each atom at the origin of a periodic supercell of 20 Bohrs.

As shown by Sgiarovello *et al.* [12], the localization tensor and thus the variances and covariances, are real. Moreover, they are obviously symmetric in α and β . Consequently there exists a set of Cartesian axes where they are diagonal and their eigenvalues are also real numbers. In the discussion of our results we will always work in this particular frame so that we do not need to consider the off-diagonal elements of the localization tensor.

2.5 Results

2.5.1 Structural and electronic properties

We will consider the two binary oxides BaO and α -PbO, the ferroelectric perovskites BaTiO₃ and PbTiO₃ as well as the trigonal ferroelectric LiNbO₃. BaO has a rocksalt structure while the tetragonal α phase of lead oxide is formed of parallel layers of Pb and O atoms. As discussed in Sec. 1.2, BaTiO₃ and PbTiO₃ have a high-temperature cubic perovskite structure with five atoms per unit cell. As the temperature is lowered, the former compound undergoes a sequence of three ferroelectric phase transitions transforming to tetragonal, orthorhombic and rhombohedral structures while the latter compound undergoes one single transition from the cubic to the tetragonal phase. Finally, LiNbO₃ has a trigonal symmetry with 10 atoms per unit cell. It undergoes a single transition from a centrosymmetric paraelectric R3c phase to a ferroelectric R3c ground state. We will consider explicitly the cubic, tetragonal and rhombohedral phases of BaTiO₃, the cubic phase of PbTiO₃ as well as the two phases of LiNbO₃.

The electronic structures of these compounds have been previously studied [69,104, 109–111] and are illustrated in Figs. 2.1 and 2.2. They are formed of well-separated groups of bands. Each of them has a marked dominant orbital character and can be labeled by the name of the atomic orbital that mainly composes the energy state in the solid. In all compounds, the bands at the Fermi level are mainly composed of O 2p states that show significant interactions with other atomic orbitals such as the well known O 2p-Ti 3d hybridization in $BaTiO_3$ and $PbTiO_3$ or the O 2p-Nb 5d hybridization in $LiNbO_3$. The band structures in the ferroelectric phases of $BaTiO_3$ and $LiNbO_3$ are similar to those in their paraelectric phases. The phase transitions principally affect the band gap and the spread of the O 2p bands while the positions of the deeper lying bands remain quite constant. The main difference in the electronic structures of BaO and $BaTiO_3$ on one hand and PbO and $PbTiO_3$ on the other hand comes from the presence or absence of Pb 6s electrons (that form the so called lonepair in PbO). These electrons show a strong hybridization with the O 2p states. As a consequence, the O 2p and Pb 6s bands are degenerate at the R point in $PbTiO_3$ and around the Z point in PbO. Consequently, we have to consider them as one single group of bands in the decomposition of the localization tensor.

2.5.2 Localization tensor and Born effective charges

As the total localization tensor is meaningless in pseudopotential calculations that do not include covariances with the core states, we focus on the variances of the different groups of bands. The values can be found in the Tables 2.1, 2.2 and 2.3 where they are compared to the variances of the dominant atomic orbitals. We do not report any values associated to the deepest lying Ti 3s and Ti 3p bands although they have been included in our pseudopotential calculation. Their variances are in fact close to the atomic ones and they do not show any sizeable covariance with other bands in $BaTiO_3$ and $PbTiO_3$.



Figure 2.1: Band structures of BaO, cubic BaTiO₃, cubic PbTiO₃ and α -PbO.

Figure 2.2: Band structure in the paraelectric phase of $LiNbO_3$.



Table 2.1: Variances (Bohr²) of the Ba 5s, O 2s, Ba 5p and O 2p bands for the isolated atomic systems Ba^{2+} and O, BaO and the cubic (C), tetragonal (T) and rhombohedral (R) phases of $BaTiO_3$.

System	Str.	Element	Band			
			$\operatorname{Ba}5\mathrm{s}$	O 2s	Ba $5p$	O 2p
Atom	_	$\langle r^2 \rangle_c$	1.011	0.929	1.370	_
BaO	_	$\langle r^2 \rangle_c$	1.065	1.552	2.023	2.199
BaTiO_3	\mathbf{C}	$\langle r^2 \rangle_c$	1.091	0.950	2.189	1.875
	Т	$\langle r_{\perp}^2 angle_c$	1.091	0.945	2.180	1.852
		$\langle r_{\parallel}^{\overline{2}} \rangle_c$	1.088	0.965	2.175	1.842
	\mathbf{R}	$\langle r_{\perp}^2 \rangle_c$	1.092	0.963	2.196	1.862
		$\langle r_{\parallel}^{\overline{2}} \rangle_c$	1.092	0.949	2.189	1.804

Table 2.2: Variances (Bohr²) of the O 2s, Pb 5d and Pb 6s +O 2p bands in PbTiO₃, α -PbO and for the isolated atomic systems Pb²⁺ and O.

System	Element	Band		
		O 2s	Pb~5d	Pb 6s + O 2p
Atom	$\langle r^2 \rangle_c$	0.929	0.657	—
$\rm PbTiO_3$	$\langle r^2 \rangle_c$	1.874	1.490	1.749
PbO	$\langle r_{\perp}^2 \rangle_c$	2.234	1.142	2.178
	$\langle r_{\parallel}^{\overline{2}} \rangle_{c}$	1.724	0.990	1.968

In the cubic crystals BaO, BaTiO₃ and PbTiO₃ as well as in the atomic systems, the reported tensors are isotropic so that we only mention their principal values $\langle r^2 \rangle_c$. This is no more true in the ferroelectric phases of BaTiO₃ and the two phases of LiNbO₃ where a weak anisotropy can be observed. The tensors have an uniaxial character as the corresponding dielectric ones: they are diagonal when expressed in the principal axes and the elements $\langle r_{\perp}^2 \rangle_c$ and $\langle r_{\parallel}^2 \rangle_c$ refer to Cartesian directions perpendicular and parallel to the optical axis (that has the direction of the spontaneous polarization). A much stronger anisotropy is observed in α -PbO where the localization tensor has the same symmetry as in the ferroelectric phases of BaTiO₃. Due to its particular structure formed of atomic Pb-O planes the electrons of each group of bands are more delocalized in a direction parallel ($\langle r_{\perp}^2 \rangle_c$) to the atomic planes¹ than perpendicular interactions between atoms inside a layer are stronger than between atoms of different

¹In α -PbO, the optical axis is perpendicular to the atomic layers.

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

Table 2.3: Variances (Bohr²) in the two phases of LiNbO₃ and for the inner orbitals of Nb⁵⁺, Li⁺ and O.

layers.

Examining the variances of the different groups of bands we see that the Ba 5s electrons show a similar degree of localization both in BaO and BaTiO₃ also equivalent to that of the corresponding atomic orbital. In contrast, the O 2s electrons behave differently in the materials under investigation: in BaTiO₃ and LiNbO₃, their variance is close to the atomic one while they show a significant larger delocalization in the three other compounds. It is in fact surprising to see the degree of delocalization of the inner bands such as the O 2s, Ba 5p, Nb 4p or Pb 5d bands. In some cases such as $BaTiO_3$, the electrons of these bands are even more strongly delocalized than those of the bands at the Fermi level. These results suggest that the corresponding atomic orbitals are chemically not inert but present non-negligible covalent interactions. An interesting observation can be made for the O 2s and Pb 5d bands in $PbTiO_3$ and α -PbO. The delocalization induced by the covalent interactions that generate these bands tends to disappear when we consider them as one single group. In order to compute the variance of the whole O 2s and Pb 5d bands, we have to use Eq. (2.20). As an example let us consider PbTiO₃. The different elements can be summarized in a matrix where the diagonal elements are the variances $(Bohr^2)$ and the off-diagonal elements the covariances (Bohr²) of the individual groups

$$\left(\begin{array}{rrr} 1.874 & -0.240 \\ -0.240 & 1.490 \end{array}\right)$$

The total variance of the (O 2s + Pb 5d) group considered as a whole reduces to 0.734 Bohr². For α -PbO, we obtain similar values of 0.732 Bohr² for $\langle r_{\perp}^2 \rangle_c$ and 0.701 Bohr² for $\langle r_{\parallel}^2 \rangle_c$. These values can be compared to the mean spread of the atomic orbitals $\frac{1}{6}(0.929 + 5 \times 0.657) = 0.702$ Bohr².

The results presented above show that inner orbitals such as O 2s, Ba 5p, Nb 4p or Pb 5d are chemically not inert in the materials under investigation. This observation

	$PbTiO_3$	α -PbO	
Band	Z_{Pb}^*	$Z^*_{Pb\perp}$	$Z_{Pb\parallel}^*$
Core	14.00	14.00	14.00
O 2s	0 + 3.47	0 + 1.89	0 + 0.26
Pb 5d	-10 - 3.36	-10 - 1.80	-10 - 0.40
Pb $6s + O 2p$	-2 + 1.78	-2 + 1.06	-2 + 0.48
Tot	2 + 1.89	2 + 1.15	2 + 0.34

Table 2.4: Band-by-band decomposition of the Born effective charges (a. u. of charge) in PbTiO₃ and α -PbO. The contributions have been separated into a reference nominal value and an *anomalous* charge.

seems in contradiction with the conclusions drawn from partial density of states analysis [110] that these states are rather inert. Nevertheless the inspection of the Born effective charges in BaO, BaTiO₃ or LiNbO₃ [69, 102, 104] confirms our observations that will now be illustrated for α -PbO and PbTiO₃. This points out that the global shape of the band structure is less sensitive to the underlying covalent interactions than the variance of the localization tensor or the Born effective charges.

In order to investigate the connection between the localization tensor and the Born effective charges we report in Table 2.4 the band-by-band decomposition of Z_{Pb}^* in PbTiO₃ and α -PbO. In the perovskite, this tensor is isotropic while in α -PbO it has the same symmetry as the localization tensor. The contribution of each group of bands has been separated into a reference nominal value and an *anomalous* charge ². For α -PbO, we observe the same anisotropy as for the localization tensor: the covalent interactions inside an atomic layer $(Z_{Pb\perp}^*)$ generate larger *anomalous* contributions than the interactions involving atoms of different layers $(Z_{Pb\parallel}^*)$. By looking at the O 2s and Pb 5d bands we see that they generate important anomalous charges that confirm our observations concerning the variances of these bands. Interestingly, in both materials these contributions cancel out when they are summed. We observe thus the same tendencies for the Born effective charges and the localization tensor: the effects induced by the covalent interactions between inner orbitals tend to disappear when the resulting bands are considered together.

2.6 Discussions

Based on the simple model exposed in Sec. 2.3.2 we can suggest the following mechanism to explain the results presented in the preceding section. The atomic orbitals

 $^{^{2}}$ The Born effective charges are usually compared to an isotropic nominal value that is the charge expected in a purely ionic compound. All deviations with respect to this reference nominal value are referred to as *anomalous*.

O 2s and Pb 5d (for which the hypothesis of zero overlap (2.22) is reasonable) present weak covalent interactions that generate the corresponding energy bands in $PbTiO_3$ and α -PbO. When we construct maximally localized Wannier functions for each individual group, the resulting orbitals are delocalized on Pb and O atoms so that during an atomic displacement an interatomic transfer of charges – generating anomalous Born effective charges - is possible. The fact that the variance of the global (O 2s + Pb 5d) group of bands is close to the mean spread of the atomic orbitals suggests that the maximally localized Wannier functions constructed on these bands are similar to the original atomic orbitals. In other words, they are confined on a single atom. This confinement also suppresses the interatomic charge transfer so that the anomalous charges disappear. We can make similar observations for the Ba 5p and O 2s bands in BaO and BaTiO₃, although, in the latter compound, the cancellation in the Born effective charges and the variance is not as complete as in the three remaining ones. This suggests that in the lead oxides as well as in BaO, the inner bands Pb 5d and O 2s (respectively Ba 5p and O 2s) mainly result from hybridizations between two types of atomic orbitals. In contrast, in $BaTiO_3$ the Ba 5p and O 2s bands are formed of more than two types of atomic orbitals.

Looking now at the bands at the Fermi level, we see that their variance is significantly larger in BaO and α -PbO than in the corresponding perovskites and that it remains nearly constant in the different phases of BaTiO₃ and LiNbO₃. This latter observation seems surprising for two reasons. (i) In BaTiO₃, the LDA band gap presents drastic changes when passing from the cubic (1.72 eV) to the rhombohedral (2.29 eV) phase. In LiNbO₃, we observe a similar strong variation when passing from the paraelectric (2.60 eV) to the ferroelectric (3.48 eV) phase. These increases suggest much stronger localization of the O 2p electrons in the ferroelectric phases. (ii) The giant Born effective charges observed in the paraelectric phases [69, 102, 103] imply an important reorganization of the electronic cloud during an atomic displacement. It appears surprising that this reorganization has such small effects on the localization tensor.

Considering point (i), we note that the correlation between the band gap and the localization tensor is not as tight as one might think. The variance of the O 2p bands for instance is significantly larger in BaO than in BaTiO₃ in spite of the fact that its LDA band gap (1.69 eV) is close to the gap in the cubic phase of BaTiO₃.

Considering point (ii), we note that it is possible to have an important reorganization of the electronic charge *without* affecting the localization tensor significantly. Following the ideas of the Harrison model [106], the giant effective charges in ferroelectrics result from dynamical orbital hybridizations changes generating interatomic transfers of charges. In Figure 2.3 (a) we have drawn schematically an O centered Wannier function in the cubic phase of BaTiO₃ along a Ti - O chain. Due to the O 2p - Ti 3d hybridization, this Wannier function has a finite probability on the neighboring Ti₁ and Ti₂ atoms. According to the Harrison model, a fraction of electrons is transferred from Ti₁ to Ti₂ during a displacement $d\tau$ of the O atom (Figure 2.3 (b)). Even if the quantity of charges involved in this process is small, the large scale on which this transfer takes place (of the order of the lattice parameter) implies a shift



Figure 2.3: Oxygen centered Wannier functions in the cubic phase (solid line) of $BaTiO_3$ (a) and its variation during the transition to the tetragonal phase (dashed line) (b).

of the Wannier function center larger than the underlying atomic displacement and explains the *anomalous effective charges*. During the transition from the cubic to the tetragonal phase, the central O atom is displaced by few percent of the lattice constant $a \left(\frac{d\tau}{a} = 0.045\right)$ with respect to Ti₁ and Ti₂. The resulting shift of the Wannier function center generates the spontaneous polarization in the ferroelectric phase.

Based on this simple picture the origin of the small variations of the O 2p variance during the phase transitions becomes more obvious: when the electrons are transferred from Ti₁ to Ti₂ their distance to the initial Wannier function center remains unaffected and their distance to the displaced Wannier function center slightly decreases due to its shift towards Ti₂. Mathematically speaking, due to the fact that the variations do not depend on the direction of the atomic displacement, they are of the second order in $\frac{d\tau}{a}$.

In order to get a numerical estimate of the charges transferred during this process and its impact on the localization tensor we can consider a one dimensional model Wannier function whose square is the sum of three delta-Dirac functions

$$|W_n(x)|^2 = \frac{1}{2} \left\{ \frac{2 - Z'_O}{2} \left[\delta(x - a) + \delta(x + a) \right] + Z'_O \delta(x) \right\}.$$
 (2.33)

This model only takes into account the delocalization of the electrons on different atoms (third term of Eq. (2.25)) while it completely neglects the delocalization of the electronic cloud on the individual atoms (first and second term of Eq. (2.25)). In this particular case we can identify the localization tensor to the second moment of the Wannier function. This is no more completely true in a real, three-dimensional crystal. In BaTiO₃ for instance, the O 2p group contains 9 different Wannier functions per unit cell located on three different O atoms. These orbitals extend in different spatial directions so that their *average* spread in the *x*-direction is lower than the spread of one single Wannier function as the one shown in Figure 2.3.

In Eq. (2.33), Z'_O represents the probability of the electrons to be found on the O atom. It can be computed from the value of the O 2p variance in the paraelectric phase of BaTiO₃ and the lattice constant *a* using the relation $\int x^2 |W_n(x)|^2 dx = \langle r^2 \rangle_{c,O2p}$. This yields $Z'_O = 1.73$. This quantity allows an estimate of the static charge of the O atom in BaTiO₃ by subtracting three times Z'_O from the charge due to the nucleus and the core electrons O 1s and O 2s. This yields $Z_{O,st} = 4 - 3 \cdot 1.73 = -1.19 \ e$.

When the O atom is displaced, the shift of the Wannier function center is directly related to the quantity of charges ε transferred from Ti₁ to Ti₂. The value of ε can be computed from the value of the effective charge generated by the O 2p electrons $(Z_{O2p}^* = -9.31)$ in the cubic phase [103] by taking into account that the anomalous charges are generated by three Wannier functions located on the same O atom [29]. To get the polarization due to one single Wannier function, we have to divide this quantity by 3 since each of them brings a similar contribution to Z_{O2p}^* . In the tetragonal phase, the model Wannier function writes

$$|W_n(x)|^2 = \frac{1}{2} \left\{ \frac{2 - Z'_O - \varepsilon}{2} \delta(x+a) + Z'_O \delta(x-d\tau) + \frac{2 - Z'_O + \varepsilon}{2} \delta(x-a) \right\}.$$
 (2.34)

By identifying twice its first moment to $Z^*_{O2p} d\tau/3$ one gets $\varepsilon = 0.0614$ at the transition from the cubic to the tetragonal state. It implies a decrease in the spread of the model Wannier function of 0.18 Bohr².

This variation is larger than the observed one (0.023 Bohr^2) . Part of the discrepancy is probably due to the fact that we considered Z_{O2p}^* to be constant along the path of atomic displacement from the paraelectric to the ferroelectric phase. Using the value of Z_{O2p}^* in the tetragonal phase we obtain a value of 0.0467 for ε while the variance decreases of 0.12 Bohr². Moreover, one has to bear in mind that the localization tensor in BaTiO₃ is an average value that has to be taken over 9 Wannier functions. Six of them are centered on O atoms that lie in a plane perpendicular to the direction of the spontaneous polarization. They are probably less affected by the phase transition. As a consequence, the variation of the Wannier function located on the remaining O atom (the one represented on Figure 2.3) is expected to be larger than the variation of the localization tensor.

In summary, even if there is no formal connection between the real Wannier functions in BaTiO₃ or LiNbO₃ and Eq. (2.33), this simple model shows that small variations of the localization tensor are compatible with giant effective charges and their interpretation in terms of the Harrison model. As illustrated with the model Wannier function, the transfer of charges along the Ti–O chains only implies a slight decrease in the spread of one single Wannier function. This *decrease* is expected to be larger than the decrease in the variance because this latter quantity is an average value over 9 Wannier functions that are not modified to the same extent during the phase transition.

2.7 Conclusions

The characterization of electron localization in extended systems had been a challenging problem that was only solved recently. Thanks to the modern theory of polarization, it is now possible to study the electronic polarization and localization length from a unified formalism. In this Chapter, we used a plane-wave-pseudopotential approach to DFT to compute the electron localization tensor for various oxides. Our study was based on the work on semiconductors performed by Sgiarovello and co-workers but used linear-response techniques to compute the first-order wave functions.

In order to investigate the properties of electrons occupying individual groups of bands independently, we first set-up a band-by-band decomposition of the localization tensor. In analogy with the field of statistics we had to distinguish between variance and covariance in this decomposition. The significance of these new concepts was illustrated in terms of Wannier functions and explained on a simple model. The variance allows to get some insight into the hybridizations of atomic orbitals. The covariance can be useful to help constructing maximally localized Wannier functions: it identifies the bands that have to be considered together in order to improve their localization. We also made a connection between the localization tensor and the Born effective charges and we discussed the difference between all-electron and pseudopotential calculations.

We applied these techniques to binary oxides (BaO and α -PbO) and ferroelectric oxides (BaTiO₃, PbTiO₃ and LiNbO₃). By considering first the electrons of the inner bands we showed that some of them present a strong delocalization with respect to the situation in an isolated atom. This observation suggests that the underlying atomic orbitals are chemically not inert but present non-negligible covalent interactions. This fact had been confirmed from an inspection of the Born effective charges.

Finally, the variations of the O 2p variance during the ferroelectric phase transitions of $BaTiO_3$ and $LiNbO_3$ were found to be very small. This surprising result was explained in terms of the electronic structure of these compounds as it is interpreted in the Harrison model.

We think that, when combined with Born effective charges, the band-by-band decomposition of the localization tensor could provide a powerful tool for the qualitative characterization of bonds in solids. However, more studies are needed, for different classes of materials [112], in order to make it fully effective.

2.8 References

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

- M. Veithen, X. Gonze and Ph. Ghosez, Electron localization: Band-by-band decomposition and application to oxides, Phys. Rev. B 66, 235113 (2002).
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2.8. REFERENCES

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Chapter 3

Nonlinear response of insulators to electric fields: theory

3.1 Introduction

Having discussed the electric field perturbation in Sec. 1.4.5, we present in this Chapter two methodologies to study the nonlinear response of insulators to electric fields. The first technique uses density functional perturbation theory (DFPT) and the second one uses finite electric fields. We report the expressions that we implemented in the ABINIT code [64]. In the following Chapter, these techniques will be applied to various semiconductors and ferroelectrics.

Our interest in the nonlinear response of insulators to electric fields lies in the fact that many interesting properties are determined by this behavior. In particular, the nonlinear optical susceptibilities, Raman scattering efficiencies and electro-optic coefficients are related to third-order derivatives of the energy with respect to two or more electric fields. In contrast to the linear response formalism that is nowadays routinely applied to various systems (see for example Ref. [34]), the nonlinear response formalism has been mostly restricted to quantum chemistry problems. Although the hyperpolarizabilities of a huge number of molecules have been computed, taking into account both electronic and vibrational (ionic) contributions [113,114], applications in condensed matter physics have focused on rather simple cases [56–63].

The formalism we describe in this Chapter takes advantage of several recent theoretical developments. Nunes and Gonze [115] used Eq. (1.39) as an ansatz for a periodic energy functional. In their formalism, the polarization was computed as a Berry phase of field polarized Bloch functions (Eqs. (1.26) and (1.28)). This ansatz was justified later by Souza and co-workers [116] who showed that the minima of the functional of

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Nunes and Gonze are stationary solutions of the time dependent Schrödinger equation for sufficiently weak fields. Using perturbation theory, Nunes and Gonze showed that it is possible to obtain analytic expressions of the derivatives of the energy with respect to electric fields up to any order. In particular, at the lowest order, they recovered the same expressions of energy derivatives as given by more conventional perturbation methods [37, 117]. While Nunes and Gonze considered the response of extended systems to infinitesimal fields, Souza and co-workers [15] and Umari and co-workers [16] studied the response of extended systems to finite electric fields (FEF) by minimizing the energy functional in Eq. (1.39) with respect to the field polarized Bloch functions.

In this Chapter, we first particularize the formalism of Nunes and Gonze to the computation of selected third-order energy derivatives. We report the local density approximation (LDA) expressions of the nonlinear optical susceptibilities and the derivatives of the linear optical susceptibilities with respect to atomic displacements. We then show how these quantities can be used to compute the Raman scattering efficiencies of transverse and longitudinal optical phonons and the EO coefficients under different mechanical boundary conditions. Finally, we discuss the finite electric field method of Souza and co-workers [15].

3.2 Third-order density functional perturbation theory

3.2.1 Mixed third-order energy derivatives

In this section, we present the general framework of the computation of third order energy derivatives based on the 2n + 1 theorem [35, 36, 118]. Using the notations of Sec. 1.4.6 (see also Refs. [37, 38]), we consider three Hermitian perturbations labeled λ_1 , λ_2 and λ_3 . The mixed third-order derivatives of the Kohn-Sham energy Eq. (1.7)

$$E^{\lambda_1 \lambda_2 \lambda_3} = \frac{1}{6} \left. \frac{\partial^3 E}{\partial \lambda_1 \partial \lambda_2 \partial \lambda_3} \right|_{\lambda_1 = 0, \lambda_2 = 0, \lambda_3 = 0}$$
(3.1)

can be computed from the ground-state and first-order wave functions

$$E^{\lambda_1\lambda_2\lambda_3} = \frac{1}{6} \left(\widetilde{E}^{\lambda_1\lambda_2\lambda_3} + \widetilde{E}^{\lambda_1\lambda_3\lambda_2} + \widetilde{E}^{\lambda_2\lambda_1\lambda_3} + \widetilde{E}^{\lambda_2\lambda_3\lambda_1} + \widetilde{E}^{\lambda_3\lambda_2\lambda_1} + \widetilde{E}^{\lambda_3\lambda_1\lambda_2} \right)$$
(3.2)

with

$$\begin{split} \widetilde{E}^{\lambda_{1}\lambda_{2}\lambda_{3}} &= \sum_{\alpha} [\langle \psi_{\alpha}^{\lambda_{1}} | (T+v_{ext})^{\lambda_{2}\lambda_{3}} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{\lambda_{1}} | (T+v_{ext}+v_{Hxc})^{\lambda_{2}} | \psi_{\alpha}^{\lambda_{3}} \rangle \\ &+ \langle \psi_{\alpha}^{(0)} | (T+v_{ext})^{\lambda_{1}\lambda_{2}\lambda_{3}} | \psi_{\alpha}^{(0)} \rangle + \langle \psi_{\alpha}^{(0)} | (T+v_{ext})^{\lambda_{1}\lambda_{2}} | \psi_{\alpha}^{\lambda_{3}} \rangle] \\ &- \sum_{\alpha,\beta} \Lambda_{\beta\alpha}^{\lambda_{2}} \langle \psi_{\alpha}^{\lambda_{1}} | \psi_{\beta}^{\lambda_{3}} \rangle \end{split}$$

$$+\frac{1}{6}\int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \frac{\delta^{3} E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{\lambda_{1}}(\mathbf{r}) n^{\lambda_{2}}(\mathbf{r}') n^{\lambda_{3}}(\mathbf{r}'')$$

$$+\frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{d}{d\lambda_{2}} \frac{\delta^{2} E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Big|_{\lambda=0} n^{\lambda_{1}}(\mathbf{r}) n^{\lambda_{3}}(\mathbf{r}')$$

$$+\frac{1}{2}\int d\mathbf{r} \frac{d^{2}}{d\lambda_{1} d\lambda_{3}} \frac{\delta E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})} \Big|_{\lambda=0} n^{\lambda_{2}}(\mathbf{r}) + \frac{1}{6} \frac{d^{3} E_{Hxc}[n^{(0)}]}{d\lambda_{1} d\lambda_{2} d\lambda_{3}} \Big|_{\lambda=0} (3.3)$$

T is the kinetic energy and E_{Hxc} (v_{Hxc}) is the sum of the Hartree and exchangecorrelation energy (potential). The first-order potential $v_{Hxc}^{\lambda_2}$ can be computed as a second-order functional derivative of E_{Hxc} [36]:

$$v_{Hxc}^{\lambda_2} = \int \frac{\delta^2 E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{\lambda_2}(\mathbf{r}') \, d\mathbf{r}' + \left. \frac{d}{d\lambda_2} \frac{\delta E_{Hxc}[n^{(0)}]}{\delta n(\mathbf{r})} \right|_{\lambda=0}.$$
 (3.4)

Within the parallel gauge, the first-order Lagrange multipliers are given by

$$\Lambda_{\beta\alpha}^{\lambda_2} = \langle \psi_{\beta}^{(0)} | (T + v_{ext} + v_{Hxc})^{\lambda_2} | \psi_{\alpha}^{(0)} \rangle.$$

$$(3.5)$$

As a consequence of the 2n + 1 theorem, the evaluation of Eq. (3.3) requires no higher order derivative of the wave functions than the first one. These first-order wave functions are nowadays available in several first-principles codes. They can be computed from linear response by minimizing a stationary expression of the secondorder energy as described in Sec. 1.4.2 or equivalently by solving the corresponding Sternheimer equation [119]. It follows that the computation of third-order energy derivatives does not require additional quantities other than the calculation of secondorder energy derivatives.

Eq. (3.3) is the general expression of the third-order energy derivatives. In case at least one of the perturbations does not affect the explicit form of the kinetic energy or the Hartree and exchange-correlation energy, it can be simplified: some of the terms may be zero. This is the case for the electric field perturbations treated in this work as well as for phonon type perturbations. Further simplifications can be made in case pseudopotentials without nonlinear exchange-correlation core-correction are used.

3.2.2 The electric field perturbation

As discussed in Sec. 1.4.5, in case one of the perturbations λ_j is a macroscopic electric field \mathcal{E} , we can no more use the Kohn-Sham energy as it is defined in Eq. (1.7). Instead, we have to consider the electric field dependent energy functional, \mathcal{F} , defined in Eq. (1.39) where the polarization is computed as a Berry phase of the field-polarized Bloch functions [Eq. (1.26)]. In order to use Eq. (1.26) in practical calculations, the integration over the BZ and the differentiation with respect to **k** have to be performed on a discrete mesh of M_k **k**-points. As discussed in Sec. 1.4.3, in case of the groundstate polarization, the standard approach is to build strings of **k**-points parallel to a vector of the reciprocal space, \mathbf{G}_{\parallel} . The polarization can then be computed as a stringaveraged Berry phase [Eq. (1.28)]. Unfortunately, the adaptation of this method to the computation of the energy derivatives is plagued with several technical difficulties, like the following. The general form of the nonlinear optical susceptibility tensor of a compound is imposed by its symmetry. For example, in zinc-blende semiconductors, this tensor, expressed in *Cartesian coordinates* reduces to $\chi_{ijl}^{(2)} = \chi^{(2)} |\epsilon_{ijl}|$, where ϵ is the Levi-Civita tensor. It follows that the *reduced coordinate* formulation of $\chi_{ijl}^{(2)}$ satisfies the relation

$$\left|\frac{\chi_{ijl}^{(2)}}{\chi_{iii}^{(2)}}\right| = \frac{1}{3},\tag{3.6}$$

where at least one of the three indices i, j and l are different from the two others. When we tried to use strings of **k**-points to compute $\chi_{ijl}^{(2)}$, Eq. (3.6) was not satisfied. However, we were able to avoid these problems, by using the finite difference formula of Marzari and Vanderbilt [28] on a regular grid of special **k**-points (instead of strings)

$$\nabla f(\mathbf{k}) = \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} \left[f(\mathbf{k} + \mathbf{b}) - f(\mathbf{k}) \right], \qquad (3.7)$$

where **b** is a vector connecting a **k**-point to one of its nearest neighbors and $w_{\mathbf{b}}$ is a weight factor. The sum in Eq. (3.7) includes as many shells of first neighbors as necessary to satisfy the condition

$$\sum_{\mathbf{b}} w_{\mathbf{b}} b_{\alpha} b_{\beta} = \frac{g_{\alpha\beta}}{(2\pi)^2},\tag{3.8}$$

where b_{α} are the reduced coordinates of **b** and $g_{\alpha\beta}$ is the metric tensor associated with the real space crystal lattice.

In the case of the ground-state polarization, we cannot apply the discretization Eq. (3.7) directly to Eq. (1.26). As shown by Marzari and Vanderbilt, the discretization of Eq. (1.26) does not transform correctly under the gauge transformation

$$u_{n\mathbf{k}}(\mathbf{r}) \to e^{-i\mathbf{k}\cdot\mathbf{R}} u_{n\mathbf{k}}(\mathbf{r}).$$
 (3.9)

Since Eq. (3.9) is equivalent to a shift of the origin by one lattice vector \mathbf{R} , $\boldsymbol{\mathcal{P}}$ must change accordingly by one polarization quantum. In order to obtain a discrete expression that matches this requirement, we must combine Eq. (3.7) with the King-Smith and Vanderbilt formula [7,8]

$$\mathcal{P} = \frac{2e}{M_k \Omega_0} \sum_{\mathbf{k}} \sum_{\mathbf{b}} w_{\mathbf{b}} \mathbf{b} \Im \ln \det \left[S(\mathbf{k}, \mathbf{k} + \mathbf{b}) \right], \qquad (3.10)$$

where S is the overlap matrix between Bloch functions at \mathbf{k} and $\mathbf{k} + \mathbf{b}$ defined in Eq. (1.31).

As discussed by Nunes and Gonze [115], when we apply the perturbation expansion of the preceding section to the energy functional Eq. (1.39), we can adopt two equivalent approaches. The first possibility is the use of Eq. (1.26) for the polarization and

a discretization after having performed the perturbation expansion. The second possibility is to apply the 2n + 1 theorem directly to Eq. (3.10) in which case no additional discretization is needed. Using the notations of Nunes and Gonze, we will refer to the first case as the DAPE (discretization after perturbation expansion) formulation and to the second one as the PEAD (perturbation expansion after discretization) formulation of the third-order energy. In the following sections, we will discuss both expressions. In addition, in Sec. 4.3.1, we will compare their convergence with respect to the **k**-point sampling to the convergence of the first term (E) of Eq. (1.39) can easily be performed as it is described in the Sec. 3.2.1. In contrast, the expansion of the second term $(-\Omega_0 \mathcal{E} \cdot \mathcal{P})$ is more tricky since it explicitly depends on the polarization. In the two sections that follow, we will focus on the $-\Omega_0 \mathcal{E} \cdot \mathcal{P}$ term of Eq. (1.39). It will be referred to as E_{pol} .

3.2.3 DAPE expression

According to the formalism of the preceding section, the $\mathcal{E} \cdot \mathcal{P}$ term acts as an additional external potential that has to be added to the ionic one. The $\mathcal{E} \cdot \mathcal{P}$ perturbation is linear in the electric field and does not depend explicitly on other variables such as the atomic positions. It just enters the terms of Eq. (3.3) that involve the first derivative of v_{ext} with respect to \mathcal{E} . In other words, the only terms in Eq. (3.2) that involve the atomic perturbation of \mathcal{P} are of the form $\tilde{E}^{\lambda_1 \mathcal{E}_i \lambda_3}$ where λ_1 and λ_3 represent an arbitrary perturbation such as an electric field or an atomic displacement.

The DAPE expression of the third-order derivative of E_{pol} is written as follows

$$\widetilde{E}_{pol}^{\lambda_1 \mathcal{E}_i \lambda_3} = \frac{2ie\Omega_0}{(2\pi)^3} \int_{BZ} d\mathbf{k} \sum_{n}^{occ} \langle u_{n\mathbf{k}}^{\lambda_1} | \left(\frac{\partial}{\partial k_i} \sum_{m}^{occ} |u_{m\mathbf{k}}^{\lambda_3} \rangle \langle u_{m\mathbf{k}}^{(0)} | \right) | u_{n\mathbf{k}}^{(0)} \rangle, \tag{3.11}$$

where $u_{n\mathbf{k}}^{\lambda_j}$ are the projection of the first-order wave functions on the conduction bands. The complete expression of various third-order energy derivatives, taking into account the expansion of both E and E_{pol} , are reported in Sec. 3.3. Eq. (3.11) was derived first by Dal Corso and Mauri [117] in a slightly different context: they performed the perturbation expansion of the energy functional Eq. (1.39) using a Wannier basis. The resulting expression of the third-order energy derivatives was expressed in terms of Bloch functions by applying a unitary transform to the Wannier orbitals.

Using the finite difference expression of Marzari and Vanderbilt Eq. (3.7), Eq. (3.11) becomes

$$\widetilde{E}_{pol}^{\lambda_{1}\mathcal{E}_{i}\lambda_{3}} = \frac{2ie}{M_{k}} \sum_{\mathbf{k}} \sum_{\mathbf{b}} \sum_{n,m}^{occ} w_{\mathbf{b}}(\mathbf{b} \cdot \mathbf{G}_{i}) \\ \times \left\{ \langle u_{n\mathbf{k}}^{\lambda_{1}} | u_{m\mathbf{k}+\mathbf{b}}^{\lambda_{3}} \rangle \langle u_{m\mathbf{k}+\mathbf{b}}^{(0)} | u_{n\mathbf{k}}^{(0)} \rangle \\ - \langle u_{n\mathbf{k}}^{\lambda_{1}} | u_{m\mathbf{k}}^{\lambda_{3}} \rangle \delta_{n,m} \right\}, \qquad (3.12)$$

where \mathbf{G}_i is a basis vector of the reciprocal lattice.

3.2.4 PEAD expression

Applying directly the 2n + 1 theorem to Eq. (3.10) we obtain the alternative PEAD formulation of the third-order energy derivatives:

$$\widetilde{E}_{pol}^{\lambda_{1}\mathcal{E}_{i}\lambda_{3}} = \frac{-e}{M_{k}} \Im \sum_{\mathbf{k}} \sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b} \cdot \mathbf{G}_{i}) \\ \times \left[2 \sum_{n,m}^{occ} \langle u_{n\mathbf{k}}^{\lambda_{1}} | u_{m\mathbf{k}+\mathbf{b}}^{\lambda_{3}} \rangle Q_{mn}(\mathbf{k}, \mathbf{k} + \mathbf{b}) \\ - \sum_{n,m,l,l'}^{occ} S_{mn}^{\lambda_{1}}(\mathbf{k}, \mathbf{k} + \mathbf{b}) Q_{nl}(\mathbf{k}, \mathbf{k} + \mathbf{b}) \\ \times S_{ll'}^{\lambda_{3}}(\mathbf{k}, \mathbf{k} + \mathbf{b}) Q_{l'm}(\mathbf{k}, \mathbf{k} + \mathbf{b}) \right], \qquad (3.13)$$

where Q is the inverse of the overlap matrix S and S^{λ_j} its first-order perturbation expansion

$$S_{nm}^{\lambda_j}(\mathbf{k}, \mathbf{k} + \mathbf{b}) = \langle u_{n\mathbf{k}}^{\lambda_j} | u_{m\mathbf{k}+\mathbf{b}}^{(0)} \rangle + \langle u_{n\mathbf{k}}^{(0)} | u_{m\mathbf{k}+\mathbf{b}}^{\lambda_j} \rangle.$$
(3.14)

3.3 Computation of nonlinear optical properties

In the preceding section we have discussed the general expressions of third-order energy derivatives. We now particularize them to the computation of selected nonlinear properties.

3.3.1 Nonlinear optical susceptibilities

As shown in Sec. 1.3.1, in an insulator the polarization can be expressed as a Taylor expansion of the macroscopic electric field

$$\mathcal{P}_{i} = \mathcal{P}_{i}^{s} + \sum_{j=1}^{3} \chi_{ij}^{(1)} \mathcal{E}_{j} + \sum_{j,l=1}^{3} \chi_{ijl}^{(2)} \mathcal{E}_{j} \mathcal{E}_{l} + \cdots, \qquad (3.15)$$

where \mathcal{P}_i^s is the zero-field (spontaneous) polarization, $\chi_{ij}^{(1)}$ the linear optical susceptibility (second rank tensor) and $\chi_{ijl}^{(2)}$ the second-order nonlinear optical susceptibility (third rank tensor). In the literature on nonlinear optics, one often finds another definition of the nonlinear optical susceptibility: instead of $\chi_{ijl}^{(2)}$, it is more convenient to rely on the *d* tensor defined as

$$d_{ijl} = \frac{1}{2}\chi_{ijl}^{(2)}.$$
(3.16)

In general, the polarization depends on valence electrons as well as on ions. In the present section, we deal only with the electronic contribution: we will consider the ionic cores as clamped to their equilibrium positions. This constraint will be relaxed in the following sections where we allow for ionic displacements.

Experimentally, the electronic contribution to the linear and nonlinear susceptibilities corresponds to measurements for electric fields at frequencies high enough to get rid of the ionic relaxation but low enough to avoid electronic excitations. In case of the second-order susceptibilities, this constraint implies that both the frequency of \mathcal{E} , and its second harmonic, are lower than the fundamental absorption gap.

The general expression of the electronic nonlinear optical susceptibility depends on the frequencies of the optical electric fields [see for example Ref. [120]]. In the present context of the 2n + 1 theorem applied within the LDA to (static) DFT, we neglect the dispersion of $\chi_{ijl}^{(2)}$. As a consequence, $\chi_{ijl}^{(2)}$ satisfies Kleinman's [121] symmetry condition which means that it is symmetric under a permutation of i, j and l. In order to be able to investigate its frequency dependence, one would need either to apply the formalism of time-dependent DFT [56] or to use expressions that involve sums over excited states [55, 122–125].

Following the work of Dal Corso and co-workers [56,117] we can relate the nonlinear optical susceptibilities to a third-order derivative of the energy functional defined in Eq. (1.39) with respect to an electric field

$$\chi_{ijl}^{(2)} = -\frac{3}{\Omega_0} \mathcal{F}^{\mathcal{E}_i \mathcal{E}_j \mathcal{E}_l}$$
(3.17)

where $\mathcal{F}^{\mathcal{E}_i \mathcal{E}_j \mathcal{E}_l}$ is defined as the sum over the permutations of the three perturbations $\tilde{\mathcal{F}}^{\mathcal{E}_i \mathcal{E}_j \mathcal{E}_l}$ (3.2). Using the PEAD formulation of Sec. 3.2.2 we can express these terms as follows:

$$\widetilde{\mathcal{F}}^{\mathcal{E}_{i}\mathcal{E}_{j}\mathcal{E}_{l}} = \frac{-e}{M_{k}} \Im \sum_{\mathbf{k}} \sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b} \cdot \mathbf{G}_{j}) \left[2 \sum_{n,m}^{occ} \langle u_{n\mathbf{k}}^{\mathcal{E}_{i}} | u_{m\mathbf{k}+\mathbf{b}}^{\mathcal{E}_{l}} \rangle Q_{mn}(\mathbf{k}, \mathbf{k}+\mathbf{b}) \\ - \sum_{n,m,n',m'}^{occ} S_{mn}^{\mathcal{E}_{i}}(\mathbf{k}, \mathbf{k}+\mathbf{b}) Q_{nn'}(\mathbf{k}, \mathbf{k}+\mathbf{b}) S_{n'm'}^{\mathcal{E}_{l}}(\mathbf{k}, \mathbf{k}+\mathbf{b}) Q_{m'm}(\mathbf{k}, \mathbf{k}+\mathbf{b}) \right] \\ + \frac{2}{M_{k}} \sum_{\mathbf{k}} \sum_{n,m}^{occ} \left[\delta_{m,n} \langle u_{n\mathbf{k}}^{\mathcal{E}_{i}} | v_{hxc}^{\mathcal{E}_{i}} | u_{m\mathbf{k}}^{\mathcal{E}_{l}} \rangle - \langle u_{m\mathbf{k}}^{(0)} | v_{hxc}^{\mathcal{E}_{j}} | u_{n\mathbf{k}}^{(0)} \rangle \langle u_{n\mathbf{k}}^{\mathcal{E}_{i}} | u_{m\mathbf{k}}^{\mathcal{E}_{l}} \rangle \right] \\ + \frac{1}{6} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \frac{\delta^{3} E_{xc} [n^{0}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{\mathcal{E}_{i}}(\mathbf{r}) n^{\mathcal{E}_{i}}(\mathbf{r}') n^{\mathcal{E}_{l}}(\mathbf{r}''). \quad (3.18)$$

3.3.2 Raman susceptibilities of zone-center optical phonons

We now consider the computation of Raman scattering efficiencies of zone-center optical phonons. In the limit $q \to 0$, the matrix of interatomic force constants \widetilde{C} can be

expressed as the sum of an analytical part and a non-analytical term [38]

$$\widetilde{C}_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q}\to 0) = \widetilde{C}^{AN}_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q}=0) + \widetilde{C}^{NA}_{\kappa\alpha,\kappa'\beta}(\boldsymbol{q}\to 0).$$
(3.19)

The analytical part corresponds to the second-order derivative of the energy with respect to an atomic displacement at q = 0 under the condition of vanishing macroscopic electric field. The second term is due to the long-range electrostatic interactions in polar crystals. It is at the origin of the so-called LO-TO splitting and can be computed from the knowledge of the Born effective charges, $Z_{\kappa\alpha\beta}^*$, and the electronic dielectric tensor [38] ε_{ij} . The phonon frequencies, ω_m , and eigendisplacements, $U_m(\kappa\alpha)$, are solutions of the following generalized eigenvalue problem

$$\sum_{\kappa',\beta} \widetilde{C}_{\kappa\alpha,\kappa'\beta} U_m(\kappa'\beta) = M_\kappa \omega_m^2 U_m(\kappa\alpha), \qquad (3.20)$$

where M_{κ} is the mass of atom κ . As a convention, we choose the eigendisplacements to be normalized as

$$\sum_{\kappa,\alpha} M_{\kappa} U_m(\kappa\alpha) U_n(\kappa\alpha) = \delta_{m,n}.$$
(3.21)

In what follows we consider non-resonant Raman scattering where an incoming photon of frequency ω_0 and polarization \mathbf{e}_0 is scattered to an outgoing photon of frequency ($\omega_0 - \omega_m$) and polarization \mathbf{e}_S by creating a phonon of frequency ω_m (Stokes process). The scattering efficiency [126,127] (cgs units) corresponds to

$$\frac{dS}{d\mathcal{V}} = |\mathbf{e}_{S} \cdot R^{m} \cdot \mathbf{e}_{0}|^{2}$$
$$= \frac{(\omega_{0} - \omega_{m})^{4}}{c^{4}} |\mathbf{e}_{S} \cdot \boldsymbol{\alpha}^{m} \cdot \mathbf{e}_{0}|^{2} \frac{\hbar}{2\omega_{m}} (n_{m} + 1)$$
(3.22)

where c is the speed of light in vacuum and n_m the boson factor

$$n_m = \frac{1}{\exp(\hbar\omega_m/k_B T) - 1}.$$
(3.23)

The Raman susceptibility $\boldsymbol{\alpha}^m$ is defined as

$$\alpha_{ij}^{m} = \sqrt{\Omega_0} \sum_{\kappa,\beta} \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\beta}} U_m(\kappa\beta), \qquad (3.24)$$

where $\chi_{ij}^{(1)}$ is the electronic linear dielectric susceptibility tensor. \mathcal{V} is the angle of collection in which the outgoing photon is scattered. Due to Snell's law, \mathcal{V} is modified at the interface between the sample and the surrounding medium. Experimentally, the scattering efficiencies are measured with respect to the solid angle of the medium while Eq. (3.22) refers to the solid angle inside the sample. In order to relate theory and experiment, one has to take into account the different refractive indices of the sample

and medium. For example, in the isotropic case, Eq. (3.22) has to be multiplied [126] by $(n'/n)^2$ where n and n' are, respectively, the refractive indices of the sample and the medium.

For pure transverse optical phonons, $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\beta}$ can be computed as a mixed thirdorder derivative of the energy with respect to an electric field, twice, and to an atomic displacement under the condition of zero electric field

$$\left. \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\lambda}} \right|_{\mathcal{E}=0} = -\frac{6}{\Omega_0} \mathcal{F}^{\tau_{\kappa\lambda} \mathcal{E}_i \mathcal{E}_j}.$$
(3.25)

In case of longitudinal optical phonons with wave vector $\mathbf{q} \to 0$ in a polar crystal, Eq. (3.24) must take into account the effect of the macroscopic electric field generated by the lattice polar vibration. This field enters the computation of the Raman susceptibilities at two levels. On one hand, it gives rise to the non-analytical part of the matrix of interatomic force constants Eq. (3.19) that modifies the frequencies and eigenvectors with respect to pure transverse phonons. On the other hand, the electric field induces an additional change in the dielectric susceptibility tensor related to the nonlinear optical coefficients $\chi_{ijk}^{(2)}$. For longitudinal optical phonons, Eq. (3.25) has to be modified as follows [128]:

$$\frac{\partial \chi_{ij}}{\partial \tau_{\kappa\lambda}} = \left. \frac{\partial \chi_{ij}}{\partial \tau_{\kappa\lambda}} \right|_{\mathcal{E}=0} - \frac{8\pi}{\Omega_0} \frac{\sum_l Z_{\kappa\lambda l}^* q_l}{\sum_{l,l'} q_l \varepsilon_{ll'} q_{l'}} \sum_l \chi_{ijl}^{(2)} q_l.$$
(3.26)

The mixed third-order derivatives (3.25) can be computed from various techniques including finite differences of the dielectric tensor [129–131] or the second derivative of the electronic density matrix [132,133]. Here, we follow an approach similar to Deinzer and Strauch [60] based on the 2n + 1 theorem. The third-order energy derivatives can be computed as the sum over the 6 permutations Eq. (3.2) of $\tau_{\kappa\lambda}$, \mathcal{E}_i and \mathcal{E}_j . According to the discussion of Sec. 3.2.2, we have to distinguish between the terms that involve the discretization of the polarization such as $\tilde{\mathcal{F}}^{\tau_{\kappa\lambda}\mathcal{E}_i\mathcal{E}_j}$ or $\tilde{\mathcal{F}}^{\mathcal{E}_j\mathcal{E}_i\tau_{\kappa\lambda}}$ and those that can be computed from a straightforward application of the 2n + 1 theorem such as $\tilde{\mathcal{F}}^{\mathcal{E}_i\tau_{\kappa\lambda}\mathcal{E}_j}$. The former ones show an electric field as second perturbation. They can be computed from an expression analogous to Eq. (3.18):

$$\widetilde{\mathcal{F}}^{\tau_{\kappa\lambda}\mathcal{E}_{i}\mathcal{E}_{j}} = \frac{-e}{M_{k}} \Im \sum_{\mathbf{k}} \sum_{\mathbf{b}} w_{\mathbf{b}}(\mathbf{b} \cdot \mathbf{G}_{i}) \left[2 \sum_{n,m}^{occ} \langle u_{n\mathbf{k}}^{\tau_{\kappa\lambda}} | u_{m\mathbf{k}+\mathbf{b}}^{\mathcal{E}_{j}} \rangle Q_{mn}(\mathbf{k}, \mathbf{k}+\mathbf{b}) - \sum_{n,m,l,l'}^{occ} S_{mn}^{\tau_{\kappa\lambda}}(\mathbf{k}, \mathbf{k}+\mathbf{b}) Q_{nl}(\mathbf{k}, \mathbf{k}+\mathbf{b}) S_{ll'}^{\mathcal{E}_{j}}(\mathbf{k}, \mathbf{k}+\mathbf{b}) Q_{l'm}(\mathbf{k}, \mathbf{k}+\mathbf{b}) \right] \\
+ \frac{2}{M_{k}} \sum_{\mathbf{k}} \sum_{n,m}^{occ} \left[\delta_{m,n} \langle u_{n\mathbf{k}}^{\tau_{\kappa\lambda}} | v_{hxc}^{\mathcal{E}_{i}} | u_{m\mathbf{k}}^{\mathcal{E}_{j}} \rangle - \langle u_{m\mathbf{k}}^{(0)} | v_{hxc}^{\mathcal{E}_{i}} | u_{n\mathbf{k}}^{(0)} \rangle \langle u_{n\mathbf{k}}^{\tau_{\kappa\lambda}} | u_{m\mathbf{k}}^{\mathcal{E}_{j}} \rangle \right] \\
+ \frac{1}{6} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \frac{\delta^{3} E_{xc} [n^{0}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n^{\tau_{\kappa\lambda}}(\mathbf{r}) n^{\mathcal{E}_{i}}(\mathbf{r}') n^{\mathcal{E}_{j}}(\mathbf{r}''). \quad (3.27)$$

We obtain a similar expression for $\tilde{\mathcal{F}}^{\mathcal{E}_{j}\mathcal{E}_{i}\tau_{\kappa\lambda}}$. The remaining terms do not require any differentiation with respect to **k**. They can be computed from the first-order change of the ionic (pseudo-) potential with respect to an atomic displacement $v_{ext}^{\tau_{\kappa\lambda}}$

$$\widetilde{\mathcal{F}}^{\mathcal{E}_{i\tau_{\kappa\lambda}}\mathcal{E}_{j}} = \frac{2}{M_{k}} \sum_{\mathbf{k}} \sum_{n,m}^{occ} \left[\langle u_{n\mathbf{k}}^{\mathcal{E}_{i}} | v_{ext}^{\tau_{\kappa\lambda}} + v_{hxc}^{\tau_{\kappa\lambda}} | u_{m\mathbf{k}}^{\mathcal{E}_{j}} \rangle \delta_{n,m} - \langle u_{n\mathbf{k}}^{(0)} | v_{ext}^{\tau_{\kappa\lambda}} + v_{hxc}^{\tau_{\kappa\lambda}} | u_{m\mathbf{k}}^{(0)} \rangle \langle u_{m\mathbf{k}}^{\mathcal{E}_{i}} | u_{n\mathbf{k}}^{\mathcal{E}_{j}} \rangle \right] \\
+ \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \, \frac{d}{d\tau_{\kappa\lambda}} \frac{\delta^{2} E_{Hxc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Big|_{n^{(0)}} n^{\mathcal{E}_{i}}(\mathbf{r}) n^{\mathcal{E}_{j}}(\mathbf{r}') \\
+ \frac{1}{6} \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \frac{\delta^{3} E_{xc}[n^{0}]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}') \delta n(\mathbf{r}')} n^{\tau_{\kappa\lambda}}(\mathbf{r}) n^{\mathcal{E}_{j}}(\mathbf{r}'). \quad (3.28)$$

In pseudopotential calculations, the computation of the first-order ionic potential $v_{ext}^{\tau_{\kappa\lambda}}$ requires the derivative of local and non-local (usually separable) operators. These operations can be performed easily without any additional workload as described in Ref. [37].

In spite of the similarities between Eqs. (3.27) and (3.28) and the expression proposed by Deinzer and Strauch we can quote few differences. First, our expression of the third-order energy derivatives makes use of the PEAD fomulation for the expansion of the polarization. Moreover, Eq. (3.28) is more general since it allows the use of pseudopotentials with nonlinear core correction through the derivative of the second-order exchange-correlation energy with respect to $\tau_{\kappa\lambda}$ (third term).

3.3.3 Sum rule

As in the cases of the Born effective charges and of the dynamical matrix [134], the coefficients $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$ must vanish when they are summed over all atoms in the unit cell.

$$\sum_{\kappa} \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\alpha}} = 0.$$
(3.29)

Physically, this sum rule guarantees that the macroscopic dielectric susceptibility remains invariant under a rigid translation of the crystal. In practical calculations, it is not always satisfied although the violation is generally less severe than in case of \tilde{C} or Z^* . Even in calculations that present a low degree of convergence, the deviations from this law can be quite weak. They can be corrected using similar techniques as in case of the Born effective charges [38]. For example, we can define the mean excess of $\partial \chi_{ii}^{(1)} / \partial \tau_{\kappa\alpha}$ per atom

$$\overline{\frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\alpha}}} = \frac{1}{N_{at}} \sum_{\kappa} \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\alpha}}$$
(3.30)

and redistribute it equally between the atoms

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\alpha}} \to \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\alpha}} - \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\alpha}}.$$
(3.31)

3.3.4 Electro-optic tensor

The optical properties of a compound usually depend on external parameters such as the temperature, electric fields or mechanical constraints (stress, strain). In the present section we consider the variations of the refractive index induced by a static or low-frequency electric field \mathcal{E}_{γ} . At linear order, these variations are described by the linear EO coefficients (Pockels effect)

$$\Delta \left(\varepsilon^{-1}\right)_{ij} = \sum_{\gamma=1}^{3} r_{ij\gamma} \mathcal{E}_{\gamma}, \qquad (3.32)$$

where $(\varepsilon^{-1})_{ij}$ is the inverse of the electronic dielectric tensor and $r_{ij\gamma}$ the EO tensor.

As discussed in Sec. 1.3.4, within the Born and Oppenheimer approximation, the EO tensor can be expressed as the sum of three contributions: a bare electronic part $r_{ij\gamma}^{el}$, an ionic contribution $r_{ij\gamma}^{ion}$ and a piezoelectric contribution $r_{ij\gamma}^{piezo}$.

The electronic part is due to an interaction of \mathcal{E}_{γ} with the valence electrons when considering the ions artificially as clamped at their equilibrium positions. It can be computed from the nonlinear optical coefficients. As can be seen from Eq. (3.15), $\chi_{ijl}^{(2)}$ defines the second-order change of the induced polarization with respect to \mathcal{E}_{γ} . Taking the derivative of Eq. (3.15), we also see that $\chi_{ijl}^{(2)}$ defines the first-order change of the linear dielectric susceptibility, which is equal to $\frac{1}{4\pi}\Delta\varepsilon_{ij}$. Since the EO tensor depends on $\Delta(\varepsilon^{-1})_{ij}$ rather than $\Delta\varepsilon_{ij}$, we have to transform $\Delta\varepsilon_{ij}$ to $\Delta(\varepsilon^{-1})_{ij}$ by the inverse of the zero field electronic dielectric tensor [77]

$$\Delta(\varepsilon^{-1})_{ij} = -\sum_{m,n=1}^{3} \varepsilon_{im}^{-1} \Delta \varepsilon_{mn} \varepsilon_{nj}^{-1}.$$
(3.33)

Using Eq. (3.33) we obtain the following expression for the electronic EO tensor

$$r_{ij\gamma}^{el} = -8\pi \sum_{l,l'=1}^{3} (\varepsilon^{-1})_{il} \chi_{ll'k}^{(2)} (\varepsilon^{-1})_{l'j} \Big|_{k=\gamma}.$$
(3.34)

Eq. (3.34) takes a simpler form when expressed in the principal axes of the crystal under investigation $^{\rm 1}$

$$r_{ij\gamma}^{el} = \frac{-8\pi}{n_i^2 n_j^2} \chi_{ijk}^{(2)} \bigg|_{k=\gamma}, \qquad (3.35)$$

 $^{^{1}}$ In some cases, the electric field can induce a rotation of the principal axes. Eq. (3.35) is expressed in the principal axes of the crystal under zero electric field.

where the n_i coefficients are the principal refractive indices.

The origin of the ionic contribution to the EO tensor is the relaxation of the atomic positions due to the applied electric field \mathcal{E}_{γ} and the variations of ε_{ij} induced by these displacements. It can be computed from the Born effective charges $Z^*_{\kappa,\alpha\beta}$ and the $\frac{\partial \chi_{ij}}{\partial \tau_{\kappa\alpha}}$ coefficients introduced in Sec. 3.3.2. As shown in appendix B [see also Refs. [128,135]], the ionic EO tensor can be computed as a sum over the transverse optic phonon modes at q = 0

$$r_{ij\gamma}^{ion} = -\frac{4\pi}{\sqrt{\Omega_0}n_i^2 n_j^2} \sum_m \frac{\alpha_{ij}^m p_{m\gamma}}{\omega_m^2},\tag{3.36}$$

where α^m is the Raman susceptibility of mode m [Eq. (3.24)] and $p_{m\gamma}$ the mode polarity

$$p_{m\gamma} = \sum_{\kappa,\beta} Z^*_{\kappa,\gamma\beta} U_m(\kappa\beta)$$
(3.37)

which is directly linked to the mode oscillator strength

$$S_{m,\alpha\beta} = p_{m\alpha} \cdot p_{m\beta}. \tag{3.38}$$

For simplicity, we have expressed Eq. (3.36) in the principal axes while a more general expression can be derived from Eq. (3.33).

Finally, the piezoelectric contribution is due to a relaxation of the unit cell shape due to the converse piezoelectric effect [87]. As it is discussed in appendix B, it can be computed from the elasto-optic coefficients $\pi_{ij\mu\nu}$ and the piezoelectric strain coefficients $d_{\gamma\mu\nu}$:

$$r_{ij\gamma}^{piezo} = \sum_{\mu,\nu=1}^{3} \pi_{ij\mu\nu} d_{\gamma\mu\nu}.$$
 (3.39)

In the discussion of the EO effect, we have to specify whether we are dealing with strain-free (clamped) or stress-free (unclamped) mechanical boundary conditions. The clamped EO tensor $r_{ij\gamma}^{\eta}$ takes into account the electronic and ionic contributions but neglects any modification of the unit cell shape due to the converse piezoelectric effect [87]:

$$r_{ij\gamma}^{\eta} = r_{ij\gamma}^{el} + r_{ij\gamma}^{ion}. \tag{3.40}$$

Experimentally, it can be measured for frequencies of \mathcal{E}_{γ} high enough to eliminate the relaxations of the crystal lattice but low enough to avoid excitations of optical phonon modes (usually above ~ 100 MHz). To compute the unclamped EO tensor $r_{ij\gamma}^{\sigma}$, we have to add the piezoelectric contribution to $r_{ij\gamma}^{\eta}$:

$$r_{ij\gamma}^{\sigma} = r_{ij\gamma}^{\eta} + r_{ij\gamma}^{piezo}.$$
(3.41)

Experimentally, $r_{ij\gamma}^{\sigma}$ can be measured for frequencies of \mathcal{E}_{γ} below the (geometry dependent) mechanical body resonances of the sample [87] (usually below ~ 1 MHz).

3.4 Finite electric field techniques

The 2n + 1 theorem is not the only formalism to study the nonlinear response of insulators to electric fields. An alternative approach consists in the direct minimization of the energy functional, \mathcal{F} , defined in Eq. (1.39) for a finite electric field \mathcal{E} [15, 16, 136, 137]. Different schemes to perform these calculations have been proposed in the literature [15, 16, 138]. Here, we describe the method of Ref. [15] that has been implemented in the ABINIT code.

As explained in Sec. 1.4.5, because of the interband (Zener) tunneling, an insulator in an electric field has no true ground-state. In practical calculations, the problem of the tunneling current can partially be overcome by the use of a finite grid of **k**-points. In most calculations, a discrete mesh of **k**-points is introduced for computational reasons, to integrate quantities such as the energy or the charge density. In the presence of a finite electric field however, the use of a finite **k**-point grid plays the additional role to eliminate the possibility of runaway solutions, allowing for stable stationary solutions of Eq. (1.39) to exist.

To illustrate how the discretization procedure endows the energy functional with minima, we consider in Figure 3.1 a one dimensional system with periodic boundary conditions over a supercell of size L. Since the number of **k**-points, M, is equal to the number of unit cells in the supercell we have L = Ma where a is the lattice constant. This system is can be visualized as a ring of perimeter L [139]. For a given number of **k**-points, the energy functional will have minima only if \mathcal{E} is small enough to avoid Zener tunneling. This should happen as long as the distance across which the electrons have to tunnel to lower their energy is larger than the ring perimeter L. According to Figure 1.8, the potential energy drop across the supercell, $\Delta E = e\mathcal{E}L$, must be smaller than the band gap, E_g , of the system. In other words, the electric field must be smaller than the critical field

$$\mathcal{E}_c = \frac{E_g}{eMa}.\tag{3.42}$$

Eq. (3.42) shows that \mathcal{E}_c decreases as the number of **k**-points increases. This behavior can impose some limitations on practical calculations. One the one hand, we usually need a large number of **k**-points to obtain well-converged results. On the other hand, for large M, the critical field can be quite low (depending on the band gap of the system) and we are limited to study the effect of relatively weak fields.

For electric fields smaller than \mathcal{E}_c , the minimization of the energy functional, \mathcal{F} , can be performed using standard techniques such as a preconditioned conjugate-gradient algorithm [15,88]. At the minimum Eq. (1.39) yields the energy and polarization of an insulator in an electric field. In addition, since the field-polarized Bloch functions are stationary points of Eq. (1.39), we can use the Hellmann-Feynman argument [88] to compute forces and stresses at $\mathcal{E} \neq 0$. The force on an atom κ along direction α can be computed as the sum of the standard Hellmann-Feynman expression at zero electric field plus a contribution due to the ionic cores

$$f_{\kappa\alpha} = -\frac{\partial \mathcal{F}}{\partial \tau_{\kappa\alpha}} = -\frac{\partial E}{\partial \tau_{\kappa\alpha}} + Z_{\kappa} \mathcal{E}_{\alpha}, \qquad (3.43)$$

Figure 3.1: A one dimensional system with periodic boundary conditions over M unit cells can be visualized as a ring with perimeter L = Ma where a is the lattice constant.



where Z_{κ} is the ionic charge of the nucleus and the core electrons.

0

In case of the stress tensor

$$\tau_{\mu\nu} = \frac{1}{\Omega_0} \frac{\partial \mathcal{F}}{\partial \eta_{\mu\nu}},\tag{3.44}$$

we have to specify the electrical boundary conditions under which the strain derivatives of \mathcal{F} are computed. Let us first use Eq. (1.28) to rewrite the field coupling term in Eq. (1.39) in terms of the electronic and ionic Berry phases

$$\Omega_{0} \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{P}} = \frac{\Omega_{0}}{2\pi} \sum_{i=1}^{3} (\boldsymbol{\mathcal{E}} \cdot \mathbf{a}_{i}) (\boldsymbol{\mathcal{P}} \cdot \mathbf{G}_{i})$$
$$= \frac{e}{2\pi} \sum_{i=1}^{3} (\boldsymbol{\mathcal{E}} \cdot \mathbf{a}_{i}) (\varphi_{el}^{(i)} + \varphi_{ion}^{(i)}) \qquad (3.45)$$

When a crystal is deformed by a homogeneous strain, η ,

$$\mathbf{a}_i \longrightarrow (\mathbf{1} + \boldsymbol{\eta}) \mathbf{a}_i$$
 (3.46)

we can keep constant either the electric field, \mathcal{E} , or the potential drop across each lattice vector, $V_i = -\mathcal{E} \cdot \mathbf{a}_i$. If we keep constant the potential drop², the strain derivatives of the electric field coupling term Eq. (3.45) vanish because φ_{el} and φ_{ion} do not explicitly depend on $\boldsymbol{\eta}$. The stress tensor at constant potential can therefore be computed as the strain derivative of the zero field Kohn-Sham energy

$$\sigma_{\mu\nu}^{(V)} = \frac{1}{\Omega_0} \frac{\partial E}{\partial \eta_{\mu\nu}}.$$
(3.47)

 $^{^{2}}$ This situation is often met in practical experiments where a voltage is applied across a sample between conducting electrodes.

In contrast, if we keep constant the electric field, the derivatives of the field coupling term no more vanish. The stresses in the two cases are related by

$$\sigma_{\mu\nu}^{(\mathcal{E})} = \sigma_{\mu\nu}^{(V)} - \frac{e}{2\pi} \sum_{i=1}^{3} \mathcal{E}_{\mu}[\mathbf{a}_{i}]_{\nu}(\varphi_{el}^{(i)} + \varphi_{ion}^{(i)}).$$
(3.48)

The formalism presented in this section offers an alternative approach to compute the nonlinear response of insulators to electric fields. In fact, all quantities discussed in Sec. 3.3 can be computed from finite differences of the energy, the polarization or the forces with respect to electric fields as will be illustrated in the following Chapter. Compared to the perturbative approach of Secs. 3.2 and 3.3, the finite electric field technique has the advantage to be very general and to be easily applicable to the computation of physical quantities other than those of Sec. 3.3 such as the tunability of the dielectric constant [140] or higher-order nonlinear optical responses. Moreover, this technique allows to use the functionals for the exchange-correlation energy that are already available for zero-field ground-state calculations. In contrast, in order to apply the perturbative approach of Secs. 3.2 and 3.3, all physical quantities and expressions for the exchange-correlation energy must be implemented explicitly. However, when the additional coding is terminated, the perturbative approach offers a more systematic and elegant way to compute nonlinear response functions than the finite electric field technique. Moreover, in the perturbative approach, there are no problems related to critical fields as it is the case of the finite electric field technique.

3.5 Conclusions

In this Chapter, we presented two methodologies to study the nonlinear response of insulators to electric fields. The first technique is based on density functional perturbation theory and the second technique is based on finite electric fields.

Starting from the work of Nunes and Gonze, we reported the LDA expressions of the nonlinear optical susceptibilities and the derivatives of the linear optical susceptibilities with respect to atomic displacements as we have implemented them in the ABINIT code. We then showed how these quantities can be used to compute the Raman scattering efficiencies of transverse and longitudinal optical phonons and the clamped and unclamped EO coefficients. We finally discussed how the finite electric field technique of Souza and co-workers can be applied to compute the energy of a solid in an electric field as well as the forces on the atoms and the stress tensor under distinct electrical boundary conditions.

In Chapter 4, the present formalism will be applied to selected ferroelectrics and semiconductors.

3.6 References

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

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Chapter 4

Nonlinear response of insulators to electric fields: results

4.1 Introduction

Ferroelectric oxides are well known to exhibit unusual linear and nonlinear response properties and are currently used in many devices. In order to find better materials for such applications, it is important to understand the physical mechanisms that are at the origin of these properties and to clarify the role of the soft mode in the electromechanical coupling of these materials. Unfortunately, the experimental characterization of ferroelectrics is not always easy. In addition, experiments give no direct information about the mechanisms responsible for the observed results. For example, the measurements of nonlinear optical properties require high-quality single crystals that are not always accessible nor easy to make. Moreover, the determination of phonon frequencies from Raman spectroscopy can be quite difficult as it is the case of the E-modes in LiNbO₃.

For such reasons, accurate theoretical calculations of Raman scattering efficiencies and EO coefficients are highly desirable. On the one hand, these calculations can be used to predict the amplitude of the EO coefficients in situations where no experimental data are available. On the other hand, the microscopic quantities computed from firstprinciples help to identify the mechanisms responsible for the observed properties and to assign the peaks on an experimental Raman spectrum to specific phonon modes.

In this Chapter, we apply the formalism of Chapter 3 to selected ferroelectrics in order to (i) identify the mechanisms responsible for their large EO responses and (ii) to clarify the assignation of the *E*-modes in LiNbO_3 . The theoretical study of the Raman spectrum of ferroelectrics has the additional benefit that it will help us to understand

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the ionic contribution to the EO coefficients in these materials.

To start, we illustrate in Sec. 4.3 the formalism of the preceding Chapter by computing the nonlinear optical susceptibilities, Raman polarizabilities and EO coefficients of selected semiconductors. In particular, we compare the convergence of different expressions to compute third-order energy derivatives with respect to the number of **k**points and we discuss the effect of the approximations used for the exchange-correlation energy.

In Sec. 4.4, we discuss some of the basic ingredients required to study the Raman spectra and EO coefficients in $BaTiO_3$, $PbTiO_3$ and $LiNbO_3$. We report the nonlinear optical susceptibilities and the derivatives of the linear optical susceptibilities with respect to atomic displacements. As in case of the semiconductors, we compare the results obtained from the 2n+1 theorem to the results obtained from the finite electric field technique.

In Sec. 4.5, we discuss the Raman spectra of $PbTiO_3$ and $LiNbO_3$. We find that the theoretical Raman spectra are sufficiently accurate to be compared to the experiment and that they can be helpful to interpret experimental Raman spectra. In particular, we are able to clarify some of the ambiguities in the assignation of the phonon modes in $LiNbO_3$.

Finally, in Sec. 4.6, we study the EO tensor of the three ferroelectric oxides $LiNbO_3$, BaTiO₃ and PbTiO₃. We find that first-principles calculations are fully predictive and provide significant new insights into the microscopic origin of the EO effect in these materials. In particular, we highlight the predominant role of the soft mode in the EO coupling in $LiNbO_3$ and $BaTiO_3$, in contrast with its minor role in PbTiO₃.

4.2 Technical details

All results presented in this Chapter have been obtained with the ABINIT package [64].

The convergence study on AlAs in Sec. 4.3.1 (Figure 4.2) has been performed at the theoretical lattice constant. We used the LDA for the exchange-correlation energy, Troullier-Martins pseudopotentials [141] and a plane wave kinetic energy cutoff of 10 hartree.

For all other calculations on semiconductors, presented in Sec. 4.3 we used either the LDA or the GGA for the exchange-correlation energy. In case of the LDA, we chose the parameterization of Perdew and Wang [142] and in case of the GGA, we chose the parameterization of Perdew, Burke, Ernzerhof [143]. In order to isolate the effect of these approximations on the nonlinear optical properties from other effects, such as the dependence of these properties on the lattice constants or the parameters of the pseudopotentials, we worked at the experimental lattice constants. Moreover, we used the fhi98PP code [144] to build norm-conserving pseudopotentials. For each atom, the same parameters (cutoff radius, nonlinear exchange-correlation core-correction, ...) were used to build the LDA and GGA pseudopotentials. These calculations have been performed using a $16 \times 16 \times 16$ grid of special **k**-points and a plane-wave kinetic energy cutoff of 20 hartree. For BaTiO₃ and PbTiO₃, we used extended norm-conserving pseudopotentials [108], a plane-wave kinetic energy cutoff of 45 hartree and a 10 × 10 × 10 **k**-point grid. The theoretical atomic positions relaxed at the experimental lattice constants have been reported in Sec. 1.2. For LiNbO₃, we used the same norm-conserving pseudopotentials as in Ref. [69] as well as the Born effective charges, phonon frequencies and eigenvectors already reported in that paper. For this compound, a $8 \times 8 \times 8$ **k**-point grid and a plane wave kinetic energy cutoff of 35 hartree give converged values for $\chi_{ijl}^{(2)}$ and $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$. The theoretical lattice constants and atomic positions have been reported in Sec. 1.2.

4.3 Nonlinear response of semiconductors to electric fields

In order to illustrate the computation of third-order energy derivatives described in Chapter 3, we performed a series of calculations on various cubic AB semiconductors where A denotes the cation (f. ex. Al) and B the anion (f. ex. As). The aim of these calculations is to compare the results obtained from the 2n + 1 theorem to the results obtained from the finite electric field technique and to study the effect of the exchange-correlation functional on the nonlinear optical properties. We first discuss the computation of nonlinear optical susceptibilities. In particular, we compare the finite electric field technique to the convergence of the FEAD and DAPE formulations to the convergence of the finite electric field technique. We then discuss the computation of Raman polarizabilities and EO coefficients.

4.3.1 Nonlinear optical susceptibilities

In cubic semiconductors, the second-order nonlinear optical susceptibility tensor (Voigt notations) has a very simple form

$$\boldsymbol{d} = \begin{pmatrix} \cdot & \cdot & \cdot & d_{36} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & d_{36} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & d_{36} \end{pmatrix}.$$
(4.1)

It has only one independent element¹, $d_{36} (= \frac{1}{2}\chi_{36}^{(2)} = \frac{1}{2}\chi_{321}^{(2)})$. The computation of this element from the 2n+1 theorem has been described in Sec. 3.3.1. In order to compute d_{36} from finite electric fields, we have to apply an electric field along two (or more) distinct Cartesian directions and to study the nonlinear evolution of the polarization, \mathcal{P} , along the third direction. This is illustrated in Figure 4.1 for an LDA calculation on AlAs. The electric field is chosen along the (1,1,1) direction with an amplitude, \mathcal{E} , defined as

$$\boldsymbol{\mathcal{E}} = \mathcal{E}(1, 1, 1). \tag{4.2}$$

¹The elements of the nonlinear optical susceptibility tensor in these compounds can also be defined as $d_{ijl} = d_{36} |\epsilon_{ijl}|$, where ϵ_{ijl} are the elements of the Levy-Civita tensor.

The polarization can be decomposed into

$$\mathcal{P}_i(\mathcal{E}) = \mathcal{P}_i^L(\mathcal{E}) + \mathcal{P}_i^{NL}(\mathcal{E}) \qquad i = 1, 2, 3$$
(4.3)

where \mathcal{P}_i^L and \mathcal{P}_i^{NL} are respectively the linear and nonlinear components of \mathcal{P}_i

$$\mathcal{P}_i^L(\mathcal{E}) = \mathcal{P}_i^s + \chi^{(1)}\mathcal{E} \tag{4.4}$$

$$\mathcal{P}_i^{NL}(\mathcal{E}) = 4d_{36}\mathcal{E}^2 + \mathcal{O}(\mathcal{E}^3).$$
(4.5)

The parameters \mathcal{P}_i^s , $\chi^{(1)}$ and d_{36} have been determined by fitting the first-principles data with Eq. (4.3). The second term of the right-hand side of Eq. (4.5) is related to higher-order effects. It will not be discussed here ² although it was included in the fit. Figure 4.1 shows the dependence of \mathcal{P}_1^{NL} on \mathcal{E} . The points are the first-principles data from which we have subtracted the linear part, \mathcal{P}_1^L , and the line corresponds to Eq. (4.5). The inset of Figure 4.1 shows the values of the total polarization for various electric fields (points) and the fit of Eq. (4.3) (line) to the first-principles data. For a given field, the nonlinear polarization is about two orders of magnitude smaller than the total polarization. On the one hand, this result shows that the dependence of \mathcal{P} on \mathcal{E} is dominated by linear effects. On the other hand, we need to compute the polarization with a high accuracy of $|\Delta \mathcal{P}/\mathcal{P}| < 10^{-3}$ if we want to compute nonlinear optical susceptibilities. This requires a high degree of convergence of the wave functions obtained from the minimization of Eq. (1.39). The value of d_{36} computed from the curvature of \mathcal{P}_1^{NL} at the origin is 38 pm/V, in excellent agreement with the value computed from the 2n + 1 theorem (see Table 4.1).

The formalism of the 2n + 1 theorem presented in Sec. 3.2.2 involves an integration over the Brillouin zone and a derivative with respect to **k**. In practical calculations, these operations must be performed on a discrete mesh of special **k**-points. As explained in Sec. 3.2.2, the discretization can either be performed before (PEAD) or after (DAPE) the perturbation expansion of the energy functional Eq. (1.39). Up until now, the applications of the present formalism to real materials [56,60] made use of the DAPE formula of the third-order energy. The only application of the PEAD formula has been reported by Nunes and Gonze [115] on a one-dimensional model system. These authors observed that the PEAD formula converges better with respect to the **k**-point sampling than the DAPE formula. In order to compare the performance of these two approaches for a realistic case, we applied both of them to compute the nonlinear optical susceptibility, d₃₆, of AlAs. We performed a series of calculations on a $n \times n \times n$ grid of special **k**-points. In addition, we used the finite electric field technique (FEF) to compute the nonlinear optical susceptibility for these grids. As

$$\mathcal{P}_1^{NL} = \sum_{j,l=1}^3 \chi_{1jl}^{(2)} \mathcal{E}_j \mathcal{E}_l = 2 \sum_{j,l=1}^3 d_{1jl} \mathcal{E}_j \mathcal{E}_l = 2(d_{123} \mathcal{E}_2 \mathcal{E}_3 + d_{132} \mathcal{E}_3 \mathcal{E}_2) = 4d_{36} \mathcal{E}^2.$$

²The factor of 4 in the first term of the right-hand side of Eq. (4.5) can be obtained from the third term of the right-hand side of Eq. (3.15) and Eq. (3.16). For example, in case of \mathcal{P}_1^{NL} we obtain:

Figure 4.1: Dependence of the nonlinear polarization of AlAs on an electric field along the (1,1,1) direction. The amplitude of the electric field, \mathcal{E} , used as abscissa is defined in Eq. (4.2). The inset shows the dependence of the total polarization on \mathcal{E} .



Figure 4.2: Nonlinear optical susceptibility d_{36} of AlAs computed for various grids of $n \times n \times n$ special **k**-points. The values have been computed using the 2n + 1 theorem (PEAD and DAPE expressions) and the finite electric field technique (FEF).



			LDA			GGA	
Method	LC	AlAs	AlP	GaP	AlAs	AlP	GaP
PEAD (present)	Ε	38	22	64			
FEF (present)	\mathbf{E}	38	22	65	36	20	57
SOS [122]	\mathbf{E}	39	24	59			
PEAD (present)	Т	35	20	48			
DAPE $[56]$	Т	32	19	41			
$\operatorname{FEF}[15]$	Т	32	19	33			
SOS [122]	Т	34	21	33			
PEAD + SCI (present)	Е	24	13	38			
SOS + SCI [122]	\mathbf{E}	24	15	35			
Exp. [145]				37			
Exp. $[146]$				41			

Table 4.1: Nonlinear optical susceptibilities d_{36} (pm/V) of the semiconductors AlAs, AlP and GaP computed at the theoretical (T) and experimental (E) lattice constants (LC). The values in the lines labeled "PEAD + SCI" and "SOS + SCI" have been obtained using a scissors correction.

can be seen in Figure 4.2 the three approaches give the same value of d_{36} for large n for large n^3 . However, the PEAD formula converges faster than the DAPE formula or the FEF approach. For this reason, the PEAD formula has been applied to obtain the results presented in the following sections. It is the one that is actually available in the ABINIT code.

In Table 4.1, we report the nonlinear optical susceptibilities of AlAs, AlP and GaP computed at the experimental and theoretical lattice constants (LC) using either the PEAD expression or the FEF technique. In case of the FEF calculations, we used either the LDA or the GGA for the exchange-correlation energy. Our results are compared to the results of Dal Corso and co-workers [56] who used the 2n + 1 theorem within the DAPE formalism, the results of Souza and co-workers [15] who used a FEF technique, the results of Levine and Allan [122] who used a "sum over excited states" (SOS) technique and to the experiment. The values in the lines labeled "PEAD + SCI" and "SOS + SCI" have been obtained using a scissors correction [147].

The values computed from the PEAD expression are in good agreement with the values obtained from the FEF technique and the values of Levine and Allan. The

³The crossing between the values obtained from the PEAD expression and the values obtained from the finite electric field technique and the small difference at large n can be related to the distinct finite difference expressions used in connection with the two techniques. In case of the finite electric field technique, we use strings of k-points whereas in case of the 2n + 1 theorem (PEAD and DAPE expressions) we use the finite difference formula of Marzari and Vanderbilt Eq. (3.7). Nevertheless, this difference is small compared to the errors introduced by the LDA or the pseudopotentials and will not be discussed here.

differences between the results reported in the top of Table 4.1 and the results of Refs. [15, 56] can be related to the fact that the former ones have been obtained at the experimental lattice constants whereas the latter ones have been obtained at the theoretical lattice constants. Using the theoretical lattice constants, we obtain values of 35, 20 and 48 pm/V for the nonlinear optical susceptibilities of AlAs, AlP and GaP in better agreement with the values obtained in Refs. [15, 56].

The nonlinear optical susceptibilities computed within the GGA are smaller than those computed within the LDA. The scissors correction decreases the values of the d_{36} even further, in agreement with the discussion of Ref. [147]⁴. To the authors' knowledge, no experimental data are available for AlAs and AlP. In case of GaP, the values computed within the LDA at the theoretical lattice constant and the values computed at the experimental lattice constant making use of a scissors correction are close to the experiment. However, it is not clear that the use of a scissors correction always improves the agreement with the experiment. Moreover, it will even have a negative effect in case the LDA (or the GGA) underestimates the experimental nonlinear optical susceptibilities. In addition, it is not straightforward to isolate the error of the LDA (or GGA) from other sources of errors. Other factors can have a similar strong influence on the nonlinear optical susceptibilities. As discusses above, the d_{ij} are strongly affected by the error on the lattice constants of the crystals. Another important source of error can be the pseudopotentials used in the calculations as discussed in Ref. [56].

4.3.2 Raman polarizabilities

In the cubic AB semiconductors, the derivatives of the linear optical susceptibilities with respect to atomic displacements are defined by a single number, $\partial \chi^{(1)} / \partial \tau$. Making use of the Levy-Civita tensor, ϵ_{ijk} , we can write for the cation (A)

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{A,\lambda}} = \frac{\partial \chi^{(1)}}{\partial \tau} |\epsilon_{ij\lambda}|$$
(4.6)

and for the anion (B)

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{B,\lambda}} = -\frac{\partial \chi^{(1)}}{\partial \tau} |\epsilon_{ij\lambda}|.$$
(4.7)

The quantities $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa,\lambda}$ can be computed from various techniques. A first technique based on the 2n + 1 theorem is described in Sec. 3.3.2. A second technique consists in computing the derivatives $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa,\lambda}$ from frozen-phonon (FP) calculations by taking

$$d_{SCI} \approx d_{LDA} \left(1 - \frac{\Delta}{E_g} \right)^3,$$

where E_g is the band gap and Δ the amplitude of the scissors correction.

⁴According to the discussion of Ref. [147], we expect the LDA value of the nonlinear optical susceptibility, d_{LDA} , to be related to the value obtained making use of the LDA and a scissors correction, d_{SCI} , by the relation

Figure 4.3: Dependence of the nonlinear component of the force on Al along x in AlAs on an electric field along the (1,1,1) direction. The amplitude of the electric field, \mathcal{E} , used as abscissa is defined in Eq. (4.2). The inset shows the dependence of the total force on \mathcal{E} .



Table 4.2: Absolute values of the Raman polarizabilities (Å²) of the transverse optical phonon modes of some semiconductors. Our results have been computed at the experimental lattice constants using the 2n+1 theorem (PEAD expression), the finite electric field (FEF) technique and frozen phonon (FP) calculations. The three experimental values for GaP have been obtained by distinct experimental techniques.

	LDA					GG	А	
Method	Si	AlAs	AlP	GaP	Si	AlAs	AlP	GaP
PEAD (present)	21.53	8.66	4.79	10.70				
FEF (present)	20.24	8.23	4.55	10.19	19.26	7.58	4.26	8.41
FP (present)	21.81	8.69	4.79	10.79	20.69	7.99	4.47	8.83
DAPE [60]	23.56	7.39	5.13	11.38				
FP [60]	20.44	5.64	4.44	9.48				
FP [129]	26.16							
Exp. $[148, 149]$	23 ± 4			19, 16, 23				

finite differences of $\chi_{ij}^{(1)}$ with respect to atomic displacements. Finally, we can use the finite electric field technique to compute the first-order derivatives $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa,\lambda}$ as a second-order derivative of the force on atom κ , $f_{\kappa,\lambda}$, with respect to the electric field

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa,\lambda}} = \frac{1}{\Omega_0} \frac{\partial^2 f_{\kappa,\lambda}}{\partial \mathcal{E}_i \partial \mathcal{E}_j}.$$
(4.8)

The third method is illustrated in Figure 4.3 in case of AlAs. The amplitude of the electric field, \mathcal{E} , is defined in Eq. (4.2). The force on the cation along a Cartesian direction, λ , can be expressed as

$$f_{A,\lambda} = Z_{A,\lambda\lambda}^* \mathcal{E} + \Omega_0 \frac{\partial \chi^{(1)}}{\partial \tau} \mathcal{E}^2$$
(4.9)

where $Z^*_{A,\lambda\lambda}$ is the Born effective charge of the cation.

The data computed from first-principles have been fitted with Eq. (4.9). The points in Figure 4.3 correspond to the force on Al along x computed for different amplitudes of the electric field from which we have subtracted the first term of the right-hand side of Eq. (4.9). The line corresponds to the dependence of $f_{Al,x}$ on the electric field computed through the second term of the right-hand side of Eq. (4.9). The inset shows the dependence of the total force on the electric field (points) and the fit of Eq. (4.9) to the first-principles data (line). As in case of the polarization illustrated in Figure 4.1, the nonlinear part of the force is about two orders of magnitude smaller than the linear part. As a consequence, we need a high degree of convergence of the electronic wave functions in order to obtain a precision of $|\Delta f/f| < 10^{-3}$ that is required to compute $\partial \chi^{(1)}/\partial \tau$ accurately.

In Table 4.2, we report the Raman polarizabilities of Si, AlAs, AlP and GaP defined as

$$a = \Omega_0 \frac{\partial \chi^{(1)}}{\partial \tau}.$$
(4.10)

All values are found to be negative and we only report their absolute values. The LDA values we obtained from the 2n + 1 theorem (PEAD expression), finite electric field (FEF) and frozen-phonon (FP) calculations are very similar. They are close to the theoretical values of Refs. [60, 129]. We should note however that the Raman polarizabilities computed in Ref. [60] from the 2n + 1 theorem (DAPE expression) are in worse agreement with the values computed from frozen-phonon calculations than in our case. The absolute values of the Raman polarizabilities computed within the GGA are significantly smaller than the corresponding LDA values. This behavior is similar to what we observed for the nonlinear optical susceptibilities in Sec. 4.3.1.

4.3.3 Clamped electro-optic coefficients

The nonlinear optical susceptibilities and Raman polarizabilities discussed in Secs. 4.3.2 and 4.3.1 are related to the nonlinear response of a compound to optical electric

Figure 4.4: Graphical illustration of the (a) 7- and (b) 4-point formulas used to compute the second-order mixed derivatives of the polarization.



fields as defined in Sec. 1.3. They have been computed from the nonlinear dependence of the polarization and the forces on the electric field. In these calculation, the atoms were held fixed at their zero-field equilibrium positions. As a consequence, the nonlinear optical susceptibilities and Raman polarizabilities are determined by pure electronic processes. In addition to the electronic contribution, the clamped EO coefficients are determined by an ionic contribution due to electric field induced atomic displacements. In case we use the formalism of the 2n + 1 theorem presented in Sec. 3.3.4, the ionic contribution can be computed from Eq. (3.36).

In order to compute the EO coefficients from the finite electric field technique, we have (i) to relax the atoms within the electric field and (ii) to compute the difference between the optical dielectric tensors of the zero-field equilibrium structure and the distorted structure at non-zero electric field. In this section, we illustrate this procedure for the cubic semiconductors AlAs, AlP and GaP. In Sec. 4.6, we apply it to the perovskite ferroelectrics $BaTiO_3$ and $PbTiO_3$.

The form of the EO tensor in cubic semiconductors is given by the transpose of their nonlinear optical susceptibility tensor in Eq. (4.1). It only has one independent element, r_{63} . The computation of this element is performed in two steps. First, we study the dependence of the polarization on an electric field that is the sum of a static field, \mathcal{E}^{st} , and an optical electric field, \mathcal{E}^{o} . In analogy with the discussion of Sec. 4.3.1, the curvature of \mathcal{P} gives the nonlinear EO susceptibility d^{EO} . Second, we apply a transformation similar to Eq. (3.35) to transform d^{EO} into the clamped EO coefficient r_{63}^{η}

$$r_{63}^{\eta} = -\frac{16\pi}{n^4} d^{EO}, \qquad (4.11)$$

where n is the refractive index of the compound.

The computation of d^{EO} is not straightforward. It has to be computed as a second-

order *mixed* derivative of the polarization with respect to \mathcal{E}^{st} and \mathcal{E}^{o} . By analogy with Eq. (4.2), we consider an electric field along the (1,1,1) direction that is the sum of \mathcal{E}^{st} and \mathcal{E}^{o} .

$$\boldsymbol{\mathcal{E}} = (\mathcal{E}^{st} + \mathcal{E}^o)(1, 1, 1). \tag{4.12}$$

The nonlinear EO susceptibility can than be computed as

$$d^{EO} = \frac{1}{8} \frac{\partial^2 \mathcal{P}_k}{\partial \mathcal{E}^{st} \partial \mathcal{E}^o} \qquad k = 1, 2, 3.$$
(4.13)

In the discussions that follow, we chose \mathcal{E}^{st} and \mathcal{E}^{o} equal to 0 or $\pm \mathcal{E}$. To compute the second-order mixed derivative of \mathcal{P} , we can either use a 7-point formula or a 4-point formula [150] as illustrated in Figure 4.4. The points labeled "(i, j)" represent a polarization

$$\mathcal{P}_k(i \cdot \mathcal{E}, j \cdot \mathcal{E}) = \mathcal{P}_k(\mathcal{E}^{st} = i \cdot \mathcal{E}, \mathcal{E}^o = j \cdot \mathcal{E}).$$
(4.14)

The expressions of d^{EO} obtained from the 7- and 4-point formulas are

$$d^{EO} = \frac{-1}{16\mathcal{E}^2} \Big(\mathcal{P}_k(\mathcal{E}, 0) + \mathcal{P}_k(-\mathcal{E}, 0) + \mathcal{P}_k(0, \mathcal{E}) + \mathcal{P}_k(0, -\mathcal{E}) - 2\mathcal{P}_k(0, 0) - \mathcal{P}_k(\mathcal{E}, \mathcal{E}) - \mathcal{P}_k(-\mathcal{E}, -\mathcal{E}) \Big)$$

$$(4.15)$$

$$d^{EO} = \frac{1}{32\mathcal{E}^2} \Big(\mathcal{P}_k(\mathcal{E}, \mathcal{E}) - \mathcal{P}_k(\mathcal{E}, -\mathcal{E}) - \mathcal{P}_k(-\mathcal{E}, \mathcal{E}) + \mathcal{P}_k(-\mathcal{E}, -\mathcal{E}) \Big).$$
(4.16)

In order to use Eqs. (4.15) and (4.16) we have to apply different combinations of static and optical fields to the compound. In practice, the change in polarization induced by an optical field is computed at clamped atomic positions while the change in polarization induced by a static field is computed by taking into account the electric field induced atomic displacements. In case both static and optical electric fields are applied to the solid, we must (i) relax the atoms for an electric field \mathcal{E}^1 equal to the static component of the field and (ii) compute the polarization for an electric field \mathcal{E}^2 equal to the sum of the static and optic components of the field while keeping constant the atomic positions at the values obtained in (i). For example, in order to compute $\mathcal{P}_k(\mathcal{E},\mathcal{E})$, we first relax the atoms for an electric field $\mathcal{E}^1 = \mathcal{E}(1,1,1)$. Then, we keep constant the atomic positions and we compute the polarization for an electric field $\mathcal{E}^2 = 2\mathcal{E}(1,1,1)$. The values of \mathcal{E}^1 and \mathcal{E}^2 required to compute the polarizations used in Eqs. (4.15) and (4.16) are summarized in Table 4.3.

The EO coefficients of AlAs, AlP and GaP computed from the 2n + 1 theorem and from the finite electric field (FEF) technique are summarized in Table 4.4. In case of the finite electric field calculations, the results obtained from the 4-point formula are close to the results obtained from the 7-point formula. For example, using Eqs. (4.15) and (4.16) to compute the clamped EO coefficient of AlAs we obtained respectively -1.118 and -1.130 pm/V. The LDA values of r_{63}^{η} computed from the 2n+1 theorem and from finite electric fields are very close. Moreover, they are close to the corresponding GGA values. This behavior is opposite to the behavior observed for the nonlinear

(i, j)	\mathcal{E}^1	${\cal E}^2$
(0,0)	0	0
(1, 0)	$\mathcal{E}(1,1,1)$	$\mathcal{E}(1,1,1)$
(-1, 0)	$-\mathcal{E}(1,1,1)$	$-\mathcal{E}(1,1,1)$
(0, 1)	0	$\mathcal{E}(1,1,1)$
(0, -1)	0	$-\mathcal{E}(1,1,1)$
(1, 1)	$\mathcal{E}(1,1,1)$	$2\mathcal{E}(1,1,1)$
(-1, 1)	$-\mathcal{E}(1,1,1)$	0
(1, -1)	$\mathcal{E}(1,1,1)$	0
(-1, -1)	$-\mathcal{E}(1,1,1)$	$-2\mathcal{E}(1,1,1)$

Table 4.3: Electric fields used to relax the atomic positions, \mathcal{E}^1 , and electric fields used to compute the polarization, \mathcal{E}^2 , for the values of *i* and *j* used in Figure 4.4.

Table 4.4: Clamped EO constant r_{63}^{η} (pm/V) of AlAs, AlP and GaP computed at the experimental lattice constant using the 2n + 1 theorem (PEAD expression) and the finite electric field (FEF) technique. The values obtained from the 2n + 1 theorem are split into the electronic and ionic contributions.

Method	XC	Contribution	AlAs	AlP	GaP
PEAD	LDA	$\operatorname{Electronic}$	-1.69	-1.25	-2.24
		Ionic	0.64	0.50	0.64
		Total	-1.05	-0.75	-1.60
\mathbf{FEF}	LDA	Total	-1.12	-0.81	-1.71
\mathbf{FEF}	GGA	Total	-1.15	-0.84	-1.71
Exp. [151]		Total			-0.97

optical susceptibilities and the Raman polarizabilities. In case of these two quantities, we found the absolute GGA values to be significantly smaller than the corresponding LDA values.

The EO coefficients computed from the 2n+1 theorem are split into their electronic and ionic contributions. It is interesting to observe that both contributions are of the same magnitude and that they are of opposite sign. As a consequence, they tend to decrease the values of the EO coefficients when we take their sum.

4.4 Nonlinear response of ferroelectrics to electric fields at clamped atomic positions

In the present section, we discuss the nonlinear optical susceptibilities, d_{ij} , the optical dielectric constants, ε_{ij} , and the derivatives of the linear optical susceptibilities with respect to atomic displacements, $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$, of BaTiO₃ and PbTiO₃ in their tetragonal phase and of LiNbO₃ in its ferroelectric phase. In case of BaTiO₃ and PbTiO₃, we also compare the results obtained from the 2n + 1 theorem to the results obtained from finite electric field calculations. The quantities discussed in this section will be used in Sec. 4.5 and 4.6 to study the Raman spectrum and the EO coefficients of these materials.

In the perovskites, the nonlinear optical susceptibility tensor has the three independent elements d_{31} , d_{33} and d_{15} (Voigt notations):

$$\boldsymbol{d} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & d_{15} & \cdot \\ \cdot & \cdot & \cdot & d_{15} & \cdot & \cdot \\ d_{31} & d_{31} & d_{33} & \cdot & \cdot & \cdot \end{pmatrix}.$$
(4.17)

In LiNbO₃, this tensor has the 4 independent elements d_{31} , d_{33} , d_{15} and d_{22} :

$$\boldsymbol{d} = \begin{pmatrix} \vdots & \vdots & \vdots & \vdots & d_{15} & -d_{22} \\ -d_{22} & d_{22} & \vdots & d_{15} & \vdots & \vdots \\ d_{31} & d_{31} & d_{33} & \vdots & \vdots & \vdots \end{pmatrix}.$$
 (4.18)

In case Kleinman's symmetry rule can be applied, the number of independent elements of these tensors is further decreased since $d_{31} = d_{15}$. As discussed in Sec. 3.3.1, in case of the 2n + 1 theorem, this rule is automatically satisfied. In case of a finite electric field calculation, we will see that it is not strictly satisfied although the differences between d_{31} and d_{15} are small and due to the numerical accuracy of the calculation.

In BaTiO₃ and PbTiO₃, the $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$ coefficients take a very simple form as shown in Table 4.5. For each atom in the unit cell as defined in Table 1.1, these coefficients are determined by 5 numbers denoted *a*, *b*, *c*, *d* and *e*. In case of Ba, Pb, Ti and O₁, the number of independent elements is even smaller because a = b and c = d. In LiNbO₃, the form of $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$ is more complicated and we do not discuss these coefficients here. In Sec. 4.5, we present instead a study of the Raman spectrum of this compound.

Table 4.5: $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$ coefficients of Ba/Pb, Ti and O in the tetragonal phase of BaTiO₃ and PbTiO₃. x, y and z denote the direction of the atomic displacement, α . The rows and columns of the matrices correspond to the indexes i and j.

x	y	z
$\left(\cdot \cdot a \right)$	$\left(\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array} \right)$	$\begin{pmatrix} c & \cdot & \cdot \end{pmatrix}$
(· · ·)	$\cdot \cdot b$	$\cdot d \cdot$
$(a \cdot \cdot)$	$\left(\begin{array}{cc} \cdot & b \\ \end{array} \right)$	$(\cdot \cdot e)$

Table 4.6: Nonlinear optical susceptibilities (pm/V) and electronic dielectric constants of the perovskite ferroelectrics BaTiO₃ and PbTiO₃ in their tetragonal phase. Reported are the theoretical values computed from density functional perturbation theory (DFPT, PEAD expression) and the finite electric field (FEF) technique as well as the experimental values reported in Refs. [152–156] for BaTiO₃ and Refs. [157–159] for PbTiO₃.

Material	Method	d_{15}	d_{31}	d_{33}	ε_{11}	ε_{33}
$BaTiO_3$	\mathbf{DFPT}	-11.10	-11.10	-18.38	6.49	5.85
	\mathbf{FEF}	-10.74	-10.73	-17.60	6.31	5.72
	Exp.	-17.0	-15.7	-6.8	5.19	5.05
$PbTiO_3$	\mathbf{DFPT}	-27.76	-27.76	-5.70	7.31	6.79
	$\mathbf{F}\mathbf{E}\mathbf{F}$	-26.42	-26.15	-5.35	7.12	6.67
	Exp.	-37.9	-42.8	+8.5	6.64	6.63

The results obtained from the 2n+1 theorem and from the finite electric field (FEF) technique are summarized in the Tables 4.6, 4.7 and 4.8. To compute the nonlinear optical susceptibilities, the electronic dielectric constants and the $\partial \chi_{ij}^{(1)}/\partial \tau_{\kappa\alpha}$ coefficients from finite electric fields, we used an approach similar to the one described in Sec. 4.3, in which we applied electric fields along the (1,0,0), (0,0,1) and (1,0,1) directions. As in case of the semiconductors, the agreement between the results obtained from the 2n + 1 theorem and those obtained from the finite electric field technique is very good. The absolute values of the nonlinear optical susceptibilities are in reasonable agreement with the corresponding experimental values. All susceptibilities are found to be negative. In case of BaTiO₃, this result corresponds to what has been observed experimentally. In contrast, the experimental values of d_{33} in PbTiO₃ and d_{22} in LiNbO₃ are positive. We should note however that nonlinear optical susceptibilities are difficult to measure accurately and that the values reported by different authors are often in substantial disagreement [87]. It is therefore not easy to say whether this discrepancy is due to the theoretical calculation or to the experiment.

Table 4.7: Nonlinear optical susceptibilities (pm/V) and electronic dielectric constants of LiNbO₃ computed from density functional perturbation theory (DFPT, PEAD expression).

Method	d_{31}	d_{22}	d_{33}	ε_{11}	ε_{33}
DFPT	-8.08	-1.30	-30.22	5.59	5.51
Exp. [160]	-4.64	+2.46	-41.7		
Exp. [128]	-6.25	+3.6	-37.5		
Exp. [161]				5.0	4.6

Table 4.8: Independent elements of $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$ (Bohr⁻¹) in BaTiO₃ and PbTiO₃ computed from the 2n + 1 theorem (DFPT, PEAD expression) and the finite electric field (FEF) technique.

		Bal	IiO_3	Pb]	CiO_3
		\mathbf{DFPT}	FEF	\mathbf{DFPT}	\mathbf{FEF}
Ba/Pb	a,b	-0.0038	-0.0043	-0.0265	-0.0259
	$^{\mathrm{c,d}}$	-0.0065	-0.0063	-0.0826	-0.0798
	е	0.0218	0.0213	-0.0486	-0.0477
Ti	a,b	-0.0873	-0.0860	-0.1407	-0.1383
	$^{\mathrm{c,d}}$	-0.1290	-0.1235	-0.1563	-0.1495
	е	-0.3100	-0.2983	-0.1276	-0.1222
01	a,b	0.0335	0.0332	0.0621	0.0613
	$^{\mathrm{c,d}}$	0.1208	0.1153	0.1927	0.1849
	е	0.2468	0.2380	0.1786	0.1725
O_2	а	-0.0029	-0.0027	-0.0240	-0.0236
	b	0.0606	0.0598	0.1291	0.1265
	с	-0.0063	-0.0061	-0.0363	-0.0347
	d	0.0209	0.0207	0.0825	0.0791
	е	0.0207	0.0194	-0.0012	-0.0013

In case of Ba or Pb, the absolute values of a, c and e are significantly smaller than the corresponding values for Ti or O₁. A similar behavior has been observed for the Born effective charges [103], Z^* : the anomalous effective charges of Ba or Pb are smaller then the anomalous effective charges of Ti or O₁. The amplitude of the Born effective charges in these compounds can be explained from their electronic structure as interpreted within the bond orbital model of Harrison [106]: the Ba atom in BaTiO₃ and, to a much lower extent, the Pb atom in PbTiO₃ are close to a fully ionized configuration whereas there is a partly covalent interaction between Ti and O₁. During an atomic displacement, the parameters that determine the covalent interactions between Ti 3d and O₁ 2p atomic orbitals (the hopping integrals) vary. As discussed in Sec. 2.3.2, this variation produces a dynamical charge transfer between Ti and O₁, which is at the origin of the anomalous effective charges of these atoms. The derivatives of the linear optical susceptibility with respect to atomic displacements can be expressed as derivatives of the Born effective charges with respect to an electric field:

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\alpha}} = \frac{1}{\Omega_0} \frac{\partial Z_{\kappa,\alpha j}^*}{\partial \mathcal{E}_i}.$$
(4.19)

The amplitude of these quantities therefore depends on the way the dynamical charge transfer is affected by an electric field. In case of Ba and Pb, this transfer of charges is close to zero and, because of the ionic configuration of these atoms, it is only slightly affected by an electric field. In contrast, because of the partly covalent interactions between Ti and O₁ the transfer of charges between these atoms is more sensitive to an electric field. The amplitude of the $\partial \chi_{ij}^{(1)} / \partial \tau_{\kappa\alpha}$ coefficients can therefore be interpreted from similar arguments as the amplitude of the Born effective charges.

4.5 Raman spectra of ferroelectrics

The theoretical determination of Raman spectra is highly desirable since it can be used to associate Raman lines on an experimental spectrum to specific phonon modes. In the present section, we show that the Raman spectra obtained from first-principles are sufficiently accurate to be compared to the experiment. We first illustrate the method for tetragonal PbTiO₃. We then discuss the Raman spectra in the ferroelectric phase of LiNbO₃ and we try to clarify some ambiguities in the assignation of the E-modes in this compound.

4.5.1 Tetragonal PbTiO₃

In the P4mm phase of PbTiO₃, the zone-center optical phonons can be classified into

$$3A_1 + B_1 + 4E.$$

All modes are Raman active. In addition, the A_1 and E modes are infrared active. At the Γ -point, they are split into transverse (TO) and longitudinal (LO) components.

Table 4.9: Frequencies (cm^{-1}) of the transverse and longitudinal optical phonon modes in the tetragonal phase of PbTiO₃. Experimental data has been obtained by Raman (Ra) spectroscopy.

		Transv	verse modes		Longitudinal modes				
		Present	$\operatorname{Ra}\left[162 ight]$	Ra [159]		Present	$\operatorname{Ra}\left[162 ight]$	Ra~[159]	
A_1	TO1	151	148	149	LO1	189		194	
	TO2	357	362	359	LO2	442		465	
	TO3	653	650	647	LO3	791		795	
E	TO1	79	89	87	LO1	117	130	128	
	TO2	202	220	219	LO2	269	290	289	
	TO3	269	290	289	LO3	416	440	441	
	TO4	484	508	505	LO4	656	720	687	
B_1		283		289					

The theoretical frequencies of all zone-center phonon modes are reported in Table 4.9 where they are compared to the experiment.

As discussed in Sec. 3.3.2, the Raman scattering efficiencies can be computed from the projection of the Raman susceptibility tensors, α^m , on the polarization vectors of the incoming and scattered photons (3.22). For a given crystal, the form of α^m depends on the symmetry and the polarization of the phonon mode eigenvector [126, 163]. For the A_1 modes in PbTiO₃, polarized along z, we can write

$$A_1(z) = \begin{pmatrix} a & \cdot & \cdot \\ \cdot & a & \cdot \\ \cdot & \cdot & b \end{pmatrix}.$$
 (4.20)

The E modes in PbTiO₃ are polarized in the plane perpendicular to z. In case the eigenvectors are polarized along x or y, the Raman susceptibilities can be expressed as

$$E(x) = \begin{pmatrix} \cdot & \cdot & e \\ \cdot & \cdot & \cdot \\ e & \cdot & \cdot \end{pmatrix}, \qquad E(y) = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & e \\ \cdot & e & \cdot \end{pmatrix}.$$
(4.21)

Finally, the Raman susceptibility of the B_1 modes can be written as⁵

$$B_1 = \begin{pmatrix} c & \cdot & \cdot \\ \cdot & c & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}.$$
(4.22)

The method presented in Sec. 3.3.2 gives no information about the shape or the width of the Raman peaks. In order to draw a theoretical Raman spectrum, we use

⁵Since the B_1 modes are infrared inactive, it is not possible to define a polarization for these modes.

the following convention: for each normal mode, we use a normalized Lorentzian centered around the theoretical phonon frequency with a half width at half maximum of 5 cm⁻¹.⁶ These Lorentzians are then multiplied by the corresponding theoretical scattering efficiencies computed from Eq. (3.22).

Figure 4.5 shows two theoretical (a) and the corresponding experimental [162] (b) Raman spectra of PbTiO₃. The bottom spectra have been obtained for a x(zz)yscattering configuration in which the incoming photon has its wave vector, \mathbf{k}_0 , along x and its polarization, \mathbf{e}_0 , along z while the scattered photon has its wave vector, \mathbf{k}_S , along y and its polarization, \mathbf{e}_S , along z. Projecting the Raman susceptibilities given in Eqs. (4.20), (4.21) and (4.22) on \mathbf{e}_0 and \mathbf{e}_S , we see that (i) only the A_1 modes can be detected in this configuration and (ii) the intensity of the Raman peaks depends on the element b of their Raman susceptibility. Due to wave vector conservation, the wave vector of the phonons created in a Stokes process, \mathbf{q} , can be computed as the difference

$$\mathbf{q} = \mathbf{k}_0 - \mathbf{k}_S. \tag{4.23}$$

It follows that the wave vector of the phonons detected in a x(zz)y scattering configuration is parallel to the (1,-1,0) direction⁷. Because the A₁ modes are polarized along z, the modes in the bottom spectrum of Figure 4.5 (a) are purely transverse.

The spectra in the top of Figures 4.5 (a) and (b) have been obtained for a x(zx)y configuration where the wave vector and polarization of the incoming photon (scattered photon) are along x and z (y and x). Projecting the Raman susceptibilities in Eqs. (4.20), (4.21) and (4.22) on \mathbf{e}_0 and \mathbf{e}_S , we see that only the E modes can be detected in this configuration. Because the E-modes are polarized in the xy plane, both transverse and longitudinal modes are visible in this configuration⁸.

The qualitative agreement between the theoretical and experimental spectra in Figure 4.5 is very good. In case of the A_1 modes, the TO3 mode has the strongest scattering efficiency while the TO2 mode has the weakest scattering efficiency. In case of the E modes, the LO4 mode at 656 cm⁻¹ has the weakest scattering efficiency. It does not even appear on the experimental spectrum although it is reported in Ref. [162] to be around this frequency.

$$E(x, y) = \frac{1}{\sqrt{2}}(E(x) + E(y))$$
$$E(x, -y) = \frac{1}{\sqrt{2}}(E(x) - E(y)).$$

⁶This value was arbitrarily chosen.

 $^{^7\}mathrm{Here},$ we consider the limit $\mathbf{q}\to \mathbf{0}$ along this direction

⁸The expression of the Raman susceptibilities in Eq. (4.21) is only valid for modes strictly polarized along x or y. In the x(zx)y configuration, the phonon wave vector is along (1,-1,0) and the transverse and longitudinal modes are respectively polarized along (1,1,0) and (1,-1,0). The corresponding susceptibility tensors can be expressed as linear combinations of the tensors in Eq. (4.21)

Figure 4.5: Theoretical (a) and experimental [162] (b) Raman spectra of PbTiO₃. The top spectra have been obtained for a x(zx)y scattering configuration. They show the transverse and longitudinal E modes. The bottom spectra have been obtained for a x(zz)y configuration. They show the transverse A₁ modes.



Table 4.10: Frequencies (cm^{-1}) of the transverse and longitudinal A_1 modes in the ferroelectric phase of LiNbO₃. Experimental data has been obtained by Raman (Ra) and Infrared (IR) spectroscopy.

	Transv	verse modes	Lor	Longitudinal modes			
	$\mathbf{Present}$	Ra [164]	Ra [161]		$\mathbf{Present}$	IR [161]	
T O1	243	252	252	LO1	287	273	
TO2	288	275	276	LO2	348	306	
TO3	355	332	333	LO3	413	423	
TO4	617	632	634	LO4	855	869	

4.5.2 Ferroelectric LiNbO₃

In the ferroelectric phase of $LiNbO_3$, the zone-center phonon modes can be classified into

$$4A_1 + 5A_2 + 9E$$
.

The A_1 and E modes are Raman and infrared active. The frequencies of the corresponding transverse and longitudinal modes are reported in the Tables 4.10 and 4.11. The A_2 modes are neither Raman nor infrared active and will not be discussed here. The Raman susceptibility of the A_1 modes is given in Eq. (4.20) while the Raman susceptibilities of the E modes can be written as

$$E(y) = \begin{pmatrix} c & \cdot & \cdot \\ \cdot & -c & d \\ \cdot & d & \cdot \end{pmatrix}, \qquad E(x) = \begin{pmatrix} \cdot & c & d \\ c & \cdot & \cdot \\ d & \cdot & \cdot \end{pmatrix}.$$
(4.24)

Figures 4.6 show the theoretical (a) and experimental [164,166] (b) Raman spectra of LiNbO₃ obtained for a x(zz)y scattering configuration. As in case of PbTiO₃, only the transverse A_1 modes can be detected in this configuration. The qualitative agreement between theory and experiment is very good. The TO1 and TO4 modes are correctly predicted to have the strongest scattering efficiency. The TO2 peak appears weaker on the theoretical spectrum than on the experimental spectrum. This effect is not related to the intrinsic scattering efficiency of the TO2 mode. It is rather a consequence of the fact that the TO1 peak in Figure 4.6 (b) is quite broad and that it overlaps with the TO2 peak. This is not the case for the theoretical spectrum since we use a constant width to represent the Raman peaks in Figure 4.6 (a). Finally the scattering efficiency of the TO3 mode is weaker than that of the other modes in agreement with the experiment, although the theoretical efficiency is so small that this peak does not appear in Figure 4.6 (a).

The analysis of the E modes in LiNbO₃ is more difficult. In the literature, many different frequencies have been reported, which were differently assigned (see f. ex.



Figure 4.6: Theoretical (a) and experimental [164,166] (b) Raman spectrum of LiNbO₃ for a x(zz)y scattering configuration. The spectra show the transverse A_1 modes.

Table 4.11: Frequencies (cm^{-1}) of the transverse and longitudinal E modes in the ferroelectric phase of LiNbO₃. Experimental data has been obtained by Raman (Ra) and Infrared (IR) spectroscopy. The values in brackets are not assumed to be related to first-order phonons.

		Transverse r	nodes				Longit	udinal m	odes	
	Present	\mathbf{Ra}	\mathbf{Ra}	\mathbf{Ra}	\mathbf{IR}		Present	\mathbf{Ra}	\mathbf{Ra}	\mathbf{IR}
		[165, 166]	[167]	[161]	[161]			[165]	[167]	[161]
TO1	155	153	155	152	152	LO1	197	195	198	198
		(177)						(186)		
TO2	218	238	238	238	236	LO2	224	240	243	238
TO3	264	264	265	264	265	LO3	298	299	295	296
TO4	330	322	325	321	322	LO4	349	345		342
TO5	372				363	LO5	384		371	
TO6	384	369	371	367		LO6	423	424	428	418
TO7	428	432	431	434	431	LO7	452	456	454	450
TO8	585	580	582	579	586	LO8	675		668	660
		(610)						(625)		
TO9	677	663	668		670	LO9	863	878	880	878

Ref. [69] for a more complete discussion). This comes from the fact that the properties of lithium niobate crystals strongly depend on the internal and external defects [168]. In particular, Raman spectroscopy is very sensitive to small modifications in the structure and to the stoichiometry of the samples [165, 169].

For the transverse optic phonons, most authors seem to agree on seven modes around 152, 237, 265, 322, 368, 431 and 580 cm⁻¹. For the two missing modes, different frequencies have been suggested including those around 180 and 610 cm⁻¹ (values in brackets in Table 4.11). Our calculation reproduces the seven modes mentioned above but we do not find any phonon frequencies around 180 and 610 cm⁻¹. For the two remaining modes, we suggest instead that one of them has a frequency of about 670 cm⁻¹ in agreement with Refs. [161,166,167]. Moreover, we suggest that the Raman and infrared peaks around 370 cm⁻¹ do not correspond to one transverse optical phonon but to two transverse optical phonons. One of them can only be detected by infrared spectroscopy while the other one can only be detected by Raman spectroscopy.

In Figure 4.7, we compare a theoretical (a) and an experimental [165, 166] (b) Raman spectrum of LiNbO₃ obtained for a x(yz)y scattering configuration. In this configuration, the transverse and longitudinal E modes can be detected. As in case of the A_1 modes, the qualitative agreement between theory and experiment is very good. In Table 4.12, we compare the theoretical and experimental infrared oscillator strengths (computed from Eq. (3.38)) and Raman scattering efficiencies. Experimentally, it is difficult to determine absolute Raman scattering efficiencies accurately. We therefore report the intensities of the Raman peaks relative to the intensity of the TO1 peak.

The TO5 mode has an oscillator strength of $3.59 \cdot 10^{-4}a.u.$, in good agreement with the experiment, and a weak Raman scattering efficiency. Due to its significant

Figure 4.7: Theoretical (a) and experimental [165,166] (b) Raman spectrum of LiNbO₃ for a x(yz)y scattering configuration. The spectra show the transverse and longitudinal E modes.



	Th	eory	Exp	periment
Mode	IR	Ra	IR [161]	m Ra~[165, 166]
	S_m	I/I_{TO1}	S_m	I/I_{TO1}
TO1	5.85	1.00	6.02	1.00
TO2	0.55	0.91	0.53	0.83
TO3	4.38	0.15	4.58	0.39
TO4	2.71	0.38	2.70	0.55
TO5	3.59	0.04	3.59	
TO6	0.15	0.32		0.68
TO7	0.31	0.17	0.40	0.22
TO8	14.33	0.88	13.43	0.78
TO9	0.37	0.01	1.06	0.12

Table 4.12: Infrared (IR) mode oscillator strengths (10^{-4} a. u.) and reduced Raman (Ra) scattering efficiencies of the transverse E modes in LiNbO₃.

oscillator strength, this mode is easy to detect by infrared spectroscopy and it gives rise to a measurable LO-TO splitting. In contrast, this mode is difficult to detect by Raman spectroscopy. The TO6 mode has a weak oscillator strength and a significant Raman scattering efficiency. As can be seen in Figure 4.7 it gives rise to a well-defined Raman peak. In contrast, due to its weak oscillator strength, this mode is difficult to detect by infrared spectroscopy and it does not give rise to a sizeable LO-TO splitting (see also Table 4.11).

The distinct characteristics of the TO5 and TO6 modes give a first argument in favor of our assumption that there are two transverse optical modes around 370 cm⁻¹. A stronger argument comes from an experiment of Claus and co-workers [167]. The authors of Ref. [167] used Raman spectroscopy to measure the dependence of the phonon frequencies on the angle between the phonon wave vector, \mathbf{q} , and the z-axis of LiNbO₃. In case of the mode around 370 cm⁻¹ they observed no angular dependence of the frequency, indicating that this mode has a negligible infrared oscillator strength. The characteristics of the mode measured by Claus and co-workers are therefore compatible with the characteristics of the TO6 mode. These observations cannot be explained if we assume only one mode at this frequency because an oscillator strength of $3.59 \cdot 10^{-4}a.u$. is not compatible with the absence of angular dispersion of the phonon frequency.

To summarize, our study has shown that the theoretical calculation of Raman efficiencies can help the interpretation of experimental Raman spectra. In particular, we have shown that LiNbO_3 has two *E*-modes around 370 cm⁻¹ whereas previous studies suggest that it only has one *E*-mode around this frequency.

In the following section, we will study the EO tensor in $BaTiO_3$, $PbTiO_3$ and $LiNbO_3$. The results of this section will help us to understand the unusual ionic contribution to the EO coefficients of these materials.

4.6 Electro-optic tensor in ferroelectric oxides

4.6.1 Ferroelectric LiNbO₃

The EO tensor in the ferroelectric phase of $LiNbO_3$ has the four independent elements (Voigt notations) r_{13} , r_{33} , r_{22} and r_{51} :

$$\mathbf{r} = \begin{pmatrix} \cdot & -r_{22} & r_{13} \\ \cdot & r_{22} & r_{13} \\ \cdot & \cdot & r_{33} \\ \cdot & r_{51} & \cdot \\ r_{51} & \cdot & \cdot \\ -r_{22} & \cdot & \cdot \end{pmatrix}.$$
 (4.25)

As discussed in Sec. 4.5.2, the TO modes can be classified into $4A_1 + 5A_2 + 9E$. The A_1 and E modes are simultaneously Raman and IR active. Only the A_1 modes couple to r_{13} and r_{33} , while the E modes are linked to r_{22} and r_{51} . In Table 4.13, we report the four clamped and unclamped coefficients, as well as the contribution of each optical phonon and the piezoelectric contribution. For comparison, we also mention the coefficients computed by Johnston [128] from measurements of IR and Raman intensities (IR + R) as well as the results of a bond-charge model (BCM) calculation by Shih and Yariv [170]. The first-principles calculations correctly predict the sign of the four EO coefficients [70]. The absolute values are also well reproduced by our method, especially if we take into account that NLO properties are generally difficult to determine accurately. The experimental values are sensitive to external parameters such as temperature changes [171] and the stoichiometry of the samples. For example, using crystals of various compositions, Abdi and co-workers measured absolute values between 1.5 pm/V and 9.9 pm/V for r_{22}^{σ} [172]. These difficulties support the need for sophisticated theoretical tools to predict NLO properties. In contrast to the models of Refs. [128,170], our method is predictive and does not use any experimental parameters. Moreover, it reproduces the clamped EO coefficients r_{13}^{η} , r_{33}^{η} and r_{22}^{η} better than the semiempirical models.

The EO coefficients of LiNbO₃ are significantly larger than the EO coefficients of the semiconductors discussed in Sec. 4.3.3. This different behavior can be explained from the decomposition of the EO coefficients into their electronic and ionic contributions. In Sec. 4.3.3, we observed that these contributions are of the same order of magnitude in semiconductors and that they are of opposite sign. As a consequence, they cancel out, giving a small r_{63}^{η} . In contrast, the EO coefficients of LiNbO₃ are dominated by the ionic contribution of the A₁ TO1 and the E TO1 modes. In addition, the contributions of these modes are much lager than the electronic and ionic contributions in the semiconductors. This can be explained as follows. At the paraelectric-ferroelectric phase transition, the unstable A_{2u} and E_u modes of the paraelectric phase (see Sec. 1.2) transform to *low-frequency* and *highly polar* modes in the ferroelectric phase [69], generating a large EO response if they exhibit, in addition, a *large Raman susceptibility*. The A₁ TO1 and E TO1 modes of the ferroelectric phase have a strong overlap

of respectively 0.82 and 0.68 with the unstable A_{2u} and E_u modes of the paraelectric phase and combine giant polarity [69] and large Raman susceptibility (see Figures 4.6 and 4.7 and Table 4.14).

As discussed in Sec. 3.3.4, the piezoelectric contribution to the EO coefficients is related to deformations of the cell shape due to the converse piezoelectric effect and the changes in the indices of refraction induced by these deformations. Using Eq. (3.39), this contribution can be computed as the product of the piezoelectric strain coefficients, $d_{\gamma\alpha\beta}$, and the elasto-optic coefficients, $\pi_{ij\alpha\beta}$. The computation of the piezoelectric strain coefficients is more difficult than the computation of the piezoelectric stress coefficient, $e_{\gamma\alpha\beta}$. Both quantities are related through the linear system of equations [173]

$$e_{\gamma\alpha\beta} = \sum_{\mu\nu} d_{\gamma\mu\nu} c_{\mu\nu\alpha\beta} \tag{4.26}$$

where $c_{\mu\nu\alpha\beta}$ are the elastic constants. The values of $\pi_{ij\alpha\beta}$, $e_{\gamma\alpha\beta}$, $c_{\mu\nu\alpha\beta}$ computed from finite differences and $d_{\gamma\alpha\beta}$ computed by solving Eq. (4.26) are summarized in Table 4.15.

The unclamped EO coefficients in LiNbO₃ are also reported in Table 4.13. As the piezoelectric coefficients d_{31} and d_{33} are small compared to d_{15} and d_{22} , the piezoelectric effect is important for r_{22}^{σ} and r_{51}^{σ} and negligible for r_{13}^{σ} and r_{33}^{σ} . The unclamped EO coefficient r_{51}^{σ} is nearly twice as large as the clamped one. Moreover, its theoretical value is in better agreement with the experiment than that of the clamped one. This suggests that the piezoelectric contribution was not entirely eliminated during the measurement of r_{51}^{η} ; the correct value of the clamped coefficient might be closer to the theoretical 14.9 pm/V.

4.6.2 Tetragonal BaTiO₃ and PbTiO₃

As discussed in Sec. 4.5.1, in the tetragonal phase of $BaTiO_3$ and $PbTiO_3$, the TO modes can be classified into $3A_1 + 4E + B_1$. The EO tensor can be written as

$$\mathbf{r} = \begin{pmatrix} \cdot & \cdot & r_{13} \\ \cdot & \cdot & r_{13} \\ \cdot & \cdot & r_{33} \\ \cdot & r_{42} & \cdot \\ r_{42} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix}.$$
 (4.27)

It has only three independent elements: r_{13} , and r_{33} , coupling to the A_1 modes, and r_{42} , linked to the E modes. The B_1 -mode is IR inactive and does not influence the EO tensor. The values of the clamped EO coefficients of the two compounds computed from the 2n + 1 theorem and the finite electric field (FEF) technique are reported in Table 4.16. We also report the decomposition of the EO coefficients into their electronic and ionic contributions as obtained from the 2n + 1 theorem. As in case of

		A ₁ -modes E-:			E-mod	-modes	
		ω_m	r_{13}	r_{33}	ω_m	r_{22}	r_{51}
$\operatorname{Electronic}$			1.0	4.0		0.2	1.0
Ionic	TO1	243	6.2	18.5	155	3.0	7.5
	TO2	287	-0.2	-0.4	218	0.4	1.5
	TO3	355	-0.1	0.0	264	0.6	1.3
	TO4	617	2.8	4.8	330	-0.3	1.2
	TO5				372	-0.2	0.4
	TO6				384	-0.1	-0.2
	TO7				428	0.2	0.2
	TO8				585	0.7	2.1
	TO9				677	0.0	0.0
	Sum of ionic		8.7	22.9		4.4	13.9
Strain			0.8	0.1		3.0	13.7
Clamped	$\mathbf{Present}$		9.7	26.9		4.6	14.9
	Exp. [168]		8.6	30.8		3.4	28
	IR + R [128]		12	39		6	19
	BCM [170]			25.9			20.5
Unclamped	Present		10.5	27.0		7.5	28.6
	Exp. [168]		10.0	32.2		6.8	32.6
	Exp. [172]					9.9	

Table 4.13: EO tensor (pm/V) in LiNbO₃ : electronic, ionic and piezoelectric contributions, and comparison with experiment, for the clamped and unclamped cases. The ionic part is split into contributions from TO modes (ω_m in cm⁻¹).

Table 4.14: Raman susceptibilities and mode polarities $(10^{-2} a. u.)$ of the A₁ TO modes in LiNbO₃, BaTiO₃ and PbTiO₃.

	$ m LiNbO_3$			BaTiO_3			PbTiO ₃		
	p_3	α_{11}	α_{33}	p_3	α_{11}	α_{33}	p_3	α_{11}	$lpha_{33}$
TO1	3.65	-0.70	-2.02	1.22	-0.16	-0.13	1.25	-0.67	-0.43
TO2	0.45	0.30	0.53	3.25	-1.18	-2.73	2.18	-0.75	-0.33
TO3	0.67	0.18	-0.05	1.74	-1.26	-2.55	2.68	-2.42	-2.28
TO4	3.82	-1.96	-3.23						

Property	Coefficient	Theory	Experiment
Elastic	c_{11}	1.96	2.03
(N/m^2)	c_{12}	0.71	0.53
	c_{13}	0.70	0.75
	c_{14}	0.05	0.09
	c_{33}	2.58	2.45
	c_{44}	0.66	0.60
	c_{66}	0.63	0.75
Piezoelectric stress	e_{15}	3.44	3.7
(C/m^2)	e_{22}	2.41	2.5
	e_{31}	0.15	0.2
	e_{33}	1.42	1.3
Piezoelectric strain	d_{15}	5.59	6.8
$(10^{-11}C/N)$	d_{22}	2.16	2.1
	d_{31}	-0.10	-0.1
	d_{33}	0.60	0.6
Elasto-optic	π_{11}	-0.0048	-0.026
	π_{12}	0.0583	0.09
	π_{13}	0.1421	0.133
	π_{14}	-0.0778	-0.075
	π_{31}	0.1131	0.179
	π_{33}	0.0640	0.071
	π_{41}	-0.1444	-0.151
	π_{44}	0.1329	0.146

Table 4.15: Theoretical and experimental [168, 174] values of the independent elastic constants, piezoelectric stress coefficients, piezoelectric strain coefficients and elastooptic coefficients in $LiNbO_3$. Voigt notations are used for all coefficients.

Table 4.16: Electronic and ionic contributions of individual TO modes (ω_m in cm⁻¹) to the clamped EO coefficients (pm/V) in the P4mm phase of PbTiO₃ and BaTiO₃. For comparison, we also report the value of r_{33}^{η} computed from the finite electric field (FEF) technique.

	$PbTiO_3$						$BaTiO_3$			
	A_1 -modes		E-m	odes	А	A_1 -modes				
	ω_m	\mathbf{r}_{13}^{η}	r_{33}^η	ω_m	\mathbf{r}_{42}^{η}	ω_m	r_{13}^{η}	r_{33}^η		
Elec.		2.1	0.5		2.2		1.0	2.1		
TO1	151	3.9	2.9	79	16.4	161	1.0	1.0		
TO2	357	1.4	0.7	202	10.5	300	5.7	16.3		
TO3	653	1.6	1.8	269	0.2	505	1.2	2.9		
TO4				484	1.2					
Tot		9.0	5.9		30.5		8.9	22.3		
\mathbf{FEF}			5.9					22.6		
Exp. [176]		13.8	5.9							
Exp. [177]							10.2	40.6		
Exp. [87]							8	28		

the semiconductors, there is a good agreement between the values computed from the two techniques.

For PbTiO₃, we found only measurements of r_{13}^{η} and r_{33}^{η} , which agree well with our theoretical results. Moreover, our calculation predicts that PbTiO₃ exhibits a large r_{42}^{η} , in spite of its low r_{33}^{η} . Combined with other advantageous features, such as small thermo-optic coefficients [175], this suggests that PbTiO₃ might be an interesting candidate for EO applications if properly oriented.

In BaTiO₃, the low temperature structure is rhombohedral. The P4mm phase is unstable and exhibits, in the harmonic approximation, an unstable E-mode that prevents the use of Eq. (3.36) to compute r_{42}^{ion} . The theoretical estimates of r_{13}^{η} and r_{33}^{η} are reasonably accurate and reproduce the correct trends, despite an underestimation of the theoretical r_{33}^{η} . The origin of the error can be attributed to various sources. First, the values computed for the P4mm phase correspond to an extrapolation of the EO tensor to 0 K, while experimental results are obtained at room temperature. Also, linear and NLO susceptibilities can be relatively inaccurate within the LDA. In this context, note the use of the LDA optical refractive indexes in Eqs. (3.35) and (3.36), overestimating the experimental values by about 10 %.

4.6.3 Discussion

We compare now the NLO response of the three compounds. r_{13}^{η} is similar for all of them, while r_{33}^{η} is significantly smaller in PbTiO₃ than in LiNbO₃ and BaTiO₃. In the

	${\operatorname{BaTiO}}_3$]	$PbTiO_3$			
κ	$\sqrt{\Omega_0} \frac{\partial \chi_{33}^{(1)}}{\partial \tau_{\kappa 3}}$	$u(\kappa,3)$	$lpha_{33}(\kappa)$	$\sqrt{\Omega_0} \frac{\partial \chi_{33}^{(1)}}{\partial \tau_{\kappa 3}}$	$u(\kappa,3)$	$lpha_{33}(\kappa)$		
	(a.u.)	(10^{-2})	a.u.)	(a.u.)	(10^{-2})	² a.u.)		
Ba/Pb	0.45	-0.014	-0.01	-1.00	-0.006	0.01		
Ti	-6.46	0.257	-1.66	-2.64	0.216	-0.57		
O_1	5.15	-0.167	-0.86	3.69	0.059	0.22		
O_2/O_3	0.43	-0.240	-0.10	-0.02	-0.316	0.01		
Tot			-2.73			-0.32		

Table 4.17: Decomposition of the Raman susceptibility of the A_1 TO2 mode in BaTiO₃ and PbTiO₃ into contributions from the individual atoms in the unit cell.

latter two compounds, the magnitude of r_{33}^{η} is dominated by one particular phonon mode. In BaTiO₃, the TO2 mode at 300 cm⁻¹ has a similar strong overlap (92%) with the unstable mode in the paraelectric phase than the TO1 modes in LiNbO₃, as previously discussed. In PbTiO₃, all A₁ modes contribute almost equally to r_{33}^{η} . The TO2 mode at 357 cm⁻¹ has the strongest overlap (73%) with the soft mode in the cubic phase. Surprisingly, its contribution to r_{33}^{η} is 23.5 times smaller than the contribution of the corresponding TO2 mode in BaTiO₃.

To identify the origin of the distinctive behavior of PbTiO₃, we report in Table 4.14 the mode polarities and Raman susceptibilities of the A₁ TO modes. In the three compounds, α has two independent elements α_{11} and α_{33} that determine the amplitude of r_{13}^{η} and r_{33}^{η} . α_{33} is large for the TO1 mode in LiNbO₃ and the TO2 mode in BaTiO₃. On the other hand, it is the smallest for the TO2 mode in PbTiO₃, in agreement with experiments as discussed in Sec. 4.5.1. Combined with a higher frequency ($\omega_{PbTiO_3}^2/\omega_{BaTiO_3}^2 = 1.41$), a lower polarity ($p_{BaTiO_3}/p_{PbTiO_3} = 1.49$), and a larger value of the refractive index ($n_{PbTiO_3}^4/n_{BaTiO_3}^4 = 1.35$), this weak Raman susceptibility ($\alpha_{BaTiO_3}/\alpha_{PbTiO_3} = 8.27$) explains the weak contribution of the TO2 mode to r_{33}^{η} in PbTiO₃.

The microscopic origin of the lower A_1 TO2 mode Raman susceptibility in PbTiO₃, compared to BaTiO₃, is explained by the decomposition of α_{33} into contributions of the individual atoms in the unit cell (see Table 4.17 and Table 1.1 for the labels of the atoms). In both perovskites, the major contributions to the Raman susceptibility of the A_1 TO2 modes are $\alpha_{33}(Ti)$ and $\alpha_{33}(O_1)$; α_{33} is mostly due to the displacements of the atoms located on the Ti–O chains oriented along the polar direction. First, the derivatives of $\chi_{33}^{(1)}$ versus atomic displacement are of opposite sign for Ti and O_1 atoms, and significantly larger in BaTiO₃ than in PbTiO₃. Second, the opposing displacements of Ti and O_1 atoms in the TO2 mode in BaTiO₃ produce contributions that add to yield a giant α_{33} . On the other hand, the in-phase displacements of Ti and O_1 in PbTiO₃ produce contributions that cancel out, giving a small α_{33} . This distinct behavior goes beyond a simple mass effect. Changing the mass of Pb to that of Ba in the dynamical matrix of PbTiO₃ has no significant effect on the relative Ti–O displacement. Large atomic displacements of opposite direction along the Ti–O chains are therefore needed to generate a large α_{33} and potentially a large r_{33} .

4.7 Conclusions

In this Chapter, we studied nonlinear optical properties of selected semiconductors and ferroelectrics. We applied both the 2n+1 theorem and the finite electric field technique. From the results obtained in this study, we can draw the following conclusions:

First, as it has been illustrated on several examples, the formalism of the 2n + 1 theorem (PEAD and DAPE expressions) and the finite electric field technique can equivalently be used to study nonlinear optical properties. However, the PEAD formula converges faster with respect to the number on **k**-points than the DAPE formula or the finite electric field technique.

Second, the Raman spectra computed from first-principles can be helpful to interpret experimental Raman spectra. In particular, we were able to clarify some of the problems in the assignation of the E-modes in the ferroelectric phase of LiNbO₃. By comparing the theoretical Raman scattering efficiencies and infrared mode oscillator strengths to the corresponding experimental values, we showed that LiNbO₃ has two E-modes around 370 cm⁻¹.

Third, the difference between the EO properties of ferroelectrics and semiconductors can be explained from the ionic contribution to the EO coefficients. In the semiconductors, the ionic and electronic contributions are small and tend to cancel each other out. In contrast, in the ferroelectric phase of $LiNbO_3$ and $BaTiO_3$, the large EO response originates in the giant contribution of the successor of the soft mode, which combines low frequency, high polarity and high Raman susceptibility.

In the next Chapter, we will take advantage of the dominant contribution of the successor of the soft mode to build a model that allows us to study the finite temperature dependence of the EO coefficients and refractive indices of BaTiO₃.

4.8 References

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

- M. Veithen, X. Gonze and Ph. Ghosez, First-Principles Study of the Electro-Optic Effect in Ferroelectric Oxides, Phys. Rev. Lett. 93, 187401 (2004).
- M. Veithen and Ph. Ghosez, First-Principles study of the dielectric and dynamical properties of lithium niobate, Phys. Rev. B 65, 214302 (2002).

◊ R. Loudon, The Raman Effect in Crystals, Adv. Phys. 13, 423 (1964).

Chapter 5

Temperature dependence of the electrooptic tensor and refractive indices of $BaTiO_3$

5.1 Introduction

In the previous Chapter, we studied the EO properties of LiNbO₃, BaTiO₃ and PbTiO₃ for their quantum mechanical ground-state at 0 K. These calculations gave a qualitative insight into the mechanisms responsible for the large EO responses of these materials. However, we must be careful when we compare the computed values of the EO coefficients to experimental values measured at room temperature. It is well known that physical properties of ferroelectrics strongly depend on temperature and that they can present a divergent behavior in the vicinity of a phase transition. In case of LiNbO₃ and PbTiO₃, we expect the values of the EO coefficients computed at 0 K to be a good approximation of their room temperature values since the phase transition temperatures are quite high: 1480 and 763 K. In contrast, in case of BaTiO₃, the rhombohedral phase is stable at 0 K whereas the tetragonal phase discussed in Sec. 4.6.2 is stable at room temperature. The EO coefficients computed for this phase are therefore an extrapolation from 0 K and their comparison to experiment is questionable. Moreover, we were not able to compute the value of r_{42} for this phase since the ionic contribution to this coefficient is determined by an unstable *E*-mode.

In optical applications, it is mandatory to know precisely the dependence of the relevant properties on temperature. For instance, the temperature dependence of the EO coefficients and refractive indices often imposes serious limitations on modulators and other devices. In order to work at low operating voltage, the EO coefficients of a material should be as high as possible. Unfortunately, it has been observed that the higher the EO coefficients of a material, the stronger usually their temperature

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dependence [87].

Optical properties can also be used as an experimental probe. For example, it is possible to determine the phase diagram [178] and polarization [179,180] of disordered ferroelectrics from measurements of their birefringence as a function of temperature and composition. Moreover, it is possible to study ferroelectricity in ferroelectric thin films from measurements of their EO response [181].

In this Chapter, we introduce a method to compute the *finite temperature* dependence of the EO coefficients and refractive indices of ferroelectrics using a firstprinciples effective Hamiltonian [17]. This method is well suited for compounds in which the soft mode plays a dominant role and is applied to tetragonal BaTiO₃. We compare our approach with the model of DiDomenico and Wemple [182], a formalism widely used to discuss the temperature dependence of the optical properties in ferroelectrics [179, 180, 183]. In particular, we show why this model is valid although its underlying hypothesis is not satisfied.

In Sec. 5.2, we report the parameters of the lattice Wannier function and the effective Hamiltonian used in this study. In Sec. 5.3, this Hamiltonian is applied to study the temperature dependence of the polarization, the structural parameters, the dielectric tensor and the piezoelectric tensor of $BaTiO_3$. In Sec. 5.4, we extend this approach to study the temperature dependence of the EO coefficients and refractive indices of this compound. In Sec. 5.5, we report the results obtained for the tetragonal phase and in Sec. 5.6, we compare our approach with the Model of DiDomenico and Wemple.

5.2 Effective Hamiltonian for BaTiO₃

In this section, we describe the BaTiO₃ effective Hamiltonian of Ghosez and co-workers [184] used in this study. In this model, the full lattice Hamiltonian is projected on the subset of degrees of freedom defined by the unstable phonon branch of the cubic phase and the macroscopic (homogeneous) strain. To each unit cell, i, we associate a localized atomic displacement pattern that corresponds to the lattice Wannier function of the unstable phonon branch, $\boldsymbol{\xi}_i$. These Wannier functions define an orthonormal basis that spans the effective Hamiltonian subspace. Within this basis, a given set of values of the coordinates corresponds directly to a particular pattern of atomic displacement. This approach is different from the approach of Zhong and co-workers [17,18] who only used the soft mode at the Γ -point to built the localized atomic displacement pattern. Since the ferroelectric phase transition involves only small structural distortions, the Hamiltonian is expressed as a low-order Taylor expansion around the high-symmetry cubic structure. All the expansion parameters are determined from first-principles total energy and linear response calculations. The temperature dependent properties of the Hamiltonian are studied using classical Monte Carlo simulations on a big supercell containing M unit cells with periodic boundary conditions.

5.2.1 Lattice Wannier function of BaTiO₃

The lattice Wannier function of $BaTiO_3$ is constructed following the method described in Ref. [185]. The discussion that follows is close to that of $KNbO_3$ in Ref. [22]. It is also similar to the discussion of $PbTiO_3$ in Ref. [21] with the only difference that the lattice Wannier functions in $BaTiO_3$ and $KNbO_3$ are build from the eigenvectors of the dynamical matrix while the lattice Wannier function of $PbTiO_3$ is build from the eigenvectors of the force constant matrix. The choice of the dynamical matrix has the advantage that the effective Hamiltonian can be used in molecular dynamics simulations since the form of the kinetic energy is greatly simplified.

Following the discussion of Ref. [22], we can build a Ti-centered lattice Wannier function from the eigenvectors of the dynamical matrix at the high symmetry **q**-points Γ , X, M and R that correspond to the unstable phonon modes Γ_{15} , X_5 and M'_3 as well as the Ti-dominated stable phonon modes R'_{25} , X_1 and M'_5 [65,74]. To obtain an explicit form for the lattice Wannier function, we consider the symmetric coordination shells surrounding a Ti-site and identify the independent displacement patterns of each shell that transform according to the vector representation of the site symmetry group O_h . For a given shell there can be more than one pattern of displacements with a given transformation property. To each such pattern corresponds an independent amplitude parameter. By including the displacements of shells up to first neighbor Ba and second neighbor Ti shells as well as selected displacements of O shells at first, second and fourth neighbors, we obtain a total of 13 parameters. The first shell of Ba atoms has 2 independent displacement patterns. There are 1, 2 and 2 parameters for the zeroth, first and second shells of Ti atoms and 2, 3 and 1 parameters for the first, second and fourth shells of oxygen atoms. These displacement patterns are shown in Figure 5.1 for the z component of the lattice Wannier function.

To determine the numerical values of the parameters, we build the normalized eigenvectors¹ of the dynamical matrix, $v_{\mathbf{q}}(\kappa\alpha)$, for the phonon modes Γ_{15} , X_5 , M'_3 , R'_{25} , X_1 and M'_5 (the index κ labels an atom and α a Cartesian direction) from the parameterized lattice Wannier function using

$$v_{\mathbf{q}}(\kappa\alpha) = \sum_{j} e^{i\mathbf{q}\cdot\mathbf{R}_{j}} \hat{\xi}_{j}(\kappa\alpha)$$
(5.1)

where \mathbf{R}_j is a direct lattice vector and $\hat{\xi}_j(\kappa\alpha)$ is a lattice Wannier function centered at the Ti site in the jth unit cell. Eq. (5.1) specifies each component of the eigenvectors as a linear combination of the parameters to be determined. The values determined by solving the linear system of equations are reported in Table 5.1. As can be seen, the magnitude of these values decays rapidly with shell-radius. As a consequence, the lattice Wannier function is well localized around the Ti site. This justifies the fact that we did not include more shells in the construction of the lattice Wannier function.

¹The eigenvectors of the dynamical matrix, $v(\kappa\alpha)$, are related to the eigendisplacements defined in Eq. (3.20) by $v(\kappa\alpha) = \sqrt{M_{\kappa}}U(\kappa\alpha)$, where M_{κ} is the mass of atom κ .

Figure 5.1: z component of the Ti-centered lattice Wannier function of BaTiO₃. Ba, Ti and O atoms are represented by open squares, solid squares and circles respectively. Parameters labeling the displacement patterns correspond to the length of the displacements (arrows) of the atoms. a denotes the lattice parameter of the cubic unit cell.




Ba-parameters	b_1	0.0022330
	\mathbf{b}_{1p}	-0.0213426
Ti-parameters	d_0	0.8013753
	d_{1a}	-0.0408339
	d_{1b}	-0.0025517
	d_{2a}	-0.0029953
	d_{2b}	0.0052709
O-parameters	O_{1a}	-0.2082255
	O_{1b}	-0.2653019
	O_{2a}	-0.0043680
	O_{2b}	-0.0129174
	O_{2c}	0.0374073
	O_4	0.0003538

Table 5.1: Values of the lattice Wannier function parameters.

5.2.2 Determination of the parameters of the effective Hamiltonian

Following the work of Waghmare and Rabe [21], the effective Hamiltonian is expressed as the sum of five parts: a local mode self-energy, a short-range interaction between local modes, a long-range dipole-dipole interaction, an elastic energy and an interaction between local modes and macroscopic strains

$$\mathcal{H}_{eff}(\{\boldsymbol{\xi}_r\}, \{\boldsymbol{\eta}\}) = \mathcal{H}_{self}(\{\boldsymbol{\xi}_r\}) + \mathcal{H}_{short}(\{\boldsymbol{\xi}_r\}) \\ + \mathcal{H}_{dpl}(\{\boldsymbol{\xi}_r\}) + \mathcal{H}_{elas}(\{\boldsymbol{\eta}\}) + \mathcal{H}_{int}(\{\boldsymbol{\xi}_r\}, \{\boldsymbol{\eta}\}).$$
(5.2)

 $\boldsymbol{\xi}_r$ is the amplitude of the displacement along the lattice Wannier function in cell r and $\boldsymbol{\eta}$ the strain tensor.

The self-energy is the only part of the effective Hamiltonian that takes into account anharmonic interactions. It includes isotropic terms up to eighth order in $|\boldsymbol{\xi}_r|$ and cubic anisotropy at fourth order:

$$\mathcal{H}_{self}(\{\boldsymbol{\xi}_r\}) = \sum_r \left[A |\boldsymbol{\xi}_r|^2 + B |\boldsymbol{\xi}_r|^4 + C(\xi_{rx}^4 + \xi_{ry}^4 + \xi_{rz}^4) + D |\boldsymbol{\xi}_r|^6 + E |\boldsymbol{\xi}_r|^8 \right].$$
(5.3)

To evaluate the short-range interaction between local modes, we consider quadratic interactions up to third nearest neighbors with the most general form allowed by the space group symmetry:

$$\mathcal{H}_{short}(\{\boldsymbol{\xi}_r\}) = \sum_r \sum_{\hat{d}=nn1} \left\{ a_L(\boldsymbol{\xi}_r \cdot \hat{d})(\boldsymbol{\xi}_r(\hat{d}) \cdot \hat{d}) + a_T[\boldsymbol{\xi}_r \cdot \boldsymbol{\xi}_r(\hat{d}) - (\boldsymbol{\xi}_r \cdot \hat{d})(\boldsymbol{\xi}_r(\hat{d}) \cdot \hat{d})] \right\}$$

$$+\sum_{r}\sum_{\hat{d}=nn2} \left\{ b_{L}(\boldsymbol{\xi}_{r}\cdot\hat{d})(\boldsymbol{\xi}_{r}(\hat{d})\cdot\hat{d}) + b_{T1}(\boldsymbol{\xi}_{r}\cdot\hat{d}_{1})(\boldsymbol{\xi}_{r}(\hat{d})\cdot\hat{d}_{1}) + b_{T2}(\boldsymbol{\xi}_{r}\cdot\hat{d}_{2})(\boldsymbol{\xi}_{r}(\hat{d})\cdot\hat{d}_{2}) \right\} \\ +\sum_{r}\sum_{\hat{d}=nn3} \left\{ c_{L}(\boldsymbol{\xi}_{r}\cdot\hat{d})(\boldsymbol{\xi}_{r}(\hat{d})\cdot\hat{d}) + c_{T}[\boldsymbol{\xi}_{r}\cdot\boldsymbol{\xi}_{r}(\hat{d}) - (\boldsymbol{\xi}_{r}\cdot\hat{d})(\boldsymbol{\xi}_{r}(\hat{d})\cdot\hat{d})] \right\}.$$
(5.4)

The sums over \hat{d} in Eq. (5.4) are taken over the first (nn1), second (nn2) and third (nn3) nearest neighbors of site r that are located respectively in the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions. $\boldsymbol{\xi}_r(\hat{d})$ denotes the lattice Wannier function at a neighbor of site r in \hat{d} direction. The second neighbor sites are located along the diagonal of a square of side a (a is the lattice constant of the cubic unit cell). The unit vector \hat{d}_1 is in the plane of the square perpendicular to this diagonal, while \hat{d}_2 is perpendicular to the plane of the square. To describe the long-range interactions, we use a dipole-dipole form parameterized by the mode effective charge \overline{Z}^* and the electronic dielectric constant ε_{∞}

$$\mathcal{H}_{dpl}(\{\boldsymbol{\xi}_r\}) = \sum_r \sum_{\mathbf{d}} \frac{(\overline{Z}^*)^2}{\varepsilon_{\infty}} \frac{\boldsymbol{\xi}_r \cdot \boldsymbol{\xi}_r(\mathbf{d})) - 3(\boldsymbol{\xi}_r \cdot \hat{d})(\boldsymbol{\xi}_r(\hat{d}) \cdot \hat{d})}{|\mathbf{d}|^3}.$$
 (5.5)

The sum over \mathbf{d} in Eq. (5.5) is taken over all neighbors of site r.

The elastic energy is given by a second-order expansion of the energy with respect to the homogeneous strain variables $\eta_{\mu\nu}$

$$\mathcal{H}_{elas}(\{\boldsymbol{\eta}\}) = Nf \sum_{\mu=1}^{3} \eta_{\mu\mu} + \frac{N}{2} C_{11} \sum_{\mu=1}^{3} \eta_{\mu\mu}^{2} + \frac{N}{2} C_{12} \sum_{\substack{\mu,\nu=1\\\mu\neq\nu}}^{3} \eta_{\mu\mu} \eta_{\nu\nu} + \frac{N}{4} C_{44} \sum_{\substack{\mu,\nu=1\\\mu\neq\nu}}^{3} \eta_{\mu\nu}^{2}$$
(5.6)

and the coupling between the strain and the local modes is given by the expression

$$\mathcal{H}_{int}(\{\boldsymbol{\xi}_{r}\},\{\boldsymbol{\eta}\}) = g_{0}\left(\sum_{\mu=1}^{3}\eta_{\mu\mu}\right)\sum_{r}|\boldsymbol{\xi}_{r}|^{2} + g_{1}\sum_{\mu=1}^{3}\left(\eta_{\mu\mu}\sum_{r}\xi_{r\mu}^{2}\right) + g_{2}\sum_{\substack{\mu,\nu=1\\\mu<\nu}}^{3}\eta_{\mu\nu}\sum_{r}\xi_{r\mu}\xi_{r\nu}.$$
 (5.7)

The parameters used in the effective Hamiltonian have been obtained from LDA total energy and linear response calculations performed at the experimental lattice constant of $BaTiO_3$ as described in Ref. [21]. Their values are summarized in Table 5.2.

A	2.9080	a_L	0.3718	C_{11}	123.0243
B	11.5242	a_T	-0.4832	C_{12}	47.1910
C	23.2260	b_L	0.2302	C_{44}	192.6313
D	-53.1421	b_{T1}	0.0354	g_0	-7.2916
E	169.9803	b_{T2}	-0.1047	g_1	-51.8323
\overline{Z}^*	1.9220	c_L	0.2094	g_2	-2.2036
ε_{∞}	6.7467	c_T	-0.0389	f	3.0611

Table 5.2: Parameters in the effective Hamiltonian (units eV per unit cell, except for $\overline{Z}^* / \varepsilon_{\infty}$ which is dimensionless).

5.3 Structural & dielectric properties

5.3.1 Technical details

We solve the Hamiltonian using Monte Carlo (MC) simulations on a $12 \times 12 \times 12$ supercell (8640 atoms) with periodic boundary conditions. We typically do 15000 sweeps to equilibrate the system and 165000 additional sweeps to compute the average values $\langle \xi_{\alpha} \rangle$ and $\langle \eta_{\mu\nu} \rangle$ and the correlation functions [19,186] to get $\chi^{(1)}_{\alpha\beta}$ and $d_{\gamma\mu\nu}$. At each temperature, up to six calculations are carried out using different seeds to generate the random numbers. The linear term, f, in Eq. (5.6) is set to zero in the simulations, to compensate for the first-principles underestimate of the lattice constant.

5.3.2 Spontaneous polarization and spontaneous strain

Figure 5.2 shows the temperature dependence of the spontaneous polarization, \mathcal{P}^s , and spontaneous strain, η^s , computed from the average normal mode coordinate and strain

$$\mathcal{P}^{s} = \frac{\overline{Z^{*}}}{\Omega_{0}} \langle \boldsymbol{\xi} \rangle \tag{5.8}$$

$$\eta^s = \langle \eta \rangle. \tag{5.9}$$

At high temperature, we find that \mathcal{P}_x^s , \mathcal{P}_y^s and \mathcal{P}_z^s are close to zero indicating that the system is in the paraelectric phase. The tensile strains, η_1^s , η_2^s and η_3^s , are equal ² and the shear strains (Voigt notations), η_4^s , η_5^s and η_6^s are zero. Consequently, the high

²The elastic energy defined in Eq. 5.6 depends quadratically on the strain. We might therefore expect that the tensile strains, η_1^s , η_2^s and η_3^s , vanish in the cubic phase. The non-zero values of η_1^s , η_2^s and η_3^s in Figure 5.2, are due to the parameterization of the interaction between the strain and the local modes defined in Eq. (5.7) that depends on the average value of the squared local mode coordinates. These terms to not vanish in the cubic phase. Since \mathcal{H}^{int} depends linearly on the tensile strains (first and second term), η_1^s , η_2^s and η_3^s are non-zero in the cubic phase.

	Phase	Heff	Heff $[17]$	$\operatorname{Exp}[17]$
T_c (K)	O-R	190	200	183
	T-O	240	230	278
	C-T	335	297	403
$\mathcal{P}^s \ (C/m^2)$	R	0.45	0.43	0.33
	Ο	0.37	0.35	0.36
	Т	0.30	0.28	0.27

Table 5.3: Calculated phase transition temperatures, T_c , and saturated spontaneous polarizations, \mathcal{P}_s , of BaTiO₃. Our results are compared to the effective Hamiltonian calculations of Ref. [17] and to the experimental values quoted in the same reference.

temperature phase of BaTiO₃ is correctly predicted to be cubic. As the system is cooled down past 330 K, \mathcal{P}_z^s increases and becomes significantly larger than \mathcal{P}_x^s and \mathcal{P}_y^s . This indicates the transition to the tetragonal phase. The homogeneous strain variables confirm that the shape of the unit cell becomes tetragonal at this temperature. Two other phase transitions occur as the temperature is reduced further. The transition from the tetragonal to the orthorhombic phase occurs at 240 K (sudden increase of \mathcal{P}_x^s) and the transition from the orthorhombic to the rhombohedral phase occurs at 190 K (sudden increase of \mathcal{P}_y^s).

The sequence of transitions exhibited by the simulation is the same as observed experimentally. In Table 5.3, we compare the corresponding phase transition temperatures and spontaneous polarizations to the values of Zhong and co-workers [17, 18] obtained from a different parameterization of the effective Hamiltonian and to the experimental values. The theoretical results of the present study are close to the theoretical results of Ref. [17]. The T_c 's predicted from both effective Hamiltonians deviate from the experimental T_c 's. As discussed in Ref. [187], this discrepancy can be attributed to an incorrect modeling of the thermal expansion in the effective Hamiltonian.

5.3.3 Dielectric and piezoelectric tensor

In this section we discuss the temperature dependence of the static dielectric tensor and the piezoelectric tensor. We focus on the tetragonal phase, which is the most important one for practical applications since it is stable at room temperature. In the Monte Carlo simulations, the static dielectric susceptibilities and the piezoelectric coefficients can be expressed as correlation functions. Following Ref. [186], we can write

$$\chi_{\alpha\beta}^{(1)} = \frac{\beta \overline{Z^*}}{\Omega_0} \left(\frac{1}{M} \langle \sum_i \xi_{i\alpha} \sum_j \xi_{j\beta} \rangle - M \langle \xi_\alpha \rangle \langle \xi_\beta \rangle \right)$$
(5.10)

Figure 5.2: Temperature dependence of the spontaneous polarization and the spontaneous strain in the cubic (C), tetragonal (T), orthorhombic (O) and rhombohedral (R) phases of $BaTiO_3$.



Figure 5.3: Temperature dependence of the static dielectric constants in the cubic (C) and tetragonal (T) phases of $BaTiO_3$. Our results are compared to the results of the effective Hamiltonian calculations of Garcia and Vanderbilt (GV) [20] and to the experiment [177]. The bottom and top *x*-axes correspond respectively to the theoretical and experimental temperatures (see text).



$$d_{\gamma\mu\nu} = \beta \overline{Z^*} \left(\langle \eta_{\mu\nu} \sum_{j} \xi_{j\gamma} \rangle - M \langle \eta_{\mu\nu} \rangle \langle \xi_{\gamma} \rangle \right)$$
(5.11)

where $\beta = \frac{1}{kT}$.

In Figure 5.3, we show the temperature dependence of the static dielectric coefficients ε_{11} and ε_{33} . Our results are compared to the results of Garcia and Vanderbilt [20] who used the effective Hamiltonian of Refs. [17,18] and to the experimental results [177]. As discussed in Sec. 5.3.2, the theoretical phase transition temperatures systematically underestimate the experiment. In order to provide a meaningful comparison of our results to experiment, we rescaled the theoretical temperatures as in Ref. [19]. The bottom x-axis in Figure 5.3 shows the temperatures used in the Monte Carlo simulations while the top x-axis shows the corresponding experimental temperatures after a linear adjustment of the scale in order to match the theoretical and experimental phase transition temperatures. Our results are in good agreement with the results of Garcia and Vanderbilt. Both models correctly predict a divergence of the dielectric constants at the cubic to tetragonal phase transition. In the tetragonal phase, ε_{33} diverges at the transition to the cubic phase. At room temperature, the theoretical value of 120 is in excellent agreement with the experimental value of 130. ε_{11} is correctly predicted to diverge at the transition from the tetragonal to the Figure 5.4: Temperature dependence of the piezoelectric constants in the cubic (C) and tetragonal (T) phases of $BaTiO_3$. Our results are compared to the results of the effective Hamiltonian calculations of Garcia and Vanderbilt (GV) [19] and to the experiment [177]. The bottom and top x-axes correspond respectively to the theoretical and experimental temperatures (see text).



orthorhombic phase. The amplitude of the divergence is underestimated by the effective Hamiltonian of Ghosez and co-workers. We obtain a value of about 2200 that underestimates the experimental value of 4400 by a factor of 2.

Figure 5.4 shows the temperature dependence of the piezoelectric coefficients d_{31} and d_{33} . The temperatures on the top x-axis have been rescaled as described above. Our simulations and those of Garcia and Vanderbilt [19] correctly predict d_{31} and d_{33} to diverge at the transition from the tetragonal to the cubic phase and to vanish in the cubic phase. At room temperature, the theoretical d_{31} (-33 pC/N) and d_{33} (105 pC/N) are in good agreement with the experimental values of -33 and 90 pC/N [177]. In case of the piezoelectric coefficient d_{24} (not shown in Figure 5.4), the agreement between theory and experiment is less good. We obtain a value of 42 pC/N that strongly underestimates the experimental value of 564 pC/N.

5.4 EO coefficients & refractive indices

5.4.1 Formalism

The principal refractive indices, n_i , can be computed as the square root of the eigenvalues of the optical dielectric tensor. At finite temperature, T, we can write

$$\langle \varepsilon_{ij}(\boldsymbol{\xi}_r, \boldsymbol{\eta}) \rangle = \delta_{ij} + 4\pi \langle \chi_{ij}^{(1)}(\boldsymbol{\xi}_r, \boldsymbol{\eta}) \rangle.$$
(5.12)

(1)

Let us write $\boldsymbol{\xi}_r$ and $\boldsymbol{\eta}$ as

$$\begin{aligned} \boldsymbol{\xi}_r &= \langle \boldsymbol{\xi} \rangle + \delta \boldsymbol{\xi}_r \\ \boldsymbol{\eta} &= \langle \boldsymbol{\eta} \rangle + \delta \boldsymbol{\eta} \end{aligned} \tag{5.13}$$

where $\delta \boldsymbol{\xi}_r$, $\delta \boldsymbol{\eta}$ denote the deviations from the average values. If we develop $\langle \chi_{ij}^{(1)}(\boldsymbol{\xi}_r, \boldsymbol{\eta}) \rangle$ as a Taylor expansion about the paraelectric structure, we can separate the terms depending on $\langle \boldsymbol{\xi} \rangle$ and $\langle \boldsymbol{\eta} \rangle$ only from those involving also $\delta \boldsymbol{\xi}_r$ and $\delta \boldsymbol{\eta}$. At finite temperature, the dielectric susceptibility can therefore be expressed as

$$\langle \chi_{ij}^{(1)}(\boldsymbol{\xi}_r, \boldsymbol{\eta}) \rangle = \chi_{ij}^{(1)}(\langle \boldsymbol{\xi} \rangle, \langle \boldsymbol{\eta} \rangle) + \langle \chi_{ij}^{(1)}(\langle \boldsymbol{\xi} \rangle, \langle \boldsymbol{\eta} \rangle, \delta \boldsymbol{\xi}_r, \delta \boldsymbol{\eta}) \rangle.$$
(5.14)

The first term of the right hand side of Eq. (5.14) describes the variations of $\chi_{ij}^{(1)}$ due to the average crystal lattice distortions. It is responsible for the discontinuity of n_i at the phase transition in ferroelectrics such as BaTiO₃ (see Ref. [188]). Following Ref. [188], we consider terms up to the second order in the Taylor expansion of $\chi_{ij}^{(1)}(\langle \boldsymbol{\xi} \rangle, \langle \boldsymbol{\eta} \rangle)$

$$\chi_{ij}^{(1)}(\langle \boldsymbol{\xi} \rangle, \langle \boldsymbol{\eta} \rangle) = \chi_{ij}^{(1)}(0,0) + \sum_{\alpha} \frac{\partial \chi_{ij}^{(1)}}{\partial \xi_{\alpha}} \bigg|_{0,0} \langle \xi_{\alpha} \rangle + \sum_{\mu,\nu} \frac{\partial \chi_{ij}^{(1)}}{\partial \eta_{\mu\nu}} \bigg|_{0,0} \langle \eta_{\mu\nu} \rangle + \frac{1}{2} \sum_{\alpha,\beta} \frac{\partial^2 \chi_{ij}^{(1)}}{\partial \xi_{\alpha} \partial \xi_{\beta}} \bigg|_{0,0} \langle \xi_{\alpha} \rangle \langle \xi_{\beta} \rangle + \frac{1}{2} \sum_{\mu,\nu} \sum_{\mu',\nu'} \frac{\partial^2 \chi_{ij}^{(1)}}{\partial \eta_{\mu\nu} \partial \eta_{\mu'\nu'}} \bigg|_{0,0} \langle \eta_{\mu\nu} \rangle \langle \eta_{\mu'\nu'} \rangle + \sum_{\alpha} \sum_{\mu,\nu} \frac{\partial^2 \chi_{ij}^{(1)}}{\partial \xi_{\alpha} \partial \eta_{\mu\nu}} \bigg|_{0,0} \langle \xi_{\alpha} \rangle \langle \eta_{\mu\nu} \rangle.$$
(5.15)

In Eq. (5.15), the first-order derivative of $\chi_{ij}^{(1)}$ with respect to ξ_{α} and the mixed second-order derivatives of $\chi_{ij}^{(1)}$ with respect to ξ_{α} and $\eta_{\mu\nu}$ are zero by symmetry ³.

³The soft mode in the paraelectric phase is polar (infrared active). The quantities $\frac{\partial \chi_{ij}^{(1)}}{\partial \xi_{\alpha}}$ and $\frac{\partial^2 \chi^{(1)}}{\partial \xi_{\alpha}}$

 $[\]frac{\partial^2 \chi_{ij}^{(1)}}{\partial \xi_\alpha \partial \eta_{\mu\nu}}$ are related to the Raman susceptibilities of the soft mode in different centrosymmetric configurations of BaTiO₃. They are zero by symmetry because in a centrosymmetric crystal, a phonon mode cannot be simultaneously Raman and infrared active.

The second term in the right hand side of Eq. (5.14) represents the variations of $\chi_{ij}^{(1)}$ due to thermal fluctuations and to their correlations [189]. It determines the variations of n_i in the paraelectric phase. This term is difficult to compute in practice. However, in usual ferroelectrics such as BaTiO₃, the variations of n_i in the paraelectric phase are small compared to their variation at the phase transition. Following Ref. [188], we will neglect the second term of the right hand side of Eq. (5.14) since we are interested in the variation of n_i below the phase transition temperature (T_c) where we expect the first term to dominate. We note that this approximation is not always valid. In disordered ferroelectrics such as Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) or Pb(Zn_{1/3}Nb_{2/3})O₃ (PZN), large anomalies of n_i have been observed above T_c where $\langle \boldsymbol{\xi} \rangle$ and $\langle \boldsymbol{\eta} \rangle$ are zero [180, 190]. Consequently, the first term of Eq. (5.14) is constant and these anomalies are related to the second term.

The linear EO effect is related to the first-order change of the optical dielectric tensor induced by a static or low frequency electric field, \mathcal{E} . Using an approach similar to the one presented in Sec. 3.3.4, the unclamped EO coefficient, $r_{ij\gamma}^{\sigma}$, can be decomposed into three terms:

$$r_{ij\gamma}^{\sigma} = r_{ij\gamma}^{el} - \frac{4\pi}{n_i^2 n_j^2} \sum_{\alpha=1}^3 \left. \frac{\partial \chi_{ij}^{(1)}}{\partial \xi_{\alpha}} \right|_{\langle \xi \rangle, \langle \eta \rangle} \frac{\partial \langle \xi_{\alpha} \rangle}{\partial \mathcal{E}_{\gamma}} \\ - \frac{4\pi}{n_i^2 n_j^2} \sum_{\mu,\nu=1}^3 \left. \frac{\partial \chi_{ij}^{(1)}}{\partial \eta_{\mu\nu}} \right|_{\langle \xi \rangle, \langle \eta \rangle} \frac{\partial \langle \eta_{\mu\nu} \rangle}{\partial \mathcal{E}_{\gamma}}.$$
(5.16)

The first term is a bare electronic part. Its value is assumed independent of temperature in the ferroelectric phase and equal to that reported in Table 4.16. It vanishes in the cubic phase. The last two terms correspond to the ionic and strain contributions ⁴. They depend on (i) the variation of $\langle \boldsymbol{\xi} \rangle$ and $\langle \boldsymbol{\eta} \rangle$ in the field and (ii) the variation of $\chi_{ij}^{(1)}$ with atomic displacements and strains. The relaxations of the atomic positions and macroscopic strains within the field are related to the static dielectric susceptibility tensor $\chi_{\alpha\gamma}^{(1)}$ and the piezoelectric tensor $d_{\gamma\mu\nu}$:

$$\frac{\partial \langle \xi_{\alpha} \rangle}{\partial \mathcal{E}_{\gamma}} = \frac{\Omega_0}{\overline{Z}^*} \chi^{(1)}_{\alpha\gamma}$$
(5.17)

$$\frac{\partial \langle \eta_{\mu\nu} \rangle}{\partial \mathcal{E}_{\gamma}} = d_{\gamma\mu\nu}. \tag{5.18}$$

They can be computed from Eqs. (5.10) and (5.11). The dependence of $\chi_{ij}^{(1)}$ on $\langle \boldsymbol{\xi} \rangle$ and $\langle \boldsymbol{\eta} \rangle$ can be estimated through Eq. (5.15):

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \xi_{\alpha}} \bigg|_{\langle \boldsymbol{\xi} \rangle, \langle \eta \rangle} = \sum_{\beta=1}^{3} \left. \frac{\partial^{2} \chi_{ij}^{(1)}}{\partial \xi_{\alpha} \partial \xi_{\beta}} \right|_{0,0} \langle \xi_{\beta} \rangle$$
(5.19)

⁴This decomposition is different from the one of Sec. 3.3.4. As it is discussed in Appendix B, the derivative $\frac{\partial \xi_{\alpha}}{\partial \mathcal{E}_{\gamma}}$ involves a coupling with the strain that is not included in the ionic contribution of Sec. 3.3.4.

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \eta_{\mu\nu}}\bigg|_{\langle \boldsymbol{\xi} \rangle, \langle \eta \rangle} = \frac{\partial \chi_{ij}^{(1)}}{\partial \eta_{\mu\nu}}\bigg|_{0,0} + \sum_{\mu', \nu'=1}^{3} \frac{\partial^2 \chi_{ij}^{(1)}}{\partial \eta_{\mu\nu} \partial \eta_{\mu'\nu'}}\bigg|_{0,0} \langle \eta_{\mu'\nu'} \rangle.$$
(5.20)

5.4.2 Determination of parameters

In Sec. 5.4.1, we used a second-order Taylor expansion to describe the dependence of $\chi_{ij}^{(1)}$ on atomic positions and strains. In case of the strain, η , this quadratic approximation is reasonable since the unit cell deformations at the phase transition are rather small in most ferroelectrics. In contrast, the internal distortions are larger and the purely quadratic dependence of $\chi_{ij}^{(1)}$ on $\langle \boldsymbol{\xi} \rangle$ is questionable. To check this hypothesis, we computed the optical dielectric constants of BaTiO₃ as a function of atomic displacements along the soft-mode eigenvector polarized along z while keeping constant the cubic lattice parameters. Figure 5.5 shows the dependence of ε_{xx} and ε_{zz} on the polarization associated with these distortions. We also show the corresponding double-well potential. The variation of ε appears *highly anharmonic*. We had to use an 8th order polynome to fit the data in Figure 5.5 (a) [solid line] and the curvature of $\varepsilon(\mathcal{P}_z)$ decreases as \mathcal{P}_z increases. Consequently, a second-order expansion around the cubic phase will lead to a strong overestimate of the value of ε_{zz} in the tetragonal phase of BaTiO₃.

In spite of that, the use of a quadratic approximation may be justified in a different way. As discussed in Sec. 5.3.2, $\langle \boldsymbol{\xi} \rangle$ and $\langle \boldsymbol{\eta} \rangle$ are discontinuous at the phase transition of BaTiO₃ and their temperature dependence in the tetragonal phase is small. In practice, we can use the formula

$$\frac{\partial^2 \chi_{ij}^{(1)}}{\partial \xi_\alpha \partial \xi_\beta} \bigg|_{0,0} \cong \frac{1}{\xi_{F\beta}} \frac{\partial \chi_{ij}^{(1)}}{\partial \xi_\alpha} \bigg|_{\xi_F, \eta=0}, \qquad (5.21)$$

where ξ_F denotes the position of the minimum of the double well potential in the positive z-direction, as an approximation of the coefficients of the quadratic terms in the second-order Taylor expansion of $\chi_{ij}^{(1)}(\langle \boldsymbol{\xi} \rangle, \langle \boldsymbol{\eta} \rangle)$. The variation of ε_{xx} and ε_{zz} that corresponds to this quadratic approximation is shown by the dotted lines in Figure 5.5 (a).

For the $r_{ij\gamma}^{\sigma}$, Eq. (5.21) is accurate around the tetragonal phase⁵ since the tangents to the solid curve and the corresponding dotted curve in Figure 5.5 (a) have the same slope at the minima of the double well potential. Indeed, Eq. (5.21) is equivalent to a linear approximation of $\partial \chi_{ii}^{(1)} / \partial \xi_{\alpha}$ around these minima

$$\frac{\partial \chi_{ij}^{(1)}}{\partial \xi_{\alpha}} \bigg|_{\langle \xi \rangle, \langle \eta \rangle} \cong \sum_{\beta=1}^{3} \frac{1}{\xi_{F\beta}} \frac{\partial \chi_{ij}^{(1)}}{\partial \xi_{\alpha}} \bigg|_{\xi_{F}, \eta=0} \langle \xi_{\beta} \rangle.$$
(5.22)

⁵For the other phases, it might be necessary to go beyond the second-order Taylor expansion of $\chi_{ij}^{(1)}(\langle \boldsymbol{\xi} \rangle, \langle \boldsymbol{\eta} \rangle)$ and to compute the exact values of the derivatives of $\chi_{ij}^{(1)}$.

Figure 5.5: Dependence of the optical dielectric constants (a) and energy (b) on the polarization in $BaTiO_3$. The points correspond to the values computed for various internal distortions. The solid lines correspond to a polynomial fit and the dotted lines to the quadratic approximation explained in the text.



For n_1 and n_3 , Eq. (5.21) reproduces the correct behavior but leads to an overestimate of n_3 as can be seen in Figure 5.5 (a).

The derivatives of $\chi_{ij}^{(1)}$ appearing in Eq. (5.15) are computed within the LDA. The second order derivative of $\chi_{ij}^{(1)}$, as defined in Eq. 5.21, are computed on a $10 \times 10 \times 10$ grid of special **k**-points. We use the 2n + 1 theorem to compute the first-order derivatives of $\chi_{ij}^{(1)}$ in a structure where the soft-mode eigenvector was frozen with an amplitude corresponding to the double-well potential minimum, while keeping constant the experimental cubic lattice. To take into account the variations of the soft mode eigenvectors at the phase transition, these first-order derivatives were projected on the eigenvectors of the soft E and A₁ modes in the tetragonal phase. The strain derivatives in Eq. (5.15) are computed from finite differences on a $6 \times 6 \times 6$ grid of special **k**-points.

Table 5.4: First- and second-order derivatives of $\chi_{ij}^{(1)}$. The second-order derivatives with respect to ξ are reported in 10⁻⁵ bohr⁻². The strain derivatives are dimensionless. They are reported in Voigt notations.

$\partial\chi^{(1)}_{11}/\partial\eta_1$	-0.0657804
$\partial\chi^{(1)}_{22}/\partial\eta_1$	0.2680479
$\partial\chi^{(1)}_{23}/\partial\eta_4$	0.1026835
$\partial\chi^{(1)}_{11}/\partial\eta_1\partial\eta_1$	0.7692116
$\partial\chi^{(1)}_{22}/\partial\eta_1\partial\eta_1$	0.2204320
$\partial\chi^{(1)}_{11}/\partial\eta_1\partial\eta_2$	1.3173122
$\partial\chi^{(1)}_{33}/\partial\eta_1\partial\eta_2$	0.2063500
$\partial\chi^{(1)}_{23}/\partial\eta_1\partial\eta_4$	-0.1142776
$\partial \chi^{(1)}_{31}/\partial \eta_1 \partial \eta_5$	0.2633623
$\partial\chi^{(1)}_{11}/\partial\eta_4\partial\eta_4$	0.6583961
$\partial\chi^{(1)}_{22}/\partial\eta_4\partial\eta_4$	3.2084150
$\partial\chi^{(1)}_{12}/\partial\eta_4\partial\eta_5$	-0.1149256
$\partial \chi^{(1)}_{33}/\overline{\partial \xi_3 \partial \xi_3}$	-3.4355776
$\partial \chi^{(1)}_{22}/\partial \xi_3 \partial \xi_3$	-1.1950726
$\partial\chi^{(1)}_{32}/\partial\xi_3\partial\xi_2$	-0.9530569

The values of all independent coefficients appearing in Eq. (5.15) are summarized in Table 5.4.

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Results 5.5

Figure 5.6 shows the principal refractive indices (a) and the stress-free EO coefficients (b) in the cubic and tetragonal phases of $BaTiO_3$. As discussed in Sec. 5.3, the predicted T_c 's do not perfectly match the experimental values. In order to obtain calculated values comparable with experimental values, we rescale the temperatures as in Sec. 5.3.3. The bottom x-axis shows the temperatures used in the MC simulations while the top x-axis shows the corresponding experimental temperatures after a linear adjustment of the scale in order to match the theoretical and experimental T_c 's.

The LDA value of the refractive index in the cubic phase ($n_c = 2.59$) is about 7 % larger than the experimental value [191] (2.4). In order to compare the theoretical and experimental values of n_1 and n_3 in the tetragonal phase, we report in Figure 5.6 (a) the difference between the refractive indices of the cubic and tetragonal phases. The internal distortions related to the spontaneous polarization mainly determine the variation of n_1 and n_3 while the spontaneous strain only plays a minor role. In particular, Figure 5.6: Temperature dependence of the refractive indices (a) and EO coefficients (b) in the cubic (C) and tetragonal (T) phases of $BaTiO_3$. The open (solid) symbols correspond to the theoretical (experimental [177,191]) values. The bottom and top x-axes correspond respectively to the theoretical and experimental temperatures (see text).



the discontinuous evolution of n_1 and n_3 at the phase transition is due to the discontinuous evolution of the spontaneous polarization and the spontaneous strain discussed in Sec. 5.3.2. The values of $\partial^2 \chi_{33}^{(1)} / \partial \xi_3^2$ and $\partial^2 \chi_{11}^{(1)} / \partial \xi_3^2$ [see Table 5.4] are negative. Consequently, n_1 and n_3 are smaller in the tetragonal phase than in the cubic phase and they decrease as the temperature decreases. Because the first coefficient is about two times more negative than the second the variation of n_3 is more pronounced than that of n_1 . At room temperature, the effective Hamiltonian predicts a large negative birefringence in agreement with the experiment although the theoretical value (-0.095) is somewhat more negative than the experimental value (-0.056 [191]).

The model Hamiltonian properly reproduces the finite temperature dependence of the EO tensor. The three coefficients vanish in the cubic phase as requested by symmetry. Also, r_{13}^{σ} and r_{33}^{σ} diverge at the cubic \rightarrow tetragonal transition while r_{42}^{σ} diverges at the tetragonal \rightarrow orthorhombic transition. According to Eqs. (5.16), (5.17) and (5.18), these divergences have the same origin as those of the static dielectric and piezoelectric tensors. At room temperature, the theoretical r_{13}^{σ} (25 pm/V) and r_{33}^{σ} (122 pm/V) are in reasonable agreement with the experimental values [177] of 8 and 105 pm/V. r_{42}^{σ} is correctly predicted to be about one order of magnitude larger than r_{13}^{σ} and r_{33}^{σ} even if our result (622 pm/V) underestimates the experimental value of 1300 pm/V (not shown in Figure 5.6 (b)). Part of this discrepancy comes from the theoretical value of the static dielectric constant ε_{11} (2600) that underestimates the experimental value (4400) [177] as discussed in Sec. 5.3.3.

5.6 Model of DiDomenico and Wemple

We can now compare our approach with the model of DiDomenico and Wemple [182] conventionally used to explain the temperature dependence of optical properties in ferroelectrics. In this latter model, the linear EO effect is described as a quadratic effect biased by the spontaneous polarization. In the paraelectric phase, the linear EO tensor is zero by symmetry and the lowest-order EO effect is quadratic. Using the polarization \mathcal{P}_{α} as the basic variable, we can write

$$\Delta \left(\varepsilon^{-1}\right)_{ij} = \sum_{\alpha,\beta=1}^{3} g_{ij\alpha\beta} \mathcal{P}_{\alpha} \mathcal{P}_{\beta}$$
(5.23)

where $g_{ij\alpha\beta}$ is the quadratic polarization-optic tensor. In the ferroelectric phase, \mathcal{P}_{α} can be expressed as the sum of a spontaneous and an induced part

$$\mathcal{P}_{\alpha} = \mathcal{P}_{\alpha}^{s} + \sum_{\beta=1}^{3} \chi_{\alpha\beta}^{(1)} \mathcal{E}_{\beta}.$$
 (5.24)

With the hypothesis that (i) the g-coefficients remain constant at the phase transition and (ii) the dependence of the optical dielectric tensor on \mathcal{P} is purely quadratic, we obtain the following expressions in the ferroelectric phase

$$r_{ij\gamma} = 2 \sum_{\alpha,\beta=1}^{3} g_{ij\alpha\beta} \mathcal{P}^{s}_{\alpha} \chi^{(1)}_{\beta\gamma}$$
(5.25)

$$\varepsilon_{ij}(\boldsymbol{\xi}_F, \eta_F) = \varepsilon_{ij}(0, 0) - n_i^2 n_j^2 \sum_{\alpha, \beta=1}^3 g_{ij\alpha\beta} \mathcal{P}_{\alpha}^s \mathcal{P}_{\beta}^s.$$
(5.26)

As demonstrated above, in the case of BaTiO₃, the dependence of ε_{ij} on the polarization is highly anharmonic and a similar behavior in other ferroelectrics may be expected. Consequently, the use of Eqs. (5.25) and (5.26) is questionable. If we compute the *g*-coefficients from a similar approximation as in Eq. (5.21), we can justify

Exp. [183] Exp. (i,j,α,β) Present [87](3,3,3,3)17.8 15 ± 3 103 (2,2,3,3)5.0 3.8 ± 0.6 (3,2,3,2)4.5 7 ± 1.5 9

Table 5.5: Second-order clamped polarization optic coefficients $g_{ij\alpha\beta}$ (10⁻² m⁴ C⁻²) of cubic BaTiO₃.

the use of Eqs. (5.25) and (5.26). However, the so computed g-coefficients can no more be identified to the quadratic polarization-optic coefficients of the *paraelectric* phase: according to Eq. (5.22), they define the slope of $\varepsilon_{ij}(\mathcal{P})$ in the *ferroelectric* phase.

With the approximation that the ferroelectric distortion is restricted to the soft mode eigenvector, the *g*-coefficients can be related to the second-order derivatives of $\chi_{ii}^{(1)}$ as given by Eq. (5.21)

$$g_{ij\alpha\beta} = \frac{-4\pi}{n_i^2 n_j^2} \frac{\Omega_0^2}{2(\overline{Z}^*)^2} \left. \frac{\partial^2 \chi_{ij}^{(1)}}{\partial \xi_\alpha \partial \xi_\beta} \right|_{0,0}.$$
 (5.27)

The theoretical values of the clamped $g_{ij\alpha\beta}$ reported in Table 5.5 are close to the experimental values. On the one hand, this agreement gives a further justification of the approximations used in our approach and validates the use of an effective Hamiltonian to predict optical properties. On the other hand, Eq. (5.27) may be used to compute the $g_{ij\alpha\beta}$ coefficients in situations, where no experimental data are available.

5.7 Conclusions

In this Chapter, we have presented an efficient method to compute the temperature dependence of the EO coefficients and the refractive indices of ferroelectrics from a first-principles effective Hamiltonian. We have successfully applied this formalism to $BaTiO_3$ in its tetragonal phase.

We first described the $BaTiO_3$ effective Hamiltonian used in this study. We reported the parameters of the lattice Wannier function and of the energy expansion and we showed that this effective Hamiltonian correctly predicts the finite temperature dependence of the spontaneous polarization, the spontaneous strain, the static dielectric tensor and the piezoelectric tensor.

We then proposed an extension of the effective Hamiltonian to study the temperature dependence of the EO coefficients and indexes of refraction of ferroelectrics. We showed that the dependence of the optical dielectric tensor on the structural parameters is highly anharmonic. This result a priori invalidates the usual hypothesis, which assumes a quadratic dependence of the optical dielectric constants on these parameters. Nevertheless, we showed that it is possible to justify the use of a quadratic approximation by using a modified expression of the second-order terms, which includes most of the anharmonic dependence.

We applied this formalism to BaTiO₃ in its tetragonal phase. The discontinuous evolution of the refractive indexes at the transition from the cubic to the tetragonal phase and the negative birefringence at room temperature can be explained from the internal distortions related to the spontaneous polarization and the negative values of the parameters $\partial^2 \chi_{ij}^{(1)} / \partial \xi_{\alpha} \partial \xi_{\beta}$. Our model correctly predicts the EO coefficients to vanish in the cubic phase and to diverge at the phase transitions. These divergences have the same origin as the divergences of the static dielectric and piezoelectric coefficients.

We compared our formalism to the model of DiDomenico and Wemple, which describes the linear EO effect in ferroelectrics as a quadratic effect biased by the spontaneous polarization. Although we showed that the dependence of the optical dielectric constants on the polarization is highly anharmonic, this model can be justified if we modify the definition of the quadratic polarization optic coefficients to take into account higher-order effects.

It is interesting to note that models similar to the model of DiDomenico and Wemple are used to describe the piezoelectric effect in ferroelectrics as a quadratic effect biased by the spontaneous polarization. These models assume that the strain in the paraelectric phase depends quadratically on the polarization [4] (electrostrictive effect). The results presented in this Chapter call into question the hypothesis of a quadratic dependence. We must therefore be careful when we apply such models in practical situations such as the study of fatigue in ferroelectrics [192].

5.8 References

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

- ◊ M. Veithen and Ph. Ghosez, Temperature dependence of the electro-optic tensor and refractive indices of BaTiO₃ from first-principles, accepted for publication in Phys. Rev. B.
- & W. Zhong, D. Vanderbilt and K. M. Rabe, Phase Transitions in BaTiO₃ from First Principles, Phys. Rev. Lett. 73, 1861 (1994).
- A. Garcia and D. Vanderbilt, Electromechanical behavior of BaTiO₃ from first principles, Appl. Phys. Lett. 72, 2981 (1998).
- ◊ U. V. Waghmare and K. M. Rabe, Ab initio statistical mechanics of the ferroelectric phase transition in PbTiO₃, Phys. Rev. B 55, 6161 (1997).

 P. Bernasconi, M. Zgonik and P. Günter, Temperature dependence and dispersion of electro-optic and elastooptic effect in perovskite crystals, J. Appl. Phys. 78, 2651 (1995).

Conclusions and Perspectives

First-principles calculations performed within density functional theory are a powerful tool to study the ground-state and linear response properties of materials. In this work, we extended this formalism to study the electron localization tensor and the nonlinear response to electric fields of ferroelectrics and other insulators. The techniques we developed are based on recent theoretical advances such as the modern theory of polarization, the theory of Wannier functions, the effective Hamiltonian approach and the density functional perturbation theory. Our work can be summarized as follows.

As a first step, we studied the electron localization tensor. This formalism makes it possible to quantify the degree of electron localization in materials. We set up a bandby-band decomposition of the localization tensor that allows to study the localization of electrons occupying individual groups of bands in a solid and to overcome the problems in the definition of the localization tensor in pseudopotential calculations. In contrast to the polarization or the Born effective charges, which are, in the parallel gauge, equal to the sum of the contributions of the individual bands, we had to distinguish between the variance and the covariance in the band-by-band decomposition of the localization tensor. We applied this formalism to several oxides and we showed that the bandby-band decompositions of the Born effective charges and the localization tensor are sensitive probes to study the electronic structure of materials. In addition, we observed only small variations of electron localization during the phase transitions of BaTiO₃ and LiNbO₃. This surprising result was explained in terms of the electronic structure of these compounds as interpreted in the Harrison model.

As a second step, we presented two methods to study the nonlinear responses of insulators to electric fields. The first method considers the response to infinitesimal fields. It allows a systematic study of nonlinear response properties from density functional perturbation theory. However, in order to use this technique, each response property and approximation of the exchange-correlation energy has to be implemented explicitly. We reported the LDA expressions of the nonlinear optical susceptibilities, the electro-optic coefficients and the Raman scattering efficiencies of transverse and longitudinal optical phonons. The second method considers the response to finite electric fields. It consists in the iterative minimization of an electric field dependent energy functional. Various linear and nonlinear response properties can be computed from finite differences and do not require any additional implementations. Moreover, most

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approximations of the exchange-correlation energy available for ground-state calculations at zero electric field can also be used in finite electric field calculations.

As a third step, we applied both methods to various ferroelectrics and semiconductors. The main results of this study can be summarized as follows. First, the two methods can equivalently be used to study the nonlinear response of insulators to electric fields. However, the perturbative approach within the PEAD formulation converges faster with respect to the k-point sampling than the DAPE formulation or the finite electric field technique. Second, by comparing theoretical infrared oscillator strengths and Raman scattering efficiencies to the experiment, we were able to clarify some of the ambiguities in the assignation of the E-modes of $LiNbO_3$. This shows that the theoretical computation of Raman spectra is a powerful tool to interpret experimental Raman spectra. Third, the amplitude of the electro-optic coefficients in $BaTiO_3$ and $LiNbO_3$ is mainly determined by the ionic contribution of the successor of the soft mode in the ferroelectric phase that combines a high polarity, a high Raman susceptibility and a low frequency. In contrast, the contribution of a similar mode in PbTiO₃ is much weaker because of its low Raman susceptibility. This result underlines the important contribution of the soft mode to the electro-optic coefficients of $BaTiO_3$ and $LiNbO_3$ in line with its well-known contributions to the dielectric constants and with its dominant role in the ferroelectric phase transition of these materials. It also points out the distinct behavior of $PbTiO_3$, in spite of its perovskite structure similar to BaTiO₃.

As a fourth step, using the fact that the electro-optic coefficients in $BaTiO_3$ and $LiNbO_3$ are dominated by the successor of the soft mode in the ferroelectric phase, we developed in Chapter 5 a model to study the finite temperature dependence of optical properties of ferroelectrics. This model consists in an extension of the standard effective Hamiltonian to take into account the dependence of the optical dielectric constants on atomic positions and strains. We applied the model to $BaTiO_3$ in its tetragonal phase and we showed that it correctly predicts the temperature dependence of the electro-optic coefficients and the refractive indexes. In addition, we were able to give a microscopic interpretation of the model of DiDomenico and Wemple and to explain why this model is successful in many situations although the dependence of the optical dielectric constants on the polarization is not quadratic as erroneously assumed.

The theoretical advances presented in Chapter 2 and 3 have been implemented in the ABINIT code. They are therefore freely accessible for future investigations and open new perspectives.

A first potential application is the systematic computation of Raman scattering efficiencies. Together with the infrared oscillator strengths, the theoretical Raman scattering efficiencies can help to study the lattice dynamics of complex materials from experimental infrared and Raman spectroscopy.

A second application is the systematic computation of electro-optic coefficients of complex materials in order to find better materials for optical applications. We can suggest two fields that might be interesting to investigate in the future. First, disordered ferroelectrics such as PZN-PT are known to exhibit excellent piezoelectric properties. It has been shown recently that these materials also have unusual electrooptic properties [193] that might be interesting to study from first-principles. Second, the structure and polarization of thin ferroelectric films can be tuned by epitaxial strain induced by the lattice mismatch between the ferroelectric film and the substrate. It has been suggested recently that this strain engineering can also be used to tune the electro-optic properties of such films [47].

Concerning the potential theoretical developments, we mentioned above that the finite electric field technique allows the use of most approximations of the exchangecorrelation energy that are available for zero-field ground-state calculations. This technique therefore makes it possible to study the effect of these approximations on the linear and nonlinear optical susceptibilities in a systematic way.

Finally, our work can also serve as a basis for further implementations in the ABINIT code in order to compute anharmonic force constants [58], the tunability of the dielectric constant [140], or the magnetoelectric coupling coefficients of multiferroics [51]. In addition, the localization tensor in connection with the finite electric field technique might be used to study the dielectric breakdown in solids [116].

Appendix A

Relation between the localization tensor and the optical conductivity

The optical conductivity (imaginary part of the optical dielectric tensor) of a given material is related to its absorption coefficient, the probability of the valence electrons to perform optical transitions to the *unoccupied* conduction bands under the influence of an electromagnetic field. If we consider only "vertical" band-to-band transitions (thus neglecting elementary excitations like the electron-hole interaction or the electron-phonon coupling) this quantity writes in the dipolar approximation [101]

$$\varepsilon_{\alpha\beta}^{\prime\prime}(\omega) = \frac{4\pi^2 e^2}{m_e^2 \omega^2 \hbar} \sum_{n=1}^N \sum_{m=N+1}^\infty \int_{BZ} \frac{2d\mathbf{k}}{(2\pi)^3} p_{nm}^{\alpha}(\mathbf{k}) p_{mn}^{\beta}(\mathbf{k}) \delta\left(\omega_{mn}(\mathbf{k}) - \omega\right)$$
(A.1)

where m_e is the electron mass, $\mathbf{p}_{nm}(\mathbf{k}) = -i\hbar \langle \psi_{n\mathbf{k}} | \nabla \psi_{m\mathbf{k}} \rangle$ and $\hbar \omega_{mn}(\mathbf{k}) = \varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}}$. The matrix elements of the momentum operator can equivalently be expressed as

$$\mathbf{p}_{nm}(\mathbf{k}) = -m_e \omega_{nm}(\mathbf{k}) \langle u_{n\mathbf{k}} | \partial_{\mathbf{k}} u_{m\mathbf{k}} \rangle.$$
(A.2)

It has been shown by Souza, Wilkens and Martin [13] that ε'' is related to the localization tensor by the relation

$$\int_{0}^{\infty} \varepsilon_{\alpha\beta}^{\prime\prime}(\omega) \, d\omega = \frac{8\pi^{2}e^{2}N}{\hbar\Omega_{0}} \left\langle r_{\alpha}r_{\beta}\right\rangle_{c}.$$
 (A.3)

In order to see the effect of the band by band decomposition, we will write ε'' as

$$\varepsilon_{\alpha\beta}^{\prime\prime}(\omega) = \sum_{i=1}^{N_g} \left\{ \varepsilon_{\alpha\beta}^{\prime\prime}(\omega; \mathcal{G}_i) + \sum_{j\neq i}^{N_g} \varepsilon_{\alpha\beta}^{\prime\prime}(\omega; \mathcal{G}_i, \mathcal{G}_j) \right\}$$
(A.4)

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where

ε

$$\varepsilon_{\alpha\beta}^{\prime\prime}(\omega;\mathcal{G}_{i}) = \frac{4\pi^{2}e^{2}}{m_{e}^{2}\omega^{2}\hbar} \sum_{n\in\mathcal{G}_{i}} \sum_{m=1}^{\infty} \int_{BZ} \frac{2d\mathbf{k}}{(2\pi)^{3}} p_{nm}^{\alpha}(\mathbf{k}) p_{mn}^{\beta}(\mathbf{k}) \delta\left(\omega_{mn}(\mathbf{k})-\omega\right) \quad (A.5)$$

$$\overset{\prime\prime}{}_{\alpha\beta}(\omega;\mathcal{G}_{i},\mathcal{G}_{j}) = \frac{-4\pi^{2}e^{2}}{m_{e}^{2}\omega^{2}\hbar} \sum_{n\in\mathcal{G}_{i}} \sum_{m\in\mathcal{G}_{j}} \int_{BZ} \frac{2d\mathbf{k}}{(2\pi)^{3}} p_{nm}^{\alpha}(\mathbf{k}) p_{mn}^{\beta}(\mathbf{k}) \delta\left(\omega_{mn}(\mathbf{k})-\omega\right). \quad (A.6)$$

The first sum of Eq. (A.5) has to be taken over the bands of group \mathcal{G}_i while the second sum extends over all bands (unoccupied or not) except those of group \mathcal{G}_i . In Eq. (A.6), the two sums extend over the bands of group \mathcal{G}_i and \mathcal{G}_j . It is easy to show that $\varepsilon''_{\alpha\beta}(\omega;\mathcal{G}_i)$ and $\varepsilon''_{\alpha\beta}(\omega;\mathcal{G}_i,\mathcal{G}_j)$ are related to the variances and covariances by the relations

$$\int_{0}^{\infty} \varepsilon_{\alpha\beta}^{\prime\prime}(\omega; \mathcal{G}_{i}) d\omega = \frac{8\pi^{2}e^{2}n_{i}}{\hbar\Omega_{0}} \langle r_{\alpha}r_{\beta}\rangle_{c} (\mathcal{G}_{i})$$
(A.7)

$$\int_{0}^{\infty} \varepsilon_{\alpha\beta}^{\prime\prime}(\omega; \mathcal{G}_{i}, \mathcal{G}_{j}) d\omega = \frac{8\pi^{2}e^{2}n_{i}n_{j}}{\hbar\Omega_{0}} \langle r_{\alpha}r_{\beta} \rangle_{c} (\mathcal{G}_{i}, \mathcal{G}_{j}).$$
(A.8)

Thanks to these definitions, the physical meaning of the covariance becomes now obvious: If the total localization tensor was simply the sum of the variances $\langle r_{\alpha}r_{\beta}\rangle_c(\mathcal{G}_i)$, the expression of the dielectric tensor (A.1) would not only contain transitions between occupied and unoccupied states, but also transitions between occupied states themselves. It is by adding the covariances $\langle r_{\alpha}r_{\beta}\rangle_c(\mathcal{G}_i,\mathcal{G}_j)$ that one compensates the effect of these forbidden transitions in order to get a physically correct quantity.

Appendix B

Expressions of the clamped and unclamped EO tensors

B.1 Macroscopic approach

As discussed in Sec. 3.3.4, the optical properties of a compound are modified by an electric field \mathcal{E}_{γ} or a mechanical constraint (a stress $\sigma_{\mu\nu}$ or a homogeneous strain $\eta_{\mu\nu}$). At linear order, the variations of ε_{ij}^{-1} can be described using either the variables $(\mathcal{E}_{\gamma}, \eta_{\mu\nu})$ or $(\mathcal{E}_{\gamma}, \sigma_{\mu\nu})$ [173,183]

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r^{\eta}_{ij\gamma} \mathcal{E}_{\gamma} + \sum_{\mu,\nu=1}^{3} \pi_{ij\mu\nu} \eta_{\mu\nu}, \qquad (B.1)$$

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r^{\sigma}_{ij\gamma} \mathcal{E}_{\gamma} + \sum_{\mu,\nu=1}^{3} \wp_{ij\mu\nu} \sigma_{\mu\nu}, \qquad (B.2)$$

where $r_{ij\gamma}^{\eta}$ and $r_{ij\gamma}^{\sigma}$ are respectively the clamped (strain-free) and unclamped (stressfree) EO coefficients, $\pi_{ij\mu\nu}$ are the elasto-optic (strain-optic) coefficients and $\varphi_{ij\mu\nu}$ are the piezo-optical (stress-optical) coefficients. In order to relate Eqs. (B.1) and (B.2), we can express the strain as beeing induced by the stress or by the electric field (converse piezoelectric effect)

$$\eta_{\mu\nu} = \sum_{\mu',\nu'=1}^{3} S_{\mu\nu\mu'\nu'} \sigma_{\mu'\nu'} + \sum_{\gamma=1}^{3} d_{\gamma\mu\nu} \mathcal{E}_{\gamma}, \qquad (B.3)$$

where $S_{\mu\nu\mu'\nu'}$ are the elastic compliances and $d_{\gamma\mu\nu}$ the piezoelectric strain coefficients.

If we assume, for example, that the unit cell is free to relax within the electric field (stress-free mechanical boundary conditions) we can either use Eq. (B.2) (in which case the second term of the right-hand side is zero) or Eq. (B.1) to compute $\Delta(\varepsilon^{-1})_{ij}$.

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In the latter case, the strain induced by the electric field can be obtained from the second term of the right-hand side of Eq. (B.3)

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r^{\sigma}_{ij\gamma} \mathcal{E}_{\gamma}$$
$$= \sum_{\gamma=1}^{3} r^{\eta}_{ij\gamma} \mathcal{E}_{\gamma} + \sum_{\mu,\nu=1}^{3} \sum_{\gamma=1}^{3} \pi_{ij\mu\nu} d_{\gamma\mu\nu} \mathcal{E}_{\gamma}.$$
(B.4)

Using this identity, we obtain the following relation between the unclamped and the clamped EO coefficients

$$r_{ij\gamma}^{\sigma} = r_{ij\gamma}^{\eta} + \sum_{\mu,\nu=1}^{3} \pi_{ij\mu\nu} d_{\gamma\mu\nu}.$$
 (B.5)

B.2 Microscopic approach

In order to derive the expressions of the clamped and unclamped EO tensor of Sec. 3.3.4, we use a Taylor expansion of the electric enthalpy [194] F. Similar developments have already been applied to determine the lattice contribution of the static dielectric tensor and of the piezoelectric tensor [195, 196]. They are based on an expansion of F up to the second order in the atomic coordinates $R_{\kappa\alpha}$, the homogeneous strain $\eta_{\mu\nu}$ and the macroscopic electric field \mathcal{E}_{γ} . In this section, we extend these developments to the third order.

The electric enthalpy of a solid in an electric field is obtained by the minimization

$$F(\boldsymbol{\mathcal{E}}) = \min_{\mathbf{R},\eta} F(\mathbf{R},\eta,\boldsymbol{\mathcal{E}}).$$
(B.6)

We denote $\mathbf{R}(\mathcal{E})$, $\eta(\mathcal{E})$ the atomic positions and the strain that minimize F at constant \mathcal{E} and \mathbf{R}_0 , η_0 (= 0) their values at $\mathcal{E} = 0$. For small fields, we can expand the function $F(\mathbf{R}, \eta, \mathcal{E})$ in powers of \mathcal{E} around $\mathcal{E} = 0$:

$$F(\mathbf{R},\eta,\mathcal{E}) = F(\mathbf{R},\eta,0) - \Omega_0 \sum_{i=1}^{3} \mathcal{P}_i(\mathbf{R},\eta) \mathcal{E}_i - \frac{\Omega_0}{8\pi} \sum_{i,j=1}^{3} \varepsilon_{ij}(\mathbf{R},\eta) \mathcal{E}_i \mathcal{E}_j$$
$$-\frac{\Omega_0}{3} \sum_{i,j,k=1}^{3} \chi_{ijk}^{(2)}(\mathbf{R},\eta) \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k + \cdots$$
(B.7)

where Ω_0 is the volume of the primitive unit cell in real space and $\mathcal{P}(\mathbf{R}, \eta)$, $\varepsilon_{ij}(\mathbf{R}, \eta)$ and $\chi_{ijk}^{(2)}(\mathbf{R}, \eta)$ are the macroscopic polarization, electronic dielectric tensor and nonlinear optical coefficients at zero macroscopic electric field and for a given configuration (\mathbf{R}, η) . At non-zero field, these quantities are defined as partial derivatives of F with respect to \mathcal{E} . For example, the electric field dependent electronic dielectric tensor can be computed from the expression

$$\varepsilon_{ij}\left(\mathbf{R}(\mathcal{E}), \eta(\mathcal{E}), \mathcal{E}\right) = -\frac{4\pi}{\Omega_0} \frac{\partial^2 F}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \bigg|_{\mathbf{R}(\mathcal{E}), \eta(\mathcal{E}), \mathcal{E}}.$$
(B.8)

Let $\tau_{\kappa\alpha} = \mathbf{R}_{\kappa\alpha} - \mathbf{R}_{0,\kappa\alpha}$ be the displacement of atom κ along direction α and $\tau_{\kappa\alpha}^{\lambda} (\eta_{\mu\nu}^{\lambda})$ the first-order modification of the atomic position (strain) induced by a perturbation λ

$$\tau_{\kappa\alpha}^{\lambda} = \left. \frac{\partial \tau_{\kappa\alpha}}{\partial \lambda} \right|_{\lambda=0}, \quad \eta_{\mu\nu}^{\lambda} = \left. \frac{\partial \eta_{\mu\nu}}{\partial \lambda} \right|_{\lambda=0}. \tag{B.9}$$

In the discussion that follows, we will study the effect of an electric field perturbation and a strain perturbation on the electric enthalpy F in order to obtain the formulas to compute the elasto-optic coefficients as well as the clamped and the unclamped EO tensors.

B.2.1 Elasto-optic coefficients ($\mathcal{E} = 0$)

The elasto-optic tensor can be computed from the *total* derivative of the dielectric tensor with respect to $\eta_{\mu\nu}$ at zero electric field

$$\frac{d\varepsilon_{ij}\left(\mathbf{R},\eta,0\right)}{d\eta_{\mu\nu}}\Big|_{\mathbf{R}_{0},\eta_{0}} = \left.\frac{\partial\varepsilon_{ij}\left(\mathbf{R},\eta\right)}{\partial\eta_{\mu\nu}}\Big|_{\mathbf{R}_{0},\eta_{0}} + 4\pi\sum_{\kappa\alpha}\left.\frac{\partial\chi_{ij}^{(1)}\left(\mathbf{R},\eta\right)}{\partial\tau_{\kappa\alpha}}\right|_{\mathbf{R}_{0},\eta_{0}}\tau_{\kappa\alpha}^{\eta_{\mu\nu}}.$$
 (B.10)

The derivative in the first term of the right-hand side is computed considering the ionic cores as artificially clamped at their equilibrium positions. The remaining terms represent the ionic contribution to the elasto-optic tensor. They involve derivatives of the linear dielectric susceptibility $\chi_{ij}^{(1)}$ with respect to the atomic positions that have to be multiplied by the first-order strain induced atomic displacements $\tau_{\kappa\alpha}^{\eta_{\mu\nu}}$ [Eq. (B.9)]. To compute these quantities we use the fact that F is minimum at the equilibrium for an imposed strain η . This condition implies

$$\frac{\partial F(\mathbf{R},\eta)}{\partial \tau_{\kappa\alpha}}\Big|_{\mathbf{R}(\eta),\eta} = 0.$$
(B.11)

Since we are interested in first-order atomic displacements we can write $\tau_{\kappa\alpha}(\eta) = \sum_{\mu,\nu=1}^{3} \tau_{\kappa\alpha}^{\eta\mu\nu} \eta_{\mu\nu} + \mathcal{O}(\eta^2)$. Solving the extremum equation (B.11) to the linear order in η , we obtain

$$\sum_{\kappa',\alpha'} \left. \frac{\partial^2 F\left(\mathbf{R},\eta\right)}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'}} \right|_{\mathbf{R}_0,\eta_0} \tau_{\kappa'\alpha'}^{\eta_{\mu\nu}} = - \left. \frac{\partial^2 F\left(\mathbf{R},\eta\right)}{\partial \eta_{\mu\nu} \partial \tau_{\kappa\alpha}} \right|_{\mathbf{R}_0,\eta_0}.$$
 (B.12)

The second derivatives on the left side of Eq. (B.12) define the matrix of interatomic force constants at zero macroscopic electric field which enables the computation of the

transverse phonon frequencies ω_m and eigendisplacements $U_m(\kappa \alpha)$. By decomposing $\tau_{\kappa \alpha}^{\eta_{\mu\nu}}$ in the basis of the zone-center phonon-mode eigendisplacements

$$\tau_{\kappa\alpha}^{\eta_{\mu\nu}} = \sum_{m} \tau_{m}^{\eta_{\mu\nu}} U_{m}(\kappa\alpha)$$
(B.13)

and using Eqs. (3.20), (3.21) we derive the following expression for the first-order strain induced atomic displacements

$$\tau_m^{\eta_{\mu\nu}} = \frac{-1}{\omega_m^2} \left. \frac{\partial^2 F\left(\mathbf{R}, \eta\right)}{\partial \eta_{\mu\nu} \partial \tau_m} \right|_{\mathbf{R}_0, \eta_0},\tag{B.14}$$

where

$$\frac{\partial^2 F\left(\mathbf{R},\eta\right)}{\partial \eta_{\mu\nu} \partial \tau_m} \bigg|_{\mathbf{R}_0,\eta_0} = \sum_{\kappa,\alpha} \left. \frac{\partial^2 F\left(\mathbf{R},\eta\right)}{\partial \eta_{\mu\nu} \partial \tau_{\kappa\alpha}} \right|_{\mathbf{R}_0,\eta_0} U_m(\kappa\alpha). \tag{B.15}$$

If we introduce Eqs. (B.13) and (B.14) into Eq. (B.10) and use the definition of the Raman susceptibility Eq. (3.24) and the transformation Eq. (3.33), we finally obtain the formula to compute the elasto-optic tensor

$$\pi_{ij\mu\nu} = \frac{-1}{n_i^2 n_j^2} \left. \frac{\partial \varepsilon_{ij} \left(\mathbf{R}, \eta \right)}{\partial \eta_{\mu\nu}} \right|_{\mathbf{R}_0, \eta_0} + \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega_0}} \sum_m \frac{\alpha_{ij}^m}{\omega_m^2} \left. \frac{\partial^2 F \left(\mathbf{R}, \eta \right)}{\partial \eta_{\mu\nu} \partial \tau_m} \right|_{\mathbf{R}_0, \eta_0}.$$
(B.16)

To simplify, we write Eq. (B.16) in the principal axes of the crystal under investigation. A more general expression can be obtained from Eq. (3.33).

Eq. (B.16) is different from the approach used previously by Detraux and Gonze to study the elasto-optic tensor in α -quartz [86]. The authors of Ref. [86] used finite differences with respect to strains to compute the the total derivative of ε_{ij} . In their approach, the atoms where relaxed to their equilibrium positions in the strained configurations. In case of Eq. (B.16), the first term of the right-hand side is computed at clamped atomic positions while the effect of the strain-induced atomic relaxations is taken into account by the second term.

B.2.2 Clamped EO coefficients $(\eta = 0)$

The clamped EO tensor can be computed from the *total* derivative of the electric field dependent dielectric tensor Eq. (B.8) with respect to \mathcal{E}

$$\frac{d\varepsilon_{ij}\left(\mathbf{R},\eta_{0},\boldsymbol{\mathcal{E}}\right)}{d\mathcal{E}_{\gamma}}\Big|_{\boldsymbol{R}_{0},\boldsymbol{\mathcal{E}}=0} = \frac{\partial\varepsilon_{ij}\left(\mathbf{R}_{0},\eta_{0},\boldsymbol{\mathcal{E}}\right)}{\partial\mathcal{E}_{\gamma}}\Big|_{\boldsymbol{\mathcal{E}}=0} + 4\pi\sum_{\kappa\alpha}\frac{\partial\chi_{ij}^{(1)}\left(\mathbf{R},\eta_{0}\right)}{\partial\tau_{\kappa\alpha}}\Big|_{\boldsymbol{R}_{0}}\tau_{\kappa\alpha}^{\mathcal{E}_{\gamma}}.$$
 (B.17)

The derivative in the first term is computed considering the ionic cores as artificially clamped at their equilibrium positions. This term represents the bare electronic contribution to the EO tensor that can be computed from the nonlinear optical coefficients

$$\frac{\partial \varepsilon_{ij} \left(\mathbf{R}_{0}, \eta_{0}, \boldsymbol{\mathcal{E}} \right)}{\partial \mathcal{E}_{\gamma}} \bigg|_{\boldsymbol{\mathcal{E}}=0} = \left. 8\pi \chi_{ijk}^{(2)} \right|_{k=\gamma} \tag{B.18}$$

related to a third-order partial derivative of F

$$\chi_{ijk}^{(2)} = \chi_{ijk}^{(2)} \left(\mathbf{R}_0, \eta_0 \right) = \frac{-1}{2\Omega_0} \frac{\partial^3 F\left(\mathbf{R}_0, \eta_0, \boldsymbol{\mathcal{E}} \right)}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k} \bigg|_{\boldsymbol{\mathcal{E}}=0}.$$
 (B.19)

The remaining terms in Eq. (B.17) represent the ionic contribution to the EO tensor. They involve derivatives of the linear dielectric susceptibility $\chi_{ij}^{(1)}$ with respect to the atomic positions that have to be multiplied by the first-order electric field induced atomic displacements $\tau_{\kappa\alpha}^{\mathcal{E}\gamma}$ [Eq. (B.9)]. To obtain these quantities, we proceed the same way as in case of the elasto-optic tensor. Using the equilibrium condition

$$\frac{\partial F}{\partial \tau_{\kappa\alpha}} = 0 = \frac{\partial F(\mathbf{R}, \eta_0, 0)}{\partial \tau_{\kappa\alpha}} \bigg|_{\mathbf{R}(\mathcal{E})} - \Omega_0 \sum_{i=1}^3 \frac{\partial \mathcal{P}_i(\mathbf{R}, \eta_0)}{\partial \tau_{\kappa\alpha}} \bigg|_{\mathbf{R}(\mathcal{E})} \mathcal{E}_i - \frac{\Omega_0}{8\pi} \sum_{i,j=1}^3 \frac{\partial \varepsilon_{ij}(\mathbf{R}, \eta_0)}{\partial \tau_{\kappa\alpha}} \bigg|_{\mathbf{R}(\mathcal{E})} \mathcal{E}_i \mathcal{E}_j + \cdots$$
(B.20)

and expanding $\tau_{\kappa\alpha}$ to the first-order in the electric field, we obtain

$$\sum_{\kappa',\alpha'} \left. \frac{\partial^2 F\left(\mathbf{R},\eta_0,0\right)}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'}} \right|_{\mathbf{R}_0} \tau_{\kappa'\alpha'}^{\mathcal{E}_{\gamma}} = \Omega_0 \frac{\partial \mathcal{P}_{\gamma}\left(\mathbf{R},\eta_0\right)}{\partial \tau_{\kappa\alpha}} \right|_{\mathbf{R}_0}.$$
 (B.21)

This expression is similar to Eq. (B.12). The second-order derivatives of F on the left side are the interatomic force constants and the derivative of the zero field polarization with respect to $\tau_{\kappa\alpha}$ on the right side is the Born effective charge tensor $Z^*_{\kappa,\gamma\alpha}$ of atom κ . Decomposing $\tau^{\mathcal{E}\gamma}_{\kappa\alpha}$ in the basis of the zone-center phonon-mode eigendisplacements [Eq. (B.13)] and using the orthononormality constraint Eq. (3.21) we derive the following expression for the first-order electric field induced atomic displacements

$$\tau_m^{\mathcal{E}_{\gamma}} = \frac{1}{\omega_m^2} \sum_{\kappa,\alpha} Z_{\kappa,\gamma\alpha}^* U_m(\kappa\alpha).$$
(B.22)

If we introduce Eqs. (B.18) and (B.22) into Eq. (B.17) we finally obtain the formula to compute the total derivative of the dielectric tensor

$$\frac{d\varepsilon_{ij}\left(\mathbf{R},\mathcal{E}\right)}{d\mathcal{E}_{\gamma}}\bigg|_{\boldsymbol{R}_{0},\mathcal{E}=0} = 8\pi\chi_{ijk}^{(2)}\bigg|_{k=\gamma}$$

$$+4\pi \sum_{m} \frac{1}{\omega_{m}^{2}} \left(\sum_{\kappa,\alpha} \frac{\partial \chi_{ij}^{(1)}(\mathbf{R})}{\partial \tau_{\kappa\alpha}} U_{m}(\kappa\alpha) \right) \\ \times \left(\sum_{\kappa',\beta} Z_{\kappa',\gamma\beta}^{*} U_{m}(\kappa'\beta) \right).$$
(B.23)

Using the definition of the Raman susceptibility [Eq. (3.24)], the mode polarity [Eq. (3.37)] and the transformation [Eq. (3.33)] we obtain the expression of the clamped EO tensor

$$r_{ij\gamma}^{\eta} = \left. \frac{-8\pi}{n_i^2 n_j^2} \chi_{ijl}^{(2)} \right|_{l=\gamma} - \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega_0}} \sum_m \frac{\alpha_{ij}^m p_{m\gamma}}{\omega_m^2}$$
(B.24)

As in case of the elasto-optic tensor [Eq. (B.16)], we have written Eq. (B.24) in the principal axes of the crystal under investigation.

B.2.3 Unclamped EO tensor ($\sigma = 0$)

In order to compute the unclamped EO tensor, we have to take into account both the electric field induced atomic displacements $\tau_{\kappa\alpha}^{\mathcal{E}\gamma}$ and the electric field induced strain $\eta_{\mu\nu}^{\mathcal{E}\gamma}$ when computing the total derivative of ε_{ij}

$$\frac{d\varepsilon_{ij} \left(\mathbf{R}, \eta, \boldsymbol{\mathcal{E}}\right)}{d\mathcal{E}_{\gamma}} \bigg|_{\boldsymbol{R}_{0}, \eta_{0}, \boldsymbol{\mathcal{E}}=0} = \frac{\partial \varepsilon_{ij} \left(\mathbf{R}_{0}, \eta_{0}, \boldsymbol{\mathcal{E}}\right)}{\partial \mathcal{E}_{\gamma}} \bigg|_{\boldsymbol{\mathcal{E}}=0} + 4\pi \sum_{\kappa\alpha} \frac{\partial \chi_{ij}^{(1)} \left(\mathbf{R}, \eta_{0}\right)}{\partial \tau_{\kappa\alpha}} \bigg|_{\boldsymbol{R}_{0}} \tau_{\kappa\alpha}^{\mathcal{E}_{\gamma}} + 4\pi \sum_{\mu,\nu=1}^{3} \frac{\partial \chi_{ij}^{(1)} \left(\mathbf{R}_{0}, \eta\right)}{\partial \eta_{\mu\nu}} \bigg|_{\eta_{0}} \eta_{\mu\nu}^{\mathcal{E}_{\gamma}}.$$
(B.25)

The electronic contribution [first term of Eq. (B.25)] is the same as for the clamped EO tensor. It can be computed from the nonlinear optical coefficients [Eq. (B.18)]. To compute $\tau_{\kappa\alpha}^{\mathcal{E}_{\gamma}}$ and $\eta_{\mu\nu}^{\mathcal{E}_{\gamma}}$, we can use an equilibrium condition similar to Eq. (B.20) where we require that the first-order derivatives of F with respect to $\tau_{\kappa\alpha}$ and $\eta_{\mu\nu}$ vanish. Expanding $\tau_{\kappa\alpha}$ and $\eta_{\mu\nu}$ to the first-order in the electric field, we obtain the system of coupled equations [see also Ref. [140]]

$$\sum_{\kappa',\alpha'} \frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_{\kappa\alpha} \partial \tau_{\kappa'\alpha'}} \bigg|_{\mathbf{R}_{0},\eta_{0}} \tau_{\kappa'\alpha'}^{\mathcal{E}_{\gamma}} + \sum_{\mu,\nu} \frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_{\kappa\alpha} \partial \eta_{\mu\nu}} \bigg|_{\mathbf{R}_{0},\eta_{0}} \eta_{\mu\nu}^{\mathcal{E}_{\gamma}} = \Omega_{0} \frac{\partial \mathcal{P}_{\gamma}(\mathbf{R},\eta)}{\partial \tau_{\kappa\alpha}} \bigg|_{\mathbf{R}_{0},\eta_{0}}$$
(B.26)
$$\sum_{\mu',\nu'} \frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \eta_{\mu\nu} \partial \eta_{\mu'\nu'}} \bigg|_{\mathbf{R}_{0},\eta_{0}} \eta_{\mu'\nu'}^{\mathcal{E}_{\gamma}} + \sum_{\kappa',\alpha'} \frac{\partial^2 F(\mathbf{R},\eta,0)}{\partial \tau_{\kappa'\alpha'} \partial \eta_{\mu\nu}} \bigg|_{\mathbf{R}_{0},\eta_{0}} \tau_{\kappa'\alpha'}^{\mathcal{E}_{\gamma}} = \Omega_{0} \frac{\partial \mathcal{P}_{\gamma}(\mathbf{R},\eta)}{\partial \eta_{\mu\nu}} \bigg|_{\mathbf{R}_{0},\eta_{0}}$$
(B.27)

Because of the coupling between $\tau_{\kappa\alpha}^{\mathcal{E}_{\gamma}}$ and $\eta_{\mu\nu}^{\mathcal{E}_{\gamma}}$, defined by the mixed second-order derivatives $\frac{\partial^2 F}{\partial \tau_{\kappa\alpha} \eta_{\mu\nu}}$, the second term of the right-hand side of Eq. (B.25) is different from that of Eq. (B.17). That means that the sum of the first and second term of Eq.

(B.25) is not identical to the clamped EO coefficients $r_{ij\gamma}^{\eta}$. Moreover, the third term of Eq. (B.25) is different from the piezoelectric contribution of Sec. B.1.

In order to obtain the decomposition of $r_{ij\gamma}^{\sigma}$ into electronic, ionic and piezoelectric contributions defined previously, we can solve Eq. (B.26) for $\tau_{\kappa\alpha}^{\mathcal{E}\gamma}$. In the basis of the zone-center phonon mode eigendisplacements we can write

$$\tau_{n}^{\mathcal{E}_{\gamma}} = \frac{p_{n\gamma}}{\omega_{n}^{2}} - \frac{1}{\omega_{n}^{2}} \sum_{\mu\nu} \left. \frac{\partial^{2}F\left(\mathbf{R},\eta,0\right)}{\partial\tau_{n}\partial\eta_{\mu\nu}} \right|_{\mathbf{R}_{0},\eta_{0}} \eta_{\mu\nu}^{\mathcal{E}_{\gamma}}.$$
(B.28)

If we insert this relation into Eq. (B.25) and use the transformation Eq. (3.33) we obtain the following expression of the unclamped EO tensor in the principal axes

$$r_{ij\gamma}^{\sigma} = \frac{-8\pi}{n_i^2 n_j^2} \chi_{ijl}^{(2)} \bigg|_{l=\gamma} - \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega_0}} \sum_m \frac{\alpha_{ij}^m p_{m\gamma}}{\omega_m^2} \\ - \frac{4\pi}{n_i^2 n_j^2} \sum_{\mu,\nu} \left[\frac{\partial \chi_{ij}^{(1)} (\mathbf{R}, \eta, \boldsymbol{\mathcal{E}})}{\partial \eta_{\mu\nu}} \bigg|_{\mathbf{R}_0, \eta_0, \boldsymbol{\mathcal{E}}=0} \\ - \frac{1}{\sqrt{\Omega_0}} \sum_m \frac{\alpha_{ij}^m}{\omega_m^2} \frac{\partial^2 F (\mathbf{R}, \eta, 0)}{\partial \tau_m \partial \eta_{\mu\nu}} \bigg|_{\mathbf{R}_0, \eta_0, \boldsymbol{\mathcal{E}}=0} \right] \eta_{\mu\nu}^{\mathcal{E}\gamma}.$$
(B.29)

The sum of the first and second term of the right-hand side of Eq. (B.29) is equal to the clamped EO coefficient $r_{ij\gamma}^{\eta}$. The product of the conversion factor times the bracket in the third term of Eq. (B.29) is equal to the elasto-optic coefficient $\pi_{ij\mu\nu}$ [Eq. (B.16)]. Finally, by definition of the converse piezoelectric effect, $\eta_{\mu\nu}^{\mathcal{E}_{\gamma}}$ is equal to the piezoelectric strain coefficient $d_{\gamma\mu\nu}$. We obtain thus the following expression of the unclamped EO coefficients that is equal to the one derived in Sec. B.1 from pure macroscopic arguments

$$r_{ij\gamma}^{\sigma} = r_{ij\gamma}^{\eta} + \sum_{\mu,\nu=1}^{3} \pi_{ij\mu\nu} d_{\gamma\mu\nu}.$$
 (B.30)

It is worth noting that the so-called piezoelectric contribution not only takes into account the change of the linear optical susceptibility with strain (third term of the right-hand side of Eq. (B.25)) but also includes the modification of the ionic contribution, with respect to the clamped case, that is associated to the modification of the ionic relaxation induced by the strain.

Glossary

Abbreviations

BZ	Brillouin zone
DAPE	Discretization after perturbation expansion
DFT	Density functional theory
DFPT	Density functional perturbation theory
EO	Electro-optic
FEF	Finite electric fields
GGA	Generalized gradiend approximation
LDA	Local density approximation
PEAD	Perturbation expansion after discretization

Notation for crystals

\mathbf{a}_i	basis vector of the real space crystal lattice
\mathbf{G}_i	basis vector of the reciprocal lattice
Ω_0	volume of the primitif unit cell
L	size of the Born- von Karman supercell

Notation for electronic properties

k	wavevector of the Bloch functions
${\cal G}_i$	group of bands
$\psi_{n\mathbf{k}}(\mathbf{r})$	electronic Bloch function
$u_{n\mathbf{k}}^{n\mathbf{k}}(\mathbf{r})$	periodic part of the Bloch function
$W_n^{n\mathbf{R}}(\mathbf{r}-\mathbf{R})$	electronic Wannier function
$ \mathbf{R}n\rangle$	Dirac notation of the electronic Wannier function $W_n(\mathbf{r} - \mathbf{R})$
e	charge of the proton
m_e	mass of an electron
E	Kohn-Sham energy at zero electric field
${\mathcal F}$	electric field dependent energy functional
E_g	electronic band gap at zero electric field
Ω	spread of Wannier functions: $\Omega = \Omega_I + \widetilde{\Omega}$

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Ω_I	gauge invariant part of Ω
$\widetilde{\Omega}$	gauge dependent part of Ω
$\langle r_{\alpha}r_{\beta} angle_{c}$	element of the localization tensor

Notation for dynamic properties

$ au_{\kappa \alpha}$	displacement of atom κ along the Cartesian direction α
$C_{\kappa\alpha,\kappa'\alpha'}$	interatomic force constants
$U_m(\kappa\alpha)$	normalized phonon mode eigendisplacements
$p_{m\alpha}$	mode polarities
$oldsymbol{\xi}_i$	amplitude of the displacement along the lattice Wannier function in cell i
$\overline{Z^*}$	mode effective charge of the soft mode in the cubic phase of ${ m BaTiO_3}$
\mathcal{V}	angle of collection in a Raman scattering experiment

General physical quantities

T_c	phase transition temperature of a ferroelectric
$oldsymbol{\mathcal{E}} \ \mathcal{\mathcal{P}} \ \mathcal{\mathcal{P}}^s$	macroscopic electric field macroscopic polarization spontaneous polarization of a ferroelectric
$egin{array}{lll} f_{\kappalpha} \ \sigma_{\mu u} \ \eta_{\mu u} \end{array}$	force on atom κ along the Cartesian direction α elements of the stress tensor elements of the (homogeneous) strain tensor
$c_{\mu u\mu' u'} \ d_{\gamma\mu u} \ e_{\gamma\mu u}$	elastic constants piezoelectric strain coefficients piezoelectric stress coefficients
$arepsilon_{ij}^{arepsilon_{ij}} \chi_{ij}^{(1)} \ arepsilon_{lphaeta}} \ arepsilon_{lphaeta} \ \chi_{lphaeta}^{(1)} \ \chi_{lphaeta}^{(1)}$	elements of the optical dielectric tensor elements of the optical dielectric susceptibility tensor elements of the static dielectric tensor elements of the static dielectric susceptibility tensor
$\begin{array}{l} \chi^{(2)}_{ijl} \\ r^{\sigma}_{ij\gamma} \\ r^{\eta}_{ij\gamma} \\ \pi_{ij\mu\nu} \\ \wp_{ij\mu\nu} \end{array}$	elements of the nonlinear optical susceptibility tensor elements of the stress-free (unclamped) EO tensor elements of the strain-free (clamped) EO tensor elasto-optic (strain-optic) coefficients piezo-optic (stress-optic) coefficients

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