Ab-initio lattice dynamics in

LiNbO$_3$ and LiTaO$_3$

Dissertation

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Chapter 1

Introduction

The ability of physics to provide an understanding of our Universe lies in the essential interrelation between experiment and theory. But physics does not provide us only reliable representations of the causes acting in nature. Its powerful experimental devices and theoretical methods are the underlying reason of the explosive technological development of our time.

LiNbO$_3$ and LiTaO$_3$ represent only one example of the essential impact of both experimental and theoretical investigations on their technological applications. Particularly, LiNbO$_3$ has been the subject of many experimental studies due to its applications in electro-optic and integrated optical devices. Also, the doped LiNbO$_3$ with rare-earth and transition metals could be used, for instance, as a material for tunable lasers.

The previous theoretical studies devoted to LiNbO$_3$ and LiTaO$_3$ focused on their electronic structure, being an attempt to understand the microscopic origin of the paraelectric-to-ferroelectric phase transition of these materials. The \textit{ab initio} lattice dynamics investigations performed so far were mainly aimed to identify the role of the individual atoms vibrations in the energetic of the phase transition.

The lack of a reliable model for the zone-center lattice dynamics in these compounds motivated us to investigate this issue by means of \textit{ab initio} frozen-phonon calculations. On the background of the obtained phonon frequencies and eigenvectors, we unambiguously identified all zone-center modes for LiNbO$_3$ and the $A_1$ ones for LiTaO$_3$. Due to the above mentioned enlargement of the technological applications of LiNbO$_3$ by doping with various ions, we focused on the analysis of the
ground-state properties of this material when doped with Fe and Cr. Even if the theoretical approach used in our calculations is not predictive with respect to the optical properties of the physical systems in study, a certain insight on this problem could be gained from the analysis of the effect of the atomic positions relaxation on the impurities energy levels localized in the optical band gap.
Chapter 2

LiNbO$_3$ and LiTaO$_3$: an overview

Introduction

Ferroelectrics are extremely useful materials with a large technological impact, being used as transducers, actuators, dielectrics, and nonvolatile memories. These physical systems provide also the opportunity to understand the physics involved in fundamental phenomena as spontaneous polarization, piezoelectricity, phase transitions under various temperature, pressure and composition conditions.

Among the ferroelectric systems most studied in the last decade are perovskite oxides, generally denoted by $ABO_3$ in which $A$ is an alkali or rare-earth element, and $B$ may represent different transition metals. For the theory, the major challenge was to explain the underlying physics involved in their ferroelectric instability and to understand why different materials behave in a different way [Coh92, Coh93, SC93]. Once this fundamental understanding reached, there is a hope to be able in future to computationally design useful materials performing $ab$ initio calculations based on the density functional theory (DFT) (see, e.g., Ref. [Coh00]).

The interest in developing new ferroelectric materials with a relevant technological impact was renewed by the discovery of giant piezoelectric response in a single crystal solid solution PbZn$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PZN-PT) and PbMg$_{1/3}$Nb$_{2/3}$O$_3$-PbTiO$_3$ (PMN-PT) [PS97] for which a theoretical insight was recently gained through first-principle calculations [FC00].

Of course, the experimental and theoretical research activity was not confined only to perovskite-like ferroelectric materials. Among other systems, LiNbO$_3$ has
attained special attention due to its various application in nonlinear optics and magneto-optics. Particularly, its transition temperature $T_C=1480 \text{ K}$ is among the highest known ferroelectric transition temperatures.

### 2.1 LiNbO$_3$ and LiTaO$_3$: experimental results

In ferroelectric phase, LiNbO$_3$ as well as LiTaO$_3$ have ten atoms in their rhombohedral unit cells which belong to the space group $R3c$. The atomic arrangement is given by oxygen octahedra disposed along the polar trigonal axis $C_3$ (see Fig. 2.1).

Each Nb(Ta) atom is displaced from the center of the oxygen octahedra along the trigonal axis. The next oxygen octahedron along the polar axis is empty and the following one contains a Li atom also displaced from the oxygen octahedron face along the $Oz$ axis. At the Curie temperature $T_C=1480 \text{ K}$ LiNbO$_3$ undergoes a ferroelectric-to-paraelectric phase transition of second order [JK70, TM87], whereas for LiTaO$_3$ this second-order structural phase transition [Gla68] occurs at much lower transition temperature of $950 \text{ K}$. In the paraelectric phase, the structure of LiNbO$_3$ and LiTaO$_3$ belongs to the $R3c$ space group. In this case, the Nb(Ta) atoms are situated in the centers of the oxygen octahedra and the Li atoms positions lie on the face between two consecutive oxygen octahedra.

As was described by Landau in his phenomenological theory valid for a general phase transition from a disordered to an ordered phase [LL59], the paraelectric-to-ferroelectric phase transition is characterized by the appearance of an order parameter (spontaneous polarization) and by a reduction in symmetry compared to that of the high-temperature phase. The symmetry of the low-temperature phase is given by all symmetry elements common to the paraelectric group and the group of the spontaneous polarization which appears in the ferroelectric phase along a given direction (see the Ref. [BZ74] for a more detailed discussion).

From microscopical point of view, the experimental data concerning the paraelectric to ferroelectric phase transition could be interpreted within two different theoretical models for this phase transition, namely the displacive and order-disorder model.

In the displacive picture, the local potential as a function of the normal coordinates is slightly anharmonic and presents only a single minimum. In consequence, the decay of the order parameter (macroscopic spontaneous polarization) when Curie
Figure 2.1: The ferroelectric structure of LiNbO₃. The hexagonal unit cell is sketched by thin lines and the rhombohedral one by thick lines. The atoms which belong to the rhombohedral unit cell are painted dark.
temperature is approached from below is a result of the shift of the minimum of the potential energy of the ions towards their centrosymmetrical positions in paraelectric phase. Within this model, depending on the number of atoms in the unit cell above and below the transition temperature, a structural phase transition from paraelectric-to- (anti)ferroelectric phase can fall in one of the following classes:

- **ferrodistortive** transitions, when the number of formula units per unit cell does not change at Curie temperature;

- **antiferrodistortive** transitions, when the number of formula units in the low symmetry phase unit cell is an integer multiple of the number of formula units in the high symmetry phase unit cell.

When the electrical properties of low-symmetry phase are taken into account, one can distinguish between the *ferroelectric* and *antiferroelectric* 'ferro' and 'antiferrodistortive' phase transitions. In the ferroelectric phase transition, the low-symmetry phase exhibits a macroscopic polarization whereas in the antiferroelectric one, there is no macroscopic polarization in the low-symmetry phase due to the appearance of two or more sublattices polarized in opposite directions (the magnitude of the sublattice polarization being the same).

As was pointed out by Cochran [Coc59, Coc60], the displacive model corresponds to the condensation of one (or more) of the normal mode displacements of the crystalline lattice at the critical temperature $T_C$. The vanishing frequency of this soft mode when the critical temperature is approached from above results in a frozen-in atomic displacements. These static components of the soft mode correspond to the atomic distortions which drive the paraelectric phase into the ferroelectric one. In consequence, in this model the structure of the low-temperature phase is determined by the superposition of the frozen-in soft mode displacements and the structure of the paraelectric phase.

If the phase transition is a ferrodistortive one, the wavevector of the unstable phonon is located at the center of the Brillouin zone, whereas for an antiferrodistortive phase transition the soft mode involves an instability at the Brillouin zone boundary.

In the *order-disorder* model, the local potential as a function of the normal coordinates presents two or more minima, being largely anharmonic. In this case, the macroscopic polarization vanishes at critical temperature due to an increasing
disorder of the orientation of the microscopical dipoles. These electric dipoles can vibrate in the potential wells even in the paraelectric phase and the high temperature to low temperature phase transition is associated with unstable pseudo spin modes [Sco74].

In the light of the above considerations, the mechanism of the structural phase transition from the paraelectric to ferroelectric phase in LiNbO₃ is still not unambiguously elucidated. Because during the phase transition there is no change in the number of atoms in the unit cell, according to the displacive picture the structural transformation in LiNbO₃ at the critical temperature involves a phonon instability at the center of the Brillouin zone. Thus the experimental challenge was to observe the existence of a temperature dependent soft phonon, which must have, according to the group theory, the $A_{2g}$ symmetry in the paraelectric phase and the $A_1$ symmetry in the ferroelectric one.

Temperature-dependent Raman scattering measurements performed by Johnston and Kaminow [JK70] for LiNbO₃ and LiTaO₃ over a large temperature range from 90 to 1100 K supported the displacive model for both compounds by detecting a vanishing frequency for the lowest $A_1$ transversal optic (TO) mode. The softness of one of the $A_1$ TO modes in these materials was also evidenced by means of infrared reflectivity measurements effected by Servoin and Gervais [SG79]. Also, the increase of the dielectric constant near the Curie temperature in LiNbO₃ observed by Nassau et al. [NLL66] was interpreted in the Ref. [JK70] as an evidence to a displacive-type phase transition in this material.

In contrast to these results, the inelastic neutron scattering measurements performed by Chowdhury et al. [CPS78] failed to observe the softening of any of the $A_1$ modes. However, they identified only three $A_1$ modes due to the use of a longitudinal scattering experimental configuration and thus the conclusion of their study may be ill founded. Surprisingly, a more clear evidence for an order-disorder phase transition in LiNbO₃ was obtained by Okamoto et al. [OWS85] by means of temperature-dependent Raman scattering experiments. Their Raman spectra recorded from room temperature to 1225 K showed a softening of one $A_1$ mode and were analyzed with the help of a damped harmonic oscillator coupled with a Debye-like relaxation mode model. Within this model, the decrease of the frequency of one $A_1$ mode from 274 cm$^{-1}$ to 100 cm$^{-1}$ was interpreted as being due to the rapid increase in damping of its linewidth with the increase of temperature, whereas its
quasiharmonic frequency was found to be nearly temperature independent.

As was stressed by Ridah et al. [RBFM97, RFB97], the Raman scattering exhibits a strong dependence on crystal stoichiometry. Basically, all the previous experiments were performed using congruent samples, described by the ratio $x_c = [\text{Li}]/([\text{Li}]+[\text{Nb}])$ rather far away from the value of 50%. As it will be discussed in more detail in the next Chapter, the presence of a large amount of intrinsic defects in congruent samples could affect the accuracy of the obtained results, e.g. through the appearance of localized vibrational modes induced by these lattice defects. Recently, using a nearly stoichiometric sample ($x_c=49.74\%$), Ridah et al. [RFB97] found only a large softening of the lowest $A_1$ mode, the frequency of which does not vanish when the critical temperature $T_C$ is approached. Based on this experimental result, they concluded that the ferroelectric-paraelectric phase transition of LiNbO$_3$ has mainly an order-disorder character.

The nature of the phase transition in LiTaO$_3$ was the subject of the same controversy – displacive versus order-disorder mechanism. Early results reported by Johnston and Kaminow [JK70] suggested that the phase transition in LiTaO$_3$ is described by the displacive model. The validity of this picture was contested by Penna et al. [PCP76, PPWA77]. In their temperature-dependent Raman scattering measurements they did not observe any softening of any $A_1$ modes. Instead, their Raman spectra showed the presence of a highly temperature-dependent central mode whose shape could be fitted by a Debye-like relaxation mode. This finding together with the observation of polariton saturation phenomenon led them to conclude that the mechanism responsible for the phase transition in LiTaO$_3$ is given by temperature-dependent dynamical domain fluctuations associated with the breaking of the long-range order along the ferroelectric axis. However, this conclusion was not supported by elastic constant measurements performed by Tomeno [Tom82] and dielectric susceptibilities and conductivities data obtained by Tomeno et al. [TM88]. These experimental results suggested an intermediate character between the displacive and order-disorder for the ferroelectric phase transition of this material described by a coupling between the soft mode and mobile defects, or Li-ion displacements. A certain degree of softness of the lowest $A_1$ mode was also observed by Zhang et al. [ZS86], and the spectral line shapes of their Raman data were interpreted as an evidence for the coupling between this “soft” mode and a Debye-type relaxation mode caused probably by oxygen defects.
2.1 LiNbO$_3$ and LiTaO$_3$: experimental results

The order-disorder picture describes well the Raman spectra measured in a temperature range 290 to 1200 K by Raptis [Rap88], who also noticed a certain softening of $A_1$ modes. Moreover, the temperature dependence of these spectra could be interpreted by supposing the presence of an intermediate phase within a temperature range of 100 K below the critical point characterized by a mixed ferro-paraelectric symmetries. However, no softening of any of $A_1$ modes was found in Raman and hyper-Raman spectra recorded from 14 to 2000 K by Tezuka et al. [TSI94]. In both phases, the hyper-Raman spectra presented a strong Debye-type relaxational mode which was interpreted as a clear indication of an order-disorder model for the phase transition in LiTaO$_3$. The same conclusion was reached by means of inelastic neutron scattering performed by Cheng et al. [CHL+93] in both ferroelectric and paraelectric phases.

Beside the already mentioned suggestion of Tomeno et al. [TM88] that the phase transition in LiTaO$_3$ has an intermediate character between displacive and order-disorder, the temperature dependence of the LiTaO$_3$ structure in ferro- and paraelectric phase investigated by Abrahams et al. [ABHL73] pointed to the same conclusion. In their neutron scattering experiments, Abrahams et al. found a displacement-like behaviour in the ferroelectric phase whereas in the paraelectric one they ascertained that the Li ions are occupying with equal probability two sites displaced along the $c$-axis with 0.374 Å above and below the oxygen atoms plane at $z=1/4$ (see Fig. 2.2). In consequence, the paraelectric-to-ferroelectric phase transition was associated with a gradual ordering of the Li atoms. The same conclusion was reached through similar neutron scattering measurements performed by Samulesen et al. [SG76]. As a final picture of these experimental evidences, it seems that in LiTaO$_3$ the Li ions present an order-disorder-type displacements, whereas Ta atoms exhibit a displacive-type ones.

Unfortunately, a similar study of the structure parameters in the paraelectric phase of LiNbO$_3$ could not be performed because of a rather narrow range of temperature between its critical point $T_c=1480$ K and the melting one at $T=1530$ K. The absence of any reliable experimental evidences concerning the Li positions in the high-temperature phase of LiNbO$_3$ precludes a clear support for a order-disorder mechanism for the phase transition in this material.
2.2 Previous theoretical results

One of the first attempts to analyze the phase transitions in ferroelectric materials was done by Lines [Lin69a, Lin69b] who developed an effective Hamiltonian which describes through several parameters fitted to the experimental results the ionic motion in a ferroelectric system. Moreover, the temperature dependent properties of the studied systems were predicted using classical statistics. When applied to LiTaO$_3$ [Lin69c, Lin72], the theoretical description of its phase transition was that of a mixture of displacive and order-disorder characteristics, with Li ions moving in a triple potential well with minima at the centrosymmetric site as well as at $\pm 0.4$ Å.
2.2 Previous theoretical results

with respect to this site. Also, a mean field-like behaviour of the dielectric relaxation in LiTaO$_3$ and LiNbO$_3$ was studied by Prieto et al. [PAG84, PG87].

A quantum mechanic calculation for the same material was performed by Bakker et al. [BHK93, BHK98] using a temperature dependent triple well potential also fitted to some experimental results. These calculations explained a previously observed resonance at 32 cm$^{-1}$ at room temperature in their time-resolved measurements of phonon polaritons [BHK92] as a tunneling of the Li ions through the central and the lowest well. A double potential well was used by Birnie [Bir91] in order to describe in a thermodynamical approach the Li atoms as Frenkel defects. In this case, Li atoms are hopping between their centrosymmetric positions and the normally vacant octahedral sites in the para- and ferroelectric structures.

The nature of the ferroelectric instability in LiNbO$_3$ and LiTaO$_3$ was studied from the first principles by Inbar and Cohen [IC95, IC96, IC97] using the full-potential linearized augmented plane wave method (FLAPW). They have shown that the Li displacements are not described by a triple potential wells as was assumed in the previous models of Lines and Bakker et al.. Instead, the displacement of Li atoms along the experimental ferroelectric coordinates can be described by a single anharmonic potential well. A deep double well was found for coupled displacements of oxygen and lithium atoms. The electronic origin of this order-disorder character of the oxygen distortions lies in the hybridization between the oxygen 2$p$ states and the $d$ states of the transition metal. This hybridization results in a movement of the oxygen atoms towards the transition metal ones, and the resulting electric field on Li sites displaces them from their centrosymmetric positions. In addition, because the zone-center potential-energy surfaces in both LiNbO$_3$ and LiTaO$_3$ look very similar, it was concluded by Inbar and Cohen that the difference in the transition temperatures in these compounds can be ascribed to the differences in their energetics at the zone boundary. Similar results were obtained later by Yu and Park [YP97].

More recently, Parliński et al. [PLK00] derived the phonon-dispersion relations for both paraelectric and ferroelectric phases of LiNbO$_3$. In their study, they found a double potential well associated with the displacements of Li atoms along the polar axis which supports the order-disorder picture of the paraelectric-to-ferroelectric phase transition in this material. Moreover, the phonon frequencies at several high-symmetry points were predicted, whereas the eigenvectors were not calculated.
2.3 Motivation

For LiNbO$_3$, an *ab initio* investigation of the lattice dynamics at Γ point was essentially required by a controversial phonon attribution of Raman and infrared active $A_1$ and $E$ modes. The underlying reason of this situation lies in the observation that the Raman measurements are very sensitive to small changes in the structure of this material. Therefore, the phonon frequencies calculated for stoichiometric LiNbO$_3$ could be used to unambiguously assign the phonon modes in question. Moreover, the frozen-phonon calculations provide also the displacement patterns which are not fully available from the experiment. These normal vibration modes can be further used in the development of lattice dynamics models for non-stoichiometric and doped LiNbO$_3$.

In addition, the study of the zone-center lattice dynamics of this compound from first principles represents also an opportunity to test the reliability of using *ab initio* methods when they are applied to a relatively complex structure. In previous *ab initio* calculations, the lattice instability of LiNbO$_3$ was investigated for the experimental structure. The use of this setup is essentially due to the failure of the ground-state calculations performed within DFT to predict to proper phase transition in some ferroelectric materials when using the theoretical lattice parameters. In consequence, our aim was to determine if this instability also occurs when the structure that minimizes the total energy of the system under study is used, i.e. for the *fully optimized* structure of LiNbO$_3$. Besides the use of the experimental lattice parameters, Inbar and Cohen [IC96] simulated the ferroelectric instability in LiNbO$_3$ by a uniform scaling of the crystal structure along the linear path between experimentally determined paraelectric and ferroelectric structures. In our study the para- to ferroelectric phase transition was investigated according to the atomic displacements given by the group theory.

Since the physical properties of LiNbO$_3$ depend significantly on the presence of both intrinsic and extrinsic defects, the doped LiNbO$_3$ with various trivalent ions was intensively studied over the last years. Performing *ab initio* spin-polarized calculations, we focused on the analysis of the ground-state properties of LiNbO$_3$ doped with Fe and Cr. Particularly, we investigated the role of the charge compensation mechanism for the Fe impurity as well as the effect of the relaxation of *all* atomic coordinates on the electronic properties of Cr impurity ions.

For LiTaO$_3$, the present study was carried out to gain an insight into the origin
of the differences between the lattice dynamics in LiTaO$_3$ and LiNbO$_3$ as evidenced by Raman spectroscopy. To be more specific, since the atomic mass of Ta atoms $m_{Ta} = 180.95$ is almost twice larger than those of Nb atoms ($m_{Nb} = 92.91$), a common physical intuition leads us to foresee that the Raman frequencies will be shifted to lower values in LiTaO$_3$ by comparison with the corresponding values in LiNbO$_3$.

However, the Raman spectra of these compounds recorded for $A_1$ modes show a different picture (see Fig. 2.3). For three modes, the Raman frequencies in LiTaO$_3$

![Raman spectra](image)

Figure 2.3: Raman spectra of $A_1$ TO modes recorded for LiNbO$_3$ and LiTaO$_3$ (P. Bouson, private communication)

are indeed lower than those in LiNbO$_3$. As was noted by Kojima [Koj93] and also by Repelin [RHP99], the substitution of Nb sites by Ta atoms results in one $A_1$ mode (TO$_3$) with a frequency slightly higher than in LiNbO$_3$. Intuitively, this experimental behaviour could be explained assuming a negligible Ta ions contribution in this mode.

Such an intuitive explanation could represent nowadays only a starting point
in understanding the physics behind this behaviour. From the comparison of the 
*ab initio* zone-center lattice dynamics obtained for LiTaO$_3$ with that of LiNbO$_3$, 
the atomic displacements responsible for the observed experimental shift in $A_1$-TO$_3$ 
frequencies can be determined. Moreover, the underlying electronic origin of this 
difference in $A_1$-TO$_3$ vibration patterns can be also identified.
Chapter 3

The Fundamentals of the Density Functional Theory

Introduction

The basic aim of physics as a fundamental science of human knowledge is to predict the behaviour of physical systems. This requires the elaboration of concepts that express the properties of physical objects as they are accessible to human perception. By comparing them with an reference object for that property, numbers associated with these physical properties could be obtained. This genesis of the quantitative laws allowed therefore amazing predictions and explanations regarding the structure of the Universe that enclose the human existence: a new planet in our solar system - Pluto, the periodic movement of the comets and when are they visible from the Earth, why do the tides exist etc.

All these quantitative explanations were possible for physical systems that could be described in terms of the notions generated by the human experience which basically relies on the intrinsic limited human perception. What happens if the physical system could not be satisfactory represented in terms of our current sensorial experience?

Unfortunately, the answer to this so fundamental question is not known. Fortunately, its absence gives the opportunity to physics to be a live science, largely opened to new mathematical and philosophical perspectives. Nevertheless, it is ex-
3.1 The Variational Principle in Quantum Mechanics

It is extraordinary that the human intelligence could devise quantitative tools which could handle such frontier situations. Particularly, the quantum mechanics allows reliable quantitative predictions of the properties of various physical systems such as atoms, molecules and solids, whose technological applications essentially determine the standard of our life.

3.1 The Variational Principle in Quantum Mechanics

The time evolution of a quantum state of any physical system can be determined by solving its time-dependent Schrödinger equation:

\[ i\hbar \frac{\partial}{\partial t} \Phi(R, r, t) = \hat{H} \Phi(R, r, t), \]  

(3.1)

where \( R \) and \( r \) denote the ensemble of positions vectors of the system’s nuclei and electrons, correspondingly, and \( \hat{H} \) is the Hamiltonian of the studied system (nuclei and electrons). Unfortunately, there is no hope in solving analytically this fundamental equation even for simple systems such as isolated atoms, with the notable exception of the hydrogen atom. Therefore, in order to determine the quantum state of a physical system, further unavoidable simplifying assumptions regarding the structure of its Hamiltonian must be taken into account.

The physical systems of interest for solid state physics as well as for atomic and molecular physics can be visualized as a frame of nuclei of charge \( Z_o \) enclosed by a sea of electrons. Because of a significant difference between the electron mass and that of a nuclei, the quantum state of an \( N \)-electron system without time dependent interactions can be described within the Born-Oppenheimer approximation by the following time-independent Schrödinger equation:

\[ \hat{H} \Psi(r) = E \Psi(r), \]  

(3.2)

where the electronic Hamiltonian operator \( \hat{H} \) is given by (in atomic units \( m = \hbar = \)
3.1 The Variational Principle in Quantum Mechanics

\[ e^2 = 1 \]

\[ \hat{H} = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^{N} v(r_i) + \frac{1}{2} \sum_{i,j=1}^{N} \frac{1}{|r_i - r_j|}, \]  

(3.3)

or in a more compact form:

\[ \hat{H} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee}. \]  

(3.4)

and \( \mathbf{r} \) represents the positions vectors of the electrons (for a given set of nuclei coordinates). In the above equation, the external potential \( v(r_i) \) felt by the \( i \)-th electron is, e.g., the potential due to static nuclei at \( \mathbf{R}_\alpha \)

\[ v(r_i) = -\sum_{\alpha} \frac{Z_\alpha}{|r_i - \mathbf{R}_\alpha|}. \]  

(3.5)

Defining the total energy \( E \) of the \( N \) electron system as a functional of its \( N \)-particle Hilbert space functions by

\[ E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \]  

(3.6)

it is proven in standard quantum mechanics books (see for instance, Messiah [Mes72], Merzbacher [Mer70]) that instead of solving the time-independent Schrödinger equation (3.2), the ground-state eigenvalues and eigenfunctions of the system under consideration can be determined \( \text{via} \) the following variational principle

\[ \delta E[\Psi] = 0. \]  

(3.7)

Because the physical meaning of the wave functions in quantum mechanics requires them to be normalized to unity, the above variational principle must be reformulated as

\[ \delta \left[ \langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle \right] = 0. \]  

(3.8)
where the total energy $E$ of the system appears as a Lagrange multiplier, associated 
with the normalization constraint $\langle \Psi | \Psi \rangle = 1$.

The variational principle (3.7) is also satisfied by an excited-state eigenfunction, 
but the corresponding eigenvalue will be above the ground-state energy only if that 
excited-state function is orthogonal to ground-state one. From the mathematical 
point of view, no essential reduction of the initial difficulty in solving the time-

independent Schrödinger equation is gained by reformulating it as a variational 
equation. However, for the ground-state eigenfunctions and eigenvalues a remarkable 
simplification of the variational principle (3.7) could be obtained due to the work 
of Hohenberg and Kohn [HK64]. This reformulation of the variational principle for 
ground-state quantum systems, together with the one-electron equation elaborated 
by Kohn and Sham [KS65] on its grounds, provides the physical foundations of 
modern computation schemes designed for quantitative predictions of ground-state 
properties of physical systems.

3.2 The Hohenberg-Kohn Theorems

To evaluate the total energy of the physical system in question first one should note 
that the external potential $v$ as well as the total number of electrons $N$ completely 
determine the form of the Hamiltonian of the that system. In consequence, instead 
of the defining relation (3.6) the total energy can be expressed as a functional of the 
total number of electrons $N$ and the external potential $v$: $E[N, v]$.

The fundamental observation of Hohenberg and Kohn was that for ground-state 
properties of an electron gas containing $N$ particles in some general external poten-
tial (Coulombian or not) $v(\mathbf{r})$, the electron density

$$
\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \ldots \mathbf{r}_N.
$$

can be regarded as the basic variable of that system.

In their original paper, Hohenberg and Kohn stated that, for a nondegenerate 
ground-state, the external potential $v(\mathbf{r})$ is a unique functional of $\rho(\mathbf{r})$, apart from 
a trivial additive constant. The proof of this first Hohenberg-Kohn theorem can be 
found in their article, as well as in more recent monographs dedicated to density
3.2 The Hohenberg-Kohn Theorems

functional theory (see for instance, Parr and Yang [PY89] and Eschrig [Esc96]). In the context of this theorem, the total energy of the ground state is a functional only of the electron density \( \rho(\mathbf{r}) \) and for a given external potential \( v(\mathbf{r}) \) it can be written as

\[
E_v[\rho] = T[\rho] + V_{\text{ext}}[\rho] + V_{\text{ee}}[\rho] \\
= F_{HK}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r},
\]

(3.9)

where the quantity \( F_{HK}[\rho] \) defined by

\[
F_{HK}[\rho] = T[\rho] + V_{\text{ee}}[\rho].
\]

(3.10)

is a universal functional, independent on any external potential \( v(\mathbf{r}) \) and valid for any number of electrons \( N \). The knowledge of this universal functional \( F_{HK}[\rho] \) would result in obtaining an exact equation for the ground-state density. The proof of this assertion is given by the second Hohenberg-Kohn theorem, namely the functional \( E_v[\rho] \) assumes its minimum value for the ground-state electron density \( \rho(\mathbf{r}) \) if the admissible functions are restricted by the condition

\[
N[\rho] = \int \rho(\mathbf{r})d\mathbf{r} = N.
\]

(3.11)

The second Hohenberg-Kohn leads to the following reformulation of the variational principle (3.7)

\[
\delta \left\{ E_v[\rho] - \mu \left[ \int \rho(\mathbf{r})d\mathbf{r} - N \right] \right\} = 0.
\]

(3.12)

where the Lagrange multiplier \( \mu \) required by the constraint (3.11) represents the chemical potential.

There is still one uncomfortable limitation of the original formulation of the variational principle (3.12) given by Hohenberg and Kohn. A closer look at the conditions that must be fulfilled by the ground-state electron density \( \rho_0(\mathbf{r}) \) solution of the variational principle (3.12) shows that it must correspond to an antisymmet-
ric ground-state wave function of the Hamiltonian (3.3) which describes the considered system with some external potential \( \nu(r) \) (such a electron density is called \( \nu \)-representable). The problem is that the required conditions for an electron density to be \( \nu \)-representable are not known.

As was shown by Levy [Lev79] (also by Lieb [Lie83]), the \( \nu \)-representability condition for the ground-state electron density can be replaced by a weaker condition. This new condition can be easily determined if one performs the ground-state energy minimization first over all wave functions that give the same electron density \( \rho(r) \) and afterwards searching over all \( \rho(r) \)

\[
E_0 = \min_{\Psi} \langle \Psi | T + V_{ee} + \mathbf{V}_{ne} | \Psi \rangle
\]

\[
= \min_{\rho} \left\{ \min_{\Psi} \langle \Psi | T + \mathbf{V}_{ee} + \mathbf{V}_{ne} | \Psi \rangle \right\} \tag{3.13}
\]

\[
= \min_{\rho} \left\{ \min_{\Psi} \langle \Psi | T + \mathbf{V}_{ee} | \Psi \rangle + \int \rho(r) \nu(r) d\mathbf{r} \right\},
\]

or in a more compact notation

\[
E_0 = \min_{\rho} \left\{ F_{\text{LL}} [\rho] + \int \rho(r) \nu(r) d\mathbf{r} \right\}. \tag{3.14}
\]

The domain of the Levy-Lieb functional \( F_{\text{LL}} [\rho] \) defined by

\[
F_{\text{LL}} [\rho] = \min_{\Psi} \langle \Psi | T + \mathbf{V}_{ee} | \Psi \rangle. \tag{3.15}
\]

introduced in the last line of the above ground-state energy minimization is given by the antisymmetric wave functions which by quadrature lead to an electron density \( \rho(r) \) (such a electron density is called \( N \)- representable). As the Hohenberg-Kohn functional \( F_{\text{HK}} [\rho] \), the Levy-Lieb functional \( F_{\text{LL}} [\rho] \) is also universal. In consequence, in this constrained-search approach of the density functional theory the variational principle (3.12) is satisfied by all electron densities that are \( N \)-representable and this constraint is obviously less restrictive than the one expressed in the initial Hohenberg-Kohn formulation.
3.3 The Kohn-Sham Equations

The power of the variational principle (3.12) becomes apparent in combination with the universality of the Hohenberg-Kohn functional $F_{HK} [\rho]$. Unfortunately, the form of the latter is not known, and this situation raised a question mark regarding the usefulness of the Hohenberg-Kohn theory.

This discouraging difficulty induced by the unknown expression of the Hohenberg-Kohn functional was overpassed by Kohn and Sham [KS65]. The basic idea of their work was the introduction of a noninteracting reference system described by the Hamiltonian

$$
\hat{H}_0 = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i=1}^{N} v(\mathbf{r}_i)
$$

$$
= \sum_{i=1}^{N} \hat{h}_i. \tag{3.16}
$$

such that the ground-state electron density is the same as for interacting system. Using the $N$ lowest eigenfunctions $\psi_i$ of the one-electron Hamiltonian $\hat{h}_i = -\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i)$ the kinetic energy functional $T_0 [\rho]$ for non-interacting system given by

$$
T_0 [\rho] = \sum_{i=1}^{N} \langle \psi_i | -\frac{1}{2} \nabla_i^2 | \psi_i \rangle. \tag{3.17}
$$

can be calculated exactly. This represents a good approximation to the true kinetic energy and an essential improvement over the Thomas-Fermi model, in which the variation of semiclassical total energy with respect to particle density yields the kinetic energy density proportional to $\rho^2(\mathbf{r})$ (see Ref. [PY89] for more details). It was shown in a literature (see, for instance, the comprehensive exposition of the Jones and Gunnarsson [JG89]) that a poor evaluation of kinetic energy results in a significant quantitative difference between the calculated atomic and molecular properties and the ones experimentally observed.

Dividing the electron-electron interaction energy functional $V_{ee} [\rho]$ into a classical
part $J[\rho]$ (including electrostatic self-interaction) defined by
\[
J[\rho] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} d\mathbf{r}_1 d\mathbf{r}_2, \tag{3.18}
\]
and in a non classical part, the Hohenberg-Kohn functional can be written as
\[
F_{HK}[\rho] = T_0[\rho] + J[\rho] + E_{xc}[\rho]. \tag{3.19}
\]
This relation defines the exchange-correlation energy functional $E_{xc}[\rho]$ that incorporates the non-classical corrections to electron-electron interactions and the (small) difference between the true kinetic energy of the interacting electron gas and that of the Kohn-Sham non-interacting reference system.

With the above definitions, the ground-state electron density that minimizes the total energy of the system via the variational principle (3.12) must satisfy the corresponding Euler-Lagrange equation
\[
\mu = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xe}(\mathbf{r}) + \frac{\delta T_0[\rho]}{\delta \rho(\mathbf{r})} = v_{eff}(\mathbf{r}) + \frac{\delta T_0[\rho]}{\delta \rho(\mathbf{r})}, \tag{3.20}
\]
where the exchange-correlation potential $v_{xe}(\mathbf{r})$ is given by the functional derivative of the exchange-correlation functional $E_{xc}[\rho]$ with respect to the electron density $\rho$ at the point $\mathbf{r}$:
\[
v_{xe}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \tag{3.21}
\]

If the effective potential $v_{eff}(\mathbf{r})$ were known, the Euler-Lagrange equation would be solved and thus all ground-state properties of the considered physical system would be determined. Unfortunately, this is not the case because the effective potential is in turn a function of the unknown ground-state electron density.

In their approach, Kohn and Sham showed that the Euler-Lagrange equation (3.20) is equivalent to a system of $N$ one-electron equations that describes $N$ non-
3.4 The Local Density Approximation

interacting electrons moving in the external potential \( v_{eff}(\mathbf{r}) \)

\[
\left[ -\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}) \right] \psi_i^{KS}(\mathbf{r}) = \varepsilon_i \psi_i^{KS}(\mathbf{r}). \tag{3.22}
\]

Therefore, the electron density is given by

\[
\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i^{KS}(\mathbf{r})|^2. \tag{3.23}
\]

and thus all ground-state properties of the considered system can be computed. Particularly, the total energy can be determined from the following relation

\[
E = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] \tag{3.24}
\]

\[- \int \rho(\mathbf{r}) v_{xc}(\mathbf{r}) d\mathbf{r}.
\]

which can be easily derived from the expression of the Hohenberg-Kohn functional (3.19).

Because the Kohn-Sham scheme is based on the Hohenberg-Kohn functional, the corresponding ground-state electron density must be noninteracting \( \nu \)-representable. However, it can be shown that by redefining the kinetic functional within the constrained-search approach, this limitation can be relaxed such that the corresponding ground-state density must fulfill only the \( N \)-representability condition.

### 3.4 The Local Density Approximation

To obtain the ground-state electron density within the Kohn-Sham approach, the form of the exchange-correlation functional \( E_{xc}[\rho] \) must be known. An accurate expression for the exchange-correlation functional is essential for obtaining meaningful results regarding the ground-state properties of the studied physical system. The search for a reliable form of this functional was and still is a challenge in the density functional theory.

One of the most popular approximation of the exchange-correlation functional
3.4 The Local Density Approximation

$E_{xc}[\rho]$ is given by the local density approximation (LDA), which was first proposed by Hohenberg and Kohn in their paper. In this approximation, the exchange-correlation functional is expressed as

$$
E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}(\rho(\mathbf{r})) \, d\mathbf{r}.
$$

(3.25)

where $\varepsilon_{xc}^{\text{hom}}(\rho)$ represents the exchange-correlation energy density determined for an uniform electron gas of density $\rho(\mathbf{r})$. An explicit form of this exchange-correlation energy density can be obtained by dividing it in an exchange and correlation part

$$
\varepsilon_{xc}^{\text{hom}}(\rho) = \varepsilon_{x}^{\text{hom}}(\rho) + \varepsilon_{c}^{\text{hom}}(\rho),
$$

(3.26)

so that, generally, the exchange-correlation functional can be written as

$$
E_{xc}[\rho] = E_{x}[\rho] + E_{c}[\rho].
$$

(3.27)

From physical point of view, the exchange energy represents the contribution to the total energy due to the antisymmetry of the many-body electron wave functions; that is, because of the Pauli exclusion principle, two electrons cannot come arbitrarily close to each other. But even when two electrons are described by the same quantum numbers except the spin one, the direct Coulomb interaction would tend to put them apart, thus lowering the total energy of the system and the corresponding energy contribution is named correlation energy. The expression of the exchange contribution averaged over Hartree-Fock orbitals which yield a certain total density $\rho$ in a homogeneous electron gas, $\varepsilon_{x}^{\text{hom}}(\rho)$, is known analytically due to Dirac [Dir30], being given by

$$
\varepsilon_{x}^{\text{hom}}(\rho) = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} \rho(\mathbf{r})^{\frac{1}{3}},
$$

(3.28)
for all electron densities $\rho(r)$. In terms of Wigner-Seitz radius defined by

$$r_s = \left( \frac{4\pi \rho(r)}{3} \right)^{-\frac{1}{3}},$$

it can be rewritten as

$$\varepsilon_c^{\text{hom}}(\rho) = -\frac{0.458}{r_s}.$$ (3.29)

For solids, typical values of Wigner-Seitz radius are between 2 and 5. The analytical form of the correlation part $\varepsilon_c^{\text{hom}}(r)$ was determined with the tools of the many-body perturbation theory [FW71] for the limiting cases of high densities ($r_s \ll 1$) [GMB57, Pin63]

$$\varepsilon_c^{\text{hom}}(\rho) = -0.0480 + 0.0311 \ln r_s - 0.0116 r_s + 0.002 r_s \ln r_s,$$  \hspace{1cm} (3.30)

and low densities ($r_s \gg 1$) [NP66]

$$\varepsilon_c^{\text{hom}}(\rho) = -\frac{0.88}{r_s}. \hspace{1cm} (3.31)$$

The results for $1 \leq r_s \leq 100$ were obtained by Ceperley and Adler [CA80] by means of quantum Monte Carlo calculations, and they were parametrized by Perdew and Zunger [PZ81] to the following analytic expression

$$\varepsilon_c^{\text{hom}}(\rho) = -\frac{0.1423}{1 + 1.0529 \sqrt{r_s} + 0.3334 r_s}. \hspace{1cm} (3.32)$$

The corresponding final formula for the exchange-correlation functional is largely used in current computer simulations of ground-state properties of atoms, molecules and solids.

Even if the electron gas in these physical systems is highly inhomogeneous, their ground-state properties were predicted often by the LDA calculations with a surprisingly good accuracy. The physical ground of this agreement between LDA and experimental results was emphasized by Gunnarsson et al. [GJL79]. However, one
should note the main drawbacks of this approximation. The LDA \textit{ab initio} calculations performed for solids usually fail to predict their experimental equilibrium lattice parameters, and this misprediction could dramatically affect their physics. Also, the LDA bulk equation for solids are often inaccurate and the molecular binding energies are usually too large.

However, a significant gain in accuracy upon the LDA results could be obtained by using its \textit{spin-density} extension. As was emphasized in Ref. [PY89], the underlying reason of this improvement even when the \textit{local spin-density} approximation (LSDA) is applied to systems in the absence of the magnetic field lies in the fact that in this approach electrons with different spin quantum numbers feel a different spin-dependent potential, which is clearly a better approximation for systems with an odd number of electrons. Moreover, the LSDA allows the investigations of magnetic systems that exhibit spontaneous magnetic phenomena. In a similar fashion as in LDA, the exchange-correlation energy is a functional of spin-up $\rho_{\uparrow}$ and spin-down $\rho_{\downarrow}$ electron densities

$$E_{xc}^{LSDA}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \rho(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}(\rho(\mathbf{r}), \zeta) d\mathbf{r}. \quad (3.33)$$

where $\rho = \rho_{\uparrow} + \rho_{\downarrow}$ is the total electron density, $\varepsilon_{xc}^{\text{hom}}(\rho)$ represents the exchange-correlation energy per particle for a homogeneous spin-polarized electron gas and $\zeta$ expresses the relative spin polarization

$$\zeta = \frac{\rho_{\uparrow} - \rho_{\downarrow}}{\rho}.$$ 

A detailed expressions for the exchange and correlation part of this functional can be found elsewhere (see, e.g., the above cited reference and references therein).

Despite of this development, there are physical situations where L(S)DA reaches its limits. For instance, the L(S)DA lattice parameters for bcc Fe are by 3 - 4\% smaller than the experimental ones, and this underestimation results in the total energy of ferromagnetic bcc phase higher than that calculated for fcc phase. Of course, the fundamental reason of the L(S)DA failure to reproduce, qualitatively or quantitatively, the physical properties of interest is its local treatment of the exchange-correlation electronic potential. As was shown by Gunnarsson and Jones
[GJ81], a supplementary inaccuracy of the total energy calculated within this approximation is due to a large contribution in energy of the unphysical self-energy of the tightly bound core electrons in atoms and molecules. Additionally, the same problem appears in solids where the valence electrons get localized on atomic sites. In such cases, typically encountered in $3d$ transition metal oxides (MnO, FeO and NiO) as well as in the $f$ electron systems, the electron-electron correlations are too strong to be adequately treated within this approximation.

## 3.5 The Generalized Gradient Approximation

The simplest choice to overcome the limitations induced by the local treatment of the exchange-correlation electronic potential is to take into account the inhomogeneity of the electron gas in the expression of the exchange-correlation functional $E_{xc}[\rho]$ as a gradient of the electron density. In this generalized gradient approximation (GGA), Perdew et al. [PBE96] proposed the following expression for the exchange-correlation energy as a functional of the electron spin densities (known as PBE GGA)

$$E_{xc}^{\text{GGA}}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \rho(\mathbf{r}) \varepsilon_{xc}^{\text{hom}}(\rho(\mathbf{r})) F_{xc}^{\text{GGA}}(r_{s}, \zeta, s(\mathbf{r})) d\mathbf{r}, \quad (3.34)$$

where $F_{xc}^{\text{GGA}}(r_{s}, \zeta, s(\mathbf{r}))$ is the enhancement factor over LDA exchange, $s(\mathbf{r})$ represents an dimensionless density gradient

$$s(\mathbf{r}) = \frac{\left| \nabla \rho(\mathbf{r}) \right|}{2k_{F}\rho(\mathbf{r})}.$$

This exchange-correlation functional yields essentially the same results as that derived by Perdew and Wang [PW92] (known as PW91 GGA) as a analytic fit to a first-principles numerical GGA as described in Ref. [PBW96]. Moreover, it improves PW91 over the linear response of the uniform gas and uniform scaling, while retains the correct features of the LSDA.

Because by its construction the GGA exchange-correlation functional allows for considering the inhomogeneity effects of the electron gas more than L(S)DA does, GGA generally improves the atomic and molecular total energies, correct the LDA
overbinding for small molecules, and yields an improved activation energy barriers in chemical reactions. It also delivers a better cohesive energies for solids. As a shortcoming, GGA softens the bonds in solids, with a corresponding increase of the lattice parameters. This feature could affect the physics of the systems whose total energies are extremely sensitive to the total volume, as is the case of the ferroelectric materials. However, GGA predicts correctly the ferromagnetic ground-state of Fe in the bcc structure, removing thus the LDA’s misprediction.

The main reason why the improvements produced by GGA over the LDA results are not systematical lies in a rather crude approximation of the inhomogeneous electron gas with a slowly varying electron gas as assumed in GGA. Moreover, as presented in detail by Filippi in Ref. [FGU96], the exact exchange-correlation functional must fulfill several analytical properties. However, the currently used exchange-correlation functionals developed on an \textit{ab-initio} or semiempirical ground satisfy only some of these known properties.

Particularly for GGA functionals with the general form given by Eq. (3.34), the expression of the enhancement factor is still a matter of debate. The form chosen by Perdew \textit{et al.} [PBE96] for the exchange part of the enhancement factor

\[ F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\kappa}{\mu s^2}}. \tag{3.35} \]

relies on the value of \( \kappa = 0.804 \) determined from the Lieb-Oxford bound constraint, \( \mu = 0.21951 \) being a constant.

By fitting the exchange atomic energies from He to Ar obtained with the above formula to their exact values, Zhang and Yang [ZY98] obtained for the parameter \( \kappa \) the value of 1.245 (the resulting exchange-correlation functional is known as revPBE), which resulted in a better accuracy for the atomic total energies and molecule atomization energies in comparison with those obtained by Perdew \textit{et al.} in their paper.

As was pointed out by Perdew \textit{et al.} [PBE98], this value of the \( \kappa \) parameter restricts the applicability of the GGA to the atomic and molecular systems, while it may worsen the results obtained for solids because it was determined by a fit to a particular set of physical systems. In fact, the revPBE leads to bondlengths too large and cohesive energies too small when applied to solids. Even more, the revPBE improvement for atomic systems does not hold for all type of bonds.
Several other forms of the exchange-correlation functional are currently available. Besides the options already mentioned, one could use the PRBE GGA proposed by Hammer et al. [HHN99] which gives a better chemisorption energies then PBE, but larger lattice parameters. There are also several semiempirical GGA functionals [Bec88, LYP88] the results of which could be reliable for small molecules, but are less accurate for solids than those determined from the first principles.

In consequence, when performing \textit{ab initio} calculations special attention must be paid to the exchange-correlation functional chosen. One should be aware that, depending on the choice, certain ground-state properties of the system system could be well reproduced whereas other physical properties could be less accurate determined.

### 3.6 The Self Interaction Correction and Beyond

As was emphasized in a previous section, the localized electronic states determines a significant error in total energies computed within the LSDA. A further improvement of the DFT predictions could be obtained starting from the observation of Perdew and Zunger [PZ81] that LSDA (and later on GGA) contains spurious self-interactions of the electrons due to the use of approximate exchange-correlation functionals.

The self-interaction contribution to the total energy comes from the fact that for the one-electron density determined by the \( i \)-th orbital with spin \( s \) the corresponding electron-electron interaction energy must vanish for an one-electron system

\[
J[\rho_i^s] + E_x[\rho_i^s, 0] = 0, \\
E_c[\rho_i^s, 0] = 0.
\] (3.36)

For the \textit{exact} exchange-correlation energy functional the above relations always hold. Particularly, these conditions are fulfilled in the Hartree-Fock method. But for an approximate functionals as both LDA and GGA are, these relations are not fulfilled, and this leads, for instance, to an error of 5\% in the LDA total energy of hydrogen atom.

In the self-interaction corrected (SIC) approach, an approximate exchange-correlation energy functional is constructed in such a way that it satisfies the relations (3.36). In this case, the resulting SIC exchange-correlation potential presents an
3.6 The Self Interaction Correction and Beyond

orbital dependence, which causes the SIC orbitals to be non-orthogonal. This technical problem can be overpassed via Gram-Schmidt orthogonalization method, and the SIC ground-state properties are considerably improved over those predicted by LDA [BTSG97]. However, one should keep in mind that SIC eliminates only the LSDA self-interaction problem; it cannot remove the intrinsic limitations of this approximation.

A general way for improving the accuracy of the ab initio calculations could be obtained by constructing exchange-correlation functionals with a significant non-local character. This aim can be reached by writing the exchange-correlation functional

\[
E_{\text{exc}}[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} h(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow]) d\mathbf{r}_1 d\mathbf{r}_2
\]

\[
= \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow])}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \tag{3.37}
\]

in terms of exchange-correlation hole \(\rho_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow]) = \rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow])\), where the pair correlation function

\[
h(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow]) = h_x(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow]) + h_c(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow]).
\]

must satisfy the following sum rules

\[
\int \rho(\mathbf{r}_2)h_x(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow])d\mathbf{r}_2 = -1
\]

\[
\int \rho(\mathbf{r}_2)h_c(\mathbf{r}_1, \mathbf{r}_2; [\rho_\uparrow, \rho_\downarrow])d\mathbf{r}_2 = 0. \tag{3.38}
\]

The exchange-correlation hole describes the depletion of the electron charge density around a given electron due to Pauli principle exclusion and Coulomb repulsions, and the exchange-correlation energy (3.37) can be interpreted as the electrostatic interaction between an electron located at \(\mathbf{r}_1\) and the density \(\rho_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2)\) of the exchange-correlation hole that surrounds it. It is important to note that the exchange-correlation hole for any physical system is essentially nonlocal, i.e. it is a
functionals of the spin-polarized charge density. The LSDA simply corresponds to

\[ \rho_{xc}(\mathbf{r}_1, \mathbf{r}_2; [\rho_1, \rho_2]) = \rho_{xc}^{\text{unif}}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_1, \rho_2). \]

where \( \rho_{xc}^{\text{unif}}(|\mathbf{r}_1 - \mathbf{r}_2|; \rho_1, \rho_2) \) represents the exchange-correlation hole density of the homogeneous spin-polarized electron gas. In this approximation, the LSDA exchange-correlation hole is only a function of the local spin-polarized charge density and this actually results in the spurious self-interaction of a one-electron system. The reason why LSDA predictions are, however, in a reasonable agreement with the experimental results obtained for real, i.e., highly inhomogeneous, physical systems resides in the isotropic character of the Coulomb interaction between a point charge and its exchange-correlation hole. Because of this, the exchange-correlation energy depends only on the isotropic part (i.e., the spherical average) of the exchange-correlation hole (for more details see, for example, Ref. [GL76, Esc96]).

In the weighted density approximation (WDA) the exchange-correlation potential is constructed at each \( \mathbf{r} \) as a functional of the charge density throughout the whole space. Therefore, this approach is computationally demanding. Another difficulty of this method is represented by the unknown form of the exchange-correlation hole for an electrical inhomogeneous system. Choosing different analytical expressions for the exchange-correlation hole subject to the constraint (3.38), the WDA results described with a better accuracy than LSDA various physical systems as atoms [GCR+93], molecules [ST96], semiconductors and metals [Sin93]. Also, it was shown in series of recent calculations performed by Mazin at al [MS98] that in the case of ferroelectric materials the lattice parameters calculated within this approximation are substantially improved relative to their LDA values. Because the ferroelectric properties are highly sensitive to the volume, the WDA predictions of the ferroelectric behaviour of materials could be more accurate than those obtained within LDA and GGA.

As a final remark, using the actual approximations for the exchange-correlation functional, reliable results for the ground-state properties of atoms, molecules and solids can be currently obtained, even if with a different degree of accuracy. One can only hope that future developments of the density functional theory will provide the same level of accuracy for all ground-state properties regardless the specific nature of the studied system.
Chapter 4

The Linear Augmented Plane Wave Method

Introduction

The Linear Augmented Plane Wave (LAPW) method allows within the framework of the DFT to perform accurate calculations of electronic properties for a large variety of physical systems such as high-temperature superconductors [CPK89, CPK90], ferroelectric oxides [CK90, YK95] or materials containing transition metals [LS92]. This \textit{ab initio} method is not only a powerful tool in understanding the electronic bulk properties of materials. Using the supercell approach, the LAPW method was successfully used in studying the phenomena related to the surfaces of different materials as well as the influence of impurities on the bulk properties. Also, using the \textit{linear response approach} [Res85] or the \textit{direct method} [KM81] it is now possible to obtain reliable results for the lattice dynamics of the crystals.

4.1 Why LAPW?

As was depicted in the previous chapter, the understanding of the ground-state physical properties of various system as atoms, molecules and solids can be achieved by searching for the electron density that minimizes the total energy of the system. Introducing a noninteracting reference system, Kohn and Sham devised a practical
scheme to determine the ground-state electron density and therefore all ground-state properties can be predicted.

The practical problem that still must be addressed is to find a recipe for the numerical solution of the Kohn-Sham equations (3.22). The general approach is to expand the Kohn-Sham orbitals $\psi_i^{KS}(\mathbf{r})$ over a complete set of orthonormal basis functions $\phi_\nu(\mathbf{r})$

$$\psi_i^{KS}(\mathbf{r}) = \sum_{\nu=1}^{\infty} c_\nu \phi_\nu(\mathbf{r}), \quad (4.1)$$

In case of solids, the subscript $i$ denotes the wave vector $\mathbf{k}$, the band index $n$ and the spin quantum number $s$ (in the scalar relativistic approximation).

Using the Rayleigh-Ritz variational principle, the Kohn-Sham equation becomes a set of algebraic equations

$$\sum_{\mu=1}^{\infty} (H_{\mu\nu} - \varepsilon S_{\mu\nu}) c_\nu = 0, \quad (4.2)$$

where the Hamiltonian and overlap matrix elements are given by

$$H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle, \quad (4.3)$$

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle.$$

From computational point of view, the secular determinant equation (4.2) can be casted as a generalized eigenvalue equation for which efficient numerical algorithms exists (see, e.g., Ref. [PFTV89] and the references therein).

Even though the principles of the quantum mechanics require the use of a complete basis set of functions, that is an infinite set of linear independent functions that span the corresponding Hilbert space, in numerical calculations this requirement cannot be accomplished. As a practical consequence, the convergence of the physical quantities of interest as total energy, charge density, magnetic moment etc. with respect to the number of basis functions must be carefully checked in order to obtain meaningful results.

There are different options for choosing the basis set functions. Perhaps the
most alluring one is the use of the plane waves. The main motivation for that is their analytical simplicity, which could lead to a straightforward numerical implementation. Unfortunately, this is not a workable scheme because it would require a prohibitive number of plane waves in order to describe the strong oscillations of the valence wavefunctions near the nuclei.

This fundamental difficulty can be surpassed in two different approaches. In the *pseudopotential* method, a smooth pseudopotential is constructed to substitute the nuclear potential. In consequence, there are no longer core electrons and the valence wavefunctions can be represented as a sum of plane waves. Obviously, this method is suitable for studying the electronic properties of physical systems principally due to valence electrons as the chemical bonding in semiconductors, whereas no information concerning the core states is essential.

In the *all electron* methods such as Linear Muffin-Tin Orbital (LMTO) method or Linear Augmented Plane Wave (LAPW) method the core states are explicitly determined. To describe the large oscillations of the valence wavefunctions near the nuclei, in both methods the basis functions are replaced by numerical solutions of the Schrödinger equation in a region around the nuclei. This augmentation of the basis functions in the vicinity of nuclei is accomplished by dividing the space into muffin-tin (MT) spheres around the nuclei and the interstitial region (IR). Whereas in the LAPW method the basis function is the plane wave (see below), in the LMTO method the basis set is composed by spherical Hankel functions centered on each atom from the unit cell. An important advantage of these *all electron* methods shared also by the pseudopotential approach is given by the possibility of constructing analytical expressions for Hamiltonian and overlap matrix elements which can therefore easily be implemented in a computer code.

The major advantage of the LMTO method consists in a relatively good completeness of the basis with already small number of basis functions, maybe as few as 9 per atom in the case of *spd* elements. As a direct consequence, the calculations performed within this method may be fast and not necessarily dependent on significant computer resources, that makes the LMTO method well suited for the study of large systems (up to several hundreds of atoms). However, as a possible shortcoming of the LMTO method one can mention the lack of a systematic procedure to check the convergence of the results with respect to the number of basis functions. The problem is, no satisfactory smooth procedure to enhance the dimension of the
4.2 The LAPW Basis Set

4.2.1 The precursor: APW Method

Starting from the observation that near the nuclei the potential and hence the wave functions are strongly varying while between the atoms they are smoother, Slater [Sla37] developed the Augmented Plane Wave (APW) method in which the space is divided into non-overlapping muffin-tin (MT) spheres around the nuclei and the interstitial region (IR). Inside the MT spheres the crystal potential was originally assumed to be spherically symmetric, while in the interstitial region it was taken to be constant. This muffin-tin approximation of the crystal potential leads to accurate values of the ground-state total energy for close packed structures (fcc,
4.2 The LAPW Basis Set

hcp). Its predictions are still reasonable for bcc-type structures, but the accuracy of the results decreases for low-symmetric and open structures.

With the above approximations on the muffin-tin potential form, the APW basis set is given by radial solutions of Schrödinger’s equation inside the MT spheres and plane waves in the IR:

\[
\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \begin{cases} 
\frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} & \mathbf{r} \in \text{IR} \\
\sum I \sum l m q_{lm}^I (\mathbf{k} + \mathbf{G}) u_I^l (\varepsilon_I, r_I) Y_{lm} (\hat{r}_I) & \mathbf{r}_I \in \text{MT},
\end{cases}
\]  

(4.4)

In the defining relation of the APW basis functions (4.4), \(\Omega\) is the unit cell volume, \(\mathbf{k}\) denotes a wave vector within the first Brillouin zone, \(\mathbf{G}\) is the reciprocal lattice vector and \(\mathbf{r}_I = \mathbf{r} - \mathbf{R}_I\) is a vector within the MT sphere of the \(I\)-th atom located at \(\mathbf{R}_I\) (see Fig. 4.1). Also, \(\hat{r}_I\) represents the angular part of the vector \(\mathbf{r}_I\), \(q_{lm}^I (\mathbf{k} + \mathbf{G})\) are the expansion coefficients for the \(I\)-th atom and \(u_I^l (\varepsilon_I, r_I)\) is the numerical solution of the radial Schrödinger’s equation for the spherical component of the potential \(V(r_I)\) in the \(I\)-th MT sphere. In atomic units

\[
\left\{ -\frac{d^2}{dr_I^2} + \frac{l(l + 1)}{r_I^2} + V(r_I) - \varepsilon_l \right\} r_I u_I^l (\varepsilon_I, r_I) = 0.
\]  

(4.5)

and the solution of this equation must be regular at the origin.

The radial functions \(u_I^l (\varepsilon_I, r_I)\) determined by (4.5) are orthogonal to any eigenstate of the same Hamiltonian that vanishes at the surface of the MT sphere, that is assumed to be the case for deep core states. This important property can be proven by integrating the following relation

\[
(\varepsilon_1 - \varepsilon_2) r_I u_1^l (\varepsilon_1, r_I) u_2^l (\varepsilon_2, r_I) = u_2^l (\varepsilon_2, r_I) \frac{d^2}{dr_I^2} (r u_1^l (\varepsilon_1, r_I))
\]

\[
- u_1^l (\varepsilon_1, r_I) \frac{d^2}{dr_I^2} (r u_2^l (\varepsilon_2, r_I)).
\]  

(4.6)

constructed for two different eigenvalues \(\varepsilon_1\) and \(\varepsilon_2\) of the same spherically averaged Hamiltonian.
The I-th MT sphere

The interstitial region IR

The interstitial region IR

The I-th MT sphere

r_I

r

R_I

Figure 4.1: In the APW method, the space is divided into MT spheres and interstitial region.

The expansion coefficients \( a_{lm}(k + G) \) are determined from the requirement that the basis set functions are continuous at the sphere boundaries. This constraint is imposed by the requirement for the kinetic energy to be well defined through the crystal, and leads for each I-th MT sphere to [Lou67]

\[
a_{lm}^{I}(k + G) = \frac{4\pi^{2}i}{\sqrt{\Omega u(S_I)}} e^{i(k + G) \cdot R_I} Y_{lm}^{*}(\sqrt{|k + G|^2}) j_l(|k + G|). \tag{4.7}
\]

where the \( S_I \) is the radius of the MT sphere located at \( R_I \). In the above relation, the parameter \( \varepsilon_l \) was set to the band energy in order to simplify the expression of the secular determinant. However, this choice results in an energy dependence of the basis set (4.4) and in consequence, the energy bands (at a fixed \( k \) point) cannot be obtained by one diagonalization. Instead, it is necessary to construct the secular determinant as a function of energy and to search for its roots. The main drawback of this computational scheme consists in the fact that it is time expensive, especially
for a general \( \mathbf{k} \) points and for systems with many bands.

Another nuisance within the APW method is the presence of the radial functions \( u_\ell(\varepsilon_l, r_I) \) in the denominator of \( a_{lm} \) (4.7). There are in general values of the energy parameter \( \varepsilon_l \) for which the radial function \( u_\ell(\varepsilon_l, r_I) \) has a node on the sphere boundary. At these energies the radial functions and the plane waves are decoupled (asymptote problem). If an energy band falls into the vicinity of such energies, additional numerical problems have to be managed.

### 4.2.2 The Standard LAPW Basis Set

The LAPW method is a modification of the APW method proposed by Andersen [And73, And75] which essentially surpasses the above mentioned difficulties. In this case, inside each MT sphere and for each azimuthal quantum number \( l \), the basis function is a linear combination of the radial functions \( u_\ell(\varepsilon_l, r)Y_{lm}(\mathbf{r}) \) and their energy derivative \( i_u(\varepsilon_l, r)Y_{lm}(\mathbf{r}) \) at a fixed energy \( \varepsilon_l \). This option corresponds essentially to the linearization of the energy dependence of the radial solution \( u(\varepsilon, r) \) around \( \varepsilon_l \). It allows us to find all KS energies \( \varepsilon_{K,s,n} \), for each \( \mathbf{k} \) point, by just one diagonalization [Sin94].

These linear combinations of radial functions and their energy derivatives are again matched smoothly by plane waves at the sphere boundaries. In this way, the plane waves are augmented inside each MT sphere, and the LAPW basis functions are

\[
\phi_{\mathbf{k} + \mathbf{G}}(\mathbf{r}) = \begin{cases} 
\frac{1}{\sqrt{M}} e^{i(\mathbf{k} + \mathbf{G})\cdot \mathbf{r}} & \mathbf{r} \in \text{IR} \\
\sum_I \sum_{lm} \left[ a^I_{lm}(\mathbf{k} + \mathbf{G})u^I(\varepsilon^I_l, r_I) + b^I_{lm}(\mathbf{k} + \mathbf{G})i_u^I(\varepsilon^I_l, r_I) \right] Y_{lm}(\mathbf{r}_I) & \mathbf{r}_I \in \text{MT},
\end{cases}
\]

(4.8)

where the functions \( Y_{lm}(\mathbf{r}) \) represent a complex spherical harmonic \((Y_{l-m}(\mathbf{r}) = (-1)^mY_{lm}(\mathbf{r}))\) and \( a^I_{lm}(\mathbf{k} + \mathbf{G}) \) and \( b^I_{lm}(\mathbf{k} + \mathbf{G}) \) are two energy-independent expansion coefficients.

The radial function \( u^I_l(\varepsilon_l, r_I) \) in t(4.8) is the solution of the same equation (4.5)
as in the APW method while its energy derivative \( \dot{u}_l^I (\varepsilon_i, r_I) \) satisfies

\[
\left\{ - \frac{d^2}{dr_I^2} + \frac{l(l + 1)}{r_I^2} + V(r_I) - \varepsilon_i \right\} r_I \dot{u}_l^I(\varepsilon_i^I, r_I) = r_I u_l^I(\varepsilon_i^I, r_I). \tag{4.9}
\]

in the non-relativistic case. In the current implementations of the LAPW method the radial functions and their energy derivatives are determined by solving the relativistic radial equations in a spherically symmetric potential as proposed by Koelling et al. [KA75]. The relativistic treatment is taken into account only in the MT spheres and neglected in the interstitial region because the relativistic corrections are relevant only when the kinetic energy is large, i.e., near the nuclei.

Because of the use of the radial energy derivative \( \dot{u}_l^I (\varepsilon_i^I, r_I) \) for the augmentation of the plane waves, there is no asymptote problem in the LAPW method. The reason is, if the radial function \( u_l^I (\varepsilon_i^I, r_I) \) is equal to zero, then either its energy derivative or its radial derivative is in general different from zero, i.e., the plane waves and radial functions are not decoupled at the corresponding MT sphere. Moreover, this choice for the LAPW basis set inside the MT spheres allows for a non problematic treatment of the non-spherical potentials inside the spheres as required by the full-potential calculations.

Using the normalization condition

\[
\int_0^{s_I} [r_I u_l^I (\varepsilon_i^I, r_I)]^2 dr_I = 1, \tag{4.10}
\]

and the orthogonalization one

\[
\int_0^{s_I} r_I^2 u_l^I (\varepsilon_i^I, r_I) \dot{u}_l^I (\varepsilon_i^I, r_I) dr_I = 0, \tag{4.11}
\]

one can provide an indication as to the range over which the linearization energy represents a reliable approximation. To obtain this criterion, the APW radial function at the band energy \( \varepsilon \) is expanded by Taylor’s theorem

\[
u_l^I (\varepsilon, r_I) = u_l^I (\varepsilon_i, r_I) + (\varepsilon - \varepsilon_i) \dot{u}_l^I (\varepsilon_i, r_I) + O((\varepsilon - \varepsilon_i)^2), \tag{4.12}
\]
where \( O((\varepsilon - \varepsilon_l)^2) \) represents the errors that are quadratic in this energy difference. In consequence, the linearization errors are reasonable if the following relation

\[
|\varepsilon - \varepsilon_l| \|\hat{u}_l(\varepsilon_l, r_I)\| \leq 1, \quad (4.13)
\]

is fulfilled, where \( \|\hat{u}_l(\varepsilon_l, r_I)\| \) stands for the norm of the energy derivative of the radial function

\[
\|\hat{u}_l(\varepsilon_l, r_I)\| = \int_0^{s_I} \left[ r_J \hat{u}_l' (\varepsilon_l, r_I) \right]^2 dr_J. \quad (4.14)
\]

In addition, the relation (4.12) expresses that in the LAPW method the errors in the wavefunction is of order \( (\varepsilon - \varepsilon_l)^2 \) and this, with the variational principle, determines errors of order \( (\varepsilon - \varepsilon_l)^4 \) in the band energy. From these high order of errors in the wavefunction and in band energy one can infer that the LAPW basis set can be used to describe electronic states over a relatively large energy range. In addition, all valence bands can be treated with a single set for \( \varepsilon_l \).

However, a typical problem of all-electron treatment is the presence in the energy spectrum of two physical states with the same orbital quantum number \( l \) but different principal quantum numbers, where the lowest of these states is not sufficiently localized within the MT sphere to be treated as true core state (such high lying core states are called semi-core states). Since in such cases the semi-core state with \( l \) character is no longer orthogonal to the valence state described by the same \( l \), the augmentation of plane waves to both numerical solutions would result in the linear dependency of the basis set which would lead to unphysical solutions of the Kohn-Sham equation (so called ghost states). Apart from several historically interesting attempts to solve this problem [Sin94], the local orbital extension of the LAPW basis set proposed by Singh [Sin91] is now well established.

Within this approach, the semi-core states are described by local orbitals. For a given \( l \) quantum number, a local orbital consists of a linear combination of two radial functions \( u_l(\varepsilon_{1l}, r_I) \) and \( u_l(\varepsilon_{2l}, r_I) \) taken at two different values of the energy parameter \( \varepsilon_l \) (in the semi-core part of the energy spectrum and in the valence part,
respectively) and one energy derivative $\dot{u}(\varepsilon_I, r_I)$ taken at one of these energies

$$
\phi_{lm}^{ILO}(\mathbf{r}) = \left[ a_{lm}^I u^I_l(\varepsilon^{I}, r_I) + b_{lm}^I \dot{u}^I_l(\varepsilon_{1,l}, r_I) \\
+ c_{lm}^I u^I_l(\varepsilon_{2,l}, r_I) \right] Y_{lm}(\mathbf{r}_I).
$$

(4.15)

The expansion coefficients $a_{lm}^I$, $b_{lm}^I$ and $c_{lm}^I$ are determined by the requirement that the local orbital should be normalized and has zero value and slope at the $I$-th sphere boundary. One should note that in the above equation the expansion coefficients do not depend on the wave vector $\mathbf{k} + \mathbf{G}$ as in the case of the standard LAPW basis functions (see Eq. (4.8)).

### 4.2.3 The Construction of the Expansion Coefficients

The expansion coefficients $a_{lm}^I(\mathbf{k} + \mathbf{G})$ and $b_{lm}^I(\mathbf{k} + \mathbf{G})$ from Eq. (4.8) are determined by the requirement that the value and slope of the basis functions are continuous at the surface of the $I$-th MT sphere. As in the APW method, these coefficients are obtained using the value and radial derivative of the angular momentum decomposition of the plane waves.

The numerical effort required by the evaluation of the expansion coefficients as well as their subsequent use in the calculation of the charge density inside the MT-spheres can be significantly reduced using the symmetry of the system under consideration. If there are symmetry related atoms, it is useful not to calculate the complex spherical harmonic functions $Y_{lm}(\mathbf{r})$ in the local coordinate systems parallel to the global one. Instead, for a given sphere, the local coordinate system is rotated about the center of that sphere using the rotational part $\mathbf{R}$ of the space group operation that generates the respective atom from the representative atom. In this case, inside the $I$-th MT sphere the basis functions are given by

$$
\phi_{\mathbf{k} + \mathbf{G}}(\mathbf{r}) = \sum_{lm} \left[ a_{lm}^I(\mathbf{k} + \mathbf{G}) u^I_l(\varepsilon^{I}, r_I) \\
+ b_{lm}^I(\mathbf{k} + \mathbf{G}) \dot{u}^I_l(\varepsilon_{1,l}, r_I) \right] Y_{lm}(\mathbf{Rr}_I),
$$

(4.16)

and the angular momentum decomposition of the plane waves gets the following
expression:

$$
\frac{1}{\sqrt{\Omega}} e^{i |\mathbf{k} + \mathbf{G}| \mathbf{r}} = \frac{4\pi}{\sqrt{\Omega}} e^{i |\mathbf{k} + \mathbf{G}| \mathbf{R}_I} \sum_{lm} j_l^I(\lVert \mathbf{k} + \mathbf{G} \rVert |\mathbf{r}_I|) \\
\times Y_{lm}^*(\hat{\mathbf{R}(\mathbf{k} + \mathbf{G}))} Y_{lm}(\hat{\mathbf{R}\mathbf{r}_I}).
$$

(4.17)

Using the radial derivative of the above angular momentum decomposition of the plane waves, the expansion coefficients $a_{lm}^I(\mathbf{k} + \mathbf{G})$ and $b_{lm}^I(\mathbf{k} + \mathbf{G})$ are readily obtained as

$$
a_{lm}^I(\mathbf{k} + \mathbf{G}) = \frac{4\pi}{\sqrt{\Omega}} e^{i |\mathbf{k} + \mathbf{G}| \mathbf{R}_I} R_{MT}^2 Y_{lm}^*(\hat{\mathbf{R}(\mathbf{k} + \mathbf{G}))} \times \\
\left[ \dot{u}_l^I(\varepsilon_I^l, \mathbf{r}_I) \frac{d}{dr_I} \dot{j}_l^I(\lVert \mathbf{k} + \mathbf{G} \rVert |\mathbf{r}_I|) - j_l^I(\lVert \mathbf{k} + \mathbf{G} \rVert |\mathbf{r}_I|) \frac{d}{dr_I} \dot{u}_l^I(\varepsilon_I^l, \mathbf{r}_I) \right],
$$

(4.18)

$$
b_{lm}^I(\mathbf{k} + \mathbf{G}) = \frac{4\pi}{\sqrt{\Omega}} e^{i |\mathbf{k} + \mathbf{G}| \mathbf{R}_I} R_{MT}^2 \hat{Y}_{lm}^*(\hat{\mathbf{R}(\mathbf{k} + \mathbf{G}))} \times \\
\left[ \dot{j}_l^I(\lVert \mathbf{k} + \mathbf{G} \rVert |\mathbf{r}_I|) \frac{d}{dr_I} u_l^I(\varepsilon_I^l, \mathbf{r}_I) - u_l^I(\varepsilon_I^l, \mathbf{r}_I) \frac{d}{dr_I} \dot{\dot{j}}_l^I(\lVert \mathbf{k} + \mathbf{G} \rVert |\mathbf{r}_I|) \right].
$$

where the radial derivative of the spherical Bessel functions of order $l$ as well as the radial functions and their radial derivative must be evaluated at the boundary of the corresponding MT sphere.

### 4.3 Solving the Kohn-Sham Equation

#### 4.3.1 Setup of the Hamiltonian and Overlap Matrices

In the LAPW method the Kohn-Sham equation is solved by expanding the corresponding Kohn-Sham wavefunctions in the LAPW basis functions $\phi_{k + \mathbf{G}}(\mathbf{r})$

$$
\psi_{n}^{KS}(\mathbf{r}) = \sum_{|\mathbf{k} + \mathbf{G}| \leq G_{\text{max}}} c_{n}(\mathbf{k} + \mathbf{G}) \phi_{k + \mathbf{G}}(\mathbf{r}),
$$

(4.19)
where for each \( \mathbf{k} \) vector within the first Brillouin zone the cutoff parameter \( G_{\text{basis}} \) limits the number of lattice vectors \( \mathbf{G} \) used in the above expansion and thus, it determines the size of the basis set. Using the LAPW basis functions the Hamiltonian \( H \) and the overlap \( S \) matrices are block diagonal for each \( k \) point in the irreducible Brillouin zone, so that their matrix elements (4.3) can be expressed only in terms of a given irreducible \( k \) point (see Appendix A to Ref. [YK94])

\[
S_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \langle \phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) | \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) \rangle, \\
H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \langle \phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) | \hat{H} | \phi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) \rangle.
\]

(4.20)

Using the explicit form of the LAPW basis functions (4.8), the overlap matrix elements can be decomposed into interstitial and sphere components

\[
S_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \frac{1}{\Omega} \int_{\mathcal{R}} e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}} d\mathbf{r} + \sum_{I} S_{I}(\mathbf{G}, \mathbf{G}'),
\]

(4.21)

where \( S_{I}(\mathbf{G}, \mathbf{G}') \) represent the contributions to the overlap matrix from the \( I \)-th MT sphere.

The same decomposition can be performed for the Hamiltonian matrix elements taking into account that in the framework of the DFT, the sphere component can be also decomposed into spherical and non-spherical contributions

\[
H_{\mathbf{G},\mathbf{G}'}(\mathbf{k}) = \frac{1}{\Omega} \int_{\mathcal{R}} e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \left[ \hat{T} + \hat{V} \right] e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} d\mathbf{r} \\
+ \sum_{I} \left[ H_{I}(\mathbf{G}, \mathbf{G}') + V_{I}^{NS}(\mathbf{G}, \mathbf{G}') \right].
\]

(4.22)

In the above equation \( H_{I}(\mathbf{G}, \mathbf{G}') \) are the spherical contributions to the Hamiltonian matrix (the \( l = 0 \) part of the crystal potential in the \( I \)-th MT sphere) and \( V_{I}^{NS}(\mathbf{G}, \mathbf{G}') \) denote the non-spherical contributions from the same potential.
4.3.2 The Interstitial Matrix Elements

The interstitial contributions to the overlap matrix are

\[
\frac{1}{\Omega} \int_{I_R} e^{i(G' - G) \cdot r} d \mathbf{r} = \frac{1}{\Omega} \int_{\Omega} e^{i(G' - G) \cdot r} \Theta(\mathbf{r}) d \mathbf{r} = \Theta(G - G'), \tag{4.23}
\]

where \( \Theta(\mathbf{r}) \) is the Heaviside function in the real space and \( \Theta(G - G') \) represents an analytical function in the reciprocal space imitating the effect of Heaviside function in case of Fourier transformation on a discrete mesh with the cutoff parameter \( G_{\text{max}} = 2G_{\text{basis}} \), see Ref. [Sin94] for details.

In a similar way, the interstitial contributions to the Hamiltonian matrix are

\[
\frac{1}{\Omega} \int_{I_R} e^{-i(k + G) \cdot r} \left[ \hat{T} + \hat{V} \right] e^{i(k + G') \cdot r} d \mathbf{r} =
\]

\[
= \frac{1}{\Omega} \int_{\Omega} e^{-i(k + G) \cdot r} \left[ \hat{T} + \hat{V} \right] e^{i(k + G') \cdot r} d \mathbf{r} \tag{4.24}
\]

\[
= V(G - G') + (k + G')^2 \Theta(G - G').
\]

where the potential energy contribution \( V(G - G') \) and the kinetic energy contribution \( (k + G')^2 \Theta(G - G') \) to \( H_{G,G'}(k) \) must be calculated up to the same cutoff parameter \( G_{\text{max}} \) as for the interstitial contribution to the overlap matrix elements.

4.3.3 The Spherical Matrix Elements

As has been already stated, the power of the LAPW method derives from the possibility of obtaining analytical expressions for certain physical quantities which then can be in a straightforward way implemented into a code. In this context, the evaluation of the spherical components of the Hamiltonian matrix elements and the sphere contribution of the overlap matrix can be easily done using the normalization (4.10) and orthogonality (4.11) conditions as well as the orthonormalization condition for spherical harmonics \( Y_{lm} \). In the non-relativistic case the expressions of these matrix
4.3 Solving the Kohn-Sham Equation

Elements are given by

\[
S_I(G, G') = \sum_{lm} \left[ a^{I*}_{lm}(k + G) a^{I}_{lm}(k + G') + b^{I*}_{lm}(k + G) b^{I}_{lm}(k + G') \| \hat{u}^I \|^2 \right],
\]

\[
H_I(G, G') = \sum_{lm} \left\{ \left[ a^{I*}_{lm}(k + G) a^{I}_{lm}(k + G') + b^{I*}_{lm}(k + G) b^{I}_{lm}(k + G') \| \hat{u}^I \|^2 \right] \varepsilon^I_I + \frac{1}{2} \left[ a^{I*}_{lm}(k + G) b^{I}_{lm}(k + G') + b^{I*}_{lm}(k + G) a^{I}_{lm}(k + G') \right] \right\},
\]

where the expansion coefficients \( a^{I}_{lm}(k + G) \) and \( b^{I}_{lm}(k + G) \) are previously calculated (see section (4.2.3)).

4.3.4 The Non-Spherical Matrix Elements

In the LAPW method the potential felt by the valence electrons is expanded in Fourier series in the interstitial region and in lattice harmonics on a radial grid inside the MT spheres

\[
V(r) = \begin{cases} 
\sum_{|G| \leq G_{pol}} V_G e^{i G \cdot r} & r \in IR \\
\sum_{I} \sum_{LM} V^I_{LM}(r_I) Y_{LM}(\hat{r}_I) & r_I \in MT,
\end{cases}
\]

where the cutoff parameter \( G_{pol} \) limits the number of reciprocal lattice vectors used in the above Fourier expansion. It is important to note that the convergence of the calculations must be carefully checked with respect to this cutoff parameter. For instance, special attention must be paid when using the GGA form for the exchange-correlation functional because the gradients in the charge density are evaluated on a mesh determined by \( G_{pol} \). The function \( Y^I_{LM}(\hat{r}_I) \) is the lattice harmonics defined
4.3 Solving the Kohn-Sham Equation

by

\[ \sum_{\tilde{\mathbf{r}}} \mathbf{R} Y_{lm}(\tilde{\mathbf{r}}_I) = \sum_{m} c_{lm}^I Y_{lm}(\mathbf{r}_I) \]

\[ = \sum_{L=I,M} Y_{LM}^I(\mathbf{r}_I). \]  \hspace{1cm} (4.27)

The lattice harmonics are the symmetrized spherical harmonics and are constructed using the symmetry operations \( \mathbf{R} \) compatible with the space group of the crystal in question. The magnetic quantum number \( M \) is that \( m \) for which the corresponding coefficient \( c_{lm}^I \) is different from zero.

With these considerations, the analytical expression of the non-spherical Hamiltonian matrix components \( V_{I}^{NS}(\mathbf{G}, \mathbf{G}') \) is given by

\[ V_{I}^{NS}(\mathbf{G}, \mathbf{G}') = \sum_{lm,l'm'} \sum_{LM} \left[ a_{lm}(\mathbf{k} + \mathbf{G}) a_{lm}^*(\mathbf{k} + \mathbf{G}') V_{l'l',LM,I}^{uu} \right. \]

\[ + a_{lm}^*(\mathbf{k} + \mathbf{G}) b_{l'm'}^I(\mathbf{k} + \mathbf{G}') V_{l'l',LM,I}^{u'u} \]

\[ + b_{lm}^*(\mathbf{k} + \mathbf{G}) a_{l'm'}(\mathbf{k} + \mathbf{G}') V_{l'l',LM,I}^{uu'} \]

\[ + b_{lm}^*(\mathbf{k} + \mathbf{G}) b_{l'm'}(\mathbf{k} + \mathbf{G}') V_{l'l',LM,I}^{u'u'} \right] \]

\[ \times \int Y_{lm}^I(\mathbf{r}_I) Y_{l'm'}^J(\mathbf{r}_I) Y_{LM}^I(\mathbf{r}_I) d\Omega, \]  \hspace{1cm} (4.28)

where \( V_{l'l',LM,I}^{uu} \), \( V_{l'l',LM,I}^{u'u} \), \( V_{l'l',LM,I}^{uu'} \), \( V_{l'l',LM,I}^{u'u'} \) represent the integrals over radial function and their energy derivatives

\[ V_{l'l',LM,I}^{uu} = \int_0^{r_I} s_I^2 u_L^I(\varepsilon_I^I, r_I) V_{LM}^I(r_I) u_L^I(\varepsilon_I^J, r_I) dr_I. \]  \hspace{1cm} (4.29)

with similar expressions for the remaining terms (see, for example, Ref. [KA75]).

The expression of the non-spherical contributions \( V_{I}^{NS} \) to the Hamiltonian matrix
can be further simplified performing the integral over the solid angle
\[
\int Y^*_{l m}(\hat{\mathbf{r}} I) Y_{l' m'}(\hat{\mathbf{r}} I) Y^I_{L M}(\hat{\mathbf{r}} I) d\Omega =
\]
\[
= \mathcal{C}_{L, m - m'} G_{l l' m m' m''}(m - m'),
\]
where the Gaunt coefficients \( G_{ll'l'm'm''} \) defined by
\[
G_{ll'l'm'm''} = \int Y^*_{l m}(\hat{\mathbf{r}} I) Y_{l' m'}(\hat{\mathbf{r}} I) Y_{l'' m''}(\hat{\mathbf{r}} I) d\Omega.
\]
are different from zero only if \( m = m' + m'' \). Other constraints for a non-zero Gaunt coefficients are that \( l + l' + l'' \) must be even and the azimuthal quantum numbers \( l, l' \) and \( l'' \) must verify the triangle inequality \(|l' - l''| \leq l \leq l' + l''\).

### 4.3.5 The Brillouin Zone Integration

The determination of the physical quantities as total energy, forces, charge densities etc. for a solid crystals requires the evaluation of the integrals over the Brillouin zone such as
\[
I = \int_{BZ} f(\mathbf{k}) d\mathbf{k},
\]
where the integrand \( f(\mathbf{k}) \) is a periodic function of wave vector \( \mathbf{k} \) in the reciprocal space. These type of integrals are numerically computed using the special points method (see [Bal73], [CC73] and [MP76]) or the tetrahedron method (see [JA71], [LT72] and [BJA94]).

In the special points approach, the periodic function \( f(\mathbf{k}) \) can be expanded in terms of symmetrized plane waves as
\[
f(\mathbf{k}) = \sum_{m=0}^{\infty} f_m A_m(\mathbf{k}),
\]
where the stars \( A_m(k) \) are given by

\[
A_m(k) = \sum_{T \in \mathcal{R}R_m} e^{ikT}.
\] (4.34)

In the relation (4.34) that defines the stars, the sum is taken over all lattice vectors \( T \) related by symmetry operations \( \mathcal{R} \) of the lattice point group to some lattice vector \( R_m \). The lattice vectors \( R_m \), whose module is denoted in the following by \( c_m \), are in ascending order so that \( c_{m-1} \leq c_m \leq c_{m+1} \) and \( c_1 = 0 \). By summing over all the stars of equivalent lattice vectors, the function \( f(k) \) will possess the full symmetry of the Bravais lattice.

In this case, the Brillouin zone integration of the function \( f(k) \) is equal to \( f_0 \) and the aim of the special points technique is to determine a set of vectors \( k_i \) such that

\[
f_0 = \sum_{i=1}^{n} w_i f(k_i).
\] (4.35)

The equation (4.35) is valid when the weight factors \( w_i \) of the vectors \( k_i \) verify the following relations

\[
\sum_{i=1}^{n} w_i = 1
\] (4.36)

\[
\forall m, \sum_{i=1}^{n} w_i A_m(k_i) = 0,
\] (4.37)

where \( n = 1, ..., N \) and \( N \) must be as large as possible. Chadi and Cohen [CC73] constructed the special points starting from two \( k \) vectors \( k_1 \) and \( k_2 \) which satisfy the relation (4.37) for \( N = N_1 \) and \( N = N_2 \). Then the vectors \( k \) defined by the relation

\[
k_i = k_1 + \mathcal{R}_i k_2.
\] (4.38)

satisfy the relation (4.37) for both \( N_1 \) and \( N_2 \). In this way a larger \( k \)-mesh can be generated till the integral (4.32) is evaluated with a sufficient accuracy.

In the approach of Monkhorst and Pack [MP76] the special points are generated
from a uniformly spaced grid in the Brillouin zone making use of the lattice point-group symmetry operations. The \( k \)-meshes obtained within this method can usually be used with the same efficiency as those constructed within the Chadi and Cohen approach for evaluating integrals over the Brillouin zone.

The special points method is well suitable for insulators because in this case the functions to be integrated over the Brillouin zone are smooth. For metals these functions are discontinuous at the Fermi surface and thus this method yields a slow convergence. However this drawback can be overpassed using a broadening scheme as described in [MP89].

The tetrahedron method is equally applicable to insulators and metals. In this approach, the reciprocal space is divided into tetrahedra. The eigenvalues and eigenvectors are calculated for each \( k \)-vector at the corners of the tetrahedra. Inside each tetrahedron the band energies are interpolated linearly (a quadratic order interpolation scheme is also possible, see [MBM87]) and the integration for each tetrahedron can be performed in this case analytically. Therefore, in this approach the integral \( I \) over the Brillouin zone (4.32) takes the following expression

\[
\int_{BZ} f(k) d\mathbf{k} = \sum_i \int_{V_i} f(k) d\mathbf{k} = \sum_i V_i \sum_{j=1}^4 W_j(k_1, k_2, k_3, k_4) f(k_j),
\]

where \( V_i \) represents the volume of the \( i \)-th tetrahedron and \( W_j \) stands for the weight corresponding to the wave vector \( k_j \) in that tetrahedron. The analytical expression of the weight factor \( W_j \) depends also on the nature of the physical quantity to be integrated in the reciprocal space. For instance, in the case of the density of states (DOS) of elementary excitations described by the dispersion relation \( \epsilon(k) \), the integral \( I \) has the following form

\[
I(\epsilon) = \int_{\epsilon(k)=\epsilon} \frac{dS}{|\nabla_k \epsilon(k)|},
\]

and it must be evaluated over constant energy surface \( \epsilon(k) = \epsilon \). This integral can be analytically calculated assuming that the energy \( \epsilon(k) \) can be linearly expanded inside of the each \( i \)-th tetrahedron. With this assumption, the coefficients of the
energy expansion can be expressed only in terms of the corner energies (for more details see, for instance, Ref. [LT72, RF75]).

Unfortunately, several drawbacks limit the actual applications of this method. In order to use the minimum number of \( \mathbf{k} \) points in Eq. (4.39), in the traditional implementations of this method the \( \mathbf{k} \) vectors must belong to the irreducible Brillouin zone. However, the division of the irreducible Brillouin zone into tetrahedra is a cumbersome procedure. Also, when applied to insulators, the tetrahedron method needs more \( \mathbf{k} \) points than the special-point approach in order to reach the same degree of accuracy of the calculated physical quantities. In addition, the Brillouin zone integration performed within the tetrahedron method requires the knowledge of the matrix elements for all irreducible \( \mathbf{k} \) points and all bands at the same time.

In the improved tetrahedron method developed by Blöchl at al. these shortcomings were removed. They showed that, instead of performing the sum (4.39) over the tetrahedra which is inefficient in the sense that the same \( \mathbf{k} \) vector is used more than once, the expectation value of an operator \( \hat{A} \) can be expressed as a weighted sum over the irreducible \( \mathbf{k} \) vectors and over all occupied bands \( n \)

\[
\langle \hat{A} \rangle = \sum_{\mathbf{k},n} W_n(\mathbf{k}) A_n(\mathbf{k}), \quad (4.41)
\]

where the weights \( W_n(\mathbf{k}) \) are independent of the matrix elements \( A_n(\mathbf{k}) \) given by

\[
A_n(\mathbf{k}) = \int \phi_n^*(\mathbf{k}) \hat{A} \phi_n(\mathbf{k}). \quad (4.42)
\]

In this approach, the irreducible \( \mathbf{k} \) vectors are obtained by applying the space-group symmetry operations to a mesh of equally spaced points in the reciprocal space, thus avoiding finding the irreducible part of the first Brillouin zone. Furthermore, they developed a correction formula for the errors due to the linear interpolation of the matrix elements \( A_n(\mathbf{k}) \) inside of each tetrahedron. As a result, a given accuracy of the calculations performed for metals is obtained using less \( \mathbf{k} \) points than in the traditional implementation of this method.

Finally, if in the special points scheme the spectral functions can be evaluated with a rather low accuracy, in the tetrahedron method these functions can be computed with a high accuracy in a reasonable computational time.
4.3 Solving the Kohn-Sham Equation

4.3.6 The Valence Charge Density

A similar expression as that derived for the crystalline potential (4.26) holds also for the valence charge density

\[ \rho(r) = \begin{cases} \sum_{|G| \leq G_{\text{cut}}} \rho_G e^{iG \cdot r} & \quad r \in \text{IR} \\ \sum_I \sum_{LM} \rho_{LM}^I (r_I) Y_{LM}(r_I) & \quad r_I \in \text{MT}, \end{cases} \quad (4.43) \]

With this option, there are no approximations in the shape of the computed potential and charge density and the resulting LAPW method is called full potential LAPW (FPLAPW).

Using the calculated Kohn-Sham eigenfunctions, in the interstitial region IR the valence electron density can be expressed as

\[ \rho^{IR}(r) = \sum_{k,n} W_n(k) \sum_{G,G'} c_n(k + G) c_n^*(k + G') e^{i(G-G') \cdot r}, \quad (4.44) \]

where \( n \) are the band indices, \( c_n(k + G) \) represent the band eigenvector coefficients for the \( n \)-th band corresponding to the \( k \) vector within the irreducible Brillouin zone and \( W_n(k) \) is a weight factor that includes both the \( k \) point weight and the occupancy of that state (given by the Fermi function). The interstitial charge density is usually symmetrized by projecting it onto the stars \( \Phi(r) \) defined in a similar way as the stars \( A_m(k) \) (see (4.34)) by

\[ \Phi(r) = \frac{1}{N} \left[ \{ \hat{R}_1 \} v_1 + \ldots + \{ \hat{R}_N \} v_N \right] e^{iG \cdot r} \]

\[ = \frac{1}{N} \sum_{\hat{R}} e^{i\hat{R}G(r-v_\text{R})}. \quad (4.45) \]

In the above definition of the stars \( \Phi(r) \), \( \hat{R} \) represents the rotational part of the space group operation \( \{ \hat{R} | v_\text{R} \} \) and \( N \) is the number of point group operations. Constructed in this way, the stars possess the lattice symmetry.

Inside each MT sphere, the valence electron density is given by the following
4.3 Solving the Kohn-Sham Equation

expression:

$$\rho^I(r) = \sum_{k,n} W_n(k) \sum_{l m} \sum_{G,G'} c^*_n(k + G)c_n(k + G')$$

$$\left\{ a^I_{l m}(k + G)u_l(r_I) a^I_{l' m'}(k + G)u_{l'}(r_I)$$

$$+ b^I_{l m}(k + G)\dot{u}_l(r_I) a^I_{l' m'}(k + G)\dot{u}_{l'}(r_I)$$

$$+ a^I_{l m}(k + G)u_l(r_I) b^I_{l' m'}(k + G)\dot{u}_{l'}(r_I)$$

$$+ b^I_{l m}(k + G)\dot{u}_l(r_I) b^I_{l' m'}(k + G)\dot{u}_{l'}(r_I) \right\}$$

$$\times Y^*_{l m}(\mathbf{r}_I) Y_{l' m'}(\mathbf{r}_I).$$

(4.46)

In this case the required symmetrization of the charge density is obtained by projecting it onto the lattice harmonics.

4.3.7 The Core Charge

In the FPLAPW method, the core states are computed self-consistently using the spherical part of the crystal potential in the MT spheres. The eigenvalues and the eigenstates of the core electrons are calculated using a full relativistic atomic code because it is important to take into account the spin-orbit coupling for a proper description of these states. In this approximation, the core states do not hybridize with the valence ones.

Usually, even when choosing the largest MT radii compatible with a given crystal structure, the core states are not completely confined inside the MT spheres. This situation requires the need to handle with the core tails that extend outside of the MT spheres. These core tails are computed using a smooth continuation of the potential from inside the spheres to outside of them. Finally, the calculated core charge density must be converted to the LAPW representation of the charge density, namely to project it onto the lattice harmonics inside the MT sphere and on stars in the interstitial region.
4.4 The Forces in LAPW method

To calculate accurately the phonon frequencies as well as to perform reliable molecular dynamics simulations, it is essential that the \textit{ab initio} calculations must be performed using the atomic configuration of the physical system under consideration which has the lowest total energy. Even if the equilibrium geometry can be determined by fitting the total energies obtained for different atomic configurations with respect to the corresponding atomic positions, this approach is not suitable in practice for systems containing many atoms. However, the equilibrium atomic configuration can be obtained for complex systems with reasonable computational effort via the atomic forces.

According to the Hellmann-Feynman (HF) theorem [Hel37, Fey39] the force acting on an the \textit{I}-th atom is equal to the electrostatic force on its nucleus. Due to the inherent approximations in the form of the exchange-correlation functional in the DFT as well as the use of a finite number of basis functions in all \textit{ab initio} calculations, the calculated charge density and, in consequence, the electric field are only approximate. Therefore, the calculated HF forces could be sufficiently inaccurate to result in wrong results for the studied physical system. However, since the HF forces can be alternatively derived from the variation of total energy of the system due to the shift of the atoms, the forces can be calculated with the same accuracy as the total energy.

It was first noted by Pulay [Pul69] that the use of an incomplete basis function set (IBS) determines a correction to the HF forces. This correction vanishes if the basis function set is independent of atomic positions, as is the case of pseudopotential method [LHC79]. In the \textit{all electron} methods with a dual representation of the basis functions, the dependence of the augmentation of the basis set on the atomic positions complicates further the analytical expression of the atomic forces.

Using the expression of the variation of the total energy in DFT determined by the small atomic displacements, Yu \textit{et al.} [YSK91] showed that the force acting on the \textit{I}-th atom can be written as the sum of three different contributions

\[ \mathbf{F}_I = \mathbf{F}_I^{HF} + \mathbf{F}_I^{BS} + \mathbf{F}_I^{core}, \]  

where in addition to the pseudopotential method there is a correction given by core states \( \mathbf{F}_I^{core} \).
4.4 The Forces in LAPW method

The Hellmann-Feynman force $F_I^{HF}$ can be expressed in terms of the electrostatic potential $V^{e_s}(r_I)$ felt by the $I$-th nucleus as the following

$$F_I^{HF} = Z_I \nabla I V^{e_s}(r_I)\big|_{r_I=0}$$

$$= Z_I \sum_{m=-1}^{1} \lim_{r_I \to 0} \frac{V^{e_s}_{1,m}(r_I)}{r_I} \nabla I \left[ r_I Y_{1m}(r_I) \right],$$

(4.48)

where $V^{e_s}_{1,m}(r_I)$ is the $l = 1$ component of the electrostatic potential $V^{e_s}(r_I)$ in the spherical harmonics expansion. Because the core states are computed in a spherically symmetric crystalline potential $V_{c/I}$, the core correction is given by

$$F_I^{core} = -\sum_{m=-1}^{1} \int_{r_I} \rho_{core}(r_I) \nabla \left[ V^{e_s}_{1m} Y_{1m}(r_I) \right] dI.$$

(4.49)

It was explicitly shown by Yu at al. that the expression for the incomplete basis set (IBS) correction must contain a term which arises from the discontinuity of the second derivative of the KS wave functions at the MT sphere boundaries

$$F_I^{IBS} = \int_{MT} \rho_{val}(r_I) \nabla \left[ V^{e_s} Y(r_I) \right] dI$$

$$+ \sum_{k,n} W_n(k) \sum_{G,G'} c_n^*(k+G')c_n(k+G)$$

$$\times \left[ (G^2 - \epsilon_n) \int \phi_{k+G'}(r)\phi_{k+G}(r)dS_I \right.$$

$$- i(G - G') \langle \phi_{k+G}(r) | \hat{H} - \epsilon_n | \phi_{k+G}(r) \rangle_{MT}.\right]$$

(4.50)

The detailed derivation of the IBS contribution in terms of LAPW basis set can be found in Ref. [YSK91] and an exposition of its implementation in a LAPW code in Ref. [KWS96].

A different approach in determining the LAPW forces was used by Soler at al. [SW89]. Starting from the variation of the kinetic energy functional and using the form of electrostatic energy as expressed in Weinert’s method [Wei81], they also derived the analytical expression of the LAPW forces and it was shown [SW93] that
these two approaches are equivalent.

In addition to the already mentioned checks of the convergence of calculations, the convergence of the computed forces must be carefully verified for each studied system.
Chapter 5

Frozen Phonon Method

Introduction

The lattice dynamics of the crystalline solids can be investigated by means of two \textit{ab initio} methods: the \textit{linear-response approach} and the \textit{direct approach}. In the linear response method the dynamical matrix is obtained from the response of the electron density to any periodic perturbation of the crystalline lattice. Initially, the linear response to phonon displacements was obtained by inverting the dielectric matrix [Mar69, CDD79]. This procedure is computationally cumbersome because the dielectric matrices must be constructed from the eigenvalues and eigenfunctions over the whole energy spectrum of the unperturbed system for many \( k \) points in the Brillouin zone; additionally, the inversion of a large matrices as currently involved in such calculations possess serious numerical difficulties. Nowadays, these drawbacks were mainly overpassed by evaluating the linear response within the Green’s function method as suggested by Baroni \textit{et al.} or by using a variational approach together with a less computationally demanding conjugate-gradient algorithm as implemented by Gonze \textit{et al.} [GAT92]. Although within the linear response method one can study lattice perturbations of arbitrary wave vectors, no anharmonic effects can be taken into account.

Unlike the linear response approach, the anharmonicity of the lattice dynamics can be analyzed within the direct method. Depending on the underlying quantities used to build the dynamical matrix, one can distinguish between two variants of this method. In the \textit{direct force-constant} approach, the forces computed via the
5.1 Description of the method

Hellmann-Feynman theorem (see Chap.3) assuming a finite range of interaction in a total energy supercell calculation are used to construct the force-constant matrix, from which the dynamical matrix is obtained through a Fourier transformation. Therefore, the phonon frequencies for arbitrary wave vectors are calculated from the diagonalization of this dynamical matrix. Usually, the force-constant matrix elements are evaluated from a finite set of interplanar force constants obtained by displacing entire planes of atoms along certain symmetry directions. This procedure allows also for the determination of the phonon dispersion for that symmetry directions [KM82, WC92, KFH95, FEF95]. The frozen phonon approach will be presented in detail in the following section.

5.1 Description of the method

Since a detailed theoretical description of the lattice dynamics of the crystalline solids can be found in many textbooks (see, e.g., Born and Huang [BH88] or Maradudin [HM74]), in the following only a short summary will be presented.

The physical system under study is represented by a crystal composed of \( N \) unit cells and \( n \) atoms in each unit cell, subject to the Born-von Karman periodic boundary conditions. The classical motion of ions is described by the Lagrangian \( L = T - \Phi \) constructed from the kinetic \( T \) and potential energy \( \Phi \) given by

\[
T = \frac{1}{2} \sum_{l=1}^{N} \sum_{\alpha=1}^{3} \sum_{\kappa=1}^{n} m_{\kappa}(\dot{u}_{\alpha}^{l,\kappa})^2,
\]

\[
\Phi = \frac{1}{2} \sum_{l'l'=1}^{N} \sum_{\alpha,\beta=1}^{3} \sum_{\kappa,\kappa'=}^{n} \frac{\partial^2 \Phi}{\partial u_{\alpha}^{l',\kappa'} \partial u_{\beta}^{l,\kappa}} u_{\alpha}^{l,\kappa} u_{\beta}^{l',\kappa'},
\]

\[
= \frac{1}{2} \sum_{l'l'=1}^{N} \sum_{\alpha,\beta=1}^{3} \sum_{\kappa,\kappa'=}^{n} \Phi_{\alpha\beta}(l,\kappa;l',\kappa') u_{\alpha}^{l,\kappa} u_{\beta}^{l',\kappa'},
\]

where \( u_{\alpha}^{l,\kappa} \) \((\alpha=1,3)\) represents the Cartesian displacement of the \( \kappa \)-th atom \((\kappa = 1, n)\) in the \( l \) unit cell \((l = 1, N)\), whose equilibrium position is denoted by \( \mathbf{R}_{\kappa}^{l} \) (with respect to an origin located at some atom in crystal). Also, the Taylor expansion of the potential energy was restricted by the 2nd order (the 1st order being zero at equilibrium), that will result in the harmonic approximation.
5.1 Description of the method

The Euler-Lagrange equation

\[
\frac{d}{dt} \frac{\partial T}{\partial u^{i}_{\alpha}} + \frac{\partial \Phi}{\partial u^{i}_{\alpha}} = 0
\]  

(5.2)

leads to a set of \(3nN\) coupled equations of motion of the atoms in crystal

\[
m_{\kappa} a^{i}_{\alpha} = -\sum_{l'=1}^{N} \sum_{\beta=1}^{3} \sum_{\kappa'=1}^{n} \Phi_{\alpha \beta}(l_{\kappa}, l'_{\kappa'}) a^{i}_{\beta} a^{l'_{\kappa'}}. \tag{5.3}
\]

Due to the spatial periodicity of the lattice, within the harmonic approximation one can always choose a solution of the following form

\[
a^{i}_{\alpha}(t) = \frac{1}{\sqrt{m_{\kappa}}} A^{i}_{\alpha}(q) e^{i(q R_{\kappa} - \omega t)}, \tag{5.4}
\]

which represents a plane wave travelling parallel to the wave vector \(q\). With this choice, the system of coupled equations of motion (5.3) becomes decoupled in \(q\)

\[
\omega^2 A^{i}_{\alpha}(q) = \sum_{\beta=1}^{3} \sum_{\kappa'=1}^{n} \left( \frac{1}{\sqrt{m_{\kappa} m_{\kappa'}}} \sum_{l'=1}^{N} \Phi_{\alpha \beta}(l_{\kappa}, l'_{\kappa'}) e^{i q (R_{l'} - R_{l})} \right) A^{l'_{\kappa'}}_{\beta}(q) \tag{5.5}
\]

\[
= \sum_{\beta=1}^{3} \sum_{\kappa'=1}^{n} D^{\kappa' \kappa}_{\alpha \beta}(q) A^{l'_{\kappa'}}_{\beta}(q),
\]

where \(D^{\kappa' \kappa}_{\alpha \beta}(q)\) are the elements of the dynamical matrix \(D(q)\). Thus, the lattice dynamics will be described by a system of \(3n\) linear homogeneous equations in the \(3n\) unknown amplitudes \(A^{i}_{\alpha}(q)\) for each wave vector \(q\). Due to the Born-von Karman boundary conditions, the number of wave vectors \(q\) which lead to different dynamical states of the crystal equals its number of unit cells \(N\). At a given \(q\), the \(3n\) values of the eigenfrequencies \(\omega^{2}_{\alpha}(q)\) and the corresponding eigenvectors \(A^{i}_{\alpha}(q)\) can be obtained by solving the secular equation

\[
\left| D^{\kappa' \kappa}_{\alpha \beta}(q) - \delta_{\alpha \beta} \omega^2 \right| = 0. \tag{5.6}
\]

The displacement pattern obtained for a particular amplitude \(A^{i}_{\alpha}(q) (j = 1, 3n)\) and
the corresponding eigenvalue \( \omega_j^2(q) \),

\[
u^{\kappa}(t) = \frac{1}{\sqrt{m_\kappa}} A^{\kappa}_\alpha(q) e^{i(q R_\kappa - \omega_j(q) t)} \tag{5.7}
\]

represents the normal mode of the crystal described by the wave vector \( q \) and the branch index \( j \). The peculiar feature of a normal mode is that it does not mix with any other normal modes.

The general solution of (5.5) can be written as a linear combination of the normal modes \( q_j \)

\[
u^{\kappa}(t) = \frac{1}{\sqrt{m_\kappa}} \sum_{q} \sum_{j=1}^{3n} A^{\kappa}_\alpha(q) e^{i(q R_\kappa - \omega_j(q) t)} Q_j^q \tag{5.8}
\]

\[
u^{\kappa}(t) = \frac{1}{\sqrt{m_\kappa}} \sum_{q} \sum_{j=1}^{3n} A^{\kappa}_\alpha(q) e^{i(q R_\kappa - \omega_j(q) t)} Q_j^q(t)
\]

where \( Q_j^q(t) = Q_j^q e^{-i\omega_j t} \) are the time-dependent complex normal coordinates. One can prove that, the classical Hamiltonian function \( H = T + \Phi \) of the system can be expressed in terms of the complex normal coordinates as

\[
H = \frac{1}{2} \sum_{q} \sum_{j=1}^{3n} \left\{ (\dot{Q}_j^q(t))^* \dot{Q}_j^q(t) + \omega_j^2(q) (Q_j^q(t))^* Q_j^q(t) \right\}, \tag{5.9}
\]

which leads to the following equation of motion of the complex normal coordinates

\[
\frac{\partial^2 Q_j^q(t)}{\partial t^2} + \omega_j^2(q) Q_j^q(t) = 0. \tag{5.10}
\]

Since the Equation (5.10) describes the motion of an uncoupled harmonic oscillator, one can infer that the physical meaning of the harmonic approximation used in the derivation of (5.5) consists in the modeling of the crystal vibrations as a superposition of \( 3nN \) uncoupled harmonic oscillations.

The first step in solving the secular equation (5.6) is to evaluate the elements of the dynamical matrix \( D^{\kappa\kappa'}_{\alpha\beta}(q) \). For a given unit cell \( l \), this requires the knowledge of the force constants \( \Phi_{\alpha\beta}(l\kappa, l\kappa') \) for all pairs of atoms \((l\kappa; l\kappa')\). However, in current
5.1 Description of the method

calculations, these force constants are computed only in large supercells in order to ensure that the interaction between a given atom in the unit cell $l$ and those at the boundary of the supercell is negligible. In other terms, the dimension of the used supercell must exceed the spatial range of the forces between atoms. Unfortunately, this requirement of the direct force-constant approach still could lead to a numerical effort beyond the computational capabilities available nowadays when attempting to obtain accurate results even for simple metals (see, e.g., Ref. [FEF95]).

The frozen-phonon approach [KM81] was designed to overcome the above mentioned drawbacks of the direct force-constant method when confining to the study of the lattice dynamics at a given wave vector $q$. Following Kunc et al. [DV83] (see also Ref. [CKH86, SK88]) the phonon frequencies and displacement patterns at a fixed wave vector $q$ can be calculated from the two structures, one distorted consistently with the symmetry of the phonon in question, and the undistorted (equilibrium) one.

The practical problem which must be solved in this approach is to generate the distorted crystal structures corresponding to the atomic displacements involved in that phonon. Unfortunately, usually these vibrations patterns are not known a priori. However, this difficulty can be overpassed with the help of the group theory.

The physical background of the application of the group theory in solid state physics is done by Wigner’s theorem which states: "If $\hat{R}$ is a symmetry operation of the Hamiltonian $\hat{H}$ that describes the physical system under study

$$\hat{R}\psi(r) = E\psi(r)$$

then

$$\hat{R}\hat{H}\psi(r) = E\hat{R}\psi(r)$$

so that $\hat{R}\psi(r)$ is also an eigenfunction of $\hat{H}$ and has the same energy $E$ as the eigenfunction $\psi(r)$". In consequence, if the physical system in question is described by the symmetry operations of a certain point group or space group $G$, then the eigenfunctions of its Hamiltonian $\hat{H}$ must belong to one of the irreducible representations $\Gamma_l$ of $G$. 
5.1 Description of the method

In case of the lattice vibrations of a crystalline solid, the group theory is used in labeling the normal modes and in predicting the forms of their eigenvectors. The assignment of the normal modes of vibration to irreducible representations of the space group $G$ can be accomplished by analyzing the transformation under the symmetry operations of that space group of an $3n$-dimensional vector $\eta$ whose components are the Cartesian displacements (5.8) of the atoms in the unit cell. At a fixed wave vector $q$, the fully reducible matrix representation of the space-group symmetry operations $\{R|v\}$ can be written as

$$D^q_\eta(\{R|v\}) = D^q_1 \oplus D^q_2 \oplus \ldots \oplus D^q_i \oplus \ldots,$$

(5.11)

where $D^q_i$ is the matrix representation of that space-group symmetry operation belonging to the spatial-group irreducible representations $\Gamma^q_i$.

If the same spatial-group irreducible representation $\Gamma^q_i$ appears $p$ times in the above relation, the corresponding normal coordinate $Q_j$ which also spans this irreducible representation (see Chapter 2 of the Ref. [HM74]) can be always expressed as a linear superposition of the symmetry-adapted displacements (symmetry coordinates)

$$Q^q_j = \sum_{l=1}^{p} a_{jk} S^q_l.$$

(5.12)

where for the simplicity of the notation the dimension of the spatial-group irreducible representation $\Gamma^q_i$ was assumed to be equal to one. The physical meaning of the above equation is that the crystal symmetry alone does not yet determine the displacement patterns of phonons in question (as is the case, for instance, of the $\Gamma$-TO mode in SiC).

The symmetry coordinates $S^q_i$ can be obtained as a linear combination of the Cartesian displacements $v^{\alpha,q}_\alpha$ of the atoms in the unit cell commensurate with the wave vector $q$

$$S^q_i = \sum_{\alpha=1}^{3} \sum_{k=1}^{n} b^q_{\alpha} v^{\alpha,q}_\alpha.$$

(5.13)

where the coefficients $b^q_{\alpha}$ are determined only from the symmetry considerations such
that the corresponding symmetry-adapted displacements transform also according to the spatial-group irreducible representation $\Gamma_i^q$ in question (see Cracknell [Cra75] p. 107 and Bhagavantam and Venkatarayudu [BV69] p. 78). Correspondingly, the Cartesian displacement $u_\alpha^q$ can be expressed in terms of the symmetry coordinates $S_t^q$ as

$$u_\alpha^q = \sum_{t=1}^{p} \epsilon_\alpha^q S_t^q,$$

(5.14)

(see also Appendix A). It follows that the kinetic energy becomes

$$T = \frac{1}{2} \sum_{t,t'=1}^{p} \sum_{\alpha=1}^{3} \sum_{\kappa=1}^{n} \epsilon_\alpha^\kappa m_\kappa e_\alpha^{\kappa} \dot{S}_t^q \dot{S}_{t'}^q,$$

$$= \frac{1}{2} \sum_{t,t'=1}^{p} F_{t't'} S_t^q S_{t'}^q,$$

(5.15)

and the potential energy is given by

$$\Phi = \frac{1}{2} \sum_{t,t'=1}^{p} \frac{\partial^2 E(S_1^q \ldots S_p^q)}{\partial S_t^q \partial S_{t'}^q} S_t^q S_{t'}^q,$$

$$= \frac{1}{2} \sum_{t,t'=1}^{p} F_{t't'} S_t^q S_{t'}^q,$$

(5.16)

where the force matrix elements $F_{t't'}$ are determined from self-consistent calculations of the total-energy evaluated for the undisplaced structure and those generated for different combinations $S_1^q \ldots S_p^q$.

Following the same steps that led to (5.5), the equation of motion of the atoms vibrating according to the symmetry of the given irreducible representation of the space group at the wave vector $q$ is given by

$$\omega^2 S_t^q \sum_{\alpha=1}^{3} \sum_{\kappa=1}^{n} \epsilon_\alpha^\kappa m_\kappa e_\alpha^{\kappa} = \sum_{t'=1}^{p} F_{t't'} S_{t'}^q,$$

(5.17)

The secular determinant of dimension $p$ to be solved is

$$|F - \omega^2 G| = 0,$$

(5.18)
where the expressions of the kinetic-energy matrix elements $G_{\nu'}$ are

$$G_{\nu'} = \sum_{\alpha=1}^{3} \sum_{\kappa=1}^{n} c_{\alpha\kappa}^{\nu} m_{\kappa} c_{\alpha\nu'}^{\kappa}.$$  \hfill (5.19)

The main limitation of this approach comes from the requirement that the phonon's wavelengths must be commensurate with the dimension of the supercell used in calculations. If for a zone-center phonon only the unit cell must be used, the size of a supercell required by a phonon at a general $q$ point in the Brillouin zone could generally involve a prohibitive numerical effort.

### 5.2 LO/TO splitting

A common limitation of both variants of the direct method arises when applied to polar crystals. For these compounds, only the TO modes can be handled, in which the atomic displacements are perpendicular to wave vector $q$. The reason is given by the fact that the force-constants as well as the total energies are calculated using supercells which are by definition subject to periodic boundary conditions. The presence of the macroscopic field generated by the atomic vibrations along the wave vector $q$ (LO modes) destroys the crystal symmetry and thus, no band-structure like calculations can be performed in this case.

The proper 	extit{ab initio} treatment of the LO/TO splitting requires the evaluation of the Born effective charge tensor associated with the atoms of the $\kappa$-th sublattice defined as

$$Z_{\kappa,\alpha\beta} = Z_{\kappa} + \frac{\Omega}{e} \left. \frac{\partial P_{\alpha}^{e\kappa}}{\partial u_{\beta}} \right|_{E=0},$$  \hfill (5.20)

where $Z_{\kappa}$ is the charge of the nuclei of the sublattice, $\Omega$ represents the volume of the unit cell, and $P_{\alpha}^{e\kappa}$ is the $\alpha$-th Cartesian component of the electronic part of the macroscopic polarization induced by the displacement of the sublattice in the $\beta$ Cartesian direction $u_{\beta}$ in zero electric field $E$. As shown in Ref. [ZVKS95], the
5.3 Application to LiNbO$_3$ and LiTaO$_3$

The dynamical matrix has the following expression

$$D_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = D^{(0)}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) + \frac{4\pi e^2}{\Omega} \frac{(Z_{\kappa}^*\mathbf{q})_\alpha (Z_{\kappa'}^*\mathbf{q})_\beta}{\epsilon_\infty(\mathbf{q})} .$$ \hspace{1cm} (5.21)

where $D^{(0)}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})$ represents an analytic function, $\epsilon_\infty(\mathbf{q})$ is the optical macroscopic dielectric function, and $\mathbf{q}$ is a unit wave vector. The last term in the above equation describes the effect of the macroscopic electric field generated by LO modes. Particularly at the $\Gamma$ point, the LO-phonon frequencies and eigenvectors can be evaluated from

$$D^{LO}_{\kappa\alpha,\kappa'\beta} = D^{TO}_{\kappa\alpha,\kappa'\beta} + \frac{4\pi e^2}{\Omega} \frac{(Z_{\kappa}^*\mathbf{q})_\alpha (Z_{\kappa'}^*\mathbf{q})_\beta}{\epsilon_\infty(0)} \bigg|_{\mathbf{q}=0} .$$ \hspace{1cm} (5.22)

where $D^{TO}$ is the zone-center TO dynamical matrix calculated without macroscopic field.

The $\textit{ab initio}$ calculation of the electronic polarization $P^e$ whose derivative with respect to the atomic displacements gives the Born effective charge tensor can be accomplished using the DFT linear-response theory [YK94, GL97] or as Berry’s phase [KSV93, Res94]. The details of the evaluation of LO/TO splitting in ferroelectric materials can be found in Ref. [ZVKSR95, WYK97, LWYK97].

5.3 Application to LiNbO$_3$ and LiTaO$_3$

In the following, the application of the frozen-phonon method in connection with the zone-center lattice dynamics in LiNbO$_3$ and LiTaO$_3$ is briefly presented. Some details regarding the implementation of this method when applied to $\Gamma$ phonons in BaTiO$_3$ could be found in Ref. [CK90].

In the case of LiNbO$_3$ and LiTaO$_3$, at the $\Gamma$ point, after projecting out 3 translation (acoustic) modes which result in zero vibration frequency, the atomic displacements in the ferroelectric phase are split by the symmetry into four $A_1$, five $A_2$ and nine double-degenerate $E$ modes. The symmetry coordinates were constructed for each irreducible representation of the $R3c$ group. The coefficients of the linear transformation (5.13) are listed in the Appendix A.
5.3 Application to LiNbO$_3$ and LiTaO$_3$

To diagonalize the secular determinant (5.18), the force matrix elements $F_{ij'}$ are evaluated from a polynomial fit of the total energy as a function of symmetry coordinates corresponding to each mode. To obtain meaningful results, a reliable fit (in the sense that the calculated eigenfrequencies and eigenvectors remain essentially unchanged when adding new data) must be obtained for each mode in question. In the case of LiNbO$_3$, a good least-square fit for $A_1$ modes was obtained from the data of 90 different structures, 127 for $A_2$ modes. In case of LiTaO$_3$, a good least-square fit for the $A_1$ modes was obtained using the data from 170 different geometries.

If only the symmetry coordinates were used in a least-square fit of the total energy calculated for the $E$ modes, this approach would result in a prohibitively high number of geometries needed to be considered. In consequence, for these modes the multidimensional total-energy fit was performed considering both symmetry coordinates and the symmetrized forces.

The least-square total-energy fit in function of both symmetry coordinates and the symmetrized forces was obtained starting from the following expression of the "chi-square" $\chi^2$ function

$$
\chi^2 = \sum_{i=1}^{M} \left( \frac{E_i - E(S_1 \cdots S_p)}{\sigma_i} \right)^2 + \bar{c} \sum_{j=1}^{p} \sum_{i=1}^{M} \left( \frac{f_{ji} - \frac{\partial E(S_1 \cdots S_p)}{\partial S_j}}{\sigma_{ji}} \right)^2,
$$

(5.23)

where $M$ represents the total number of energies $E_i$ calculated for different geometries, $\sigma_i$ and $\sigma_{ji}$ stand for the standard deviation of each data point (for instance, for the cases when mixing data points obtained for calculations performed with different accuracies). Also, the $\bar{c}$ parameter is a constant which takes into account the appropriate dimensional scaling of the $\chi^2$ function. The fitting procedure was performed assuming a second-order polynomial form of the function $E(S_1 \cdots S_p)$. The symmetrized forces $f_{ji}$ are obtained from the relation

$$
f_{ji} = -\sum_{k=1}^{3n} \frac{\partial E(S_1 \cdots S_p)}{\partial u_k} \frac{\partial u_k}{\partial S_i} \frac{\partial S_i}{\partial S_j}
$$

(5.24)

$$
= \sum_{k=1}^{3n} c_{ki} F_k.
$$

where $F_k$ is the calculated force on atom $k$ and the coefficients $c_{ki}$ are given by
(5.14). From the minimization of the function \( \chi^2 \) with respect of the coefficients of
the second-order polynom \( E(S_1 \ldots S_p) \), the analytical expression of the resulting set
of equations was implemented into a Fortran program. Using this code, a reliable
fit for the \( E \) modes required the data from only 262 different structures. A different
approach in using the computed forces in the frozen-phonon method can be found
in Ref. [SW89, YSK91].

Since the symmetry coordinates belonging to different irreducible representations
at a given wave vector \( \mathbf{q} \) do not mix, the dynamical matrix whose diagonalization
delivers all TO modes at \( \Gamma \) has a block-diagonal form:

\[
\begin{pmatrix}
A_1 & 4 \times 4 \\
& A_2 & 5 \times 5 \\
& & E & 9 \times 9 \\
& & & E & 9 \times 9
\end{pmatrix}
\]

all other elements of this matrix being equal to zero.
Chapter 6

Ab initio zone-center lattice dynamics in LiNbO$_3$

6.1 Method

The Kohn-Sham equations were solved self-consistently using the FLAPW method (see Chap. 3) with the addition of local orbital basis functions [Sin91] as implemented in WIEN97 FLAPW code [BSL97]. As was depicted in a previous Chapter, in this method there is no shape approximation imposed on the potential, nor on electronic charge density. Moreover, the core states are treated fully relativistically using the spherical component of the crystal potential whereas the semicore and valence states are computed in the full crystal potential with the spin-orbit coupling evaluated within the scalar relativistic approximation. The use of the local orbitals (LO) relaxes the linearization errors and also allows the treatment of the high lying core (semicore) states and valence ones in one energy window, that ensures a proper orthogonality between these states. The exchange-correlation energy functional was evaluated within the local density approximation (LDA), using the Perdew and Wang parametrization [PW92] of the quantum Monte Carlo data obtained by Ceperley and Adler [CA80] for the homogeneous electron gas.

The integration over the Brillouin zone was performed on a $4 \times 4 \times 4$ special $k$-points mesh using the improved tetrahedron method as described in Ref. [BJA94]. The convergence of our calculations with respect to a denser $k$-mesh was carefully
checked. The use of a finer $6 \times 6 \times 6$ $k$-mesh resulted in the absolute total energy difference of less than 1 mRy (see Fig. 6.1). From this figure one can also infer that the average difference in the total energy trends obtained for the equilibrium structure (see below) and two displaced structures according to A$_1$ phonon symmetry is also less than 1 mRy. We also tested if the total energies calculated are changing significantly when increasing the cutoff parameter $G_{\text{max}}$ that controls the accuracy with which the potential and charge density in the interstitial region are calculated by means of the Fourier expansion (see Chap. 3). Choosing for the cutoff parameter $G_{\text{max}}$ a value of 11 and keeping fixed the parameter $R_{\text{min}},K_{\text{max}}$, we repeated the above calculations. As is presented in Fig. 6.2, with this value of $G_{\text{max}}$ parameter we obtained the same differences of less than 1 mRy for both total energy and total energy trends. Moreover, a difference of same magnitude describes the total energies calculated with the both settings. These observations determined us to perform all frozen phonon calculations with the cutoff parameter $G_{\text{max}}=10$.

For a well convergent calculation, the electron density computed within the full
potential LAPW method should not depend on the chosen radii of the (non overlapping) muffin-tin spheres. Because of this feature of the FPLAPW approach and also in order to allow the atoms to move during the structure optimization process, we have chosen the muffin-tin radii of 1.9 a.u. for Nb and 1.6 a.u. for Li and O, close to the values used by Inbar and Cohen [IC95, IC96] in their FLAPW calculation.

The convergency of the total energy with respect to the number of augmented plane waves used was also carefully checked. The dimension of the basis set is controlled by the parameter $R_{\text{min}}K_{\text{max}}$, where $R_{\text{min}}$ represents the minimum value of the chosen muffin-tin radii and $K_{\text{max}}$ is the cutoff parameter that limits the number of basis functions (see the relation (4.19) from Chap. 3). As depicted in Fig. 6.3, when increasing the value of the $R_{\text{min}}K_{\text{max}}$ parameter from 7 as previously used to 8, we found only a rigid ”translation” of the total energies to lower values. Because the frozen phonon approach relies on the total energy differences between the equilibrium structure and the distorted ones, all our subsequent calculations were performed setting this cutoff parameter to 7.0, that generated, on the average,
Figure 6.3: Total energy differences (with respect to $E_{\text{tot}} = -16194$ Ry) obtained for two different LAPW basis sets (see text)

980 LAPW basis functions for each $k$-point.

6.2 Ground-state structure

In order to perform truly \textit{ab initio} frozen phonon calculations, first the equilibrium structure that minimizes the total energy of the system under consideration must be obtained. However, because the exchange-correlations are evaluated in a approximate way, it could happen that no ferroelectric instability is found for the calculated lattice parameters, if they are too much underestimated. Such situations are usually overcome by using the experimental lattice constants instead of the computed ones. In consequence, one of our initial tasks was to check if the zone-center lattice dynamics in LiNbO$_3$ could be investigated using the calculated lattice parameters or the experimental ones.

The simultaneous optimization of the volume and the $c/a$ ratio for the paraelectric phase of LiNbO$_3$ resulted in the values of lattice parameters (in the hexagonal
setting) \(a_H = 5.1378 \text{ Å} \) and \(c = 13.4987 \text{ Å}\). As compared to the experimental data \((a_H = 5.1483 \text{ Å} \) and \(c = 13.8631 \text{ Å}\), see Ref. [ARB66, AHR66]), that corresponds to a volume underestimated by \(~3\%\) and a \(c/a\) ratio deviating by \(~2\%\) from experiment, i.e. quite good agreement by the standards of first-principles calculations based on DFT. In the subsequent optimization of atomic positions, we kept the lattice parameters fixed. In Table 6.1 we explicitly list the Cartesian coordinates of all ten atoms in the unit cell, in order to specify the numbering of atoms the discussion of phonon eigenvectors later in this section. The fully optimized paraelectric

### Table 6.1: Numbering of atoms in the primitive cell and their Cartesian coordinates in ferroelectric LiNbO\(_3\)

<table>
<thead>
<tr>
<th></th>
<th>Nb1</th>
<th>Nb2</th>
<th>Li1</th>
<th>Li2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
<th>O5</th>
<th>O6</th>
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<tbody>
<tr>
<td>(x/a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.278</td>
<td>0.029</td>
<td>0.249</td>
<td>0.299</td>
<td>-0.039</td>
<td>-0.259</td>
</tr>
<tr>
<td>(y/a)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.127</td>
<td>0.304</td>
<td>-0.177</td>
<td>0.127</td>
<td>-0.323</td>
<td>0.196</td>
</tr>
<tr>
<td>(z/c)</td>
<td>0</td>
<td>(\frac{1}{2})</td>
<td>0.281</td>
<td>0.781</td>
<td>0.401</td>
<td>0.401</td>
<td>0.401</td>
<td>0.568</td>
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</tbody>
</table>

structure was found energetically instable with respect to the symmetry-lowering atom displacements. The paraelectric phase has one internal coordinate whereas the ferroelectric phase has four (see Fig. 6.4). These four parameters are actually related to the four symmetry coordinates which can be introduced to describe the \(A_1\)-TO phonons. Therefore, in the course of accumulating total energy data for our frozen phonon calculations (see next section), we were able simultaneously to optimize the ferroelectric ground-state structure to quite good accuracy. Moreover, the calculated forces have been used in the process of structure optimization. The experimental and calculated atomic positions (in the hexagonal coordinates, following [ARB66, AHR66]) for both paraelectric and ferroelectric phases are given in Table 6.2. The agreement between theory and experiment in all internal parameters is quite good, indicating a presumably nonproblematic applicability of LDA for the study of lattice dynamics in LiNbO\(_3\). The energy difference we found between paraelectric and ferroelectric phases is essentially the same as determined by Inbar and Cohen [IC95, IC97, IC96].
Figure 6.4: The four internal crystal-structure parameters of the LiNbO$_3$ in the ferroelectric phase.
6.3 \( A_1 \) modes

<table>
<thead>
<tr>
<th>phase</th>
<th>Nb</th>
<th>Li</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>para</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{4} )</td>
<td>( \frac{1}{3} )</td>
<td>( \frac{1}{12} )</td>
</tr>
<tr>
<td></td>
<td>( 0.049^c )</td>
<td>( 0.041^c )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 0.283^c )</td>
<td>( 0.279^c )</td>
<td>( 0.346^c )</td>
</tr>
<tr>
<td></td>
<td>( 0.067^c )</td>
<td></td>
<td>( 0.066^c )</td>
</tr>
<tr>
<td>ferro</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

\(^c\)Experimental: Ref. [ARB66, AHR66]; \(^c\)Calculation.

6.3 \( A_1 \) modes

The zone-center lattice dynamics in LiNbO\(_3\) was experimentally investigated by means of Raman spectroscopy measurements [Koj93, SM97] or by neutron scattering [CPS78]. The early experiments used congruent samples and only recently (see, e.g., Ref. [RBFM97]) the frequencies of \( A_1 \) modes could be determined for nearly stoichiometric crystals. As was pointed out in several papers [MGS99, RHB99], the physical properties of LiNbO\(_3\) depend significantly on the presence of both intrinsic and extrinsic defects. In particular, the Raman spectroscopy is very sensitive to the stoichiometry of the LiNbO\(_3\) crystals, that results in the shift of some lines, or in apparent appearance of new lines. In consequence, the displacement patterns corresponding to different modes have not yet been unambiguously attributed, to our best knowledge. However, some insight concerning this problem could be gained using the \(^7\)Li - \(^6\)Li isotope effect in Ref. [Koj93], that helped to identify the lines involving mostly the Li\(^+\) cation vibrations. Moreover, the difference between the LiNbO\(_3\) and LiTaO\(_3\) spectra allowed to assign the Raman lines involving Ta\(^{5+}\) and Nb\(^{5+}\) cation displacements.

To solve the dynamical equation of motion, the total energy then has been calculated for a number of trial geometries corresponding to different points in the four-dimensional space of the symmetry coordinates corresponding to \( A_1 \) modes, and a second-order polynomial fit \( E_{\text{tot}}(S_1 \cdots S_4) \) was constructed. In order to obtain a good total-energy fit for the \( A_1 \) modes (in a sense that the results remain relatively unaffected by the addition of extra total energy data), we considered more than 90 different geometries. The accuracy of our fit is based on a careful treatment of the geometry of the total-energy hypersurface, which is presented in detail in the
following.

The diagonalization of the dynamical matrix provides the frequencies and eigenvectors of four modes labeled TO₁ to TO₄. The calculated frequencies can be directly compared with the results of Raman or infrared measurements. The eigenvectors define the normal coordinates of four harmonic modes; this information, related to the participance of individual atoms in each of four vibration modes, is not available from the experiment (apart from some qualitative information related to the isotope shift, that is discussed below). The transformation to normal coordinates $S_{TO₁} \cdots S_{TO₄}$ in 4-dimensional space of $(S₁ \cdots S₄)$ is the following (see Appendix A for more details):

$$
\begin{pmatrix}
S_{TO₁} \\
S_{TO₂} \\
S_{TO₃} \\
S_{TO₄}
\end{pmatrix} =
\begin{pmatrix}
0.685 & 0.660 & 0.307 & -0.028 \\
0.069 & -0.997 & -0.034 & 0.024 \\
0.018 & 0.009 & -0.331 & -0.943 \\
0.069 & 0.099 & -0.934 & 0.336
\end{pmatrix}
\begin{pmatrix}
S₁ \\
S₂ \\
S₃ \\
S₄
\end{pmatrix}.
$$

Fig. 6.5 shows the cuts of the total energy hypersurface along the directions of these four normal coordinates. This helps to get an idea about the quality of our fit and about the anharmonicity of four modes. The raw data points are shown as circles, the abscissa values of which are projections of their $(S₁ \cdots S₄)$ positions onto the direction of the normal coordinate in question. The sizes are inversely proportional to the distance in the 4-dimensional space between the data point and the normal coordinate line. I.e., the largest circles represent the displacements essentially along a normal coordinate. The 2d order fit of the total energy hypersurface along each normal coordinate is shown by solid line, and the fit by a 4th-order polynomial is shown by dashed line for two modes (TO₁ and TO₄) that exhibit the largest deviation from the harmonic behavior. For the cut along the normal coordinates corresponding to the TO₂ and TO₃ modes, the deviation of the higher-order polynomial fit from the 2d-order fit is negligible. Therefore these two modes can be left out in case of a subsequent analysis of anharmonic corrections based on a total energy fit to a higher-order polynomial, similarly to how it was attempted by Inbar and Cohen[IC96].

The calculated frequencies of the $A₁$ modes are shown in Table 6.3 in comparison...
Figure 6.5: The cut of the total energy fit along the directions of normal displacements in the 4-dimensional space of symmetry coordinates corresponding to the $A_1$ symmetry of LiNbO$_3$. The circles’ sizes are inversely proportional to the distances of corresponding data points from the direction of normal displacement. Solid lines represent the 2d-order polynomial fit, dashed lines – the 4th order fit.
Table 6.3: Calculated and measured frequencies (cm\(^{-1}\)) of four \(A_1\)-TO modes in LiNbO\(_3\)

<table>
<thead>
<tr>
<th></th>
<th>calc. (^7)LiNbO(_3)</th>
<th>exp. (^7)LiNbO(_3)</th>
<th>calc. (^6)LiNbO(_3)</th>
<th>exp. (^6)LiNbO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>present Ref.</td>
<td>PLK00 Ref.</td>
<td>Koj93 Ref.</td>
<td>RFB97 Ref.</td>
</tr>
<tr>
<td>TO(_1)</td>
<td>208</td>
<td>239</td>
<td>256</td>
<td>252</td>
</tr>
<tr>
<td>TO(_2)</td>
<td>279</td>
<td>320</td>
<td>275</td>
<td>273</td>
</tr>
<tr>
<td>TO(_3)</td>
<td>344</td>
<td>381</td>
<td>332</td>
<td>331</td>
</tr>
<tr>
<td>TO(_4)</td>
<td>583</td>
<td>607</td>
<td>637</td>
<td>632</td>
</tr>
</tbody>
</table>

with the experimental data. We selected as those the results of the most recent publications [SM97, RFB97] as well as Ref. [Koj93] including the information on the \(^7\)Li – \(^6\)Li isotope shift. Older measurements [SW66, KJ67, CBWS72] provided actually also very close estimations for the frequencies. The agreement between our calculation and experimental values is very good for TO\(_2\) and TO\(_3\) modes, that were mentioned above to be largely harmonic. The corresponding eigenvectors are shown in Table 6.4.

One can see that TO\(_2\) is essentially the \(z\)-vibration of Li ions in antiphase to Nb

Table 6.4: Calculated eigenvectors of four \(A_1\) modes in LiNbO\(_3\)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Nb1</th>
<th>Nb2</th>
<th>Li1</th>
<th>Li2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
<th>O5</th>
<th>O6</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO(_1)</td>
<td>{ x, y, z }</td>
<td>0, 0, 0.39</td>
<td>0, 0, 0.09</td>
<td>0, 0, 0.09</td>
<td>-0.01, -0.33, -0.33</td>
<td>0.07, 0.07, 0.07</td>
<td>-0.03, -0.33, -0.33</td>
<td>-0.04, -0.33, -0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO(_2)</td>
<td>{ x, y, z }</td>
<td>0, 0, 0.18</td>
<td>0, 0, -0.68</td>
<td>0, 0, -0.68</td>
<td>-0.01, -0.01, -0.01</td>
<td>0.01, 0.01, 0.01</td>
<td>-0.00, -0.00, -0.00</td>
<td>-0.01, -0.01, -0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO(_3)</td>
<td>{ x, y, z }</td>
<td>0, 0, 0.02</td>
<td>0, 0, -0.00</td>
<td>0, 0, -0.00</td>
<td>-0.38, 0.38, 0.38</td>
<td>0.31, 0.31, 0.31</td>
<td>0.08, 0.08, 0.08</td>
<td>0.31, 0.31, 0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO(_4)</td>
<td>{ x, y, z }</td>
<td>0, 0, 0.06</td>
<td>0, 0, 0.04</td>
<td>0, 0, 0.04</td>
<td>-0.38, 0.38, 0.38</td>
<td>0.31, 0.31, 0.31</td>
<td>0.07, 0.07, 0.07</td>
<td>0.31, 0.31, 0.31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
with respect to a (relatively rigid) oxygen cage. In fact this is the only $A_1$ mode which exhibits a substantial amount of Li movement. One can observe that in the experimentally measured frequencies of $^6$Li-doped LiNbO$_3$ [Koj93] only the TO$_2$ mode presents an isotope effect, increasing its frequency by 14 cm$^{-1}$ (see Table 6.3). Our calculation of this effect also indicates that only the TO$_2$ mode is affected, its frequency being increased by 19 cm$^{-1}$. The isotope effect is clearly expected to be larger in the calculation (where we assumed 100% of Li atoms to have a reduced mass) than in an experiment.

Recently, Repelin et al. [RHPB99] measured the $^7$Li – $^6$Li isotope shift of the Raman lines in ceramic samples of LiNbO$_3$ and reported the increase also in the frequency of the TO$_3$ line, from 334 to 364 cm$^{-1}$. One should note, however, that the line in question has the lowest intensity among all $A_1$ TO modes, and the spectra obtained from ceramic samples contain a complicated mixture of all $A_1$ and $E$ lines. A tiny feature in the Raman spectrum of $^6$LiNbO$_3$ interpreted as a shifted TO$_3$ line in Ref. [RHPB99] (see Fig. 3 therein) may well have a different origin in the spectrum of a ceramic sample, related for instance with defects. To our mind, from the spectra shown in Fig. 3 of Ref. [RHPB99] one cannot rule out that the $A_1$-TO$_3$ remains unaffected by the isotope shift, as clearly follows from our calculation.

The displacement pattern in the TO$_1$ mode is similar to that in the soft mode of cubic perovskites (for instance, KNbO$_3$) in the sense that Nb vibrates in antiphase with the oxygen sublattice along the trigonal axis, leaving Li relatively static. The frozen-phonon calculations in cubic KNbO$_3$ (see, e.g., Refs. [SB92, PNB94]) have shown that this mode is instable against off-center displacements along the trigonal axis. Even as stabilized by an appropriate symmetry lowering in tetragonal [PNB94] or orthorhombic [PB94] structure of KNbO$_3$, the TO$_1$ mode generally maintains its original displacement pattern. In LiNbO$_3$, the $A_1$-TO$_1$ is the ultimately stabilized soft mode of the paraelectric phase. The total energy profile related to this displacement is quite asymmetric as is well seen in Fig. 6.5 from the comparison with the parabolic fit. This anharmonicity of the $A_1$-TO$_1$ mode was also found by Inbar and Cohen [IC96], who obtained an excellent agreement between the experimental TO$_1$ frequency and the calculated one by solving the Schrödinger equation for one-dimensional noninteracting anharmonic oscillators. Because of anharmonicity of this mode, the experimental frequency is substantially higher than that calculated in the harmonic approximation. A low Li content in the eigenvector of the TO$_1$ mode is
consistent with the fact that the Li displacement contributes only insignificantly to the total energy lowering in the para- to ferroelectric transition, as pointed out by Inbar and Cohen [IC96]. This is in spite of the fact that the magnitude of Li displacement is actually relatively large in the transition.

Another example of an anharmonic mode is the TO$_4$, the total energy profile of which is also shown in Fig. 6.5. In order to understand the physical origin of its anharmonicity, the atom displacements in this mode can be compared with those of the harmonic mode TO$_3$. In TO$_3$, the whole oxygen octahedra are rigidly rotated along the polar axis, that results in a relatively soft and harmonic vibration. In the TO$_4$ mode, the stretching of individual octahedra takes place. It requires much higher energy and determines a strong anharmonic behaviour of this mode. A suggestive visualization of these modes is presented in Appendix A of this work.

Whereas there is an overall agreement between our calculated frequencies and those by Parlinski et al.[PLK00] also listed in Table 6.3, one can see a systematic shift of frequencies upwards as compared to ours. The reason for this may be that the force constants in Ref. [PLK00] were calculated from the set of geometries with atoms shifted from their equilibrium positions. For modes with pronounced anharmonicity, the forces on atoms calculated under such displacements are larger than would follow from the harmonic approximation for the total energy profile near the equilibrium. The “harmonic” TO$_2$ and TO$_3$ modes must be relatively insensitive to the amplitude of individual atomic displacements for which the forces are calculated. But the fact that these modes are mixed with two anharmonic ones in the course of constructing the dynamical matrix apparently affects the accuracy with which all four frequencies are calculated.

In our calculation, we used many geometries and controlled our data (total energies and forces) used for the total energy fit to be well within the harmonic region, discarding the rest. Therefore the calculated frequencies are typically close to, or less than, the experimental values.

### 6.4 $A_2$ modes

The $A_2$ modes are not detectable by means of Raman nor infrared spectroscopy. However the study of the dispersion in certain phonon branches by inelastic neutron scattering[CP78] revealed the frequencies of three $A_2$ modes at $\Gamma$ (see Table 6.5).
6.5 $E$ modes

The other modes were, to our knowledge, addressed only in a recent first-principles calculation by Parlinski et al.[PLK00]. In our calculation, we used 127 different geometries to obtain an accurate second-order total energy fit in the 5-dimensional space of symmetry coordinates. The calculated frequencies are shown in Table 6.5 and the eigenvectors in Table 6.6.

It is well seen that the $^6$Li → $^7$Li substitution would only affect the softest mode. Its frequency is close to that of the second $A_1$ mode, and even the eigenvector components are similar. In both cases, the vibration pattern is that of Nb vs. Li on the background of essentially static oxygen atoms; the difference is that two identical atoms in the unit cell (both Nb, or both Li) vibrate in phase in the $A_1$ and in antiphase in the $A_2$ mode. In generally, the $A_2$ modes have comparable contributions from the displacements along the trigonal $z$ axis and in the $xy$ plane. Exceptions are the softest mode which includes essentially the Nb vs. Li antiphase $z$-movement, and the hardest one which, similarly to the $A_1$-TO$_4$ mode, includes a distortion of the oxygen octahedra and its $z$-stretching. The displacement patterns involved in the $A_2$ phonons are presented in Appendix B.

6.5 $E$ modes

The dependence of the Raman spectra on the stoichiometry of the samples resulted in a controversial assignment of the nine $E$ modes in the study of Raman vibrations in LiNbO$_3$. A review on this controversy can be found, e.g., in Ref. [RBFM97]. The present calculations are based on the stoichiometric structure of LiNbO$_3$ with no
6.5 \( E \) modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Nb1</th>
<th>Nb2</th>
<th>Li1</th>
<th>Li2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
<th>O5</th>
<th>O6</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO1</td>
<td>( x )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>-0.01</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.03</td>
<td>-0.03</td>
<td>0.00</td>
<td>-0.03</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.24</td>
<td>-0.24</td>
<td>-0.66</td>
<td>0.66</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>-0.05</td>
<td>-0.05</td>
</tr>
<tr>
<td>TO2</td>
<td>( x )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.08</td>
<td>0.24</td>
<td>-0.16</td>
<td>0.08</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.23</td>
<td>-0.05</td>
<td>-0.18</td>
<td>0.23</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>-0.51</td>
<td>0.51</td>
<td>-0.14</td>
<td>0.14</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>-0.12</td>
<td>-0.12</td>
</tr>
<tr>
<td>TO3</td>
<td>( x )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.23</td>
<td>-0.03</td>
<td>0.26</td>
<td>0.23</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.17</td>
<td>0.28</td>
<td>-0.11</td>
<td>-0.17</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.04</td>
<td>-0.04</td>
<td>0.11</td>
<td>-0.11</td>
<td>0.28</td>
<td>0.28</td>
<td>-0.28</td>
<td>-0.28</td>
<td>-0.28</td>
</tr>
<tr>
<td>TO4</td>
<td>( x )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>-0.25</td>
<td>0.24</td>
<td>-0.01</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.28</td>
<td>0.13</td>
<td>0.15</td>
<td>-0.28</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>-0.42</td>
<td>0.42</td>
<td>-0.19</td>
<td>0.19</td>
<td>-0.12</td>
<td>-0.12</td>
<td>0.12</td>
<td>-0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>TO5</td>
<td>( x )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.33</td>
<td>0.21</td>
<td>0.12</td>
<td>0.33</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.06</td>
<td>0.26</td>
<td>-0.31</td>
<td>0.06</td>
<td>-0.31</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0.06</td>
<td>-0.06</td>
<td>0.02</td>
<td>-0.02</td>
<td>-0.23</td>
<td>-0.23</td>
<td>-0.23</td>
<td>0.23</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Intrinsic defects, so it unambiguously identifies the first-order \( E \) modes and provides the information about atom displacement patterns in each of them.

The \( E \) modes have been studied experimentally by several groups [SW66, KJ67, CBWS72], but some of the earlier studies faced a problem of detecting, or proper assignment, of nine Raman lines. Ridah et al. [RBFM97] emphasized the dependence of the Raman spectra (the frequency resolution, but also the position of some lines) on the crystal composition. In earlier studies, the crystals of congruent composition have been used, with Li deficiency of almost 3% and hence noticeable amount of intrinsic defects. In the study of Ridah et al. [RBFM97] the results obtained with both congruent and nearly stoichiometric single crystals have been compared, and high-resolution spectra obtained for the latter sample made it possible to find evidence of two new first-order Raman lines. Moreover, it was shown that several other lines have been erroneously attributed to first-order phonons in earlier studies.

The problem of attribution of different \( E \) modes could be up to now accessed
only indirectly, via the study of $^7\text{Li} - ^6\text{Li}$ isotope shift, or analyzing the differences between phonon frequencies in LiNbO$_3$ and LiTaO$_3$. An example of such a semi-quantitative analysis has been recently presented by Repelin et al.[RHP99]. An introduction of a limited set of nearest-neighbors stretching and bending force constants and fitting the phonon frequencies calculated herewith to experimental ones enabled the reconstruction of displacement patterns within all $A_1$ and $E$ modes. These calculations were not based on first-principles calculations of the underlying electronic structure. Moreover, the quality of the analysis was necessarily dependent on the ad hoc selection of interaction constants and probably not unambiguous, taken the necessity to fit many force parameters to just few experimental frequency values.

In the present study, we restrict ourselves to zone-center phonons only, but we tried to get a good description of the total-energy hypersurface associated with nine symmetry coordinates of the $E$ mode. We used displacements of different magnitudes and incorporated both total energy values and forces in our fitting procedure. The distribution of calculated total energy values reveals substantial anharmonicity along some directions in the 9-dimensional space, so that corresponding (harmonic) frequencies tend to be lower for some modes than the experimental values.

The calculated $E$-mode frequencies are shown in Table 6.7 in comparison with other experimental and calculated data; the phonon eigenvectors – in Table 6.8. The Nb and Li vibrations in the $E$ modes are confined to the $(x, y)$-plane; apart from this observation, the displacement patterns which can be visualized in Appendix C are quite complicated. One should note that since the $E$ modes are doubly degenerate, the definition of eigenvectors is not unique. Actually, they are defined up to a rotation in the $(x, y)$-plane. An additional information is available from the isotope shift of frequencies, that was, to our knowledge, reported for the $E$ modes only recently in the above mentioned work by Repelin et al.[RHP99] (using, however, only ceramic samples). Our calculated frequencies with different masses, as well as the information contained in the eigenvectors, help us to assign the phonon lines in the following way.

For three low-frequency and four high-frequency modes, one can see a good agreement between our calculated results and those selected in Ref. [RBFM97] as first-order phonons in the nearly stoichiometric crystal. The largest deviation is for the TO$_8$ mode which has a noticeable anharmonic contribution seen in the cut of
6.5 $E$ modes

Table 6.7: Calculated and measured frequencies (cm$^{-1}$) of nine $E$-TO modes in LiNbO$_3$

<table>
<thead>
<tr>
<th></th>
<th>$^5$LiNbO$_3$</th>
<th>$^7$LiNbO$_3$</th>
<th>$^6$LiNbO$_3$</th>
<th>$^6$LiNbO$_3$</th>
<th>Ref.</th>
<th>present Ref.</th>
<th>present Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO$_1$</td>
<td>151</td>
<td>157</td>
<td>153</td>
<td>151</td>
<td>[PLK00]</td>
<td>[RFM97]</td>
<td>[RHB99]</td>
</tr>
<tr>
<td>TO$_2$</td>
<td>167</td>
<td>214</td>
<td>177</td>
<td>168</td>
<td>[RFM97]</td>
<td>[RHB99]</td>
<td></td>
</tr>
<tr>
<td>TO$_3$</td>
<td>236</td>
<td>269</td>
<td>238</td>
<td>237</td>
<td>[RHB99]</td>
<td>[RHB99]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>264</td>
<td>265</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO$_4$</td>
<td>307</td>
<td>349</td>
<td>322</td>
<td>319</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO$_5$</td>
<td>334</td>
<td>419</td>
<td></td>
<td>334</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO$_6$</td>
<td>352</td>
<td>423</td>
<td>370</td>
<td>371</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO$_7$</td>
<td>432</td>
<td>446</td>
<td>432</td>
<td>431</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO$_8$</td>
<td>526</td>
<td>605</td>
<td>580</td>
<td>532</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TO$_9$</td>
<td>617</td>
<td>690</td>
<td>610</td>
<td>617</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

the total energy hypersurface along the direction of the corresponding displacement pattern. The isotope shift is largest for the TO$_6$ mode (by 19 cm$^{-1}$ as calculated, compared to 17 cm$^{-1}$ in the experiment) and also noticeable in the calculation for the TO$_7$ mode, that was however not detected in Ref. [RHB99]. As for the remaining two modes in the intermediate frequency region, we assign our TO$_4$ to the 325 cm$^{-1}$ mode of Ref. [RHB99] on the basis that it exhibits a strong isotope shift. The TO$_5$ mode with the calculated frequency close to 344 cm$^{-1}$ was not explicitly listed among the $E$(TO) frequencies in Ref. [RFM97] nor in Ref. [RHB99], although the corresponding feature may be found in the spectra shown in Fig. 2 of Ref. [RFM97] and Fig. 3 of Ref. [RHB99], in the latter case – indeed unaffected by the isotope shift. The line observed at 264 cm$^{-1}$ and missing in our calculation may be a signature of a quite intense $A_1$-TO$_2$ mode of close frequency. We assume that this transition, forbidden in the $X(ZY)Z$ geometry, may become observable due to anharmonicity, or to the presence of defects. It is noteworthy that Claus et al. [CBWS72] who measured the Raman scattering for the angle $\Theta$ between the optical axis of the crystal and the phonon wave vector varying from 0 to $\pi/2$ found that the $E$(TO) line at 265 cm$^{-1}$ for $\Theta = 0$ transforms smoothly into the $A_1$(TO) line at 255 cm$^{-1}$ for $\Theta = \pi/2$. This is the only mode in LiNbO$_3$ which undergoes a transformation from $E$(TO) to the $A_1$(TO) character.
### 6.5 $E$ modes

Table 6.8: Calculated eigenvectors of nine $E$ modes in LiNbO$_3$

<table>
<thead>
<tr>
<th>Mode</th>
<th>Nb1</th>
<th>Nb2</th>
<th>Li1</th>
<th>Li2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
<th>O5</th>
<th>O6</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO$_1$</td>
<td>(x)</td>
<td>-0.20</td>
<td>0.49</td>
<td>-0.00</td>
<td>0.03</td>
<td>-0.00</td>
<td>-0.29</td>
<td>-0.13</td>
<td>-0.08</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>-0.44</td>
<td>-0.05</td>
<td>-0.03</td>
<td>-0.01</td>
<td>0.28</td>
<td>0.26</td>
<td>0.03</td>
<td>0.38</td>
<td>0.14</td>
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<tr>
<td></td>
<td>(z)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.09</td>
<td>0.01</td>
<td>0.09</td>
<td>0.01</td>
<td>-0.09</td>
</tr>
<tr>
<td>TO$_2$</td>
<td>(x)</td>
<td>-0.07</td>
<td>0.17</td>
<td>0.00</td>
<td>0.11</td>
<td>-0.19</td>
<td>0.23</td>
<td>-0.02</td>
<td>-0.14</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>-0.16</td>
<td>-0.02</td>
<td>-0.12</td>
<td>-0.06</td>
<td>-0.01</td>
<td>0.03</td>
<td>0.37</td>
<td>-0.18</td>
<td>0.16</td>
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<td>(z)</td>
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<td>0</td>
<td>0</td>
<td>0.34</td>
<td>-0.34</td>
<td>+0.00</td>
<td>-0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>TO$_3$</td>
<td>(x)</td>
<td>0.18</td>
<td>-0.03</td>
<td>0.28</td>
<td>-0.54</td>
<td>0.04</td>
<td>-0.01</td>
<td>0.16</td>
<td>-0.03</td>
<td>-0.21</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>-0.07</td>
<td>-0.19</td>
<td>0.46</td>
<td>-0.02</td>
<td>0.21</td>
<td>0.04</td>
<td>0.08</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>-0.12</td>
<td>-0.12</td>
<td>0.25</td>
<td>-0.12</td>
</tr>
<tr>
<td>TO$_4$</td>
<td>(x)</td>
<td>0.46</td>
<td>-0.29</td>
<td>0.01</td>
<td>0.03</td>
<td>0.14</td>
<td>0.11</td>
<td>-0.17</td>
<td>-0.37</td>
<td>-0.09</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0.07</td>
<td>-0.36</td>
<td>-0.04</td>
<td>-0.03</td>
<td>0.02</td>
<td>0.36</td>
<td>0.17</td>
<td>0.08</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.21</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>-0.21</td>
</tr>
<tr>
<td>TO$_5$</td>
<td>(x)</td>
<td>0.11</td>
<td>-0.18</td>
<td>0.36</td>
<td>0.23</td>
<td>-0.05</td>
<td>-0.17</td>
<td>0.03</td>
<td>0.08</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0.14</td>
<td>-0.03</td>
<td>-0.48</td>
<td>-0.55</td>
<td>0.17</td>
<td>0.01</td>
<td>-0.02</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
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<td>0</td>
<td>0</td>
<td>0.17</td>
<td>-0.12</td>
<td>-0.06</td>
<td>-0.12</td>
<td>0.17</td>
</tr>
<tr>
<td>TO$_6$</td>
<td>(x)</td>
<td>-0.28</td>
<td>0.16</td>
<td>0.47</td>
<td>-0.28</td>
<td>0.05</td>
<td>0.23</td>
<td>-0.14</td>
<td>-0.18</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>-0.03</td>
<td>0.23</td>
<td>0.05</td>
<td>-0.38</td>
<td>-0.25</td>
<td>0.08</td>
<td>0.07</td>
<td>-0.16</td>
<td>-0.17</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.12</td>
<td>-0.05</td>
<td>0.17</td>
<td>-0.05</td>
<td>-0.12</td>
</tr>
<tr>
<td>TO$_7$</td>
<td>(x)</td>
<td>-0.14</td>
<td>0.11</td>
<td>-0.19</td>
<td>0.24</td>
<td>0.26</td>
<td>0.30</td>
<td>0.27</td>
<td>-0.27</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>-0.04</td>
<td>0.10</td>
<td>-0.16</td>
<td>0.08</td>
<td>0.12</td>
<td>0.13</td>
<td>0.17</td>
<td>-0.20</td>
<td>-0.16</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.14</td>
<td>-0.29</td>
<td>0.15</td>
<td>-0.29</td>
<td>0.14</td>
</tr>
<tr>
<td>TO$_8$</td>
<td>(x)</td>
<td>0.13</td>
<td>-0.01</td>
<td>0.01</td>
<td>-0.01</td>
<td>-0.41</td>
<td>0.01</td>
<td>0.09</td>
<td>0.20</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>-0.06</td>
<td>-0.14</td>
<td>0.01</td>
<td>-0.00</td>
<td>0.09</td>
<td>-0.24</td>
<td>0.29</td>
<td>-0.13</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.17</td>
<td>-0.15</td>
<td>0.32</td>
<td>-0.15</td>
<td>-0.17</td>
</tr>
</tbody>
</table>
A different assignment, namely that our TO$_4$ line corresponds to the measured 264 cm$^{-1}$ and the TO$_5$ line to that at 322 cm$^{-1}$, seems unsatisfactory because in both cases the calculated harmonic frequencies are then much larger than in the experiment which is difficult be to explained. Moreover – and more important – the observed isotope shift of the 322 cm$^{-1}$ line contradicts to the near absence of Li contribution in the calculated TO$_5$ line.
Chapter 7

Ab initio zone-center lattice dynamics in LiTaO$_3$

7.1 Method

Since the total-energy calculations presented in this Chapter were also performed within density functional formalism using the full-potential LAPW+LO method [Sin91, BSL97] similar to that described in the previous Chapter for LiNbO$_3$, in the following I am going to present only a short description of the computational setup used in our calculations.

In all our frozen-phonon computations the exchange-correlations were treated within the local density approximation (LDA) as parametrized by Perdew and Wang [PW92]. The Brillouin zone was sampled by a 4$\times$4$\times$4 special $k$-points mesh and the integrals over it were evaluated using the improved tetrahedron method [BJA94]. As depicted in Fig 7.1 when using a denser 6$\times$6$\times$6 mesh of $k$ points, we obtained an absolute total-energy difference of less than 1 mRy. The same result was found for the differences in the total-energy trends and this enabled us to perform all ab initio calculations using only 13 $k$-points in the irreducible wedge of the Brillouin zone.

A comparison of the accuracy of the total energies calculated with two different values of the cutoff parameter - 9.0 and 9.5, respectively - is presented in Fig 7.2. These values of the $R_{\text{min}}K_{\text{max}}$ parameter, together with non-overlapping muffin-
Figure 7.1: Total energy differences (with respect to $E_{\text{tot}} = -63396 \text{ Ry}$) obtained for $R_{\text{min}} K_{\text{max}} = 7$ and $G_{\text{max}} = 10$ for two different sets of $k$-points.

Figure 7.2: Total energy differences (with respect to $E_{\text{tot}} = -63396 \text{ Ry}$) obtained for two different LAPW basis sets (see text).
7.2 A₁ modes

The lattice dynamics of LiTaO₃ at Γ was studied by solving the dynamical equation of motion in the four-dimensional space spanned by the A₁ symmetry coordinates S₁...S₄ generated from the atomic positions as described in Appendix A. The reliable polynomial total-energy fit \( E_{\text{tot}}(S_1, S_2, S_3, S_4) \) was obtained from the total energies calculated for 170 different structures compatible with the A₁ mode symmetry. The equilibrium structure which minimizes the total amount energy data was obtained from the same fit, and the resulting positions are listed in Table 7.1, whereas the corresponding coordinates in hexagonal setting are presented in Table 7.2. One can observe a very good agreement between the experimental and theoretical values of the atomic coordinates, and this represents a supplementary proof of the reliability of the setup used in our \textit{ab initio} calculations.

Table 7.1: Numbering of atoms in the primitive cell and their Cartesian coordinates in LiTaO₃

<table>
<thead>
<tr>
<th></th>
<th>Ta1</th>
<th>Ta2</th>
<th>Li1</th>
<th>Li2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
<th>O5</th>
<th>O6</th>
</tr>
</thead>
<tbody>
<tr>
<td>x/a</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.280</td>
<td>0.034</td>
<td>0.246</td>
<td>0.297</td>
<td>-0.043</td>
<td>-0.254</td>
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<tr>
<td>y/a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.122</td>
<td>0.306</td>
<td>-0.181</td>
<td>0.122</td>
<td>-0.319</td>
<td>0.196</td>
</tr>
<tr>
<td>z/c</td>
<td>0</td>
<td>1/2</td>
<td>0.282</td>
<td>0.782</td>
<td>0.405</td>
<td>0.405</td>
<td>0.405</td>
<td>0.572</td>
<td>0.572</td>
<td>0.572</td>
</tr>
</tbody>
</table>
Table 7.2: The experimental and theoretical atomic positions in hexagonal coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>Ta</th>
<th>Li</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.279c</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.050c</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.282c</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.344c</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.049c</td>
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<td>0</td>
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<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>0.071c</td>
</tr>
</tbody>
</table>

cExperimental: Ref. [ABHL73]; cCalculation.

In the same way as for LiNbO₃, we checked the quality of our total-energy fit by plotting our data in the four-dimensional space of the A₁ symmetry coordinates along the normal coordinates given by

$$
\begin{align*}
S_{TO_1} & = \begin{pmatrix} 0.303 & 0.894 & 0.319 & -0.084 \end{pmatrix} \\
S_{TO_2} & = \begin{pmatrix} 0.445 & -0.833 & 0.156 & 0.295 \end{pmatrix} \\
S_{TO_3} & = \begin{pmatrix} 0.003 & 0.176 & -0.215 & 0.961 \end{pmatrix} \\
S_{TO_4} & = \begin{pmatrix} 0.102 & 0.159 & -0.954 & -0.236 \end{pmatrix}
\end{align*}
$$

(7.1)

As presented in Fig. 7.3, the cut of the total-energy hypersurface along the normal coordinates corresponding to all A₁-TO modes clearly shows that these modes are harmonic, the closest data points to these directions in the four-dimension space being more appropriately fitted by a second-order polynomial than by a fourth-order one. From this observation, one can infer that for these modes the deviation form the harmonic behaviour should be negligible.

The same conclusion is obtained from the comparison of the calculated A₁ frequencies with the experimental Raman data shown in Table 7.3. The selected experimental data are actually in good agreement with the earlier results published by Kaminow and Johnston [KJ67]. The infrared spectroscopy data obtained by Barker et al. suggested a frequency of 241 cm⁻¹ for the TO₂ mode, but their fit of the measured reflectivity with classical oscillators required the use of six A₁ modes instead of four. This apparent breaking down of the group theory predictions was explained by Penna et al. assuming a lowering of the unit cell symmetry from C₃ᵥ to C₃ due to a distortion of the oxygen octahedra. However, this assumption is not supported
Figure 7.3: The cut of the total energy fit along the directions of normal displace-
mments in the 4-dimensional space of symmetry coordinates corresponding to the $A_1$ 
symmetry of LiTaO$_3$. The meaning of the used symbols is the same as in Fig. 6.5
Table 7.3: Calculated and measured frequencies (cm$^{-1}$) of four $A_1$-TO modes in LiTaO$_3$

<table>
<thead>
<tr>
<th></th>
<th>cal. LiTaO$_3$</th>
<th>exp. LiTaO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO$_1$</td>
<td>194</td>
<td>206</td>
</tr>
<tr>
<td>TO$_2$</td>
<td>242</td>
<td>253</td>
</tr>
<tr>
<td>TO$_3$</td>
<td>360</td>
<td>356</td>
</tr>
<tr>
<td>TO$_4$</td>
<td>599</td>
<td>600</td>
</tr>
</tbody>
</table>

by neutron measurements performed by Abrahams et al. [ABHL73]. Moreover, no recent Raman measurement assigned nine phonons to $A_1$ modes as in their study.

The largest systematic difference of up to 11 cm$^{-1}$ between the calculated frequency and corresponding experimental values is found for TO$_1$ and TO$_2$ modes. This difference is small as compared to that for anharmonic modes in LiNbO$_3$ (46 cm$^{-1}$ for TO$_1$ and 50 cm$^{-1}$ for TO$_4$), that supports the above conclusion of essentially harmonic character of all $A_1$ vibrations in LiTaO$_3$. This is especially true for the TO$_3$ and TO$_4$ modes. As could be expected, the frequencies of all modes but TO$_3$ are lower in LiTaO$_3$ than in LiNbO$_3$. The hardening of the TO$_3$ mode on changing from niobate to tantalate is counter-intuitive and is analyzed in detail below.

The displacement of each atom in these vibrational modes can be determined from the calculated eigenvectors shown in Table 7.4, which are specified with respect to the equilibrium atomic positions listed in Table 7.1.

The displacement pattern in the TO$_1$ mode of LiTaO$_3$ resembles that in LiNbO$_3$ in the sense that Ta vibrates in antiphase with the oxygen sublattice along the polar axis. However, whereas the contribution of Li in this mode is almost negligible in LiNbO$_3$, it has a substantial participation in LiTaO$_3$.

As in LiNbO$_3$, the TO$_2$ mode is given by a $z$ vibration of Ta atoms in antiphase to Li, but in this case the oxygen cage exhibits also a significant movement along the trigonal axis.

Whereas the Li contribution is negligible in the harmonic TO$_3$ mode of LiNbO$_3$, it is significant in the similar mode of LiTaO$_3$. Moreover, this mode is dominated by oxygen sublattice displacements in the $x0y$ plane following the same pattern as in LiNbO$_3$. Therefore, in this mode the oxygen octahedra are also rigidly rotated
7.3 Comparison with LiNbO$_3$ data

Table 7.4: Calculated eigenvectors of four $A_1$ modes in LiTaO$_3$

<table>
<thead>
<tr>
<th>Mode</th>
<th>Ta1</th>
<th>Ta2</th>
<th>Li1</th>
<th>Li2</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
<th>O5</th>
<th>O6</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO1</td>
<td>$x$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.11</td>
<td>-0.03</td>
<td>-0.08</td>
<td>0.11</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>-0.11</td>
<td>0.08</td>
<td>-0.03</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>0.16</td>
<td>0.16</td>
<td>0.45</td>
<td>0.45</td>
<td>-0.28</td>
<td>-0.28</td>
<td>-0.28</td>
<td>-0.28</td>
<td>-0.28</td>
</tr>
<tr>
<td>TO2</td>
<td>$x$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.03</td>
<td>-0.07</td>
<td>0.04</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.07</td>
<td>0.00</td>
<td>0.07</td>
<td>-0.06</td>
<td>-0.00</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>0.29</td>
<td>0.29</td>
<td>-0.51</td>
<td>-0.51</td>
<td>-0.21</td>
<td>-0.21</td>
<td>-0.21</td>
<td>-0.21</td>
<td>-0.21</td>
</tr>
<tr>
<td>TO3</td>
<td>$x$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.09</td>
<td>-0.29</td>
<td>0.38</td>
<td>-0.09</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.39</td>
<td>0.27</td>
<td>0.12</td>
<td>0.39</td>
<td>-0.12</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>-0.02</td>
<td>-0.02</td>
<td>0.14</td>
<td>0.14</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-0.01</td>
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</tr>
<tr>
<td>TO4</td>
<td>$x$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.38</td>
<td>0.27</td>
<td>0.10</td>
<td>-0.38</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.09</td>
<td>0.28</td>
<td>-0.37</td>
<td>-0.09</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.06</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.10</td>
</tr>
</tbody>
</table>

along the trigonal axis as we previously found for LiNbO$_3$.

The displacement pattern in TO$_4$ mode is almost the same in both LiTaO$_3$ and LiNbO$_3$. However, in LiTaO$_3$ the stretching of the oxygen octahedra specific to this mode is accompanied by a larger displacement of the oxygen sublattice along the trigonal axis than in LiNbO$_3$. In consequence, this mode exhibits an harmonic behaviour in LiTaO$_3$ while it is largely anharmonic in LiNbO$_3$.

7.3 Comparison with LiNbO$_3$ data

Since $A_1$-TO$_3$ mode in LiNbO$_3$ and LiTaO$_3$ is largely harmonic, one can infer from the corresponding atomic displacement patterns that a substantial contribution of Li movement in TO$_3$ mode of LiTaO$_3$ is responsible for the experimentally observed shift of the Raman frequencies in these compounds. In order to elucidate the electronic origin of the different behaviour of Li ions in this mode, we investigated the energy profiles associated with $A_1$-TO$_3$ displacement patterns in both compounds.

As depicted in Fig. 7.4, the potential energy wall related to $A_1$-TO$_3$ atomic vibrations in LiTaO$_3$ has higher curvature than that obtained for LiNbO$_3$. Since a
7.3 Comparison with LiNbO$_3$ data

![Graph showing energy (mRy) vs. normal coordinate (a.u.).]

Figure 7.4: Total energy profiles of $A_1$-TO$_3$ mode in LiNbO$_3$ (LNO) and LiTaO$_3$ (LTO)

higher curvature of the potential energy profile results in a higher frequency of the harmonic vibrational mode, this result shows that indeed the calculated eigenvectors corresponding to this mode in both materials are appropriately determined in the harmonic approximation.

As was previously stressed by Inbar and Cohen [IC96], the electronic structures of LiNbO$_3$ and LiTaO$_3$ are very similar. This conclusion emerges also from Fig. 7.5, in which the charge density is plotted in a crystalline plane containing the optical axis $e$ and the oxygen atoms labeled by the number 1 in Table 6.1 and Table 7.1. These charge density plots were obtained for the $A_1$-TO$_3$ normal coordinate (see Eq. (7.1)) set to the value of 0.061 a.u.

One can observe that in both cases there is only a weak covalency between Li atoms and O ones, which lead to a pronounced ionic character of Li ions in these compounds. On the contrary, Nb and Ta atoms exhibit a significant covalent bonding with the surrounding oxygen atoms. A supplementary proof of the ionic behaviour of Li ions comes from the analysis of the density of states of LiNbO$_3$.
Figure 7.5: Charge density contours plot for LiNbO$_3$ (left) and LiTaO$_3$ (right). These density maps were plotted in the crystalline plane determined by the trigonal axis $C_3$ and the oxygen atom O1 (see Table 6.1 and Table 7.1). The interval between iso-density curves in the maps corresponds to 0.11 $e$/a.u.$^3$. 
7.3 Comparison with LiNbO$_3$ data

illustrated in Fig. 7.6 and Fig. 7.7. These figures indicate that there is a very small hybridization between the Li states and whose of the surrounding atoms. Actually, Li is fully stripped of its valence electron and bounds to its neighbours purely ionically. The same holds for LiTaO$_3$ (see Figs. 7.8 and 7.9).

This qualitative picture of the ionic versus covalent character of the chemical bonding of these atoms can be refined by means of the effective atomic charges analysis, which values can be obtained from the electronic charge distribution presented in Table 7.5. Before proceeding with the physical interpretation of the above

<table>
<thead>
<tr>
<th></th>
<th>LiNbO$_3$</th>
<th></th>
<th>Li</th>
<th>O</th>
<th>Interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_{MT}$(a.u.)</td>
<td>1.90</td>
<td>1.60</td>
<td>1.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge</td>
<td>36.875</td>
<td>2.085</td>
<td>7.211</td>
<td>14.810</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>LiTaO$_3$</th>
<th></th>
<th>Li</th>
<th>O</th>
<th>Interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_{MT}$(a.u.)</td>
<td>1.88</td>
<td>1.65</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge</td>
<td>68.557</td>
<td>2.098</td>
<td>7.374</td>
<td>14.447</td>
<td></td>
</tr>
</tbody>
</table>

numerical values, one should mention that in the FP-LAPW method the electron charge located inside the MT spheres does of course depend on the sphere radii, while the interstitial charge distribution cannot be clearly split into contributions from individual atoms.

Let us define the (static) effective atomic charges of a given atom in a solid as the difference between its neutral electronic configuration (described by the atomic number Z) and the calculated charge inside the corresponding MT sphere. Using this definition, the ionic character of Li ions in these materials is evidenced by the value of their effective charge: +0.92 in LiNbO$_3$ and +0.90 in LiTaO$_3$. The covalent bonding between the transition metal ions and the oxygen ones determines an effective charge of +4.12 for Nb ions and of +4.44 for the Ta ones. However, the calculated effective charge for O ions has the value of +0.79 in LiNbO$_3$ and of +0.63 in LiTaO$_3$, and differs significantly from the ideal value of −2, as expected in a pure ionic picture. The origin of this difference can be related to the large amount of interstitial electronic charge. Since from the charge density plots as well
7.3 Comparison with LiNbO₃ data

![Graph showing DOS of Nb and Li atoms in LiNbO₃](image1)

Figure 7.6: Total density of states of Nb and Li atoms in LiNbO₃

![Graph showing DOS of O and Li atoms in LiNbO₃](image2)

Figure 7.7: Total density of states of O and Li atoms in LiNbO₃
7.3 Comparison with LiNbO$_3$ data

Figure 7.8: Total density of states of Ta and Li atoms in LiTaO$_3$

Figure 7.9: Total density of states of O and Li atoms in LiTaO$_3$
as from the density of states we concluded that Li atoms are mainly ionized, one can consider that the interstitial charge is shared only by Nb(Ta) and O ions. Assuming the (admittedly ill-defined) case in which the whole amount of interstitial electronic charge is attributed to oxygen atoms, one obtains the value of \(-1.68\) in LiNbO\(_3\) and of \(-1.78\) in LiTaO\(_3\) for the effective charge of the oxygen ions.

Despite of the above mentioned limits of the effective charge concept when used in the FP-LAPW method, it can be used to sketch a qualitatively model of our problem. Since Li atoms are essentially ionized in both compounds, it seems that the presence of Li displacements in the \(A_1\)-TO\(_3\) mode in LiTaO\(_3\) (absent in the similar mode in LiNbO\(_3\)) is due to the delicate interplay between the ionicity of the atoms that participate in this mode and the distances that separate them (listed in Table 7.6). In LiNbO\(_3\) as well as in LiTaO\(_3\) the effect of the Coulomb electric field at the Li site is to induce off-center displacements of these ions towards the Nb ones from the second shell. This tendency is compensated by the repulsive Coulomb

Table 7.6: Distances between Li ions and the surrounding atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>LiNbO(_3)</th>
<th>LiTaO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shell No.</td>
<td>Distance (a.u.)</td>
</tr>
<tr>
<td>Nb(Ta)</td>
<td>1</td>
<td>5.595</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.159</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>3.799</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.276</td>
</tr>
</tbody>
</table>
7.4 A two coupled oscillators model

A qualitative understanding of the absence of different Li contribution in the $A_1$ modes of LiNbO$_3$ and LiTaO$_3$, can be gained considering a model of two coupled
harmonic oscillators described by the following Lagrangian:

$$L = \sum_{i=1}^{2} m_i \dot{z}_i^2 - \frac{k_1 z_1^2}{2} - \frac{k_2 z_2^2}{2} - \frac{k(z_1 - z_2)^2}{2}$$ \hspace{1cm} (7.2)$$

where $k_1$ and $k_2$ are the stiffnesses of the uncoupled harmonic motions, while $k$ describes the coupling between the harmonic oscillators. The values of the masses $m_i$ depend on the modes in question.

In this case, the Euler-Lagrange equation (5.2) leads to a second-order system of two coupled equations

$$\begin{cases}
m_1 \ddot{z}_1 + (k_1 + k) z_1 - k z_2 = 0 \\
m_2 \ddot{z}_1 + (k_2 + k) z_2 - k z_1 = 0
\end{cases}$$ \hspace{1cm} (7.3)$$

Making use of the following matrices

$$Z = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}, \quad A = \begin{pmatrix} \frac{k_1 + k}{m_1} & \frac{-k}{m_1} \\ \frac{-k}{m_2} & \frac{k_2 + k}{m_2} \end{pmatrix}$$ \hspace{1cm} (7.4)$$

its expression can be written as

$$\frac{d^2}{dt^2} Z + AZ = 0$$ \hspace{1cm} (7.5)$$

which exhibits a striking resemblance to the simple harmonic equation of motion.

In consequence, in the same way as described in Chapter 4, the harmonic solution of Eq. (7.5) can be obtained by solving the secular equation of the system

$$\begin{vmatrix} \frac{k_1 + k}{m_1} - \omega^2 & \frac{-k}{m_1} \\ \frac{-k}{m_2} & \frac{k_2 + k}{m_2} - \omega^2 \end{vmatrix} = 0$$ \hspace{1cm} (7.6)$$

The calculated eigenfrequencies show that, for a given set of elastic constants $k_1, k_2$
and \( k \), the effect of the coupling between two harmonic oscillations is to mix the angular frequencies \( \omega_1^0 = k_1/m_1 \) and \( \omega_2^0 = k_2/m_2 \) of the uncoupled motions.

The elastic constants \( k_1 \) and \( k_2 \) of the uncoupled harmonic oscillations can be easily computed from the shape of the potential felt by the atoms that undergo pure (uncoupled) displacements. The corresponding data are given in Table 7.7. Since we also know the theoretical values of the angular frequencies \( \omega \) in both \( \text{LiNbO}_3 \) and \( \text{LiTaO}_3 \), we attempt to explain the different Li contribution in \( A_1 \) modes of these materials by means of a different value of the coupling elastic constant \( k \).

In our model, we assume that in the case of \( \text{LiNbO}_3 \) there is an initial coupling the Nb vibrations (with respect to a fixed oxygen cage) with oxygen \( O_{xy} \) displacements in the \( x0y \)-plane, because their frequencies are the closest. As a result of this coupling, the frequencies are shifted upwards and apart to higher frequencies. The highest frequency corresponds to the calculated \( \text{TO}_3 \) phonon, in which there is no Li contribution. A further coupling between the remaining frequency with the Li vibrations leads to the final picture of three \( A_1 \) modes with a substantial Li contribution only in \( \text{TO}_2 \) mode.

Unlike \( \text{LiNbO}_3 \), in the case of \( \text{LiTaO}_3 \) the initial coupling is realized between the Li and \( O_{xy} \) vibrations, now closest in their frequencies due to the softness of the "pure Ta" mode (see Table 7.7). In consequence, both resulting split modes will contain the Li vibrations. Due to the coupling of one of the split frequencies with Ta displacements (with respect to a fixed oxygen octahedra), the resulting picture is that of the presence of Li movements in all three \( A_1 \) modes.

Table 7.7: The angular frequencies for the uncoupled harmonic oscillators.

<table>
<thead>
<tr>
<th>Vibrations</th>
<th>( \text{LiNbO}_3 ) ( \omega_0 ) (cm(^{-1}))</th>
<th>( \text{LiNbO}<em>3 ) ( O</em>{xy} )</th>
<th>( \text{LiTaO}_3 ) ( \omega_0 ) (cm(^{-1}))</th>
<th>( \text{LiTaO}<em>3 ) ( O</em>{xy} )</th>
<th>( \text{LiTaO}_3 ) ( \omega_0 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>89.82</td>
<td>91.02</td>
<td>60.46</td>
<td>93.53</td>
<td>117.65</td>
</tr>
<tr>
<td>Li</td>
<td>130.42</td>
<td>95.99</td>
<td>13.88</td>
<td>95.99</td>
<td>13.88</td>
</tr>
<tr>
<td>( m_{\text{eff}} ) (a.m.u.)</td>
<td>185.81</td>
<td>95.99</td>
<td>361.89</td>
<td>95.99</td>
<td>13.88</td>
</tr>
</tbody>
</table>

On the background of these physical considerations, we solved the secular equation Eq. (7.6) in terms of the coupling constant \( k \) using the "true" \( A_1 \) mode phonon frequencies previously calculated. In the following, for \( \text{LiNbO}_3 \) \( k_{12} \) describes the coupling between Nb and \( O_{xy} \) vibrations and \( k_{23} \) is associated with the coupling between one of the split frequency with Li oscillations. In the case of \( \text{LiTaO}_3 \), the primary
coupling is between \( O_{xy} \) and Li vibrations and is characterized by the interaction constant \( k_{12} \); the secondary coupling between the lowest of two split frequencies and the Ta vibrations described by \( k_{23} \). The calculated values of these elastic constants are presented in Table 7.8.

Table 7.8: The coupling elastic constant \( k_{\text{coupl}} \). The unit used is Ry/(a.u.)²

<table>
<thead>
<tr>
<th>Coupling elastic constant</th>
<th>LiNbO₃</th>
<th>LiTaO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{12} )</td>
<td>5.73</td>
<td>5.91</td>
</tr>
<tr>
<td>( k_{23} )</td>
<td>4.31</td>
<td>3.41</td>
</tr>
</tbody>
</table>

To summarize the results presented in this section, the frozen-phonon calculations performed for \( A_1 \) modes in LiTaO₃ showed a substantial contribution of Li vibrations in three of these modes while in LiNbO₃ they are present only in TO₃. The difference can be assigned in the framework of a two coupled harmonic oscillators described above to a different coupling of the Li, \( O_{xy} \), and Nb(Ta) vibrations in these compounds described by different elastic coupling constants (see Table 7.8).
Chapter 8

Transition metal impurities in LiNbO$_3$

Introduction

As was stressed in a previous Chapter, some of the physical properties of undoped lithium niobate, as its lattice dynamics revealed by Raman spectroscopy experiments, are highly sensitive to the presence of intrinsic defects. The same conclusion applies to its optical properties, for instance the refractive index depends strongly on the stoichiometry of this compound, as was shown in Ref. [SB93]. This dependence could seriously restrict the technological applications of LiNbO$_3$ and in consequence, a defect-free material is desirable for industrial purposes. With such a (nearly) stoichiometric single crystal, it was shown in [BK97] how undoped lithium niobate can be used to improve the performances of the nonvolatile holographic storage devices, or in [BRO+00] how a two-dimensional nonlinear photonic crystal with potential applications in optics can be constructed.

However, the potential applications area of LiNbO$_3$ can be considerably enlarged by doping it intentionally with various impurity ions as K [XY+97], Mg [MBP00, XH00], Cu [PHB00], Cr [LBF+98, MGK99]. In this way, one can obtain efficient waveguide devices based on LiNbO$_3$:Mg:Tl [CZ+98], high-density holographic optical memories based on single LiNbO$_3$:Td:Fe crystals [LTFC00] or on multidomain LiNbO$_3$:Y:Fe crystals [OTS+00]. A review of the influence of intrinsic
and extrinsic defects on the photorefractive properties of LiNbO$_3$ can be found in Ref. [KS88].

### 8.1 Intrinsic and extrinsic defects in LiNbO$_3$

The intrinsic defects are always present in congruent LiNbO$_3$ crystals, characterized by a stoichiometry parameter $x_c (x = [\text{Li}] / ([\text{Li}]+[\text{Nb}]))$ less than 50% even when these crystals are grown from a stoichiometric melt $x_{\text{melt}} = 50\%$. The common lattice defects encountered in these Li-poor crystals are the following [MGS99]: lithium vacancy $v_{\text{Li}}^+$, lithium on structural vacancy $\text{Li}^+_v$, antisite defect $\text{Nb}_{\text{Li}}^{5+}$, niobium vacancy $v_{\text{Nb}}^{5+}$, niobium on structural vacancy $\text{Nb}_v^{5+}$, oxygen vacancy $\text{O}_v^{2-}$ and interstitial oxygen $O_i$. These intrinsic defects are grouped in complexes which fulfill the charge compensation requirement: $\text{Nb}_{\text{Li}}^{5+} + 4v_{\text{Li}}$, $5\text{Nb}_v^{5+} + 4v_{\text{Nb}}$, $2\text{Nb}_{\text{Li}}^{5+} + 2\text{Nb}_v^{5+} + 3v_{\text{Li}} + 3v_{\text{Nb}}$, or the site sequence (along the c-axis) Li Nb v Nb Li v Li Nb v instead of Li Nb v Li Nb v Li Nb v, where v denotes the structural vacancy (see, e.g., Ref. [MGS99] and references therein). If these defects are disposed along the polar axis c, then their site symmetry is $C_3$, otherwise it has the lowest symmetry $C_1$. This difference in defect site symmetry can be experimentally evidenced by means of electron spin resonance (ESR). Note that, however, the angular dependence of the ESR signal for a defect with the $C_3$ site symmetry will be described by the same symmetry if no other defect is present in its nearest neighborhood. For instance, as exposed in detail in Ref. [KS88], the photorefractive properties of undoped LiNbO$_3$ are influenced by two intrinsic defects, namely a hole trapped at $O^{2-}$ subject to a low symmetry crystal field due to a nearby Li vacancy and an electron self-trapped as a small polaron at a Nb site giving rise to the Nb$^{4+}$ center in a nearly axially symmetric crystal field.

It is important to note that the crystal imperfection determined by the above mentioned presence of various intrinsic defects in congruent LiNbO$_3$ crystals can not be properly described by the crystal composition $x_c$ because of the possible presence of stoichiometric defects (for instance, Li$_{\text{Nb}}$ + Nb$_{\text{Li}}$) which do not alter the crystal stoichiometry. A quantitative description of the influence of these intrinsic defects on the physical properties of LiNbO$_3$ can be, however, accomplished by using the parameter $\zeta$, introduced in Ref. [MGS99]. This parameter is proportional to the relative concentration of all intrinsic defects in this material and was set to zero.
for the perfectly ordered LiNbO$_3$ crystal. In this way, the results obtained for different congruent and nearly stoichiometric LiNbO$_3$ crystals could be quantitatively associated with different degrees of crystal imperfection of the used samples.

The intrinsic defects present in LiNbO$_3$ play an essential role in restoring the charge neutrality with respect to the crystalline lattice when it is doped with different impurity ions. If the impurities which enter the crystalline matrix do not form self-compensated complexes, the charge neutrality of the lattice is realized by means of a local or distant charge compensators given by a single intrinsic defect or complexes of them, which are not charged compensated. A detailed description of the trivalent ion centers in LiNbO$_3$ including their symmetry and possible charge compensation mechanism was done by Malovichko et al. [MGKS99]. By means of ESR, optical absorption and luminescence studies performed on congruent, nearly stoichiometric and stoichiometric LiNbO$_3$ crystals for different chromium concentrations, they identified a strong interrelation between the intrinsic and extrinsic defect subsystems which can determine a different quantitative and even qualitative behaviour of the studied properties. For instance, their ESR spectra obtained for stoichiometric compounds revealed the absence of some ESR lines present in congruent samples and appearance of new chromium centers. Moreover, the reduction of the concentration of intrinsic defects result also in a significant narrowing of ESR lines, a decrease of the asymmetry of these lines as well as a vanishing relative intensities of forbidden transitions.

The features of ESR spectra recorded in Ref. [MGKS99] for stoichiometric LiNbO$_3$ crystals doped with a small concentrations $x_{Cr}$ of Cr$^{3+}$ ions (from 0.02 to 0.1 wt.%) as well as a high chromium concentration ($x_{Cr}$=1 wt.%) could be explained assuming that these impurity ions occupy the Li sites, an assumption consistent with luminescence results obtained by Lhommedé et al. [LFB+98]. Also, the recent high-pressure spectroscopic studies of near-stoichiometric LiNbO$_3$ doped with 0.1% Cr performed by Kamińska et al. [KSA+00] pointed to the same conclusion. The charge compensation mechanism in this case consists in two Cr$^{3+}_{Li}$ which are compensated by five niobium vacancies $v_{Nb^{5+}}$.

The dependence of electro-optical (EO) properties on the presence of both non-stoichiometric intrinsic defects and chromium impurities in pure and low Cr-doped ($x_{Cr}$=0.06 at.%) congruent and nearly stoichiometric LiNbO$_3$ crystals was analyzed by Chad et al. [CFA+98]. In agreement with the above mentioned ESR and
minescence results, they assumed that the behaviour of the EO properties in their samples is due to the substitution of Li ions by chromium, whereas the number of Nb antisite defects varies with the crystal composition.

Of course, this model of Cr ions occupying only Li positions could lead to wrong predictions if the concentration of impurity ions is relatively large. In such cases, the formation of Cr\textsuperscript{3+}-Cr\textsuperscript{3+} dimers could be possible, as evidenced in a series of studies\cite{JLKY90, SMMG91, JGSC93, CYYR93}. In particular, the pair of Cr ions at Li and Nb sites is charge compensated. However, one should note that the cited experimental evidences pointing to this conclusion were obtained for congruent crystals. Since the subsystem of intrinsic defects is essentially different for each particular congruent sample and the analyzed physical properties depend strongly on the presence of the intrinsic defects, the formation of such self-compensated dimer could be experimentally ill founded.

More recently, Grachev et al. \cite{GM00} interpreted the observed features of their experimental EPR data recorded for nonstoichiometric LiNbO\textsubscript{3} crystals doped with a high Cr concentration (x_Cr=1 wt.\%) as an evidence for a low-symmetry Cr\textsubscript{Li}\textsuperscript{3+} - Cr\textsubscript{Li}\textsuperscript{3+} pairs, which are charge-compensated by niobium vacancies. In addition, by means of EPR, ENDOR and optical-absorption studies performed on LiNbO\textsubscript{3} samples having very low concentration of intrinsic defects and also doped with the same high concentration of chromium impurities, they observed, besides the main Cr\textsubscript{Li}\textsuperscript{3+} center, the presence of another Cr\textsuperscript{3+} center substituting niobium. The existence of this new center is due to the fact that a small amount of intrinsic defects can serve as charge compensators only for a given number of Cr ions at Li sites which defines a threshold concentration x_Cr\textsuperscript{thresh}. If the chromium concentration x_Cr overcomes x_Cr\textsuperscript{thresh}, then the Cr ions are constrained to replace Nb ions in addition to Li.

In LiNbO\textsubscript{3} codoped with modifiers as Mg [KDS\textsuperscript{+99}, KSA\textsuperscript{+00}] and Zn [JGSC\textsuperscript{+93}, TTJ\textsuperscript{00}], the Cr\textsubscript{Nb}\textsuperscript{3+} center can appear at low concentration of Cr impurities. In this case, the Cr ions start to be located also at Nb sites if the concentration of the modifier ions is larger than a threshold value.

### 8.2 Fe impurity in LiNbO\textsubscript{3}

From experimental point of view, the iron impurities in LiNbO\textsubscript{3} were intensively studied due to their influence on photorefractive properties of the matrix as described
in Ref. [KS88]. The ESR studies performed for congruent samples revealed a main
axial Fe$^{3+}$ center at a Li site. Another centers of this impurity ion were identified
in congruent LiNbO$_3$ heavily doped with Mg or in stoichiometric samples after a
reduction treatment, as described in detail in Ref. [MGSF93].

From theoretical point of view, the physical properties of an impurity system
which can be investigated within the DFT formalism are ground-state properties
such as electric field gradients at impurity site as well as at its neighborhood envi-
ronment, magnetic moments at any lattice site etc. By comparing the total energies
obtained for different positions of the same impurity ions in the same (super)cell
one can also infer which impurity configuration is energetically favorable. Moreover,
even if the Kohn-Sham eigenstates do not have any physical meaning except for the
highest occupied KS orbital, starting from the identification of the impurity lev-
els one can construct models to predict its optical behaviour which is not properly
described by DFT.

These models can be developed if the impurity states of interest can be identified
with no ambiguity, i.e., if they are lying in the band gap of the ferroelectric material
under consideration. For instance, the study of the electronic structure of iron
impurity in KNbO$_3$ performed by Postnikov et al. [PPB98] showed a significant
hybridization of the Fe 3$d$ states with those of O and Nb and this, corroborated
with a small band gap in this material, preclude any analysis of its optical properties
within such approximate model.

In the case of LiNbO$_3$ doped with transition metals as Fe and Cr, its photore-
fractive behaviour is explained by the presence of the impurity energy levels in the
optical band gap for several charge states of these impurities. In consequence, the
main goal of the present study in what regards impurities was to identify the posi-
tion of their localized energy levels. If they were in the calculated optical band gap
of LiNbO$_3$, this finding would stimulate further investigations of the ground-state
properties of this material doped with transition metals.

The electronic structure of Fe isolated impurity in perfectly ordered LiNbO$_3$
crystal was calculated for a 40 atoms supercell in which one Nb atom was replaced
by an Fe one. This supercell was generated by [111], [1$ar{1}$1] and [11$ar{1}$] lattice vectors of
fully optimized unit cell of undoped LiNbO$_3$. The energy levels of this impurity were
determined from \textit{ab-initio} spin-polarized total energy calculations performed within
the framework of DFT with essentially the same setup as that used in frozen-phonon
8.2 Fe impurity in LiNbO$_3$

calculations. For Fe we have chosen the same muffin-tin radius as for the substituted Nb atom (1.9 a.u.); the Fe 3$s$ and 3$p$ states were treated as semi-core states. The Brillouin zone integrations were carried out within the improved tetrahedron method on a $3 \times 3 \times 3$ mesh of special $k$-points. Since the Brillouin zone corresponding to the supercell in question is spanned by smaller primitive vectors than for normal unit cell of LiNbO$_3$, the cutoff parameter equal to 7.0 resulted in this case, on the average, to 3934 basis functions.

As the reference data, we present in Fig. 8.1 the total density of states (DOS) obtained for the stoichiometric LiNbO$_3$. The calculated optical gap has the value of

![Graph showing DOS vs Energy](image)

Figure 8.1: Total density of states for undoped LiNbO$_3$

3.4 eV, slightly different from those of 3.1 eV reported by Inbar and Cohen [IC96]. The reason for this small difference could be the use of different values for lattice parameters, namely, Inbar and Cohen used in their band-structure calculations the experimental lattice parameters whereas we used the optimized ones. However, as usually in LDA-based calculations, the theoretical band gap underestimates the experimental one of 3.78 eV.

The total density of states resulting from these spin-polarized calculations is presented in Fig. 8.2 and the contribution of the partial density of states corresponding to Fe 3$d$ energy levels is shown in Fig. 8.3. As can be seen from the comparison
Figure 8.2: Total density of states (for both spin components) obtained for a 40-atoms supercell of LiNbO$_3$ with one Fe impurity at Nb site

Figure 8.3: 3$d$ partial density of states of the Fe impurity at Nb site
8.2 Fe impurity in LiNbO$_3$

of these data with the total density of states obtained for undoped LiNbO$_3$ (see Fig. 8.1), the impurity 3d states hybridizes with those of Nb and O over an energy range of 7 eV. More important for our study, several groups of these impurity states are localized in the optical band gap above the Fermi level. This theoretical finding agrees well with the optical absorption data which, besides the absorption bands assigned to intervalence electronic transitions, revealed the presence of absorption bands due to crystal field transitions (see Ref. [KS88] for more details).

The magnetic moment at Fe site determined from our spin-polarized calculations is equal to 2.32 $\mu_B$. As presented in Table 8.1, this value of the magnetic moment essentially originates from the 3d states of the impurity ion. Since the interstitial

Table 8.1: Partial atomic charges evaluated at Fe site when substituting Nb ions together with that of its neighboring ions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>Distance (a.u.)</th>
<th>Majority spin</th>
<th>Minority spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.077</td>
<td>3.061</td>
<td>3.780</td>
<td>0.013</td>
</tr>
<tr>
<td>O</td>
<td>3.598</td>
<td>0.795</td>
<td>1.813</td>
<td>0.006</td>
</tr>
<tr>
<td>O</td>
<td>3.897</td>
<td>0.794</td>
<td>1.761</td>
<td>0.006</td>
</tr>
<tr>
<td>Li</td>
<td>5.955</td>
<td>0.998</td>
<td>0.036</td>
<td>0.006</td>
</tr>
<tr>
<td>Li</td>
<td>5.764</td>
<td>0.999</td>
<td>0.037</td>
<td>0.006</td>
</tr>
</tbody>
</table>

contribution to the total magnetic moment of the unit cell is very small, only 0.20 $\mu_B$, one can conclude that it is mainly localized at Fe site. Also, from the partial atomic charges listed in Table 8.1 one can assign$^1$ the value of +2.45 for the effective charges of Fe ion. The difference from the expected value of +3 derives from the dependence of this quantity on the chosen MT radius of 1.9 a.u. and from the absence of any charge compensation mechanism for this impurity. Moreover, the Fe impurity is located at the Nb site, whereas the experimental results indicate that it more probably enters the Li sites. One should also note that in LiNbO$_3$ doped with Fe, the magnetic impurity can be found in two different valence states, +2 or +3, whose ratio depends on the reduction-like or oxidation-like thermal treatment of the doped crystal. For samples measured in "as growth" state, the experimental data indicate a concentration of 15% for Fe$^{2+}$ and of 85% for Fe$^{3+}$ [CDGP73, KDGB76, KKK$^+$77].

A better background for a comparison with the experimental data can be ob-

---

$^1$See the discussion of the limits of this concept presented in the previous Chapter
tained considering the more realistic case in which the Fe impurity replaces one Li atom situated at 3.79 Å from the origin. This situation was modeled by a 80-atoms supercell generated by [200], [020] and [002] lattice vectors of the unit cell. The computational setup used in our spin-polarized calculations for this supercell was essentially the same as that previously reported. The main difference resides in using the smearing technique for the Brillouin zone integrations with a Gaussian broadening of 0.01 Ry [FH83]. Moreover, the self-consistent total-energy calculations were carried out using only the $\Gamma$ point in the reciprocal space. The cutoff parameter $R_{\text{min}} K_{\text{max}}$ was set to 5.8 which generated 4583 basis functions.

As in the previous case, from the comparison of the total density of states presented in Fig. 8.4 with the partial density of states corresponding to the impurity 3$d$ levels shown in Fig. 8.5 one can observe that the Fe 3$d$ states are also localized in the optical band gap of the undoped LiNbO$_3$. In addition, these levels are more narrow than those of Fe at Nb site. This difference could be related to the use of a larger supercell which diminishes the interaction between the impurity ions.

The calculated magnetic moment at Fe site is equal to 3.06 $\mu_B$, slightly higher than that obtained when Fe substitutes for Nb. In Table 8.2 we present the partial charges obtained for the impurity at Li site and its neighboring ions. As in the

Table 8.2: Partial atomic charges evaluated at Fe site when substituting Li ions together with that of its neighboring ions.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>Distance (a.u.)</th>
<th>Majority spin</th>
<th>Minority spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$s$</td>
<td>$p$</td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>3.809</td>
<td>1.054</td>
<td>3.024</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>4.271</td>
<td>0.792</td>
<td>1.830</td>
</tr>
<tr>
<td>Nb</td>
<td>3</td>
<td>5.595</td>
<td>0.997</td>
<td>2.772</td>
</tr>
<tr>
<td>Nb</td>
<td>4</td>
<td>5.764</td>
<td>0.997</td>
<td>2.772</td>
</tr>
</tbody>
</table>

previous studied case, the listed values clearly indicate that the impurity magnetic moment is exclusively related to its 3$d$ states. Moreover, the partial atomic charges of its neighboring ions as well as the insignificant contribution of the interstitial charge of 0.07 $\mu_B$ to the total magnetic moment of the unit cell show that the spin-density is mainly localized at the impurity site. The corresponding effective charge of 2.24 suggests a nominal valence of +2 rather than +3 for this impurity. This difference could be assigned to the simplicity of model used in our calculations, in
8.2 Fe impurity in LiNbO₃

Figure 8.4: Total density of states or a 80-atoms supercell of LiNbO₃ with one Fe impurity at Li site

Figure 8.5: 3d partial density of states of the Fe impurity at Li site
which the Fe impurity is not charge compensated.

8.3 Cr impurity in LiNbO$_3$

The main achievement of the spin-polarized calculations reported in the previous section for an Fe impurity in 40-atoms and 80-atoms supercell free of any charge compensation mechanism, is the presence of impurity d states in the optical band gap. This result encourage us to proceed with the study of ground-state properties of Cr-doped LiNbO$_3$. To facilitate a meaningful comparison with experimental results, a charge compensation mechanism was built into the supercell used in our calculations.

To keep the computational effort feasible, we have chosen to study a self-compensated pair Cr$_{Li}^{3+}$-Cr$_{Nb}^{3+}$ in a 80-atoms supercell spanned also by [200],[020] and [002] (see Fig. 8.6). In this 80-atoms supercell, one Nb and Li atom along the polar axis, separated by a distance of 10.54 Å, were substituted by two Cr atoms. Since the distance that separates the impurity ions is rather large, the practical model used in the discussion of our spin-polarized calculations results will be that of an isolated and charge compensated Cr-impurity. Moreover, no intrinsic defects present were taken into account in our model.

The muffin-tin radii for the substituting Cr atoms are the same as those for the substituted Nb and Li atoms. The 3s and 3p states of chromium impurity were calculated using the local orbitals in the valence energy window. The integrations over the first Brillouin zone were performed on a 3×3×3 grid of k-points, using the smearing technique with a Gaussian broadening of 0.01 Ry. The cutoff parameter $R_{min}K_{max}$ was set to 5.8 which generated on the average 4455 basis functions for each k-vector. The Fourier expansion of the charge density and potential in the interstitial region was performed by choosing for the $G_{max}$ parameter the value of 9. Using this setup, we optimized the atomic positions of all 80 atoms of our supercell according to the calculated Hellmann-Feynman forces. This relaxation of the atoms around their equilibrium positions was performed in order to come as closer as possible to the experimental situation.

The 3d partial density of states obtained for Cr replacing Nb ions in the unrelaxed supercell structure is presented in Fig. 8.7. As in the case of Fe impurity, the 3d states of Cr ions are mainly localized in the optical band gap of the undoped LiNbO$_3$. The
Figure 8.6: The ferroelectric structure of 80-atoms supercell of LiNbO$_3$ with two Cr atoms substituting Nb and Li; only the closest atoms to the polar $C_3$ axis are shown. The (oxygen) atoms indicated as light are outside of the rhombohedral unit cell shown.
Figure 8.7: 3d partial density of states of the Cr impurity at Nb site (unrelaxed structure)

Figure 8.8: 3d partial density of states of the Cr impurity at Li site (unrelaxed structure)
8.3 Cr impurity in LiNbO₃

peculiar feature of these impurity states consists in a high density of levels near the Fermi level such that almost all electrons which populate the majority-spin 3d band are energetically very close to the Fermi energy. Also, the occupied and unoccupied levels of the majority-spin band are separated by a very small band gap of 0.08 eV.

The localized 3d states of this impurity give raise to a magnetic moment equal to 1.98 $\mu_B$, the contribution of other states to this values being negligible (see Table 8.3). The effective charge has the value of +2.63, close to the ideal value of +3 experimentally assigned to this impurity ion in LiNbO₃ (see, for example, Ref. [MGKS99] and references therein).

The 3d partial density of states calculated for Cr at Li site in the same unrelaxed supercell structure is shown in Fig. 8.8. In this case one can observe that the majority-spin 3d states are mainly localized at ~-1.3 eV below the Fermi level. Moreover, the minority-spin band is less populated with electrons (0.26) than that obtained for Cr ion at Nb site (0.64).

As presented in Table 8.4, the substitution of Li ions with a Cr impurity lead to

Table 8.3: Partial atomic charges (in the MT sphere) for Cr substituting Nb, along with its nearest neighboring ions (unrelaxed structure).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>Distance (a.u.)</th>
<th>Distance (a.u.)</th>
<th>Majority spin</th>
<th>Minority spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1</td>
<td>1.050 3.007 2.602 0.013</td>
<td>1.044 2.998 0.636 0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>3.598 0.789 1.765 0.006 0.001</td>
<td>0.790 1.768 0.004 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>3</td>
<td>3.897 0.792 1.768 0.007 0.001</td>
<td>0.793 1.775 0.005 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>4</td>
<td>5.595 0.998 0.006 0.001</td>
<td>0.998 0.003 0.006 0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>4</td>
<td>5.764 0.998 0.006 0.001</td>
<td>0.998 0.003 0.006 0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.4: Partial atomic charges (in the MT sphere) for Cr substituting Li, along with its nearest neighboring ions (unrelaxed structure).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>Distance (a.u.)</th>
<th>Majority spin</th>
<th>Minority spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1</td>
<td>0.988 2.820 2.558 0.002</td>
<td>0.982 2.812 0.259 0.002</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>3.809 0.792 1.818 0.010 0.002</td>
<td>0.791 1.812 0.007 0.002</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>3</td>
<td>4.271 0.793 1.808 0.008 0.002</td>
<td>0.792 1.805 0.007 0.002</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>4</td>
<td>5.595 0.997 2.772 0.636 0.024</td>
<td>0.997 2.772 0.622 0.024</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>4</td>
<td>5.764 0.997 2.773 0.636 0.025</td>
<td>0.997 2.773 0.611 0.024</td>
<td></td>
</tr>
</tbody>
</table>
8.3 

A magnetic moment of 2.31 $\mu_B$ with a 3$d$ character. The calculated effective charge is in this case by 0.57 higher than the expected one in a pure ionic picture. This difference could be determined by a rather small MT radius ($R_{MT}=1.6$ a.u.) used for Cr ions at Li site.

It should be mentioned that the magnetic density spills considerably out of a small Cr$_{Li}$ MT sphere into the interstitial, so that the interstitial contribution to the total magnetic moment is 1.41 $\mu_B$ out of 6 $\mu_B$ for the supercell with two Cr impurities. However, from the spin-density contour plots presented in Fig. 8.9 one can infer that the spin density is mainly localized around the Cr impurities.

The relaxation of the atomic coordinates under the constraint of preserving the supercell symmetry could lead to a change of the electronic structure described above due to the change of the distances between the atoms. As becomes apparent from Table 8.5, during the relaxation process the distance $d_{Cr_{Nb}-Cr_{Li}}$ separating

<table>
<thead>
<tr>
<th>Structure</th>
<th>$d_{Cr_{Nb}-Cr_{Li}}$ (a.u.)</th>
<th>Cr$_{Nb}$</th>
<th>Cr$_{Li}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>O</td>
<td>Li</td>
</tr>
<tr>
<td>relaxed</td>
<td>20.087</td>
<td>3.609</td>
<td>3.906</td>
</tr>
</tbody>
</table>

the chromium impurities increases, together with a significant rearrangement of the atomic positions of their neighboring atoms, especially for the atoms around the Cr ions at Li site.

The electronic origin of this enhancement of the distance between the impurity ions can be investigated from the comparison of the total density of states of Cr ions at Li site in the unrelaxed (Fig. 8.10) and relaxed (Fig. 8.11) supercell structures. One can observe a gradual decrease of the hybridization between Cr 3$d$ states and those of the O1 2$p$ (from the first shell of the neighboring atoms) corroborated with a stronger hybridization of the impurity 3$d$ states and O2 2$p$ (from the second shell) states. This interplay leads Cr impurity at Li site to move towards a centrosymmetric position. On the contrary, Cr impurity at Nb site tends the preserve its unrelaxed position (with respect to its neighbors).

The effect of the atomic positions relaxation on the electronic structure of the Cr impurity substituting for Nb ions is depicted in Fig. 8.12. The main difference with
Figure 8.9: Charge density (left) and magnetic (spin) density (right) obtained for the unrelaxed 80-atoms supercell. The maps were plotted in the crystalline plane determined by the trigonal axis $C_3$ and the oxygen atom of Cartesian coordinates (3.083,1.899,18.733) labeled by the symbol X. In the right panel, the dashed lines refer to negative difference spin-densities. The unit used is the same as in Fig. 7.5.
Figure 8.10: Local density of states of Cr impurity at Li in the unrelaxed 80-atoms supercell together with those of its neighboring oxygen atoms.

Figure 8.11: Local density of states of Cr impurity at Li in the relaxed 80-atoms supercell together with those of its neighboring oxygen atoms.
8.3 \textit{Cr} impurity in LiNbO$_3$

Figure 8.12: 3\textit{d} partial density of states of the \textit{Cr} impurity at Nb site (relaxed structure)

respect to the similar density of states obtained for the unrelaxed structure consists in a larger band gap of 0.35 eV between the occupied and the empty majority-spin 3\textit{d} levels. Also, the number of \textit{d}-like electrons inside the impurity's MT sphere that populate the majority-spin band is larger than in the case of the unrelaxed structure. An opposite behaviour can be observed for the 3\textit{d} minority-spin band.

The comparison of the atomic effective charges computed for the relaxed structure and listed in Table 8.6 with the similar data obtained for the unrelaxed structure (see Table 8.3) shows that in the case of the relaxed structure the magnetic moment has increased from 1.98 \(\mu_B\) to 2.29 \(\mu_B\). Moreover, the effective charge of \textit{Cr} impurity at Nb site has the value of 2.58, being slightly lower than that previously evaluated.

The partial 3\textit{d} density of states obtained for \textit{Cr} at Li site in the relaxed 80-atoms supercell are presented in Fig. 8.13. These density of states present almost the same features as those calculated for the unrelaxed structure. However, they are different through a deeper energy localization of the majority-spin 3\textit{d} states at \(-1.51\) eV with respect to the Fermi level.
8.3 Cr impurity in LiNbO$_3$

Table 8.6: Partial atomic charges (in the MT sphere) for Cr substituting Nb, along with its nearest neighboring ions (relaxed structure).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>Distance (a.u.)</th>
<th>Majority spin</th>
<th>Minority spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$s$</td>
<td>$p$</td>
<td>$d$</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
<td>1.048</td>
<td>3.002</td>
<td>2.789</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>3.609</td>
<td>0.788</td>
<td>1.780</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>3.906</td>
<td>0.793</td>
<td>1.776</td>
</tr>
<tr>
<td>Li</td>
<td>4</td>
<td>5.562</td>
<td>0.997</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Also, as can be deduced from the analysis of the partial atomic charges listed in Table 8.7, the relaxation of the atomic positions leads to a slightly reduction of the occupation of the majority-spin 3$d$ band and an opposite trend for the minority-spin band. In consequence, the magnetic moment of Cr impurity at Li site is reduced to 2.09 $\mu_B$ whereas its effective charge has the value of 3.63, still too high with respect to the nominal value of +3. This difference could be related to the absence of any intrinsic defects in our model which, in consequence, play an essential role in preserving the charge neutrality of the real lattice.

The interstitial charge contribution to the total magnetic moment of the relaxed supercell is equal to 1.35 $\mu_B$. The spin-density maps plotted in the same plane as those for unrelaxed structure show the same localization of the spin density around the impurity ions. Therefore, the predicted magnetic moments must be, on the average, by 0.65 $\mu_B$ higher than those deduced from the partial atomic charges analysis.

In summary, the effect of the relaxation of all atomic coordinates on the mag-
8.3 \textit{Cr} impurity in LiNbO$_3$

![Graph showing DOS vs Energy](image)

Figure 8.13: 3$d$ partial density of states of the \textit{Cr} impurity at Li site (relaxed structure)

The magnetic properties of the Cr-doped LiNbO$_3$ is to increase the value of the magnetic moment for Cr impurity at Nb site due to a higher population of its 3$d$ majority spin band associated with a depletion of the corresponding minority spin band. An opposite behaviour is observed for Cr at Li site. Since in the relaxed structure the 3$d$ states are deeper in energy (with respect to Fermi level) for both impurities than in the unrelaxed one, one can conclude that the relaxation of the atomic positions could have a significant influence on the optical properties of the Cr-doped LiNbO$_3$. Unfortunately, this qualitative conclusion cannot be quantitatively refined because DFT allows us to predict \textit{only} the ground-state properties of the physical system under study.

Even if the (static) effective charges as could be defined within LAPW method depend on the MT radii and cannot take into account for the interstitial electronic charge, a qualitative picture of the valency of Cr impurities can be reached by analyzing the trends of their effective charges. Such analysis is meaningful since we preserve the same computational setup during our \textit{ab initio} spin-polarized calcu-
lations. The tendency observed is that of a slightly decrease of effective charges evaluated for Cr ion at Nb site (by 0.05 electrons) whereas there is an opposite trend for Cr impurity at Li site. Moreover, since our full-potential calculations do not depend on the chosen MT radii, one can assume that, for a larger MT radii of the Cr impurities, a larger amount of electronic charge can be assigned to these impurities. This means, in the framework of our model, the effective charge of Cr ion at Li site should be close to +4 while for Cr impurity substituting for Nb it seems to be close to +3. One should note that for Cr impurity at Li site there is a large difference from the expected ideal value of +3 obtained within a pure ionic model. The reason of this disagreement could also lie in the absence of any intrinsic defects in our model, and it was experimentally shown that these intrinsic defects ensure the charge compensation of Cr impurities which enters at Li site.

Finally, the ground-state properties like the electric gradient field EFG and the hyperfine field HF (their defining relations are given in Appendix F) predicted for Cr impurities at Nb and Li sites as well as for their nearest neighbors are listed in Table 8.8 and Table 8.9. These predictions can be hopefully directly compared with experimental measurements, if the latter become available.

Table 8.8: Ground-state properties of Cr impurity at Nb site together with those of its neighboring atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>$V_{zz}$</th>
<th>$\eta$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td></td>
<td>-0.837</td>
<td>0.000</td>
<td>-189.229</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>3.867</td>
<td>0.574</td>
<td>0.251</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>-3.106</td>
<td>0.489</td>
<td>0.231</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>0.068</td>
<td>0.000</td>
<td>-0.084</td>
</tr>
<tr>
<td>Li</td>
<td>4</td>
<td>0.115</td>
<td>0.389</td>
<td>0.381</td>
</tr>
</tbody>
</table>

Table 8.9: Ground-state properties of Cr impurity at Li site together with those of its neighboring atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>Shell</th>
<th>$V_{zz}$</th>
<th>$\eta$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td></td>
<td>2.371</td>
<td>0.000</td>
<td>-201.745</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>3.694</td>
<td>0.446</td>
<td>1.071</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>4.741</td>
<td>0.681</td>
<td>3.190</td>
</tr>
<tr>
<td>Nb</td>
<td>3</td>
<td>4.158</td>
<td>0.000</td>
<td>3.421</td>
</tr>
<tr>
<td>Nb</td>
<td>4</td>
<td>-2.793</td>
<td>0.658</td>
<td>7.796</td>
</tr>
</tbody>
</table>
Chapter 9

Conclusions

In the framework of the density functional theory, we fully optimized the equilibrium ground-structure of LiNbO$_3$ in its both paraelectric and ferroelectric phases using the full-potential linearized plane wave method as implemented in WIEN97 code. The exchange-correlation energy functional was evaluated within the local density approximation. With this setup the lattice parameters and all internal geometry parameters were found in a good agreement with the experimental values.

The $\Gamma$-TO phonon frequencies calculated within frozen-phonon method are in a good agreement with the experimental data available for the $A_1$ and $E$ modes in nearly stoichiometric samples. We found out that the anharmonic effects play a significant role for the softest and the hardest of the $A_1$ modes. Since the $A_2$ modes are infrared and Raman silent, from our $ab$ initio frozen-phonon calculations we predict the frequencies of these modes. Also, we analyzed the calculated frequencies of the $E$ modes on the basis of their behaviour with respect to the $^{6}$Li isotope effect and on this background we proposed a different assignment of these modes than that experimentally assumed. In addition, we predicted the displacement patterns of all $\Gamma$-TO modes from the calculated eigenvalues whereas only a limited information on this subject is experimentally available.

Since the physical properties of LiNbO$_3$ depend significantly on the presence of both intrinsic and extrinsic defects, the doped LiNbO$_3$ with various trivalent ions was intensively studied over the last years. Particularly, we focused on the analysis of the ground-state properties of LiNbO$_3$ doped with Fe and Cr. The iron impurity replacing one Nb ion was modeled by a 40 atoms supercell spanned by [\$\Gamma11\$, [\$\Gamma\Gamma1\$] and
[111], whereas the Fe impurity at Li site was investigated with the help of a 80 atoms supercell generated by [200], [020] and [002] lattice vectors of the unit cell. Even if no charge compensation mechanism was taken into account in the study of this impurity, we obtained a strong localization of the impurity 3d states in the optical band gap of the undoped LiNbO$_3$, in agreement with the experimentally observed absorption bands due to crystal field transitions. We carried out more realistic calculations for Cr impurity in a 2×2×2 supercell, assuming a self-compensated pair Cr$_{Nb}$-Cr$_{Li}$. For this system, we particularly paid attention to the effect of the relaxation of all atomic coordinates on the electronic properties of these impurity ions. The most significant difference between the electronic structure computed for the relaxed and unrelaxed supercell consists in a deeper energy localization of the Cr impurities 3d states in the optical band gap. Also, during the relaxation process the magnetic moment evaluated for Cr ion at Nb site increased whereas an opposite tendency was observed for Cr impurity at Li site. Moreover, the ground-state properties like the electric gradient field and the hyperfine field for both Cr impurities were predicted.

We also investigated the zone-center lattice dynamics in LiTaO$_3$ with the frozen-phonon method in order to gain an insight regarding the experimentally observed shift of the $A_1$-TO$_3$ frequency to higher values compared to LiNbO$_3$. We ascribe this behaviour to a substantial contribution of Li vibrations in the corresponding eigenvector of LiTaO$_3$ while it is absent in LiNbO$_3$. In addition, we described the different participation of Li ions in the first three $A_1$ modes of these compounds by means of a two coupled classical oscillators model.
Appendix A

Symmetry coordinate coefficients for LiNbO3 and LiTaO3

The symmetry coordinate coefficients \( b_\alpha \) (see Eq. (5.13)) for the \( A_1 \) modes are listed in Table (A.1), while those corresponding to \( A_2 \) and \( E \) modes in Table (A.2), Table (A.3) and Table (A.4). One should note that, since the \( E \) modes are doubly degenerate, there are two sets of symmetry coordinates.

Table A.1: Symmetry coordinates coefficients for \( A_1 \) modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Cartesian Coord.</th>
<th>Symmetry Coefficients of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x )</td>
<td>Nb1 Nb2 Li1 Li2 O1 O2 O3 O4 O5 O6</td>
</tr>
<tr>
<td>TO1</td>
<td>( y )</td>
<td>0 0 0 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>1 1 0 0 (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3})</td>
</tr>
<tr>
<td>TO2</td>
<td>( x )</td>
<td>0 0 0 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0 0 0 1 1 (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3}) (-\frac{1}{3})</td>
</tr>
<tr>
<td>TO3</td>
<td>( z )</td>
<td>0 0 0 0 0 0 0 0 0 0</td>
</tr>
<tr>
<td></td>
<td>( x )</td>
<td>0 0 0 0 0 0 (-\frac{\sqrt{3}}{2}) (-\frac{\sqrt{3}}{2}) 0 (\frac{\sqrt{3}}{2}) (\frac{\sqrt{3}}{2})</td>
</tr>
<tr>
<td>TO4</td>
<td>( y )</td>
<td>0 0 0 0 0 0 (-\frac{\sqrt{3}}{2}) (-\frac{\sqrt{3}}{2}) 0 (\frac{\sqrt{3}}{2}) (\frac{\sqrt{3}}{2})</td>
</tr>
<tr>
<td></td>
<td>( z )</td>
<td>0 0 0 0 0 0 0 0 0 0</td>
</tr>
</tbody>
</table>

With the above notations, the \( A_1 \) symmetry coordinates are constructed from
the Cartesian positions of the atoms as the following:

\[
S1 = z(\text{Nb}1) + z(\text{Nb}2) - \frac{1}{3} [z(\text{O}1) + z(\text{O}2) + z(\text{O}3) + z(\text{O}4) + z(\text{O}5) + z(\text{O}6)]
\]

\[
S2 = z(\text{Li}1) + z(\text{Li}2) - \frac{1}{3} [z(\text{O}1) + z(\text{O}2) + z(\text{O}3) + z(\text{O}4) + z(\text{O}5) + z(\text{O}6)]
\]

\[
S3 = x(\text{O}1) + x(\text{O}4) - \frac{1}{2} [x(\text{O}2) + x(\text{O}3) + x(\text{O}5) + x(\text{O}6)]
\]

\[
+ \frac{\sqrt{3}}{2} [y(\text{O}2) - y(\text{O}3) + y(\text{O}5) - y(\text{O}6)]
\]

\[
S4 = y(\text{O}1) - y(\text{O}4) - \frac{1}{2} [y(\text{O}2) + x(\text{O}3) - x(\text{O}5) - x(\text{O}6)]
\]

\[
- \frac{\sqrt{3}}{2} [y(\text{O}2) - y(\text{O}3) - y(\text{O}5) + y(\text{O}6)]
\]

with similar expressions for the \(A_2\) and \(E\) symmetry coordinates.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Cartesian Coord.</th>
<th>Symmetry Coefficients of</th>
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<tr>
<td></td>
<td>(\text{Nb}1)</td>
<td>(\text{Nb}2)</td>
</tr>
<tr>
<td>(\text{TO}_1)</td>
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<td>0</td>
</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(z)</td>
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<td>(\text{TO}_4)</td>
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</tr>
<tr>
<td></td>
<td>(y)</td>
<td>0</td>
</tr>
<tr>
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<td>(z)</td>
<td>0</td>
</tr>
<tr>
<td>(\text{TO}_5)</td>
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<tr>
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<td>(y)</td>
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</tr>
<tr>
<td></td>
<td>(z)</td>
<td>0</td>
</tr>
<tr>
<td>(\text{TO}_2)</td>
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</tr>
<tr>
<td></td>
<td>(y)</td>
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</tr>
<tr>
<td></td>
<td>(z)</td>
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</tbody>
</table>
Table A.3: Symmetry coordinates coefficients for $E$ modes (first partner)

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<th>Symmetry Coefficients of</th>
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<td></td>
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<td></td>
<td>$y$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>$y$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>0</td>
</tr>
<tr>
<td>$TO_3$</td>
<td>$x$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$y$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>0</td>
</tr>
<tr>
<td>$TO_4$</td>
<td>$x$</td>
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</tr>
<tr>
<td></td>
<td>$y$</td>
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</tr>
<tr>
<td></td>
<td>$z$</td>
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</tr>
<tr>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>$z$</td>
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</tr>
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<td>$z$</td>
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<tr>
<td>Mode</td>
<td>Cartesian Coord.</td>
<td>Symmetry Coefficients of</td>
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<tr>
<td>------</td>
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<td>---------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb1</td>
</tr>
<tr>
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</tr>
<tr>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>z</td>
</tr>
<tr>
<td>TO2</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y</td>
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<tr>
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</tr>
<tr>
<td></td>
<td></td>
<td>x</td>
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<td></td>
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<td>y</td>
</tr>
<tr>
<td>TO4</td>
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<td></td>
<td></td>
<td>x</td>
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<tr>
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<td>y</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
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<tr>
<td>TO6</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
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<td>TO7</td>
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<td>x</td>
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<td>TO8</td>
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<tr>
<td></td>
<td></td>
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</tr>
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</tr>
<tr>
<td>TO9</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y</td>
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<tr>
<td></td>
<td></td>
<td>z</td>
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</tbody>
</table>
As a final remark, one should note that in order to obtain to $c_\alpha$ coefficients of the Eq. (5.14), three translational modes along the $Ox$, $Oy$ and $Oz$ axis must be added to the matrix $B$ of the $b_\alpha$ coefficients. Then, the coefficients $c_\alpha$ can be calculated by inverting the matrix $B$. 
Appendix B

Graphical representation of the $A_1$ modes in LiNbO$_3$

Figure B.1: a) A 3D representation of four $\Gamma$ $A_1$ phonons in LiNbO$_3$. The grey circles represent the equilibrium positions of the atoms, whereas the dark ones denote that obtained according to the displacement pattern; b) A top view of these modes.
$A_1$-TO$_2$ mode

$A_1$-TO$_3$ mode
$A_1\text{-}TO_4$ mode
Appendix C

Graphical representation of the $A_2$ modes in LiNbO$_3$

Figure C.1: a) A 3D representation of five $\Gamma A_2$ phonons in LiNbO$_3$. The grey circles represent the equilibrium positions of the atoms, whereas the dark ones denote that obtained according to the displacement pattern; b) A top view of these modes.
$A_2$-TO$_2$ mode

$A_2$-TO$_3$ mode
$A_2\text{-TO}_4$ mode

$A_2\text{-TO}_5$ mode
Appendix D

Graphical representation of the $E$ modes in LiNbO$_3$

Figure D.1: a) A 3D representation of nine $\Gamma$ $E$ phonons in LiNbO$_3$. The grey circles represent the equilibrium positions of the atoms, whereas the dark ones denote that obtained according to the displacement pattern; b) A top view of these modes.
$E$-TO$_2$ mode

$E$-TO$_3$ mode
$E$-TO$_4$ mode

$E$-TO$_5$ mode
$E\text{-TO}_6$ mode

$E\text{-TO}_7$ mode
Appendix E

Graphical representation of the $A_1$ modes in LiTaO$_3$

Figure E.1: a) A 3D representation of four $\Gamma A_1$ phonons in LiNbO$_3$. The grey circles represent the equilibrium positions of the atoms, whereas the dark ones denote that obtained according to the displacement pattern; b) A top view of these modes.
$A_1$-TO$_2$ mode

$A_1$-TO$_3$ mode
$A_1\text{-TO}_4$ mode
Appendix F

Ground-state properties of Cr-doped LiNbO₃

The quantity $V_{zz}$ listed in Table (8.8) and Table (8.9) represents the largest component of the traceless EFG tensor

$$V_{xx} + V_{yy} + V_{zz} = 0$$  \hspace{1cm} (F.1)

and the asymmetry parameter $\eta$ is defined by

$$\eta = \frac{|V_{xx} - V_{yy}|}{|V_{zz}|}$$  \hspace{1cm} (F.2)

The hyperfine field $H_F$ is proportional with the spin-density computed at the nucleus:

$$H_e = \frac{8\pi}{3\mu_B^2} \left[ \rho_{up}(0) - \rho_{down}(0) \right]$$  \hspace{1cm} (F.3)

The units used are $10^{21}$ V/m² for the electric field gradient and kGauss for the hyperfine field.
Presentation of the results of the present study

Refereed publications


Presentations at workshop and conferences


Poster title: "Calcul \textit{ab initio} des phonons \Gamma-TO dans LiNbO$_3$"
Vasile Caciuc, Andrei V. Postnikov et Gunnar Borstel.


Poster title: "Zone-center phonons in LiNbO$_3$ and LiTaO$_3$: A comparative first-principles study"
V. Caciuc, A.V. Postnikov and G. Borstel.
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