

## ABSTRACT

YU, LIPING. First Principles Studies of Interface Dielectric Properties of Polymer/metal-oxide Nanocomposites. (Under the direction of Dr. Jerry Bernholc).

This thesis is devoted to studying interface dielectric properties of polymer nanocomposites from first principles. We aim to understand at atomic scale the role of interface effects and the dielectric finite size effects of nanoparticles in determining the effective dielectric properties of polymer nanocomposites.

To study surface effects from first principles, we first investigate the two common methods, namely dipole correction and Coulomb cutoff, used to eliminate the artificial effects introduced by using the supercell approximation. We implement Coulomb cutoff technique in a plane-wave-based density functional theory code and compare it with dipole correction for the same system under the same conditions. By comparison, both methods are shown to be equivalent and able to remove the artificial effects of periodic images very accurately. We also find that a combination of these two methods offers an easy way to distinguish the localized bound states of interest from highly delocalized unoccupied states while using a relatively small supercell, and to ascertain the convergence of the results with respect to supercell size.

To understand the dielectric properties at the atomic scale, we develop a new nanoscale averaging model to connect the macroscopic quantities to the corresponding microscopic ones. This model allows us to compute the spatially resolved local dielectric permittivity, including the critically important ionic contributions, for interfaces and other complex structures. In this model, a simple way of evaluating real-space decay length of the nonlocal dielectric functions is also proposed.

By using the dipole correction and our averaging model in supercells, we calculate the optical and static local dielectric permittivity profiles for polymer (polypropylene) / metal-oxide ( $\text{PbTiO}_3$  and alumina) nanocomposites. Our *ab-initio* results show that metal-oxide/polymer interface effects are very localized and are mostly confined to the metal-oxide surface side, and that nanoscale metal-oxide slabs can on average retain the macroscopic value of bulk dielectric permittivity. These findings suggest that classical mixing laws associated with macroscopic composites can be applied to model the overall dielectric constant of a real polymer/metal-oxide nanocomposite system.

First Principles Studies of Interface Dielectric Properties of Polymer/metal-oxide  
Nanocomposites

by  
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## DEDICATION

To my family.

## BIOGRAPHY

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# Chapter 1

## Introduction

Polymer nanocomposites are usually defined as the composites of polymers with dispersed inorganic nanofillers. The nanofiller can be an insulator, a semiconductor or a metal, and can have spherical, cylindrical, or flake shapes. The polymer can be conductive or non-conductive. The combination of polymers with nanofillers could yield many novel, unique and improved properties, and offers the potential to tailor materials for special purposes. Since 1990s, an intensive research and development effort has been devoted to the synthesis of various types of polymer-nanocomposites and to understanding of the basic principles that determine their electronic, optical and magnetic properties [1]. At present, a number of polymer-nanocomposite-based devices, such as light emitting diodes, photodiodes, solar cells, gas sensors, and field effect transistors, have been developed. Due to the improved long-term stability of polymer-nanocomposites and many other advantages, the research in this field continues to grow.

Unlike applications of nanotechnology in the photonics and electronics area, the use of the polymer nanocomposites in the field of dielectrics and electrical insulation has not attracted a lot of interest until very recently [2, 3, 4, 5]. In 1994, the term “nanometric dielectric” [6] was introduced as a future research area associated with polymer-nanocomposite dielectrics. However, only after 1999, experimental data [7, 8] started to be reported, suggesting that polymer nanocomposites can gain many advantages in the field of bulk electric insulation. In particular, it has been demonstrated that polymer nanodielectrics can generally exhibit significant improvements in dielectric strength [2], as well as an order of magnitude improvement in voltage endurance [9].

The current increasing need for high-power density and high voltage capacitors, gate dielectrics, memories and power-storage devices has stimulated a new wave of research interest in polymer nanocomposites [10, 11, 12, 3, 13, 14, 15]. By incorporating high-permittivity inorganic nanoparticles into a polymer matrix with low dielectric loss and high dielectric strength, one may be able to develop new composite materials that have improved dielectric properties (resistivity, dielectric strength, permittivity and dielectric losses) and retain the unique attributes of polymers such as ease of production, light weight, and often ductility, etc.. By varying the size and percentage of filler nanoparticles, the polymer nanocomposites may be fabricated with tailored dielectric properties for specific applications.

In experiment, designing composite materials for specific electric applications with a classical ‘trial and error’ approach is quite expensive in both time and money. However, using theory and modern computers, the desired properties can be modeled, estimated and corrected. In this thesis, we have undertaken a theoretical study of the permittivity properties of polymer nanocomposites, aimed at providing *ab-initio* data for mesoscopic modeling and guiding of experiments.

The most distinctive feature of polymer nanocomposites, in comparison with conventional *micro*-composites, is the extremely high interface area between the nanoparticles and the polymer matrix. The smaller the size of the embedded nanoparticles, the larger the surface area to volume ratio, which leads to larger interface regions. For filler nanoparticles with modest loadings, the surface area associated with the internal interfaces becomes dominant in nanocomposites [16]. The properties of these interface areas may differ substantially from those of both the base polymer matrix and the nanoparticle material. As a consequence, the interface area may play a pivotal role in determining the overall dielectric properties of nanocomposites. It means that a truly new material, differing from its constituents, can be created due to the interface zone which can be adjusted by controlling nanoparticle sizes.

In addition to interfaces, dielectric properties of the polymer nanocomposites also depend on the polymer [17] and nanofiller materials [18] themselves. For nanoparticles, especially ferroelectric materials [19, 20], the size effects may also become very important.

The understanding of how different factors determine dielectric properties of polymer nanocomposites is far from being satisfactory. Most of the models proposed so far

are based on the classical electrodynamics, such as the multi-core model [4], various mixing models [21] and the classical effective medium method [22, 23]. In these models, the effective properties of composites are generally taken as functions of properties of bulk constituents, volume fraction of components, shape and arrangement of fillers, and polymer-filler interface. The size effects of the nanofiller are totally ignored, and the properties of interfaces are often assumed, or based on very crude classical approximations, irrespective of (physically attached or chemically bonded) interface structures. Therefore, the properties predicted by these models are very qualitative even for a very simple system[23].

Indeed, the regions of surfaces and interfaces in polymer nanocomposites are generally of the order of nanometers. At this length scale, the theory of macroscopic electrodynamics is no longer valid. The methods based on this classical theory then are neither able to describe and predict correctly the dielectric behaviors across surfaces and interfaces, nor can they determine whether the size dependence of dielectric properties of nanostructures arises from a quantum confinement effect or from increased surface-to-volume ratio. Therefore, to understand the interface properties and finite size effects, one has to rely on quantum mechanical theory.

Density functional theory (DFT) [24, 25] is today the most widely used quantum mechanical approach today for electronic structure calculations. It has been proved to be remarkably successful in interpreting and predicting properties of many-electron systems. In this thesis, we perform DFT-based first principles calculations to study the surface and interface dielectric effects in polymer nanocomposites. By focusing on the polymer(polypropylene)/metal-oxide ( $\text{PbTiO}_3$  and alumina) nanocomposites, the *ab-initio* calculations can bring up general, in-depth new insights that classical methods cannot provide.

Most of the *ab-initio* methods used to study surface properties typically adopt the supercell technique and assume periodic boundary conditions in all three directions. The periodically repeated supercell, containing both the slabs and the vacuum, often generates two major problems, not present in isolated slabs. First, there are interactions between periodic images of the slab, even for symmetric non-polar slab. Second, for an asymmetric slab with two surfaces having different work functions, or a slab with a non-vanishing polarization normal to the surface, a fictitious electric field is induced to enforce the periodicity of the potential at the supercell boundaries. The charge density self-consistently

achieved under this fictitious field influences the atomic relaxations, energetics, electronic band structure, and also the dielectric response properties.

In order to study the dielectric properties of the surfaces as correcting as possible, one needs to get rid of spurious interactions between slab replicas and the unphysical electric field. Therefore, in the first part of this thesis, we will compare the two common methods that have been proposed for this purpose and choose the one that is good for our dielectric calculations. Furthermore, one should notice that the dielectric response function at the microscopic scale is in principle nonlocal. To understand the local macroscopic permittivity from the microscopic point of view, a special treatment is needed. In our work, we also propose a new model that can efficiently extract the spatially resolved local dielectric permittivity across a surface or interface with nanoscale resolution.

The rest of the thesis is organized as follows: in Chapter 2, we outline the general DFT-based methods that are needed for our dielectric permittivity calculations. In Chapter 3, we investigate the methods that are used to eliminate the unphysical image interactions created by using a supercell in DFT calculations for surfaces. Chapter 4 presents and discusses our first-principles results for polymer/metal-oxide nanocomposites. This chapter also details a new model we developed to study nano-resolved local dielectric permittivity profiles for large complex systems. Finally, our conclusions are summarized in Chapter 5.

## Chapter 2

# Methodology

This chapter outlines some general DFT-based theories related to our dielectric permittivity calculations.

### 2.1 Density functional theory

Density functional theory (DFT) is a quantum-mechanical theory used to calculate the electronic structure for many-electron systems. It has become a common tool in first-principles calculations aimed at interpreting or predicting the properties of atoms, molecules and solids. There are a large amount of literature on DFT, including excellent reviews and overviews [26, 27, 28, 29, 30, 31, 32, 33, 34, 35]. In this section, we briefly describe two core elements of DFT, the Hohenberg-Kohn theorem [24] and Kohn-Sham equations [25], focusing on the basic concepts. Some approximations involved in DFT are also described briefly.

Before describing DFT, we look at the traditional ways in quantum mechanics to solve many-electron problems. For a system of  $N$  interacting electrons under an external potential  $v(\mathbf{r})$  (usually the Coulomb potential of nuclei<sup>1</sup>), a stationary electron state is described by a wavefunction  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  satisfying the non-relativistic Schrödinger's

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<sup>1</sup>Since nuclei have much larger masses than electrons, they are considered as static in studying the electronic properties. This is called the Born-Oppenheimer approximation.

equation (SE)<sup>2</sup>

$$\hat{H}\Psi = \left[ \hat{T} + \hat{V} + \hat{U} \right] \Psi = \left[ \sum_i^N -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_i^N v(\mathbf{r}_i) + \sum_{i<j}^N U(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi = E\Psi, \quad (2.1)$$

where  $\hat{T}$  and  $\hat{U}$  are so-called universal operators, representing the electron kinetic energy and the electron-electron interaction energy respectively, and  $\hat{V}$  is the system-dependent (i.e., nonuniversal) potential energy from the external field. In this equation, it is the  $\hat{U}$  term by which the much more complicated many-particle problem differs from the separable single-particle problem. The usual approaches to Schrödinger's equations are based on the expansion of the wave function in Slater determinants [36]. The simplest one is the Hartree-Fock method [37]. The more sophisticated approaches, e.g., configuration interaction methods, have also been developed during the decades of struggling with quantum many-body problems. However, due to the huge number of the degrees of freedom in  $\Psi$ 's for a large and complex system, these methods require too many computational resources to be applied to systems.

DFT provides an alternative and much more versatile way to solve the above many-body Schrödinger's equation (2.1). It systematically maps the many-body problem, with  $\hat{U}$ , onto a single-body problem without  $\hat{U}$  by using the charge density as the key variable which only has three continuous degrees of freedom. The charge density  $\rho(\mathbf{r})$ , which for a normalized  $\Psi$  is defined as

$$\rho(\mathbf{r}) = N \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (2.2)$$

In DFT, knowledge of the  $\rho(\mathbf{r})$  leads to the knowledge of the ground-state wave functions and the potential, and hence one can compute the all other ground-state observables.

### 2.1.1 The Hohenberg-Kohn theorem

At the heart of DFT, the Hohenberg-Kohn (HK) theorem states that for a non-degenerate ground state system, the external potential  $v(\mathbf{r})$  is uniquely determined by the corresponding ground state (GS) electronic density  $\rho_0(\mathbf{r})$ , to within an additive constant.

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<sup>2</sup>Spin effects are neglected here since we are dealing with non-magnetic materials and only electric properties are of interest in this work.

For a given GS  $\rho_0(\mathbf{r})$ , one can determine external potential  $v(\mathbf{r})$  and calculate the corresponding ground state wave function  $\Psi_0(\mathbf{r}_0, \mathbf{r}_2 \cdots, \mathbf{r}_N)$ . It means that for ground states Eq.(2.2) is invertible and  $\Psi_0$  is a unique functional of  $\rho_0$ <sup>3</sup>

$$\Psi_0(\mathbf{r}_0, \mathbf{r}_2 \cdots, \mathbf{r}_N) = \Psi[\rho_0(\mathbf{r})]. \quad (2.3)$$

So both  $\Psi_0$  and  $\rho_0$  are equivalent and carry exactly the same information. Consequently, any ground state observable  $\hat{O}$  is also a functional of GS  $\rho_0$ ,

$$O_0 = O[\rho_0] = \langle \Psi[\rho_0] | \hat{O} | \Psi[\rho_0] \rangle. \quad (2.4)$$

For the observable of GS energy, its functional can be written as

$$E_0 = E[\rho_0] = \langle \Psi[\rho_0] | \hat{T} + \hat{U} + \hat{V} | \Psi[\rho_0] \rangle = \min_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle \quad (2.5)$$

and has the variational property

$$E[\rho_0] \leq E[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle + \int d^3r \rho(\mathbf{r}) v(\mathbf{r}) \equiv F[\rho] + V[\rho], \quad (2.6)$$

where  $\rho$  is the arbitrary density in the same potential  $\hat{V}$ , and the internal-energy functional  $F[\rho]$  is independent of  $v(\mathbf{r})$  and only determined by  $\hat{T}$  and  $\hat{U}$ . It implies that any density different from  $\rho_0$  would result in an energy greater than GS  $E_0$  and GS  $E_0$  is obtained only by GS  $\rho_0$ .

The above HK theorem has been proved by several ways. The original proof, given by HK [24], is to show that a contradiction to the variational principle is obtained assuming that  $\Psi_0$  is not uniquely determined by  $\rho_0$ . A constrained-search proof consisting of Equations (2.5) and (2.6) was given independently by M. Levy [38] and E.Lieb [39]. In addition to these two classic proofs, several other alternative proofs have also been found. One of these is the so-called ‘strong form of the HK theorem’, based on the inequality [40, 41, 42]

$$\int d^3r \Delta \rho(\mathbf{r}) \Delta v(\mathbf{r}) < 0 \quad (2.7)$$

which means that a change in the potential must also change the density and hence there are no two local potentials with the same GS charge density.

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<sup>3</sup>For degenerate ground states, several of the degenerate GS wave functions produce the same density and hence the unique function  $\Psi[\rho]$  does not exist. However, the energy functional still exist and can be minimized by  $\rho_0$ .

Therefore, the HK theorem is rigorous. It exactly reduces the  $N$ -body problem to the determination of a three-dimensional function  $\rho(\mathbf{r})$  which minimize  $E[\rho]$ . However, HK is still of little use since  $F[\rho]$  is unknown.

### 2.1.2 The Kohn-Sham equations

The introduction of the Kohn-Sham (KS) equations [25] is the breakthrough in applications of the DFT. The system of interacting electrons is mapped onto a fictitious KS system of noninteracting electrons with the same GS electronic density.

Considering a system of interacting electrons, the exact energy functional can be written as

$$E[\rho] = T[n] + U[n] + V[n] = T_s[\rho] + U_H[\rho] + E_{XC}[\rho] + V[\rho], \quad (2.8)$$

where the subscript  $s$  denotes ‘single particle’, and the exchange correlation energy is defined as  $E_{XC} = T - T_s + U - U_H$ . In terms of single particle orbitals  $\phi_i(\mathbf{r})$  of a noninteracting system with density  $\rho(\mathbf{r})$ ,  $T_s$ <sup>4</sup> can be expressed as

$$T_s = -\frac{\hbar^2}{2m} \sum_i^N \int d^3r \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}). \quad (2.9)$$

The minimization of  $E[\rho]$  gives

$$\begin{aligned} 0 &= \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta U_H[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})} \\ &= \frac{T_s[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r}). \end{aligned} \quad (2.10)$$

In this equation,  $v_H(\mathbf{r})$  denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, and  $v_{XC}(\mathbf{r})$  is called the exchange-correlation potential, which includes all the many-body interactions.

For a noninteracting KS system, its orbitals are given by Schrödinger’s equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (2.11)$$

and yield

$$\rho_s(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2. \quad (2.12)$$

---

<sup>4</sup>A nonrelativistic treatment is assumed here. The treatment can also be scalar relativistic (using the relativistic kinetic-energy operator and other simple relativistic corrections, but no spin-orbit coupling) and relativistic (using Dirac’s equation, also which includes spin-orbit coupling).

The minimization condition for the energy functional of this system is simply

$$0 = \frac{\delta E_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{T_s[\rho]}{\delta \rho(\mathbf{r})} + v_s(\mathbf{r}). \quad (2.13)$$

Comparing this with Eq.(2.10), one finds the same  $\rho \equiv \rho_s$  if the potential  $v_s$  is chosen to be

$$\begin{aligned} v_s(\mathbf{r}) &= v(\mathbf{r}) + v_H(\mathbf{r}) + v_{XC}(\mathbf{r}) \\ &= v(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})} \end{aligned} \quad (2.14)$$

By the HK theorem,  $v_s$  is uniquely defined. Since both  $v_H$  and  $v_{XC}$  depend on  $\rho$ , which depends on the  $\phi_i$ , which in turn depends on  $v_s$ . The Eqs.(2.11)-(2.14) can be solved self-consistently, starting with an initial guess of  $\rho(\mathbf{r})$ , calculating the  $v_s(\mathbf{r})$ , and then solving the differential equation (2.11) for the  $\phi_i$ . From the new charge density calculated from  $\phi_i$  by Eq.(2.12), one starts again and repeats the procedure until convergence is reached.

From the solved  $\rho_0$  and  $\epsilon_i$ , one can then calculate the total energy of the interacting system by

$$E_0 = \sum_i^N \epsilon_i - \frac{e^2}{2} \int \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3 r v_{XC}(\mathbf{r})\rho_0(\mathbf{r}) + E_{XC}[\rho_0]. \quad (2.15)$$

The equation (2.15) shows that  $E_0$  is not just the sum over all  $\epsilon_i$ , but also includes three additional terms which account for particle-particle interactions. The  $\epsilon_i$  should be taken as artificial objects and are actually introduced as the eigenvalues of an auxiliary single-body equation whose eigenfunctions yield the correct density. Only this density has a strict physical meaning in KS equations. However, in many situations,  $\epsilon_i$  do empirically provide a reasonable first approximation to the actual energy levels of extended systems. In solid state physics, this approximation, behind most band structure calculations, often gives results that agree well with experimental photo-emission and inverse photo-emission data [43]. The eigenfunctions can also be interpreted as zero-order approximations to quasi-particle wave functions.

### 2.1.3 Approximations to the exchange-correlation energy

In Eq.(2.8), the exchange-correlation energy functional  $E_{XC}[\rho]$  contains all the many-body effects of the problem and is typically much smaller than the known terms  $T_s$ ,  $U_H$  and  $V$ . It is often decomposed as  $E_{XC} = E_X + E_C$ , where  $E_X$  is due to the Pauli

principle (exchange energy) and  $E_C$  is due to correlations. The exchange energy can be expressed explicitly in terms of single-particle orbitals as

$$E_X[\{\phi_i[\rho]\}] = -\frac{e^2}{2} \sum_{jk} \int d^3r d^3r' \frac{\phi_j^*(\mathbf{r}) \phi_k^*(\mathbf{r}') \phi_j(\mathbf{r}') \phi_k(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.16)$$

However it has no general exact expression in terms of the density. For the correlation energy  $E_c$ , the general explicit expression is also unknown, neither in terms of the densities nor orbitals. Therefore, in order to make DFT calculations practical, one has to make reasonably simple approximations for  $E_{XC}$ . Up to now, there exist three major types of such approximated functionals [35], namely, local (TF, LDA and  $X\alpha$ ), semilocal or gradient-dependent (GEA and GGA), and nonlocal (hybrids[44], orbital functionals such as meta-GGAs[45], EXX[46] and SIC[32], and integral-dependent functionals such as ADA[47]). Here I only shortly describe the two most popular functionals: the local-density approximation (LDA) and the generalized gradient approximation (GGA).

### Local-density approximation

LDA is the simplest one and was introduced by Kohn and Sham [25] in 1965. The exchange-correlation energy in LDA is written as

$$E_{XC}^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{XC}(\rho(\mathbf{r})) d^3r = \int \rho(\mathbf{r}) \{\epsilon_X + \epsilon_C\} d^3r \quad (2.17)$$

and the exchange-correlation potential is given as

$$v_{XC}^{LDA}(\mathbf{r}) = \frac{\delta E_{XC}^{LDA}}{\delta \rho(\mathbf{r})} = \epsilon_{XC}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \frac{\partial \epsilon_{XC}(\rho(\mathbf{r}))}{\partial \rho(\mathbf{r})}, \quad (2.18)$$

assuming that  $E_{XC}$  depends solely upon the value of the electronic density at each point in space. The most successful LDA is based on the homogeneous electron gas model. In this model, the per volume exchange energy  $\epsilon_{XC}$  is known exactly,

$$\epsilon_X^{hom} = -\frac{3e^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \rho^{4/3}, \quad (2.19)$$

and so the LDA for  $E_X$  is

$$E_X^{LDA}[\rho] = -\frac{3e^2}{4} \left(\frac{3}{\pi}\right)^{1/3} \int d^3r \rho(\mathbf{r})^{4/3}. \quad (2.20)$$

The analytic expressions for the  $\epsilon_c^{hom}$  of the homogeneous electron gas is unknown except in the high- and low-density limits corresponding to infinitely-weak and infinitely-strong correlations [26]. The earlier approximation for  $\epsilon_c$ , based on perturbation theory [48, 49], became outdated with the advent of highly precise of Quantum Monte Carlo (QMC) calculations for electron gas by Ceperley and Alder [50]. Modern expressions for  $\epsilon_c$  are parameterized by interpolating the accurate values obtained from QMC calculations and reproducing the exactly known limiting behaviors. Various approaches, using different analytic forms for  $\epsilon_C$ , have generated several LDA's for the correlation functional, including Perdew-Zunger [51], Cole-Perdew [52], Perdew-Wang [53] etc..

The LDA has proven to be amazingly successful, particularly in condensed matter systems. The partial reason for this success comes from systematic error cancellation [54, 49, 55]: LDA typically underestimates  $E_C$  but overestimates  $E_X$ , resulting in unexpectedly good values of  $E_{XC}$ . This error cancellation is not accidental, but caused by that fact that for any density LDA  $xc$  hole satisfies the correct sum rule.

The LDA also has some well-known limitations, and is not often accurate enough for quantum chemistry applications. For instance, LDA can underestimate a semiconductor band gap by up to 50%. In molecules and solids, LDA badly overestimates the cohesive energies and bond strengths, and underestimate the bond lengths. In addition, for a finite system, the LDA potential  $v_{XC}$  decays exponentially, exhibiting an incorrect long-range behavior, while the true  $v_{XC}$  decays much slower in a Coulombic manner. The artificially rapid decay manifests itself in the number of Kohn-Sham orbitals that the LDA potential can bind. The LDA potential can not support a Rydberg series and those states it does bind are too high in energy. This results in the HOMO energy being too high in energy, so that any predictions for the ionization potential based on Koopmans' theorem [56] are not good [34].

### Generalized gradient approximation

Any real system is spatially inhomogeneous, i.e., it has a spatially varying density  $\rho(\mathbf{r})$  and the electrons are exposed to spatially varying electric fields produced by the nuclei. The GGA is the simplest extension of LDA to include the spatial variation as a term  $\nabla\rho(\mathbf{r})$  in the functional. The general form for the exchange-correlation energy functional in GGA

is written as

$$E_{XC}^{GGA} = \int \epsilon_{XC}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))\rho(\mathbf{r})d^3r. \quad (2.21)$$

Unlike LDA which has only one expression for  $\epsilon_{XC}^{hom}$  with the various parametrizations (i.e., different ways of writing it), GGA is not unique: different choices of the functional  $\epsilon_{XC}(\rho, \nabla\rho)$  can lead to very different GGA. In quantum chemistry, GGAs are often obtained by fitting parameters to test sets of selected molecules. In physics, GGAs tend to emphasize the exact constraints. Nowadays, there are many GGA-type functionals available. The most popular (and maybe the most reliable) GGAs are BLYP (Becke’s exchange functional [57] combined with the correlation functional of Lee, Yang and Parr [58]) in chemistry and PBE [59] (Perdew, Burke and Ernzerhof) in physics. PBE GGAs are designed to improve PW91 (Perdew and Wang) GGAs [60] which have some unphysical wiggles in the PW91  $xc$  potential for small and large reduced-density gradients, and do not satisfy some exactly known features of  $E_{XC}$ .

GGA functionals usually yield much better atomic energies and binding energies than LDA, and give reliable results for all main types of chemical bonds (covalent, ionic, metallic and hydrogen bridge). However, GGAs are still local and they can reproduce only phenomenon due to charge overlap. For the van der Waals interactions that have a non-local character, both GGA and LDA fail [61].

#### 2.1.4 Pseudopotentials

To make the DFT calculations more practical, pseudopotentials (PP) are often used for ions. Using PP, the basis set size and the number of electrons are greatly reduced in solving KS equations. The ionic potentials enter the KS equation (2.14) as parts of the external potential  $v_{ext}$ . For large system in DFT, especially in solids, the strong Coulomb potentials of the nuclei and the effects of the tightly bound core electrons are replaced by pseudopotentials acting on the valence electrons. The idea behind the PP is that chemical binding in molecules and solids is dominated by the outer (valence) electrons of each atom. The inner (core) electrons retain a atomic-like configuration and their orbitals change very little when the atom is put in a different chemical environment. Hence, it is reasonable to freeze the core electrons with the nucleus, and leave only the valence electronic density to be determined self-consistently for the system of interest.

The aim of pseudopotential theory is to find useful pseudopotentials that can faithfully represent the scattering of electrons over a desired energy range. The scattering properties of a localized potential can be concisely described by phase shifts. For any potential that gives the same phase shift, the scattering cross-section and all properties of the wave function outside the scattering region are exactly same [62]. Therefore, a simple and weak effective potential without nodes can be used to reproduce all scattering properties of a true potential with nodes. On the other hand, it means that the pseudopotentials are not unique.

The earlier developed pseudopotentials are usually local and not accurate enough for all the properties of interest [63, 64, 65]. However it is worth mentioning here that the orthogonalized plane wave (OPW) method, introduced by Herring [66, 67] is the direct antecedent of modern pseudopotential and projector augmented wave (PAW) methods [68, 69]. Modern pseudopotentials, based on “*ab initio* norm-conserving” [70] concepts, have now been widely used for much of the current research and for development of new methods in electronic structure theory.

Modern norm-conserving PPs are generated from all-electron KS calculations and are not fitted to experiment. They are constructed using the following requirements (see Fig. 2.1.4):

- All-electron and pseudo valence eigenvalues must agree for a chosen atomic reference configuration;
- All-electron and pseudo valence wave functions must be the same beyond a given core radius  $r_c$ , which is usually located around the outermost maximum of the atomic wave function;
- The integrated all-electron and pseudo charge inside  $r_c$  must be equal for each wave function (norm-conservation).

From the first two requirements, it follows that the potentials outside  $r_c$  are also same. Inside the  $r_c$ , the pseudo potential and the wave function differ from all-electron counterparts and are usually much smoother. The last point is crucial. It has been shown [70] that the norm-conservation condition actually implies that the logarithmic derivatives of the all-electron and pseudo wave functions match at  $r_c$  to second order in  $\epsilon - \epsilon_{\text{bound}}$ ,

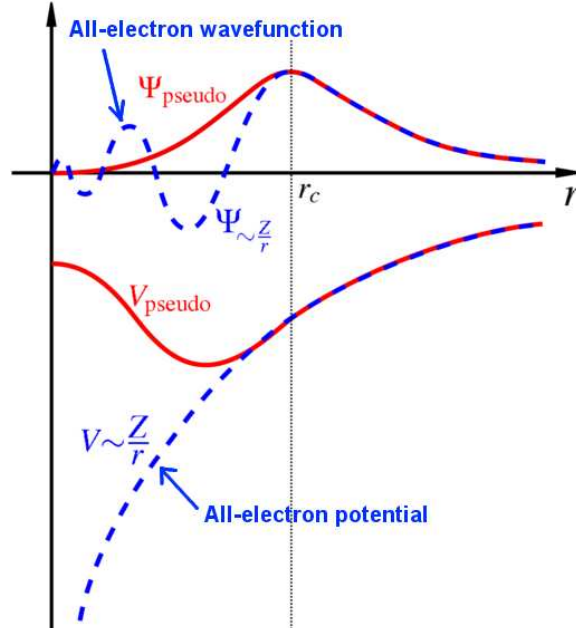


Figure 2.1: Comparison of a wave function of the Coulomb potential of the nucleus (blue) to the one of the pseudopotential (red). The all-electron and the pseudo wave functions and the potentials match beyond a certain cutoff radius  $r_c$ .

which means the same scattering phase shifts for both all-electron and pseudo potentials to linear order in energy around the chosen energy  $\epsilon_l$ . Therefore, this point ensures good scattering properties and good transferability.

Norm-conserving PP has been extended by Blöchl [71] and Vanderbilt [72], who showed that “ultrasoft pseudopotentials” can be defined by using auxiliary localized functions to improve the accuracy of norm-conserving PP and to reduce the computational cost. More recently, the advent of the PAW method [68, 69, 73] has completed reformulation of the OPW methods into a form that is particularly appropriate for DFT calculations of total energies and forces. Both norm-conserving and ultrasoft PPs can be derived from PAW methods as special cases.

### 2.1.5 Supercells

In solid state physics, we are dealing with crystal structures in which the positions of atoms are repeated periodically in space. A supercell refers to a repeating unit cell of

the crystal that contains one or several primitive cells. In real cases, instead of studying the enormous number of electrons and nuclei of crystal, one studies these properties in a supercell cell using Born-von Karman (or periodic) boundary conditions (PBCs). Combined with plane-wave expansions, PBCs have been extensively applied to the quantum *ab initio* studies of properties of crystalline solids. Due to its simplicity and a unified numerical scheme for both periodic and aperiodic systems, the supercell method has been extended to study aperiodic systems, such as defects in solids [74], substitutional alloys, and other finite systems, such as molecules [75], wires and slabs. For finite systems, enough empty space between the periodic replicas has to be inserted into a supercell, so that the interactions between them are weak. In this work, we focus on surface and interface systems, using this supercell method. In order to eliminate the artificial interaction of the replicas and reduce the computational cost, some additional techniques need to be employed. In the next chapter we investigate two most commonly used such methods.

In a periodic potential, i.e.,  $U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r})$  for all  $\mathbf{R}$  in a Bravais lattice, the Bloch theorem states that the eigenstates  $\psi$  of a one-electron Hamiltonian  $H = \hbar^2 \nabla^2 / 2m + U(\mathbf{r})$  have a special form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad (2.22)$$

where  $u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$ . The Born-von Karman boundary conditions further impose that the eigen wave-function must be periodic over a volume commensurate with the supercell of the underlying Bravais lattice, i.e.,

$$\psi(\mathbf{r} + N_i \mathbf{a}_i) = \psi(\mathbf{r}), \quad i = 1, 2, 3, \quad (2.23)$$

where  $\mathbf{a}_i$  are the three supercell vectors and  $N_i$  are all integers of orders of  $N^{1/3}$ , where  $N = N_1 N_2 N_3$  is the total number of the supercells in the crystal. Under this condition, the wave vector  $\mathbf{k}$  must be real and has the form

$$\mathbf{k} = \sum_{i=1}^3 \frac{m_i}{N_i} \mathbf{b}_i, \quad m_i \text{ integer}. \quad (2.24)$$

It follows from above equation that the  $k$ -space volume  $\Delta \mathbf{k}$  for each allowed  $\mathbf{k}$  can be written as

$$\Delta \mathbf{k} = \frac{\mathbf{b}_1}{N_1} \cdot \left( \frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3} \right) = \frac{1}{N} (\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3) = \frac{1}{N} \cdot \frac{(2\pi)^3}{v} = \frac{(2\pi)^3}{V}. \quad (2.25)$$

Hence the number of allowed wave vectors in the reciprocal cell is equal to the number of supercells in the crystal. In the limit of a large (macroscopic) crystal, the  $\Delta\mathbf{k}$  goes to zero and  $\mathbf{k}$  can then be taken as a continuous variable.

All possible eigenstates  $\psi_{i,\mathbf{k}}$  can be specified by  $\mathbf{k}$  within the first Brillouin zone (BZ) and the band index  $i$ . Many properties, such as the charge density, total energies, etc., which are functions of  $\psi_{i,\mathbf{k}}$ , are obtained by a sum or integration in  $\mathbf{k}$  over the first BZ. For a general function  $f_i(\mathbf{k})$ , its average value per cell becomes,

$$\bar{f}_i = \frac{1}{N_k} \sum_{\mathbf{k}} f_i(\mathbf{k}) \rightarrow \frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} d\mathbf{k} f_i(\mathbf{k}) = \frac{\Omega_{\text{cell}}}{2\pi^d} \int_{\text{BZ}} \mathbf{k} f_i(\mathbf{k}). \quad (2.26)$$

In real calculation, integration is often take over in an irreducible BZ, instead of the full BZ, by considering the symmetries in a crystal. Moreover, special  $k$ -points are often chosen for efficient integration of smooth periodic functions. In our work, we choose the most widely used Monkhorst-Park [76] special  $k$ -points. This special  $k$ -point choosing method leads to a uniform set of points determined by a simple formula valid for any crystal:

$$\mathbf{k}_{n_1, n_2, n_3} \equiv \sum_{i=1}^3 \frac{2n_i - N_i - 1}{2N_i} \mathbf{G}_i, \quad (2.27)$$

where  $\mathbf{G}_i$  is are the reciprocal vectors corresponding to the supercell in the crystal.

### 2.1.6 Plane wave basis

In practice, a numerical solution of the KS equations (Eq.2.11) typically proceeds by expanding the KS orbitals in a suitable set of basis functions and solving the resulting secular equation for the coefficients in this expansion. Many basis functions have been constructed, such as plane waves (PW), linear combinations of atomic orbitals (LCAO), orthogonized PW (OPW), linear muffin tin orbitals (LMTO), linear augmented plane waves (LAPW), Gaussian type orbitals (GTO), etc. In this work, all calculations are done in the Quantum-Espresso code with a PW basis [77]. Hence, in the following we only describe PW methods. The PW have many attractive features: they are naturally periodic, orthogonal, independent of atomic positions, fixed by the crystal structure and by the cutoff, and they have no basis set superposition errors, and can use Fast Fourier Transformations (FFTs) efficiently.

A PW basis set is defined as

$$\varphi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}, \quad \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}, \quad (2.28)$$

where  $\Omega$  is the volume of the crystal,  $\mathbf{G}$  is the reciprocal lattice vector and  $E_{\text{cut}}$  is the cutoff of the kinetic energy. With this definition, the normalization becomes:

$$\langle \mathbf{k} + \mathbf{G} | \mathbf{k} + \mathbf{G}' \rangle = \delta_{\mathbf{G}, \mathbf{G}'}. \quad (2.29)$$

An eigenfunction expanded in this PW basis can be written as

$$\phi_{i,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{G}} \langle \mathbf{r} | \mathbf{k} + \mathbf{G} \rangle. \quad (2.30)$$

By inserting Eq.(2.30) into the KS equation (2.11), multiplying from the left by  $\langle \mathbf{k} + \mathbf{G}' |$  and by integrating as in Eq.(2.29), we obtain the KS equations in the PW basis as

$$\sum_{\mathbf{G}} \langle \mathbf{k} + \mathbf{G}' | -\frac{\hbar^2}{2m} \nabla^2 + v_s(\mathbf{r}) | \mathbf{k} + \mathbf{G} \rangle c_{i,\mathbf{G}} = \varepsilon_i c_{i,\mathbf{G}'}. \quad (2.31)$$

The matrix element of a kinetic operator is simply

$$\langle \mathbf{k} + \mathbf{G}' | -\frac{\hbar^2}{2m} \nabla^2 | \mathbf{k} + \mathbf{G} \rangle = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}, \mathbf{G}'}. \quad (2.32)$$

For a crystal, the KS potential is periodic and can be expanded as

$$v_s(\mathbf{r}) = \sum_m v_s(\mathbf{G}_m) e^{i\mathbf{G}_m \cdot \mathbf{r}}, \quad (2.33)$$

where

$$v_s(\mathbf{G}) = \frac{1}{\Omega_{\text{cell}}} \int v_s(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} d\mathbf{r}. \quad (2.34)$$

Thus the matrix element of the potential becomes

$$\langle \mathbf{k} + \mathbf{G}' | v_s | \mathbf{k} + \mathbf{G} \rangle = \sum_m v_s(\mathbf{G}_m) \delta_{\mathbf{G}' - \mathbf{G}, \mathbf{G}_m}, \quad (2.35)$$

which is nonzero only if  $\mathbf{G}$  and  $\mathbf{G}'$  differ by some reciprocal lattice vector  $\mathbf{G}_m$ .

## 2.2 Density functional perturbation theory

DFT is a powerful approach to calculate the ground state charge density and the total energy, which give access to a wide number of experimental observables. Density functional perturbational theory (DFPT) extends the scope of DFT. Compared to finite-difference methods, DFPT is more powerful and provides an easy and systematic way to calculate quantities related to derivatives of the total energy (or charge density) with respect to a small perturbation of the potential applied to the system. DFPT was first proposed by Baroni, Giannozzi and Testa [78] as the linear response to atomic displacement and then generalized to various other perturbations [79, 80, 81]. Their formalism is based on the Sternheimer equation, Green's functions and sum-over-states techniques. A different formalism of DFPT, due to Gonze [82, 83, 84], is based on the variational principle, providing more accurate expressions for the energy derivatives, and giving also access to arbitrary order of perturbations based on the  $2n+1$  theorem [85]. Both methods have been commonly used and discussed in detail in the review by Baroni et al. [86].

The basic ansatz behind DFPT is that a general observable of the system  $X$ , such as the wavefunction, electron density, potential, energy, etc., can be expanded as a small perturbation series in  $\lambda$  around their unperturbed values  $X^{(0)}$ , i.e.,

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \dots \quad (2.36)$$

The expansion coefficients are given by simple numerical coefficients:

$$X^{(n)} = \frac{1}{n!} \left. \frac{d^n X}{d\lambda^n} \right|_{\lambda=0}. \quad (2.37)$$

The applied potential, external to the electronic system, is supposed to be known through all orders, and our goal is to calculate the  $X^{(n)}$  for other quantities.

The variation of the Kohn-Sham orbitals,  $\phi_n^{(1)}(\mathbf{r})$ , can be obtained by standard first-order perturbation theory, i.e., the Sternheimer equation [87],

$$(H_{\text{KS}}^{(0)} - \epsilon_n^{(0)})|\phi_n^{(1)}\rangle = -(V_{\text{KS}}^{(1)} - \epsilon_n^{(1)})|\phi_n^{(0)}\rangle \quad (2.38)$$

where  $H_{\text{KS}}^{(0)}$  is the unperturbed KS Hamiltonian,

$$V_{\text{KS}}^{(1)}(\mathbf{r}) = V^{(1)}(\mathbf{r}) + e^2 \int \frac{\rho^{(1)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \left. \frac{dv_{xc}[\rho]}{d\rho} \right|_{\rho=\rho^{(0)}(\mathbf{r})} \rho^{(1)}(\mathbf{r}) \quad (2.39)$$

is the first order correction to the Kohn-Sham potential, and

$$\epsilon_n^{(1)} = \langle \phi_n^{(0)} | V_{KS}^{(1)} | \phi_n^{(0)} \rangle \quad (2.40)$$

is the first order variation of the KS eigenvalue  $\epsilon_n^{(0)}$ . The first order variation of the charge density can be obtained as

$$\rho_n^{(1)} = 2 \sum_{n=1}^{N/2} \phi_n^{(0)*}(\mathbf{r}) \phi_n^{(1)}(\mathbf{r}) + c.c. \quad (2.41)$$

$$= 2 \sum_{n=1}^{N/2} \sum_{m \neq n} \phi_n^{(0)*}(\mathbf{r}) \phi_m^{(0)*}(\mathbf{r}) \frac{\langle \phi_m^{(0)} | V_{KS}^{(1)} | \psi_n^{(0)} \rangle}{\epsilon_n^{(0)} - \epsilon_m^{(0)}}. \quad (2.42)$$

Equations (2.38)-(2.41) form a set of self-consistent equations for the perturbed system analogous to standard KS equations. Eqs.(2.38) are linearly coupled to each other. Thus the set of  $\phi^{(1)}$ 's is the solution of a problem of dimension  $(NM/2 \times NM/2)$ , where  $M$  is the size of the basis set used for representing  $\phi$ 's. Since only occupied states are needed to construct the right side of equation (2.38), the computational cost of determining the density response to a perturbation is of the same order as that needed to calculate the unperturbed ground-state density. On the other hand, Equation (2.42) indicates that the contribution to the electron-density response from products of the occupied states cancel. Therefore the response of the system to an external perturbation depends only on the component of the perturbation that couples the occupied-state manifold with the empty-state one [86]. All the above applies to insulators. For metallic systems, a finite density of states occurs at the Fermi energy and a change in the occupation number may also occur upon the application of a perturbation. A modification of DFPT to treat metal systems have been discussed by de Gironcoli [88].

In this work we use DFPT to calculate the bulk dielectric permittivity given as the second derivative of the total energy with respect to the applied electric field. Both high-frequency and low-frequency dielectric permittivities are considered. The perturbation potential due to a homogeneous electric field is linear in space, but it breaks the periodicity of the crystalline lattice:

$$v^{(1)} = \sum_{\alpha} E_{\alpha} \cdot r_{\alpha}. \quad (2.43)$$

To deal with this problem, the long-wave method is commonly used. A linear potential is

obtained as the limit of  $\mathbf{q}$  approaching 0 for

$$v(\mathbf{r}) = \lim_{\mathbf{q} \rightarrow \mathbf{0}} \lambda \frac{2 \sin(\mathbf{q} \cdot \mathbf{r})}{|\mathbf{q}|} = \lim_{\mathbf{q} \rightarrow \mathbf{0}} \lambda \left( \frac{e^{i\mathbf{q} \cdot \mathbf{r}}}{i|\mathbf{q}|} - \frac{e^{-i\mathbf{q} \cdot \mathbf{r}}}{i|\mathbf{q}|} \right). \quad (2.44)$$

In DFPT the high-frequency permittivity mainly comes from the electronic contribution and can be obtained as [84]

$$\begin{aligned} \epsilon_{\alpha\beta}^{\infty} &= \delta_{\alpha\beta} - \frac{4\pi}{\Omega_0} 2E_{\text{el}}^{\varepsilon_{\alpha}^* \varepsilon_{\beta}} \left\{ u^{(0)}; u^{\varepsilon_{\alpha}}, u^{\varepsilon_{\beta}} \right\} \\ &= \delta_{\alpha\beta} - \frac{1}{\pi^2} \int_{\text{BZ}} \sum_m^{\text{occ}} s \left( \left\langle u_{m\mathbf{k}}^{\varepsilon_{\alpha}} | H_{\mathbf{k},\mathbf{k}}^{(0)} - \epsilon_{m\mathbf{k}}^{(0)} | u_{m\mathbf{k}}^{\varepsilon_{\beta}} \right\rangle - \left\langle u_{m\mathbf{k}}^{\varepsilon_{\alpha}} | i u_{m\mathbf{k}}^{k_{\beta}} \right\rangle - \left\langle i u_{m\mathbf{k}}^{k_{\alpha}} | u_{m\mathbf{k}}^{\varepsilon_{\beta}} \right\rangle \right) d\mathbf{k} \\ &\quad - \frac{4\pi}{\Omega_0} \int_{\Omega_0} \frac{dv_{\text{xc}}}{d\rho} |_{\rho^{(0)}(\mathbf{r})} [\rho^{\varepsilon_{\alpha}}(\mathbf{r})]^* \rho^{\varepsilon_{\beta}}(\mathbf{r}) d\mathbf{r} - 16\pi^2 \sum_{\mathbf{G} \neq 0} \frac{[\rho^{\varepsilon_{\alpha}}(\mathbf{G})]^* \rho^{\varepsilon_{\beta}}(\mathbf{G})}{|\mathbf{G}|^2}. \end{aligned} \quad (2.45)$$

At low frequencies, phonons are coupled to macroscopic electric fields. Hence, to compute the low-frequency permittivity tensor, one has to include the ionic (or lattice) response to the electric field perturbation. The polarization due to the ionic displacement induced by the field can be dominant, especially for polar materials. Following Gonze et al., at the long-wavelength limit, one derives the low-frequency permittivity tensor:

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega} \sum_{\kappa\kappa'} \sum_{\alpha'\beta'} Z_{\kappa,\alpha\alpha'}^* \left[ \tilde{C}(\mathbf{q} = 0) - M\omega^2 \right]_{\kappa\alpha',\kappa'\beta'}^{-1} Z_{\kappa,\beta\beta'}^*, \quad (2.46)$$

where  $Z_{\kappa,\alpha\beta}^*$  is the Born effective charge, defined as the proportionality coefficient relating the induced dipole moment per unit cell along  $\alpha$  and atom displacement along  $\beta$  at zero macroscopic electric field. It also describes the linear relation between the force on the atom and the applied macroscopic electric field. Hence, it can be calculated in two ways:

$$Z_{\kappa,\alpha\beta}^* = \Omega \frac{\partial P_{\alpha}}{\partial \tau_{\kappa\beta}(\mathbf{q} = 0)} = \frac{\partial F_{\kappa,\alpha}}{\partial \varepsilon_{\beta}}. \quad (2.47)$$

By using eigendisplacements  $U_{m\mathbf{q}}(\kappa\beta)$  of  $\tilde{C}(\mathbf{q} = 0)$  and by defining the mode-oscillator strength tensor

$$S_{m,\alpha\beta} = \left( \sum_{\kappa\alpha'} Z_{\kappa,\alpha\alpha'}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa\alpha') \right) \cdot \left( \sum_{\kappa'\beta'} Z_{\kappa',\beta\beta'}^* U_{m\mathbf{q}=\mathbf{0}}(\kappa'\beta') \right) \quad (2.48)$$

eq.(2.46) can be written in a simpler form

$$\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2 - \omega^2}. \quad (2.49)$$

## 2.3 Modern polarization theory

Electric polarization is a basic quantity in the theory of the dielectrics. The classical definition of polarization, expressed in terms of the dipole moment per unit volume, i.e., with obvious notations,

$$\mathbf{P} = \frac{e}{\Omega} \left( \sum_{\kappa} Z_{\kappa} R_{\kappa} - \int_{\Omega} d\mathbf{r} \rho(\mathbf{r}) \mathbf{r} \right), \quad (2.50)$$

is only valid for a finite system. For an extended system, this definition is only acceptable if the polarization elements are discrete. However, in a real dielectric, the electronic density is continuous and there is no unique way to find the dipole moment as a sum of dipoles by ‘cutting’ the charge density into discrete finite regions. Hence, the dipole of a unit cell is ill-defined. The origin for this non-uniqueness comes from the unbound position vector  $\mathbf{r}$  in Eq.(2.50).

Therefore, a proper definition of bulk polarization in a crystal requires that the expression in terms of  $\mathbf{r}$  be replaced by a different form. This can be done by using the relation between polarization field  $\mathbf{P}(\mathbf{r}, t)$  and polarization current  $\mathbf{j}(\mathbf{r}, t)$ :

$$\frac{d\mathbf{P}(\mathbf{r}, t)}{dt} = \mathbf{j}(\mathbf{r}, t), \quad (2.51)$$

which indicates that a static change in the polarization can be calculated from adiabatic evolution of a system with time. Since the polarization current is a physically measurable unique quantity, the change in polarization  $\Delta\mathbf{P}$  can be strictly determined through currents and be taken as a fundamental definition of polarization,

$$\mathbf{P}(\mathbf{r}, t) = \int^t dt' \mathbf{j}(\mathbf{r}, t'). \quad (2.52)$$

In this definition, the  $\mathbf{j}$  should be specified as the current that flows through the material under the condition of zero internal macroscopic field, which ensures the periodicity of the Hamiltonian and excludes influence of extrinsic charges.

The definition of polarization in Eq.(2.52) is physically correct but is not sufficient for applications. The quantum mechanical resolution to the polarization problem for an extended crystalline has been derived only in 1990s, and is known as the modern polarization theory (MPT) [89, 90, 91]. It makes polarization calculations practical using the already well-proven tool of the electronic structure theory.

According to MPT, the bulk polarization is defined as a Berry phase of the electronic Bloch wavefunctions. The detailed derivation of the theory can be found in the references [92, 89, 93, 90]. Here, only some main formulas of the theory are outlined and discussed briefly.

Let us consider two states  $\lambda_1$  and  $\lambda_2$  of a crystal, connected by a continuous adiabatic transformation of the Hamiltonian described by revolution of a variable  $\lambda$ , which usually parameterizes displacements of atoms in a unit cell. During the transformation, the macroscopic electric field is always required to vanish. The change in electronic polarization  $\Delta \mathbf{P}$  induced by this transformation can then be obtained from Eq. (2.52) with time  $t$  replaced by  $\lambda$ ,

$$\Delta \mathbf{P} = \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial \mathbf{P}}{\partial \lambda}. \quad (2.53)$$

The first derivative of  $\mathbf{P}$  with respect to  $\lambda$  is well defined in the infinite system and is given by [92]

$$\frac{\partial \mathbf{P}}{\partial \lambda} = -\frac{2ie\hbar}{\Omega m_e} \sum_{\mathbf{k}} \sum_i^{\text{occ}} \sum_j^{\text{empty}} \frac{\langle \psi_{i\mathbf{k}}^\lambda | \mathbf{p} | \psi_{j\mathbf{k}}^\lambda \rangle \langle \psi_{j\mathbf{k}}^\lambda | \partial V_{\text{KS}}^\lambda / \partial \lambda | \psi_{i\mathbf{k}}^\lambda \rangle}{(\epsilon_{i\mathbf{k}}^\lambda - \epsilon_{j\mathbf{k}}^\lambda)^2} + c.c. \quad (2.54)$$

where  $\Omega$  is volume of the crystal. It has been proved [89] that the integral of Eq.(2.54) over a closed loop in parameter space results in a change in polarization which takes the form

$$\oint d\lambda \frac{\partial \mathbf{P}}{\partial \lambda} = \frac{e\mathbf{R}}{\Omega_0}, \quad (2.55)$$

where  $\Omega_0$  and  $\mathbf{R}$  correspond to the unit cell volume and a lattice vector. This suggests that the electronic polarization is well-defined modula  $e\mathbf{R}/\Omega_0$ . Furthermore the integral in Eq.(2.53) has been shown to be independent of path between  $\lambda_1$  and  $\lambda_2$  and can be computed from

$$\int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial \mathbf{P}}{\partial \lambda} = \mathbf{P}(\lambda_1) - \mathbf{P}(\lambda_2), \quad (2.56)$$

where  $\mathbf{P}(\lambda)$  is given in terms of geometric Berry phase [94]  $\gamma$  by

$$\mathbf{P}(\lambda) = \frac{e}{\pi} \gamma = -\frac{2e}{8\pi^3} \text{Im} \int_{\text{BZ}} d\mathbf{k} \sum_i^{\text{occ}} \left\langle u_{i\mathbf{k}}^\lambda | \nabla_{\mathbf{k}} | u_{i\mathbf{k}}^\lambda \right\rangle, \quad (2.57)$$

where  $u_{i\mathbf{k}}(\mathbf{r})$  are the periodic part of the Bloch wavefunction and obey the “periodic gauge condition”

$$u_{i,\mathbf{k}+\mathbf{G}}^\lambda(\mathbf{r}) = e^{i\mathbf{G}\cdot\mathbf{r}} u_{i,\mathbf{k}}^\lambda(\mathbf{r}). \quad (2.58)$$

The physics behind Eq.(2.57) becomes more transparent when this expression is written in terms of centers of the Wannier functions  $W_i^{(\lambda)}(\mathbf{r})$  of the occupied bands,

$$\mathbf{P}(\lambda) = -\frac{2e}{\Omega_0} \sum_i^{\text{occ}} \int \mathbf{r} |W_i^{(\lambda)}(\mathbf{r})|^2 d\mathbf{r} \quad (2.59)$$

## Chapter 3

# Equivalence of dipole correction and Coulomb cutoff techniques in supercell calculation

In *ab initio* calculations of surfaces or non-periodic systems one frequently relies on the supercell approximation, where the periodic replicas of the system are separated by enough empty space to avoid spurious interactions between successive images. However, a vacuum separation is not sufficient to screen dipolar interaction that appears in asymmetrically charged or polar systems. The *dipole correction* and *Coulomb cutoff* methods are often used to eliminate such interactions between periodic replicas. In this work, these methods are compared under the same conditions in the framework of plane-wave-based Density Functional Theory (DFT). The dipole correction method is shown to be equivalent to the rigorous Coulomb cutoff formalism in calculations of total energy, force, charge density and self-consistent potential. We demonstrate that the band structures obtained by these methods coincide for localized bound states and that the corrections have essentially no influence on occupied energy bands, only substantially affecting unoccupied bands. By comparing the results of the two methods, the localized bound states of interest can be easily distinguished from highly delocalized unoccupied states using a relatively small supercell. This comparison offers substantial savings in computational time when ascertaining convergence with supercell size. The accuracy of the dipole correction method is also con-

firmed by comparing the results for a model ferroelectric BaTiO<sub>3</sub> slab with a Berry phase calculation of polarization for the bulk system. (Most of this chapter has been published in Phys.Rev.B 77, 245102(2008))

### 3.1 Introduction

The plane-wave method with Born-von Kármán periodic boundary conditions (PBC's) is one of the most important state-of-the-art techniques in electronic structure calculations for systems ranging from bulk solids to molecules and surfaces [95]. The systems are considered to be repeated periodically in three-dimensional space and the supercell approximation is commonly adopted when non-periodic systems, such as surfaces, nanostructures or molecules are investigated. When necessary, e.g., for modeling surfaces, a vacuum region is inserted into the supercell to separate the periodic replicas along the aperiodic direction(s). However, the supercell approximation artificially introduces spurious dipole interactions between periodic images when there is a net dipole moment or charge in the cell <sup>1</sup>. The dipole interactions lead to results that display strong dependence on cell size and shape, possibly introducing artifacts into the calculations.

The issue of eliminating the undesired interactions between the periodic images has been extensively discussed in the literature. Several different methods have been proposed [98, 99, 100, 96, 101, 102, 103, 104, 105, 106, 107, 97, 108, 109, 110]: Makov and Payne [96] correct the electrostatic energy functional (but not the potential) for an aperiodic system by adding a dipole-dependent term in a cubic supercell. Kantorovich [105] generalized this method to cells of arbitrary shape. Another kind of method obtains the electrostatic potential by subtracting out countercharge matching multiple moment of the charge distribution, and solving for that part using boundary conditions of an isolated system [106, 110]. A different approach is to introduce a modified Coulomb potential with a spatial cutoff [102, 103, 108, 109]. This Coulomb cutoff formalism can remove all spurious image interactions introduced by the long range part of the Coulomb potential, including dipole and all higher order multipole interactions. It has been demonstrated to be exact

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<sup>1</sup>Note that higher order multipole corrections are negligible in a polar slab system. The quadrupole-quadrupole interaction decays as  $L^{-5}$ , where  $L$  is the linear dimension of a supercell. It is clearly negligible for supercells as large as the ones used in typical calculations [96]. Moreover, it has been shown that adding the quadrupole corrections does not noticeably improve the accuracy of the results [97].

and rigorous for clusters [102, 103], slabs [107] and even wires [108]. For polar slabs, the simple to implement dipole correction method, which introduces a correcting dipole in the vacuum region, has been widely used in calculations [111, 112]. It was originally proposed by Neugebauer and Scheffler [100] and later corrected by Bengtsson [104].

Unfortunately, the above methods have never been consistently compared to each other. It is therefore difficult to know which one is the most suitable for the system at hand. In particular, it is not clear yet whether the simple dipole correction [104, 100] is sufficiently effective in cancelling the spurious interactions due to PBC's in planar polar slabs.

In this paper we compare the dipole correction method [104] with the exact Coulomb cutoff formalism [107, 108] that we implemented in the plane-wave based density-functional code PWSCF [77], in which the dipole correction method was already coded as an option. We studied the convergence of these two techniques via computation of the total energy, force, charge density, potential and electron band structure. Our results demonstrate that the dipole correction method is equivalent to the Coulomb cutoff formalism. As such, both methods can completely cancel the spurious interactions between periodic images in a polar slab system. As already noted in Ref. [108], we find that the corrections to the band structure substantially affect the unoccupied electronic states, but have negligible influence on the occupied ones. This finding is important when studying optical or excited state properties of polar slabs. In fact, as will be described below, comparisons between the two methods provide a cost-effective avenue for confirming the convergence of the results with respect to supercell size.

### 3.2 Coulomb cutoff formalism and dipole correction technique

In the supercell approach, periodic images of the system interact with each other through the long-range Coulomb potential, *i.e.*, the electrostatic potential  $V(\mathbf{r})$  that satisfies the Poisson equation with PBC's. It has the form of a convolution

$$V(\mathbf{r}) = \int_{\text{all space}} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' = \int n(\mathbf{r}') v(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'. \quad (3.1)$$

In reciprocal space for a 3D periodic system with reciprocal lattice vectors  $\mathbf{G}$ , Eq.(3.1) can be written using the convolution theorem as

$$V(\mathbf{G}) = n(\mathbf{G})v(\mathbf{G}), \quad (3.2)$$

where  $n(\mathbf{G})$  and  $v(\mathbf{G})$  are the Fourier transforms of the charge density  $n(\mathbf{r})$  and long-range Coulomb potential  $v(\mathbf{r})$ .

To remove all undesired interactions between periodic replicas in the Coulomb cutoff formalism [102, 107, 108], one replaces Eq.(3.2) with a modified one

$$\tilde{V}(\mathbf{G}) = \tilde{n}(\mathbf{G})\tilde{v}(\mathbf{G}) \quad (3.3)$$

where the Fourier integral

$$\tilde{v}(\mathbf{G}) = \int_{\text{all space}} \tilde{v}(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d^3\mathbf{r} \quad (3.4)$$

corresponds to a modified Coulomb interaction

$$\tilde{v}(|\mathbf{r} - \mathbf{r}'|) = \begin{cases} \frac{1}{|\mathbf{r} - \mathbf{r}'|} & \text{for } |z - z'| < L \\ 0 & \text{otherwise.} \end{cases} \quad (3.5)$$

The modified charge density  $\tilde{n}(\mathbf{r})$  is still 3D periodic, but the range of the cutoff parameter  $L$  must be equal to the supercell dimension in the aperiodic direction, and at least twice the slab thickness [108]. Here, the slab thickness is defined as the distance between the two surfaces outside the slab where charge densities are essentially zero, and not the distance between the top and bottom atomic surfaces of the slab. By choosing  $L$  and the slab thickness in this way, the densities belonging to different slab images will not overlap and cannot interact through  $\tilde{v}(\mathbf{r})$ .

In plane-wave-based DFT calculations, the electrostatic energy is decomposed into three terms: Hartree, ion-electron and ion-ion interaction. Within the Coulomb cutoff formalism, each term has an analytic form in reciprocal space for a 2D slab system (refer to Refs. [107, 108] for the exact expressions). The divergent terms at  $G = 0$  are shown to cancel exactly when the cutoff is applied to both the ionic and Hartree potentials. The regular spherical energy cutoff still can be applied after separating surface terms that need higher cutoff  $G_c$  and special care (see discussion in Appendix B of Ref. [107]).

The dipole correction method [104] is based on the observation that the electrostatic potentials on the two sides of an isolated slab with nonzero net dipole moment  $m$  are different, and the use of PBC's introduces an artificial uniform electric field in the supercell that cancels the potential jump across the slab. To eliminate the unwanted electric field, one introduces a dipole layer in the mid-vacuum region of the supercell. Furthermore, a true external electric field  $E_{\text{ext}}$  can also be applied to the slab in the same way by adjusting the strength of the additional sawtooth-like potential [113, 111, 114]

$$V^{\text{dip}}(z) = -e \left( \frac{4\pi m}{c} - E_{\text{ext}} \right) z, \quad -\frac{c}{2} < z < \frac{c}{2}. \quad (3.6)$$

The dipole-corrected potential  $V(\mathbf{r})$ , total energy  $E_{\text{tot}}$  and Hellmann-Feynman forces  $\mathbf{F}_I$  become

$$V(\mathbf{r}) = V^{\text{dip}}(z) + V^0(\mathbf{r}), \quad (3.7)$$

$$E_{\text{tot}} = E_{\text{tot}}^0 + \left( \frac{2\pi m}{c} - E_{\text{ext}} \right) Am, \quad (3.8)$$

$$\mathbf{F}_I = \mathbf{F}_I^0 + eZ_I \left( E_{\text{ext}} - \frac{4\pi m}{c} \right) \hat{z}, \quad (3.9)$$

where  $V^0(\mathbf{r})$ ,  $E_{\text{tot}}^0$  and  $\mathbf{F}_I^0$  are the calculated electrostatic potential, total energy and force without dipole correction,  $Z_I$  is the ionic charge of I-th atom and  $A$  is the area of the surface unit cell.

We should stress that the Coulomb cutoff and dipole-correction methods correspond to two different physical procedures, rather than mathematical transformations of the same expression. The former is considered to be exact, rigorous, and able to remove all spurious interactions between periodic images. However, it is more complex to implement and needs modifications for including non-zero electric field. In contrast, the dipole correction can simultaneously cancel the undesired artificial electric field due to PBC's and include an external electric field applied to a slab, but it is difficult to ascertain whether the artificial electric field completely cancels all interactions between the periodic replicas. The two methods may also differ in their convergence properties with respect to supercell size. In order to investigate these issues, it is necessary and fruitful to compare these methods under the same conditions and for the same physical system.

To accomplish this, we implement the Coulomb cutoff formalism in the PWSCF [77] code, where the dipole correction method was already programmed [115]. We are thus able

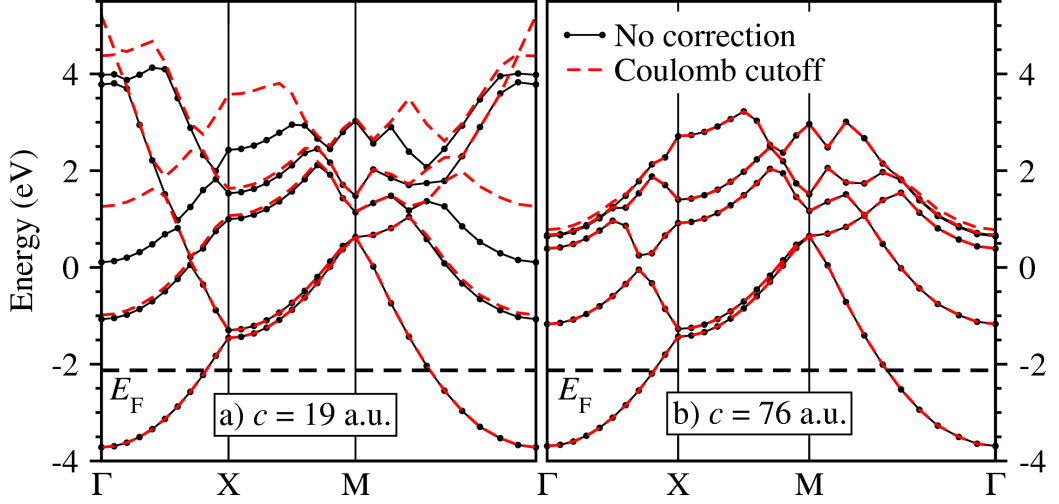


Figure 3.1: Band structures of Na sheet with and without Coulomb cutoff correction in supercell thicknesses of 19 a.u. (a) and 76 a.u. (b). The Fermi energies in the two supercells have been aligned.

to perform calculations with no correction, dipole correction, and Coulomb cutoff, in the same supercell and with the same inputs (such as cutoff energy, k-points, pseudopotentials, etc.). The slab is centered in the middle of the supercell along  $z$  direction and the supercell size is chosen large enough so that the Coulomb cutoff formalism exactly removes all the undesired interactions. Our calculations use the cutoff energy of 30 Ry, Vanderbilt ultra-soft pseudopotentials [72] with Perdew-Zunger (LDA) parameterization of the exchange-correlation functional [116], and an in-plane Monkhorst-Pack k-point grid of  $8 \times 8$  [76].

### 3.3 Results and discussion

As a first test of the implementation of the Coulomb cutoff formalism in the PWSCF code, we computed the total energy and the electronic band structure of a non-polar Na sheet in a supercell of size  $7.6 \times 7.6 \times 19$  a.u. As expected, the total energies from calculations with and without the Coulomb cutoff are the same, *i.e.*, -0.651110 Ry, because the sheet is non-polar. The electronic band structure, which agrees very well with that in Ref. [108], shows that the occupied band states obtained with the Coulomb cutoff correction applied are essentially the same as the ones obtained without the correction, while the unoccupied bands start to differ as their energies increase (see Fig. 3.1a). In the Ref. [108], the authors

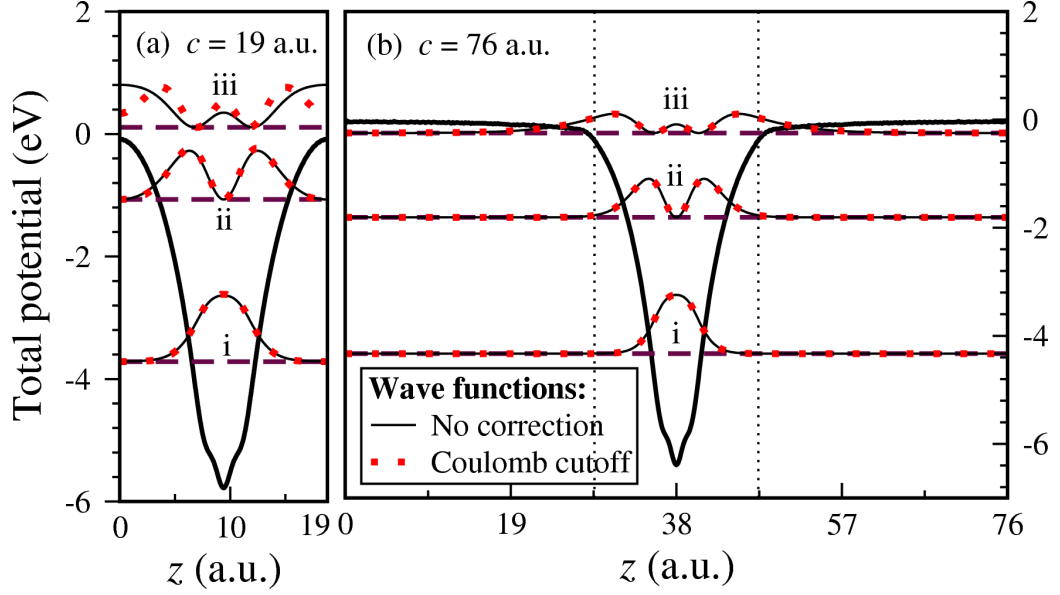


Figure 3.2: Plane-averaged total potential (thick black curves) along the normal direction of the Na-layer slab with no correction in supercells of thicknesses of (a) 19 a.u. and (b) 76 a.u. The three lowest energy bands at the  $\Gamma$  point and their corresponding electron densities without correction and with Coulomb cutoff correction are also shown.

also found the same effect for a Si chain and stated it is due to greater delocalization of states at higher energies.

To understand this effect more explicitly, we plot in Fig. 3.2a the planar average of the total potential and squares of the wave functions of the three lowest band states at  $\Gamma$ . It shows that the supercell of 19 a.u. thickness is too small for the potential to become flat in the vacuum region. In this small cell, the third lowest  $\Gamma$  state does not decay to zero in vacuum, which inevitably leads to overlap interactions between states belonging to neighbor slab images. This state then behaves like a bulk one and the Coulomb cutoff correction is no longer valid. It changes both the bulk-like wave function and its band energy. When calculations are performed in a larger supercell (76 a.u.) with more vacuum, the flat vacuum potential around the slab is recovered (see Fig. 3.2b) and the band structure difference between results with and without the Coulomb-cutoff correction disappears (see Fig. 3.1b). In this large supercell, the third lowest  $\Gamma$  state is well localized within about 25 a.u. from the slab and the Coulomb correction does not affect it.

From Figs. 3.1-3.2, we conclude that differences between results obtained with and

Table 3.1: Calculated total energy, force on the oxygen atom and dipole moment per unit area for a water-molecule sheet in a supercell of size  $5.67 \times 5.67 \times 23$  a.u. See text.

|                   | Total Energy (Ry) | $F_z(\text{O})$ (Ry/a.u.) | Dipole moment(e/a.u.) |
|-------------------|-------------------|---------------------------|-----------------------|
| No correction     | -34.335063        | 0.014020                  | 0.018996              |
| Dipole correction | -34.329478        | 0.014475                  | 0.016516              |
| Coulomb cutoff    | -34.329477        | 0.014497                  | 0.016518              |
| Double cell       | -34.329482        | 0.014355                  | —                     |

without the Coulomb cutoff only occur for those unoccupied states that overlap with their periodic images due to limited size of the vacuum region. These differences disappear in a very large supercell, as they should, since there are no dipole interactions between nonpolar repeated slab images.

For a more meaningful comparison between the two techniques we now turn to a highly polar slab: a layer of water molecules in a supercell geometry, for direct comparison with a previous investigation [104].

Table 3.1 shows the total energies, forces and dipole moments for a water-molecule sheet in a supercell of size  $5.67 \times 5.67 \times 23$  a.u., for the cases of no correction, Coulomb cutoff and dipole correction, respectively. The dipole moment is calculated from the electron charge density and the point charges of ions. As a reference, we also performed the same calculation in a nonpolar double cell, where we positioned two water slabs with dipoles in opposite directions so that no net dipole moment exists in the simulation cell. The results show that both Coulomb cutoff and dipole correction give essentially the same total energy, forces and dipole moment, which also agree very well with the results of the double cell calculation where no correction is needed.

Fig. 3.3 shows the convergence of total energy with respect to the supercell size  $c$  ( $a$  is fixed at 5.67 a.u.) with and without the corrections. At supercell sizes  $c/a \geq 3$ , the Coulomb cutoff and the dipole corrections are essentially converged, while without a correction the convergence is much slower. This behavior agrees well with what is reported for the Coulomb cutoff formalism in Ref. [108, 102]. Surprisingly and to the best of our knowledge, no such convergence tests have ever been published for the dipole correction. In supercells with sizes  $c/a < 3$ , the Coulomb cutoff correction is not converged, while the dipole correction is essentially converged at  $c/a = 2$ . As mentioned in Sec.II, the supercell

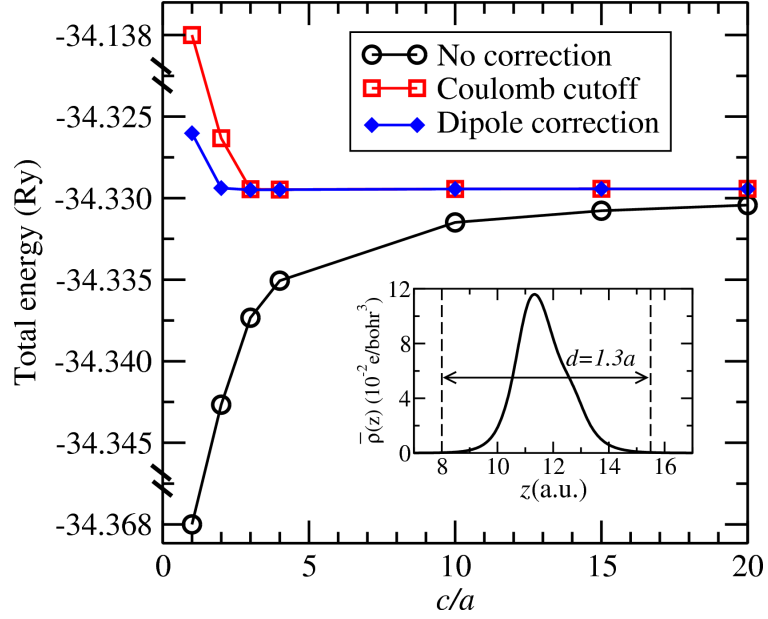


Figure 3.3: Variation of the total energy of a water-sheet slab with various supercell sizes, calculated with no correction, dipole correction and Coulomb cutoff. The inset shows the plane-averaged charge density of the water molecule sheet. Its effective thickness  $d$  is  $1.3a$ . See text.

size for the Coulomb cutoff method should be at least twice the slab thickness. The thickness of the water sheet is about  $1.3a$ ; therefore the Coulomb cutoff cannot eliminate all spurious interactions between replicas for a supercells smaller than  $c = 2.6a$ .

In Fig. 3.4 we plot the planar average of the electrostatic potential in the  $z$ -direction for a water sheet in a supercell of size  $5.67 \times 5.67 \times 23$  a.u. Except in the mid-region of the vacuum, the dipole correction and Coulomb cutoff methods give an essentially the same electrostatic potential. Both potentials introduce characteristic dipole layers in the vacuum, which allow for proper extraction of the work functions of the two inequivalent slab surfaces. As evident from the figure, the dipole potential in the Coulomb cutoff method has a shape that is similar to the electrostatic potential of the slab, but with an opposite sign. This is why the size of the supercell has to be at least twice the slab thickness. In contrast, the simple step-like potential in the dipole correction method allows for a significantly smaller vacuum region and thus a smaller supercell. The dipole method should thus be preferred for large slab systems.

The calculated band structures of the  $\text{H}_2\text{O}$  sheet are shown in Fig. 3.5 for the

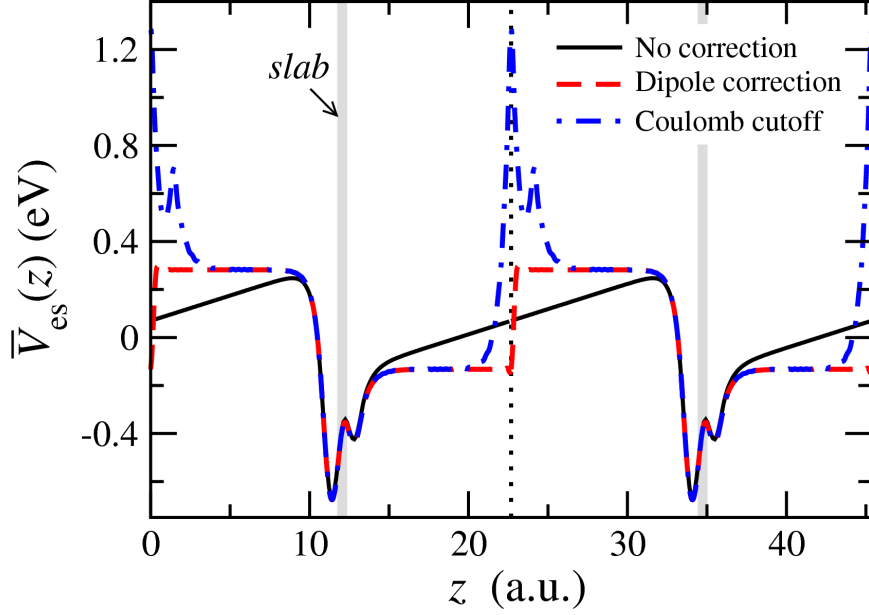


Figure 3.4: Planar average of the electrostatic potential ( $V_{\text{es}}$ ) for the water sheet with Coulomb cutoff, dipole and no correction. The positions of the periodic images of the water slab are shown as vertical gray lines. The vertical dotted line shows the position of the cell boundary in the middle of the vacuum region.

cases of (i) Coulomb cutoff, (ii) dipole correction and (iii) no correction. Similar to the case of the nonpolar Na sheet (Fig. 3.1), we observe differences only in the unoccupied states. In Fig. 3.5a for a small supercell, the Coulomb cutoff and dipole corrections agree for all occupied bands and the lowest unoccupied band within the whole Brillouin zone, and for the second lowest unoccupied band at k-points between X and M, while disagreeing for all other states. For convenience, we call the former *coincident* and the latter *non-coincident* states. By examining their wave functions, we find that all coincident states are well-localized bound states that decay to zero in the vacuum of the supercell (see the  $i = 1$  curve in Fig. 3.6a for an example), while all non-coincident states are delocalized and spread over the whole supercell (see the  $i = 3$  curve in Fig. 3.6a for an example). As a result, the two methods here do not work accurately for the overlapping non-coincident states and behave differently. In a larger supercell ( $c = 113$  a.u.), the non-coincident states in Fig. 3.5a become coincident states and both correction techniques coincide again.

The comparison between Fig. 3.5a and Fig. 3.5b shows that the non-coincident states in the small supercell ( $c = 23$  a.u.) are far from convergence and cannot be taken

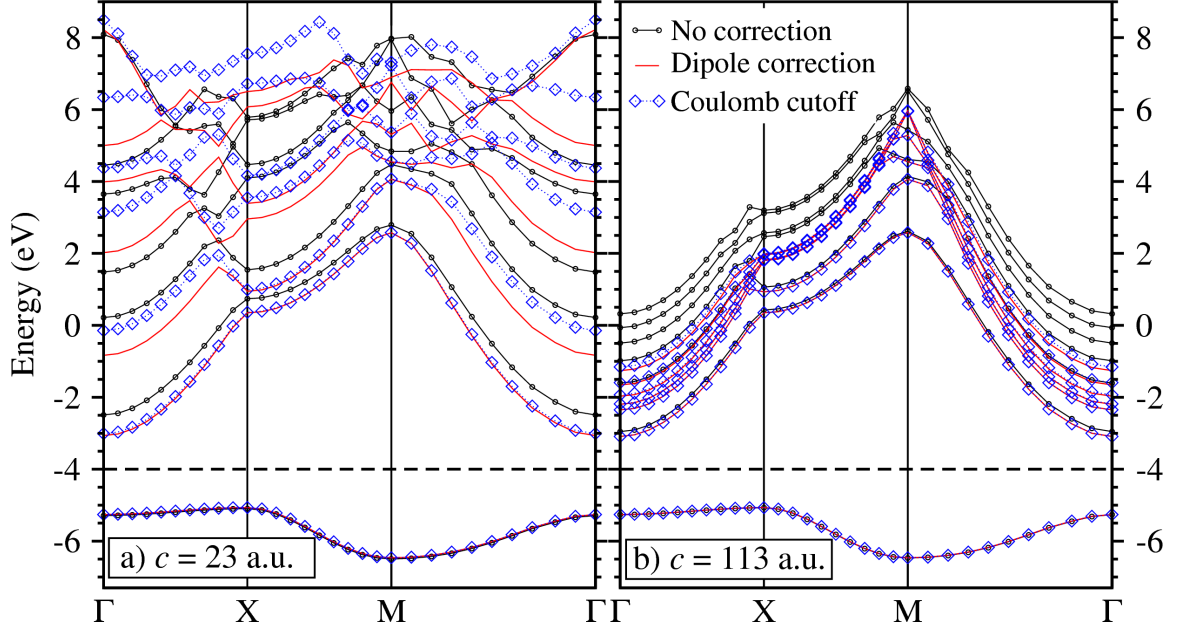


Figure 3.5: Band structures of the water sheet with Coulomb cutoff, dipole or no correction, in supercells with thicknesses of (a) 23 a.u. and (b) 113 a.u. The dashed line separates occupied states from the unoccupied ones. All band structures have been aligned so that the lowest occupied states coincide.

as correct band states. It follows that to obtain a converged band structure, especially for the unoccupied states, one needs a huge supercell even with Coulomb cutoff or dipole correction. Moreover, there also exist unbound non-coincident continuum states (not shown in the figure), which have higher energies and in principle need an infinitely large supercell to represent them. Strictly speaking, it is therefore impractical to calculate the high-energy band structure for an isolated polar slab using the supercell technique. However, in this work we are interested in low-energy unoccupied non-coincident states, which are well localized near the slab. The corrections made to the coincident states by both techniques are substantial in the small supercell, but become much smaller as the supercell size increases. For instance, the difference between the direct band gaps at  $\Gamma$  calculated with (2.23 eV) and without (2.73 eV) the correction is about 0.5 eV in the small supercell (Fig. 3.5a), but it is about 0.14 eV in the large supercell (Fig. 3.5b). This difference occurs because the empty coincident states are still spread out in the vacuum and are therefore substantially affected by the electric field in the vacuum region, which is due to periodic boundary conditions. The

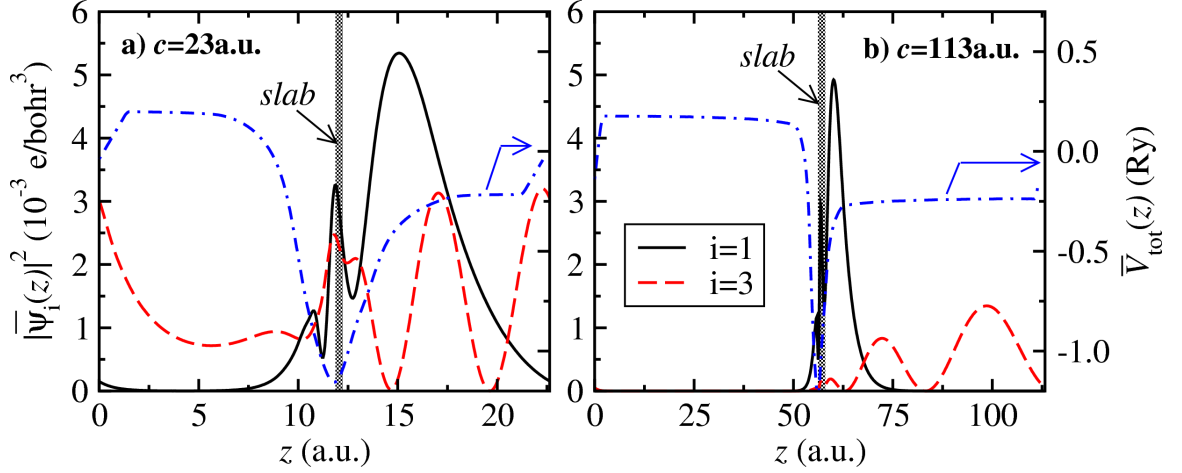


Figure 3.6: Plane-averaged electron densities associated with the first and third lowest unoccupied states at  $\Gamma$  of the water sheet along the aperiodic  $z$  direction in supercells of thicknesses (a) 23 a.u. and (b) 113 a.u. with dipole correction. The different vacuum potentials on the two sides of the polar slab result in a series of potential wells in the total potential of the periodically repeated supercell (see the dot-dashed blue curve). The third lowest conduction states in (b) are confined to the lower potential well in the vacuum region.

electric field obviously decreases as the length of the supercell is increased. After removing this field by either the Coulomb cutoff or the dipole correction, it is amazing to find that the corrected coincident bands in this small supercell ( $c = 23$  a.u., see Fig. 3.5a) are almost identical to the ones calculated in a much larger supercell ( $c = 113$  a.u., see Fig. 3.5b) and thus can be taken as converged results.

The above results show that the convergent results for well-localized bound states can be obtained with either Coulomb cutoff or dipole correction in a relatively small supercell. To distinguish these states from highly delocalized or unbound continuum empty states, one can simply perform calculations with both techniques and compare the respective results. In this way, one can confirm the convergence for states of interest without having to carry out calculations for several supercell sizes, thereby saving large amounts of computer time.

To assess the computational cost of the two corrections we show in Table 3.2 the average CPU time needed to run a single self-consistent iteration for a test system. The corrections increase only slightly the computational time compared to the “no correction” case, and they both cost about the same.

Table 3.2: Average CPU time in seconds for one self-consistent iteration with and without the corrections for a molecular sheet of water in a supercell of size  $5.67 \times 5.67 \times 113$  a.u. (25 bands and  $16 \times 16 \times 2$  kpoints are used for this test). All calculations are carried out on an IBM SP4, using from 1 to 8 CPUs.

| #procs | No Correction | Coulomb Cutoff | Dipole correction |
|--------|---------------|----------------|-------------------|
| 1      | 400           | 410            | 427               |
| 2      | 234           | 239            | 247               |
| 4      | 127           | 130            | 133               |
| 8      | 74            | 78             | 79                |

In general, our tests have shown that the dipole correction and the Coulomb cutoff techniques produce almost identical results for the total energy, force, charge density, electrostatic potential and the band structure. Therefore, we can conclude that the addition of a self-consistent dipole to screen the interaction between periodic replicas of a polar supercell leads to very accurate results. Actually, the additional external dipole layer in the vacuum can be seen as an effective capacitor. The charge on the plates of the capacitor produces an electric field that compensates the artificial electric field due to the PBC's imposed on the polar slab. The external field introduces a potential drop in the vacuum region where the wave functions are essentially zero and thus are not affected. Consequently, the whole supercell has a zero net dipole moment and all periodic interactions are effectively screened.

### 3.4 Comparison to Hartree-Fock theory

In order to confirm even more strongly the validity of the two techniques, we decided to follow an approach similar to that of Fu *et al.* [117], who carried out a Hartree-Fock (HF) calculation for genuinely isolated slabs with a localized basis set. They calculated the bulk spontaneous polarization  $P_s$  of ferroelectric BaTiO<sub>3</sub> from a bulk truncated slab with ideal ferroelectric distortions. Their HF result of 0.245 C/m<sup>2</sup> agrees well with the bulk value of 0.240 C/m<sup>2</sup> obtained independently with a Berry phase calculation [89], demonstrating that indeed one can recover the theoretical bulk value of polarization using genuinely isolated slabs.

However, a similar isolated slab calculation in density functional theory is ham-

pered by the fact that the DFT-LDA gap in BaTiO<sub>3</sub> is much too small. Due to the small band gap and the high value of polarization in bulk-truncated BaTiO<sub>3</sub> slab, Zener (inter-band) tunneling occurs [118, 119]. This results in metallicity for polar slabs thicker than three atomic layers, and thus in charge transfer from one side to the other. This transfer reduces the depolarization field and eventually leads to zero polarization as the thickness of the slab increases. Hence the bulk spontaneous polarization derived from a planar metallic slab is zero. This behavior is in contrast with the HF result, where the calculated band gap is much larger [120]. To circumvent this problem, we created fictitious bulk and slab structures of BaTiO<sub>3</sub> in which the ferroelectric distortions are artificially reduced to 1/10 of the physical ones. In this fictitious system, the corresponding polarization and depolarization fields are also reduced, and thus the slabs used in our DFT-LDA calculation for deriving bulk polarization are still insulators. We have performed polarization calculations with the reduced distortions using DFT-LDA with dipole correction. From the slab geometry we obtain  $P_s = 0.0230$  C/m<sup>2</sup>, in excellent agreement with the value of 0.0238 C/m<sup>2</sup> derived from Berry-phase calculations. Therefore we can conclude that the dipole correction (or equivalently the Coulomb cutoff formalism) yield results that are equivalent to the ones acquired for isolated slabs in a localized basis scheme [117].

As an additional example, we re-examine by using the dipole correction method in DFT-LDA, the surface properties (primary polarization) of isolated ferroelectric BaTiO<sub>3</sub> slab, which was previously studied by Fu et al.[117] within the scheme of *ab initio* Hartree-Fock theory with localized basis, enabling them to consider isolated slabs.

In the calculations, we adopt lattice constants (i.e.  $a_0 = 7.4251$  a.u. and  $c_0/a_0 = 1.0093$ ) of relaxed perovskite bulk BaTiO<sub>3</sub>. The values of ferroelectric distortion relative to fixed Ba are:  $\Delta(\text{Ti}) = -0.0118c_0$ ,  $\Delta(\text{O}_I) = 0.0184c_0$ , and  $\Delta(\text{O}_{II}) = 0.0123c_0$ . In slab calculations a fix vacuum length of six lattice constants ( $6c_0 = 45$  a.u.) is used for separating periodic replicas and is enough for the charge density, electrostatic potential, total energy and occupied bands to reach convergence.

Following the steps in ref.[117], we calculate spontaneous polarizations  $P_n$  for an  $n$ -layer bulk-truncated ferroelectric BaTiO<sub>3</sub> slab with asymmetric terminations (one TiO<sub>2</sub> and one BaO surfaces). In DFT-LDA with dipole correction applied, the spontaneous

polarization of the slab can be conveniently evaluated as

$$P_n = -\frac{\Delta V_n}{4\pi l_n} = -\frac{\Delta V_n}{2\pi n c_0}, \quad \text{or} \quad = \int_0^c \bar{\rho}_{\text{tot}}(z) z dz \quad (3.10)$$

where  $\Delta V_n$  is the planar averaged electrostatic potential difference across the slab, and  $l_n = n c_0/2$  is the thickness of  $n$ -layer slab. As shown in ref.[117],  $P_n$  can also be approximated as

$$P_n \approx \sigma_\infty + \frac{2p_\infty}{n c_0}, \quad (3.11)$$

where  $\sigma_\infty$  and  $p_\infty$  are two asymptotic constants of surface charges and surface dipoles, i.e., their values for  $n = \infty$  in our DFT-LDA calculation. The quantity  $P_\infty$  is related to bulk spontaneous polarization through electronic dielectric constant  $\epsilon_\infty$  as  $P_s = \epsilon_\infty P_\infty$ .

In Fig.3.7, we plot the calculated polarizations  $P_n$  as function of  $1/n$  for slabs of two to twelve atomic layers, and fit them by Eq.(3.11) with and without dipole correction. Without dipole correction, the intercept at the origin gives  $P_\infty = 0.018 \text{ C/m}^2$ , which corresponds to bulk spontaneous polarization of  $P_s = 0.110 \text{ C/m}^2$  far away from  $0.241 \text{ C/m}^2$  obtained in a Berry phase calculation [89]. With dipole correction,  $P_\infty = \sigma_\infty = 0.0 \text{ C/m}^2$ , which means zero spontaneous polarization for infinite ferroelectric BaTiO<sub>3</sub> slab. Hence, the bulk spontaneous polarization of  $0.241 \text{ C/m}^2$  cannot be recovered in the middle region of infinite long slab with bulk-truncated structure. It seems to be contrary to the Hartree-Fock calculation, from which the bulk properties are quickly obtained in the slab mid-region.

Actually, the above conclusion comes from fitting  $P_n$  as a function of  $n$  using Eq.(3.11), which is based on the assumption that surface dipoles and surface charges approach constant values as  $n$  increases, and that the bulk properties can be recovered quickly in the midregion of the slab. In other words, Eq.(3.11) assumes that the polarization  $P_n$  or depolarization field  $E_p$  in the slab midregion become invariant as the thickness of the bulk-truncated slab increases. In this case, the potential difference  $\Delta V_n$  across a polar slab, which equals the product of the depolarization field and the slab thickness at zero electric field (i.e.  $\Delta V_n = E_p \cdot l_n$ ), will increase infinitely as  $n \rightarrow \infty$ . This cannot occur in our real physical system because when  $\Delta V_n$  is greater than the band gap, the dielectric slab will undergo an electrical breakdown and become metallic [83], which is known as interband (or Zener) tunneling [118, 119]. Therefore there exists a critical thickness ( $d_c$ ) beyond which the insulating polar slab will turn into a metallic one. Once the slab becomes metallic, the

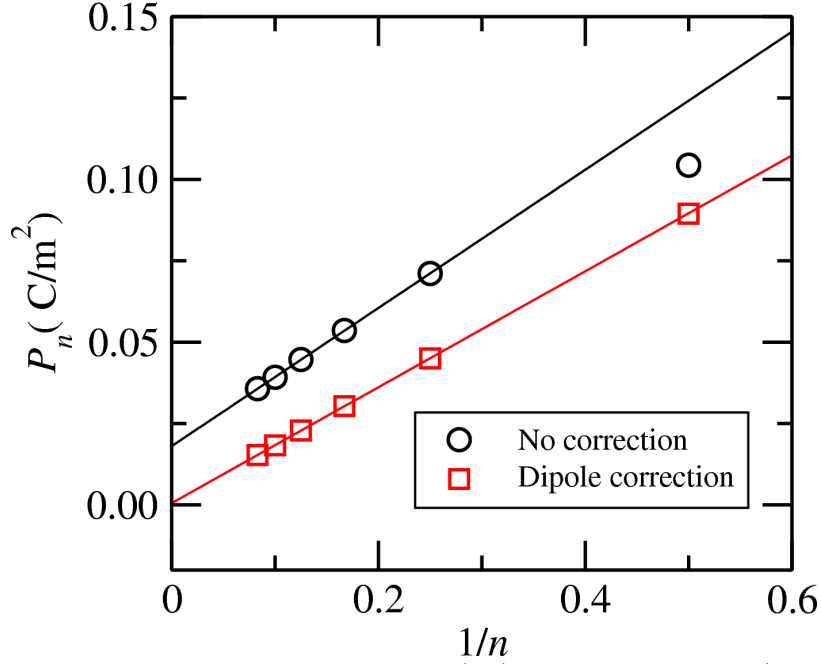


Figure 3.7: Dipole moment per unit volume ( $P_n$ ) as a function of  $1/n$  with and without dipole correction for isolated BaTiO<sub>3</sub> slabs. The solid lines represent two fits to Eq.(3.11). The two intercepts at the origin are 0.0 and 0.018 C/m<sup>2</sup>.

charges start transfer from one surface to the other. This charge transfer reduces polarization or the depolarization field in the slab and could lead to  $\Delta V_n$  becoming a constant, only related to the asymmetric surface properties of two sides, such as the work function. Hence the assumption of Eq.(3.11) is only valid for insulating slabs where charges are prohibited from transferring between the two surfaces, and is no longer true once the slab becomes metallic.

For an isolated BaTiO<sub>3</sub> slab with bulk-truncated geometry, its critical thickness can be estimated from the bulk band gap  $V_g$ , bulk electronic dielectric constant  $\epsilon_\infty$  and bulk spontaneous polarization  $P_s$  via

$$d_c = \frac{\epsilon_\infty V_g}{4\pi P_s}. \quad (3.12)$$

Using  $P_s = 0.241 \text{ C/m}^2$ ,  $V_g = 2.08 \text{ eV}$ , and  $\epsilon_\infty = 6.09$ , calculated for bulk BaTiO<sub>3</sub> with our DFT-LDA scheme, one obtains  $d_c = 8.8 \text{ a.u.}$ , larger than thickness  $c_0 = 7.5 \text{ a.u.}$  of a two-layer slab and less than  $2c_0$  of a four-layer slab. It suggests that bulk-truncated BaTiO<sub>3</sub> slab with more than three atomic layers will turn metallic. From our band structure

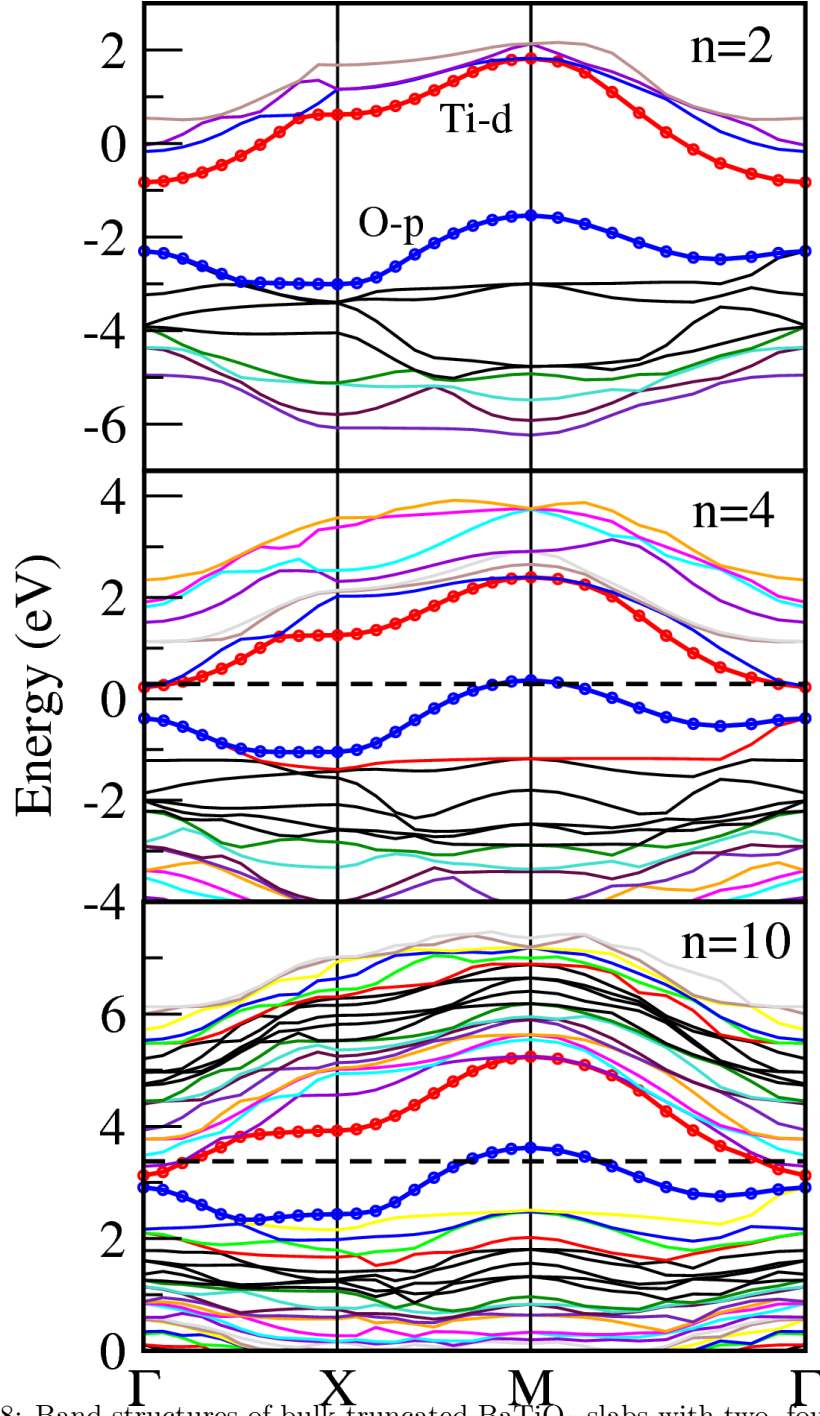


Figure 3.8: Band structures of bulk-truncated  $\text{BaTiO}_3$  slabs with two, four and ten atomic layers. The dashed lines mark the Fermi energies and surface states near the respective Fermi energies are highlighted by dotted curves.

calculations for BaTiO<sub>3</sub> slab with two, four and ten layers (shown in Fig.3.8), one can find that a two-layer slab is insulating and slabs with four and ten layers are metallic. Their band structures are similar to BaTiO<sub>3</sub> slabs with both sides terminated by TiO<sub>2</sub> surfaces [112]. At  $n = 2$ , the highest valence band is the O-p state in the TiO<sub>2</sub> surface layer and the Ti-d state in this layer corresponds to the lowest unoccupied band. As  $n$  increases, Ti-d states in the TiO<sub>2</sub> surface layer move down to the mid-band-gap and cross the Fermi energy level at  $\Gamma$  point. At the same time, the O-p states in the TiO<sub>2</sub> subsurface layer on the other side of slab move upward to the mid-band-gap and cross the Fermi energy level at the M k-point. Both Ti-d and O-p states become partially occupied and conducting then. The charge exchange between these states leads to global charge transfer across the slab, compensating the depolarization field.

As the BaTiO<sub>3</sub> slab becomes metallic, the net change of potential across the slab with  $n \geq 4$  (see Fig. 3.9) approaches quickly a constant (4.11 eV), which is of the same order of magnitude as the bulk band-gap (2.08 eV). Therefore, it is physically true that the calculated asymptotic value of polarization goes to zero as  $\Delta V/4\pi l_n \rightarrow 0$  with  $l_n \rightarrow \infty$ , and the surface charge density of slab cannot allow for bulk spontaneous polarization. In the Hartree-Fock calculation, the bandgap could be more than six times larger than the one from DFT-LDA calculation [120]. From Eq.(3.12), one can see that this big bandgap in Hartree-Fock calculation makes the slab with  $n \leq 12$  still insulating and the assumptions of Eq.(3.11) can apply. Hence it is also true in Hartree-Fock calculation that the bulk-properties are recovered in the midregion of the slab at a relatively small number of layers  $n$ .

To confirm the above argument, we perform the same calculations in the scheme of DFT-LDA with dipole correction for artificial BaTiO<sub>3</sub> bulk and slab structures in which the ferroelectric distortions are artificially reduced to 1/10 of the real ones adopted above. In this fictitious system, the corresponding polarization and depolarization field are then also reduced and the critical thickness of slab is so long that slabs with  $n \leq 10$  still remain insulating. The fit of  $P_n$  versus  $1/n$  for the dipole correction results in Fig.3.10 gives the asymptotic value of polarization  $P_\infty = \sigma_\infty = 0.00345$  C/m<sup>2</sup>. Using  $\epsilon_\infty = 6.67$  calculated within our DFT-LDA scheme we deduce that  $P_s = 0.0230$  C/m<sup>2</sup>, in excellent agreement with the value of 0.0238 C/m<sup>2</sup> obtained from our Berry-phase calculations. Without dipole correction, we get that  $P_\infty = 0.0135$  C/m<sup>2</sup> and  $P_s = 0.0899$  C/m<sup>2</sup>, which is almost four

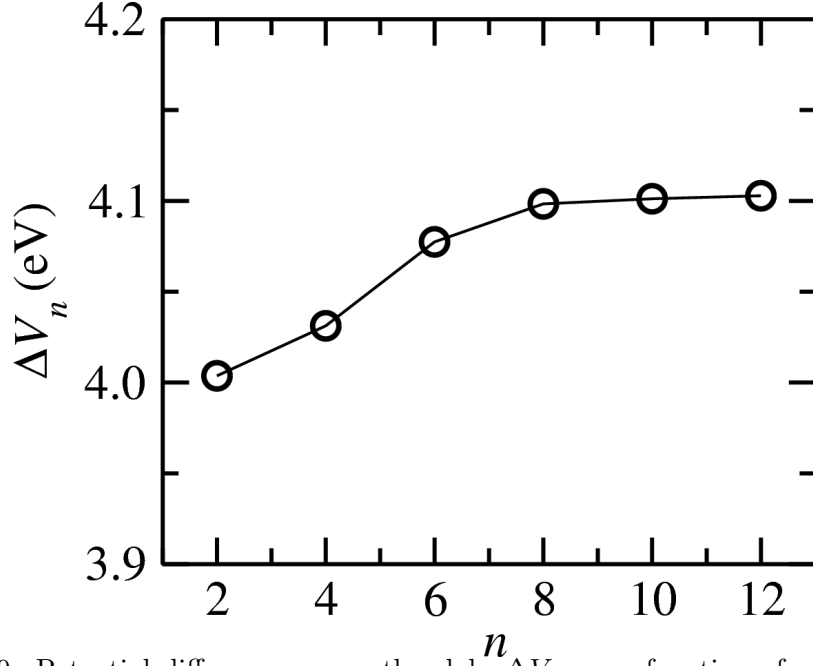


Figure 3.9: Potential difference across the slab,  $\Delta V_n$ , as a function of  $n$ , calculated from DFT-LDA with dipole correction for isolated BaTiO<sub>3</sub> slabs with bulk-truncated geometries.

times of the bulk polarization calculated from the Berry phase. This suggests that the dipole correction is essential for slab calculations within DFT-LDA scheme. Therefore, in this situation, the dipole correction implemented DFT-LDA yields equivalent results for isolated slabs as a calculation with localized basis set, analogous to a Hartree-Fock calculation [117], which proves once again that the dipole correction works well and can also simulate a truly isolated slab accurately.

Since dipole correction is shown to be able to remove all spurious interactions, our result also illustrates that an isolated ferroelectric BaTiO<sub>3</sub> with bulk-truncated structure can not exist in the vacuum at zero field (i.e. open circuit boundary condition). After structural relaxation with dipole correction, it has been confirmed that a ferroelectric BaTiO<sub>3</sub> or PbTiO<sub>3</sub> slab becomes paraelectric and has zero net dipole moment due to strong depolarization field [111]. On the other hand, an isolated nonpolar or polar dielectric slab could also turn metallic in finite electric field [115] during DFT-LDA calculation, and its dielectric properties would change essentially as well. So to determine the dielectric properties of an isolated slab in finite electric field, it is crucial to check if the slab becomes metallic and to

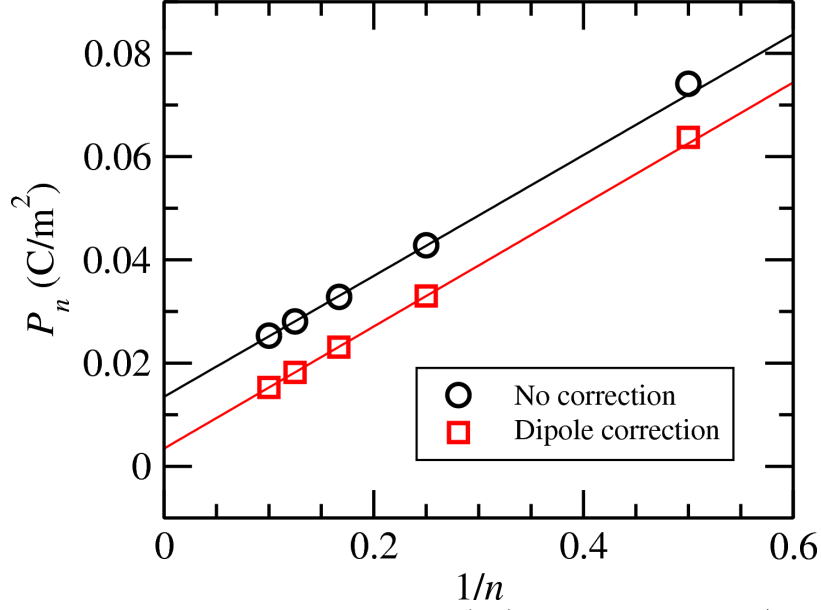


Figure 3.10: Dipole moment per unit volume ( $P_n$ ) as a function of  $1/n$  with and without dipole correction for isolated  $\text{BaTiO}_3$  slabs with ferroelectric distortion reduced to 1/10 of the real relaxed one. The solid lines represent two fits with Eq.(3.11). The two intercepts at the origin are 0.0135 and 0.00345 C/m<sup>2</sup>.

find out the range of the electric fields in which the slab's polarization scales linearly [121].

### 3.5 Conclusions

This work shows that the dipole correction and the Coulomb cutoff formalism techniques are equally effective in eliminating the spurious interactions between periodic images of polar supercells. The results of either technique are equivalent to the ones that would be obtained for isolated slabs, as previously demonstrated in HF calculations with a localized orbital basis. In general, we conclude that both techniques have different relative strengths, which can be exploited in different contexts: The Coulomb cutoff formalism can be applied not only to slab geometries, but also to arbitrary-shape nanostructures. However, for slab geometries the dipole correction is preferred because a smaller supercell is sufficient for achieving convergence. Moreover, electric fields can be trivially included in the dipole correction method.

Finally, it is found that both corrections have essentially no influence on occupied

band states and affect only unoccupied bands. The corrections made to the electrostatic potentials by using the two methods differ only in the mid-region of the vacuum. Therefore, for those highly delocalized states which extend to the mid-vacuum-region, the two methods differ and do not work correctly. By comparing the results of dipole and Coulomb cutoff corrections, the highly delocalized unoccupied states can be easily distinguished from localized bound states in a relatively small supercell calculation. This identification is important when determining excited states and optical properties from slab calculations. In general, careful convergence studies should be performed when calculating properties involving unoccupied electronic states. Judicious comparisons between the results of the two corrections make this task much easier and less costly.

## Chapter 4

# Dielectric properties of polypropylene/metal-oxide interfaces

Nanoscale-resolved dielectric properties of polypropylene / metal-oxide (alumina,  $\text{PbTiO}_3$ ) interfaces and of the corresponding surfaces are investigated via first-principles calculations. In order to ascertain the locality of the atomically-resolved permittivity profiles, we propose a simple procedure to directly evaluate the real-space decay length of nonlocal effects in the dielectric susceptibility. Based on this decay length, the microscopic dielectric response is derived by using a convolution of rectangular and gaussian filters as the averaging weight function. This procedure converges quickly to the bulk values in slabs of only moderate thicknesses, while providing atomic-layer-resolved permittivity profiles even in the presence of significant relaxations and surface structure. Our results show that (i) the surface- and interface-induced modifications to the dielectric permittivity in polymer/metal-oxide composites are localized to only a few atomic layers; (ii) the interface effects are mainly confined to the metal-oxide side; and (iii) metal-oxide particles larger than a few nanometers should retain the average macroscopic value of their bulk dielectric permittivity.

## 4.1 Introduction

Recently, the growing need for high-power energy density capacitors and electrical energy storage devices has stimulated intensive research efforts on polymer-ceramic nanocomposites in which metal oxide nanoparticles are incorporated into a polymer matrix [11, 12, 3, 14, 15]. Polymers such as polypropylene generally have high dielectric strength, good flexibility and easy processability at low temperatures, but also have a low dielectric constant which limits their ability to store energy. On the other hand, metal oxides, such as ferroelectric  $\text{PbTiO}_3$ , possess very high dielectric permittivity, but are brittle, have low dielectric breakdown fields and need high temperature sintering. When these two materials are integrated into a nanocomposite, they offer the possibility of achieving high energy and power densities, potentially enabling a broad range of applications in aerospace, automotive and power industries [3].

The combination of the high- $k$  metal-oxide nanoparticles with polymers usually results in an effective composite dielectric permittivity,  $\epsilon$ , higher than the pure polymer matrix and lower than the nanoparticles [11]. The general understanding of the role of interface effects is currently still limited to a qualitative level [3, 23], and is mainly based on classical approximations such as various mixing models [21], and the classical effective medium method [22]. However, as the incorporated particles shrink to nanometer sizes, their dielectric properties may become quite different from the corresponding bulk materials. The large interfacial area also leads to significant interfacial volume, which may affect the properties of both the nanoparticles and the polymer. These effects are investigated at the microscopic, quantum-mechanical level in this work.

Recently, Giustino and Pasquarello [121] developed a first-principles theory for investigating atomic-scale permittivity profiles across interfaces between insulators. It has been successfully applied to several systems, such as  $\text{Si}/\text{SiO}_2$  [121],  $\text{SiO}_2/\text{C}_{12}\text{H}_{25}\text{-chain}$  [122], and metal/ $\text{SrTiO}_3$  interfaces [123]. In this theory, a local susceptibility is introduced to describe variations of the dielectric response over length scales of the order of interatomic distances. It assumes that the nonlocality of the microscopic susceptibility tensor occurs at smaller distances. In fact, this assumption may not be always true. For a homogeneous system, as already shown by Giustino and Pasquarello [121], the typical real-space decay length  $\xi$  of the nonlocal effects in the dielectric function is *larger* than the spreads of

maximally localized Wannier functions [124]. The latter are usually of the order of interatomic distances [125]. In particular, for a system where the lattice contribution dominates the low-frequency dielectric response, we will show that the decay length  $\xi$  can be much larger than an interatomic distance. Furthermore,  $\xi$  may differ substantially between systems. Therefore, to properly average and obtain nanoscale-resolved, local and physically meaningful permittivity profiles, one needs to determine the decay length  $\xi$  of the nonlocal susceptibility for each specific system under investigation.

In this work, we will evaluate  $\xi$  directly by calculating the spatial spread of the charge density induced by slightly displacing each non-equivalent atom from its equilibrium position. Using the calculated  $\xi$ , we introduce a modified averaging model that ensures the locality of the dielectric permittivity profile extracted from *ab initio* calculations, while efficiently filtering out the physically uninteresting oscillations due to the lattice periodicity. The resulting profiles are flat in the bulk-like region and atomically smooth in the interface and surface regions, while still providing nanoscale resolution.

The main goal of the present work is to investigate the local dielectric permittivity profiles of polymer/metal-oxide nanocomposites, which are being considered for high power density capacitors. These composites would combine the advantages of polymers, which are light, flexible and can withstand high electric fields, but have low dielectric constants, with those of oxides, which are usually brittle and heavy, with low breakdown fields, but their dielectric constants are usually much larger. A composite material, consisting of oxide particles embedded in a polymeric matrix, would avoid the brittleness of the bulk oxides while still taking advantage of their large dielectric constants. We choose isotactic polypropylene (iPP) as the host polymer matrix, because it is one of the most commonly used capacitor dielectrics. For metal oxides, we select alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and tetragonal PbTiO<sub>3</sub>, representing two categories of materials of current interest, a non-ferroelectric and a high- $k$  ferroelectric. We calculate the optical and static dielectric permittivity profiles across both single bare slabs of these materials and of their interfaces with iPP, with the goal of understanding the nanoscale variation of surface- and interface-induced changes to the local dielectric properties. These quantities, which may be very hard to measure, are needed for accurate mesoscopic modeling of dielectric properties of the complex nanocomposites [126].

The rest part of this chapter is organized as follows. In section 4.2, we briefly

review the theory of local dielectric permittivity theory, focusing on aspects important to nanoscale averaging. Section 4.3 describes the procedures used to evaluate of the decay length  $\xi$  of the microscopic susceptibility and to obtain the permittivity profiles. Section 4.4, Results, introduces and discusses the dielectric permittivity profiles across metal-oxide and iPP slabs and their interfaces. The summary and conclusions of the paper are presented in Section 4.5.

## 4.2 Theory of local dielectric permittivity

In the following we assume that the interface is oriented along the  $z$  axis and each material is periodic in the plane parallel to interface, referred as the  $xy$ -plane. Focusing on the dielectric permittivity across the surface or interface, we eliminate the in-plane dependence by taking a planar average of the corresponding microscopic quantity, e.g., for the charge density we define  $\bar{\rho}(z) = \frac{1}{S} \int_S \rho(\vec{r}) dx dy$ , where  $S$  is the area of the  $xy$  cross section of the unit cell. This transverse averaging has no effect on the Poisson equation [127]. Starting from the plane-averaged quantities and following Giustino and Pasquarello [121], we derive elements of the local dielectric permittivity theory, focusing on the connection between microscopic and macroscopic quantities.

At the microscopic scale in the linear regime, the susceptibility  $\chi(z, z')$  and permittivity  $\varepsilon(z, z')$  are defined through

$$\bar{D}(z) = \int \varepsilon(z, z') \bar{E}(z') dz', \quad (4.1)$$

and

$$\bar{P}(z) = \int \chi(z, z') \bar{E}(z') dz', \quad (4.2)$$

which are related to each other by

$$\varepsilon(z, z') = \delta(z - z') + 4\pi\chi(z, z'). \quad (4.3)$$

In Eq.(4.1)-(4.2),  $\bar{P}(z)$  and  $\bar{E}(z)$  correspond to the induced polarization [128] and the change of the total electric field due to an applied external field. They can be obtained from the induced charge density using

$$\frac{d}{dz} \bar{E}(z) = 4\pi \bar{\rho}_{\text{ind}}(z) \quad (4.4)$$

and

$$\frac{d}{dz}\bar{P}(z) = -\bar{\rho}_{\text{ind}}(z). \quad (4.5)$$

The microscopic electric displacement  $\bar{D}(z)$  in Eq.(4.1) is defined as  $\bar{D}(z) = \bar{E}(z) + 4\pi\bar{P}(z)$  and satisfies

$$\frac{d}{dz}\bar{D}(z) = 0, \quad (4.6)$$

which shows that  $\bar{D}(z)$  is a constant.

The microscopic permittivity  $\varepsilon(z, z')$  and susceptibility  $\chi(z, z')$  as defined in Eq. (4.1)-(4.2) are nonlocal and usually vary very rapidly over interatomic distances. In order to obtain measurable local dielectric properties from the microscopic quantum-mechanical results, a spatial averaging procedure needs to be adopted. Denoting the averaging distance as  $r_0$ , it must be significantly larger than the interatomic distance, so that the dielectric response function can be considered local. For nanostructures, in order to obtain a physically transparent position-dependent local dielectric permittivity near a surface or an interface,  $r_0$  needs to be as small as possible, but it should not be smaller than the decay length  $\xi$  of the nonlocal susceptibility.

In terms of these properly averaged quantities, Eqs.(4.1) and (4.2) can simplify to

$$\bar{\bar{D}}(z) = \varepsilon(z)\bar{\bar{E}}(z) \text{ and } \bar{\bar{P}}(z) = \chi(z)\bar{\bar{E}}(z), \quad (4.7)$$

where the double bars indicate the averages taken over the  $xy$ -plane and  $z$  direction. Naturally, Eq.(4.7) defines our local dielectric permittivity and susceptibility.

In practical applications, considering that  $\bar{\bar{D}}(z)$  is continuous, it is convenient to express the local permittivity in terms of the polarization  $\bar{\bar{P}}(z)$ , i.e.

$$\varepsilon(z) = 1 + 4\pi\chi(z) = 1 + \frac{4\pi\bar{\bar{P}}(z)}{D - 4\pi\bar{\bar{P}}(z)}, \quad (4.8)$$

where  $D$  is the external field of a finite system. For an extended system,  $D = E_{\text{av}} + 4\pi P$ , where  $E_{\text{av}}$  corresponds to the average self-consistent electric field, and  $P$  is the field-induced macroscopic polarization in the supercell. The latter can be determined by Berry phase method [89]. Thus, Eq. (4.8) together with Eq. (4.5) establish a direct link between the induced charge density and the local permittivity. By calculating  $\bar{\rho}_{\text{ind}}(z)$  with the atoms fixed or relaxed in the finite electric field, we can obtain the corresponding optical and static permittivity profiles.

In addition to the above, Giustino and Pasquarello [121] also analyzed the local permittivity in terms of discrete effective electronic and ionic polarizabilities. For the electron charge density, decomposition into maximally localized Wannier functions [124] provides a discrete representation of the local contributions. They define the effective electronic polarizability  $\alpha_{\text{elec}}^{(n)}$  for each Wannier function by relating its induced dipole to the electric field at its center  $z_n$ :

$$e(z_n^E - z_n^{E=0}) \equiv \alpha_{\text{elec}}^{(n)} \bar{\bar{E}}(z_n). \quad (4.9)$$

This definition relates the variation of the dielectric response to the specific features of the local bonding arrangement.

In analogy with  $\alpha_{\text{elec}}^{(n)}$ , they also define the effective ionic polarizability as

$$\sum_{\beta} Z_{I,z\beta}^D (R_{I\beta}^E - R_{I\beta}^{E=0}) \equiv \alpha_{\text{ion}}^{(I)} \bar{\bar{E}}(R_{Iz}), \quad (4.10)$$

where  $R_{I\beta}$  and  $Z_{I,z\beta}^D$  represent the coordinate and the dynamical charge of the ion  $I$ . The dynamical charge is determined from the linear relation between the force on an atom  $F_{I\beta}$  and the effective local field  $\bar{\bar{E}}_z$ ,

$$Z_{I,z\beta}^D \equiv \frac{\partial F_{I\beta}}{\partial \bar{\bar{E}}(R_{Iz})}. \quad (4.11)$$

In our calculations, based on  $\alpha_{\text{ion}}^{(I)}$ , we also define an effective layer ionic polarizability by

$$\alpha_{\text{layer}} \equiv \frac{1}{S} \sum_I \alpha_{\text{ion}}^{(I)}, \quad (4.12)$$

where  $S$  is the transverse area of the simulation cell and the summation is over all atoms belonging to the same layer. The Eq. (4.12) is well justified because  $\bar{\bar{E}}$  is almost the same for all the atoms belonging to the same layer.

In Eqs. (4.9-4.10), the  $\alpha_{\text{elec}}^{(n)}$  and  $\alpha_{\text{ion}}^{(I)}$  describe the extent of electronic and ionic contributions to the local polarization around the center of the Wannier function or the ion, respectively. However, because of non-locality, the contributions of nearby Wannier functions and ions should also be considered when evaluating the local permittivity at a given position, depending on the decay length of the nonlocal microscopic susceptibility. For a layered structure, the neighboring layers should also be included.

## 4.3 Methodology and calculations

### 4.3.1 Evaluation of the decay length of the nonlocal susceptibility

As seen in Sec.4.2, the local dielectric permittivity should be obtained from a suitable averaging procedure. Only when the average is taken over a distance  $r_0$  that is larger than the decay length  $\xi$  of the microscopic susceptibility, can the derived permittivity profiles be considered local and physically meaningful. The determination of  $\xi$  is thus the key for ascertaining the locality of the derived permittivity profile.

The microscopic susceptibility  $\chi(\mathbf{r}, \mathbf{r}')$  can be equivalently defined as the linear response of the charge density  $\delta\rho(\mathbf{r})$  to an external potential perturbation  $\delta V_{\text{ext}}(\mathbf{r}')$ , i.e.,

$$\delta\rho(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta V_{\text{ext}}(\mathbf{r}') d\mathbf{r}', \quad (4.13)$$

which can be formally written in term of a functional derivative

$$\chi(\mathbf{r}, \mathbf{r}') = \frac{\delta\rho(\mathbf{r})}{\delta V_{\text{ext}}(\mathbf{r}')} . \quad (4.14)$$

From this definition, for a given very localized external potential disturbance at position  $\mathbf{r}'$ , the corresponding induced charge density  $\delta\rho$  at  $\mathbf{r}$  characterizes the nonlocality of the microscopic susceptibility  $\chi(\mathbf{r}, \mathbf{r}')$ . The spatial decay of  $\delta\rho$  can then be used to obtain the decay length  $\xi$  of  $\chi(\mathbf{r}, \mathbf{r}')$ . We therefore evaluate  $\xi$  directly from the decay of the induced charge density by displacing an ion by a very small amount  $\Delta u$  from its equilibrium position in a supercell, resulting in a very localized dipolar external potential that quickly screened by the electrons. The supercell is chosen large enough that the induced charge density does not overlap between the cells.

In general, the induced charge density profile  $\delta\rho(\mathbf{r})$  in an insulator should have a small, but slowly decaying tail, corresponding to screening by the finite dielectric constant. However, in density functional theory the screening is rather rapid [129], both when using LDA or GGA. In our supercells we observe a rather rapid decay, sometimes with small oscillations, which still decay to zero before reaching the supercell boundary. In order to provide a physically meaningful lower bound of nonlocality of  $\chi(\mathbf{r}, \mathbf{r}')$ , we define  $\xi$  due to a particular atom as spatial extent the region containing 95% of  $|\delta\rho|$ , *viz.*

$$\int_{z_0-\xi/2}^{z_0+\xi/2} |\delta\rho(z)| dz / \int_L |\delta\rho(z)| dz = p = 95\%, \quad (4.15)$$

where  $z_0$  is the  $z$  coordinate of the atom being displaced and  $L$  is the supercell size along  $z$ .

In fact, the above method for obtaining  $\xi$  corresponds to calculating the broadening width of a dynamical charge [130] for a given atom along a certain direction. Within a linear regime, the dynamical charge and its broadening width (*i.e.*,  $\xi$ ) show little dependence on the magnitude of  $\Delta u$  for the same atom at different  $\mathbf{r}$ , even for a nonuniform material. This is shown in Fig. 4.1, where the  $\xi$  is calculated by displacing atoms at different positions with varying  $\Delta u$  in an isolated (001) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> slab. In principle, the smaller  $\Delta u$  correspond to a more localized disturbance and should yield more accurate  $\xi$ . Nevertheless, for consistency with permittivity calculations, we choose  $\Delta u$  to be the maximum atomic displacement caused by the electric field used for deducing dielectric functions. However, the dynamical charge and its broadening width are different for atoms with different numbers of valence electrons and ionicities. For example, by displacing Al and O atoms we find  $\xi = 8.9$  and  $4.3$  *bohr*, respectively. To ensure the locality of the dielectric permittivity everywhere in the slab considered in the next sections, we choose the maximum  $\xi$  of all atoms in our averaging procedure.

### 4.3.2 Nanoscale averaging model

The averaging procedure can be explicitly defined by using a real normalized weight function  $f$ , which satisfies

$$\int f(z - z') dz' = 1; \quad f(z - z') = 0, \quad |z - z'| > r_0. \quad (4.16)$$

For the electric field we then have

$$\bar{\bar{E}}(z) = \int \bar{f}(z - z') \bar{E}(z') dz'. \quad (4.17)$$

Eq.(4.17) shows that  $\bar{\bar{E}}(z)$  depends on the choice of the  $f$ . The electric displacement is invariant after any averaging because of Eq.(4.6), *i.e.*,  $\bar{\bar{D}}(z) = \bar{D}(z)$ . As a result, the dielectric permittivity derived from Eq.(4.7) is not unique and depends on the choice of the weight function  $f$ .

In actual calculations two kinds of weight functions are commonly used. One is a rectangular filter [131]

$$f_l(z) = \frac{1}{l} \Theta\left(\frac{l}{2} - |z|\right), \quad (4.18)$$

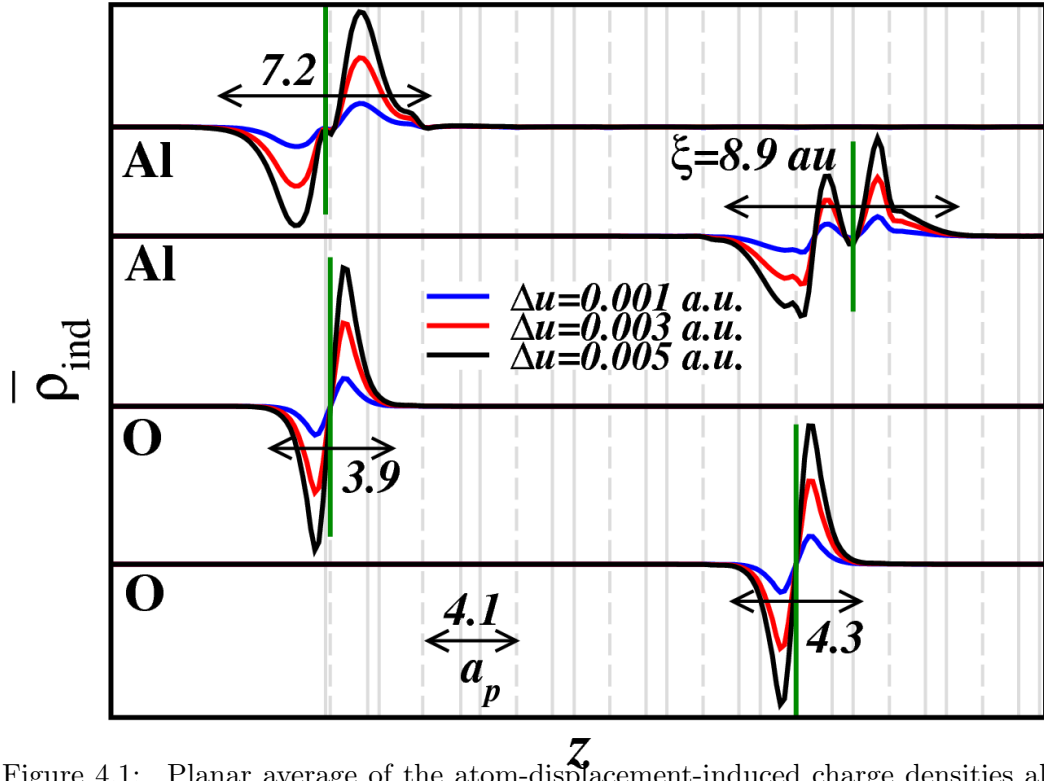


Figure 4.1: Planar average of the atom-displacement-induced charge densities along  $z$  in a  $(001)\alpha\text{-Al}_2\text{O}_3$  slab. Vertical lines indicate planes of O (dashed line) and Al (solid line) atoms. The green vertical segments denote the positions of the atoms being moved. The periodic interlayer distance in the middle of slab is indicated as  $a_p$ .

where  $\Theta$  is a unit-step function and  $l$  is the layer periodicity. The  $f_l$  is best suited for a superlattice composed of undistorted crystalline layers. However, for a system with varying planar distances, this method is not efficient in filtering oscillations that are due to different layer spacings. The other commonly used function is the Gaussian broadening kernel [121]

$$f_\sigma(z) = \frac{1}{\sqrt{2\pi}\sigma} e^{-z^2/2\sigma^2}, \quad (4.19)$$

which is continuous at any  $z$  and suitable for disordered systems with only short-range order. However, since  $f_\sigma$  does not explicitly include the periodic lattice spacing information, it is less efficient in flattening the permittivity profile in the bulk-like region away from the interface.

In this work, we are mainly dealing with crystalline slabs, which usually contain uniformly spaced atomic planes in the regions far away from surfaces or interfaces, while near surfaces or interfaces this spacing becomes non-uniform. The slab must be thick enough to recover bulk permittivity in its middle region, but we are particularly interested in the widths of the surface or interface regions. Efficient averaging, which would quickly lead to a flat permittivity profile in the middle of the slab while preserving the main features in the surface and interface regions would thus provide maximum physical insight and minimize the computational expense. We thus choose as  $f$  a convolution of the two broadening functions

$$f_{l\sigma}(z) = \int f_l(z - z') f_\sigma(z' - z'') dz' dz''. \quad (4.20)$$

Similarly to the decay length of the induced charge density, there is also some arbitrariness in defining the broadening width  $r_0$  of this convolution. In order to be consistent with the numerical definition of  $\xi$ , we define  $r_0$  through Eq.(4.15), with  $|\delta\rho(z)|$  replaced by  $f_{l\sigma}(z)$ . To ensure the locality of the extracted dielectric functions, we further require that

$$r_0 \geq \xi. \quad (4.21)$$

In our calculations,  $l$  is set to the lattice spacing of the bulk region away from the surface or interface, and  $\sigma$  is then constrained by the above condition (Eq.(4.21)). To confirm that  $f_{l\sigma}(z)$  satisfies Eq.(4.21) for the particular choices of  $l$  and  $\sigma$ , we also validate this condition visually by plotting normalized  $|\delta\rho|$  and  $f_{l\sigma}$  in the same figure and centered at the same position. This procedure provides a robust lower bound of  $\sigma$  that satisfies Eq.(4.21).

Table 4.1: Bulk dielectric constants and lattice parameters for monoclinic iPP, hexagonal  $\text{Al}_2\text{O}_3$  and tetragonal  $\text{PbTiO}_3$ . GGA was used for iPP and  $\text{Al}_2\text{O}_3$ , and LDA for  $\text{PbTiO}_3$ . See text.

|                    | iPP        |       | $\text{Al}_2\text{O}_3$ |           | $\text{PbTiO}_3$ |       |
|--------------------|------------|-------|-------------------------|-----------|------------------|-------|
|                    | Expt.[133] | Calc. | Expt.[134]              | Calc.     | Expt.[135]       | Calc. |
| $a(\text{\AA})$    | 6.65       | 6.73  | 4.76                    | 4.77      | 3.91             | 3.86  |
| $b$                | 20.96      | 21.13 | —                       | —         | —                | —     |
| $c$                | 6.51       | 6.53  | 12.99                   | 13.04     | 4.14             | 4.01  |
| $\alpha(^{\circ})$ | 99.30      | 99.17 | —                       | —         | —                | —     |
| $\epsilon(\infty)$ | 2.30       | 2.25  | 3.25                    | 3.22      | 7.13             | 7.24  |
| $\epsilon(0)$      | 2.20-3.35  | 2.30  | 9.4,11.6                | 9.8, 12.2 | 32-35            | 36.4  |

The actual averaging with  $f_{l\sigma}$  is easily carried out in reciprocal space, by multiplying each Fourier coefficient with the weight

$$f_G = \frac{\sin(Gl/2)}{Gl/2} e^{-G^2\sigma^2/2}. \quad (4.22)$$

### 4.3.3 Calculations

The calculations were performed using density functional theory and ultrasoft pseudopotentials, as implemented in the QUANTUM-ESPRESSO package [77]. For alumina and iPP slabs and their interfaces, we use the exchange and correlation functional in the generalized gradient approximation (GGA). For the  $\text{PbTiO}_3$  slab and  $\text{PbTiO}_3/\text{iPP}$  interface, the local density approximation is used, because the GGA catastrophically overestimates both equilibrium volume and  $c/a$  of  $\text{PbTiO}_3$  [132]. The wave functions and the augmented charge density are represented by plane-wave basis sets with energy cutoffs of 30 and 300 Ry, respectively. All atoms in the supercell are relaxed until the atomic forces are less than 3 meV/ $\text{\AA}$ . Our calculated bulk dielectric constants and lattice parameters of  $\alpha\text{-Al}_2\text{O}_3$ , tetragonal  $\text{PbTiO}_3$  and monoclinic iPP are in excellent agreement with experimental ones (see Table 4.1).

The slab structures used to investigate the oxide surfaces and oxide/polymer interfaces are constructed in an orthorhombic supercell, with periodically repeated slabs or stacked films separated by a 20  $\text{\AA}$  vacuum region along the  $z$ -axis. We derive the optical and static local dielectric profiles from Eqs.(4.7) as described in Section II. The induced charge densities appearing in Eqs.(4.4)-(4.5) are calculated as differences between the to-

tal charge densities corresponding to two oppositely directed macroscopic electric fields of  $\pm 0.001$  a.u.. The finite electric field can be applied by either using the dipole correction method [104, 111], or the method based on Berry-phase theory of polarization [136, 137]. Here we choose the former one, because it removes well the artificial periodic image interactions due to supercell approach [138], while avoiding the convergence issues related to the latter method [139].

## 4.4 Results and discussion

In this section we first consider metal oxide slabs in vacuum, which enable analysis of permittivity profiles near surfaces, for both paraelectric ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and ferroelectric (PbTiO<sub>3</sub>) slabs. We also examine a polypropylene slab, to establish its permittivity profile. In the last subsection we analyze the metal-oxide/polymer interfaces, and compare their dielectric profiles to those of the constituent materials. The computed profiles can also be used in mesoscopic modeling of dielectric properties of nanocomposites.

### 4.4.1 Metal-oxide slabs

#### $\alpha$ -Al<sub>2</sub>O<sub>3</sub> slabs

For alumina, we consider two surfaces, the single-O-layer-terminated (110) and the single-Al-layer-terminated (001) surface. From bond-counting rules of Harrison [140], both surfaces should be chemically stable and charge neutral. The latter surface has been observed in the experiment [141]. The relaxed surface structures in our calculations agree very well with other *ab initio* calculations [142].

For both kinds of slabs, our calculated  $\xi$ 's (5.9 *bohr* for (110)-slabs and 8.9 *bohr* for (001)-slabs) are found to be larger than their layer stacking periodicities (4.5 *bohr* for (110)-slabs and 4.1 *bohr* for (001)-slabs). To obtain the local dielectric permittivities, we choose the averaging weight functions, as described in Sec.4.3.2, with  $l = 4.5$  *bohr* and  $\sigma = 1.2$  ( $r_0 = 6.8$  *bohr*) for the (110)slabs, and  $l = 4.1$  *bohr* and  $\sigma = 3.0$  ( $r_0 = 12.7$  *bohr*) for (001) slabs. We have confirmed that the weight functions with these parameter values are broader than their corresponding induced charge density profiles by plotting them together in the same figure (see Sec.4.3.2).

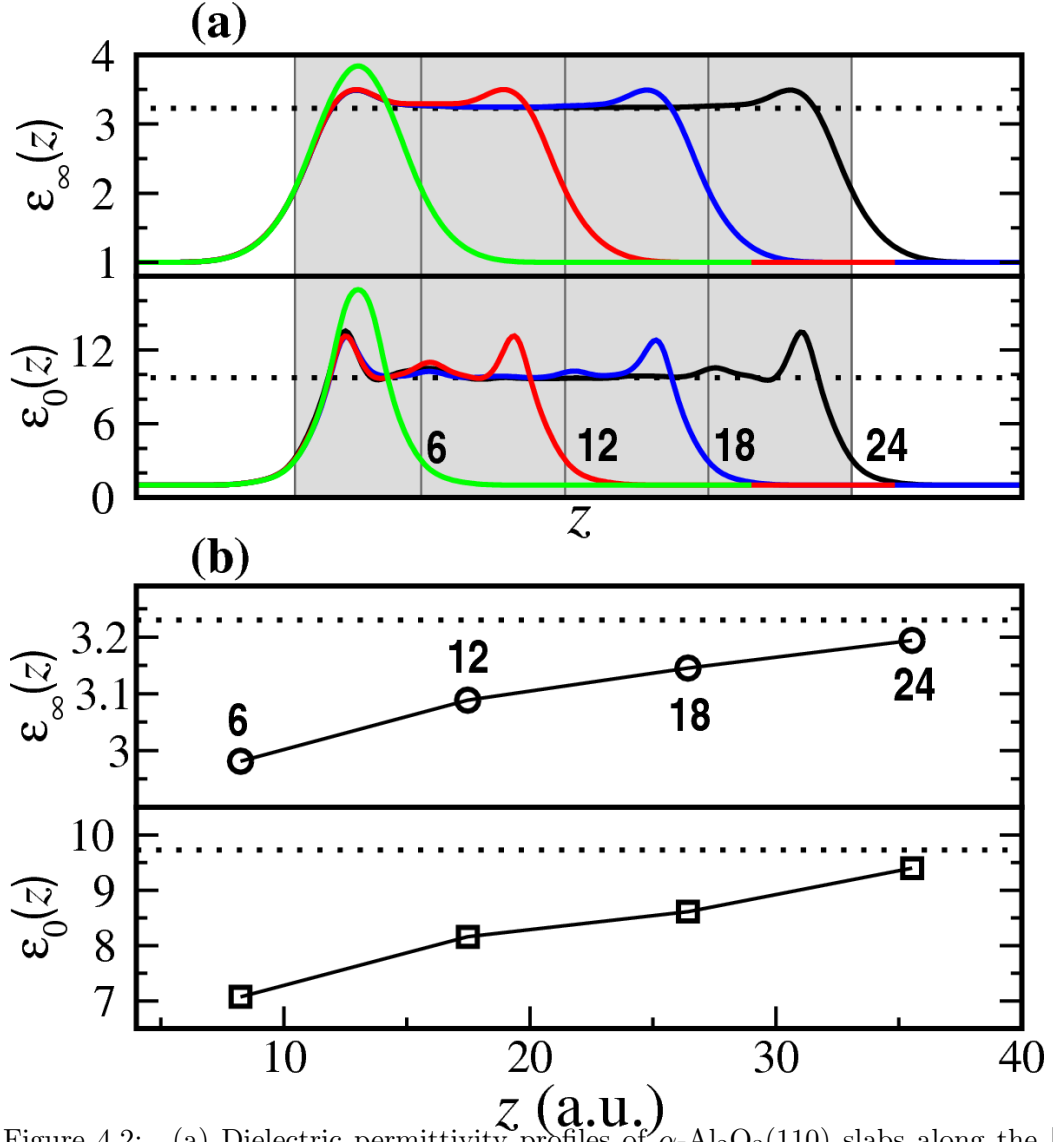


Figure 4.2: (a) Dielectric permittivity profiles of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(110) slabs along the [110] direction. Vertical lines represent the edge planes of the corresponding slabs. All slabs are aligned at the leftmost surface. (b) Overall effective dielectric permittivities, both high frequency and static, of the four  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(110) slabs in (a). The horizontal dotted lines show the corresponding bulk permittivities. The number of layers in slab are indicated in the figure.

To investigate the size dependence of the slab permittivities, we calculated the optical and static permittivity profiles for both kinds of slabs with sizes of 6 to 24 atomic layers. Fig. 4.2(a) shows these profiles for alumina (110) slabs. For slabs thicker than 12 atomic layers ( $\sim 26$  bohr), the optical permittivity profile in the middle of the slab is flat and matches the corresponding bulk value very well (within 1%). For the static permittivity, a flat bulk-like permittivity is obtained for 18 layers and beyond. In the surface regions of these slabs, both the optical and static permittivity profiles have the same shape and are independent of slab thickness. The permittivities increase near the surface and then decrease quickly when approaching the outermost surface layer. As the slab size goes below 18 (or 12) atomic layers, the static (or optical) dielectric permittivity in the slab interior is affected by the surfaces. This coupling becomes stronger as the slab size decreases. As a result, the bulk-like dielectric behavior can no longer be recovered in the mid-region of such thin slab. For instance, in the middle of a six-layer (110) slab, both the static and optical permittivities are much larger than the corresponding bulk ones. The results for alumina (001) slabs are similar and not shown.

Overall, the combined effects of the two surface regions lead to a reduced effective dielectric permittivity for a thin slab, when compared to the bulk value. This can be seen in Fig. 4.2(b), where the slab thickness is defined as the distance between the two outermost surface layers. However, the decrease in the overall dielectric permittivity becomes smaller as the slab thickness increases. For a (110) slab with 24 atomic layers ( $18.7\text{\AA}$ ), the effective permittivity is already very close (within 5%) to the bulk value. This implies that alumina slabs with thicknesses greater than a few nanometers can have bulklike dielectric properties. Similar dependence of permittivity on the slab thickness has also been found in finite Si systems [121, 143].

Fig. 4.2 also shows that the ionic contribution dominates the static dielectric permittivity across the entire slab. To understand in more detail how the ionic contributions determine the surface dielectric properties, we calculated the dynamical charges  $Z^D$  and effective ionic layer polarizabilities, according to Eqs. (4.11-4.12), for an 18-layer alumina(110) slab. Fig. 4.3(a) indicates that the effective dynamical charges in the middle of slab agree well with the corresponding dynamical charges in the bulk. In the surface region, both Al and O have reduced effective charges in their corresponding outermost layers.

From the calculated  $Z^D$ , we obtain the effective ionic layer polarizability profile,

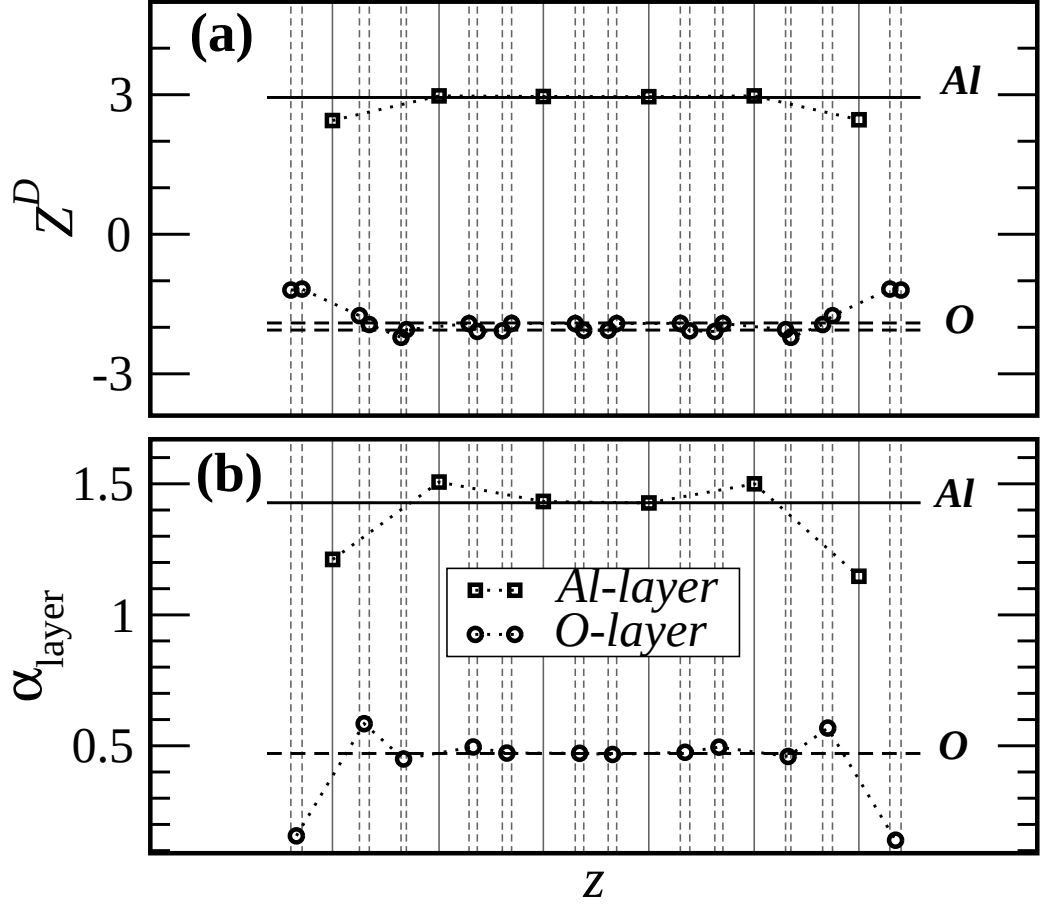


Figure 4.3: Dynamical charges (a) and effective ionic layer polarizability (b) for an 18-layer alumina(110) slab as same as the one used Fig. 4.2. The two horizontal lines in (a) correspond to the dynamical charges of Al (solid) and O (dashed) respectively in bulk. The two horizontal lines in (b) are only shown for the convenience of comparison between surface and interior. Vertical lines denote the positions of Al (solid) and O (dashed) planes along  $z$ .

shown in Fig. 4.3b. We observe that the Al layers are much more polarizable than the O layers. The ionic layer polarizability profiles of both Al and O layers display features similar to the static permittivity profile. Clearly, the enhancement of the local dielectric permittivity close to the surface is due to the second outermost Al layer and second outermost O layer, which are more polarizable than the corresponding layers in the slab interior. When approaching the outermost surface layer, the local static permittivity decreases quickly because of the much lower polarizabilities of the outermost layers.

### (001) $\text{PbTiO}_3$ slabs

In the ionic limit, a (001)-oriented  $\text{PbTiO}_3$  slab can be considered as an alternating stack of neutral  $\text{PbO}$  and  $\text{TiO}_2$  layers. We consider a (001) slab with 13 atomic layers. The calculated decay length of  $\chi(z, z')$  for this slab is about 8.2 *bohr* (about 3 atomic layers), confirming that this slab is thick enough to avoid the surface-surface interactions.

In a zero-field calculation, open-circuit boundary conditions are adopted. However, under these conditions any ferroelectric slab with a net polarization perpendicular to the surface relaxes into a paraelectric nonpolar structure. This is because the net polarization leads to surface charges that give rise to a huge depolarization field inside the slab. The depolarization field contributes a positive electrostatic energy, which is large enough to completely destabilize the bulk ferroelectric state [111]. For instance, a 13-layer  $\text{TiO}_2$ -terminated free-standing  $\text{PbTiO}_3$  slab, which was obtained by truncating a relaxed bulk structure, relaxes into an anti-centrosymmetric layered domain structure and becomes nonpolar as a whole. From the outermost surface to the innermost layer, the relative displacement between the metal and the oxygen atoms (rumpling) oscillates in sign from layer to layer, and its amplitude decreases rapidly to zero, as shown in Fig. 4.4.

To preserve ferroelectricity in such a slab, the depolarization field must be screened. In real systems, this screening may be provided by free charges from metallic electrodes, or by compensating surface layers, which may include adsorbates or charged defects, such as cation or oxygen vacancies. In our calculations, we use Nb- and Sc-doped surfaces to compensate the depolarization field. This charge-compensating method has already been employed to stabilize domain walls in other  $\text{PbTiO}_3$  calculations [144]. Specifically, in the  $2 \times 2$  13-layer  $\text{TiO}_2$ -terminated  $\text{PbTiO}_3$  slab, we replace three Ti atoms by Nb on one surface, and three Ti atoms by Sc on the other surface, creating a delta-like compensating

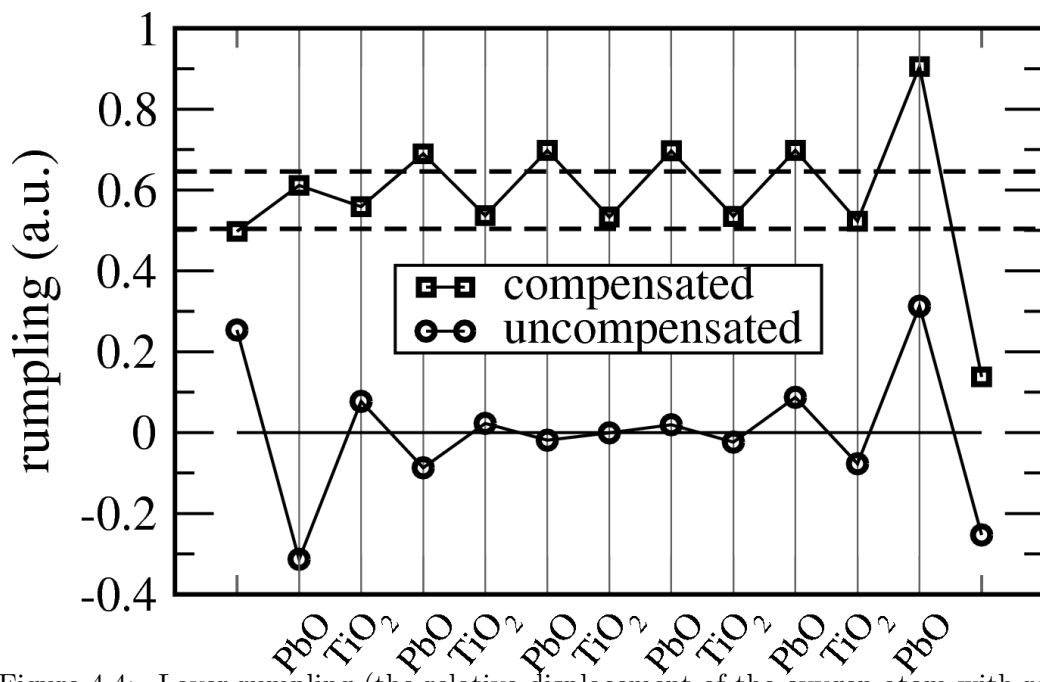


Figure 4.4: Layer rumpling (the relative displacement of the oxygen atom with respect to the metal atom along  $c$ ) for free standing  $\text{PbTiO}_3$  slabs with (square) and without (circle) surface charge compensation. Horizontal dashed lines represent the corresponding rumpling of the  $\text{TiO}_2$  and PbO layers in the bulk.

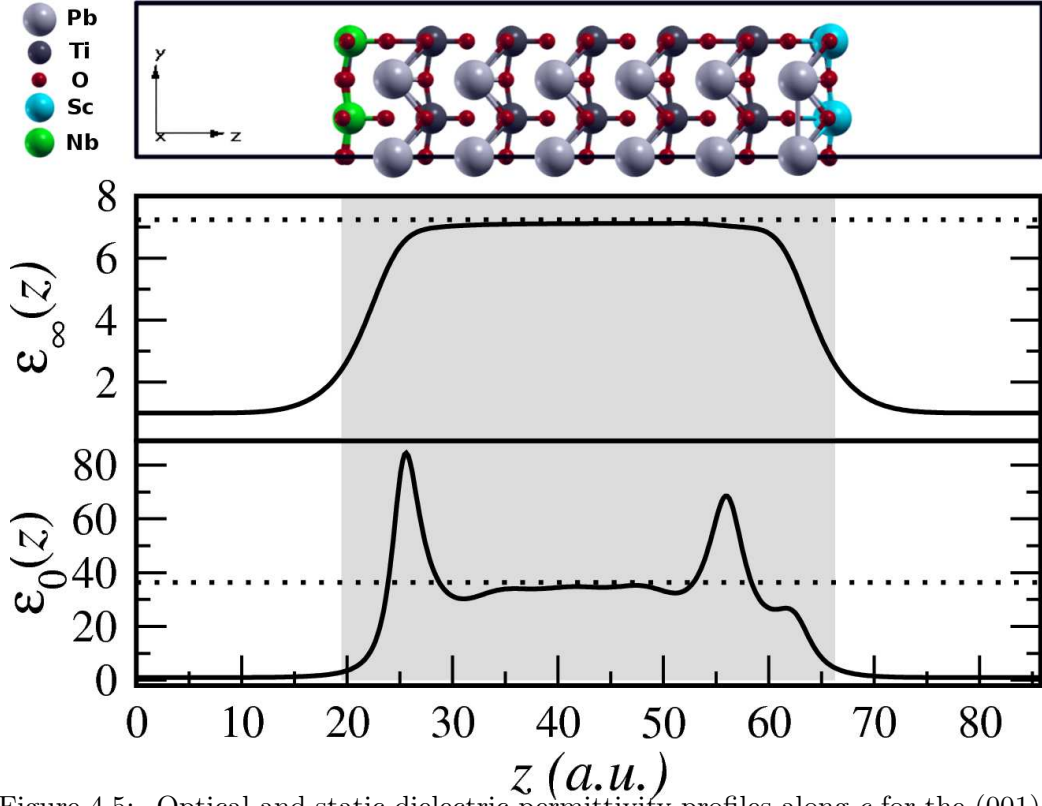


Figure 4.5: Optical and static dielectric permittivity profiles along  $c$  for the (001)  $\text{PbTiO}_3$  slab with the left side terminated by a  $(\text{Nb}_{3/4}\text{Ti}_{1/4})\text{O}_2$  surface and the right side terminated by a  $(\text{Sc}_{3/4}\text{Ti}_{1/4})\text{O}_2$  surface. Horizontal dotted lines represent the bulk permittivities.

surface charge densities of about  $\pm 0.0141 \text{ } e/\text{bohr}^2$ , which are very close to those induced by spontaneous bulk polarization of  $\text{PbTiO}_3$  ( $0.0134 \text{ } e/\text{bohr}^2$ ). After relaxation, this slab now remains in a single domain ferroelectric state (see Fig. 4.4), with slightly increased layer rumpling parameters and  $c/a$  ratio in the middle of the slab.

The local dielectric permittivity profiles for this compensated slab are shown in Fig. 4.5. In the averaging model we use  $l = 7.63 \text{ bohr}$ , which is equal to the lattice spacing in the slab interior, and  $\sigma = 2.5$ . The resulting weight function ( $r_0 \sim 13.0 \text{ bohr}$ ) is broader than the induced charge density profile ( $\xi \sim 8.2 \text{ bohr}$ ). For these choices we observe that in the slab interior both the optical and static dielectric permittivity profiles are flat and slightly lower than the corresponding bulk values. This permittivity reduction originates from the slightly over-compensating surface charges. As a response to the remanent surface charges, the lattice constant  $c$  in the slab mid-region increases by about 1%. For a strained bulk with

this enlarged  $c$  and  $a$  fixed at its theoretical bulk value, we find that the optical and static permittivities become 7.13 and 33.95, respectively, matching very well the corresponding permittivities in the slab interior.

In the surface regions, similarly to Si slabs [121], the optical dielectric permittivity is reduced due to lower electronic polarizability at the surface. However, the static permittivity is substantially enhanced in the subsurface layers, and differs in shape at the two surfaces. In order to better understand this enhancement, we also calculate the dynamical charges and effective ionic layer polarizabilities for this slab. As shown in Fig. 4.6(a), the atoms in the two outermost surface layers have smaller dynamical charges, while within the slab interior the effective dynamical charges coincide well with the corresponding ones in the bulk. From the discrete effective ionic layer polarizability profile (Fig. 4.6(b)), one can observe similar characteristics as in the continuous local permittivity profile in Fig. 4.5. At the left side of the slab, the outermost surface layer of  $(\text{Nb}_{3/4}\text{Ti}_{1/4})\text{O}_2$  is much less polarizable, leading to a lower local permittivity. The sub-surface layer of  $\text{PbO}$  and the third-inner-surface layer of  $\text{TiO}_2$  have larger polarizabilities and result in a higher local permittivity in the nearby region. At the other side of the slab, the outermost  $(\text{Sc}_{3/4}\text{Ti}_{1/4})\text{O}_2$  surface layer is also much less polarizable. Interestingly, the least polarizable layer is the sub-surface layer of  $\text{PbO}$ . The combined effect of these two layers produces a small local permittivity peak at the surface. The more polarizable third and fourth inner-surface layers induce a significantly larger local dielectric permittivity peak, as shown in Fig. 4.5.

#### 4.4.2 Polypropylene slabs

Here we only consider the most common crystal phase of iPP, the  $\alpha$ -phase [133]. The unit cell is monoclinic, with the lattice parameters as shown in Table 4.1. The cell contains four parallel chains arranged along the  $b$  axis. Each chain consists of three  $-\text{CH}_2-\text{CH}(\text{CH}_3)-$  monomers and has a three-fold helical conformation. In our slab calculations, for computational reasons, an orthorhombic supercell is used instead of the monoclinic one, which only amounts to a change of the angle between  $a$  and  $c$  from  $99.17^\circ$  to  $90^\circ$ . In this supercell, the chain conformation and unit chain length are preserved, and the change in the dielectric permittivity is less than 3%. It is therefore reasonable to assume that the surface dielectric properties are essentially unaffected by this change of the unit cell.

We study the dielectric permittivity profiles across iPP slabs that consist of two bi-

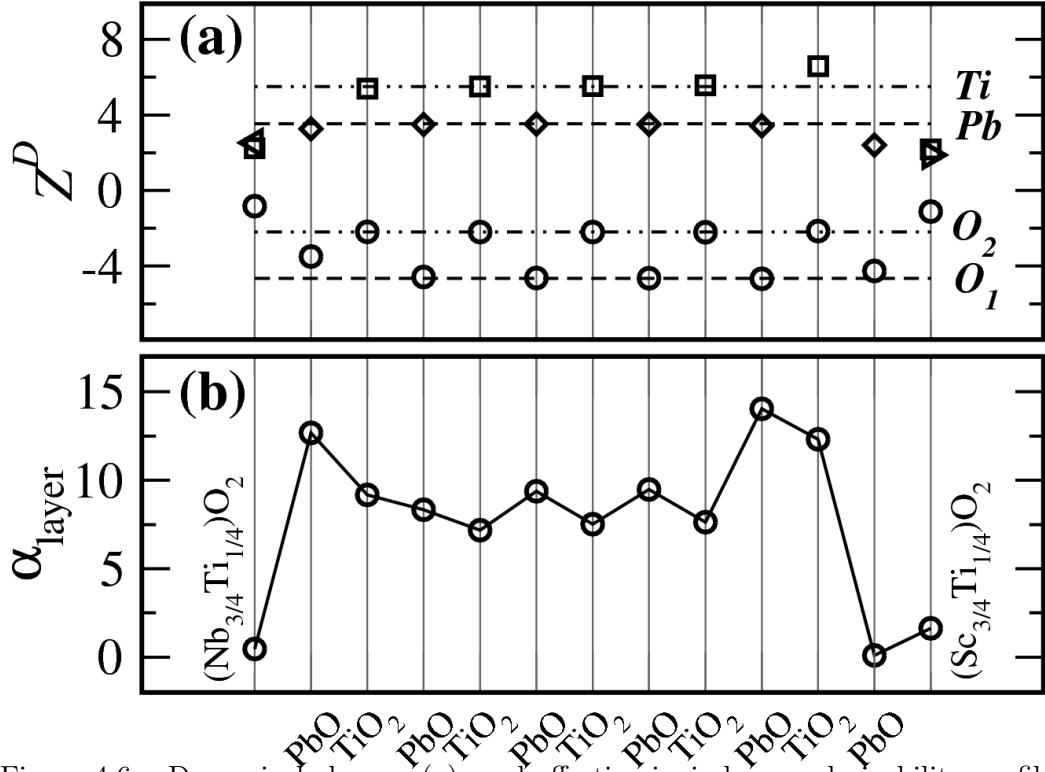


Figure 4.6: Dynamical charges (a), and effective ionic layer polarizability profile (b) for the  $\text{PbTiO}_3$  slab shown in Fig. 4.5. Vertical lines represent the positions of the atomic layers. In (a), bulk dynamical charges of Pb, Ti and O are indicated by horizontal lines. The triangles at left- and right-most layers represent the dynamical charges of Nb and Sc atoms, respectively. The dynamical charges of surface Ti are similar to those of Nb and Sc, as indicated by the overlapping squares and triangles.

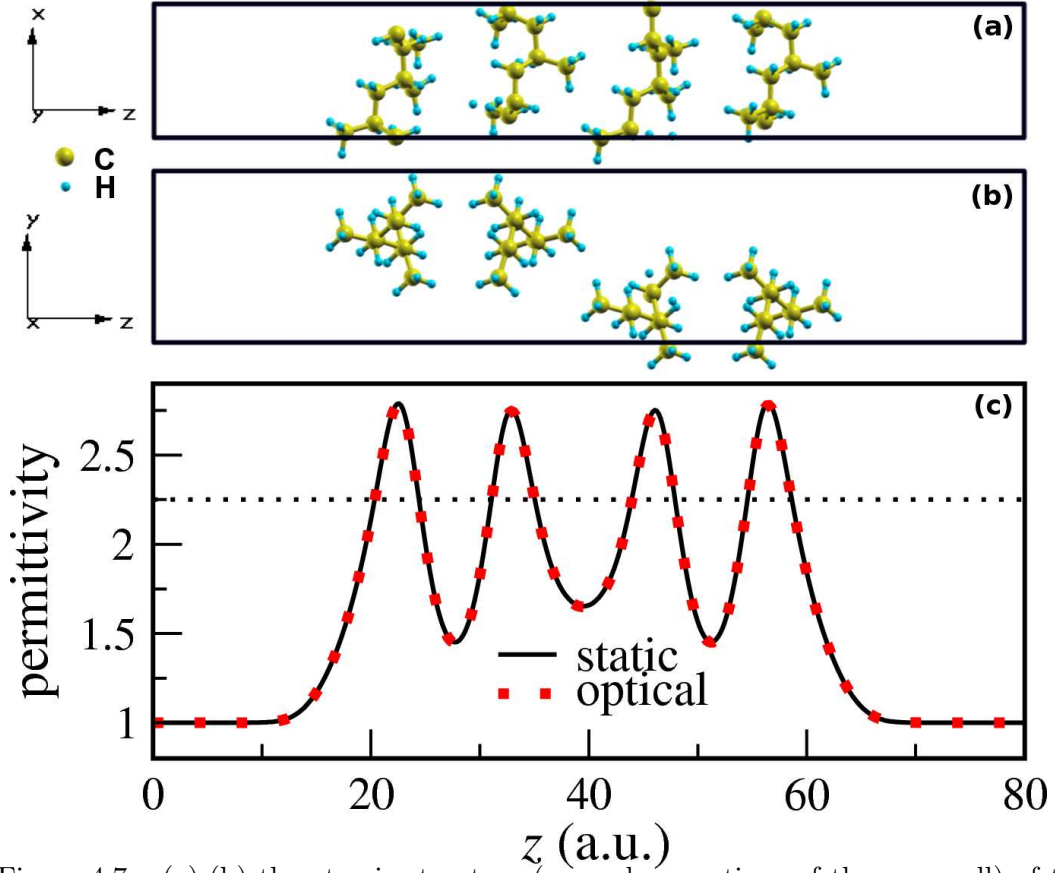


Figure 4.7: (a)-(b) the atomic structure ( $xz$  and  $yz$  sections of the supercell) of the iPP slab with single-methyl surfaces. The double-methyl surface in the text refers to the surface between the surface and subsurface layers shown here. (c) Optical and static dielectric permittivity profiles for the single-methyl-terminated slab along  $z$ .

layers parallel to the  $ac$  plane and terminated by either single- or double-methyl groups (see Fig. 4.7(a)-(b)). The in-plane lattice parameters were chosen equal to the DFT-optimized  $a$  and  $c$  values in the monoclinic cell. The single-layer thickness along  $z$  is  $20.0 \text{ bohr}$ , which is much larger than the  $\xi$  of only  $4.9 \text{ bohr}$  along the surface normal. In order to see the permittivity variation across the chain and in the interchain region, and to compare with the iPP/alumina(110) interface profiles below, we choose the same averaging model as the one we used for alumina(110) slabs, *i.e.*,  $l = 4.5 \text{ bohr}$  and  $\sigma = 1.2$ , corresponding to a  $r_0$  of  $6.8 \text{ bohr}$ .

Fig. 4.7(c) shows the permittivity profiles for the iPP slab with single-methyl

surfaces. For the double-methyl-terminated slabs, the permittivity profiles look very similar and thus are not shown. The figure shows that the lattice contributions to the static dielectric permittivity can be neglected, as in bulk iPP, because of vanishing dynamical charges. The permittivity profile decays very smoothly from the surface to the vacuum, similarly to the drop in permittivity from the chain to the interchain region. Inside the slab, the permittivity oscillates from chain to chain around the bulk value. Near the surface, the peak permittivity at the chain increases slightly, while the interchain permittivity decreases with the increase in interchain distance. This implies that lower chain packaging density in iPP would lead to a lower effective permittivity, as would be expected.

#### 4.4.3 iPP/metal-oxide interfaces

The atomic structure of interfaces between polypropylene and metal oxides has not yet been determined. For chemisorbed polypropylene, it could be quite complex and depend on the morphology and quality of the surface of the oxide. In this initial study we thus only examine physisorbed polypropylene, where all the bonds maintain their initial saturation.

##### iPP/alumina interface

We only consider the single-methyl iPP surface being physisorbed to the oxygen terminated alumina (110) surface. This interface can be constructed in a moderate size orthorhombic supercell with a lattice mismatch along the chain direction of less than 4%, while other kinds of interfaces would require a much larger supercell to achieve a physically reasonable lattice mismatch.

In the current orthorhombic supercell, two iPP chains are stacked parallel to the  $xy$  surface of a 18-layer  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(110) slab (see Fig.4.8). Since iPP polymer is more flexible than the oxide, the in-plane lattice parameters are chosen from the corresponding theoretically relaxed values of bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, namely  $a = \sqrt{3}a_{\text{Al}_2\text{O}_3} = 8.26 \text{ \AA}$ ,  $b = c_{\text{Al}_2\text{O}_3} = 13.04 \text{ \AA}$ . The iPP chains are aligned along  $y$  (i.e.  $b$ ) direction and elongated by 3.2%, whereas along  $x$ -direction ( $a$ ) the interchain distance is increased by 26.5%. As a result, the iPP chain density in the surface plane is decreased by 23.4% relative to the slab in Sec.4.4.2. Along  $z$ -direction, as mentioned in Sections 4.4.1-4.4.2, the calculated nonlocality lengths for alumina

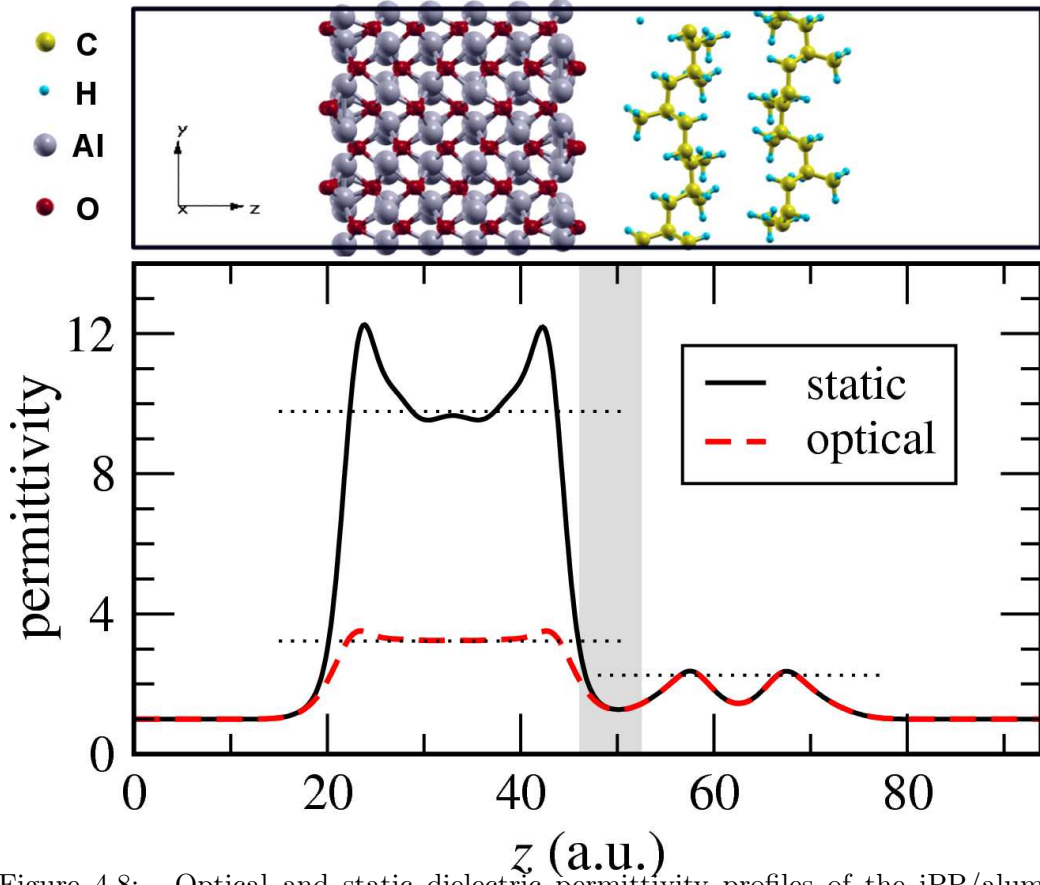


Figure 4.8: Optical and static dielectric permittivity profiles of the iPP/alumina(110) interface. The  $yz$  section of the supercell is shown at the top. The vertical grey bar represents the interface region. The bulk dielectric permittivities corresponding to each slab component are marked by horizontal dotted lines.

and iPP are  $6.8 \text{ bohr}$  and  $4.9 \text{ bohr}$ , respectively. To obtain the local permittivity profiles and be consistent with Sections 4.4.1-4.4.2, we use  $l = 4.5 \text{ bohr}$  and  $\sigma = 1.2$ , corresponding to  $r_0$  of  $6.8 \text{ bohr}$ .

Fig. 4.8(c) shows the optical and static local dielectric permittivity profiles for this interface. In the interior of the alumina slab, both the optical and static permittivities are flat and coincide well with the corresponding bulk values. However, on the iPP side, the permittivity is decreased by about 14% from its theoretical bulk value. This is because the in-plane iPP packing density is reduced by 23.4%. As already seen from Fig. 4.7 in Sec.4.4.2, a lower chain density yields lower dielectric permittivity. In the interface region,

the interface permittivity profiles of alumina and iPP are quite similar to those of their corresponding isolated surfaces (see Fig. 4.2(a) and Fig. 4.7(c)). Proceeding from  $\text{Al}_2\text{O}_3$  to the iPP, the permittivity is enhanced in  $\text{Al}_2\text{O}_3$  close to the interface and then decreases quickly to the smaller dielectric constant of the iPP. The variation of the permittivity across iPP part of interface is quite smooth and similar to the permittivity decay from the middle of the chain position to the interchain region. This shows that the interface dielectric effects at the iPP side are insignificant and that the dielectric properties of the interface are dominated by the alumina component. The width of the transition region between alumina and iPP depends thus on the characteristics of the alumina side and is very short, only about 6-7 atomic layers (11 *bohr*).

### **iPP/PbTiO<sub>3</sub> interface**

Here, we only consider physisorbed polypropylene on surface charge compensated PbTiO<sub>3</sub> slab, so that the depolarization field is realistic. To construct a model structure for this interface, we use an orthorhombic supercell containing a 13-layer PbTiO<sub>3</sub> slab and a 4-layer slab of isotactic polypropylene (iPP). The two slabs are joined together at the  $(\text{Sc}_{3/4}\text{Ti}_{1/4})\text{-O}_2$  surface, as shown in Fig. 4.9. In the plane of the interface, we use a  $2 \times 2$  unit cell of relaxed PbTiO<sub>3</sub>, as in the previous subsection. For iPP, one unit of the chain is then matched to  $a_{\text{supercell}}$ , which results in a 23% elongation of its LDA relaxed length, and a 16% elongation of the experimental length. This elongation, although seemingly large, is still much smaller than the experimental breakage elongation of 47% [145]. After atomic relaxations, we find that the conformation of the chain remains the same and its dielectric permittivity changes very little. Therefore, we expect that this model interface structure can still describe the major dielectric features of a physisorbed-polymer/ferroelectric interface.

To obtain the local dielectric permittivity profile, we adopt the same averaging model as for the PbTiO<sub>3</sub> slab. We can then easily compare the permittivity profiles of the bare slab with those of the PbTiO<sub>3</sub>/iPP slab. The calculated local permittivity profiles of iPP/PbTiO<sub>3</sub> are displayed in Fig. 4.9. Both optical and static permittivity profiles in PbTiO<sub>3</sub> and iPP slab interiors are flat and satisfactorily match the corresponding bulk values. In the interface region, the permittivity decreases rapidly from that of PbTiO<sub>3</sub> to the iPP value. The transition region is about 15 *bohr* thick and mostly confined to the PbTiO<sub>3</sub> side, while at the iPP side the permittivity profile at the interface differs very little

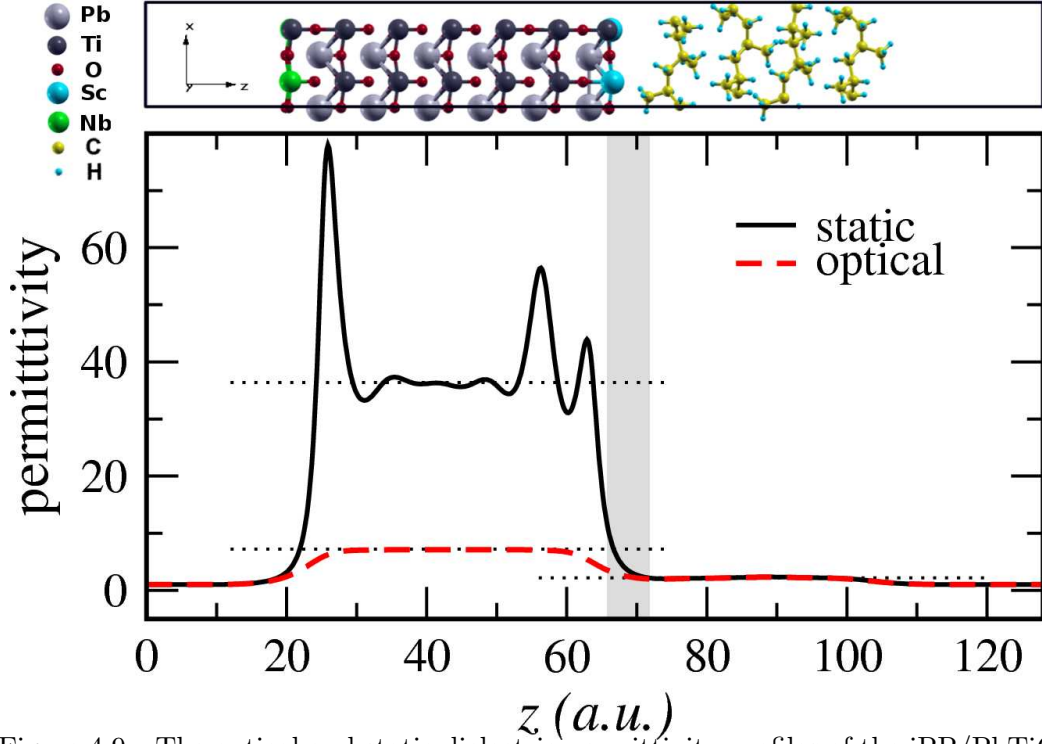


Figure 4.9: The optical and static dielectric permittivity profiles of the  $iPP/PbTiO_3$  interface. The  $ixz$  section of the interface structure is shown at the top. The grey vertical bar represents the interface region. The three dotted horizontal lines mark the optical and static permittivity of bulk  $iPP$ , and optical and static permittivities of bulk  $PbTiO_3$ , respectively.

from that of bulk  $iPP$ . At the  $PbTiO_3$  side of the interface, the static permittivity still exhibits two peaks. Compared to the free  $(Sc_{3/4}Ti_{1/4})O_2$  surface in Fig. 4.5, the peak closer to the  $iPP$  becomes higher and surpasses the bulk value of  $PbTiO_3$ .

The increased permittivity peak at the  $PbTiO_3$  side of the interface originates from the attachment of  $iPP$ . A comparison of discrete, effective ion-layer polarizability profiles shows that the two outermost surface layers (i.e.,  $(Sc_{3/4}Ti_{1/4})O_2$ ) and  $PbO$ ) of  $PbTiO_3$  become much more polarizable when attached to the  $iPP$  polymer. By evaluating the individual ionic polarizabilities of all twelve atoms in the  $(Sc_{3/4}Ti_{1/4})O_2$  layer, we find that the major cause for the increased layer polarizability comes from the  $Sc$  atom that is located closest to the side methyl branch of the  $iPP$  chain. For this  $Sc$  atom, the dynamical charge is increased from 1.90 at the free surface to 2.98 at the interface, and its ionic polarizability correspondingly increases from 66.65 to 269.79. The four  $O$  atoms nearest to

this Sc atom and the nearby Ti atom also have increased ionic polarizabilities and contribute considerably to the increased layer polarizability. From the charge density difference profile (i.e.,  $\Delta\rho(z) = \rho_{\text{iPP/PbTiO}_3} - \rho_{\text{iPP}}(z) - \rho_{\text{PbTiO}_3}(z)$ ), we find that the charge density around these six atoms is partially transferred into the middle of the interface. As a result, these ions are screened by fewer electrons and become more polarizable. For the other two Sc and four O atoms that are farther away from the iPP chain, the charge transfers are very small and their polarizabilities remain almost unchanged. Similarly, for the subsurface PbO layer, as affected by the  $(\text{Sc}_{3/4}\text{Ti}_{1/4})\text{O}_2$  layer, the four Pb atoms are become more polarizable and increase the effective ionic polarizability of this layer.

## 4.5 Summary and conclusions

This work focused on evaluating dielectric permittivity profiles across metal oxide slabs and metal oxide-polymer interfaces. In order to obtain local permittivity profiles with high resolution, the nonlocality decay length  $\xi$  of the microscopic susceptibility tensor is explicitly determined for each system across the slab or interface. The  $\xi$  is obtained by introducing small displacements in the atomic positions and evaluating the width of the change in the charge density induced by this disturbance. Using the physical condition that the averaging width of the nonlocal susceptibility must be greater than the nonlocality length, we proposed a new procedure for obtaining nanoscale-resolved local dielectric permittivity profile along a given direction. It combines the advantages of the two common averaging models: rectangular filtering and Gaussian kernel. It converges quickly to the bulk value in slabs of only moderate thicknesses, while providing atomic-layer-resolved permittivity profiles even in the presence of significant relaxations and surface structure.

This model was used to obtain dielectric permittivity profiles for alumina,  $\text{PbTiO}_3$ , and iPP slabs, and for physisorbed interfaces of alumina/iPP and  $\text{PbTiO}_3$ /iPP. The calculations show that the surface and interface effects on dielectric permittivity are very localized (within only a few atomic layers) and that the interface effects are mainly confined to the metal oxide side.

For polypropylene slabs the permittivity profiles indicate that the surface effects can be neglected and the effective permittivity of the slab depends mostly on the packing density of the chains. Since the effective permittivity is lowered significantly by nanovoids,

the free volume in nanocomposites could be a major factor for reducing their effective permittivity.

For both alumina and  $\text{PbTiO}_3$  slabs, the static dielectric permittivity is enhanced in the subsurface region, but decays rapidly when approaching the outermost layer. The discrete effective ionic layer polarizability profile shows that these effects are due to the more polarizable subsurface layers and less polarizable outermost surface layers.

Overall, due to their very localized surface permittivity effects, alumina slabs and particles with sizes larger than a few nanometers can retain their average macroscopic values of bulk dielectric permittivity.

For the ferroelectric  $\text{PbTiO}_3$  slab, our results show that its effective dielectric permittivity strongly depends on the electrostatic boundary conditions, *i.e.* the depolarization field. In the slab interior, the permittivity depends on the tetragonality ratio  $c/a$ , which can be modified by the residual depolarization field. Therefore, the bulk-like permittivity can only be obtained after the depolarization field is completely screened, which requires a slab with thickness of more than a few nanometers. However, in a real system, the screening is imperfect. Hence, different surface terminations, defects, molecular or cluster adsorption, etc., will in general affect the effective permittivity of the slab.

While we have only considered physisorbed interfaces, chemically-bonded interfaces should have similar properties outside of the immediate bonding region. However, the bonding at the interface will affect surface charges, which would certainly affect the depolarization field. One should therefore search for bonding configurations that would enhance the screening of the depolarization field, thereby lowering the minimum sizes of the oxide particles at which their bulk permittivities are preserved. In general, however, since the range of interface effects extends only over a few atomic layers in charge-compensated slabs, classical mixing laws associated with macroscopic composites should be applicable for modeling the overall dielectric properties of a real polymer/metal-oxide nanocomposite system. Alternatively, a nanoscale computer simulation of the nanocomposite, using the bulk dielectric constants for its constituents, could be employed to arrive at a more detailed description of the dielectric properties, provided that the nanoparticles are larger than a few nanometers.

## Chapter 5

# Summary and Conclusions

In this thesis, we have studied the interface and surface dielectric properties of polymer(polypropylene)/metal-oxide(alumina and  $\text{PbTiO}_3$ ) nanocomposites from first principles.

In our first principles calculations, we model the surface and interface structures using slabs or stacked slabs in supercells, using periodic boundary conditions. Since we are mainly concerned with polar slabs or slabs with asymmetric surfaces, some artificial effects are also introduced, which would substantially affect the dielectric properties of systems of interest. To eliminate these effects, some additional techniques need to be adopted. We compared two such methods, the dipole correction and the Coulomb cutoff technique, and identify the preferred one for our dielectric studies.

By comparing the two methods, we find that they are equally effective in eliminating the spurious interactions between periodic images of polar supercells. The results of either technique are equivalent to the ones that would be obtained for isolated slabs, as previously demonstrated in HF calculations with a localized orbital basis. In general, we conclude that both techniques have different relative strengths, which can be exploited in different contexts: The Coulomb cutoff formalism can be applied not only to slab geometries, but also to arbitrary-shape nanostructures. However, for slab geometries the dipole correction is preferred because a smaller supercell is sufficient for achieving convergence. Moreover, electric fields can be trivially included in the dipole correction method.

In particular, we found that both corrections have essentially no influence on occupied band states and affect only unoccupied bands. The corrections made to the electrostatic

potentials by using the two methods differ only in the mid-region of the vacuum. Therefore, for those highly delocalized states which extend to the mid-vacuum region, the two methods differ and do not work correctly. By comparing the results of dipole and Coulomb cutoff corrections, the highly delocalized unoccupied states can be easily distinguished from the localized bound states in a relatively small supercell calculation. This identification is important when determining excited states and optical properties from slab calculations. In general, careful convergence studies should be performed when calculating properties involving unoccupied electronic states. Judicious comparisons between the results of the two corrections make this task much easier and less costly.

To understand the local dielectric permittivity at the atomic scale, one needs to deal with nonlocality of the microscopic dielectric response functions. In this work, in order to ensure the locality of the extracted permittivity profile, the nonlocality decay length ( $\xi$ ) of microscopic susceptibility tensor in real space is explicitly determined for each system under investigation along a given direction. We artificially introduce a very localized potential disturbance by moving an atom a little bit from its equilibrium position. The spatial broadening width of this potential-disturbance-induced charge density is used to represent  $\xi$ . Based on the calculated  $\xi$ , we propose a new averaging model for obtaining nanoscale-resolved local dielectric permittivity profile along a given direction. This model combines the advantages of the two common averaging models: rectangular filtering and Gaussian kernel, and is especially good for interface or surface systems.

With the dipole correction method and our averaging model, we study from first principles the local dielectric permittivity profiles for alumina,  $\text{PbTiO}_3$ , and iPP slabs, and physisorbed interfaces of iPP/alumina and iPP/ $\text{PbTiO}_3$ . Our calculations show that the surface and interface dielectric permittivity in polymer/metal-oxide slabs is very localized (only a few atomic layers), and the interface effects are mainly confined to the metal-oxide side.

For iPP slabs, the permittivity profiles indicate that the surface effects can be neglected and that the effective permittivity of the slab depends on the chain packing density. The lower the density, the lower the effective permittivity. It means that the nanofiller-induced free volume in nanocomposites could be a major factor in reducing the effective permittivity of nanocomposites.

For both alumina and  $\text{PbTiO}_3$  slabs, the static dielectric permittivity is enhanced

in the subsurface region. It decays rapidly when approaching the outermost surface layers. The discrete effective ionic layer polarizability profile illustrates that the increase and decrease in the static permittivity, respectively are due to the more polarizable inner surface layers and less polarizable outermost surface layers.

Overall, due to its very localized surface permittivity effects, alumina slabs with size larger than a few nanometers can retain the average macroscopic value of bulk dielectric permittivity. The size dependence of the permittivity mainly comes from slab surface effects.

For ferroelectric  $\text{PbTiO}_3$  slab, our results suggest that the slab dielectric permittivity strongly depends on the electrostatic boundary conditions, i.e., the depolarization field. In the slab interior, the permittivity depends on the tetragonality ( $c/a$ ), which can be modified by the residual depolarization field. Therefore the bulk-like permittivity can only be obtained after the depolarization field is completely screened, which requires width of more than a few nanometers. In a real system, however, the screening is imperfect. Hence, different surface terminations, defects, molecular or cluster adsorptions, etc., will in general affect the effective permittivity of the slab.

Finally, we should mention that the interface structure models in our calculations are very simple. In the future, chemically bonded structure and other surface configurations should also be considered. As expected, our results suggest that properly prepared nanocomposite dielectrics can substantially increase the permittivity of the polymer host. It also means that a nanocomposite dielectric can be fabricated with tailored dielectric properties, i.e., controllable permittivity as a function of the volume percentage of incorporated high- $k$  nanoparticles. On the other hand, the localized nature of the surface or interface dielectric permittivity makes quantitative tests of our predictions difficult. However, based on the predicted short range of interface-induced changes to the dielectric permittivity, classical mixing laws associated with macroscopic composites can be applied to model the overall dielectric constant of a real polymer/metal-oxide nanocomposite system. Alternatively, a nanoscale computer simulation of the nanocomposite, using the bulk dielectric constants for its constituents, could be employed to arrive at a more detailed description of the dielectric properties, provided that the nanoparticles are larger than a few nanometers in diameter.

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