TITLE OF PROPOSED RESEARCH:

First-principles modeling of ferroelectric oxides

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1) **Research Background**

Ferroelectrics oxides known as perovskites are very important functional materials used in many technological applications [1], such as transducers, gate dielectrics for MOSFETs, EO modulators, IR detectors and non-volatile RAMs. The applications of ferroelertrics rely on their special properties to diplay spontaneous electrical polarisation and switching under external electric fields. Due to the practical applications of ferroelectrics, the physics of polarisation in ferroelectrics has been a very active research area since its discovery in the 1920 by Valasek [2]. Good insight of the physical and thermodynamical properties of ferroelectrics can be calculated using the well-known phenomenological Dovonshire-Ginzburg-Landau (DGL) theory [3]. In DGL theory of ferroelectrics, the parameters of the theory is phenomenological in nature, and have to be measured experimentally. This approach used to be one of the most popular theoretical tools in the ferroelectrics research community, and its application in describing ferroelectric effects has been very successful in the past. The Theory Group of School of Physics, USM, has been very active in the theoeritcal research of ferroelectrics since 1990s, and has published extensively, mainly using the DGL approach (see the selected publications as listed in Ref. [4]). However, to capture the atomistic origin of the ferroelectric effects of a chemically-specific crystal, we need to go beyond the phenomenological theory. The research project proposed here aims at investigating ferroelectric properties of crystals with an alternative, powerful approach: the first-principles method.

Generically, the physical properties of a crystalline solid material are determined by the electronic structure at the atomic scale. This is essentially a complex, many-body system governed by the law of quantum mechanics. To determine the physical properties of a crsytal structure by computationally solving the Schroedinger equation from first-principles is a numerically demanding task. A well-established scheme to calculate electronic properties of solid crystal by first-principles is based on the Nobel-prize-winning Density Functional Theory, DFT [5] first proposed in the 1960s. It is a universal approach to the quantum mechanical many-body problem, where the system of interacting electrons is mapped in a unique manner onto an effective noninteracting system with the same total density. DFT has made it a practical feasibility to carry out numerical computation to obtain realistic properties of solid state systems [6]. DFT has since been one of the most important tools in understanding the physics and detailed atomistic mechanisms of condensed matter systems developed on a sound theoretical foundation [7]. Many numerical packages have been developed since 1980s to implement DFT on computers, leading to many important break through in condensed matter and quantum chemistry. Kohn and Pople were conferred the Noble prize in 1998 because of their original work in developing first-principle calculation methods.

In first-principles calculation, we can predict, at least in principle, many of the relevant ferroelectric properties by supplying the crystal structure and bases of a ferroelectric crystal [8]. The essential physical properties, in particular the electric dipole polarisation, of these systems can be calculated by manipulating the DFT codes which takes care of all the relevant quantum interactions and the physics of polarisation in the crystal lattice. A very comprehensive review of first-principles calculation on ferroelectric oxides in bulk, thin film, superlattices and nano structures can be found in Ref. [9]. In practice, supercells mimicking the configurations of the ferroelectric crystal (e.g. a thin film) are built, and their physical properties probed by cleverly manipulating the DFT codes. By building supercell models representing these structures, we can calculate and obtain computationally the ferroelectric properties of the materials represented by of these supercells. As such, the ferroelectric effects of a chemically-specific perovskite oxide can be understood at a more fundamental level than that offered by DGL theory. Since the seminar paper that successfully elucidates the original of ferroelectricity in $PbTiO_3$ and $BaTiO_3$ by Cohen [10] using first-principles method in 1990s, DFT has enjoyed tremendous popularity due to its supreme power to address the physics of ferroelectrics at the fundamental, atomistic level. It is to be stressed that density functional theory software packages offer a powerful approach to investigate the ferroelectric system. The astonishing achievements of first-principles method in ferroelectrics research, and its future prospect, are well discussed in the review paper by one of the most important figures in this field, Cohen [11].

Comparatively, bulk perovskites are much easier to calculate, hence better understood, than ferroelectric thin films. First-principle calculations on the latter form are relatively scarce. The precise effects of the substrate,

growth orientation, surface termination, boundary conditions and thickness on the finite-temperature ferroelectric properties of ultrathin films are not particularly well established [12]. They vary from case to case. In some cases thin films exhibit striking features that are quite unexpected from the bulk. Superlattices comprised of ferroelectric thin layers are artificial structures that offer a higher level of complexity than the ferroelectric thin films. The research of ferroelectric properties of superlattices is a frontier research topic. Other than being a very challenging condensed matter system in which the interplay between the underlying atomistic interactions is yet to be fully explored, superlattices also offers a highly promising way to purpose-design a functional ferroelectric material.

This research proposes to make use of the DFT computational tools to investigate the ferroelectric effects of some chemically-specific perovskite oxides ABO_3 structures, in particular in the form of thin film and superlattice. Ultimately the insight gained from the first-principle modelling will help us in the designing of more powerful functional ferroelectric materials.

Referrences

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2) **Objective(s) of the Research**

- To calculate from first-principles the ferroeletric characteristics of a generic perovskite oxides structure in the forms of bulk, thin film and superlattice.

- To study the interplay between the ferroelectric properties of perovskite oxides and the interfaces in thin flim-substrate, and in superlattice structures, by using first-principles methods.
- To theoretically design optimised ferrolectric structures that has potential applications in solid state devices.
- To develop our local human capital in computational condensed physics / computational materials science researches.

3) **Research Method**

Description of Research Method

This is basically a computational research project which uses a computer cluster to run computationally intensive parallel codes from readily available DFT software packages such as ABINIT [1], WIEN2k [2], VASP [3] and CRYSTAL [4]. These software packages compliment each other in their functionalities and features. The latest ABINIT and WIEN2k codes are currently available in the School of Physics, whereas currently only older versions of VASP and CRYSTAL are available. All these codes will be installed in the computer cluster in the school of physics. The cluster has in it MPI capability to run parallel codes. We will run the DFT packages in parallel mode in the cluster. Configuring a computer cluster and setting them to run parallel codes from scratch is no trivial task. Fortunately, the principle investigator of this research proposal (YTL) has picked up the know-how of installing, configuring and actually running the DFT codes in parallel mode through the research experience in an earlier FRGS grant "Ab initio study of electronic structures of advanced solid materials" between Oct 07 – Feb 10.

The planned procedure to investigate the ferroelectric properties of a generic perovskites are as followed:

1. Initially, as a warming-up, we shall reproduce the bulk ferroelectric properties (at zero temperature and zero pressure) of the prototypical ABO_3 perovskite ($PbTiO_3$, $BaTiO_3$ etc.) as reported in [5], which is a very comprehensive review of the topic. These ferroelectric properties, among others, include e.g. the Born effective charges of the atoms in the ABO_3 compound, the various phonon modes and their dispersion relations, and also the range of ferroelectric instability as a function of the geometry of the crystal structures.

2. Generically, after a crystal structure has been constructed (may it be bulk, surface, thin film or superlattice), it has to be relaxed and optimised, usually by using the built-in molecular dynamics functionality in the DFT software packages. Such structural optimisation is sort of a routine procedure in DFT calculations. It is usually done before actually carrying out the abstraction of the physical properties subsequently. ABINIT and VASP software packages provide many useful functionalities that are capable of performing respond-function and Berry-phase calculations. These functionalities are very much relevant for our proposed research, and shall be employed to calculate the ferroelectric properties, such as polarisation and phonon dispersion relation.

3. Once the bulk results in (1) have been reproduced, we are then ready to proceed to consider perovskites in the form of single thin films. This is done by constructing supercells of isolated slabs in vacuum with two free surfaces. The electronic and structural properties of such a slab can be calculated by the DFT software packages by simply supplying the structure of the supercell mimicking the thin film. Constructing supercell models in DFT calculations are kind of a routine task. There exist many resources, in particular the tutorial manuals of DFT software packages, that provide comprehensive training on supercell construction.

4. The main purpose of this calculation is to investigate the interplay between the thin film's properties with the perovskite's ferroelectricity. In particular, the ferroelectric polarisation along and perpendicular to the film's surface is strongly dependent on the thin film's physical characters, such as its thickness, the free surface's Miller index, the lattice constants, as well as the A, B atoms of the perovskite oxides. As a step-by-step strategy, we shall first reproduce the thin film's ferroelectric results as reported in the literature [5]. Once successful, we shall proceed to apply the technique to other perovskite thin films that are not yet been investigated in the literature (there are plenty of such compound around). This exploration offers a possibility to discovering some otherwise unknown yet interesting ferroelectric properties of other perovskite oxides films.
5. The next step would be to construct a structure with higher complexity. Specifically, we shall use supercell method to construct an interface between a chemically-specific bulk substrate (it could be a dielectric or a perovskite of different type) and a chemically-specific perovskite thin film. Strain will be induced in both substrate and ferroelectric thin film due to lattice misfit between the two generically different lattice structures at the interface. Due to the thinness of the ferroelectric film, the strain effect near the interface will modify the ferroelectric properties of the film at the free surface. The effects of such a coupling between the strain and the

ferroelectric properties of the film shall be investigated with DFT codes. Among the ferroelectric properties, we specifically want to investigate how the polarisation of the thin film gets modified by the strain effect. Constructing supercell models with varying thickness, relative surface orientations between different combinations of substrate-thin film compounds shall provide us the insight of the effects of these physical parameters on the thin films's ferroelectric properties. In particular, the method shall allow us to investigate the existence (or non-existence) of critical thickness (below which the ferroelectricity of the perovskite oxide vanishes – a highly valuable information for practical applications) of a given perovskite oxide film sitting on a given substrate. Ref. [5] reviewed many such kind of calucaltions.

6. We shall also construct superlattice of perovskite oxides using supercell method. A good example of how to perform first-principles calculation of the strain effect on the ferroelectric properties in $(PbTiO_3)_1$ $(PbZrO_3)_1$ superlattice can be found in Ref. [7]. Properties of the superlattice shall be abstracted by skilfully manipulating the functionalities that are readily coded in the DFT software packages.

7. Finally, the results calculated with first-principles method shall be checked against those obtained via the phenomenological DGL theory. Such a consistency check will be used as a benchmark for the reliability of the results obtained by the first-principle calculation.

References

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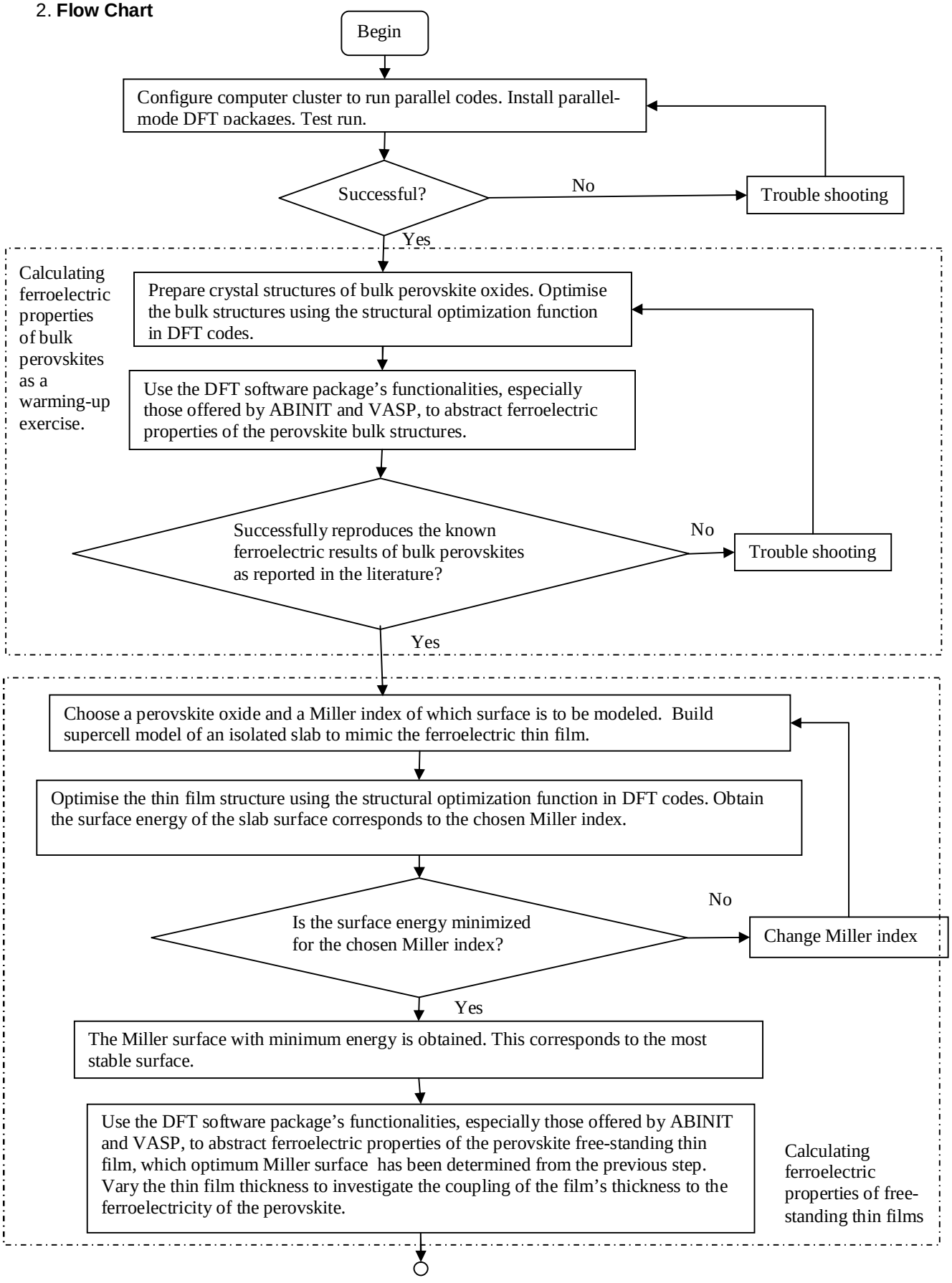
2. **Flow Chart**



2. **Flow Chart** (cont.)