First-Principles Calculations of Complex Oxide Perovskites

David-Alexander Robinson Sch.

08332461

The University of Dublin, Trinity College

(Dated: 24th August 2011)

Recent developments in epitaxial techniques have allowed for the growth of complex oxide heterostructures with unprecedented control over structural quality and chemical composition, with atomic layer precision. For instance $SrTiO_3$ with record high electron mobility has been achieved, and characteristics of a two dimensional electron gas (2DEG) at the interface of two insulators such as $LaAlO_3$ and $SrTiO_3$ have been reported in the literature. Despite the rapid progress basic parameters such as band gaps and band alignments of perovskite oxides, which are essential ingredients in the design of heterostructure based devices, are largely unknown. Here first-principles calculations were used to investigate the electronic structure and band alignments of a series of perovskites ABO_3, for varying both A and B cations. The calculations were based on the Density Functional Theory method in both the Generalised Gradient Approximation (GGA) and the screened Hybrid Functional formulation by Heyd-Scuseria-Ernzerhof (HSE) as implemented in the Vienna Ab-Initio Simulation Package (VASP). While the GGA is know to severely underestimate band gaps, the HSE is expected to result in much more accurate values for both band gaps and band alignments. The variation of band gaps and band alignments were rationalised in terms of the atomic orbital energies and atomic sizes. This data will serve as the basis in the electronic structure design of complex oxide heterostructures with potential applications in novel electronic devices.

PACS numbers:

I. DESCRIPTION OF GROUP

I have been working in the Computational Materials Theory Group led by Prof. Chris Van de Walle, in the Materials department at the University of California Santa Barbara (UCSB). The group is composed of a project scientist, eight postdoc researchers and five graduate students. All of the group members have an undergraduate background in Physics or Materials Physics. The group was founded in 2004 and has graduated two graduate students since then.

The group research activity centres on Materials Physics with emphasis on electronic structure theory. All the research is connected by a common first-principles approach using computational methods in which the quantum mechanical equations are solved using supercomputing.

Some specific areas of research are Oxide and Nitride Semiconductors, and Hydrogen storage materials;

- Many oxide semiconductors may be used as transparent semiconductors. These compounds, such as ZnO, TiO_2, In_2O_3 and Ga_2O_3 are wide band gap semiconductors, and do not absorb light in the visible range, with the latter remaining transparent well into the ultraviolet range. Research on the origin of unintentional n-type conductivity in these compounds is investigated. ZnO when grown shows n-type conductance, which was believed to be due to Oxygen vacancies, was found to be due to impurities with atomic hydrogen being a main candidate to explain many of the experimental results using first-principles methods.[1]

- Nitride Semiconductors are of increasing commercial importance as they are used in blue and ultraviolet Light Emitting Diodes, and are candidates for green LEDs. These blue LEDs may in turn be used to create white light sources using suitable phosphors. Investigation of the electronic structure and properties of such materials is therefore of high importance. Again, using first-principles methods the group was able to identify sources of n-type conductivity in InN, and explain the loss in efficiency in green LEDs and lasers.[2]

- Hydrogen can have strong effects on the electronic and structural properties of many materials, as it can bind to and create defects in semiconductors. The Group has investigated the effects of hydrogen in a wide range of semiconductors and insulators. In the case of metal hydrides the specific mechanisms of hydrogenation and dehydrogenation have been proposed solely based on first-principles calculations[3].[4]

II. PROJECT DESCRIPTION

A. Introduction & Theory

Complex Oxide Perovskites are any crystal structure of the general form ABO_3, where in general A is any mono- di- or trivalent ion and B is any transition metal cation or any trivalent ion. These compounds are some of the most abundant in the Earth's crust. Moreover perovskites in general are know to display almost all solid state physical phenomenon, from electrical properties of insulators, semiconductors and metals, to semiconductor-metal insulators, and superconductivity, amongst many others. In addition, all oxide perovskites have a near simple cubic structure, and have a lattice constant in the region around $4\mathring{A}$.[5]

The wide range of properties displayed by semiconducting oxide perovskites makes them interesting candidates for the construction of novel electronic devices. Yet, their electrical properties are not well documented.

In this project a large range of semiconducting oxide perovskites were investigated, with the range of $A = Li, K, Mg, Ca, Sr, Ba, Sc, Y, La, Gd$ and $B = Ti, Zr, Hf, Nb, Ta$ or Al, Ga, In.

To compute the electronic properties of these perovskites from first principles requires solving the Schrödinger Equation for the many-electron problem

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \mathcal{H}\Psi(\vec{r},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right)\Psi(\vec{r},t) \tag{1}$$

However this can only be solved using approximation techniques.

The first of these is to employ Hartree-Fock methods (HF). In this approach, the many-electron wavefuntion is written as an anti-symmetric linear combination of single electron wavefunctions, reducing the problem to one of non-interacting particles. This however gives overestimates of the electronic band gap.

As an improvement, one may use Density Functional Theory (DFT). This replaces the many-electron problem with a single-particle in an effective potential[6,7] The 1998 Nobel Prize was awarded to Walter Kohn for his work on the development of DFT. This again gives rise to problems with the calculation of the band gaps however, this time giving results which are too small.

Thus the use of screened Hybrid Functionals is adopted, as developed by Heyd-Scuseria-Ernzerhof (HSE).[8,9] This mixes both HF and DFT exchange potential to give a more accurate description of the electronic structure, and a good calculation of the band gap.

B. Computational Methods

The DFT and hybrid functionals are implemented using the Vienna Ab-Initio Simulation Package code (VASP).[10] This is a self-consistent iterative method, which works to minimise the energy of the system by filling up electron bands and relaxing the lattice constant in turn. In this way it solves the quantum mechanical Schrdinger equation. These calculations uses first principles methods.

The Projector Augmented Wave (PAW) potentials are used to represent the interactions between the valance electrons and the inert ion cores. These are compiled into an input POTCAR file for the specific perovskite. The supercell ion positions, periodic boundary conditions and plane wave basis set in the POSCAR input file. A special k-point mesh is used for integrations over the first Brillouin zone in reciprocal space as defined in the KPOINTS input file. Finally the cut off energy, electron smearing, algorithms to be used and convergence tolerance levels are set in the INCAR file. These files are then submitted using a job submission script.

High Performance Computing is used to run this code in parallel on supercomputing clusters. The jobs are submitted to either of the California NanoSystems Institute (CNSI), UCSB on the Lattice, Guild and Knot clusters, or the Texas Advanced Computing Centre, U Texas on the Lonestar cluster.

Computer programing and editing languages are used to edit and submit the jobs on Linux systems, such as Bash and VI, and plotting software is used to analyse the results, such as xmgrace.

III. PROJECT OUTCOMES

A. Results & Analysis

The following tables of data on the electrical properties of oxide perovskites were compiled.

TABLE I: Electronic properties for oxide perovskites using GGA

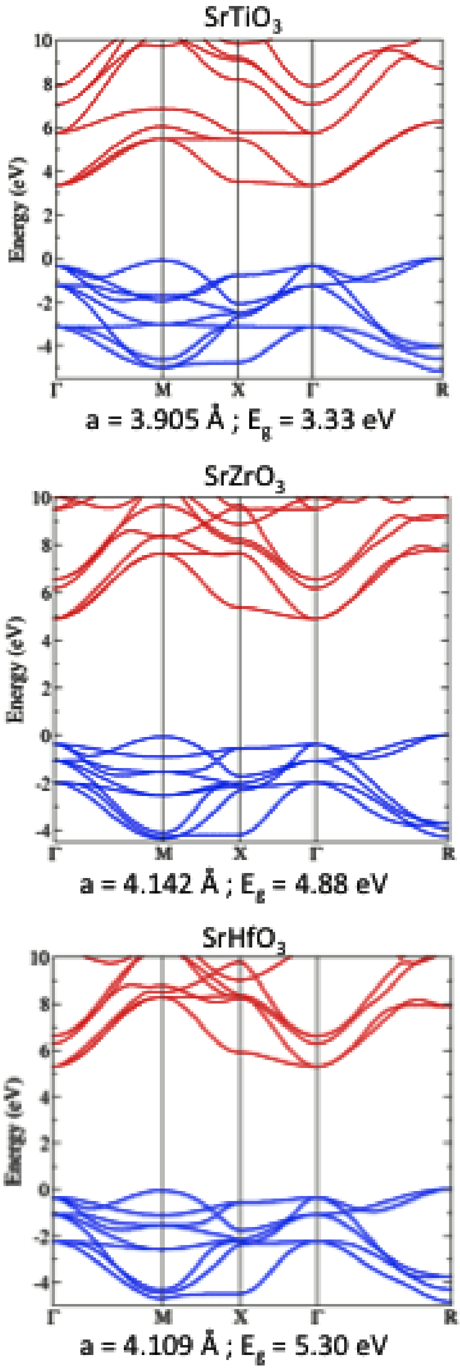
Compound	a($\mathring{A}$)	$E_g(\Gamma\text{-}\Gamma)$ (eV)	$E_g(\mathrm{R}\text{-}\Gamma)$ (eV)
$BaHfO_3$	4.203	3.75	3.50
$BaTiO_3$	4.038	1.67	1.54
$BaZrO_3$	4.251	3.21	2.99
$CaHfO_3$	4.105	4.02	3.65
$CaTiO_3$	3.896	2.12	1.70
$CaZrO_3$	4.161	3.47	3.17
$GdAlO_3$	3.726	3.43	2.90
$GdGaO_3$	3.843	3.42	2.81
$GdInO_3$	4.131	3.03	1.61
$LaAlO_3$	3.810	3.62	3.49
$LaGaO_3$	3.928	3.42	3.34
$LaInO_3$	4.214	3.03	1.61
$LiNbO_3$	3.989	2.23	1.55
$LiTaO_3$	3.963	3.08	2.30
$LiVO_3$	3.728	0.82	0.03
$MgHfO_3$	4.074	1.21	0.79
$MgTiO_3$	3.851	2.12	1.60
$MgZrO_3$	4.131	0.99	0.66
$ScAlO_3$	3.646	2.23	1.42
$ScGaO_3$	3.814	2.14	1.29
$ScInO_3$	4.156	1.70	0.47
$SrHfO_3$	4.142	4.04	3.70
$SrTiO_3$	3.948	1.97	1.65
$SrZrO_3$	4.194	3.46	3.18
$YAlO_3$	3.718	3.41	2.80
$YGaO_3$	3.862	3.35	2.67
$YInO_3$	4.175	2.89	1.75

TABLE II: Electronic properties for oxide perovskites using HSE

Compound	a($\mathring{A}$)	E_g(Γ-Γ) (eV)	E_g(R-Γ) (eV)	E_g [GGA] (eV)	E_g diff (eV)
$BaHfO_3$	4.180	5.29	5.03	3.50	1.54
$BaTiO_3$	3.993	3.28	3.18	1.54	1.64
$BaZrO_3$	4.228	4.74	4.51	2.99	1.51
$CaHfO_3$	4.075	5.72	5.29	3.65	1.64
$CaTiO_3$	3.851	3.88	3.41	1.70	1.71
$CaZrO_3$	4.133	5.16	4.80	3.17	1.63
$GdAlO_3$	3.684	4.94	4.33	2.90	1.43
$GdGaO_3$	3.796	4.90	4.23	2.81	1.42
$GdInO_3$	4.804	4.96	3.29	1.61	1.68
$LaAlO_3$	3.777	5.04	4.89	3.49	1.39
$LaGaO_3$	3.874	5.01	4.75	3.34	1.41
$LaInO_3$	4.132	4.63	3.25	1.61	1.64
$LiNbO_3$	3.909	3.95	3.06	1.55	1.52
$LiTaO_3$	3.928	4.59	3.76	2.30	1.46
$LiVO_3$	3.666	1.87	1.03	0.03	0.99
$MgHfO_3$	4.038	2.68	2.19	0.79	1.40
$MgTiO_3$	3.800	3.80	3.18	1.60	1.58
$MgZrO_3$	4.096	2.41	2.01	0.66	1.35
$ScAlO_3$	3.606	3.85	2.86	1.42	1.44
$ScGaO_3$	3.737	3.72	2.71	1.29	1.42
$ScInO_3$	4.052	3.10	1.27	0.47	0.79
$SrHfO_3$	4.109	5.68	5.30	3.70	1.60
$SrTiO_3$	3.905	3.68	3.33	1.65	1.69
$SrZrO_3$	4.142	5.28	4.88	3.18	1.70
$YAlO_3$	3.681	5.06	4.36	2.80	1.56
$YGaO_3$	3.795	4.99	4.24	2.67	1.57
$YInO_3$	4.084	4.46	2.78	1.75	1.03

It was found that on performing HSE calculation band gap widening of 1.54±0.16 eV was found compared to those of GGA.

The electronic band structure of all of these perovskites were plotted. As a sample of those plotted, the following comparative plots are given.



a = 3.905 Å ; E_g = 3.33 eV

a = 4.142 Å ; E_g = 4.88 eV

a = 4.109 Å ; E_g = 5.30 eV

FIG. 1: Band Structure comparison of Strontium Oxide Perovskites using HSE

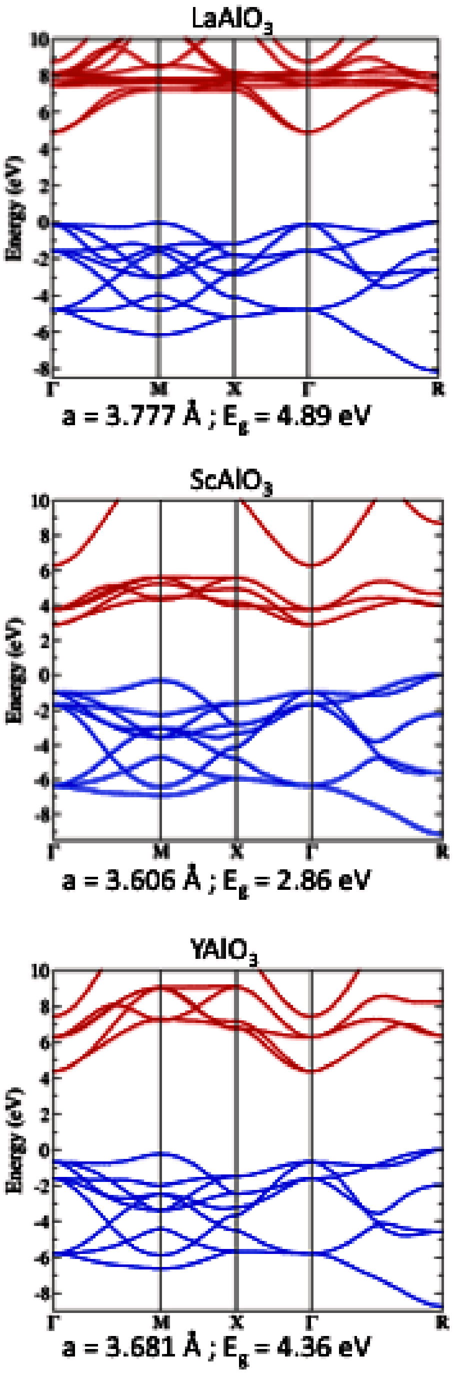


FIG. 2: Band Structure comparison of Aluminium Oxide Perovskites using HSE

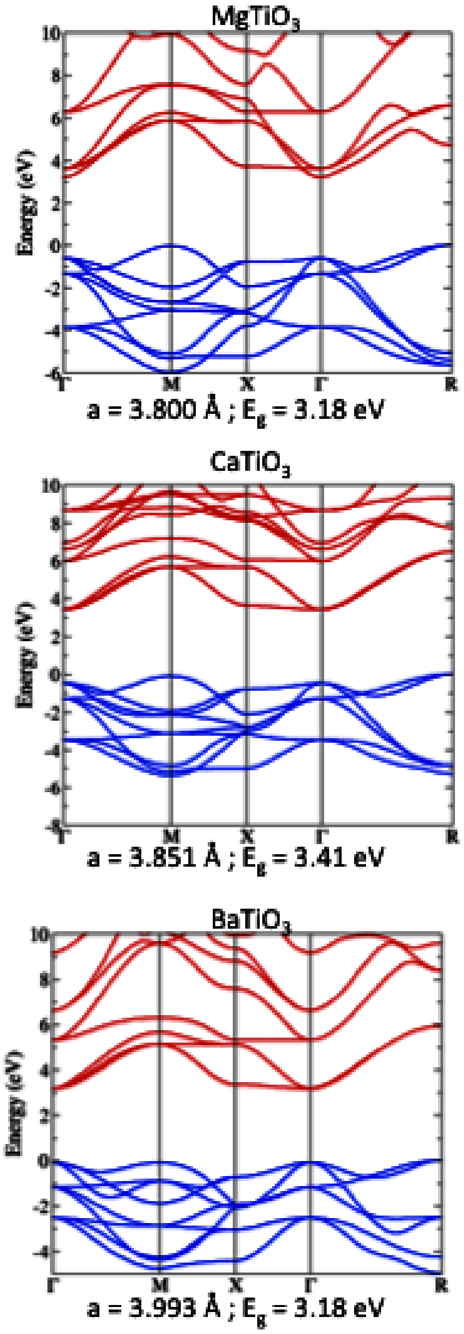


FIG. 3: Band Structure comparison of Titanium Oxide Perovskites using HSE

Comparisons were made between the bandstructure plots of similar perovskites to discern the changes induced in the electronic structure by varying the A or B ion. It was found that the B cation is the main influence on the conduction band, with the bottom of the conduction band minimum being made of a B t_{2g} triplet state in general, and the second band a B e_g doublet. This however was not the case for MgTiO$_3$, which instead has a Mg s-state for the conduction band minimum.

Moreover, it was found the the top three valence bands are composed of Oxygen p-states for all of these oxide perovskites. These bands are triply degenerate at the Γ point, and separate away from the centre of the zone.

Finally, it was confirmed that these oxide perovskites are indirect band gap semiconductors, with the Valance Band Maximum (VBM) at the R point and the Conduction Band Minimum (CBM) at the Γ point.

B. Learning Outcomes

From this research project I have learnt a large about modern theoretical approaches to condensed matter physics. I have become familiar with the methods of DFT and HSE, and their use in performing first principles calculations. I know have a good working knowledge of perovskite materials and their common properties, both structural and electronic.

In addition, I have gotten well acquainted with the methods of high performance computing, and parallel processing. I have gained fluency with the Linux terminal system and Bash, as well as with other command line based software.

I have also been able to learn a lot about the general research environment. I have gained an inside look at how a research group works, and how the research is carrier out, in an international setting. From this, I have been able to assess my own aptitude to research, and improve it by working in new ways.

On top of these things, I have gained a great amount of industry know-how. Each week I attended many seminars, at least three of which were regular. Of these, one was a career development workshop series, and another a scientific writing and presentation series. These two were especially useful, as I had the opportunity to develop skills in writing scientific talks, abstracts and papers, presenting these talks, and also poster preparation and presentation abilities. The third weekly seminar was a general scientific series, which helped to give me a more broad view of cutting edge scientific research.

Finally, I have learnt a huge amount about America, and American culture. I have had this great opportunity to travel all around the country, and see several different states and cities. This has been an excellent experience, which has broadened my outlook.

In all, I have discovered that I have a great drive for research, and that I wish to continue my studies after graduation with the goal of entering academic life.

IV. EVALUATION OF PROGRAM EXPERIENCE

Overall I would evaluate the program very well. It was a well structured program, which included many seminar series, some social programs, and a solid planned research project. I am of the opinion that everything was very well organised. The program is one which is of huge benefit to those who partake in it. I am sure that I have gotten many rewards from being involved in it, from academic and career orientated rewards, to social and cultural rewards also.

V. SUMMARY & CONCLUSIONS

To conclude, I would like to thank my project supervisor here at UCSB, Dr. Anderson Janotti, as well as Prof. Chris Van de Walle, and all the members of the Computational Materials Theory group, the CISEI and SURE programs, The University of Dublin, Trinity College, and all those staff who helped to make the program run smoothly. I would also like to talk the Science Foundation Ireland (SFI) and the National Science Foundation (NSF) for funding the program, and giving me this chance to come to the US for research.

---

[1] A. Janotti, C. G. Van de Walle, Nature Materials **6, 44** (2007).

[2] A. Janotti, C. G. Van de Walle, Phys. Stat. Sol. A **207, 5** (2010).

[3] C. G. Van de Walle, J. Neugebauer, Nature **423, 626** (2003).

[4] C.G. Van de Walle, A. Peles, A. Janotti, G.B. Wilson-Short, Physica B Condensed Matter **404, 793** (2009).

[5] Wolfram, T. Eillialtioğlu, Ş. Electronic and Optical Properties of d-Band Perovskites. Cambridge; Cambridge University Press, 2006.

[6] P. Hohenberg and W. Kohn, Phys. Rev. **136 B864** (1964).

[7] W. Kohn and L. J. Sham, Phys. Rev. **140 A1133** (1965).

[8] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118, 8207** (2003).

[9] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124, 219906(E)** (2006).

[10] J. Hafner, Computer Physics Communications **177 1-2** (2007).