THEORETICAL INSIGHTS OF DEFECTS IN MODULATING FUNCTIONAL PROPERTIES OF VARIOUS ADVANCED ENERGY MATERIALS

DEEPIKA GILL

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JUNE 2023

© Indian Institute of Technology Delhi (IITD), New Delhi, 2023.

Theoretical Insights of Defects in Modulating Functional Properties of Various Advanced Energy Materials

by

Deepika Gill

Department of Physics

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

Indian Institute of Technology Delhi

June 2023

Dedicated to my parents and supervisor

Certificate

This is to certify that the thesis entitled “**Theoretical Insights of Defects in Modulating Functional Properties of Various Advanced Energy Materials.**” being submitted by **Deepika Gill**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in Physics is a record of bonafide research work carried out by her under my supervision and guidance. She has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard. The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Prof. Saswata Bhattacharya
Thesis Supervisor
Department of Physics,
Indian Institute of Technology Delhi,
Hauz Khas, New Delhi 110016, India.
Date:.......
Place: New Delhi

Acknowledgments

First and foremost, I would want to take this chance to convey my sincere thanks to Professor Saswata Bhattacharya, who oversaw my thesis, for his unwavering support, wise counsel, tolerance, and inspiration. He enabled me to begin my studies in the same way that parents enable their newborn to take their first steps. I owe him a great deal of gratitude for our stimulating conversations about physics, research techniques, leadership qualities, philosophy, and a variety of other topics. These discussions have not only improved my understanding of physics but have also helped me develop into a well-rounded and inquisitive individual. He gave me considerable support and inspired bravery when things became difficult, and I owe him a great deal. He has always been an inspiration to me because of his contagious energy, love of physics, dynamic personality, and drive to achieve great things. He consistently believed in my talents, which inspired me to pursue a career in research, for which I am really grateful. I appreciate the thoughtful questions and ideas from Professors B. K. Mani, N. M. Anoop Krishnan and J. P. Singh, who make up the remainder of my student research committee in addition to my adviser. DISCERE group members Shikha Saini, Pooja Basera, Ekta Arora, Manish Kumar, Arunima Singh, Manjari Jain, Preeti Bhumla, Sajjan Sheoran, Ankita Phutela, Sanchi Monga, Ruman Moulik, Riya Gupta, Shantanu Pathak have my deepest gratitude for their assistance during my doctoral studies. I have had several enjoyable conversations with them on physics. I'm also appreciative to my other team members, Professors K. K. Pant, Sreedevi Upadhyayula, and Sameer Sapra, and Priyesh Yadav, Dr. Arindam Modak, and Dr. Sachin Tomar for our productive conversations and collaborations. I appreciate all the resources provided by the Indian Institute of Technology Delhi in New Delhi for my research efforts and travel funding. I'd like to express my gratitude to the University Grants Commission (UGC) for providing money for my study. I also thank the Council of Scientific Industrial Research (CSIR) for helping me out financially by paying for my travel. I am very appreciative of my family since without their unwavering support it would not have been able to complete this thesis. I will always be grateful to my parents for their unending love and blessings. I might not be who I am now without their wishes, motivation, and emotional support. Each of my victories or setbacks was felt by them as their own. Last but not least, I humbly thank the Almighty for bestowing upon me five senses and undying love.

Thank you!

Deepika Gill

Abstract

The necessity to switch to renewable energy sources has become critical due to the world's increasing energy demands and the depletion of fossil fuel reserves. The answer to the current problem is to use renewable energy sources, which are economical, ecologically responsible, and abundant in nature. Advanced solid-state materials that are utilized to solve environmental problems have attracted a lot of scientific interest. The three kinds of innovative energy materials—solid-state electrolyte materials for all-solid-state batteries, perovskite materials for solar cells and optoelectronic devices and catalysts for H_2 production and bio-mass conversion are the core topics of this thesis. The most widely used kind of energy storage in both autos and portable gadgets is the lithium-ion battery. Its use in large-scale energy applications is hindered by the usage of flammable liquid electrolytes. The use of solid-state electrolytes in place of liquid electrolytes, as in all-solid-state batteries, improves battery design and assures safety. LISICON oxide-based materials are been explored as solid-state electrolytes since they are easy to synthesize and environmentally friendly. However, they exhibit poor ionic conductivity at room temperature. Hence, we look at the impact of point defects on the ion transport properties, namely Li-vacancy, substitution at the P site with Si, Ge and Al. We do ab-initio molecular dynamics (AIMD) simulations to determine the diffusional characteristics of the pristine and defected materials. We explain how the point defects play a pivotal role in modifying the ion transport properties in oxide-based solid state electrolytes. On the other hand in optoelectronics, lead halide perovskites have become an effective compound semiconductor replacement for traditional solar materials. The materials in this class have a good optical band gap, long carrier diffusion length, high charge carrier mobility, and low cost of production. However, their widespread use is constrained by worries about the toxicity of lead and intrinsic instability. As an alternative to conventional lead halide perovskites, several derivatives of these have been proposed. Double perovskites like $Cs_2M(I)M(III)X_6$ (M = metal, X = halogen) and layered hybrid perovskites have been developed in an effort to combat toxicity and instability. However, these lead-free halide double perovskites and layered hybrid perovskites do not demonstrate the same efficiency as that of lead halide perovskites. Therefore, we do point defects in these materials to improve their stability, electronic and optical properties. Since double perovskites and layered hybrid perovskites do not meet all the criteria and lack at some points, we focus on a new type of inorganic layered type perovskite i.e., Ruddlesden Popper phases of chalcogenides. Here, we study the polaronic and excitonic effects with the number of perovskites units in a layer. To address optical features such as dielectric function, absorption spectra, exciton binding energy, and polaronic effects in perovskites, we use a robust methodological approach that combines many layers of theories into a single multi-scale simulation. Density functional theory (DFT) is used in this thesis work to predict the ground-state properties, ab initio atomistic thermodynamics is used to predict thermodynamic stability, many-body perturbation theory (GW, BSE, and model-BSE) is used to predict excited-state properties, the Wannier-Mott approach is used to calculate the exciton binding energy and exciton lifetime, and density functional perturbation theory (DFPT) is used to determine the exciton lifetime. Lastly, engineering an effective and optimized catalyst is the ultimate objective of research in heterogeneous catalysis. This is because there are many different catalytic processes. Consider what restricts the usefulness of current catalysts as a useful technique for finding acceptable catalysts. Understanding the intended functionality at an atomistic level is crucial for the development and logical design of catalytic materials. In this thesis, we study role of O-vacancy on the surface of the catalyst in facilitating the dissociation of the SO_3 which is the most endothermic reaction step in the S-I cycle for H_2. We also study the effect of surrounding ligands on the catalytic activity of the single-atom-Ru in partial hydrogenation of the xylose/glucose into useful sweeteners, which are popular in medical as well as industrial areas.

सार

ऊर्जा की बढ़ती मांग और जीवाश्म ईंधन भंडार की कमी के कारण अक्षय ऊर्जा स्रोतों पर स्विच करने की आवश्यकता महत्वपूर्ण हो गई है। वर्तमान में इसका एकमात्र उपाय नवीकरणीय ऊर्जा स्रोतों का उपयोग करना है, जो किफायती, पारिस्थितिक रूप से जिम्मेदार हो, और प्रकृति में प्रचुर मात्रा में पाए जाते हो। उन्नत ठोस-राज्य सामग्री जिनका उपयोग पर्यावरण की ऊर्जा सम्भंदित समस्याओं को हल करने के लिए किया जाता है, जिस कारण ये वैज्ञानिक शोध का केंद्र बने हुए है। तीन प्रकार की नवीन ऊर्जा सामग्री -सभी ठोस-राज्य बैटरी के लिए ठोस-राज्य इलेक्ट्रोलाइट सामग्री, सौर सेल/ऑप्टोइलेक्ट्रॉनिक उपकरणों के लिए पेरोसाइट सामग्री, और H_2 उत्पादन और जैव-द्रव्यमान रूपांतरण के लिए उत्प्रेरक, इस थीसिस के मुख्य विषय हैं। मोबाइल और डिजिटल डिवाइस में सबसे व्यापक रूप से इस्तेमाल किया जाने वाला ऊर्जा भंडारण और पोर्टेबल गैजेट लिथियम-आयन बैटरी है। ज्वलनशील तरल इलेक्ट्रोलाइट्स की उपस्थिति ने उनके बड़े पैमाने पर व्यावसायीकरण में बाधा उत्पन्न की है। तरल इलेक्ट्रोलाइट्स की जगह ठोस-अवस्था इलेक्ट्रोलाइट्स का उपयोग, जैसा कि सभी ठोस-राज्य बैटरी में होता है, बैटरी डिजाइन में सुधार करता है और सुरक्षा का आश्वासन देता है। LISICON ऑक्साइड-आधारित सामग्री को ठोस-अवस्था इलेक्ट्रोलाइट्स के रूप में खोजा गया है क्योंकि वे संश्लेषित करना आसान है और पर्यावरण के अनुकूल है। हालांकि, वे खराब आयनिक चालकता प्रदर्शित करते हैं कमरे के तापमान पर। इसलिए, हम आयन परिवहन गुण पर बिंदु दोष के प्रभाव को देखते हैं, अर्थात् Li-रिक्ति, Si, Ge और Al के साथ P साइट पर प्रतिस्थापन। हम प्राचीन और दोषपूर्ण सामग्री की विसारक विशेषताओं को निर्धारित करने के लिए आणविक गतिकी (AIMD) सिमुलेशन की हैं। हम समझाते हैं कि कैसे बिंदु दोष ऑक्साइड-आधारित ठोस अवस्था इलेक्ट्रोलाइट्स में आयन परिवहन गुण संशोधित करने में महत्वपूर्ण भूमिका निभाते हैं। वहीं दूसरी ओर ऑप्टोइलेक्ट्रॉनिक्स में, लेड हैलाइड पेरोसाइट्स एक प्रभावी यौगिक सेमीकंडक्टर बन गए हैं, जो परंपरागत सौर सेल सामग्री को प्रतिस्थापित कर सकता है। ये सामग्री अच्छे ऑप्टिकल बैंड का प्रदर्शन करती हैं अंतराल, लंबी वाहक प्रसार लंबाई, उच्च चार्ज वाहक गतिशीलता, और उत्पादन की कम लागत। हालांकि, सीसा की विषाक्तता और आंतरिक अस्थिरता ने उनके बड़े पैमाने पर व्यावसायीकरण में बाधा डाली है। पारंपरिक लेड हलाइड पेरोसाइट्स के विकल्प के रूप में कई पेरोसाइट्स प्रस्तावित किए गए हैं। $Cs_2M(I)M(III)X_6$ (M = धातु, X = हलोजन) जैसे डबल पर्कोसाइट्स और स्तरित संकर पर्कोसाइट्स विषाक्तता और अस्थिरता से निपटने

के प्रयास में विकसित किए गए हैं। हालाँकि, ये लेड-फ्री हैलाइड डबल पर्कोव्साइट्स और लेयर्ड हाइब्रिड पर्कोव्साइट्स करते हैं उच्च शक्ति रूपांतरण दक्षता का प्रदर्शन नहीं करते हैं, जैसा कि लेड हैलाइड पेरोसाइट्स के रूप में होता है। प्रदर्शन नहीं करते। इसलिए, उनकी स्थिरता, इलेक्ट्रॉनिक और ऑप्टिकल गुणों में सुधार करने के लिए हम ऐसी सामग्रियों में दोषों की भूमिका का अध्ययन करते हैं। जैसा डबल पर्कोव्साइट्स और लेयर्ड हाइब्रिड पर्कोव्साइट्स सभी मानदंडों को पूरा नहीं करते हैं और कुछ में कमी है, हम एक नए प्रकार के अकार्बनिक स्तरित प्रकार के पेरोसाइट पर ध्यान केंद्रित करते हैं, जैसे कि चाकोजेनाइड रुडल्सडेन पॉपर पेरोव्स्काइट्स। यहां, हम एक परत में पेरोसाइट इकाइयाँ की संख्या के साथ पोलरोनिक और एक्साइटोनिक प्रभावों का अध्ययन करते हैं। परावैद्युत फलन, अवशोषण जैसी प्रकाशीय विशेषताओं, स्पेक्ट्रा, एक्सिटोन बाइंडिंग एनर्जी, और पेरोसाइट्स में पोलरोनिक प्रभाव का अध्ययन के लिए हम एक मजबूत पद्धति का उपयोग करते हैं, जो सिद्धांतों की कई परतों को एक बहु-स्तरीय अनुकरण में जोड़ता है। Density functional theory (DFT) का उपयोग इस थीसिस कार्य में जमीन-राज्य गुणों की भविष्यवाणी करने के लिए किया जाता है, *ab initio* Molecular dynamics का उपयोग थर्मोडायनामिक स्थिरता की भविष्यवाणी करने के लिए किया जाता है, many body Perturbation theory (GW, BSE, and model-BSE) उत्साहित राज्य गुणों की भविष्यवाणी करने के लिए प्रयोग किया जाता है, Wannier-Mott दृष्टिकोण का उपयोग एक्सिटोन बाइंडिंग एनर्जी और एक्साइटन लाइफटाइम की गणना के लिए कियाजाताहै, और घनत्व कार्यात्मक गड़बड़ी सिद्धांत (DFPT) का उपयोग एक्साइटन जीवनकाल को निर्धारित करने के लिए किया जाता है। अंत में, इंजीनियरिंग में एक प्रभावी और अनुकूलित उत्प्रेरक अनुसंधान का अंतिम उद्देश्य है। ऐसा इसलिए है क्योंकि कई अलग-अलग उत्प्रेरक प्रक्रियाएं हैं। विचार करना स्वीकार्य खोजने के लिए एक उपयोगी तकनीक के रूप में वर्तमान उत्प्रेरक की उपयोगिता को क्या प्रतिबंधित करता है उत्प्रेरक। विकास के लिए एक परमाणु स्तर पर इच्छित कार्यक्षमता को समझना महत्वपूर्ण है और उत्प्रेरक सामग्री का तार्किक डिजाइन। इस थीसिस में, हम O-रिक्ति की भूमिका का अध्ययन करते हैं जो SO_3 के वियोजन को सुविधाजनक बनाने में उत्प्रेरक की सतह पर महत्वपूर्ण भूमिका निभाता है। SO_3 का वियोजन, H_2 उत्पादन के लिए S-I चक्र में सबसे अधिक एंडोथर्मिक चरण है।हम Ru एकल परमाणु की उत्प्रेरक गतिविधि पर आसपास के लिगेंड की भूमिका का भी अध्ययन करते हैं, जिसका उपयोग जाइलोज/ग्लूकोज के हाइड्रोजनीकरण के लिए जाइलिटोल/सोर्बिटोल में किया जाता है, जो चिकित्सा और उद्योगों में मांग में हैं।

List of Publications

1. **D. Gill**, M. Kumar, P. Basera, S. Bhattacharya “Understanding the ionic diffusivity in (meta)stable (un)doped solid state electrolyte fromfirst- principles: A case study of LISICON" J. Phys. Chem. C 124, 17485 (2020).

2. **D. Gill**, P. Bhumla, M. Kumar, S.Bhattacharya “High-throughput screening for band gap engineering by sub lattice mixing of $Cs_2AgBiCl_6$ from first- principles" J. Phys. Mater. 4, 025005 (2021).

3. **D. Gill**, A. Singh, M. Jain, S.Bhattacharya “Exploring Exciton and Polaron Dominated Photophysical Phenomena in RuddlesdenPopper Phases of $Ba_{n+1}Zr_nS_{3n+1}$ (n = 1-3) from Many Body Perturbation Theory" J. Phys. Chem. Lett. 12, 6698 (2021).

4. **D. Gill**, G. Yadav, S. Bhattacharya “Sn/Ge Substituted in $((C_nH_{2n-1}NH_3)_2PbI_4$; n=3-6): An Emerging 2D Layered Hybrid Perovskites with Enhanced Optoelectronic Properties" J. Phys. Chem. C 2022 126 (32), 13957-13966.

5. S. Tomar, **D.Gill**, K. Kondamudi, S. Upadhayula, S. Bhattacharya “SO_3 decomposition over silica modified b-SiC supported $CuFe_2O_4$ catalyst: Effects of Si treated support and Fe-O-vacancy-Cu on catalyst activity” Nanoscale 14, 6876 (2022).

6. A. Modak, **D. Gill**, A. Mankar, V. Bhasin, C. Nayak, K. K. Pant, S. Bhattacharya “Ru-Single Atom Decorated Ordered Mesoporous Polymer for High Yield Synthesis of Sugar Alcohols under Microwave Conditions" Nanoscale 14, 15875 (2022).

7. P. Yadav, **D. Gill**, S. Khurana, R. S. Lamba, S. Bhattacharya, S. Sapra “Enhanced Luminescence and Interstitial Site Mn^{2+} Doping in Two-Dimensional Na-In Halide Perovskite" J.Phys.Chem.C accepted.

8. M. Kumar, A. Singh, **D. Gill**, S. Bhattacharya “Optoelectronic Properties of Chalcogenide Perovskites from Anybody Perturbation Theory" J. Phys. Chem. Lett. 12, 5301

(2021).

9. M. Jain, **D. Gill**, P. Bhumla, S. Bhattacharya “Theoretical Insights of Excitonic in Lead Bromide Perovskites" Apple. Phys. Lett. 118, 192103 (2021).
10. P. Bhumla, **D. Gill**, S. Sheoran, S. Bhattacharya “Origin of Rashba Spin- splitting and Strain Tunability in Ferroelectric Bulk $CsPbF_3$" J. Phys. Chem. Lett. 12 (39), 9539-9546.
11. P. Basera, A. Singh, **D. Gill**, S. Bhattacharya “Capturing Excitonic Effects in Lead Iodide Perovskites from Many-Body Perturbation Theory" J. Mater. Chem. C 9 (47), 17113-17123.
12. M. Jain, **D. Gill**, S. Monga and S. Bhattacharya “Theoretical evaluation of oxynitride, oxyfluoride and nitrofluoride perovskites with promising photon absorption properties for solar water splitting” arXiv:2301.04335.
13. A. Modak, **D. Gill**, K. Sharma,V. Bhasin,K. K. Pant, S. N. Jha,D. Bhattacharyyac and S. Bhattacharya“Hydrogenolysis of biomass-derived xylose to xylitol and 1,2-diols under microwave condition by hydroxylated Ru single-atom on phosphine-modified silica” to be submitted.

Contents

Certificate i

Acknowledgements ii

Abstract iv

List of Publications vi

List of Symbols vi

List of Figures xiii

1 Introduction 1

1.1 Why advanced energy materials? 1

1.2 A brief introduction to imperfection or defects in solids 2

1.3 Thermodynamics of defects 2

1.4 Solid solutions 4

1.5 The Hume-Rothery Rules for the Solid Solution 4

1.6 Properties affected or controlled by the by point defects 6

1.7 Role of point defects in advance energy materials 6

1.8 Problems and Challenges 8

1.9 A short overview 10

2 Theoretical methodology 14

2.1 Computer simulation 14

2.2 First principles calculation 15

2.3 Introduction to many body physics: A theoretical framework 17

2.4 Wavefunction 19

2.5 Time independent Schrödinger equation 21

2.6 Born-Oppenheimer approximation 22

2.7 Wavefunction based approximation 23

2.8 The Hartree approximation 23

2.9 The Hartree-Fock approximation 25

2.10 Functional 28

2.11 Density Functional Theory 29

 2.11.1 The Thomas-Fermi Model 29

 2.11.2 Hohenberg and Kohn Theorem 30

  2.11.2.1 Kohn-Sham equations 34

 2.11.3 Exchange and correlation energy 36

2.12 Basis set 40

 2.12.1 The Plane wave basis set 41

 2.12.2 Numeric atom-centred basis functions 43

 2.12.3 Plane wave pseudopotential method 43

 2.12.4 Norm-conserving pseudopotential 45

 2.12.5 Vanderbilt Ultrasoft pseudopotential 45

 2.12.6 Projector augmented-wave method (PAW) 46

2.13 Introduction: Beyond DFT 48

2.14 GW method 50

2.15 Bethe-Salpeter Equation (BSE) 55

 2.15.1 Optical response using BSE 59

 2.15.2 Challenges while performing BSE calculations 61

2.16 Exciton models and lifetimes 62

2.17 Wannier exciton 63

2.18 Optical transition 64

 2.18.1 Fermi's golden rule 64

2.19 Wannier approach 66

 2.19.1 k.p perturbation theory 66

2.20 Excitonic parameters 68

2.21 Exciton lifetime 68

2.22 Geometry optimization 69

2.23 Molecular dynamics . . . 70
2.23.1 *Ab Initio* Molecular Dynamics . . . 71
2.23.2 Integration algorithms . . . 73
2.23.3 Ensembles . . . 73
3 Role of defects in modulating the ionic-diffusivity in solid state electrolytes for battery materials 78
3.1 Introduction . . . 78
3.2 Methodology . . . 80
3.3 Results and Discussions . . . 81
3.3.1 Formation energy of defects . . . 81
3.3.2 Change in amplitude of vibration with temperature and doping . . . 84
3.3.3 Tracer diffusivity and ionic conductivity . . . 85
3.3.4 Estimation of jump rate . . . 87
3.3.5 Polarization and lattice softening . . . 89
3.4 Conclusion . . . 93
4 Bandgap engineering by doing sublattice mixing in double perovskites 94
4.1 Introduction . . . 94
4.2 Methodology . . . 96
4.3 Results and Discussions . . . 96
4.3.1 Validation of exchange-correlation (ϵ_{xc}) functional for $Cs_2AgBiCl_6$ . . . 96
4.3.2 Screening of conformers based on band gap values and stability against decomposition . . . 97
4.3.3 Inconsistency in the band gap with different percentage of substitution . 101
4.3.4 Optical properties of potential conformers . . . 105
4.3.5 Spectroscopic limited maximum efficiency (SLME) . . . 108
4.4 Conclusion . . . 110
5 Exploring the effects of the defects in layered hybrid perovskite 111
5.1 Introduction . . . 111
5.2 Methodology . . . 113
5.3 Results and Discussions . . . 114
5.3.1 Benchmarking of DFT functionals . . . 114

5.3.2 Thermodynamic Stability 118
5.3.3 Structural Stability 120
5.3.4 Electronic Properties 121
5.3.5 Optical properties 123
5.3.6 Spectroscopic limited maximum efficiency (SLME) 124
5.3.7 Wannier-Mott approach and exciton binding energy 126
5.3.8 Electron-phonon coupling strength 127
5.4 Conclusion 132

6 Exciton and polaron dominated photo-physical phenomena in Ruddlesden popper phases of chalcogenide perovskites 133
6.1 Introduction 133
6.2 Methodology 134
6.3 Results 136
6.4 Conclusions 149

7 Role of defects and surrounding on the catalytic activity of the catalyst in energy fuel and bio-mass conversion 151
7.1 Introduction 151
7.2 SO_3 decomposition over silica-modified β-SiC supported $CuFe_2O_4$ catalyst: atomistic insights 151
7.2.1 Computational details 152
7.2.2 Result 153
7.3 Partial hydogenation of the xylose/glucose into useful sweatners using single Ru-atom catalyst surrounded by different ligands. 155
7.3.1 Computational 156
7.3.2 Results 156
7.4 Conclusion 160

8 Summary 161

A Appendix 164
A.1 Band gap, tolerance factor, octahedral factor and enthalpy of decomposition of different configurations 164

A.2 Path of decomposition of $Cs_2AgBiCl_6$ into binary/ternary compounds on alloying with monovalent, trivalent and divalent configurations 168

List of Figures

1.1 Diagrammatic representation of surface defects such as flaws at grain boundaries, edge dislocations, and point defects such as vacancies, substitutions, and interstitial defects. 3

1.2 Schematic presentation of strain in the lattice on doing substitutional point defect. 5

1.3 Partial density of states and absorption spectra of (a) pristine ($Cs_8Ag_4Bi_4Cl_{24}$) and (b) defected $Cs_8Ag_3Au_1Bi_4Cl_{24}$ double perovskites along with respective optimized geometries. 7

1.4 Schematic illustration of point defects in different energy materials viz., LISICON, perovskites, catalysts and their applications in automobile, electronic devices, solar cells, and optoelectronic devices, H_2 production and biomass conversion. 8

1.5 Schematic illustration of various energy materials as input, and several challenges and steps to be followed to have accurate prediction of the electronic, ion transport, optical properties and thermodynamic stability for their application in different energy fields. 10

2.1 Multi-scale simulation in different length and time scales. 16

2.2 The polar coordinates of a spherical symmetric system 20

2.3 Schematic flowchart of Hartree method for solving the many electron system. . 26

2.4 Schematic flowchart of Hartree-Fock method for many-body system. 28

2.5 Schematic of the interacting and non-interacting electron systems possessing same ground density. 35

2.6 Jacob's ladder, illustrating the variation of the accuracy and the commputational cost with different exchange-correlation functionals. 38

2.7 Flow-chart for the solution of the Kohn-Sham equations using self-consistent method. 40

2.8 Schematic representation of all electron wavefunction (shown with solid line) and its corresponding pseudo wavefunction (shown with dashed line) and along with the respective external Coulomb potential and pseudopotential [1]. 44

2.9 Photoemission and inverse photoemission spectroscopies along with optical band gap are shown schematically. 48

2.10 Spectral function representation for both interacting many particles and non-interacting single particle excitation. 51

2.11 The illustration of the quasiparticle and noninteracting particle excitation peaks. 52

2.12 The pentagon of Hedin. In the GW approximation, the vertex function (Γ) is omitted. 54

2.13 Schematic diagram of many body interaction (exchange and the direct interaction)term. 60

2.14 Flow chart for the BSE calculations. 60

2.15 Work flow diagram for *ab-initio* molecular dynamics (AIMD). 72

3.1 (a) Gaussian curve fit of the average temperature of $\mathrm{Li_4SiO_4}$ during AIMD run of time period 30 ps, 40 ps and 50 ps, respectively at 300 K. (b) Formation energy per atom ($\mathrm{E_f}$), with increase in Li-$\boxtimes$ in $\mathrm{Li_{56}Si_{14}O_{56}}$, using HSE06 functional. 81

3.2 Formation energy per atom (E_f) of different structures are represented as a function of (a) P-substitution at Li and Li-$\boxtimes$ (for $\mathrm{Li}_{56-y-x}\mathrm{P}_y\mathrm{Si}_{14}\boxtimes_x\mathrm{O}_{56}$), (b) P-substitution at Si and Si-$\boxtimes$ (for $\mathrm{Li}_{56}\mathrm{Si}_{14-y-x}\mathrm{P}_y\boxtimes_x\mathrm{O}_{56}$) and (c) P-substitution at Si, along with Si-vacancy and Li-$\boxtimes$ (for $\mathrm{Li}_{56-x}\mathrm{Si}_{14-y-k}\mathrm{P}_y\boxtimes_x\boxtimes_k\mathrm{O}_{56}$). The color bar represents E_f in eV. A guide to eye for the configuration with minimum E_f is marked with red arrows. (d) Optimized structure of the system with P-substitution at Si-site. 83

3.3 Histogram showing the amplitude of vibration of Li-ions at 300 K, 600 K and 900 K in $\mathrm{Li}_{56-x}\mathrm{Si}_{14-y}\mathrm{P}_y\boxtimes_x\mathrm{O}_{56}$ for (a) $x = 0$ and $y = 0$, (b) $x = 2$ and $y = 2$ and (c) $x = 4$ and $y = 4$. (d) Histogram of amplitude of vibration of Li-ions in $\mathrm{Li}_{56-x}\mathrm{Si}_{14-y}\mathrm{P}_y\boxtimes_x\mathrm{O}_{56}$ at 300 K, where values of x and y are (0, 2, and 4). The colored dotted lines correspond to gaussian curve fitting. 85

3.4 Histogram showing the amplitude of vibration of Li-ions at 300 K, 600 K and 900 K in $\mathrm{Li}_{56-x}\mathrm{Si}_{14-y}\mathrm{P}_y \boxtimes_x \mathrm{O}_{56}$ for (a) $x = 0$ and $y = 0$, (b) $x = 2$ and $y = 2$ and (c) $x = 4$ and $y = 4$. (d) Histogram of amplitude of vibration of Li-ions in $\mathrm{Li}_{56-x}\mathrm{Si}_{14-y}\mathrm{P}_y \boxtimes_x \mathrm{O}_{56}$ at 300 K, where values of *x* and *y* are (0, 2, and 4). The colored dotted lines correspond to gaussian curve fitting. 86

3.5 Jump rates of pristine and defected systems at different temperatures for different planes. 88

3.6 Contour density plots of Li-ion diffusion for $\mathrm{Li}_4\mathrm{SiO}_4$ in (a) bc-plane (b) ac-plane, at 600 K. 88

3.7 Charge density plot for plane with miller indices (001) at a distance 11 Å from origin for (a) $\mathrm{Li}_{56}\mathrm{Si}_{14}\mathrm{O}_{56}$, (b) $\mathrm{Li}_{54}\mathrm{Si}_{12}\mathrm{P}_2 \boxtimes_2 \mathrm{O}_{56}$ at 600 K. Note that Si and P labeled atoms in (a) and (b) are lying slightly above the given plane. During whole AIMD simulation at 600 K, radial distribution of (c) single Li w.r.t. all O (d) all Li w.r.t. all O, (e) single Li w.r.t. all Si (f) all Li w.r.t. all Si. Here different color corresponds to three different configurations in $\mathrm{Li}_{56-x}\mathrm{Si}_{14-y}\mathrm{P}_y \boxtimes_x \mathrm{O}_{56}$. 90

3.8 Schematic diagram of the effect of lattice softening on activation barrier (lower panel) and simulated one (upper panel). With increasing lattice softness, i.e., with decreasing bond strength, the activation barrier gets reduced for the defected systems. 92

4.1 Convergence of *k*-mesh for (a) imaginary and (b) real part of dielectric function using PBE ϵ_{xc} functional. Band gap of $\mathrm{Cs}_2\mathrm{AgBiCl}_6$, using (c) HSE06 and (d) HSE06+SOC ϵ_{xc} functionals with different values of Hartree-Fock exchange fraction (α). (e) Band edge alignment of VBM and CBm with PBE, PBE+SOC and HSE06+SOC. 97

4.2 (a) Variation of tolerance and octahedral factor for different conformers. Band gap vs ΔH_D using (b) PBE+SOC (Here, the highlighted region shows the promising configurations that lie within the band gap of 0.0 to 1.5 eV) and (c) HSE06+SOC ϵ_{xc} functionals (highlighted region shows the promising configurations that lie within the band gap of 1.0 to 2.3 eV). (Here, red, blue and green color circular dots correspond to M(I) (e.g., substitution of 25% Au at Ag-site ($(25\%)Au_{Ag}$)), M(II) (e.g., substitution of Sn at Ag- and Bi-site simultaneously ($Sn_{Ag,Bi}$)) and M(III) (e.g., substitution of 25% Sb at Bi-site ($(25\%)Sb_{Bi}$)), respectively) (d) Enthalpy of decomposition for decomposition of pristine and alloyed double perovskites into binary/ternary compounds, using HSE06+SOC ϵ_{xc} functional. 98

4.3 Band structure of (a) $Cs_8Ag_4Sb_1Bi_3Cl_{24}$, (b) $Cs_8Ag_4Sb_2Bi_2Cl_{24}$, (c) $Cs_8Ag_4Sb_3Bi_1Cl_{24}$ and (d) $Cs_8Ag_4Sb_4Cl_{24}$ using PBE+SOC ϵ_{xc} functional. 101

4.4 Partial density of states (pDOS) for Sb substitution at Bi-sites of $Cs_2AgBiCl_6$, using HSE06+SOC ϵ_{xc} functional. Different color corresponds to different atoms in the system. 102

4.5 Electron localized function (ELF) for $Cs_2AgBiCl_6$ and Sb substituted configurations. 104

4.6 (a) Partial density of states (pDOS) of pristine and alloyed $Cs_2AgBiCl_6$ calculated using HSE06+SOC ϵ_{xc} functional. (b) Band structure of (i) $Cs_8Ag_3Au_1Bi_4Cl_{24}$, (ii) $Cs_8Ag_2Au_2Bi_4Cl_{24}$, (iii) $Cs_8Ag_1Au_3Bi_4Cl_{24}$ and (iv) $Cs_8Au_4Bi_4Cl_{24}$, using PBE+SOC ϵ_{xc} functional. 105

4.7 Variation of imaginary part of dielectric constant (Im(ε)) of $Cs_2AgBiCl_6$ sublattice mixed with (a) monovalent (M(I)), (d) divalent (M(II)) and (g) trivalent (M(III)) cations, respectively. Variation of real part of dielectric constant (Re(ε)) of $Cs_2AgBiCl_6$ sublattice mixed with (b) monovalent (M(I)), (e) divalent (M(II)) and (h) trivalent (M(III)) cations, respectively. Absorption coefficient of $Cs_2AgBiCl_6$ sublattice mixed with (c) monovalent (M(I)), (f) divalent (M(II)) and (i) trivalent (M(III)) cations, respectively. Note that all calculations have been done using HSE06+SOC ϵ_{xc} functional. 106

4.8 Variation of SLME w.r.t. the thickness of solar cell absorber. 108

5.1 (a) A 3D cubic perovskite structure with chemical formula ABX_3, where A, B and X are organic cation, divalent metal cation and monovalent halide anion, respectively. (b) Schematic drawing of 2D layered structure of the $(R\text{-}NH_3)_2BX_4$ hybrids. 112

5.2 Crystal structures for compounds: (a) cyclopropyl ammonium tetraiodoplumbate (CPPI, n = 3), $(C_3H_5NH_3)_2PbI_4$, (b) cyclobutyl ammonium tetraiodoplumbate (CBPI, n = 4), $(C_4H_7NH_3)_2PbI_4$, (c) cyclopentyl ammonium tetraiodoplumbate (CPEPI, n = 5), $(C_5H_9NH_3)_2PbI_4$, and (d) cyclohexyl ammonium tetraiodoplumbate (CHXPI, n = 6), $(C_6H_{11}NH_3)_2PbI_4$. 113

5.3 Calculated band structures along with the density of states (DOS) of CPPI. The band paths are along the high symmetry *k*-points Γ (0, 0, 0), F (0, 0.5, 0), Q (0, 0.5, 0.5), and Z (0, 0, 0.5) of BZ. 115

5.4 (a) Band edge alignment for for CPPI using PBE, PBE+SOC, HSE06 and HSE06+SOC functionals. (b) Variation in the bandgap of CPPI with α. The point inside blue ellipse represents the calculated bandgap, which is very close to the experimental bandgap. (c) Imaginary part of the dielectric function calculated using HSE06+SOC with different Hartree-Fock exact exchange (i.e., α = 0.25, 0.30, 0.40 and 0.50). 116

5.5 (a) Partial density of states of $(C_3H_5NH_3)_2PbI_4$; (b) Partial density of states of inorganic cage of $(C_3H_5NH_3)_2PbI_4$. 117

5.6 Partial density of states of inorganic cage of (a) $(C_3H_5NH_3)_2PbI_4$; (b) $(C_4H_7NH_3)_2PbI_4$; (c) $(C_5H_9NH_3)_2PbI_4$; (d) $(C_6H_{11}NH_3)_2PbI_4$. Notably, since VBM and CBm are contributed by In and Pb orbitals (organic moieties mainly contribute in the deep of the conduction and valence band). Hence, only inorganic cage has been taken into account. 118

5.7 Variation of (a) imaginary (Im (ε)) and (b) real (Re (ε)) parts of dielectric function with energy; (c) variation of absorption coefficient with wavelength for ($(C_nH_{2n\text{-}1}NH_3)_2PbI_4$; n=3-5) using HSE06+SOC functional 119

5.8 Formation energy (eV/atom) of different mixed conformers (the blue dotted line is the reference line corresponding to prototypical material (CPPI)), and their respective bandgap using HSE06+SOC with α = 25%. 121

5.9 Radial distribution of stable phanses of $(C_3H_5NH_3)_2Pb_{1-x}Sn_xI_4$ at two different temperatures i.e., 0K and 400K. 122

5.10 Calculated octahedral factor for different conformers. 123

5.11 Calculated total and partial density of states for (a) $(C_3H_5NH_3)_4Pb_2I_8$, (b) $(C_3H_5NH_3)_4SnPbI_8$, (c) $(C_3H_5NH_3)_4Sn_2I_8$, and (d) $(C_3H_5NH_3)_4GePbI_8$ using the HSE06+SOC with α = 25%. The VBM is set to 0 eV. 125

5.12 (a) Calculated imaginary part of the dielectric function, Im(ε), and (b) calculated real part of the dielectric function, Re(ε) for different stable conformers using HSE06+SOC with α = 25%. 126

5.13 (a) Calculated absorption coefficient, and (b) SLME vs film thickness, of different stable conformers using HSE06+SOC with α = 25%. 126

5.14 Single Mn^{+2} substitutionally doped at In-site of 2D RP $(PEA)_4NaInCl_8$ (a) optimized crystal structure of unit cell (b) band structure and (c) partial Density of States (pDOS). Single Mn^{+2} interstitially doped 2D RP $(PEA)_4NaInCl_8$ (d) optimized crystal structure of unit cell, (e) band structure and (f) pDOS. (g) Variation of absorption coefficient with the wavelength doped at In-site of 2D RP $(PEA)_4NaInCl_8$. (h) As a function of the displacement of atoms, the formation energies in two different charges states i.e., q=0 and q=1 are plotted. 130

5.15 (a) Optimized crystal structure, (b) band structure, and (c) partial Density of States (pDOS) of 2D $(PEA)_4NaInCl_8$. 131

6.1 (a) Real (Re(ε)) and imaginary (Im(ε)) part of dielectric function for $Ba_{n+1}Zr_nS_{3n+1}$ (n=[1-3]) RP phases using PBE exchange-correlation ϵ_{xc} functional. (b) Variation of imaginary part (Im(ε)) of dielectric function with number of occupied (NO) and unoccupied (NV) bands using BSE for Ba_2ZrS_4. 135

6.2 Optimized crystal structure of $Ba_{n+1}Zr_nS_{3n+1}$ (n=[1-3]) Ruddlesden-Popper phases (RP phases). 137

6.3 Variation of inverse of the dielectric function ε^{-1} with respect to |q+G| for (a) Ba_2ZrS_4, (b) $Ba_3Zr_2S_7$, and (c) $Ba_4Zr_3S_{10}$, respectively. The red curve is obtained by fitting based on Eq. (5). The mBSE calculated spectra with different k-mesh for (d) Ba_2ZrS_4, (e) $Ba_3Zr_2S_7$ and (f) $Ba_4Zr_3S_{10}$, respectively. 139

6.4 Model-BSE (mBSE) calculation with dense k-mesh and low NBANDS for Ba_2ZrS_4. Here, NBANDSO and NBANDSV correspond to number of occupied and vacant orbitals, respectively. 139

6.5 Imaginary part (Im (ε)) of the dielectric functional for $Ba_3Zr_2S_7$ using BSE and mBSE. 140

6.6 Imaginary part (Im (ϵ)) of the dielectric function for (a) Ba_2ZrS_4, (b) $Ba_3Zr_2S_7$, (c) $Ba_4Zr_3S_{10}$ using single shot GW (G_0W_0) and BSE. Im(ε) of dielectric function for (d) Ba_2ZrS_4 (e) $Ba_3Zr_2S_7$ and (f) $Ba_4Zr_3S_{10}$ along E || xy direction and Im(ε) of dielectric function for (g) Ba_2ZrS_4 (h) $Ba_3Zr_2S_7$ and (i) $Ba_4Zr_3S_{10}$ along E || z direction, using G_0W_0 and BSE. Here, coloured region is indicating the energy window that lies in visible region of electromagnetic spectra. . . 142

6.7 Full width at half maximum (FWHM) of exciton peak using mBSE@G_0W_0@PBE approach with dense k-mesh. Broadening of exciton peak is mainly due to electron-hole interaction. Here, Γ corresponds to the FWHM. 143

6.8 Electronic (Im (ε_e) and Re (ε_e)) (a)-(c) and ionic (Im (ε_i) and Re (ε_i)) (d)-(f) contribution to dielectric function for Ba_2ZrS_4, $Ba_3Zr_2S_7$ and $Ba_4Zr_3S_{10}$. Red and black color correspond to real (Re(ε)) and imaginary (Im(ε)), respectively. . 145

6.9 Capturing excitonic peak and estimation of E_B for the RP phases of $Ba_{n+1}Zr_nS_{3n+1}$ (n=[1-3]) using mBSE@G_0W_0@PBE method. 146

6.10 Variation of the bandgap with strain along different axis. 146

7.1 Free energy profile for adsorption and dissociation of SO_3 on the surface of $CuFe_2O_4$/β-SiC (UT) and $CuFe_2O_4$/β-SiC (T) catalyst, respectively. 153

7.2 Reaction profile for the decomposition of SO_3 with initial state (IS), transition state (TS) and final state (FS) on (a) $CuFe_2O_4$ cluster and (b) $CuFe_2O_4$ cluster with oxygen vacancy. Structure and charge density difference contours for SO_3 adsorbed on top of cluster (c) $CuFe_2O_4$, (d) $CuFe_2O_4$ with O-vacancy) and (e) Fe_2O_3 with O-vacancy. In charge density difference plots cyan and yellow colour correspond to the negative and positive charge, respectively. 154

7.3 Partial density of states (pDOS) for (a) isolated SO_3, SO_3 adsorbed over the cluster (b) $CuFe_2O_4$, (c) $CuFe_2O_4$ with O-vacancy and (d) Fe_2O_3 with O-vacancy. Here, blue and red color correspond to S and O states, respectively. . . 155

7.4 (a) Variation in the enumerated adsorption energy strength for glucose and xylose on the Ru-atom surrounded by different ligands. (b) The calculated Hirshfeld charge for the Ru atom in Ru-PPh, Ru-AmPh, and Ru-Cat, respectively. (c) The computed H-bonding energies between xylose (C5) and PPh, AmPh, and Cat, respectively. Energy minimized structures of (d) Ru-PPh-MesoSi, (e) Ru-AmPh, and (f) Ru-Cat along with their respective electron density difference plots; and (g) the change in Gibbs free energy for the partial hydrogenation of xylose to xylitol in the presence of different ligands (using PBE exchange–correlation functional); in the electron density difference plot, the cyan and the yellow colors correspond to the negative and positive charge densities, respectively.. 157

7.5 (a) Reaction profile for the adsorption and partial hydrogenation of the carbonyl group of the xylose with initial state (SI), transition state (TS) and final state (FS) on the single Ru atom surrounded by triphenylphosphine (Ru-PPh-MesoSi). (b) Reaction profile for the desorption of xylitol from the single Ru atom surrounded by triphenylphosphine (Ru-PPh-MesoSi). 158