UNDERSTANDING DEFECTS AND EXCITED-STATE PROPERTIES IN PEROVSKITES FROM MANY-BODY PERTURBATION THEORY

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by

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Department of Physics

Submitted

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

to the

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Dedicated to my parents

Certificate

This is to certify that the thesis entitled "**Understanding Defects and Excited-State Properties in Perovskites from Many-Body Perturbation Theory**" being submitted by **Manish Kumar**, 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 him under my supervision and guidance. He 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.

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Abstract

Oxide perovskites such as $SrTiO_3$ and $CaTiO_3$ are the potential candidates to be used as a photocatalyst due to their exceptional electronic structure, high chemical stability, non-toxicity, and low cost. They exhibit suitable conduction and valence band-edge positions for reduction and oxidation of water to produce hydrogen and oxygen. Therefore, they can be exploited to generate hydrogen via water splitting, which is a clean, sustainable, and abundant source of energy. However, owing to their wide band gap, they absorb only UV irradiation (which consists $\sim$4% of the solar spectrum). Hence, several works are dedicated to expand optical response toward the visible region by reducing the band gap through doping with metals, nonmetals, or the combination of different elements. Despite significant amount of research is done, both experimentally and theoretically on these systems, it is still an open question concerning the kind of dopants or codopants, that could reduce the band gap while retaining the photocatalytic efficiency. In view of this, we systematically study the role of monodoping as well as codoping of a metal and nonmetal in $SrTiO_3$ in enhancing the photocatalytic efficiency for water splitting. Moreover, we investigate the effects of intrinsic defect (viz. O-vacancy) in $CaTiO_3$ to disentangle the role of O-vacancy for water splitting and N_2 fixation reaction.

On the other hand, lead halide perovskites have emerged as an efficient compound semiconductor alternative to conventional materials used in photovoltaics. This class of materials has suitable optical band gap, long carrier diffusion length, high charge carrier mobility and low manufacturing cost. However, the concerns regarding toxicity of lead and phase instability restricts their usage on large scale. In an attempt to deal with toxicity and instability, lead-free halide double perovskites such as $Cs_2M(I)M(III)X_6$ (M = metal, X = halogen) and chalcogenide perovskites ABX_3 (A, B = metals, X = chalcogen) have emerged. In this work, we aim to design lead-free halide double perovskites with improved optoelectronic properties since they have not shown the efficiency as that of lead halide perovskites. Furthermore, the excitonic and polaronic effects are unraveled in the case of chalcogenide perovskites.

We employ a robust methodological approach that integrates various levels of theories combined into one multi-scale simulation to address the optical properties such as dielectric function, absorption spectra, exciton binding energy and polaronic effects in perovskites. In this thesis work, the state-of-the-art methodologies that are used to obtain the desired objectives are: (i) density functional theory (DFT) for ground-state properties, (ii) *ab initio* atomistic thermodynamics to predict the stability, (iii) many-body perturbation theory (GW, BSE and model-BSE) for excited-state properties, (iv) Wannier-Mott approach to determine the exciton binding energy and exciton lifetime, and (v) density functional perturbation theory (DFPT) for including ionic contribution to dielectric function and to capture the electron-phonon coupling.

सार

ऑक्साइड पैरोव्स्काइट्स जैसे कि $SrTiO_3$ और $CaTiO_3$ सामर्थ्यवान उम्मीदवार हैं जिन्हें उनकी असाधारण इलेक्ट्रॉनिक संरचना, उच्च रासायनिक स्थिरता, गैर-विषाक्तता और कम लागत के कारण फोटोकैटलिस्ट के रूप में उपयोग किया जा सकता है। वे हाइड्रोजन और ऑक्सीजन का उत्पादन करने के लिए पानी का अपचयन और ऑक्सीकरण के लिए उपयुक्त चालन और संयोजकता बैंड-एज स्थिति प्रदर्शित करते हैं। इसलिए, पानी के विभाजन के माध्यम से हाइड्रोजन उत्पन्न करने के लिए उनका दोहन किया जा सकता है, जो ऊर्जा का एक स्वच्छ, टिकाऊ और प्रचुर स्रोत है। हालांकि, उनके व्यापक बैंड अंतराल के कारण, वे केवल यूवी विकिरण (जो सौर स्पेक्ट्रम का लगभग 4% होता है) को अवशोषित करते हैं। इसलिए, धातुओं, अधातुओं या विभिन्न तत्वों के संयोजन के साथ मादन (डोपिंग) के माध्यम से बैंड अंतराल को कम करके दृश्य क्षेत्र की ओर ऑप्टिकल प्रतिक्रिया का विस्तार करने के लिए कई कार्य समर्पित हैं। इन प्रणालियों पर प्रायोगिक और सैद्धांतिक दोनों तरह से विस्तृत मात्रा में शोध किए जाने के बावजूद, यह अभी भी एक खुला प्रश्न है कि किस तरह के अपमिश्रक (डोपेंट) या कोडोपेंट हैं, जो फोटोकैटलिटिक दक्षता को बनाए रखते हुए बैंड अंतराल को कम कर सकते हैं। इसे ध्यान में रखते हुए, हम पानी के विभाजन के लिए फोटोकैटलिटिक दक्षता को बढ़ाने में $SrTiO_3$ में मोनोडोपिंग के साथ-साथ धातु और अधातु के कोडोपिंग की भूमिका का व्यवस्थित रूप से अध्ययन करते हैं। इसके अलावा, हम पानी के विभाजन और N_2 निर्धारण प्रतिक्रिया के लिए O-रिक्ति की भूमिका को सुलझाने के लिए $CaTiO_3$ में आंतरिक दोष (अर्थात O-रिक्ति) के प्रभावों की जांच करते हैं।

दूसरी ओर, लैड हैलाइड पैरोव्स्काइट्स एक कुशल यौगिक अर्धचालक फोटोवोल्टिक में प्रयुक्त पारंपरिक सामग्रियों के विकल्प के रूप में उभरे हैं। सामग्री के इस वर्ग में उपयुक्त ऑप्टिकल बैंड अंतराल, लंबी वाहक प्रसार लंबाई, उच्च आवेश वाहक गतिशीलता और कम विनिर्माण लागत है। हालांकि, लैड की विषाक्तता और चरण अस्थिरता के बारे में चिंताएं बड़े पैमाने पर उनके उपयोग को प्रतिबंधित करती हैं। विषाक्तता और अस्थिरता से निपटने के प्रयास में, लैड-रहित हैलाइड डबल पैरोव्स्काइट्स जैसे $Cs_2M(I)M(III)X_6$ (M = धातु, X = हैलोजन) और चाल्कोजेनाइड पैरोव्स्काइट्स ABX_3 (A, B = धातु, X = चाल्कोजेन)) उभरे हैं। इस काम में, हमारा लक्ष्य बेहतर ऑप्टोइलेक्ट्रॉनिक गुणों के साथ लैड-रहित हैलाइड डबल पैरोव्स्काइट्स को डिज़ाइन करना है क्योंकि उन्होंने लैड हैलाइड पैरोव्स्काइट्स जैसी दक्षता नहीं दिखाई है। इसके अलावा, चाल्कोजेनाइड पैरोव्स्काइट्स के मामले में एक्साइटोनिक और ध्रुवीय प्रभाव सुलझाये हैं।

हम एक मजबूत कार्यप्रणाली दृष्टिकोण को नियोजित करते हैं जो ऑप्टिकल गुणों जैसे कि परावैद्युत फलन, अवशोषण स्पेक्ट्रा, एक्साइटन बाध्यकारी ऊर्जा और पैरोव्स्काइट्स में ध्रुवीय प्रभाव को संबोधित करने के लिए एक बहु-स्तरीय अनुरूपण में संयुक्त सिद्धांतों के विभिन्न स्तरों को एकीकृत करता है। इस शोध-प्रबन्ध कार्य में, वांछित उद्देश्यों को प्राप्त करने के लिए उपयोग की जाने वाली अत्याधुनिक पद्धतियां हैं: (i) ग्राउंड-स्टेट गुणों के लिए घनत्व कार्यात्मक सिद्धांत (डीएफटी), (ii) स्थिरता की भविष्यवाणी करने के लिए आदित परमाणु ऊष्मा गतिकी, (iii) एक्साइटिड-स्टेट गुणों के लिए बहुपिंडी क्षोभ सिद्धांत (जीडब्ल्यू, बीएसई और मॉडल-बीएसई), (iv) ऐक्साइटॉन बाध्यकारी ऊर्जा और ऐक्साइटॉन जीवनकाल निर्धारित करने के लिए वैनियर-मॉट दृष्टिकोण, और (v) घनत्व कार्यात्मक क्षोभ सिद्धांत (डीएफपीटी) परावैद्युत फलन में आयनिक योगदान को शामिल करने और इलेक्ट्रॉन-फोनॉन युग्मन के अध्ययन के लिए।

List of Publications

1. **Manish Kumar**, Pooja Basera, Shikha Saini, and Saswata Bhattacharya, “Role of defects in photocatalytic water splitting: Monodoped vs codoped $SrTiO_3$”, The Journal of Physical Chemistry C **124**, 10272 (2020).

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