The 3rd International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/3/20230365

Recent trend of using computational science tools in organic-inorganic hybrid perovskite materials research

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Abstract. Organic-inorganic hybrid perovskite materials have been considered promising candidates for solar cells in the future, and computational science tools have been widely used in the research on the structure and various properties of these perovskite materials. Researchers have also focused on finding the composition of ions which they need for specific purposes and have discovered new candidates with better performance in the organic-inorganic hybrid perovskite materials family. In this review, notable computational ways to assist the organic-inorganic hybrid perovskite materials research in recent years, including First Principals calculations or Density Functional Theory (DFT) calculations, and machine learning tools, have been summarized and discussed. The review shows various applications for First Principals and DFT calculations in this area, and also highlights the prominent potential for machine learning tools in finding new perovskite material candidates for novel solar cells.

Keywords: perovskite, organic-inorganic hybrid, first principles, DFT, machine learning.

1. Introduction

Perovskite has been considered impressive materials with very high power conversion efficiency (PCE) and an easy process to fabricate. And organic-inorganic hybrid perovskites have become one of the most promising groups of perovskite materials to be applied in solar cells or electronic-photonic devices in the future.

To investigate the properties and structures of the organic-inorganic hybrid perovskite materials, researchers have had computational tools to do calculation sor simulations in many different ways. This includes first-principles calculations, usually based on density functional theory (DFT), and other tools. Besides the calculations, machine learning has also become an essential tool in organic-inorganic hybrid perovskite materials development.

The study reviews some notable recent reports about the utilization of calculation and machine learning tools in organic-inorganic hybrid perovskite materials studies. This review includes the general introduction of each study and the comparison and summary of those computational tools' assistant roles. The review shows a significant and diverse usage of computational science in organic-inorganic hybrid perovskite materials and devices studies and also a future potential in this and other material science research fields.

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DOI: 10.54254/2755-2721/3/20230365

2. The first principles calculations on organic-inorganic hybrid perovskite materials

2.1. The calculations of optical and electronic properties

The first principles calculations have been generally utilized in discovering the optical and electronic properties of organic-inorganic hybrid perovskite materials. Some groups have made some specific work in this area.

H. Kawai and K. Yamashita investigated the hot-carrier lifetimes from electron-phonon interaction in $CsPbI_3$ and PbI_3^-, and they found that while the holes in $CsPbI_3$ have longer lifetimes at a region below the valence band along with a small density of state, they don't show the same characters in PbI_3^-. They found that the difference here means the slow hot-hole cooling is the small density of state in the valence band. Using the calculation of Eliashberg functions, they predicted that the carrier decay mechanism here is not motivated by the A-site cations, which means the description of organic-inorganic hybrid halide perovskite materials can be extended from fully inorganic materials like $CsPbI_3$ [1].This work successfully revealed the origin of slow hot-hole cooling by first principles calculations, and helped to make researchers rely on the already-known mechanism to analyze the hybrid perovskite materials.

Later, H. Fujiwara group looked at the hybrid perovskite materials deeper by calculating to show the optical characteristics and operational principles of the solar cells. Their group used density functional theory calculations to build the structure of a hybrid perovskite. The DFT calculations found that $MAPbI_3$ is a direct-transition semiconductor, which doesn't fit the experimental result. They then calculated the band gap using generalized gradient approximation and self-consistent GW approximation with spin-orbit and discovered inconsistencies between the two methods. The indirect was contributed by the splitting of the conduction band by the spin-orbit coupling effect. This led to the conclusion that band splitting is very sensitive to the orientation and position of the A-site. The details of the calculation show that the PbI_3^- induces the transitions. The study also focused on the phenomenon of reduced absorption in hybrid perovskites when FA+ replaces MA+. At the same time, the study also believes that this phenomenon stems from strong hydrogen bonding interactions. Finally, by checking the operation of conventional hybrid perovskite solar cells, a new model to explain the properties was suggested and discussed [2].

Another example eyed on the phase transformation. Li-Min Liu's group used nonlocal van der Waals correlation in first principles calculations to investigate $MAPbI_3$. In the calculation, they described the electron-ion interaction by the projector augmented wave method, and replaced the semi-local generalized gradient approximation with the nonlocal van der Waals correlation to better fit the structure and bonds in the octahedron structure. The calculation results reflect the geometric structures and the electronic and optical properties of $MAPbI_3$ with these two phases - tetragonal and orthorhombic phases. Their work shows the critical role of MA^+ ions in the stability of the crystal structure of the perovskites. They also discovered that the phase transition is derived from the different torsion and arrangement of PbI_6 octahedron structures, and marked the decrease of band gap when the orthorhombic phase transfers to the tetragonal phase, with an effect on the carrier mass. Their further calculation revealed the valence band maximum and the conduction band minimum are contributed by different atoms' p orbitals, and is not directly from the organic molecules. However, the organic molecules still influence the electronic features by affecting the structure [3].

As these reports showing, the calculations of the specific hybrid perovskite materials have helped to discover the breakthrough to describe the properties of the materials.

2.2. The calculations on mixed organic-inorganic hybrid perovskite materials

Mixed organic-inorganic hybrid perovskites are various and have interesting properties. Mixed hybrid perovskites in mixed-organic molecules, mixed-metal ions, and mixed-halide types have been studied by researchers. People have discovered that the difference between these ions contributes to the properties gap between each candidate and that mixing them is a convenient and effective way to improve the properties and performance.

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In Chiyung Yam's research, researchers investigated the mixed cation methylammonium-formamidinium groups of perovskite by first-principles calculations. They focused on $FAPbI_3$, which has better stability but is common to have phase transition. Therefore, adding some MA^+ had been considered to be helpful as many experiments showed. The researchers explained the reason why the difference ratio of FA^+/MA^+ leads to different electronic and optical properties and proposed the best ratio in theory as well. They noted that DFT calculations often underestimate the band gap while the lack of spin-orbit interaction can overestimate it, so the Perdew-Burke-Ernzerhof theory has been chosen for this work. They calculated different ratios of mixed perovskites and compared the result, found the lattice constant is going down in linear with the decrease of FA^+,when the FA^+/MA^+ equals 1, the system reaches the most stable condition. They also found that with the decrease of FA^+, the band gap becomes wider. As a result, the absorption spectra has a blue shift [4].

This gives us a direction to design the novel hybrid perovskite with mixed cations. Some similar work has been done on the anions. Xiao-Qing Lu and Xue-Feng Liu led a research on the mixed B ions. The research aimed to focus on the micro structure and electronic-optic properties of $MASn_xPb_{1-x}I_3$, and revealed that the MA^+ doesn't participate in the frontline orbital transition. They also found that with the ratio of Sn/Pb increasing, the band gap narrows, which suggest that $MASnI_3$ has advantage to be the light absorbing layer in perovskite solar cells [5]. A more recent study led by S. Tao and Maria A. Loi investigated the $FASn_xPb_{1-x}I_3$ instead. Their work combined the DFT calculation with the experimental study to discover the electronic structure of these perovskites with a variation of compositional ratios. This calculation applied a different feature compared with the previous $MASn_xPb_{1-x}I_3$ study's report. The Tao and Loi group stated that all the mixed perovskites have a narrower band gap compared to either of the neat compounds. This nonlinear result is proved by the result of the PL characterization experiment. This new research denies the previous understanding that stability correlates with Pb ions, suggests that low Sn concentration may cause the material to be defective. As a result, the work concludes that to get a band gap energy covered by the mixtures requires high Sn compounds [6].

A relative work on mixed Pb-Sn hybrid perovskites kept an eye on the intrinsic defects in the materials. Oleg V. Prezhdo and WanZhen Liang and their group calculated the MA_2SnPbI_6 or the MA mixed-Pb/Sn perovskite with Pb/Sn ratio being 1, with density function theory. They also used non-adiabatic molecular dynamic simulations to assist in discovering the structure and role of intrinsic defects. To achieve their goal, they performed the calculations with and without the intrinsic point defects, and compared their properties with the neat compounds that are relative hybrid perovskites. They evaluated the result and showed the oxidation of Sn is the result of the generation of defects such as V_{Sn}, V_{Pb}, and i_I, with i_I being the most easily to be generated. At the same time, it will create a defective vacancy. Their result later described the details of how each kind of defect here influences the electronic-optics properties like carrier lifetime and the process like hot carrier relaxation compared with other twos [7]. This work effectively brought a new topic in mixed metal perovskite materials research by using first principle calculations, which helped the researchers to understand the nature of intrinsic defects and their influence. Generally, this shows that the calculation plus experiment way of research is very helpful for perovskite application engineers.

Another similar work of mixed metal perovskites expanded the combination of elements in a more diverse way. Xin-Feng Diao, Yan-Lin Tang and Quan Xie worked on the doped $FAPbI_3$ calculation. Doped $FAPbI_3$ may combine more than two metal elements at the same time, and the metal to be added may replace Pb or even the organic part of the perovskite. In their work, they discussed the replacement of FA by Cs (inorganic) and replaced Pb by non-toxic ions like Ca, Zn, Ge, Sr, Sn and Ta. They found some doped candidates have promising performances, which makes them potential alternate for $FAPbI_3$. They also selected a mixed perovskite $FA_{0.75}Cs_{0.25}Sn_{0.25}Ge_{0.75}I_3$, which has similar properties compared with another candidate, but doesn't include toxic Pb ions[8]. Their work is very helpful for researchers to find lead-free solar cell materials, which is better for the environment when it starts industrial usage.

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Finally, people can also find researchers made calculation on mixed halide ions perovskite materials. Marina R. Filip led a group to discover the mixed I-Br perovskites by first principles calculations and experimental results. They focused their sight on the optoelectronic properties of $CsPb(Br_xI_{1-x})_3$ and $FA_{0.83}Cs_{0.17}Pb(Br_xI_{1-x})_3$ perovskites with DFT and DFPT calculations according to specific conditions. They discussed the relationship between structures and properties in mixed halide perovskites materials by comparing calculated results to experimental measurements. Further discussion was about the idea of behavior according to the modeling and calculations, which gave a promising picture for efficient photovoltaic devices made from the homovalent alloyed perovskites [9].

These calculations of various kinds of mixed hybrid perovskite materials have proposed a convenient application for computational assistance in perovskites studies. Also, a theoretical analysis of mixed hybrid perovskites is more achievable for researchers in some situations when they are supposed to find out the best combination by multiple attempts.

Generally, first principles calculation is very common in hybrid perovskite materials research, and density functional theory is a major theory in practice. But the overestimate or underestimate of some properties like band gaps should also be considered. Therefore, researchers may choose adjusted methods to avoid or offset them. The calculations are always done along with experiments to corroborate each other's results and help to draw a complete picture of the materials people investigate.

3. Machine learning in organic-inorganic hybrid perovskite materials exploration

As the research has noted, organic-inorganic hybrid perovskites are in a very diverse group and their performances are under the control of multiple parameters or issues. As a result, it is very difficult to discover the underlying mechanism for those perovskites. Machine Learning can also replace the traditional trail-and-error methods to find the ideal combination of perovskite in a large scale of candidates.

We reviewed two examples that searched for lead-free perovskite materials with the help of machine learning methods. Jinlan Wang group and Yiqiang Zhan, Hao Zhang group both created methods that based on the combination of DFT calculation and machine learning technology to practice quick screening and find targeted lead-free hybrid organic-inorganic perovskites candidates. By using machine learning technology, they only need to select the most promising candidates to perform DFT calculations, which accelerates the process dramatically. These methods are based on enough material data and theory or methodology includes gradient boosted regression algorithm, hyper-parameters selection and density functional theory [10] [11]. In addition, Wang's work highlights that they added a last-place elimination feature selection procedure to further adjust the method [10]. These methods are not just available for lead-free hybrid organic-inorganic perovskites discovery and design. If the data that builds the machine learning practice is large enough, people can adjust these methods to meet the requirements for other work in materials research as well.

Another paper from the Yiqiang Zhan and Hao Zhang group linked machine learning technology to experimental realization. They invented a forward-inverse method to study the mixed hybrid perovskite $MASn_xPb_{1-x}I_3$ and find high-performance solar cell materials. The method was based on five algorithms – linear regression, support vector regression, k-nearest neighbor regression, random forest regression and gradient boosting regression with a neutral network. They found an asymmetrically bowing relationship between Sn-Pb ratio and band gap, which matched the fabricated material well. An optimized Sn-Pb ratio near 0.6 is established and obtained for high-performance hybrid perovskite solar cells here according to the research [12].

These machine learning usage examples are very fresh for traditional material science research. However, they fit the features of current hybrid organic-inorganic perovskite materials development well. By accelerating the discovery process, it is very possible that machine learning tools will be a convenient tool in the future study and application of perovskite solar cells.

As these recent works with first-principle calculations and machine learning shows, researchers are now using computational tools occasionally. Combining experimental and computational tools to make research results mutually verifiable and complete is a common way to make computational science

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useful in the workplace. The calculations of material structure can give a unique aspect to understanding the theoretical part of material behavior. And the development of data-driven and machine learning emphasizing materials research will be rapid and significant as well, according to the review.

4. Conclusion

This paper reviews twelve recent research on organic-inorganic hybrid perovskite materials which have used computational tools. They include the first principle calculations on the structures and electronic-optic properties for both neat and mixed hybrid perovskites. These studies also include the examples of using machine learning methods to discover new high-performance or stable organic-inorganic hybrid perovskite solar cell materials. To conclude the review, it is clear that there will be more methods to be invented and applied in this area to further reveal the properties and science of perovskites and to design and fabricate higher-performance and more efficient organic-inorganic hybrid perovskite solar cells or electronic-optic devices. Although this article has mentioned various significant applications for calculations and other tools, the summary and reflection is still limited and the work that has been done is very small. This paper doesn't reveal the complete picture of the extensive applications of computational science in the discovery and development of perovskite materials.

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