

Recent advances of computational simulation on polarons in organic-inorganic hybrid perovskites

Yijia Zou

University College London, Gower Street, London, WC1E 6BT, United Kingdom

yijia.zou.21@ucl.ac.uk

Abstract. Organic-inorganic hybrid perovskites are prized for their exceptional properties and ease of use, finding applications in high-efficiency, cost-effective solar cells. Hybrid perovskite materials, belonging to the perovskite family, possess unique crystallographic and electronic structures that benefit from versatile phase transitions and component modifications. The crystal structure and electronic characteristics of perovskites facilitate the generation of polarons, which are quasiparticles that readily form in organic-inorganic hybrid perovskites due to the coupling of excess electrons or holes to ionic vibrations and play a pivotal role in shaping the electronic properties. This review delves into the polarons within organic-inorganic hybrid perovskites, in which the formation and interaction of polarons within the crystal lattice and their profound impact on material properties. Computational simulations offer insights into polaron characteristics, such as phonon density of states, carrier-phonon coupling, and polaron dynamics. Therefore, it is of vital importance to make clear the fundamental properties focusing on polarons in perovskite, since a comprehensive understanding of them would significantly facilitate the enhancement of the electronic and optoelectronic characteristics, and eventually contribute to the release of their full potential in real-world applications.

Keywords: Perovskite, polaron, dynamics, theoretic simulation, photovoltaics

1. Introduction

Organic-inorganic hybrid perovskites have attracted significant attention for their unique properties and straightforward fabrication processes, garnering extensive research in energy conversion, sensors, and electronic devices [1]. Particularly, in the field of solar cells, these materials have demonstrated high photovoltaic conversion efficiency and low manufacturing costs [2], making them a promising candidate for next-generation photovoltaic materials. Typically, perovskite possesses a component of ABX_3 , with the positive covalent A ions tending to have larger diameters, while the B ions have smaller ones. X is an anion, usually a halogen atom, forming an octahedral space structure [3]. The versatility of perovskite materials in accommodating various anions and cations, while adhering to the Goldschmidt tolerance factor rule, underpins their wide-ranging applications [4]. The incorporation of organic ions unlocks numerous structural and chemical possibilities, leading to tunable functionality and a diverse array of multi-properties [5]. For instance, in perovskite solar cells, replacing the methylammonium group (MA) with formamidinium (FA) in $MAPbI_3$ perovskite lowers the energy band gap from 1.55 eV to 1.4 eV, widening the photo-responsive range and boosting device efficiency [6]. In hybrid perovskite lasers,

formamidinium lead halide perovskite-based devices have been designed to ensure stability under room temperature laser pulses at 402 nm wavelength, lasting over 150 fs [7].

Owing to the flexibility of the structure and components of perovskite, especially the soft lattice properties that make polaron a feasible quasi-particle in perovskite [8]. In this context, a comprehensive exploration of the properties of polarons in organic-inorganic hybrid perovskites will be given, probing their formation, interactions within the crystal lattice, the potential influence on material characteristics, and computationally derived parameters. The research begins by scrutinizing carrier behavior, encompassing both electrons and holes, shaping the electronic properties of these inclusion crystals. Subsequently, it delves into the intricate interplay between carriers and lattice vibrations following polaron formation. Meanwhile, essential parameters, such as phonon density of states, carrier-phonon coupling, and polaron dynamics, which decisively influence polaron properties and bridge the gap between theoretical understanding and experimental observations.

In summation, this review will introduce the world of polarons within organic-inorganic hybrid inclusion crystals, elucidating their genesis and unveiling insights gleaned through computational simulations. As these materials continue to captivate researchers and fuel innovation across diverse domains, a comprehensive grasp of their foundational characteristics becomes indispensable for harnessing their full potential.

2. Charge Carriers in Organic-Inorganic Hybrid Perovskites

Perovskite solar cell architecture comprises multiple layers, typically organized in p-i-n or n-i-p configurations. These layers include the perovskite absorber, electron transport material (ETM), hole transport material (HTM), bottom metal electrode, and top transparent conducting layer [9]. When incident photons are absorbed by the perovskite layer, excitons (electron-hole pairs) are primordially generated, and rapidly dissociate into free carriers (electrons and holes), due to the low binding energy. These free carriers then traverse the carrier transport layers to reach their respective electrodes, generating an electric current that flows through the external circuit [10]. These processes enable the conversion of light into electrical energy, therefore, the charge separation efficiency, carriers' mobility, lifetime, and recombination rates, all of these dynamic process plays a key role in determining the voltage output, short-circuit current, and finally the overall effectiveness, which underscores their pivotal role in optimizing perovskite solar cell performance and reliability.

2.1. Carrier mobility in perovskite photovoltaics

One essential parameter is carrier mobility, which refers to the ability of charge carriers to move under the influence of an electric field. Higher carrier mobility typically leads to more efficient charge transport and, consequently, better solar cell performance.

There are various methods to characterize the carrier transport characterization of hybrid perovskites, including photoluminescence (PL) [11], microwave conductivity (MC) [12], terahertz (THz) spectroscopy [13], and Hall measurements [14]. PL relies on emitted photons from excited carriers to trace their behavior, offering insights into carrier lifetimes and energy band structures. MC and THz spectroscopy utilize dielectric responses to measure free carrier dynamics, providing information about carrier mobility and transport mechanisms, and highlighting the differing approaches to characterizing carrier behavior in materials [15]. While, Hall measurements determine carrier type, density, and mobility by applying a perpendicular magnetic field to the current [5]. These distinct techniques collectively provide a comprehensive view of carrier transport in materials, each focusing on different aspects of carrier behavior, as summarized in Figure 1 [16].

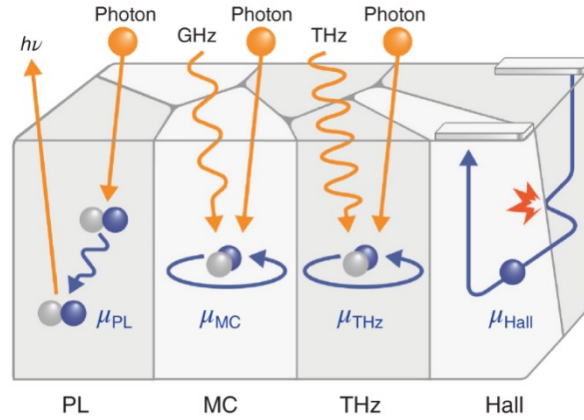


Figure 1. The principles of carrier transport characterization by photoluminescence (PL), microwave conductivity (MC), terahertz (THz) spectroscopy, and Hall measurements [16].

Typically, the photoconductivity of the excited charge carrier could be expressed as:

$$\sigma = en\mu \quad (1)$$

where e is the elementary charge, n is the photoinduced charge-carrier density and μ the charge-carrier mobility [17]. The carrier mobility could be primarily impacted by increasing carrier mass, introducing additional scattering, trapping carriers, and creating energy barriers, respectively. All of these properties could be influenced by a pre-formed polaron in the materials. Therefore, the carrier mobility could be treated as a key indicator of how polarons affect organic-inorganic perovskite materials, which makes research about polarons essential.

2.2. Carrier diffusion properties in perovskite photovoltaics

Another factor that influences the efficiency of photovoltaic devices is the carrier diffusion length, which represents the average distance that charge carriers can travel in the absorber material before recombining. A longer diffusion length increases the probability of carriers contributing to overall photocurrent generation. The carrier diffusion length was defined as:

$$L_D = \sqrt{D\tau} \quad (2)$$

Where D is the diffusion coefficient and τ is carrier lifetime. The diffusion coefficient can be related to carrier mobility following the Einstein relation:

$$D = \left(\frac{k_B T}{e}\right) \mu \quad (3)$$

where k_B is the Boltzmann constant and T is the temperature (K), respectively.

Lots of computational studies on, MAPbI₃ and FAPbI₃, have shown promising values for both mobility (μ) and carrier lifetime (τ) [15]. These findings indicate that these materials possess substantial carrier diffusion lengths, enabling efficient charge migration within the absorber layer. However, a recent study showed that the carrier mobility and lifetime would be significantly impacted by the readily formed polarons and their behaviors in perovskite. Strong electron-phonon interactions play a pivotal role in shaping the unique characteristics of hybrid perovskites that distinguish them from conventional semiconductors [18]. Polaron formation results in an effective carrier mass increase, exerting a substantial influence on both electrical and optical properties. This underscores the importance of understanding polaron effects as we delve into their potential impact in subsequent discussions.

3. Formation of polarons in perovskite photovoltaics

The term “polaron” was introduced by Solomon Pekar in 1946 to describe electrons moving in dielectric crystals, where the atom deviates from its equilibrium positions to screen the charge of the electrons. This produces quasiparticles consisting of electrons or holes surrounded by a virtual phonon cloud. When an excess charge is injected, the ions in its vicinity are displaced, creating a polarization cloud that follows the charge carrier as it propagates through the crystal [19]. The spatial extent of the polaron wave function and the associated structural distortions allow the identification of two general types of polarons: small and large polarons, which arise from the difference in the magnitude of the range of interaction between carriers and phonons.

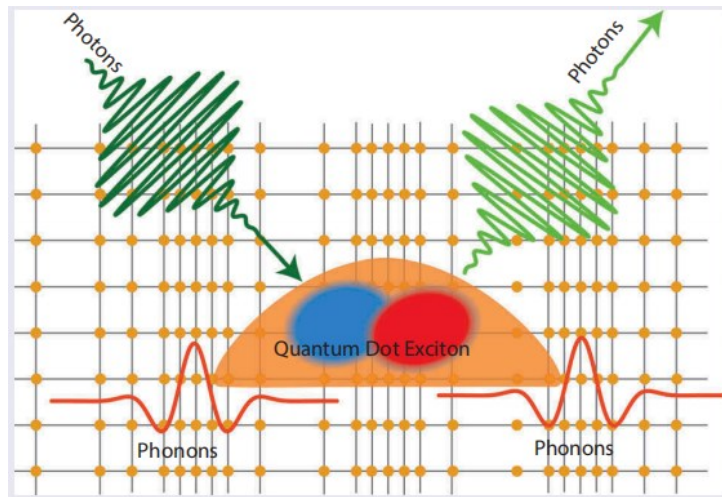


Figure 2. Polarons formed by electrons or holes surrounded by a virtual phonon cloud [20].

The impact of polarons on charge carriers includes reducing their mobility, decreasing conductivity, and shortening their lifetimes. Both small polarons and large polarons exhibit these effects, with the distinction lying in the strength of their interactions with lattice vibrations and their respective influence scopes. Small polarons typically have relatively weaker interactions with lattice vibrations, affecting a localized area, whereas large polarons involve stronger interactions with lattice vibrations, exerting a more significant influence over a broader range, resulting in a more pronounced impact on charge carriers [21]. These phenomena contribute to the degradation of charge carrier performance. The prevailing view is that charge carriers are ‘protected’ from scattering by their incorporation into large polarons. The mechanism of polarization or Fröhlich interaction is a significant component of the exciton-phonon interaction and plays a crucial role in the formation and dynamics of polarons. The exciton-phonon interaction involves two main mechanisms: one is the short-range deformation interaction, which is characterized by the deformation potential and strongly affects small excitons, while the other is the polarization or Fröhlich interaction, resulting from the Coulombic interaction of charge carriers in excitons with the lattice’s macroscopic field, particularly dominant for larger excitons [22].

To delve deeper into the mechanisms of polarons, an essential aspect lies in computational simulations of materials. Theoretical models for polarons have primarily relied on quantum field theory effective Hamiltonians. The Fröhlich Hamiltonian, using the continuum approximation, describes large polarons [23], while the Yamasita-Kurosawa and Holstein models capture small polarons, becoming foundational theories in polaron research and facilitating subsequent computational advancements [24, 25]. Additional theoretical models, including analytical schemes, quantum Monte Carlo, dynamical mean-field theory (DMFT), and multiscale modeling, have emerged [26-29]. All of these methods were trying to establish a sophisticated tool to describe the phonon and carrier interaction properties. Recently, an extended first-principles approach based on density functional theory (DFT) has provided accurate microscopic descriptions of both large and small polarons, predicting material-specific polaron

properties. The field of computational simulations for polarons is continually evolving, providing a vital tool for gaining a deeper understanding of the nature and behavior of these quasi-particles. Current trends encompass the ongoing refinement of theoretical models as discussed above [30].

4. Computational simulation for polarons

The utilization of multiscale modelling to comprehensively investigate polaron properties, material-specific studies, and the harnessing of high-performance computing platforms not only hold the potential to enhance our comprehension of polarons but also offer new possibilities for materials science and electronic device engineering, fostering growth and innovation in related fields. This segment of the discussion will delve into specific computable parameters to shed light on the world of polarons in the realm of computational simulations.

4.1. Evaluation for density of state of phonon

The phonon density of states (PDOS) is predominantly a function of the local atomic structure and is sensitive to the atomic-level stresses and microstructure. The PDOS reflects the vibrational modes of a material, which are intimately connected to the arrangement of atoms in the crystal lattice [31]. The specific positions of atoms, their bonding, and their interactions with neighboring atoms also significantly influence the phonon frequencies and energy levels.

Variations in local atomic structure, including features like grain boundaries, dislocations, and defects, can alter the PDOS, impacting the thermal and mechanical properties of materials. In addition, phonon characteristics, including their modes, frequencies, and direct interaction with carriers, exert influences on the interaction between excitons and phonons, as do the properties of polarons. The amplitudes and frequencies of phonons in different modes directly shape the stability and distribution of excitons, while higher-frequency phonons typically lead to stronger electron-phonon interactions, resulting in significant alterations in band structures and energy level shifts. The direct interaction between phonons and charge carriers triggers the localization and gives rise to polaron formation. Grain boundaries and defects also influence charge carriers and collectively impact polaron properties through their interplay. Researchers employ techniques like DFT calculations, molecular dynamics simulations, and inelastic neutron scattering experiments to analyze the PDOS, providing insights into a material's structural and vibrational properties.

The most mentioned method for the calculation of PDOS is the DFT method. By calculating the potential energy of the lattice and the vibrational modes of the atoms, the energy and frequency of the phonons can be obtained, and thus the phonon density of states. More specifically, begin by performing a DFT-based electronic structure calculation, the material's electronic band structure and electron density could also be computed as well [32]. The advantages of calculating phonon-carrier interaction parameters lie in its provision of precise, cost-effective, controllable, and theoretically guided research methodology. This requires choosing an appropriate exchange-correlation functional to approximate the electron-electron interactions. These calculations provide information about electronic energy, wave functions, and charge density. Furthermore, unlike classical DFT, DFPT (Density functional perturbation theory) introduces a perturbation potential for calculating the relationship between atomic displacements and lattice vibrations, both are crucial factors that influence carrier dynamics [33], which can be further utilized to calculate phonon frequencies and amplitudes, facilitating the study of phonon-carrier interactions [34]. Within the DFT framework, the lattice energy changes were computed by the force constant matrix near the equilibrium positions of the atoms in an account of atomic displacements, revealing phonon vibrational properties. By solving the eigenvalue problem of the dynamical matrix, precise calculations of phonon frequencies and amplitudes can be obtained. Allowing for comprehensive analysis of phonon behavior and intuitive visualization through phonon density of states plots. However, these computations often demand significant computational resources and time, resulting in higher costs and limitations for large-scale applications. DFT sometimes resorts to approximate methods, potentially introducing errors, especially in cases involving strong interactions or unconventional materials. In contrast, DFPT, as an extension of DFT, excels in handling complex crystal structures and strong

interaction materials. DFPT offers a more comprehensive treatment of non-harmonic effects of phonons, particularly in the study of phonon-carrier scattering processes, contributing to a more accurate understanding of phonon characteristics.

Molecular Dynamics (MD) simulates the motion of atoms or molecules within a material to investigate phonon behavior. Unlike static calculations, MD provides dynamic information about how phonons evolve over time, enabling the study of processes such as phonon heat transport and scattering dynamics. MD naturally accounts for the non-harmonic effects of phonons since it considers atomic interactions and displacements, including higher-order effects. MD calculates the auto-correlation functions of the displacements and velocities of the atoms [35]. These functions provide information about atomic vibrations, which are related to phonon mode frequencies and amplitudes, that influence carrier dynamics by affecting processes such as carrier mobility and diffusion length. And the PDOS could be estimated via the frequency spectrum of phonon density after Fourier-transforming of the auto-correlation functions [36].

In summary, the PDOS calculation in hybrid perovskite materials reveals the distribution of vibrational energy levels and provides essential information about the interactions between electrons and lattice vibrations. This knowledge contributes to a deeper understanding of the material's thermal and electronic properties, guiding its application in various technological contexts, including the modulation of polaronic properties and the manipulation of electrical and optical characteristics.

4.2. Electron-phonon and hole-phonon coupling

In perovskite semiconductors, a readily formed polaron that originates from electron-phonon coupling influences charge transport, thermal conductivity, and even the optical properties of the material [37]. DFPT-based electron-phonon coupling calculations usually take into account the effect of phonon vibrations on the electron energy bands by means of a perturbed electronic structure and then determine the strength of the electron-phonon coupling by calculating the change in the energy bands of the electrons [16]. After performing a ground-state DFT calculation to obtain the electronic energy band structure, the phonon modes, and frequencies could be obtained via DFPT. The perturbation of the electron energy bands by phonon displacements is introduced and the change in the electron energy bands is calculated. Finally, the electron-phonon coupling matrix element is used to represent the electron-phonon coupling strength [38]. The binding energy assesses carrier localization, where a higher value implies tighter carrier-phonon interaction, potentially leading to polaron localization, reflecting polaron stability and postponed electronic transport.

The abovementioned DFPT often struggles with strong electron correlation and excitonic effects, but these limitations can be overcome using the Bethe–Salpeter equation method and Green's and Wannier functions (GW). By employing Wannier functions, local electronic density states, and excitonic states can be considered, enabling a more precise investigation of exciton formation and properties within strongly correlated electronic systems. These advantages were achieved by connecting electronic-phonon coupling parameters with the overlap integrals of Wannier functions [39]. Electron-phonon coupling calculations have also been performed using Green's function-based methods, in which the main idea is that the GW calculation considers self-energy corrections to electronic bands, while the BSE addresses coupling in excited states, making it suitable for electronic-phonon coupling calculations [19].

These methods provide diverse pathways to compute electron-phonon coupling parameters, which further provides critical theoretical support for comprehending and applying hybrid perovskite materials.

4.3. Polaron Binding Energy in Perovskite Photovoltaics

The binding energy of a polaron represents the strength of the electron-phonon coupling in the material. It is defined as the energy difference between the ground state energy of the crystal with the polaron and without the polaron. A higher binding energy indicates a more strongly bound polaron. The polaron binding energy consists of two terms: the molecular deformation energy and the electron-phonon term. Due to the significant influence of the large polaron effect arising from the Coulomb interaction between

charge carriers and lattice optical phonons, it is imperative to incorporate a tight-binding (TB) model for hybrid perovskites based on Density Functional Theory (DFT) calculations. This inclusion is necessary to mitigate self-interaction errors, as the TB model lacks a Coulomb interaction term when operating within the strong coupling approximation [40]. The wavefunction of the large polaron can be expressed as a composite of two constituent components, namely, the “electron” and “ionic” parts, adhering to the Born-Oppenheimer (BO) approximation. Within this approximation framework, the total energy of the polaron is ascertained by minimizing equation (1) through the variation of the electron wavefunction ψ :

$$E = \langle \psi | H_0 | \psi \rangle - E^P \quad (4)$$

$$E^P = \frac{1}{2\epsilon} \int dr V^P(r) \rho(r) \quad (5)$$

Herein, H_0 represents the Hamiltonian governing the behavior of the electron devoid of any influence from the polaron effect. The term $\rho(r) = |\psi(r)|^2$ designates the charge density associated with the state $\psi(r)$, E^P denotes the screening energy, and V^P stands for the lattice’s polarization potential, arising in response to the Coulomb potential of $\rho(r)$ [23]. Through a comparative analysis of energies in the presence and absence of the large polaron effect, it becomes feasible to compute the binding energy of the large polaron. The significance of this binding energy lies in its ability to quantify the strength of the interaction between phonons and charge carriers, as well as the phonons’ capacity to either bind or localize these carriers. A larger binding energy indicates a more intense interaction between phonons and charge carriers, which may lead to the localization of carriers within the material and the formation of polarons [41]. The binding energy can be illustrated in Figure. 3 and is usually measured in meV.

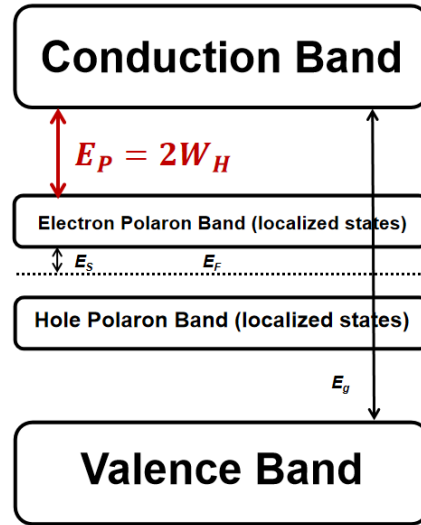


Figure 3. Schematic band diagram for materials showing localization of charge carriers due to electron-phonon coupling. E_P is the polaron binding energy, W_H is the polaron hopping energy, E_S is the charge carrier generation energy, and E_F is the Fermi level.

4.4. Polaron Mobility in Perovskite Photovoltaics

“Polaron mobility,” another key parameter in condensed matter physics, quantifies the ability of polarons to move freely within condensed matter materials. Polaron mobility reflects the extent to which polarons can move through the material and is often measured in terms of the mobility of charge carriers, such as electrons or holes [42]. Various factors wield influence over polaron mobility, encompassing the potency of electron-phonon interactions with stronger interactions typically resulting in localized polarons and diminished mobility [43].

Small polarons are inclined to engage in phonon-assisted hopping, primarily as a consequence of the destabilization of charge carrier localization due to thermally induced atomic distortions in the vicinity of the trapping site. This phenomenon results in intermittent hop events, leading to incoherent motion characterized by typically modest mobility, often less than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [19]. This mobility tends to increase as the temperature is elevated, primarily due to the augmented thermal distortions. In contrast, large polarons are predisposed to exhibit a coherent, free-carrier-like motion. The substantial effective mass of large polarons plays a pivotal role in dictating their high mobility, as it serves to safeguard polaron motion against intermittent scattering events with the phonon field. Nevertheless, this mobility diminishes as temperature rises, owing to the heightened efficacy of scattering processes [44]. Moreover, the presence of impurities or defects (which can scatter polarons), diminishes their mobility [45]. A comprehensive grasp of and enhancement in polaron mobility is pivotal for the formulation of semiconductor devices and the advancement of materials research [46].

Moreover, it is customary in scientific investigations to undertake a rigorous quantitative examination of the mobility of large polarons and to compute transport properties tailored to specific materials. Such analyses are commonly executed through the utilization of either the Boltzmann equation or the Feynman, Hellwarth, Iddings, and Platzman (FHIP) approach. For the FHIP mobility (μ_{FHIP}), an initial low-temperature approximation was initially introduced and is expressed as follows [19]:

$$\mu_{\text{FHIP}} = \left(\frac{w}{v}\right)^3 \frac{3e}{4m} \frac{\exp(\beta')}{\Omega \alpha \beta'} \exp\left(\frac{v^2 - w^2}{w^2 v}\right) \quad (6)$$

where w and n are Feynman variational parameters, m represents the band effective mass, Ω is the phonon frequency, α is the coupling constant and

$$\beta' = \hbar\Omega/k_B T \quad (7)$$

FHIP accounts for non-adiabatic effects, where charge carriers' motion may not synchronize with lattice vibrations. Furthermore, FHIP excels at capturing the quantum mechanical aspects of charge transport, encompassing both wave-like and particle-like behaviors of charge carriers, making it essential for studying polaronic systems. This comprehensive approach allows for a detailed exploration of charge carrier interactions with the lattice and their consequential impact on mobility and transport properties.

For example, one of the methods is based on constructing the maximally localized Wannier functions (MLWFs) from the DFT band structure to define an effective tight-binding Hamiltonian, which is then subsequently used to compute the mobility via the Kubo formula [33]. Importantly, it does not make any assumption either about the polaron character of the mobility (small or large polarons) or about the dependence on the temperature.

Binding energy significantly influences charge transport, primarily through its impact on mobility, carrier trapping, and polaron formation. Higher binding energies imply stronger attachment of charge carriers to the lattice, hindering their mobility and reducing overall conductivity. Materials with substantial binding energies tend to trap charge carriers for longer durations, hampering their contribution to charge transport and causing delays. Additionally, strong binding energies between charge carriers and phonons can result in the formation of large polarons, further affecting charge mobility and overall transport properties.

5. Conclusions

In this work focusing on a comprehensive exploration of polarons in organic-inorganic hybrid perovskites, we have journeyed through the intricacies of these materials, beginning with an introduction to organic-inorganic hybrid perovskites, charge carriers, and the concept of polarons. Our investigation has yielded valuable insights into the significance of polarons on charge carrier dynamics.

This research emphasizes the crucial role of computational simulations in advancing our understanding of materials science and the unique polaron characteristics of hybrid perovskite materials.

The computed parameters PDOS, electron-phonon coupling, polaron binding energy, and polaron mobility form a foundational framework for customizing materials for specific applications.

The significance of this inquiry lies in its potential to drive innovation in materials science and electronic device engineering. A deep understanding of polaron behavior enables the development of materials with enhanced thermal and electronic properties, fuelling advancements in technologies such as highly efficient solar cells, cutting-edge semiconductors, and pioneering electronic devices. Computational simulations for polarons hold immense promise, serving as both a path to academic progress and a catalyst for technological breakthroughs that will shape our future in materials science and electronics.

References

- [1] Zhang A, Lv Q. Organic-Inorganic Hybrid Perovskite Nanomaterials: Synthesis and Application. *ChemistrySelect*, 2020, 5(41): 12641-12659.
- [2] Jeon N J, Noh J H, Kim Y C, et al. Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. *Nature materials*, 2014, 13(9): 897-903..
- [3] Mercier N. Hybrid halide perovskites: Discussions on terminology and materials. *Angewandte Chemie International Edition*, 2019, 58(50): 17912-17917.
- [4] Ji L J, Sun S J, Qin Y, et al. Mechanical properties of hybrid organic-inorganic perovskites. *Coordination Chemistry Reviews*, 2019, 391: 15-29.
- [5] Rose G. De novis quibusdam fossilibus quae in montibus Uraliis inveniuntur. typis AG Schadii, 1839.
- [6] Chan W K, Chen J, Zhou D, et al. Hybrid Organic–Inorganic Perovskite Superstructures for Ultrapure Green Emissions. *Nanomaterials*, 2023, 13(5): 815.
- [7] Fu Y, Zhu H, Schrader A W, et al. Nanowire lasers of formamidinium lead halide perovskites and their stabilized alloys with improved stability. *Nano letters*, 2016, 16(2): 1000-1008.
- [8] Chen W, Shi Y, Chen J, et al. Polymerized hybrid perovskites with enhanced stability, flexibility, and lattice rigidity. *Advanced Materials*, 2021, 33(48): 2104842.
- [9] Wang H, Wang X, Zhang H, et al. Organic-inorganic hybrid perovskites: Game-changing candidates for solar fuel production. *Nano Energy*, 2020, 71: 104647.
- [10] Trifiletti V, Degousée T, Manfredi N, et al. Molecular doping for hole transporting materials in hybrid perovskite solar cells. *Metals*, 2019, 10(1): 14.
- [11] Kirchartz T, Márquez J A, Stollerfoht M, et al. Photoluminescence-based characterization of halide perovskites for photovoltaics. *Advanced energy materials*, 2020, 10(26): 1904134.
- [12] Peng J, Chen Y, Zheng K, et al. Insights into charge carrier dynamics in organo-metal halide perovskites: from neat films to solar cells. *Chemical Society Reviews*, 2017, 46(19): 5714-5729.
- [13] Jin Z, Peng Y, Fang Y, et al. Photoinduced large polaron transport and dynamics in organic–inorganic hybrid lead halide perovskite with terahertz probes. *Light: Science & Applications*, 2022, 11(1): 209.
- [14] Pang T, Sun K, Wang Y, et al. Hysteresis effects on carrier transport and photoresponse characteristics in hybrid perovskites. *Journal of Materials Chemistry C*, 2020, 8(6): 1962-1971.
- [15] Fujiwara H, Kato Y. Carrier Transport Properties. *Hybrid Perovskite Solar Cells: Characteristics and Operation*, 2021: 151-171.
- [16] *Hybrid Perovskite Solar Cells: Characteristics and Operation*. John Wiley & Sons, 2021.
- [17] Johnston M B, Herz L M. Hybrid perovskites for photovoltaics: charge-carrier recombination, diffusion, and radiative efficiencies. *Accounts of chemical research*, 2016, 49(1): 146-154.
- [18] Yamada Y, Kanemitsu Y. Electron-phonon interactions in halide perovskites. *NPG Asia Materials*, 2022, 14(1): 48.
- [19] Franchini C, Reticioli M, Setvin M, et al. Polarons in materials. *Nature Reviews Materials*, 2021, 6(7): 560-586.

- [20] Reiter D E, Kuhn T, Axt V M. Distinctive characteristics of carrier-phonon interactions in optically driven semiconductor quantum dots. *Advances in Physics: X*, 2019, 4(1): 1655478.
- [21] Zhang H, Park N G. Polaron in perovskite solar cells: its effect on photovoltaic performance and stability. *Journal of Physics: Energy*, 2023.
- [22] Plekhanov V. Isotope effects in solid state physics. Academic Press, 2000.
- [23] Sio W H, Verdi C, Poncé S, et al. Ab initio theory of polarons: Formalism and applications. *Physical Review B*, 2019, 99(23): 235139.
- [24] Yamashita J, Kurosawa T. On electronic current in NiO. *Journal of Physics and Chemistry of Solids*, 1958, 5(1-2): 34-43.
- [25] Holstein T. Studies of polaron motion: Part II. The “small” polaron. *Annals of Physics*, 1959, 8(3): 343-389.
- [26] Setvin M, Franchini C, Hao X, et al. Direct view at excess electrons in TiO₂ rutile and anatase. *Physical review letters*, 2014, 113(8): 086402.
- [27] Miyata K, Meggiolaro D, Trinh M T, et al. Large polarons in lead halide perovskites. *Science Advances*, 2017, 3(8): e1701217.
- [28] Reticioli M, Setvin M, Hao X, et al. Polaron-driven surface reconstructions. *Physical Review X*, 2017, 7(3): 031053.
- [29] Giustino F. Electron-phonon interactions from first principles. *Reviews of Modern Physics*, 2017, 89(1): 015003.
- [30] Louie S G, Chan Y H, da Jornada F H, et al. Discovering and understanding materials through computation. *Nature Materials*, 2021, 20(6): 728-735.
- [31] Wormald J L, Hawari A I. Generation of phonon density of states and thermal scattering law using ab initio molecular dynamics. *Progress in Nuclear Energy*, 2017, 101: 461-467.
- [32] Bassani F, Liedl G L, Wyder P. *Encyclopedia of condensed matter physics*, 2005.
- [33] Motta C, Sanvito S. Electron–phonon coupling and polaron mobility in hybrid perovskites from first principles. *The Journal of Physical Chemistry C*, 2018, 122(2): 1361-1366.
- [34] Ganose A M, Park J, Faghaninia A, et al. Efficient calculation of carrier scattering rates from first principles. *Nature communications*, 2021, 12(1): 2222.
- [35] Meggiolaro D, Ambrosio F, Mosconi E, et al. Polarons in metal halide perovskites. *Advanced Energy Materials*, 2020, 10(13): 1902748.
- [36] *Handbook of Materials Modeling: Applications: Current and Emerging Materials*. Springer International Publishing, 2020.
- [37] Antonius G, Louie S G. Theory of exciton-phonon coupling. *Physical Review B*, 2022, 105(8): 085111.
- [38] Wang Z, Shi W, Lortz R, et al. Superconductivity in 4-Angstrom carbon nanotubes—A short review. *Nanoscale*, 2012, 4(1): 21-41.
- [39] Leng X, Jin F, Wei M, et al. GW method and Bethe–Salpeter equation for calculating electronic excitations. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2016, 6(5): 532-550.
- [40] Zheng F, Wang L. Large polaron formation and its effect on electron transport in hybrid perovskites. *Energy & Environmental Science*, 2019, 12(4): 1219-1230.
- [41] Natanzon Y, Azulay A, Amouyal Y. Evaluation of polaron transport in solids from first principles. *Israel Journal of Chemistry*, 2020, 60(8-9): 768-786.
- [42] Lu N, Li L, Geng D, et al. A review for polaron dependent charge transport in organic semiconductor. *Organic Electronics*, 2018, 61: 223-234.
- [43] Shi Z, Guo J, Chen Y, et al. Lead - free organic–inorganic hybrid perovskites for photovoltaic applications: recent advances and perspectives. *Advanced Materials*, 2017, 29(16): 1605005.
- [44] Fu J, Ramesh S, Melvin Lim J W, et al. Carriers, Quasi-particles, and Collective Excitations in Halide Perovskites. *Chemical Reviews*, 2023.

- [45] Shuai Z, Wang L, Li Q. Evaluation of charge mobility in organic materials: from localized to delocalized descriptions at a first principles level. *Advanced Materials*, 2011, 23(9): 1145-1153.
- [46] Maiti A, Pal A J. Carrier recombination in CH₃NH₃PbI₃: why is it a slow process? *Reports on Progress in Physics*, 2022, 85(2): 024501.