

MANY-BODY THEORETICAL STUDIES OF EXCITONIC EFFECTS AND CARRIER DYNAMICS IN PEROVSKITE-INSPIRED SEMICONDUCTORS

SANCHI



DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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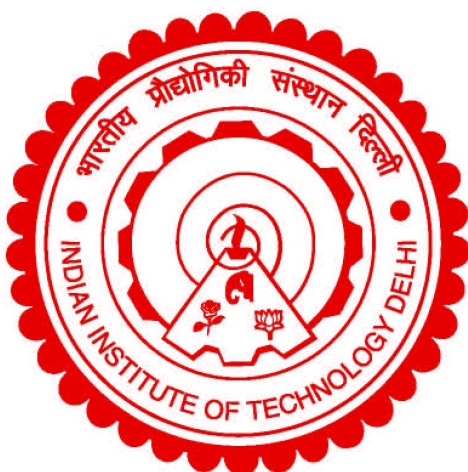
by

SANCHI

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 and my brother

Certificate

This is to certify that the thesis entitled “**Many-Body Theoretical Studies of Excitonic Effects and Carrier Dynamics in Perovskite-Inspired Semiconductors**” being submitted by **Sanchi**, 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 in 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

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Abstract

The pursuit of sustainable energy solutions has positioned lead halide perovskites at the forefront of photovoltaic (PV) research, with power conversion efficiencies exceeding 27%. However, their practical deployment remains hindered by intrinsic lead toxicity and limited environmental stability. This thesis investigates lead-free perovskite-inspired materials—including antiperovskites, chalcogenides, and vacancy-ordered halides—as structurally robust and environmentally benign alternatives. While their ground-state properties are increasingly well understood, device performance is ultimately governed by excited-state processes—such as exciton formation, electron–phonon coupling, and non-radiative recombination—which remain insufficiently resolved. To address this gap, a multiscale first-principles approach is employed, combining density functional theory (DFT), many-body perturbation theory (*GW*/BSE), density functional perturbation theory, the Fröhlich polaron model with the Feynman path-integral variational method for polaron transport, and non-adiabatic molecular dynamics (NAMD).

Within this framework, we systematically investigate antiperovskite nitrides X_3NA ($X = \text{Mg, Ca, Sr, Ba}$; $A = \text{Sb, As}$), a class of materials characterized by inverted cation–anion positions relative to conventional perovskites, which gives rise to distinct bonding and electronic characteristics. By examining how band structure and dielectric response jointly influence excitonic and polaronic behavior, we identify Sb-based compounds as particularly promising for efficient charge transport. We further demonstrate how cation substitution and structural symmetry in X_3NSb regulate non-radiative recombination through a delicate balance of band gap, non-adiabatic (NA) coupling, and electronic decoherence. Extending this analysis to carbide antiperovskites M_6CSe_4 ($M = \text{Ca, Sr}$), derived from zero-dimensional Cs_4PbX_6 -type perovskites, we correlate carrier relaxation dynamics—including non-radiative recombination and hot-carrier cooling—with lattice fluctuations and the underlying electronic landscape. Large energy-level spacing suppresses NA coupling, creating a relaxation bottleneck that enables slow hot-carrier cooling alongside nanosecond-scale recombination lifetimes—both of which

are advantageous for high-performance PV operation.

Chalcohalides emerge as a compelling class of lead-free absorbers, combining structural stability with suitable band gaps and strong dielectric response. Within this family, the quasi-one-dimensional compound BiSeI provides an ideal platform to probe the effects of reduced dimensionality. By tracking the evolution from bulk to Janus and exfoliated monolayer structures, and ultimately to the isolated monochain, we examine how quantum confinement and dielectric screening shape excitonic properties, including binding energies, spatial distributions, and bright–dark exciton splitting. Furthermore, the role of external dielectric environments is assessed to establish practical routes for tuning excitonic behavior in low-dimensional systems. Finally, vacancy-ordered halides are investigated as lead-free alternatives offering superior resilience against environmental degradation. This study elucidates the consequences of intrinsically limited electronic connectivity and outlines viable strategies for its mitigation. We first examine $A_3Bi_2I_9$ ($A = Cs, MA, FA$), where electronically isolated structural units are shown to induce strong carrier localization and hindered transport. Building on these insights, we demonstrate that Ag incorporation—forming the layered compound $Cs_2AgBi_2I_9$ —successfully restores electronic connectivity, enhances band dispersion, and significantly improves charge-carrier mobility. In parallel, Mo-alloyed Cs_2ZrCl_6 is investigated to uncover how octahedral isolation, in conjunction with dopant-induced states, gives rise to dual visible–near-infrared emission. Notably, the two emission channels—originating from host self-trapped excitons within the regular octahedra and Mo-related impurity states—function as decoupled radiative pathways with negligible inter-channel coupling. Collectively, these results provide a coherent framework for the independent tuning of charge transport and light-emission characteristics in vacancy-ordered halide materials.

सतत ऊर्जा समाधानों की खोज ने लेड हैलाइड पेरोव्स्काइट्स को फोटोवोल्टाइक अनुसंधान के अग्रणी स्थान पर स्थापित किया है, जिनकी शक्ति-रूपांतरण दक्षता (PCE) 27% से अधिक हो चुकी है। तथापि, इनका व्यावहारिक अनुप्रयोग लेड की अंतर्निहित विषाक्तता तथा सीमित पर्यावरणीय स्थिरता के कारण अभी भी चुनौतीपूर्ण बना हुआ है। यह शोध प्रबंध लेड-मुक्त पेरोव्स्काइट-प्रेरित पदार्थ — जिनमें एंटीपेरोव्स्काइट्स, चाल्कोहैलाइड्स तथा रिक्तिका-क्रमबद्ध (vacancy-ordered) हैलाइड्स शामिल हैं — का अध्ययन संरचनात्मक रूप से सुदृढ़ एवं पर्यावरण-अनुकूल विकल्पों के रूप में करता है। यद्यपि इनके मूल-अवस्था (ground-state) गुणों की समझ काफी विकसित हो चुकी है, वास्तविक उपकरण प्रदर्शन अंततः उत्तेजित-अवस्था प्रक्रियाओं — जैसे एक्साइटॉन निर्माण, इलेक्ट्रॉन-फोनॉन युग्मन तथा गैर-विकिरणीय पुनर्संयोजन — द्वारा नियंत्रित होता है, जिनका पूर्णतः स्पष्ट होना अभी शेष है। इस अंतराल को दूर करने के लिए एक बहु-स्तरीय प्रथम-सिद्धांत दृष्टिकोण अपनाया गया है, जिसमें घनत्व फलनिक सिद्धांत (DFT), बहुकणीय विक्षोभ सिद्धांत (GW/BSE), घनत्व फलनिक विक्षोभ सिद्धांत (DFPT), पोलारॉन परिवहन के लिए फेनमैन पाथ-इंटीग्रल वेरिएशनल पद्धति के साथ फ्रोलिख पोलारॉन मॉडल, तथा नॉन-एडियाबेटिक आणविक गतिकी (NAMD) का संयोजन किया गया है।

इस रूपरेखा के अंतर्गत, एंटीपेरोव्स्काइट नाइट्राइड्स X_3NA ($X = Mg, Ca, Sr, Ba$; $A = Sb, As$) का व्यवस्थित अध्ययन किया गया है। यह पदार्थ वर्ग पारंपरिक पेरोव्स्काइट्स की तुलना में धनायन-ऋणायन स्थानों के उलट विन्यास के कारण विशिष्ट बंधन और इलेक्ट्रॉनिक गुण प्रदर्शित करता है। बैंड संरचना तथा परावैद्युत अनुक्रिया (dielectric response) के संयुक्त प्रभाव का विश्लेषण करते हुए हमने Sb-आधारित यौगिकों को कुशल आवेश परिवहन के लिए विशेष रूप से आशाजनक पाया है। हम आगे यह प्रदर्शित करते हैं कि X_3NSb में धनायन प्रतिस्थापन और संरचनात्मक सममिति, बैंड गैप, गैर रुद्धोष्म (nonadiabatic) युग्मन तथा इलेक्ट्रॉनिक असम्बद्धता के सूक्ष्म संतुलन के माध्यम से गैर-विकिरणीय पुनर्संयोजन को नियंत्रित करती है। इसी विश्लेषण को कार्बाइड एंटीपेरोव्स्काइट्स M_6CSe_4 ($M = Ca, Sr$) तक विस्तारित करते हुए, हमने वाहक रिलैक्सेशन गतिकी — जिसमें गैर-विकिरणीय पुनर्संयोजन और हॉट-कैरियर शीतलन शामिल हैं — का जाली उतार-चढ़ाव तथा अंतर्निहित इलेक्ट्रॉनिक परिदृश्य के साथ सह-संबंध स्थापित किया है। ऊर्जा स्तरों के बीच बड़ा अंतराल गैर रुद्धोष्म युग्मन को दबा देता है, जिससे एक विश्राम अवरोध (relaxation bottleneck)

उत्पन्न होता है। यह धीमी हॉट-कैरियर शीतलन के साथ नैनोसेकंड-स्केल पुनर्संयोजन जीवनकाल को सक्षम बनाता है — जो उच्च-प्रदर्शन फोटोवोल्टाइक संचालन के लिए अत्यंत लाभप्रद है।

चाल्कोहैलाइड्स लेड-मुक्त अवशोषकों के एक आकर्षक वर्ग के रूप में उभरते हैं, जो संरचनात्मक स्थिरता को उपयुक्त बैंड गैप और प्रबल परावैद्युत अनुक्रिया के साथ जोड़ते हैं। इस वर्ग के भीतर, अर्ध-एक-आयामी (quasi-one-dimensional) यौगिक BiSeI कम-आयामीता के प्रभावों की जांच के लिए एक आदर्श मंच प्रदान करता है। बल्क (bulk) से जेनस (Janus) और एक्सफोलिएटेड मोनोलेयर (exfoliated monolayer) संरचनाओं, और अंततः पृथक मोनोचेन (monochain) तक के क्रमिक विकास का विश्लेषण करते हुए, हमने स्पष्ट किया है कि क्वांटम परिरोधन (confinement) तथा परावैद्युत स्क्रीनिंग एक्साइटॉनिक गुणों — जैसे बंधन ऊर्जा, स्थानिक वितरण तथा ब्राइट-डार्क एक्साइटॉन विभाजन — को कैसे आकार देते हैं। साथ ही, निम्न-आयामी प्रणालियों में एक्साइटॉनिक व्यवहार को समायोजित करने के व्यावहारिक मार्ग स्थापित करने हेतु बाह्य परावैद्युत वातावरण की भूमिका का भी मूल्यांकन किया गया है।

अंत में, रिक्तिका-क्रमबद्ध हैलाइड्स की जांच लेड-मुक्त प्रणालियों के रूप में की जाती है जो पर्यावरणीय क्षरण के प्रति उच्च प्रतिरोधक क्षमता प्रदान करती हैं। यह अध्ययन इनकी स्वाभाविक रूप से सीमित इलेक्ट्रॉनिक संपर्कता (connectivity) के प्रभाव को स्पष्ट करता है तथा इसे दूर करने की व्यवहार्य रणनीति प्रस्तुत करता है। हम पहले $A_3Bi_2I_9$ ($A = Cs, MA, FA$) पर विचार करते हैं, जहाँ इलेक्ट्रॉनिक रूप से पृथक संरचनात्मक इकाइयाँ मजबूत वाहक स्थानीयकरण और बाधित परिवहन को जन्म देती हैं। इन अंतर्दृष्टि के आधार पर, हम दिखाते हैं कि Ag समावेश द्वारा निर्मित स्तरीकृत यौगिक $Cs_2AgBi_2I_9$, इलेक्ट्रॉनिक संपर्कता को पुनः स्थापित करता है, बैंड प्रसार को बढ़ाता है और वाहक गतिशीलता में महत्वपूर्ण सुधार करता है। इसके समानांतर, Mo-मिश्रित Cs_2ZrCl_6 की जांच यह प्रदर्शित करने के लिए की जाती है कि कैसे ऑक्टाहेड्रल अलगाव और डोपेंट-प्रेरित अवस्थाएँ मिलकर होस्ट सेल्फ-ट्रैप्ड एक्साइटॉन्स और अशुद्धि स्तरों के बीच अंतर्क्रिया के माध्यम से दोहरी दृश्य-निकट-अवरक्त उत्सर्जन उत्पन्न करती हैं। उल्लेखनीय है कि ये दोनों उत्सर्जन चैनल स्वतंत्र रूप से कार्य करते हैं और इनके बीच नगण्य युग्मन पाया जाता है। सामूहिक रूप से, ये परिणाम रिक्तिका-क्रमबद्ध सामग्रियों में आवेश परिवहन और प्रकाश-उत्सर्जन गुणों के स्वतंत्र अनुकूलन के लिए एक सुसंगत रूपरेखा प्रदान करते हैं।

List of Publications

1. **S. Monga**^{*}, and S. Bhattacharya^{*}, “*Tuning nonradiative recombination via cation substitution in inorganic antiperovskite nitrides*”, Physical Review Materials **10**, 024602 (2026).
2. **S. Monga**^{*}, M. Jain, C. Draxl, and S. Bhattacharya^{*}, “*Theoretical insights into inorganic antiperovskite nitrides (X_3NA : $X= Mg, Ca, Sr, Ba$; $A= As, Sb$): An emerging class of materials for photovoltaics*”, Physical Review Materials **8**, 105403 (2024).
3. **S. Monga**^{*}, and S. Bhattacharya^{*}, “*Tunable Carrier Dynamics in Carbide Antiperovskites via A-Site Cation Substitution*” (manuscript under review), arXiv:2512.24093.
4. **S. Monga**^{*}, and S. Bhattacharya^{*}, “*Dimensionality-Driven Excitonic Engineering in Bi-SeI: An Ab Initio Many-Body Study*” (manuscript under review), arXiv:2503.13020
5. M. Jain^{*}, **S. Monga**, and S. Bhattacharya^{*}, “*Exploring the Role of Four-Phonon Scattering in the Lattice Thermal Transport of $LaMoN_3$* ”, The Journal of Physical Chemistry Letters **17**, 1370 (2026).
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catalytic activity in Cr(VI) reduction, green H₂ generation and CO sensing: An experimental study supported by DFT", *Nanoscale* **17**, 5941 (2025).

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11. M. Jain*, D. Gill, **S. Monga**, and S. Bhattacharya*, "*Oxynitride, Oxyfluoride, and Nitrofluoride Perovskites: Theoretical Evaluation of Photon Absorption Properties for Solar Water Splitting*", *The Journal of Physical Chemistry C* **127**, 15620 (2023).
12. S. Sheoran*, **S. Monga**, A. Phutela, and S. Bhattacharya*, "*Coupled spin-valley, Rashba effect, and hidden spin polarization in WSi₂N₄ family*", *The Journal of Physical Chemistry Letters* **14**, 1494 (2023).

[†]: Equal contribution

*: Corresponding authors

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Introduction

1.1 Motivation

Can we envision a future powered entirely by clean, abundant solar energy—where rooftops, windows, and flexible surfaces silently convert sunlight into electricity with unprecedented efficiency, while lighting our world with vibrant, energy-efficient displays? Semiconductors lie at the heart of this vision. They drive not only photovoltaics (PVs) and light-emitting diodes (LEDs) but also photodetectors, sensors, and emerging quantum technologies that will shape a carbon-neutral society.

Among the many materials explored in the quest for sustainable optoelectronics, lead halide perovskites (LHPs) have emerged as true disruptors. Since their first demonstration in solar cells in 2009 [12], single-junction perovskite PVs have surged from 3.8% to over 27% certified power-conversion efficiency (PCE) by 2026, with tandem devices exceeding 34% [13]. Perovskite LEDs have simultaneously achieved external quantum efficiencies surpassing 30% across the visible spectrum [14, 15, 16]. These remarkable advances originate from a unique combination of strong optical absorption, long carrier diffusion lengths, defect tolerance, tunable band gaps, and compatibility with low-cost solution processing [17, 18].

At the atomic level, LHPs adopt the ABX_3 structure—a three-dimensional (3D) network of corner-sharing $[BX_6]$ octahedra with A-cations occupying the interstitial cavities (Fig. 1.1). Their remarkable optoelectronic response arises from a delicate interplay of antibonding band-edge states, strong dielectric screening, relativistic effects, and a soft polar lattice [19, 20]. This synergy promotes efficient free-carrier generation at room temperature while suppressing non-radiative energy losses, allowing laboratory-scale devices to achieve excellent efficiencies [21]. Despite this spectacular success, two formidable obstacles block the path to large-scale commercialization: the toxicity of lead and intrinsic instability under moisture, heat, oxygen, and

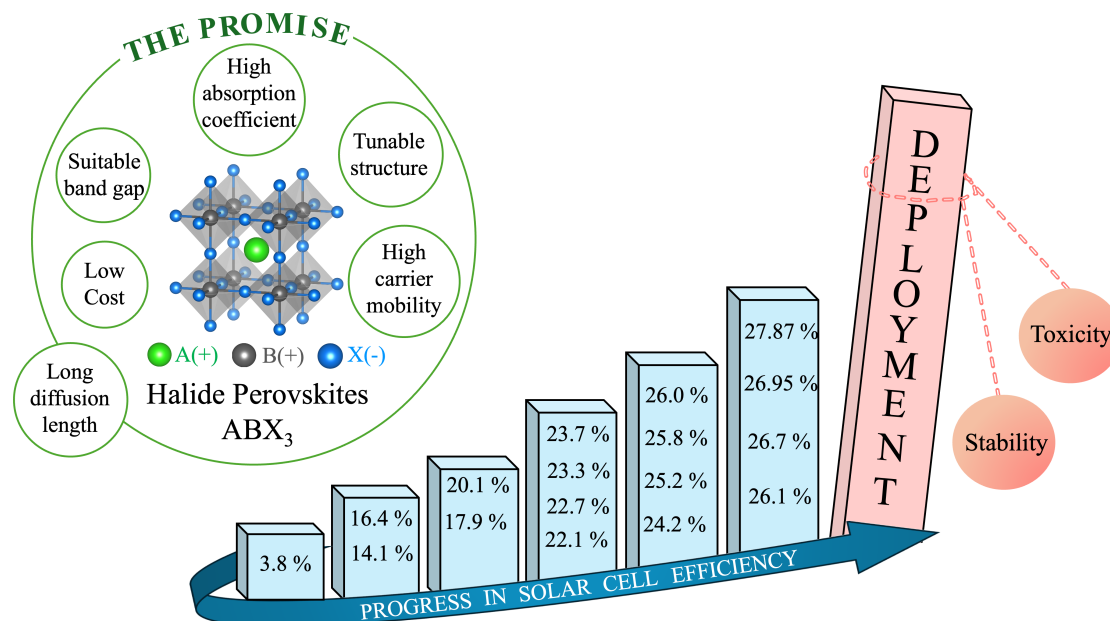


Figure 1.1: Schematic illustration of the conventional ABX_3 halide perovskite structure and the dramatic rise in photovoltaic efficiency enabled by their exceptional optoelectronic properties. Despite this success, long-term instability and lead toxicity remain major obstacles to large-scale technological deployment.

illumination [22, 23]. These challenges have ignited a global search for lead-free alternatives that preserve the remarkable optoelectronic qualities of LHPs while offering superior chemical robustness and environmental compatibility.

1.2 Perovskite-inspired materials: Expanding the design space

Perovskite-inspired materials (PIMs) constitute a broad and chemically diverse class of semiconductors that extend beyond the conventional ABX_3 perovskite framework while retaining many of the electronic attributes responsible for the remarkable optoelectronic performance of LHPs. Owing to their compositional flexibility, structural diversity, and potential for stable lead-free optoelectronics, these materials have emerged as a promising platform for next-generation semiconductor design. In the context of this thesis, PIMs encompass materials that are either structurally derived from the parent perovskite lattice—such as antiperovskites and vacancy-ordered derivatives—or electronically inspired by the design principles underlying the exceptional performance of LHPs (Fig. 1.2). The latter category includes compounds containing stereochemically active ns^2 lone-pair cations analogous to Pb^{2+} , which can promote defect tolerance, strong dielectric screening, high polarizability, and favorable band-edge char-

acteristics [24]. The rapidly expanding design space of PIMs encompasses diverse bonding

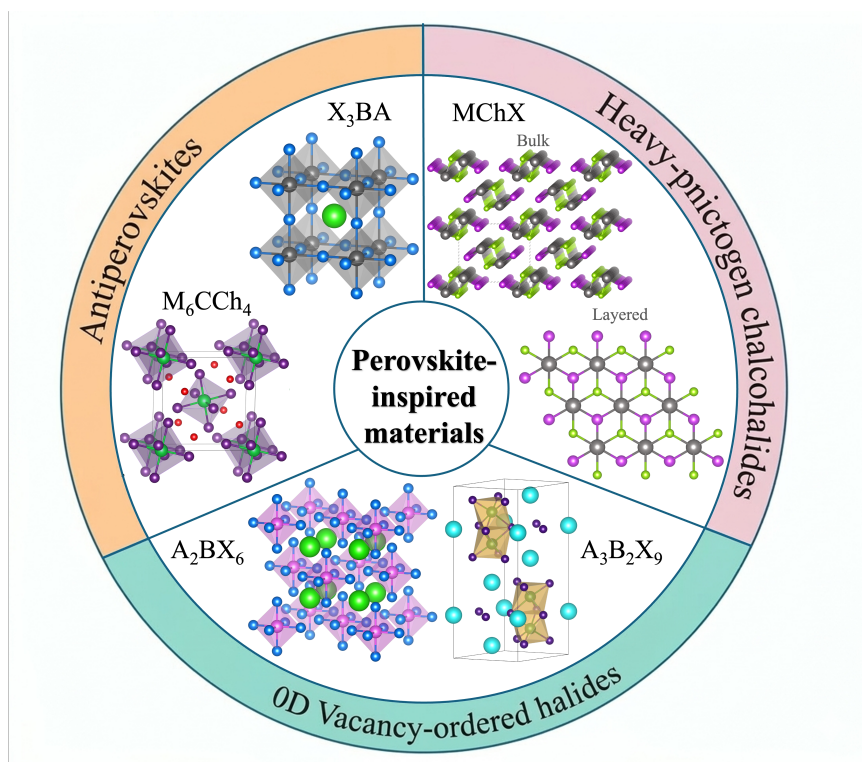


Figure 1.2: Representative families of perovskite-inspired materials (PIMs) investigated in this thesis: antiperovskites and derivatives, vacancy-ordered halides, and heavy-pnictogen chalcogenides.

motifs, mixed-anion chemistries, ordered vacancies, and varying levels of structural connectivity. These variations generate electronic environments substantially different from those of conventional LHPs, making PIMs an attractive platform for exploring structure-dependent excited-state phenomena. Among the many emerging PIM families, three classes are particularly relevant to this thesis because of their distinct crystal architectures and optoelectronic characteristics (Fig. 1.2):

- **Antiperovskites** constitute structurally inverted analogues of conventional perovskites, in which the positions of cations and anions are reversed relative to the ABX_3 lattice, giving rise to fundamentally distinct bonding characteristics and electronic structures [25, 26]. This broad materials family includes oxide, nitride, halide, and mixed-anion antiperovskites, as well as quaternary derivatives and emerging low-dimensional variants [27]. Among these, nitride antiperovskites of the form X_3NA ($X = \text{Mg, Ca, Sr, Ba}$; $A = \text{P, As, Sb, Bi}$) have attracted considerable attention because of their suitable band gaps, low carrier effective masses, and strong visible-light absorption, resulting in exceptionally high theoretical spectroscopic-limited maximum efficiencies (SLME) [28, 29, 30]. In parallel,

mixed-anion carbide–chalcogenide antiperovskites such as M_6CCh_4 ($M = Ca, Sr, Ba$; $Ch = S, Se, Te$) combine strong covalent bonding with optoelectronic characteristics comparable to or surpassing those of prototypical LHPs [31]. The chemical versatility and tunable lattice environments of antiperovskites therefore make them promising candidates for exploring lead-free optoelectronic functionality across a wide range of structural and electronic regimes.

- The ordered removal of B-site cations from the conventional ABX_3 lattice gives rise to **vacancy-ordered halides**, producing low-connectivity structures such as $A_3B_2X_9$ and A_2BX_6 [32, 33]. The resulting reduction in octahedral connectivity suppresses long-range electronic hybridization, yielding electronically low-dimensional structures characterized by narrow band dispersion and enhanced carrier localization. This reduced connectivity often improves structural rigidity and environmental stability relative to 3D LHPs, enabling greater resistance to moisture, heat, and prolonged illumination. At the same time, the electronically isolated octahedral units can limit charge transport and hinder efficient free-carrier extraction in PV applications [34]. Conversely, the same localization effects strengthen excitonic confinement and electron–phonon interactions, frequently leading to the formation of self-trapped excitons (STEs) [35]. These STEs commonly produce broadband emission with large Stokes shifts, making vacancy-ordered halides promising candidates for light-emitting applications, including phosphors, scintillators, and LEDs [36]. Importantly, compositional engineering provides effective routes to partially restore electronic connectivity and tailor excited-state behavior, thereby enabling improved optoelectronic performance across this material family.
- **Heavy-pnictogen chalcahalides** ($MChX$; $M = Bi, Sb$; $Ch = S, Se$; $X = I, Br, Cl$) represent an electronically inspired class of PIMs that reproduces many of the key electronic advantages of LHPs without relying on a common structural framework. These compounds exploit the stereochemically active ns^2 lone pairs of heavy-metal cations to induce strong hybridization with anion p orbitals, giving rise to dispersive antibonding valence-band states, high dielectric polarizability, and defect-tolerant electronic structures [37]. Their mixed-anion frameworks implement a “split-anion” strategy that combines soft halides with more covalent chalcogenides, thereby enhancing thermodynamic stability while enabling highly tunable band gaps across the visible spectrum [38]. To-

gether with their strong optical absorption and favorable band-edge alignment with established charge-transport layers [39, 40], these characteristics make chalcogenides promising candidates for next-generation optoelectronic applications. Structurally, many chalcogenides crystallize into highly anisotropic quasi-one-dimensional motifs composed of covalently bonded ribbons or chains weakly coupled through van der Waals interactions. Such low-dimensional anisotropic frameworks also provide an ideal platform for investigating excitonic effects and many-body interactions in reduced-dimensional semiconductors relevant to nanoscale optoelectronic applications.

1.3 Excited-state physics: The hidden frontier

Although many PIMs exhibit promising ground-state electronic properties, their device efficiencies often remain substantially below theoretical limit [41, 42, 34]. This disparity underscores that semiconductor functionality is governed not only by static electronic structure, but also by the complex many-body interactions that emerge under excited-state conditions. Following photoexcitation, the semiconductors evolve through a coupled interplay among electron–hole interactions, dielectric screening, lattice polarization, dynamic disorder, and carrier-relaxation pathways. These microscopic processes collectively determine carrier generation, transport, recombination, and energy dissipation, thereby shaping the overall optoelectronic response of the material.

In conventional LHPs, the coexistence of small exciton binding energies (few meV), strong dielectric screening, and large-polaron formation creates near-ideal conditions for efficient carrier separation and long-range charge transport [43, 44, 45]. The PIMs explored in this thesis, however, span a far broader structural and chemical landscape characterized by substantial variations in bonding character, structural dimensionality, lattice flexibility, and dielectric response. Such diversity can profoundly reshape Coulomb interactions, electron–phonon coupling, and carrier localization, often giving rise to excited-state phenomena fundamentally distinct from those observed in conventional LHPs. Understanding how these microscopic interactions evolve across chemically diverse PIMs therefore remains one of the central challenges in the rational design of next-generation lead-free optoelectronic materials.

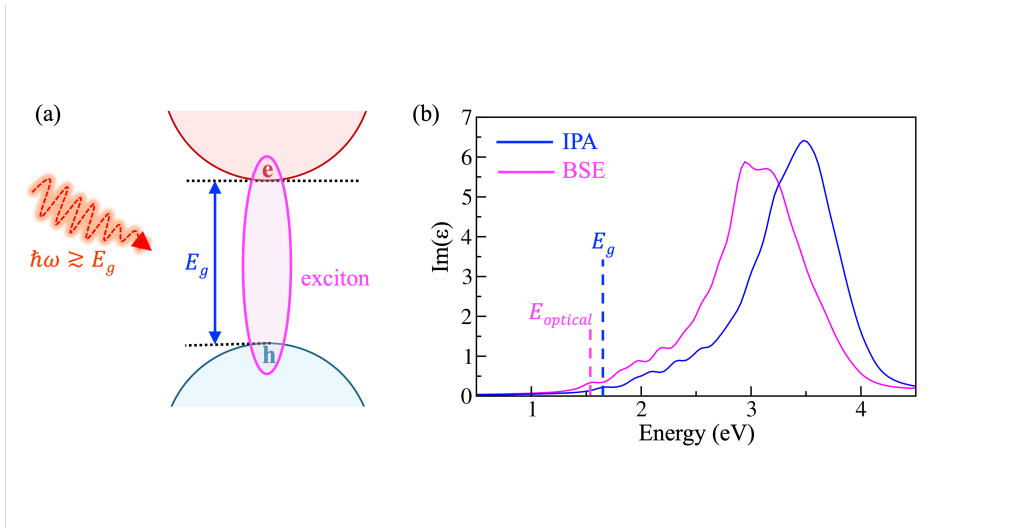


Figure 1.3: (a) Schematic illustration of exciton formation following photoexcitation. (b) Optical absorption spectra calculated within the independent-particle approximation (IPA) and the Bethe–Salpeter equation (BSE), illustrating the emergence of bound excitonic states below the quasiparticle band gap (E_g).

Excitonic effects

One of the most direct manifestations of many-body interactions in semiconductors is the formation of excitons—correlated electron–hole pairs bound by Coulomb attraction (Fig. 1.3 (a)). The stability of these quasiparticles is quantified by the exciton binding energy E_b , defined as the difference between the quasiparticle band gap E_g and the optical gap E_{optical} . Excitonic interactions profoundly reshape the optical response of semiconductors by redistributing oscillator strength and introducing discrete bound states below the quasiparticle continuum. As a result, the optical absorption onset becomes red-shifted relative to the independent-particle picture and is frequently accompanied by pronounced excitonic resonances (Fig. 1.3 (b)) [10]. The strength and spatial character of excitons are governed by the interplay among dielectric screening, carrier effective masses, lattice connectivity, and electronic dimensionality.

In low-dimensional and weakly screened materials, enhanced electron–hole attraction often drives a crossover from weakly bound Wannier–Mott excitons, typical of highly screened 3D semiconductors, toward more localized Frenkel-like excitons with substantially larger binding energies [46, 47]. Such strongly bound excitons can remain stable at room temperature, producing sharp excitonic peaks and enhanced light–matter interactions that are advantageous for LEDs, lasing, and photodetection applications [48]. Conversely, excessively large exciton binding energies can hinder efficient free-carrier generation and charge separation, thereby lim-

iting PV performance. Consequently, excitonic behavior can be systematically tuned through changes in composition, dielectric environment, and structural dimensionality [49, 50].

Electron–phonon coupling and polaron formation

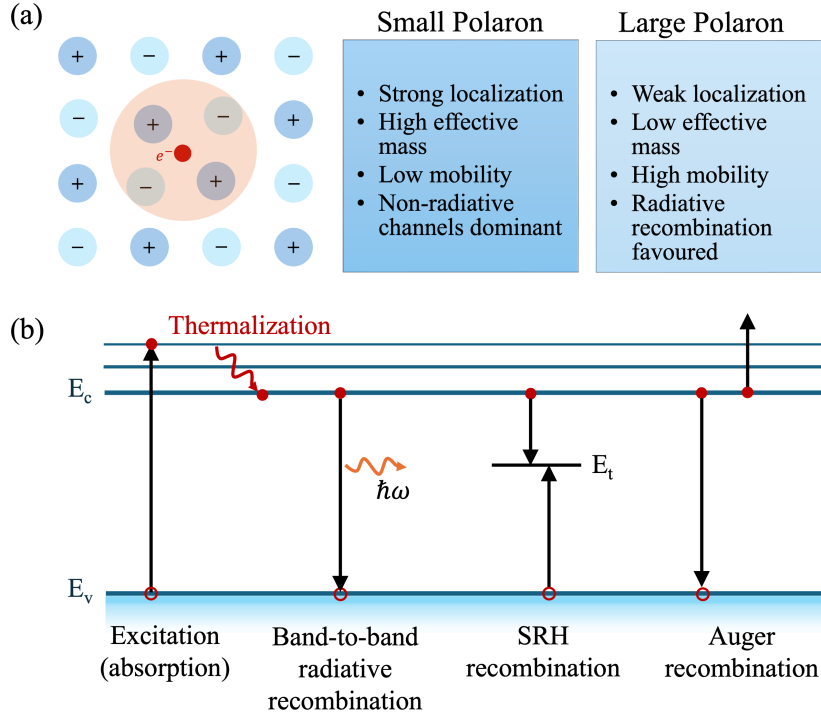


Figure 1.4: (a) Illustration of polaron formation in a polar lattice, along with the contrasting characteristics of small- and large-polaron regimes. (b) Representative carrier-relaxation pathways following excitation, including carrier thermalization, radiative recombination, and non-radiative decay processes.

Beyond electron–hole interactions, electron–phonon coupling constitutes another defining aspect of excited-state physics in semiconductors. Following photoexcitation, carriers continuously interact with lattice vibrations, dynamically polarizing the surrounding crystal and forming composite quasiparticles known as polarons (Fig. 1.4 (a)) [11]. The spatial extent of the resulting lattice distortion critically determine carrier effective masses, mobility, scattering rates, and recombination kinetics. In the weak-to-intermediate coupling regime, carriers remain delocalized over many lattice sites, forming large polarons that dynamically screen charged defects and impurities. Such screening suppresses carrier scattering and reduces non-radiative capture processes, and is widely regarded as a key contributor to the exceptional defect tolerance and long carrier lifetimes observed in LHPs [45, 10].

In contrast, sufficiently strong electron–phonon coupling can localize carriers over one or a few lattice sites, leading to the formation of small polarons. These localized quasiparticles exhibit

larger effective masses, reduced carrier mobility, and enhanced multi-phonon non-radiative relaxation due to stronger coupling with local vibrational modes. Polaron formation therefore plays a central role in determining whether photoexcited carriers remain mobile and long-lived or become localized and rapidly dissipate their energy into the lattice [51]. Understanding how bonding environments, and lattice flexibility govern electron–phonon interactions is thus essential for predicting carrier transport and energy-loss mechanisms in lead-free PIMs.

Carrier relaxation and non-radiative recombination

Once an electron is promoted from the valence to the conduction band, the resulting hot-carrier population undergoes a complex cascade of relaxation processes driven by the intricate interplay among electron–phonon coupling, lattice fluctuations, electronic decoherence, and electron–hole interactions. As illustrated schematically in Fig. 1.4 (b), dominant relaxation pathways include ultrafast carrier thermalization through phonon scattering, radiative band-to-band recombination, defect-assisted Shockley–Read–Hall (SRH) recombination, Auger recombination, and multi-phonon non-radiative decay. Among these processes, hot-carrier cooling and non-radiative recombination constitute the principal energy-loss channels in semiconductor devices. By rapidly dissipating excess electronic energy into lattice vibrations as heat, they impose intrinsic limitations on open-circuit voltage, PCE, carrier lifetime, and photoluminescence quantum yield.

To unravel these non-equilibrium processes at an atomistic level, real-time non-adiabatic molecular dynamics (NAMD) simulations provide a powerful first-principles framework [52, 53]. By explicitly propagating the electronic density matrix alongside the classical or semiclassical motion of the nuclei, NAMD captures the time-dependent non-adiabatic couplings responsible for carrier relaxation and recombination. Because these couplings depend sensitively on lattice dynamics and electronic-state mixing, even subtle structural perturbations—including changes in crystal symmetry, octahedral tilting, cation substitution, lattice strain, and intrinsic defects—can alter non-radiative carrier lifetimes by several orders of magnitude [54, 55, 56, 57, 58]. Such perturbations modify orbital overlap, phonon spectra, and decoherence dynamics, thereby reshaping the efficiency of carrier-relaxation pathways.

While the non-equilibrium excited-state kinetics of conventional LHPs have been extensively investigated, lead-free PIMs remain a comparatively unexplored frontier. Recent studies on vacancy-ordered halides have shown that A-site cation engineering, lattice compression, and

structural dimensionality can strongly influence orbital hybridization, carrier delocalization, and hot-carrier lifetimes [59, 60]. For example, enhanced structural connectivity induced by partial cation substitution in $\text{Cs}_3\text{Bi}_2\text{I}_9$ has been found to improve carrier delocalization and substantially prolong carrier lifetimes relative to electronically isolated zero-dimensional analogues [61]. Despite these advances, systematic first-principles investigations of carrier relaxation and non-radiative recombination remain limited across many important PIM families.

1.4 Computational approach and scope of this thesis

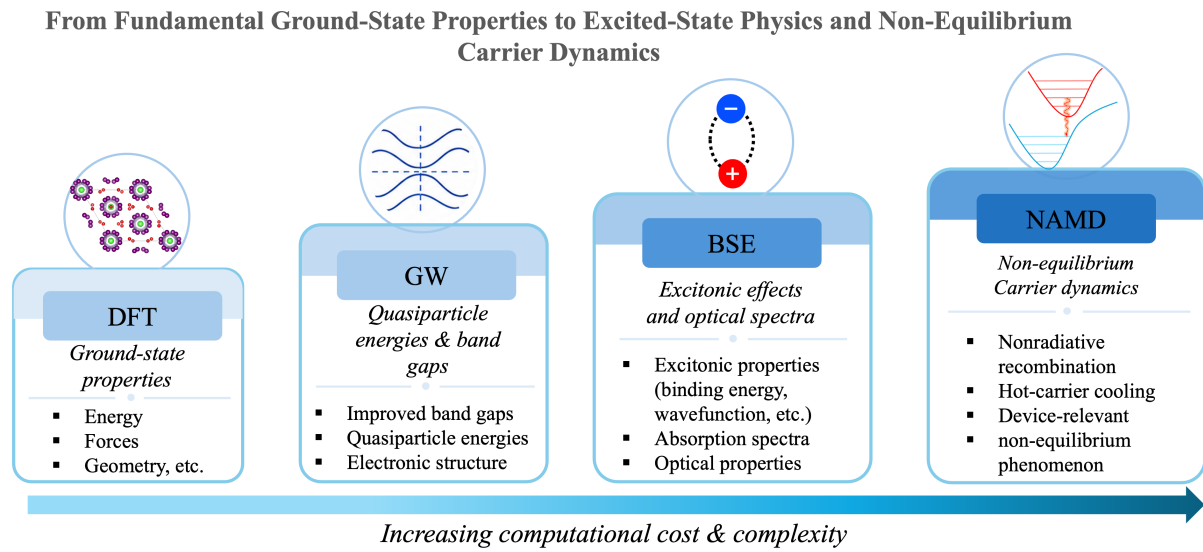


Figure 1.5: Hierarchy of first-principles theoretical approaches employed in this thesis, spanning ground-state density functional theory (DFT), many-body perturbation theory (GW /BSE), and real-time non-adiabatic molecular dynamics (NAMD).

Capturing the complex excited-state physics of PIMs requires theoretical frameworks capable of simultaneously describing quasiparticle corrections, excitonic interactions, lattice polarization, and non-equilibrium carrier dynamics. While conventional density functional theory (DFT) has proven highly successful for predicting ground-state structural and electronic properties, its approximate treatment of exchange–correlation effects and dynamical screening often limits its ability to accurately describe excited-state phenomena and many-body interactions. Quantitative investigations of excited-state processes therefore demand advanced first-principles methodologies beyond standard DFT. In this thesis, quasiparticle electronic structures and optical excitations are investigated within the framework of many-body perturbation theory (MBPT) using the GW approximation and the Bethe–Salpeter equation (BSE), enabling an

accurate description of electronic screening and electron–hole interactions. Non-equilibrium carrier dynamics are explored through real-time NAMD simulations, which explicitly capture the interplay between electronic excitations and lattice motion. Complementary approaches based on density functional perturbation theory, and polaron models are further employed to investigate carrier–phonon coupling. Although these methodologies are now well established both theoretically and computationally, their substantial computational cost continues to limit their routine application to chemically and structurally complex materials systems. Figure 1.5 summarizes the hierarchy of computational techniques employed throughout this work.

The central objective of this thesis is to develop a microscopic understanding of excited-state phenomena across representative families of lead-free PIMs. Particular emphasis is placed on elucidating how crystal chemistry, structural dimensionality, dielectric screening, and lattice dynamics collectively govern excitonic effects, polaron formation, hot-carrier relaxation, and non-radiative recombination. This work seeks to establish fundamental structure–property–dynamics relationships that govern energy conversion and dissipation in lead-free semiconductors, while simultaneously providing guiding principles for the rational design of next-generation optoelectronic materials.

1.5 Organization of the thesis

The thesis is organized as follows.

- **Chapter 2:** This chapter presents the theoretical foundations and computational framework employed throughout this thesis. The methodologies introduced here provide the basis for investigating ground-state electronic structure, excited-state many-body interactions, lattice dynamics, and non-equilibrium carrier processes in PIMs. Together, these complementary approaches enable a unified understanding of the microscopic mechanisms governing the optoelectronic performance of lead-free semiconductors.
- **Chapter 3:** This chapter investigates lead-free inorganic antiperovskite nitrides (X_3NA , $X = Mg, Ca, Sr, Ba$; $A = As, Sb$) as promising alternatives to conventional LHPs for PV applications. It begins with a systematic analysis of their structural stability and ground-state electronic properties using DFT. The role of many-body effects is subsequently explored through quasiparticle calculations within the GW approximation, followed by the evaluation of optical spectra and excitonic properties using the BSE formalism and the

Wannier–Mott model. In addition, polaronic effects—including carrier–phonon coupling strength, effective-mass renormalization, and charge-carrier mobility—are investigated. Collectively, this study provides microscopic insight into the optoelectronic behavior of antiperovskite nitrides and identifies the Sb-based compounds as particularly promising PV absorbers. Chapter 3 is based on the author’s published work reported in Ref. [62].

- **Chapter 4:** Building upon the promising optoelectronic properties of X_3NSb ($X = Ca, Sr, Ba$) antiperovskite nitrides established in Chapter 3, this chapter investigates the microscopic mechanisms governing non-radiative electron–hole recombination dynamics. Particular emphasis is placed on understanding the coupled influence of X-site cation chemistry and crystal symmetry on excited-state carrier relaxation through a comparative study of cubic and hexagonal phases. Real-time NAMD simulations are employed to examine how variations in lattice dynamics, band-gap fluctuations, non-adiabatic coupling strengths, and electronic decoherence collectively regulate carrier lifetimes. The analysis reveals that subtle changes in crystal symmetry and lattice dynamics can substantially modify recombination lifetimes, providing microscopic insight into the factors governing non-radiative losses in antiperovskite semiconductors. The contents of this chapter are adapted from the published work in Ref. [63].
- **Chapter 5:** This chapter investigates the electronic structure, optical response, and excited-state carrier dynamics of the carbide antiperovskites M_6CSe_4 ($M = Ca, Sr$) as emerging lead-free materials for PV and optoelectronic applications. Ground- and excited-state electronic properties are examined using DFT and MBPT, enabling an accurate description of quasiparticle band structures, optical absorption, and excitonic effects. Both compounds are identified as direct-gap semiconductors with visible-to-near-infrared band gaps and moderate exciton binding energies. Furthermore, NAMD simulations reveal that A-site cation substitution strongly modulates lattice fluctuations, non-adiabatic coupling strengths, and electronic decoherence, thereby producing markedly different carrier-relaxation pathways and recombination lifetimes. In particular, enhanced dynamic disorder in Ca_6CSe_4 induces larger band-gap fluctuations and faster decoherence while simultaneously suppressing non-radiative recombination through weaker non-adiabatic couplings, resulting in carrier lifetimes nearly an order of magnitude longer than those in Sr_6CSe_4 . Hot-carrier cooling in both systems occurs on picosecond timescales, with

pronounced slowing near the band edges. Collectively, these findings establish a counterintuitive structure–dynamics relationship in which enhanced lattice fluctuations can intrinsically prolong carrier lifetimes, thereby providing microscopic insight into lattice-driven carrier dynamics and guiding the rational design of next-generation lead-free optoelectronic materials. The contents of this chapter are adapted from the preprint Ref. [64].

- **Chapter 6:** Orthorhombic heavy-pnictogen chalcogenides of the form MChX exhibit highly anisotropic quasi-one-dimensional crystal structures, excellent chemical stability, and promising optoelectronic characteristics. Their weak interchain interactions make them attractive candidates for exfoliation into reduced-dimensional forms with tunable excited-state properties. In this chapter, we investigate the evolution of the electronic structure, optical response, and excitonic properties of BiSeI across bulk, monolayer, and one-dimensional monochain geometries using first-principles DFT and MBPT within the *GW*/BSE framework. The calculations reveal a pronounced enhancement of quasiparticle band gaps and exciton binding energies with decreasing dimensionality, driven by quantum confinement and reduced dielectric screening. In particular, exciton binding energies evolve from weakly bound bulk excitons to strongly confined excitonic states in the monochain limit. Reduced dimensionality further modifies the excitonic fine structure by increasing bright–dark exciton splitting and introducing multiple dark excitonic states below the first bright excitation, with important implications for exciton radiative dynamics and optical emission processes. The influence of environmental dielectric screening is additionally examined through substrate-supported structures, demonstrating substantial renormalization of excitonic interactions in reduced dimensions. Collectively, these findings establish BiSeI as a highly tunable platform for exploring strong excitonic effects and many-body interactions in low-dimensional semiconductors, while highlighting its potential for future excitonic and nanoscale optoelectronic applications. The results and discussion presented in this chapter are adapted from the preprint Ref. [65].
- **Chapter 7:** This chapter focuses on low-dimensional vacancy-ordered halides, with particular emphasis on the influence of structural dimensionality and compositional engineering on their electronic and optical properties. It begins with an investigation of the electronic structure of $A_3\text{Bi}_2\text{I}_9$ ($A = \text{Cs}, \text{MA}, \text{FA}$) to elucidate the band-edge characteristics and carrier localization arising from reduced octahedral connectivity in zero-

dimensional systems. The study then examines the layered derivative $\text{Cs}_2\text{AgBi}_2\text{I}_9$, demonstrating how partial Ag incorporation enhances electronic connectivity, increases band dispersion, and improves charge-transport behavior, consistent with the experimentally reported enhancement in PV performance for indoor applications. Finally, dopant engineering in vacancy-ordered double perovskites is explored through Mo alloying in Cs_2ZrCl_6 , where the interplay between host excitons and dopant-induced states gives rise to dual visible–near-infrared emission associated with electronically isolated octahedra. Collectively, these results establish how dimensionality and compositional tuning govern excitonic confinement, charge transport, and light-emission behavior in vacancy-ordered halide systems. The contents of this chapter are adapted from Refs. [66, 67, 68].

- **Chapter 8:** This chapter summarizes the key findings of the present work and highlights their broader implications. It further outlines prospective directions for future research building upon the outcomes of this thesis.

Theoretical Methodology

2.1 First-principles modeling of materials

A fundamental understanding of materials requires a quantum-mechanical description of interacting electrons and nuclei, which ultimately governs their physical properties. In condensed matter systems, this naturally leads to a complex many-body problem, where the motion of each particle is strongly correlated with that of all others. Although the Schrödinger equation formally provides a complete description, its direct solution for realistic systems quickly becomes intractable due to the exponential scaling with the number of degrees of freedom.

This intrinsic difficulty was succinctly articulated by Dirac:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

First-principles (*ab initio*) methods address this challenge by reformulating the many-body problem into tractable computational frameworks through a series of controlled and systematically improvable approximations. By relying solely on fundamental physical constants—rather than empirical or system-specific parameters—these approaches enable predictive modeling of material properties based on atomic composition and crystal structure. Modern implementations, supported by advanced numerical algorithms and high-performance computing, now permit simulations of systems comprising hundreds to thousands of atoms. Consequently, first-principles modeling serves as a powerful bridge between theory and experiment, providing microscopic insight into physical mechanisms that are often difficult to access experimentally, while also guiding the rational design of novel materials.

This thesis employs first-principles computational methods to investigate the structural, electronic, and optical properties, and charge-carrier dynamics of perovskite-inspired materials. Particular emphasis is placed on excitonic properties including binding energies and real-space wavefunctions, electron–phonon interactions, encompassing polaron formation, effective mass renormalization, and charge-carrier mobility, and nonradiative recombination mechanisms, all of which play critical roles in determining the performance of optoelectronic devices. While the underlying theoretical frameworks are well established in the literature [69, 70, 71], the following sections provide a concise yet rigorous overview of the key methodologies and computational approaches adopted in this work. These include density functional theory (DFT) [72], many-body perturbation theory (MBPT) [73], nonadiabatic molecular dynamics (NAMD) [74, 71], density functional perturbation theory (DFPT) [75], and theoretical models of excitons [76] and polarons [77], which together constitute the computational and theoretical foundation of the subsequent chapters.

2.2 Time-independent many-body Schrödinger equation

The quantum-mechanical description of a material begins with the time-independent many-body Schrödinger equation for a system consisting of N_e electrons and N_n nuclei:

$$\hat{H}\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = E\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}), \quad (2.1)$$

where Ψ is the many-body wavefunction that depends on the spatial and spin coordinates of all electrons $\{\mathbf{r}_i\}$ ($i = 1, \dots, N_e$) and the positions of all nuclei $\{\mathbf{R}_I\}$ ($I = 1, \dots, N_n$), and E is the total energy of the system.

The full Hamiltonian reads

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}, \quad (2.2)$$

where $\hat{T}_e$ and $\hat{T}_N$ denote the kinetic energies of electrons and nuclei, respectively, and $\hat{V}_{ee}$, $\hat{V}_{eN}$, and $\hat{V}_{NN}$ represent the electron–electron, electron–nucleus, and nucleus–nucleus Coulomb interactions, respectively, given by (in atomic units)

$$\hat{T}_e = -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2, \quad (2.3)$$

$$\hat{T}_N = -\frac{1}{2} \sum_{I=1}^{N_n} \frac{1}{M_I} \nabla_I^2, \quad (2.4)$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.5)$$

$$\hat{V}_{eN} = - \sum_{i=1}^{N_e} \sum_{I=1}^{N_n} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}, \quad (2.6)$$

$$\hat{V}_{NN} = \frac{1}{2} \sum_{I \neq J}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (2.7)$$

Here, M_I and Z_I are the mass and atomic number of the I -th nucleus, respectively.

Although formally exact, the direct solution of this equation is computationally prohibitive for realistic materials because the many-body wavefunction depends on $3(N_e + N_n)$ coordinates and scales exponentially with system size. A crucial simplification is provided by the **Born–Oppenheimer (BO) approximation**, which exploits the large mass difference between nuclei and electrons ($M_I \gg m_e$). Owing to their much larger mass, nuclei evolve on significantly slower timescales than electrons, allowing an effective decoupling of electronic and nuclear degrees of freedom. Consequently, the total wavefunction can be factorized as

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = \psi_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}), \quad (2.8)$$

where ψ_e is the electronic wavefunction that depends parametrically on the nuclear positions, and χ describes the nuclear motion. Within this framework, the electronic Schrödinger equation is solved for fixed nuclear configuration

$$\hat{H}_e \psi_e = E_e(\{\mathbf{R}_I\}) \psi_e, \quad (2.9)$$

with the electronic Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{V}_{\text{ext}} + \hat{V}_{ee}, \quad (2.10)$$

where $\hat{V}_{\text{ext}} \equiv \hat{V}_{eN}$ is the external potential exerted by the nuclei on the electrons. The nuclear dynamics are then treated separately on the potential energy surface defined by the electronic energy $E_e(\{\mathbf{R}_I\})$ together with the nucleus–nucleus repulsion $\hat{V}_{NN}$.

Even after applying the BO approximation, solving the resulting electronic problem remains nontrivial due to the $3N_e$ degrees of freedom, necessitating further simplifications. A natural starting point is the independent-particle picture, in which each electron moves in an effective potential generated by the average field of all other electrons and the nuclei. The Hartree approximation embodies this idea by expressing the many-electron wavefunction as a simple product of single-particle spin-orbitals [78, 79]:

$$\psi_e(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) \approx \prod_{i=1}^{N_e} \phi_i(\mathbf{r}_i), \quad (2.11)$$

where each $\mathbf{r}_i$ includes both spatial and spin coordinates, and $\phi_i(\mathbf{r}_i)$ denotes a single-electron spin-orbital. This ansatz neglects exchange and correlation effects, treating electrons as independent particles interacting only through a mean electrostatic potential. While conceptually useful, the Hartree approximation violates the antisymmetry requirement of fermionic wavefunctions and neglects electron correlation.

The Hartree–Fock (HF) method corrects this by constructing the many-electron wavefunction as a single Slater determinant of spin-orbitals [80, 81]:

$$\psi_e(\mathbf{r}_1, \dots, \mathbf{r}_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_{N_e}(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_{N_e}(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_{N_e}) & \phi_2(\mathbf{r}_{N_e}) & \cdots & \phi_{N_e}(\mathbf{r}_{N_e}) \end{vmatrix}. \quad (2.12)$$

This construction ensures the required antisymmetry of the wavefunction under particle exchange and introduces an exact nonlocal exchange interaction that eliminates self-interaction errors present in the Hartree approximation. Despite incorporating exact exchange, HF remains a mean-field theory and does not account for electron correlation effects arising from the instantaneous Coulomb interaction between electrons. To incorporate these correlation effects, wavefunction-based post-HF methods, such as configuration interaction, Møller–Plesset perturbation theory, and coupled-cluster theory, extend the description beyond a single-determinant framework. While these approaches can achieve high accuracy, their computational cost scales steeply with system size, typically ranging from $\mathcal{O}(N^5)$ to $\mathcal{O}(N^7)$ or higher, which restricts their applicability to relatively small systems.

These limitations motivate the search for alternative formulations. DFT provides such a framework by reformulating the electronic many-body problem in terms of the ground-state electron density $n(\mathbf{r})$ rather than the many-electron wavefunction. This approach offers an excellent balance between accuracy and computational efficiency, making it the cornerstone of modern first-principles materials modeling.

2.3 Density functional theory

Within this framework, the central quantity is the electron density $n(\mathbf{r})$, which serves as the fundamental variable for describing the ground-state properties of an interacting electron system. Within the probabilistic interpretation of quantum mechanics, the electron density associated

with a many-electron wavefunction ψ_e (composed of N_e orthonormal electron orbitals) represents the probability density of finding an electron at a given position in space and is defined as

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} \langle \psi_e | \delta(\mathbf{r} - \mathbf{r}_i) | \psi_e \rangle. \quad (2.13)$$

Here, N_e is the total number of electrons. Unlike the wavefunction, which depends on $3N_e$ variables, $n(\mathbf{r})$ depends only on three spatial coordinates, making it computationally far more tractable for large systems.

Early attempts to express the total energy directly as a functional of the electron density were made by Thomas, Fermi, and Dirac in the 1920s and 1930s [82, 83, 84]. These approaches, collectively known as the Thomas–Fermi–Dirac model, provided an initial framework for density-based descriptions but relied on oversimplified approximations and neglected important quantum-mechanical effects, particularly electron correlation. These limitations motivated the development of a more rigorous foundation, which was established through the two theorems proved by Hohenberg and Kohn in the mid-1960s [85].

2.3.1 Hohenberg–Kohn formalism

Theorem 1: *For any system of interacting electrons in an external potential $V_{\text{ext}}(\mathbf{r})$, this potential is uniquely determined, up to an additive constant, by the ground-state electron density $n(\mathbf{r})$.*

Proof: This theorem establishes a one-to-one correspondence between the ground-state density and the external potential. Consequently, the density uniquely determines the Hamiltonian and, therefore, all ground-state properties of the system.

The proof proceeds by contradiction. Assume that two distinct external potentials, $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$, differing by more than a constant, give rise to the same ground-state electron density $n(\mathbf{r})$. These potentials define two different Hamiltonians, $\hat{H}$ and $\hat{H}'$, with corresponding ground-state wavefunctions ψ and ψ' , and energies E and E' , respectively.

According to the variational principle,

$$E < \langle \psi' | \hat{H} | \psi' \rangle. \quad (2.14)$$

Writing $\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{\text{ext}}$, this becomes

$$E < \langle \psi' | \hat{T}_e + \hat{V}_{ee} | \psi' \rangle + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}). \quad (2.15)$$

Since ψ' is the ground state of $\hat{H}'$,

$$E' = \langle \psi' | \hat{T}_e + \hat{V}_{ee} | \psi' \rangle + \int d\mathbf{r} V'_{\text{ext}}(\mathbf{r}) n(\mathbf{r}). \quad (2.16)$$

Substituting into the inequality above yields

$$E < E' + \int d\mathbf{r} n(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})]. \quad (2.17)$$

Reversing the roles of $\hat{H}$ and $\hat{H}'$, one similarly obtains

$$E' < E + \int d\mathbf{r} n(\mathbf{r}) [V'_{\text{ext}}(\mathbf{r}) - V_{\text{ext}}(\mathbf{r})]. \quad (2.18)$$

Adding both inequalities leads to the contradiction

$$E + E' < E + E', \quad (2.19)$$

thereby establishing one-to-one correspondence between the external potential and the electron density.

Theorem 2: *There exists a universal energy functional $E[n]$ such that, for a given external potential $V_{\text{ext}}(\mathbf{r})$, the ground-state energy is obtained by minimizing this functional. The minimizing density is the exact ground-state density.*

Proof: The total energy can be written as

$$E[n] = F[n] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}), \quad (2.20)$$

where $F[n]$ is a universal functional containing the kinetic ($\hat{T}_e$) and electron–electron ($\hat{V}_{ee}$) interaction energies.

Let $n_0(\mathbf{r})$ denote the true ground-state density associated with $V_{\text{ext}}(\mathbf{r})$, with corresponding wavefunction ψ_0 and energy E_0 . For any trial density $n(\mathbf{r}) \neq n_0(\mathbf{r})$, associated with a trial wavefunction ψ , the variational principle implies

$$E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle < \langle \psi | \hat{H} | \psi \rangle. \quad (2.21)$$

This implies

$$E[n_0] < E[n], \quad (2.22)$$

showing that the functional is minimized by the true ground-state density.

Although these theorems establish a rigorous foundation, they do not provide the explicit form of $F[n]$, which limits their direct applicability. This challenge is overcome by the Kohn–Sham (KS) scheme [86].

2.3.2 Kohn–Sham approach

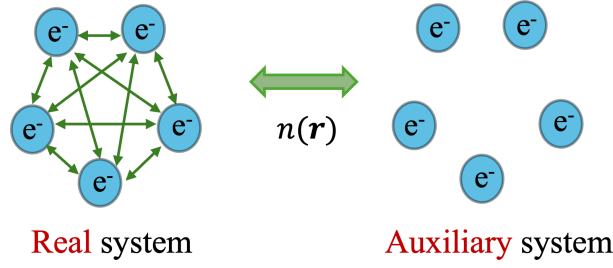


Figure 2.1: Mapping of the real interacting system onto an auxiliary non-interacting system with the same ground-state density.

Kohn and Sham introduced a formulation in which the interacting many-electron system is mapped onto an auxiliary system of non-interacting electrons that reproduces the same ground-state density (Fig. 2.1). Within this framework, the auxiliary system is described by a set of single-particle wavefunctions $\psi_i^\sigma(\mathbf{r})$, known as KS orbitals, which satisfy an effective one-electron Schrödinger-like equation,

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{KS}}^\sigma(\mathbf{r}) \right] \psi_i^\sigma(\mathbf{r}) = \epsilon_i^\sigma \psi_i^\sigma(\mathbf{r}), \quad (2.23)$$

where $V_{\text{KS}}^\sigma(\mathbf{r})$ is the KS effective potential acting on an electron with spin σ at position $\mathbf{r}$. The ground-state electron density is constructed from these orbitals as

$$n(\mathbf{r}) = \sum_{\sigma} \sum_i^{N_{\sigma}} |\psi_i^\sigma(\mathbf{r})|^2. \quad (2.24)$$

The total energy functional within the KS scheme is expressed as

$$E[n] = T_s[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{\text{H}}[n] + E_{\text{xc}}[n], \quad (2.25)$$

where $T_s[n]$ is the kinetic energy of the non-interacting auxiliary system, written in terms of the KS orbitals as (in atomic units)

$$T_s = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int |\nabla \psi_i^\sigma(\mathbf{r})|^2 d\mathbf{r}. \quad (2.26)$$

Here, $V_{\text{ext}}(\mathbf{r})$ represents the external potential due to the nuclei, and $E_{\text{H}}[n]$ is the classical Hartree energy describing the Coulomb interaction between electrons (in atomic units),

$$E_{\text{H}}[n] = \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.27)$$

All many-body effects beyond these contributions are incorporated into the exchange–correlation functional $E_{xc}[n]$, defined as

$$E_{xc}[n] = F[n] - (T_s[n] + E_H[n]), \quad (2.28)$$

which captures the difference between the true interacting system and the non-interacting reference. It can be formally expressed as

$$E_{xc}[n] = \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{ee} \rangle - E_H[n], \quad (2.29)$$

where $\langle \hat{T} \rangle$ and $\langle \hat{V}_{ee} \rangle$ denote the exact kinetic and electron–electron interaction energies of the interacting system, respectively. Thus, $E_{xc}[n]$ plays a central role in determining the electronic structure in atoms, molecules, and solids. The effective KS potential is obtained as the functional derivative of the total energy with respect to the density,

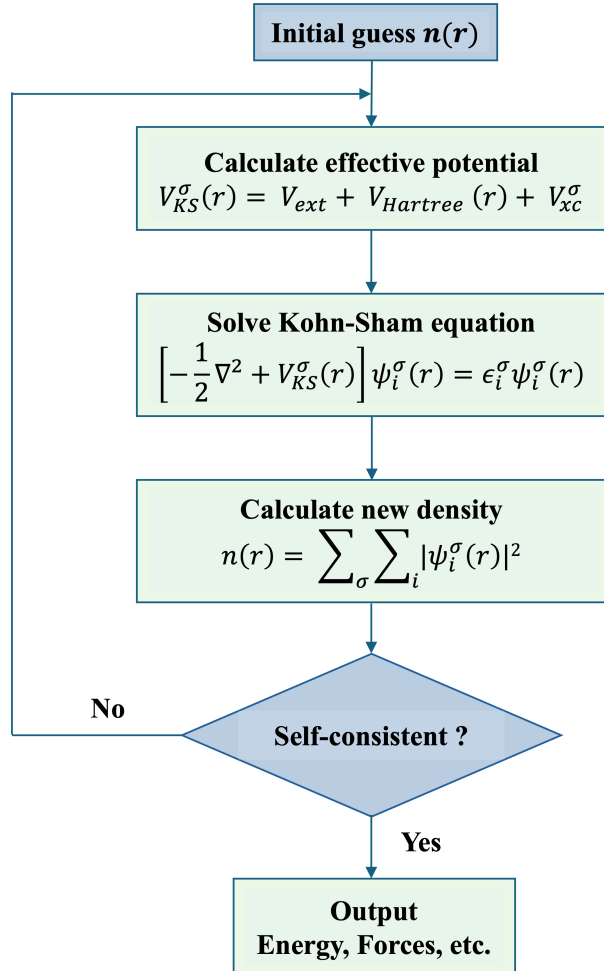


Figure 2.2: Schematic representation of the self-consistent procedure used to solve the Kohn–Sham (KS) equations.

$$V_{KS}^\sigma(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^\sigma(\mathbf{r}), \quad (2.30)$$

where $V_H(\mathbf{r})$ is the Hartree potential and $V_{xc}^\sigma(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r}, \sigma)$ is the exchange–correlation potential.

Since the KS potential depends on the electron density, and the density itself is constructed from the KS orbitals, the equations must be solved self-consistently (as illustrated in Fig. 2.2). Starting from an initial guess for the density, the KS equations are iteratively solved until convergence is achieved, yielding the ground-state density and total energy. The accuracy of this approach ultimately depends on the choice of the exchange–correlation functional, whose exact form remains unknown and must be approximated in practical calculations.

2.3.3 Exchange–correlation functional

Within the KS framework, all many-body effects beyond the classical electrostatic interaction and non-interacting kinetic energy are embedded in $E_{xc}[n]$. The exchange and correlation contributions in $E_{xc}[n]$ originate from distinct physical mechanisms. Exchange arises from the antisymmetry of the many-electron wavefunction, imposed by the Pauli exclusion principle, and leads to an effective interaction between electrons with parallel spins. Correlation, on the other hand, accounts for the correlated motion of electrons arising from their mutual Coulomb repulsion, beyond mean-field descriptions such as HF theory. In this sense, it represents the residual interaction energy not captured within independent-particle approximations.

For practical implementations, the exchange–correlation energy is often expressed in terms of the energy density per particle,

$$E_{xc}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(\mathbf{r}) d\mathbf{r}, \quad (2.31)$$

Since the exact form of $E_{xc}[n]$ is unknown, a hierarchy of approximations has been developed. These are commonly organized in the form of “Jacob’s ladder” (depicted in Fig. 2.3) where each successive rung incorporates additional physical information, thereby improving accuracy at the expense of increased computational cost. Conceptually, this hierarchy progresses from simple local descriptions toward increasingly non-local and physically complete treatments.

2.3.3.1 Local density approximation (LDA)

The first rung of Jacob’s ladder is LDA [86], where the exchange–correlation energy at a given point depends only on the local electron density:

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \varepsilon_{xc}^{unif}(n(\mathbf{r})) d\mathbf{r}. \quad (2.32)$$

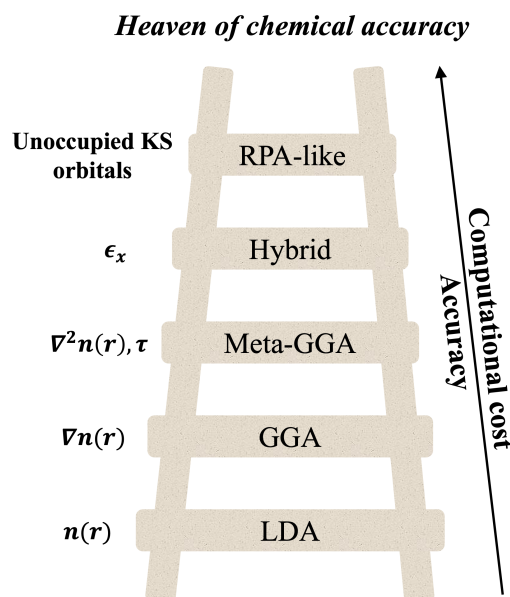


Figure 2.3: Jacob’s ladder of exchange–correlation functionals, depicting the progressive improvement in accuracy and the associated rise in computational cost, approaching the ideal limit of chemical accuracy at the highest rungs [1].

where $\varepsilon^{\text{unif}}_{xc}(n(\mathbf{r}))$ denotes the exchange–correlation energy per electron of a locally homogeneous electron gas with density $n(\mathbf{r})$, for which $\varepsilon_{xc}^{\text{unif}}$ is known with high accuracy. Although the LDA performs well for systems with slowly varying electron densities, its accuracy generally deteriorates in strongly inhomogeneous environments.

2.3.3.2 Generalized gradient approximation (GGA)

The second rung (GGA) [87] improves upon LDA by incorporating information about the spatial variation of the density:

$$E_{xc}^{\text{GGA}}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r}. \quad (2.33)$$

By accounting for density gradients, GGA provides a better description of inhomogeneous systems and significantly improves structural properties such as bond lengths and binding energies. A widely used example is the Perdew–Burke–Ernzerhof (PBE) functional [88]. Nevertheless, GGA remains semi-local and does not fully capture non-local exchange and correlation effects [89].

2.3.3.3 Meta-GGA

The third rung of Jacob’s ladder is formed by meta-GGA functionals [90], which extend the semi-local framework by incorporating additional quantities beyond the electron density and its gradient. In particular, meta-GGA functionals depend on the kinetic energy density,

$$\tau(\mathbf{r}) = \sum_i^{\text{occ}} \frac{1}{2} |\nabla \psi_i(\mathbf{r})|^2, \quad (2.34)$$

and, certain formulations also include the Laplacian of the electron density, $\nabla^2 n(\mathbf{r})$. The exchange–correlation energy is thus expressed as

$$E_{\text{xc}}^{\text{meta-GGA}}[n] = \int n(\mathbf{r}) \varepsilon_{\text{xc}}(n, |\nabla n|, \tau) d\mathbf{r}. \quad (2.35)$$

The inclusion of $\tau(\mathbf{r})$ provides access to information about the local electronic environment, such as orbital character and inhomogeneity, enabling meta-GGA functionals to satisfy additional exact constraints that are inaccessible at the GGA level. As a result, they generally offer improved accuracy for diverse systems, including molecules and solids. Despite these advances, meta-GGA functionals also remain semi-local in nature and therefore inherit some of the intrinsic limitations of lower-rung approximations. In particular, the self-interaction error is only partially corrected, and non-local exchange–correlation effects are not fully captured. This often leads to systematic underestimation of band gaps and inaccuracies in systems where electron localization is important, such as defects, surfaces, and strongly correlated materials.

2.3.3.4 Hybrid functionals

The fourth rung of Jacob’s ladder introduces hybrid functionals, originally proposed by Becke in 1993 [79], which incorporate a fraction of exact exchange from HF theory into the density functional framework. The exchange–correlation energy is expressed as

$$E_{\text{xc}}^{\text{hyb}} = \alpha E_x^{\text{HF}} + (1 - \alpha) E_x^{\text{DFT}} + E_c^{\text{DFT}}, \quad (2.36)$$

where α is the mixing parameter controlling the contribution of non-local HF exchange. This approach partially corrects the self-interaction error present in semi-local functionals and improves the overall description of electronic structure. As a consequence, hybrid functionals provide a more reliable prediction of quantities such as band gaps, ionization potentials, and reaction barriers. However, the explicit evaluation of the non-local exchange term is computationally demanding, particularly for periodic and large-scale systems.

To alleviate this limitation, screened hybrid functionals were developed by Heyd, Scuseria, and Ernzerhof (HSE) [91, 92]. In this approach, the Coulomb interaction is partitioned into short-range (SR) and long-range (LR) components using a screening parameter ω . The computationally expensive HF exchange is retained only in the short-range part, while the long-range exchange and correlation are treated using a semi-local functional, typically PBE. The exchange–correlation energy of the HSE functional is given by

$$E_{xc}^{\text{HSE}} = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}, \quad (2.37)$$

where the standard choice $\alpha = 0.25$ and $\omega = 0.11 \text{ bohr}^{-1}$ defines the widely used HSE06 functional, providing a balanced compromise between accuracy and computational efficiency. Hybrid functionals thus represent a significant improvement over semi-local approximations, particularly for systems where an accurate description of electronic structure is essential. Nevertheless, their computational cost and the presence of empirical parameters motivate the development of more rigorous many-body approaches.

In this thesis, structural and ground-state properties are primarily obtained using GGA, mainly in the PBE form, while hybrid functionals, specifically HSE06, are employed to achieve an improved description of electronic properties. All calculations are performed using state-of-the-art electronic structure packages, including Vienna *Ab initio* Simulation Package (VASP) [93, 94], Quantum ESPRESSO (QE) suite [95], and the `exciting` code [96].

2.3.4 Basis set

The KS equations derived earlier in the chapter recast the many-body problem of interacting electrons into an effective single-particle framework. Solving these equations numerically requires an appropriate representation of the KS orbitals $\psi_i(\mathbf{r})$. This is achieved through a basis-set expansion, which expresses each orbital as a linear combination of known functions:

$$\psi_i(\mathbf{r}) = \sum_{\alpha} c_{i\alpha} \phi_{\alpha}(\mathbf{r}), \quad (2.38)$$

where $\phi_{\alpha}(\mathbf{r})$ denotes the basis functions and $c_{i\alpha}$ are variational coefficients determined by minimizing the total energy. Substituting this expansion into the KS eigenvalue equation leads to a generalized matrix eigenvalue problem:

$$(\mathbf{H} - \varepsilon_i \mathbf{S}) \mathbf{c}_i = 0, \quad (2.39)$$

where $\mathbf{H}$ contains the Hamiltonian matrix elements and $\mathbf{S}$ is the overlap matrix, which becomes the identity for orthonormal basis sets. The choice of basis set plays a crucial role in balancing computational efficiency and accuracy.

Basis sets in DFT can broadly be categorized into three classes: (i) plane-wave and real-space grid approaches (typically used with pseudopotentials or projector-augmented-wave methods), (ii) localized atomic-like orbitals, and (iii) atomic-sphere-based methods. Plane waves are particularly advantageous for periodic systems because they are orthonormal, energy-independent, and free of Pulay forces, which enables direct application of the Hellmann–Feynman theorem. Localized basis sets, such as linear combinations of atomic orbitals (LCAO) or numeric atom-centered orbitals (NAOs), are more efficient for finite or for achieving linear scaling in very large systems due to matrix sparsity. Atomic-sphere methods, such as the linearized augmented plane-wave (LAPW) approach, provide an accurate all-electron description by partitioning space into atomic spheres and an interstitial region. For a more detailed discussion of these methods and the general strategies for solving the KS equations, the reader is referred to Refs.[97, 98, 99, 100].

In this thesis, multiple first-principles frameworks are employed depending on the problem under investigation. These include the projector-augmented-wave (PAW) method implemented in VASP, norm-conserving pseudopotentials within QE interfaced with YAMBO [101, 102] and PYXAID (PYthon eXtension for Ab Initio Dynamics) [52, 53], and the full-potential LAPW method as implemented in the `exciting` code. The following sections describe the underlying basis-set formalism used in these approaches.

2.3.4.1 Plane-wave basis and Bloch’s theorem

For periodic systems satisfying $V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r})$, where $\mathbf{T}$ is a Bravais lattice vector, Bloch’s theorem states that the single-particle eigenfunctions can be written as [103]:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad (2.40)$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is lattice-periodic, i.e., $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{n\mathbf{k}}(\mathbf{r})$, and $\mathbf{k}$ is the wave vector that lies within the first Brillouin zone (BZ). For each $\mathbf{k}$, multiple eigenstates exist, distinguished by the band index n .

The KS equation takes the form:

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_{j\mathbf{k}}(\mathbf{r}) = \varepsilon_{j\mathbf{k}} \psi_{j\mathbf{k}}(\mathbf{r}), \quad (2.41)$$

where

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n] + V_{\text{xc}}[n]. \quad (2.42)$$

The ground-state electron density is constructed from the occupied KS states as:

$$n(\mathbf{r}) = 2 \frac{\Omega_c}{(2\pi)^3} \sum_j \int_{\text{BZ}} |\psi_{j\mathbf{k}}(\mathbf{r})|^2 \Theta(E_F - \varepsilon_{j\mathbf{k}}) d\mathbf{k}, \quad (2.43)$$

where Ω_c is the unit-cell volume, the factor of 2 accounts for spin degeneracy, Θ is the step function, and E_F denotes the Fermi energy.

Brillouin-zone sampling

The evaluation of physical quantities therefore involves integration over the Brillouin zone. In practice, this integral is replaced by a discrete sum over a finite set of k -points:

$$\frac{\Omega_c}{(2\pi)^3} \int_{\text{BZ}} \dots \Theta(E_F - \varepsilon_{j\mathbf{k}}) d\mathbf{k} \approx \frac{1}{N_{kpt}} \sum_{\mathbf{k}} f_{j\mathbf{k}} \dots, \quad (2.44)$$

where N_{kpt} is the number of sampling points, and $f_{j\mathbf{k}}$ are occupation factors. Because the lattice-periodic part $u_{n\mathbf{k}}(\mathbf{r})$ varies smoothly with $\mathbf{k}$, accurate results can be obtained using a finite k -point mesh [104, 105, 106, 107]. Increasing the density of the mesh systematically improves convergence. Larger supercells require fewer k -points due to the reduced Brillouin zone size, while metallic systems necessitate denser sampling to properly resolve the Fermi surface.

Plane-wave expansion and Fourier representation

The Bloch form naturally enables a plane-wave expansion:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (2.45)$$

where $\mathbf{G}$ are reciprocal lattice vectors. Substituting this into the KS equation yields a matrix eigenvalue problem [70]:

$$\sum_{\mathbf{G}} \left[\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}',\mathbf{G}} + V_{\text{eff}}(\mathbf{G}' - \mathbf{G}) \right] c_{j\mathbf{k}}(\mathbf{G}) = \varepsilon_{j\mathbf{k}} c_{j\mathbf{k}}(\mathbf{G}'). \quad (2.46)$$

In practice, the expansion is truncated using a kinetic-energy cutoff:

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}, \quad (2.47)$$

and convergence is achieved by increasing E_{cut} .

The electron density in reciprocal space is then given by:

$$n(\mathbf{G}) = \frac{2}{N_{kpt}} \sum_{j\mathbf{k}} f_{j\mathbf{k}} \sum_{\mathbf{G}'} c_{j\mathbf{k}}^*(\mathbf{G}' - \mathbf{G}) c_{j\mathbf{k}}(\mathbf{G}'). \quad (2.48)$$

Since $n(\mathbf{r}) \propto |\psi|^2$, the Fourier components of the electron density extend up to twice the plane-wave cutoff of the wavefunctions. A direct evaluation of the density in reciprocal space involves a double summation over reciprocal lattice vectors and therefore scales as N_G^2 , where N_G denotes the number of plane waves (or reciprocal lattice vectors) included in the basis set. For large systems, this procedure becomes computationally demanding. In practice, the density is evaluated efficiently by transforming between reciprocal and real space using fast Fourier transforms (FFT), which reduce the computational scaling to approximately $N \ln N$, where N represents the number of grid points used to represent the wavefunctions and electron density [70]. This computational efficiency constitutes one of the major advantages of plane-wave-based methods.

2.3.4.2 Pseudopotential approximation

Solving the KS equations for a system containing N electrons is computationally demanding, particularly within a plane-wave basis. This is primarily due to the need for a large number of plane waves to represent both the tightly bound core states and the rapidly oscillating valence wavefunctions in the vicinity of the nuclei [108]. Consequently, all-electron (AE) calculations become prohibitively expensive.

The pseudopotential approximation offers an efficient alternative by exploiting the fact that most material properties are predominantly governed by valence electrons. Within this framework, illustrated in Fig. 2.4, the strong ionic potential together with the chemically inert core electrons is replaced by a smoother, effective potential acting on pseudo(PS) wavefunctions. As a result, the PS wavefunctions are significantly less oscillatory than their AE counterparts, enabling an accurate representation using a substantially reduced plane-wave basis.

In an AE framework, the Pauli exclusion principle enforces orthogonality between core and valence states. As a consequence, valence wavefunctions develop pronounced oscillations in the vicinity of the nuclei, where the strong ionic potential and core states dominate. These oscillations ensure orthogonality but significantly increase the complexity of their representation in a plane-wave basis. In the pseudopotential approach, this rapidly varying behavior is removed by constructing PS wavefunctions that are smooth and nodeless within a chosen cutoff radius

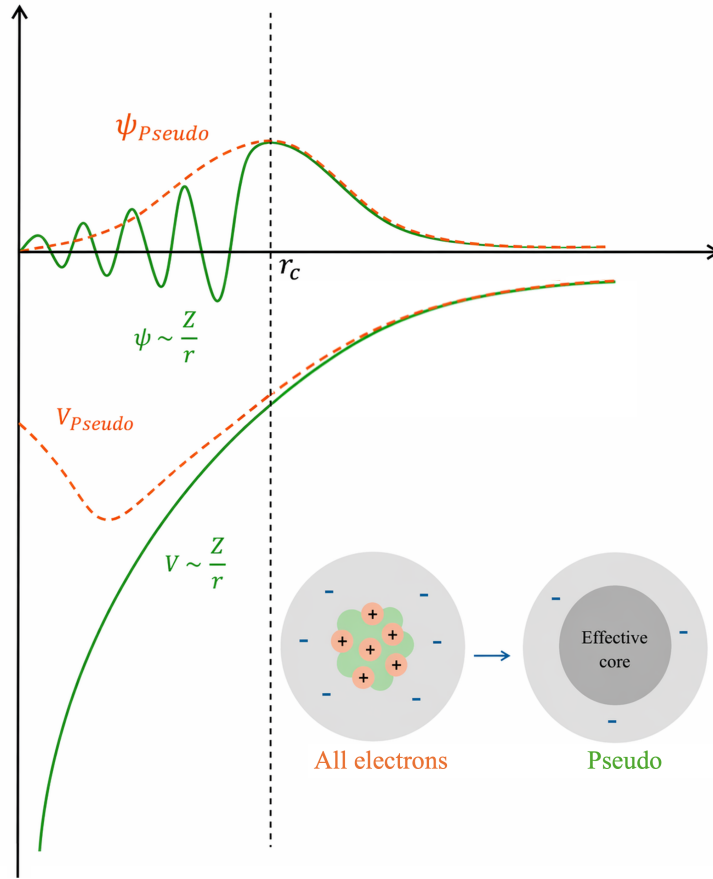


Figure 2.4: Schematic depiction of the external Coulomb potential alongside the all-electron and pseudo wavefunctions, and the corresponding pseudopotential.

r_c , while reproducing the AE wavefunctions outside this region:

$$\psi_{nl}^{AE}(r) = \psi_{nl}^{PS}(r), \quad \text{for } r \geq r_c. \quad (2.49)$$

The cutoff radius r_c plays a central role in determining the characteristics of the pseudopotential. A larger r_c yields a softer pseudopotential, allowing convergence with fewer plane waves, but may reduce its transferability, i.e., its ability to accurately reproduce valence properties in different chemical environments. Conversely, a smaller r_c leads to harder but more transferable pseudopotentials. An additional advantage of this framework is that relativistic effects can be incorporated efficiently while retaining a computationally tractable description of valence electrons.

2.3.4.2.1 Norm-conserving pseudopotentials

Norm-conserving pseudopotentials, introduced by Hamann, Schlüter, and Chiang, are constructed to preserve essential physical properties of the all-electron system [109]. These pseudopotentials are energy-independent and satisfy the following conditions:

1. *Eigenvalue matching*: The pseudo and all-electron valence eigenvalues are identical for a given atomic configuration:

$$\epsilon_{nl}^{\text{AE}} = \epsilon_{nl}^{\text{PS}}. \quad (2.50)$$

where n is the principal quantum number and l is the angular momentum quantum number.

2. *Wavefunction matching beyond the core*: The pseudo- and all-electron wavefunctions coincide outside the core region:

$$\psi_{nl}^{\text{AE}}(r) = \psi_{nl}^{\text{PS}}(r), \quad \text{for } r \geq r_c. \quad (2.51)$$

3. *Norm conservation*: The integrated charge density within the core region is preserved:

$$\int_0^{r_c} |\phi_{nl}^{\text{AE}}(r)|^2 r^2 dr = \int_0^{r_c} |\phi_{nl}^{\text{PS}}(r)|^2 r^2 dr. \quad (2.52)$$

4. *Matching of logarithmic derivatives*: The energy derivatives of the logarithmic derivatives of the wavefunctions match at r_c :

$$\left[(r\phi_{nl}^{\text{AE}}(r))^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \phi_{nl}^{\text{AE}}(r) \right]_{r_c} = \left[(r\phi_{nl}^{\text{PS}}(r))^2 \frac{d}{d\epsilon} \frac{d}{dr} \ln \phi_{nl}^{\text{PS}}(r) \right]_{r_c} \quad (2.53)$$

These constraints ensure that both the scattering properties and the electrostatics of the atomic core are faithfully reproduced, thereby enhancing the transferability of the pseudopotential across diverse chemical environments. In practice, norm-conserving pseudopotentials are constructed from atomic all-electron calculations by partitioning the electronic states into core and valence manifolds, and further subtracting the Hartree and exchange-correlation contributions of the valence electrons from the all-electron potential. The resulting pseudopotential typically comprises both local and non-local components. There exists an inherent degree of freedom in the pseudization process, necessitating a balance between numerical precision and computational efficiency. Specifically, the choice of the cutoff radius (r_c) dictates the hardness of the potential: smaller radii yield harder potentials with superior transferability at the cost of a higher plane-wave kinetic energy cutoff, whereas larger radii produce softer potentials that accelerate convergence but may limit accuracy in high-pressure or varying coordination environments.

2.3.4.2.2 Ultrasoft pseudopotentials

Norm-conserving pseudopotentials can become inefficient for systems with localized valence orbitals (e.g., $2p$, $3d$ states), where a large plane-wave cutoff is required. Ultrasoft pseudopotentials overcome this limitation by relaxing the norm-conservation constraint, allowing for smoother pseudo-wavefunctions and significantly reducing the basis set size.

In this approach, the pseudo-wavefunction is decomposed into two contributions [110]:

1. A smooth ultrasoft valence wavefunction that does not satisfy norm conservation.
2. An augmentation charge that compensates for the missing charge within the core region.

The inclusion of augmentation charges introduces additional terms into the KS formalism, increasing the computational complexity per iteration. However, the reduction in plane-wave cutoff typically leads to an overall gain in efficiency. Ultrasoft pseudopotentials are non-local within the core region and become effectively local outside it, with their transferability enhanced through self-consistent dependence on the charge density.

2.3.4.2.3 Projector augmented-wave method

The PAW method, introduced by Blöchl [111], provides a unified framework that bridges pseudopotential approaches and all-electron methods such as the LAPW formalism [97, 112, 113]. The essential idea is to establish a transformation that connects the true all-electron KS wavefunction $|\phi_s\rangle$ with a corresponding smooth pseudo-wavefunction $|\tilde{\phi}_s\rangle$, while systematically restoring the correct nodal behavior in the core region.

This mapping is defined through a linear transformation operator $\hat{T}$:

$$|\phi_s\rangle = \hat{T}|\tilde{\phi}_s\rangle. \quad (2.54)$$

In analogy with LAPW-based schemes, space is divided into atom-centered augmentation regions Ω_a (surrounding each atom a) and an interstitial region. Each augmentation region is defined by a cutoff radius r_c^a , chosen such that the spheres do not overlap. Outside Ω_a , the pseudo and all-electron wavefunctions coincide, and therefore the transformation operator modifies the wavefunction only within the augmentation regions. It can thus be expressed as a sum of atomic contributions:

$$\hat{T} = 1 + \sum_a \hat{T}^a, \quad (2.55)$$

where $\hat{T}^a$ acts locally within Ω_a .

To construct $\hat{T}$, one introduces atom-centered all-electron partial waves $|\phi_j^a\rangle$, corresponding pseudo partial waves $|\tilde{\phi}_j^a\rangle$, and a set of localized projector functions $|\tilde{p}_j^a\rangle$. These projector functions are confined within Ω_a and are orthonormal to the pseudo partial waves. The transformation operator then takes the form:

$$\hat{T} = 1 + \sum_{a,j} \left(|\phi_j^a\rangle - |\tilde{\phi}_j^a\rangle \right) \langle \tilde{p}_j^a|. \quad (2.56)$$

Applying this operator yields the explicit relation between the all-electron and pseudo wavefunctions:

$$|\phi_s\rangle = |\tilde{\phi}_s\rangle + \sum_{a,j} \left(|\phi_j^a\rangle - |\tilde{\phi}_j^a\rangle \right) \langle \tilde{p}_j^a | \tilde{\phi}_s \rangle. \quad (2.57)$$

The construction ensures that the following conditions are satisfied:

- Inside the augmentation region ($\mathbf{r} \in \Omega_a$):

$$\phi_s(\mathbf{r}) = \phi_s^a(\mathbf{r}), \quad \tilde{\phi}_s(\mathbf{r}) = \tilde{\phi}_s^a(\mathbf{r}). \quad (2.58)$$

- Outside the augmentation region:

$$\phi_s(\mathbf{r}) = \tilde{\phi}_s(\mathbf{r}), \quad \phi_s^a(\mathbf{r}) = \tilde{\phi}_s^a(\mathbf{r}). \quad (2.59)$$

Within each augmentation sphere, the wavefunctions are expanded in terms of partial waves as:

$$\phi_s^a(\mathbf{r}) = \sum_j \phi_j^a(\mathbf{r}) \langle \tilde{p}_j^a | \tilde{\phi}_s \rangle, \quad \tilde{\phi}_s^a(\mathbf{r}) = \sum_j \tilde{\phi}_j^a(\mathbf{r}) \langle \tilde{p}_j^a | \tilde{\phi}_s \rangle. \quad (2.60)$$

The smooth pseudo-wavefunctions $|\tilde{\phi}_s\rangle$ serve as the variational degrees of freedom and can be efficiently expanded in a plane-wave basis with a relatively low kinetic-energy cutoff, owing to their smoothness. The partial waves and projector functions are constructed from radial functions combined with spherical harmonics, allowing for an accurate reconstruction of the all-electron wavefunction in the core region. The PAW method achieves near all-electron accuracy while retaining the computational efficiency characteristic of plane-wave approaches.

2.3.4.3 Linearized augmented plane-wave method

The LAPW method provides an accurate all-electron description of the KS problem by exploiting the distinct spatial character of the electronic wavefunctions. The unit cell is partitioned into two regions: non-overlapping muffin-tin (MT) spheres centered at atomic sites and the interstitial region (IR) between them, as depicted in Fig. 2.5 [112].

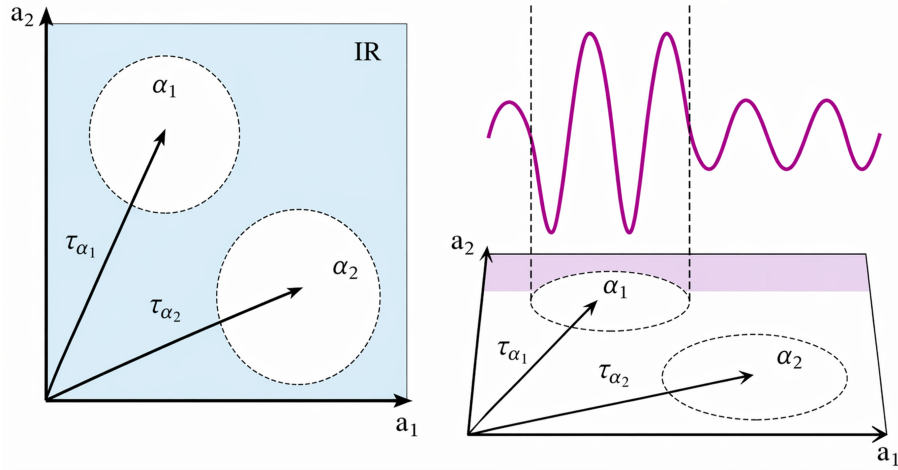


Figure 2.5: Schematic illustration of a unit cell within the (L)APW framework.

The basis functions are defined differently in these two regions. In the interstitial region, where the potential varies smoothly, plane waves form a natural basis:

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}, \quad \mathbf{r} \in \text{IR}, \quad (2.61)$$

where Ω is the unit-cell volume.

Inside a muffin-tin sphere of atom α , located at $\mathbf{R}_\alpha$, the basis functions are expanded in terms of atomic-like functions:

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \sum_{l,m} [A_{lm}^\alpha(\mathbf{k} + \mathbf{G}) u_l^\alpha(r_\alpha, \epsilon_l^\alpha) + B_{lm}^\alpha(\mathbf{k} + \mathbf{G}) \dot{u}_l^\alpha(r_\alpha, \epsilon_l^\alpha)] Y_{lm}(\hat{r}_\alpha), \quad (2.62)$$

for $r_\alpha \leq R_{\text{MT}}^\alpha$, where $r_\alpha = |\mathbf{r} - \mathbf{R}_\alpha|$. Here, the functions $Y_{lm}(\hat{r}_\alpha)$ represent spherical harmonics associated with the angular momentum quantum numbers l and m , describing the angular dependence of the basis functions inside the muffin-tin spheres, $u_l^\alpha(r_\alpha, \epsilon_l^\alpha)$ are radial solutions of the scalar-relativistic Schrödinger equation evaluated at fixed linearization energies ϵ_l^α , while $\dot{u}_l^\alpha$ denotes their energy derivatives:

$$\dot{u}_l^\alpha(r_\alpha, \epsilon_l^\alpha) = \left. \frac{\partial u_l^\alpha(r_\alpha, E)}{\partial E} \right|_{E=\epsilon_l^\alpha}. \quad (2.63)$$

The coefficients A_{lm}^α and B_{lm}^α are determined by enforcing continuity of both the basis functions and their first radial derivatives at the MT sphere boundary. This construction ensures a smooth matching between the plane-wave description in the IR region and the atomic-like representation inside the spheres.

The inclusion of energy derivatives of the radial functions is the key feature that distinguishes LAPW from the original augmented plane-wave (APW) method [97]. In APW, the radial functions depend explicitly on the eigenvalues, leading to a nonlinear eigenvalue problem. In contrast, the LAPW approach introduces fixed energy parameters ϵ_l^α and expands the basis linearly

around them, thereby transforming the problem into a standard linear eigenvalue problem with controllable errors [114].

To further improve the flexibility of the basis, particularly for semicore and localized states, additional local orbitals (lo) are introduced [115]. These are confined within individual MT spheres and vanish in the interstitial region:

$$\phi_\mu(\mathbf{r}) = [a_\mu u_l^\alpha(r_\alpha, \epsilon_l^\alpha) + b_\mu \dot{u}_l^\alpha(r_\alpha, \epsilon_l^\alpha)] Y_{lm}(\hat{r}_\alpha) \delta_{\alpha\alpha_\mu} \delta_{ll_\mu} \delta_{mm_\mu}, \quad (2.64)$$

for $\mathbf{r}$ inside a specific MT sphere, and zero elsewhere. The coefficients a_μ and b_μ are chosen such that the local orbitals are normalized and smoothly matched at the sphere boundary. In practice, the LAPW basis size is controlled by the plane-wave cutoff in the interstitial region, typically expressed through the dimensionless parameter $R_{\text{MT}}G_{\text{max}}$, where R_{MT} is the smallest muffin-tin radius. Convergence is achieved by systematically increasing this parameter and by including an appropriate number of local orbitals.

Overall, the LAPW+lo method provides a full-potential, all-electron description without relying on pseudopotentials. By combining plane waves in the interstitial region with atom-centered basis functions inside muffin-tin spheres, it achieves high accuracy and serves as a reliable reference for validating pseudopotential-based approaches. In a specific investigation within this thesis, the LAPW formalism implemented in the `exciting` code was employed to compute band gaps, serving as an independent validation of results obtained using the PAW method in VASP.

2.4 Many-body perturbation theory

Although DFT offers a computationally efficient and remarkably accurate framework for ground-state properties, its extension to excited-state phenomena is fundamentally limited. In particular, KS eigenvalues do not, in general, correspond to physical excitation energies, as the KS orbitals are auxiliary constructs designed solely to reproduce the exact ground-state density. A notable exception is the highest occupied KS eigenvalue, which is equal to the negative of the ionization potential. While DFT often yields qualitatively reasonable band structures, it systematically underestimates fundamental band gaps. This shortcoming originates from the incomplete treatment of electron correlation within approximate exchange–correlation functionals, as well as the absence of the derivative discontinuity [116, 117], which plays a crucial role in determining the true QP gap.

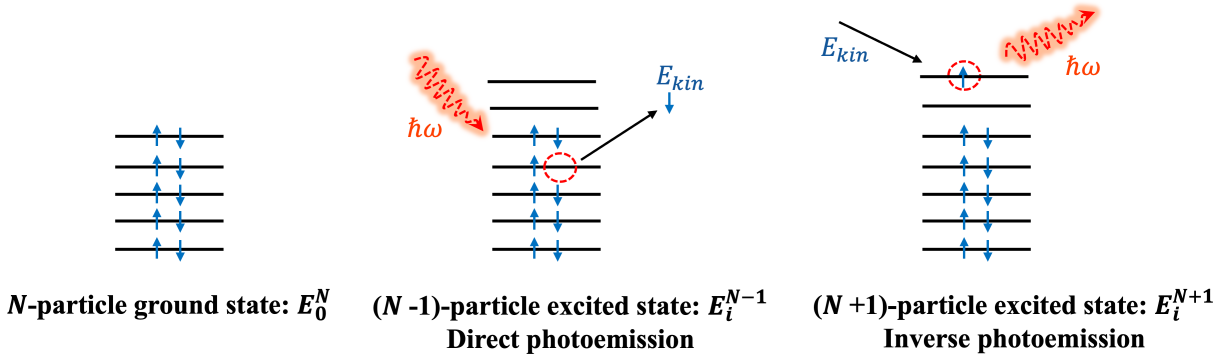


Figure 2.6: Schematic illustration of direct and inverse photoemission spectroscopy. In both processes, the particle number changes due to electron removal or addition. The corresponding energy differences are given by $\varepsilon_i = E_0^N - E_i^{N-1}$ (direct photoemission) and $\varepsilon_i = E_i^{N+1} - E_0^N$ (inverse photoemission).

To overcome these limitations, it is instructive to examine how excitation energies are accessed experimentally. The fundamental band gap is measured by direct and inverse photoemission spectroscopy (DPES and IPES), whose processes are illustrated schematically in Fig. 2.6. In DPES, an incident photon ejects an electron from the N -electron ground state, leaving the system in an $(N - 1)$ -electron state. The measured kinetic energy of the emitted electron yields the ionization potential (IP), which within a many-body framework is the total-energy difference

$$\epsilon_i = E_0^N - E_i^{N-1}, \quad \epsilon_i < E_F \quad (2.65)$$

where E_0^N is the ground-state energy of the neutral system and E_i^{N-1} is the energy of the i -th state of the $(N - 1)$ -electron system. Conversely, IPES injects an electron into the system, producing an $(N + 1)$ -electron state. The emitted photon energy gives the electron affinity (EA):

$$\epsilon_i = E_i^{N+1} - E_0^N, \quad \epsilon_i \geq E_F \quad (2.66)$$

The difference $\text{IP} - \text{EA}$ is the fundamental *quasiparticle* (QP) band gap. Both spectroscopies involve changes in the particle number from N to $N \pm 1$, and therefore probe charged excitations. The standard KS framework of DFT is not designed to describe such charged excitations within a rigorous theoretical framework. More generally, it also fails to capture neutral excitations involving correlated electron–hole (e – h) pairs. These limitations necessitate theoretical approaches that explicitly incorporate many-body effects [118, 73].

Many-body perturbation theory provides the required framework by establishing a direct link between the electronic structure and experimentally measurable excitation spectra. Its central quantity is the time-ordered Green’s function, which describes the propagation of an added or

removed particle in an interacting system and thereby, connects the N -electron ground state to the $(N \pm 1)$ -electron excited states.

Within MBPT, two complementary Green's-function-based approaches are widely employed to describe different classes of excitations:

- (i) The **one-particle Green's function** formalism, within the GW approximation, is used to describe charged (QP) excitations. The poles of the Green's function correspond to the energies required to add or remove an electron, making this approach directly comparable to PES and IPES experiments.
- (ii) The **two-particle Green's function** formalism leads to the Bethe–Salpeter equation (BSE) [119, 120], which describes neutral excitations, such as those observed in optical absorption spectroscopy. In this case, an electron is promoted from the valence band to the conduction band, leaving behind a hole. The resulting e – h pair interacts via the Coulomb interaction and may form a bound state known as an exciton, requiring an explicit treatment of e – h correlations.

2.4.1 The one-particle Green's function

The time-ordered single-particle Green's function is defined as

$$G(\mathbf{r}, \sigma, t, \mathbf{r}', \sigma', t') = -i \langle N | \hat{T} [\hat{\psi}(\mathbf{r}, \sigma, t) \hat{\psi}^\dagger(\mathbf{r}', \sigma', t')] | N \rangle, \quad (2.67)$$

where $|N\rangle$ is the ground-state wavefunction of the N -electron system, $\hat{T}$ is the time-ordering operator, σ denotes the spin, and $\hat{\psi}^\dagger$ and $\hat{\psi}$ are fermionic creation and annihilation field operators. The physical content of G follows immediately from the two possible time orderings:

- For $t > t'$ the Green's function describes the propagation of an extra electron with spin σ' injected at $(\mathbf{r}', t')$ and removed at $(\mathbf{r}, t)$. This process corresponds to inverse photoemission (electron addition).
- For $t < t'$ it describes the propagation of a hole created by electron removal at $(\mathbf{r}, t)$ and filled at $(\mathbf{r}', t')$, corresponding to direct photoemission.

Thus, G acts as a propagator that naturally maps the N -electron ground state onto the charged excited states probed by PES and IPES.

For stationary systems, it is convenient to Fourier transform the Green's function with respect to the time difference $t - t'$. The resulting frequency-domain Green's function reads (Lehmann spectral representation)

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \times \left[\frac{\Theta(\epsilon_i - E_F)}{\omega - (\epsilon_i - i\eta)} + \frac{\Theta(E_F - \epsilon_i)}{\omega - (\epsilon_i + i\eta)} \right] \quad (2.68)$$

where Θ is the Heaviside step function, $\psi_i(\mathbf{r})$ are the transition amplitudes between the N - and $(N \pm 1)$ -electron states, and two terms in the brackets correspond to two time orderings in G . The poles of this function correspond to the exact many-body excitation energies.

$$\varepsilon_i = \begin{cases} E_i^{N+1} - E_0^N & \text{(electron addition),} \\ E_0^N - E_i^{N-1} & \text{(electron removal).} \end{cases} \quad (2.69)$$

Experimentally, the quantity measured in photoemission is the photocurrent, which—to an excellent approximation—is proportional to the spectral function of the system. The spectral function is obtained from the imaginary part of the Green's function:

$$A(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{1}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}', \omega) \text{sgn}(E_F - \omega) \quad (2.70)$$

$$= \sum_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \delta(\omega - \varepsilon_i) \quad (2.71)$$

Eq. (2.71) shows that $A(\omega)$ consists of a series of δ -function peaks located at the many-body excitation energies. In the non-interacting limit these peaks remain infinitely sharp; each corresponds to an independent-particle excitation with infinite lifetime. In a real interacting solid, the addition or removal of an electron is accompanied by a dynamical rearrangement of the surrounding charge density. The injected electron repels its neighbors, creating a region of depleted electron density known as the *Coulomb hole* (or screening cloud). Conversely, electron removal eliminates the associated Coulomb hole and allows the remaining electrons to relax. A schematic illustration of this process in the context of photoemission is given in Fig. 2.7. The propagating object is therefore never a bare electron or hole; it is a QP—a composite excitation consisting of the bare particle dressed by its induced polarization cloud. The interaction of this QP with the medium is encoded in the self-energy operator Σ , which incorporates all exchange and correlation effects beyond the mean-field (Hartree) level. Because of screening, the effective interaction between QPs is the screened Coulomb interaction W , which is substantially weaker than the bare Coulomb interaction. Consequently, QPs often behave as weakly interacting entities.

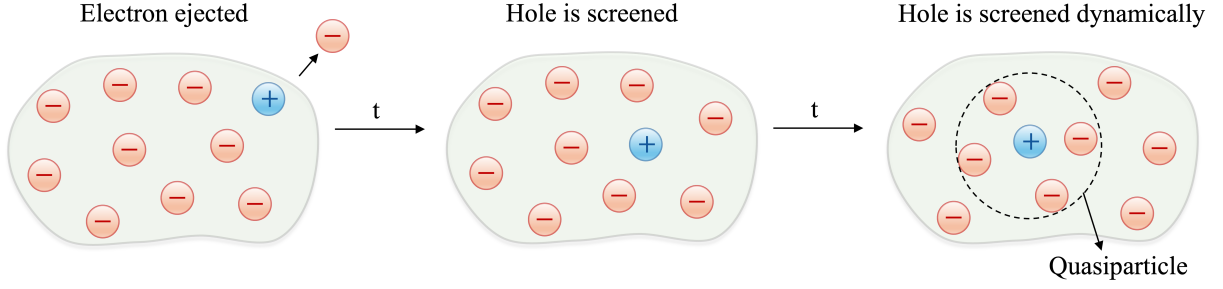


Figure 2.7: Illustration of *quasiparticle* (QP) formation in photoemission spectroscopy. An electron is removed from the system, leaving behind a hole. The surrounding electrons rearrange to screen the missing charge, forming a polarization cloud that travels with the hole. The resulting composite object—the QP—has renormalized energy and finite lifetime.

Electron–electron interactions redistribute the spectral weight. The sharp δ -peaks of the non-interacting spectral function broaden and may acquire satellite structures, as illustrated in Fig. 2.8. When a dominant peak survives the redistribution, it is identified as the QP excitation. Its position defines the QP energy ϵ_i^{QP} , its width Γ_i is inversely proportional to the QP lifetime ($\tau_i \sim 1/\Gamma_i$), and the integrated weight under the peak is the renormalization factor Z_i ($0 < Z_i \leq 1$). The factor Z_i quantifies the overlap between the bare-particle state and the dressed QP state; $1 - Z_i$ is the incoherent weight transferred to satellites (e.g., plasmons).

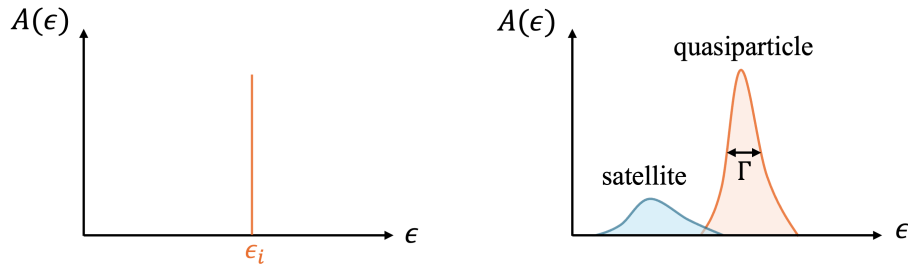


Figure 2.8: Spectral function in the non-interacting (left) and interacting (right) limits. In the non-interacting case, each state appears as a δ -function peak. Interactions broaden the peaks, shift their positions, and generate satellite features. The dominant peaks correspond to QP excitations.

For an isolated, well-defined QP, the spectral function near the peak acquires an approximate Lorentzian lineshape:

$$A(\omega) \approx \left| \frac{1}{\pi} \frac{Z_i}{[\omega - (\epsilon_i + i\Gamma)]} \right| \quad (2.72)$$

The transition from infinitely sharp δ -peaks (non-interacting limit) to finite-width Lorentzians (interacting case) is the spectroscopic signature of many-body interactions and constitutes the foundation of the QP picture that underpins the *GW* approximation.

The one-particle Green's function therefore provides a rigorous, experimentally accessible de-

scription of charged excitations. Its poles and residues directly map onto the energies and amplitudes measured by PES and IPES. The subsequent sections of this chapter will show how the GW approximation systematically constructs an accurate self-energy that yields these QP energies and spectral functions. Neutral excitations, however, require the two-particle Green's function and those extensions are discussed later when optical properties are addressed.

2.4.2 Dyson equation

The time-ordered Green's function G of an interacting many-body system is formally related to a non-interacting reference Green's function G_0 through the Dyson equation:

$$G(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}, \mathbf{r}'; \omega) + \int \int G_0(\mathbf{r}, \mathbf{r}''; \omega) \Sigma(\mathbf{r}'', \mathbf{r}'''; \omega) G(\mathbf{r}''', \mathbf{r}'; \omega) d^3\mathbf{r}'' d^3\mathbf{r}''' \quad (2.73)$$

where Σ is the nonlocal, energy-dependent, and generally non-Hermitian self-energy operator. Σ incorporates all many-body exchange and correlation effects beyond the mean-field approximation: its real part leads to a renormalization of QP energies, while its imaginary part determines QP lifetimes.

The reference Green's function $G_0(\mathbf{r}, \mathbf{r}'; \omega)$ is constructed from the eigenstates of an effective single-particle Hamiltonian $\hat{h}_0$, defined as

$$\hat{h}_0 \phi_i^0(\mathbf{r}) = \epsilon_i^0 \phi_i^0(\mathbf{r}), \quad (2.74)$$

where the Hamiltonian is given by

$$\hat{h}_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}). \quad (2.75)$$

Substituting the Lehmann representation of G into the Dyson equation leads to the QP equation:

$$\hat{h}_0(\mathbf{r})\psi_i(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_i) \psi_i(\mathbf{r}') d^3\mathbf{r}' = \epsilon_i \psi_i(\mathbf{r}), \quad (2.76)$$

which is nonlinear in the eigenvalue ϵ_i . As a consequence, the QP wavefunctions $\psi_i(\mathbf{r})$ are, in general, not orthonormal, in contrast to the eigenstates of a single-particle Hamiltonian. Moreover, this equation must be solved self-consistently, since the self-energy itself depends on the QP energies.

Iterating Eq. (2.73) yields the formal series expansion

$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 \Sigma G_0 + \cdots, \quad (2.77)$$

which can be interpreted as a geometric series. Each term represents successive scattering processes (single, double, triple, and higher order), with Σ acting as an effective scattering potential.

2.4.3 *GW* approximation: Hedin's equations

Having established the Green's function formalism and the QP picture, we now introduce a practical framework for computing the self-energy [121]. An exact description of interacting many-body systems can be formulated in terms of a closed set of coupled equations derived by Hedin in 1965. These equations provide a formally exact, self-consistent scheme for determining the Green's function and the self-energy. They involve five central quantities: the vertex function Γ , the polarizability P , the screened Coulomb interaction W , the Green's function G , and the self-energy Σ . The coupled equations are given by

$$\Gamma(1, 2; 3) = \delta(1, 2)\delta(1, 3) + \int d(4, 5, 6, 7) \frac{\delta\Sigma(1, 2)}{\delta G(4, 5)} G(5, 6) \Gamma(6, 7; 3) G(7, 4) \quad (2.78)$$

$$P(1, 2) = -i \int d(3, 4) G(1, 3) \Gamma(3, 4; 2) G(4, 1) \quad (2.79)$$

$$W(1, 2) = v(1, 2) + \int d(3, 4) v(1, 3) P(3, 4) W(4, 2) \quad (2.80)$$

$$G(1, 2) = G_0(1, 2) + \int d(3, 4) G_0(1, 3) \Sigma(3, 4) G(4, 2) \quad (2.81)$$

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3) W(1^+, 4) \Gamma(3, 2; 4) \quad (2.82)$$

where $1 \equiv (\mathbf{r}_1, t_1, \sigma_1)$, v is the bare Coulomb interaction and 1^+ denotes a time infinitesimally later than t_1 , ensuring proper time ordering.

These equations are exact but highly nontrivial to solve due to their self-consistent and functional nature (Fig. 2.9). In particular, the vertex function Γ , which depends on three space-time coordinates, introduces significant computational complexity through its dependence on the functional derivative of the self-energy with respect to the Green's function.

A major simplification arises in the *GW* approximation, where vertex corrections are neglected by approximating

$$\Gamma(1, 2; 3) \approx \delta(1, 2)\delta(1, 3). \quad (2.83)$$

Under this assumption, the self-energy reduces to

$$\Sigma(1, 2) = i G(1, 2) W(1^+, 2), \quad (2.84)$$

which gives the name “*GW*”. In this approximation, the polarizability becomes

$$P(1, 2) = -i G(1, 2) G(2, 1), \quad (2.85)$$

and the screened Coulomb interaction W is obtained from a Dyson-like equation involving the bare interaction and the polarizability.

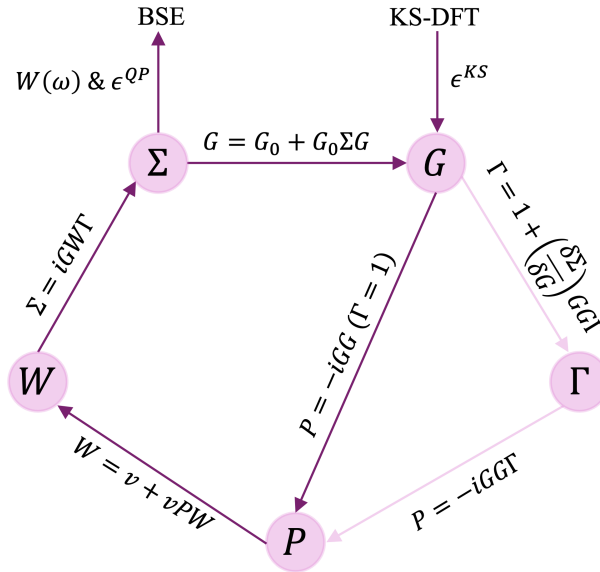


Figure 2.9: Schematic representation of Hedin's pentagon, illustrating the interconnection between the Green's function G , its non-interacting counterpart G_0 , the irreducible vertex function Γ , the polarizability P , the screened Coulomb interaction W , and the self-energy Σ through Hedin's equations. The *GW* approximation (maroon arrows) follows a simplified pathway by neglecting the explicit evaluation of Γ (pink arrows). Starting from KS orbitals and energies, *GW* yields QP corrections and the screened interaction W , which can be further employed in Bethe–Salpeter equation calculations of optical excitations.

The *GW* self-energy can be interpreted as a dynamically screened generalization of the exchange term in HF theory, where the bare Coulomb interaction is replaced by the screened interaction W . The frequency dependence of W reflects the dynamical response of the electronic system and is essential for describing QP excitations.

In practical calculations, different levels of self-consistency are employed. Fully self-consistent *GW* (sc*GW*) [122, 123] requires iterative updates of both G and W , but is computationally demanding. More commonly, perturbative approaches such as single-shot *GW* (G_0W_0), where both quantities are constructed from a reference mean-field calculation, are widely used due to their favorable balance between accuracy and computational cost [124]. The following subsection outlines how this formalism is implemented in practice to compute QP energies.

2.4.4 Computational implementation

In practice, Eq. (2.76) is solved perturbatively by assuming that the QP wavefunctions are well approximated by the KS states, yielding:

$$\epsilon_i^{\text{QP}} = \epsilon_i^{\text{KS}} + \langle \psi_i^{\text{KS}} | \Sigma(\epsilon_i^{\text{QP}}) - V_{\text{xc}} | \psi_i^{\text{KS}} \rangle. \quad (2.86)$$

The above equation is nonlinear due to the explicit frequency dependence of the self-energy $\Sigma(\omega)$. In practice, it is solved perturbatively by linearizing the self-energy around the KS eigenvalue ϵ_i^{KS} :

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) \approx \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_i^{\text{KS}}/\hbar) + (\omega - \epsilon_i^{\text{KS}}/\hbar) \left. \frac{\partial \Sigma(\mathbf{r}, \mathbf{r}'; \omega)}{\partial \omega} \right|_{\omega=\epsilon_i^{\text{KS}}}. \quad (2.87)$$

Substituting this expansion into the QP equation yields the perturbative expression

$$\epsilon_i^{\text{QP}} \approx \epsilon_i^{\text{KS}} + Z_i \langle \psi_i^{\text{KS}} | \Sigma(\epsilon_i^{\text{KS}}) - V_{\text{xc}} | \psi_i^{\text{KS}} \rangle, \quad (2.88)$$

where the renormalization factor

$$Z_i = \left[1 - \left\langle \psi_i^{\text{KS}} \left| \frac{\partial \Sigma(\omega)}{\partial \omega} \right| \psi_i^{\text{KS}} \right\rangle_{\omega=\epsilon_i^{\text{KS}}} \right]^{-1} \quad (2.89)$$

accounts for the energy dependence of the self-energy and represents the QP weight.

Within the GW approximation, the self-energy is expressed as

$$\Sigma^{GW} = iG_0W = iG_0v + iG_0(W - v) = \Sigma_x + \Sigma_c, \quad (2.90)$$

where Σ_x is the exchange contribution, analogous to the HF exchange and evaluated using the bare Coulomb interaction v , while Σ_c is the correlation contribution arising from dynamical screening through the screened Coulomb interaction W . The latter is frequency dependent and constitutes the most computationally demanding part of the calculation.

The G_0W_0 scheme is implemented through the following sequence of steps:

1. *Ground-state calculation:* Perform a DFT calculation to obtain the KS eigenvalues ϵ_i^{KS} and eigenfunctions ψ_i^{KS} , which define the non-interacting Green's function

$$G_0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i \frac{\psi_i^{\text{KS}}(\mathbf{r}) \psi_i^{\text{KS}*}(\mathbf{r}')}{\omega - \epsilon_i^{\text{KS}} + i\eta \text{sgn}(\epsilon_i^{\text{KS}} - E_F)}. \quad (2.91)$$

At this stage, the exchange part of the self-energy is evaluated as

$$\langle \psi_i^{\text{KS}} | \Sigma_x | \psi_i^{\text{KS}} \rangle = - \sum_j^{\text{occ}} \iint d^3\mathbf{r} d^3\mathbf{r}' \frac{\psi_i^{\text{KS}*}(\mathbf{r}) \psi_j^{\text{KS}}(\mathbf{r}) \psi_j^{\text{KS}*}(\mathbf{r}') \psi_i^{\text{KS}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.92)$$

2. *Polarizability*: Construct the independent-particle polarizability within the random-phase approximation (RPA), $P_0 = -iG_0G_0$.
3. *Dielectric function*: Compute the dielectric matrix $\varepsilon = 1 - vP_0$ and obtain its inverse ε^{-1} .
4. *Screened interaction*: Evaluate the screened Coulomb interaction $W_0 = \varepsilon^{-1}v$.
5. *Correlation self-energy*: Compute the correlation part of the self-energy $\Sigma_c = iG_0(W_0 - v)$ which involves numerical integration over frequency.
6. *QP energies*: Finally, evaluate the QP energies using Eq. (2.88).

Although the G_0W_0 approach is not self-consistent, it can be regarded as the first iteration of a fully self-consistent GW cycle (see Fig. 2.10). In partially self-consistent schemes such as GW_0 , only the QP energies (and hence G) are updated while keeping W fixed at W_0 . In contrast, fully self-consistent GW (sc GW) iteratively updates both G and W until convergence is achieved, thereby providing a more consistent description of many-body effects at a higher computational cost.

In this thesis, QP corrections are computed within the G_0W_0 , GW_0 , and fully self-consistent GW frameworks. The underlying DFT calculations were performed using VASP and QE, while the many-body perturbation theory calculations were carried out using VASP and the YAMBO code.

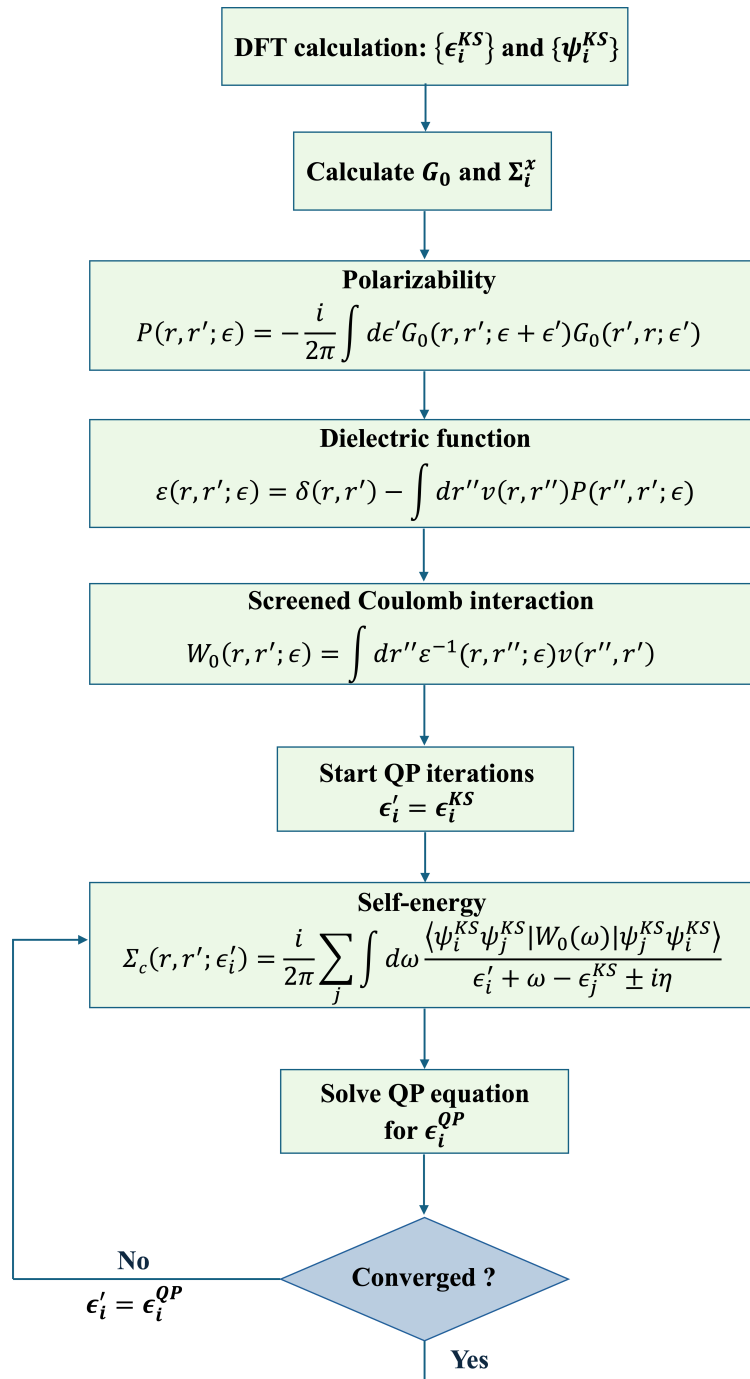
2.4.5 Frequency dependence and the plasmon-pole model (PPM)

The evaluation of the correlation part of the self-energy,

$$\Sigma_c = iG_0(W - v), \quad (2.93)$$

involves a convolution over frequency, which constitutes one of the main computational challenges in GW calculations. This difficulty arises because both G_0 and $W(\omega)$ exhibit poles in close proximity to the real frequency axis, rendering direct numerical integration along the real axis numerically unstable and computationally demanding.

To overcome this issue, several strategies have been developed to treat the frequency dependence of $W(\omega)$. Among these, PPM provides an efficient and widely used approximation. In

Figure 2.10: Schematic representation of the single-shot GW (G_0W_0) implementation.

this approach, the frequency dependence of the inverse dielectric function $\varepsilon^{-1}(\mathbf{q}, \omega)$ is approximated by a simple analytic form characterized by one (or a few) effective poles. Physically, this approximation is motivated by the observation that the dielectric response of many materials is often dominated by collective charge excitations (plasmons), allowing ε^{-1} to be represented by a single-pole function.

The parameters of the model are determined by enforcing physically motivated constraints, such as reproducing the static dielectric function $\varepsilon(\mathbf{q}, \omega = 0)$ and satisfying sum rules (e.g.,

the f -sum rule). Common implementations include the Hybertsen–Louie and Godby–Needs models, which differ in how these constraints are imposed. Once the analytic form of ε^{-1} is specified, the screened interaction $W(\omega)$ can be expressed in a closed form, enabling the frequency integration in the self-energy to be carried out analytically via residue calculus. This significantly reduces the computational cost compared to full-frequency methods.

Despite its efficiency, the plasmon-pole approximation introduces limitations. In particular, it may not fully capture the detailed frequency dependence of the dielectric response, especially in systems where multiple excitation channels are important, such as molecules or strongly correlated materials. Moreover, the imaginary part of the self-energy is restricted to the pole structure of the model, which can affect the accurate description of QP lifetimes. More accurate treatments of the frequency dependence include full-frequency approaches such as contour deformation techniques, where the integration is performed in the complex frequency plane to avoid poles on the real axis, as well as numerical integration along the imaginary axis followed by analytic continuation. While these methods provide improved accuracy, they are computationally more demanding.

In the calculations presented in this work using the YAMBO package, PPA within the Godby–Needs model is employed to evaluate the frequency-dependent dielectric screening, owing to its favorable balance between computational efficiency and accuracy, particularly for extended systems with well-defined plasmonic excitations.

2.4.6 Bethe–Salpeter equation

Neutral excitations, such as optical absorption, electron energy loss, and inelastic scattering processes, involve the creation of correlated e – h pairs without changing the total number of electrons in the system. While the GW approximation provides an accurate description of single-particle excitations, it fails to describe optical spectra due to the neglect of e – h interactions. In fact, optical spectra obtained within the independent QP picture can significantly deviate from experiments, both in peak positions and intensities, and completely miss bound excitonic states.

A rigorous treatment of neutral excitations requires a two-particle formalism based on the two-particle Green’s function. Within many-body perturbation theory, this leads to the Bethe–Salpeter equation, which describes the correlated dynamics of e – h pairs and provides access to the full excitation spectrum, including both bound excitons below the band gap and resonant

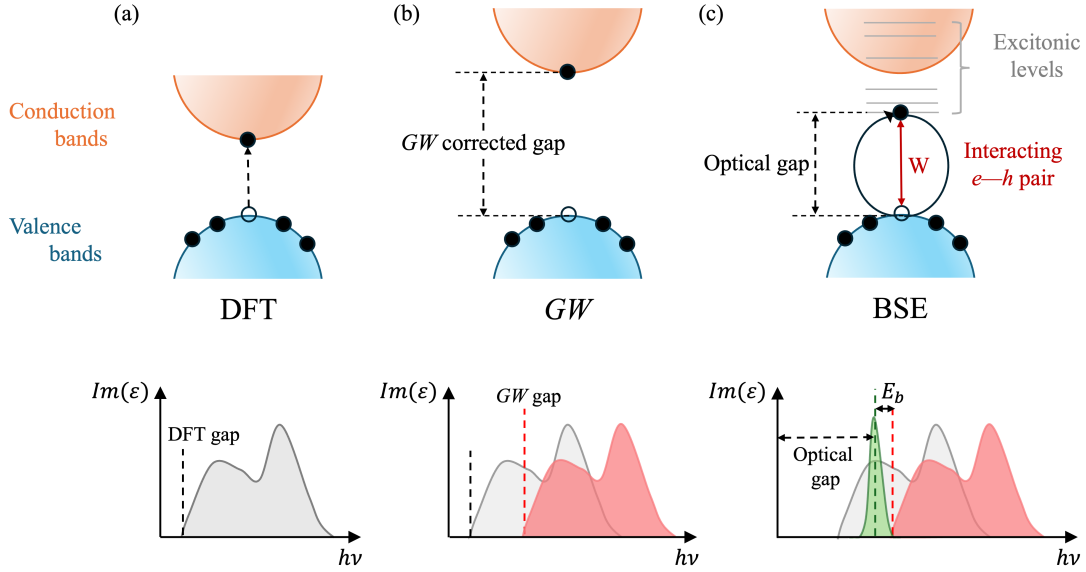


Figure 2.11: Schematic illustration of three successive levels of approximation and their predictive accuracy. (a) The independent-particle DFT approach, which typically underestimates the band gap. (b) The QP GW approximation, where band gap corrections lead to improved agreement with experimental values. (c) The Bethe–Salpeter equation (BSE), which incorporates electron–hole interactions, providing a more complete many-body description and accurately reproducing optical absorption spectra in close agreement with experiments.

excitations above it [119, 120].

2.4.6.1 Two-particle correlation function

The interacting $e-h$ correlation function L satisfies the Bethe-Salpeter equation in the form:

$$L(1, 2; 1', 2') = L_0(1, 2; 1', 2') + \int d(3, 4, 5, 6) L_0(1, 4; 1', 3) K(3, 5; 4, 6) L(6, 2; 5, 2'), \quad (2.94)$$

where K is the $e-h$ interaction kernel, $L_0(1, 2, 1', 2') = G(1, 2')G(2, 1')$ is the non-interacting correlation function which corresponds to free $e-h$ pair i.e., without the interaction K . Notably, L depends on four time-variables, from two creation processes (electron and hole) and two annihilation processes. However, for optical excitations, we consider only simultaneous creation and simultaneous annihilation events, which reduces the number of independent time variables from four to two. In the absence of external perturbations, time-translational invariance implies that only the difference between these two times is physically relevant. Consequently, the above equation can be reformulated by performing a one-dimensional Fourier transform from time to energy, leading to $L(1, 2, 1', 2', \omega)$ where the indices now denote only spatial and spin

coordinates. The non-interacting correlation function can be expressed as

$$L_0(1, 2, 1', 2'; \omega) = i \sum_{v,c} \left[\frac{\psi_c(\mathbf{r}_1) \psi_v^*(\mathbf{r}'_1) \psi_v(\mathbf{r}_2) \psi_c^*(\mathbf{r}'_2)}{\omega - (E_c - E_v) + i0^+} - \frac{\psi_v(\mathbf{r}_1) \psi_c^*(\mathbf{r}'_1) \psi_c(\mathbf{r}_2) \psi_v^*(\mathbf{r}'_2)}{\omega + (E_c - E_v) - i0^+} \right], \quad (2.95)$$

where v and c denote valence (occupied) and conduction (unoccupied) states, respectively.

Including e - h interaction, the full L becomes

$$L(1, 2, 1', 2'; \omega) = i \sum_S \left[\frac{\chi_S(\mathbf{r}_1, \mathbf{r}'_1) \chi_S^*(\mathbf{r}'_2, \mathbf{r}_2)}{\omega - \Omega_S + i0^+} - \frac{\chi_S(\mathbf{r}_2, \mathbf{r}'_2) \chi_S^*(\mathbf{r}'_1, \mathbf{r}_1)}{\omega + \Omega_S - i0^+} \right], \quad (2.96)$$

where S represents the correlated e - h excitations of the system, Ω_S are the excitation energies, and χ_S are the excitonic amplitudes expressed as:

$$\chi_S(r, r') = \sum_v \sum_c^{\text{empty}} \left(A_{vc}^S \psi_c(\mathbf{r}) \psi_v^*(\mathbf{r}') + B_{vc}^S \psi_v(\mathbf{r}) \psi_c^*(\mathbf{r}') \right), \quad (2.97)$$

where A_{vc}^S and B_{vc}^S are the coupling coefficients.

2.4.6.2 BSE eigenvalue problem

Substituting the expressions in Eqs.(2.95)–(2.97) into BSE (Eq.(2.94)) leads to a generalized eigenvalue problem:

$$(E_c - E_v) A_{vc}^S + \sum_{v'c'} K_{vc,v'c'}^{AA}(\Omega_S) A_{v'c'}^S + \sum_{v'c'} K_{vc,v'c'}^{AB}(\Omega_S) B_{v'c'}^S = \Omega_S A_{vc}^S, \quad (2.98)$$

$$(E_c - E_v) B_{vc}^S + \sum_{v'c'} K_{vc,v'c'}^{BB}(\Omega_S) B_{v'c'}^S + \sum_{v'c'} K_{vc,v'c'}^{BA}(\Omega_S) A_{v'c'}^S = -\Omega_S B_{vc}^S. \quad (2.99)$$

where

$$K_{vc,v'c'}^{AA}(\Omega_S) = i \int d(3, 4, 5, 6) \psi_v(\mathbf{r}_4) \psi_c^*(\mathbf{r}_3) K(3, 5, 4, 6; \Omega_S) \psi_{v'}^*(\mathbf{r}_5) \psi_{c'}(\mathbf{r}_6), \quad (2.100)$$

$$K_{vc,v'c'}^{AB}(\Omega_S) = i \int d(3, 4, 5, 6) \psi_v(\mathbf{r}_4) \psi_c^*(\mathbf{r}_3) K(3, 5, 4, 6; \Omega_S) \psi_{v'}^*(\mathbf{r}_6) \psi_{c'}(\mathbf{r}_5), \quad (2.101)$$

with similar expressions for K^{BA} and K^{BB} . The above Eqs.(2.98)–(2.99) exhibit a block-matrix structure. The diagonal blocks are defined by the QP energy differences $(E_c - E_v)$ and the interaction matrix elements K^{AA} and K^{BB} , while the off-diagonal blocks are formed by the coupling terms K^{AB} and K^{BA} . Setting these off-diagonal terms to zero ($K^{AB} = K^{BA} = 0$) decouples the Eqs.(2.98)–(2.99) into two independent equations corresponding to the A and B.

$$(E_c - E_v) A_{vc}^S + \sum_{v'c'} K_{vc,v'c'}^{AA}(\Omega_S) A_{v'c'}^S = \Omega_S A_{vc}^S. \quad (2.102)$$

This is equivalent to expressing the excited states as e - h pair configurations.

$$|N, S\rangle = \sum_v \sum_c^{\text{hole elec}} A_{vc}^S \hat{a}_v^\dagger \hat{b}_c^\dagger |N, 0\rangle =: \sum_v \sum_c^{\text{hole elec}} A_{vc}^S |vc\rangle, \quad (2.103)$$

where $\hat{a}_v^\dagger$ and $\hat{b}_c^\dagger$ are the hole and electron creation operators, and $|N, 0\rangle$ is the many-body ground state. The above expansion is known as Tamm–Dancoff approximation (TDA).

2.4.6.3 Electron–hole interaction kernel

The e – h interaction kernel K is obtained from the functional derivative of the self-energy with respect to the Green's function.

$$K(3, 5; 4, 6) = \frac{\delta[V_{coul}\delta(3, 4) + \Sigma(3, 4)]}{\delta G(6, 5)}. \quad (2.104)$$

Within the GW approximation, $\Sigma = iGW$, and neglecting the functional derivative of the screened interaction W with respect to G , the kernel separates into exchange and direct contributions:

$$\begin{aligned} K(3, 5; 4, 6) &= -i\delta(3, 4)\delta(5^-, 6)v(3, 6) + i\delta(3, 6)\delta(4, 5)W(3^+, 4) \\ &=: K^x(3, 5; 4, 6) + K^d(3, 5; 4, 6). \end{aligned} \quad (2.105)$$

The exchange term, K^x , arises from the bare Coulomb interaction v , whereas the direct term K^d involves the screened Coulomb interaction W . Physically, the exchange term primarily governs local-field effects and fine structure of the excitation spectrum (e.g., singlet–triplet splitting), whereas the direct term accounts for the attractive interaction between the electron and hole, which leads to the formation of bound excitonic states.

In the basis of valence (v) and conduction (c) states, the matrix elements of the direct and exchange contributions are given by:

$$\begin{aligned} \langle vc | K^{AA,d}(\Omega_S) | v'c' \rangle &= \int d\mathbf{r} d\mathbf{r}' \psi_c^*(\mathbf{r})\psi_{c'}(\mathbf{r})\psi_v(\mathbf{r}')\psi_{v'}^*(\mathbf{r}') \\ &\times \frac{i}{2\pi} \int d\omega e^{-i\omega 0^+} W(\mathbf{r}, \mathbf{r}', \omega) \\ &\times \left[\frac{1}{\Omega_S - \omega - (E_c^{QP} - E_v^{QP}) + i0^+} \right. \\ &\quad \left. + \frac{1}{\Omega_S + \omega - (E_c^{QP} - E_v^{QP}) + i0^+} \right]. \end{aligned} \quad (2.106)$$

$$\langle vc | K^{AA,x} | v'c' \rangle = \int d\mathbf{r} d\mathbf{r}' \psi_c^*(\mathbf{r})\psi_v(\mathbf{r})v(\mathbf{r}, \mathbf{r}')\psi_{c'}(\mathbf{r}')\psi_{v'}^*(\mathbf{r}'). \quad (2.107)$$

The matrix elements involve integrals over QP electron and hole wavefunctions. While these integrals are formally straightforward, their practical evaluation depends on the specific features of the electronic system and may require specialized computational techniques. In addition to the real-space integration, the e – h interaction kernel K requires a frequency integration, which can be treated using models such as the plasmon-pole approximation in which

$$W(\mathbf{r}, \mathbf{r}'; \omega) = \sum_l W_l(\mathbf{r}, \mathbf{r}') \frac{\omega_l}{2} \left(\frac{1}{\omega - \omega_l + i0^+} - \frac{1}{\omega + \omega_l - i0^+} \right), \quad (2.108)$$

where ω_l represents the plasmon frequency, and $W_l(\mathbf{r}, \mathbf{r}')$ describes the spatial dependence of the plasmon mode l .

2.4.6.4 Static screening approximation

For most semiconductors and extended systems, the QP transition energies ($E_c^{QP} - E_v^{QP}$) are close to the excitation energies Ω_S . Consequently, the quantity $\Omega_S - (E_c^{QP} - E_v^{QP})$ is much smaller than the characteristic plasmon frequencies. This separation of energy scales justifies the *static screening approximation*, in which the direct term simplifies to:

$$\langle vc | K^{AA,d} | v'c' \rangle \approx - \int d\mathbf{r} d\mathbf{r}' \psi_c^*(\mathbf{r}) \psi_{c'}(\mathbf{r}) W(\mathbf{r}, \mathbf{r}', \omega = 0) \psi_v(\mathbf{r}') \psi_{v'}^*(\mathbf{r}'). \quad (2.109)$$

This renders the kernel frequency independent and significantly simplifies the solution of the BSE. However, for finite systems such as atoms and molecules, where the difference $\Omega_S - (E_c^{QP} - E_v^{QP})$ can be comparable to the plasmon energies, the full frequency dependence of W must be retained. In that case an iterative self-consistent procedure is followed: an initial $\Omega_S^{(0)}$ is obtained with static screening, the kernel is updated with the new excitation energies, a first-order perturbative correction is computed, and the cycle is repeated until convergence of Ω_S .

In practical implementations the workflow therefore reduces to (i) computing the screened interaction W in the static limit, (ii) constructing the complete kernel K , and (iii) diagonalizing the BSE Hamiltonian to obtain the excitonic eigenvalues Ω_S and eigenvectors A_{vck}^S . Although the procedure involves a chain of approximations and is far from a fully self-consistent solution of Hedin's equations, it has been shown to reproduce experimental optical spectra with high accuracy for a broad class of materials.

2.4.6.5 Optical absorption spectrum

The optical response of a material is fundamentally described by the macroscopic dielectric function $\epsilon_M(\omega)$, which is obtained from the microscopic dielectric matrix in the long-wavelength limit ($q \rightarrow 0$).

$$\epsilon_M(\omega) = \lim_{q \rightarrow 0} [\epsilon_{G=0, G'=0}^{-1}(q, \omega)]^{-1} \quad (2.110)$$

The optical absorption spectrum is directly related to $\text{Im}(\epsilon_M(\omega))$, which describes the probability of photon absorption at a given frequency.

Within the independent-particle approximation (IPA), where e - h interactions are neglected, optical absorption arises from vertical transitions between valence and conduction states. In this case, the imaginary part of the dielectric function is given by

$$\text{Im}(\varepsilon_M(\omega)) = \frac{16\pi e^2}{\omega^2} \sum_{v,c} |\langle v | \hat{\mathbf{e}} \cdot \hat{\mathbf{v}} | c \rangle|^2 \delta(\omega - (E_c^{\text{QP}} - E_v^{\text{QP}})), \quad (2.111)$$

where $\hat{\mathbf{e}}$ is the light polarization vector and $\hat{\mathbf{v}}$ is the velocity operator. The transitions are governed by single-particle matrix elements between QP states.

A more accurate description of optical spectra requires the inclusion of e - h interactions, which is achieved by solving BSE, which yields neutral excitation energies Ω_S and the corresponding excitonic states $|S\rangle$. In this framework, optical absorption is expressed as transitions from the ground state to correlated e - h pairs (excitons), and the dielectric function becomes

$$\text{Im}(\varepsilon_M(\omega)) = \frac{16\pi e^2}{\omega^2} \sum_S |\langle 0 | \hat{\mathbf{e}} \cdot \hat{\mathbf{v}} | S \rangle|^2 \delta(\omega - \Omega_S), \quad (2.112)$$

where the summation runs over all excitonic states. This formulation naturally captures bound excitons and the redistribution of oscillator strength induced by Coulomb interactions.

The excitonic optical matrix elements are evaluated by expanding the excitonic states in the e - h basis:

$$\langle 0 | \hat{\mathbf{v}} | S \rangle = \sum_{v\mathbf{c}\mathbf{k}} A_{v\mathbf{c}\mathbf{k}}^S \langle v\mathbf{k} | \hat{\mathbf{v}} | c\mathbf{k} \rangle, \quad (2.113)$$

$A_{v\mathbf{c}\mathbf{k}}^S$ are the BSE eigenvectors, describing the weight of each e - h transition contributing to the excitonic state. In the absence of e - h interaction, these coefficients reduce to single transitions, and the BSE expression recovers the independent-particle limit. A crucial aspect in practical calculations is the evaluation of the single-particle matrix elements $\langle v | \hat{\mathbf{v}} | c \rangle$, particularly when pseudopotentials are employed. The velocity operator is defined through the commutator

$$\hat{\mathbf{v}} = i[\hat{H}, \mathbf{r}], \quad (2.114)$$

which reduces to the momentum operator $\mathbf{p}$ for local potentials. However, in the presence of non-local pseudopotentials V_{ps} , the commutator does not vanish, and an additional contribution must be included:

$$\langle v | \hat{\mathbf{v}} | c \rangle = \langle v | \mathbf{p} + i[V_{\text{ps}}, \mathbf{r}] | c \rangle. \quad (2.115)$$

This generalized expression ensures a consistent evaluation of optical matrix elements and is essential for accurately capturing transition intensities. Overall, the BSE framework provides a robust and predictive description of optical absorption, accounting for both QP corrections

and excitonic effects, which are crucial in materials with strong Coulomb interactions such as low-dimensional and ionic systems.

2.5 Excitonic models and classification

Excitons are electrically neutral QPs arising from the Coulomb attraction between a photoexcited electron in the conduction band and the corresponding hole in the valence band. Absorption of a photon with energy $\hbar\omega \gtrsim E_g$ promotes an electron across the band gap, generating an $e-h$ pair. Owing to their mutual electrostatic interaction, this pair can form a bound state known as an exciton. The stability of this state is quantified by the exciton binding energy E_b , defined as the energy needed to separate the $e-h$ pair into free charge carriers. Depending on their spatial extent and binding energy, excitons are broadly classified into *Frenkel* and *Wannier–Mott* types, as shown in Fig. 2.12.

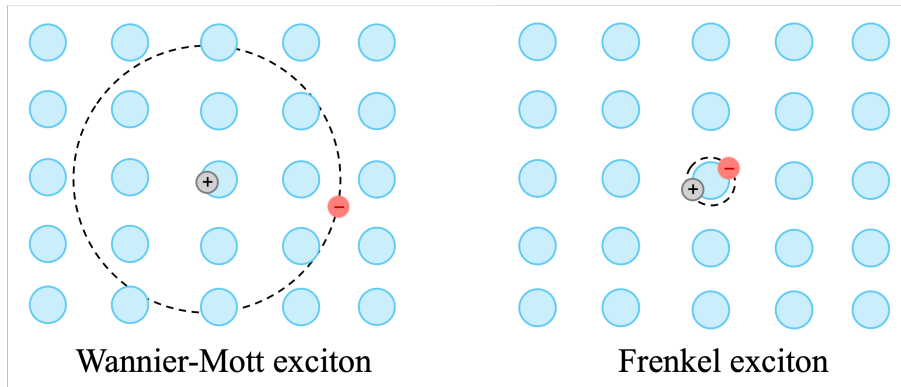


Figure 2.12: Schematic representation of Wannier–Mott (delocalized) and Frenkel (localized) excitons, emphasizing their different spatial extents.

1. **Frenkel excitons** correspond to tightly bound $e-h$ pairs with a spatial extent comparable to the lattice constant or molecular size. They typically arise in systems with weak dielectric screening, large band gaps, and localized electronic states. As a result, Frenkel excitons exhibit large binding energies, ranging from hundreds of meV to several eV, and are therefore stable at room temperature. They are commonly observed in organic semiconductors, molecular crystals, and wide-gap insulators [76, 125]. Owing to their localized character, charge transport in such systems proceeds predominantly via hopping mechanisms rather than band-like motion.
2. **Wannier–Mott excitons**, in contrast, represent the delocalized limit, where the $e-h$ pair

extends over many lattice constants. These excitons are characteristic of inorganic semiconductors with large dielectric constants and small effective carrier masses [76, 125]. Strong dielectric screening weakens the Coulomb interaction, leading to relatively small binding energies, typically on the order of few meVs.

Accurate treatment of excitonic effects generally requires the rigorous many-body GW –BSE framework discussed earlier in this chapter. Nevertheless, for weakly bound excitons in semiconductors, the essential physics can often be captured within the simpler Wannier–Mott model, which describes the exciton as a hydrogen-like e – h pair interacting through a screened Coulomb potential. Since crystal systems investigated in Chapter 3 of this thesis exhibit weakly bound excitonic character, the following sections primarily employ the Wannier–Mott formalism to describe their optical and excitonic properties. Building upon this model, the theoretical framework for optical transitions, radiative recombination, and excitonic transition strengths is developed using Fermi’s Golden Rule and $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, while the full GW –BSE formalism is utilized in the remaining chapters for quantitative many-body calculations.

2.5.1 Wannier–Mott formalism

Drawing an analogy with the hydrogen atom, the Wannier–Mott model describes excitons in semiconductors as bound e – h pairs interacting through a screened Coulomb potential. In a direct-gap material, the effective two-particle Hamiltonian for the exciton is expressed as:

$$H_{\text{exc}} = E_g - \frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 - \frac{e^2}{4\pi\epsilon_0\epsilon_r|\mathbf{r}_e - \mathbf{r}_h|}, \quad (2.116)$$

where E_g is the QP band gap, m_e^* and m_h^* are the effective masses of the electron and hole, respectively, and ϵ_r is the static relative dielectric constant of the material that screens the Coulomb interaction.

To decouple the system, the coordinates are transformed into center-of-mass ($\mathbf{R}$) and relative ($\mathbf{r}$) coordinates:

$$\mathbf{R} = \frac{m_e^*\mathbf{r}_e + m_h^*\mathbf{r}_h}{m_e^* + m_h^*}, \quad \mathbf{r} = \mathbf{r}_e - \mathbf{r}_h, \quad \mu = \frac{m_e^*m_h^*}{m_e^* + m_h^*}, \quad (2.117)$$

with μ representing the reduced effective mass. This transformation separates the Hamiltonian into independent center-of-mass and relative-motion components. The relative motion, which determines the binding properties of the exciton, satisfies the Schrödinger-like equation:

$$\left(-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 - \frac{e^2}{4\pi\epsilon_0\epsilon_r|\mathbf{r}|} \right) \phi_n(\mathbf{r}) = E_n \phi_n(\mathbf{r}). \quad (2.118)$$

The solutions $\phi_n(\mathbf{r})$ are hydrogenic envelope functions. The full excitonic wavefunction is then constructed as [126]:

$$\psi_{n\mathbf{K}}(\mathbf{R}, \mathbf{r}) = e^{i\mathbf{K}\cdot\mathbf{R}} \phi_n(\mathbf{r}) \phi_c(\mathbf{r}_e) \phi_v(\mathbf{r}_h), \quad (2.119)$$

where ϕ_c and ϕ_v are the Bloch functions for the conduction and valence bands, respectively.

The total energy is given by:

$$E_{n\mathbf{K}} = E_g + E_b(n) + \frac{\hbar^2 \mathbf{K}^2}{2(m_e^* + m_h^*)}, \quad (2.120)$$

where the exciton binding energy for the n -th state is defined as [76]:

$$E_b(n) = -\frac{\mu}{m_0 \varepsilon_r^2} \frac{E_{Ry}}{n^2}. \quad (2.121)$$

Here, $E_{Ry} \approx 13.6$ eV is the Rydberg energy and m_0 is the electron rest mass. Furthermore, the spatial extent of the exciton is characterized by the effective Bohr radius:

$$r_{\text{exc}} = \frac{\varepsilon_r m_0}{\mu} n^2 a_0, \quad (2.122)$$

where $a_0 \approx 0.529$ Å is the Bohr radius of the hydrogen atom.

2.5.2 Optical transitions and Fermi's golden rule

While the Wannier–Mott model provides an excellent description of the bound excitonic states, calculating experimentally observable quantities—such as optical absorption spectra, oscillator strengths, and radiative lifetimes—requires a proper treatment of the light–matter interaction. This is achieved within time-dependent perturbation theory using Fermi's Golden Rule. Fermi's golden rule provides the fundamental framework for calculating transition rates between quantum states under a time-dependent perturbation, such as the absorption or emission of a photon [127, 128]. The transition rate Γ_{if} from an initial state $|i\rangle$ to a final state $|f\rangle$ is given by:

$$\Gamma_{if} = \frac{2\pi}{\hbar} |\langle f | H' | i \rangle|^2 \delta(E_f - E_i \mp \hbar\omega), \quad (2.123)$$

where H' is the perturbation Hamiltonian and $\hbar\omega$ is the photon energy. This rate is inversely proportional to the radiative lifetime of the excited state and forms the basis for computing optical spectra.

2.5.2.1 Light-matter interaction Hamiltonian

The interaction between a charge carrier and an external electromagnetic field is characterized by a scalar potential $\phi(\mathbf{r}, t)$ and a vector potential $\mathbf{A}(\mathbf{r}, t)$. The corresponding electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields are given by:

$$\mathbf{E} = -\nabla\phi - \frac{\partial\mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}. \quad (2.124)$$

The Hamiltonian for an electron with mass m and charge e in the presence of this field and the periodic crystal potential $V(\mathbf{r})$ is:

$$H = \frac{1}{2m} (\mathbf{p} - e\mathbf{A})^2 + e[\phi + V(\mathbf{r})]. \quad (2.125)$$

Under typical experimental conditions with moderate light intensity, the quadratic $\mathbf{A}^2$ term is small and can be neglected. Additionally, adopting the Weyl gauge ($\phi = 0$) and the Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$), the commutator $[\mathbf{A}, \mathbf{p}] = 0$ [129]. The total Hamiltonian can then be partitioned into the unperturbed part H_0 and the time-dependent perturbation H' :

$$H_0 = \frac{\mathbf{p}^2}{2m} + eV(\mathbf{r}), \quad (2.126)$$

$$H' = -\frac{e}{m} \mathbf{A} \cdot \mathbf{p}. \quad (2.127)$$

For a monochromatic plane wave, the vector potential is $\mathbf{A} = A_0 \hat{\epsilon} [e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}]$, where $\hat{\epsilon}$ is the polarization unit vector. In the visible and ultraviolet range, the wavelength is much larger than the lattice constant ($\mathbf{k} \cdot \mathbf{r} \ll 1$), allowing for the **electric dipole approximation** ($e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$).

Using the commutation relation $[H_0, \mathbf{r}] = -i\hbar\mathbf{p}/m$, the momentum matrix element is related to the position matrix element by:

$$\langle \psi_c | \mathbf{p} | \psi_v \rangle = im\omega_{cv} \langle \psi_c | \mathbf{r} | \psi_v \rangle, \quad (2.128)$$

where $\hbar\omega_{cv} = E_c - E_v$. Thus, the transition rate becomes directly proportional to the square of the dipole matrix element:

$$\Gamma_{if} \propto |\langle \psi_v | \hat{\epsilon} \cdot \mathbf{r} | \psi_c \rangle|^2. \quad (2.129)$$

2.5.3 The $\mathbf{k} \cdot \mathbf{p}$ perturbation theory

Near band extrema, the electronic structure and optical matrix elements are efficiently described by $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. Within this framework, the Hamiltonian acting on the cell-periodic

part of the Bloch function, $u_{n,\mathbf{k}}$, is given by:

$$H_{\mathbf{k},\mathbf{p}} = \frac{p^2}{2m} + V(\mathbf{r}) + \frac{\hbar}{m} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar^2 k^2}{2m}. \quad (2.130)$$

Treating the $\mathbf{k}$ -dependent terms as a perturbation and applying second-order perturbation theory yields the energy dispersion

$$E_{n,\mathbf{k}} = E_{n,0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0} | \mathbf{k} \cdot \mathbf{p} | u_{n',0} \rangle|^2}{E_{n,0} - E_{n',0}}. \quad (2.131)$$

Comparing this with the parabolic band approximation [130] $E_n(\mathbf{k}) = E_n(0) + \frac{\hbar^2}{2m} \sum_{ij} \left(\frac{m}{m^*}\right)_{ij} k_i k_j$ gives the inverse effective mass tensor:

$$\left(\frac{m}{m^*}\right)_{ij} = \delta_{ij} + \frac{2}{m} \sum_{n' \neq n} \frac{\langle u_{n,0} | \mathbf{p} | u_{n',0} \rangle^2}{E_{n,0} - E_{n',0}}. \quad (2.132)$$

This framework provides both the effective masses (needed for the Wannier–Mott model) and the interband momentum matrix elements (needed for optical transition strengths).

2.5.4 Excitonic transition parameters

Within the Wannier–Mott formalism, an excitonic state $|n\rangle$ is expressed as a coherent superposition of independent e – h transitions across the Brillouin zone. The momentum matrix element connecting the crystal ground state $|0\rangle$ to the excitonic state $|n\rangle$ is therefore

$$\langle n | \hat{\mathbf{p}} | 0 \rangle = \sum_{\mathbf{k}} \langle n | \mathbf{k} \rangle \langle \psi_{c,\mathbf{k}} | \hat{\mathbf{p}} | \psi_{v,\mathbf{k}} \rangle, \quad (2.133)$$

where $\langle n | \mathbf{k} \rangle$ denotes the excitonic amplitude in reciprocal space.

Near the band extrema, the interband momentum matrix element varies slowly with $\mathbf{k}$. Under this approximation,

$$\langle \psi_{c,\mathbf{k}} | \hat{\mathbf{p}} | \psi_{v,\mathbf{k}} \rangle \approx \langle \psi_c | \hat{\mathbf{p}} | \psi_v \rangle. \quad (2.134)$$

The excitonic transition matrix element then simplifies to

$$\langle n | \hat{\mathbf{p}} | 0 \rangle \approx \langle \psi_c | \hat{\mathbf{p}} | \psi_v \rangle \sum_{\mathbf{k}} \langle n | \mathbf{k} \rangle. \quad (2.135)$$

The summation term corresponds to the real-space exciton envelope function evaluated at zero relative separation. Defining the envelope function via the Fourier transform

$$\phi_n(\mathbf{r}) = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \langle \mathbf{k} | n \rangle, \quad (2.136)$$

one obtains at $\mathbf{r} = 0$

$$\phi_n(0) = \sum_{\mathbf{k}} \langle \mathbf{k} | n \rangle. \quad (2.137)$$

Consequently, the squared transition matrix element becomes

$$|\langle n | \hat{\mathbf{p}} | 0 \rangle|^2 \propto |\langle \psi_c | \hat{\mathbf{p}} | \psi_v \rangle|^2 |\phi_n(0)|^2. \quad (2.138)$$

This result has a clear physical meaning: optical transitions (absorption or emission) are local processes that require finite spatial overlap between the electron and hole. Hence, the probability density $|\phi_n(0)|^2$ directly governs the excitonic oscillator strength. For a hydrogenic Wannier–Mott exciton in three dimensions, the probability density at the origin for the state with principal quantum number n is

$$|\phi_n(0)|^2 = \frac{1}{\pi r_{\text{exc}}^3 n^3}, \quad (2.139)$$

This expression shows that the optical transition strength scales inversely with the cube of the exciton radius – more compact excitons exhibit significantly stronger light-matter coupling. Additionally, due to the symmetry of hydrogenic wavefunctions, only s -type states ($l = 0$) have non-zero amplitude at $\mathbf{r} = 0$ and are optically bright within the electric dipole approximation.

2.5.5 Radiative lifetime of excitons

The radiative lifetime τ_{exc} characterizes the average time an exciton survives before recombining radiatively via photon emission. It is given by the inverse of the spontaneous emission rate obtained from Fermi's Golden Rule. Starting from the transition rate

$$\Gamma_{if} \propto \sum_{\mathbf{k}} |\langle \psi_{v,\mathbf{k}} | \hat{\mathbf{e}} \cdot \mathbf{r} | \psi_{c,\mathbf{k}} \rangle|^2, \quad (2.140)$$

and using the relation between position and momentum matrix elements

$$|\langle \psi_{v,\mathbf{k}} | \hat{\mathbf{e}} \cdot \mathbf{r} | \psi_{c,\mathbf{k}} \rangle|^2 = \frac{1}{m_0^2 \omega^2} |\langle \psi_{v,\mathbf{k}} | \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_{c,\mathbf{k}} \rangle|^2, \quad (2.141)$$

the interband momentum matrix element can be evaluated using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. Combining this with the excitonic envelope contribution yields the total transition rate

$$\Gamma_{if} \propto V_{\text{exc}} |\phi_n(0)|^2 |\langle \psi_{v,\mathbf{k}_0} | \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_{c,\mathbf{k}_0} \rangle|^2, \quad (2.142)$$

where V_{exc} is the effective exciton volume and $\mathbf{k}_0$ corresponds to the band-edge wavevector.

The radiative lifetime of the exciton is therefore

$$\tau_{\text{exc}} = \frac{1}{\Gamma_{if}}. \quad (2.143)$$

This expression reveals that the exciton lifetime is highly sensitive to both the dielectric environment (which controls r_{exc} and thus $|\phi_n(0)|^2$) and the strength of the interband optical matrix element. Materials with strong dielectric screening or symmetry-forbidden transitions at the band edge generally exhibit longer radiative lifetimes, while compact excitons with large dipole matrix elements recombine more rapidly.

2.6 Theoretical framework: Nonadiabatic molecular dynamics

A quantitative description of excited-state dynamics in optoelectronic materials requires going beyond the BO approximation, which decouples the fast electronic motion from the slow nuclear dynamics. Although the BO approximation has proven highly effective for describing ground-state properties, it breaks down in the presence of strong nonadiabatic (NA) coupling between electronic excitations and lattice vibrations. Under such conditions, atomic motion can drive transitions between electronic states. These transitions govern essential processes such as hot-carrier relaxation, charge transfer, and nonradiative recombination, which ultimately determine the efficiency of next-generation optoelectronic devices. Traditional adiabatic molecular dynamics, constrained to a single potential energy surface, simply cannot model these interstate electronic transitions or capture their excited-state relaxation pathways.

NAMD provides the essential framework to capture these processes by explicitly treating the coupled evolution of electrons and nuclei. This approach permits the real-time simulation of energy exchange between excited carriers and phonons, uncovering microscopic relaxation pathways that directly correlate with spectroscopic observations. In this work, all NAMD simulations utilize the PYXAID package [52, 53]. Ground-state molecular dynamics trajectories are initially obtained using QE and are then used as inputs in PYXAID to evaluate the time-dependent NA coupling elements and simulate the carrier dynamics.

2.6.1 Time-dependent Schrödinger equation (TD-SE)

The starting point for NAMD is the total TD-SE for a system of N_e electrons ($\mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_{N_e}\}$) and N_N nuclei ($\mathbf{R} = \{\mathbf{R}_1, \dots, \mathbf{R}_{N_N}\}$):

$$i\hbar \frac{\partial \Psi(\mathbf{r}, \mathbf{R}, t)}{\partial t} = \hat{H}(\mathbf{r}, \mathbf{R}, t) \Psi(\mathbf{r}, \mathbf{R}, t). \quad (2.144)$$

The total wavefunction is expanded in a basis of adiabatic electronic states $\psi_i(\mathbf{r}; \mathbf{R}(t))$ and nuclear wavefunctions $\chi_i(\mathbf{R}(t), t)$:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i \chi_i(\mathbf{R}(t), t) \psi_i(\mathbf{r}; \mathbf{R}(t)). \quad (2.145)$$

Substituting this expansion into the TD-SE and projecting onto the electronic state ψ_i (i.e., multiplying by ψ_i^* and integrating over electronic coordinates) yields a set of coupled equations that govern the time evolution of the nuclear wave packets $\chi_i(\mathbf{R}(t), t)$ on the individual electronic potential energy surface

$$i\hbar \frac{\partial \chi_i(\mathbf{R}(t), t)}{\partial t} = \sum_j \left[\left(T_{\text{nuc}} + \tilde{E}_i(t, \mathbf{R}) \right) \delta_{ij} - \hbar^2 \frac{\mathbf{d}_{ij}^{(1)}}{M} \cdot \nabla_{\mathbf{R}} - \hbar^2 \frac{d_{ij}^{(2)}}{2M} \right] \chi_j(\mathbf{R}(t), t). \quad (2.146)$$

where T_{nuc} is the nuclear kinetic energy and $\tilde{E}_i(t, \mathbf{R})$ represents the adiabatic potential energy surface obtained by solving the stationary Schrödinger equation:

$$H_{\text{el}}(\mathbf{r}, t; \mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R}(t)) = \tilde{E}_i(t, \mathbf{R}) \psi_i(\mathbf{r}; \mathbf{R}(t)), \quad (2.147)$$

and $\mathbf{d}_{ij}^{(1)}$ and $d_{ij}^{(2)}$ are the first- and second-order NA couplings:

$$\mathbf{d}_{ij}^{(1)} = \langle \psi_i(\mathbf{r}; \mathbf{R}(t)) | \nabla_{\mathbf{R}} \psi_j(\mathbf{r}; \mathbf{R}(t)) \rangle, \quad (2.148)$$

$$d_{ij}^{(2)} = \langle \psi_i(\mathbf{r}; \mathbf{R}(t)) | \nabla_{\mathbf{R}}^2 \psi_j(\mathbf{r}; \mathbf{R}(t)) \rangle. \quad (2.149)$$

Similar to the uncorrected electronic energy $\tilde{E}_i(t, \mathbf{R})$, the second-order NA coupling term is a scalar quantity that depends parametrically on the nuclear coordinates. Its diagonal contributions can therefore be incorporated as a correction to the adiabatic potential energy surface, yielding the renormalized energy:

$$E_i(\mathbf{R}) = \tilde{E}_i(\mathbf{R}) - \hbar^2 \sum_j \frac{d_{ij}^{(2)}}{2M}. \quad (2.150)$$

The off-diagonal elements of the second-order coupling are usually omitted because they are assumed to be of higher-order and much smaller than the first-order derivative coupling term

$\left(\hbar^2 \frac{\mathbf{d}_{ij}^{(1)}}{M} \cdot \nabla_{\mathbf{R}}\right)$ [131, 132, 133]. Nevertheless, under specific conditions these terms may play an important role [134]. Incorporating the diagonal correction into the adiabatic potential energy surface, Eq. (2.146) can be cast into the simplified form:

$$i\hbar \frac{\partial \chi_i(\mathbf{R}(t), t)}{\partial t} = \sum_j \left[(T_{\text{nuc}} + E_i(t, \mathbf{R})) \delta_{ij} - \hbar^2 \frac{\mathbf{d}_{ij}^{(1)}}{M} \cdot \nabla_{\mathbf{R}} \right] \chi_j(\mathbf{R}(t), t). \quad (2.151)$$

A complete solution of the general TD-SE, Eq. (2.144) requires the simultaneous treatment of Eqs. (2.151) and (2.147), thereby describing the fully coupled electron–nuclear dynamics. The electronic part (Eq. (2.147)) corresponds to the stationary electronic Schrödinger equation, which can be solved using the well-established methods of solid-state electronic structure theory discussed earlier in this chapter. In contrast, solving the nuclear equations of motion (Eq. (2.151)) is considerably more challenging due to the high computational cost and complexity involved. This difficulty has motivated the development of advanced semiclassical approximations that form the foundation of modern NAMD methodologies.

2.6.2 Semiclassical NAMD

To make NAMD computationally tractable, PYXAID adopts a semiclassical description where nuclei are treated as classical point particles. Within this approximation, the operators in Eq. (2.151) are substituted using the classical nuclear momentum $\mathbf{P}$ as:

$$T_{\text{nuc}} \equiv -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \longrightarrow \frac{P^2}{2M}, \quad (2.152)$$

$$-\hbar^2 \frac{\mathbf{d}_{ij}^{(1)}}{M} \cdot \nabla_{\mathbf{R}} \longrightarrow -i\hbar \mathbf{d}_{ij}^{(1)} \cdot \frac{\mathbf{P}}{M}. \quad (2.153)$$

Although this semiclassical treatment substantially reduces the computational complexity, a fully self-consistent description in which the nuclei dynamically respond to changes in the electronic state—such as in on-the-fly surface hopping with force recalculation at every time step—remains prohibitively expensive for condensed-matter systems containing a large number of atoms.

To further simplify the problem, PYXAID employs the Classical Path Approximation (CPA) [52]. Within the CPA, the nuclei evolve along a precomputed classical trajectory $\mathbf{R}(t)$ that is assumed to be only weakly influenced by the electronic state. This approximation is justified when photoexcitation induces structural changes that are small compared to thermal nuclear fluctuations. Consequently, a single ground-state adiabatic molecular dynamics trajectory is generated and subsequently reused for all electronic calculations and stochastic realizations.

Under the CPA, the total wavefunction is expanded in the adiabatic basis:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{i=0}^{N_b-1} c_i(t) \psi_i(\mathbf{r}; \mathbf{R}(t)), \quad (2.154)$$

where N_b denotes the basis size. Substituting this ansatz into the TD-SE yields the equation of motion for the electronic amplitudes $c_i(t)$:

$$i\hbar \frac{dc_i(t)}{dt} = \sum_{j=0}^{N_b-1} (\varepsilon_i \delta_{ij} - i\hbar d_{ij}(t)) c_j(t). \quad (2.155)$$

where the time-dependent NA coupling is defined as

$$d_{ij}(t) = \left\langle \psi_i \left| \frac{\partial}{\partial t} \psi_j \right. \right\rangle = \mathbf{d}_{ij}^{(1)} \cdot \frac{\mathbf{P}}{M}. \quad (2.156)$$

In numerical implementations, this coupling is evaluated from the overlap of electronic wavefunctions at successive time steps:

$$d_{ij}(t) \approx \frac{\langle \psi_i(t) | \psi_j(t + \Delta t) \rangle - \langle \psi_i(t + \Delta t) | \psi_j(t) \rangle}{2\Delta t}. \quad (2.157)$$

Eq. (2.155) can be written in compact matrix form as

$$\frac{d\mathbf{c}}{dt} = \overleftrightarrow{H}(t) \mathbf{c}(t), \quad (2.158)$$

where the matrix $\overleftrightarrow{H}(t)$ contains the adiabatic energies on the diagonal ($H_{ii} = \varepsilon_i$) and the NA couplings on the off-diagonal elements ($H_{ij} = -i\hbar d_{ij}$). This Hamiltonian can be further extended to incorporate additional physical effects such as external electromagnetic fields [135, 136, 137] or spin-orbit coupling (SOC) [137, 138]:

$$H_{ij} = H_{ij}^{\text{NAC}} + H_{ij}^{\text{field}} + H_{ij}^{\text{SOC}}. \quad (2.159)$$

2.6.3 Integration schemes for the TD-SE

The temporal evolution of the electronic subsystem is dictated by the TD-SE in Eq. (2.158). Consequently, implementing a numerically stable and efficient integration scheme is a fundamental prerequisite for accurately capturing these dynamics. Within the CPA, the nuclear trajectory is precomputed independently of the electronic dynamics, leading to two distinct propagation time scales: the nuclear time step, dt_{nuc} , used to evolve the ionic motion, and the considerably smaller electronic time step, dt_{el} , employed for propagating the electronic degrees of freedom. Dynamical quantities are therefore labeled by the pair $(t_{\text{nuc}}; t_{\text{el}})$, with typically $n_{\text{el}} = dt_{\text{nuc}}/dt_{\text{el}}$ electronic substeps performed within each nuclear step.

To propagate the electronic coefficients, there are several numerical integration schemes ranging from simple finite-difference methods to advanced unitary propagators. These approaches differ in their numerical stability, conservation properties, computational cost, and scalability to large basis sets. The simplest implementations are second-order finite-difference schemes, such as the leapfrog/Euler algorithm, combined with either linear or symmetric interpolation of the Hamiltonian between consecutive nuclear time steps. Although computationally inexpensive per propagation step, these methods require extremely small electronic time steps ($dt_{\text{el}} \approx 1\text{--}10$ attoseconds) to maintain numerical stability and do not strictly conserve the norm of the wavefunction.

A more accurate alternative is provided by the analytic propagator, which assumes that the Hamiltonian remains approximately constant over a single nuclear time step and integrates the TD-SE exactly within each interval through matrix exponentiation. Because the Hamiltonian is Hermitian, the propagator can be evaluated through matrix diagonalization. This scheme is norm-conserving and time-reversible, allowing significantly larger electronic time steps, potentially up to dt_{nuc} . However, repeated diagonalization becomes computationally expensive for large active spaces.

To improve efficiency without sacrificing numerical stability—particularly for large basis sets and non-Markovian approaches—a propagator based on the Liouville–von Neumann formalism combined with symmetric Trotter factorization [139, 140] is employed. This approach preserves exact norm conservation and time reversibility while avoiding repeated diagonalization, making it especially suitable for large-scale NAMD simulations. The formalism underlying this scheme is discussed in the following subsection and is employed throughout the present work.

2.6.3.1 Liouville formalism and symmetric Trotter factorization

The equations of motion in Eq. (2.158) can be expressed in terms of the Liouville operator:

$$\begin{aligned}
 iL &= \sum_{i=0}^{N-1} \dot{c}_i \frac{\partial}{\partial c_i} \\
 &= \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} \left(-\frac{i}{\hbar} H_{ij} \right) c_j \frac{\partial}{\partial c_i} \\
 &= \sum_{i=0}^{N-1} \left(-\frac{i}{\hbar} H_{ii} \right) c_i \frac{\partial}{\partial c_i} + \sum_{i=0}^{N-1} \sum_{j>i}^{N-1} -\frac{i}{\hbar} \left(H_{ij} c_j \frac{\partial}{\partial c_i} + H_{ji} c_i \frac{\partial}{\partial c_j} \right)
 \end{aligned} \tag{2.160}$$

$$= \sum_{i=0}^{N-1} iL_i^{(1)} + \sum_{i=0}^{N-1} \sum_{j>i}^{N-1} iL_{ij}^{(2)}, \quad (2.161)$$

which can be written in a symmetric factorized form:

$$\begin{aligned} \exp(iL \cdot dt_{\text{el}}) = & \exp\left(i \sum_{i=0}^{N-1} L_i^{(1)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(iL_{01}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(iL_{02}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \cdots \\ & \exp\left(iL_{0(N-1)}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(iL_{12}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \cdots \exp\left(iL_{1(N-1)}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \\ & \cdots \exp\left(iL_{(N-2)(N-1)}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(iL_{(N-2)(N-1)}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \cdots \\ & \exp\left(iL_{1(N-1)}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \cdots \exp\left(iL_{12}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(iL_{0(N-1)}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \cdots \\ & \exp\left(iL_{02}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(iL_{01}^{(2)} \cdot \frac{dt_{\text{el}}}{2}\right) \exp\left(i \sum_{i=0}^{N-1} L_i^{(1)} \cdot \frac{dt_{\text{el}}}{2}\right). \end{aligned} \quad (2.162)$$

The elementary propagators $\exp(iL^{(1)}dt)$ and $\exp(iL^{(2)}dt)$ act as [53]:

$$\exp(iL_i^{(1)}dt): c_i \rightarrow \left[\cos\left(\frac{dt}{\hbar}\varepsilon_i\right) - i \sin\left(\frac{dt}{\hbar}\varepsilon_i\right) \right] c_i, \quad (2.163)$$

$$\exp(iL_{ij}^{(2)}dt): \begin{pmatrix} c_i \\ c_j \end{pmatrix} \rightarrow \begin{pmatrix} \cos(dt \cdot \beta_{ij}) & \sin(dt \cdot \beta_{ij}) \\ -\sin(dt \cdot \beta_{ij}) & \cos(dt \cdot \beta_{ij}) \end{pmatrix} \begin{pmatrix} c_i \\ c_j \end{pmatrix}, \quad (2.164)$$

with $\alpha_i = -iH_{ii}/\hbar$ and $\beta_{ij} = -iH_{ij}/\hbar$. The phase propagators (2.163) govern the phase evolution of individual electronic states, whereas the transfer operators (2.164) describe population transfer between pairs of states. Since each elementary propagator is unitary, the norm of the propagated amplitudes is conserved exactly, ensuring strict conservation of the total wavefunction norm throughout the dynamics. This formulation permits the use of comparatively large electronic time steps while maintaining numerical stability. Furthermore, the symmetric Trotter decomposition in Eq. (2.162) guarantees time reversibility of the propagator, consistent with the underlying symmetry of the equations of motion. Compared to the analytic integration scheme, the principal advantage of this approach lies in the absence of matrix diagonalization. Because all propagation steps are explicit and computationally efficient, the method remains highly scalable and particularly well suited for simulations involving large basis sets.

2.6.4 Surface hopping algorithms

Solving the electronic TD-SE determines the coherent time evolution of the electronic coefficients $c_i(t)$. However, such a coherent superposition of adiabatic states does not directly

correspond to the observed physical picture, where the system is effectively localized on a particular electronic state. Trajectory surface hopping (TSH) methods address this issue by propagating an ensemble of classical nuclear trajectories while allowing stochastic transitions between adiabatic electronic states [141, 142].

The most widely used TSH framework is the **Fewest Switches Surface Hopping (FSSH)** method introduced by Tully [143, 144, 145]. In FSSH, the nuclei evolve classically on a single adiabatic potential energy surface at a given time, while stochastic hops between electronic states are introduced to reproduce the quantum populations obtained from the TD-SE. The probability for a transition from the current state i to another state j during a small time interval Δt is given by

$$g_{i \rightarrow j}(t) = \max \left(0, \frac{-2\Delta t \operatorname{Re} [c_i^*(t) H_{ij}(t) c_j(t)]}{|c_i(t)|^2} \right), \quad (2.165)$$

where the total probability of leaving state i is $g_i(t) = \sum_{j \neq i} g_{i \rightarrow j}(t)$. A random number $\xi \in [0, 1]$ is then compared with the cumulative hopping probabilities to determine whether a hop occurs and, if so, the final state of the trajectory.

Although FSSH successfully describes ultrafast relaxation processes in systems with dense manifolds of electronic states, it neglects electronic decoherence arising from the spatial separation of nuclear wave packets evolving on different electronic states (Fig. 2.13). In a fully

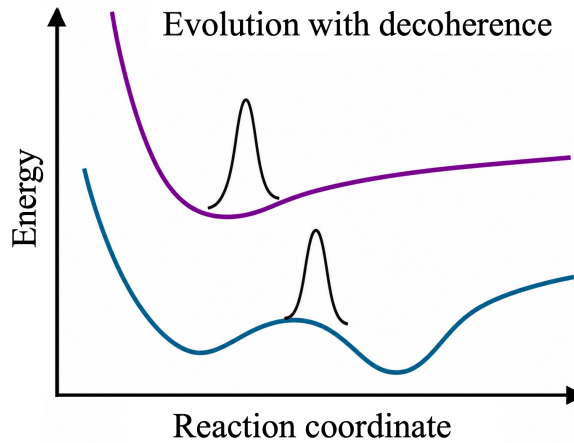


Figure 2.13: Schematic illustration of the divergence of nuclear wavepackets associated with different electronic states, leading to decoherence within the electronic subsystem. Such decoherence effects are absent in purely classical treatments of nuclear motion, as in FSSH, but can be incorporated within semiclassical approaches such as DISH.

quantum-mechanical treatment, this wavepacket divergence causes the off-diagonal elements

of the electronic density matrix to decay, converting a coherent superposition into a statistical mixture. Because nuclear motion is treated classically in standard FSSH, decoherence effects are not described consistently. As a result, FSSH often overestimates transition rates, particularly in systems with localized or energetically well-separated electronic states, such as molecules, quantum dots, and many semiconducting materials.

To explicitly incorporate decoherence within a surface-hopping framework, the decoherence-induced surface hopping (DISH) method was developed [146, 53]. In this approach, decoherence is interpreted as a stochastic collapse of the electronic wavefunction onto one of the adiabatic states according to the Born probability, $|c_i(t)|^2$. Such stochastic collapses mimic the loss of electronic phase coherence arising from the divergence of nuclear wavepackets evolving on different potential energy surfaces. The strong influence of decoherence on quantum dynamics is exemplified by the quantum Zeno effect [147, 148, 149, 150], in which frequent collapses can strongly suppress transitions and effectively localize the system in a particular state. By incorporating stochastic decoherence events, DISH naturally captures this physics and provides a more realistic description of long-timescale NA processes.

The DISH algorithm can be summarized through the following sequence of steps:

1. **Coherent propagation between decoherence events:** The electronic wavefunction is first propagated coherently by solving the TD-SE along the classical nuclear trajectory. For a given adiabatic state i , decoherence occurs when the elapsed time since the last collapse event, $t_i(t)$, exceeds the corresponding state-dependent decoherence time $\tau_i(t)$:

$$t_i(t) > \tau_i(t). \quad (2.166)$$

The decoherence time is evaluated as

$$\frac{1}{\tau_i(t)} = \sum_{\substack{j=1 \\ j \neq i}}^{N_b} |c_j(t)|^2 r_{ij}, \quad (2.167)$$

where r_{ij} denotes the pairwise decoherence rate between states i and j . Since $\tau_i(t)$ depends explicitly on the instantaneous electronic populations, the resulting dynamics possesses a non-Markovian character.

2. **Wavefunction collapse and projection:** Once a decoherence event is triggered for state i , the electronic wavefunction undergoes stochastic projection according to the Born

probability distribution. With probability $|c_i(t)|^2$, the wavefunction collapses onto state i . Otherwise, the decohered state is removed from the superposition by setting

$$c_i(t) \rightarrow 0, \quad (2.168)$$

followed by renormalization of the remaining amplitudes. After the collapse event, the decoherence timer $t_i(t)$ is reset to zero.

3. **Surface hopping procedure:** A change of the active electronic surface occurs in two possible situations:

- (a) If the wavefunction collapses onto state i and the nuclei are not currently evolving on this state, the trajectory hops to surface i .
- (b) If state i is projected out while the nuclei are propagating on surface i , the trajectory hops to another state $j \neq i$ with probability proportional to $|c_j(t)|^2$.

4. **Detailed balance correction within CPA:** Under CPA, upward transitions in energy are weighted by a Boltzmann factor

$$\exp\left(-\frac{E_j - E_i}{k_B T}\right), \quad E_j > E_i. \quad (2.169)$$

in order to maintain detailed balance:

In practical implementations, the decoherence rates r_{ij} are precomputed along the classical molecular dynamics trajectory using the optical response formalism [151, 152, 153, 154]. This approach provides a parameter-free and experimentally motivated description of decoherence, since the associated pure-dephasing times are directly related to homogeneous spectral linewidths. By explicitly incorporating stochastic decoherence events, the DISH framework provides a physically consistent description of both ultrafast carrier relaxation and slower non-radiative recombination processes in condensed-matter systems.

2.7 Density functional perturbation theory

DFPT provides an efficient framework to study the response of a system to small external perturbations. Among such perturbations, lattice vibrations (phonons) play a central role, as they directly influence a wide range of physical properties, including thermal conductivity,

specific heat, thermal expansion, and scattering processes. Furthermore, electron–phonon interactions are crucial for understanding superconductivity and the temperature dependence of optical spectra [75]. This section outlines the linear-response formalism that forms the basis for implementing the method.

2.7.1 Lattice dynamics from electronic structure theory

Within the BO approximation, the nuclear motion is described by a Schrödinger equation in which electrons provide an effective potential energy surface. The nuclear wavefunction $\chi(\mathbf{R})$ and corresponding eigenvalues E satisfy:

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} + E(\mathbf{R}) \right] \chi(\mathbf{R}) = E \chi(\mathbf{R}), \quad (2.170)$$

where M_I and $\mathbf{R}_I$ denote the mass and position of the I -th nucleus, respectively, and $\mathbf{R} \equiv \{\mathbf{R}_I\}$ represents the full set of nuclear coordinates. The function $E(\mathbf{R})$ corresponds to the BO potential energy surface, obtained as the ground-state electronic energy for fixed ionic positions.

At equilibrium, the forces acting on all nuclei vanish:

$$\mathbf{F}_I \equiv -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0. \quad (2.171)$$

The vibrational properties are determined from the second derivatives of the total energy, i.e., the Hessian matrix:

$$\frac{1}{\sqrt{M_I M_J}} \frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} - \omega^2 = 0, \quad (2.172)$$

whose eigenvalues yield the phonon frequencies ω .

Using the Hellmann–Feynman theorem, the forces can be written as:

$$\mathbf{F}_I = -\left\langle \psi(\mathbf{R}) \left| \frac{\partial \hat{H}_{BO}}{\partial \mathbf{R}_I} \right| \psi(\mathbf{R}) \right\rangle, \quad (2.173)$$

where $\psi(\mathbf{R})$ is the electronic ground-state wavefunction and $\hat{H}_{BO}$ is the BO Hamiltonian:

$$\hat{H}_{BO} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (2.174)$$

The force can also be expressed in terms of the electronic density $n(\mathbf{r})$:

$$\mathbf{F}_I = -\int d\mathbf{r} n(\mathbf{r}) \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{II}(\mathbf{R})}{\partial \mathbf{R}_I}, \quad (2.175)$$

where

$$E_{II}(\mathbf{R}) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad V_{\text{ext}}(\mathbf{r}) = - \sum_I \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}|}. \quad (2.176)$$

Taking derivatives of the forces leads to the interatomic force constants:

$$\frac{\partial^2 E(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} = \int d\mathbf{r} \frac{\partial n(\mathbf{r})}{\partial \mathbf{R}_J} \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}_I} + \int d\mathbf{r} n(\mathbf{r}) \frac{\partial^2 V_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}_I \partial \mathbf{R}_J} + \frac{\partial^2 E_{II}(\mathbf{R})}{\partial \mathbf{R}_I \partial \mathbf{R}_J}. \quad (2.177)$$

2.7.2 Linear response formulation

To compute the variation of the electronic density and wavefunctions, DFPT employs first-order perturbation theory. The change in KS orbitals $|\psi_n\rangle$ is obtained from:

$$(\hat{H}_{\text{SCF}} - \epsilon_n) |\Delta\psi_n\rangle = -(\Delta V_{\text{SCF}} - \Delta\epsilon_n) |\psi_n\rangle. \quad (2.178)$$

Here, the self-consistent Hamiltonian is given by:

$$\hat{H}_{\text{SCF}} = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{SCF}}(\mathbf{r}), \quad (2.179)$$

with

$$V_{\text{SCF}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}(\mathbf{r}). \quad (2.180)$$

The first-order variation of the potential is:

$$\Delta V_{\text{SCF}}(\mathbf{r}) = \Delta V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{dV_{xc}}{dn}|_{n=n(\mathbf{r})} \Delta n(\mathbf{r}), \quad (2.181)$$

and the corresponding eigenvalue correction is:

$$\Delta\epsilon_n = \langle \psi_n | \Delta V_{\text{SCF}} | \psi_n \rangle. \quad (2.182)$$

For non-magnetic systems, the first-order change in the charge density is:

$$\Delta n(\mathbf{r}) = 4 \sum_{n=1}^{N/2} \psi_n^*(\mathbf{r}) \Delta\psi_n(\mathbf{r}). \quad (2.183)$$

The correction to the wavefunction can be expressed as:

$$\Delta\psi_n(\mathbf{r}) = \sum_{m \neq n} \frac{\psi_m(\mathbf{r}) \langle \psi_m | \Delta V_{\text{SCF}} | \psi_n \rangle}{\epsilon_n - \epsilon_m}. \quad (2.184)$$

Substituting the above expression into the density variation given in Eq.(2.183) yields:

$$\Delta n(\mathbf{r}) = 4 \sum_{n=1}^{N/2} \sum_{m \neq n} \psi_n^*(\mathbf{r}) \psi_m(\mathbf{r}) \frac{\langle \psi_m | \Delta V_{\text{SCF}} | \psi_n \rangle}{\epsilon_n - \epsilon_m}. \quad (2.185)$$

The contributions involving only occupied states cancel, leaving terms involving transitions to unoccupied (conduction) states. To avoid explicit summation over empty states, a projection operator onto the unoccupied subspace,

$$P_c = 1 - \sum_v |\psi_v\rangle\langle\psi_v|, \quad (2.186)$$

is introduced. The linear equation is then reformulated as:

$$\left(\hat{H}_{\text{SCF}} + \alpha P_v - \epsilon_v\right) |\Delta\psi_v\rangle = -P_c \Delta V_{\text{SCF}} |\psi_v\rangle, \quad (2.187)$$

where P_v projects onto occupied states. This equation can be solved iteratively with trial functions orthogonal to the occupied manifold, resulting in a computational effort comparable to standard self-consistent KS calculations.

2.8 Polarons

In polar semiconductors, charge carriers do not propagate as bare particles but interact strongly with the surrounding ionic lattice. This interaction induces a redistribution of charges, generating a polarization field that screens the carrier and accompanies it during its motion. As originally proposed by Landau [155] and later formulated by Pekar [156], this self-induced lattice distortion gives rise to a composite QP—consisting of the charge carrier dressed by its polarization cloud—known as a *polaron* (Fig. 2.14).

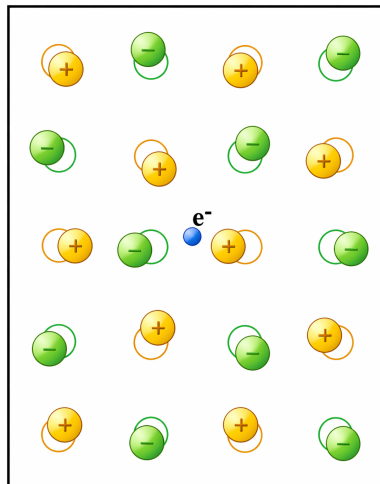


Figure 2.14: Schematic illustration of a polaron in a polar crystal. The charge carrier induces a lattice polarization, forming a coupled electron–phonon QP.

The presence of the polarization cloud modifies the intrinsic properties of the carrier, leading to mass renormalization, finite self-energy, and altered transport behavior. Depending on the

spatial extent of the lattice distortion, polarons are classified into two limiting regimes. When the distortion extends over many lattice sites, the continuum *large polaron* (Fröhlich) model applies, dominated by long-range coupling to longitudinal optical (LO) phonons. By contrast, when the distortion is strongly localized, a *small polaron* (Holstein type) forms. The materials studied in this work fall within the large-polaron or intermediate regime, justifying the use of the Fröhlich Hamiltonian.

2.8.1 Fröhlich Hamiltonian and coupling constant

The long-range electron–phonon interaction is well described by the Fröhlich Hamiltonian [77], in which the lattice is treated as a polarizable dielectric continuum. For a carrier of effective mass m^* , the Hamiltonian reads

$$H = \frac{\mathbf{p}^2}{2m^*} + \sum_{\mathbf{q}} \hbar\omega_{\text{LO}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{\mathbf{q}} \left(V_{\mathbf{q}} a_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} + V_{\mathbf{q}}^* a_{\mathbf{q}}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}} \right), \quad (2.188)$$

where the first term describes the carrier kinetic energy, the second—the LO phonons, and the last—their interaction. The coupling matrix element exhibits a characteristic long-range Coulomb form,

$$|V_{\mathbf{q}}| = \frac{\hbar\omega_{\text{LO}}}{q} \left(\frac{4\pi\alpha}{V} \frac{\hbar}{2m^*\omega_{\text{LO}}} \right)^{1/2}. \quad (2.189)$$

Here, α denotes the dimensionless Fröhlich coupling constant, which quantifies the strength of the electron–phonon interaction and is defined as

$$\alpha = \frac{1}{\epsilon^*} \sqrt{\frac{R_\infty}{\hbar\omega_{\text{LO}}}} \sqrt{\frac{m^*}{m_0}}, \quad \frac{1}{\epsilon^*} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}, \quad (2.190)$$

where ϵ_∞ and ϵ_0 denote the high-frequency and static dielectric constants, respectively, while ω_{LO} denotes the LO phonon frequency.

2.8.2 Feynman variational approach

A direct solution of the Fröhlich Hamiltonian is complicated by the time-retarded nature of the electron–phonon interaction. Feynman resolved this difficulty by rewriting the problem using the imaginary-time path integral [157]. After integrating out the phonons exactly, the electron is described by the effective action

$$S_{\text{eff}}[\mathbf{r}(\tau)] = \int_0^\beta d\tau \frac{m^*}{2} |\dot{\mathbf{r}}|^2 - \frac{\alpha\hbar\omega_{\text{LO}}}{2\sqrt{2}} \int_0^\beta d\tau \int_0^\beta d\sigma \frac{e^{-\omega_{\text{LO}}|\tau-\sigma|}}{|\mathbf{r}(\tau) - \mathbf{r}(\sigma)|}. \quad (2.191)$$

To obtain analytic expressions, Feynman introduced a quadratic trial action

$$S_{\text{trial}} = \int_0^\beta d\tau \frac{m^*}{2} |\dot{\mathbf{r}}|^2 + \frac{m^*(v^2 - w^2)}{2v} \int_0^\beta d\tau \int_0^\beta d\sigma e^{-w|\tau - \sigma|} |\mathbf{r}(\tau) - \mathbf{r}(\sigma)|^2, \quad (2.192)$$

which describes the electron harmonically coupled to a fictitious particle representing the polarization cloud. The variational parameters v and w are optimized using the Jensen–Feynman inequality or, at finite temperature, using the extension by Ōsaka.

The renormalized polaron mass follows from the curvature of the polaron dispersion within the Feynman model:

$$m_p = m^* \frac{v}{w}. \quad (2.193)$$

In the weak-coupling limit, the variational solution reduces to the perturbative expansion

$$\frac{m_p}{m^*} = 1 + \frac{\alpha}{6} + \frac{\alpha^2}{40} + \mathcal{O}(\alpha^3). \quad (2.194)$$

Further, the width of the relative electron–cloud coordinate yields the polaron radius in the Schultz definition [158]:

$$r_f = \sqrt{\frac{\hbar}{m^* \omega_{\text{LO}}}} f(v, w), \quad (2.195)$$

where $f(v, w)$ is evaluated using the optimized variational parameters.

2.8.3 Polaron mobility

The temperature-dependent DC mobility is evaluated using the linear-response formalism developed by Hellwarth and co-workers [159, 160, 161, 11]. The mobility takes the form

$$\mu_p = \frac{3\sqrt{\pi}e}{m^* \alpha \omega_{\text{LO}}} \frac{\sinh(\beta/2)}{\beta^{5/2}} \frac{w^3}{v^3} \frac{1}{K(a, b)}, \quad (2.196)$$

where $\beta = \hbar \omega_{\text{LO}} / k_B T$ and $K(a, b)$ is the polaron response kernel,

$$K(a, b) = \int_0^\infty du \left[u^2 + a^2 - b \cos(vu) \right]^{-3/2} \cos(u). \quad (2.197)$$

The auxiliary parameters are

$$a^2 = (\beta/2)^2 + \frac{(v^2 - w^2)}{w^2 v} \beta \coth(\beta v/2), \quad (2.198)$$

$$b = \frac{(v^2 - w^2)}{w^2 v} \frac{\beta}{\sinh(\beta v/2)}. \quad (2.199)$$

This formulation directly links the microscopic material properties (ϵ_∞ , ϵ_0 , ω_{LO} , m^*) to the macroscopic charge-carrier mobility. In this work, these quantities are computed using the

`PolaronMobility.jl` package developed by Frost [11], which implements the Fröhlich Hamiltonian, Feynman's variational path-integral approach, and the finite-temperature mobility theory of Hellwarth and co-workers [159]. When parametrized with *ab initio* data, this unified framework enables predictive evaluation of polaron formation, mass renormalization, and charge-transport behavior in perovskite-inspired materials.

Theoretical Insights into Inorganic Antiperovskite Nitrides (X_3NA ; $X = \text{Mg, Ca, Sr, Ba}$; $A = \text{As, Sb}$): An Emerging Class of Materials for Photovoltaics

3.1 Introduction

Lead halide perovskites have emerged as leading materials in photovoltaic research due to their exceptional electronic and optical properties. Their power-conversion efficiencies (PCEs) have increased dramatically from 3.8% in 2009 to over 27% in 2026 [162, 163, 13]. Despite these remarkable advances, their long-term operational instability and susceptibility to environmental degradation remain major obstacles to large-scale commercial deployment [22, 23]. These limitations have driven extensive efforts toward the discovery of lead-free alternatives that retain comparable optoelectronic performance while offering improved structural stability.

In this context, antiperovskites—formed by reversing the ionic configuration in conventional perovskites—have recently attracted considerable attention [2, 3, 164, 4, 5, 165]. These materials adopt the general chemical formula X_3BA , where X is a cation and A and B are anions of different sizes [27]. This inverted ionic arrangement results in fundamentally distinct band-edge compositions compared to halide perovskites, thereby broadening the accessible design space for functional materials.

A number of theoretical studies have explored the electronic properties of inorganic antiperovskites [28, 29, 30, 166, 167, 168, 169]. For instance, Mochizuki *et al.* [170] examined the structural stability and electronic properties of both known and yet-unsynthesized compounds, identifying candidates with favorable light-absorption characteristics. Zhong *et al.* [171] established correlations between the tolerance factor and key physical properties such as the band gap, dielectric constant, and Young's modulus, providing guidelines for photovoltaic material

design. While hybrid antiperovskites have been proposed theoretically [172, 173], experimental validation of their photovoltaic potential remains limited. In contrast, several nitride-based inorganic antiperovskites (i.e., X_3NA , $X = \text{Mg, Ca, Sr, Ba}$; $A = \text{P, As, Sb, Bi}$) have, however, been successfully synthesized [4, 5, 165] and exhibit promising electronic characteristics. However, most previous studies have primarily focused on electronic structure, while detailed investigations of excitonic and polaronic effects—crucial for understanding optical response and materials’ suitability for optoelectronic applications—remain scarce.

To address this gap, this chapter presents a systematic investigation of the electronic, optical, excitonic, and polaronic properties of selected antiperovskite nitrides, namely Mg_3NSb , Ca_3NSb , Sr_3NSb , Ba_3NSb , Ca_3NAs , and Sr_3NAs . By combining density-functional theory (DFT) with hybrid exchange–correlation functionals [92, 91] and many-body perturbation theory (MBPT) [121, 174], we systematically analyze the electronic structure, evaluate the electronic and ionic contributions to the dielectric screening, and compute exciton binding energies, electron-phonon coupling strengths, and charge-carrier mobilities.

3.2 Computational methodology

First-principles calculations are performed within the framework of DFT [85, 86] using the Vienna *Ab initio* Simulation Package (VASP) [93, 94], which employs the projector augmented-wave (PAW) method [93, 111], and the full-potential all-electron code **exciting** [96], based on the linearized augmented plane-wave (LAPW) method. Experimental crystal structures [2, 5, 4] are adopted as initial inputs, with the corresponding lattice parameters listed in Table 3.4.

Structural relaxations are carried out using VASP within the generalized gradient approximation (GGA) employing the Perdew–Burke–Ernzerhof (PBE) functional [88]. Atomic positions are optimized until the Hellmann–Feynman forces fall below 0.01 eV/Å, while the total energy is converged to within 0.01 meV. A plane-wave kinetic energy cutoff of 550 eV is used throughout. Γ -centered k -point meshes of $6 \times 6 \times 6$, $4 \times 4 \times 3$, and $4 \times 4 \times 4$ are adopted for the $Pm\bar{3}m$, $Pbnm$, and $P6_3/mmc$ phases, respectively. Dynamical stability is assessed by computing phonon dispersion relations using the PHONOPY package [175, 176] with $2 \times 2 \times 2$ supercells. In **exciting**, muffin-tin radii of 1.89, 2.01, 2.07, and 2.47 Bohr are used for N, Mg, Sr, and Sb, respectively, with a basis-set cutoff defined by $R_{\text{MT}}|G + k|_{\text{max}} = 8.0$.

Electronic band structures and densities of states are computed using both semilocal PBE and

hybrid HSE06 [92] exchange–correlation functionals. Spin–orbit coupling (SOC) is included in all calculations. Effective carrier masses are obtained by parabolic fitting of the band edges using the SUMO package [177]. Many-body quasiparticle corrections are incorporated via GW calculations [121, 174]. Both single-shot GW (G_0W_0) and self-consistent GW (sc GW) approaches are considered. While G_0W_0 calculations exhibit a strong dependence on the underlying DFT starting point, sc GW provides reduced sensitivity at significantly higher computational cost. To assess the reliability of the G_0W_0 approach, benchmark calculations are performed for Mg_3NSb and Sr_3NSb (Table 3.1). The close agreement between sc GW and G_0W_0 @HSE06 results justifies the use of G_0W_0 @HSE06 for all systems studied, ensuring a balance between accuracy and computational efficiency. The number of unoccupied bands in-

Table 3.1: Fundamental band gaps (in eV) of Mg_3NSb and Sr_3NSb obtained using G_0W_0 and sc GW methods including SOC.

X_3NA	G_0W_0 @PBE	G_0W_0 @HSE06	sc GW
Mg_3NSb	0.88	1.41	1.47
Sr_3NSb	0.50	1.14	1.20

cluded in the GW calculations is carefully converged. Representative convergence tests for Mg_3NSb are presented in Table 3.2, and optimal values of 120 for X_3NSb ($\text{X} = \text{Mg}, \text{Ca}, \text{Sr}$), 360 for Ba_3NSb , and 640 for X_3NAs ($\text{X} = \text{Ca}, \text{Sr}$) are identified.

Table 3.2: Convergence of the G_0W_0 @PBE band gap (in eV), without SOC, with respect to the number of empty bands for Mg_3NSb .

Empty bands	60	120	180	240
E_g (eV)	1.04	1.14	1.15	1.14

To incorporate excitonic effects, we solve the Bethe–Salpeter equation (BSE) [178, 179, 47] within the Tamm–Dancoff approximation on top of G_0W_0 @HSE06. The BSE Hamiltonian is constructed using 22 occupied and 22 unoccupied states, as validated by convergence tests (Fig. 3.1). In these compounds, the small exciton binding energies indicate weakly bound Wannier-like excitons that are spatially extended in real space but localized near the band extrema in reciprocal space. Consequently, accurate BSE calculations require dense k -point sam-

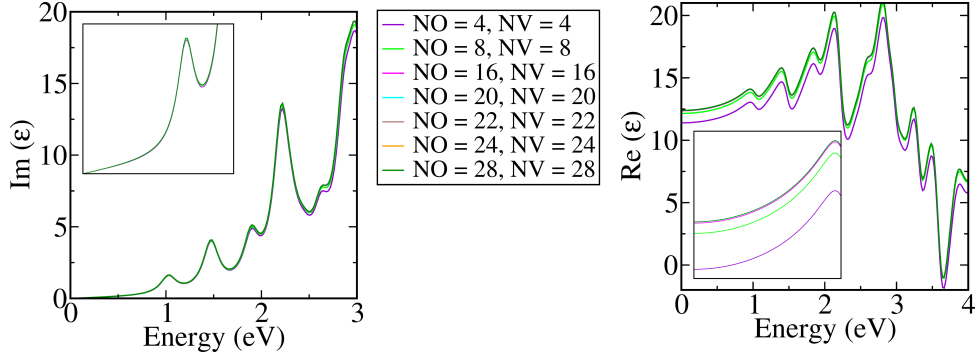


Figure 3.1: Convergence of the dielectric function of Mg_3NSb with the number of occupied (NO) and unoccupied (NV) orbitals in the BSE formalism.

pling, which poses significant computational challenges, particularly at the $G_0W_0@HSE06$ level. The optical spectra of Mg_3NSb computed using $\text{BSE}@G_0W_0@HSE06$ for $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $6 \times 6 \times 6$ k -grids are shown in Fig. 3.2. A systematic shift in the position of the first excitonic peak with increasing k -grid density highlights the slow convergence of excitonic features. However, achieving fully converged spectra within the full BSE framework is computationally prohibitive, especially in larger systems.

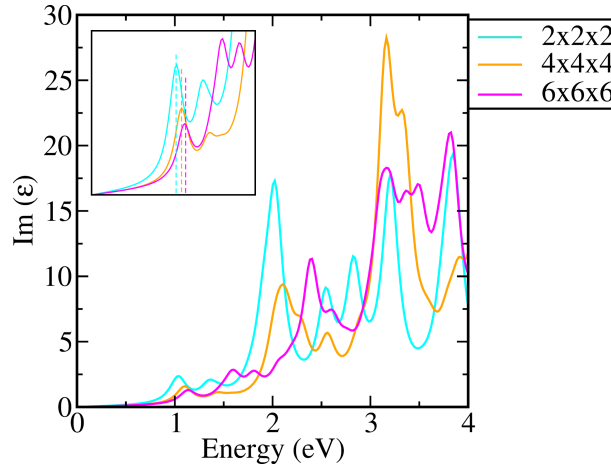


Figure 3.2: Optical spectra obtained by $\text{BSE}@G_0W_0@HSE06$ using $2 \times 2 \times 2$, $4 \times 4 \times 4$, and $6 \times 6 \times 6$ k -grids for Mg_3NSb .

To systematically quantify the impact of k -point sampling beyond the limits of full BSE calculations, we employ the model BSE (mBSE) approach [43] on top of PBE for Mg_3NSb . Within this framework, the screened Coulomb interaction is approximated by neglecting the off-diagonal elements of $W_{GG'}$, and a scissor operator—defined as the difference between the GW and DFT band gaps—is applied to correct the electronic structure. The mBSE calculations reveal a strong dependence of the exciton binding energy E_b on k -grid density. In particular, E_b decreases by nearly 50% when increasing the grid from $6 \times 6 \times 6$ to $10 \times 10 \times 10$ (Table 3.3), demonstrating

that insufficient k -point sampling leads to a substantial overestimation of exciton binding energies in BSE-type calculations. Calculations beyond a $10 \times 10 \times 10$ grid are computationally unfeasible.

Table 3.3: Exciton binding energy E_b (in meV) for Mg_3NSb using the mBSE approach.

k -grid	$6 \times 6 \times 6$	$8 \times 8 \times 8$	$10 \times 10 \times 10$
E_b	131.3	98.3	77.3

Owing to the prohibitive computational cost of fully converged BSE results and the small magnitude of the exciton binding energies, a fully first-principles description becomes impractical. Therefore, the final quantitative evaluation of excitonic properties—including binding energies, radii, and electron–hole probability densities—is carried out using the Wannier–Mott effective-mass model [46]. This approach is well justified for weakly bound, spatially extended excitons and provides a computationally efficient alternative to first-principles methods. In this framework, the electronic contribution to dielectric screening is obtained from $\text{BSE}@G_0W_0@\text{HSE06}$, while the ionic contribution is computed separately using density functional perturbation theory (DFPT) [75] with $20 \times 20 \times 20$, $16 \times 16 \times 16$, and $14 \times 14 \times 14$ k -point grids for the $Pm\bar{3}m$, $Pbnm$, and $P6_3/mmc$ phases, respectively.

Carrier–phonon interactions are further described within the Fröhlich polaron framework [77], employing the Hellwarth [159] and Feynman [157, 11] formalisms to evaluate polaron parameters and charge-carrier mobilities.

3.3 Results and discussion

3.3.1 Crystal structure and stability

To assess the structural stability of X_3NA antiperovskites, we first evaluate the Goldschmidt tolerance factor, t [180, 181], a widely used descriptor for perovskite formability. It is defined as

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)} \quad (3.1)$$

where r_A , r_B , and r_X are the ionic radii of the anions A and B, and the cation X, respectively. Typically, t is calculated using Shannon’s ionic radii. However, Shannon radii are not reported

Table 3.4: Space group, experimental lattice parameters, Goldschmidt tolerance factor t and distortion parameters: average bond length d_0 (Å), bond angle variance σ^2 (deg²), and bond length distortion index D , of X_3NA antiperovskites.

X_3NA	Space group	a (Å)	b (Å)	c (Å)	t	d_0 (Å)	σ^2 (deg ²)	$D \times 10^{-6}$
Mg_3NSb	$Pm\bar{3}m$	4.35 [2]	4.35	4.35	0.94	2.19	0	0
Ca_3NSb	$Pm\bar{3}m$	4.85 [3]	4.85	4.85	0.93	2.44	0	0
Sr_3NSb	$Pm\bar{3}m$	5.17 [4]	5.17	5.17	0.90	2.59	0	0
Ba_3NSb	$P6_3/mmc$	7.53 [4]	7.53	6.64	0.89	2.69	19.24	7
Ca_3NAs	$Pbnm$	6.72 [5]	6.71	9.52	0.86	2.40	0.05	777
Sr_3NAs	$Pbnm$	7.15 [5]	7.18	10.14	0.85	2.58	0.22	2004

for anionic pnictogens X^{3-} ($X = \text{N, P, As, Sb, Bi}$). Mochizuki *et al.* [170] report anionic radii of 1.37 Å, 1.90 Å, and 2.21 Å for N, As, and Sb, respectively. The calculated tolerance factors (Table 3.4) lie in the range 0.85–0.94, indicating overall structural stability across the series. For $X_3\text{NSb}$ ($X = \text{Mg, Ca, Sr}$), t values close to unity favor the formation of the ideal cubic $Pm\bar{3}m$ phase, in agreement with experimental observations [2, 3, 4]. In contrast, the reduced value of t for Ba_3NSb reflects increasing ionic size mismatch, leading to structural distortions and stabilization of the hexagonal $P6_3/mmc$ phase. A further decrease in t for Ca_3NAs and Sr_3NAs promotes octahedral tilting, resulting in orthorhombic $Pbnm$ structures. The unit cells of the ground-state structures of all phases are shown in Fig. 3.3. In the ideal cubic structure, (Fig. 3.3 (a)), the A-site anion (Sb^{3-}) occupies the cuboctahedral center, while B-site anions (N^{3-}) are located at the corners and are surrounded by six X-site cations, forming NX_6 octahedra.

To further quantify these distortions, we evaluate average bond lengths, bond-angle variances, and bond-length distortion indices (Table 3.4) using the following expressions [182, 183]:

$$\text{average bond length } (d_0) = \frac{\sum_{i=1}^6 d_i}{6} \quad (3.2)$$

$$\text{bond angle variance } (\sigma^2) = \frac{\sum_{i=1}^{12} (\theta_i - 90)^2}{11} \quad (3.3)$$

$$\text{Distortion index } (D) = \frac{1}{6} \frac{\sum_{i=1}^6 |d_i - d_0|}{6} \quad (3.4)$$

where, d_i is the individual N–X intraoctahedral bond length and θ_i are the X–N–X intraoctahe-

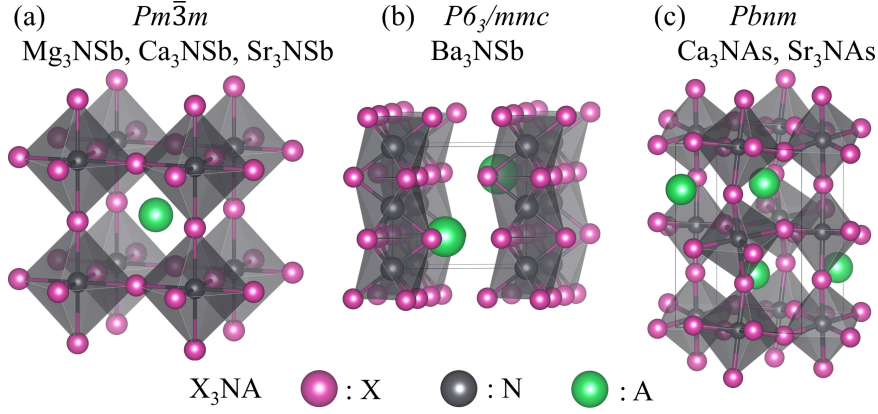


Figure 3.3: Unit cells of the antiperovskites X_3NA with space groups (a) $Pm\bar{3}m$, (b) $P6_3/mmc$, and (c) $Pbnm$. Mg_3NSb , Ca_3NSb , and Sr_3NSb crystallize in the cubic $Pm\bar{3}m$ phase in their ground state [2, 3, 4], whereas Ba_3NSb adopts a hexagonal $P6_3/mmc$ structure [4]. Ca_3NAs and Sr_3NAs crystallize in the orthorhombic $Pbnm$ phase [5].

dral bond angles. We observe a systematic increase in the average N–X bond length from Mg to Ba, reflecting the increasing ionic radius of the X-site cation. This trend enhances cation–anion repulsion, which destabilizes the ideal cubic framework and drives octahedral distortions, as evident in Ba_3NSb . In contrast, smaller A-site anions such as As promote cooperative tilting of the NX_6 octahedra, stabilizing lower-symmetry orthorhombic phases in Ca_3NAs and Sr_3NAs . The larger bond-angle variance and distortion index in Sr_3NAs compared to Ca_3NAs further highlight the role of cation size in amplifying structural distortions. To further confirm

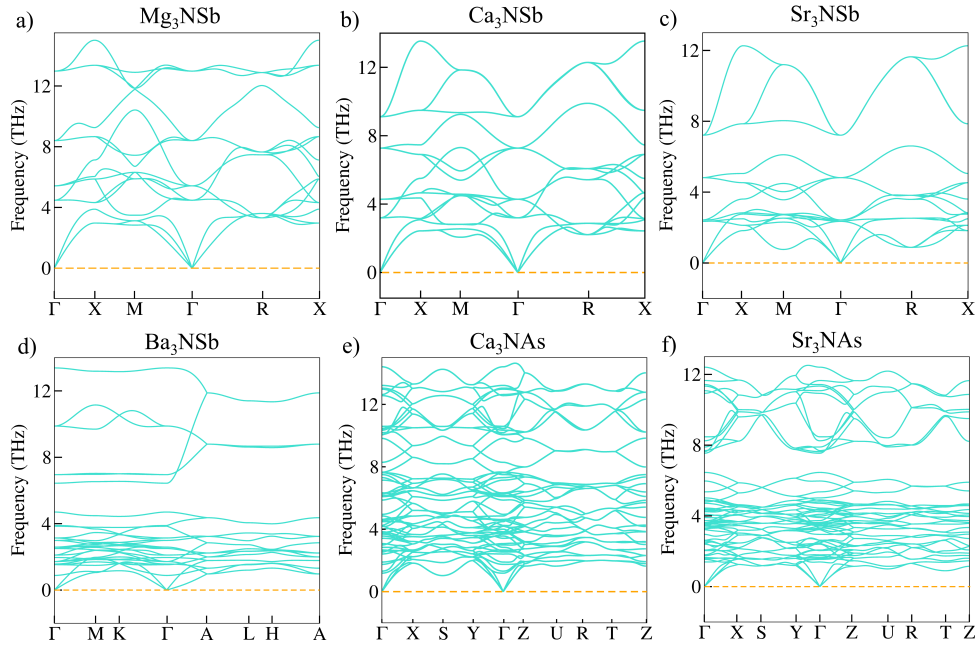


Figure 3.4: Phonon band structures obtained by DFPT using $2 \times 2 \times 2$ supercells of the X_3NA antiperovskites.

the dynamical stability, we compute phonon dispersion using DFPT (Fig. 3.4). The absence of imaginary frequencies across the Brillouin zone, demonstrate the dynamical stability of all investigated compounds.

3.3.2 Electronic structure

We begin by assessing the electronic structure using different levels of theory to establish a reliable description of the band gaps. As expected, the semilocal PBE functional significantly underestimates the band gaps (Table 3.5), a well-known limitation of this approach. In contrast, the hybrid HSE06 functional yields band gaps in much closer agreement with available experimental data, providing a more accurate starting point for subsequent many-body calculations. Electronic band structures obtained using HSE06 are shown in Fig. 3.5. All investigated

Table 3.5: Fundamental band gaps (in eV) for X_3NA antiperovskites computed using different levels of theory, including SOC effects. Values obtained using `exciting` are given in parentheses. With the exception of Mg_3NSb , all materials exhibit direct band gaps at the Γ point.

Material	PBE	HSE06	$G_0 W_0$ @PBE	$G_0 W_0$ @HSE06	Exp.
Mg_3NSb	0.55 (0.54)	1.23 (1.18)	0.88	1.41	$1.30^d, 1.10^i$ [165]
Ca_3NSb	0.41	1.02	1.09	1.33	-
Sr_3NSb	0.16 (0.19)	0.87 (0.87)	0.52	1.14	1.15 [4]
Ba_3NSb	0.50	1.16	1.36	1.57	-
Ca_3NAs	0.82	1.63	1.64	1.91	-
Sr_3NAs	0.71	1.56	1.14	1.52	-

compounds, except Mg_3NSb , exhibit direct band gaps at the Γ point. However, in Mg_3NSb , the conduction band minimum (CBM) is located at the M point, and the valence band maximum (VBM) lies at Γ , resulting in an indirect band gap. To incorporate many-body effects, we perform $G_0 W_0$ @HSE06 calculations, which yield substantial quasiparticle corrections to the band gaps. The resulting values—1.41 eV (Mg_3NSb), 1.33 eV (Ca_3NSb), 1.14 eV (Sr_3NSb), 1.57 eV (Ba_3NSb), 1.91 eV (Ca_3NAs), and 1.52 eV (Sr_3NAs)—all lie below 2 eV, placing these materials within the optimal range for photovoltaic absorption. Notably, the result for Sr_3NSb is in excellent agreement with experiment [4], while a slight overestimation is observed for Mg_3NSb [165]. Parabolic fitting of the band edges leads to estimation of effective electron and

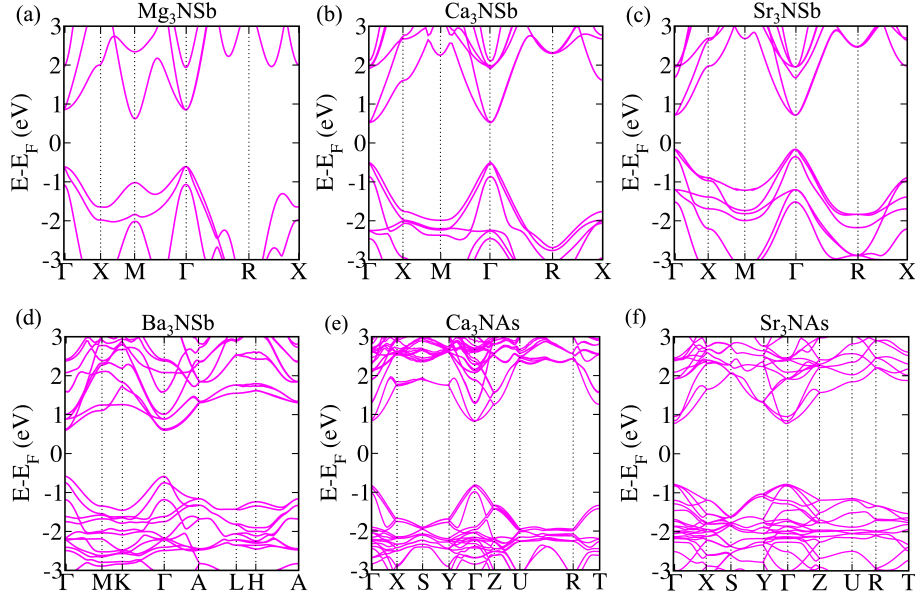


Figure 3.5: Electronic band structures of (a) Mg_3NSb , (b) Ca_3NSb , (c) Sr_3NSb , (d) Ba_3NSb , (e) Ca_3NAs , and (f) Sr_3NAs obtained by HSE06.

hole masses (Table 3.5) which are smaller than the free-electron mass, indicating potentially high charge-carrier mobilities. In Sr_3NSb , Ba_3NSb , and Ca_3NAs , the hole effective mass is smaller than the electron effective mass, suggesting enhanced hole transport. The calculated values are in good agreement with previous reports [170, 29].

Table 3.6: Effective electron mass (m_e^*), hole mass (m_h^*), and reduced mass (μ), in units of the free electron mass m_0 , obtained from parabolic fitting of HSE06 band edges using the SUMO package [9].

	Mg_3NSb	Ca_3NSb	Sr_3NSb	Ba_3NSb	Ca_3NAs	Sr_3NAs
m_e^*	0.18	0.21	0.23	0.76	0.37	0.14
m_h^*	0.34	0.23	0.21	0.17	0.32	0.62
μ	0.12	0.11	0.11	0.14	0.17	0.12

Figure 3.6 shows the atom- and symmetry-projected partial densities of states (PDOS) obtained using the HSE06 functional. In Mg_3NSb , the VBM is dominated by hybridized N- p and Sb- p states, whereas the CBM primarily originates from Mg- s orbitals, enabling optically allowed p - s transitions. In Ca_3NSb , Sr_3NSb , Ba_3NSb , Ca_3NAs , and Sr_3NAs , the VBM mainly consists of hybridized N- p and A- p states, while X- d orbitals dominate the CBM. Consequently, dipole-allowed p - d transitions are expected. These findings reveal a striking distinction from conventional halide perovskites: in the studied antiperovskites, the A-site anion actively contributes to the band edges, thereby playing a pivotal role in shaping both the electronic structure

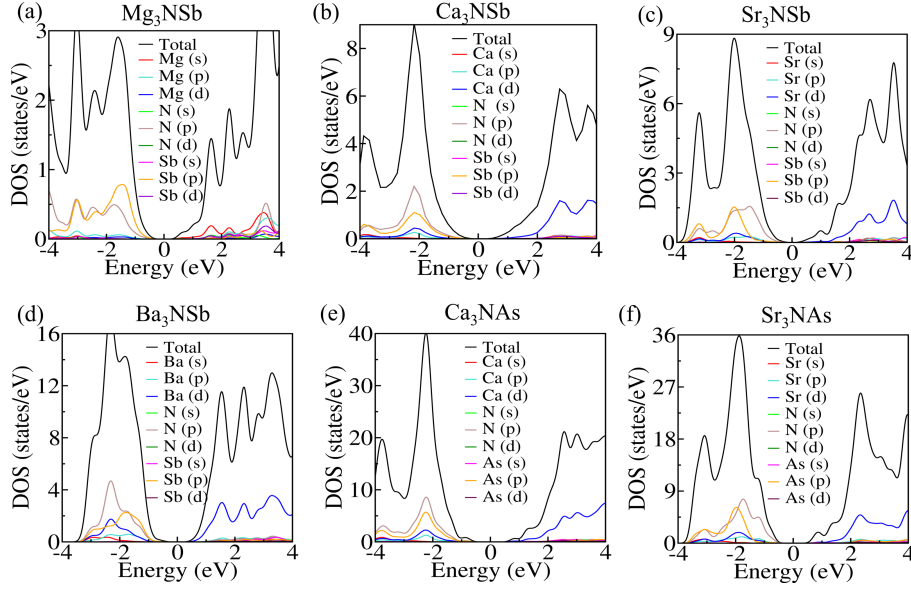


Figure 3.6: Atom-projected partial density of states (PDOS) of (a) Mg_3NSb , (b) Ca_3NSb , (c) Sr_3NSb , (d) Ba_3NSb , (e) Ca_3NAs , and (f) Sr_3NAs obtained by HSE06.

and the optical transitions.

3.3.3 Dielectric and excitonic properties

Although these materials exhibit favorable band gaps and low effective carrier masses, such characteristics alone are insufficient to establish their suitability as photovoltaic absorbers. The formation of bound electron–hole pairs (excitons) can impede charge separation and thus warrants careful evaluation. Accordingly, we examine their optical response and excitonic properties at the absorption onset. The exciton stability is quantified by the binding energy E_b , defined as the difference between the fundamental (quasiparticle) gap and the optical absorption onset.

Given the small exciton binding energies and the associated Wannier-like character of excitons in these systems, we employ the Wannier–Mott effective-mass model [46] to estimate E_b . According to this model, E_b is expressed as

$$E_b = \frac{\mu}{\epsilon_{eff}^2} R_\infty, \quad (3.5)$$

where μ is the reduced mass, R_∞ is the Rydberg constant, and ϵ_{eff} is the effective dielectric constant which lies between the high-frequency value ϵ_∞ and the long-wavelength limit ϵ_0 . ϵ_∞ and ϵ_0 are the zero frequency limits of the electronic ($\epsilon_e = 1 + 4\pi\alpha_e$) and total dielectric constants ($\epsilon_{total} = 1 + 4\pi(\alpha_e + \alpha_{ion})$), respectively (Table 3.7), where α_e and α_{ion} are the

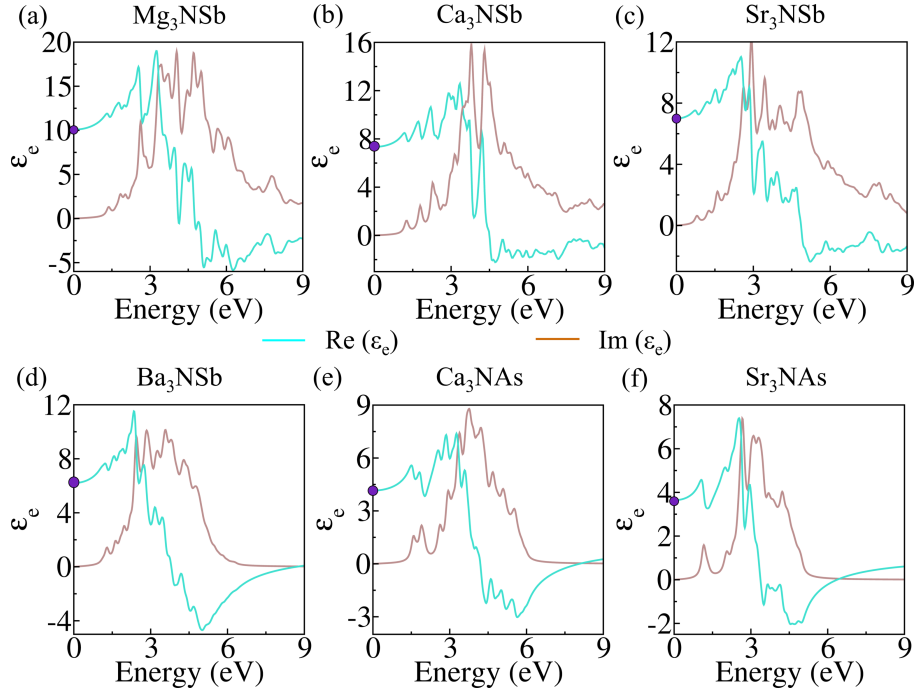


Figure 3.7: Real and imaginary part of the electronic dielectric function of the investigated antiperovskites obtained by BSE / $G_0 W_0$.

electronic and the ionic polarizability, respectively. Real and imaginary parts of ϵ_e , determined by the BSE on top of $G_0 W_0$ @HSE06 are depicted in Fig. 3.7. DFPT calculations are performed to compute the ionic contribution to the dielectric screening, $\epsilon_{ion} = 1 + 4\pi\alpha_{ion}$ (see Fig. 3.8). Hence, the total dielectric constant can be written as, $\epsilon_{total} = \epsilon_e + \epsilon_{ion} - 1$, with its zero-frequency limit, $\epsilon_0 = \epsilon_\infty + \epsilon_i - 1$. To the best of our knowledge, no experimental values for ϵ_{eff} have been reported in the literature. In non-polar materials, typically ϵ_0 does not differ from ϵ_∞ . In other words, contributions from the lattice screening can be ignored. This is, however, not the case in polar materials like perovskites [184, 185, 186, 187]. Depending on to which extent, the lattice contributions are effective, one ends up with an upper and a lower bound to the binding energy (Table 3.7).

In a recent study, Filip and colleagues [188] included the phonon screening into the expression of E_b using four distinct materials parameters i.e., the reduced effective mass (μ), static high and low frequency dielectric constants, and the longitudinal optical (LO) phonon frequency (ω_{LO}). The electronic and ionic contributions to the dielectric screening are illustrated in Fig. 3.7 and 3.8, respectively. For materials with multiple scattering channels due to different LO phonon modes, Hellwarth *et al.* [159] suggested two approximations to compute the effective LO phonon frequency $\omega_{LO,eff}$. Here, we use their athermal ‘B’ scheme [11] to estimate $\omega_{LO,eff}$

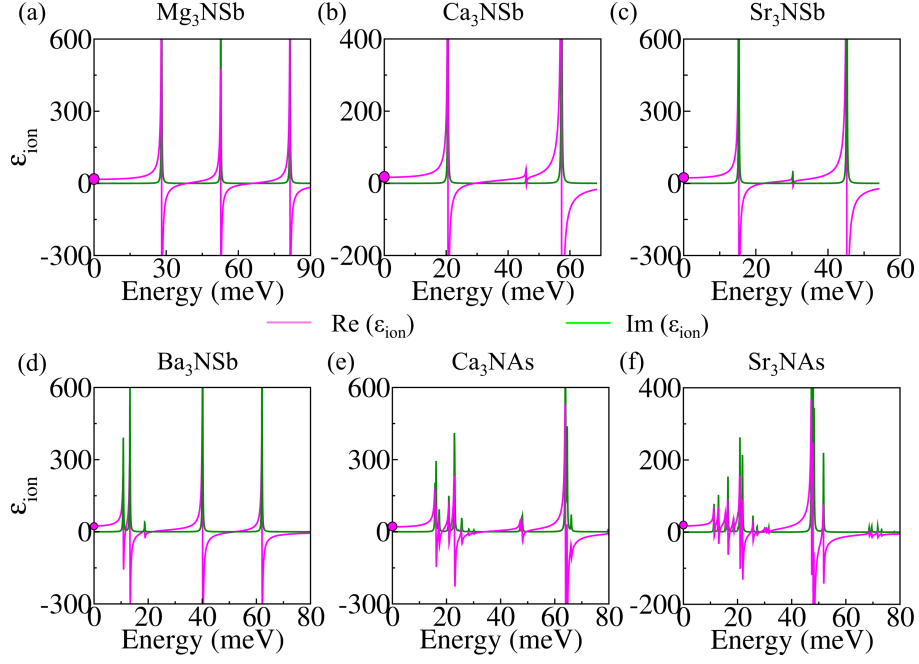


Figure 3.8: Real and imaginary part of the ionic dielectric function of the investigated antiperovskites obtained by DFPT.

using the following relations:

$$\frac{W_{LO,eff}^2}{\omega_{LO,eff}^2} = \sum_{i=1}^m \frac{W_{LO,i}^2}{\omega_{LO,i}^2} \quad (3.6)$$

$$W_{LO,eff}^2 = \sum_{i=1}^m W_{LO,i}^2, \quad (3.7)$$

where $\omega_{LO,i}$ is the frequency of the i^{th} -LO mode, $W_{LO,i}$ is the weight of the i^{th} -LO phonon mode, and $W_{LO,eff}$ is the effective weight from all the modes. Using these four parameters, we estimate the phonon-screening correction to the exciton binding energy, assuming isotropic and parabolic electronic band dispersion, which is given by the following expression:

$$\Delta E_b = -2\omega_{LO} \left(1 - \frac{\epsilon_\infty}{\epsilon_0} \right) \frac{\sqrt{1 + \frac{\omega_{LO}}{E_b}} + 3}{\left(1 + \sqrt{1 + \frac{\omega_{LO}}{E_b}} \right)^3} \quad (3.8)$$

We find (Table 3.7) that the contribution of phonon screening to E_b is significant in these materials and hence, cannot be neglected. After incorporating the phonon-screening correction, the values of E_b are 6 meV, 11 meV, 18 meV, 29 meV, 108 meV, and 102 meV for Mg_3NSb , Ca_3NSb , Sr_3NSb , Ba_3NSb , Ca_3NAs , and Sr_3NAs , respectively. Notably, for Mg_3NSb , Ca_3NSb and Sr_3NSb , E_b is smaller than $k_B T$ at room temperature, where k_B is the Boltzmann constant, while for Ba_3NSb , it is slightly larger. This implies that excitons can easily dissociate into free charge carriers in these materials. Moreover, these values are comparable with that of the well-known photovoltaic compound MAPbI_3 . However, Ca_3NAs and Sr_3NAs show higher exciton

Table 3.7: Upper bound ($E_{b,max}$) and lower bound ($E_{b,min}$) of exciton binding energies (in meV), obtained by considering ϵ_∞ or ϵ_0 , respectively, in the Wannier-Mott model; LO phonon frequency (ω_{LO}) at Γ ; correction to the exciton binding energy by phonon screening (ΔE_b) estimated using the static electronic dielectric constant (in meV), and percentage contribution of this phonon correction ($\frac{\Delta E_b}{E_b} \times 100(\%)$).

Material	ϵ_∞	$E_{b,max}$	ϵ_0	$E_{b,min}$	ω_{LO}	ΔE_b	$\frac{\Delta E_b}{E_b}(\%)$
Mg ₃ NSb	10.1	16	25.9	2	37	-10	41
Ca ₃ NSb	8.0	23	24.7	2	34	-12	52
Sr ₃ NSb	7.0	31	28.9	2	27	-13	39
Ba ₃ NSb	6.6	44	29.4	2	27	-15	32
Ca ₃ NAs	4.2	134	25.6	4	36	-26	19
Sr ₃ NAs	3.6	123	19.9	4	30	-21	16

binding energies. This behavior is also reflected in the exciton temperature, i.e., the temperature up to which an exciton is stable before dissociating into a free electron and a free hole. It can be estimated as $T_{exc} = E_b/k_B$. The resulting values along with other excitonic properties are summarized in Table 3.8.

We further determine the exciton radius using the expression:

$$r_{exc} = \frac{m_0}{\mu} \epsilon_{eff} a_0 \quad (3.9)$$

where $a_0 = 0.529\text{\AA}$ is the Bohr radius. We find that in all investigated materials, the electron-hole pairs are distributed over many lattice constants, justifying the use of the Wannier-Mott model. For good photo-conversion efficiency of solar cells, the exciton lifetime τ_{exc} should be high enough so that the photo-generated charge carriers can be extracted before recombination. τ_{exc} is proportional to the inverse probability of the electron-hole wavefunction at zero separation, $|\phi_n(0)|^2$, i.e., $\tau_{exc} \propto 1/|\phi_n(0)|^2$ with $|\phi_n(0)|^2 = 1/\pi r_{exc}^3$. We observe the following trend: $\tau_{exc}(\text{Ca}_3\text{NAs}) < \tau_{exc}(\text{Sr}_3\text{NAs}) < \tau_{exc}(\text{Ba}_3\text{NSb}) < \tau_{exc}(\text{Sr}_3\text{NSb}) < \tau_{exc}(\text{Ca}_3\text{NSb}) < \tau_{exc}(\text{Mg}_3\text{NSb})$. In summary, the antimonide nitrides $X_3\text{NSb}$ ($X = \text{Mg, Ca, Sr, Ba}$) have lower exciton binding energies, larger exciton radii, and longer exciton lifetimes than Ca_3NAs and Sr_3NAs , owing to relatively larger dielectric screening of the Coulomb interaction between electrons and holes, thus indicating better performance in photovoltaic applications.

Table 3.8: Exciton parameters for the studied antiperovskites. The corresponding properties of MAPbI_3 are listed for comparison [10].

Material	E_b (meV)	T_{exc} (K)	r_{exc} (nm)	$ \phi_n(0) ^2(10^{24}m^{-3})$
Mg_3NSb	6	110	5.8	1.6
Ca_3NSb	11	127	5.6	1.8
Sr_3NSb	18	216	4.3	3.9
Ba_3NSb	29	342	3.0	11.4
Ca_3NAs	108	1269	1.4	108.5
Sr_3NAs	102	1198	1.8	58.9
MAPbI_3	16 ^a	187	4.7	5.7

^a The reported experimental values of E_b lie within the range of 16–30 meV at low temperatures [43, 189, 44, 190, 191, 192].

3.3.4 Polaronic properties

Polar materials often exhibit polaron formation, which significantly influences charge-carrier transport. The interaction between charge carriers and polar lattice vibrations is well described by the Fröhlich model [77]. Fröhlich introduced a dimensionless coupling constant to quantify the strength of this interaction,

$$\alpha = \frac{1}{\epsilon^*} \sqrt{\frac{R_\infty}{\hbar\omega_{LO}}} \sqrt{\frac{m^*}{m_0}}, \quad (3.10)$$

where, ω_{LO} is the LO phonon frequency, $\hbar$ is the Planck constant, R_∞ is the Rydberg constant, m^* is the effective charge-carrier mass in units of the free-electron mass m_0 , and $\frac{1}{\epsilon^*} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}$ is an effective screening parameter. The computed carrier-phonon coupling constants (α), polaron masses ($\frac{m_p}{m^*}$), polaron radii (r_f), and carrier mobilities (μ_p) are summarized in Table 3.9. For both electrons and holes, we find that $\alpha \leq 2$, indicating weak coupling of the charge carriers with phonons. In this weak coupling regime, large polarons are formed. Their spatial extent can be estimated using the Schultz polaron radius r_f [158], confirming that in all cases the polarons extend over multiple unit cells. Feynman extended the Fröhlich's polaron model to give an expression for the effective polaron mass[157],

$$m_p = m^* \left(1 + \frac{\alpha}{6} + \frac{\alpha^2}{40} + \dots \right) \quad (3.11)$$

Based on this relation, the effective electron and hole masses are enhanced by approximately 7% – 43% upon polaron formation in the studied materials. We further estimate an upper bound

Table 3.9: Polaron parameters corresponding to electrons (e) and holes (h) in the studied antiperovskites. The corresponding properties of MAPbI₃ are listed for comparison [11].

Material	Carrier	α	$\frac{m_p}{m^*}$	r_f (Å)	μ_p (cm ² /Vs)
Mg ₃ NSb	e	0.4	1.07	186	713
	h	0.6	1.11	156	323
Ca ₃ NSb	e	0.8	1.19	126	196
	h	0.8	1.20	123	170
Sr ₃ NSb	e	0.8	1.15	102	363
	h	1.2	1.24	86	127
Ba ₃ NSb	e	1.0	1.19	94	228
	h	0.9	1.17	99	210
Ca ₃ NAs	e	1.6	1.33	90	98
	h	1.4	1.28	98	64
Sr ₃ NAs	e	1.7	1.36	77	135
	h	2.0	1.43	70	21
MAPbI ₃	e	2.4	1.37	29	136 ^a
	h	2.7	1.10	25	94

^a A value of 115 cm²/Vs has been achieved experimentally [45].

for the charge-carrier mobilities (μ_p) using Feynman's variational solution of the Fröhlich polaron Hamiltonian and the corresponding polaron response function [193, 159, 157, 11]. The mobility is given by

$$\mu_p = \frac{(3\sqrt{\pi}e)}{m^*\alpha\omega_{LO,eff}} \frac{\sinh \frac{\beta}{2}}{\beta^{\frac{5}{2}}} \frac{w^3}{v^3} \frac{1}{K(a,b)}, \quad (3.12)$$

where, e is the elementary charge, $\beta = \frac{\hbar\omega_{LO,eff}}{k_B T}$ is the reduced thermodynamic temperature in units of the phonon energy ($\hbar\omega_{LO,eff}$), and T is the absolute temperature. The function

$$K(a,b) = \int_0^\infty du [u^2 + a^2 - b \cos(vu)]^{-3/2} \cos(u) \quad (3.13)$$

describes the polaron response to a change in the driving force, with

$$a^2 = (\beta/2)^2 + \frac{(v^2 - w^2)}{w^2 v} \beta \coth(\beta v/2), \quad b = \frac{(v^2 - w^2)}{w^2 v} \frac{\beta}{\sinh(\beta v/2)}. \quad (3.14)$$

Here, w and v are temperature-dependent variational parameters determined by minimizing the polaron free energy. Our results indicate that Mg₃NSb, Ca₃NSb, Sr₃NSb, and Ba₃NSb

exhibit substantially higher charge-carrier mobilities than the widely studied photovoltaic material MAPbI_3 . It should be noted that the present approach neglects polaron-induced lattice distortions and scattering from acoustic phonons [194]. Consequently, the experimentally measured mobilities may be lower than the values reported here.

3.4 Conclusion

In summary, we have conducted a detailed analysis of electronic, optical, excitonic, and polaronic properties in inorganic antiperovskite nitrides. Our electronic-structure calculations reveal effective electron and hole masses smaller than the free electron mass, indicative of high charge-carrier mobilities. We find that all considered materials have band gaps in the visible range of the solar spectrum, making them suitable for photovoltaic applications. By employing the Wannier-Mott model, we obtain low exciton binding energies (6-29 meV), specifically in Mg_3NSb , Ca_3NSb , Sr_3NSb , and Ba_3NSb . This indicates that free charge carriers are predominantly generated upon light absorption. The computed Fröhlich coupling constants indicate weak electron-phonon coupling and thus formation of large polarons in all studied antiperovskites. We find high charge-carrier mobilities in Sb-based antiperovskites, as estimated by the Hellwarth polaron model. Moreover, despite exhibiting an indirect band gap, among the studied antiperovskites, Mg_3NSb has the highest mobilities of $713 \text{ cm}^2/\text{Vs}$ and $323 \text{ cm}^2/\text{Vs}$ for electrons and holes, respectively. From all these results we suggest Mg_3NSb , Sr_3NSb , Ca_3NSb , and Ba_3NSb to be favorable candidates for photovoltaic applications.

Tuning Nonradiative Recombination via Cation Substitution in Inorganic Antiperovskite Nitrides

4.1 Introduction

Antiperovskites, derived from an ionic inversion of the conventional perovskite lattice, have recently attracted growing attention as promising candidates for photovoltaic and optoelectronic applications [27, 170, 171, 2, 164, 4, 28, 29, 62]. These compounds adopt the general formula X_3BA , where X is a cation and A and B are anions of different sizes. The inverted ionic configuration fundamentally modifies electronic structure and lattice dynamics relative to lead halide perovskites (LHPs), while also substantially expanding the accessible compositional and structural space. However, antiperovskites remain comparatively underexplored, and to date only Mg_3NSb has been experimentally synthesized as a thin film [165].

In our previous work in chapter 3, we carried out a systematic first-principles investigation of the electronic, optical, excitonic, and polaronic properties of inorganic antiperovskite nitrides X_3NA ($X = Mg, Ca, Sr, Ba$; $A = As, Sb$). Within this family, Ca_3NSb , Sr_3NSb , and Ba_3NSb emerged as particularly promising direct-band-gap photovoltaic candidates, exhibiting optimal band gaps, low electron and hole effective masses ($\frac{m_{e/h}^*}{m_e} < 1$), small exciton binding energies (< 30 meV), and high carrier mobilities exceeding those of the benchmark $MAPbI_3$ perovskite [11]. Despite these favorable properties, their nonradiative recombination dynamics have not yet been explored.

Photovoltaic performance is critically limited by nonradiative recombination processes, which dissipate photoexcited carrier energy as heat. In recent years, *ab initio* nonadiabatic molecular dynamics (NAMD) simulations have substantially advanced the understanding of carrier lifetimes in LHPs, demonstrating that nonradiative pathways can be strategically suppressed

through strategies such as surface passivation, compositional engineering, and dimensionality control [195, 196, 197]. Several of these computational predictions have also been corroborated experimentally [198, 199, 54, 200].

In this work, we investigate the nonradiative recombination dynamics of $X_3\text{NSb}$ ($X = \text{Ca}, \text{Sr}, \text{Ba}$) antiperovskites using real-time time-dependent density functional theory (TDDFT) [201] combined with NAMD. These compounds span two distinct crystallographic motifs. Ca_3NSb and Sr_3NSb crystallize in the high-symmetry cubic $Pm\bar{3}m$ phase, enabling a controlled assessment of alkaline-earth cation size effects at fixed symmetry. In contrast, Ba_3NSb stabilizes in a lower-symmetry hexagonal $P6_3/mmc$ structure. To disentangle symmetry-driven effects from purely chemical ones, we additionally consider the hexagonal $P6_3/mmc$ polymorph of Sr_3NSb , allowing a direct comparison between cubic and hexagonal phases at identical chemical composition. Hexagonal phases are denoted by the subscript “hexa” (e.g., $\text{Ba}_3\text{NSb}_{\text{hexa}}$ and $\text{Sr}_3\text{NSb}_{\text{hexa}}$), while compositions without subscripts refer exclusively to the cubic $Pm\bar{3}m$ phase. Together, this four-model set constitutes a minimal yet physically well-justified framework for elucidating how cation chemistry and crystal symmetry independently and cooperatively govern lattice fluctuations, electronic structure, nonadiabatic couplings, and nonradiative recombination lifetimes in antiperovskite nitrides. Our results establish a clear structure-property-dynamics relationship and provide fundamental design principles for engineering antiperovskite materials with suppressed nonradiative losses.

4.2 Computational methodology

We perform *ab initio* NAMD simulations using the decoherence-induced surface hopping (DISH) method [202, 146], within the classical path approximation, as implemented in the PYXAID package [52, 53]. In this framework, the nuclear motion—associated with heavier and slower atoms—is treated semiclassically, whereas the electronic degrees of freedom are described quantum mechanically using TDDFT [201]. Decoherence, arising from elastic electron–phonon scattering that disrupts superpositions between electronic states, plays a critical role in regulating quantum transitions. Since decoherence typically occurs on timescales shorter than those of interband transitions, its inclusion is essential for accurately capturing nonradiative electron–hole recombination processes. In the DISH algorithm, quantum transitions emerge as a consequence of decoherence, which provides the physical basis for surface

hops. Decoherence time is estimated as the pure-dephasing time, evaluated via the second-order cumulant approximation of optical response theory [203].

First-principles density functional theory (DFT) calculations [85, 86] are performed using the Vienna Ab initio Simulation Package (VASP) [94, 93]. The projector augmented-wave (PAW) method [111] is employed to accurately describe the interactions between valence electrons and the ionic cores. Structural optimization is carried out using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [88]. A Γ -centered k -point mesh of $6 \times 6 \times 6$ and a plane-wave cutoff energy of 550 eV are used to ensure convergence. The atomic positions are relaxed until the Hellmann–Feynman forces on each atom are less than 10^{-3} eV/Å. The calculated lattice parameters are listed in Table 4.1 and they show good agreement with previously reported values [5, 4]. For electronic structure calculations, the hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional [92] is employed, including the spin–orbit coupling (SOC).

Table 4.1: Optimized lattice parameters of $X_3\text{NSb}$ ($X = \text{Ca}, \text{Sr}, \text{Ba}$) unit cells at 0 K.

$X_3\text{NSb}$	Ca_3NSb	Sr_3NSb	$\text{Sr}_3\text{NSb}_{\text{hexa}}$	$\text{Ba}_3\text{NSb}_{\text{hexa}}$
Space group	$Pm\bar{3}m$	$Pm\bar{3}m$	$P6_3/mmc$	$P6_3/mmc$
$a = b$ (Å)	4.87	5.25	7.28	7.66
c (Å)	4.87	5.25	6.37	6.76
$\alpha = \beta$ (°)	90	90	90	90
γ (°)	90	90	120	120

Ab initio molecular dynamics (AIMD) simulations are carried out using the Quantum Espresso (QE) package [95]. Supercell of dimension $2 \times 2 \times 2$ are constructed for all studied antiperovskites. Following geometry optimization, these supercells are heated to 300 K for a total simulation time of 13 ps with a time step of 1 fs, employing the Verlet algorithm within the canonical (NVT) ensemble. The initial 8 ps of each trajectory is considered for thermal equilibration, and the subsequent 5 ps is used for the generation of the nonadiabatic (NA) Hamiltonian. All NAMD simulations are performed at the Γ -point using the PBE exchange-correlation functional. The use of a single k -point is justified by the direct band gap nature of these antiperovskite nitrides, with both the valence band maximum (VBM) and conduction band minimum (CBM) located at the Γ -point (see Fig. 4.2). To extend the observation window for recombination dynamics, the NA Hamiltonian extracted from this 5 ps segment is iterated multiple

times. The first 50 geometries are chosen as initial configurations, and for each geometry, 10,000 stochastic realizations are performed to ensure convergence. SOC effects are excluded from the NAMD simulations, as they do not significantly alter the band gap magnitude (see Table 4.2), while introducing a substantial increase in computational cost.

Scissor correction in band gap for NAMD simulations:

The GGA-PBE functional is known to underestimate band gaps. Our previous work in Chapter 3 [62] demonstrates that, for Sr_3NSb , the quasiparticle G_0W_0 approximation on top of HSE06+SOC yields band gaps in excellent agreement with experiment (see Table 4.2). However, using hybrid functionals or beyond in NAMD simulations is computationally prohibitive. Therefore, for the present study, we employ the PBE functional, which offers a reasonable balance between computational cost and accuracy, and is widely used for both inorganic and organic perovskites [197, 204, 205]. In order to correct for the band gap underestimation in PBE-based NAMD simulations, a scissor operator is applied. The magnitude of this scissor correction corresponds to the difference between $G_0W_0@HSE06+SOC$ and time averaged PBE band gaps, thereby enabling a more realistic estimation of recombination lifetimes. It is important to note that the objective here is to obtain a qualitative understanding of lifetime trends rather than absolute quantitative accuracy. The time-averaged band gaps, obtained by averaging the instantaneous band gaps over a 5 ps MD trajectory, along with the band gaps computed using hybrid HSE06 functional, and the G_0W_0 approximation, are reported in Table 4.2.

Table 4.2: Canonically averaged PBE band gap ($\langle\text{PBE}\rangle$), hybrid HSE06 band gaps without and with SOC, $G_0W_0@HSE06+SOC$ gaps, and experimental reported band gap values (in eV).

X_3NSb	$\langle\text{PBE}\rangle$	HSE06	HSE06+SOC	$G_0W_0@HSE06+SOC$	Exp.
Ca_3NSb	0.54	1.16	1.02	1.33 [62]	-
Sr_3NSb	0.38	0.96	0.87	1.14 [62]	1.15 [4]
$\text{Sr}_3\text{NSb}_{\text{hexa}}$	0.61	1.36	1.31	1.62	-
$\text{Ba}_3\text{NSb}_{\text{hexa}}$	0.59	1.29	1.16	1.57 [62]	-

4.3 Results and discussion

4.3.1 Geometric structure

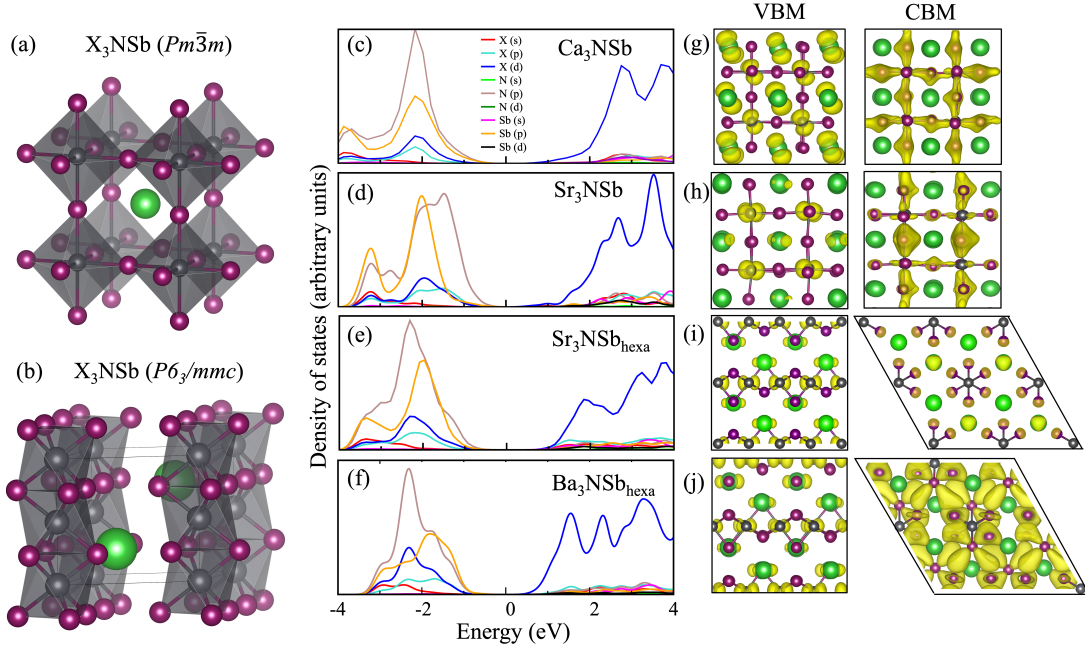


Figure 4.1: Unit cells of (a) cubic ($Pm\bar{3}m$) X_3NSb and (b) hexagonal ($P6_3/mmc$) X_3NSb . Panels (c–f) show the atom- and orbital-resolved density of states computed using the HSE06 functional including spin-orbit coupling (SOC). Panels (g–j) illustrate the corresponding spatial charge distributions of the valence band maximum (VBM) and conduction band minimum (CBM) for Ca_3NSb , Sr_3NSb , Sr_3NSb_{hexa} , and Ba_3NSb_{hexa} , respectively. Grey, purple, and green spheres in (a, b) denote nitrogen, X-site cations, and antimony atoms, respectively.

Fig. 4.1 (a) and (b) show the cubic ($Pm\bar{3}m$) and hexagonal ($P6_3/mmc$) unit cells of X_3NSb ($X = Ca, Sr, \text{ and } Ba$) antiperovskite nitrides. Ca_3NSb and Sr_3NSb crystallize in the cubic $Pm\bar{3}m$ phase, whereas Ba_3NSb adopts a distorted hexagonal $P6_3/mmc$ structure in its ground state (hereafter denoted as Ba_3NSb_{hexa}). In the ideal cubic structure (Fig. 4.1 (a)), Sb atoms occupy the cuboctahedral center, while N-centered NX_6 octahedra are arranged at the corners of the unit cell.

Substituting Ca with Sr at the X-site leads to an increase in the X–N bond length from 2.437 Å to 2.598 Å, accompanied by an expansion of the lattice parameters (Table 4.1). However, the substantially larger ionic radius of Ba destabilizes the cubic framework through enhanced Ba–N repulsion, favoring a symmetry-lowered hexagonal arrangement. Consequently, Ba_3NSb_{hexa} exhibits a further increase in the average Ba–N bond length to 2.686 Å.

Although Sr_3NSb adopts the cubic structure in its ground state, we also consider its hexagonal ($P6_3/mmc$) polymorph to enable a direct assessment of symmetry effects at fixed chemical composition. In $\text{Sr}_3\text{NSb}_{\text{hexa}}$, the average Sr-N bond length slightly decreases to 2.525 Å relative to the cubic phase, reflecting a modified local coordination environment induced by symmetry lowering. Within the hexagonal phases, X-N bond lengths increase systematically with increasing X-site cation size.

4.3.2 Static electronic properties

Fig. 4.1 (c-j) depicts the atom- and orbital-resolved density of states (DOS) near the band edges together with the real-space charge distributions associated with the VBM and CBM. Across all X_3NSb antiperovskites, the VBM is dominated by N and Sb p orbitals, while the CBM primarily arises from the X-site d orbitals. In contrast to conventional LHPs, where A-site cations make negligible contributions to the frontier electronic states, the A-site atoms in X_3NSb (A=Sb) contribute significantly to the band edges, highlighting the active role of all atomic constituents in these antiperovskites.

Substituting Ca with Sr in the cubic phase reduces Sb $5p$ –N $2p$ hybridization (Fig. 4.1 (d)), likely due to the increased Sb–N distances from 4.224 Å in Ca_3NSb to 4.545 Å in Sr_3NSb . In $\text{Sr}_3\text{NSb}_{\text{hexa}}$, however, reduced symmetry, altered coordination, and slightly shorter Sb–N distances (4.497 Å) enhance Sb $5p$ –N $2p$ overlap relative to Sr_3NSb . $\text{Ba}_3\text{NSb}_{\text{hexa}}$ also exhibits strong Sb $5p$ –N $2p$ mixing at the VBM. Remarkably, this enhanced hybridization persists despite the monotonic increase in Sb–N distances from $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (4.497 Å) to $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (4.644 Å). This indicates that the incorporation of Ba, accompanied by reduced symmetry and local lattice distortions in the hexagonal phase, modifies the bonding environment in a way that strengthens Sb–N hybridization even at longer Sb–N bond distances.

The electronic band structures calculated using the HSE06 hybrid functional including SOC are presented in Fig. 4.2. All compounds exhibit direct band gaps at the Γ point, with values of 1.02 eV, 0.87 eV, 1.31 eV and 1.18 eV for Ca_3NSb , Sr_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and $\text{Ba}_3\text{NSb}_{\text{hexa}}$, respectively. Among the cubic phases, the band gap decreases from Ca_3NSb to Sr_3NSb , consistent with the findings of Mochizuki *et al.* [170], who reported a positive correlation between the band gap and the inverse lattice constant in cubic inorganic antiperovskite nitrides. This trend originates from the lowering of the X d orbital energies with increasing ionic radius, which reduces the CBM energy and narrows the band gap [171]. In $\text{Sr}_3\text{NSb}_{\text{hexa}}$, the gap increases

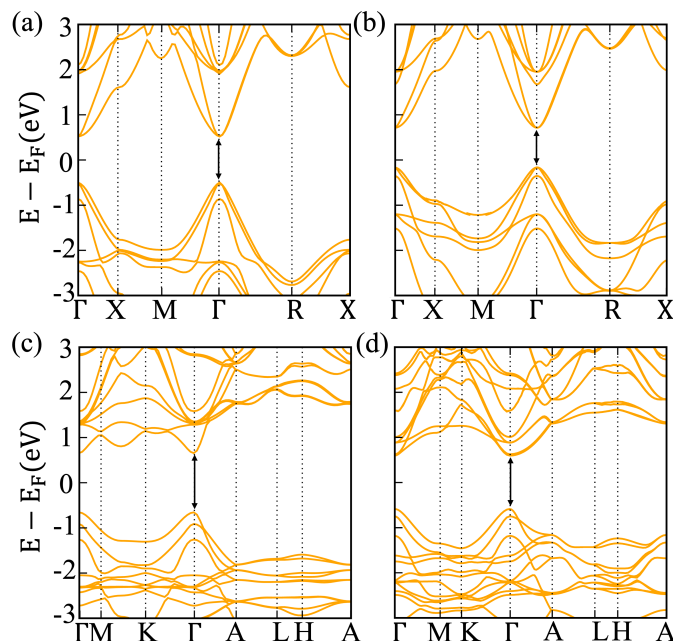


Figure 4.2: Electronic band structures of (a) Ca_3NSb , (b) Sr_3NSb , (c) $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and (d) $\text{Ba}_3\text{NSb}_{\text{hexa}}$ computed using the HSE06 functional with SOC. All compounds exhibit direct band gaps at the Γ point, with values of 1.02 eV, 0.87 eV, 1.31 eV, and 1.18 eV for Ca_3NSb , Sr_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and $\text{Ba}_3\text{NSb}_{\text{hexa}}$, respectively.

substantially relative to its cubic counterpart, highlighting the gap-widening effect induced by symmetry-lowering distortions. Similarly, moving from Sr_3NSb to $\text{Ba}_3\text{NSb}_{\text{hexa}}$ results in an increase in the band gap, in contrast to the decreasing trend from Ca_3NSb to Sr_3NSb with an increase in the X-site cation size. This reversal further highlights that crystal symmetry plays a decisive role in determining the electronic gap. Such distortion-driven band gap widening is well established in conventional perovskites [206, 207, 208] and is clearly manifested in X_3NSb antiperovskites. However, within the hexagonal family, the band gap decreases with increasing X-site cation size, from $\text{Sr}_3\text{NSb}_{\text{hexa}}$ to $\text{Ba}_3\text{NSb}_{\text{hexa}}$, mirroring the trend observed in the cubic phase. Thus, both the X-site cation size and the crystal's structural symmetry play an important role in tuning the electronic properties of X_3NSb antiperovskites.

4.3.3 Dynamical structural and electronic properties

AIMD simulations provide valuable insights into the time-dependent structural behavior of these compounds. Upon thermal excitation to 300 K, atomic fluctuations arise that influence electron-phonon interactions. We begin by quantifying the atomic-level fluctuations using the root mean square fluctuation (RMSF) of each species over a 5 ps trajectory (Table 5.4). Within

Table 4.3: Root mean square fluctuation (RMSF) of the atomic positions for the X-site ion, N, and Sb atoms in Å for Ca_3NSb , Sr_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and $\text{Ba}_3\text{NSb}_{\text{hexa}}$.

X_3NSb	X	N	Sb
Ca_3NSb	0.085	0.087	0.065
Sr_3NSb	0.068	0.097	0.067
$\text{Sr}_3\text{NSb}_{\text{hexa}}$	0.068	0.098	0.062
$\text{Ba}_3\text{NSb}_{\text{hexa}}$	0.057	0.099	0.062

the cubic phases (Ca_3NSb and Sr_3NSb), the RMSF of the X-site cations decreases systematically from Ca to Sr, reflecting the suppression of thermal motion with increasing cation mass. In contrast, nitrogen exhibits a monotonic increase in RMSF with increasing X-site ionic radius. This trend is consistent with the progressive elongation of X–N bonds and the accompanying increase in lattice free volume, which permits larger vibrational amplitudes of the lighter N atoms despite the heavier surrounding cations. A comparison between Sr_3NSb and its hexagonal polymorph $\text{Sr}_3\text{NSb}_{\text{hexa}}$ isolates the role of symmetry on atomic dynamics. While the RMSF of the Sr cations remains essentially unchanged across the two phases, the fluctuation of N is slightly increased, whereas that of Sb is reduced in the hexagonal structure. The reduced Sb RMSF indicates that the anisotropic coordination environment in the hexagonal phase imposes additional geometric constraints on the Sb-centered bonding network, thereby limiting its thermal displacement relative to the cubic phase. Notably, the shorter average X–N bond length in $\text{Sr}_3\text{NSb}_{\text{hexa}}$ does not lead to reduced N fluctuations, indicating that local symmetry breaking, rather than bond length alone, control N dynamics in the hexagonal phase. The same behavior persists in $\text{Ba}_3\text{NSb}_{\text{hexa}}$, where the heavy Ba cations exhibit the smallest RMSF among all X-site cations, while Sb fluctuations remain comparable to those in $\text{Sr}_3\text{NSb}_{\text{hexa}}$ and the N RMSF is slightly larger. Overall, these results demonstrate that atomic fluctuations in X_3NSb antiperovskites arise from an interplay between cation mass, bond geometry, and crystal symmetry.

Thermal excitation induces a noticeable expansion in the intra-octahedral X–N bond lengths, with time-averaged values of 2.449 Å, 2.626 Å, 2.532 Å, and 2.688 Å for Ca_3NSb , Sr_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and $\text{Ba}_3\text{NSb}_{\text{hexa}}$, respectively. These values are obtained by averaging all intra-octahedral X–N bond lengths over the entire 5 ps AIMD trajectory. To quantify the variability of these bond lengths, we construct histograms for the X–N distributions, shown in Fig. 4.3 (a–d). The corresponding standard deviations (σ) reveal a systematic reduction in bond-length fluctu-

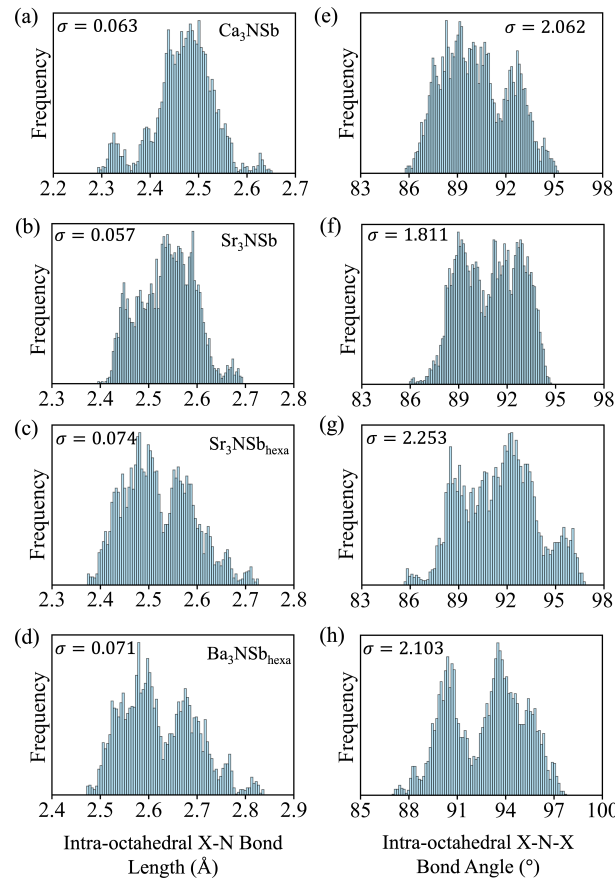


Figure 4.3: Statistical distribution of (a-d) intra-octahedral X-N bond lengths and (e-h) intra-octahedral X-N-X bond angles, computed using AIMD simulations, for Ca_3NSb (a, e), Sr_3NSb (b, f), $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (c, g) and $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (d, h). Standard deviations (σ) of the bond length and bond angle fluctuations are listed.

ations with increasing X-site cation size within a given symmetry: σ decreases from Ca_3NSb (0.063 Å) to Sr_3NSb (0.057 Å), and from $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (0.074 Å) to $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (0.071 Å). At fixed chemical composition, a clear symmetry effect is observed— Sr_3NSb exhibits substantially narrower bond-length distributions than its hexagonal polymorph—indicating enhanced structural flexibility upon symmetry lowering. A similar behavior is observed for the intra-octahedral X-N-X bond angle distributions (Fig. 4.3(e-h)). Sr_3NSb shows the smallest angular fluctuations ($\sigma = 1.811^\circ$), reflecting the rigidity of its NX_6 octahedra. While Ca_3NSb exhibits larger angular variability ($\sigma = 2.062^\circ$), consistent with the lighter Ca^{2+} cation. The hexagonal phases display enhanced angular fluctuations relative to cubic structures, with $\sigma = 2.253^\circ$ for $\text{Sr}_3\text{NSb}_{\text{hexa}}$ and 2.103° for $\text{Ba}_3\text{NSb}_{\text{hexa}}$.

These thermally driven structural fluctuations directly influence the electronic structure through electron-phonon interactions. To quantify this effect, we analyze the instantaneous energies

of the VBM and CBM along the AIMD trajectory, with statistical distributions shown in Fig. 4.4(a–d), together with the corresponding band gap histograms (Fig. 4.4(e–h)). The data reveal a clear correlation between lattice dynamics and temporal fluctuations of the band-edge eigenvalues. Across all four compositions, the VBM exhibits larger energy fluctuations than the CBM. The standard deviation of the VBM energy follows the trend: $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (0.0373) > $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (0.0341) > Ca_3NSb (0.0259) > Sr_3NSb (0.0102), which mirrors the hierarchy of octahedral flexibility identified earlier. In contrast, the CBM fluctuations follow a distinct order: Ca_3NSb (0.0141) > $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (0.0090) > $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (0.0085) > Sr_3NSb (0.0064), indicating a weaker and qualitatively different sensitivity of the conduction band edge to local structural distortions.

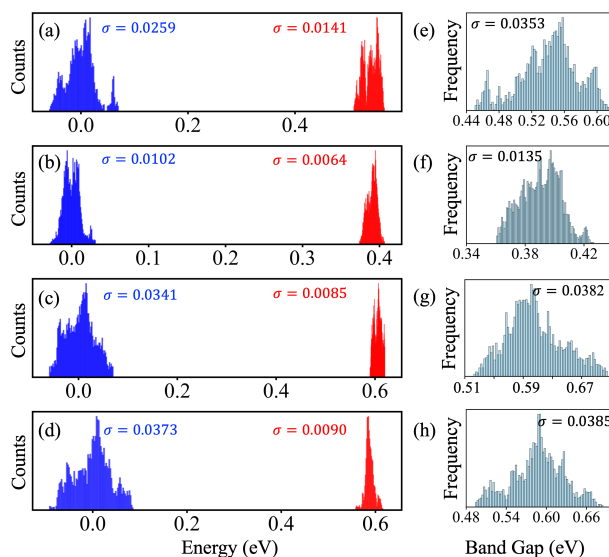


Figure 4.4: Statistical distribution of (a–d) VBM (blue) and CBM (red), and (e–h) corresponding band gap distributions, computed using AIMD simulations, for Ca_3NSb (a, e), Sr_3NSb (b, f), $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (c, g), and $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (d, h), respectively. Standard deviations (σ) of the energy fluctuations are listed.

Among studied antiperovskites, Sr_3NSb exhibits the narrowest energy distributions for both VBM and CBM, resulting in the smallest variation of the instantaneous band gap with a standard deviation of $\sigma = 0.0135$ eV (Fig. 4.4(e)). In comparison, Ca_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$ and $\text{Ba}_3\text{NSb}_{\text{hexa}}$ display significantly larger band gap fluctuations, with standard deviations of approximately 0.0353 eV, 0.0382 eV and 0.0385 eV, respectively. The suppressed band-edge fluctuations in Sr_3NSb point to comparatively weaker electron–phonon coupling and reduced nonradiative recombination losses at finite temperature.

4.3.4 Electron-vibrational interactions

The extent of thermal fluctuations in Kohn–Sham orbital energies indicates the strength of electron–vibration interactions. Inelastic electron–phonon scattering, captured by NA coupling, facilitates energy exchange between electrons and vibrations, enabling nonradiative transitions between electronic states. In contrast, elastic scattering disrupts coherence between the initial and final states during an electronic transition. Although it does not involve direct energy exchange, it significantly influences nonradiative recombination, as transitions can only proceed once quantum coherence between the initial and final states is established. The loss of coherence typically acts to suppress or slow down these transitions, as exemplified by the quantum Zeno effect [148, 209]. Thus, both elastic and inelastic processes play an important role in governing the nonradiative recombination dynamics.

NA coupling, characterizing inelastic electron-vibration scattering, is calculated as:

$$d_{ij} = -i\hbar\langle\varphi_i|\nabla_R|\varphi_j\rangle \cdot \dot{R} = -i\hbar\langle\varphi_i|\frac{\partial}{\partial t}|\varphi_j\rangle \quad (4.1)$$

where, d_{ij} is the NA coupling between the states i and j . φ_i and φ_j are their corresponding wavefunctions, and $\dot{R}$ denotes the instantaneous nuclear velocity, determined by the kinetic energy, which is proportional to temperature. $\langle\varphi_i|\nabla_R|\varphi_j\rangle$ represents the matrix element which quantifies how electronic wavefunctions depend on atomic displacements and requires the wavefunction of VBM and CBM to be confined within the same spatial area. As shown in Fig. 4.1 (g-j), the VBM and CBM states reside primarily on different atomic species, leading to a reduced spatial overlap between electron and hole wavefunctions and, consequently, a suppression of the NA coupling. Nevertheless, the magnitude of NA coupling remains finite due to minor contributions from secondary atomic orbitals. Table 5.6 summarizes the averaged and root mean squared NA couplings for all compounds. Among them, Sr_3NSb exhibits the weakest NA coupling, consistent with its rigid octahedral framework, narrow band-edge distributions, and relatively localized VBM, which altogether the sensitivity of the electronic states to lattice vibrations. Upon transitioning to the hexagonal phase, $\text{Sr}_3\text{NSb}_{\text{hexa}}$ displays an enhanced NA coupling compared to its cubic counterpart, reflecting the increased structural distortions in the symmetry-lowered bonding environment. However, the coupling remains smaller than in Ca_3NSb and $\text{Ba}_3\text{NSb}_{\text{hexa}}$, which may be attributed to the larger orbital overlap in these structures. Overall, larger NA coupling values signify stronger electron–lattice interactions, which facilitate faster nonradiative recombination processes.

Table 4.4: Canonically averaged scaled band gaps (in eV), with original band gaps included in parenthesis, along with the averaged absolute nonadiabatic (NA) coupling, root mean square (RMS) value of NA coupling, pure-dephasing time (τ_{deph}), and nonradiative electron-hole recombination lifetime (τ_{NRR}) for the VBM-CBM transition in Ca_3NSb , Sr_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and $\text{Ba}_3\text{NSb}_{\text{hexa}}$.

X_3NSb	Gap (eV)	NA coupling (meV)	RMS NA coupling (meV)	τ_{deph} (fs)	τ_{NRR} (ns)
Ca_3NSb	1.33 (0.54)	0.57	1.02	20.3	1.36
Sr_3NSb	1.14 (0.38)	0.26	0.50	52.8	3.48
$\text{Sr}_3\text{NSb}_{\text{hexa}}$	1.62 (0.61)	0.33	0.57	17.6	4.90
$\text{Ba}_3\text{NSb}_{\text{hexa}}$	1.57 (0.59)	0.65	1.17	17.5	2.23

To characterize elastic electron–phonon interactions, we compute the decoherence times, estimated as pure-dephasing time of the optical response theory. Under the second-order cumulant approximation, the pure-dephasing function is expressed as:

$$D_{ij}(t) = \exp\left(\frac{-1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' C_{ij}(t'')\right) \quad (4.2)$$

where $C_{ij}(t) = \langle \delta E_{ij}(t) \delta E_{ij}(0) \rangle$ is the unnormalized autocorrelation function (un-ACF) of the phonon-induced band gap fluctuation. $E_{ij}(t) = E_{ij}(t) - \langle E_{ij} \rangle$ represents the fluctuation of the energy gap between states i and j , and $\langle E_{ij} \rangle$ denotes the ensemble-averaged band gap. The pure-dephasing (or decoherence) time is extracted by fitting $D_{ij}(t)$ (Fig. 4.5) to a Gaussian decay function of the form: $f(t) = \exp(-0.5(\frac{t}{\tau})^2)$, with the corresponding values summarized in Table 5.6. The initial value of the un-ACF, $C_{ij}(0)$, represents the square of band gap fluctuation. The calculated band gap variances (in Fig. 4.4 (e-h)) corroborate the initial values of the un-ACF (upper inset of Fig. 4.5), which decrease in the sequence: $\text{Sr}_3\text{NSb} < \text{Ca}_3\text{NSb} < \text{Sr}_3\text{NSb}_{\text{hexa}} < \text{Ba}_3\text{NSb}_{\text{hexa}}$. Greater initial value of un-ACF and more asymmetric ACF favor faster dephasing. The pure dephasing times decrease in the opposite order: $\text{Ba}_3\text{NSb}_{\text{hexa}} < \text{Sr}_3\text{NSb}_{\text{hexa}} < \text{Ca}_3\text{NSb} < \text{Sr}_3\text{NSb}$, as expected. The suppression of decoherence/pure dephasing in the Ca_3NSb and hexagonal systems ($\text{Sr}_3\text{NSb}_{\text{hexa}}$ and $\text{Ba}_3\text{NSb}_{\text{hexa}}$) is attributed to enhanced electronic energy level fluctuations in comparison to Sr_3NSb . The pure-dephasing times of X_3NSb compounds (17-53 fs) are much shorter than the electron-hole recombination lifetimes, underscoring the importance of including decoherence into the NAMD simulations.

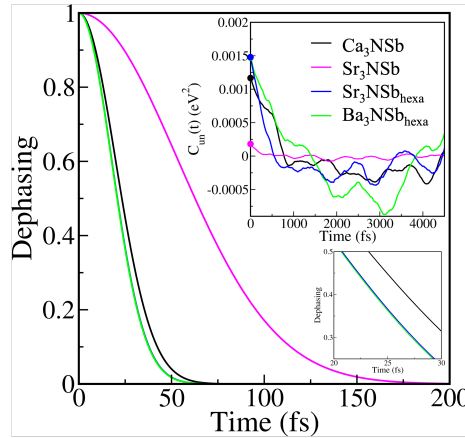


Figure 4.5: Pure dephasing functions corresponding to the VBM–CBM transition in Ca₃NSb (black), Sr₃NSb (magenta), Sr₃NSb_{hexa} (blue), and Ba₃NSb_{hexa} (green). The upper inset displays the unnormalized autocorrelation function (un-ACF), whose initial value (indicated by solid circles) represents the square of the band gap fluctuations. A higher initial un-ACF value typically corresponds to a shorter pure dephasing time. The lower inset is the zoomed view of the dephasing function showing almost overlapping curves for Sr₃NSb_{hexa} (blue), and Ba₃NSb_{hexa} (green).

4.3.5 Nonradiative electron-hole recombination

Fig. 4.6 depicts the time evolution of first-excited state populations during nonradiative electron-hole recombination in X₃NSb antiperovskites. Given that intraband relaxation in semiconductors typically occurs on sub-picoseconds timescales, we assume that the electron and hole have already relaxed to the CBM and VBM, respectively. Recombination time constants are extracted by fitting the population decay to an exponential function, $P(t) = \exp(-t/\tau)$, and the resulting lifetimes are also summarized in Table 5.6.

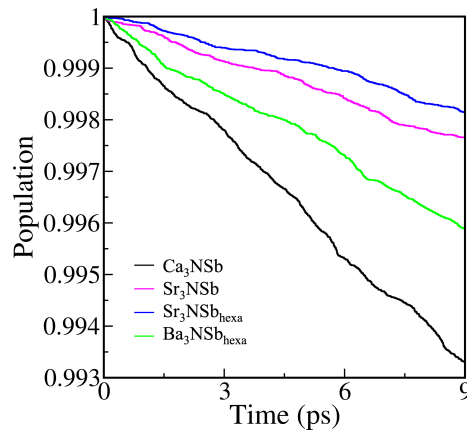


Figure 4.6: Nonradiative electron–hole recombination dynamics associated with the VBM–CBM transition in Ca₃NSb (black), Sr₃NSb (magenta), Sr₃NSb_{hexa} (blue), and Ba₃NSb_{hexa} (green).

NAMD simulations reveal the following trend in recombination lifetimes: $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (4.90 ns) > Sr_3NSb (3.48 ns) > $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (2.23 ns) > Ca_3NSb (1.36 ns). These lifetimes are mainly governed by the combined influence of the band gap, the strength of NA coupling, and the pure-dephasing time. Larger band gaps and weaker NA coupling, and quick dephasing suppress electronic transitions, thereby reducing nonradiative recombination rates.

Ca_3NSb exhibits the shortest nonradiative recombination lifetime, reflecting the combined effect of its small band gap and strong NA coupling. Although $\text{Ba}_3\text{NSb}_{\text{hexa}}$ shows even stronger NA coupling, its larger band gap and faster electronic dephasing suppress recombination relative to Ca_3NSb . Within the cubic phase, substitution of Ca by Sr localizes the VBM and reduces structural and electronic fluctuations, leading to weaker NA coupling. However, Sr_3NSb still exhibits a shorter lifetime than its hexagonal polymorph because its lattice rigidity limit band-gap fluctuations and prolong electronic coherence. $\text{Sr}_3\text{NSb}_{\text{hexa}}$ displays the longest recombination lifetime, driven by the synergistic combination of a larger band gap, reduced NA coupling, and rapid dephasing. Among the two hexagonal systems, the comparatively stronger NA coupling and smaller band gap of $\text{Ba}_3\text{NSb}_{\text{hexa}}$ lead to faster nonradiative recombination than in $\text{Sr}_3\text{NSb}_{\text{hexa}}$.

Overall, these results demonstrate that nonradiative carrier lifetimes in X_3NSb antiperovskites are governed by a delicate balance between band gap, lattice-driven NA coupling, and dephasing times. Crucially, symmetry lowering within a fixed chemical composition (Sr_3NSb) emerges as an effective strategy for suppressing nonradiative losses, underscoring the importance of structural motifs—beyond chemistry alone—in designing photovoltaic materials.

4.4 Conclusion

Using a combination of NAMD and TDDFT, we investigated the influence of X-site cation substitution and structural symmetry on nonradiative electron-hole recombination dynamics in Ca_3NSb , Sr_3NSb , $\text{Sr}_3\text{NSb}_{\text{hexa}}$, and $\text{Ba}_3\text{NSb}_{\text{hexa}}$. Band structure calculations reveal that all compounds are direct band gap semiconductors with both the VBM and CBM located at the Γ point. In the cubic phase (Ca_3NSb and Sr_3NSb), increasing X-site cation size narrows the band gap through a downward shift of the X d orbitals that primarily govern the CBM. A similar cation-size dependence of the band gap is observed in the hexagonal phase. However, relative to the cubic structures, lattice distortions in $\text{Sr}_3\text{NSb}_{\text{hexa}}$ and $\text{Ba}_3\text{NSb}_{\text{hexa}}$ result in wider band

gaps, consistent with trends reported for symmetry-lowered halide perovskites.

AIMD simulations show that Sr_3NSb exhibits the narrowest X-N bond length and X-N-X bond angle distributions, reflecting the rigidity of its NX_6 octahedral framework, while Ca_3NSb displays moderately enhanced flexibility. The hexagonal phases, $\text{Sr}_3\text{NSb}_{\text{hexa}}$ and $\text{Ba}_3\text{NSb}_{\text{hexa}}$, exhibit the largest structural fluctuations due to reduced symmetry. These structural trends are directly reflected in the band gap distribution. The combination of rigid octahedra, narrow band-edge fluctuations, and a relatively localized VBM results in the weakest NA coupling in Sr_3NSb . Although NA coupling increases in its hexagonal polymorph, it remains weaker than in Ca_3NSb and $\text{Ba}_3\text{NSb}_{\text{hexa}}$, consistent with its larger band gap and reduced orbital overlap between the VBM and CBM.

Pure-dephasing times, governed by band gap fluctuations, follow the trend Sr_3NSb (52.8 fs) > Ca_3NSb (20.3 fs) > $\text{Sr}_3\text{NSb}_{\text{hexa}}$ (17.6 fs) > $\text{Ba}_3\text{NSb}_{\text{hexa}}$ (17.5 fs), exhibiting an opposite trend to the magnitude of band gap fluctuations. Larger band gap variability accelerates dephasing, as observed in the hexagonal phases relative to the cubic structures. The two hexagonal systems exhibit comparable dephasing times due to similar band-edge fluctuations, while Sr_3NSb displays the slowest dephasing overall.

Ultimately, nonradiative recombination lifetimes are governed by the interplay between band gap magnitude, NA coupling strength, and pure-dephasing time. $\text{Sr}_3\text{NSb}_{\text{hexa}}$ exhibits the longest lifetime due to its wide band gap, weak NA coupling, and rapid dephasing. Its cubic counterpart undergoes faster recombination as a result of its smaller band gap and longer dephasing time. Although $\text{Ba}_3\text{NSb}_{\text{hexa}}$ and Ca_3NSb exhibit comparable NA coupling strengths, the larger band gap and faster dephasing in $\text{Ba}_3\text{NSb}_{\text{hexa}}$ lead to slower recombination relative to Ca_3NSb . Overall, both X-site cation chemistry and structural symmetry play decisive roles in shaping structural dynamics, electronic fluctuations, and nonradiative recombination in X_3NSb antiperovskites. These findings establish clear design principles for achieving long-lived excited states through symmetry and lattice engineering.

Tunable Carrier Dynamics in Carbide Antiperovskites via A-Site Cation Substitution

5.1 Introduction

The search for materials with tunable electronic structure and strong light-matter interactions has revitalized interest in antiperovskites—electronically inverted perovskites with the general formula X_3BA (X = cation; A , B = anions of different sizes). Their structural flexibility and rich chemical tunability give rise to diverse emergent properties, positioning them as promising candidates for photovoltaics [210, 25], thermoelectrics [211, 212], superconductivity [213, 214], solid electrolytes [215, 216, 217], superionic conductors [218], and topological insulators [219].

Among these, inorganic nitride antiperovskites (X_3NA ; X = Mg, Ca, Sr, Ba; A = P, As, Sb, Bi) have been widely explored for optoelectronic applications owing to their favorable band gaps, dispersive band edges, high carrier mobilities, and strong near-edge optical absorption [62, 28, 29, 30, 166, 220, 170, 64]. Expanding the chemical space, Hahn and coworkers [221] proposed quaternary antiperovskites of the form X_6B_2AA' and $X_6BB'A_2$, identifying several thermodynamically stable compounds as potential photovoltaic absorbers. More recently, imide-based defect antiperovskites $AE_5AsPn(NH)_2$ (AE = Ca, Sr; Pn = Sb, Bi) have further broadened the accessible bonding motifs and electronic landscapes in this family [222].

In contrast, carbide-based antiperovskites remain relatively underexplored, particularly with regard to their excited-state and dynamical properties [223, 224, 225, 226]. A notable advance by Guo *et al.* [31] predicted a family of carbide antiperovskites M_6CCh_4 (M = Ca, Sr, Ba; Ch = S, Se, Te) through ion inversion from the Cs_4PbX_6 -type structure. Among these, Ca_6CSe_4 and Sr_6CSe_4 stand out with suitable band gaps, high carrier mobilities, and strong

visible-light absorption—comparable to the benchmark halide perovskite MAPbI₃. Their distinct bonding and lattice flexibility are expected to profoundly influence electron-phonon interactions and nonadiabatic dynamics, making them an ideal platform for studying carrier relaxation. Nevertheless, while their ground-state electronic structure has been characterized, key aspects—including quasiparticle corrections, optical response, and especially carrier relaxation dynamics—remain largely unexplored.

Excited-state processes are central to the performance of optoelectronic devices. Upon above-gap photoexcitation, hot electrons and holes are generated. These carriers rapidly dissipate excess energy via electron–phonon scattering as they relax toward the band edges, often preceding efficient charge extraction. Concurrently, nonradiative recombination provides an additional decay channel that depletes carrier populations. Understanding and controlling these competing processes is therefore essential for optimizing carrier lifetimes and charge transport. At the microscopic level, these phenomena arise from the strong coupling between structural and electronic dynamics, driven by electron-phonon interactions and nonadiabatic (NA) transitions. Accurately describing the coupled electron–nuclear dynamics requires methods that go beyond static electronic-structure calculations. *Ab initio* nonadiabatic molecular dynamics (NAMD) combined with time-dependent density functional theory (TDDFT) [201], has emerged as a powerful framework for this purpose. These simulations have provided valuable insights into carrier relaxation in conventional perovskites [227, 228], demonstrating excellent agreement with ultrafast spectroscopic experiments [198, 199, 54, 200].

In the present study, we address this gap through a comprehensive investigation of the electronic structure and carrier dynamics in the carbide antiperovskites Ca₆CSe₄ and Sr₆CSe₄. Using many-body perturbation theory (MBPT) [229, 118], we first obtain an accurate quasiparticle description of the band structure and evaluate excitonic effects. Subsequently, TDDFT combined with NAMD is employed to examine hot-carrier cooling and nonradiative recombination. Our results reveal that A-site cation substitution plays a decisive role in modulating lattice fluctuations, NA couplings, and electronic decoherence times, leading to pronounced differences in carrier lifetimes. In particular, Ca₆CSe₄ exhibits enhanced decoherence and weaker NA couplings, which together result in significantly prolonged recombination times. Furthermore, both materials display a distinct hot-carrier cooling bottleneck near the band edges, with relatively faster cooling in Ca₆CSe₄ driven by stronger intraband NA interactions. Overall, these findings provide microscopic insight into carrier relaxation pathways in antiperovskites and underscore

the critical role of lattice-mediated dynamics in shaping their excited-state behavior.

5.2 Computational methodology

NAMD simulations are performed in conjunction with TDDFT using the decoherence-induced surface hopping (DISH) approach [202, 146], as implemented in the PYXAID package [52, 53]. Within this framework, nuclear motion is treated semi-classically, while the electronic degrees of freedom are described quantum mechanically. The DISH formalism explicitly incorporates decoherence effects, which govern the probabilities of NA transitions (hops) between adiabatic potential energy surfaces. This approach has been successfully applied to a wide range of systems, including bulk [230, 204, 231] and two-dimensional halide perovskites [232, 233, 234], transition metal dichalcogenides [235, 236], and semiconducting quantum dots [237], yielding results in good agreement with experiments.

First-principles calculations are performed using the Quantum ESPRESSO (QE) suite [95, 238], employing norm-conserving Troullier–Martins pseudopotentials from the PseudoDojo library [239]. Structural optimization is carried out within the generalized gradient approximation using the PBE functional [88], until the Hellmann–Feynman forces on each atom are less than 10^{-4} eV/Å. A plane-wave kinetic-energy cutoff of 80 Ry and a charge-density cutoff of 320 Ry are used, along with a Γ -centered $11 \times 11 \times 11$ k -point mesh. Hybrid functional calculations are performed using the HSE06 functional [92]. Phonon dispersions are computed using the Phonopy package [175, 176], employing a $2 \times 2 \times 2$ supercell to assess the dynamical stability of the studied materials.

Quasiparticle corrections are obtained using the single-shot GW (G_0W_0) calculations within the MBPT framework as implemented in YAMBO [102, 101, 240]. QE is used to generate the self-consistent and non-self-consistent PBE wavefunctions with a plane-wave cutoff of 80 Ry, which serve as the starting point for all G_0W_0 and Bethe–Salpeter equation (BSE) calculations. The resulting calculations provide both the underlying PBE band structures and the quasiparticle-corrected G_0W_0 band structures used in the analysis. The frequency dependence of the dielectric function is treated using the plasmon-pole approximation [241]. Electron–hole interactions are included by solving the BSE within the Tamm–Dancoff approximation [119]. Key computational parameters used in the DFT and MBPT calculations within YAMBO are provided in Table 5.1.

Table 5.1: Summary of computational parameters employed in the YAMBO package for DFT (PBE), $G_0 W_0$ @PBE, and BSE@ $G_0 W_0$ @PBE calculations for Ca_6CSe_4 and Sr_6CSe_4 .

Method	Parameter	Ca_6CSe_4	Sr_6CSe_4
DFT (PBE)	Plane wave cutoff	80 Ry	80 Ry
	Number of bands	800	800
	k -grid	$6 \times 6 \times 6$	$6 \times 6 \times 6$
$G_0 W_0$	Exchange cutoff	50 Ry	50 Ry
	XC potential cutoff	50 Ry	50 Ry
	GW bands	600	600
	Dielectric cutoff	10 Ry	10 Ry
	k -grid	$6 \times 6 \times 6$	$6 \times 6 \times 6$
BSE	Static screening bands	600	600
	Valence/conduction bands	8	8
	k -grid	$6 \times 6 \times 6$	$6 \times 6 \times 6$

Ab initio molecular dynamics (AIMD) simulations are performed using QE on the $2 \times 2 \times 2$ supercell of both compounds. The systems are equilibrated at 300 K in the canonical (NVT) ensemble for 8 ps using a time step of 1 fs. The first 3 ps are discarded for equilibration, while the subsequent 5 ps are used for production runs. Thermal stability is evaluated by monitoring the total energy, and verifying the structural integrity throughout the equilibrated trajectory. All AIMD and NAMD calculations are conducted at the Γ point, as both materials exhibit direct band gaps at Γ . To ensure statistical convergence, the NAMD simulations are repeated over 50 randomly selected initial configurations and 10,000 stochastic realizations. Spin-orbit coupling (SOC) effects are not included in the DFT, MBPT, or NAMD calculations, as their contribution to the band gap and overall band dispersion is negligible, consistent with previous reports [31].

5.3 Results and discussion

5.3.1 Crystal structure and stability

The crystal structures of the carbide antiperovskites $M_6\text{CSe}_4$ ($M = \text{Ca}, \text{Sr}$) are derived from zero-dimensional (0D) perovskite Cs_4PbX_6 , which adopts the $R\bar{3}c$ space group [31, 242]. In

Cs_4PbX_6 , isolated PbX_6 octahedra are separated by Cs cations. Through ion inversion, this structure is transformed into the antiperovskite $M_6\text{CSe}_4$, resulting in a significantly enhanced structural connectivity. The atomic arrangement of $M_6\text{CSe}_4$ is illustrated in Fig. 5.1 (a), which shows the primitive unit cell. In contrast to the parent 0D structure, the $M_6\text{C}$ octahedra in

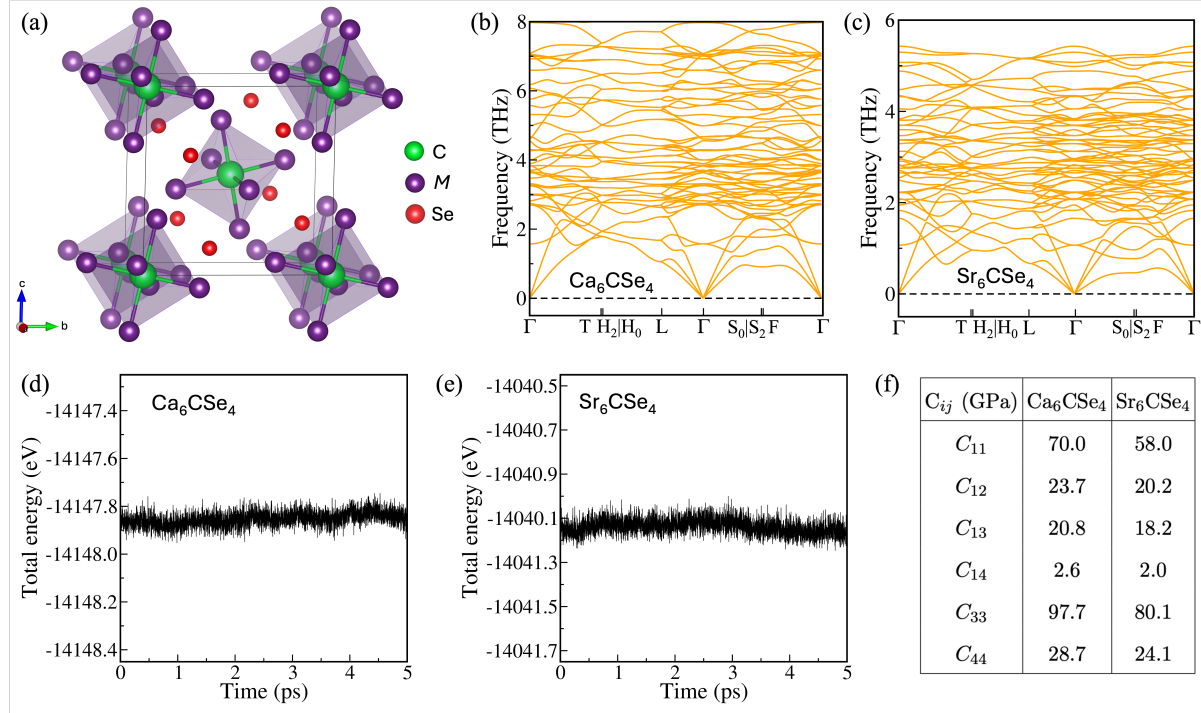


Figure 5.1: Structural and stability analysis of $M_6\text{CSe}_4$ ($M = \text{Ca}, \text{Sr}$): (a) primitive unit cell; phonon dispersion for (b) Ca_6CSe_4 and (c) Sr_6CSe_4 ; total energy as a function of simulation time from *ab initio* molecular dynamics simulations in the canonical (NVT) ensemble at 300 K for (d) Ca_6CSe_4 and (e) Sr_6CSe_4 ; and (f) calculated elastic constants C_{ij} (in GPa), confirming mechanical stability.

$M_6\text{CSe}_4$ are no longer isolated. The central C atoms form bonds with both the surrounding M -site cations (Ca or Sr) and interstitial Se atoms, as revealed by the electron localization function in Fig. 5.2. This enhanced connectivity increases the electronic dimensionality of the lattice, which is favorable for photoinduced charge transport. Substituting Ca with Sr at the M site increases the intra-octahedral M -C bond length from 2.427 Å to 2.603 Å, and the inter-octahedral C-C distance from 7.151 Å to 7.579 Å. Consequently, the lattice constant of the primitive unit cell expands from 8.23 Å in Ca_6CSe_4 to 8.71 Å in Sr_6CSe_4 , consistent with previous reports [31].

To assess dynamical stability, we calculate the phonon dispersion plots, shown in Fig. 5.1 (b) and (c). The absence of imaginary frequencies throughout the Brillouin zone confirms that both Ca_6CSe_4 and Sr_6CSe_4 are dynamically stable. Thermal stability at room temperature is

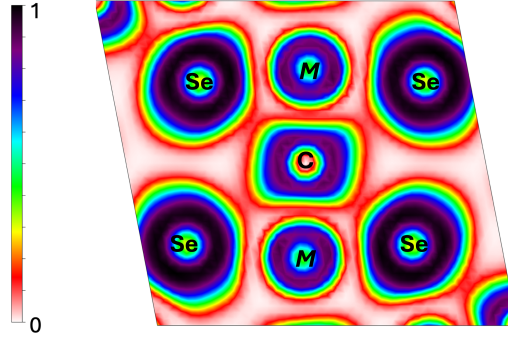


Figure 5.2: Electron localization function (ELF) of M_6CSe_4 ($M = \text{Ca}, \text{Sr}$) showing the bonding interaction between C and Se atoms, where Se atom links two adjacent octahedra. Consequently, the octahedra in M_6CSe_4 are not isolated, unlike in its parent-structure Cs_4PbX_6 .

verified using AIMD simulations in the canonical (NVT) ensemble at 300 K (Fig. 5.1 (d) and (e)). The total energy remains nearly constant, with no bond breaking observed, indicating robust thermal stability. Mechanical stability is evaluated by calculating the elastic constants. For Trigonal(I) systems, there are six independent elastic constants: C_{11} , C_{12} , C_{13} , C_{14} , C_{33} , and C_{44} . These satisfy the Born stability criteria [243]:

$$C_{11} - |C_{12}| > 0$$

$$(C_{11} + C_{12})C_{33} > 2C_{13}^2$$

$$C_{44} > 0$$

$$(C_{11} - C_{12})C_{44} > 2C_{14}^2$$

The calculated elastic constants (Fig. 5.1 (f)) satisfy all four conditions for both compounds, thereby confirming their mechanical stability.

5.3.2 Electronic properties

We investigate the electronic structure of Ca_6CSe_4 and Sr_6CSe_4 using density functional theory (DFT) and many-body perturbation theory (GW). Figure 5.3 (a, d) shows the electronic band structures computed using the PBE (orange dashed lines) and single-shot GW ($G_0 W_0 @ \text{PBE}$) (blue solid lines) approaches for both compounds. At the PBE level, both materials exhibit direct band gaps at the Γ point. Substituting Ca with Sr at the M site substantially reduces the band gap, demonstrating that varying A-site cation provides an effective route for band-gap engineering in this family of antiperovskites. While the PBE functional captures the qualitative band dispersion, it is well known to underestimate band gaps. Calculations using the hybrid

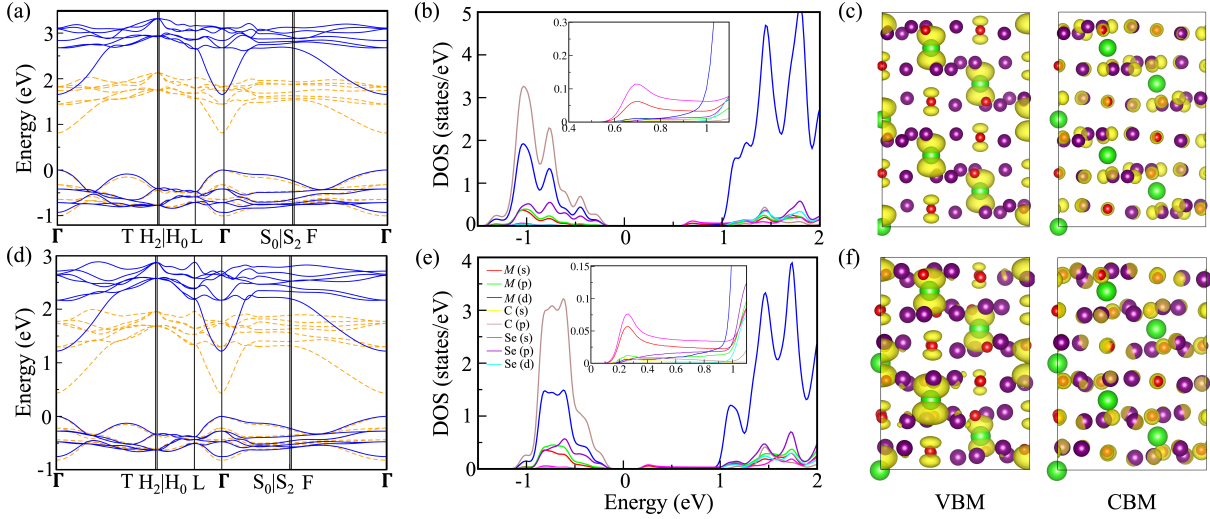


Figure 5.3: Electronic band structures of Ca_6CSe_4 (a) and Sr_6CSe_4 (b), calculated using PBE (orange dashed lines) and $G_0 W_0$ @PBE (blue solid lines), with corresponding atom- and orbital-resolved density of states (DOS) shown in (c) and (d), respectively.

HSE06 functional give values of 1.39 eV for Ca_6CSe_4 and 1.03 eV for Sr_6CSe_4 . A more accurate quasiparticle description is obtained within the $G_0 W_0$ approximation, which opens the fundamental gaps to 1.66 eV and 1.22 eV, respectively (Table 5.2). The systematic increase in band gap from PBE to HSE06 to $G_0 W_0$ highlights the importance of many-body corrections in these compounds. Notably, the $G_0 W_0$ correction shifts the band edges while preserving their dispersion and nature of the band gap.

Table 5.2: Band gaps (in eV) of $M_6\text{CSe}_4$ ($M = \text{Ca}, \text{Sr}$) calculated using different levels of theory. The exciton binding energy E_b (eV) is estimated as the difference between the $G_0 W_0$ @PBE gap and the lowest bright excitation from the BSE.

$M_6\text{CSe}_4$	PBE	HSE06	$G_0 W_0$ @PBE	BSE	E_b
Ca_6CSe_4	0.79	1.39	1.66	1.54	0.12
Sr_6CSe_4	0.40	1.03	1.22	1.02	0.20

Further insights into carrier transport is provided by the effective masses extracted from parabolic fitting near the band edges (Table 5.3). The electron effective masses are smaller than the free-electron mass ($m_e^*/m_0 < 1$) and lower than the corresponding hole masses, suggesting high electron mobilities.

The orbital character of the band edges is revealed by the atom- and orbital-projected density of states (PDOS) shown in Fig. 5.3 (b, e). The valence band maximum (VBM) is dominated by hybridized C- p and Se- p states with a noticeable contribution from M- d orbitals, consistent

Table 5.3: Effective masses of electrons and holes at the band edges, in units of the rest mass of electron (m_0), obtained from parabolic fitting of the band edges and computed using the PBE functional. The coordinates of the high-symmetry points are: Γ (0,0,0), T (0.5,0.5,0.5), L (0.5, 0, 0), S_0 (0.5,-0.5,0), and F (0.5,0,0.5).

Path	Ca ₆ CSe ₄		Sr ₆ CSe ₄	
	m_e^*	m_h^*	m_e^*	m_h^*
$\Gamma \rightarrow \text{T}$	0.25	0.24	0.21	0.22
$\Gamma \rightarrow \text{L}$	0.21	0.48	0.17	0.44
$\Gamma \rightarrow S_0$	0.22	1.60	0.18	1.52
$\Gamma \rightarrow \text{F}$	0.23	0.31	0.19	0.30

with the corresponding charge density distributions presented in Fig. 5.3 (c, f). In contrast, the conduction band minimum (CBM) exhibits predominant s -character from the M and Se atoms. The participation of formally empty M - d states near the VBM arises from the small energy separation between the ns and $(n-1)d$ levels in Ca and Sr, which enables partial d -occupation and facilitates M -C bonding [31]. This orbital mixing is consistent with observations in other antiperovskite systems [170, 166, 221] and plays an important role in shaping the band dispersion and optical transitions.

While quasiparticle calculations within the $G_0 W_0$ approximation provide an accurate description of the fundamental (quasiparticle) band gap, they do not incorporate the electron-hole interactions that govern optical excitations. To account for excitonic effects, we solve the BSE on top of the $G_0 W_0$ electronic structure. This approach leads to a pronounced red-shift of the lowest-energy absorption peak (see Fig. 5.4 (a,c)), reflecting the formation of bound excitonic states. The exciton binding energies of the first bright (optically allowed) exciton, determined as the difference between the $G_0 W_0$ band gap and the lowest dipole-allowed optical excitation, are summarized in Table 5.2. These zero-temperature binding energies are relatively large, reaching 120 meV for Ca₆CSe₄ and 200 meV for Sr₆CSe₄. It should be noted that these values represent upper bounds, as finite-temperature effects are not included. In realistic conditions, lattice polarization, electron-phonon interactions, and dynamical screening are expected to reduce the effective exciton binding energies [43, 244]. The real-space distribution of the electron component of the first bright exciton is illustrated in Fig. 5.4 (b,d), with the hole fixed 1 Å above the atom contributing most strongly to the VBM, within a $6 \times 6 \times 6$ supercell. In

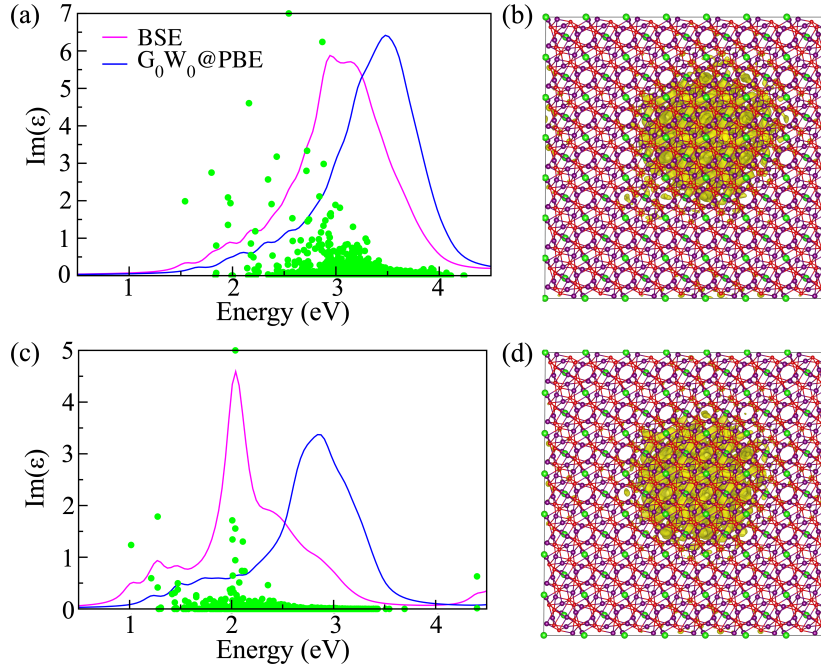


Figure 5.4: Imaginary part of the dielectric function obtained from G_0W_0 @PBE (blue) and BSE@ G_0W_0 @PBE (magenta) approaches, along with the spatial distribution of the first bright exciton, with the hole fixed 1 Å above the atoms contributing most to the valence band maximum (VBM), for Ca_6CSe_4 (a,b) and Sr_6CSe_4 (c,d). The green circles in panels (a) and (c) represent the relative oscillator strengths, normalized to a maximum value of 1 and rescaled for visual clarity. The exciton wavefunctions shown in panels (b) and (d) are visualized using an isosurface value of $0.038 \text{ e}/\text{\AA}^3$ over a $6 \times 6 \times 6$ supercell. Green, purple, and red spheres denote C, M (Ca/Sr), and Se atoms, respectively.

both compounds, the exciton wavefunction extends over multiple unit cells, consistent with Wannier-type character. Notably, Ca_6CSe_4 exhibits a slightly larger exciton spatial extent compared to Sr_6CSe_4 .

5.3.3 Dynamical properties

All preceding calculations are performed on optimized 0 K structures, providing a static description of the electronic and optical properties. At finite temperature, however, thermal fluctuations dynamically modulate the crystal lattice, which in turn perturbs the instantaneous electronic structure and influences carrier relaxation pathways. To capture these effects, we perform AIMD simulations at 300 K in the canonical (NVT) ensemble. Thermal excitation induces an expansion of both intra- and inter-octahedral bonds. The average M -C bond length increases to 2.429 Å in Ca_6CSe_4 and 2.608 Å in Sr_6CSe_4 , while the inter-octahedral C-C distance expands to 7.188 Å and 7.635 Å, respectively. The larger expansion observed in Sr_6CSe_4 indicates

its softer lattice. Thermal disorder is quantified by computing the root-mean-square fluctuation (RMSF) of atomic positions over the last 5 ps of the AIMD trajectories (Table 5.4). Substituting

Table 5.4: Root-mean-square fluctuation (RMSF) of atomic positions (in Å) for the M -site, C, and Se atoms in Ca_6CSe_4 and Sr_6CSe_4 , averaged over the last 5 ps of the AIMD trajectories.

$M_6\text{CSe}_4$	M	C	Se
Ca_6CSe_4	0.089	0.072	0.068
Sr_6CSe_4	0.069	0.072	0.068

Ca with Sr significantly reduces the RMSF at the metal sites, reflecting the larger ionic radius and heavier mass of Sr, which suppress vibrational amplitudes. In contrast, the fluctuations of C and Se atoms remain nearly identical in both compounds. Overall, Sr_6CSe_4 exhibits smaller atomic displacements than Ca_6CSe_4 , indicating greater structural rigidity at finite temperature.

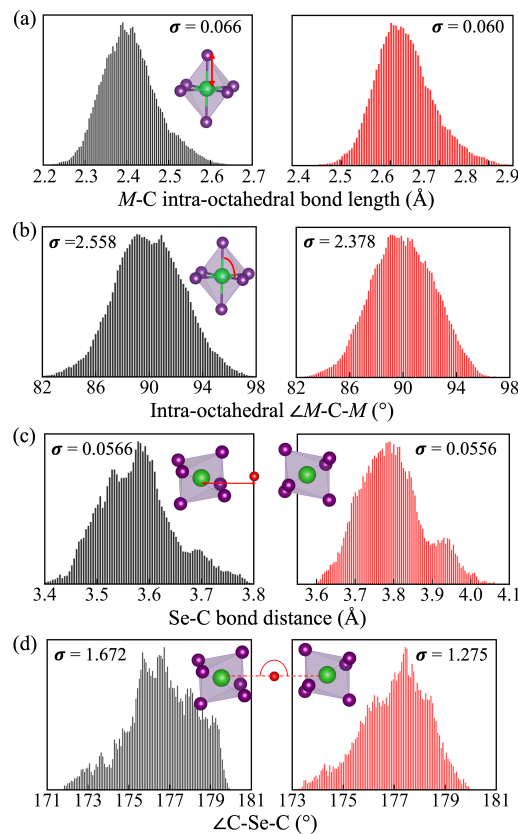


Figure 5.5: Statistical distributions of (a) intra-octahedral M -C bond lengths, (b) $\angle M$ -C- M bond angles, (c) Se-C bond distances, and (d) $\angle C$ -Se-C bond angles obtained from the last 5 ps of the AIMD trajectories for Ca_6CSe_4 (black) and Sr_6CSe_4 (red). Standard deviations (σ) of the fluctuations are also reported.

Deeper insight into the nature of these fluctuations is obtained from the statistical distribu-

tions of key structural parameters extracted from the last 5 ps of the trajectories (Fig. 5.5). These include intra-octahedral M -C bond lengths, $\angle M$ -C- M bond angles, Se-C distances, and $\angle C$ -Se-C bond angles. The bond angles $\angle M$ -C- M and $\angle C$ -Se-C reflect distortions of the M_6C octahedra. The distributions are noticeably broader for Ca_6CSe_4 than for Sr_6CSe_4 , with larger standard deviations, indicating stronger deviations from ideal octahedral geometry and a more dynamically disordered lattice. These structural fluctuations directly modulate orbital overlap and thereby perturb the instantaneous electronic structure. As shown in Fig. 5.6

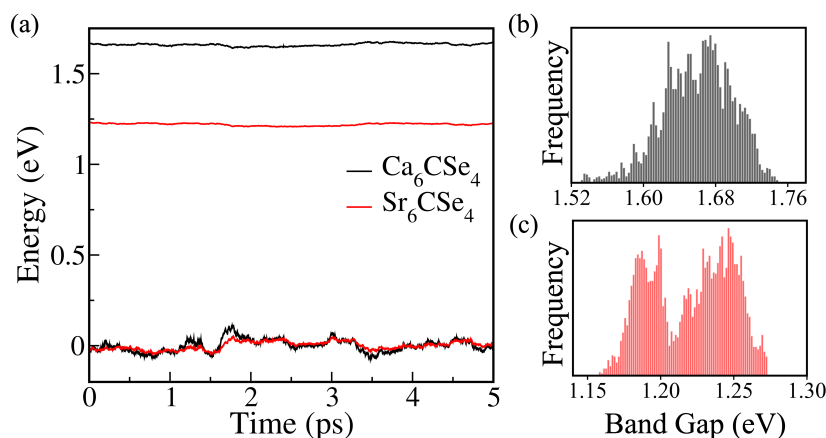


Figure 5.6: (a) Time evolution of the VBM and CBM energies for Ca_6CSe_4 (black) and Sr_6CSe_4 (red). Panels (b) and (c) show the statistical distributions of the band gap for Ca_6CSe_4 and Sr_6CSe_4 , respectively. The band gaps are scaled to the $G_0 W_0$ @PBE values. The standard deviation is larger for Ca_6CSe_4 ($\sigma = 0.0386$ eV) than for Sr_6CSe_4 ($\sigma = 0.0279$ eV).

(a), the VBM exhibits significantly larger temporal energy fluctuations than the CBM in both materials. This asymmetry originates from their distinct orbital characters: the VBM consists of directional C- p , Se- p , and M - d states that are highly sensitive to bond-angle distortions, whereas the CBM is dominated by more isotropic M - s and Se- s states. Consequently, thermal lattice motion couples more strongly to the valence band edge. Consistent with its larger structural disorder, Ca_6CSe_4 displays stronger VBM fluctuations than Sr_6CSe_4 . The enhanced fluctuations in Ca_6CSe_4 are also reflected in the band-gap distributions, depicted in Fig. 5.6 (b,c). The standard deviation of the band gap is larger for Ca_6CSe_4 ($\sigma = 0.0386$ eV) than for Sr_6CSe_4 ($\sigma = 0.0279$ eV). These dynamic band-edge fluctuations influence carrier localization and electronic coherence, thereby playing an important role in non-radiative recombination and HC relaxation dynamics.

5.3.4 Hot-carrier relaxation

To probe hot-electron relaxation, we simulate photoexcitation from the VBM to the CBM+5 state, corresponding to excitation energies of 2.0–2.14 eV. The subsequent intraband relaxation of electrons within the conduction band is tracked from the CBM+5 state and shown in Fig. 5.7 (b,e). The decay of the excited-state population is fitted to an exponential function, $f(t) =$

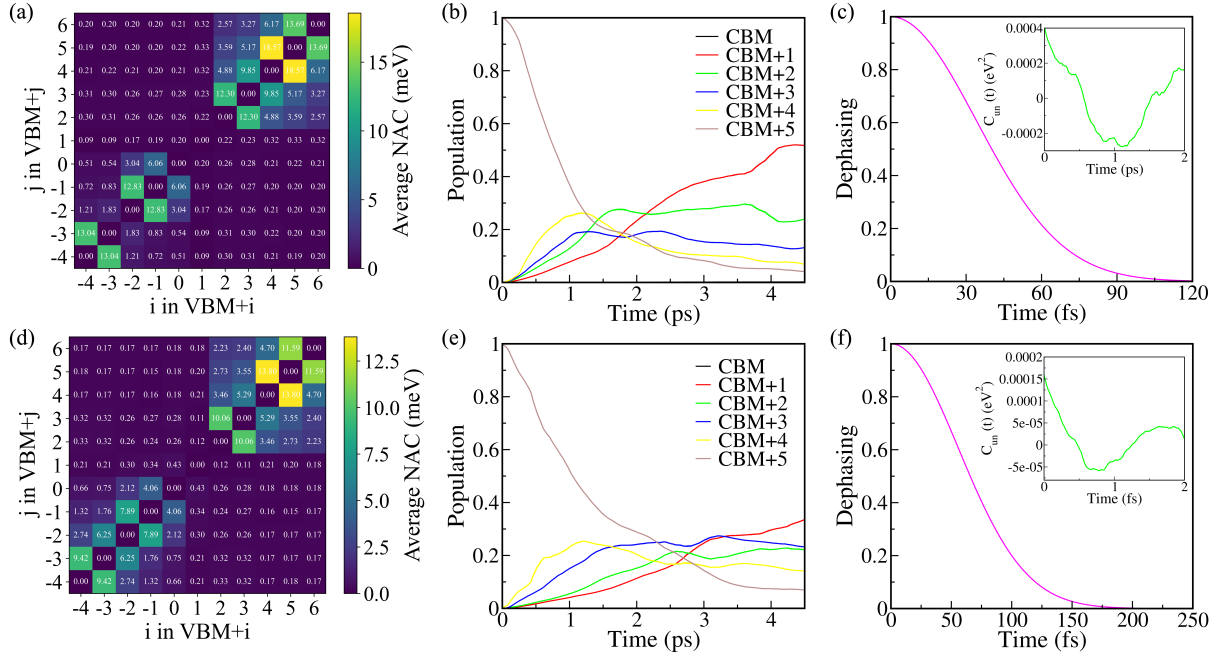


Figure 5.7: (a, d) Averaged absolute nonadiabatic (NA) couplings among states spanning VBM-4 to CBM+5 for Ca_6CSe_4 and Sr_6CSe_4 , respectively. (b, e) Time evolution of hot-electron relaxation following excitation to CBM+5 for Ca_6CSe_4 and Sr_6CSe_4 . (c, f) Pure-dephasing functions corresponding to the CBM+5 to CBM transition for Ca_6CSe_4 and Sr_6CSe_4 . Insets display the unnormalized auto-correlation function, $C_{un}(t)$. The initial value, $C_{un}(0)$, represents the squared band-gap fluctuation amplitude; larger fluctuations lead to faster dephasing.

$\exp(-t/\tau)$, yielding cooling times of 1.1 ps for Ca_6CSe_4 and 1.6 ps for Sr_6CSe_4 . As the electron approaches the band edge, the relaxation slows markedly (Table 5.5), with particularly long lifetimes at the CBM+1 state (6.8 ps for Ca_6CSe_4 and 9.1 ps for Sr_6CSe_4). This bottleneck originates from the large energy separation between CBM+1 and CBM (Fig. 5.8)—0.614 eV in Ca_6CSe_4 and 0.856 eV in Sr_6CSe_4 —which suppresses phonon-assisted transitions.

To elucidate the microscopic origin of the cooling behavior, we analyze the role of electron-phonon interactions. Inelastic electron-phonon scattering governs energy dissipation by enabling transitions between electronic states via lattice vibrations. The strength of this inter-

Table 5.5: Hot-carrier relaxation lifetimes (in ps) corresponding to the VBM+*i* (hot-hole relaxation) and CBM+*i* states (hot-electron relaxation).

Transition	Ca ₆ CSe ₄	Sr ₆ CSe ₄
CBM+5	1.1	1.6
CBM+4	1.0	1.5
CBM+3	1.2	2.1
CBM+2	2.4	3.8
CBM+1	6.8	9.1
VBM-1	4.2	6.8
VBM-2	2.4	2.7
VBM-3	3.0	1.9
VBM-4	2.5	2.3

action is quantified by the NA coupling:

$$d_{ij} = -i\hbar \langle \varphi_i | \frac{\partial}{\partial t} | \varphi_j \rangle = -i\hbar \frac{\langle \varphi_i | \nabla_R \hat{H} | \varphi_j \rangle}{\varepsilon_i - \varepsilon_j} \dot{R}, \quad (5.1)$$

where $\varphi_{i/j}$ and $\varepsilon_{i/j}$ are the Kohn–Sham wavefunctions and eigenvalues, $\hat{H}$ is the Kohn–Sham Hamiltonian, and $\dot{R}$ is the nuclear velocity. In practice, d_{ij} is evaluated from wavefunction overlaps along the AIMD trajectory, and its magnitude directly determines the probability of nonradiative transitions.

The averaged absolute NA coupling matrices, depicted as heat maps Fig. 5.7 (a,d), show that couplings between adjacent states are stronger than the nonadjacent states, confirming the dominant role of sequential intraband transitions in hot-electron relaxation. Nevertheless, finite off-diagonal elements indicate that non-adjacent jumps also contribute. Importantly, Ca₆CSe₄ exhibits systematically larger NA couplings across the conduction-band manifold compared to Sr₆CSe₄, which directly explains its faster cooling dynamics. This difference stems from the smaller energy separation between the conduction band states in Ca₆CSe₄ which enhance the denominator term in Eq. (5.1). The slowing down of cooling rate at the CBM+1 state can also be attributed to the large energy separations (0.614 eV in Ca₆CSe₄ and 0.856 eV in Sr₆CSe₄) and correspondingly weak NA coupling (0.22 and 0.12 meV, respectively). This quantitative inverse scaling directly explains the observed HC cooling dynamics: rapid relaxation at high energies (~ 1 ps) and a pronounced slowdown near the band edge (up to ~ 9 ps), where large energy gaps suppress phonon-assisted transitions.

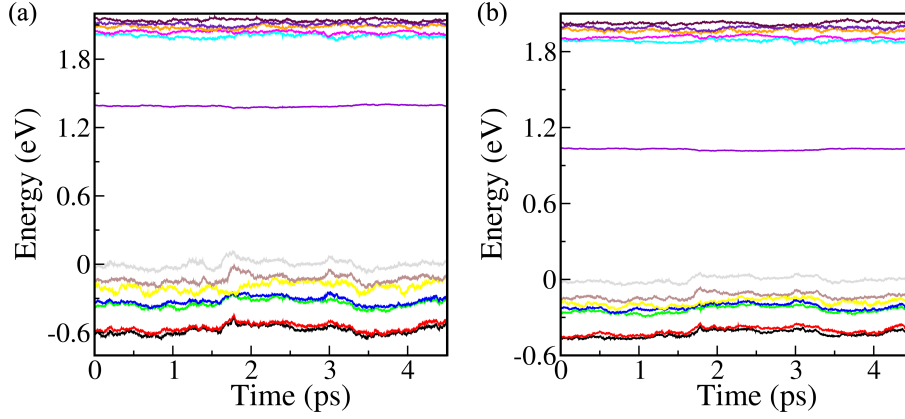


Figure 5.8: Time evolution of the electronic energy levels (from VBM-4 to CBM+5) over a 4.5 ps time window for (a) Ca_6CSe_4 and (c) Sr_6CSe_4 . The gray and violet lines denote the VBM and CBM, respectively.

In addition to inelastic scattering, elastic electron-phonon interactions also influence carrier dynamics by disrupting quantum coherence between electronic states. This decoherence is captured by the pure-dephasing function, obtained via the second-order cumulant expansion:

$$D_{ij}(t) = \exp \left(-\frac{1}{\hbar^2} \int_0^t dt' \int_0^{t'} dt'' C_{ij}(t'') \right), \quad (5.2)$$

where $C_{ij}(t) = \langle \delta E_{ij}(t), \delta E_{ij}(0) \rangle$ is the unnormalized autocorrelation function of the phonon-induced energy-gap fluctuations between states i and j , with $C_{un}(0)$ denoting its initial value. This quantity represents the squared amplitude of band-gap fluctuations, with larger values leading to faster dephasing. Here, $\delta E_{ij}(t) = E_{ij}(t) - \langle E_{ij} \rangle$ denotes the instantaneous deviation of the energy gap from its ensemble average. The pure-dephasing time is extracted by fitting $D_{ij}(t)$ to a Gaussian function of the form $\exp[-0.5(t/\tau)^2]$. As shown in Fig. 5.7 (c,f), Ca_6CSe_4 exhibits a larger value of $C_{un}(0)$, indicating stronger energy-gap fluctuations and hence faster decoherence (34.2 fs for Ca_6CSe_4 and 55.8 fs for Sr_6CSe_4). Although faster dephasing generally reduces transition probabilities, the significantly stronger NA couplings in Ca_6CSe_4 dominate, resulting in overall faster hot-electron cooling.

Hot-hole relaxation exhibits behavior qualitatively similar to hot-electron cooling. To investigate hot-hole dynamics, we promote an electron from VBM-4 to the CBM and monitor the evolution of hole populations within the valence-band manifold. The population decay and corresponding pure-dephasing functions are shown in Fig. 5.9. Relaxation proceeds predominantly via sequential intraband transitions (VBM-4 $\rightarrow$ VBM-3 $\rightarrow$ VBM-2 $\rightarrow$ VBM-1 $\rightarrow$ VBM), consistent with the dominance of adjacent-state couplings observed in the NA matrices (Fig. 5.7(a,d)). The initial relaxation from VBM-4 exhibits comparable lifetimes in both com-

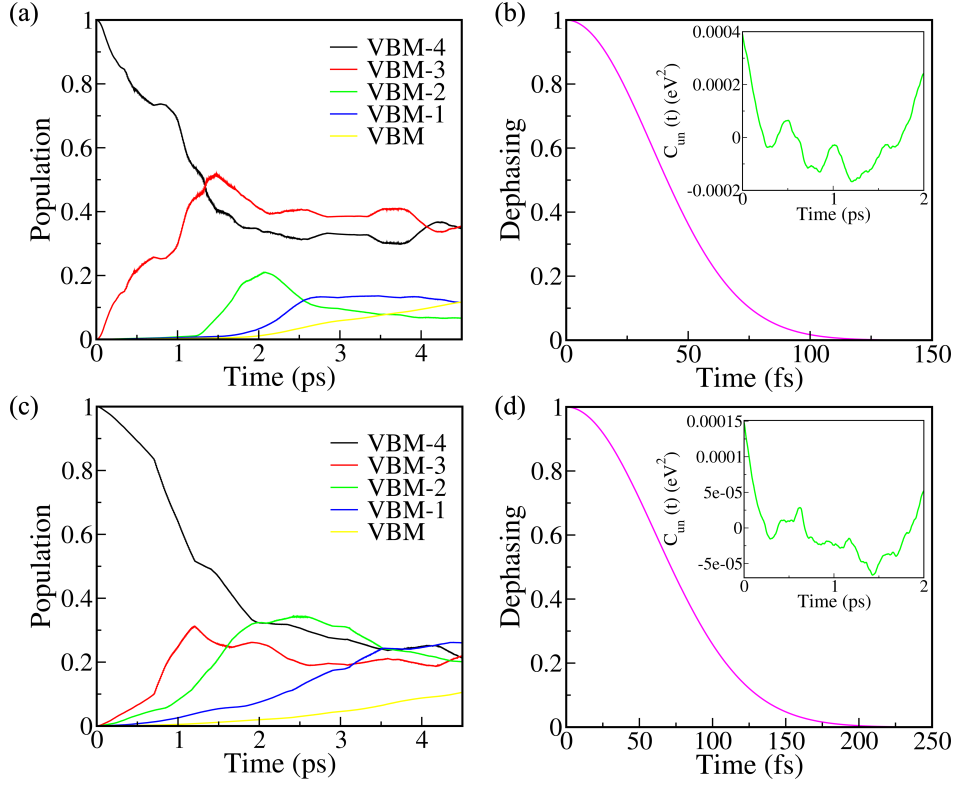


Figure 5.9: Hot-hole relaxation from VBM-4 to the VBM in (a) Ca_6CSe_4 and (c) Sr_6CSe_4 . Panels (b) and (d) show the corresponding pure-dephasing functions for the VBM-4 to VBM transition in Ca_6CSe_4 and Sr_6CSe_4 , respectively. The insets in (b) and (d) display the unnormalized autocorrelation functions of the VBM-4–VBM energy-gap fluctuations. A larger initial value, $C_{un}(0)$, indicates stronger gap fluctuations and generally corresponds to a shorter pure-dephasing time.

pounds, 2.5 ps for Ca_6CSe_4 and 2.3 ps for Sr_6CSe_4 . Thus occurs despite stronger NA coupling in Ca_6CSe_4 , due to faster dephasing (35.1 fs in Ca vs 60.8 fs in Sr) which suppresses electronic transitions. In Ca_6CSe_4 , the larger energy separation between the VBM-2 and VBM-3 states (0.125 eV) reduces the NA coupling (1.83 meV), slowing relaxation at this step. In contrast, Sr_6CSe_4 has smaller energy spacings (0.038 eV) and stronger NA coupling (6.25 meV), leading to faster relaxation through these states. Closer to the band edge, a pronounced slowdown occurs at VBM-1, with lifetimes of 4.2 ps (Ca_6CSe_4) and 6.8 ps (Sr_6CSe_4). This slowdown arises from large energy separation and reduced NA couplings, which are weaker in Sr_6CSe_4 (4.06 meV vs 6.06 meV in Ca), leading to a longer lifetime at VBM-1 and transient hole accumulation.

Overall, both hot-electron and hot-hole cooling in $M_6\text{CSe}_4$ occur on the picosecond timescale (1–9 ps), with a clear slowdown near the band edges. This behavior contrasts with much faster HC cooling in conventional semiconductors, such as ~ 50 fs in GaAs, ~ 0.4 ps in non-

nanostructured Si, and $\sim 2\text{--}3$ ps in CIGS [245, 246, 247, 248]. In lead halide perovskites such as MAPbI_3 , cooling times vary widely depending on excitation conditions and sample morphology, ranging from sub-picosecond relaxation in bulk films to tens or hundreds of picoseconds (and even nanoseconds) under specific conditions [249]. These results demonstrate that HC relaxation in $M_6\text{CSe}_4$ can be systematically tuned through composition-driven modifications of the electronic structure and lattice dynamics.

5.3.5 Nonradiative recombination

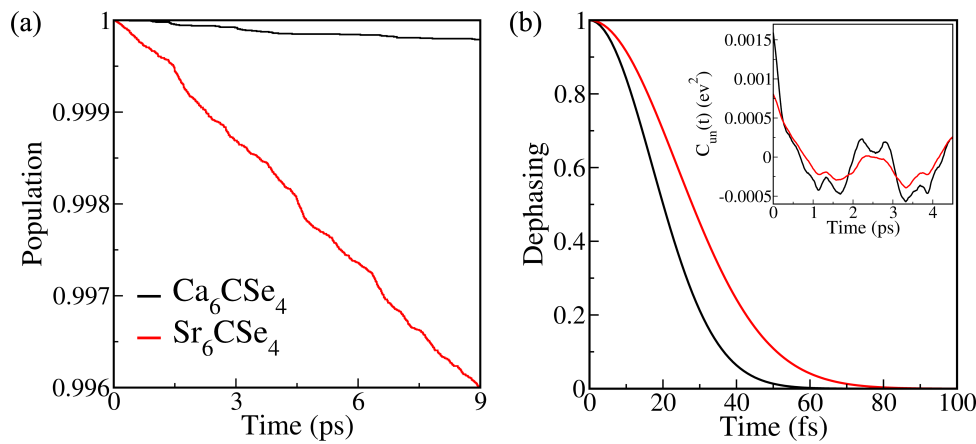


Figure 5.10: Time evolution of the population of the first excited state corresponding to the VBM–CBM transition.

Figure 5.10 (a) shows the time evolution of the excited-state population associated with the VBM–CBM transition in $M_6\text{CSe}_4$. Because intraband HC cooling occurs on picosecond timescales—much faster than recombination—we assume that electrons and holes have relaxed to the CBM and VBM, respectively, before recombination takes place. The decay of the excited-state population is fitted with a single exponential function $\exp(-t/\tau)$, yielding non-radiative recombination lifetimes of 40.3 ns for Ca_6CSe_4 and 2.2 ns for Sr_6CSe_4 (Table 5.6). The nearly order-of-magnitude difference highlights a strong suppression of non-radiative recombination in the Ca-based compound. The recombination lifetimes are governed by the interplay of three key factors: the band-gap magnitude, the strength of NA couplings, and the electronic decoherence time [231, 234]. To obtain quantitatively reliable estimates, the time-averaged PBE band gaps are rescaled to the $G_0 W_0$ @PBE values.

First, Sr_6CSe_4 exhibits significantly stronger NA couplings—more than twice those of Ca_6CSe_4 , thereby accelerating nonradiative recombination. Notably, the stronger coupling in Sr_6CSe_4 occurs despite its reduced structural fluctuations. This counterintuitive result is explained by

Table 5.6: Canonically averaged scaled band gaps (in eV), with original band gaps included in parenthesis, averaged absolute NA coupling ($\langle |d_{ij}| \rangle$), root mean square (RMS) NA coupling (d_{ij}^{RMS}), pure-dephasing time (τ_ϕ), and nonradiative recombination lifetime (τ_{nr}) for the VBM–CBM transition.

$M_6\text{CSe}_4$	Gap (eV)	$\langle d_{ij} \rangle$ (meV)	d_{ij}^{RMS} (meV)	τ_ϕ (fs)	τ_{nr} (ns)
Ca_6CSe_4	1.66 (0.77)	0.20	0.34	17.0	40.3
Sr_6CSe_4	1.22 (0.37)	0.43	0.76	23.7	2.2

its smaller band gap, which reduces the energy denominator in the NA coupling expression (Eq. (5.1)) and thereby amplifies d_{ij} . Second, electronic decoherence modulates the recombination rate. The pure-dephasing times extracted from Fig. 5.10 (b) are 17.0 fs for Ca_6CSe_4 and 23.7 fs for Sr_6CSe_4 . Faster decoherence in Ca_6CSe_4 , driven by its larger band-gap fluctuations (Fig. 5.6), suppresses electronic transitions between the VBM and CBM, thereby reducing the recombination rate. This behavior is consistent with the higher initial value of the unnormalized autocorrelation function, $C_{\text{un}}(0)$ in Ca_6CSe_4 . Collectively, the larger band gap, weaker NA couplings, and faster decoherence in Ca_6CSe_4 act cooperatively to inhibit non-radiative recombination, resulting in its substantially longer carrier lifetime. In contrast, Sr_6CSe_4 combines a smaller band gap, stronger NA couplings, and slower decoherence, all of which favor faster recombination.

The predicted lifetimes can be placed in the broader context of hybrid halide perovskites such as MAPbI_3 , which typically exhibit intrinsic theoretical lifetimes in the range of ~ 0.8 –3 ns, extending beyond 10 ns when structural effects such as twin boundaries or nuclear quantum effects are considered [250, 251, 252, 253]. Experimentally, carrier lifetimes in MAPbI_3 have been further enhanced from the nanosecond to the microsecond regime through strategies such as defect passivation and interface engineering [254]. In this context, the intrinsic lifetimes of the present compounds—particularly Ca_6CSe_4 —indicates intrinsically suppressed nonradiative recombination, highlighting their potential as promising candidates for high-efficiency photovoltaic applications.

5.4 Conclusion

In summary, we present a comprehensive first-principles investigation of the electronic structure and excited-state carrier dynamics in the carbide antiperovskites Ca_6CSe_4 and Sr_6CSe_4 .

Our $G_0 W_0$ -BSE calculations reveal direct band gaps in the visible-to-infrared range for both compounds, along with moderate exciton binding energies, providing a reliable description of their optical response. NAMD simulations further elucidate the key factors governing carrier dynamics. HC cooling occurs on the picosecond timescale and exhibits pronounced band-edge bottlenecks arising from large energy level separations and weak NA couplings, with faster cooling in Ca_6CSe_4 . This intrinsic slowing of carrier relaxation, compared to conventional semiconductors, suggests potential for HC retention. In parallel, nonradiative recombination lifetimes are dictated by a delicate interplay between band gap, NA coupling strength, and electronic decoherence. Notably, Ca_6CSe_4 exhibits a significantly longer lifetime of 40.3 ns—nearly an order of magnitude higher than the 2.2 ns obtained for Sr_6CSe_4 . This contrasting behavior between cooling and recombination reflects the combined influence of band-gap magnitude, NA coupling, and decoherence dynamics.

These findings identify A-site cation substitution as an effective strategy to tune the electronic structure, lattice fluctuations, and electron-phonon interactions, thereby enabling control over excited-state dynamics. The coexistence of picosecond-scale cooling, pronounced band-edge bottlenecks, and nanosecond carrier lifetimes highlights carbide antiperovskites as promising lead-free materials for optoelectronic and photovoltaic applications. These results motivate future experimental efforts aimed at fully realizing the potential of these materials. More broadly, this work establishes composition-driven lattice engineering as a powerful framework for tailoring excited-state dynamics in antiperovskites and related material systems.

Dimensionality-Driven Excitonic Engineering in BiSeI: An Ab Initio Many-Body Study

6.1 Introduction

Chalcohalides, with the general formula $MChX$ (M = metal cation, Ch = divalent chalcogen: S/Se, X = monovalent halogen: Cl/Br/I), are an emerging class of materials for optoelectronics and solar-light harvesting applications, owing to their earth abundance, non-toxicity, and low environmental impact [37]. A key advantage over lead halide perovskites (LHPs) is their enhanced structural stability, which arises from the covalent nature of M – Ch bonds, in contrast to the predominantly ionic bonding in LHPs. Among chalcohalides, bismuth seleniodide (BiSeI), a heavy pnictogen chalcohalide, exhibits promising optoelectronic properties, including a suitable band gap (1.29–1.32 eV), low effective carrier masses, and high dielectric constants [255, 256, 257, 258, 259, 260].

BiSeI is a quasi-one-dimensional (1D) anisotropic crystal composed of $[(BiSeI)_\infty]_2$ chains bound by weak van der Waals (vdW) interactions, forming a characteristic chain-like structure (Fig. 6.1 (a)). Despite its indirect band gap, strong optical absorption arises from a nearby direct transition, with energy close to the Shockley–Queisser limit [257]. Early device studies on BiSeI–BiSI alloys showed limited photovoltaic performance [261], which was subsequently attributed to suboptimal alignment with transport layers [262]. More recently, Ganose *et al.* [263] employed quasiparticle (QP) self-consistent GW ($QSGW$) approach and Boltzmann transport theory, revealing low effective masses along the $BiChI$ ($Ch = S, Se$) chains, strong near-edge absorption, and high spectroscopically limited maximum efficiency (SLME) of approximately 25% for BiSeI. While a few studies have employed density functional theory (DFT) and GW methods to explore BiSeI’s electronic properties, a systematic investigation of excitonic effects

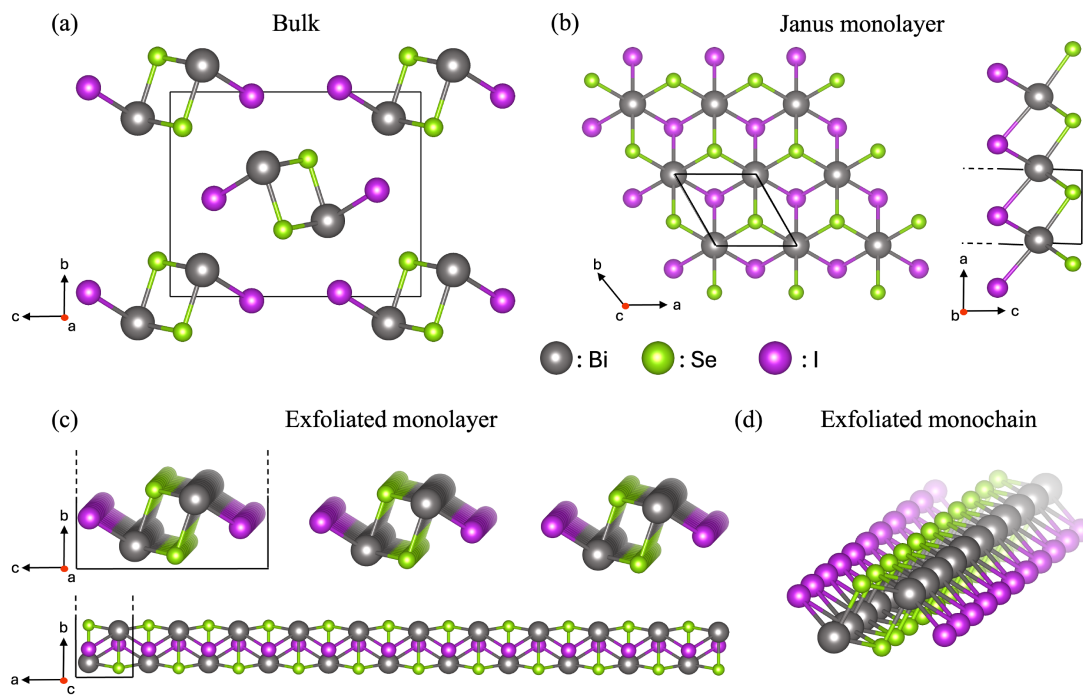


Figure 6.1: Crystal structures of (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer, and (d) exfoliated monochain BiSeI. The black boxes indicate the unit cells of the respective structures. The exfoliated monolayer in (c) is obtained by cleaving a layer from the bulk structure in panel (a) along the a - c plane, while the monochain in (d) is extracted as a one-dimensional $[\text{BiSeI}]_{\infty}$ chain from the bulk. The Janus monolayer structure shown in panel (b) was proposed theoretically in earlier studies [6, 7, 8].

in BiSeI remains absent.

The layered, chain-like crystal structure of BiSeI renders it a promising candidate for the fabrication of low-dimensional systems through exfoliation or mechanical cleavage [264, 265, 266, 267, 268, 269, 270]. Low-dimensional systems exhibit physical properties distinct from their bulk counterparts, primarily due to enhanced geometric confinement and reduced dielectric screening. These effects give rise to the formation of strongly bound electron–hole pairs, or excitons, which remain stable even at room temperature [271, 272, 273]. The optical properties of low-dimensional materials are predominantly governed by these strongly bound excitons, which can be leveraged in a range of optoelectronic applications, including photovoltaic solar cells, light-emitting diodes, and photodetectors [274, 275, 276, 277, 278]. Furthermore, dimensional reduction offers novel opportunities, such as blue shifting of the band gap due to quantum confinement effects enabling tunable light emission without altering the material’s composition, which could otherwise introduce deep trap states. Despite these advantages, low-dimensional chalcogenides, including BiSeI, remain underexplored compared to their bulk counterparts.

In this study, we investigate the dimensionality–driven evolution of electronic, optical and ex-

citonic properties in BiSeI, including its bulk form, an exfoliated two-dimensional (2D) monolayer, a one-dimensional monochain, and a theoretically predicted Janus monolayer [279, 280, 6]. Using DFT [281] and single-shot GW ($G_0 W_0$) calculations within the many-body perturbation theory (MBPT) framework [121, 119, 282], we compute QP band structures, revealing a notable widening of band gaps with reduced dimensionality. To account for electron–hole interactions, we solve the Bethe-Salpeter equation (BSE) within the Tamm-Dancoff approximation [179, 283, 120] using the YAMBO package [102, 101, 240]. Our results show a significant increase in the exciton binding energy with decreasing dimensionality. We further examine the magnitude and sign of bright-dark exciton splitting (Δ_{bd}), a critical factor for optoelectronic performance, and its variation with dimensionality and spin-orbit coupling (SOC). We find that all structures exhibit positive Δ_{bd} , except the Janus monolayer. Additionally, we incorporate substrate-induced dielectric screening using effective mass models for 2D [284, 285] and 1D [286] systems, finding a substantial reduction in exciton binding energy due to substrate effects. With suitable infrared-to-visible band gaps, large absorption coefficients ($> 10^4 \text{ cm}^{-1}$), and tunable excitonic properties, BiSeI emerges as a promising candidate for next-generation optoelectronic and excitonic applications.

6.2 Computational methodology

The first-principles calculations within the DFT framework are performed using the Vienna *ab initio* Simulation Package (VASP) [287, 288, 94, 98] and the Quantum Espresso (QE) suite [95]. To incorporate interactions between valence and core electrons, fully relativistic projector augmented wave (PAW) [93] and norm-conserving pseudopotentials [239] are used for VASP and QE, respectively. The semicore $4d$ and $5d$ states for iodine and bismuth are explicitly included in the valence electrons due to their importance in the electronic structure, as discussed in the literature [289, 290]. Geometry optimization is performed with the VASP code using the PBEsol [291] functional, a revised version of PBE [88] for solids. It accurately predicts lattice constants for systems with vdW interactions without explicitly accounting for them [262, 292]. Bulk BiSeI is lattice optimized until the residual forces on the atoms are less than $10^{-3} \text{ eV/\AA}$, with a plane wave kinetic energy cut-off of 500 eV. The relaxed lattice parameters (see Table 6.4) closely align with the experimental values, with an error under 1 % [293]. This optimized bulk structure is used to exfoliate low-dimensional structures, followed by relaxation

of their atomic positions. A 20 Å vacuum is applied in low-dimensional structures to prevent fictitious interactions between periodic images.

In order to include electron many-body effects and accurately estimate the fundamental band gap [229, 118], we use $G_0 W_0$ [282] approximation on top of PBE functional for calculating the electronic band structures. In this approach, the electronic self-energy is evaluated within Hedin’s GW framework, where the dynamically screened Coulomb interaction is described within the random phase approximation (RPA). The frequency dependence of the dielectric function is treated using the plasmon-pole approximation (PPA) [241]. Optical absorption spectra without electron–hole interactions are computed within the RPA using the $G_0 W_0$ QP energies ($G_0 W_0$ -RPA). To incorporate excitonic effects, we solve BSE within the Tamm–Dancoff approximation [119]. All $G_0 W_0$ and BSE calculations are performed within the framework of many-body perturbation theory using the YAMBO package [102, 101, 240]. QE is used for the starting point ground state electronic structure calculations with a plane-wave kinetic energy cut-off of 50 Ry. The truncated Coulomb potential with slab and cylindrical geometry is used for the 2D and 1D structures to avoid interaction between repeated images along the non-periodic directions [294]. This approach allows us to achieve well-converged QP gaps with moderate vacuum spacing and computationally feasible k -point grids [295]. In order to speed up the convergence of electronic Green’s function with respect to the number of unoccupied bands and k -grid, we use the Bruneval-Gonze terminator [296] and the random integration method (RIM) [297]. The computational settings used in DFT and GW /BSE calculations are listed in Table 6.1–6.3.

Table 6.1: Computational settings for the DFT (PBE) calculations of bulk, Janus monolayer, exfoliated (exf.) monolayer and monochain BiSeI.

	Bulk	Janus monolayer	Exf. monolayer	Exf. Monochain
Plane wave cutoff	50 Ry	50 Ry	50 Ry	50 Ry
Number of bands	800	600	600	600
k -grid	$12 \times 6 \times 5$	$24 \times 24 \times 1$	$15 \times 1 \times 6$	$40 \times 1 \times 1$

Table 6.2: Computational settings for the *GW* (on top of PBE) calculations of bulk, Janus monolayer, exfoliated (exf.) monolayer and monochain BiSeI.

	Bulk	Janus monolayer	Exf. monolayer	Exf. Monochain
Exchange cutoff	40 Ry	40 Ry	40 Ry	40 Ry
XC potential cutoff	DFT value	DFT value	DFT value	DFT value
<i>GW</i> bands	600	200	400	400
Dielectric cutoff	8 Ry	8 Ry	8 Ry	8 Ry
<i>k</i> -grid (<i>GW</i> /BSE)	12×6×5	24×24×1	15×1×6	40×1×1

Table 6.3: Computational settings for BSE (on top of *GW*@PBE) calculations of bulk, Janus monolayer, exfoliated (exf.) monolayer and monochain BiSeI.

	Bulk	Janus monolayer	Exf. monolayer	Exf. Monochain
Static screening bands	600	200	400	400
BSE bands	187-198	41-56	91-102	91-102
Valence bands	6	8	6	6
Conduction bands	6	8	6	6
<i>k</i> -grid (<i>GW</i> /BSE)	12×6×5	24×24×1	15×1×6	40×1×1

6.3 Results and discussion

6.3.1 Crystal structure and stability

Bulk BiSeI crystallizes in an orthorhombic structure with the *Pnma* space group, as shown in Fig. 6.1 (a). The optimized lattice parameters are listed in Table 6.4. Its structure comprises $[(\text{BiSeI})_\infty]_2$ parallel ribbons oriented along the *a*-axis, which are held together by weak vdW interactions. Within each ribbon, Bi and Se atoms are covalently bonded, while I atoms form ionic bonds with the Bi-Se framework [298, 280, 299, 300]. The presence of weak vdW interactions between adjacent ribbons makes it a strongly quasi-1D material [293]. These ribbons are arranged in parallel layers forming a layered chain-like structure. A monolayer is obtained by exfoliating the bulk crystal along the *a*–*c* plane. While 1D monochain is obtained by extracting a $[\text{BiSeI}]_\infty$ ribbon from the bulk structure. To evaluate the feasibility of exfoliating the 2D monolayer and the 1D monochain, we compute their exfoliation energies using the expression

Table 6.4: Lattice parameters of the theoretically optimized structures of bulk BiSeI, Janus monolayer, exfoliated monolayer and monochain BiSeI.

	a (Å)	b (Å)	c (Å)
Bulk	4.18	8.63	10.64
Janus monolayer	4.19	4.19	-
Exfoliated monolayer	4.18	-	10.64
Exfoliated Monochain	4.18	-	-

[301, 302]:

$$E_{exf} = E_{nD}/N_{nD} - E_{bulk}/N_{bulk} \quad (6.1)$$

where $E_{nD/bulk}$ and $N_{nD/bulk}$ represent the total energies and number of atoms in n-dimensional or bulk structures, respectively. The estimated E_{exf} values for the 2D monolayer and the 1D monochain are 200 meV and 212 meV. These values are lower than those of some experimentally exfoliated structures, indicating their experimental viability [303, 304, 301]. Fig. 6.1 (c,d) illustrates the exfoliated 2D monolayer and 1D monochain structures, exhibiting $P2_1m$ space group symmetry with vacuum along the b and b/c axis, respectively. We also examine the theoretically proposed BiSeI Janus monolayer [6, 7, 8], which was constructed using the experimentally realized BiTeI monolayer [305]. As shown in Fig. 6.1 (b), the Janus BiSeI structure exhibits $P3m1$ space group symmetry.

The stability of low-dimensional materials is a crucial factor that must be thoroughly assessed. To examine their dynamical stability, we compute the phonon dispersion relations, as depicted in Fig. 6.2. The absence of negative frequencies throughout the phonon spectrum confirms the dynamical stability of these structures. To investigate thermal stability, we perform *ab-initio* molecular dynamics (AIMD) simulations in the canonical (NVT) ensemble at 300 K for a duration of 10 ps with a time step of 1 fs. The evolution of system's total energy over time is presented in Fig. 6.3. The total energy remains nearly constant throughout the simulation, with no bond breaking observed. The structures retain their integrity, closely resembling the equilibrium configurations at 0 K, indicating thermal stability at room temperature.

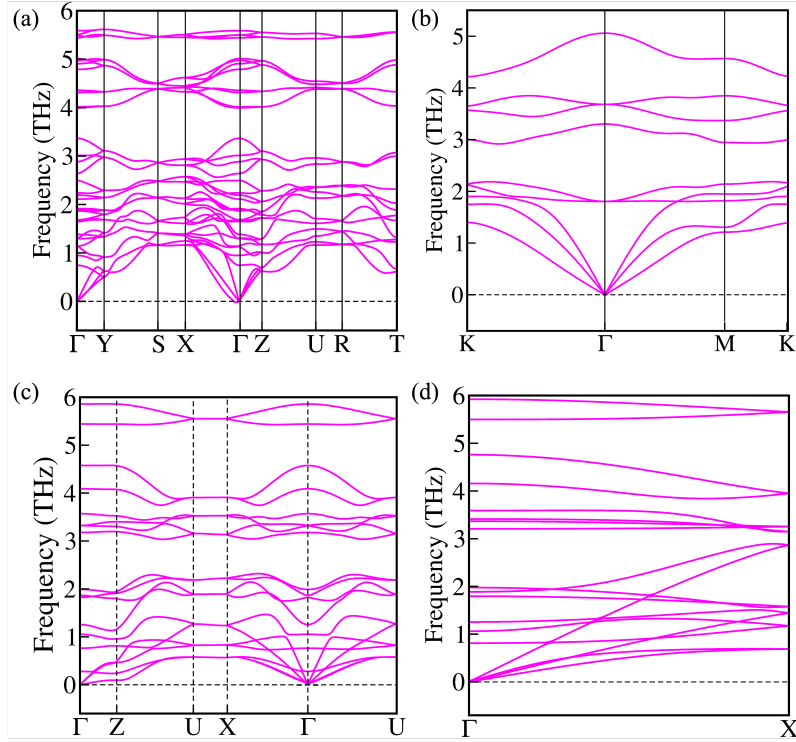


Figure 6.2: Phonon band structure for (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer, and (d) exfoliated monochain of BiSeI obtained using density functional perturbation theory (DFPT).

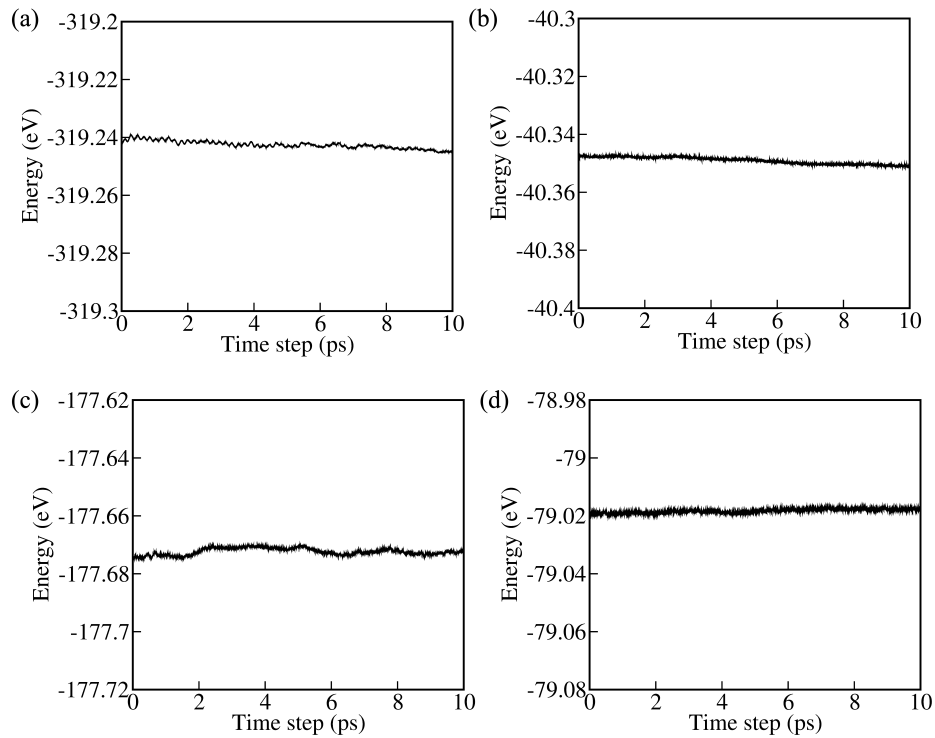


Figure 6.3: Total energy as a function of time step obtained from molecular dynamics simulations in the canonical (NVT) ensemble at 300 K for (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer, and (d) exfoliated monochain of BiSeI.

6.3.2 Electronic structure

To investigate the electronic properties of bulk BiSeI and its low-dimensional derivatives, we analyze their electronic band structures, obtained using PBE and $G_0 W_0$ @PBE methods (Fig. 6.4). Arrows in the band structure indicate their lowest indirect and direct band gaps. All

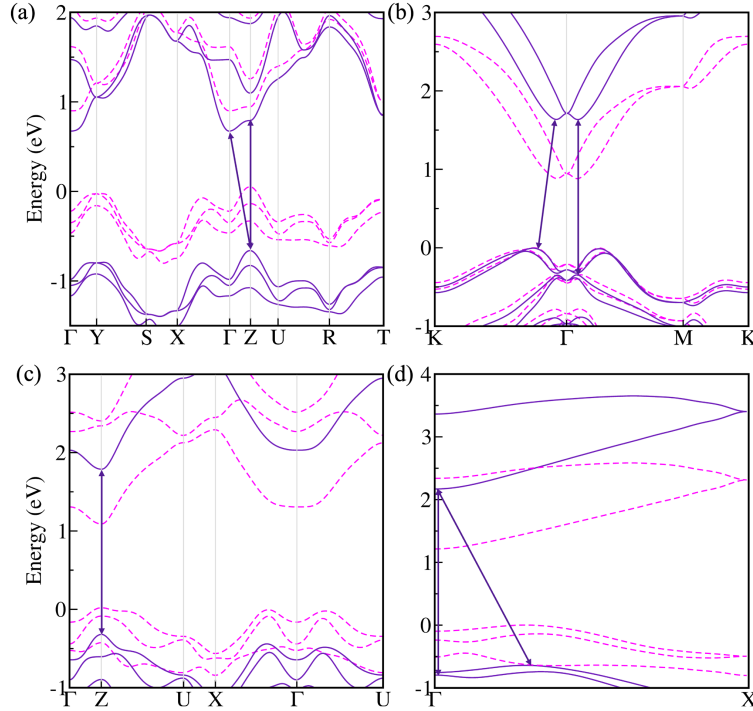


Figure 6.4: Electronic band structures of (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer and (d) exfoliated monochain of BiSeI computed using PBE (dashed) and $G_0 W_0$ @PBE (solid) methods, including spin-orbit coupling (SOC). Arrows indicate the lowest indirect and direct fundamental band gaps for each structure.

structures, except the exfoliated 2D monolayer, are found to be indirect band gap semiconductors. The corresponding band gap values are summarized in Table 6.5. In bulk BiSeI (Fig. 6.4 (a)), the valence band maximum (VBM) occurs between the Γ and Z high-symmetry points, while the conduction band minimum (CBM) is located at the Γ point. Valence bands exhibit higher dispersion compared to conduction bands both parallel and perpendicular to the atomic chains, suggesting significant interchain coupling and relatively higher hole mobility compared to electron mobility. The conduction bands are however highly non-parabolic and possess maximum dispersion along the chain direction (a -axis). Dimensional reduction leads to a notable increase in the band gap, which can be attributed to quantum confinement effects. For the 2D Janus monolayer (see Fig. 6.4 (b)), an indirect band gap is observed with both VBM and CBM lying between the Γ and K points. Furthermore, the difference between the two lowest indirect

Table 6.5: Lowest indirect (ID) and direct (D) band gaps (in eV) computed using PBE without SOC, PBE+SOC and $G_0 W_0$ @PBE+SOC approaches.

	PBE		PBE+SOC		$G_0 W_0$ @PBE	
	ID	D	ID	D	ID	D
Bulk	1.56	1.69	0.85	0.89	1.33	1.46
Janus monolayer	1.67	2.17	0.88	1.15	1.64	1.98
Exfoliated monolayer	1.82	1.88	-	1.07	-	2.14
Exfoliated monochain	1.91	2.33	1.22	1.46	2.81	2.97

band gaps and the two lowest direct band gaps is merely 10 meV. However, for the exfoliated 2D monolayer (Fig. 6.4 (c)), there is a direct band gap with both VBM and CBM located at the Z point. Notably, this direct gap character emerges upon the inclusion of SOC. Similar to bulk, valence bands are more dispersive than conduction bands. Lastly, the exfoliated 1D monochain shows an indirect band gap, with VBM located between the Γ and X points and CBM at the Γ point.

Since the PBE functional is known to significantly underestimate band gaps, we perform $G_0 W_0$ calculations on top of PBE to incorporate many-body effects. This results in systematically larger QP band gaps compared to PBE. While the inclusion of QP corrections leads to a systematic increase in the band gap, the overall shape of the band structure and nature of the band gap (indirect or direct) remains unchanged. These QP corrections are more pronounced in low-dimensional structures, attributed to the reduced dielectric screening, which enhances electron–electron interactions. Interestingly, the energy difference between direct and indirect QP band gaps is relatively small for the bulk (0.13 eV) and the 1D monochain (0.16 eV), whereas the 2D Janus monolayer exhibits a more substantial difference of 0.34 eV. Since, $G_0 W_0$ results are sensitive to the DFT starting point, we performed additional calculations using partial self-consistent GW (GW_0) for bulk BiSeI. The resulting indirect and direct band gaps are 1.36 eV and 1.49 eV, respectively – differing from $G_0 W_0$ by only ~ 30 meV. Given this small discrepancy, we proceeded with $G_0 W_0$ for all subsequent calculations. Furthermore, due to the presence of heavy elements in BiSeI, SOC plays a significant role in shaping the electronic band structure, often shifting band edges by more than 0.5 eV (see Table 6.5). Thus, to ensure accuracy, all calculations reported in this work incorporate SOC effects.

Fig. 6.5 shows the atomic orbital- and symmetry-projected partial density of states, calculated using the PBE functional. Across all dimensions, VBM is primarily determined by the hybridization of I- p and Se- p orbitals, with smaller contributions from Bi- s and Bi- p orbitals located deeper within the valence band. The interaction between Bi- s and anionic- p orbitals is expected to increase the valence band dispersion, akin to other halides with ns^2 lone-pairs [306, 307], thereby reducing hole effective masses and enhancing hole mobility. On the other hand, CBM is predominantly characterized by Bi- p orbitals with notable contributions from I- p and Se- p orbitals. This hybridization between cationic- p and anionic- p orbitals in the valence and conduction bands leads to substantial cross-band hybridization, imparting a mixed ionic-covalent character to the material. The mixed character, in turn, is known to impart strong lattice polarization and large dielectric constants [306, 307].

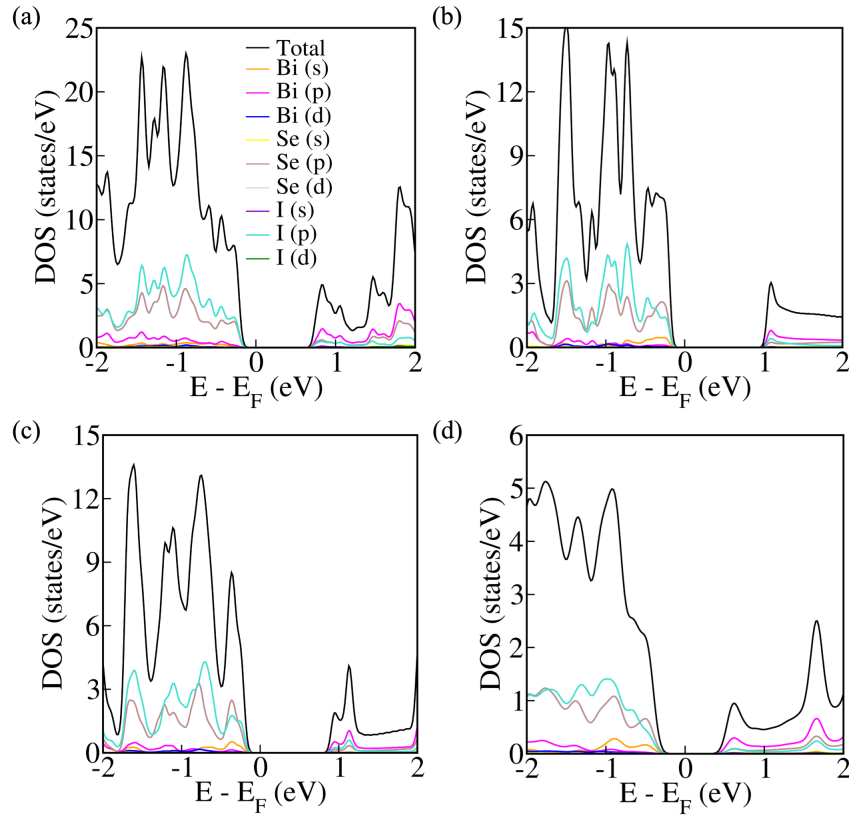


Figure 6.5: Atomic orbital- and symmetry-projected partial density of states (DOS) for (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer, and (d) exfoliated monochain obtained using PBE functional, incorporating SOC.

6.3.3 Optical properties and excitonic effects

Further, to incorporate electron–hole interactions, we compute the optical absorption spectra by solving BSE on top of QP band structures, as illustrated in Fig. 6.6. The solid and dotted curves represent spectra obtained with (BSE@ G_0W_0) and without (G_0W_0 -RPA) electron–hole interactions, respectively. The direct G_0W_0 band gap is indicated by the vertical dashed black line, while colored solid lines denote excitonic transitions (oscillator strengths). The first bright (optically allowed) exciton is identified as the excitonic state with finite oscillator strength, defined here as exceeding 5% of the maximum value. The exciton binding energy is calculated as the difference between the QP band gap and the excitation energy.

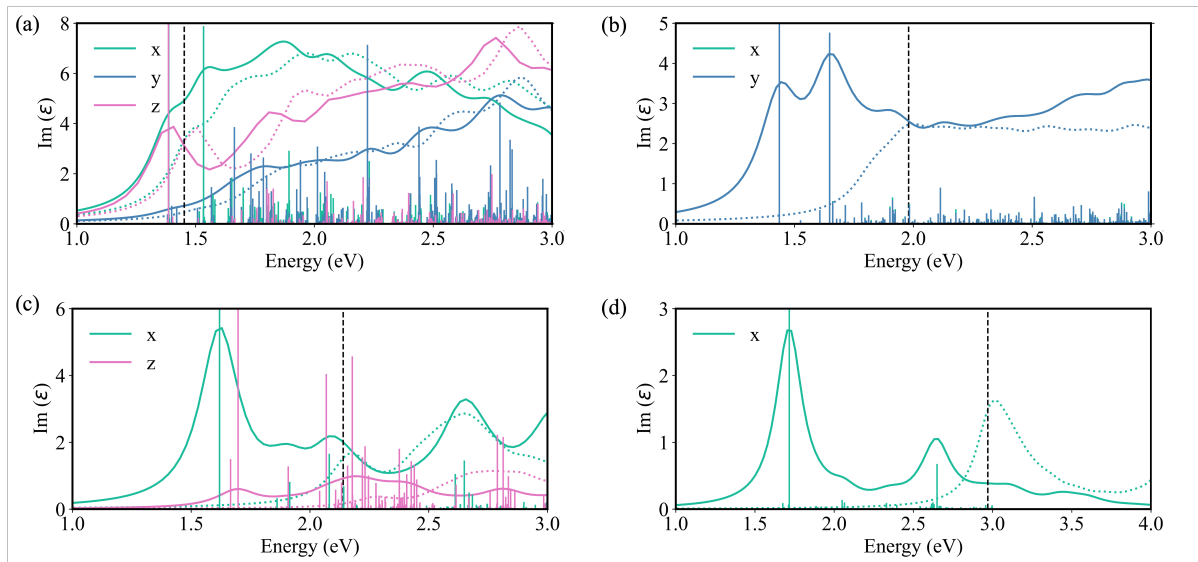


Figure 6.6: Absorption spectra for (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer, and (d) exfoliated monochain BiSeI, estimated at the G_0W_0 -RPA (dotted curve) and BSE@ G_0W_0 (solid curve) levels, along each polarization direction. The vertical dashed black line indicates the G_0W_0 direct band gap. The colored vertical lines indicate the oscillator strengths of the excitonic transitions, scaled proportionally to the intensity of $\text{Im}(\epsilon)$ in each panel for visualization purposes. The anisotropy in the absorption spectrum originates from the intrinsic geometric anisotropy of the crystal.

Including electron–hole interactions induces a significant red shift in the optical spectra across all configurations. Notably, the presence of finite oscillator strength below the G_0W_0 direct band gap confirms the existence of bound excitons, highlighting the importance of excitonic effects in shaping the optical response of these materials. In the bulk material, the first bright exciton peak appears at 1.39 eV ($E \parallel x$ and z) and 1.40 eV ($E \parallel y$), corresponding to exciton binding energies (E_b) of 70 meV, 70 meV, and 60 meV, respectively (see Fig. 6.6 (a)). Sev-

eral dark excitons (i.e. optically inactive excitonic states) are observed below the first bright exciton. Notably, the theoretically estimated optical band gap at 0 K is slightly larger than the experimental band gap (1.29 eV at 290 K [308]), likely due to the exclusion of temperature-dependent effects in the theoretical calculations. Recent experiments by Nielsen *et al.* [309] have demonstrated pronounced electron–phonon interactions in bulk BiSeI. While a detailed treatment of such interactions is beyond the scope of the present study, they are expected to play a crucial role in renormalizing both the band gap and the excitation energies.

In the isotropic 2D Janus monolayer, the first bright excitonic peak occurs at 1.43 eV, with a large binding energy of 0.55 eV, as depicted in Fig. 6.6 (b). These excitons are doubly degenerate, both optically active, and no dark excitonic states are observed below the optical band gap. For the exfoliated monolayer (Fig. 6.6 (c)), the first bright excitonic peak appears at 1.62 eV (*x*-polarization) and 1.66 eV (*z*-polarization), with corresponding binding energies of 0.52 and 0.48 eV, respectively. Notably, both 2D monolayers approximately follow the linear scaling relation between the QP band gap (E_g) and E_b , namely $E_b \approx E_g/4$, as proposed by Jiang *et al.* [310] for 2D semiconductors. Unlike the Janus monolayer, multiple dark excitons exist below the optical band gap in the exfoliated monolayer. In the 1D monochain (Fig. 6.6 (d)), the first bright exciton appears at 1.72 eV, with a remarkably high binding energy of 1.25 eV. This exciton is doubly degenerate, comprising one dark and one bright component, with several additional dark states lying energetically below it. Across all dimensionalities, the absorption onset spans the infrared to visible region of the solar spectrum, highlighting the potential for solar-harvesting applications. To further assess their potential, we compare the calculated absorption coefficients (α) with the AM1.5G solar flux (shown in grey in Fig. 6.7). All materials display large absorption coefficients ($\alpha > 10^4 \text{ cm}^{-1}$) and a substantial spectral overlap with the solar irradiance, confirming their capability to effectively harness solar energy.

We observe that the optical response of BiSeI is dominated by strongly bound excitons. However, a material’s photo- or electro-luminescence yield critically depends on the nature of its lowest energy excitonic state — whether it is optically active (bright) or inactive (dark). When dark excitons lie below the first bright exciton, they introduce non-radiative decay channels that suppress light emission, particularly at low temperatures. Therefore, accurate determination of both the magnitude and sign of the bright–dark exciton splitting (Δ_{bd}) is essential, not only for understanding fundamental excitonic physics but also for advancing optoelectronic applications. Beyond light emission, low-lying dark excitons—if strongly bound—can serve as a

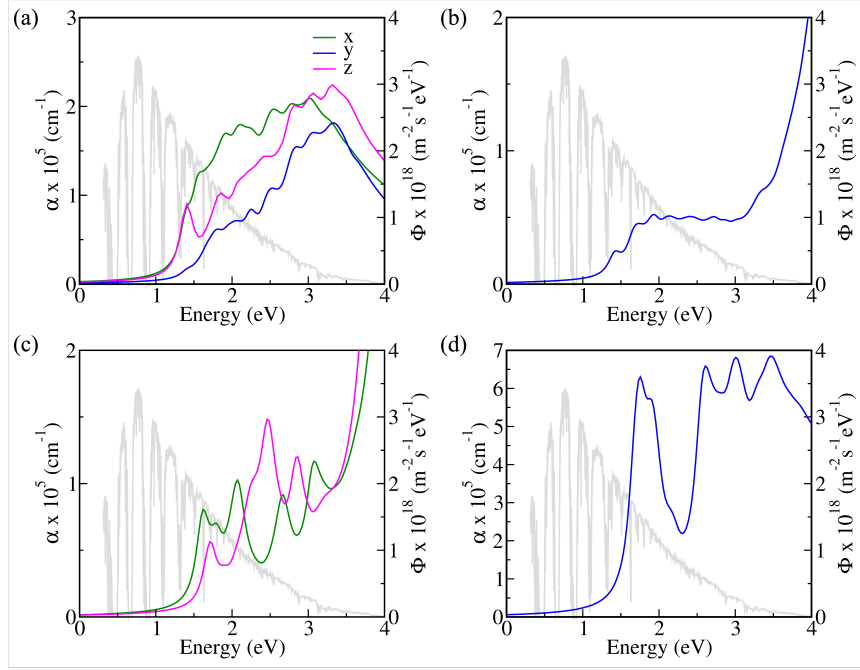


Figure 6.7: Absorption coefficient (α) as a function of photon energy for (a) bulk BiSeI, (b) Janus monolayer, (c) exfoliated monolayer, and (d) exfoliated monochain, shown along different polarization directions. The absorption spectra exhibit pronounced anisotropy with respect to polarization in both the bulk and its exfoliated low-dimensional forms, attributed to the intrinsic geometric anisotropy of the crystal structure. For comparison, the solar photon flux (AM1.5G spectrum) is plotted in grey.

platform for realizing exotic phenomena such as excitonic Bose–Einstein condensation [311]. Fig. 6.8 (a) presents Δ_{bd} , defined as the difference between the excitation energies of the first bright exciton and the lowest dark exciton, with and without SOC. Our results show that Δ_{bd} is highly sensitive to the system’s dimensionality. As the quantum and dielectric confinement increases—from bulk to exfoliated monolayer to monochain— Δ_{bd} increases significantly. In these cases, the bright exciton lies above the dark states, resulting in a positive Δ_{bd} . Interestingly, the Janus monolayer exhibits a considerably smaller splitting than the exfoliated monolayer. Upon including SOC, a notable reduction in Δ_{bd} is observed across all configurations. For the case of Janus monolayer, SOC reverses the sign of the splitting, yielding a negative Δ_{bd} , which implies that the lowest-energy exciton is optically bright. Fig. 6.8 (b) and (c) schematically illustrate qualitative excitonic band structures corresponding to positive and negative Δ_{bd} , respectively. In bulk BiSeI, the SOC-corrected Δ_{bd} is approximately 7 meV, equivalent to the thermal energy at ~ 81 K. Consequently, excitons excited optically at low temperature rapidly relax into the lower-energy dark states, where they can become trapped. However, as temperature increases, thermal excitation can promote excitons into bright states,

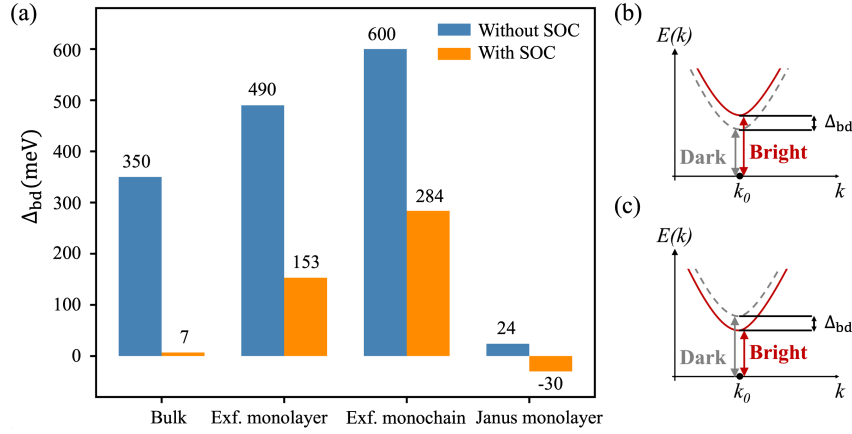


Figure 6.8: (a) Bright–dark exciton splitting (Δ_{bd} in meV) for bulk BiSeI, exfoliated monolayer, exfoliated monochain, and Janus monolayer, calculated using BSE@ $G_0 W_0$ @PBE for the x-polarization direction, without (blue) and with SOC (orange). (b) and (c) depict qualitative exciton band structures for representative cases where the lowest-energy exciton is dark and bright, respectively. Here, Δ_{bd} is defined as the difference between the excitation energy of the first bright exciton and the lowest dark exciton, as indicated in panel (b) and (c).

enabling radiative recombination. Thus, dark excitons no longer fully suppress diffusion but merely slow it down. In contrast, for the exfoliated monolayer and monochain, Δ_{bd} exceeds 30 meV, potentially inhibiting exciton diffusion even at room temperature.

For a detailed analysis of the optical transitions associated with the first bright exciton, we superimpose the exciton weights ($|A_{cvk}^\lambda|$) onto the $G_0 W_0$ @PBE band structures, as shown in Fig 6.9 [312]. The exciton wavefunction is expressed in the electron–hole product basis as: $\sum_{cvk} A_{cvk}^\lambda \phi_{ck} \phi_{vk}$. The coefficients A_{cvk}^λ quantify the contribution of each electron–hole pair (from valence band v to conduction band c at k -point k) to the exciton wavefunction labeled by λ [313, 314, 315]. The red shades in Fig 6.9 represent the vertical electronic transitions from the direct band gaps that predominantly contribute to the formation of the first bright exciton in the respective material corresponding to the x -polarization direction. We note that the dominant k -point regions and band-to-band transitions contributing to the first bright exciton remain essentially the same for all polarization directions, with differences arising primarily in the magnitude of the exciton weights. In bulk BiSeI, the first bright exciton originates from transitions between the VBM and CBM, predominantly localized at the Z high-symmetry point in reciprocal space and along the Z– Γ and Z–U directions, as depicted in Fig 6.9 (a). For the Janus monolayer (Fig. 6.9 (b)), the dominant contributions occur along the Γ –K and Γ –M paths, involving the highest valence band and lowest conduction band. Similar to bulk BiSeI,

in the exfoliated monolayer shown in Fig 6.9 (c), the strongest contributions remain centered around the Z point, in addition to the contributions from the Z– Γ and Z–U directions, between the VBM and CBM. For the exfoliated monochain, the first bright exciton, located at 1.72 eV, arises from transitions from VBM-2 and VBM-3 to CBM and CBM+1 at the Γ point. However, accurately interpolating exciton weights onto the band structure necessitates a dense k -grid, which exceeds our current computational scope. Consequently, while the relevant results have been successfully generated and analyzed, we have omitted the corresponding plot.

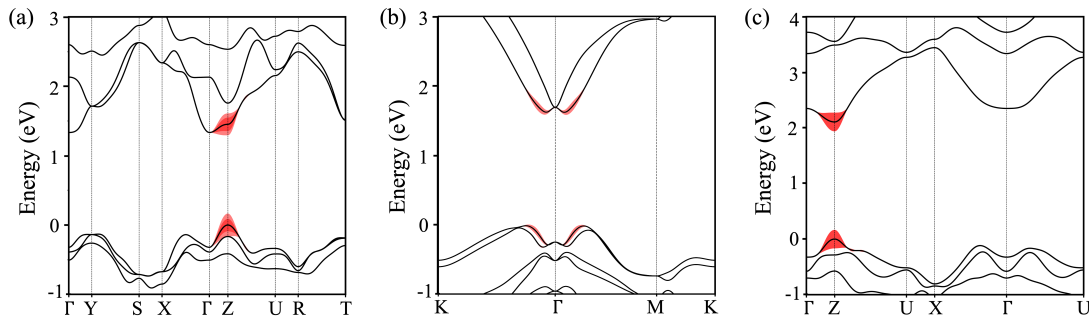


Figure 6.9: The first bright exciton formation in (a) bulk BiSeI, (b) Janus monolayer, and (c) exfoliated monolayer BiSeI for x -polarization direction. The exciton weights $|A_{cvk}^\lambda|$ (depicted in red shades) are superimposed on the $G_0 W_0$ @PBE band structures (including SOC) to visually inspect which electron and hole states, and k -points primarily contribute to the first bright exciton. Thicker red lines indicate larger weights, i.e., a stronger contribution from the corresponding k -point and band pair.

To visualize the first bright exciton in real space, we plot its isosurface on the atomic lattice of BiSeI, as shown in Fig 6.10. The exciton wavefunction is computed by fixing the hole at a position 1 Å above the unit cell, centered on the atom that predominantly contributes to the VBM. In bulk BiSeI (Fig. 6.10 (a,b)), the wavefunction of the first bright exciton reveals the spatial distribution of the electron, with the hole located on an iodine atom. The exciton exhibits anisotropic spatial distribution with large electron–hole separation along the atomic chain direction (a -axis), consistent with the quasi-1D nature of the crystal. In this phase, the exciton extends over multiple unit cells and has a relatively low binding energy and large radius, features characteristic of Wannier-type excitons. In contrast, the Janus monolayer (Fig. 6.10 (c)) hosts an exciton that spans only 3-4 unit cells. In the exfoliated monolayer and monochain structures (Fig. 6.10 (d, e)), the exciton is primarily distributed along a single atomic chain, accompanied by a substantial increase in E_b . This progression from weakly bound excitons in bulk BiSeI to strongly bound excitons with smaller radius in its low-dimensional derivatives demonstrates the fundamental impact of reduced dimensionality on excitonic properties.

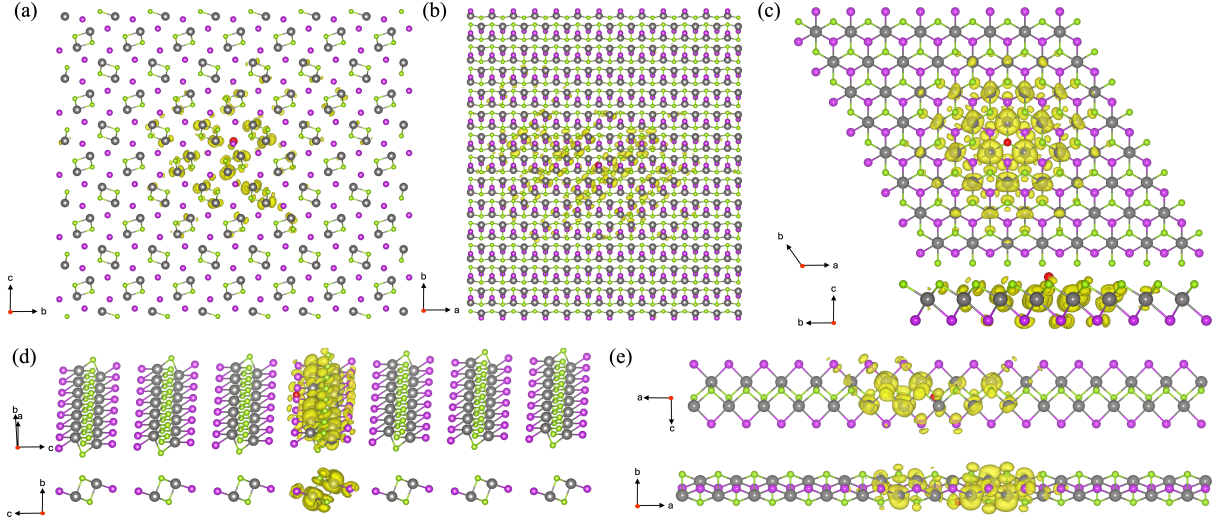


Figure 6.10: Top and side views of the wave functions corresponding to the first bright exciton for (a,b) bulk BiSeI calculated using $12 \times 6 \times 5$ supercell, (c) Janus monolayer ($6 \times 6 \times 1$ supercell), (d) exfoliated monolayer ($6 \times 1 \times 6$ supercell), and (e) exfoliated monochain ($15 \times 1 \times 1$ supercell) of BiSeI. The red dot represents the position of the hole, fixed at a position $1 \text{ \AA}$ above the atom contributing most significantly to the valence band maximum. The isosurface value is set to $0.16 \text{ e/\AA}^3$. Grey, green and pink circles represent Bi, Se, and I atoms, respectively.

6.3.4 Effect of substrate screening on exciton binding energy

In low-dimensional materials, the exciton binding energy is highly sensitive to the surrounding dielectric environment due to the reduced and non-local nature of dielectric screening. Herein, we adopt a computationally efficient effective mass model [284, 285] to systematically investigate the impact of substrate-induced screening on excitonic properties in low-dimensional systems, where BSE calculations become computationally demanding. For the 2D monolayers, considering the in-plane anisotropy, the excitonic Hamiltonian can be written as [284]:

$$H = -\frac{\hbar^2}{2\mu_x} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\mu_y} \frac{\partial^2}{\partial y^2} + V_{2D}(x, y)$$

where, $\mu_{x,y}$ are the reduced exciton masses along the x and y directions, respectively, obtained from the $G_0 W_0$ band structures, and V_{2D} is the Coulomb potential due to a point charge located at the origin in the 2D dielectric space. Keldysh derived an expression for this interaction potential between charges in a 2D material [316]:

$$V_{2D}(r) = \frac{e^2}{4\varepsilon_0(\varepsilon_1 + \varepsilon_2)r_0} \left[H_0\left(\frac{r}{r_0}\right) - Y_0\left(\frac{r}{r_0}\right) \right]$$

where H_0 and Y_0 are the zeroth-order Struve and Bessel functions of the second kind. ε_1 and ε_2 are the dielectric constants of the surrounding medium, and $r_0 = \frac{4\pi\chi_{2D}}{\varepsilon_1 + \varepsilon_2}$ is the screening length

dependent on the 2D polarizability (χ_{2D}). The values of the reduced exciton masses and χ_{2D} are listed in Table 6.6. At large separations, the potential reduces to a $\frac{1}{r}$ form, while at short

Table 6.6: The 2D polarizability (χ_{2D}) and reduced exciton mass ($\mu_{x/y}$) along the in-plane directions (expressed in units of the electron rest mass m_e).

Material	χ_{2D} (Å)	μ_x, μ_y (m_e)
Janus monolayer	5.60	0.073, 0.073
Exfoliated monolayer	3.79	0.064 _x , 0.079 _z

range it diverges logarithmically, with the transition scale set by r_0 . To simplify the numerical implementation, we adopt the approximation to the Keldysh potential proposed by Cudazzo *et al* [285]:

$$V_{2D}(r) = \frac{e^2}{2\pi\epsilon_0(\epsilon_1 + \epsilon_2)r_0} \left[\ln\left(\frac{r}{r+r_0}\right) + [\gamma - \ln(2)]e^{\frac{-r}{r_0}} \right]$$

where γ is the Euler constant. This approximation closely matches the exact Keldysh form in both short- and long-range limits. We use a variational approach to calculate the ground-state exciton energy, assuming a trial wavefunction of the form:

$$\psi(x, y) = \sqrt{\frac{2}{\pi a_x a_y}} \exp\left(-\sqrt{\left(\frac{x}{a_x}\right)^2 + \left(\frac{y}{a_y}\right)^2}\right)$$

Here, a_x and a_y are variational parameters representing the exciton radii along the lateral axes of the monolayers. The lowest-energy eigenvalue of H gives the exciton binding energy. To

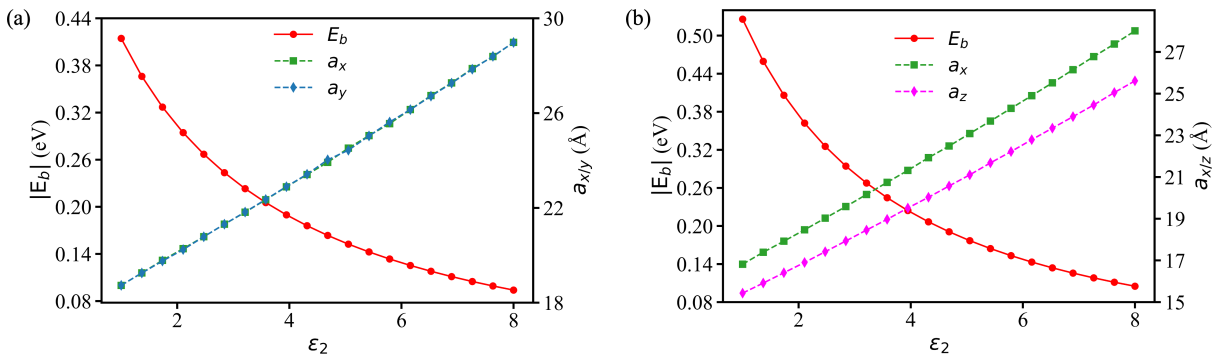


Figure 6.11: Exciton binding energy E_b and radius $a_{x/y}$ along the lateral axes, as a function of substrate dielectric constant ϵ_2 for the (a) Janus and (b) exfoliated BiSeI monolayers.

simulate the realistic environment of suspended or supported monolayers, we fix the dielectric constant of the top environment to $\epsilon_1 = 1$ (vacuum), while varying the bottom dielectric constant (ϵ_2) to model different substrate materials (see Fig. 6.11). For the freestanding (i.e.,

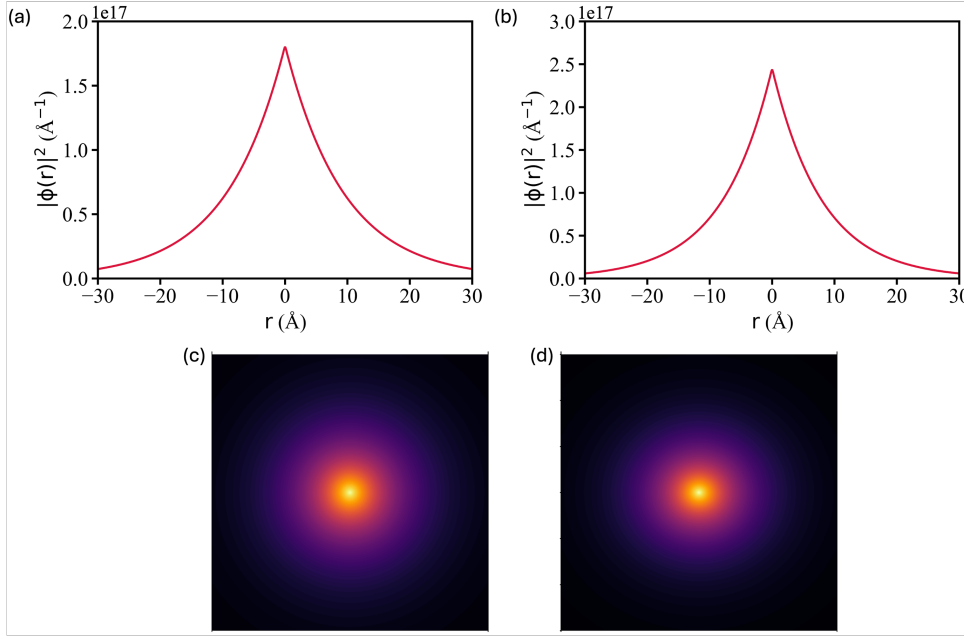


Figure 6.12: Exciton wavefunction distribution and squared exciton wavefunction $|\psi_1|^2$, shown in $30 \text{\AA} \times 30 \text{\AA}$, calculated using the effective mass model, for the lowest energy bright exciton state of the Janus monolayer (a,c) and exfoliated monolayer (b, d).

$\varepsilon_2 = 1$) Janus and exfoliated BiSeI monolayers, we obtain exciton binding energies of approximately 0.41 eV and 0.53 eV, respectively. The latter agrees well with our BSE calculated value, while the former is slightly underestimated. Our analysis reveals a substantial reduction in E_b upon substrate screening. For example, when placed on a SiO_2 substrate ($\varepsilon_2 = 3.9$) [317], E_b decreases to 0.19 eV and 0.22 eV for the Janus and exfoliated monolayer, corresponding to nearly 50 % reduction in both cases. This reduction is accompanied by an increase in the exciton radius, as evidenced by its nearly linear growth with increasing ε_2 . Furthermore, we present the spatial distribution of the exciton wavefunction $|\psi_1|^2$ for the lowest-energy exciton in Fig. 6.12, plotted over a $30 \text{\AA} \times 30 \text{\AA}$ region. Panels (a, c) correspond to the suspended Janus monolayer, while (b, d) show the exfoliated monolayer, highlighting the difference in their excitonic radii.

To extend this analysis to the 1D BiSeI monochain, we employ a similar effective-mass framework appropriate for strongly bound excitons. The relative motion of the electron-hole pair along the chain axis (x -direction) is described within the two-band effective-mass approximation by the 1D Schrödinger equation[318, 319]:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + W_{\text{eff}}(x) \right] \phi(x) = -E_b^M \phi(x), \quad (6.2)$$

where $\mu = m_e^* m_h^* / (m_e^* + m_h^*)$ is the reduced effective mass, $\phi(x)$ is the exciton envelope

function, and $W_{\text{eff}}(x)$ denotes the screened electron–hole interaction potential.

The BiSeI chain is modeled as a cylindrical wire with an effective radius R , extracted from its structural cross-section. The screened Coulomb interaction is constructed in reciprocal space as

$$\tilde{W}(q) = -\frac{e^2 \tilde{V}_{\text{bare}}(q)}{1 + \alpha_{1D}^0 q^2 \tilde{V}_{\text{bare}}(q)}, \quad (6.3)$$

where α_{1D}^0 is the static 1D polarizability per unit length, defined as $A^\perp(\epsilon_1(0) - 1)/4\pi$, obtained from the macroscopic dielectric response of the supercell for polarization along the chain direction. Here, $A^\perp$ denotes the cross-sectional area of the supercell in the yz plane. The reduced exciton mass is $0.16 m_e$ and α_{1D}^0 is $5.43 \text{ \AA}^2$. Two forms of the bare interaction $\tilde{V}_{\text{bare}}(q)$ are employed: (i) a softcore potential expressed in terms of the zeroth-order modified Bessel function K_0 , given by $2K_0(|q|R)$, and (ii) a regularized form involving the first-order modified Bessel function K_1 , given by $4(q^2 R^2)^{-1} [1 - |q|R K_1(|q|R)]$. Due to the non-analytic nature of the screened interaction, the exciton binding energy is evaluated variationally using the trial wavefunction

$$\phi(x) = \sqrt{\frac{2s^3}{a_{\text{exc}}^3}} |x| \exp\left(-\frac{s|x|}{a_{\text{exc}}}\right), \quad (6.4)$$

where s is a variational parameter and a_{exc} is the effective exciton Bohr radius. Minimization of the Hamiltonian expectation value with respect to s yields the binding energy E_b^M and the corresponding exciton radius.

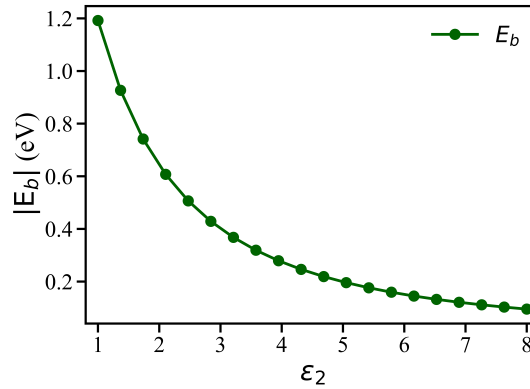


Figure 6.13: Exciton binding energy E_b as a function of substrate dielectric constant ϵ_2 for the exfoliated BiSeI monochain.

For the freestanding BiSeI monochain ($\epsilon_2 \approx 1$), the model predicts $E_b^M \approx 0.94 \text{ eV}$ and 1.19 eV using the softcore and modified softcore potentials, respectively. The latter shows excellent agreement with the BSE result of 1.25 eV . The strong quantum confinement and weak dielectric screening in 1D give rise to significantly enhanced binding energies compared to bulk and 2D

counterparts. When the chain is supported on a substrate (e.g., SiO_2 with $\varepsilon_2 = 3.9$), the additional environmental screening weakens the electron–hole interaction, reducing E_b^M to ~ 0.28 eV, corresponding to a decrease of nearly 76% (see Fig. 6.13).

6.4 Conclusion

In summary, we have systematically investigated the electronic and optical properties of bulk, Janus monolayer, exfoliated monolayer and monochain BiSeI using *ab initio* methods based on DFT (PBE) and many-body approaches (*GW*/BSE). Electronic band gaps computed using $G_0 W_0$ method on top of PBE orbitals provide quantitatively reliable band gaps. Among the four configurations, bulk BiSeI, the Janus monolayer, and the 1D monochain exhibit indirect band gaps, while the exfoliated monolayer transitions from an indirect to direct band gap upon inclusion of SOC. A systematic increase in the fundamental band gap and QP correction is observed with decreasing dimensionality, attributed to enhanced quantum confinement and reduced dielectric screening. Across all configurations, the band gaps fall within the infrared to visible range of the solar spectrum and exhibit substantial spectral overlap with the AM1.5G solar flux. The corresponding absorption coefficients exceed 10^4cm^{-1} , highlighting the potential of BiSeI for light-harvesting applications.

The excitonic properties, analyzed via BSE, reveal a clear dimensionality-driven evolution. Bulk BiSeI hosts excitons with large radius and small binding energies (~ 70 meV). Upon dimensionality reduction, there is a significant enhancement in the binding energies. The Janus and exfoliated monolayers exhibit comparable values, while the 1D monochain demonstrates a remarkably large value of 1.25 eV. In both the exfoliated monolayer and monochain, exciton wavefunctions are predominantly confined within individual atomic chains. Exciton fine structure analysis further reveals that the bright-dark splitting (Δ_{bd}) increases with decreasing dimensionality, from 7 meV in the bulk BiSeI to 153 meV in the exfoliated monolayer and 284 meV in the monochain. Interestingly, the Janus monolayer exhibits a negative Δ_{bd} , indicating that the lowest-energy exciton is optically active. The small splitting in bulk and negative value in the Janus monolayer, combined with their favorable band gaps and strong absorption coefficients, make them promising for solar-light harvesting applications. Conversely, the large positive values in the exfoliated monolayer and monochain (>30 meV) could suppress exciton diffusion at room temperature. Nevertheless, their large binding energies and long-lived dark

excitons governing the optical response make them attractive for excitonic devices requiring controlled exciton transport, storage, or manipulation.

Furthermore, we demonstrate that substrate-induced dielectric screening can be an effective means of modulating excitonic properties in low-dimensional BiSeI. When placed on a SiO₂ substrate, the exciton binding energy in both monolayers decreases by nearly 50%, yielding values of 0.19 eV (Janus) and 0.22 eV (exfoliated). In the exfoliated monochain, screening leads to even larger reduction ($\sim 76\%$), resulting in $E_b=0.28$ eV. Overall, our study provides a comprehensive understanding of how dimensionality governs the electronic and excitonic properties of BiSeI. The tunable excitonic behavior, strong light–matter interaction, and potential for substrate modulation underscore BiSeI’s promise for next-generation optoelectronic and excitonic devices.

Electronic Structure and Many-Body Effects in 0D Lead-Free Perovskite-Inspired Materials

7.1 Introduction

The rapid development of lead halide perovskites has demonstrated their remarkable optoelectronic performance in photovoltaic (PV) and light-emitting applications [320]. However, persistent concerns regarding lead toxicity and the long-term instability of these materials have intensified efforts to identify environmentally benign and structurally robust alternatives. In this context, low-dimensional metal halides have emerged as promising candidates [321]. Their reduced metal-halide connectivity often leads to enhanced structural rigidity and improved resistance to thermal and environmental degradation. Consequently, many of these materials maintain their structural and optical characteristics even under prolonged exposure to humid conditions [322, 323]. Such intrinsic stability makes low-dimensional metal halides attractive platforms for the development of durable optoelectronic devices.

Vacancy-ordered perovskites form a significant subclass of low-dimensional metal halides. These materials are obtained by the systematic and ordered removal of B-site cations from the conventional ABX_3 perovskite lattice. In this thesis, focus is placed on two important structural families of such vacancy-ordered compounds [32]. The first, with general formula $A_3\square B_2^{3+}X_9$ ($\square$ denotes a vacancy), forms when one-third of the B-sites are systematically unoccupied, yielding either isolated face-sharing $[B_2X_9]^{3-}$ bioctahedra [33] or layered octahedral networks [324]. The second family, vacancy-ordered double perovskites (VODPs) with composition $A_2\square B^{4+}X_6$, consists of alternating tetravalent vacancies and structurally isolated $[BX_6]^{2-}$ octahedra separated by A^+ cations [325]. Despite their structural differences, both families share a defining characteristic: suppressed inter-octahedral coupling and reduced electronic dimen-

sionality.

Among vacancy-ordered halides, Bi-based iodides have been extensively studied for PV applications owing to their suitable bandgaps, chemical robustness, and solution processability [326, 42]. Early PV devices based on $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{MA}_3\text{Bi}_2\text{I}_9$ ($\text{MA} = \text{CH}_3\text{NH}_3$) exhibited power conversion efficiencies (PCEs) of $\sim 1\%$ and 0.12% [42, 34], respectively. These efficiencies were later improved to 3–4% through advances in precursor chemistry, morphology control, and interface engineering [327, 328, 329]. Such developments demonstrate that Bi-based iodides are electronically active absorbers. Nevertheless, further progress in their PV performance remains constrained by their intrinsic zero-dimensional (0D) electronic structure. The crystal lattice consists of electronically isolated $[\text{Bi}_2\text{I}_9]^{3-}$ bioctahedra, which suppress band dispersion, promote strong excitonic confinement, and favor the formation of small polarons. Consequently, devices suffer from limited photocurrent generation and inefficient long-range carrier transport, imposing a fundamental structural limit on their performance [34]. Overcoming this intrinsic limitation requires strategies that partially restore electronic connectivity while maintaining a lead-free composition and high chemical stability.

In this chapter, the electronic structure of $\text{A}_3\text{Bi}_2\text{I}_9$ ($\text{A} = \text{Cs}$, $\text{MA} = \text{CH}_3\text{NH}_3$, $\text{FA} = \text{CH}(\text{NH}_2)_2$) nanocrystals is first investigated to establish the fundamental band-edge characteristics of these 0D Bi-based halides. The intrinsic structural bottleneck arising from the electronically isolated $[\text{Bi}_2\text{I}_9]^{3-}$ units is subsequently addressed via compositional engineering, specifically by incorporating Ag into the $\text{Cs}_3\text{Bi}_2\text{I}_9$ framework. The resulting layered compound, $\text{Cs}_2\text{AgBiI}_9$, features extended Ag–I–Bi networks that enhance orbital hybridization, increase the electronic dimensionality, and lead to significantly improved PCE in indoor PV devices. By systematically comparing the electronically isolated architecture of $\text{Cs}_3\text{Bi}_2\text{I}_9$ with the more connected framework of $\text{Cs}_2\text{AgBiI}_9$, the critical role of electronic dimensionality in controlling excitonic confinement and charge transport properties in Bi-based halides is elucidated.

While reduced dimensionality limits long-range carrier transport in PVs, it can be highly beneficial for light-emission applications. In VODPs of the form $\text{A}_2\text{B}^{4+}\text{X}_6$, the weak inter-octahedral coupling promotes strong carrier localization and frequently leads to the formation of self-trapped excitons (STEs) [35]. These STEs typically produce broadband emission with large Stokes shifts, making VODPs promising candidates for phosphors and light-emitting devices. However, many VODPs suffer from weak photoluminescence or inefficient near-infrared (NIR) emission [330]. These limitations often stem from indirect band gaps or parity-forbidden

transitions that suppress radiative recombination.

Among such compounds, Cs_2ZrCl_6 has gained prominence as a robust host lattice for luminescent dopants due to its high structural stability, strong quantum confinement, and pronounced electron–phonon coupling [331]. Although the pristine material supports the formation of STEs [332, 48], its large band gap and inefficient excitation pathways result in relatively weak intrinsic photoluminescence [333]. To overcome these limitations, dopant engineering has been extensively explored. The incorporation of aliovalent ns^2 , d -, or f -electron dopants introduces localized electronic states within the band gap, creating additional radiative pathways and enabling tunable emission across the visible to infrared regions [334, 36]. Nevertheless, achieving controllable dual visible–NIR emission from a single VODP host remains a significant challenge. In many doped systems, dopant-centered transitions tend to dominate, often obscuring the interaction between host STEs and impurity states.

To address this challenge, we investigate Mo-alloyed Cs_2ZrCl_6 . The incorporation of Mo^{4+} introduces additional electronic states associated with Mo-centered octahedra. The coexistence of host $[\text{ZrCl}_6]^{2-}$ and dopant $[\text{MoCl}_6]^{2-}$ units offers a unique platform to explore the interplay between host STE emission and dopant-driven optical transitions. Combining experimental spectroscopic observations with first-principles calculations, we elucidate the origin of the observed dual visible–NIR emission and clarify the role of dopant-induced electronic states within the electronically isolated octahedral framework.

Accordingly, this chapter examines three closely related problems, carried out in collaboration with experimental groups, that collectively explore how structural dimensionality and compositional engineering govern localization physics in vacancy-ordered halides. Specifically, we (i) investigate $\text{A}_3\text{Bi}_2\text{I}_9$ ($\text{A} = \text{Cs}, \text{MA}, \text{FA}$) to clarify the composition and dispersion of the band-edge states in 0D Bi-based halides; (ii) analyze the layered derivative $\text{Cs}_2\text{AgBi}_2\text{I}_9$ to determine how Ag incorporation restores electronic connectivity and modifies charge-transport tendencies; and (iii) study Mo-alloyed Cs_2ZrCl_6 to elucidate the origin of dual visible–NIR emission arising from the interplay between host excitons and dopant-induced electronic states within a VODP framework.

7.2 Computational methodology

First-principles calculations are performed using density functional theory (DFT) [85, 86] and many-body perturbation theory (MBPT) [121, 174]. Depending on the material system and the physical properties investigated, the calculations are carried out using the Vienna *ab initio* Simulation Package (VASP) [93, 94], Quantum ESPRESSO (QE) [95], and the YAMBO code [102, 101, 240]. The specific computational procedures adopted for each material system are described in the following subsections.

Electronic Properties of $A_3Bi_2I_9$

The electronic properties of $A_3Bi_2I_9$ ($A = Cs, MA, FA$) materials are investigated using first-principles DFT calculations performed with the VASP code. The interaction between core and valence electrons is treated using projector-augmented wave (PAW) [93] pseudopotentials. Structural relaxations are performed using the Perdew–Burke–Ernzerhof (PBE) [88] exchange–correlation functional within the generalized gradient approximation (GGA). Atomic positions are optimized until the Hellmann–Feynman forces are smaller than 10^{-3} eV Å⁻¹. An electronic convergence threshold of 10^{-5} eV and a plane-wave kinetic energy cutoff of 550 eV are employed in the self-consistent calculations. Spin–orbit coupling (SOC) effects are included in the electronic structure calculations in order to account for relativistic contributions associated with the heavy Bi atoms.

Electronic structure, excitonic, polaron, and defect calculations for $Cs_3Bi_2I_9$ and $Cs_2AgBi_2I_9$

Ground-state DFT calculations are performed using the QE package with scalar-relativistic norm-conserving Troullier–Martins pseudopotentials [335]. The experimental crystal structure is adopted as the starting point, and atomic positions are optimized using the PBE [291] exchange–correlation functional. A plane-wave kinetic energy cutoff of 60 Ry is employed, and the Brillouin zone is sampled using a Γ -centered $5 \times 5 \times 2$ k -point grid. Electronic band structures and density of states are computed using the PBE functional including SOC effects. The static ionic dielectric constant is calculated using density functional perturbation theory (DFPT) [75].

Many-body perturbation theory calculations are carried out using the YAMBO code. Quasi-

particle (QP) corrections to the band gap are obtained within the single-shot GW (G_0W_0) approximation, with the energy dependence of the self-energy treated using the Godby–Needs plasmon-pole model [241]. The kinetic energy cutoffs for the exchange and correlation parts of the GW self-energy are set to 40 Ry and 4 Ry, respectively. The absorption spectra, including excitonic effects, are obtained by solving the Bethe–Salpeter equation (BSE) [119] with a scissor correction corresponding to the difference between the G_0W_0 and DFT band gaps. Charge–carrier interactions with longitudinal optical (LO) phonons are described using the Fröhlich mesoscopic polaron model [77], and carrier mobilities are estimated using Feynman’s variational approach [159, 11, 157].

Electronic Structure Calculations of Mo-Alloyed Cs_2ZrCl_6

To investigate the effect of Mo incorporation on the electronic structure of Cs_2ZrCl_6 , spin-polarized DFT calculations are performed using the VASP package with PAW pseudopotentials. Structural relaxations are carried out using the PBE exchange–correlation functional until the Hellmann–Feynman forces on each atom are smaller than $0.01 \text{ eV } \text{\AA}^{-1}$. The self-consistent electronic calculations employ an energy convergence criterion of 10^{-8} eV and a plane-wave kinetic energy cutoff of 600 eV. The Brillouin zone is sampled using a Γ -centered $4 \times 4 \times 4$ k -point grid. Mo substitution is modeled using a $2 \times 2 \times 1$ supercell containing 36 atoms, where Mo atoms replace Zr sites. The electronic structures of both pristine and Mo-substituted systems are analyzed through band structure calculations and atom-projected density of states in order to identify dopant-induced electronic states and their interaction with the host electronic bands.

7.3 Results and discussion

7.3.1 Electronic properties of $\text{A}_3\text{Bi}_2\text{I}_9$ ($\text{A} = \text{Cs}, \text{MA}, \text{FA}$) halides

The $\text{A}_3\text{Bi}_2\text{I}_9$ ($\text{A} = \text{Cs}, \text{MA} = \text{CH}_3\text{NH}_3, \text{FA} = \text{CH}(\text{NH}_2)_2$) compounds adopt the hexagonal $P6_3/mmc$ space group at room temperature (see Fig. 7.1). Their structures consist of isolated inorganic frameworks in which pairs of $[\text{BiI}_6]^{3-}$ octahedra share faces to form $[\text{Bi}_2\text{I}_9]^{3-}$ bioctahedral units. This structural motif differs fundamentally from the corner-sharing octahedral network observed in conventional lead-halide perovskites such as MAPbI_3 . The voids between these bioctahedral units are occupied by the A-site cations.

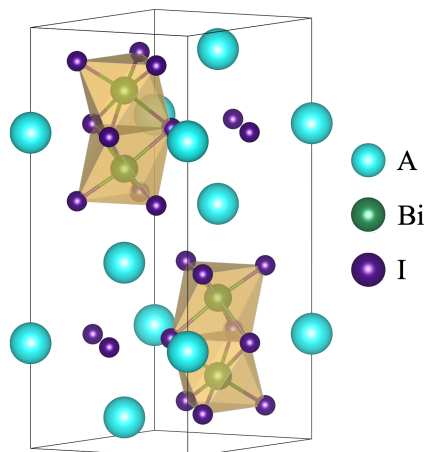


Figure 7.1: Crystal structure of $A_3Bi_2I_9$ ($A = Cs, MA, FA$) showing face-sharing $[BiI_6]^{3-}$ octahedra forming $[Bi_2I_9]^{3-}$ bioctahedral units.

To understand the electronic properties of these compounds, we analyze their electronic band structures and atom- and orbital-projected density of states (DOS) obtained from DFT calculations. All three materials exhibit semiconducting behavior with indirect band gaps. The calculated indirect (direct) band gaps are 1.81 (1.92) eV, 1.79 (1.89) eV, and 1.78 (1.82) eV for $Cs_3Bi_2I_9$, $MA_3Bi_2I_9$, and $FA_3Bi_2I_9$, respectively (Fig. 7.2 (a–c)). The small energy difference between the indirect and direct band gaps (≤ 0.11 eV) implies that optical absorption near the band edge is only weakly affected by the indirect character of the fundamental gap, since direct transitions remain energetically accessible at slightly higher energies. A systematic reduction in the band gap is observed with increasing size of the A-site cation. This trend can be attributed to structural distortions induced by the larger organic cations, which modify the Bi–I bonding environment and influence the electronic structure. In addition, the organic–cation–containing systems exhibit reduced band dispersion compared to inorganic $Cs_3Bi_2I_9$, reflecting enhanced carrier localization associated with the electronically isolated bioctahedral units. Consequently, $Cs_3Bi_2I_9$ is expected to exhibit relatively higher carrier mobility than its MA- and FA-based counterparts.

The orbital character of the band edges is further examined using the projected density of states (Fig. 7.2 (d–f)). For all three materials, the valence band maximum (VBM) is primarily composed of I- p orbitals, whereas the conduction band minimum (CBM) mainly originates from hybridized Bi- p and I- p states. The A-site cations do not directly contribute to the electronic states near the band edges; instead, they influence the electronic structure indirectly through structural distortions and modifications of the crystal-field environment.

Despite the comparatively improved band dispersion in $Cs_3Bi_2I_9$, its electronic structure re-

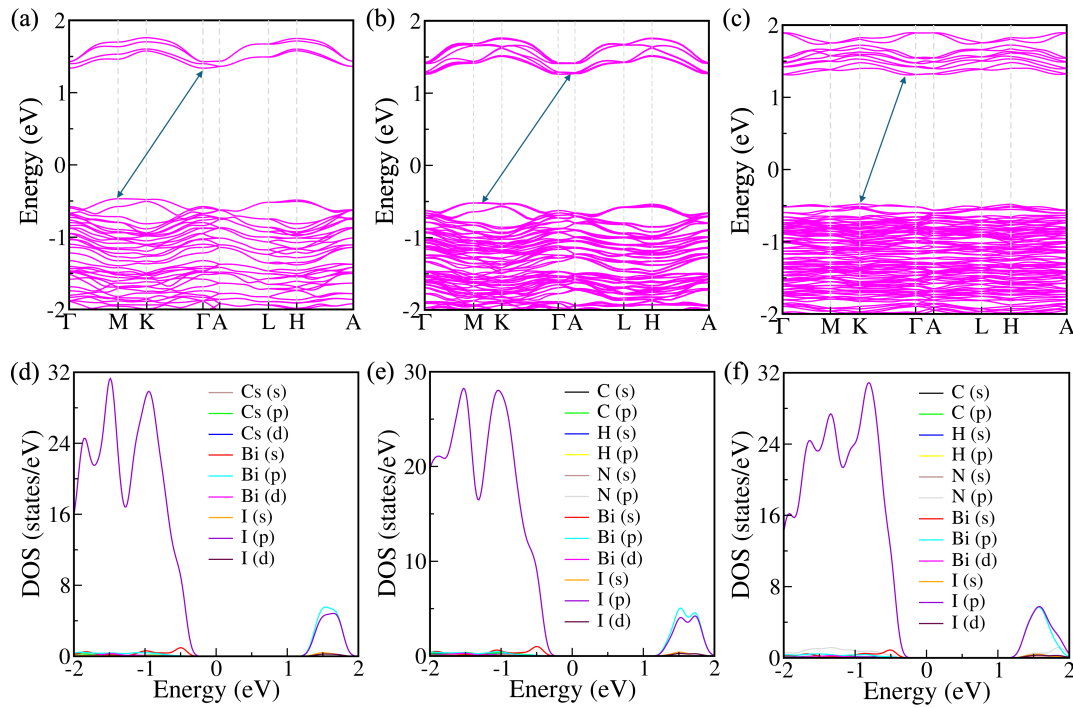


Figure 7.2: Electronic band structures and orbital-projected density of states (DOS) of $\text{Cs}_3\text{Bi}_2\text{I}_9$ (a,d), $\text{MA}_3\text{Bi}_2\text{I}_9$ (b,e), and $\text{FA}_3\text{Bi}_2\text{I}_9$ (c,f), calculated using the PBE functional with spin–orbit coupling (SOC) included.

mains governed by isolated $[\text{Bi}_2\text{I}_9]^{3-}$ bioctahedral units, which restrict long-range electronic connectivity. As a result, carrier transport in this system is still limited by the intrinsically 0D nature of the inorganic framework.

7.3.2 Restoring electronic connectivity in Bi-based halides: $\text{Cs}_2\text{AgBi}_2\text{I}_9$

One promising strategy to enhance electronic connectivity in $\text{Cs}_3\text{Bi}_2\text{I}_9$ is the incorporation of Ag, which transforms the structure into the layered compound $\text{Cs}_2\text{AgBi}_2\text{I}_9$ (shown in Fig. 7.3 (a)). This structural modification introduces extended Ag–I–Bi networks that promote stronger orbital hybridization and improved electronic delocalization. To elucidate the microscopic origin of the experimentally observed enhancement in PV performance upon Ag incorporation, we investigate the electronic structure, excitonic properties, and carrier–phonon interactions in $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_2\text{AgBi}_2\text{I}_9$ using first-principles calculations.

The calculated electronic band structures, shown in Fig. 7.3 (b,c), reveal that both compounds are indirect band-gap semiconductors. In $\text{Cs}_3\text{Bi}_2\text{I}_9$, the VBM occurs at the M point, while the CBM lies along the Γ –A direction. In contrast, $\text{Cs}_2\text{AgBi}_2\text{I}_9$ exhibits the VBM between the M and K points and the CBM at the Γ point. The calculated band gaps with and without SOC are

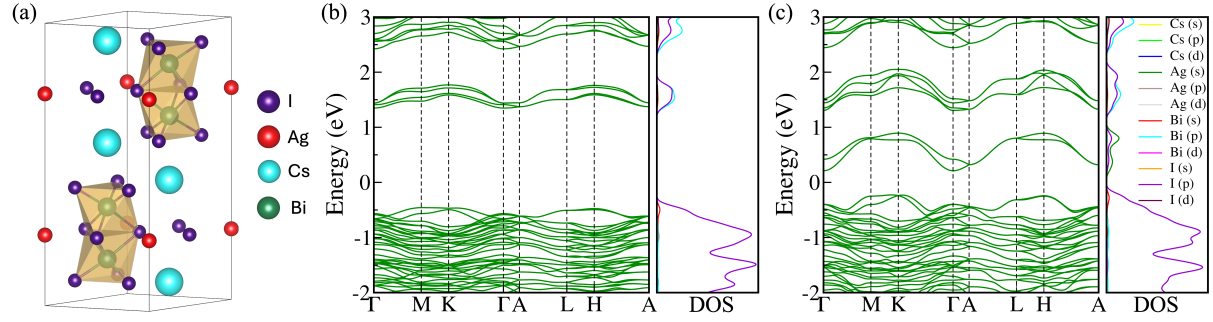


Figure 7.3: (a) Unit cell of $\text{Cs}_2\text{AgBi}_2\text{I}_9$. Electronic band structures and orbital-projected density of states (DOS) of (b) $\text{Cs}_3\text{Bi}_2\text{I}_9$ and (c) $\text{Cs}_2\text{AgBi}_2\text{I}_9$ calculated using the PBE functional including SOC.

summarized in Table 7.1. A significant reduction in the band gap is observed upon inclusion of SOC, reflecting the strong relativistic effects associated with the heavy Bi atoms.

Table 7.1: Calculated indirect and direct band gaps (in eV) using PBE and PBE+SOC methods, and carrier effective masses for $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_2\text{AgBi}_2\text{I}_9$ computed by parabolic fitting of the PBE+SOC band edges. Effective masses are given in units of the free electron mass (m_0).

Material	PBE		PBE+SOC		Effective mass (PBE+SOC)	
	Indirect	Direct	Indirect	Direct	m_e^*	m_h^*
$\text{Cs}_3\text{Bi}_2\text{I}_9$	2.14	2.26	1.81	1.92	4.0	9.8
$\text{Cs}_2\text{AgBi}_2\text{I}_9$	0.59	0.75	0.46	0.60	0.6	2.1

The projected density of states (Fig. 7.3 (b,c)) shows that the VBM in both materials is mainly composed of I- p orbitals. However, the nature of the CBM changes significantly upon Ag incorporation. In $\text{Cs}_3\text{Bi}_2\text{I}_9$, the CBM arises primarily from hybridized Bi- p and I- p states, whereas in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ it is predominantly composed of Ag- d orbitals with smaller contributions from iodine. This orbital reorganization lowers the CBM energy while leaving the VBM largely unaffected, resulting in a substantial reduction of the band gap in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ (Table 7.1). Carrier effective masses obtained from parabolic fitting of the band edges indicate that electrons are lighter than holes in both materials. Importantly, Ag incorporation significantly reduces both electron and hole effective masses, suggesting improved carrier transport in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ compared with $\text{Cs}_3\text{Bi}_2\text{I}_9$.

To obtain quantitatively reliable band gaps, many-body effects are included by performing G_0W_0 calculations on top of PBE functionals. The resulting QP direct band gaps are 2.67 eV for

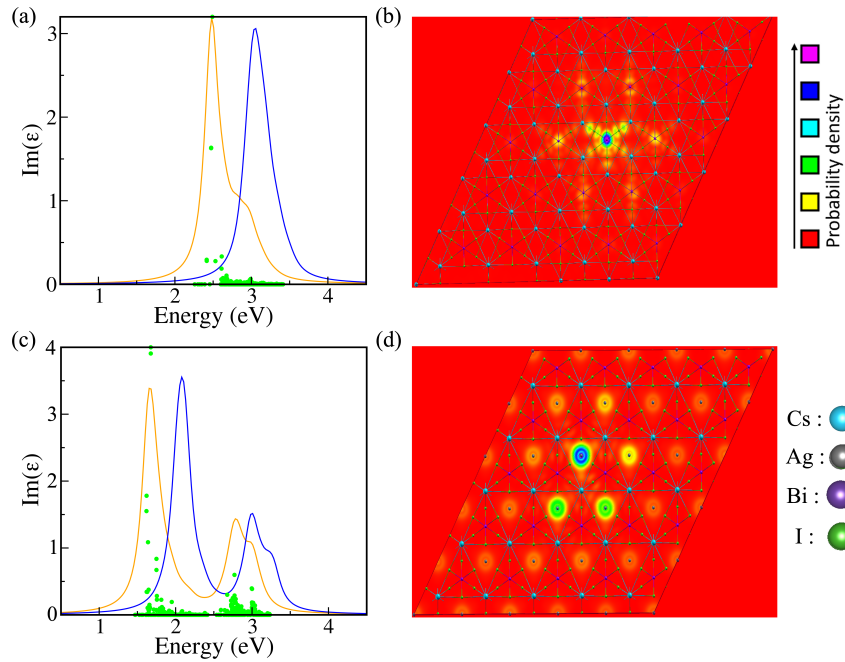


Figure 7.4: Absorption spectra computed using $G_0W_0@PBE$ (blue) and $\text{BSE}@G_0W_0@PBE$ (orange), along with the wavefunction of the first bright exciton obtained by fixing the hole 1 Å above the atom contributing most strongly to the VBM in a $5 \times 5 \times 1$ supercell. Results are shown for $\text{Cs}_3\text{Bi}_2\text{I}_9$ (a,b) and $\text{Cs}_2\text{AgBi}_2\text{I}_9$ (c,d). The green circles in (b) and (d) indicate the scaled oscillator strength.

$\text{Cs}_3\text{Bi}_2\text{I}_9$ and 1.60 eV for $\text{Cs}_2\text{AgBi}_2\text{I}_9$, indicating substantial QP corrections relative to the PBE values. However, the G_0W_0 approach does not account for electron–hole interactions, which lead to the formation of bound electron–hole pairs (excitons). These excitonic effects are incorporated by solving the BSE. The calculated absorption spectra without and with electron–hole interactions are presented in Fig. 7.4 (a,c). The resulting optical gaps from BSE are 2.41 eV for $\text{Cs}_3\text{Bi}_2\text{I}_9$ and 1.56 eV for $\text{Cs}_2\text{AgBi}_2\text{I}_9$. Consequently, the exciton binding energies—obtained as the difference between the G_0W_0 QP gap and the lowest optically bright BSE excitation—are 260 meV and 40 meV, respectively. This significant reduction in binding energy indicates a transition from strongly bound excitons in $\text{Cs}_3\text{Bi}_2\text{I}_9$ to weakly bound Wannier–Mott excitons in $\text{Cs}_2\text{AgBi}_2\text{I}_9$. The spatial character of the excitons further supports this picture. By fixing the hole on an iodine atom and mapping the electron probability density in a $5 \times 5 \times 1$ supercell, we observe that the electron density in $\text{Cs}_3\text{Bi}_2\text{I}_9$ is largely localized around Bi atoms with additional contributions from surrounding I atoms (Fig. 7.4 (b)). In contrast, the electron density in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ is markedly more delocalized and shifts toward the Ag atoms (Fig. 7.4 (d)), consistent with the dominant Ag character of the CBM.

The reduced exciton binding energy and increased spatial extent in the Ag-containing com-

pound can be attributed to the combined effects of smaller carrier effective masses and enhanced dielectric screening (see Table 7.2). The electronic contribution to the dielectric screening (ϵ_∞) is obtained from MBPT calculations, while the ionic contribution (ϵ_{ionic}) is computed using DFPT. The total static dielectric constant is given by $\epsilon_0 = \epsilon_\infty + \epsilon_{\text{ionic}} - 1$, and the corresponding values are summarized in Table 7.2. These results show that $\text{Cs}_2\text{AgBiI}_9$ exhibits significantly stronger dielectric screening compared to $\text{Cs}_3\text{Bi}_2\text{I}_9$.

Table 7.2: Electronic static dielectric constant (ϵ_∞), total static dielectric constant (ϵ_0), longitudinal optical phonon frequency (ω_{LO}), electron–phonon coupling strength (α), polaron radius (r_f), and polaron mobility (μ_p) for $\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_2\text{AgBi}_2\text{I}_9$.

Material	ϵ_∞	ϵ_{static}	ω_{LO} (cm^{-1})	α	r_f ($\text{\AA}$)	μ_p ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
$\text{Cs}_3\text{Bi}_2\text{I}_9$	5.6	10.6	89.6	5.0	21	1.7
$\text{Cs}_2\text{AgBi}_2\text{I}_9$	6.4	14.7	95.4	2.1	34	36.2

In halide perovskites and related materials, carrier dynamics are strongly governed by electron–phonon interactions, particularly the coupling between charge carriers and polar lattice vibrations. Coupling with longitudinal optical (LO) phonons gives rise to the formation of polarons, which renormalize the carrier effective masses and significantly influence charge carrier mobility. This interaction is well described by the Fröhlich model [77], a continuum theory that characterizes the long-range coupling between charge carriers and LO phonons in polar semiconductors. The strength of this electron–phonon coupling is quantified by the dimensionless Fröhlich coupling constant, α .

$$\alpha = \frac{1}{\epsilon^*} \sqrt{\frac{R_\infty}{\hbar \omega_{\text{LO}}}} \sqrt{\frac{m^*}{m_0}}, \quad (7.1)$$

where ω_{LO} is the LO phonon frequency [159], $\hbar$ is the reduced Planck constant, R_∞ is the Rydberg constant, and m^* is the carrier effective mass expressed in units of the free-electron mass m_0 . The effective screening parameter is defined as $1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_0$. The calculated polaron parameters, including the Fröhlich coupling constant (α), polaron radius (r_f), and polaron mobility (μ_p), are summarized in Table 7.2. $\text{Cs}_3\text{Bi}_2\text{I}_9$ exhibits intermediate electron–phonon coupling ($\alpha \approx 5.0$), whereas $\text{Cs}_2\text{AgBi}_2\text{I}_9$ lies in the weak-coupling regime ($\alpha \approx 2.1$). Consequently, the polarons in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ are more spatially extended, as reflected by the larger polaron radius. Using Feynman’s variational solution [157] of the Fröhlich polaron Hamiltonian, we estimate the upper limit of the carrier mobility. The calculated mobility increases

dramatically from $1.67 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in $\text{Cs}_3\text{Bi}_2\text{I}_9$ to $36.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in $\text{Cs}_2\text{AgBi}_2\text{I}_9$. This substantial enhancement indicates that Ag incorporation significantly improves carrier transport by weakening electron–phonon scattering.

Table 7.3: Formation energies (E_f) of possible intrinsic defects in $\text{Cs}_2\text{AgBi}_2\text{I}_9$. Energies are reported in eV.

Defect	V_I	V_{Cs}	V_{Ag}	V_{Bi}	Cs_{Ag}	Cs_{Bi}	Ag_{Cs}	Ag_{Bi}	Bi_{Ag}	Bi_{Cs}
E_f (eV)	1.87	4.42	1.10	5.08	3.80	5.01	4.60	2.83	0.67	5.54
Defect	Cs_I	Ag_I	Bi_I	I_{Cs}	I_{Ag}	I_{Bi}	i_{Cs}	i_{Ag}	i_{Bi}	i_I
E_f (eV)	1.66	2.68	2.97	5.40	0.69	4.19	4.40	1.13	7.10	3.71

Despite the improved intrinsic transport properties, PV performance may still be limited by defect-assisted non-radiative recombination. Experimental measurements indicate a defect density of approximately $2 \times 10^{15} \text{ cm}^{-3}$, suggesting the presence of grain-boundary or point defects that could act as recombination centers [66].

To elucidate the defect physics, first-principles defect calculations were performed using a $2 \times 2 \times 1$ supercell. Defect formation energies were computed with the screened hybrid HSE06 functional [92], which incorporates 25% Hartree–Fock exchange and 75% PBE exchange. In this work, only neutral point defects were considered. The defect formation energy is defined as

$$E_f = E_{\text{tot}}[X^q] - E_{\text{tot}}[\text{bulk}] + \sum_i n_i \mu_i + q(\varepsilon_{VBM} + E_F), \quad (7.2)$$

where $E_{\text{tot}}[X^q]$ and $E_{\text{tot}}[\text{bulk}]$ are the total energies of the defective and pristine supercells, respectively. n_i is the number of atoms of species i added to or removed from the system, μ_i is the chemical potential of species i , ε_{VBM} denotes the valence band maximum of the pristine material, and E_F is the Fermi level referenced to ε_{VBM} .

The calculated formation energies for various intrinsic defects (vacancies, antisites, interstitials, and substitutional defects) are summarized in Table 7.3. Analysis of the defects with low formation energies reveals that most introduce shallow states near the band edges rather than deep mid-gap levels (see Fig. 7.5). This suggests that these defects are unlikely to act as efficient non-radiative recombination centers. Although the Bi_{Ag} antisite defect introduces states below the conduction band minimum, it is not expected to significantly promote non-radiative recombination. Overall, the results indicate that bulk point defects in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ are relatively

benign. Consequently, recombination losses in devices are more likely to be dominated by grain-boundary and interface defects rather than intrinsic bulk defects.

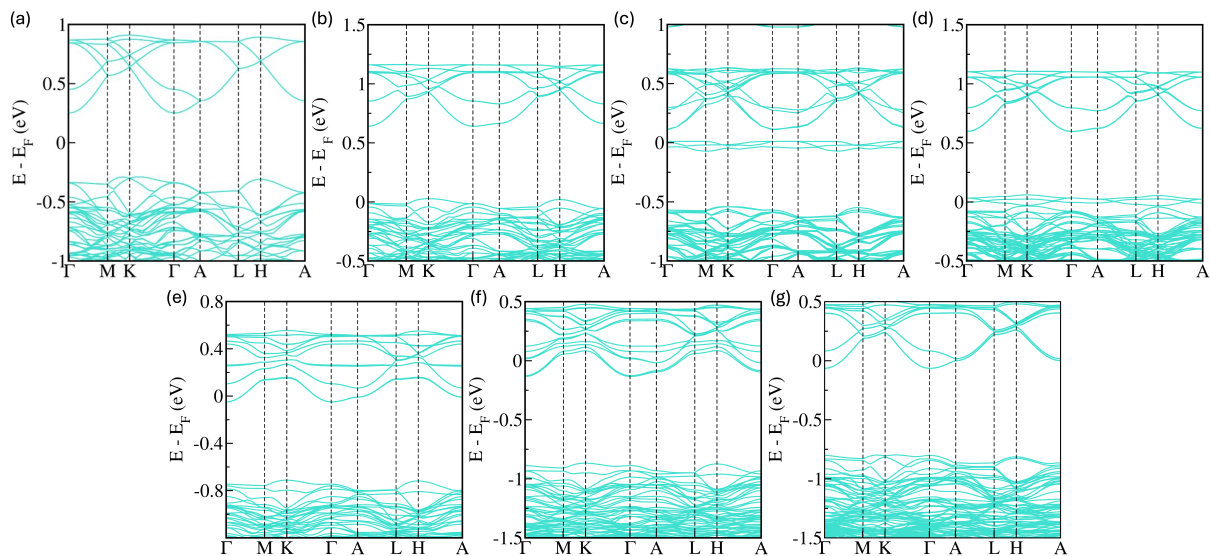


Figure 7.5: Electronic band structure for (a) pristine (b) V_{Ag} (c) Bi_{Ag} (d) I_{Ag} (e) V_I (f) Cs_I (g) i_{Ag} defected $Cs_2AgBi_2I_9$.

7.3.3 Dopant-induced dual visible–NIR emission in Mo-alloyed Cs_2ZrCl_6

Cs_2ZrCl_6 crystallizes in the vacancy-ordered double perovskite structure with space group $Fm\bar{3}m$, analogous to the K_2PtCl_6 antiferrofluorite structure. In this structure, isolated $[ZrCl_6]^{2-}$ octahedra occupy the corners and face centers of the cubic lattice, while vacancies alternate with the octahedra. The cuboctahedral cavities along the body diagonal are occupied by Cs^+ ions (Fig. 7.6 (a)). Upon Mo^{4+} incorporation, $[MoCl_6]^{2-}$ octahedra can substitute for some of the $[ZrCl_6]^{2-}$ units because Mo and Zr possess similar ionic radii and share the same octahedral coordination with halogen atoms. This substitution preserves the local structural framework while introducing dopant-induced electronic states.

To understand the impact of Mo incorporation on the electronic structure, we compute the atom-projected density of states and electronic band structures. For pristine Cs_2ZrCl_6 , the VBM is primarily derived from Cl-3p orbitals, whereas the CBM originates mainly from hybridized Zr-4d and Cl-3p states (Fig. 7.6 (b)). The band structure indicates that Cs_2ZrCl_6 is a spin-unpolarized indirect band-gap semiconductor, with the VBM and CBM located at the Γ and X points, respectively (Fig. 7.7 (a)). Mo substitution significantly modifies the electronic structure. The hybridization of Mo-4d and Cl-3p orbitals introduces strongly polarized mid-gap

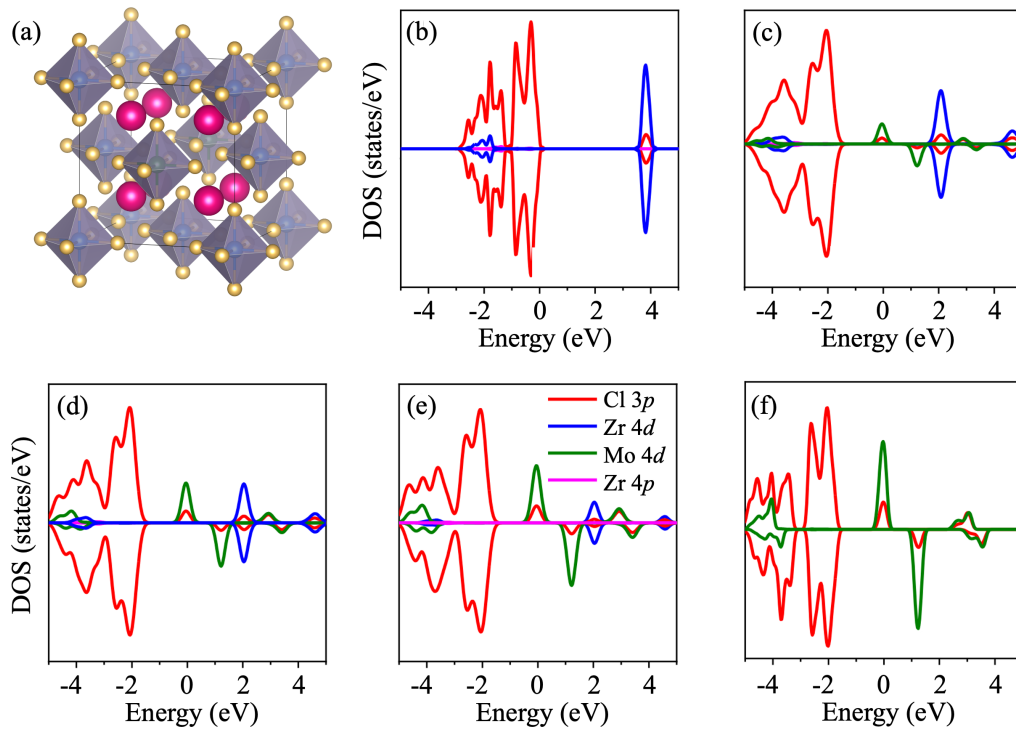


Figure 7.6: (a) Crystal structure of $\text{Mo:Cs}_2\text{ZrCl}_6$, where magenta, gold, blue, and green spheres represent Cs, Cl, Zr, and Mo atoms, respectively. Atom- and orbital-projected electronic density of states (DOS) for (b) Cs_2ZrCl_6 , (c) $\text{Cs}_2\text{Zr}_{0.75}\text{Mo}_{0.25}\text{Cl}_6$, (d) $\text{Cs}_2\text{Zr}_{0.5}\text{Mo}_{0.5}\text{Cl}_6$, (e) $\text{Cs}_2\text{Zr}_{0.25}\text{Mo}_{0.75}\text{Cl}_6$, and (f) Cs_2MoCl_6 .

states within the band gap of the host material (Fig. 7.6 (b-f)). As a result, the alloyed systems exhibit half-metallic behavior: the majority spin channel displays metallic characteristics with states crossing the Fermi level, whereas the minority spin channel retains a semiconducting character. This behavior is evident in the DOS, where states appear at the Fermi level for the spin-up channel while the spin-down channel maintains a finite band gap. With increasing Mo concentration in $\text{Mo:Cs}_2\text{ZrCl}_6$, the density of Mo-4d states near the conduction band edge increases, leading to a gradual reduction of the band gap in the spin-down channel. In contrast, the spin-up channel consistently exhibits metallic behavior. The calculated band structures for pristine Cs_2ZrCl_6 and fully substituted Cs_2MoCl_6 further illustrate the transition from a semiconducting to a half-metallic state upon Mo incorporation (Fig. 7.7 (a,b)).

Experimentally, distinct emission profiles are observed for $\text{Mo}^{4+}:\text{Cs}_2\text{ZrCl}_6$. This behavior can be attributed to the presence of structurally isolated octahedral units in vacancy-ordered perovskites, which allows the emission processes of host and dopant octahedra to remain largely independent. Figure 7.7(c) shows the calculated charge-density isosurface at the (100) facet for $\text{Cs}_2\text{Zr}_{0.75}\text{Mo}_{0.25}\text{Cl}_6$, revealing negligible electronic overlap of Cl orbitals between neighboring

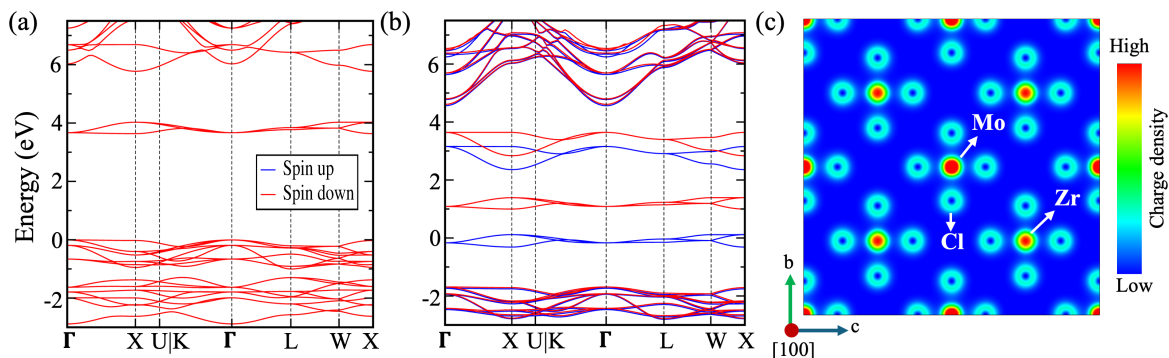


Figure 7.7: Electronic band structure for (a) Cs₂ZrCl₆, (b) Cs₂MoCl₆, and (c) Charge density isosurface at the (100) facet of Mo⁴⁺:Cs₂ZrCl₆ reveals the decoupling of Cl orbitals between adjacent polyhedral [ZrCl₆]²⁻ and [MoCl₆]²⁻ units.

polyhedral units of [ZrCl₆]²⁻ and [MoCl₆]²⁻. The charge density remains largely confined within individual octahedra, confirming weak electronic coupling between adjacent polyhedral units. Such structural isolation results in highly localized electronic states and suppresses efficient energy transfer between host and dopant octahedra. Consequently, host- and dopant-related emissions coexist, giving rise to the observed dual luminescence in Mo⁴⁺:Cs₂ZrCl₆.

Overall, Mo alloying introduces strongly polarized mid-gap states and induces half-metallic behavior in Mo:Cs₂ZrCl₆. These dopant-induced electronic states modify the band structure and play a crucial role in tuning the photoluminescence properties of this vacancy-ordered perovskite.

7.4 Conclusion and outlook

We first examined the electronic properties of A₃Bi₂I₉ (A = Cs, MA, FA) halides. These compounds crystallize in a structure composed of isolated [Bi₂I₉]³⁻ bioctahedral units, which results in a 0D inorganic framework. Our DFT calculations reveal that all three materials are indirect band-gap semiconductors with band edges primarily derived from I-*p* and Bi-*p* orbitals. The presence of isolated bioctahedra leads to limited band dispersion and relatively localized electronic states, which restrict long-range carrier transport. Although the band gap slightly decreases with increasing size of the A-site cation, the intrinsic electronic connectivity in these materials remains weak due to their 0D structural motif.

To overcome this limitation, we investigated Ag incorporation in Cs₃Bi₂I₉, which transforms the structure into the layered compound Cs₂AgBi₂I₉. This compositional modification introduces extended Ag–I–Bi networks that enhance electronic delocalization. Our calculations

show that Ag incorporation significantly reduces the band gap and carrier effective masses, leading to improved carrier transport properties. Many-body perturbation theory calculations further reveal a strong reduction in exciton binding energy from 260 meV in $\text{Cs}_3\text{Bi}_2\text{I}_9$ to 40 meV in $\text{Cs}_2\text{AgBi}_2\text{I}_9$, indicating a transition from strongly bound excitons to weakly bound Wannier–Mott excitons. In addition, enhanced dielectric screening and weaker electron–phonon coupling in $\text{Cs}_2\text{AgBi}_2\text{I}_9$ result in more spatially extended polarons and a substantial increase in the estimated carrier mobility. Defect calculations indicate that most intrinsic defects introduce shallow states near the band edges rather than deep mid-gap states, suggesting that bulk defects are relatively benign and that recombination losses are more likely associated with grain-boundary or interface defects.

Finally, we explored dopant-induced electronic properties in Mo-alloyed Cs_2ZrCl_6 , a vacancy-ordered double perovskite. Mo incorporation introduces strongly polarized mid-gap states arising from hybridization between Mo-*d* and Cl-*p* orbitals, leading to half-metallic behavior in the alloyed systems. Charge-density analysis reveals negligible electronic overlap between neighboring octahedral units, confirming the structural isolation of $[\text{ZrCl}_6]^{2-}$ and $[\text{MoCl}_6]^{2-}$ polyhedra. This weak electronic coupling suppresses efficient energy transfer between host and dopant centers, allowing host- and dopant-related emissions to coexist and giving rise to dual visible–NIR luminescence.

Overall, our results demonstrate that structural dimensionality, compositional substitution, and dopant engineering provide effective routes to tune the electronic structure and optical properties of lead-free halide materials. Restoring electronic connectivity through cation substitution can significantly improve carrier transport and reduce exciton binding energies, while dopant-induced localized states can be exploited to design multifunctional luminescent materials.

Epilogue and outlook

In this thesis, we have explored the emerging landscape of perovskite-inspired materials (PIMs)—spanning antiperovskites, chalcogenides, and vacancy-ordered halides—within a unified first-principles framework. By moving beyond static ground-state descriptions, we have elucidated the complex excited-state manifold of these systems, providing a microscopic understanding of excitonic effects, hot-carrier cooling, and nonradiative recombination dynamics.

In Chapter 3, we identified inorganic antiperovskite nitrides (X_3NA ; $X = \text{Mg, Ca, Sr, Ba}$; $A = \text{As, Sb}$) as a promising class of photovoltaic absorbers. In particular, Sb-based compounds combine suitable band gaps with dispersive band edges, weak electron–phonon coupling, and small exciton binding energies, resulting in high carrier mobilities that exceed those of benchmark lead-halide perovskites. Despite these favorable attributes, experimental realization remains limited, with only Mg_3NSb reported in thin-film form to date. This highlights a critical gap between theory and synthesis, motivating systematic experimental efforts to stabilize and grow Ca-, Sr-, and Ba-based thin films.

Beyond static descriptors, Chapter 4 extends the analysis to the carrier dynamics of direct-gap Sb-based antiperovskites, demonstrating that nonradiative recombination is governed by a subtle interplay among the fundamental band gap, non-adiabatic (NA) coupling strengths, and electronic decoherence. Notably, symmetry modulation within a fixed composition (Sr_3NSb) emerges as an effective strategy to suppress recombination losses, establishing structural symmetry as a powerful—yet often underexplored—design parameter for tuning excited-state lifetimes beyond conventional band-structure engineering.

While these inorganic antiperovskite nitrides exhibit promising theoretical efficiencies for photovoltaic applications, translating these microscopic insights into macroscopic device performance requires addressing the complexities of realistic operating conditions. In particular, incorporating finite-temperature effects into optical and excited-state calculations will be es-

sential to capture phonon-induced band-gap renormalization and thermal broadening. Furthermore, the present focus on pristine lattices should be extended to include extrinsic perturbations—such as point defects, vacancies, and impurities—which can introduce localized trap states and strongly influence nonradiative pathways. Quantifying how such defects modulate non-adiabatic couplings and carrier lifetimes remains a key challenge for predictive materials design. Given the significant computational cost associated with these advanced simulations, the development of accelerated predictive frameworks is highly desirable. In this context, data-driven approaches offer a promising complementary strategy. Machine learning models trained on physically informed electronic descriptors—such as band gaps, wavefunction overlap between valence- and conduction-band edges, and lattice dynamical features—could enable rapid screening of candidate materials. While the availability of sufficiently diverse training data remains a limiting factor at present, such approaches hold considerable long-term potential to augment first-principles methods and guide the discovery of antiperovskites with intrinsically suppressed recombination losses.

In Chapter 5, we investigated carbide-based antiperovskites (Ca_6CSe_4 and Sr_6CSe_4), which remain experimentally unrealized and thus represent a predictive frontier. Our results reveal the coexistence of picosecond-scale hot-carrier cooling bottlenecks and long nonradiative lifetimes, originating from weak nonadiabatic couplings and the distinctive electronic structure near the band edges. This combination highlights their intrinsic potential for hot-carrier energy conversion. Despite these encouraging descriptors, the transition from theoretical prediction to functional material necessitates addressing the stability of these dynamics under operational conditions. Specifically, the impact of structural disorder, lattice defects, and room-temperature excitonic correlations remains a critical open question. Moving forward, the priority lies in establishing experimentally accessible synthesis pathways and identifying chemically viable analogues that can retain these slow-relaxation properties in realistic device environments.

Extending the investigation to quasi-one-dimensional chalcogenides in Chapter 6, BiSeI emerges as a prototypical system in which excitonic properties can be systematically tuned through quantum confinement and the dielectric environment. While experimental optical gaps have been reported for the bulk phase, the fundamental characterization of its low-dimensional counterparts remains largely unexplored. Consequently, our results provide predictive benchmarks for future spectroscopic studies of low-dimensional BiSeI . In addition, prior studies indicate the emergence of Rashba-type spin splitting in Janus BiSeI monolayers, offering a versatile

platform to probe the interplay between spin degrees of freedom and excitonic behavior. In particular, the formation of spin-polarized excitons and their associated relaxation pathways represents a compelling direction for spin-selective optoelectronic applications. Looking forward, detailed investigations of temperature-dependent excitonic renormalization, along with phonon-mediated decoherence, will be essential for assessing the stability and transport of these states. Such efforts are crucial for enabling controlled excitonic functionality in next-generation spintronic and quantum optoelectronic devices, where spin and excited-state dynamics are intrinsically coupled.

Finally, Chapter 7 highlights that vacancy-ordered halides provide a complementary paradigm in which electronic connectivity can be deliberately engineered to control optoelectronic functionality. While structural isolation in $A_3\text{Bi}_2\text{I}_9$ ($A = \text{Cs}, \text{MA}, \text{FA}$) favors the formation of self-trapped excitons and limits carrier transport, Ag incorporation partially restores connectivity, promoting Wannier–Mott-like excitons and enhancing carrier mobility. In contrast, Mo-alloying in Cs_2ZrCl_6 demonstrates how controlled localization can be harnessed to stabilize self-trapped excitons, enabling dual visible–near-infrared emission. A key open question is how these engineered electronic landscapes evolve in the presence of disorder, and how such perturbations influence the competition between different carrier relaxation pathways.

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