



Title	Automated Discovery and Design Principles of Two-Dimensional Materials Using a High-Throughput First-Principles Framework
Author(s)	鈴木, 創
Degree Grantor	北海道大学
Degree Name	博士(総合化学)
Dissertation Number	甲第16857号
Issue Date	2026-03-25
DOI	https://doi.org/10.14943/doctoral.k16857
Doc URL	https://hdl.handle.net/2115/99702
Type	doctoral thesis
File Information	SUZUKI_Hajime.pdf, 全文



HOKKAIDO UNIVERSITY

**Automated Discovery and Design
Principles of Two-Dimensional
Materials Using a High-Throughput
First-Principles Framework**

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A thesis submitted in fulfillment of the requirements

for the degree of Doctor of Philosophy

in the

Information Chemistry Laboratory

Graduate School of Chemical Sciences and Engineering

February 5, 2026

Declaration of Authorship

I, Hajime Suzuki, declare that this thesis titled, “Automated Discovery and Design Principles of Two-Dimensional Materials Using a High-Throughput First-Principles Framework” and the work presented in it are my own. I confirm that:

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Abstract

Faculty of Science

Graduate School of Chemical Sciences and Engineering

Doctor of Philosophy

Automated Discovery and Design Principles of Two-Dimensional Materials

Using a High-Throughput First-Principles Framework

by Hajime Suzuki

The dissertation aims to establish design guidelines for the development of two-dimensional materials. Since the first isolation of monolayer graphene in 2004, exfoliation from layered materials such as hexagonal boron nitride, transition metal dichalcogenides, silicene, and black phosphorus has rapidly expanded the family of 2D materials. In the 2010s, bottom-up-type 2D prototypes with no bulk counterparts, such as octagraphene, graphenylene, and honeycomb–kagome vanadium oxides, were theoretically proposed, and in the 2020s some of these, including the biphenylene network and honeycomb–kagome vanadium oxide, have been experimentally realized. While theoretical predictions of such bottom-up 2D materials are active, systematic design guidelines are lacking. therefore, The dissertation aims to construct guidelines of bottom-up-type 2D prototypes.

The dissertation consists of six chapters. After the background and computational methods in Chapters 1 and 2, Chapters 3–5 clarify design principles for three classes of bottom-up 2D materials. In Chapter 3, a high-throughput first-principles workflow is developed for the honeycomb–kagome lattice to systematically explore 530 compositions and evaluate stability, magnetic configurations, and electronic structures. For 61 stable candidates, detailed magnetic analysis

reveals how elemental choice controls stability, magnetism, and Curie temperature, leading to the identification of 17 ferromagnetic metals, 12 half-metals, and 10 antiferromagnetic metals with out-of-plane anisotropy, including 12 ferromagnets with Curie temperatures above 300 K. These results provide design guidelines for spintronics and quantum information materials.

In Chapter 4, the stability and electronic structures of two-dimensional phosphorus allotropes—black phosphorus, octagonal, and kagome phases—are compared under consistent conditions. The study shows that in-plane network topology controls band-gap size and direct/indirect character, offering guidelines for semiconductor applications such as solar cells and photocatalysts. Possible synthesis routes are also examined using metal–2D interface models and gas-phase reactions between gold and yellow phosphorus, suggesting formation of gold phosphide phases.

In Chapter 5, metal adsorption on functionalized graphene is systematically evaluated to establish design rules for energy-storage materials. High-throughput screening of alkali and alkaline-earth adsorption on cyanographene indicates that Li and Na bind with suitable strengths for ion batteries. First-principles analysis of cyanographene and cyanographite as sodium-ion battery anodes shows that cyano groups promote sodium ionization and adsorption, that Na diffuses rapidly at room temperature (NEB results), and that their theoretical capacities exceed graphite's Na capacity, highlighting cyanographene and cyanographite as promising anode materials.

Chapter 6 summarizes the overall conclusions of this study.

Acknowledgements

Words cannot express my gratitude to Prof. Keisuke Takahashi for his guidance, patience and feedback throughout this journey. I will forever be grateful to him for taking me under his wing in this exciting and interesting field of Materials science. In the same manner, I am grateful for Prof. Satoshi Maeda, Prof. Tetsuya Taketsugu and Prof. Toshihiro Shimada for their support and feedback. I'd like to extend special acknowledgments to Prof. Hideki Abe from the National Institute for Materials Science (NIMS) for their feedback and assistance in this research.

I could not have made it to this point without the people from the Information Chemistry Laboratory at Hokkaido University, particularly Prof. Lauren Takahashi, Mr. Mikael Kuwahara and Dr. Fernando Garcia Escobar for their guidance, insightful discussions and feedback, especially during the latter stages of my dissertation journey.

This work is funded by Grant-in- Aid for JSPS Fellows Grant Number (JP24KJ0272).

Lastly, I would be remiss in not mentioning my family: especially my wife, son, sister and parents. Their continuous support has kept my spirits high during this journey. To my extended relatives and friends as well, whose constant encouragement has kept me going, and especially those I could meet during my doctoral studies.

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Dedicated to my wife, son, sister and parents

Chapter 1

Introduction

1.1 2D-materials Diversity and Applications

The dissertation focuses on the materials two-dimensional (2D) materials, whose thicknesses are on the order of only a few angstroms. As one of the most actively investigated classes in contemporary materials science, 2D materials exhibit exceptionally large surface-to-volume ratios and outstanding electronic, optical, and mechanical properties compared with their bulk counterparts[1, 2]. Owing to these advantages, research and development on 2D materials promises broad impact across photocatalysis, semiconductor devices, energy storage, pollutant remediation, and spintronics, among other fields [3, 4]. Since the experimental discovery of graphene in 2004, progress has accelerated markedly. To date, hundreds of 2D materials—such as silicene, phosphorene, and transition-metal dichalcogenides—have been realized experimentally, while thousands more have been designed and screened via first-principles calculations [5, 6]. Moreover, vertical stacking of disparate 2D layers (heterostructuring) is known to elicit emergent properties absent in the constituents, further expanding the design space [7, 8]. In the following sections, I introduce representative 2D materials and their applications as shown in Fig. 1.1(a).

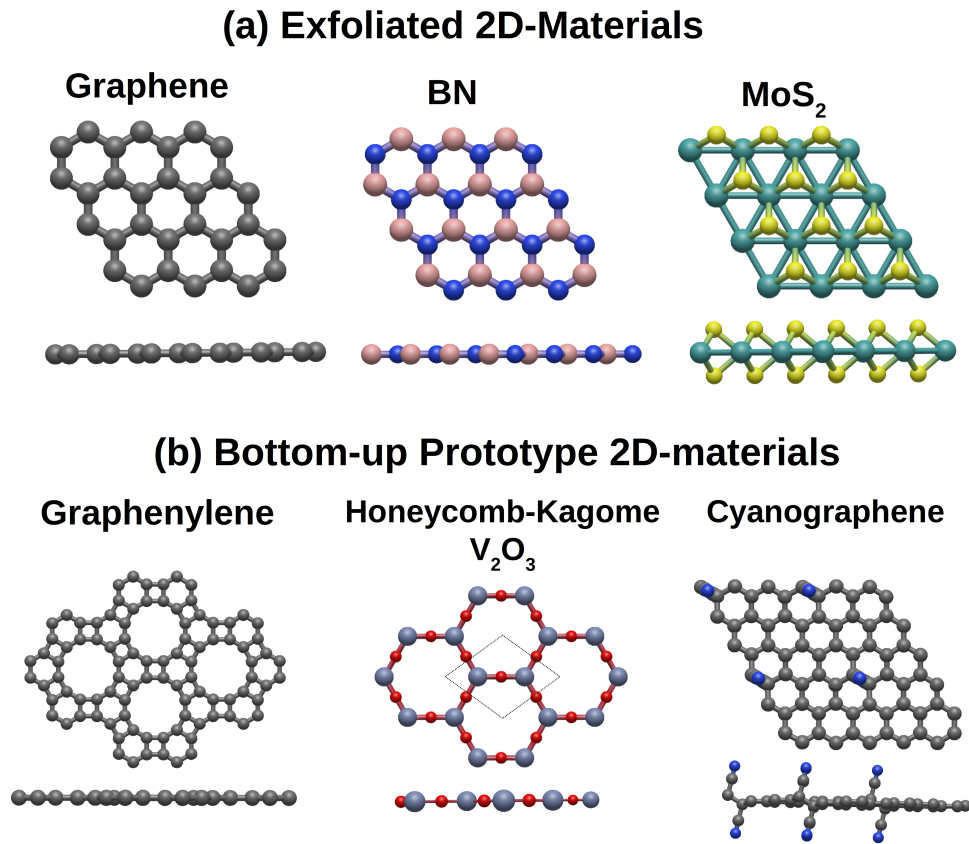


Figure 1.1. The examples of 2D-materials. (a) Exfoliated 2D-Materials from bulk layer. (b) Bottom-up Prototype 2D-materials which dose not come from bulk layer.

1.1.1 Application for Semiconductor Materials

Graphene, a single-atomic-layer sheet of carbon, was the first 2D-material to be isolated and experimentally verified in monolayer form[9, 10]. Its peculiar electronic structure—linear bands forming “Dirac cones”—was described theoretically as early as 1947, and monolayer graphene was realized experimentally in 2004 by mechanical exfoliation of graphite. Today, wafer-scale films are typically grown by chemical vapor deposition (CVD) on Cu using methane as the carbon

source, then transferred onto Si/SiO substrates for device fabrication. This platform underpins applications under active development, including gas and biosensors, high-frequency field-effect transistors, transparent and flexible electrodes, thermal spreaders, and reinforcement in composite materials[11, 12]. A persistent challenge, however, is the absence of an intrinsic band gap, which hampers suppression of the device off-state current; consequently, engineering strategies to open a gap are central to digital applications. Representative approaches include patterning into nanometer-wide graphene nanoribbons (quantum-confinement-induced gaps), applying a perpendicular electric field to bilayer graphene, and exploiting nanoporous architectures, chemical functionalization, and substrate interactions[13–17].

1.1.2 Application for Magnetic Materials

In parallel with advances in band-gap engineering of graphene, recent years have seen growing attention to the spin degree of freedom as a complementary design axis for 2D materials, accelerating both the discovery and functionalization of 2D-ferromagnets[18, 19]. 2D-ferromagnets are layered crystalline materials that retain spontaneous magnetization even in the monolayer or few-layer limit, and they are promising building blocks for the ultimate miniaturization of spintronic devices. Although pristine graphene is nonmagnetic, spin polarization can be induced via magnetic-proximity coupling to a ferromagnet or through the introduction of defects and edge states; on this basis, hybrid structures have been explored for spin injection and spin-filtering functionalities[20, 21]. Meanwhile, a growing number of intrinsically ferromagnetic 2D materials have been reported. A representative case is CrI₃[22], which exhibits strong Ising-type ferromagnetism in the

monolayer and antiferromagnetic interlayer coupling in bilayers, enabling applications such as tunnel magnetoresistance devices and spin filters[23, 24]. Furthermore, in systems such as Fe_3GeTe_2 [25], $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [26], and engineered transition-metal dichalcogenides (TMDC)[27], gate control and carrier doping have been shown to enhance ferromagnetism and raise the Curie temperature, opening avenues for optoelectronic devices that exploit coupled spin and valley degrees of freedom[28, 29]. Nonetheless, a lot of 2D-ferromagnets still suffer from low Curie temperatures at ambient conditions, air sensitivity (particularly in halides), and challenges in wafer-scale synthesis and uniform interface engineering[30–32].

1.1.3 Application for Ion Batteries

The electrochemistry of 2D materials have emerged as promising electrodes for next-generation ion batteries due to their short ion-diffusion paths and large specific surface areas[33, 34]. Graphene exhibits exceptional electrical and thermal conductivities; consequently, when used as an anode in lithium-ion batteries, it can deliver specific capacities reported as high as $\sim 669\text{mAhg}^{-1}$ under suitable structural and electrochemical conditions, substantially exceeding that of commercial graphite (372mAhg^{-1}) [35, 36]. Further improvements in ion transport and capacity have been achieved through defect engineering, heteroatom doping, interlayer-spacing control, and purposeful porosity[37–39].

Currently, the rapid growth of the electric-vehicle market has intensified interest in post-lithium-ion systems based on Na, K, and Mg, which face fewer resource constraints[40–42]. In Na-ion batteries in particular, graphite and graphene suffers from weak intercalation interactions and thus limited capacity[43]. To address this, graphene-based electrodes are being engineered to promote Na storage via interlayer expansion—achieved through functionalization and porous architectures—and by introducing additional redox-active sites[44]. Beyond graphene,

other 2D materials are attracting attention for Na-ion batteries: MXenes leverage high conductivity and hydrophilic terminations for fast charge/discharge[45]; MoS₂ utilizes a combination of intercalation and conversion reactions to sustain high capacities[46]; and black phosphorus offers very high theoretical capacity and favorable ion-transport kinetics, with nanostructuring being crucial to mitigate volume changes[47]. Overall, the tunable chemistry and high surface-to-volume ratio of 2D materials position them as strong candidates for achieving higher energy and power densities in post-Li-ion batteries.

1.1.4 Application for Catalysts

2D-materials have attracted intensive interest as catalyst supports because their atomically thin architectures expose abundant anchoring sites and facilitate high dispersion of active species[48, 49]. In particular, graphene combines high electrical conductivity, mechanical robustness, and chemical stability; by leveraging defects and surface functional groups to immobilize single atoms or nanoparticles, graphene-metal interfaces can realize strong metal-support interactions (MSI) that enable simultaneous high dispersion and anti-sintering under operation[50]. Representative studies on Pt/graphene variants report enhanced durability consistent with strengthened MSI[51]. In parallel, deploying the 2D materials themselves as catalysts has advanced rapidly. Notably, 2D conjugated/-conductive metal organic frameworks (2D-MOF) provide in-plane -conjugation for charge transport together with ultrathin morphologies that shorten diffusion pathways, which has spurred applications in electrocatalysis such as CO reduction and water splitting[52, 53]. At the same time, key challenges are well recognized. For single-atom catalysts on 2D supports, there is a persistent trade-off between dispersion and metal loading and a risk of aggregation[54]. For 2D-materials electrocatalysis, stability under electrochemical potentials (e.g., restacking, oxidation/corrosion, structural degradation) are still bottlenecks[55].

1.2 Bottom-up Prototype 2D-Materials

Graphene is now extensively studied, but it exists only as a theoretical concept for more than 50 years until the isolation of a single layer in 2004[56]. Following the synthesis of graphene, monolayers are exfoliated from various layered materials, and the diversity of two-dimensional materials, including BN, TMDCs, silicene, and black phosphorus, increases significantly. In parallel with the discovery of many two-dimensional materials by exfoliation from bulk crystals, the existence of Bottom-Up Prototype 2D-Materials with structures that do not originate from bulk phases is theoretically predicted by first-principles calculations as shown in Fig. 1.1(b). More recently, experimental reports on this type of two-dimensional material gradually appear. This section introduces the development and potential applications of Bottom-Up Prototype 2D-Materials, as well as examples of their synthesis in experiments.

1.2.1 Two-dimensional carbon allotropes

Theoretical predictions of two-dimensional carbon allotropes with planar structures other than the regular hexagonal tiling (honeycomb lattice) become active around 2010[57]. Representative examples are graphyne, which contains in-plane carbon–carbon triple bonds[58], and graphenylene, which contains nonhexagonal rings[59]. Graphyne has a planar structure in which benzene rings are connected by acetylenic chains, and it is theoretically proposed in 1987[60]. Experimental studies are also actively reported: the first organic synthesis is achieved in 2010[61], and more recently wafer-scale synthesis is demonstrated[62]. Graphyne is expected to be applied to information storage devices such as optoelectronic memory[62]. A related structure, graphdiyne, extends the sp-hybridized carbon chains connecting the hexagonal rings, and its porosity is investigated for applications in gas separation membranes[63, 64].

Graphenylene is a nonhexagonal two-dimensional carbon allotrope composed of a planar tiling of regular hexagons, squares, and dodecagons. Theoretical predictions start in 2013[59], and various applications are subsequently examined theoretically. For example, its intrinsic porosity associated with the dodecagons is expected to be useful for gas separation and desalination membranes[59, 65]. In addition, metal adsorption originating from the nonhexagonal ring structure is explored for applications as lithium-ion battery anode materials and as supports for single-atom catalysts[66, 67]. Furthermore, a related nonhexagonal carbon network, the biphenylene network, which is structurally similar to graphenylene, is synthesized on a gold surface from molecular precursors in 2021[68]. Other related structures include octagraphene, which consists of a tiling of squares and octagons, and penta-graphene, which contains pentagons, and these materials are proposed for applications such as hydrogen storage media and superconductors[69, 70]. Planar structures with non-hexagonal tilings are also being explored for other elements, including boron nitride and phosphorus allotropes[71, 72].

1.2.2 Honeycomb–Kagome Lattice

The honeycomb–kagome lattice is a two-dimensional crystal lattice with a planar structure that combines the hexagonal tiling (honeycomb lattice) and the triangular–hexagonal tiling (kagome lattice). In general, the geometric structure of two-dimensional materials is closely related to their electronic states. For example, in graphene with a honeycomb lattice, a linearly dispersing band called a Dirac cone appears, corresponding to Dirac particles with nearly zero effective mass. It is also theoretically shown that when a gap opens at the Dirac point due to spin–orbit coupling, a two-dimensional topological insulator (quantum spin Hall insulator) phase emerges[73]. Similarly, the kagome lattice exhibits a characteristic band structure, referred to as the kagome band, in which Dirac cones and flat bands

coexist[74]. In contrast to Dirac bands, flat bands have extremely small dispersion, leading to a large effective mass of electrons and a pronounced enhancement of the density of states. When a flat band lies near the Fermi level, strong electronic correlations can arise, and it has been suggested that unconventional superconductivity with a very high transition temperature may appear[75]. Furthermore, the kagome lattice is one of the prototypical frustrated lattices, and it has been proposed that, in magnetic systems, a quantum spin liquid state without long-range spin order can be realized[76]. For these reasons, two-dimensional materials based on the honeycomb–kagome lattice are expected to host a variety of quantum states that are central to modern condensed matter physics, including Dirac particles, topological insulators, flat bands, and quantum spin liquids, originating from the underlying honeycomb and kagome lattices. These quantum states hold great potential not only as platforms for next-generation spintronic and quantum information devices, but also as model systems for testing fundamental theories of strongly correlated electrons and topological phenomena[77, 78].

Research on honeycomb–kagome lattices has been conducted since around 2017, mainly focusing on transition-metal oxides such as V_2O_3 and Nb_2O_3 . In particular, V_2O_3 and Nb_2O_3 have been proposed as quantum anomalous Hall insulators that remain stable up to near room temperature, because they host spin-polarized Dirac cones together with Dirac points that are gapped by spin–orbit coupling[79, 80]. Furthermore, in recent years, V_2O_3 on platinum surfaces and Nb_2O_3 on gold surfaces have actually been synthesized by reactive evaporation under low-oxygen atmospheres[81, 82]. In this way, the honeycomb–kagome lattice is shifting from a purely theoretical concept to a realizable motif in real materials.

1.2.3 Functionalized Graphen

Bottom-up two-dimensional materials are not limited to two-dimensional carbon allotropes and honeycomb–kagome lattices, but also extend to graphene uniformly functionalized with specific groups. Attempts to introduce functional groups or modifier molecules into graphene have been made since the early days of graphene research. A representative example is graphene oxide, a two-dimensional material obtained by strong oxidation of graphite, for which applications in semiconductor technologies have been extensively investigated[83]. However, because graphene oxide contains a wide variety of defects and oxidation states, it has been difficult to control the degree of functionalization and to ensure reproducibility[84].

Uniform functionalization of graphene was first achieved in 2012 by the synthesis of fluorographene using a fluoropolymer and laser irradiation[85]. In fluorographene, fluorine atoms are introduced at high density and with high uniformity, and its application as an insulating material with a band gap of approximately 3.5 eV has been explored[86]. Furthermore, by converting the functional groups of fluorographene as a precursor, cyanographene and graphene acid, in which cyano and carboxyl groups are introduced at high density, were synthesized in 2017[87]. Owing to their electrical conductivity, biocompatibility, metal adsorption capability, and hydrophilicity, these materials have been demonstrated, both experimentally and theoretically, to be promising for a wide range of applications, including capacitors, biosensors, catalytic materials, and battery materials[88–92].

1.3 High-Throughput First-Principles Calculations toward Materials Design

1.3.1 High-Throughput Density Functional Theory Work Frame

In recent years, efforts to discover next-generation materials for societal challenges have highlighted the limitations of the traditional trial-and-error design loop of proposing compositions, tuning synthesis conditions, characterizing products, and testing performance[93, 94]. As the accessible chemical and structural space has expanded, it has become clear that intuition-driven exploration alone cannot efficiently navigate this space. In this context, first-principles calculations—particularly density functional theory (DFT)—now play a central role[95–97]. DFT enables mechanistic analysis that links composition and structure to functionality, as well as predictive evaluation of yet-unsynthesized compounds, thereby reducing costly synthesis–characterization–testing cycles. Open databases such as the Materials Project, AFLOW, and the Open Quantum Materials Database (OQMD) disseminate large volumes of DFT-based property data, built on systematic, high-throughput workflows that yield reliable, comparable datasets[98–100].

High-throughput DFT (HT-DFT) workflows operationalize these advantages by emphasizing scale and uniformity[101, 102]. Large candidate sets are generated programmatically, followed by a standardized pipeline of structural relaxation, stability and phase-relation assessment, and consistent evaluation of key properties (e.g., electronic structure, magnetism, ion diffusion). Using a single level of theory and fixed numerical parameters across all candidates ensures cross-candidate comparability, enables construction of design rules, and produces machine-learning datasets.

In practice, the Materials Project provides structures, energies, phase diagrams, and reactivity-relevant quantities for inorganic materials[98], while OQMD offers

hundreds of thousands of total-energy calculations with quantified formation-energy accuracy[100]. JARVIS extends this idea by integrating DFT, force-fields, and machine-learning models, supporting multi-property data and benchmarking[99]. Together, these platforms have turned computation into a map-making engine for the global materials design space. At the same time, HT-DFT faces challenges of computational cost and workflow management[103–105], which are addressed by filtering strategies and automated infrastructures that unify job submission, monitoring, post-processing, and database registration.

1.3.2 High-Throughput Theoretical Studies for 2D-Materials

High-throughput first-principles studies of two-dimensional materials have primarily developed around top-down approaches. Initially, exfoliable layers were systematically identified from bulk materials databases, leading to the theoretical proposal of more than one thousand two-dimensional materials[106]. Subsequently, the two-dimensional structures obtained by virtual exfoliation were used as structural prototypes, and hypothetical two-dimensional materials generated by elemental substitution were subjected to comprehensive property analyses—including stability and electronic structure—and compiled into databases such as the Computational 2D Materials Database (C2DB)[107].

More recently, high-throughput studies based on materials data from C2DB have become the mainstream, and a wide range of structures and properties have been investigated theoretically, including heterostructures formed by stacking different two-dimensional materials, magnetic materials, and ferroelectric materials[108–110]. In contrast, for bottom-up two-dimensional materials such as graphyne and the honeycomb–kagome lattice—namely, two-dimensional networks that do not have corresponding bulk crystal structures—hardly any exhaustive high-throughput first-principles exploration has been carried out, despite the large degree of freedom in designing the prototype structures themselves. Consequently,

design guidelines for bottom-up two-dimensional materials have yet to be established.

1.4 General Objective

Bottom-up two-dimensional materials exhibit diverse 2D structures that do not depend on bulk materials and offer wide design flexibility. However, their exploration is still mainly based on conventional theoretical predictions, and clear design guidelines for bottom-up two-dimensional materials have not yet been established. Therefore, the dissertation aims to establish design guidelines for bottom-up two-dimensional materials by means of high-throughput first-principles calculations.

In Chapter 3, a high-throughput first-principles workflow for honeycomb–kagome lattices is constructed, and design guidelines for two-dimensional magnetic materials are clarified. In Chapter 4, the stability and electronic structures of two-dimensional allotropes are compared under consistent computational conditions, and design guidelines for semiconductor materials are clarified. In Chapter 5, metal adsorption on functionalized graphene is compared under consistent computational conditions, and design guidelines for energy storage materials are clarified.

The dissertation provides the first example of high-throughput calculations for bottom-up two-dimensional materials and is expected to serve as a theoretical foundation for next-generation two-dimensional materials design, with potential impact across a wide range of fields, including magnetic materials, semiconductors, and energy materials.

Chapter 2

General Methodology

2.1 The Role of DFT in Materials Science

Density Functional Theory (DFT) plays a central role in materials science as a first-principles computational method that predicts electronic structure, bonding, and properties directly from atomic configurations. Since the 1990s, improvements in computational resources and software implementations have enabled its application across a wide spectrum—from bulk crystals to surfaces, defects, interfaces, and molecules—and it has been widely used in parallel with experiments for quantitative comparison and mechanistic elucidation[111]. In addition, the rise of high-throughput workflows and curated databases now allows systematic estimation of key design metrics such as phase stability, band gaps, and diffusion barriers, thereby establishing an infrastructure for screening synthesis candidates and enabling inverse design[95, 112]. As a result, materials discovery is shifting from trial-and-error to computation-driven exploration.

Against this backdrop, I first clarify the position of DFT within materials science. First-principles calculations provide a framework for predicting properties from quantum mechanics without empirical parameters and are commonly divided into two approaches: the Wave-Function methods and DFT. As a foundational Wave-Function methods, Hartree–Fock (HF) method treats many-electron systems within a mean-field approximation by averaging interparticle interactions into an effective one-body potential; however, this averaging neglects electron

correlation[113]. To remedy this, post-HF methods incorporate excited configurations, enabling more accurate energies that include electron correlation[114]. Nevertheless, such post-HF methods entail very high computational cost—typically $O(N^6) - O(N^7)$, which limits their routine applicability. By contrast, DFT usually requires only $O(N^3) - O(N^4)$ computational cost, although it achieves sufficient accuracy for meaningful comparison with experiment[115]. For this reason, DFT has become the core tool for mechanism elucidation and property prediction in materials science.

2.2 The Fundamentals of Density Functional Theory

The theoretical foundation of density functional theory (DFT) consists of the Hohenberg–Kohn theorems and the Kohn–Sham scheme. The Hohenberg–Kohn theorems show that all physical quantities of an interacting electronic system can be expressed as functionals of the electron density, thereby providing a framework in which the total energy of a many-electron system is computed from the electron density without explicitly treating the many-electron wavefunction. In this way, DFT focuses on the electron density, which describes the collective state of all electrons, instead of explicitly calculating the behavior of each electron, and can therefore be applied at a much lower computational cost than post-Hartree–Fock methods.

In the Kohn–Sham scheme, a fictitious non-interacting reference system (the Kohn–Sham auxiliary system) is introduced in place of the real interacting system, and the total energy is evaluated from Kohn–Sham orbitals by solving the Kohn–Sham equations[116]:

$$[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})]\phi_i(\mathbf{r}, s) = \varepsilon_i\phi_i(\mathbf{r}, s) \quad (2.1)$$

Here, $v_{eff}(\mathbf{r})$ denotes the Kohn–Sham effective potential, $\phi_i(\mathbf{r}, s)$ denotes the Kohn–Sham

orbitals, and ε_i denotes the eigenvalues of the Kohn–Sham orbitals. The Kohn–Sham effective potential $v_{eff}(\mathbf{r})$ is defined by Equation. 5.2:

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_{Hartree}(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2.2)$$

In this expression, $v_{ext}(\mathbf{r})$ is the external potential arising from the Coulomb interaction between nuclei and electrons, $v_{Hartree}(\mathbf{r})$ is the classical Coulomb potential describing electron–electron interactions (the Hartree potential), and $v_{xc}(\mathbf{r})$ is the exchange–correlation potential. The key point of this formulation is that the electron–correlation effects, which are treated by explicitly considering excited electronic configurations in post-Hartree–Fock methods, are incorporated in a much simpler manner in the Kohn–Sham scheme through the exchange–correlation potential.

The exchange–correlation potential $v_{xc}(\mathbf{r})$ is given by Equation. 5.3:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad (2.3)$$

where $n(\mathbf{r})$ is the electron density and $E_{xc}[n]$ is the exchange–correlation functional. The exchange–correlation functional includes not only electron correlation, but also exchange interactions and the difference in kinetic energy between the real interacting system and the Kohn–Sham auxiliary system. Because these interactions become less important between electrons that are spatially far apart, they can be approximated as a semilocal functional of the electron density (semilocal approximation).

A variety of exchange–correlation functionals based on semilocal approximations has been developed[117]. The local density approximation (LDA) is the simplest exchange–correlation functional and depends only on the local value of the electron density. The generalized gradient approximation (GGA) improves upon

LDA by including the gradient of the electron density. The meta-GGA further refines GGA by incorporating the kinetic-energy density (or equivalently the Laplacian of the electron density).

However, in these functionals, self-interaction errors and the limitations of the semilocal approximation prevent a quantitatively accurate description of the classical Coulomb interaction, exchange interaction, and electron correlation. To address these issues, the following types of exchange–correlation functionals have been developed. Hybrid functionals correct the exchange interaction by mixing a fixed fraction of the Hartree–Fock exchange term into the exchange part of LDA, GGA, or meta-GGA[118]. In the DFT+U method, an empirical Hubbard U parameter is added on top of LDA, GGA, or meta-GGA to correct the Coulomb and exchange interactions, particularly for localized orbitals[119]. In the van der Waals density functional (vdW-DF) method, a GGA-type functional is used for the exchange part, LDA is used for the local part of the correlation, and the nonlocal part of the correlation is corrected via the adiabatic-connection formalism[120].

In practice, the exchange–correlation functional is selected according to the target properties and the model. GGA functionals are used as the standard choice in most calculations[117]. For strongly correlated systems such as transition-metal oxides, DFT+U is often employed. For systems in which van der Waals interactions are important, such as physisorption systems and layered materials, vdW-DF is commonly used. For band-structure analysis, DFT+U and hybrid functionals are frequently adopted to obtain a more accurate description of the electronic structure.

2.3 Density Functional Theory for Solid State Materials

Crystals are described by periodic boundary conditions in which an identical unit cell is repeated throughout space. The periodicity is characterized by the lattice vectors $\mathbf{R}$ and the reciprocal lattice vectors $\mathbf{G}$. From Bloch's theorem, the eigenfunctions of periodic systems are expressed as Equation. 5.4:

$$\phi_{\mathbf{k}n}(\mathbf{r}) = U_{\mathbf{k}n}(\mathbf{r}) \exp[i\mathbf{k} \cdot \mathbf{r}] \quad (2.4)$$

where, $U_{\mathbf{k}n}(\mathbf{r})$ is a lattice-periodic function, n is the index assigned to each band, and $\mathbf{k}$ is wave number vector. In first-principles calculations for periodic systems, the electronic states are obtained by evaluating the eigenvalues and eigenfunctions at all $\mathbf{k}$ points in the Brillouin zone. In practice, the Brillouin zone is divided into a mesh, and the eigenvalues are computed at the sampled $\mathbf{k}$ points. These values are then integrated, as is commonly done in the Special point method[121].

The computational cost and accuracy of first-principles calculations strongly depend on the choice of basis set used to describe the wave functions. At present, the basis sets commonly used in DFT calculations are (1) plane-wave bases, (2) atomic-orbital bases, and (3) real-space bases.

In the plane-wave basis, the eigenfunctions of periodic systems are expressed as a Bloch function characterized by plane waves, as shown in Equation 5.4. Therefore, the plane wave basis uses the linear combination of plane-waves to represent wave functions, which can describe electron state in solid materials very well.

$$\phi_{\mathbf{k}n}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \quad (2.5)$$

The computational accuracy is controlled by the number of plane waves in the plane-wave basis. The number of basis functions is determined by using the kinetic energy of the plane waves as a parameter, which is called the cutoff energy.

In other words, increasing the plane-wave cutoff energy allows finer wave functions, which improves the computational accuracy but also increases the computational cost. A drawback of the plane-wave basis is that a very high cutoff energy is required to describe core electrons. However, this issue is mitigated by the pseudopotential method described later. The plane-wave basis is implemented in codes such as VASP[122], Quantum ESPRESSO[123], and GPAW[124].

In contrast, atomic-orbital and real-space bases provide alternative representations of the wave functions. Atomic-orbital basis sets represent the wave functions as linear combinations of atomic orbitals and are frequently used for systems with non-periodic boundary conditions, such as molecules. They are frequently used for systems with non-periodic boundary conditions, such as molecules. Although they are particularly efficient in terms of computational cost for large systems, they are not suitable for precise discussions of solid-state materials. Atomic-orbital basis sets are implemented in GAUSSIAN[125] and GPAW[124].

$$\phi_{kn}(\mathbf{r}) = \sum_{\mu} C_{n\mathbf{k}\mu} \Phi_{\mathbf{k}\mu}(\mathbf{r}) \quad (2.6)$$

Real-space bases, on the other hand, employ the finite-difference (FD) mode, in which the kinetic-energy operator is represented on a uniform Cartesian grid. This approach also offers high efficiency for large-scale systems and is implemented in GPAW[124].

The wave function oscillates strongly near atomic nuclei, so high numerical accuracy is required. Therefore, the projector augmented-wave (PAW) method is widely used, in which core electrons are fixed in isolated-atom states and pseudo wave functions are computed only for valence electrons[126]. The all-electron wave functions are then obtained by applying a linear transformation to the pseudo wave functions generated by the PAW method. Because core electrons generally do not contribute significantly to chemical bonding, this approach allows an efficient description of the electronic structure of materials. For this reason, the PAW

method is implemented in many DFT codes, such as VASP, Quantum ESPRESSO, and GPAW. In contrast, WIEN2k implements the linearized augmented plane-wave method, in which core electrons are represented by atom-centered localized basis functions and the valence electrons is described by plane waves[127]. This method can describe the electronic structure accurately, but its computational cost is higher than that of the PAW method.

2.4 The grid-based projector-augmented wave code

All DFT calculations are conducted using the grid based projector augmented wave (GPAW) code[124]. GPAW is an open-source first-principles code based on the Projector Augmented-Wave (PAW) method and provides three types of wave-function representations: plane-wave (PW), real-space (FD), and atomic-orbital (LCAO)[126, 128]. Therefore, it enables calculations using both atomic-orbital basis sets, as in molecular electronic-structure codes such as GAUSSIAN, and plane-wave basis sets, as in solid-state codes such as VASP, and can be applied to property predictions for a wide range of systems from molecules to bulk solids, surfaces, and two-dimensional materials. Furthermore, GPAW implements its own FD basis that uses finite differences on a uniform real-space grid, which provides high computational efficiency for large and non-periodic systems. GPAW is implemented in Python and offers an interface through the Atomic Simulation Environment (ASE)[129], which allows automated high-throughput workflows to be constructed and easily integrated with Python tools such as Pandas. In the field of two-dimensional materials, it is used as the computational engine of the Computational 2D Materials Database (C2DB), where structural, electronic, magnetic, and optical properties of many two-dimensional materials are systematically calculated with GPAW, which facilitates comparison with other theoretical studies of two-dimensional materials[107]. In addition, in a numerical error assessment relative to WIEN2k, which employs an all-electron LAPW method, the numerical error is reported to

be 1.9 meV/atom for VASP, which uses the PAW method, and 3.3 meV/atom for GPAW, indicating that GPAW can be regarded as an electronic-structure code with a level of reliability comparable to VASP and WIEN2k[130].

In this section, the methods used for structural optimization and property analysis using GPAW are described.

2.4.1 Structure Relaxation

Usually, DFT calculations treat the ground state of materials, although atomic modeling cannot always provide a stable initial structure. Thus, the structural optimization is first performed for the initial structure to get energetically stable structure. In this study, the lattice constants are first optimized by varying the lattice length in steps of 0.4% and calculating the total energy, and the lattice constants corresponding to the lowest energy are adopted. Next, the atomic positions inside the unit cell are optimized using the BroydenFletcher-GoldfarbShanno (BFGS) algorithm implemented in ASE[131]. In this optimization, the internal coordinates are relaxed until the maximum force acting on any atom is reduced below 0.1 eV Å⁻¹. The exchange–correlation functional of Perdew, Burke, and Ernzerhof (PBE) is employed with spin-polarized calculations[132].

The python3 code is here: The function of *relax* is using for optimization of atomic positions and *cell – opt* is for getting the lattice constants. The exception handlings for broken symmetry error and convergence error are applied to the optimization calculations.

```
1 def relax(calc, input='in.traj', path='./', cnum=1):
2     # Read input structure
3     atoms = io.read(path + input)
4     # Attach the calculator to the input structure for relax()
5     atoms.set_calculator(calc)
6     # Add vacuum along the z direction
7     atoms.center(axis=2, vacuum=6.0)
8     # Perform structural optimization and save the trajectory file
```

```
9     dyn = optimize.BFGS(  
10         atoms,  
11         trajectory=path + 'relax' + str(cnum) + '.traj',  
12         logfile=path + 'relax.log'  
13     )  
14     try:  
15         dyn.run(fmax=0.1)  
16     except RuntimeError as BS:  
17         raise RuntimeError('Broken symmetry!')  
18     except KohnShamConvergenceError as KS:  
19         raise KohnShamConvergenceError('gpaw.KohnShamConvergenceError  
20             : Did not converge!')  
21  
22     # Save the electronic structure  
23     calc.write(path + 'out.gpw')  
24     # Load the optimized structure from the trajectory  
25     atoms = io.read(path + 'relax' + str(cnum) + '.traj')
```

```
1 def cell_opt(atoms, rate=0.005, step=5, cnum=1):  
2     cell = atoms.get_cell()  
3     traj = Trajectory(path+'lattice'+str(cnum)+'.traj', 'w')  
4     #Divide the specified range to obtain energy  
5     for x in np.linspace(1-rate, 1+rate, step):  
6         cell_new = cell*x  
7         cell_new[2][2] =cell[2][2]  
8         atoms.set_cell(cell_new, scale_atoms=True)  
9         try:  
10             atoms.get_potential_energy()  
11         except KohnShamConvergenceError:  
12             return KohnShamConvergenceError  
13     traj.write(atoms)
```

2.4.2 Density of States and Band Structure

Density of States (DOS) and band structure are used to analyze the electronic properties of solid state materials in DFT calculations. The band structure shows how the Kohn–Sham eigenvalues vary along high-symmetry paths in reciprocal space, providing a band dispersion that reveals band gaps and electronic features such as flat bands or Dirac cone. While the band structure resolves the dispersion of individual bands, the DOS emphasizes how many electronic states are available at each energy and is therefore convenient for identifying band gaps and the contribution of different orbitals when projected DOS (PDOS) is used.

2.4.3 GLLB-SC

The Perdew–Burke–Ernzerhof (PBE) functional relies on a semilocal approximation and therefore cannot properly account for electronic correlation, which leads to an inaccurate description of the conduction bands and a systematic underestimation of band gaps. To calculate the band gap, hybrid functionals such as HSE06[118] incorporating the Fock exchange operator are often employed. Nevertheless, their high computational cost makes them unsuitable for high-throughput DFT studies. Similarly, the DFT+U method[119], which introduces empirical on-site interaction parameters, is frequently used to correct band gaps, although the need to tune the U value to reproduce experimental data limits its applicability to unknown compounds and large-scale screening. In contrast, the GLLB-SC approach enables a non-empirical evaluation of band gaps at a computational cost comparable to PBE[133]. In practice, it has been shown to yield band gaps that reproduce experimental values well for perovskite oxides[134].

GLLB-SC approach gets quasiparticle band gap E_g^{QP} to calculate Kohn-Sham band gap E_g^{KS} and derivative discontinuity Δ_{xc} :

$$E_g^{QP} = E_g^{KS} + \Delta_{xc} \quad (2.7)$$

where discontinuity Δ_{xc} is calculated from exchange correlation potential ν_{xc} and integer occupation numbers N [126].

$$\Delta_{xc} = \lim_{\delta \rightarrow 0} [\nu_{xc}(\mathbf{r}; N + \delta) - \nu_{xc}(\mathbf{r}; N - \delta)] \quad (2.8)$$

the exchange correlation potential ν_{xc} is using exchange energy density and response potential of PBEsol[135], as well as GLLB response potential[136].

2.4.4 Bader Charge Analysis

Bader charge analysis is a method to quantify charge transfer between atoms and to characterize the bonding nature as ionic or covalent. In this approach, atomic regions are defined by zero-flux surfaces of the gradient of the electron density. Each atomic charge is obtained by integrating the electron density within its Bader volume, which is determined by the shape of the charge density. Therefore, Bader charge analysis is less basis-set dependent and more easily applicable across different DFT codes and pseudopotentials. For solid-state calculations, the approach allows a consistent comparison of charge transfer at interfaces and of the effects of doping or adsorption. GPAW can be combined with grid-based algorithms that locate zero-flux surfaces in the charge density, which enables efficient solid-state charge analysis[137].

The python3 code is here:

```

1 #read structure and electronic state file
2 crystal=io.read('relax.traj')
3 calc = GPAW('out.gpw')
4 crystal.set_calculator(calc)
5 crystal.get_potential_energy()
6
7 # get electron density of all electron potential
8 rho = calc.get_all_electron_density(gridrefinement=2) * Bohr**3
9 write('density.cube', crystal, data=rho)

```

```

10
11 #apply bader algorithm to electron density file.
12 command = './bader -p all_atom -p atom_index density.cube &'
13 proc = subprocess.run(command, shell=True, stdout=subprocess.PIPE,
14                        stderr=subprocess.PIPE, text=True)

```

2.4.5 Nudged Elastic Band Method

To evaluate the probability of chemical reactions or atomic diffusion, it is necessary to determine the transition state and the activation energy. According to the Arrhenius equation, the reaction rate constant k is given by

$$k = A \exp\left(-\frac{E_a}{k_B T}\right) \quad (2.9)$$

Once the activation energy E_a is determined, the reaction rate at a given temperature can be estimated. The Nudged Elastic Band (NEB) method is a technique that explores the reaction path and transition state from initial and final states. This approach introduces intermediate images and connects neighboring images with virtual springs. Under this constraint, a structural optimization is performed so that the band of images slides over the potential-energy surface and converges to the minimum-energy path via the saddle point. In GPAW-based DFT calculations, NEB is used through the implementation in the Atomic Simulation Environment (ASE), where intermediate images are generated by the NEB algorithm and each image is relaxed using the BFGS optimization method[129].

2.4.6 Magnetic Anisotropy

Spin-orbit coupling (SOC) is a term that originates from relativistic effects and couples the spin degrees of freedom to the orbital motion, and it is indispensable for describing spin-related properties such as magnetic anisotropy and SOC gaps in the band structure. In GPAW, a standard spin-polarized DFT calculation first

obtains the eigenstates, and then the SOC Hamiltonian is applied perturbatively to the Kohn–Sham orbitals to compute spin–orbit–split band structures non-self-consistently[126]. This procedure enables the direct reuse of self-consistently converged results and thus reduces the computational cost.

Crystalline magnetic anisotropy is the orientation of spins in the crystal induced by spin–orbit coupling, which strongly affects the properties of magnetic materials. In particular, for two-dimensional magnets, the Mermin–Wagner theorem shows that an isotropic Heisenberg system with continuous spin-rotation symmetry cannot sustain long-range order at finite temperature. Therefore an out-of-plane magnetic anisotropy derived from spin–orbit coupling is required to exhibit magnetism at finite temperature for two-dimensional magnets [26]. The magnetic anisotropy energy (MAE) is calculated from energy difference including spin–orbit coupling between in-plane ($\parallel$) and out-of-plane ($\perp$) directions.

$$\text{MAE} = E^{\parallel} - E^{\perp} \quad (2.10)$$

When MAE is positive, spins aligned out of plane is energetically more stable, which means that a perpendicular easy axis exists to support long-range magnetic order at finite temperature in two-dimensional magnets.

2.5 Automated High-Throughput Calculation Program

High-throughput DFT program that combines the DFT software GPAW with the atomic modeling framework ASE. Each type of calculation is implemented as a Python class so that they can be flexibly combined according to the purpose. In addition, batch-job handling with Pandas enables sequential DFT calculations for multiple materials. The workflow of high-throughput DFT for chapter 3 is shown in Fig. 2.1.

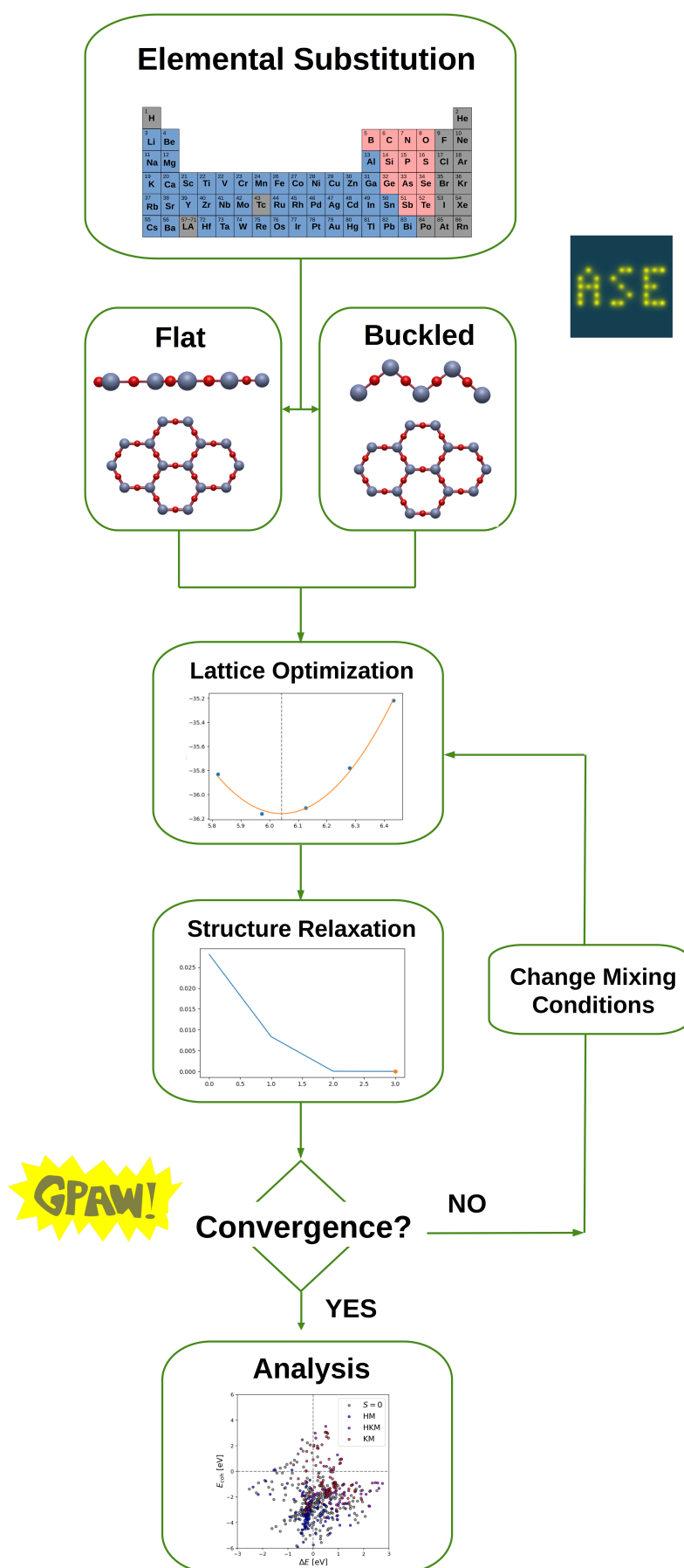


Figure 2.1. High-throughput calculation work flow in Chapter 3.

2.5.1 Initial Structure Setup

The initial structures for DFT structural optimization are generated by arranging atoms and substituting elements using the ASE *Atoms* object. In the honeycomb–kagome lattice calculations of Chapter 3, 57 elements are systematically substituted into the flat and buckled structure to construct a total of 1080 initial structures. In the metal adsorption calculations on cyanographene in Chapter 5, the initial structures are constructed by placing nine alkali and alkaline-earth metals on pre-optimized cyanographene. These initial structures serve as the starting point for structural optimization and property evaluation.

The python3 code is here.

```

1 materials_df = pd.read_csv('run.csv')
2 configurations = ['FLAT', 'BUCKLING']
3 for con in configurations:
4     for index, row in materials_df.iterrows():
5         path = './'+con+'/'+row['material']+'/'
6         comand = 'mkdir -p '+path
7         proc = subprocess.run(comand, shell=True, stdout=sys.stdout,
8                               stderr=sys.stdout, text=True)
9         create.create(path=path, elementA=row['elementA'], elementB=
10                      row['elementB'], bondL=row['bondL'], configuration=con)
11 world.barrier()

```

```

1 def create(path, elementA, elementB, bondL, configuration):
2     if configuration == 'FLAT':
3         symbol = elementA*3+elementB*2
4         bondL *= root3
5         positions = [[0.5*root3*bondL, 0.5*bondL, 0], [0.5*root3*
6                  bondL, -0.5*bondL, 0], [root3*bondL, 0, 0],
7                  [(2/3)*root3*bondL, 0, 0], [(4/3)*root3*bondL, 0,
8                  0]]
9         cell = [[root3*bondL, -bondL, 0], [root3*bondL, bondL, 0], [0,
10                  0, 0]]

```

```

9     elif configuration == 'BUCKLING':
10         symbol = elementA*3+elementB*2
11         bondL *= 1.2
12         positions = [[0.5*root3*bondL, 0.5*bondL, 0], [0.5*root3*
13                     bondL, -0.5*bondL, 0], [root3*bondL, 0, 0],
14                     [(2/3)*root3*bondL, 0, bondL],
15                     [(4/3)*root3*bondL, 0, -bondL]]
16         cell = [[root3*bondL, -bondL, 0],[root3*bondL, bondL, 0],[0,
17                     0, 0]]

```

2.5.2 Structural Optimization

For structural optimization, the *cell-opt* and *relax* functions described in the *StructureRelaxation* section are used in combination. When the self-consistent calculation does not converge for a given material, the mixing conditions in the self-consistent cycle are changed and the calculation is repeated. The mixing settings are applied in the following four patterns:

$$\begin{aligned}
 (1) & \text{mixer} = \text{MixerDif}(0.05, 5, \text{weight} = 100.0) \\
 (2) & \text{mixer} = \text{MixerDif}(0.02, 2, \text{weight} = 100.0) \\
 (3) & \text{mixer} = \text{MixerSum}(0.05, 5, \text{weight} = 100.0) \\
 (4) & \text{mixer} = \text{MixerSum}(0.05, 5, \text{weight} = 100.0)
 \end{aligned}
 \tag{2.11}$$

Here, in cases (1) and (2), MixerDif mixes the total electron density and the magnetization density separately, whereas in cases (3) and (4), MixerSum mixes the density matrices for each spin channel separately and treats the pseudo electron density as the sum over the spin channels.

The python3 code is here.

```

1 materials_df = pd.read_csv('run.csv')
2 for index, row in materials_df.iterrows():
3     path = './' + str(row['material']) + '/'

```

```
4
5 # ----- FM expand -----
6 # Change conditions and iterate until convergence
7 for cnum in range(1, 5):
8     if cnum == 5:
9         calc = calc_expand_FM1
10    try:
11        expand.cell_opt(input='in.traj', path=path, calc=calc,
12                        rate=rate, step=step, cnum=cnum)
13    # If RuntimeError: Broken symmetry! occurs, stop the
14    relaxation
15    except RuntimeError as BS:
16        txt = open('error.txt', 'a')
17        parprint(str(materials_data) + ' Broken symmetry!',
18                file=txt)
19        break
20    # If KohnShamConvergenceError occurs, record it and try the
21    next condition
22    except KohnShamConvergenceError as KS:
23        txt = open('error.txt', 'a')
24        parprint(str(materials_data) +
25                ': did not converge in relax at cnum = ' + str
26                (cnum), file=txt)
27        if cnum == 5:
28            is_break = True
29            continue
30    # If the calculation finishes normally, break the loop
31    break
32    if is_break is True:
33        continue
34
35 # ----- FM relax -----
36 # Change conditions and iterate until convergence
37 for cnum in range(1, 5):
```

```
34     if cnum == 5:
35         calc = calc_relax_FM1
36     try:
37         relax.relax(input='atoms.traj', path=path, calc=calc,
38                     cnum=cnum)
39
40     # If RuntimeError: Broken symmetry! occurs, stop the
41     relaxation
42
43     except RuntimeError as BS:
44         txt = open('error.txt', 'a')
45         parprint(str(materials_data) + ' Broken symmetry!',
46                 file=txt)
47         break
48
49     # If KohnShamConvergenceError occurs, record it and try the
50     next condition
51
52     except KohnShamConvergenceError as KS:
53         txt = open('error.txt', 'a')
54         parprint(str(materials_data) +
55                 ': did not converge in relax at cnum = ' + str
56                 (cnum), file=txt)
57
58         if cnum == 5:
59             is_break = True
60             continue
61
62     # If the calculation finishes normally, break the loop
63
64     break
65
66 if is_break is True:
67     continue
68
69 # Write the final trajectory file
70 atoms = io.read(path + 'atoms.traj')
71 atoms.write(path + 'out.traj')
72
73 # If all calculations for this material finish normally, write
74 "end"
75
76 txt = open('calculation.txt', 'a')
```

```
62     parprint(str(row['material']) + ': end', file=txt)
63     world.barrier()
64
65 # When all calculations are finished, write the final "end"
66 txt = open('calculation.txt', 'a')
67 parprint('All calculation: end', file=txt)
68 world.barrier()
```


Chapter 3

High-throughput Workflow for Honeycomb-Kagome Lattice

3.1 Introduction

Since the discovery of graphene, two-dimensional (2D) materials have attracted significant attention due to their unique electronic structures, leading to novel electronic and optical properties with potential applications in next-generation electronic devices[138–140]. The emergence of 2D ferromagnets, such as CrI_3 [22] and $\text{Cr}_2\text{Ge}_2\text{Te}_6\text{C}$ [26], has introduced layer-dependent magnetic control, substantially impacting spintronics and quantum information technologies. Recently, honeycomb-kagome lattices displaying unique electronic structures, including Dirac and flat bands, have gained attention for intriguing magnetic properties like half-metallicity and topological insulating states[77, 80, 141]. However, existing honeycomb-kagome materials mainly comprise oxides and sulfides (e.g., V_2O_3 [80, 141] and Ta_2S_3 [142]), limiting compositional variety and highlighting the need for exploration beyond these elements.

In this context, high-throughput first-principles calculations offer a powerful approach for the rapid and comprehensive screening of diverse compositions

and structures, facilitating theoretical predictions and the discovery of new functional 2D materials[107, 143, 144]. This study employs high-throughput calculations to systematically explore the relationship between elemental composition, thermodynamic stability and magnetic properties in the honeycomb-kagome lattice (H_2K_3), constructed from 45 metal elements on honeycomb sites (H) and 12 p-block elements on kagome sites (K). Thermodynamically stable magnetic candidates are identified, classified according to magnetic ordering and electronic states, providing critical insights into how elemental choices influence magnetic properties and offering guidelines for designing novel 2D magnetic materials based on honeycomb-kagome lattices.

3.2 Methodology

3.2.1 Overview of the High-throughput Work Flow

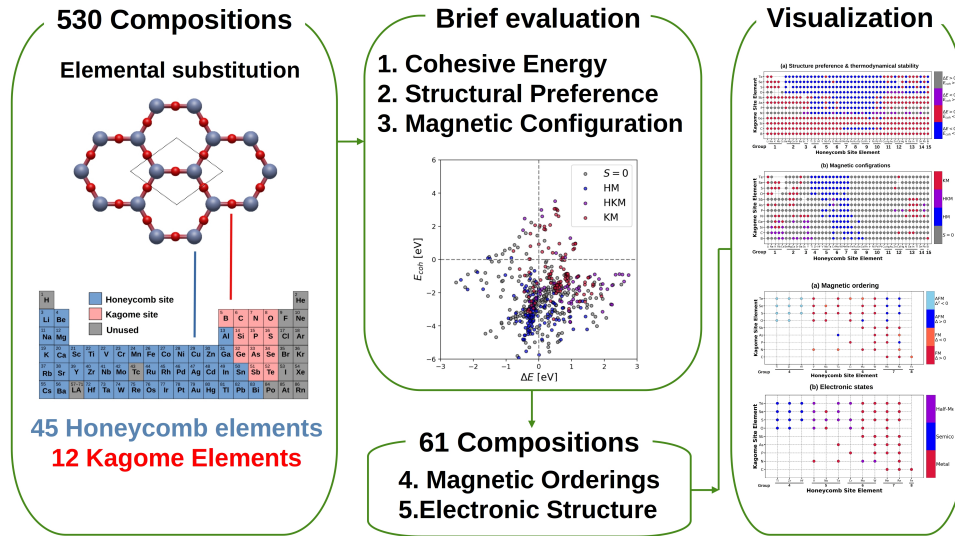


Figure 3.1. Architecture of the high-throughput calculations.

This study focuses on the honeycomb–kagome lattice, a periodic two-dimensional structure with alternating honeycomb- and kagome-like sublattices of atoms, as

illustrated in Fig. 3.1. High-throughput first-principles calculations within density functional theory (DFT) is proposed in order to unveil the stability and magnetic properties of these expanded elemental compositions. First, honeycomb site element and kagome site element are substituted to 45 metal elements and 12 p-block elements, respectively. Atomic color code: gray-Honeycomb site element, red-Kagome site element. High-throughput DFT calculation analyzes thermodynamic stability, structural preference and magnetic configurations. 61 compositions are selected as 2D-magnetic candidates. The visualization for the relationship between elemental composition, thermodynamic stability, structural preference and magnetic properties.

3.2.2 Evaluation Methods for Physical Properties

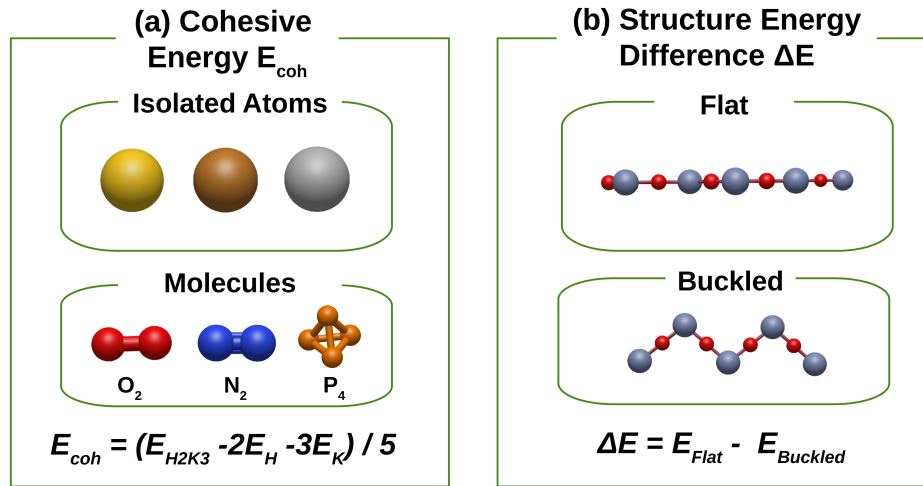


Figure 3.2. The evaluation Method for (a) cohesive energy E_{coh} and (b) structure energy difference ΔE .

The cohesive energy E_{coh} is calculated to consider thermodynamic stability[145].

$$E_{coh} = (E_{H2K3} - 2E_H - 3E_K) / 5 \quad (3.1)$$

where $E_{H_2K_3}$ is the energy of honeycomb-kagome lattice, E_H and E_K are the energy for gas phases of honeycomb site element and kagome site element, respectively. Gas phase energy for elements of O, N and P are calculated from the molecule of O_2 , N_2 and P_4 , while the other elements are calculated from the single atom as shown in Fig. 3.2(a). A negative E_{coh} means the materials can be formed from the single atom exothermically. The gas phase energy of honeycomb elements and kagome elements are shown in Table. 3.1 and 3.2, respectively.

Name	E [eV/atom]	Name	E [eV/atom]
Sc	-0.54	Os	-2.72
Ti	-1.16	Ir	-2.03
V	-2.60	Pt	-0.95
Cr	-5.44	Au	-0.18
Mn	-5.76	Hg	-0.72
Fe	-4.15	Li	-0.30
Co	-3.24	Na	-0.25
Ni	-2.47	K	-0.37
Cu	-0.24	Rb	-0.16
Zn	-0.07	Cs	-0.14
Y	-0.51	Be	0.00
Zr	-1.08	Mg	-0.12
Nb	-3.33	Ca	-0.14
Mo	-5.04	Sr	-0.09
Ru	-2.59	Ba	-0.01
Rh	-1.44	Al	-0.30
Pd	-0.18	Ga	-0.27
Ag	-0.33	In	-0.45
Cd	-0.16	Tl	-0.48
Hf	-1.02	Sn	-0.87
Ta	-1.75	Pb	-0.86
W	-2.68	Bi	-2.15
Re	-3.78		

Table 3.1. The gas phase energy of honeycomb elements.

Although flat structures have been investigated for 2D honeycomb-kagome

Name	E [eV/atom]	Name	E [eV/atom]
B	-0.45	S	-1.04
C	-1.37	Se	-0.86
Si	-0.85	Te	-0.76
Ge	-0.77	O ₂	-5.22
As	-1.69	N ₂	-8.44
Sb	-1.71	P ₄	-5.20

Table 3.2. The gas phase energy of hkagome elements. O, N and P are calculated from molecules.

lattices, expanding the elemental composition requires evaluating the possibility of stable non-flat (buckled) structures, as shown in Fig. 3.2(b). Hence, structural optimizations are conducted for both flat and buckled configurations and compared their energy differences:

$$\Delta E = E_{\text{FLAT}} - E_{\text{BUCKLED}} \quad (3.2)$$

where E_{FLAT} and E_{BUCKLED} are the energy for flat and buckled structure. A negative ΔE indicates that the flat structure is more stable than the buckled one. This approach allows efficient and straightforward structural stability assessments across numerous candidate materials.

The spin quantum number S is defined by normalizing the total magnetic moment M of the unit cell by the number of magnetic atoms in unit cell N , rounded to the nearest half-integer[109]. The number N of magnetic atoms is inferred based on the ratio $|M_H/M_K|$, where M_H and M_K are the magnetic moments associated with atoms on honeycomb and kagome sites, respectively. Based on this ratio, the system is categorized into three regimes, as shown in Fig. 3.3. For example, $N = 2$ when $|M_H/M_K| \geq 10$, corresponding to honeycomb-dominated magnetism (HM); $N = 3$ when $|M_H/M_K| \leq 0.1$, corresponding to kagome-dominated

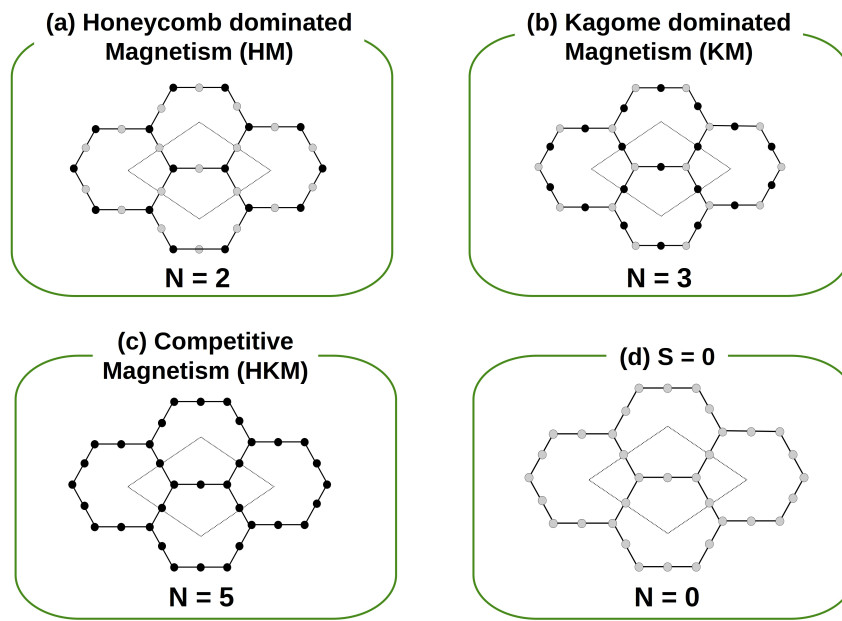


Figure 3.3. Four types of magnetic configurations. Black point represents magnetic atoms and white point represents nonmagnetic atoms. Dot lines represent unit cell.

magnetism (KM); $N = 5$ for intermediate values, indicating a competitive regime (HKM). This method is applied to provide a screening of the magnetic configuration in honeycomb–kagome lattices.

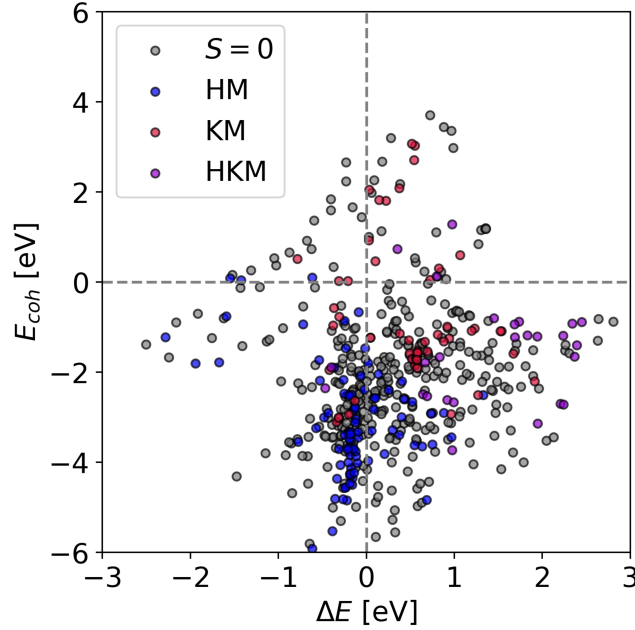


Figure 3.4. The plot analysis for ΔE , E_{coh} and magnetic configurations. ΔE means the energy difference between flat and buckled structure. A negative ΔE indicates that the flat structure is more stable. E_{coh} means cohesive energy from gas phase. A negative E_{coh} means indicates that materials can be formed from the single atom exothermically. Blue, purple, red and gray point represent honeycomb-dominated magnetism (HM), kagome-dominated magnetism (KM), honeycomb-kagome competitive magnetism (HKM) and nonmagnetic state ($S = 0$), respectively.

To analyze magnetic ordering and electronic states, candidate materials are selected with honeycomb dominated magnetism (HM), negative cohesive energy, and negative flat buckled energy difference ($\Delta E < 0$), as shown in Fig. 3.4. Out of

an initial set of 530 materials, 61 materials satisfy the criteria ($E_{coh} < 0$, $\Delta E < 0$ and HM). These candidates are thermodynamically stable, favoring flat structures and have magnetic moments localized on coplanar honeycomb sites, enabling straightforward magnetic analysis analogous to established 2D honeycomb magnetic models.

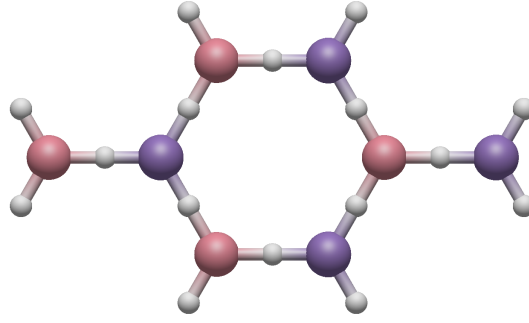


Figure 3.5. The illustration of antiferromagnetic state as Néel-type spin configuration. Atomic color code: pink-spin up atoms, purple-spin down atoms and white-nonmagnetic atoms.

Ferromagnetic (FM) and antiferromagnetic (AFM) states are calculated including spin-orbit coupling to get energies $E_{FM(AFM)}^{\parallel}$ and anisotropic energies $\Delta E_{FM(AFM)}$. Anisotropic energies are calculated from the energy differences between in-plane and out-of-plane magnetization ($\Delta E_{FM(AFM)} = E_{FM(AFM)}^{\parallel} - E_{FM(AFM)}^{\perp}$). Antiferromagnetic states are calculated by constraining the total magnetic moment to zero, using a Néel-type spin configuration, as shown in Fig. 3.5. This is implemented by flipping the spins on alternating magnetic atoms such that the total number of spin-up and spin-down electrons is equal, resulting in zero net magnetic moment in the unit cell.

The Hamiltonian H is defined as Heisenberg model to investigate magnetic ordering[109, 146].

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j - A \sum_i (S_i^z)^2 - \frac{1}{2} \sum_{ij} B_{ij} S_i^z S_j^z \quad (3.3)$$

where J is nearest neighbor exchange coupling, A is single ion anisotropy and B is nearest neighbor anisotropic. J is calculated from energies, while A and B are calculated from anisotropic energies of ferromagnetic and antiferromagnetic state[109].

$$J = \frac{E_{AFM}^{\parallel} - E_{FM}^{\parallel}}{3S^2} \quad (3.4)$$

$$A = \frac{\Delta E_{FM} + \Delta E_{AFM}}{(2S - 1)S} \quad (3.5)$$

$$B = \frac{\Delta E_{FM} - \Delta E_{AFM}}{3S^2} \quad (3.6)$$

The sums run over all magnetic sites and $J_{ij} = J$, $B_{ij} = B$ if i and j are nearest neighbors and zero otherwise. The maximum value of S_i^z is denoted by S . The ground state is FM if $J > 0$ and AFM if $J < 0$. $A = 0$ for $S = 1/2$ and $B = \Delta E_{FM}/3S^2$ for $J > 0$ and $B = -\Delta E_{AFM}/3S^2$ for $J < 0$.

Spin wave gap Δ for ferromagnetic order is calculated as following equation[109].

$$\Delta_{FM} = A(2S - 1) + 3SB \quad (J > 0) \quad (3.7)$$

The positive Δ_{FM} represents out-of-plane and negative Δ_{FM} represents in-plane ferromagnetic order. Spin wave gap Δ for antiferromagnetic order is calculated as following equation.

$$\Delta_{AFM} = -[3S(J + B) - (2S - 1)A] \sqrt{1 - \gamma^2} \quad (J < 0) \quad (3.8)$$

$$\gamma = \frac{3SJ}{3S(J + B) - (2S - 1)A} \quad (3.9)$$

The real and positive Δ_{AFM} represents out-of-plane and imaginary Δ_{AFM} represents in-plane antiferromagnetic order.

Curie temperature T_C for ferromagnetic order ($J > 0$) can be fitted to the function using Heisenberg parameters J, A, B ($S > 1/2$) [146].

$$T_C = \frac{1.52S^2J}{k_B} f\left(\frac{\Delta}{J(2S-1)}\right) \quad (3.10)$$

with

$$f(x) = \tanh^{1/4}[2\log(1 + 0.033x)] \quad (3.11)$$

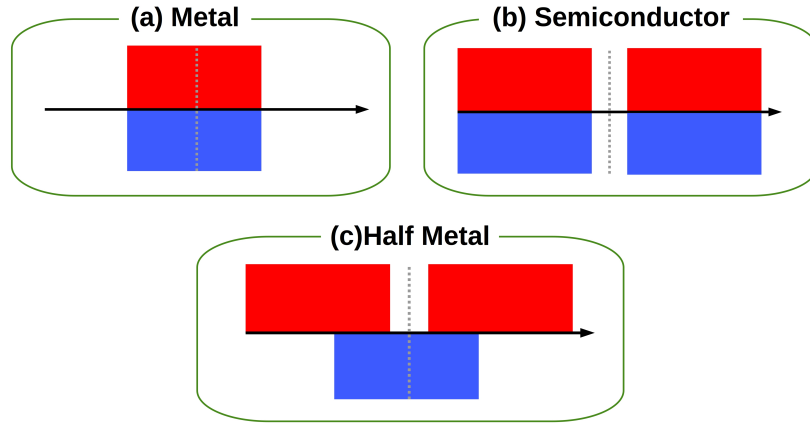


Figure 3.6. The illustration of dos for each electronic structures. Red and blue mean different spin directions.

Density of states (DOS) analysis classifies electronic states into metallic, semi-conducting, or half-metallic states, as shown in Fig. 3.6. Electronic states are classified based on DOS at the Fermi level: materials with DOS below 0.01 states eV^{-1} at the Fermi level are considered to possess a band gap.

3.2.3 Computational Details

The grid based projector augmented wave (GPAW) algorithm within density functional theory calculations is implemented[124]. The exchange correlation of Perdew Burke Ernzerhof (PBE) is implemented with spin polarization calculation[132]. Plane-wave cutoff energy is applied to 400 eV. The k point density of the Brillouin zone sampling is applied $8/\text{\AA}^{-1}$ for structure relaxation and $12/\text{\AA}^{-1}$ for magnetic properties and DOS[121]. The relaxation procedure is executed until the forces on each atom are smaller than $0.10\text{ eV \AA}^{-1}$. The vacuum of $12\text{ \AA}$ is applied in the z-direction of unit cell. The occupation smearing based on the Fermi–Dirac distribution is applied with a width of 0.05 eV.

The calculations of gas phase including isolated atom and molecules is conducted by the following setups; The plane-wave cutoff energy of 800 eV, the vacuum of $12\text{ \AA}$, and occupation numbers width of 0.00 eV, except that Pt and Ni are treated with 0.01 and 0.05 eV because of convergence issues, respectively.

3.3 Results and Discussion

Histogram analysis shows that 226 materials (43%) exhibit stability in flat structures ($\Delta E < 0$) and 471 materials (89%) are thermodynamically stable with negative cohesive energies, both of which are 205 materials (39%), as shown in Fig. 3.7. Violin plots highlight the critical influence of kagome-site elemental selection on ΔE and E_{coh} , as shown in Fig. 3.8(a)(b). Specifically, kagome-site chalcogen elements (O, S, Se, Te) show negative medians for both ΔE and E_{coh} , indicating preference for flat structures and thermodynamic stability. Conversely, nitrogen as a kagome-site element prefers flat structure but not thermodynamically stable. Other pnictogens (P, As, Sb), carbon-group elements (C, Si, Ge) and boron generally favor buckled structures but are thermodynamically stable.

Honeycomb-dominated magnetism (HM) shows different trend, as shown in

Fig. 3.8(c)(d). Chalcogens (O, S, Se, Te), pnictogens (N, P, As, Sb), and carbon exhibit negative medians for both ΔE and E_{coh} , indicating preference for flat structures and thermodynamic stability. In contrast, other elements (Si, Ge, B) favor buckled structures but remain thermodynamically stable.

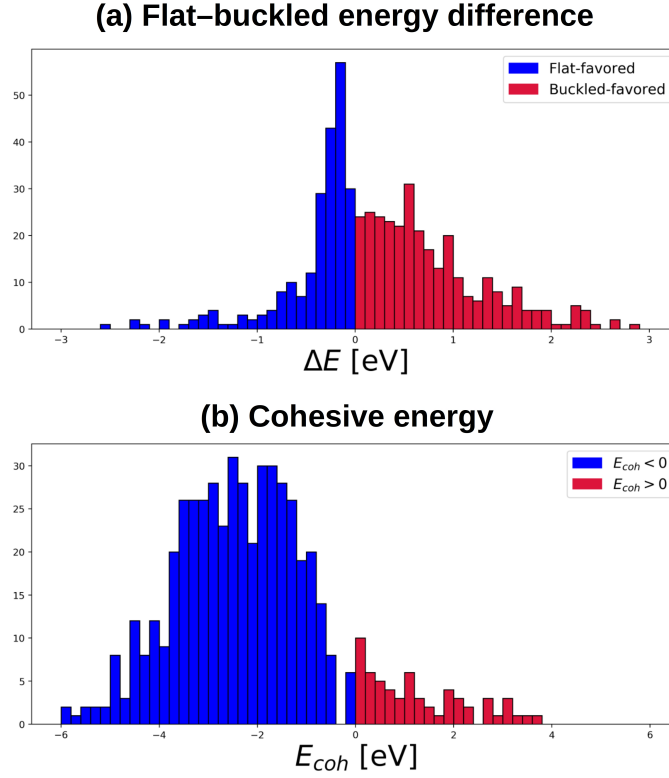


Figure 3.7. Histogram analysis for (a) Flat-buckled energy difference and (b) Cohesive energy. Blue represents flat-favored and negative cohesive energy. Red represents buckled-favored and positive cohesive energy.

The relationship between structural preference and thermodynamic stability is analyzed using heatmaps, as shown in Fig. 3.9(a). The results indicate that certain combinations of honeycomb and kagome elements favor flat structures ($\Delta E < 0$) and thermodynamic stability ($E_{\text{coh}} < 0$), represented in blue in Fig. 3.9(a). For example, combinations of group 2–10 (Be–Pt) metals with chalcogens (O, S, Se, Te), groups 4–10 (Ti–Pt) metals with pnictogens (N, P, As, Sb), and group 7–10

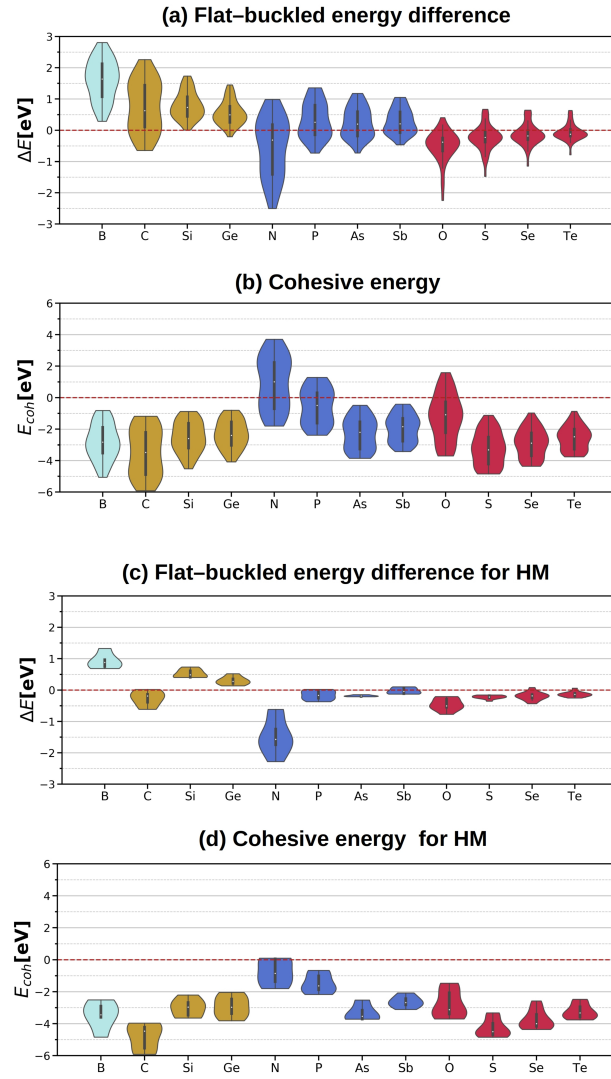


Figure 3.8. Violin plots for (a)(c) Flat-buckled energy difference and (b)(d) Cohesive energy. (c)(d) shows exclusively for honeycomb-dominated magnetism (HM). The red line represents 0 eV.

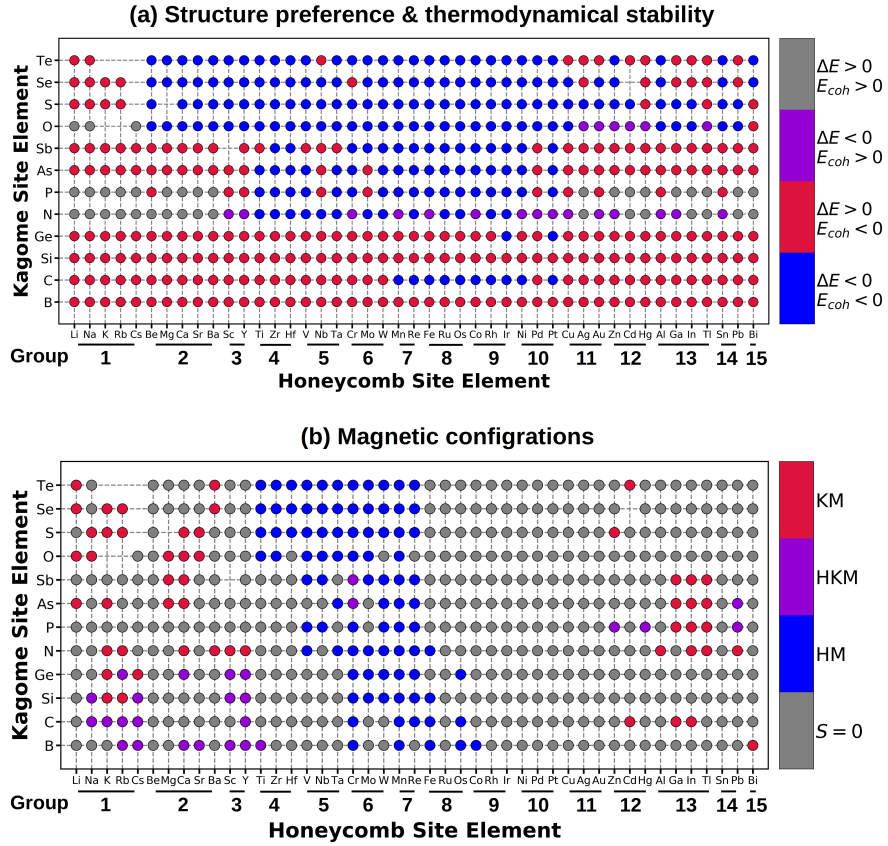


Figure 3.9. Heatmap analysis for (a) Structure preference and thermodynamic stability and (b) Magnetic configuration. ΔE : Energy between flat and buckled structure. E_{coh} : Cohesive energy. HM: Honeycomb-dominated magnetism. KM: Kagome-dominated magnetism. HKM: Honeycomb-kagome competitive magnetism. $S = 0$: Nonmagnetic state.

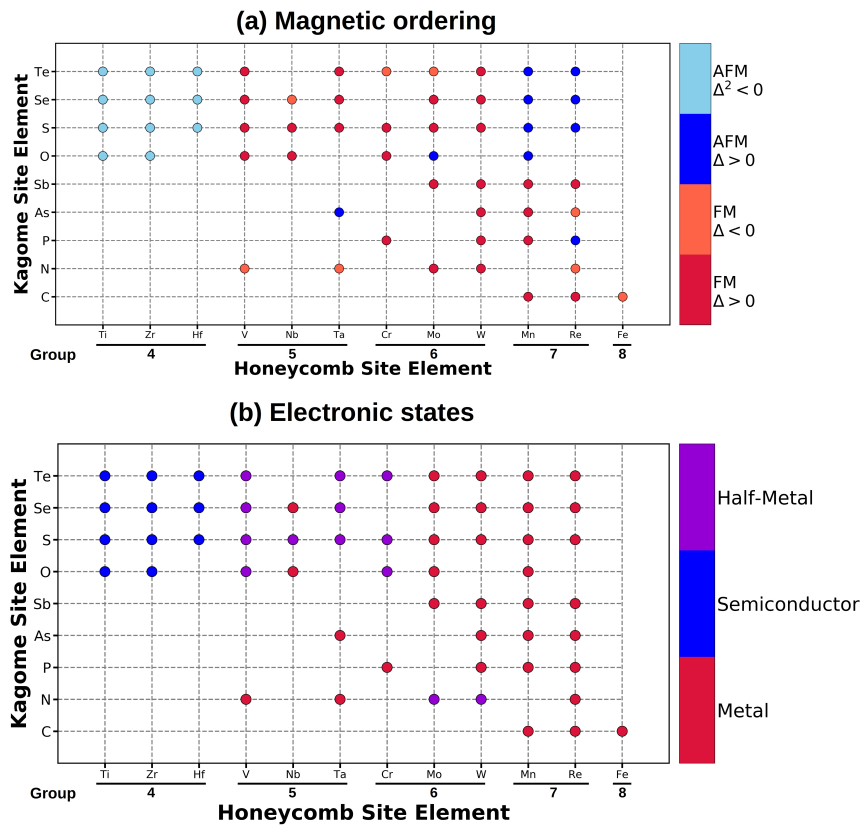


Figure 3.10. Heatmap analysis for (a)Magnetic ordering and (b)Electronic states.

J : Nearest neighbor exchange coupling. Δ : Spin wave gaps.

(Mn–Pt) metals with carbon predominantly favor flat structures and thermodynamic stability.

The relationship in magnetic configurations is analyzed using heatmaps, as shown in Fig. 3.9(b). The results indicate that groups 4–8 (Ti–Os) elements typically promote honeycomb-dominated magnetism (HM), represented in blue in Fig. 3.9(b). Specifically, chalcogens (O, S, Se, Te) favor combinations with group 4–7 (Ti–Re) metals; pnictogens (N, P, As, Sb) favor combinations with W, Mn and Re; and carbon favors combinations with Mn, Re and Fe. These combinations predominantly exhibit flat structures and thermodynamic stability, as shown in blue in Fig. 3.9(a). Moreover, heatmap analysis reveals that groups 1–3 (Li–Y) and 12–15 (Zn–Bi) elements partially favor kagome-dominated magnetism (KM, red) or honeycomb–kagome competitive magnetism (HKM, purple), as illustrated in Fig. 3.9(b).

The scatter plot analysis reveals trends between stability and magnetic configuration, as shown in Fig. 3.4. Honeycomb-dominated magnetism (HM) mainly occupies the quadrant with $\Delta E < 0$ and $E_{coh} < 0$, indicating preference for flat structures and thermodynamic stability. In contrast, kagome-dominated magnetism (KM) and honeycomb-kagome competitive magnetism mainly occupy the $\Delta E > 0$ and $E_{coh} < 0$, indicating preference for buckled structures and thermodynamic stability. Materials that exhibit honeycomb-dominated magnetism and lie in the quadrant with $\Delta E < 0$ and $E_{coh} < 0$ are selected. Their magnetic orderings and electronic states are then analyzed.

Magnetic ordering, including nearest-neighbor exchange coupling J and spin gaps Δ , is calculated to evaluate the nature of magnetism. Trends in magnetic ordering are analyzed using a heatmap, as shown in Fig. 3.10(a). The results indicate that group 4 elements (Ti, Zr, Hf) consistently exhibit antiferromagnetic ordering ($J < 0$) and imaginary spin gaps ($\Delta^2 < 0$), suggesting unstable magnetic ordering, represented as light blue in Fig. 3.10(a). In contrast, groups 5–6 (V–W) elements predominantly exhibit ferromagnetic ordering ($J > 0$), represented as red and light

red in Fig. 3.10(a). The combination of group 7 elements (Mn, Re) with chalcogens (O, S, Se, Te) generally results in antiferromagnetic ordering ($J < 0$), whereas ferromagnetic ordering ($J > 0$) frequently emerges when pnictogens (N, P, As, Sb) occupy kagome sites. These trends are depicted as blue for antiferromagnetic ordering, and red or light red for ferromagnetic ordering in Fig. 3.10(a).

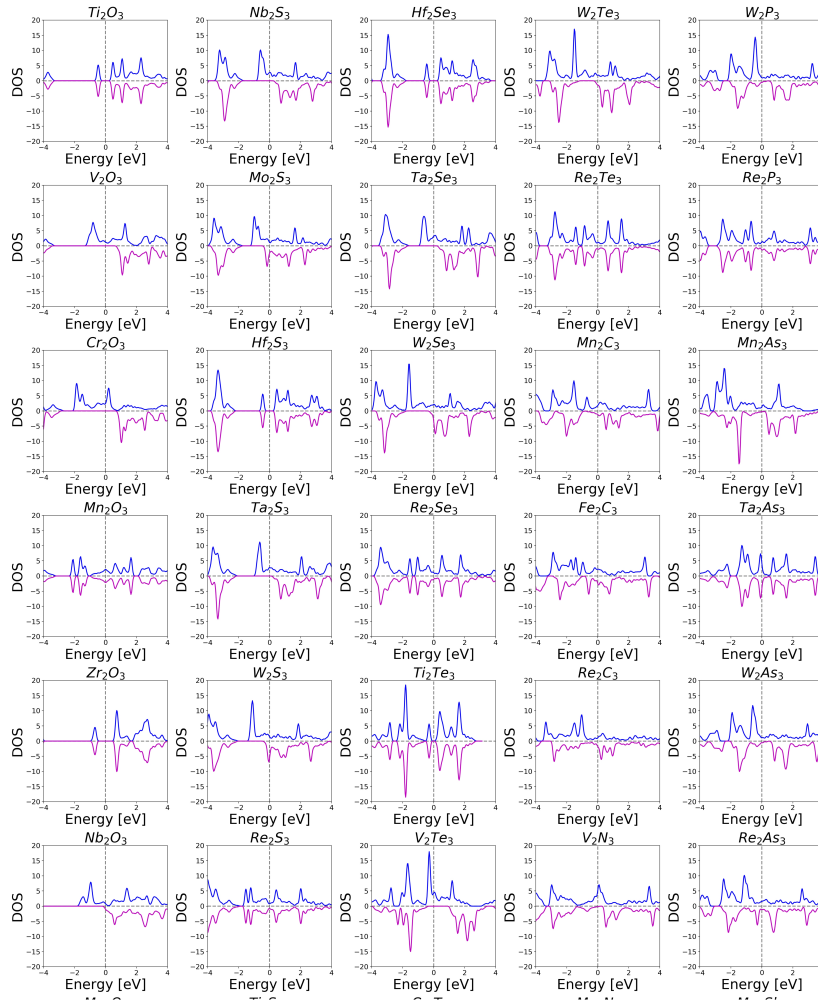


Figure 3.11. Density of states (DOS) for honeycomb kagome materials. Blue line shows spin up and pink line show spin down.

Trends in electronic states are analyzed using a heatmap, as shown in Fig. 3.10(b).

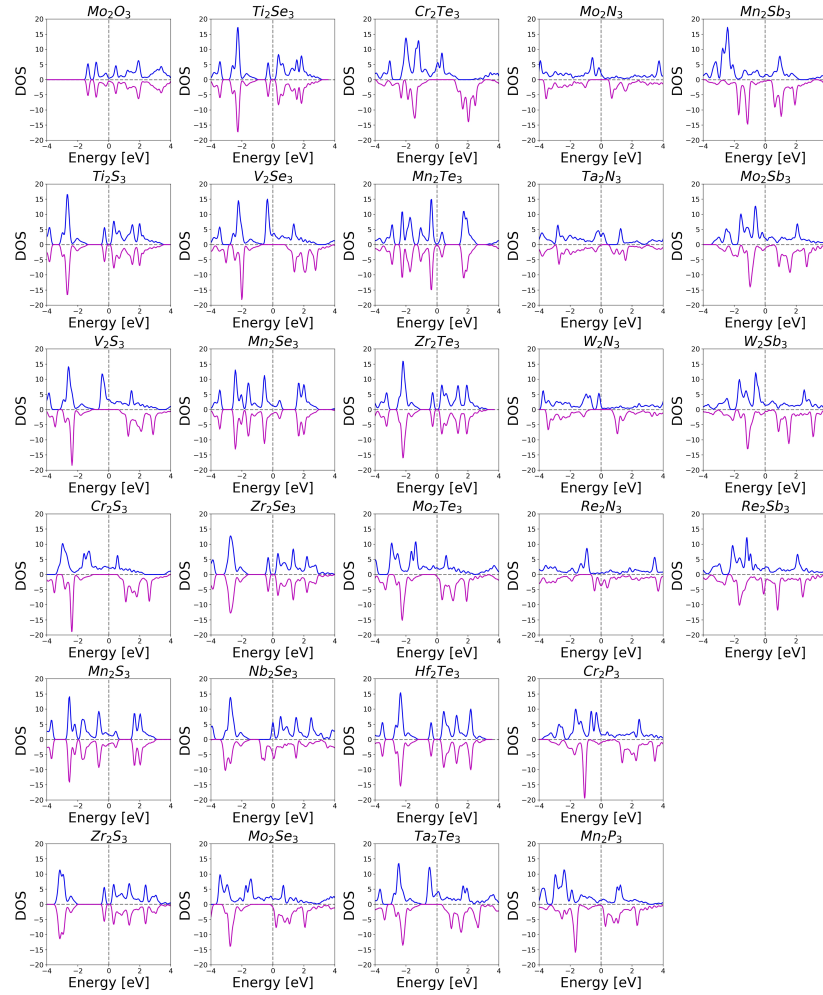


Figure 3.12. Density of states (DOS) for honeycomb kagome materials. Blue line shows spin up and pink line show spin down.

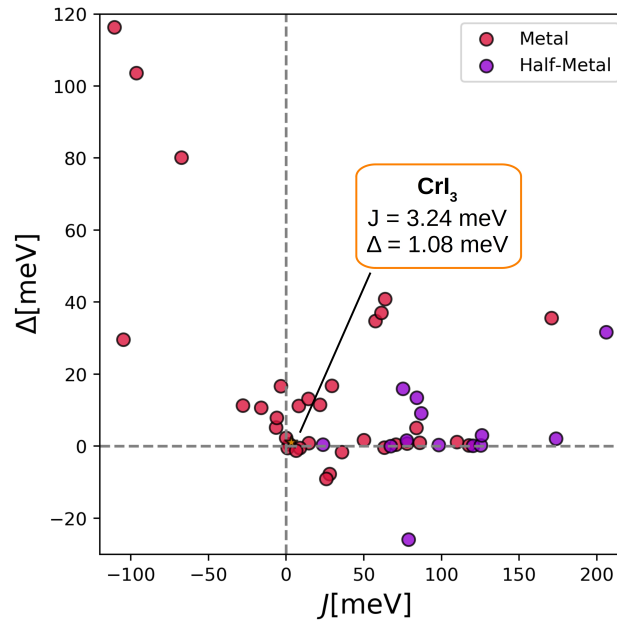


Figure 3.13. The plot analysis for J , Δ and electronic states. J represents nearest exchange interaction. $J > 0$ means ferromagnetic states are favored. Δ represents spin wave gaps. $\Delta > 0$ means out of plane easy axes. Red circles represent metal states, purple circles represent half-metal states and an orange star represents CrI_3 [146].

The results indicate that group 4 elements (Ti, Zr, Hf) consistently exhibit semiconducting behavior, represented as blue in Fig. 3.10(b). Notably, all materials within this group show unstable magnetic ordering, suggesting their suitability as nonmagnetic semiconductors. Furthermore, group 5–8 (V–Fe) elements predominantly display metallic or half-metallic states, represented as red and purple in Fig. 3.10(b), respectively. The metallic or half-metallic ferromagnetic materials are relevant for spintronic applications. In particular, half-metals exhibit 100% spin polarization at the Fermi level, facilitating fully spin-polarized currents essential for efficient spin injection. Known honeycomb–kagome lattices exhibit half-metallic electronic states as reported in previous studies [77, 80, 141, 142, 147]. The all calculated DOS is shown in Fig. 3.11 and Fig. 3.12.

Name	ΔE [eV]	E_{coh} [eV]	M [μB /atom]	S	J [meV]	Δ [meV]
(a) FM-Metal						
Nb ₂ O ₃	-0.57	-3.24	0.77	1	50	1.66
Mo ₂ S ₃	-0.18	-3.84	0.64	1	2	0.54
W ₂ S ₃	-0.24	-4.57	0.75	1	8	11.15
Mo ₂ Se ₃	-0.18	-3.33	1.16	1.5	15	0.86
W ₂ Se ₃	-0.21	-4.00	1.05	1.5	14	13.15
W ₂ Te ₃	-0.19	-3.48	1.13	1.5	30	16.76
Mn ₂ C ₃	-0.14	-4.23	0.63	1	78	0.79
Re ₂ C ₃	-0.39	-5.53	0.57	0.5	171	35.59
Cr ₂ P ₃	-0.09	-0.67	0.75	1	118	0.28
Mn ₂ P ₃	-0.25	-0.87	1.00	1	110	1.13
W ₂ P ₃	-0.26	-2.17	0.65	1	57	34.74
Mn ₂ As ₃	-0.19	-2.52	1.02	1.5	71	0.40
W ₂ As ₃	-0.21	-3.72	0.66	1	61	37.06
Mn ₂ Sb ₃	-0.06	-2.08	1.05	1.5	86	0.92
Mo ₂ Sb ₃	-0.02	-2.39	0.72	1	84	5.14
W ₂ Sb ₃	-0.13	-3.11	0.68	1	64	40.85
Re ₂ Sb ₃	-0.13	-2.79	0.59	0.5	22	11.46
(b) FM Half-Metal						
V ₂ O ₃	-0.48	-3.01	0.80	1	98	0.34
Cr ₂ O ₃	-0.54	-1.73	1.20	1.5	24	0.47
V ₂ S ₃	-0.16	-4.35	0.80	1	120	0.09
Cr ₂ S ₃	-0.25	-3.40	1.20	1.5	67	0.02
Nb ₂ S ₃	-0.24	-4.56	0.80	1	78	1.57
Ta ₂ S ₃	-0.36	-4.81	0.80	1	75	15.95
V ₂ Se ₃	-0.12	-3.87	0.80	1	125	0.19
Ta ₂ Se ₃	-0.19	-4.27	0.80	1	84	13.49
V ₂ Te ₃	-0.10	-3.33	0.80	1	126	2.99
Ta ₂ Te ₃	-0.20	-3.67	0.80	1	87	9.13
Mo ₂ N ₃	-1.59	-0.76	0.60	0.5	174	2.11
W ₂ N ₃	-1.94	-1.81	0.60	0.5	206	31.65
(c) AFM-Metal						
Mn ₂ O ₃	-0.24	-1.47	1.59	2	-16	10.65
Mo ₂ O ₃	-0.53	-2.19	0.41	0.5	-105	29.65
Mn ₂ S ₃	-0.20	-3.32	1.60	2	-7	5.16
Re ₂ S ₃	-0.18	-4.13	0.42	0.5	-67	80.11
Mn ₂ Se ₃	-0.44	-2.91	1.60	2	-6	7.85
Re ₂ Se ₃	-0.18	-3.53	0.48	0.5	-96	103.57
Mn ₂ Te ₃	-0.17	-2.50	1.60	2	-3	16.67
Re ₂ Te ₃	-0.12	-3.05	0.50	0.5	-111	116.30
Re ₂ P ₃	-0.37	-1.90	0.47	0.5	-0.2	2.27

Table 3.3. Properties for magnetic materials. Flat-buckled energy difference ΔE , cohesive energy E_{coh} , Total magnetic moment per atoms in unit cell M , Spin quantum number S , Nearest neighbor exchange coupling J , spin-wave gap Δ for (a) Metal with ferromagnetic state, (b) Half-metal with antiferromagnetic state and (c) Metal with ferromagnetic state ($\Delta > 0$, $\Delta E < 0$, $E_{coh} < 0$ and honeycomb-dominated magnetism). Note: Ta_2O_3 , V_2P_3 and Os_2C_3 are not converged because of its complex antiferromagnetic configurations.

2D magnetic material candidates with out-of-plane easy axes are identified, as listed in Table. 3.3. Specifically, 10 metals and 7 half-metals exhibit significantly larger values of J and Δ compared to CrI_3 [146] ($J = 3.24$ meV and $\Delta = 1.08$ meV), indicating robustness of magnetic ordering against thermal fluctuations, as shown in Fig. 3.13. These 2D-ferromagnetic candidates are promising for spintronic applications such as magnetic tunnel junctions in next-generation MRAM devices, owing to their strong out-of-plane anisotropy[4]. On the other hand, 2D-antiferromagnetic candidates include 10 metals exhibiting a broad range of nearest-neighbor exchange interaction J (-0.2~-111 meV) and spin wave gaps Δ (2.27~40.9 meV). The identified 2D-antiferromagnetic candidates provide opportunities for exploration of emergent topological spin phenomena in two-dimensional systems[148].

The curie temperature for magnetic ordering systems is fitted based on exchange coupling J and spin gaps Δ using eq. 3.11 to investigate magnetic stability. The results shows various curie temperature from 13K to 508K, as listed in Table.3.11. Especially, 24 materials show higher curie temperature compared to CrI_3 [146] (45K), while curie temperature of 12 materials including Ta_2S_3 [142] is above room temperature. High-Curie-temperature 2D ferromagnets enable the operation of spintronic devices above room temperature, offering robust, low-power information storage and processing[149, 150].

The heat plot of Curie temperature shows that the selection of honeycomb elements leads to high Curie temperatures. In particular, the combinations of W with Te, P, As, Sb and Ta with S, Se, Te exhibit Curie temperatures above 400 K, as shown in Fig. 3.14. These materials have a large energy difference between the antiferromagnetic and ferromagnetic states ($E_{\text{AFM}} - E_{\text{FM}}$: 172–261 meV), as well as a large spin-wave gap (Δ : 9.13–40.84 meV), which is larger than that of CrI_3 (DFT calculations reveal $E_{\text{AFM}} - E_{\text{FM}} = 7.65$ meV, $\Delta = 0.88$ meV, and $T_C = 41$ K using Eq. (3.10)). Both the large energy difference $E_{\text{AFM}} - E_{\text{FM}}$ and the large spin-wave gap Δ contribute to the high Curie temperatures of W_2Te_3 , W_2P_3 , W_2As_3 , W_2Sb_3 ,

Name	E_{coh} [eV]	J [meV]	Δ [meV]	Electronic State	T_c [K]
W ₂ Sb ₃	-3.11	64	40.85	Metal	508
W ₂ As ₃	-3.72	61	37.06	Metal	482
Ta ₂ Se ₃	-4.27	84	13.49	Half-Metal	475
Mn ₂ Sb ₃	-2.08	86	0.92	Metal	468
Ta ₂ S ₃	-4.81	75	15.95	Half-Metal	456
W ₂ P ₃	-2.17	57	34.74	Metal	452
V ₂ Te ₃	-3.33	126	2.99	Half-Metal	442
Ta ₂ Te ₃	-3.67	87	9.13	Half-Metal	442
W ₂ Te ₃	-3.48	30	16.76	Metal	433
Mo ₂ Sb ₃	-2.39	84	5.14	Metal	372
Mn ₂ As ₃	-2.52	71	0.40	Metal	328
Mn ₂ P ₃	-0.87	110	1.13	Metal	313
Nb ₂ S ₃	-4.56	78	1.57	Half-Metal	262
W ₂ Se ₃	-4.00	14	13.15	Metal	237
Cr ₂ P ₃	-0.67	118	0.28	Metal	231
V ₂ Se ₃	-3.87	125	0.19	Half-Metal	222
Mn ₂ C ₃	-4.23	78	0.79	Metal	221
V ₂ O ₃	-3.01	98	0.34	Half-Metal	213
Nb ₂ O ₃	-3.24	50	1.66	Metal	191
V ₂ S ₃	-4.35	120	0.09	Half-Metal	177
Cr ₂ O ₃	-1.73	24	0.47	Half-Metal	151
Cr ₂ S ₃	-3.40	67	0.02	Half-Metal	148
Mo ₂ Se ₃	-3.33	15	0.86	Metal	121
W ₂ S ₃	-4.57	8	11.15	Metal	77
Mo ₂ S ₃	-3.84	2	0.54	Metal	13

Table 3.4. List of curie temperature of 2D ferromagnetic materials ($S > 1/2$). The cohesive energy E_{coh} , Nearest neighbor exchange coupling J , spin-wave gap Δ , electronic states and curie temperature T_C .

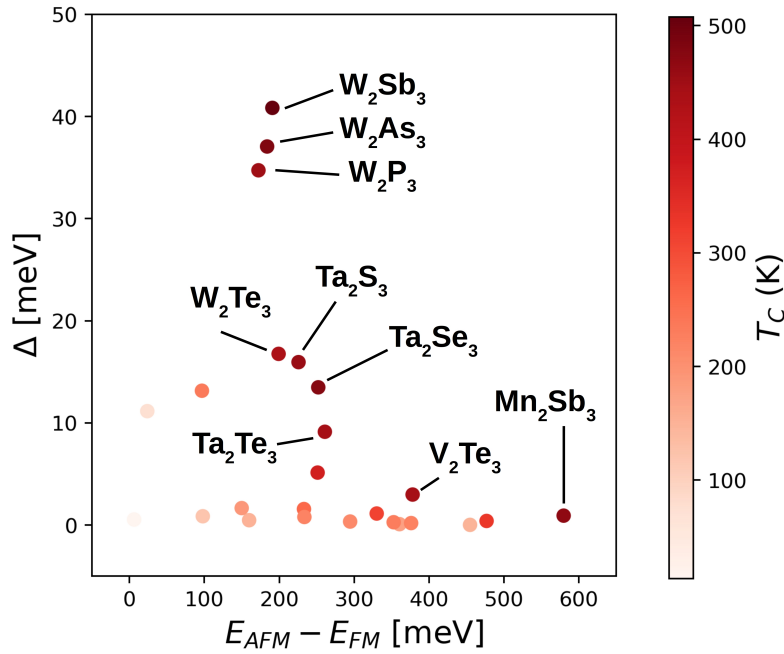


Figure 3.14. The plot for energy difference between antiferromagnetic state and ferromagnetic state $E_{AFM} - E_{FM}$, spin-wave gap Δ , electronic states and curie temperature T_C . The compositions of high curie temperature ($T_C > 400K$) are indicated.

Ta₂S₃, Ta₂Se₃, and Ta₂Te₃.

The projected density of states (PDOS) analysis is conducted to understand the bonding states of Ta₂S₃ and W₂P₃, which exhibit high Curie temperatures, as shown in Fig. 3.15. The results indicate that Ta₂S₃ has overlap between the Ta *d* and S *p* states in the energy range from -6.5 to -4.5 eV and near -3.7 eV, while W₂P₃ has overlap between the W *d* and P *p* states in the range from -4.5 to -2.5 eV and from -2.1 to -1.4 eV. These overlaps indicate strong hybridization between the Ta *d* and S *p* states in Ta₂S₃ and between the W *d* and P *p* states in W₂P₃. Such *d*-*p* hybridization enhances the exchange interaction between neighboring metal sites and stabilizes the ferromagnetic state relative to the antiferromagnetic state,

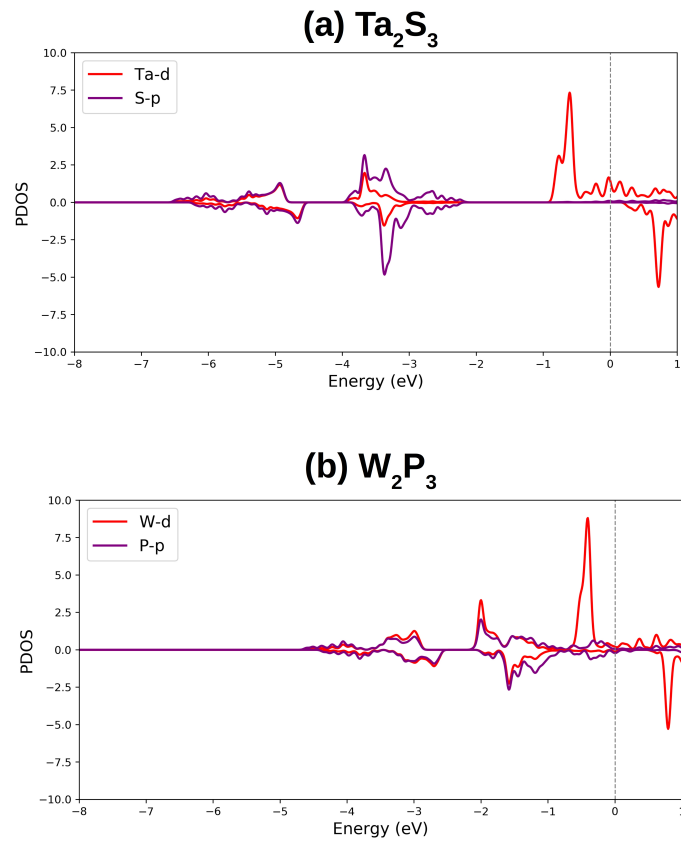


Figure 3.15. Projected density of states (PDOS) between d orbital of Honeycomb elements (red) and p orbital of kagome elements (purple). Dot line indicates Fermi level.

leading to the large energy difference $E_{\text{AFM}} - E_{\text{FM}}$.

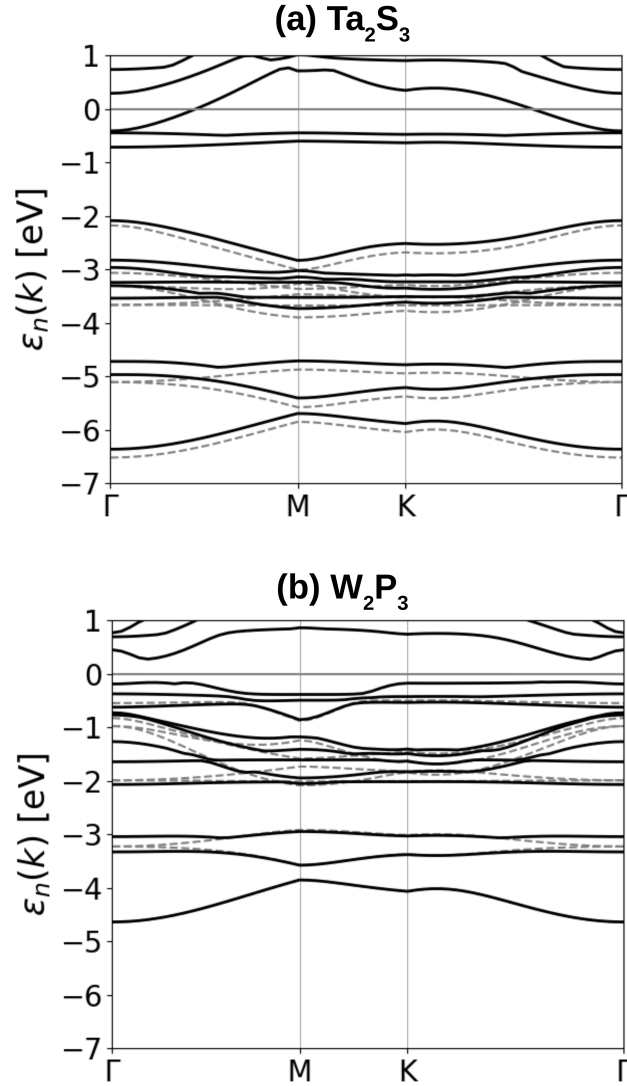


Figure 3.16. The band structure with spin-orbital coupling (black line) and without spin-orbital coupling (gray dot line).

The band-structure calculation is performed to clarify the effect of spin-orbit coupling (SOC), as shown in Fig. 3.16. The results show that the band structure of Ta_2S_3 is split by SOC in the energy range from -6.5 to -2 eV, whereas W_2P_3 exhibits spin-orbit splitting between -3.5 and -0.5 eV. Since magnetocrystalline

anisotropy arises from SOC[151], the SOC-induced band splitting bands is consistent with the large magnetic anisotropy energy and the resulting large spin-wave gap Δ .

DFT+ U calculations can provide a better description of magnetic materials than PBE. Nevertheless, it is difficult to determine proper Hubbard corrections because of the scarceness of experimental observations, which limits high-throughput calculations for magnetic materials with DFT+ U . To check the difference in Curie temperature from PBE, DFT+ U calculations are conducted for specific materials including Ta₂S₃ and W₂P₃. Hubbard U parameter are used as the same value of previous research[152, 153]. For Ta₂S₃, the critical temperature is calculated to be 578 K when $U = 1$ eV is applied to the Ta- d orbital, which is increased by 122 K from 456 K. While W₂P₃ shows the Curie temperature of 820 K when $U = 3$ eV is applied to the W- d orbital, which is increased by 368 K from 452 K. The results indicate that applying Hubbard corrections leads to an increase in the Curie temperature of Ta₂S₃ and W₂P₃. Specially, the exchange coupling J is increased from 75 meV to 112 meV in Ta₂S₃ and from 57 meV to 160 meV in W₂P₃, and the spin-wave gap Δ is decreased from 15.95 meV to 12.23 meV in Ta₂S₃ and from 34.73 meV to 17.28 meV in W₂P₃. Although Hubbard corrections reduce the spin-wave gap Δ , the increasing of the exchange coupling J leads to a higher Curie temperature of Ta₂S₃ and W₂P₃.

3.4 Conclusion

In conclusion, this study systematically explored the thermodynamic stability, structural preference, and magnetic properties of honeycomb-kagome lattices through high-throughput first-principles calculations, significantly expanding the elemental diversity previously limited to oxides and sulfides. The analysis identified crucial relationships between elemental composition, stability, magnetic ordering,

and electronic states. The further analysis for magnetic honeycomb-kagome lattices uncovers novel 2D-magnetic material candidates, including 17 ferromagnetic metals, 12 half-metals, and 10 antiferromagnetic metals, which have out-of-plane anisotropy. The Curie temperature of 17 ferromagnetic materials is higher than that of the reported 2D-magnetic material (CrI_3 , experimental T_C is 45K), while 12 ferromagnetic materials show higher Curie temperatures than 300K. In particular, the selection of Ta and W tends to lead to high Curie temperatures. The combinations of Ta with S, Se, Te and W with Te, P, As, Sb exhibit a large energy difference between ferromagnetic and antiferromagnetic states as well as a large spin-wave gap, which contributes to Curie temperatures above 400 K. The PDOS and band-structure analysis reveals that Ta_2S_3 and W_2P_3 have strong d - p hybridization and spin-orbit coupling, enhancing the exchange interaction and magnetic anisotropy. These findings provide valuable guidelines for future research in spintronics and quantum materials, demonstrating the effectiveness of computational screening methods in advancing the development of next-generation magnetic materials.

3.5 Physical Property Analysis Code for High-Throughput Calculations

The analysis for stability and magnetic moment is conducted using following code.

```

1 # Calculation of cohesive energy
2 def calc_energy(path='./', mode='atom'):
3     # Read a CSV file containing the material name and the energies
4     # of the stable bulk phase or isolated atoms.
5     if mode == 'binding':
6         energy_df = pd.read_csv('./bulk_energy.csv', index_col=0)
7     elif mode == 'atom':
8         energy_df = pd.read_csv('./atom_energy.csv', index_col=0)

```

```

9
10 # Read the gpw file
11 try:
12     calc = GPAW(path + 'out.gpw')
13 except FileNotFoundError:
14     return np.nan
15
16 # Obtain the total energy of the 2D material and divide by the
    number of atoms
17 TotalEnergy = calc.get_potential_energy(force_consistent=True)
18 atoms = io.read(path + 'out.traj')
19 atom_number = len(atoms.get_positions())
20 # Compute the free energy per atom
21 # FreeEnergy.append(TotalEnergy / atom_number)
22 # Refer to the energies of each element from the CSV file using
    the atomic symbols
23 # and compute the sum of the elemental reference energies.
24 baseEnergy = sum([energy_df.at[symbol, 'E'] for symbol in atoms
    .get_chemical_symbols()])
25 # Calculate the formation (or binding) energy per atom
26 modeEnergy = (TotalEnergy - baseEnergy) / atom_number
27 return modeEnergy

```

```

1 # Energy, spin, and magnetic elements
2 def output_results(initial_df):
3     answers_energy = []
4     answers_S = []
5     answers_M = []
6     answers_r = []
7     mhs = []
8     mks = []
9
10    for index, row in initial_df.iterrows():
11        path = './A/' + row['material'] + '/'
12        try:

```

```

13         atoms = io.read(path + 'out.traj')
14     except FileNotFoundError:
15         answers_energy.append(np.nan)
16         answers_S.append(np.nan)
17         answers_M.append(np.nan)
18         answers_r.append(np.nan)
19         continue
20
21     M = atoms.get_magnetic_moment()
22
23     # Ratio of magnetic moments for M and S in M2X3
24     ms = atoms.get_magnetic_moments()
25     mh = ms[3] # Magnetic moment on the honeycomb site
26     mk = ms[0] # Magnetic moment on the kagome site
27     r = mh / mk
28
29     # Energy
30     energy = calc_energy(path=path, mode='atom')
31     answers_energy.append(energy)
32     answers_M.append(M)
33     answers_r.append(r)
34     mhs.append(mh)
35     mks.append(mk)
36
37     return answers_energy, answers_M, answers_r, mhs, mks

```

```

1 #output to csv
2 df = pd.read_csv('./run.csv', index_col=False)
3 results = energy.output_results(df)
4
5 df['E_coh'] = results[0]
6 df['M'] = results[1] # Total magnetic moment of the unit cell
7 df['r'] = results[2] # Ratio of magnetic moments (M and S) in
   M2X3
8 df['M_h'] = results[3] # Magnetic moment on the honeycomb site

```

```

9 df['M_k'] = results[4] # Magnetic moment on the kagome site
10
11 df.to_csv('run.csv', index=False)

```

Energy difference between flat and buckling structure are calculated using following code.

```

1 df = pd.read_csv('run.csv')
2 sts = ['FLAT', 'BUCKLED']
3 answers = []
4 for index, row in df.iterrows():
5     energys = []
6     for i in range(2):
7         path = './'+sts[i]+'/' + row['material'] + '/'
8         calc = GPAW(path+'out.gpw')
9         energy = calc.get_potential_energy(force_consistent=True)
10        energys.append(energy)
11        E = (energys[0] - energys[1])/5
12        answers.append(E)
13
14 df['dE'] = answers
15 df.to_csv('run.csv', index=False)

```

The calculated data are classified into four sets according to their magnetic moments: Non-Magnetic (NM.csv), Honeycomb Ferromagnetic (HFM.csv), Kagome Ferromagnetic (KFM.csv), and Honeycomb–Kagome Ferromagnetic (HKFM.csv). These CSV files contain the total magnetic moments, the local magnetic moments on the honeycomb and kagome sites, the ratio of the local moments, the structural energy difference, the cohesive energy, the magnetic configuration, and the spin quantum number. The data in HFM.csv are used for the subsequent magnetic and electronic calculations.

$$r = [\text{magnetic moment on Honeycomb site}] / [\text{magnetic moment on Kagome site}] r < 0 \text{ means that } t$$

(3.12)

```

1 df = pd.read_csv('run.csv', index_col=False)
2
3 def calc_S(M, N):
4     M = abs(M)
5     m = M / N
6     if m > 4.5 and m <= 5.5: S = 2.5
7     elif m > 3.5 and m <= 4.5: S = 2
8     elif m > 2.5 and m <= 3.5: S = 1.5
9     elif m > 1.5 and m <= 2.5: S = 1
10    elif m > 0.5 and m <= 1.5: S = 0.5
11    elif m >= 0 and m <= 0.5: S = 0
12    else:
13        print('caution!!')
14    return S
15
16
17 magnetic_types = []
18 Ss = []
19 rs = []
20 df = pd.read_csv('run.csv')
21 for index, row in df.iterrows():
22     if abs(row['r']) > 10:
23         magnetic_type = 'HFM'
24         S = calc_S(M=row['M'], N=2)
25         r = row['r']
26     elif abs(row['r']) > 0.1 and abs(row['r']) <= 10:
27         magnetic_type = 'HKFM'
28         S = calc_S(M=row['M'], N=5)
29         r = row['r']
30     elif abs(row['r']) > 0 and abs(row['r']) <= 0.1:

```

```

31     magnetic_type = 'KFM'
32     S = calc_S(M=row['M'], N=3)
33     r = row['r']
34     elif abs(row['r']) == 0:
35         magnetic_type = 'NM'
36         S = 0
37         r = 0
38     if S == 0:
39         magnetic_type = 'NM'
40         r = 0
41     magnetic_types.append(magnetic_type)
42     Ss.append(S)
43     rs.append(r)
44
45 df['M-type'] = magnetic_types
46 df['S'] = Ss
47 df['r'] = rs
48 df['M'] = abs(df['M'])
49 df.to_csv('run.csv', index=False)
50
51 # Filter for thermodynamically and energetically stable candidates
52 df = df[(df['dE'] < 0) & (df['E_coh'] < 0)]
53
54 # Split into separate DataFrames by magnetic type
55 df_KFM = df[df['M-type'] == 'KFM']
56 df_HKFM = df[df['M-type'] == 'HKFM']
57 df_HFM = df[df['M-type'] == 'HFM']
58 df_NM = df[df['M-type'] == 'NM']
59
60 # Save each subset to a separate CSV file
61 df_KFM.to_csv('KFM.csv', index=False)
62 df_HKFM.to_csv('HKFM.csv', index=False)
63 df_HFM.to_csv('HFM.csv', index=False)
64 df_NM.to_csv('NM.csv', index=False)

```

The antiferromagnetic configurations are created using following code.

```

1 df = pd.read_csv('HFM.csv')
2 def create_afm(path, config):
3     atoms = io.read(path+'fm.gpw')
4     mags = atoms.get_magnetic_moments()
5     maxmag = max(mags)
6
7     if config == 'M2X3':
8         mags[3] = mags[3]*(-1) #Flip magnetic moments
9         mags[:3] = 0
10        atoms.set_initial_magnetic_moments(mags)
11    atoms.write(path+'in.traj')
12
13 for index, row in df.iterrows():
14     filename = row['material']
15     path = './AFM/'+filename+'/'
16     create_afm(path=path, config='M2X3')

```

The magnetic anistropy energies are calculated for both the ferromagnetic and antiferromagnetic states.

```

1 df = pd.read_csv('HFM_calculated.csv')
2 e_FMs = []
3 e_AFMs = []
4 de_FMs = []
5 de_AFMs = []
6
7 for index, row in df.iterrows():
8     filename = row['material']
9     path_FM = './FM/'+filename+'/'
10    path_AFM = './AFM/'+filename+'/'
11    calc_fm = GPAW(path_FM+'out.gpw')
12    calc_afm = GPAW(path_AFM+'out.gpw')
13    M_FM = 2 #The number of magnetic atoms
14    M_AFM = 2 #The number of magnetic atoms

```



```

15
16     #FM
17     e_x_FM = get_anisotropy(calc_fm, theta=90, phi=0)/M_FM
18     e_z_FM = get_anisotropy(calc_fm, theta=0, phi=0)/M_FM
19     de_FM = e_x_FM - e_z_FM
20
21     #AFM
22     e_x_AFM = get_anisotropy(calc_afm, theta=90, phi=0)/M_AFM
23     e_z_AFM = get_anisotropy(calc_afm, theta=0, phi=0)/M_AFM
24     de_AFM = e_x_AFM - e_z_AFM
25
26     #Energy
27     e_FM = calc_fm.get_potential_energy(force_consistent=True)/M_FM
28     e_AFM = calc_afm.get_potential_energy(force_consistent=True)/
29         M_AFM
30
31     e_FMs.append(e_FM)
32     e_AFM.append(e_AFM)
33     de_FMs.append(de_FM)
34     de_AFM.append(de_AFM)
35
36     df['e_FM'] = e_FMs
37     df['e_AFM'] = e_AFM
38     df['de_FM'] = de_FMs
39     df['de_AFM'] = de_AFM
40     df.to_csv('./JAB.csv', index=False)

```

DOS is calculated and plotted using following code.

```

1 def plot_dos(i, j, calc):
2     spin = {0: "up", 1: "down"}
3     col = ['b', 'm']
4     dos = []
5     for sp in range(2):
6         e, dos = calc.get_dos(spin=sp, npts=2001, width=0.10)
7         if row['order'] == 'FM':
8             e_f = calc.get_fermi_level()
9         elif row['order'] == 'AFM':

```

```

10     e_f = calc.get_fermi_levels()[sp]
11     if sp == 1:
12         dos = -dos
13     ax[i][j].plot(e-e_f, dos, col[sp],label=spin[sp],lw=2)
14     idx = min(range(len(e)), key=lambda i: abs(e[i]-e_f))
15     d0s.append(dos[idx])
16
17     ax[i][j].vlines(0, -20, 20, lw=2, color='gray', ls='--')
18     ax[i][j].hlines(0, -4, 4, lw=2, color='gray', ls='--')
19     ax[i][j].set_xlim(-4, 4)
20     ax[i][j].set_ylim(-20, 20)
21     ax[i][j].set_title(row['name'], size=30)
22     ax[i][j].set_xlabel('Energy [eV]', size=30)
23     ax[i][j].set_ylabel('DOS', size=30)
24     ax[i][j].tick_params(axis='both', labels=15)
25     return d0s

```

The following code calculates nearest neighbor exchange coupling J , single ion anisotropy A , nearest neighbor anisotropic B , spin wave gap Δ , and curie temperature T_C . Then these properties are outputted to csv files.

```

1 # Compute Heisenberg parameters J, A, and B
2 # N_FM : number of parallel spin nearest neighbours in the
   antiferromagnetic state
3 # N_AFM: number of antiparallel spin nearest neighbours in the
   antiferromagnetic state
4 def calc_JAB(N_FM, N_AFM):
5     N = N_FM / N_AFM
6     N_nn = N_FM + N_AFM # total number of magnetic nearest
   neighbours
7
8     # J: magnetic exchange coupling constant
9     dE = row['e_AFM'] - row['e_FM']
10    NS = N_AFM * S * S
11    J = dE / NS

```

```

12
13     # A: single-ion anisotropy
14     # B: nearest-neighbour anisotropic exchange
15     if S != 0.5:
16         A = (row['de_FM'] * (1 - N) + row['de_AFM'] * (1 + N)) /
17             ((2 * S - 1) * S)
18         B = (row['de_FM'] - row['de_AFM']) / (N_AFM * S * S)
19     elif S == 0.5:
20         A = 0
21         if J >= 0:
22             B = row['de_FM'] / (N_nn * S * S)
23         elif J < 0:
24             B = -row['de_AFM'] / ((N_AFM - N_FM) * S * S)
25
26     return J, A, B
27
28 df = pd.read_csv('JAB.csv')
29 # Remove data with S = 0 (only one entry)
30 df = df[df['S'] != 0]
31
32 Js = []
33 As = []
34 Bs = []
35 deltas = []
36 orders = []
37 order_types = []
38
39 for index, row in df.iterrows():
40     S = row['S'] # spin quantum number
41     J, A, B = calc_JAB(N_FM=0, N_AFM=3)
42
43     # delta: spin gap
44     N_nn = 3

```

```

45     if J >= 0:
46         delta = A * (2 * S - 1) + S * N_nn * B
47         order = 'FM'
48     elif J < 0:
49         gamma = (S * N_nn * J) / (S * N_nn * (J + B) - (2 * S - 1)
50             * A)
51         corr = np.sqrt(1 - gamma * gamma)
52         delta = -(S * (J + B) * N_nn - (2 * S - 1) * A) * corr
53         order = 'AFM'
54         # If delta is negative, treat as ferromagnetic even when J
55         # < 0
56         # (this case does not appear in the present data set)
57         if delta < 0:
58             print('Special FM order:' + row['material'])
59             delta = A * (2 * S - 1) + S * N_nn * B
60             order = 'FM'
61         if gamma > 1:
62             print('AFM disorder:' + row['material'])
63
64     if order == 'FM':
65         if delta >= 0:
66             order_type = 'order-FM'
67         else:
68             order_type = 'disorder-FM'
69     if order == 'AFM':
70         if delta >= 0:
71             order_type = 'order-AFM'
72         elif gamma > 1:
73             order_type = 'disorder-AFM'
74         else:
75             order_type = 'Special-FM'
76
77     Js.append(J)
78     As.append(A)

```

```
77     Bs.append(B)
78     deltas.append(delta)
79     orders.append(order)
80     order_types.append(order_type)
81
82 df['J'] = Js
83 df['A'] = As
84 df['B'] = Bs
85 df['delta'] = deltas
86 df['order'] = orders
87 df['order_type'] = order_types
88
89 # Save all data
90 df.to_csv('./total.csv', index=False)
91
92 # delta > 0: systems with magnetic order
93 order_df = df[
94     (df['order_type'] == 'order-FM') |
95     (df['order_type'] == 'order-AFM')
96 ]
97 order_df.to_csv('./order.csv', index=False)
98
99 # delta < 0: systems without magnetic order
100 disorder_df = df[
101     (df['order_type'] == 'disorder-FM') |
102     (df['order_type'] == 'disorder-AFM')
103 ]
104 disorder_df.to_csv('./disorder.csv', index=False)
105
106 # delta > 0: ferromagnetic candidate materials
107 FM_df = order_df[order_df['order'] == 'FM']
108 FM_df.to_csv('./FM.csv', index=False)
109
110 # delta > 0: antiferromagnetic candidate materials
```

```
111 AFM_df = order_df[order_df['order'] == 'AFM']
112 AFM_df.to_csv('./AFM.csv', index=False)
113
114 # S >= 1 and delta > 0: candidates for Curie (or Neel) temperature
    estimation
115 critical_df = order_df[order_df['S'] >= 1]
116 T_cs = []
117
118 for index, row in critical_df.iterrows():
119     delta = row['delta']
120     S = row['S']
121     J = row['J']
122     T0 = 1.52
123     N_nn = 3
124
125     x = delta / (J * (2 * S - 1))
126     ising = T0 * S * S * J / kB
127     tanh_025 = tanh(6 / N_nn * log(1 + 0.033 * x))**0.25
128     T_c = ising * tanh_025
129     T_cs.append(T_c)
130
131 critical_df['T_c'] = T_cs
132
133 # Ferromagnetic systems
134 FM_df = critical_df[critical_df['order'] == 'FM']
135 FM_df.to_csv('./curie.csv', index=False)
136
137 # Antiferromagnetic systems
138 AFM_df = critical_df[critical_df['order'] == 'AFM']
139 AFM_df.to_csv('./neel.csv', index=False)
```

3.6 Supplementary data for Calculated 530 Honeycomb Kagome Lattice

The results for calculated 530 honeycomb kagome lattice. M [B/atom]: Total magnetic moment per atoms in unit cell. M_H [B]: Local magnetic moment on honeycomb element. M_K [B]: Local magnetic moment on kagome element. ΔE [eV]: Flat-buckled energy difference. E_{coh} [eV]: Cohesive energy. M_{conf} : Magnetic configuration (NM: Nonmagnetic, HM: Honeycomb-dominated magnetism, KM: Kagome-dominated magnetism, HKM: Honeycomb-kagome competitive magnetism). S: Spin quantum number

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Sc2O3	0.00	0.00	0.00	-0.20	-3.25	NM	0.00
Ti2O3	0.40	0.70	-0.03	-0.21	-3.34	HM	0.50
V2O3	0.80	1.80	-0.10	-0.48	-3.01	HM	1.00
Cr2O3	1.20	2.83	-0.10	-0.54	-1.73	HM	1.50
Mn2O3	1.59	3.50	0.09	-0.24	-1.47	HM	2.00
Fe2O3	0.00	0.00	0.00	-0.32	-1.42	NM	0.00
Co2O3	0.30	0.60	0.07	-0.33	-1.30	NM	0.00
Ni2O3	0.41	0.63	0.20	-0.40	-1.08	NM	0.00
Cu2O3	0.00	0.00	0.00	-0.58	-0.12	NM	0.00
Zn2O3	0.00	0.00	0.00	-1.03	0.37	NM	0.00
Y2O3	0.00	0.00	0.00	-0.32	-3.19	NM	0.00
Zr2O3	0.40	0.45	-0.02	-0.31	-3.71	HM	0.50
Nb2O3	0.77	1.35	-0.06	-0.57	-3.24	HM	1.00
Mo2O3	0.41	0.76	-0.02	-0.53	-2.19	HM	0.50
Ru2O3	0.00	0.00	0.00	-0.58	-1.84	NM	0.00
Rh2O3	0.00	0.00	0.00	-1.76	-1.24	NM	0.00
Pd2O3	0.37	0.45	0.24	-1.21	-0.11	NM	0.00
Ag2O3	0.00	0.00	0.00	-0.62	0.73	NM	0.00
Cd2O3	0.01	0.01	-0.01	-0.68	0.92	NM	0.00
Hf2O3	0.02	0.02	0.00	-0.35	-3.68	NM	0.00
Ta2O3	0.56	1.01	-0.05	-0.77	-3.55	HM	0.50
W2O3	0.17	0.30	-0.01	-0.64	-3.03	NM	0.00
Re2O3	0.00	0.00	0.00	-0.77	-2.25	NM	0.00
Os2O3	0.00	0.00	0.00	-0.97	-2.20	NM	0.00
Ir2O3	0.00	0.00	0.00	-2.25	-1.68	NM	0.00
Pt2O3	0.19	0.25	0.12	-1.62	-0.81	NM	0.00
Au2O3	0.00	0.00	0.00	-0.88	0.66	NM	0.00
Hg2O3	0.02	-0.01	-0.02	-0.40	1.59	NM	0.00
Sc2S3	0.00	0.00	0.00	-0.27	-4.57	NM	0.00
Ti2S3	0.40	0.92	-0.06	-0.16	-4.50	HM	0.50
V2S3	0.80	1.95	-0.13	-0.16	-4.35	HM	1.00
Cr2S3	1.20	2.94	-0.16	-0.25	-3.40	HM	1.50
Mn2S3	1.60	3.64	0.01	-0.20	-3.32	HM	2.00
Fe2S3	0.00	0.00	0.00	-0.05	-3.39	NM	0.00
Co2S3	0.00	0.00	0.00	-0.39	-3.45	NM	0.00
Ni2S3	0.00	0.00	0.00	-0.48	-3.40	NM	0.00
Cu2S3	0.38	0.18	0.27	-0.24	-2.54	NM	0.00
Zn2S3	0.40	0.02	0.34	-0.42	-1.95	KM	0.50
Y2S3	0.00	0.00	0.00	-0.85	-4.69	NM	0.00
Zr2S3	0.40	0.57	-0.03	-0.22	-4.85	HM	0.50
Nb2S3	0.80	1.49	-0.08	-0.24	-4.56	HM	1.00

Table 3.5. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Mo2S3	0.64	1.20	-0.04	-0.18	-3.84	HM	1.00
Ru2S3	0.00	0.00	0.00	-0.44	-4.10	NM	0.00
Rh2S3	0.00	0.00	0.00	-0.92	-3.84	NM	0.00
Pd2S3	0.00	0.00	0.00	-0.45	-2.81	NM	0.00
Ag2S3	0.00	0.00	0.00	-0.03	-1.95	NM	0.00
Cd2S3	0.09	0.00	0.08	-0.17	-1.61	NM	0.00
Hf2S3	0.40	0.56	-0.02	-0.27	-4.82	HM	0.50
Ta2S3	0.80	1.38	-0.06	-0.36	-4.81	HM	1.00
W2S3	0.74	1.31	-0.03	-0.24	-4.57	HM	1.00
Re2S3	0.43	0.80	-0.02	-0.18	-4.13	HM	0.50
Os2S3	0.00	0.00	0.00	-0.66	-4.47	NM	0.00
Ir2S3	0.00	0.00	0.00	-1.48	-4.32	NM	0.00
Pt2S3	0.00	0.00	0.00	-0.85	-3.58	NM	0.00
Au2S3	0.30	0.14	0.22	-0.35	-2.21	NM	0.00
Hg2S3	0.00	0.00	0.00	0.24	-1.12	NM	0.00
Sc2Se3	0.00	0.00	0.00	-0.12	-4.12	NM	0.00
Ti2Se3	0.40	0.96	-0.07	-0.10	-4.02	HM	0.50
V2Se3	0.80	2.03	-0.14	-0.12	-3.87	HM	1.00
Cr2Se3	0.27	-0.77	0.05	0.08	-2.58	HM	0.50
Mn2Se3	1.60	-3.68	0.02	-0.44	-2.91	HM	2.00
Fe2Se3	0.00	0.00	0.00	-0.17	-2.89	NM	0.00
Co2Se3	0.12	0.20	0.03	-0.26	-2.99	NM	0.00
Ni2Se3	0.00	0.00	0.00	-0.31	-3.03	NM	0.00
Cu2Se3	0.45	0.18	0.29	-0.08	-2.28	NM	0.00
Zn2Se3	0.00	0.00	0.00	-0.17	-1.66	NM	0.00
Y2Se3	0.00	0.00	0.00	-0.18	-4.25	NM	0.00
Zr2Se3	0.40	0.59	-0.03	-0.34	-4.36	HM	0.50
Nb2Se3	0.80	-1.51	0.08	-0.30	-4.06	HM	1.00
Mo2Se3	1.16	2.30	-0.07	-0.18	-3.33	HM	1.50
Ru2Se3	0.00	0.00	0.00	-0.31	-3.60	NM	0.00
Rh2Se3	0.00	0.00	0.00	-0.66	-3.44	NM	0.00
Pd2Se3	0.00	0.00	0.00	-0.21	-2.52	NM	0.00
Ag2Se3	0.00	0.00	0.00	0.13	-1.77	NM	0.00
Hf2Se3	0.40	0.57	-0.02	-0.18	-4.32	HM	0.50
Ta2Se3	0.80	1.42	-0.07	-0.19	-4.27	HM	1.00
W2Se3	1.05	1.94	-0.06	-0.21	-4.00	HM	1.50
Re2Se3	0.47	0.92	-0.03	-0.18	-3.53	HM	0.50
Os2Se3	0.00	0.00	0.00	-0.67	-3.87	NM	0.00
Ir2Se3	0.00	0.00	0.00	-1.15	-3.80	NM	0.00
Pt2Se3	0.00	0.00	0.00	-0.54	-3.21	NM	0.00
Au2Se3	0.35	0.14	0.22	-0.12	-2.00	NM	0.00
Hg2Se3	0.06	0.00	0.05	0.31	-0.98	NM	0.00
Sc2Te3	0.00	0.00	0.00	-0.15	-3.54	NM	0.00
Ti2Te3	0.40	1.01	-0.09	-0.09	-3.45	HM	0.50
V2Te3	0.80	2.18	-0.21	-0.10	-3.33	HM	1.00
Cr2Te3	1.20	3.36	-0.30	-0.25	-2.48	HM	1.50
Mn2Te3	1.60	-3.84	0.08	-0.17	-2.50	HM	2.00
Fe2Te3	0.00	0.00	0.00	-0.17	-2.44	NM	0.00

Table 3.6. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Co2Te3	0.27	0.41	0.09	-0.18	-2.60	NM	0.00
Ni2Te3	0.04	0.03	0.03	-0.14	-2.74	NM	0.00
Cu2Te3	0.47	0.14	0.33	0.05	-2.08	NM	0.00
Zn2Te3	0.00	0.00	0.00	-0.21	-1.41	NM	0.00
Y2Te3	0.00	0.00	0.00	-0.17	-3.68	NM	0.00
Zr2Te3	0.40	0.62	-0.04	-0.12	-3.76	HM	0.50
Nb2Te3	0.40	0.86	-0.07	0.06	-3.30	HM	0.50
Mo2Te3	1.18	2.37	-0.10	-0.14	-2.85	HM	1.50
Ru2Te3	0.00	0.00	0.00	-0.28	-3.21	NM	0.00
Rh2Te3	0.00	0.00	0.00	-0.39	-3.17	NM	0.00
Pd2Te3	0.00	0.00	0.00	-0.03	-2.36	NM	0.00
Ag2Te3	0.06	0.00	-0.05	0.20	-1.66	NM	0.00
Cd2Te3	0.40	0.00	0.30	0.04	-1.23	KM	0.50
Hf2Te3	0.40	0.60	-0.02	-0.18	-3.69	HM	0.50
Ta2Te3	0.80	1.45	-0.09	-0.20	-3.67	HM	1.00
W2Te3	1.14	2.14	-0.09	-0.19	-3.48	HM	1.50
Re2Te3	0.49	0.98	-0.04	-0.12	-3.05	HM	0.50
Os2Te3	0.00	0.00	0.00	-0.38	-3.44	NM	0.00
Ir2Te3	0.00	0.00	0.00	-0.79	-3.49	NM	0.00
Pt2Te3	0.00	0.00	0.00	-0.31	-3.02	NM	0.00
Au2Te3	0.00	0.00	0.00	0.03	-1.91	NM	0.00
Hg2Te3	0.00	0.00	0.00	0.33	-0.87	NM	0.00
Sc2C3	0.30	-0.01	-0.12	1.17	-3.56	NM	0.00
Ti2C3	0.00	0.00	0.00	0.58	-4.59	NM	0.00
V2C3	0.00	0.00	0.00	0.11	-4.89	NM	0.00
Cr2C3	0.38	1.35	-0.13	0.02	-3.97	HM	0.50
Mn2C3	0.63	2.09	-0.18	-0.14	-4.23	HM	1.00
Fe2C3	0.46	1.19	-0.06	-0.19	-4.47	HM	0.50
Co2C3	0.00	0.00	0.00	-0.25	-4.47	NM	0.00
Ni2C3	0.00	0.00	0.00	-0.04	-4.41	NM	0.00
Cu2C3	0.00	0.00	0.00	0.57	-3.21	NM	0.00
Zn2C3	0.06	0.00	0.03	1.17	-2.08	NM	0.00
Y2C3	1.19	0.14	0.47	0.97	-3.73	HKM	0.50
Zr2C3	0.00	0.00	0.00	0.58	-4.98	NM	0.00
Nb2C3	0.00	0.00	0.00	0.30	-5.27	NM	0.00
Mo2C3	0.00	-0.07	0.00	0.13	-4.77	NM	0.00
Ru2C3	0.33	0.35	0.07	-0.29	-5.30	NM	0.00
Rh2C3	0.16	0.03	0.09	-0.12	-4.99	NM	0.00
Pd2C3	0.00	0.00	0.00	0.32	-3.77	NM	0.00
Ag2C3	0.00	0.00	0.00	1.44	-2.42	NM	0.00
Cd2C3	0.81	0.02	0.39	1.67	-1.59	KM	0.50
Hf2C3	0.00	0.00	0.00	0.63	-4.90	NM	0.00
Ta2C3	0.00	0.00	0.00	0.33	-5.56	NM	0.00
W2C3	0.00	0.00	0.00	0.10	-5.65	NM	0.00
Re2C3	0.57	1.42	-0.10	-0.39	-5.53	HM	0.50
Os2C3	0.37	0.55	0.05	-0.61	-5.92	HM	0.50
Ir2C3	0.00	0.00	0.00	-0.65	-5.81	NM	0.00
Pt2C3	0.00	0.00	0.00	-0.38	-5.01	NM	0.00

Table 3.7. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Au2C3	0.00	0.00	0.00	0.96	-3.14	NM	0.00
Hg2C3	0.31	-0.02	0.18	1.71	-1.37	NM	0.00
Sc2N3	0.60	-0.02	0.39	-0.21	0.02	KM	0.50
Ti2N3	0.00	0.00	0.00	-0.95	-1.02	NM	0.00
V2N3	0.21	0.54	-0.05	-0.72	-0.94	HM	0.50
Cr2N3	0.62	1.80	-0.17	-0.62	0.10	HM	1.00
Mn2N3	0.62	1.64	-0.11	-1.55	0.09	HM	1.00
Fe2N3	0.28	0.70	-0.03	-1.42	0.04	HM	0.50
Co2N3	0.00	0.00	0.00	-1.52	0.15	NM	0.00
Ni2N3	0.00	0.00	0.00	-1.05	0.53	NM	0.00
Cu2N3	0.00	0.00	0.00	-0.40	1.84	NM	0.00
Zn2N3	0.20	-0.04	-0.14	-0.23	2.66	NM	0.00
Y2N3	0.60	0.01	0.40	-0.31	0.03	KM	0.50
Zr2N3	0.20	-0.03	0.16	-1.13	-1.32	NM	0.00
Nb2N3	0.20	0.31	-0.02	-1.41	-1.42	NM	0.00
Mo2N3	0.60	-1.23	0.07	-1.59	-0.76	HM	0.50
Ru2N3	0.03	0.06	0.00	-1.92	-0.71	NM	0.00
Rh2N3	0.00	0.00	0.00	-1.43	-0.13	NM	0.00
Pd2N3	0.00	0.00	0.00	-0.59	1.36	NM	0.00
Ag2N3	0.00	0.00	0.00	0.18	2.68	NM	0.00
Cd2N3	0.20	-0.04	-0.13	0.28	3.19	NM	0.00
Hf2N3	0.20	-0.03	0.15	-1.10	-1.27	NM	0.00
Ta2N3	0.20	0.31	-0.02	-1.68	-1.79	HM	0.50
W2N3	0.60	1.18	-0.06	-1.94	-1.81	HM	0.50
Re2N3	0.34	0.66	-0.02	-2.28	-1.23	HM	0.50
Os2N3	0.00	0.00	0.00	-2.51	-1.38	NM	0.00
Ir2N3	0.00	0.00	0.00	-2.16	-0.90	NM	0.00
Pt2N3	0.00	0.00	0.00	-1.31	0.26	NM	0.00
Au2N3	0.00	0.00	0.00	-0.23	2.23	NM	0.00
Hg2N3	0.08	-0.01	0.08	0.72	3.71	NM	0.00
Sc2P3	0.20	0.01	0.09	0.23	-1.10	NM	0.00
Ti2P3	0.00	0.00	0.00	-0.08	-1.62	NM	0.00
V2P3	0.31	1.06	-0.10	-0.02	-1.47	HM	0.50
Cr2P3	0.75	2.29	-0.19	-0.09	-0.67	HM	1.00
Mn2P3	1.00	2.92	-0.20	-0.25	-0.87	HM	1.00
Fe2P3	0.00	0.01	0.00	-0.14	-1.04	NM	0.00
Co2P3	0.00	0.00	0.00	-0.28	-1.25	NM	0.00
Ni2P3	0.00	0.00	0.00	-0.15	-1.26	NM	0.00
Cu2P3	0.00	0.00	0.00	0.23	-0.17	NM	0.00
Zn2P3	0.94	0.06	0.53	0.35	0.73	HKM	0.50
Y2P3	0.23	0.00	0.11	0.32	-1.15	NM	0.00
Zr2P3	0.00	0.00	0.00	-0.17	-1.98	NM	0.00
Nb2P3	0.26	0.65	-0.06	0.02	-1.80	HM	0.50
Mo2P3	0.00	0.00	0.00	0.05	-1.23	NM	0.00
Ru2P3	0.00	0.00	0.00	-0.33	-1.91	NM	0.00
Rh2P3	0.00	0.00	0.00	-0.27	-1.81	NM	0.00
Pd2P3	0.00	0.00	0.00	0.17	-0.71	NM	0.00
Ag2P3	0.00	0.00	0.00	0.56	0.43	NM	0.00

Table 3.8. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Cd2P3	0.15	0.00	0.08	0.79	1.11	NM	0.00
Hf2P3	0.00	0.00	0.00	-0.31	-1.96	NM	0.00
Ta2P3	0.09	0.25	-0.02	-0.07	-2.05	NM	0.00
W2P3	0.64	1.40	-0.09	-0.26	-2.17	HM	1.00
Re2P3	0.48	0.98	-0.03	-0.37	-1.90	HM	0.50
Os2P3	0.15	0.32	-0.01	-0.62	-2.33	NM	0.00
Ir2P3	0.00	0.00	0.00	-0.73	-2.39	NM	0.00
Pt2P3	0.00	0.00	0.00	-0.27	-1.70	NM	0.00
Au2P3	0.00	0.00	0.00	0.26	-0.04	NM	0.00
Hg2P3	0.99	0.10	0.55	0.97	1.28	HKM	0.50
Sc2B3	1.39	0.70	0.25	2.21	-2.70	HKM	0.50
Ti2B3	0.63	0.41	0.09	1.95	-3.15	HKM	0.50
V2B3	0.00	0.00	0.00	1.64	-3.29	NM	0.00
Cr2B3	1.48	2.58	0.04	1.33	-2.51	HM	2.00
Mn2B3	0.61	2.04	-0.10	0.88	-2.91	HM	1.00
Fe2B3	0.58	1.95	-0.10	0.97	-3.45	HM	0.50
Co2B3	0.23	0.56	-0.02	0.75	-3.61	HM	0.50
Ni2B3	0.00	0.00	0.00	0.78	-3.77	NM	0.00
Cu2B3	0.00	0.00	0.00	1.20	-2.83	NM	0.00
Zn2B3	0.00	0.00	0.00	1.51	-1.89	NM	0.00
Y2B3	0.88	0.28	0.16	2.24	-2.72	HKM	0.50
Zr2B3	0.00	0.00	0.00	2.05	-3.52	NM	0.00
Nb2B3	0.00	0.00	0.00	1.67	-3.78	NM	0.00
Mo2B3	0.00	0.00	0.00	1.45	-3.42	NM	0.00
Ru2B3	0.16	0.43	-0.03	0.71	-4.43	NM	0.00
Rh2B3	0.13	0.16	0.01	0.61	-4.48	NM	0.00
Pd2B3	0.00	0.00	0.00	0.93	-3.49	NM	0.00
Ag2B3	0.00	0.00	0.00	1.57	-2.32	NM	0.00
Cd2B3	0.09	0.01	0.02	1.90	-1.51	NM	0.00
Hf2B3	0.49	0.20	0.07	2.13	-3.45	NM	0.00
Ta2B3	0.00	0.00	0.00	1.79	-4.00	NM	0.00
W2B3	0.00	0.00	0.00	1.53	-4.16	NM	0.00
Re2B3	0.13	0.38	-0.01	1.22	-4.04	NM	0.00
Os2B3	0.34	0.83	-0.03	0.69	-4.84	HM	0.50
Ir2B3	0.14	0.20	0.01	0.32	-5.06	NM	0.00
Pt2B3	0.00	0.00	0.00	0.29	-4.63	NM	0.00
Au2B3	0.00	0.00	0.00	0.93	-3.12	NM	0.00
Hg2B3	0.00	0.00	0.00	1.69	-1.53	NM	0.00
Sc2Si3	0.84	0.19	0.27	0.92	-2.62	HKM	0.50
Ti2Si3	0.39	0.07	0.13	0.75	-2.91	NM	0.00
V2Si3	0.00	0.00	0.00	0.73	-2.92	NM	0.00
Cr2Si3	0.84	2.75	-0.22	0.40	-2.21	HM	1.00
Mn2Si3	0.77	2.94	-0.27	0.43	-2.60	HM	1.00
Fe2Si3	0.63	1.81	-0.11	0.40	-3.00	HM	1.00
Co2Si3	0.00	0.00	0.00	0.43	-3.15	NM	0.00
Ni2Si3	0.00	0.00	0.00	0.27	-3.45	NM	0.00
Cu2Si3	0.00	0.00	0.00	0.44	-2.60	NM	0.00
Zn2Si3	0.00	0.00	0.00	0.58	-1.54	NM	0.00

Table 3.9. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Y2Si3	1.12	0.15	0.36	0.99	-2.67	HKM	0.50
Zr2Si3	0.20	0.03	0.07	0.77	-3.27	NM	0.00
Nb2Si3	0.00	0.00	0.00	0.67	-3.28	NM	0.00
Mo2Si3	0.46	1.27	-0.10	0.74	-2.93	HM	0.50
Ru2Si3	0.00	0.00	0.00	0.52	-3.88	NM	0.00
Rh2Si3	0.00	0.00	0.00	0.29	-4.00	NM	0.00
Pd2Si3	0.00	0.00	0.00	0.34	-3.16	NM	0.00
Ag2Si3	0.00	0.00	0.00	0.68	-2.13	NM	0.00
Cd2Si3	0.08	0.00	0.04	0.86	-1.23	NM	0.00
Hf2Si3	0.39	0.07	0.13	0.72	-3.20	NM	0.00
Ta2Si3	0.00	0.00	0.00	0.57	-3.53	NM	0.00
W2Si3	0.45	0.95	-0.05	0.63	-3.65	HM	0.50
Re2Si3	0.60	1.38	-0.07	0.55	-3.62	HM	0.50
Os2Si3	0.00	0.00	0.00	0.47	-4.20	NM	0.00
Ir2Si3	0.00	0.00	0.00	0.13	-4.52	NM	0.00
Pt2Si3	0.00	0.00	0.00	0.01	-4.17	NM	0.00
Au2Si3	0.00	0.00	0.00	0.33	-2.78	NM	0.00
Hg2Si3	0.19	0.02	0.09	0.98	-1.10	NM	0.00
Sc2Ge3	0.81	0.21	0.19	0.64	-2.50	HKM	0.50
Ti2Ge3	0.39	0.10	0.09	0.52	-2.77	NM	0.00
V2Ge3	0.00	0.00	0.00	0.52	-2.75	NM	0.00
Cr2Ge3	0.90	2.82	-0.16	0.13	-2.04	HM	1.00
Mn2Ge3	0.79	3.08	-0.21	0.25	-2.40	HM	1.00
Fe2Ge3	0.00	0.05	-0.01	0.35	-2.50	NM	0.00
Co2Ge3	0.00	0.00	0.00	0.20	-2.84	NM	0.00
Ni2Ge3	0.00	0.00	0.00	0.06	-3.16	NM	0.00
Cu2Ge3	0.00	0.00	0.00	0.25	-2.38	NM	0.00
Zn2Ge3	0.00	0.00	0.00	0.36	-1.39	NM	0.00
Y2Ge3	0.87	0.14	0.21	0.69	-2.54	HKM	0.50
Zr2Ge3	0.08	0.01	0.02	0.49	-3.11	NM	0.00
Nb2Ge3	0.00	0.00	0.00	0.48	-3.07	NM	0.00
Mo2Ge3	0.52	1.30	-0.07	0.52	-2.66	HM	0.50
Ru2Ge3	0.00	0.00	0.00	0.33	-3.50	NM	0.00
Rh2Ge3	0.00	0.00	0.00	0.09	-3.64	NM	0.00
Pd2Ge3	0.00	0.00	0.00	0.14	-2.87	NM	0.00
Ag2Ge3	0.00	0.00	0.00	0.50	-1.93	NM	0.00
Cd2Ge3	0.00	0.00	0.00	0.60	-1.11	NM	0.00
Hf2Ge3	0.38	0.08	0.09	0.49	-3.03	NM	0.00
Ta2Ge3	0.00	0.00	0.00	0.39	-3.31	NM	0.00
W2Ge3	0.45	0.93	-0.04	0.37	-3.40	HM	0.50
Re2Ge3	0.70	1.62	-0.06	0.30	-3.29	HM	1.00
Os2Ge3	0.43	-0.85	0.01	0.21	-3.82	HM	0.50
Ir2Ge3	0.00	0.00	0.00	-0.04	-4.08	NM	0.00
Pt2Ge3	0.00	0.00	0.00	-0.21	-3.77	NM	0.00
Au2Ge3	0.00	0.00	0.00	0.25	-2.47	NM	0.00
Hg2Ge3	0.29	0.04	0.10	0.80	-0.94	NM	0.00
Sc2As3	0.20	0.02	0.09	0.18	-2.87	NM	0.00
Ti2As3	0.00	0.00	0.00	-0.08	-3.30	NM	0.00

Table 3.10. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
V2As3	0.33	1.18	-0.13	-0.11	-3.12	NM	0.00
Cr2As3	0.79	2.65	-0.27	-0.47	-2.36	HKM	0.50
Mn2As3	1.02	3.13	-0.25	-0.19	-2.52	HM	1.50
Fe2As3	0.00	0.00	0.00	-0.19	-2.60	NM	0.00
Co2As3	0.00	0.00	0.00	-0.29	-2.82	NM	0.00
Ni2As3	0.00	0.00	0.00	-0.18	-2.90	NM	0.00
Cu2As3	0.08	0.02	0.05	0.20	-1.95	NM	0.00
Zn2As3	0.00	0.00	0.00	0.34	-1.06	NM	0.00
Y2As3	0.21	0.00	0.10	0.17	-2.93	NM	0.00
Zr2As3	0.00	0.00	0.00	-0.15	-3.65	NM	0.00
Nb2As3	0.01	0.06	-0.01	0.02	-3.37	NM	0.00
Mo2As3	0.00	0.00	0.00	0.07	-2.78	NM	0.00
Ru2As3	0.00	0.00	0.00	-0.30	-3.42	NM	0.00
Rh2As3	0.00	0.00	0.00	-0.29	-3.39	NM	0.00
Pd2As3	0.00	0.00	0.00	0.13	-2.41	NM	0.00
Ag2As3	0.00	0.00	0.00	0.48	-1.41	NM	0.00
Cd2As3	0.04	0.01	0.02	0.48	-0.76	NM	0.00
Hf2As3	0.00	0.00	0.00	-0.22	-3.61	NM	0.00
Ta2As3	0.32	0.61	-0.04	-0.15	-3.71	HM	0.50
W2As3	0.65	1.46	-0.11	-0.21	-3.72	HM	1.00
Re2As3	0.51	1.07	-0.05	-0.19	-3.37	HM	0.50
Os2As3	0.00	0.00	0.00	-0.25	-3.76	NM	0.00
Ir2As3	0.00	0.00	0.00	-0.73	-3.86	NM	0.00
Pt2As3	0.00	0.00	0.00	-0.25	-3.26	NM	0.00
Au2As3	0.00	0.00	0.00	0.28	-1.79	NM	0.00
Hg2As3	0.00	0.00	0.00	0.89	-0.49	NM	0.00
Ti2Sb3	0.00	0.00	0.00	0.02	-2.75	NM	0.00
V2Sb3	0.45	1.35	-0.12	0.10	-2.58	HM	0.50
Cr2Sb3	0.86	2.95	-0.30	-0.40	-1.90	HKM	0.50
Mn2Sb3	1.05	3.36	-0.27	-0.06	-2.08	HM	1.50
Fe2Sb3	0.02	0.09	-0.01	-0.08	-2.10	NM	0.00
Co2Sb3	0.00	0.00	0.00	-0.15	-2.38	NM	0.00
Ni2Sb3	0.00	0.00	0.00	-0.08	-2.57	NM	0.00
Cu2Sb3	0.00	0.00	0.00	0.22	-1.74	NM	0.00
Zn2Sb3	0.00	0.00	0.00	0.34	-0.86	NM	0.00
Y2Sb3	0.21	0.01	0.09	0.20	-2.53	NM	0.00
Zr2Sb3	0.00	0.00	0.00	-0.02	-3.09	NM	0.00
Nb2Sb3	0.35	0.75	-0.06	0.08	-2.83	HM	0.50
Mo2Sb3	0.72	1.91	-0.18	-0.02	-2.39	HM	1.00
Ru2Sb3	0.00	0.00	0.00	-0.12	-2.94	NM	0.00
Rh2Sb3	0.00	0.00	0.00	-0.13	-3.02	NM	0.00
Pd2Sb3	0.00	0.00	0.00	0.18	-2.19	NM	0.00
Ag2Sb3	0.00	0.00	0.00	0.42	-1.30	NM	0.00
Cd2Sb3	0.00	0.00	0.00	0.44	-0.63	NM	0.00
Hf2Sb3	0.00	0.00	0.00	-0.10	-3.04	NM	0.00
Ta2Sb3	0.11	0.31	-0.04	0.02	-3.02	NM	0.00
W2Sb3	0.68	1.56	-0.12	-0.13	-3.11	HM	1.00
Re2Sb3	0.63	1.40	-0.07	-0.13	-2.79	HM	1.00

Table 3.11. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Os2Sb3	0.00	0.00	0.00	-0.11	-3.21	NM	0.00
Ir2Sb3	0.00	0.00	0.00	-0.46	-3.43	NM	0.00
Pt2Sb3	0.00	0.00	0.00	-0.12	-2.98	NM	0.00
Au2Sb3	0.00	0.00	0.00	0.26	-1.67	NM	0.00
Hg2Sb3	0.00	0.00	0.00	0.74	-0.41	NM	0.00
Li2B3	0.00	0.00	0.00	2.63	-1.30	NM	0.00
Be2B3	0.00	0.00	0.00	1.07	-2.88	NM	0.00
Na2B3	0.20	0.04	0.06	2.81	-0.88	NM	0.00
Mg2B3	0.33	0.02	0.07	2.26	-1.52	NM	0.00
K2B3	0.29	0.04	0.07	2.64	-0.82	NM	0.00
Ca2B3	1.39	-0.21	-0.29	2.37	-1.66	HKM	0.50
Rb2B3	1.00	0.05	0.24	2.45	-0.89	HKM	0.50
Sr2B3	0.65	-0.10	-0.15	2.39	-1.41	HKM	0.50
Cs2B3	1.00	0.04	0.24	2.34	-0.92	HKM	0.50
Ba2B3	0.13	-0.07	-0.04	2.30	-1.58	NM	0.00
Al2B3	0.13	0.00	0.03	1.47	-2.91	NM	0.00
Ga2B3	0.00	0.00	0.00	1.48	-2.72	NM	0.00
In2B3	0.00	0.00	0.00	1.76	-2.33	NM	0.00
Sn2B3	0.00	0.00	0.00	1.60	-2.78	NM	0.00
Tl2B3	0.00	0.00	0.00	1.90	-2.09	NM	0.00
Pb2B3	0.00	0.00	0.00	1.96	-2.36	NM	0.00
Bi2B3	0.39	0.00	0.12	1.91	-2.21	KM	0.50
Li2Si3	0.00	0.00	0.00	1.43	-1.36	NM	0.00
Be2Si3	0.00	0.00	0.00	0.43	-2.58	NM	0.00
Na2Si3	0.64	0.03	0.29	1.73	-0.88	HKM	0.50
Mg2Si3	0.00	0.00	0.00	0.98	-1.42	NM	0.00
K2Si3	1.60	-0.04	-0.64	1.53	-1.09	KM	1.50
Ca2Si3	0.03	0.03	-0.01	1.31	-1.63	NM	0.00
Rb2Si3	1.60	-0.06	-0.64	1.52	-1.09	KM	1.50
Sr2Si3	0.40	-0.04	-0.16	1.39	-1.54	NM	0.00
Cs2Si3	0.80	0.05	0.32	1.68	-0.94	HKM	0.50
Ba2Si3	0.40	-0.04	-0.15	1.40	-1.73	NM	0.00
Al2Si3	0.16	0.00	0.08	0.66	-2.41	NM	0.00
Ga2Si3	0.03	0.00	0.02	0.88	-2.14	NM	0.00
In2Si3	0.07	0.00	0.03	1.07	-1.85	NM	0.00
Sn2Si3	0.00	0.00	0.00	1.09	-2.18	NM	0.00
Tl2Si3	0.11	0.00	0.05	1.25	-1.63	NM	0.00
Pb2Si3	0.00	0.00	0.00	1.14	-2.03	NM	0.00
Bi2Si3	0.00	0.00	0.00	0.90	-2.01	NM	0.00
Li2Ge3	0.00	0.00	0.00	1.06	-1.35	NM	0.00
Be2Ge3	0.00	0.00	0.00	0.20	-2.43	NM	0.00
Na2Ge3	0.25	0.00	0.08	1.38	-0.86	NM	0.00
Mg2Ge3	0.09	0.00	0.03	0.62	-1.36	NM	0.00
K2Ge3	1.60	-0.04	-0.48	1.23	-1.03	KM	1.50
Ca2Ge3	1.32	0.11	0.36	0.83	-1.67	HKM	0.50
Rb2Ge3	0.78	0.05	0.23	1.45	-0.80	HKM	0.50
Sr2Ge3	0.01	0.04	0.01	1.06	-1.42	NM	0.00
Cs2Ge3	1.60	-0.04	-0.47	1.19	-1.08	KM	1.50

Table 3.12. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Ba2Ge3	0.23	-0.01	0.06	1.16	-1.55	NM	0.00
Al2Ge3	0.10	0.00	0.03	0.39	-2.25	NM	0.00
Ga2Ge3	0.00	0.00	0.00	0.57	-2.01	NM	0.00
In2Ge3	0.08	0.00	0.03	0.76	-1.74	NM	0.00
Sn2Ge3	0.00	0.00	0.00	0.77	-2.09	NM	0.00
Tl2Ge3	0.14	0.00	0.05	0.93	-1.55	NM	0.00
Pb2Ge3	0.00	0.00	0.00	0.81	-1.98	NM	0.00
Bi2Ge3	0.00	0.00	0.00	0.49	-1.95	NM	0.00
Li2As3	1.40	0.02	0.77	0.94	-1.25	KM	1.00
Be2As3	0.00	0.00	0.00	0.20	-2.21	NM	0.00
Na2As3	0.20	-0.01	-0.11	1.09	-0.79	NM	0.00
Mg2As3	0.34	0.00	0.19	0.48	-1.30	KM	0.50
K2As3	1.40	-0.01	-0.75	0.92	-0.99	KM	1.00
Ca2As3	1.00	0.01	0.50	0.55	-1.84	KM	1.00
Rb2As3	0.20	0.01	0.11	1.17	-0.74	NM	0.00
Sr2As3	0.18	0.00	0.10	0.70	-1.63	NM	0.00
Cs2As3	0.20	0.01	0.10	1.18	-0.76	NM	0.00
Ba2As3	0.20	0.01	0.11	0.78	-1.81	NM	0.00
Al2As3	0.24	-0.01	0.15	0.25	-2.21	NM	0.00
Ga2As3	0.65	-0.02	0.41	0.58	-1.76	KM	0.50
In2As3	0.75	-0.01	0.45	0.69	-1.54	KM	0.50
Sn2As3	0.22	-0.04	0.16	0.59	-1.92	NM	0.00
Tl2As3	0.92	-0.02	-0.53	0.88	-1.32	KM	1.00
Pb2As3	0.60	-0.05	0.39	0.67	-1.78	HKM	0.50
Bi2As3	0.00	0.00	0.00	0.49	-1.62	NM	0.00
Li2Sb3	0.00	0.00	0.00	0.92	-1.02	NM	0.00
Be2Sb3	0.00	0.00	0.00	0.17	-1.87	NM	0.00
Na2Sb3	0.20	-0.01	-0.10	0.97	-0.69	NM	0.00
Mg2Sb3	0.99	0.00	0.53	0.38	-1.14	KM	1.00
K2Sb3	0.20	0.01	0.11	1.02	-0.65	NM	0.00
Ca2Sb3	1.00	-0.01	-0.48	0.49	-1.58	KM	1.00
Rb2Sb3	0.20	0.01	0.11	1.03	-0.64	NM	0.00
Sr2Sb3	0.08	0.00	0.05	0.60	-1.41	NM	0.00
Cs2Sb3	0.20	0.02	0.10	1.05	-0.66	NM	0.00
Ba2Sb3	0.19	0.00	0.10	0.70	-1.58	NM	0.00
Al2Sb3	0.25	-0.02	0.15	0.32	-1.82	NM	0.00
Ga2Sb3	0.53	0.00	0.31	0.58	-1.52	KM	0.50
In2Sb3	0.78	0.00	0.44	0.66	-1.33	KM	0.50
Sn2Sb3	0.21	-0.04	0.14	0.53	-1.69	NM	0.00
Tl2Sb3	0.95	0.02	0.52	0.81	-1.16	KM	1.00
Pb2Sb3	0.26	-0.04	0.17	0.62	-1.57	NM	0.00
Bi2Sb3	0.00	0.00	0.00	0.47	-1.41	NM	0.00
Li2O3	0.80	0.02	-0.86	0.10	0.46	KM	0.50
Be2O3	0.00	0.00	0.00	-0.01	-1.72	NM	0.00
Na2O3	0.80	-0.01	0.84	0.03	0.93	KM	0.50
Mg2O3	0.40	-0.01	0.43	-0.37	-0.57	KM	0.50
Ca2O3	0.40	-0.01	0.43	-0.38	-0.96	KM	0.50
Sr2O3	0.40	0.00	0.43	-0.31	-0.77	KM	0.50

Table 3.13. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Cs2O3	0.00	0.00	0.00	0.17	1.13	NM	0.00
Ba2O3	0.00	0.00	0.00	-0.26	-0.91	NM	0.00
Al2O3	0.00	0.00	0.00	-0.01	-2.60	NM	0.00
Ga2O3	0.00	0.00	0.00	-0.12	-1.01	NM	0.00
In2O3	0.00	0.00	0.00	-0.72	-0.55	NM	0.00
Sn2O3	0.00	0.00	0.00	-0.24	-0.97	NM	0.00
Tl2O3	0.00	0.00	0.00	-0.37	0.34	NM	0.00
Pb2O3	0.00	0.00	0.00	-0.29	-0.52	NM	0.00
Bi2O3	0.00	0.00	0.00	0.40	-0.43	NM	0.00
Li2S3	0.27	0.00	0.20	0.67	-1.93	NM	0.00
Be2S3	0.00	0.00	0.00	-0.05	-3.26	NM	0.00
Na2S3	0.80	0.00	0.63	0.51	-1.70	KM	0.50
K2S3	0.80	0.00	-0.62	0.56	-1.69	KM	0.50
Ca2S3	0.40	0.00	0.31	-0.34	-3.11	KM	0.50
Rb2S3	0.80	0.00	0.62	0.58	-1.65	KM	0.50
Sr2S3	0.40	0.00	0.31	-0.32	-3.01	KM	0.50
Ba2S3	0.09	0.00	0.06	-0.23	-3.13	NM	0.00
Al2S3	0.00	0.00	0.00	-0.88	-3.56	NM	0.00
Ga2S3	0.00	0.00	0.00	-0.13	-2.76	NM	0.00
In2S3	0.00	0.00	0.00	-0.05	-2.53	NM	0.00
Sn2S3	0.00	0.00	0.00	-0.18	-2.92	NM	0.00
Tl2S3	0.00	0.00	0.00	0.37	-2.06	NM	0.00
Pb2S3	0.00	0.00	0.00	-0.07	-2.71	NM	0.00
Bi2S3	0.00	0.00	0.00	0.10	-2.50	NM	0.00
Li2Se3	0.80	-0.01	0.55	0.58	-1.91	KM	0.50
Be2Se3	0.00	0.00	0.00	-0.03	-2.88	NM	0.00
Na2Se3	0.09	0.00	-0.05	0.64	-1.50	NM	0.00
Mg2Se3	0.00	0.00	0.00	-0.32	-2.24	NM	0.00
K2Se3	0.80	0.00	0.51	0.58	-1.58	KM	0.50
Ca2Se3	0.07	0.00	0.04	-0.25	-2.83	NM	0.00
Rb2Se3	0.80	0.00	-0.51	0.58	-1.56	KM	0.50
Sr2Se3	0.00	0.00	0.00	-0.22	-2.73	NM	0.00
Ba2Se3	0.40	0.00	0.25	-0.20	-2.94	KM	0.50
Al2Se3	0.00	0.00	0.00	-0.43	-3.01	NM	0.00
Ga2Se3	0.00	0.00	0.00	0.10	-2.43	NM	0.00
In2Se3	0.00	0.00	0.00	0.17	-2.23	NM	0.00
Sn2Se3	0.00	0.00	0.00	-0.09	-2.64	NM	0.00
Tl2Se3	0.00	0.00	0.00	0.48	-1.88	NM	0.00
Pb2Se3	0.00	0.00	0.00	0.01	-2.48	NM	0.00
Bi2Se3	0.00	0.00	0.00	-0.30	-2.27	NM	0.00
Li2Te3	0.80	0.00	0.59	0.57	-1.73	KM	0.50
Be2Te3	0.00	0.00	0.00	-0.12	-2.45	NM	0.00
Na2Te3	0.20	0.00	-0.13	0.63	-1.37	NM	0.00
Mg2Te3	0.00	0.00	0.00	-0.17	-1.89	NM	0.00
Ca2Te3	0.02	0.00	-0.01	-0.19	-2.49	NM	0.00
Sr2Te3	0.07	0.00	-0.04	-0.16	-2.42	NM	0.00
Ba2Te3	0.40	0.00	0.26	-0.13	-2.63	KM	0.50
Al2Te3	0.00	0.00	0.00	-0.09	-2.49	NM	0.00

Table 3.14. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Ga2Te3	0.00	0.00	0.00	0.24	-2.12	NM	0.00
In2Te3	0.00	0.00	0.00	0.31	-1.94	NM	0.00
Sn2Te3	0.00	0.00	0.00	-0.06	-2.31	NM	0.00
Tl2Te3	0.00	0.00	0.00	0.53	-1.70	NM	0.00
Pb2Te3	0.00	0.00	0.00	0.01	-2.20	NM	0.00
Bi2Te3	0.00	0.00	0.00	-0.08	-1.98	NM	0.00
Li2C3	0.01	-0.07	0.00	2.26	-1.40	NM	0.00
Be2C3	0.00	0.00	0.00	0.26	-3.47	NM	0.00
Na2C3	0.80	-0.08	-0.38	2.23	-1.19	HKM	0.50
Mg2C3	0.19	-0.01	0.09	1.62	-1.88	NM	0.00
K2C3	0.80	-0.04	-0.38	1.94	-1.21	HKM	0.50
Ca2C3	0.38	0.08	0.19	1.49	-2.22	NM	0.00
Rb2C3	0.80	-0.04	-0.37	1.83	-1.18	HKM	0.50
Sr2C3	0.40	0.08	0.20	1.35	-2.09	NM	0.00
Cs2C3	0.80	0.05	0.38	1.69	-1.23	HKM	0.50
Ba2C3	0.01	-0.10	0.00	1.31	-2.21	NM	0.00
Al2C3	0.08	0.00	-0.03	0.56	-3.49	NM	0.00
Ga2C3	0.81	0.00	0.42	0.96	-2.93	KM	0.50
In2C3	0.90	0.02	0.45	1.27	-2.51	KM	1.00
Sn2C3	0.38	-0.03	-0.18	1.06	-2.98	NM	0.00
Tl2C3	0.00	0.00	0.00	1.81	-1.87	NM	0.00
Pb2C3	0.16	0.02	-0.10	1.61	-2.39	NM	0.00
Bi2C3	0.32	-0.07	-0.14	1.42	-2.39	NM	0.00
Li2N3	0.20	-0.02	-0.13	0.99	2.98	NM	0.00
Be2N3	0.16	0.00	0.12	0.03	1.00	NM	0.00
Na2N3	0.20	-0.01	-0.15	0.97	3.36	NM	0.00
Mg2N3	0.20	0.00	-0.13	0.09	2.26	NM	0.00
K2N3	1.40	0.01	0.93	0.55	3.03	KM	1.00
Ca2N3	1.00	0.00	0.63	0.22	1.80	KM	1.00
Rb2N3	1.40	0.02	0.93	0.52	3.07	KM	1.00
Sr2N3	0.20	-0.01	-0.09	0.38	2.18	NM	0.00
Cs2N3	0.20	-0.02	-0.14	0.88	3.44	NM	0.00
Ba2N3	1.00	-0.05	-0.66	0.14	1.83	KM	1.00
Al2N3	0.31	-0.01	0.22	-0.78	0.51	KM	0.50
Ga2N3	0.07	-0.02	0.06	-0.16	1.66	NM	0.00
In2N3	0.60	0.00	-0.45	0.03	2.05	KM	0.50
Sn2N3	0.21	-0.02	0.16	-0.05	1.44	NM	0.00
Tl2N3	0.72	0.01	-0.55	0.54	2.71	KM	0.50
Pb2N3	0.54	0.02	0.39	0.38	2.08	KM	0.50
Bi2N3	0.00	0.00	0.00	0.06	1.98	NM	0.00
Li2P3	0.20	-0.01	-0.10	1.27	0.84	NM	0.00
Be2P3	0.00	0.00	0.00	0.25	-0.41	NM	0.00
Na2P3	0.20	-0.01	-0.11	1.30	1.16	NM	0.00
Mg2P3	0.20	0.00	0.11	0.55	0.53	NM	0.00
K2P3	0.20	0.01	0.10	1.35	1.18	NM	0.00
Ca2P3	0.19	0.00	0.09	0.81	0.12	NM	0.00
Rb2P3	0.20	0.01	0.10	1.35	1.20	NM	0.00
Sr2P3	0.20	0.00	0.10	0.85	0.23	NM	0.00

Table 3.15. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	M_{conf}	S
Cs2P3	0.20	0.02	0.10	1.36	1.18	NM	0.00
Ba2P3	0.20	0.00	0.10	0.91	0.06	NM	0.00
Al2P3	0.24	-0.01	0.14	0.28	-0.50	NM	0.00
Ga2P3	0.64	-0.03	0.39	0.72	0.05	KM	0.50
In2P3	0.66	-0.02	0.39	0.82	0.30	KM	0.50
Sn2P3	0.23	-0.04	0.15	0.70	-0.04	NM	0.00
Tl2P3	0.87	0.02	0.49	1.06	0.60	KM	0.50
Pb2P3	0.60	-0.05	0.37	0.80	0.12	HKM	0.50
Bi2P3	0.22	-0.05	0.15	0.66	0.24	NM	0.00

Table 3.16. The results for calculated 530 honeycomb kagome lattice.

Name	M	M_H	M_K	ΔE	E_{coh}	S	J	Δ	ordering	ES
Ti2O3	0.40	0.70	-0.03	-0.21	-3.34	0.50	-47.50		disorder-AFM	S
V2O3	0.80	1.80	-0.10	-0.48	-3.01	1.00	98.20	0.340	order-FM	HM
Cr2O3	1.20	2.83	-0.10	-0.54	-1.73	1.50	23.70	0.470	order-FM	HM
Mn2O3	1.59	3.50	0.09	-0.24	-1.47	2.00	-16.10	10.650	order-AFM	M
Zr2O3	0.40	0.45	-0.02	-0.31	-3.71	0.50	-88.50		disorder-AFM	S
Nb2O3	0.77	1.35	-0.06	-0.57	-3.24	1.00	49.90	1.660	order-FM	M
Mo2O3	0.41	0.76	-0.02	-0.53	-2.19	0.50	-105.00	29.650	order-AFM	M
Ti2S3	0.40	0.92	-0.06	-0.16	-4.50	0.50	-12.40		disorder-AFM	S
V2S3	0.80	1.95	-0.13	-0.16	-4.35	1.00	120.20	0.090	order-FM	HM
Cr2S3	1.20	2.94	-0.16	-0.25	-3.40	1.50	67.40	0.020	order-FM	HM
Mn2S3	1.60	3.64	0.01	-0.20	-3.32	2.00	-6.60	5.160	order-AFM	M
Zr2S3	0.40	0.57	-0.03	-0.22	-4.85	0.50	-8.90		disorder-AFM	S
Nb2S3	0.80	1.49	-0.08	-0.24	-4.56	1.00	77.70	1.570	order-FM	HM
Mo2S3	0.64	1.20	-0.04	-0.18	-3.84	1.00	2.10	0.540	order-FM	M
Hf2S3	0.40	0.56	-0.02	-0.27	-4.82	0.50	-12.50		disorder-AFM	S
Ta2S3	0.80	1.38	-0.06	-0.36	-4.81	1.00	75.20	15.950	order-FM	HM
W2S3	0.74	1.31	-0.03	-0.24	-4.57	1.00	7.90	11.150	order-FM	M
Re2S3	0.43	0.80	-0.02	-0.18	-4.13	0.50	-67.50	80.110	order-AFM	M
Ti2Se3	0.40	0.96	-0.07	-0.10	-4.02	0.50	-48.10		disorder-AFM	S
V2Se3	0.80	2.03	-0.14	-0.12	-3.87	1.00	125.40	0.190	order-FM	HM
Mn2Se3	1.60	-3.68	0.02	-0.44	-2.91	2.00	-6.20	7.850	order-AFM	M
Zr2Se3	0.40	0.59	-0.03	-0.34	-4.36	0.50	-7.90		disorder-AFM	S
Nb2Se3	0.80	-1.51	0.08	-0.30	-4.06	1.00	0.80	-0.470	disorder-FM	M
Mo2Se3	1.16	2.30	-0.07	-0.18	-3.33	1.50	14.50	0.860	order-FM	M
Hf2Se3	0.40	0.57	-0.02	-0.18	-4.32	0.50	-11.40		disorder-AFM	S
Ta2Se3	0.80	1.42	-0.07	-0.19	-4.27	1.00	84.00	13.490	order-FM	HM

Table 3.17. The materials which satisfy negative cohesive energy E_{coh} and flat-buckled energy difference ΔE and honeycomb-dominated magnetism (HM). M [B/atom]: Total magnetic moment per atoms in unit cell. M_H [B]: Local magnetic moment on honeycomb element. M_K [B]: Local magnetic moment on kagome element. ΔE [eV]: Flat-buckled energy difference. E_{coh} [eV]: Cohesive energy. S : Spin quantum number. J [meV] Nearest neighbor exchange coupling. Δ [meV] Spin-wave gaps. Ordering: Magnetic ordering (order-FM: $J > 0$ and $\Delta > 0$, disorder-FM: $J > 0$ and $\Delta < 0$, order-AFM: $J < 0$ and $\Delta > 0$, disorder-AFM: $J < 0$ and Δ is imaginary). ES: Electronic state (M: Metal, HM: Half-Metal, S: Semiconductor).

Chapter 4

Designing Phosphorus 2D-Allotrope

4.1 Introduction

Bulk phosphorus allotropes expand various structure, including white, red, black, and violet phosphorus. In two-dimensional materials, in addition to monolayer black phosphorus obtained by exfoliation from bulk black phosphorus[47], various phosphorus networks such as octagonal and kagome phases based on planar tiling motifs have been proposed[154, 155]. However, the relationship between the two-dimensional phosphorus networks and their electronic properties has not been fully clarified. In this chapter, first-principles calculations are performed under consistent conditions for two-dimensional phosphorus networks, and the electronic structures of the black-phosphorus, octagonal, and kagome phases are comparatively analyzed. Furthermore, the synthesis possibility for the octagonal and kagome phosphorus phases are investigated as a basis for synthesis experiments.

4.2 Methodology

The grid-based projector augmented wave software package (GPAW) within density functional theory (DFT) is implemented [124]. The calculations are performed with a plane-wave cutoff of 400 eV. The exchange–correlation of Perdew–Burke–Ernzerhof is implemented with spin polarization[132]. The exchange–correlation functional

of GLLB-SC is applied to monolayer band structure calculation to correct kohn-sham band gaps[133]. The exchange–correlation functional of vdW-DF is applied to metal-supported monolayer calculation to consider the dispersion[120]. The special k points for Brillouin-zone sampling are set to (8, 8, 1), (2, 2, 1), and (4, 4, 4) for the monolayer calculation, the metal-supported monolayer calculation, and the bulk gold phosphide calculation, respectively[121]. The relaxation procedure is executed until the forces on each atom are smaller than $0.10 \text{ eV}\text{\AA}^{-1}$. Bader charge analysis is implemented to understand the charge transfer [137, 156].

The cohesive energy E_{coh} is calculated to consider thermodynamic stability[145].

$$E_{coh} = \frac{E_{2D}}{N_P} - \frac{E_{P_4}}{4} \quad (4.1)$$

where E_{2D} is the energy of phosphorus monolayer, N_P is the number of P atoms in monolayer, and E_{P_4} is the energy of white phosphorus. A negative E_{coh} means the materials can be formed from gas phase exothermically.

The lattice mismatch between monolayer and support metals $L_{mismatch}$ is calculated to select proper metal supports[157].

$$L_{mismatch} = \frac{L_{2D} - L_{metal}}{L_{metal}} \times 100\% \quad (4.2)$$

The formation energy of the metal supported monolayer E_f is calculated to consider thermodynamic stability on metal support[158].

$$E_f = \frac{E_{all} - E_M}{N_P} - \frac{E_{P_4}}{4} \quad (4.3)$$

where E_{all} is the energy of metal supported monolayer, N_P is the number of P atoms in monolayer, E_M is the energy of metal support, and E_{P_4} is the energy of white phosphorus. A negative E_{coh} means the materials on the metal support can be formed from gas phase exothermically.

The interlayer binding energy per area between monolayer and the support metal is calculated to consider the interlayer interaction[159].

$$E_{bind} = \frac{E_{all} - E_{2D} - E_M}{A} \quad (4.4)$$

where E_{all} is the energy of metal supported monolayer, E_{2D} is the energy of free-standing monolayer, E_M is the energy of metal support, and A is the surface area.

4.3 Results and Discussion

4.3.1 Theoretical Exploration of Phosphorus 2D-Allotrope

Table 4.1. Structural and electronic properties of two-dimensional black, octagonal, and kagome phosphorus. E_{coh} : cohesive energy, E_{PBE} : the band gap calculated using PBE functional, $E_{GLLB-SC}$: the band gap calculated using GLLB-SC functional.

Phase	E_{coh} [eV/atoms]	E_{PBE} [eV]	$E_{GLLB-SC}$ [eV]
Black P	-0.12	0.90	1.20
Octagonal P	0.01	1.88	2.07
Kagome P	0.09	0.42	0.69

Two-dimensional black, octagonal, and kagome phosphorus are explored using DFT calculations. Structural and electronic properties of these two-dimensional black, octagonal, and kagome phosphorus networks are summarized in Table 5.1, while the atomic models of the two-dimensional phosphorus structures are shown in Fig. 4.1. Here, the structure of black phosphorus is derived from the corresponding bulk structure, whereas the octagonal and kagome phases are constructed from two-dimensional tilings with the (4,8) pattern and the (3,6) pattern, respectively, as shown in Fig. 4.1. The lattice constants are calculated to be 4.63 Å and 3.31 Å for black phosphorus, 6.27 Å for octagonal phosphorus, and 5.06 Å for kagome

phosphorus, and they show good agreement with previously reported bond distances[154, 155, 160].

The cohesive energy of black phosphorus is calculated to be -0.12 eV, while those of the octagonal and kagome phases are 0.01 eV and 0.09 eV, respectively, as shown in Table 5.1. These results indicate that black phosphorus is formed exothermically from the gas phase, whereas the other phases exhibit endothermic formation from the gas phase. Because the cohesive energies of the octagonal and kagome phases are slightly positive, the interface energy with a metal support can stabilize these phases.

The electronic structures of two-dimensional black, octagonal, and kagome phosphorus are then investigated. Two-dimensional black phosphorus is calculated to have a band gap of 0.90 eV using the PBE functional and 1.20 eV using the GLLB-SC functional, as shown in Table 5.1. These results indicate that black phosphorus acts as a semiconductor. The experimentally observed band gap is 1.73 eV[161], thus GLLB-SC is more suitable for reproducing the band gap of the two-dimensional phosphorus monolayer. The octagonal phase results in a band gap of 2.07 eV using the GLLB-SC functional, demonstrating that the band gap can be broadened by modifying the configuration to the octagonal phase. In the case of the kagome configuration, it is interesting that the band gap is calculated to be 0.69 eV using the GLLB-SC functional, which is smaller than the band gaps of the black and octagonal phases. Hence, modifying the configuration to the kagome phase can narrow the band gap of the two-dimensional phosphorus monolayer.

Further detailed analysis of the band structures is carried out. The band structures of two-dimensional black, octagonal, and kagome phosphorus are shown in Fig. 4.1. The projected density of states for these three two-dimensional phosphorus networks is also shown in Fig. 4.3. One can see that the band structures vary depending on the configuration of the two-dimensional phosphorus network. The results demonstrate that black phosphorus has a direct band gap, whereas the octagonal and kagome phases have indirect band gaps.

The DFT calculations show that black phosphorus has a direct band gap of 1.20 eV in the visible region, which is consistent with its promising applications in solar cells[162]. The kagome phosphorus network has an indirect band gap of 0.69 eV in the infrared region, suggesting potential for infrared optoelectronic applications. The octagonal phosphorus network has an indirect band gap of 2.07 eV, suggesting potential for photocatalytic applications. Therefore, two-dimensional phosphorus networks provide tunable band gaps from the visible to the infrared region and can be considered as candidate materials for a wide variety of applications.

Table 4.2. Properties of metal supported 2D-phosphorus. $L_{mismatch}$: Lattice mismatch between monolayer and support metals, D : the distance between monolayer and support metals, E_f : formation energy of the metal supported monolayer, E_{bind} : the interlayer binding energy per area between monolayer and support metals.

Phase	$L_{mismatch}$ [%]	D [Å]	E_f [eV/atoms]	E_{bind} [eV/Å ²]
Octagonal P on Au(100)	0.72	2.48	-0.14	-0.03
Kagome P on Cu(111)	2.17	2.76	-0.02	-0.06

The metal-supported phosphorus monolayer is considered to demonstrate the synthesis possibility of the octagonal and kagome phases. The (100) surface of gold and the (111) surface of copper are selected to support the octagonal and kagome phosphorus monolayers, respectively, as shown in Fig. 4.2. By constructing a 3×3 supercell of the 4.21 Å surface of gold and a 2×2 supercell of the 6.27 Å surface of octagonal phosphorus, a metal–monolayer interface with 0.72% lattice mismatch is obtained, which allows epitaxial growth via domain-matching epitaxy. In the same way, the 5.17 Å surface of copper and the 5.06 Å surface of kagome phosphorus are combined to obtain a metal–monolayer interface with 2.48% lattice mismatch, which allows epitaxial growth. The distances between the

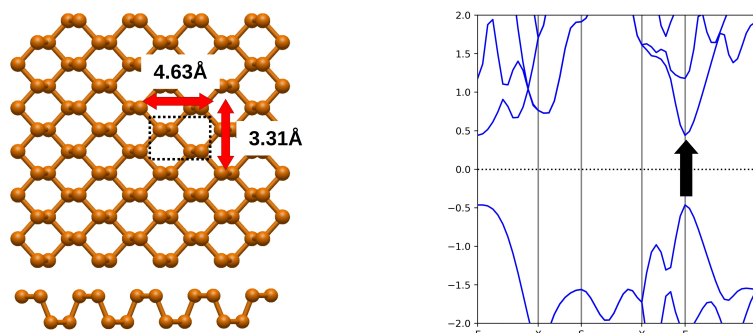
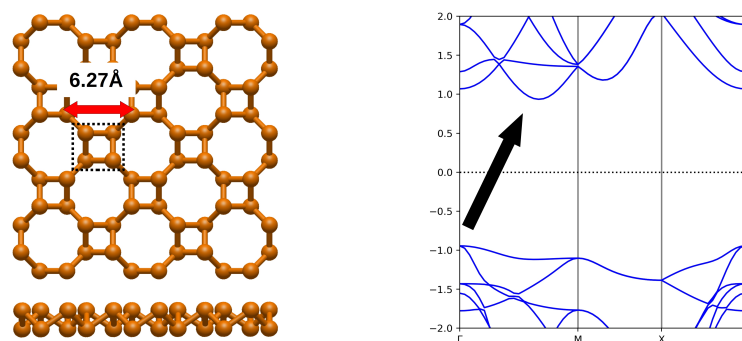
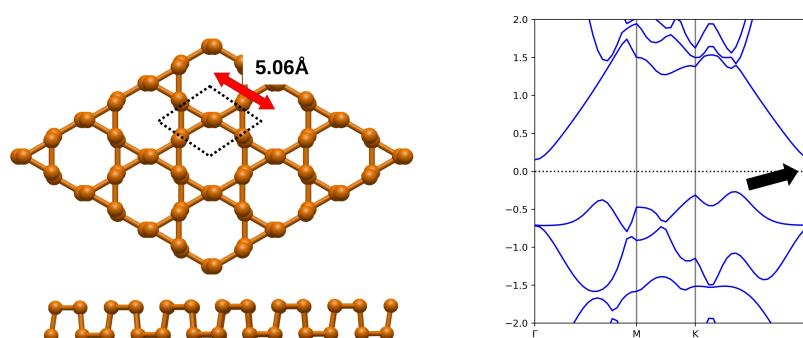
(a) Black Phosphours**(b) Octagonal Phosphours****(c) Kagome Phosphours**

Figure 4.1. The illustration and band structure of 2D-phosphorus networks. Dot lines indicate pedoric boundary.

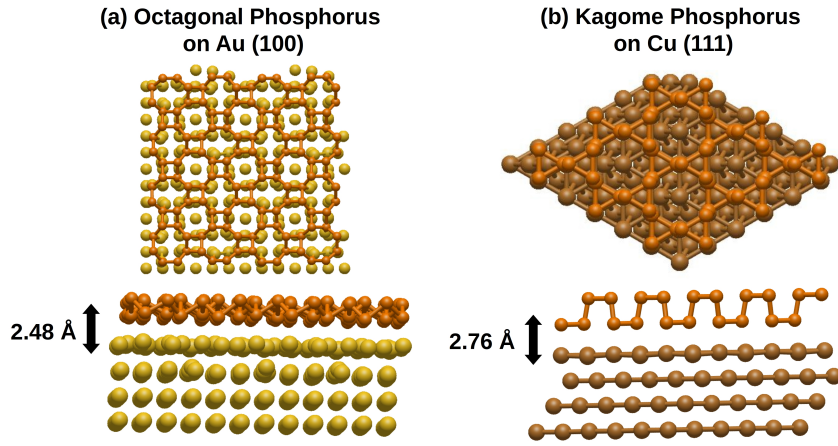


Figure 4.2. The illustration of (a) Octagonal Phosphorus on Au (100) and (b) Kagome Phosphorus on Cu (111).

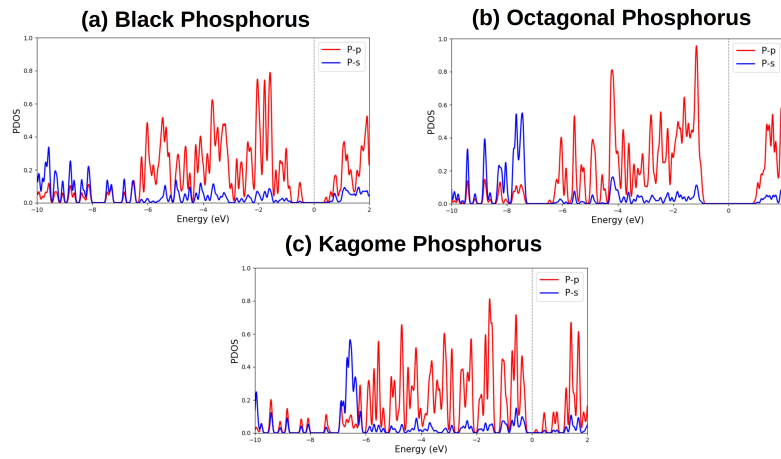


Figure 4.3. PDOS of 2D- (a) black, (b) octagonal, and (c) kagome phosphorus. red indicates p-orbital of P atom and blue indicates s-orbital of P atom.

supporting metal and the monolayer are 2.48 Å for the octagonal phosphorus and 2.76 Å for the kagome phosphorus, respectively.

The formation energy and interlayer binding energy are calculated to demonstrate the synthesis possibility of the phosphorus monolayer on metal supports, as shown in Table 5.2. The results indicate that the formation energies of the octagonal and kagome phases are -0.14 eV and -0.02 eV, respectively, so both phases can be formed exothermically from the gas phase. The interlayer binding energies of the octagonal and kagome phases are calculated to be -0.03 eV/Å² and -0.06 eV/Å², respectively, which are comparable to typical separation energies reported for mechanically exfoliated two-dimensional materials[163]. In particular, octagonal phosphorus is more stable on the gold surface, and the interlayer binding energies are moderate enough to allow exfoliation of the monolayer. Accordingly, the synthesis of octagonal phosphorus on gold is experimentally investigated.

4.3.2 Synthesization and Characterization of Gold Phosphide Phase Transformed from Gold Mesh

The synthesis experiment of 2D-phosphors on gold is conducted by annealing Au mesh in phosphorus vapor. A quartz tube with an outer diameter of 15 mm, a wall thickness of 1 mm, and a length of 100 mm is selected as the growth container, which is dried in oven after cleaning. Red phosphorus (50 mg, RP, 99.9999%, FU-RUUCHI CHEMICAL), quartz cotton, and Au mesh (300 mg, 99.95%, THE NILACO CORPORATION) are put into a quartz tube. After being sealed under a vacuum (<10 Pa) using rotary pump and turbo molecular pump, the quartz tube is put into the tube furnace. RP is located in the low-temperature zone of quartz tube, and Au mesh is in the high-temperature zone. The reactor is heated to 600 °C at a rate of 10 °C/min from room temperature and kept for 1 h of heat preservation at this temperature. After the reaction, gold mesh turns to black and white phosphorus chunk is remained, as shown in Fig. 4.4(b). The black samples is taken from

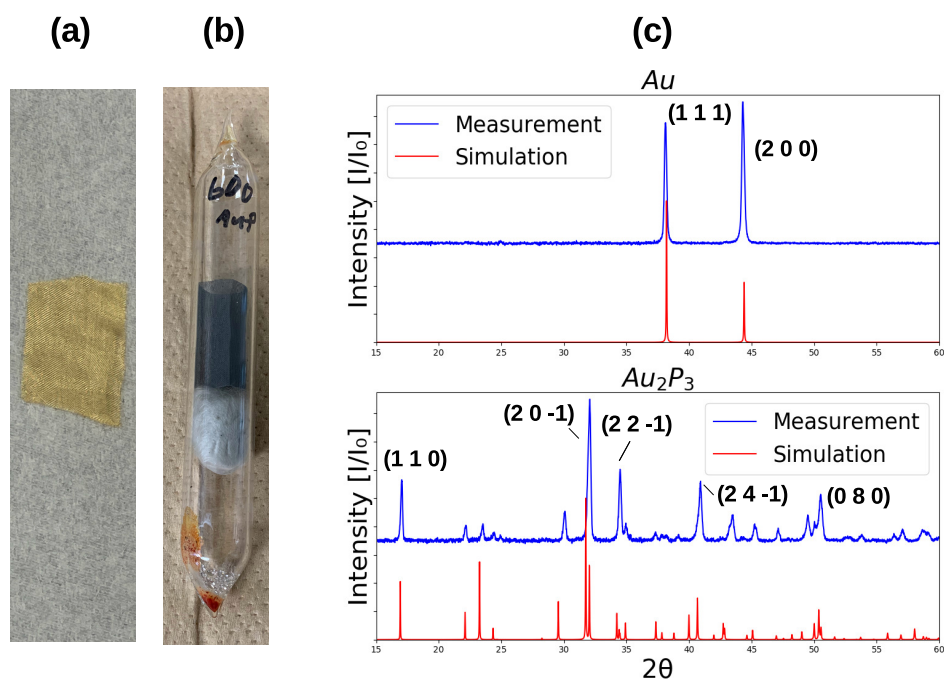


Figure 4.4. (a) Au mesh before reaction. (b) Gold phosphide (Au_2P_3) mesh in quartz tube. (c) XRD patterns of Au and Au_2P_3 mesh. Blue lines represent measured peaks and red lines represent simulated peaks.

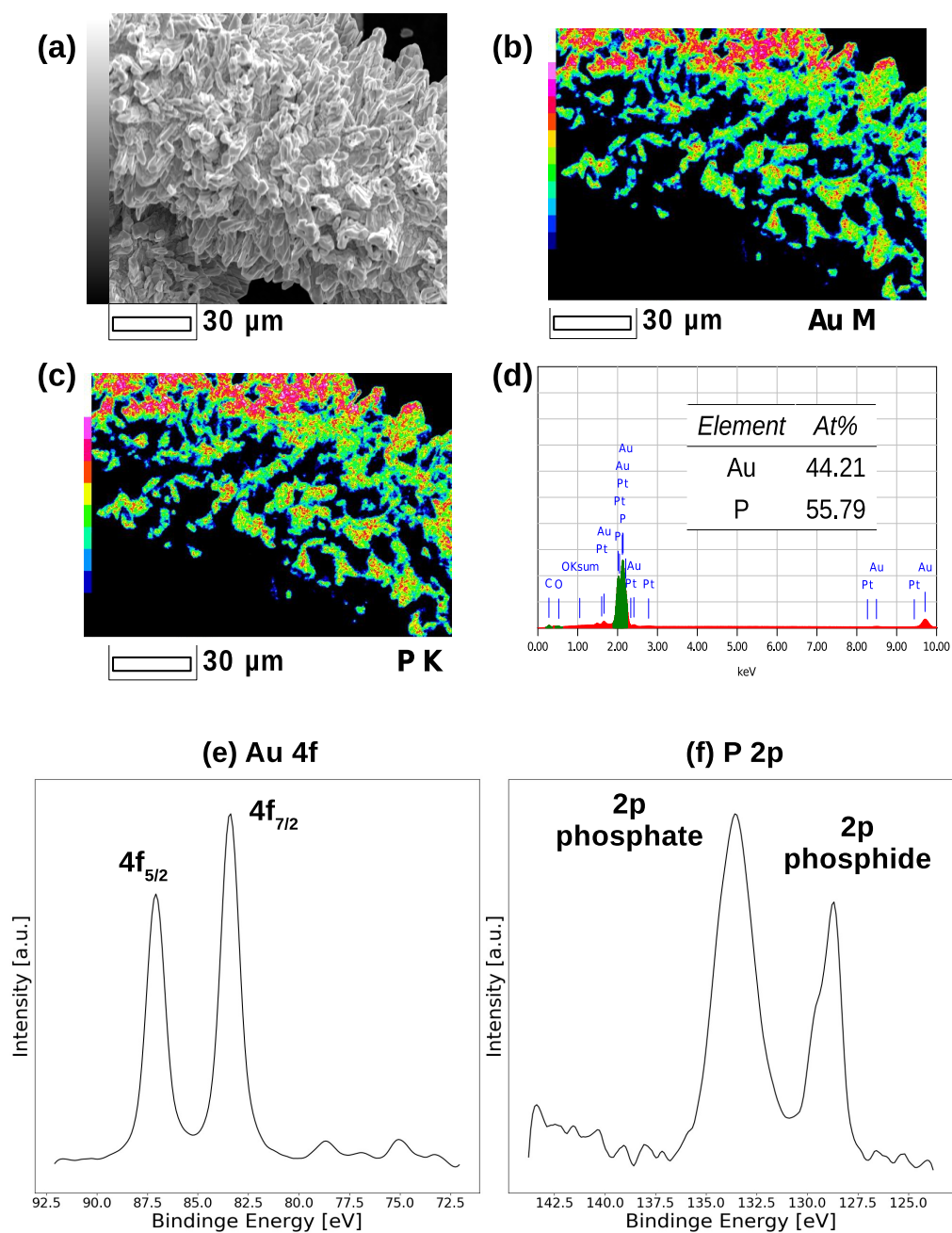


Figure 4.5. The SEM image and EDS spectrum of Au_2P_3 . (a) SEM image of the Au_2P_3 mesh. (b) Element scanning mapping of Au element and (c) P element of Au_2P_3 . (d) Element contents of Au and P in the sample. (e)(f) XPS patterns of Au 4f and P 2p orbitals of Au_2P_3 .

quartz tube and washed by water to remove white phosphorus under extra careful precautions.

The X-ray diffractometers (XRD, Rigaku, MiniFlex600) shows sample has Au_2P_3 peaks as shown in Fig. 4.4(c), which indicates that bulk gold is transformed to gold phosphide phase. Although this result differs from 2D phosphorus on a gold support, the properties of this gold phosphide phase have not been investigated in detail. Therefore, further characterization of this material is carried out.

The analysis including scanning electron microscope (SEM, Hitachi High-Tech, SU1510), and X-ray energy scattering spectroscopy (EDS) are conducted to understand the size, morphology, and composition of sample. SEM images are acquired using an accelerating voltage of 20 kV under a vacuum of 30 Pa. The sample for SEM is coated by platinum to improve electronic conductivity. SEM image and EDS spectrum indicate that Au_2P_3 crystal size is $\sim 10 \mu\text{m}$ and the ratio of P/Au is 1.26 as shown in Fig. 4.5(a) and (d).

X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9200) with a Mg-K α X-ray source (10 mA, 10 kV) is performed in order to analyze the surface electron states of Au_2P_3 as shown in Fig. 4.5(e)(f). The result indicates that the surface electron state of Au_2P_3 is characterized by Au 4f peaks at 83.4 eV and 87.1 eV and P 2p peaks at 128.7 eV and 133.5 eV. The Au peaks are shifted to lower binding energies relative to metallic Au (~ 84 eV for 4f $_{7/2}$ and ~ 88 eV for 4f $_{5/2}$), suggesting covalent environment around the Au atoms[164]. Meanwhile, the primary P peak at 128.7 eV is comparable to the peak observed in typical metal phosphides (~ 129 eV), and the higher-energy peak at 133.5 eV is attributed to surface-oxidation-induced phosphate species[164]. These observations imply that Au_2P_3 forms covalent bonds rather than ionic bonds.

Both DFT calculations and X-ray diffraction (XRD) analysis reveals matching lattice constants; the DFT-computed values are $a = 5.89 \text{ \AA}$, $b = 14.43 \text{ \AA}$, $c = 4.73 \text{ \AA}$,

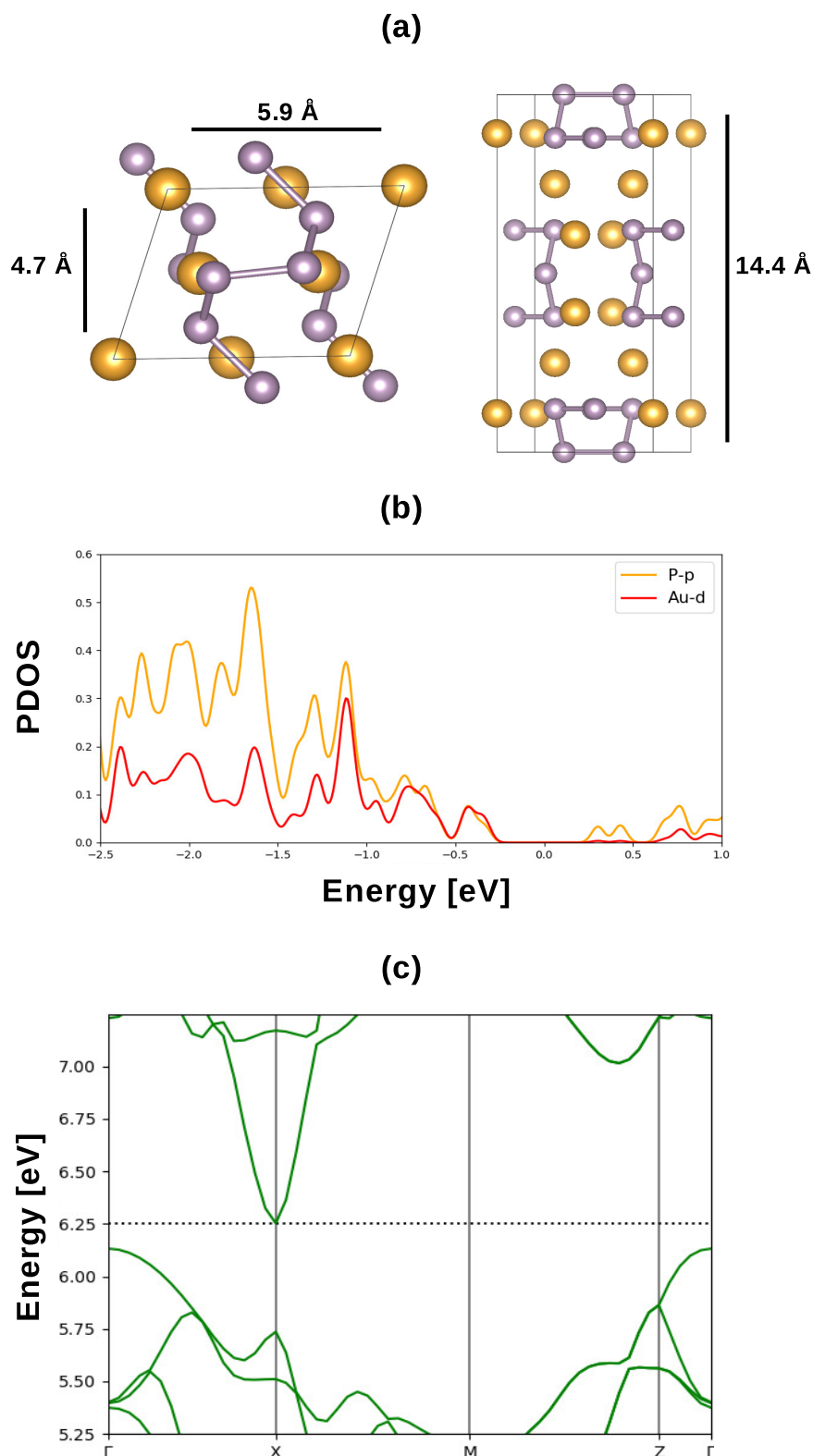


Figure 4.6. (a) The illustration of Au_2P_3 structure. Atomic color code: yellow-gold, purple-phosphorus. (b) Projected density of states (PDOS) between Au-d and P-p states. (c) The electronic band structure of Au_2P_3 . Dot line indicates Fermi level.

while experimental values are $a = 5.86 \text{ \AA}$, $b = 14.43 \text{ \AA}$, $c = 4.67 \text{ \AA}$, indicating reliable reproduction of the crystal structure, as shown in Fig. 4.6(a). Moreover, X-ray diffraction patterns are simulated using visualization for electronic and structural analysis (VESTA)[165], as shown in Fig. 4.4(c). The result shows agreement with experimental data, reinforcing structural accuracy predicted by the computational approach.

Electronic structure analysis using Bader charge distribution and projected density of states (PDOS) further aligns with X-ray photoelectron spectroscopy (XPS) findings. The Bader analysis yields subtle charge transfers of approximately $+0.1e$ on phosphorus (P) atoms and $-0.1e$ on gold (Au) atoms, indicative of a covalent bonding character. PDOS shows overlapping between Au-d and P-p states in the range of -1.1 to -0.4 eV, as shown in Fig. 4.6(b). The result supports the covalent bonding character, indicating agreement with the Bader analysis and XPS measurements.

The electronic band structure is demonstrated to understand a electronic nature of Au_2P_3 , as shown in Fig. 4.6(c). The result indicates an indirect band gap between the Γ and X points. The band gap is calculated to be 0.12 eV using PBE functional, while employing the GLLB-SC functional yields a band gap of 0.17 eV. Materials with an indirect band gap of 0.17 eV are ideally suited for mid-infrared photodetectors[166, 167]. Thus, Au_2P_3 exhibits promising semiconducting behavior with an indirect band gap.

4.4 Conclusion

Two-dimensional black, octagonal, and kagome phosphorus networks are investigated using DFT to clarify their structural stability, electronic properties, and synthesis feasibility. Black phosphorus is derived from the bulk structure, whereas the octagonal and kagome phases are constructed from (4,8) and (3,6) tilings. Cohesive-energy analysis shows that black phosphorus is exothermically formed from the

gas phase, while the octagonal and kagome phases are slightly endothermic, implying that interaction with metal supports is required to stabilize. GLLB-SC band-gap calculations reveal a direct 1.20 eV gap for black phosphorus and indirect gaps of 2.07 eV and 0.69 eV for the octagonal and kagome networks, suggesting potential applications in solar cells, photocatalysis, and infrared optoelectronics. By selecting lattice-matched Au(100) and Cu(111) surfaces, metal–monolayer interfaces with small lattice mismatch and moderate interlayer binding energies are obtained, indicating that the octagonal and kagome phosphorus monolayers can be formed and exfoliated.

A synthesis experiment of two-dimensional phosphorus on gold is carried out by annealing Au mesh in red phosphorus vapor, but XRD analysis revealed that the Au mesh is converted into crystalline Au_2P_3 rather than forming a 2D phosphorus layer, motivating further investigation of this gold phosphide. SEM–EDS characterization shows that Au_2P_3 crystals with a size of $\sim 10\ \mu\text{m}$ are obtained and that the P/Au ratio is 1.26, consistent with the stoichiometry. XPS analysis identifies Au 4f peaks shifted to lower binding energy relative to metallic Au and P 2p peaks characteristic of metal phosphides with additional surface-oxidized phosphate species, indicating that Au_2P_3 is governed by covalent rather than ionic bonding. DFT calculations reproduce the experimental lattice constants and XRD pattern, and Bader charge analysis together with PDOS confirms small charge transfer and strong overlap between Au–d and P–p states, further supporting the covalent character. Band-structure calculations reveal an indirect band gap of 0.17 eV (GLLB-SC) between the Γ and X points, placing Au_2P_3 in the regime relevant for mid-infrared photodetection and demonstrating that the synthesized gold phosphide is a promising narrow-gap semiconductor.

At the same time, the conversion to Au_2P_3 instead of a 2D phosphorus monolayer indicates that metastable two-dimensional phases require careful control of the phosphorus chemical potential, for example through molecular beam epitaxy. Indeed, boron- and phosphorus-based 2D materials supported on metal surfaces

have been obtained by molecular beam epitaxy under ultra-high vacuum conditions[168, 169]. Establishing synthesis strategies for bottom-up prototype 2D materials is therefore essential to translate theoretical design principles into experimentally accessible phases and to expand the two-dimensional materials space beyond bulk-derived structures.

Chapter 5

Theoretical Investigation of Metal-Absorption for Cyanographene

5.1 Introduction

Two-dimensional materials are reported to have more metal adsorption sites than bulk materials because of their high surface area[170]. On the other hand, graphene itself is a stable π -electron system and therefore does not readily form stable chemical bonds with metals[171]. Functionalized graphene, represented by cyanographene and graphene acid, is expected to be applied to battery materials, catalytic materials, and metal recovery, because polar functional groups promote metal adsorption[91, 92, 172]. To date, metal adsorption on functionalized graphene is investigated from both theoretical and experimental perspectives. However, most studies focus on individual elements, and comprehensive analyses of metal adsorption across multiple elements are still limited.

In Chapter 5, the adsorption of alkali and alkaline-earth metals on cyanographene are evaluated via high-throughput calculation to understand the elemental trends and their potential applications. Furthermore, based on the result of high-throughput calculations, the potential of cyanographene for sodium-ion battery applications is identified. Further detailed analyses of sodium adsorption and diffusion are carried out for cyanographene and the corresponding layered material, cyanographite[173].

5.2 Methodology

The grid-based projector augmented wave (GPAW) software package within density functional theory (DFT) calculations is implemented[124]. The exchange-correlation of vdW-DF[120] based on Perdew–Burke– Ernzerhof (PBE) [132] is implemented with spin polarization to consider the effect of van der Waals forces. All calculations are performed with a plane-wave cutoff of 400 eV. $4 \times 4 \times 1$ and $4 \times 4 \times 4$ special k points of the Brillouin zone sampling is applied to cyanographene and cyanographite, respectively[121]. The relaxation procedure is executed until the forces on each atom are smaller than $0.02 \text{ eV } \text{\AA}^{-1}$. Bader charge analysis is implemented to understand the charge transfer[137, 156]. The transition states energies are obtained using the Nudged Elastic Band (NEB) method by considering ten images between each state.

The structure of cyanographene and cyanographite is shown in Figure 5.1. Cyanographene is modeled as a supercell (3×3) of graphene, with two cyano groups on each side. In cyanographene, periodic boundary conditions are set in the x and y axes with $12 \text{ \AA}$ of vacuum in the z-axis. The interlayer distance of cyanographite is $9.90 \text{ \AA}$, which is larger than the $3.35 \text{ \AA}$ interlayer spacing of graphite[174]. This enlarged spacing provides adsorption space and promotes interactions between sodium and cyanographite. Note that experimentally reported cyanographite is a composite of paracyanogen and cyanographite with a low density of cyano groups[173]. In this study, cyanographite is modeled as layered cyanographene to enable simple calculations.

The adsorption energy (E_{ads}) of Metal atoms is calculated using the Equation 5.1:

$$E_{ads} = \frac{E_{all} - (E_{cg} + N_M E_M)}{N_M} \quad (5.1)$$

E_{ads} where E_{all} is the energy of the system, E_{cg} is the energy of cyanographene or cyanographite, E_M is the energy of metal atom in bulk metal, N_M is the number of metal atoms. Negative E_{ads} values represent exothermic adsorption and positive

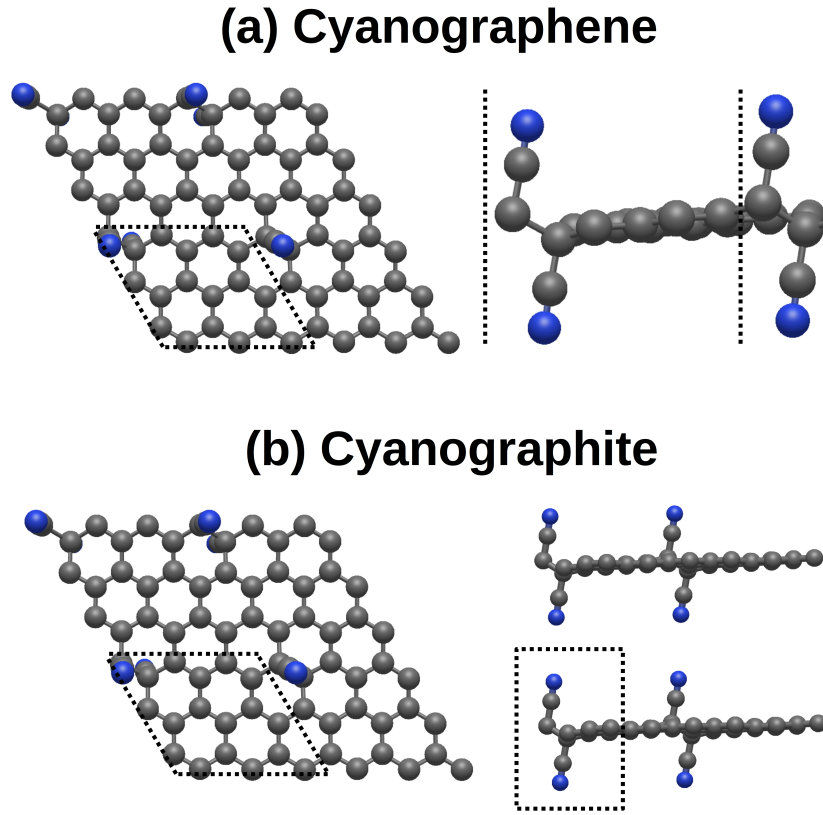


Figure 5.1. The illustration of the (a) cyanographene, (b) cyanographite. The dot stands for the periodic boundary. Atomic color code: gray-carbon, blue-nitrogen.

values represent repulsion of metal atom to cyanographene or cyanographite.

The number of alkali metals per 100 graphene carbons S is calculated by Equation 5.2:

$$S = \frac{N_M}{N_C} * 100 \quad (5.2)$$

N_M and N_C stand for the number of metals and graphene carbon in the calculated model.

The binding energy E_{bind} between graphene and CN group is calculated by Equation 5.3:

$$E_{bind} = E_{cg} - 2E_{CN} - E_g \quad (5.3)$$

E_{bind} where E_{cg} is the energy of cyanographene, E_{CN} is the energy of isolated cyano group and E_g is the energy of graphene. It indicates that graphene-CN bond is stable because the binding energy is under zero.

The average open-circuit voltages (OCV) [175] is able to be estimated from the Equation 5.4:

$$OCV = \frac{E_{cg} + N_{Na}E_{Na} - E_{all}}{N_{Na}} \quad (5.4)$$

N_{Na} stands for the number of Na in the calculated model.

5.3 Results and Discussion

5.3.1 High-throuput DFT calculation for Metal Adsorption on Cyanographene

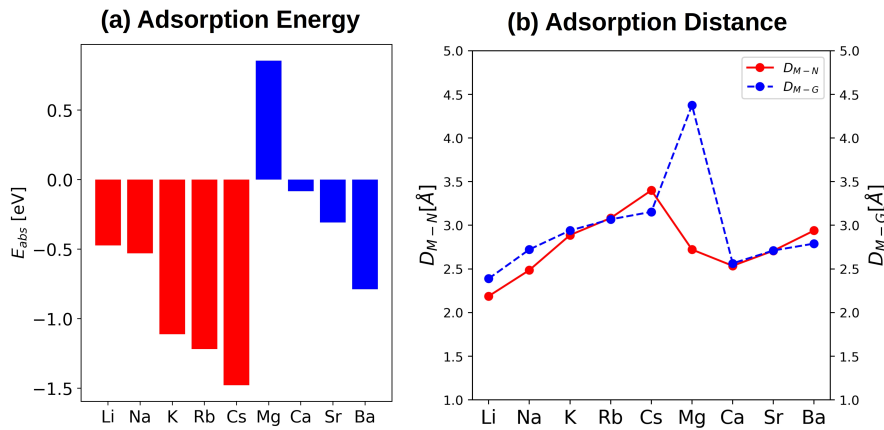


Figure 5.2. (a) The adsorption energy E_{ads} of metal atoms to cyanographene. $E_{ads} < 0$ indicates exothermic adsorption. Alkaline metals are shown as red and alkaline earth metals are shown as blue. (b) Adsorption distance between metal-nitrogen of cyano group D_{M-N} (red) and metal-carbon of graphene D_{M-G} (blue).

High-throughput DFT calculations reveal the adsorption behavior of alkali and alkaline-earth metals on cyanographene. Adsorption energies are calculated to investigate the trend in metal adsorption, as shown in Fig. 5.2(a). Mg shows an adsorption energy of +0.85 eV, indicating endothermic adsorption, whereas the

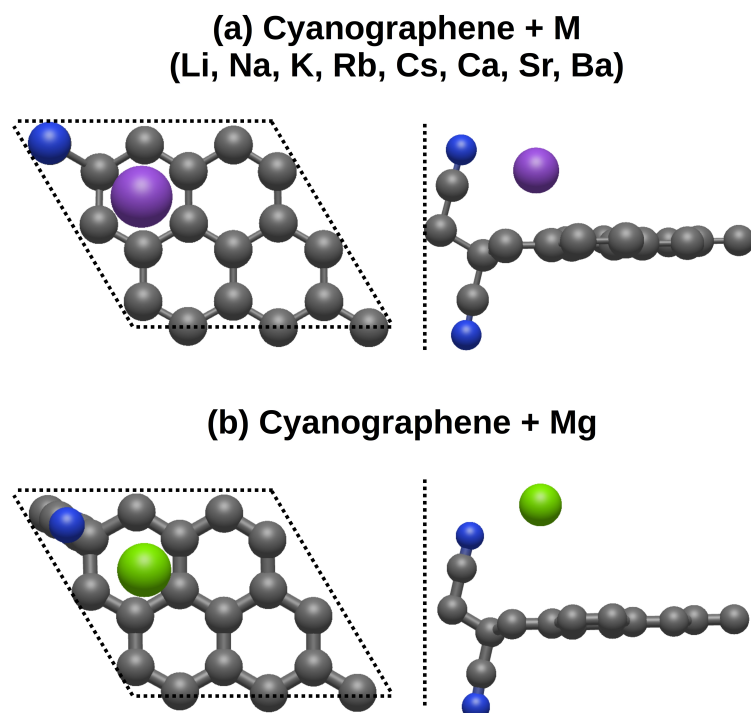


Figure 5.3. The illustration of metal adsorption to cyanographene. (a) The adsorption of Li, Na, K, Rb, Cs, Ca, Sr, and Ba. The metals are adsorbed between a cyano group and graphene. (b) The adsorption of Mg. The metal is adsorbed near a cyano group.

other metals exhibit negative adsorption energies and are therefore adsorbed on cyanographene exothermically. For both the alkali and alkaline-earth series, elements lower in the periodic table show more negative adsorption energies, corresponding to stronger adsorption on cyanographene. This trend is consistent with their smaller ionization energies.

The distances between the adsorbed metal and the nitrogen atom of the cyano group (D_{M-N}) and the graphene carbon atom (D_{M-C}) are evaluated to analyze the adsorption sites, as shown in Fig. 5.2(b). In general, elements located lower in the periodic table have larger ionic radii and tend to exhibit longer adsorption distances. Mg is an exception to this trend: its distance to graphene is 4.38 Å,

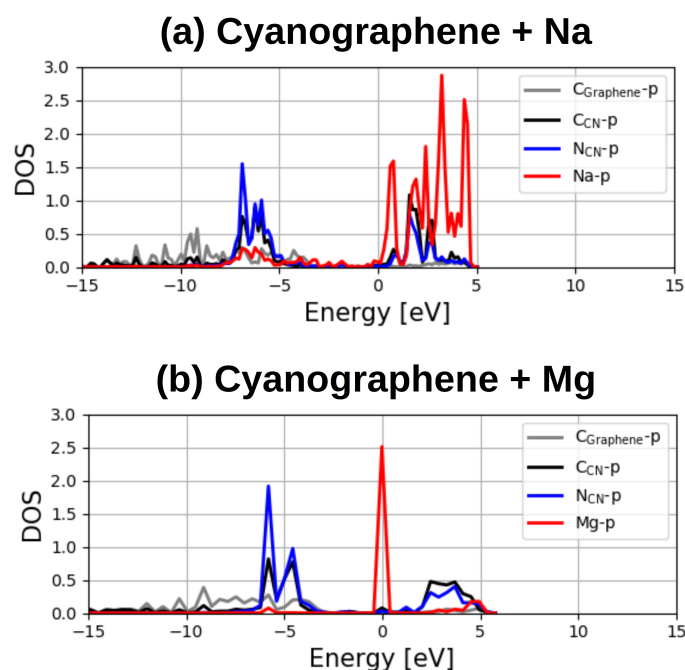


Figure 5.4. Projected density of states (PDOS) where the p-orbitals of carbon of graphene part, carbon of cyano group, nitrogen of cyanogroup and sodium are plotted in gray, black, blue and red, respectively. (a) The adsorption of Na and (b) Mg.

which is significantly larger than the 2.4–3.1 Å observed for the other metals. This difference is explained by the fact that the other metals are adsorbed between the cyano group and the graphene sheet, whereas Mg interacts only with the cyano group, as shown in Fig. 5.3.

Bader charge analysis is performed to investigate charge transfer on the metal atoms. The results show that the alkali metals (Li, Na, K, Rb, Cs) are positively charged by 0.9 electrons, whereas the alkaline-earth metals (Ca, Sr, Ba), except Mg, are positively charged by 1.3 electrons. These positive charges indicate an ion-like interaction between the metals and cyanographene, which promotes metal adsorption. In contrast, Mg has a smaller positive charge of about 0.3 electrons,

meaning that cyanographene does not significantly promote the ionization of Mg. This is consistent with the endothermic adsorption of Mg on cyanographene.

The projected density of states (PDOS) is calculated to clarify the electronic-structure difference between Na adsorption and Mg adsorption, as shown in Figure. 5.4. The PDOS between Na and the C atoms of graphene reveals overlap p states near -7 eV, whereas no overlap is observed between Mg and the C atoms of graphene. These results indicate that electron pairing between CN–Na contributes to the adsorption of Na, whereas graphene does not contribute to the adsorption of Mg.

The potential application of metal–cyanographene is evaluated based on the adsorption energy. Li, Na, and K adsorption can be applied to ion batteries. In particular, the adsorption energies of Li and Na are about -0.5 eV, which is moderate and allows both high theoretical capacity and facile ion diffusion[176]. The adsorption energies of Rb and Cs are -1.2 eV and -1.5 eV, respectively, indicating that these elements are strongly adsorbed on cyanographene. In particular, Rb adsorption can be applied to rare-metal recovery from sea water, and Cs adsorption can be applied to the recovery of radioactive element[177, 178]. Therefore, the development of cyanographene contributes to energy storage and the recovery of rare metal and radioactive element.

5.3.2 Theoretical Investigation of Cyanographene and Cyanographite for Potential Sodium-Ion Battery

High-throughput DFT calculation reveals that cyanographene has moderate adsorption of Li and Na, which can be applied ion batteries. Generally, lithium ions possess the capability to intercalate within graphite reversibly, achieving significant lithium loadings, extending to a stoichiometry of LiC_6 [36]. This process culminates in a specific capacity approximating 372 mAhg^{-1} , concomitant with

the production of graphite intercalation compounds (GICs)[179]. This reversible, nanoscale phenomenon currently underpins the majority of battery technology.

However, sodium, despite its relative abundance and cost-effectiveness as an alternative charge carrier to lithium, is unfortunately limited by its low capacity to achieve comparable loadings in graphite. Its maximum stoichiometry stands at NaC_{64} , resulting in a considerably lower capacity of approximately 35 mAhg^{-1} [180]. It has been suggested that the weak intercalation of sodium into graphite results from a large ionization energy and ionic radius[181]. Descending the periodic table, alkali metals' ionization energy decreases, while ionic radius increases, leading to weaker electrostatic coupling with graphene. This results in the weakest chemical bond between metal-graphene among alkali metals. Innovative strategies bolstering this electrostatic interaction could foster a new generation of Sodium-Ion Batteries (SIBs)[182].

Here, cyanographene and cyanographite are proposed as materials exhibiting superior storage capacity, facilitating sodium ionization. It is considered to be that the electrostatic interaction between cyano groups and sodium can result in a higher capacity than graphite. To demonstrate the application of cyanographene and cyanographite to SIBs, the adsorption and diffusion energy barrier of sodium atoms are investigated in terms of the first principle calculation.

The adsorption of sodium atoms to cyanographene and cyanographite is investigated to understand the possibility of SIBs. In cyanographene, the sodium atom is adsorbed between the cyano group and graphene part as shown in Figure 5.5(a) (CN-Na-G adsorption). The adsorption energy over cyanographene is calculated to be -0.53 eV as shown in Table 5.1. It is negative and thus the sodium atom is adsorbed in exothermic on cyanographene. The distance between the Na-N of CN is $2.47 \text{ \AA}$, while the distance between Na-C of cyanographene is $2.68 \text{ \AA}$ as shown in Table 5.1. On the other hand, the sodium atom in cyanographite is adsorbed between two CNs in interlayer (CN-Na-NC adsorption) as well as CN-Na-G adsorption, as shown in Figure 5.5(b)(c).

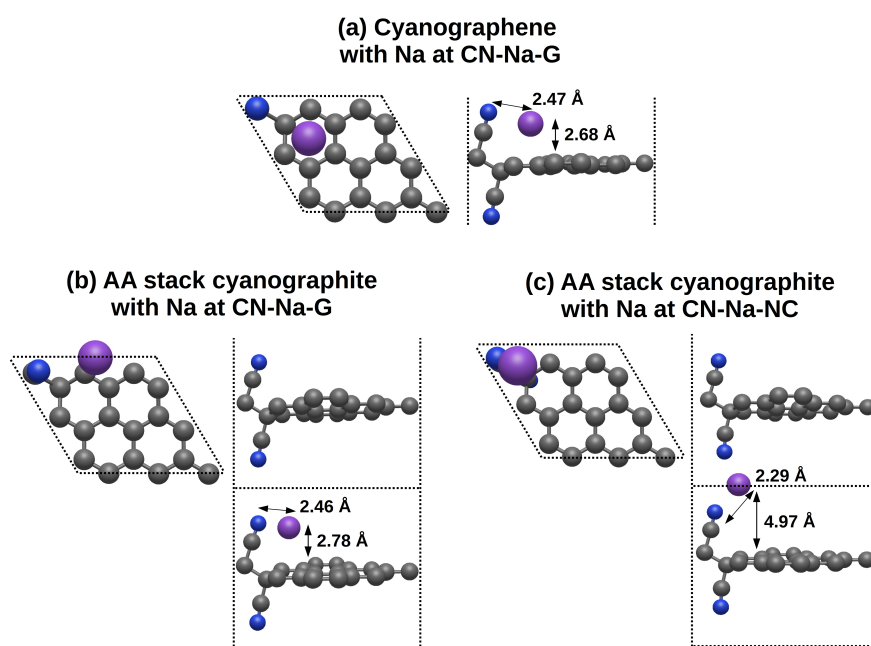


Figure 5.5. The illustration of the sodium adsorption for (a) cyanographene, (b)(c) cyanographite. (a) and (b) indicate sodium atom at CN-Na-G, while (c) indicates sodium atom at CN-Na-NC. The dot stands for the periodic boundary. Atomic color code: gray-carbon, blue-nitrogen, and purple-sodium.

The adsorption energy over cyanographite is calculated to be -0.69 eV for CN-Na-G and -1.12 eV for CN-Na-NC as shown in Table 5.1. They are negative and thus the sodium atom is adsorbed in exothermic on cyanographite. On CN-Na-G adsorption, the distance between Na-N of CN is 2.46 Å, while the distance between Na-C of cyanographite is 2.78 Å. On CN-Na-NC adsorption, the distance between the Na-N of CN is 2.29 Å, while the distance between Na-C is 4.97 Å. Because the sodium atom at CN-Na-NC has interaction with two cyano groups, the adsorption energy for CN-Na-NC of -1.12 eV is larger than CN-Na-G of -0.69 eV as shown in Figure 5.1.

Bader analysis is conducted to determine the charge transfer for the sodium atom and nitrogen of cyanographene or cyanographite, as shown in Table 5.2. Without sodium atoms, the analysis indicates that N of CN is negatively charged

Table 5.1. The adsorption energy E_{ad} and positions of sodium atom to cyanographene and cyanographite. D_{Na-N} and D_{Na-G} stand for the distance between Na-N of CN Na-C of graphene, respectively. CN-Na-G stands for the sodium adsorption between CN-graphene. CN-Na-NC stands for the sodium adsorption between two CNs in the interlayer.

Site	E_{ad} [eV]	D_{Na-N} [Å]	D_{Na-G} [Å]
Cyanographene			
CN-Na-G	-0.53	2.47	2.68
Cyanographite			
CN-Na-G	-0.69	2.46	2.78
CN-Na-NC	-1.12	2.29	4.97

by 0.89 electrons for cyanographene and 0.96 electrons for cyanographite. With the sodium atom at CN-Na-G, the analysis indicates that N of CN is negatively charged by 1.14 electrons for cyanographene and cyanographite. Also, it is observed that the sodium atom is positively charged by 0.91 electrons for cyanographene and cyanographite. With the sodium atom at CN-Na-NC, the analysis indicates that N of CN is negatively charged by 1.14 electrons for cyanographite. Also, it is observed that the sodium atom is positively charged by 0.87 electrons for cyanographite. These results indicate an ionic like interaction between Na and CN in cyanographene and cyanographite. It can be inferred that the interaction fosters sodium atoms adsorption.

The projected density of state (PDOS) is calculated to understand the electronic structure. PDOS among the graphene part, CN, and Na, is shown in Figure 5.6. PDOS among N, C of CN, and Na in cyanographite reveals overlap p-state near -7 eV as shown in Figure 5.6(d)(e), while the others have no overlap. The result indicates that there is electron paring between CN-Na.

The energy barrier for sodium atom diffusion on cyanographene and cyanographite is calculated. Energy profiles are collected in Figure 5.7. In cyanographene, the

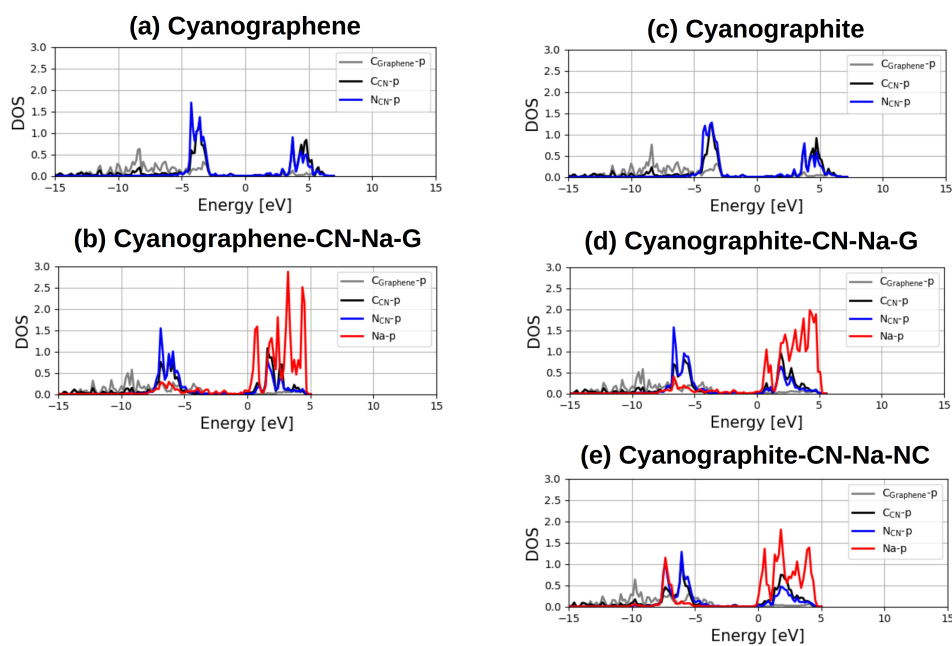


Figure 5.6. Projected density of states (PDOS) where the p-orbitals of carbon of graphene part, carbon of cyano group, nitrogen of cyanogroup and sodium are plotted in gray, black, blue and red, respectively.

Table 5.2. The charge state of cyanographene and cyanographite. V_{Na} and V_{CN} stand for the charge state from the sodium atom and nitrogen atom of cyano group, respectively. Positive values indicate a positive charge.

Site	V_{Na}	V_{CN}
Cyanographene		
Without Na	-	-0.89
CN-Na-G	0.91	-1.14
Cyanographite		
Without Na	-	-0.96
CN-Na-G	0.91	-1.14
CN-Na-NC	0.87	-1.14

diffusion path of the sodium atom is set to connect two CN-Na-G sites as shown in Figure 5.7(a). The highest energy barrier of sodium atom on cyanographene is calculated to be 0.25 eV for $A \rightarrow B$ as shown in Table 5.3. It is relatively lower than 0.48 eV of the energy barrier for lithium atoms on graphite[183]. In cyanographite, the diffusion path of sodium atom is set to connect two CN-Na-G sites and two CN-Na-NC sites as shown in Figure 5.7(b). The highest energy barrier of sodium atom on cyanographite is calculated to be 0.52 eV for $B \rightarrow C$ as shown in Table 5.3. An estimation using the Arrhenius expression indicates that an energy barrier ≤ 0.65 eV will allow facile diffusion at room temperature[182]. Thus, sodium atoms smoothly diffuse on cyanographene and cyanographite.

PDOS between Na and N in absorption site and transition state indicates the rationale for energy profiles as shown in Figure 5.8. In cyanographene energy profile (Figure 5.7 (a)), PDOS for A site has no overlap p-state between N-Na in the range above 0 eV, while transition state T_{AB} between A-B path has overlap p-state near +2 eV as shown in Figure 5.8(a)(b). The overlap p-state in T_{AB} contributes to the energy barrier of 0.25 eV as shown in Table 5.3. In cyanographite energy profile (Figure 5.7 (b)), there is overlap p-state between N-Na near -7 eV in both

Table 5.3. The energy barrier E_{bar} for the sodium atom diffusion on cyanographene and cyanographite.

Site	E_{bar} [eV]		E_{bar} [eV]	
Cyanographene				
A $\rightarrow$ B	0.25	B $\rightarrow$ A	0.15	
Cyanographite				
A $\rightarrow$ B	<0.01	B $\rightarrow$ A	<0.01	
B $\rightarrow$ C	0.52	C $\rightarrow$ B	0.09	
C $\rightarrow$ D	0.28	D $\rightarrow$ C	0.15	

cyanographite A site and transition state T_{AB} as shown in Figure 5.8(c)(d). The result indicates that cyanographite A site and transition state T_{AB} have similar bonding states, thus the energy barrier between A-B is lower than 0.01 eV as shown in Table 5.3. This is because that sodium atom moves around cyano group in A-B path as keeping the distance N-Na of 2.3 Å. PDOS for cyanographite B site has overlap p-state among two nitrogen atoms (top and bottom side) and Na in the range of -8~-7 eV, while transition state T_{BC} between B-C path has overlap p-state only one nitrogen atom (bottom side) and Na in the range of -8~-7 eV as shown in Figure 5.8 (e)(f). The results indicate that the sodium in T_{BC} loses an interaction from a nitrogen atom, which contributes to the energy barrier of 0.52 eV as shown in Table 5.3. PDOS for cyanographite C site has overlap p-state between N-Na near -7 eV, while transition state T_{CD} between C-D path has no overlap p-state as shown in Figure 5.8 (g)(h). The results indicate that sodium in T_{CD} loses an interaction from a nitrogen atom, which contributes to the energy barrier of 0.28 eV as shown in Table 5.3.

To evaluate the sodium storage, sodium atom is added to cyanographene and cyanographite one by one until they are saturated by sodium atoms. The distance between cyano group and graphene part for each number of sodium atoms is shown in Figure 5.9. In cyanographene, the distance between cyano group and

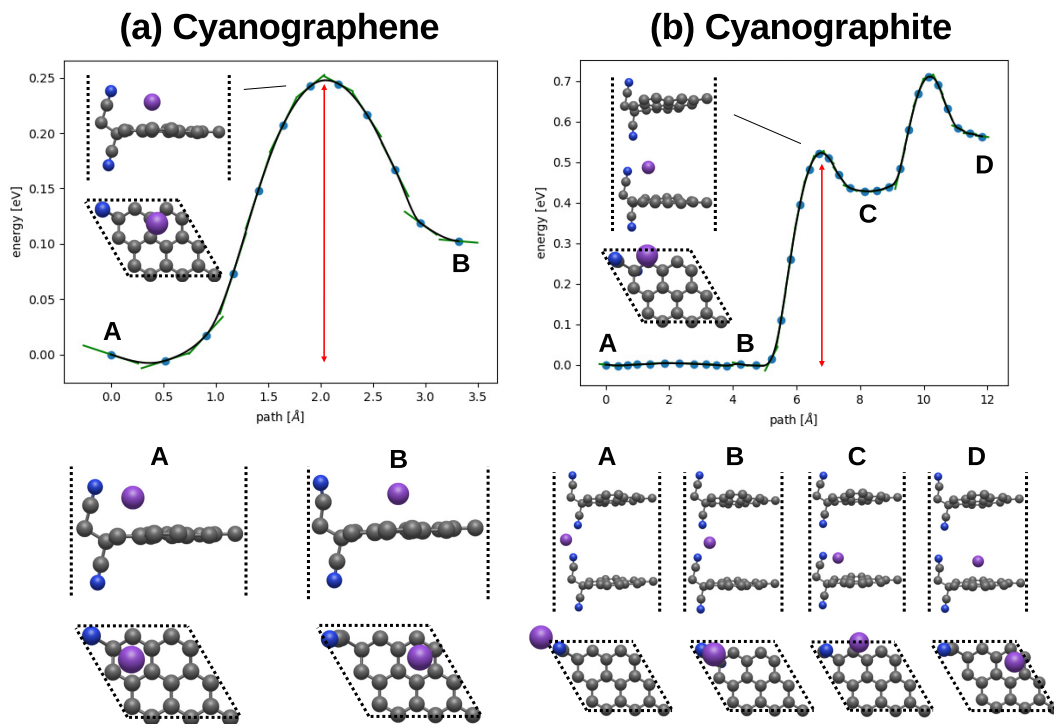


Figure 5.7. Energy profiles of NEB calculation. (a) In cyanographene, the diffusion path of the sodium atom is set to connect two CN-Na-G sites ($A \Rightarrow B$). (b) In cyanographite, the diffusion path of sodium atom is set to connect two CN-Na-G sites and two (CN-Na-NC) sites ($A \Rightarrow B \Rightarrow C \Rightarrow D$). The red arrow stands for the highest energy barrier of 0.25 eV for cyanographene and 0.52 eV for cyanographite.

graphene part increases from 1.55 to 4.22 Å when 5 sodium atoms are added. The results indicate that cyano group is removed from graphene part when 5 sodium atoms are added to cyanographene as shown in Figure 5.10(a). In cyanographite, the distance between cyano group and graphene part increases from 1.50 to 3.35 Å when 6 sodium atoms are added. The results indicate that cyano group is removed from graphene part when 6 sodium atoms are added to cyanographite as shown in Figure 5.10(b).

Moreover, PDOS is calculated to understand the cyano group divergence. PDOS among graphene part, CN, and Na is shown in Figure 5.11. In cyanographene with 4 sodium atoms and cyanographite with 5 sodium atoms, PDOS between C of CN

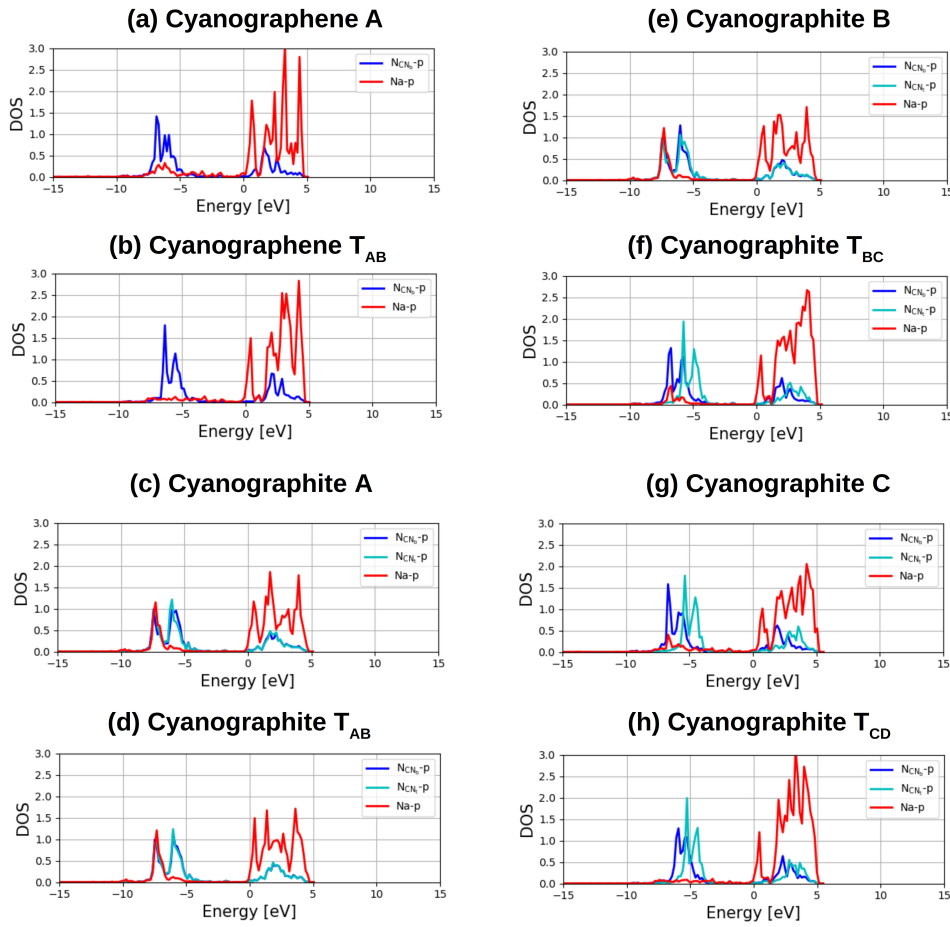


Figure 5.8. Projected density of states (PDOS) where the p-orbitals of sodium (red), nitrogen of bottom layer (blue) and top layer (cyan) plotted.

and graphene part reveals overlap p-state in the range of -7~-6 as shown in Figure 5.11(a)(c). The overlaps indicate electron pairing between graphene part and cyano group. In cyanographene with 5 sodium atoms and cyanographite with 6 sodium atoms, PDOS between C of CN and graphene part is not confirmed, while PDOS between N of CN and Na reveals overlap p-state in the range of -7~-4 eV as shown in Figure 5.11(b)(d). Also, there are overlaps p-state between C of CN and Na near -5 eV for cyanographene and cyanographite as shown in Figure 6(b)(d). The overlaps indicate electron pairing between CN-Na. Therefore, the results are corresponding to cyano group divergence from graphene and forming CN-Na bond as shown in Figure S5. The process of CN separation has no barrier,

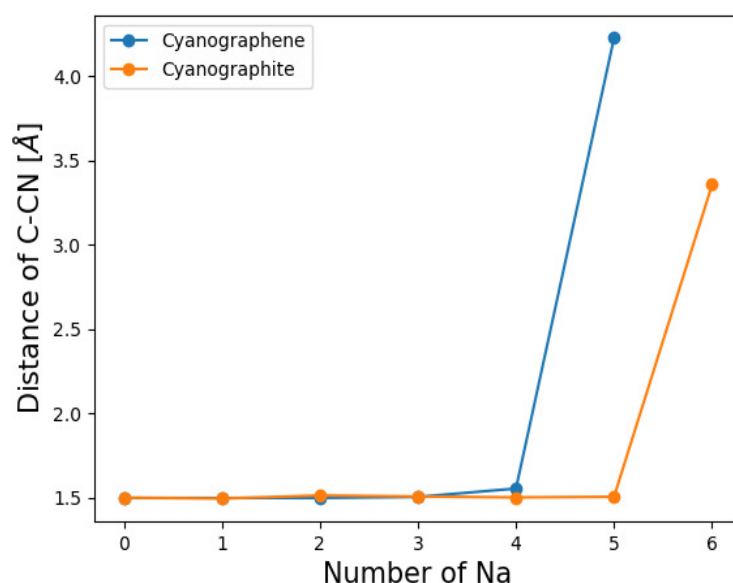


Figure 5.9. The distance between cyano group and graphene part and for each number of sodium atoms. The blue and yellow line stand for cyanographene and cyanographite, respectively.

thus it might be challenging to reform cyanographene or cyanographite.

The average open-circuit voltages (OCV) for each number of sodium atoms is calculated as shown in Figure 5.13. The results show that the first sodium adsorption has OCV of 0.53 eV for cyanographene, and 1.12 eV for cyanographite. When the 5th sodium is adsorbed in cyanographene, OCV increases from 0.15 to 0.96 eV. Also, the 6th sodium adsorption in cyanographite shows that OCV increases from 0.33 to 1.03 eV. These sudden changes of energy changes occur as cyano group is detached from graphene and formed bond to sodium as shown in Figure 5.14.

The maximum sodium adsorption is four atoms for cyanographene and five atoms for cyanographite, as shown in Figure 5.12. The closest distance between two sodium atoms is 3.58 Å for cyanographene and 3.59 Å for cyanographite. The two values of the closest distance between sodium atoms are larger than the bond length of the sodium dimer (experimental bond length is 3.08 Å[184]). Therefore sodium atoms might not agglutinate each other in cyanographene and cyanographite. The number of alkali metals per 100 graphene carbons is calculated to be 22.2

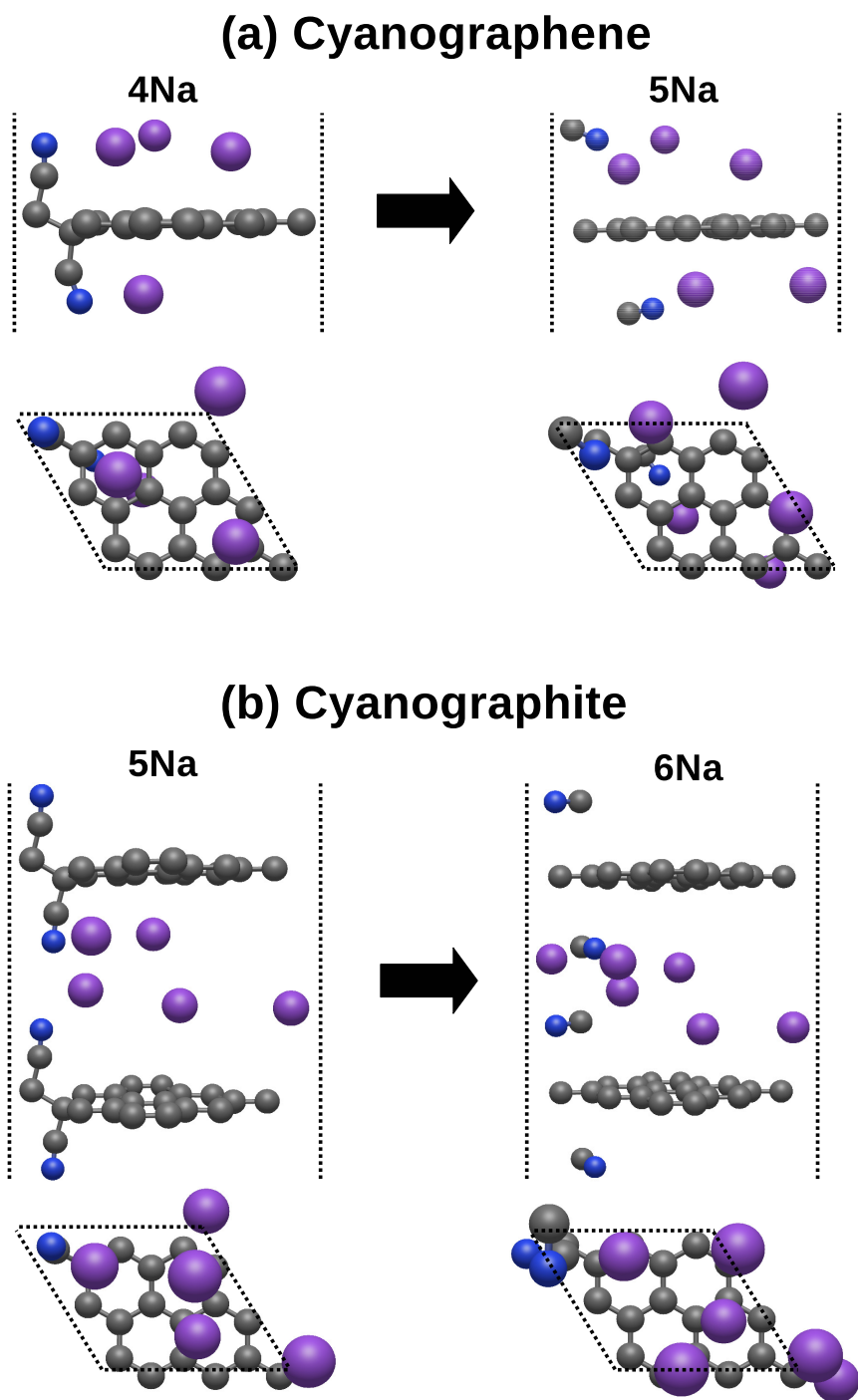


Figure 5.10. The snapshot of the cyano group divergence. The cyano group is removed from graphene part when (a) 5 sodium atoms for cyanographene and (b) 6 sodium atoms for cyanographite are added.

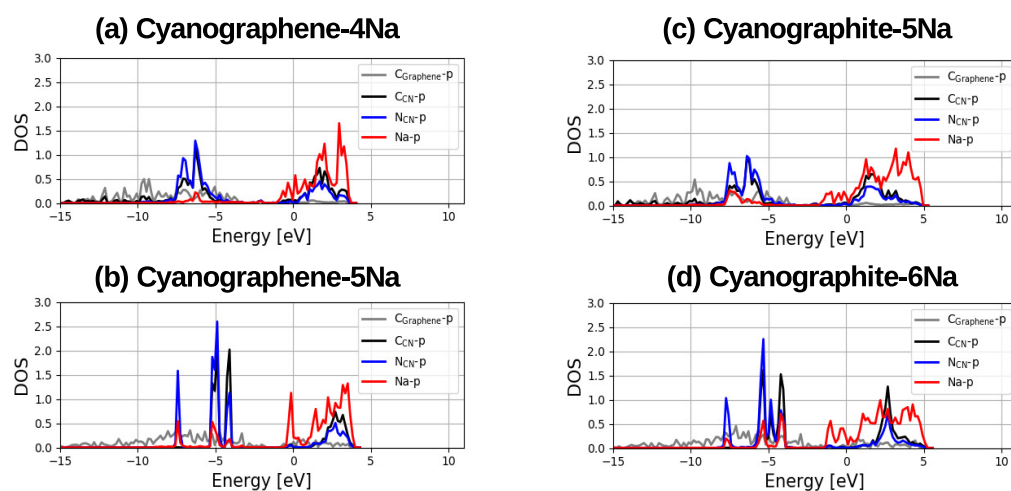


Figure 5.11. Projected density of states (PDOS) where the p-orbitals of C of graphene part, C of CN, N of CN, and Na are plotted in gray, black, blue and red, respectively.

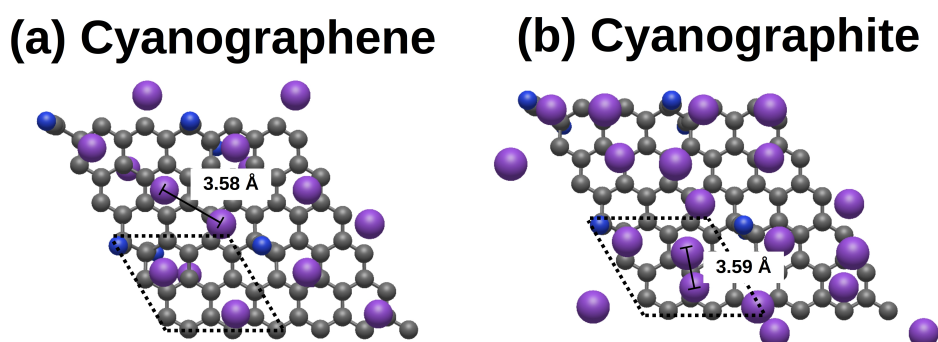


Figure 5.12. The snapshot of sodium-intercalated compounds for (a)cyanographene and (b)cyanographite.

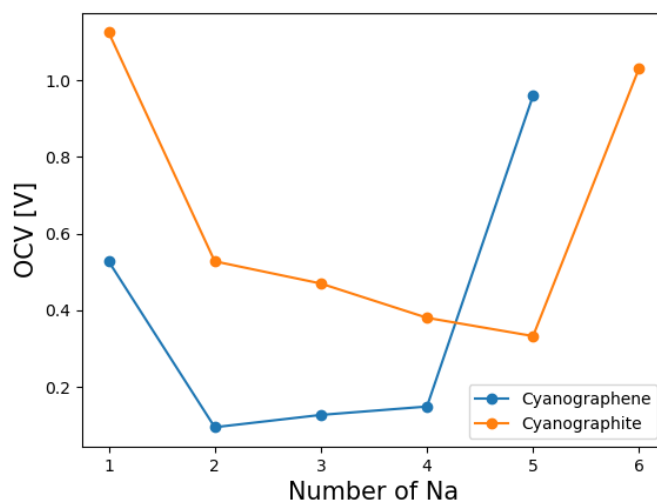


Figure 5.13. The OCV for each number of sodium atom. The blue, yellow line stand for cyanographene and cyanographite, respectively.

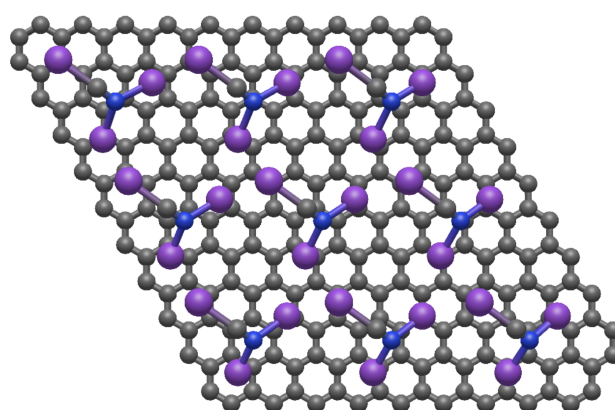


Figure 5.14. The snapshot of CN-Na bond on graphene.

for cyanographene $\text{Na}_4\text{C}_{18} - \text{CN}$ and 27.8 for cyanographite $\text{Na}_5\text{C}_{18} - \text{CN}$, which is higher than 16.7 for lithium-graphite LiC_6 [36] and 1.6 for sodium-graphite NaC_{64} [180] with Equation 5.2. N_M and N_C are 4 and 18 for cyanographene, 5 and 18 for cyanographite, 1 and 6 for lithium-graphite and 1 and 64 for sodium-graphite, respectively. The formula for cyanographene and cyanographite is derived from calculated model as shown in Figure 5.12. This result indicates that cyanographene and cyanographite have greater metal storage capacity than graphite. Hence, cyanographene and cyanographite can be used as an anode material for SIBs with a very high capacity.

5.4 Conclusion

High-throughput DFT calculations reveal elemental trends and their potential applications. The adsorption energies indicate that Mg shows endothermic adsorption, whereas the other metals are adsorbed on cyanographene exothermically. Bader charge analysis shows charge transfers of 0.9 electrons, 1.3 electrons, and 0.3 electrons for alkali metals (Li, Na, K, Rb, Cs), alkaline-earth metals (Ca, Sr, Ba), and Mg, respectively. These results indicate an ion-like interaction between the metals and cyanographene, which promotes metal adsorption, while cyanographene does not significantly promote the ionization of Mg. The PDOS between Na and the C atoms of graphene reveals overlapping p states near -7 eV, indicating that electron pairing between CN–Na contributes to the adsorption of Na. The adsorption of Li, Na, and K is related to ion battery applications, whereas the adsorption of Rb and Cs is related to the recovery of rare metals and radioactive elements. Therefore, the development of cyanographene contributes to energy storage and the recovery of rare metals and radioactive elements.

Further DFT calculations are conducted to demonstrate the potential utility of cyanographene and cyanographite in sodium-ion batteries (SIBs). Observations reveal that the sodium atom in cyanographene is adsorbed between cyano

group and graphene part. While, sodium atom in cyanographite is adsorbed between two cyano groups as well as between cyano group and graphene part. Bader charge analysis delineates the ionic like interaction between the sodium atom and cyano group, promoting sodium atom adsorption. The projected density of states (PDOS) suggests electron coupling between the sodium atom and the cyano group in cyanographite, contributing to adsorption energy of -1.12 eV for the sodium atom at the CN-Na-NC. The highest energy barrier for sodium atom diffusion on cyanographene and cyanographite is calculated to be 0.25 and 0.52 eV, respectively. Consequently, sodium atoms smoothly diffuse on cyanographene and cyanographite. Upon the addition of 5 sodium atoms to cyanographene and 6 to cyanographite, the cyano group detaches from the graphene part, subsequently interacting with the sodium atoms. The number of alkali metals per 100 graphene carbons is calculated to be 22.2 for cyanographene, 27.8 for cyanographite, which is higher than 1.6 for sodium-graphite. Thus cyanographene and cyanographite have greater sodium storage capacity than graphite. Due to interatomic spacings, sodium atoms might not coalesce within cyanographene and cyanographite, as the minimum distance between adjacent sodium atoms exceeds the bond length of the sodium dimer. Given the elevated sodium mobility and significant sodium storage capacity, it is evident that both cyanographene and cyanographite offer promising prospects as anode materials for SIBs.

Chapter 6

Conclusions

In this work, the design principles of bottom-up-type 2D prototype materials are established via high-throughput DFT calculations. In particular, automation of the high-throughput calculations is achieved by combining GPAW, ASE, and Python 3, enabling consistent evaluation of bottom-up-type 2D prototype materials. Below, the conclusions of each part of the work are briefly discussed together with their respective limitations.

6.1 General Conclusions

6.1.1 High-throughput Workflow for Honeycomb-Kagome Lattice

This study systematically investigates the thermodynamic stability, structural preference, and magnetic properties of honeycomb–kagome lattices using high-throughput first-principles calculations, extending the elemental space beyond conventional oxides and sulfides. It reveals key relationships among elemental composition, stability, magnetic ordering, and electronic states, and identifies 17 ferromagnetic metals, 12 half-metals, and 10 antiferromagnetic metals with out-of-plane anisotropy as promising 2D magnetic candidates. Seventeen ferromagnets show higher Curie temperatures than CrI_3 ($T_C = 45$ K), and 12 exceed 300 K. In particular, Ta and W

tend to yield high Curie temperatures: Ta–S/Se/Te and W–Te/P/As/Sb combinations exhibit large energy differences between ferromagnetic and antiferromagnetic states and large spin-wave gaps, resulting in $T_C > 400$ K. PDOS and band-structure analyses show that Ta_2S_3 and W_2P_3 exhibit strong d – p hybridization and spin–orbit coupling, enhancing exchange interactions and magnetic anisotropy, and providing design guidelines for spintronic and quantum materials via computational screening.

6.1.2 Designing Phosphorus 2D-Allotrope

Two-dimensional black, octagonal, and kagome phosphorus networks are studied by DFT to clarify their stability, electronic properties, and synthesis feasibility: black phosphorus derives from the bulk phase, whereas the octagonal and kagome structures are based on (4,8) and (3,6) tilings. Cohesive-energy analysis shows that black phosphorus forms exothermically from the gas phase, while the octagonal and kagome phases are slightly endothermic, indicating that interaction with metal supports is needed for stabilization. GLLB-SC calculations give a direct 1.20 eV gap for black phosphorus and indirect gaps of 2.07 eV and 0.69 eV for the octagonal and kagome phases, suggesting applications in solar cells, photocatalysis, and infrared optoelectronics. Lattice-matched Au(100) and Cu(111) surfaces provide small mismatch and moderate binding, implying that octagonal and kagome monolayers can be formed and exfoliated. Experimentally, annealing Au mesh in red phosphorus vapor yields crystalline Au_2P_3 instead of a 2D phosphorus layer; SEM–EDS confirms ~ 10 μm Au_2P_3 crystals and a P/Au ratio of 1.26, consistent with stoichiometry, while XPS shows Au 4f shifts and P 2p features typical of metal phosphides with surface phosphates, indicating predominantly covalent bonding. DFT reproduces the lattice constants and XRD, and Bader charge together with PDOS reveals small charge transfer and strong Au– d /P– p overlap,

supporting the covalent character, and band-structure calculations give an indirect 0.17 eV gap (GLLB-SC) between Γ and X , placing Au_2P_3 in the mid-infrared regime as a promising narrow-gap semiconductor.

6.1.3 Theoretical Investigation of Metal-Absorption for Cyanographene

High-throughput DFT calculations on cyanographene reveal elemental trends and potential applications: adsorption energies show that Mg adsorption is endothermic, while other metals are exothermically adsorbed, and Bader analysis gives charge transfers of 0.9, 1.3, and 0.3 electrons for alkali metals (Li, Na, K, Rb, Cs), alkaline-earth metals (Ca, Sr, Ba), and Mg, respectively, indicating ion-like interactions that promote adsorption for all but Mg. The PDOS between Na and graphene C atoms shows overlapping p states near -7 eV, suggesting CN–Na electron pairing contributes to Na adsorption; Li, Na, and K adsorption is relevant for ion battery anodes, while Rb and Cs adsorption relates to the recovery of rare and radioactive metals, highlighting cyanographene’s potential in energy storage and resource recovery. Further DFT calculations assess cyanographene and cyanographite as sodium-ion battery anodes: Na on cyanographene is adsorbed between the cyano group and graphene, whereas in cyanographite it is adsorbed both between cyano groups and between cyano and graphene. Bader analysis indicates ionic-like interaction between Na and cyano groups, and PDOS shows electron coupling at CN–Na–NC sites, yielding an adsorption energy of -1.12 eV. The highest Na diffusion barriers are 0.25 eV on cyanographene and 0.52 eV on cyanographite, indicating smooth diffusion, and upon adding 5 Na atoms to cyanographene and 6 to cyanographite, cyano groups detach and bind to Na, giving 22.2 and 27.8 Na per 100 C atoms, much higher than 1.6 for sodium–graphite. Because Na atoms remain separated beyond the Na–Na bond length, aggregation is suppressed, and the combination of high mobility and large storage capacity makes cyanographene and cyanographite promising anode materials for SIBs.

6.2 Perspective of Future Research

6.2.1 High-throughput Workflow for Honeycomb-Kagome Lattice

This study compares PBE and DFT+ U for honeycomb-kagome lattices and shows that DFT+ U modifies the Curie temperature and magnetic properties, yet the choice of an appropriate Hubbard U remains uncertain. Thus, high-throughput calculations with DFT+ U have inherent limitations. This study mainly evaluates thermodynamic stability and magnetic properties, and phonon calculations or AIMD simulations are essential to guarantee dynamical stability for synthesizable two-dimensional magnets, although the computational cost makes it impractical to evaluate all candidate materials. Therefore, it is important to leverage this study as a set of design guidelines for further theoretical investigations, including phonon calculations, AIMD, and DFT+ U studies of specific two-dimensional materials with half-metallic properties or high Curie temperatures. Overall, this study functions as a guideline that provides priorities and directions for the discovery of novel two-dimensional magnetic materials.

6.2.2 Designing Phosphorus 2D-Allotrope

Annealing the Au mesh in red phosphorus vapor produces Au_2P_3 instead of a two-dimensional phosphorus monolayer, indicating that the two-dimensional octagonal and kagome phosphorus allotropes are metastable. Growth methods with precise control of the phosphorus chemical potential, such as molecular beam epitaxy under ultra-high vacuum, are therefore essential for their experimental realization. There are several reports that bottom-up two-dimensional materials containing boron or phosphorus are obtained by molecular beam epitaxy on metal substrates. These reports suggest that the bottom-up two-dimensional phosphorus networks proposed in this study also become accessible when growth parameters such as substrate choice and temperature are optimized. On the other hand,

this study considers only a limited set of substrates, Au(100) and Cu(111), with ideal surfaces, and does not account for defects or interfacial reactions that occur during actual film growth. In the future, it is necessary to establish synthesis strategies for bottom-up 2D prototype materials by combining first-principles calculations and experiments. This approach will connect theoretical design principles to experimentally accessible two-dimensional phases and expand the space of two-dimensional materials beyond bulk-derived structures.

6.2.3 Theoretical Investigation of Metal-Absorption for Cyanographene

This study discusses the potential application of SIBs based on theoretical calculations. It does not consider stability in real battery environments, voltage profiles, initial irreversible capacity, or the effects of electrolytes and SEI formation. The calculations also assume ideal cyano-group arrangements and defect-free graphene frameworks; thus, defects, inhomogeneous cyano groups, structural degradation under high sodium loading, and detachment of cyano groups remain issues for real SIB applications. Therefore, it is important to combine experimental studies of cyanographene and cyanographite with first-principles calculations and molecular dynamics that explicitly include solvents and interfaces. This combined approach will assess their practical application as SIB anode materials and establish concrete electrode design guidelines for bottom-up prototype two-dimensional materials.

6.2.4 General Perspective

This dissertation focuses on three classes of bottom-up prototype two-dimensional materials—honeycomb–kagome lattices, two-dimensional allotropes, and functionalized graphene—and establishes design guidelines for magnetic, semiconducting, and energy-storage materials, respectively. Across these studies, high-throughput first-principles calculations are applied to bottom-up prototype two-dimensional materials for the first time, demonstrating that systematic computational screening is a powerful approach for exploring their thermodynamic stability, electronic structure, and functional properties. Since bottom-up prototype two-dimensional materials are now shifting from purely theoretical concepts toward experimentally realizable systems, this work provides a theoretical foundation for the field and offers concrete design principles that support the development of next-generation two-dimensional materials.

6.3 Contributions of this Work

The work compiled in Chapters 3, 4 and 5 has resulted in three peer-reviewed publications as listed below:

- **H. Suzuki**, F. Garcia-Escobar, K. Takahashi, 2025. *The Journal of Physical Chemistry Letters*, 16(27), 7076–7082 [185]
- **H. Suzuki**, S. Shoji, F. Garcia-Escobar, T. Tashiro, H. Abe, K. Takahashi, 2025. *physica status solidi (RRL) – Rapid Research Letters*, 2500298, [186]
- **H. Suzuki**, K. Takahashi, 2024. *Advanced Engineering Materials*, 26(7), 2301907, [187]

Below are three peer-reviewed publications in which the author contributed during this period, but are not included in this thesis:

- T. Tashiro, **H. Suzuki**, K. Takahashi. 2024. *Physical Chemistry Chemical Physics*, 26, 14440–14447. [188]

The author also delivered the following presentations about the research contained in this work:

- **H. Suzuki**, K. Takahashi. Theoretical study of Cyanographene and Cyanographite for sodium-ion battery applications. (ACS Spring 2025 , Mar 2025)
- **H. Suzuki**, K. Takahashi. 2 Dimensional Dodecagonal Nitride and Graphenylene via First Principle Calculations. (5th conference of Theory and Applications of Computational Chemistry, September 2023, Sapporo)
- **H. Suzuki**, K. Takahashi. High-throughput DFT screening for 2D-materials. (The University of Melbourne; Hokkaido University Workshop on Smart Materials, Mar 2025)

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