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Mapping Magnetic Properties of Spintronic Materials Using a First Principles Framework

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Abstract

In recent years, the field of spin electronics (Spintronics) has made significant advances in novel magnetic data storage and processing technologies in terms of energy efficiency, non-volatility, and compact design. While spintronic devices offer promising prospects, they face a persistent challenge known as the "THz-gap," which refers to the limited frequency range that current THz radiation sources can operate within. Computational simulation techniques have emerged as a pivotal tool for bridging this gap, enabling researchers to model and optimize complex nanoscopic devices based on stacks of novel low-moment ferri- or antiferro-magnetic materials (having high natural frequency) with precision, thereby facilitating advancements in this strategic field. This approach not only aids in overcoming existing technological barriers but also contributes significantly to the realization of practical applications based on theoretical predictions.

In this thesis, we present a systematic approach developed to design a protocol based on ab initio theoretical methods for exploring the potential of various novel low-moment ferrimagnetic and antiferromagnetic materials, as well as topical ferromagnetic Heusler compounds, as functional elements in spintronic devices. Specifically, we aim to map magnetic properties using density functional theory (DFT) and employ state-of-the-art materials science techniques to address the limitations of standard DFT, and comparing the effectiveness of different implementations of Hubbard corrections in describing the low-moment ferrimagnet Mn_3Ga . We then analyze magnetocrystalline anisotropy energies to assess magnetic domain stability in selected materials, including Mn_3Ga (a low-moment ferrimagnet), CrSb (an altermagnet), and CuMnAs (an antiferromagnet). Finally, we develop a practical scheme for calculating Heisenberg exchange parameters using the spin-spiral approach. These results allow us to construct a simplified classical spin Hamiltonian to study the thermodynamic behavior of promising low-moment

magnetic materials. Additionally, we compared our findings against existing literature on standard ferromagnets (such as the 3d transition metals) and a range of topical Heusler compounds, including Cu_2MnAl , Pd_2MnSn , Ni_2MnGa , Ni_2MnSn , NiVSb , and NiVSn . This comparison enables us to evaluate the performance of fully self-consistent versus magnetic force theorem-based approaches for extracting Heisenberg exchange parameters, highlighting their respective advantages and limitations within the widely used VASP code—the workhorse of ab initio electronic structure calculations in materials science—. Since there are only a few such methods currently exist in the literature for extracting these parameters from first principles, and most rely on private codes used within small research communities, by demonstrating a practical scheme available within VASP, we aim to make this valuable theoretical tool more accessible to the broader research community in magnetism and spintronics.

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1 — Introduction

Throughout human history, magnetism has always been in the spotlight for curious minds, but its working mechanics have remained a mystery for a long time. The absence of knowledge of magnetism, however, did not prevent ancient human civilizations from harnessing a naturally magnetic mineral, lodestone (magnetite), to build the first magnetic device, a compass, in ancient China around 2 BC [9]. Beyond China, the Greek and Roman civilizations had contributed documentation of the attractive properties of lodestone. These early studies and device applications must have seeded the ground for the next level of scientific study of magnetism and its subsequent technological advancements.

During the 17th century, the magnetic properties of materials became the subject of more systematic studies and gained momentum with William Gilbert's work on magnetism- he was the first to describe the Earth as a giant magnet in his book "De Magnete" [10]. Hans Christian Ørsted and André-Marie Ampère established the phenomenological connection between magnetism and electricity, which led to James Clerk Maxwell's mathematical unification of electromagnetism in the 19th century [11]. These discoveries led to practical applications of electrical engineering, such as electric motors, transformers, and electromagnets. One of the famous applications was the first magnetic recording medium in the Telegraphic invention by Valdemar Poulsen [12].

In the 20th century, a new fundamental theory of physics, quantum mechanics, emerged to understand optical emission spectra and to study the microscopic (atomic) level of magnetism and its properties. One of the most significant modern days breakthroughs in the research on magnetic devices came in 1988 when Peter Grünberg and Albert Fert separately discovered the Giant Magnetoresistance (GMR) [13, 14] effect, a quantum mechanical phenomenon where the electrical resistance of certain

stacks of magnetic and non-magnetic metallic layers changes drastically under a magnetic field which switches the orientation of one of the magnetic layers. This discovery completely changed data storage technology, enabling the development of high-density hard disk drives using GMR-based read-heads. GMR-based sensors became essential in modern computing, allowing for rapid advancements in information technology and initiating a new field of physics spintronics, which utilizes the electron's spin for information processing.

Heusler alloys are a class of materials which have gained significant attention during the last century due to their potential application in spintronic devices [15, 16, 17, 18], magnetic refrigeration [19], and micro-electromechanical system [20] due their wide range of magnetic properties such as itinerant and localized magnetism, antiferromagnetism, helimagnetism, Pauli paramagnetism or heavy-fermionic behavior [21, 22, 23, 24]. The saturation magnetization and the total spin magnetic moments can be controlled through atomic substitution. Such controllability is beneficial for applications such as MRAM cells [25] and HDD read heads [26], where efficient spin injection is critical. The Huesler alloys' crystalline structure is categorized into two main groups: Full Huesler alloys, which are represented with $L2_1$ and form of X_2YZ , which consists of 4 fcc sublattice such as Cu_2MnAl and Pd_2MnSn . The second group is half-Heusler alloys, which are represented with $C1_b$ and are formed by removing one of the X sites, such as $NiMnSn$ and $NiMnSb$.

The Ni-based full Huesler alloys exhibit a small lattice mismatch on widely employed semiconductors like InAs and GaAs [27]. Theoretical studies have demonstrated that the stable pseudomorphic growth of Ni_2MnGa on GaAs can be explained by a broad energy minimum of the tetragonal structure. This high-quality epitaxial growth is crucial for ensuring that the electronic and magnetic properties of the allow are preserved [28].

The antiferromagnetic Heusler alloy's magnetic moments are adjacently aligned in the opposite direction between the sublattices where they generate zero net magnetic moment. This magnetic property is used to pin one of the ferromagnetic (FM) magnetization direction in the GMR stacks, accomplishing a steady antiparallel magnetization configuration through the so-called exchange bias effect [29]. However, challenges with

the dominant antiferromagnetic material IrMn_3 used for exchange bias due to the rising cost of iridium [30] and the lack of alternative anti-ferromagnetic (AF) material with a Neel temperature above room temperature has stimulated active research into novel AF Heusler alloys. One of the promising materials for this role is Mn_3Ga . It crystallizes in a tetragonal DO_{22} structure, which is a slightly distorted version of the cubic L2_1 Heusler structure, and it is a low-moment ferrimagnet [31]. This tetragonal distortion was reported to possess a large uniaxial anisotropy $1 \times 10^7 \text{ erg/cm}^3$ [32], high Curie temperature of 770 K [33], and high spin polarization at Fermi energy [34]. These unique magnetic properties of Mn_3Ga led to its use in magnetic tunneling junction (MTJ) where its properties contribute to improved magnetoresistance [35]. Furthermore, Mn_3Ga is a promising candidate for THz spintronic emitters due to its ability to generate and manipulate spin currents at THz frequencies via the spin Seebeck effect (SSE) and their conversion to charge currents through the inverse spin Hall effect (ISHE) [36]. Moreover, its nearly compensated ferrimagnetic state, characterized by strong exchange interactions and low net magnetization, enables high precession frequencies, making it a potential material for bridging the THz gap.

Understanding the fundamental electronic and magnetic properties and accelerating to discovery of Heusler compounds, including Ni_2MnGa , NiVSb , and Pd_2MnAl , Mn_3Ga , requires first-principles (ab-initio) calculations, which provide crucial insights into their electronic band structure, structural stability, and spintronic potential. These computational methods, based on density functional theory (DFT), which is one of the most successful and widely employed theories for implementing computer algorithms in materials science, allow for the accurate prediction of material properties without relying on empirical parameters. Given the complex interplay of spin polarization, lattice distortions, and magnetic exchange interactions in these compounds, ab initio studies play a crucial role in identifying new materials with tailored properties for spintronic and THz applications. However, DFT alone cannot model large-scale magnetic devices (comprising thousands of atoms) or evaluate their finite-temperature thermodynamic properties, as it is inherently a ground-state (0 K) theory. To overcome these limitations, classical spin models parameterized from DFT-derived interactions become

essential, enabling the study of magnetic order, phase transitions, and excitation spectra at experimentally relevant scales.

In this thesis, we address Heusler compounds within an *ab initio* framework. We focus on the structural, electronic, and magnetic properties of Heusler compounds, with particular emphasis on Mn_3Ga . The computational investigation is carried out using DFT. We examine the bulk magnetic properties of Mn_3Ga under the influence of Hubbard corrections applied to the energy functional (LDA, GGA). The magnetocrystalline anisotropy energy of Mn_3Ga and two anti-ferromagnetic materials, CbSr and CuMnAl , were calculated in order to construct a classical Heisenberg spin Hamiltonian, which can then be used to investigate spin dynamics at the atomistic scale. To compute the spin Hamiltonian, the Heisenberg exchange parameters were determined using a practical user-level approach for utilising the built-in spin-spiral implementation in the VASP code [37, 38, 39, 40, 41]. This method was first tested on 3d ferromagnets and subsequently applied to Heusler compounds, yielding good agreement with literature values.

The Thesis is structured as follows. The concepts and formulation of Density Functional Theory (DFT), along with the Projector Augmented Wave (PAW) method, as implemented in the VASP code—a widely used simulation package in the DFT field—are presented in Chapter 2. Non-collinear magnetism within the VASP basis set, the generalized Bloch theorem for spin spiral of finite wavevectors, and spin space symmetry are described. Chapter 3 show limitation of standard DFT performance on Mn_3Ga , as well as evaluating different implementations of the DFT+U method. In Chapter 4, the magnetocrystalline anisotropy energy calculations are performed. Finally, in Chapter 5, a practical protocol for Heisenberg exchange parameter calculations using the spin spiral implementation in VASP is introduced and tested for transition metals and Heusler compounds.

2 — Theory

2.1 Density Functional Theory

One of the main quests in the physics and chemistry field is to find an efficient approach to solving many-body electron systems via the Schrodinger equation,

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (1)$$

where $\mathbf{r}$ is electron position, and N is the number of electrons in the system. Even for small systems, many-body electron wave-function (Eq. (1)) solutions demand a huge Hamiltonian Matrix configuration, which leads to a high number of elements in terms of the number of grid points where set in a computational framework for solving the Schrodinger equation. One idea would be to map the N -electron system to a one-electron wave function in the form of a Slater determinant,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \cdots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \vdots \\ \phi_N(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_N) \end{pmatrix}, \quad (2)$$

where $\phi_i(\mathbf{r}_i)$ is a single-particle wave-function where an appropriate choice needs to reflect the symmetry properties of a many-body electron system. The minimization by varying the single-particle wave function leads to the Hartree-Fock equation, and the method is referred to as the Hartree-Fock approximation (see [42, 43] for detailed derivation). However, the Hartree-Fock Method is limited to small systems and excludes the correlation effects of electrons.

The Hohenberg-Kohn theorem [44] supplies deeper physical insight into a reduction of the complicated many-body electron system to single-electron theory to ensure that knowledge of ground-state density is sufficient to calculate all physical quantities of the many-body system. The theorem established that electron density has a crucial role in finding the ground-state energy of the system, and the theorem follows two arguments:

1. The total ground state energy of any many-electron system is a functional of density
2. For any many-electrons system, the functional for the total energy has a minimum equal to the ground-state energy at the ground-state density.

In conclusion, the Hohenberg-Kohn theorem produces a justification of the density functional model that ground state energy represents in terms of ground state density,

$$E_o = E[n_o], \quad (3)$$

where n_o , and E_o are the donated ground state of density and energy of a system. The general form of ground expression by a single-particle wave function,

$$n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r}_i)|^2 \quad (4)$$

The basic facts of the density functional theory are stated by the Hohenberg-Kohn theorem, although the theorem does not give an explicit form of the energy functional $E[n]$. The explicit form was given by Kohn and Sham [45], who implemented a variational principle to minimize the energy functional using its ground-state density for deriving single-particle Schrodinger equations. The total ground-state energy is divided into four parts:

$$E[n] = T_s[n] + E_H[n] + E_{ext}[n] + E_{xc}[n], \quad (5)$$

where T_s is kinetic energy functional for non-interaction particle

$$T_s[n] = \sum_i^N \int d^3(\mathbf{r}) \phi_i^*(\mathbf{r}_i) \left(\frac{-i\hbar \nabla^2}{2m} \right) \phi_i(\mathbf{r}_i). \quad (6)$$

The $E_H[n]$ is the Hartree energy functional, which describes the average energy experienced by each electron from their interaction in the electron density,

$$E_H[n] = \int d^3(\mathbf{r})d^3(\mathbf{r}') \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (7)$$

The $E_{ext}[n] + E_{xc}[n]$ are external potentials, and the exchange-correlation functional is the exchange-correlation potential, which involves all the complicated many-body effects not represented in other energy functionals. As the Kohn-Sham theorem stated, the energy functional Eq. (5) is minimized by ground state density to derive a single-particle Schrödinger-like equation, Kohn-Sham equations,

$$\left[\frac{(-i\hbar\nabla)^2}{2m} + V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \quad (8)$$

The Schrödinger equation is replaced by a solvable expression in terms of Kohn-Sham orbitals within Eq. (8). The energy functional exhibits an explicit structure, but the exchange-correlation energy remains to be determined and must be accurately approximated for the correct solution of the Kohn-Sham equations.

2.2 Exchange-Correlation Functionals

To study materials, it is essential to incorporate many-body effects into the Density Functional Theory (DFT). The exchange-correlation energy terms deliver these effects within a simplified density approximation of the exact electron system. One of the simplest and most successful formulations to do this job is Local (spin) Density approximation (L(S)DA). First, we will address its mathematical formation and success in describing an accurate exchange-correlation energy. Subsequently, we will introduce the Generalized Gradient Approximation (GGA), an enhanced form of LDA, designed to describe inhomogeneous materials where LDA falls short more accurately. Finally, we will conclude this section with an overview of DFT+U method, which supplements the exchange-correlation functionals of LDA and GGA. Since these approaches often struggle to represent strongly localized orbitals in magnetic materials accurately, they

may not fully capture the relevant physical properties.

2.2.1 Local Spin Density Approximation (LSDA)

The Local Density Approximation (LDA) stands out as a simple yet effective method for approximating the exchange-correlation energy,

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}^{HEG}(n(\mathbf{r})) d\mathbf{r} \quad (9)$$

where $\epsilon_{xc}^{HEG}(\mathbf{r})$ is the exchange-correlation energy per electron of a homogeneous electron gas.

The LDA energy functional follows the principle that the system is represented by different local electron density contributions, which collectively determine the total energy of the system. Inside these local contributions, density is slowly changing. Each local region behaves as an infinitesimal rectangular volume, and these volumes contribute to the exchange-correlation energy obtained from the homogeneous electron gas model. When each volume is connected smoothly, the exchange and correlation energy of the entire system can be obtained.

The LDA approach often fails to describe magnetic systems because of their strongly correlated states. Thus, LDA should be enhanced with an empirical correction to accurately describe the ground state of magnetic systems. This approach, known as the Hubbard correction in the DFT framework (or DFT+U method), will be explored in the following sections.

LDA functional has been generalized to study spin-polarized magnetic materials by Parr and Yang [46] and named the local-spin-density approximation (LSDA). The mathematical steps follow the same approach as before, but with the addition of spin density to the energy functional,

$$\{n(\mathbf{r}), \mathbf{s}(\mathbf{r})\} \rightarrow E = F[n(\mathbf{r}), \mathbf{s}(\mathbf{r})]. \quad (10)$$

Spin-polarized systems include two spin densities in form of $n = n_\alpha + n_\beta$ and exchange-correlation energy become

$$E_{XC}^{LSDA}[n_\alpha, n_\beta] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}(n_\alpha, n_\beta), \quad (11)$$

where α, β are represent spin directions for quantization axis z .

2.2.2 Generalized Gradient Approximation (GGA)

The generalized gradient approximation (GGA) extends the local density approximation (LDA) by incorporating semi-local corrections based on the gradient of electron density. This enhancement refines LDA's ability to describe inhomogeneous systems, such as surfaces and interfaces, where variations in electron density occur. The exchange-correlation energy functional of GGA (E_{xc}^{GGA}) follows a similar structure to that of LDA (E_{xc}^{LDA}), but it incorporates the gradient of the electron density, making the energy of the homogeneous electron gas (ϵ_x) dependent on spatial variations in electron density,

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int n(\mathbf{r}) \epsilon_{xc}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r}. \quad (12)$$

Alongside GGA's success in describing complex systems, it often fails to accurately describe strongly correlated materials within localized d and f orbitals. Specifically, its performance is suboptimal to accurate band gap prediction or capturing the local magnetic moments. This limitation is particularly evident in transition metal oxides (TMOs) such as FeO, NiO, and MnO [47, 48].

2.2.3 DFT+U Method

The countless numerical first-principle calculations with LDA and GGA have shown that these energy functionals fail to obtain ground states and excited states of many strongly correlated systems comprising transition metals and rare-earth elements (such as NiO, Ru, Mn₃Ga). Due to limitations in accuracy and its inability to describe strongly correlated systems, DFT requires extensions beyond this approximation. Numerous studies demonstrate that the so-called DFT+U provides accurate results for strongly correlated systems [49], which the modified energy functional in LDA can be

re-written from the Hubbard correction framework,

$$E^{LDAU}[\rho^\sigma(\mathbf{r}), \{n_{m,m'}^\sigma\}] = E^{LDA}[\rho^\sigma(\mathbf{r})] + E^U[\{n_{m,m'}^\sigma\}] - E_{dc}[\{n^\sigma\}]. \quad (13)$$

Here $\rho(\mathbf{r})$ is charge density for an electron with spin σ , $n^\sigma = \text{Tr}(n_{m,m'}^\sigma)$ and $n_{m,m'}^\sigma$ is a atomic-orbital occupations within m magnetic quantum number. The last term E_{dc} corrects for double counting.

The set of orbital occupation numbers, also known as density matrix elements, can be expressed as the projection of occupied KS orbitals (ϕ_{kv}^σ) on the state of a localized basis set (λ_m)

$$n_{m,m'}^\sigma = \sum_{k,v} f_{kv}^\sigma \langle \lambda_{m'} | \phi_{kv}^\sigma \rangle \langle \phi_{kv}^\sigma | \lambda_m \rangle. \quad (14)$$

In the rotational invariant form of the atomic orbital basis set for Eq. (13) introduced by A. Liechtenstein and coworkers [50], the Hubbard correction energy reads:

$$E^U[\{n_{m,m'}^\sigma\}] = \frac{1}{2} \sum_{m,\sigma} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{m,m'}^\sigma n_{m'',m'''}^{-\sigma} + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m', m''' \rangle) n_{m,m'}^\sigma n_{m'',m'''}^{-\sigma} \} \quad (15)$$

and the double-counting part becomes

$$E_{dc}[\{n^\sigma\}] = \frac{U}{2} n(n-1) - \frac{J}{2} [n^\uparrow(n^\uparrow-1) + n^\downarrow(n^\downarrow-1)]. \quad (16)$$

Where U , J are effective Coulomb and exchange parameters, and $n = n^\uparrow + n^\downarrow$.

After inserting the set of orbital occupations number expression into Eq. (13) and Eq. (15), effective single-particle Hamiltonian can be derived from the LDA potential

$$V_{m,m'}^\sigma = \frac{1}{2} \sum_{m,\sigma} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{m'',m'''}^{-\sigma} + (\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m', m''' \rangle) n_{m'',m'''}^{-\sigma} \} - U(n - \frac{1}{2}) - J(n^\sigma - \frac{1}{2}) \quad (17)$$

The V_{ee} represents the electron-electron interaction, and its matrix elements are

$$\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_k a^k(m, m', m'', m''') F^{(k)}. \quad (18)$$

where $0 \leq k \leq 2l$ and l is angular moment number of localized basis. a_k factor can be expressed as a product of Clebsh-Gordan coefficients,

$$a^k(m, m', m'', m''') = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle. \quad (19)$$

The Coulomb interaction matrix between the localized basis Eq. (18) can be derived with spherical harmonics expression of Coulomb kernel Eq. (20),

$$\frac{1}{r_{ij}} = \frac{1}{[r_i^2 + r_j^2 - 2r_i r_j \cos\theta]^{1/2}} = \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos\theta), \quad (20)$$

and radial Slater integrals Eq. (21)

$$F^{(k)} = e^2 \int_0^\infty \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} [R_{nf}(r_i) R_{nf}(r_j)]^2 dr_i dr_j. \quad (21)$$

Where $P_k(\cos\theta)$ is Legendre polynomial and R_{nf} is radial eigenfunction. The detailed solution can be found in Judd's book [51].

To compute the V_{ee} matrix elements, the values of the radial Slater integrals are required. Specifically, for calculating matrix elements of the d -orbitals, one needs these integral values F^0, F^2 , and F^4 . In light of these mathematical tools, Coulomb and Hund (exchange) interactions (U, J) can be derived

$$U = \frac{1}{(2l+1)^2} \sum_{m, m'} \langle m, m' | V_{ee} | m, m' \rangle = F^0, \quad (22)$$

$$J = \frac{1}{2l(2l+1)} \sum_{m, m'} \langle m, m' | V_{ee} | m', m \rangle = \frac{F^2 + F^4}{14}. \quad (23)$$

Another simplified implementation of the DFT+U method was introduced by Dudarev and colleagues, in which the Coulomb and exchange terms are combined to form

an effective potential within the Hubbard energy function [52],

$$E^{LDAU}[\rho^\sigma(\mathbf{r}), \{n_{m,m'}^\sigma\}] = E^{LDA}[\rho^\sigma(\mathbf{r})] + \frac{U-J}{2} \sum_{\sigma} [\sum_m n_m^\sigma - \sum_{m,m'} n_{m,m'}^\sigma n_{m',m}^\sigma]. \quad (24)$$

2.3 Theoretical Framework for Magnetic Systems

In this section, we will focus on the DFT implementation and methods for studying the magnetic properties of materials. First, the spin-charge density will be introduced into the Kohn-Sham (KS) equations. Then, we will derive the final form of the KS equations, incorporating non-diagonal spin-charge density, to study non-collinear magnetic systems. After that, we will derive the Heisenberg Hamiltonian and explain the Bloch theorem and Spin-Space group to build a framework for investigating itinerant magnetic systems. This will allow us to extract the exchange parameters for the classical Heisenberg Hamiltonian using the so-called spin-spiral method. Finally, we will introduce the concept of magneto-crystalline anisotropy energy, which arises as a result of spin-orbit interaction in magnetic crystals with reduced symmetry.

2.3.1 Heisenberg Exchange Hamiltonian

The model spin Hamiltonian is a crucial tool for understanding the microscopic origin of magnetic ordering in solids and the thermodynamic properties of magnetic materials. The main contribution to a model spin Hamiltonian comes from the exchange field. To shed light on the exchange interaction, we will use a dimer (see Fig.2.1) of particles with spin $\frac{1}{2}$ and study the quantum Heisenberg Hamiltonian between spin $\mathbf{S}_1$ and $\mathbf{S}_2$

$$\hat{H} = -J\hat{S}_1\hat{S}_2, \quad (25)$$

The general form of a two-electron system can be expressed in joint wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2). \quad (26)$$

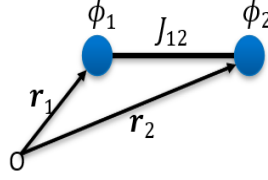


Figure 2.1: Two electron system.

The electron wave function can be split into a product of two wave functions (WF): the spatial WF $\phi(\mathbf{r})\chi(\mathbf{r})$ and the spin part χ have to carry information about its spin. Therefore, a generalized algebraic form of the electron wave function must be channeled into a new form, known as a spinor ϕ . The most general form of a two-electron spinor includes 4 different spin vector configurations: up-up, down-down, down-up, and up-down ($|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle$).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_1(\mathbf{r}_1, \mathbf{r}_2) |\uparrow\uparrow\rangle + \Psi_2(\mathbf{r}_1, \mathbf{r}_2) |\uparrow\downarrow\rangle + \Psi_3(\mathbf{r}_1, \mathbf{r}_2) |\downarrow\uparrow\rangle + \Psi_4(\mathbf{r}_1, \mathbf{r}_2) |\downarrow\downarrow\rangle. \quad (27)$$

Pauli's exclusion principle implies that the two-electron spinor should be anti-symmetric under the exchange of electrons. The first and the last terms in RHS in Eq. (27) imply that the spatial WF should be anti-symmetric when the spin basis is symmetric. The second and third terms satisfy the principle only in their combined form. The four different spinor configurations that satisfy the Pauli exclusion principle consist of three symmetric configurations, referred to as triplet states (Ψ_t), and one anti-symmetric configuration, known as the singlet state (Ψ_s),

$$\Psi_t(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) |\uparrow\uparrow\rangle, \Psi(\mathbf{r}_1, \mathbf{r}_2) |\downarrow\downarrow\rangle, \Psi(\mathbf{r}_1, \mathbf{r}_2) |\uparrow\downarrow\rangle + \Psi(\mathbf{r}_1, \mathbf{r}_2) |\downarrow\uparrow\rangle, \quad (28)$$

$$\Psi_s(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) |\uparrow\downarrow\rangle - \Psi(\mathbf{r}_1, \mathbf{r}_2) |\downarrow\uparrow\rangle. \quad (29)$$

The energies can be derived from the expectation values of the Hamiltonian for the two states. The Hamiltonian consists of two parts; the part H_o represents non-spin related terms such as kinetic energy, potential energy, etc. The part H_{spin} accounts for spin interactions. Since the Hamiltonian only includes spin-related terms, the energy differences between states arise from the symmetry properties of their spin WFs under

electron exchange,

$$\langle \psi_s | \hat{H} | \psi_s \rangle = E_s = E_o + J, \quad (30)$$

$$\langle \psi_t | \hat{H} | \psi_t \rangle = E_t = E_o - J. \quad (31)$$

Where J is the so-called *exchange integral* and $\hat{H} = \hat{H}_o + \hat{H}_{spin}$.

The energy difference between the two states includes spin energy information.

$$2J = E_s - E_t = \langle \psi(r_1, r_2) | \hat{H}_{spin} | \psi(r_2, r_1) \rangle. \quad (32)$$

To obtain spin information from a joint wave function, $\hat{H}_{spin}$ should include a joint spin operator (the simplest possible term is),

$$\hat{H}_{spin} = A \hat{S}_1 \cdot \hat{S}_2, \quad (33)$$

where A is a parameter. The expectation value (eigenvalue) of the states are

$$\epsilon_{spin} = \begin{cases} -\frac{3}{4} & \xrightarrow{\text{singlet state}} s = 0 \\ \frac{1}{4} & \xrightarrow{\text{triplet state}} s = 1 \end{cases}$$

From Eq. (32) and Eq. (33), we can define the so-called Heisenberg spin Hamiltonian,

$$\hat{H}_{spin} = -2J \hat{S}_1 \cdot \hat{S}_2. \quad (34)$$

The sign and magnitude of the exchange integral are characteristic of the magnetic properties of the systems of the electrons. In our case, the singlet state reaches the lowest energy when the exchange integral (J) is negative, whilst the triplet state reaches its lowest energy configuration when the exchange integral (J) is positive. In solid-state language, these spin alignments can be named antiferromagnetic (AFM) and ferromagnetic (FM) order, respectively.

The generalization of the Heisenberg Hamiltonian to systems containing many spins reads:

$$\hat{H}_{spin} = -2 \sum_{\langle i,j \rangle} J_{ij} \hat{S}_i \cdot \hat{S}_j, \quad (35)$$

where $\hat{S}_i$ ($\hat{S}_j$) is an operator that acts on the spin of atom i (j) and J_{ij} is exchange integral between pairs of atoms. The Notation $\langle i, j \rangle$ implies that the interaction of only nearest-neighbor atoms counts in the sum.

2.3.2 Non-Collinear Magnetism

When the system is spin-polarized, the density matrix has only a 2x2 block of diagonal elements to shape,

$$\hat{n}_\sigma(\mathbf{r}) = \begin{pmatrix} \hat{n}_1(\mathbf{r}) & 0 \\ 0 & \hat{n}_2(\mathbf{r}) \end{pmatrix}, \quad (36)$$

and is used in collinear spin-DFT calculations. In the absence of a global spin quantization axis for the whole crystal, the density matrix is not diagonal anymore, and the crystal is described as a noncollinear magnetic system. The single-particle KS equations form with two-component spinors ($\psi_{i,\sigma}(\mathbf{r})$) in a noncollinear system,

$$\sum_{\sigma} (\delta_{\sigma,\sigma'} \nabla_i + v^{eff}(\mathbf{r}_i)_{\sigma,\sigma'} - \epsilon_{i,\sigma}) \psi_{i,\sigma}(\mathbf{r}) = 0, \quad (37)$$

where the effective potential is

$$v^{eff}(\mathbf{r}_i)_{\sigma,\sigma'} = v^{ext}(\mathbf{r}_i)_{\sigma,\sigma'} + 2\delta_{\sigma,\sigma'} \int \frac{n(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_j + v_{\sigma,\sigma'}^{xc}(\mathbf{r}_i) \quad (38)$$

and spin-density matrix is

$$\hat{n}_{\sigma,\sigma'} = \sum_{i=1}^N \psi_{\sigma,i} \psi_{\sigma',i}^*, \quad (39)$$

and its matrix form

$$n(\mathbf{r}) = \begin{pmatrix} n_{11}(\mathbf{r}) & n_{12}(\mathbf{r}) \\ n_{12}(\mathbf{r}) & n_{22}(\mathbf{r}) \end{pmatrix}. \quad (40)$$

Exchange-correlation energy (E_{xc}) can be approximated when electrons have collinear spin. Therefore, the spin-density matrix Eq. (38) needs to diagonalize locally with Unitary transform matrix U (From Sakurai [53]) also known as spin-1/2 rotation

matrix

$$U = \begin{pmatrix} U_{11}(\mathbf{r}) & U_{12}(\mathbf{r}) \\ U_{12}(\mathbf{r}) & U_{22}(\mathbf{r}) \end{pmatrix} \begin{pmatrix} \exp(\frac{1}{2}i\phi) \cos \frac{1}{2}\theta & \exp(-\frac{1}{2}i\phi) \sin \frac{1}{2}\theta \\ -\exp(\frac{1}{2}i\phi) \sin \frac{1}{2}\theta & \exp(-\frac{1}{2}i\phi) \cos \frac{1}{2}\theta \end{pmatrix}, \quad (41)$$

and the transformation between Eq. (36) and Eq. (40) in matrix form

$$\begin{pmatrix} n_{11}(\mathbf{r}) & n_{12}(\mathbf{r}) \\ n_{12}(\mathbf{r}) & n_{22}(\mathbf{r}) \end{pmatrix} = U(\theta, \phi)^+ \begin{pmatrix} n_{11}(\mathbf{r}) & 0 \\ 0 & n_{22}(\mathbf{r}) \end{pmatrix} U(\theta, \phi). \quad (42)$$

Rewriting this matrix equation in a simplistic way

$$\sum_{\sigma, \sigma'} U_{i, \sigma} n_{\sigma, \sigma'} U_{i, \sigma'}^+ = n_i. \quad (43)$$

The relation between the diagonalized spin-density and the unitary operation can be expressed as shown in Eq. 43,

$$\frac{\delta n_i}{\delta n_{\sigma, \sigma'}} = U_{i, \sigma} U_{i, \sigma'}^+ \quad (44)$$

Now, we can express exchange-correlation potential ($v_{\sigma, \sigma'}^{xc}$) in terms of the diagonalized spin-density matrix,

$$v_{\sigma, \sigma'}^{xc} = \frac{\delta E_{xc}}{\delta n_{\sigma, \sigma'}} = \sum_{i=1}^2 \frac{\delta E_{xc}}{\delta n_i} \frac{\delta n_i}{\delta n_{\sigma, \sigma'}} = \sum_{i=2}^2 \frac{\delta E_{xc}}{\delta n_i} U_{i, \sigma'} U_{i, \sigma}^+. \quad (45)$$

The exchange-correlation potential is reformulated in matrix form to present the results more clearly, with the matrix elements populated according to Eq. 45

$$v_{\sigma, \sigma'}^{xc} = \begin{pmatrix} v_{11}^{xc} & v_{12}^{xc} \\ v_{21}^{xc} & v_{22}^{xc} \end{pmatrix} = \begin{pmatrix} \frac{\delta E_{xc}}{\delta n_1} U_{1,1} U_{1,1}^+ + \frac{\delta E_{xc}}{\delta n_2} U_{2,1} U_{2,1}^+ & \frac{\delta E_{xc}}{\delta n_1} U_{1,2} U_{1,1}^+ + \frac{\delta E_{xc}}{\delta n_2} U_{2,2} U_{2,1}^+ \\ \frac{\delta E_{xc}}{\delta n_1} U_{1,2} U_{1,1}^+ + \frac{\delta E_{xc}}{\delta n_2} U_{2,2} U_{2,1}^+ & \frac{\delta E_{xc}}{\delta n_1} U_{1,2} U_{1,2}^+ + \frac{\delta E_{xc}}{\delta n_2} U_{2,2} U_{2,2}^+ \end{pmatrix} \quad (46)$$

Before finalizing the exchange-correlation potential matrix, the first matrix elements will showcase how to obtain the final expression of $v_{\sigma,\sigma'}^{xc}$,

$$U_{1,1}U_{1,1}^+ = \exp\left(\frac{1}{2}i\phi\right) \cos \frac{1}{2}\theta * \exp\left(-\frac{1}{2}i\phi\right) \cos \frac{1}{2}\theta = \cos^2 \frac{\theta}{2} + \sin^2 \frac{\theta}{2}. \quad (47)$$

From trigonometric identities $\cos^2 \frac{\theta}{2} = \frac{1}{2}(\cos \theta + 1)$, $\sin^2 \frac{\theta}{2} = \frac{1}{2}(\cos \theta - 1)$. Then, v_{11}^{xc} become

$$v_{11}^{xc} = \frac{1}{2} \sum_{i=2}^2 \frac{\delta E_{xc}}{\delta n_i} + \frac{1}{2} \left(\frac{\delta E_{xc}}{\delta n_1} - \frac{\delta E_{xc}}{\delta n_2} \right) \cos \theta. \quad (48)$$

From the previous steps, we can finalize the exchange-correlation potential matrix Eq. 46

$$\begin{aligned} v_{\sigma,\sigma'}^{xc} &= \begin{pmatrix} v_{11}^{xc} & v_{12}^{xc} \\ v_{12}^{xc} & v_{22}^{xc} \end{pmatrix} = \\ &\begin{pmatrix} \frac{1}{2} \sum_{i=1}^2 \frac{\delta E_{xc}}{\delta n_i} + \frac{1}{2} \left(\frac{\delta E_{xc}}{\delta n_1} - \frac{\delta E_{xc}}{\delta n_2} \right) \cos \theta & \frac{1}{2} \left(\frac{\delta E_{xc}}{\delta n_1} - \frac{\delta E_{xc}}{\delta n_2} \right) \exp(-i\phi) \sin \theta \\ \frac{1}{2} \left(\frac{\delta E_{xc}}{\delta n_1} - \frac{\delta E_{xc}}{\delta n_2} \right) \exp(i\phi) \sin \theta & \frac{1}{2} \sum_{i=1}^2 \frac{\delta E_{xc}}{\delta n_i} - \frac{1}{2} \left(\frac{\delta E_{xc}}{\delta n_1} - \frac{\delta E_{xc}}{\delta n_2} \right) \cos \theta \end{pmatrix} \\ &= \frac{1}{2} \sum_{i=1}^2 \frac{\delta E_{xc}}{\delta n_i} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} \left(\frac{\delta E_{xc}}{\delta n_1} - \frac{\delta E_{xc}}{\delta n_2} \right) + \begin{pmatrix} \cos \theta & \exp(-i\phi) \sin \theta \\ \exp(i\phi) \sin \theta & -\cos \theta \end{pmatrix}. \end{aligned} \quad (49)$$

The last matrix can be formed with the Unitary rotation and Pauli operations

$$\begin{pmatrix} \cos \theta & \exp(-i\phi) \sin \theta \\ \exp(i\phi) \sin \theta & -\cos \theta \end{pmatrix} = \mathbf{U}^+ \sigma_z \mathbf{U}. \quad (50)$$

The exchange-correlation potential has been formulated within the context of non-diagonal spin density. The single-particle Kohn-Sham equation now adopts a modified form, which, when paired with a suitable basis set, is prepared for application in noncollinear spin-density functional calculations.

2.3.3 Projector Augmented-Wave Method for Non-Collinear Magnetic System

P.E. Bloch proposed the projected augmented-wave (PAW) method [54] to bridge the gap between pseudopotential and augmented-wave methods [55]. This method preserves the periodicity of electronic structures with a plane wave basis set and simultaneously avoids the asymptotic behavior of waves around the nuclei, allowing for accurate modeling of electronic structures. The PAW formalism involves two fragments, namely the envelope function that maps the electron's behavior outside of the atom-centered regions and the partial-wave expansion within the atom-centered spheres. This decomposition of basis sets in wave-function description helps to navigate rapid oscillation around nuclei while sustaining smooth behavior in the bond region. These properties of the PAW method make it a versatile and powerful tool for ab initio calculations.

Hobs *et al.* [56] extended the PAW method into the noncollinear magnetic framework by a basis set described in terms of spinor wave functions, and the new basis set was implemented within VASP to solve the single-particle KS equation (Eq. (37)).

The all-electron (AE) wave function is transformed into a pseudo (PS) wave function representation to overcome the numerical challenges of representing the wave function near the nuclei. To address this, the linear transformation operator $\hat{T}$ is used to establish a bridge between an auxiliary smooth wave function $|\tilde{\Psi}\rangle$ and the all-electron wave function $|\Psi\rangle$, which represents a single-particle electron in the DFT framework,

$$|\Psi\rangle = \hat{T} |\tilde{\Psi}\rangle, \quad (51)$$

This transformation enables the calculation of physical quantities of the AE system within the PS wave function framework. As an example, the ground state of AE can be obtained from PS wave functions with $\hat{T}$ operator

$$\hat{T}^* \hat{H}_o \hat{T} |\tilde{\Psi}\rangle = \epsilon_o \hat{T}^* \hat{T} |\tilde{\Psi}\rangle. \quad (52)$$

The Eq. (52) will have a complete solution when operator $\hat{T}$ carries WF information

close the nuclei

$$\hat{T} = \hat{1} + \sum_R \hat{T}^R, \quad (53)$$

where $\hat{T}^R$ is a sum of local, atom-centered contribution within Ω_R region enclosing the atom. The target function inside each augmented sphere represents partial waves ϕ_i with index i referring to the atomic side R_i . The partial waves inside the augmented spheres region transfer to auxiliary smooth partial wave function $\tilde{\phi}_i$ with linear transformation operator $\hat{T}$,

$$|\phi_i\rangle = \left(1 + \hat{T}^R\right) |\tilde{\phi}_i\rangle \quad \text{within } \Omega_R \quad \leftrightarrow \quad \hat{T}^R |\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle. \quad (54)$$

The next step is to define a partial wave function outside the augmented sphere and continue on a surface,

$$\langle r|\phi_i\rangle = \langle r|\tilde{\phi}_i\rangle \quad \text{outside of } \Omega_R. \quad (55)$$

The PS-AE wave function can form into smooth partial waves after Eq. (55) reveals a complete set inside the augmented sphere,

$$|\Psi\rangle = \sum_i P_i |\tilde{\phi}_i\rangle \quad \text{within } \Omega_R, \quad (56)$$

Since we require the transformation $\hat{T}$ to be linear, P_i must be linear functionals of the PS wave functions. Hence the coefficients are scalar products

$$P_i = \langle \tilde{p}_i | \tilde{\Psi} \rangle \quad (57)$$

of PS wave function with some fixed functions $\langle \tilde{p}_i |$, so called projection functions. There is exactly one projector function for each PS partial wave. The most general form of the projection function chosen by Bloch is

$$\langle \tilde{p}_i | = \sum_j (\{\langle f_k | \tilde{\phi}_l \rangle\})_{ij}^{-1} \langle f_i |, \quad (58)$$

where l is angular momentum quantum number, the $|f_i\rangle$ is any set of linearly independent functions, and the projection function will be localized if the function $|f_i\rangle$ is

localized.

The expansion of the auxiliary all-electron (AE) wave function at a single center within the augmentation sphere, denoted by Ω_R , is identical to the auxiliary AE wave function itself. Consequently, the projection function must satisfy the identity condition

$$|\Psi\rangle = \sum_i |\phi_i\rangle \langle \tilde{p}_i | \Psi \rangle \quad \leftrightarrow \quad \sum_i \langle \tilde{\phi}_i | \tilde{p}_i \rangle = 1, \quad (59)$$

and this relation implies that

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}. \quad (60)$$

In summary, using identity at Eq. (59), linear operation will form

$$\tilde{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i|, \quad (61)$$

the transformation set was completed, and the AE wave function can be formed from the PS wave function (see Fig.2.2) by

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle. \quad (62)$$

The final expression has three components:

- Auxiliary {PS} wave function $\tilde{\Psi}_i$ which avoids strong oscillations of the all-electron wave function in the core region, and increases computational efficiency thanks to lower energy cutoffs and larger integration time.
- Auxiliary {PS} partial wave function $\tilde{\phi}_i$ is smooth counterpart of partial wave.
- Projection function $\tilde{p}_i$ for each PS wave function localized within augmentative sphere.

The PS wave functions are constructed in reciprocal space using the 2N eigenspinors to describe non-collinear magnetism [56].

$$\langle \mathbf{r} | \tilde{\Psi}^\alpha \rangle = \frac{1}{\sqrt{\Omega_R}} \sum_{\mathbf{k}} C_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (63)$$

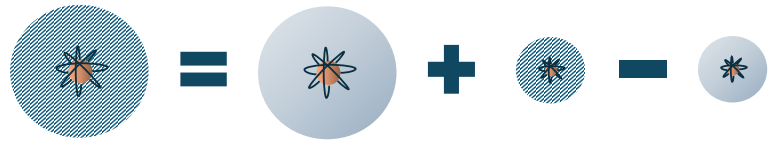
$$\psi = \tilde{\psi} + \sum_i (|\phi_i\rangle\langle\tilde{p}_i|\tilde{\psi}\rangle - |\tilde{\phi}_i\rangle\langle\tilde{p}_i|\tilde{\psi}\rangle)$$


Figure 2.2: Compositions of the all-electron wavefunction within the PAW method.

Here, α index introduced the spin component and Ω_R represents the volume of the Wigner-Seitz cell. The final expression for the total energy of the non-collinear system can be derived from the previous expression by applying the appropriate Hamiltonian.

2.3.4 Spin-Space Groups

An accurate description of the symmetry properties of non-collinear magnetic systems introduces a new class of operations that allow for the independent transformation of spin and spatial variables. To achieve this transformation, Spin-Space groups have been introduced [57, 58, 59] that extend traditional symmetry operations to account for both spatial and spin transformation of two-component spinor (Φ),

$$\{\alpha_s|\alpha_R|\mathbf{t}\}\Phi(\mathbf{r}) = \mathbf{U}(\alpha_s)\Phi(\alpha_R^{-1}\mathbf{r} - \alpha_R^{-1}\mathbf{t}), \quad (64)$$

where α_s and α_R are spin and space rotations, $\mathbf{t}$ is space translation and $\mathbf{U}$ is spin- $\frac{1}{2}$ rotation matrix. When the spin and spatial rotation angles are aligned (i.e., $\alpha_s = \alpha_R$), the Hamiltonian remains invariant under the inclusion of spin-orbit coupling within this framework. Consequently, the relative angle between the spin and the lattice plays a significant role. Conversely, the spin and spatial alignment can be independent of each other and have a crucial role in spin-spiral ab initio calculations.

2.3.5 Generalized Bloch Theorem

The Bloch theorem states that the eigenstates of a Hamiltonian with a periodic potential remain invariant under Bravais lattice translations and can be expressed as the product of a plane wave and a function possessing the same periodicity as the Bravais

lattice.

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{n\mathbf{r}}(\mathbf{r}). \quad (65)$$

In the spin-spiral framework, the exchange-correlation field satisfies the same periodicity conditions under rotational angle $\mathbf{q} \cdot \mathbf{R}_n$, where $\mathbf{q}$ is the wave propagation vector and $\mathbf{R}_n$ is the Bravais lattice vector. The general translation operation, which produces a spin spiral, combines a lattice translation and a spin rotation

$$T_n = \{\alpha\mathbf{q} \cdot \mathbf{R}_n | \epsilon | \mathbf{R}_n\}, \quad (66)$$

where ϵ is a unit element of the group of such operations, and $\alpha\{\mathbf{q} \cdot \mathbf{R}_n\}$ is a rotation by an angle $\mathbf{q} \cdot \mathbf{R}_n$ around the z-axis. The generalized Bloch theorem (Eq. (65)) implies that eigenstates can be written as

$$\Psi_{\mathbf{qk}}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r})U_{-\mathbf{q}\cdot\mathbf{R}_n} \begin{pmatrix} u_{\mathbf{qk}}^{\uparrow}(\mathbf{r}) \\ u_{\mathbf{qk}}^{\downarrow}(\mathbf{r}) \end{pmatrix} \quad (67)$$

where $U_{-\mathbf{q}\cdot\mathbf{R}_n}$ is spin 1/2 rotation matrix,

$$U_{-\mathbf{q}\cdot\mathbf{R}_n} = \begin{pmatrix} \exp(-i\mathbf{q} \cdot \frac{\mathbf{R}_n}{2}) & 0 \\ 0 & \exp(i\mathbf{q} \cdot \frac{\mathbf{R}_n}{2}) \end{pmatrix} \quad (68)$$

2.3.6 *Ab-initio* Calculation of Heisenberg Exchange Parameters

Deflected local moments/spin modes from their equilibrium position at the atomic scale create excited states of spins that propagate along the crystal. This wave-vector-dependent propagation is known as a spin wave. In the quasi-particle picture, the collective excitation is called a magnon. The characteristic timescale of a magnon is much larger than the timescale of an electron's orbital motion. For example, the magnon energy in a transition metal is a few tenths of an eV, while the *d*-band width is a few eV. From this physical picture, we can draw an adiabatic approximation for the systems that evolve from a certain magnetic moment configuration to another state

with a different magnetic moment configuration with zero electron relaxation time. This evolution of magnetic moments can represent a series of snapshots of different magnetic moment configurations at fixed times, called a frozen magnon.



Figure 2.3: (a) All spins in a given lattice direction are aligned due to exchange interaction. (b) A single-flipped spin creates an excited state. (c) The wave-vector-dependent quantized form is called a magnon, where the spin vectors precess on the surface of cones, with a constant phase angle between successive spins that are separated by the inter-atomic lattice spacing. The figure is adapted from reference [1].

The adiabatic case can be interpreted as the expectation value of the magnetic moment as a function of time being almost equal to the expectation value of the stationary state of fast electronic motion with respect to time parameters:

$$\langle \mathbf{M}_i(t) \rangle \approx \langle \mathbf{M}_i \rangle_{\text{fast}}(t) \quad (69)$$

From the Heisenberg Hamiltonian (Eq. (35)) with adiabatic modification, the total energy per unit cell due to magnetic interactions can be expressed by the following formula:

$$\mathbf{E}_M = -\frac{1}{2N} \sum_{n,m,i,j} J(\mathbf{R}_{ni}, \mathbf{R}_{mj}) \mathbf{M}_{mi} \cdot \mathbf{M}_{nj}, \quad (70)$$

Where N is the number of the unit cells in the crystal and $\mathbf{R}_n$ is the translation vector with atomic position vector $\mathbf{r}_i$ inside the unit cell. The n, m index represents the unit cell, i, j the atoms inside each cell. $J(\mathbf{R}_{ni}, \mathbf{R}_{mj})$ contains interatomic interaction information within the unit-cell.

In the spin spiral framework, the local magnetic moment (MM) propagates along a given $\mathbf{q}$ vector, varying with the phase angle (ϕ) relative to the lattice vector ($\mathbf{R}_i$) of

the propagated atom,

$$\mathbf{M}_i^q = M_i \begin{bmatrix} \cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i) \sin(\theta_i) \\ \sin(\mathbf{q} \cdot \mathbf{R}_i + \phi_i) \sin(\theta_i) \\ \cos(\theta_i) \end{bmatrix} \quad (71)$$

where θ_i is the tilted angle of the local magnetic moment over the z-axis.

For simplifying the notation of the next derivations, the inter-atomic distance inside the super-cell is rearranged as $\mathbf{R}_{ni} - \mathbf{R}_{mj} \equiv \mathbf{R}_{ij}$. Then, the Eq. (70) for the energy of a spin spiral with wave vector $\mathbf{q}$ become (see Appendix A for extensive derivation of spin spiral energy formula),

$$\begin{aligned} \mathbf{E}_M(\mathbf{q}; \Theta; \Phi) = & -\frac{1}{2} \sum_{\mathbf{R}_{i,j}} J(\mathbf{R}_{i,j}) M_i M_j \\ & \times \left\{ \sin(\theta_i) \sin(\theta_j) [\cos(\mathbf{q} \cdot \mathbf{R}_{ij} + \phi_i - \phi_j)] + \cos(\theta_i) \cos(\theta_j) \right\}. \end{aligned} \quad (72)$$

The total energy expressed in Eq. (72) is a function of the propagation wave vector $\{\mathbf{q}\}$. As a result, it is convenient to convert to real space interactions $J(\mathbf{R}_{i,j})$ to reciprocal space by the Fourier transform

$$J_{i,j}(\mathbf{q}) = \sum_{\mathbf{R}_{ij}} J(\mathbf{R}_{ij}) \exp^{i\mathbf{q} \cdot \mathbf{R}_{ij}}, \quad (73)$$

The right-hand side of total energy equation (Eq. (72)) becomes,

$$\begin{aligned} \mathbf{E}_M(\mathbf{q}; \Theta; \Phi) = & -\frac{1}{2} \sum_{i,j} M_i M_j \\ & \times \left\{ \sin(\theta_i) \sin(\theta_j) \Re [J_{i,j}(\mathbf{q}) \exp(i(\phi_i - \phi_j))] \right. \\ & \left. + \cos(\theta_i) \cos(\theta_j) J_{i,j}(\mathbf{0}) \right\}. \end{aligned} \quad (74)$$

From the Fourier transform relation, we can define the symmetry relation of exchange parameters in reciprocal space

- $J_{ij}(\mathbf{q}) = J_{ij}(-\mathbf{q})$

- $\Re[J_{ij}(\mathbf{q})] = \Re[J_{ij}(-\mathbf{q})]$.
- $\Im[J_{ij}(\mathbf{q})] = -\Im[J_{ij}(-\mathbf{q})]$.
- $J_{ij}(\mathbf{q}) = J_{ij}(\hat{C}^{-1}\mathbf{q})$

where $\hat{C}$ represents a crystal point group symmetry operation. The final symmetry relation holds a particular significance as it substantially reduces computational time. This reduction is achieved by restricting the sampling of propagation wave vectors $\mathbf{q}$ to the irreducible wedge of the Brillouin zone. By utilizing symmetry operations, the full Brillouin zone can be effectively represented while reducing computational complexity.

2.3.6.1 One Magnetic Atom In The Unit Cell

When there is only one magnetic atom in the unit cell, the interaction will map between the same basis position ($\mathbf{r}_i$ or $\mathbf{r}_j$) among the unit cells ($\mathbf{R}_i, \mathbf{R}_j$) as illustrated in Fig.2.4. To simplify the expression of the total energy of the interaction in notation, the interaction distance between atom i in two different cells $n, m, \mathbf{R}_n + \mathbf{r}_i - (\mathbf{R}_m + \mathbf{r}_i)$ reformed in $\mathbf{R}$. For simplicity the atom i is label as 1, M_1, θ_1 and M_2, θ_2 are assumed equal to M, θ .

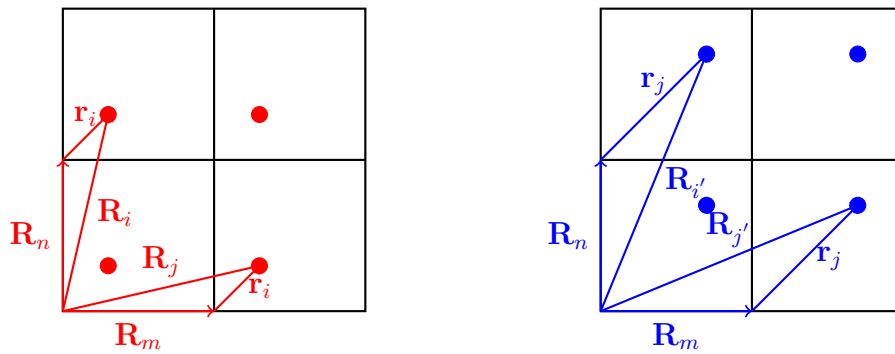


Figure 2.4: Illustration of exchange interaction between same atom i (j) in the single-atom unit cell. This figure depicts the exchange interaction occurring at the same atomic site i (j) within a unit cell containing a single atom.

The total energy of interactions Eq. (74) for magnetic atom 1 become,

$$E_{11}(\mathbf{q}) = -M^2 \sin^2 \theta \Re[J_{11}(\mathbf{q})] - M^2 J_{11}(0) \cos^2 \theta \quad (75)$$

The Fourier transform of $J_{11}(\mathbf{q})$ from Eq. (73) becomes,

$$J_{11}(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{R}} J_{11}(\mathbf{R}) \exp(i\mathbf{q} \cdot \mathbf{R}). \quad (76)$$

Now, two propagation vector conditions are required to determine from the complex-valued Heisenberg parameters in reciprocal space at any $\mathbf{q}$ vector,

- $\mathbf{q} = \mathbf{q} \rightarrow E_{11}(\mathbf{q}) = -M^2 \sin^2 \theta \operatorname{Re}[J_{11}(\mathbf{q})] - M^2 J_{11}(0) \cos^2 \theta$
- $\mathbf{q} = \mathbf{0} \rightarrow E_{11}(\mathbf{0}) = -M^2 \sin^2 \theta \operatorname{Re}[J_{11}(\mathbf{0})] - M^2 J_{11}(0) \cos^2 \theta$

From two energy condition differences $E_{11}(\mathbf{q}) - E_{11}(\mathbf{0})$, $J_{11}(q)$ and $J_{11}(0)$ can reorganize in LHS of the equation after diving both sides by $M^2 \sin^2 \theta$,

$$J_{11}(\mathbf{q}) - J_{11}(\mathbf{0}) = -\frac{E_{11}(\mathbf{q}) - E_{11}(\mathbf{0})}{M^2 \sin^2 \theta}. \quad (77)$$

Defining a complex (in general) coefficient $\tilde{J}_{ij}(q) \equiv J_{ij}(q) - \delta_{ij} J_{ij}(0)$, Eq. (77) can now be re-written,

$$\tilde{J}_{11}(\mathbf{q}) = -\frac{E_{11}(\mathbf{q}) - E_{11}(\mathbf{0})}{M^2 \sin^2 \theta}. \quad (78)$$

2.3.6.2 More Than One Magnetic Atom In The Unit Cell

Now, we will consider there are two magnetic atoms in the unit cell, the interaction will happen between the two basis's position $(\mathbf{r}_i, \mathbf{r}_j)$ among the unit cells $(\mathbf{R}_i, \mathbf{R}_j)$. In this case, the interaction of atomic moments is divided into two parts: Spin interaction inside the same unit cell as illustrated in Fig.2.5, and spin interaction among the different unit cells as illustrated in Fig.2.6.

To simplify the expression of the total energy of the interaction in notation, the interaction distance between atom i and j , $\mathbf{R}_i + \mathbf{r}_i - (\mathbf{R}_j + \mathbf{r}_j)$ expressed in terms of $\mathbf{R}$. The atoms i and j are labeled as 1, 2 for simplicity, M_1, θ_1 and M_2, θ_1 assumed to be equal to M, θ . The symmetry operations of real and imaginary parts of $J(\mathbf{q})$ will be labeled as **SO** in the next steps.

The energy of the interaction illustrated in Fig.2.5 contain 1-2 and 2-1 bases inter-

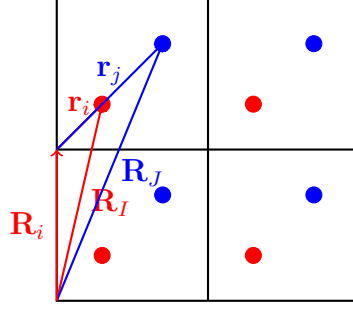


Figure 2.5: Illustration of the exchange interaction between two atom i, j inside unit-cell. This figure represents the exchange interaction occurring between two distinct atomic sites, i and j , within a single unit cell.

action energies,

$$E(\mathbf{q}, \phi) = E_{12}(\mathbf{q}, \phi_1) + E_{21}(\mathbf{q}, \phi_2). \quad (79)$$

From Eq. (72) after applying Fourier transform Eq. (74), E_{12} and E_{21} are

$$E_{12}(\mathbf{q}) = -M^2 \sin^2 \theta \text{Re}[J_{12}(\mathbf{q}) \exp(i\Delta\phi)] - M^2 J_{12}(\mathbf{0}) \cos^2 \theta, \quad (80)$$

$$E_{21}(\mathbf{q}) = -M^2 \sin^2 \theta \text{Re}[J_{21}(\mathbf{q}) \exp(-i\Delta\phi)] - M^2 J_{21}(\mathbf{0}) \cos^2 \theta. \quad (81)$$

Now, two propagation vector conditions are used to derive the propagation energies at any arbitrary $\mathbf{q}$ vector ($\mathbf{q}$) with phase angle 0 ($\Delta\phi = 0$), and $\mathbf{q} = 0$ with phase angle 90 ($\Delta\phi = \pi/2$),

- $\{\mathbf{q}, 0\} \rightarrow E_{12}(\mathbf{q}, 0) = -M^2 \sin^2 \theta \text{Re}[J_{12}(\mathbf{q})] - M^2 J_{12}(\mathbf{q}) \cos^2 \theta$
- $\{\mathbf{0}, \pi/2\} \rightarrow E_{12}(\mathbf{0}, \frac{\pi}{2}) = -M^2 \sin^2 \theta \text{Re}[\cancel{J_{12}(\mathbf{0})}^{\text{SO} \rightarrow 0} \exp(i\frac{\pi}{2})] - M^2 J_{12}(\mathbf{0}) \cos^2 \theta$
- $\{\mathbf{q}, 0\} \rightarrow E_{21}(\mathbf{q}, 0) = -M^2 \sin^2 \theta \text{Re}[J_{21}(\mathbf{q})] - M^2 J_{21}(\mathbf{0}) \cos^2 \theta$
- $\{\mathbf{0}, \pi/2\} \rightarrow E_{21}(\mathbf{0}, \frac{\pi}{2}) = -M^2 \sin^2 \theta \text{Re}[\cancel{J_{21}(\mathbf{0})}^{\text{SO} \rightarrow 0} \exp(i\frac{\pi}{2})] - M^2 J_{21}(\mathbf{0}) \cos^2 \theta$

Using the relations above, and $J_{21}(\mathbf{q}) = J_{12}(-\mathbf{q})$ symmetry relation, the energy differences ($E(\mathbf{0}, \pi/2) - E(\mathbf{q}, 0)$) can be re-written from Eq.(80),

$$\begin{aligned} E(\mathbf{0}, \frac{\pi}{2}) - E(\mathbf{q}, 0) &= \cancel{M^2 J_{12}(\mathbf{0}) \cos^2 \theta} + M^2 \sin^2 \theta \Re[J_{12}(\mathbf{q})] \\ &\quad + \cancel{M^2 J_{12}(\mathbf{0}) \cos^2 \theta} - \cancel{M^2 J_{21}(\mathbf{0}) \cos^2 \theta} \\ &\quad + M^2 \sin^2 \theta \Re[J_{12}(-\mathbf{q})] + \cancel{M^2 J_{21}(\mathbf{0}) \cos^2 \theta}. \end{aligned} \quad (82)$$

The final step in calculating the real part of $J_{12}(\mathbf{q})$ involves utilizing the symmetry relation between the real parts of J_{12} , J_{21} : $\Re[J_{12}(\mathbf{q})] = \Re[J_{12}(-\mathbf{q})]$, and dividing by $2M^2 \sin^2(\theta)$ both sides of the equation,

$$\Re[J_{mi,nj}(\mathbf{q})] = \frac{E_{mi}(\mathbf{0}, \frac{\pi}{2}) - E_{mj}(\mathbf{q}, 0)}{2M^2 \sin^2 \theta}. \quad (83)$$

The derivation of the imaginary part of $J_{12}(\mathbf{q})$ will be shown in the second part of the interaction map between i and j in Fig. 2.6.

This second part of the interaction between atoms i and j includes contributions from energy differences across distinct unit cells $(\mathbf{R}_n, \mathbf{R}_m)$ interaction mapping as shown in Fig.2.6. The labeling pattern is consistent with that used in the first part of the interaction, maintaining the same indices ($i = 1, j = 2$), and parameters (M, θ) .

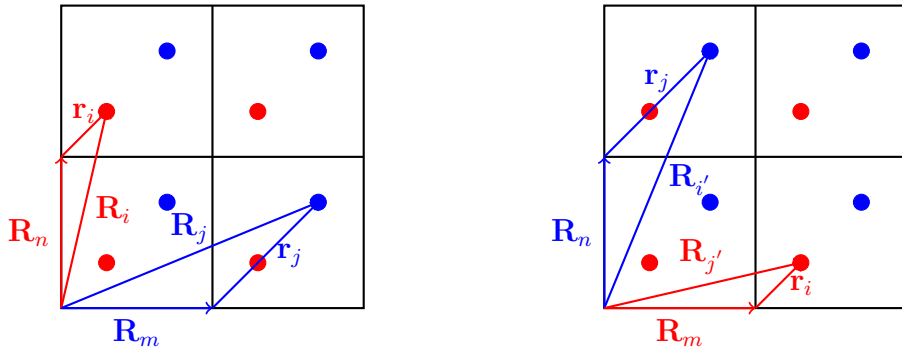


Figure 2.6: Illustration of the exchange interaction between two atoms i, j outside the unit Cell. This figure represents the exchange interaction taking place between two distinct atomic sites, i and j , located outside the unit cell.

The energy of the interaction illustrated in Fig.2.6 contain 1-1 and 2-2, 1-2, and 2-1 bases interaction energies,

$$E(\mathbf{q}, \phi) = E_{11}(\mathbf{q}, \phi) + E_{22}(\mathbf{q}, \phi) + E_{12}(\mathbf{q}, \phi) + E_{21}(\mathbf{q}, \phi). \quad (84)$$

The mathematical steps are analogous to those used in the first part of the interaction to calculate the real part of the exchange constant ($\Re[J_{12}(\mathbf{q})]$), and the result yields,

$$\Re[J_{21}(\mathbf{q})] = \frac{E(\mathbf{0}, \frac{\pi}{2}) - E(\mathbf{q}, 0)}{2M^2 \sin^2 \theta} + \frac{E_{11}(\mathbf{q}) - E_{11}(\mathbf{0})}{2M^2 \sin^2 \theta} + \frac{E_{22}(\mathbf{q}) - E_{22}(\mathbf{0})}{2M^2 \sin^2 \theta}. \quad (85)$$

When the unit cell lacks inversion symmetry, the imaginary component of the Heisen-

berg exchange constant $\Im[J_{12}(q)]$ also contributes to the real-space Heisenberg exchange constant in its Fourier transform. Again, two special spin spirals are used to derive the propagation energies at any arbitrary $\mathbf{q}$ vector ($\mathbf{q}$) with phase angle 0 ($\Delta\phi = 0$), and phase angle 90 ($\Delta\phi = \pi/2$),

- $\{\mathbf{q}, 0\} \rightarrow E_{12}(\mathbf{q}, 0) = -M^2 \sin \theta \operatorname{Re}[J_{12}(\mathbf{q})] - M^2 J_{12}(\mathbf{q}) \cos^2 \theta$
- $\{\mathbf{q}, \pi/2\} \rightarrow E_{12}(\mathbf{q}, \frac{\pi}{2}) = -M^2 \sin \theta \frac{\operatorname{Re}[J_{12}(\mathbf{q}) \exp(i\frac{\pi}{2})] = -\Im[J_{12}(q)]}{\operatorname{Re}[J_{12}(\mathbf{q}) \exp(i\frac{\pi}{2})]} - M^2 J_{12}(\mathbf{0}) \cos^2 \theta$
- $\{\mathbf{q}, 0\} \rightarrow E_{21}(\mathbf{q}, 0) = -M^2 \sin \theta \operatorname{Re}[J_{21}(\mathbf{q})] - M^2 J_{21}(\mathbf{0}) \cos^2 \theta$
- $\{\mathbf{0}, \pi/2\} \rightarrow E_{21}(\mathbf{q}, \frac{\pi}{2}) = -M^2 \sin \theta \frac{\operatorname{Re}[J_{21}(\mathbf{q}) \exp(-i\frac{\pi}{2})] = \Im[J_{21}(q)]}{\operatorname{Re}[J_{21}(\mathbf{q}) \exp(-i\frac{\pi}{2})]} - M^2 J_{21}(\mathbf{0}) \cos^2 \theta$

After straight forward mathematical steps and symmetry operations (see Appendix B), the final expression of $\Im[J_{12}(\mathbf{q})]$ can be re-written as,

$$\begin{aligned} \Im[J_{21}(\mathbf{q})] = & \frac{E(\mathbf{q}, \frac{\pi}{2}) - E(\mathbf{q}, 0)}{2M^2 \sin^2 \theta} + \frac{E_{11}(\mathbf{0}) - E_{11}(\mathbf{q})}{2M^2 \sin^2 \theta} \\ & + \frac{E_{22}(\mathbf{0}) - E_{22}(\mathbf{q})}{2M^2 \sin^2 \theta} + \Re[J_{21}(\mathbf{q})]. \end{aligned} \quad (86)$$

Now that different magnetic configuration interactions energies were established from differences in total energies as a function of $\mathbf{q}$ and $\Delta\phi$, calculating real space Heisenberg exchange constants ($J_{ij}(\mathbf{r}_i, \mathbf{r}_i)$) from inverse Fourier transform (IFT) is ready (see Appendix C for mathematical steps),

$$\begin{aligned} J_{ij}(\mathbf{r}_i, \mathbf{r}_i - \mathbf{R}) = & \frac{1}{V_{BZ}} \int_{BZ} \left\{ \Re[J_{ij}(\mathbf{q})] \cos(\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})) \right. \\ & \left. - \Im[J_{ij}(\mathbf{q})] \sin(\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})) \right\} d^3 \mathbf{q}. \end{aligned} \quad (87)$$

The inverse Fourier Transform (IFT) is now reformulated for each magnetic interaction configuration. First, the IFT is calculated for the interaction involving a single magnetic basis, where $\mathbf{R} = R$, and $\Im[J_{ij}] = 0$,

$$J_{ii}(\mathbf{r}_i, \mathbf{r}_i - \mathbf{R}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} \left\{ -\frac{E_{ii}(\mathbf{q}) - E_{ii}(\mathbf{0})}{M^2 \sin^2 \theta} \right\} d^3 \mathbf{q}. \quad (88)$$

Secondly, the IFT is calculated for the interaction involving two magnetic atoms inside

the unit cell, where $\mathbf{R} = 0$,

$$J_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{V_{BZ}} \int_{V_{BZ}} \left\{ \frac{E(\mathbf{0}, \frac{\pi}{2}) - E(\mathbf{q}, 0)}{2M^2 \sin^2 \theta} \right\} d^3 \mathbf{q}. \quad (89)$$

Finally, the IFT is calculated for the interaction involving two magnetic atoms outside the unit cell, where $\mathbf{R} = R$,

$$J_{ij}(\mathbf{r}_i, \mathbf{r}_j - \mathbf{R}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} \left\{ \frac{E(\mathbf{0}, \frac{\pi}{2}) - E(\mathbf{q}, 0)}{2M^2 \sin^2 \theta} + \frac{E_{ii}(\mathbf{q}) - E_{ii}(\mathbf{0})}{2M^2 \sin^2 \theta} + \frac{E_{jj}(\mathbf{q}) - E_{jj}(\mathbf{0})}{2M^2 \sin^2 \theta} \right\} d^3 \mathbf{q}, \quad (90)$$

where V_{BZ} is the volume of reciprocal space within the Brillouin zone boundary.

2.3.6.3 Andersen's Magnetic Force Theorem

Andersen's force theorem states that when the densities $(n(\mathbf{r}), s(\mathbf{r}))$ of the magnetic system is subjected to a small perturbation, the energy difference between the ground state and the perturbed state can be calculated by their KS band energies (ϵ_i) and the results yield an approximate value of the total energy differences of the two states calculated by Self-Consistent field. The total energy can be expressed as the sum of the density of states $[D(E)]$ up to fermi energy,

$$E = \int_{-\infty}^{E_f} E D(E) dE - E_r. \quad (91)$$

where the first term on the right hand side called band energies (eigenvalues sum E_{eig}) and E_r term includes sum all of non-band-energy contribution (e.g., Hartree energy, exchange-correlation, and external potential). When the perturbation introduced to system, its energy will change from equilibrium to the perturbed state, and the change can be parameterized by a set of quantities $\{X_i\}$. The change in the total energy will be formulated as a function of $\{X_i\}$,

$$\delta E = \sum_i \frac{\delta E}{\delta X_i} \delta X_i. \quad (92)$$

The spin spiral perturbation is specified by a set of $\{\Delta X_i\}$ parameters. First, with the effective potential held fixed, the Schrödinger equation is solved for the new parameter set $\{X_i + \Delta X_i\}$, yielding a new density and energy eigenvalues. This first variation is denoted as δ_1 . In the subsequent step, the potential relaxes to achieve self-consistency using the same parameter set $\{X_i + \Delta X_i\}$. This second variational step is referred to as δ_2 . Consequently, the total variation can be expressed as $\delta = \delta_1 + \delta_2$. Then, the change in total energy is formulated as,

$$\delta E = \delta E_1 + \delta E_2 - \delta E_r, \quad (93)$$

and change in band energies,

$$\delta E = \delta E_1 + \delta E_2, \quad (94)$$

The final form will be obtained from writing out the term δE_r and applying the first-order perturbation theory on δE_2

$$\delta E = \delta E_2 - \int_{\delta\Omega} n^2 \frac{d\epsilon_{xc}}{dn} \delta\sigma \cdot d\mathbf{S}, \quad (95)$$

where $d\sigma$ is surface element, and $\delta\mathbf{S}$ is representing spin state change in the perturbed system volume Ω due to the applied perturbation.

The Eq. (95) is called Andersen's magnetic force theorem [60, 61, 62] and states that energy changes of the two-state created by small perturbations can be calculated by differences in their sum of eigenvalues ($E_{eig}^1 - E_{eig}^2$). In computational terms, energy changes in slightly perturbed systems can be efficiently addressed using a Non-Self-Consistent Field (NSCF) approach, significantly reducing the computational time required for spin-spiral calculations.

2.3.7 The Magnetocrystalline Anisotropy Energy

In the previous sections, magnetic interactions were modeled using an effective classical Heisenberg Hamiltonian, which is isotropic and lacks directional dependence. However, the intrinsic magnetic energy of a magnetic material exhibits directionality bound to

certain crystallographic directions and is called magnetocrystalline anisotropy. The fundamental physics of this phenomenon is that the antiferromagnetic or ferromagnetic order parameter of a material determines a preferential direction within the crystal.

Macroscopically, the magnetization reaches saturation at a significantly lower magnetic field along the preferred crystallographic direction, known as the easy axis. Conversely, the direction that requires the highest magnetic field to achieve magnetization is referred to as the hard axis. The required energy to change direction between the easy axis and hard axis can be formulated as the work done per unit volume by an external field in magnetizing a ferromagnetic sample at a constant temperature

$$E_{mc} = \int_0^M \mu_o \mathbf{H} d\mathbf{M}, \quad (96)$$

E_{mc} is magnetocrystalline anisotropy energy (MAE) that is the integrated area of the magnetization curve as a function of the magnetic field along a specific crystallographic direction. A textbook example of the Eq. (96) is shown in Fig.2.7

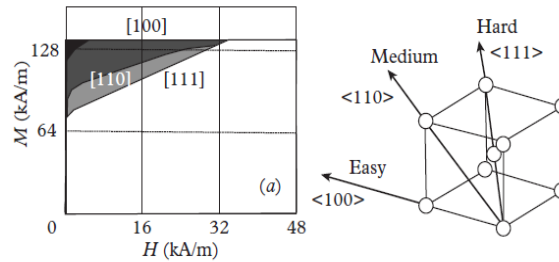


Figure 2.7: Magnetization curves for the field applied along different crystallographic directions for bcc Fe. The $\langle 001 \rangle$ is easy axis, $\langle 111 \rangle$ is the hard axis. The figure is adapted from reference [1].

From the magnetic force theorem, the Eq. (96) can be recast to obtain the MAE in the DTF picture

$$E_{mc} = \sum_{n\mathbf{k}} [\epsilon_{n\mathbf{k}}^{KS}(\mathbf{S}||\mathbf{e}_{easy}) - \epsilon_{n\mathbf{k}}^{KS}(\mathbf{S}||\mathbf{e}_{hard})], \quad (97)$$

where $\epsilon_{n\mathbf{k}}^{KS}$ is an eigenvalue of occupied band energy and $S[axis]$ is the direction of the total spin in the unit cell.

The relation between the crystalline lattice symmetry and the spin-orbit coupling creates preferential paths along crystallographic directions for the magnetic field, which is called anisotropy. The preferential behavior can be revealed from the crystal field (CF) potential of the single-ion approximation V_{CF} . The CF potential function can be decomposed in spherical coordinates in real space with the tensor function $C^{(n)}(\theta, \phi)$, which is characteristic to the intrinsic symmetries of the crystal,

$$V_{CF}(\mathbf{r}, \theta, \phi) = \sum_{n=even}^{\infty} \sum_{m=-n}^n V_{nm}(\mathbf{r}) C_n^{(n)}(\theta, \phi). \quad (98)$$

The tensor function can be expressed using any complete set of functions, provided they are compatible with a polar coordinate representation. The Stevens normalization is a suitable choice of basis set for this purpose, as it is based on trigonometric expressions that facilitate simple calculations in high-symmetry cases (a term introduced by Newman and Ng, 1989 [63]). In the microscopic picture, the crystal field potential information reads to anisotropy energy expression with Steven's normalization basis set

$$E_a = \sum_{n=even}^{\infty} \sum_{m=-n}^n \kappa_{nm} C_n^{(n)}(\theta, \phi). \quad (99)$$

The anisotropy energy [Eq. (99)] in tetragonal crystal that maintain D_4 , C_{4v} , D_{2d} and D_{4h} will be formed

$$E_{tetragonal} = K_1 \sin^2(\theta) + K_2 \sin^4(\theta) + K'_2 \sin^4(\theta) \cos(4\phi) + K_3 \sin^6(\theta) + K'_3 \sin^6(\theta) \cos(4\phi), \quad (100)$$

K_i is called the anisotropy constant. Its relation to κ_{nm} can be found in the Handbook of Magnetic Material appendix B1 [64]. The higher terms of $\sin(\theta)$ in Eq. (100) will be neglected for the sake of simplicity for DFT calculations, which yield one easy-axis and one in-plane K parameter calculations (where the crystal exhibits two-fold symmetry):

$$E_{tetragonal} = K_1 \sin^2(\theta) + K_2 \sin^4(\theta) + K'_2 \sin^4(\theta) \cos(4\phi) \quad (101)$$

3 — Optimization of Hubbard U and J Parameters for Mn₃Ga: From Linear Response to Empirical Adjustment

A central problem of the *ab initio* electronic methods is to understand and describe electronic properties and geometric optimization at the atomic level of mesoscopic systems to gain an understanding of fundamental physics and explore novel effects for applications in technology. The most significant approximation for the exchange and correlation energy functional in DFT is primarily derived on the basis of the homogeneous electron gas, and because of its nature, strongly correlated systems fail to converge their physical, magnetic, and electronic properties. By way of example, LSDA is failing dramatically to reproduce the experimental lattice parameters of DO₂₂ Mn₃Ga bulk, which are $a = 3.90 \text{ \AA}$ and $c = 7.12 \text{ \AA}$ [65, 66]. Likewise, GGA functions perform better on the optimization of the lattice parameters but underestimate them by approximately 6%. In addition, out-of-plane magnetocrystalline anisotropy energy (MAE) yields an overestimated result compared to the experimental value (1 meV [67]) (that will be discussed in the Chapter 3). These systematic problems on DFT energy functionals were improved through an alternative functional such as the hybrid functional PBE0 [68, 69] and HSE06 [70]. These functionals demonstrate themselves to perform more accurate band gaps and geometry optimization due to their HF screening function, which corrects self-interaction errors present in standard DFT. However,

they are computationally expensive. That drawback of these functionals directs us to research less expensive but momentarily in a similar accuracy domain for optimizing DO₂₂ Mn₃Ga. One of the best-established methods for this purpose is the Hubbard correction, widely referred to as DFT+U [71, 72, 73]. This method introduces an energy cost to localized orbitals to align the system with the experimental evidence. Adjustments are primarily made by modifying the 'U parameter' of the atomic site, which is prone to more localized orbitals in the unit cell.

In this chapter, we first evaluate the performance of standard exchange-correlation functionals (LDA, GGA) for volume optimization of DO₂₂-Mn₃Ga. Subsequently, we introduce the linear response approach to compute the Hubbard U parameter. We then implement an empirical multi-parameter scanning method within the Dudarev and Liechtenstein formalism to determine optimal Hubbard U parameter that yield lattice parameters and local magnetic moment consistent with experimental measurements. Finally, we apply the the multi-parameter scanning technique to fixed-volume DO₂₂ Mn₃Ga structures, initializing the unit cell with epitaxial constraints ($a = b = \sqrt{2}a_{Fe} = 4.05 \text{ \AA}$) to model coherent growth on Fe/MgO magnetic tunnel junction (MTJs) [74].

Initial lattice parameters were intentionally set distinct from experimental values to evaluate standard exchange-correlation functionals (LDA, GGA) in volume optimization of DO₂₂ Mn₃Ga. Volume relaxation results are presented in Fig.3.1. A tolerance window of $\pm 1\%$ around experimental lattice constants was defined as the favorable region (gray highlight). As Fig.3.1 shows, relaxed unit cells using GGA (red) and LDA (gree) fail to converge withing experimental tolerance (blue rectangle). LDA exhibits particularly poor performance, with both a and c -lattice parameters converging outside the favorable region. While GGA achieves agreement for the c -axis within experimental bounds, it underestimates the a -axis parameter. Crucially, the both functionals underestimate the experimental volume (Fig.3.1). This demonstrates that standard exchange-correlation functionals inadequately describe the Mn₃Ga DO₂₂ unit cell within experimentally established parameter ranges. As anticipated, the deficiency originates in the inadequate treatment of strongly correlated d -electron in Mn atoms, motivating the application of DFT+U.

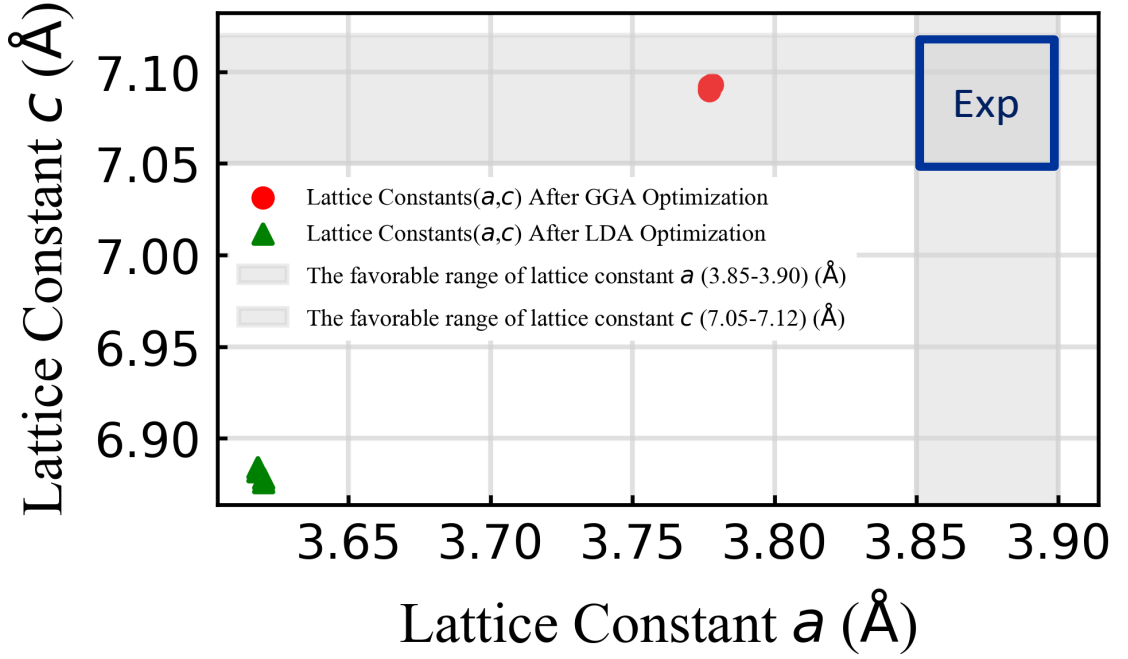


Figure 3.1: Comparison of the performance of GGA and LDA functionals in lattice parameter optimization.

Several methods have been developed to calculate the U parameter from DFT-based simulations. One of the most extensively studied approaches is the linear response method [75, 76]. This method computes Hubbard U parameter self-consistently analyzing the system's electronic response to localized perturbations to ensure that U parameter derived from material's intrinsic electronic structure.

In Linear response formulation of the LDA+ U method, Hubbard U obtained via constrained density functional calculation. Following Dederichs et al. [77], the total energy functional defined as:

$$E[\alpha_I] = \min_{n(\mathbf{r})} \{E[n(\mathbf{r})] + \sum_I \alpha_I n_I\}. \quad (1)$$

Where $E[n(\mathbf{r})]$ is the usual DFT total energy functional, and α_I are Lagrange multipliers imposing localized perturbations on the occupations n_I of Hubbard sites I .

Following Cococcioni et al [75] steps, one then defines the interacting (χ_{IJ}) and

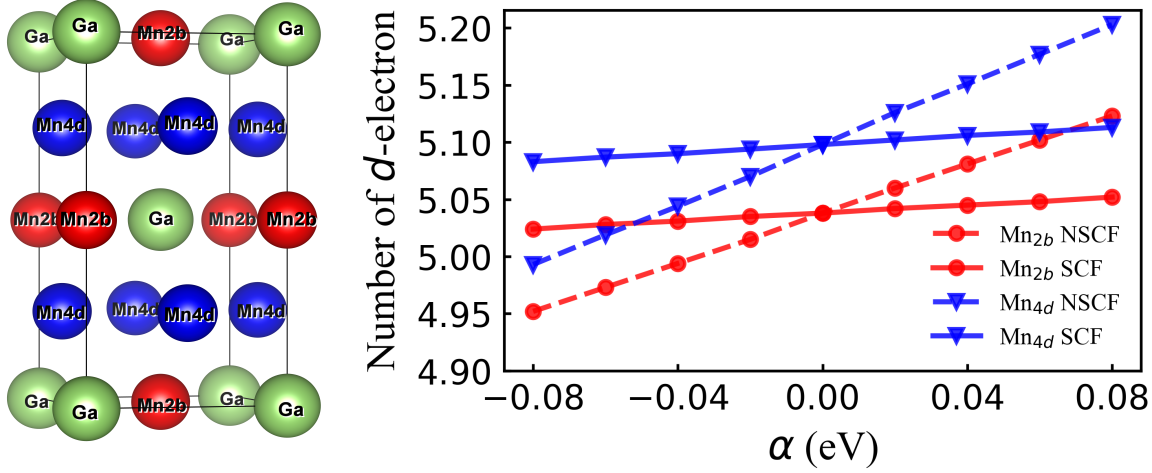


Figure 3.2: Left figure: The Wyckoff sites 2b and 4d illustration of DO_{22} Mn_3Ga . Right Figure: The dependence of the linear response of the d orbital occupation of Mn sites on potential shift α . The lines in plots illustrate the non-interacting (NSCF) and the interacting (SCF) inverse density response functions for 2b and 4d sites of Mn atom. The inverse response functions are obtained numerically by linear fit of the slop of lines.

non-interaction (χ_{IJ}^0) density response functions are

$$\chi_{IJ} = \frac{\delta^2 E}{\delta \alpha_I \delta \alpha_J} = \left. \frac{\delta n_I}{\delta \alpha_J} \right|_{\text{SCF}}, \quad (2)$$

$$\chi_{IJ}^0 = \frac{\delta^2 E^{KS}}{\delta \alpha_I^{KS} \delta \alpha_J^{KS}} = \left. \frac{\delta n_I}{\delta \alpha_J^{KS}} \right|_{\text{NSCF}}. \quad (3)$$

where “SCF” denotes the fully self-consistent response (including screening) to the localized perturbation α_J , and “NSCF” denotes the bare response of the noninteracting Kohn–Sham system that were obtained from a linear fit of the number of d -electron for each atomic site of Mn (see Fig.3.2). Finally, the Hubbard U parameter is obtained as difference between the inverses of these response functions:

$$U = \chi_0^{-1} - \chi^{-1}. \quad (4)$$

The Hubbard U parameter of each Mn site computed from Eq. (4) where the inverse response functions are obtained numerically by linear fit of occupation numbers (see Fig.3.2). The resulting values are $U_{\text{Mn}_{2b}} = 4.8$ eV and $U_{\text{Mn}_{4d}} = 4.5$ eV. Subsequent volume relaxation using these parameters yielded lattice constants $a=4.05$ Å, $c=6.03$

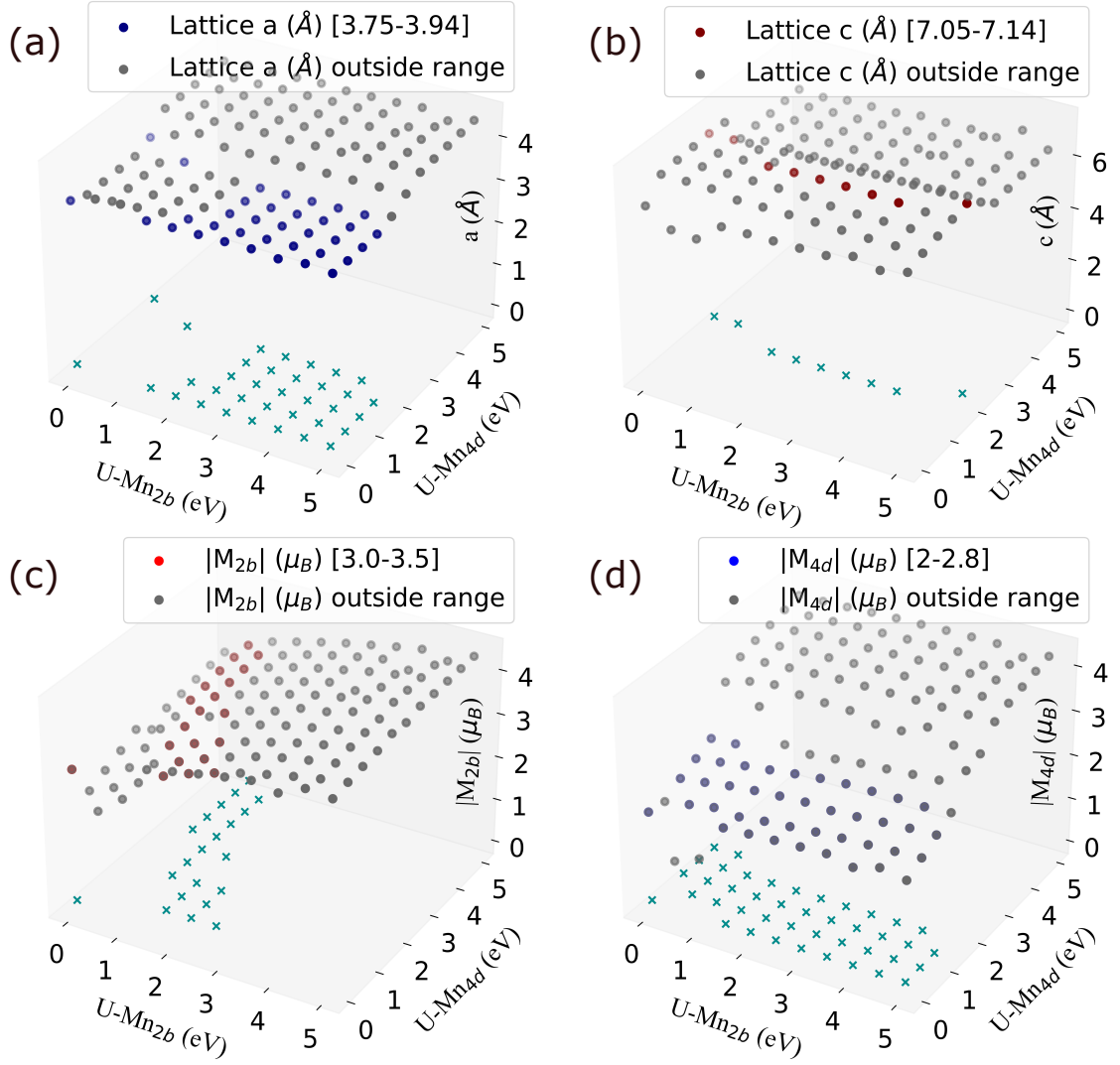


Figure 3.3: 3D representation of (a)-(b) lattice parameters (a and c) and (c)-(d) local magnetic moment optimization for Mn_{2b} and Mn_{4d} sites in Mn_3Ga via dense 121-point 2D mesh over Hubbard parameter U_{2b} and U_{4d} . Blue (red) dots highlight parameter combinations yielding magnetic moments closest to experimental values. Projection of these optimal Hubbard parameters onto U_{2b} - U_{4d} plane are marked with green crosses.

Å, which deviate from experimental values ($a_{\text{exp}}=3.90$ Å, $c_{\text{exp}}=7.12$ Å).

This discrepancy may originate from the supercell size used in the linear response calculation. As emphasized by Cococcioni et al. [75], an insufficiently large supercell can truncate screening contributions from neighboring atoms, leading to inaccurate U values. While increasing the supercell size would improve accuracy, the computational cost for Mn_3Ga —a compound with two distinct Mn sites—becomes prohibitive. Moreover, the transferability of U parameters obtained from a converged supercell to the primitive cell remains uncertain due to differences in the local atomic environment.

Given the inability of Hubbard U parameters derived from linear response approach

Table 3.1: Lattice parameters a and c , total magnetic moment m_{total} (per unit cell), and local magnetic moments m of Mn_3Ga as a function of U_{2b} and U_{4d} .

U_{2b} (eV)	U_{4d} (eV)	a (Å)	c (Å)	M_{2b} (μ_B)	M_{4d} (μ_B)	m_{total} (μ_B)
1.5	1.5	3.72	7.06	-3.237	2.581	1.925
2.0	1.5	3.73	7.10	-3.432	2.654	1.876
2.5	1.5	3.75	7.11	-3.606	2.718	1.830
3.0	1.5	3.77	7.12	-3.758	2.764	1.770
3.5	1.5	3.79	7.09	-3.908	2.767	1.625
4.0	1.5	3.81	7.07	-4.031	2.778	1.525

to reproduce the experimental volume of Mn_3Ga , we implemented an empirical multi-parameter scanning technique following Saha *et al.* [78]. This methodology systematically scans Hubbard U values for distinct atomic sites (2b and 4d) to simultaneously optimize in-plane (a), out-of-plane (c) lattice constants, and local magnetic moments at each Mn site against experimental benchmarks. Within the LDA exchange-correlation framework and using Dudarev’s DFT+ U formalism, we performed a dense 121-point parameter scan over U_{2b} and U_{4d} . As illustrated in Fig. 3.3, the lattice parameters as well as local magnetic moment of Mn sites within the tolerance window of $\pm 1\%$ around experimental values are highlighted in color (red and blue), while the silver points represent those outside the tolerance window. The green cross signs represent a projection of highlighted points on optimal Hubbard parameters axis.

Implementing Hubbard corrections requires balancing the simultaneous convergence of lattice parameters and local magnetic moments to experimental values. While applying Hubbard U parameters to Mn d -shells enhances site-specific magnetic moments, optimizing lattice parameters alone is insufficient to achieve the critical magnetic properties of Mn_3Ga . Crucially, the local magnetic moment—a key benchmark due to its direct impact on electron transport vector components—must converge to closely the experimentally established value of $2.2 \mu_B$ per formula unit [79].

This necessitates a trade-off: we prioritize magnetic moment accuracy while maintaining lattice parameters within experimental tolerance windows. As evidenced by the cross-section of optimal parameters in Fig. 3.3, the combination $U_{2b}=U_{4d}=1.5$ eV (Table 3.1) yields:

- lattice constant: $a = 3.72 \text{ Å}$, $a = 7.06 \text{ Å}$

- $Mn_{2b} = -3.237 \mu_B$, $Mn_{4d} = 2.581 \mu_B$
- Total moment: $1.925 \mu_B$

showing closest agreement with experimental magnetic properties while retaining acceptable structural accuracy.

Our subsequent Hubbard correction investigation aims to reproduce with the structural Mn_3Ga epitaxial grown on MgO substrate that has lattice constants of $a = 3.92 \text{ \AA}$ and $c = 7.04 \text{ \AA}$ from reciprocal space mapping measurement technique [80]. Our previous scanning method of Hubbard corrections was applied to obtain a desirable range of local magnetic moments at sites Mn_{4d} and Mn_{2b} and their total magnetic moment per unit formula. However, this time, the volume was fixed, and only the ions were allowed to relax, following a zero-strain approach between the Mn_3Ga composition and the MgO substrate based on the experimental observation on thin film lattice constants [80]. The local magnetic moments of Mn_{2b} and Mn_{4d} vary in the broad spectrum of the magnetic moment as a function of Hubbard's effective potential as shown in Fig. 3.4.

The local magnetic moments in Fig.3.4a-b indicated that, under a fixed volume condition ($a = 3.92 \text{ \AA}$, $c = 7.04 \text{ \AA}$), Mn_3Ga demonstrates a considerable variation in the converged values of local magnetic moments across the range of Hubbard U_{2b} and U_{4d} variation. To refine the selection of the Hubbard energy, the magnetic moment per formula unit will be examined for each combination of Hubbard parameters U_{2b} and U_{4d} , to achieve values close to the saturation magnetization of $2.53 \mu_B$. The selection process narrowed down to $U_{2b} = U_{4d} = 0-1 \text{ eV}$ range since the local magnetic moments exhibit reasonable values in that region, and higher Hubbard energies give rise to larger local magnetic moments above the experimental benchmark. Figure 3.4c exhibits 13 Hubbard energy combinations converged on the desirable range of total magnetic moment with 0-1 eV energy range. After, carefully measuring the trade-off between the total magnetic and local magnetic moment of these 13 candidates, $U_{2b} = U_{4d} = 1 \text{ eV}$ was selected which exhibits $1.87 \mu_B$ total magnetic moment per unit formula with $-3.394 \mu_B$ and $2.677 \mu_B$ local magnetic moment at 2b and 4d sites respectively.

In summary, we demonstrated in Fig.3.1 that the conventional LDA energy functional fails to achieve reasonable agreement to experiment lattice constants. We ex-

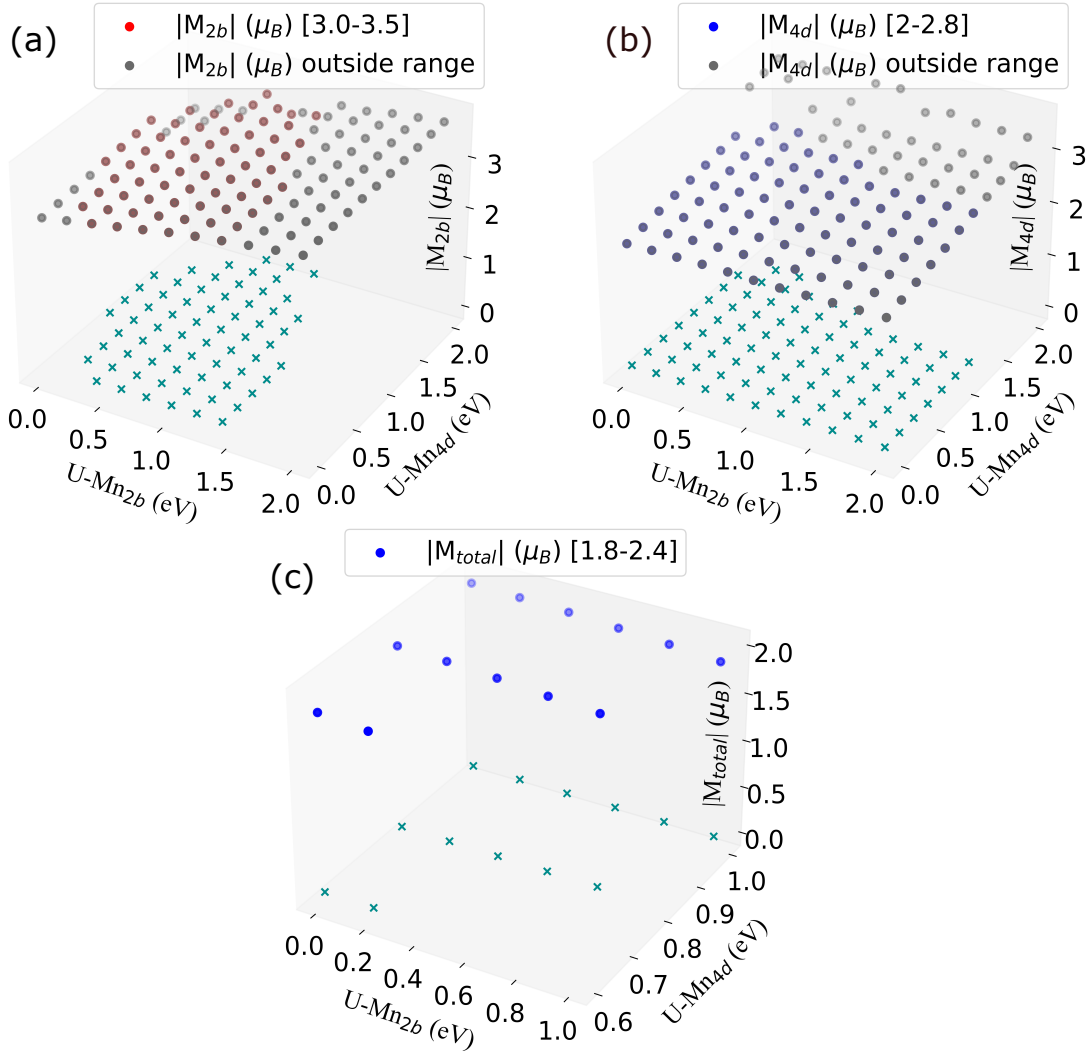


Figure 3.4: 3D representation of (a)-(b) local magnetic moment and (c) total magnetic moment optimization for Mn_{2b} and Mn_{4d} sites in fixed-volume Mn_3Ga via dense 121-point 2D mesh over Hubbard parameter U_{2b} and U_{4d} . Blue (red) dots highlight parameter combinations yielding magnetic moments closest to experimental values. Projection of these optimal Hubbard parameters onto U_{2b} - U_{4d} plane are marked with green crosses.

plored the possibility of adding Hubbard U correction to the LDA functional to overcome this failure. To chose Hubbard U parameter for Mn_{2b} and Mn_{4d} sites, we tried different techniques. First, Hubbard U parameter for each site were calculated by the linear response method (Eq. (4)). This failed to produce suitable Hubbard U parameters for Mn_3Ga 's Mn sites as to improve the calculated lattice constants and result in a better agreement to the experimental values for Mn_3Ga .

The success of the scanning technique within GGA energy functional [78] inspired its application to the LDA+ U approach with the Dudarev approach. This method, using a denser 2D grid of U_{2b} and U_{4d} values, aimed to achieve a better agreement

between the lattice constants and local magnetic moments of Mn_3Ga and experimental results. We detected several Hubbard U parameters configurations to improve the LDA performance of calculating the local magnetic moments and lattice constants of Mn_3Ga , as shown in Table.3.1. We applied the same technique for improving LDA performance on local magnetic moments of fixed volume Mn_3Ga and detected 13 Hubbard energy configurations as shown in Fig.3.4. Finally, we looked at the thin film experimental data and found values $U_{2b} = U_{4d} = 1.5$ eV, which give a reasonable agreement for both the experimental lattice constant and the magnetic moment measured in the thin films per formula unit.

Details of calculations: The calculations are performed under 500 eV cutoff energy for a plane-wave basis. The Brillouin zone integrations are done on a uniform Gamma-Centred $\mathbf{k}$ grid of 10x10x10. To test the accuracy, an 18x18x10 grid was also used when evaluating the Hubbard U parameter configuration of fixed-volume Mn_3Ga . Atomic positions are fully relaxed using the conjugate gradient algorithm until all inter-atomic forces are smaller than 0.01 eV/Å. The Vosko-Wilk-Nusair interpolation [81] was introduced into exchange-correlation energy. The valance electron configuration of Mn and Ga in the pseudo potentials used are, respectively, $3d^6 4s^1$, and $3d^{10} 4s^2 4p^1$.

4 — Investigation of Magnetocrystalline Anisotropy Energy in Spintronic Materials

4.1 Methodology

The magnetocrystalline anisotropy energy (MAE) is a crucial magnetic property from both technological and fundamental perspectives, as it determines magnetic domain stability, which is essential for magnetic information storage. The alignment of magnetic moments in an out-of-plane orientation is facilitated by the large perpendicular MAE, enabling magneto-optical recording processes [82].

There are several methods for calculating MAE; one of the pioneering attempts was developed by van Vleck [83]. The MAE stems from the relativistic spin-orbit interaction in quantum electrodynamics to interplay between the orbital and the spin degrees of freedom, which in turn couple the magnetic moments treated as localized on the atoms to the crystalline lattice. The dipole-dipole and quadrupole-quadrupole coupling was introduced and implemented to the spin Hamiltonian as Weiss molecular field contribution and solved under the perturbation theory.

The other methods presented qualitative calculation schemes such as the itinerant-electron model by Brooks [84]. However, this Thesis will concentrate on calculating the magnetic anisotropy energy (MAE) using first-principles methods. The numerical approach for calculating MAE using the VASP simulation packages was initially introduced in the theory chapter of this thesis. Now, we will lay out the steps of this

derivation. In the first step, a single electron KS equation is solved by Hamiltonian that conveys additional spin-orbit information of the system,

$$\hat{H}_{SOC} = \frac{1}{2}\xi(\mathbf{r})\mathbf{l} \cdot \boldsymbol{\sigma}, \quad (1)$$

where $\mathbf{l}$ is angular orbital momentum number, $\boldsymbol{\sigma}$ is the vector of Pauli spin matrices and $\xi(\mathbf{r})$ spin-orbit coupling (SOC) amplitude which is equal to $\frac{1}{c^2 r} \frac{\delta v(r)}{\delta r}$. The following step in the calculation scheme is the self-consistent field energy minimization of the spin-polarized KS problem where the total energy is obtained by the expectation value of the spinor wave function $\langle \Phi_o | H_o | \Phi_o \rangle$,

$$E[\rho_o, \rho_n] = T[\rho_o, \rho_n] + U_H[\rho_n] + E_{xc}[\rho_n] + E_{ext}[\rho_n] \quad (2)$$

where ρ_o is the input density matrix in the last iteration, ρ_n is the output density matrix, and in T, U_H, E_{xc}, E_{ext} are, the kinetic energy, electron-electron Coulomb interaction energy, exchange-correlation energy, and the sum of the electron-ion and ion-ion Coulomb interaction energy respectively. The final step is a non-self-consistent solution of the KS equation obtained by $H_o + H_{SOC}$ with ρ_n as the input density matrix. The change in the total energy between the last two steps is expected as small differences due to the spin-orbit interaction are small compared to the exchange splitting and the bandwidth. From the same condition, the output density matrix $\rho_{n'}$ is similar to ρ_n , such that the exchange-correlation and Coulomb terms in total energy can be neglected

$$\Delta E = E_{SOC} - E = \sum_{i,\mathbf{k}}^{occ} \epsilon'_{i,\mathbf{k}} - \sum_{i,\mathbf{k}}^{occ} \epsilon_{i,\mathbf{k}} \quad (3)$$

This relation has been called the force theorem [60]. A major result has established an intuitive relation between the density-functional theory band structure and the MAE. From this framework, the set of calculated KS of band energy in the Brillouin zone magnetic anisotropy energy can be formulated as

$$\Delta E_{MAE} = \sum_{i,\mathbf{k}}^{occ} (\hat{\mathbf{n}}_1) \epsilon'_{i,\mathbf{k}} - \sum_{i,\mathbf{k}}^{occ} \epsilon'_{i,\mathbf{k}} (\hat{\mathbf{n}}_2). \quad (4)$$

Where $\hat{\mathbf{n}}_1$ and $\hat{\mathbf{n}}_2$ represent two different arbitrarily chosen magnetic directions.

The MAE calculations demand very highly accurate energy results due to the nature of minor energy differences between different spatial magnetic moment orientations. To fulfill MAE accuracy in simulation, the symmetry of the Bravais lattice was taken into account, and an additional support grid was implemented to evaluate the augmentation charges. Additionally, the number of KS orbitals was doubled in NSCF from SCF.

A deeper understanding of MAE as a function of the magnetic quantization axis can be sought by atomic orbital contribution in the spin-orbit coupling matrix framework [85]. To produce the matrix element of the orbitals, the spin-orbit Hamiltonian (H_{so}) will be defined in the immediate vicinity of nuclei, which causes its contribution to be insignificant outside the PAW sphere. Therefore, the H_{so} has an all-electron (AE) one-center contribution from the PAW basis set.

$$\tilde{H}_{so} = \sum_{i,j} |p_i\rangle \langle \phi_i| H_{so} |\phi_j\rangle \langle p_j|. \quad (5)$$

In the zeroth-order-regular approximation, H_{so} is given by E. van Lenthe *et al.* [86],

$$H_{so}^{\alpha\beta} = \frac{\hbar^2}{(2m_e c)^2} \frac{K(r)}{r} \frac{dV(r)}{dr} \vec{\sigma}^{\alpha\beta} \cdot \vec{L}, \quad (6)$$

where σ is the vector of 2x2 Pauli spin matrices, and $\vec{L}$ is the angular momentum operator, $V(r)$ is the spherical part of effective AE potential within the PAW sphere, and $K(r) = (1 - V(r)/2m_e c^2)^{-2}$. The AE basis set extended to spherical harmonics $\phi_i(\mathbf{r}) = R_i(|\mathbf{r}|)Y_{l_i, m_i}(\hat{r})$ and where

$$R_{ij} = 4\pi \int_0^{r_c} R_i(r) \frac{K(r)}{r} \frac{dV(r)}{dr} R_j(r) dr. \quad (7)$$

From Eq. (6) and the Spherical harmonic basis set of AE, the spin-orbit Hamiltonian (H_{so}) can be rewritten as

$$H_{so}^{\alpha\beta} = \frac{\hbar^2}{(2m_e c)^2} \sum_{ij} |\tilde{p}_i\rangle \langle Y_{l_i, m_i}| R_i \frac{K(r)}{r} \frac{dV(r)}{dr} \vec{\sigma}^{\alpha\beta} \cdot \vec{L} R_j |Y_{l_j, m_j}\rangle \langle \tilde{p}_j|. \quad (8)$$

The matrix element of spin-orbit energy can be extracted after the spin-orbit operator

$(\tilde{H}_{so}^{\alpha\beta})$ on pseudo orbitals,

$$E_{ij}^{soc} = \xi \sum_{i,j} \langle Y_{l_i, m_i} | \vec{L} \cdot \vec{S} | Y_{l_j, m_j} \rangle, \quad (9)$$

where i and j represent ion indices. The l and m are orbital angular momentum and orbital magnetic numbers. ξ is the spin-orbit constant.

As an example of orbital matrix, consider $3d$ orbital structure, where the angular momentum number l is equal to 2. The corresponding matrix has a 5×5 shape, characterized by $m = -2, -1, 0, 1, 2$. Each m number corresponds to an azimuthal angle for a given orbital momentum where their shape is named as $d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{xz} , d_{yz} , d_{z^2} .

4.2 Mn₃Ga

The calculation scheme follows a two-step process analogous to that prescribed by the Force theorem. In the first step, the fully self-consistent calculation was performed to obtain the charge density of the collinear system. In the next step, the noncollinear NSCF calculation was performed from SCF charge density with Spin-Orbit coupling, and the calculation was repeated for different magnetic vector orientations. To obtain the perpendicular magnetic anisotropy (PMA), band energies for perpendicular and parallel magnetization were calculated and used in Eq. (4).

The DO₂₂ Mn₃Ga bulk structure in GGA energy functional exhibits +1.76 meV perpendicular MAE. When Hubbard U parameter was applied on each Mn site of Mn₃Ga as $U_{2b} = 1.5$ eV and $U_{4d} = 1.5$ eV, the perpendicular MAE value was reduced to +1.63 meV. The primary source of the PMA is Mn_{4d} site contribution for both XC energy functionals rather than the small contribution of Mn_{2b} site as shown Fig.4.1. The large positive contribution is shown about 0.8 meV/atom for $U_{2b} = U_{4d} = 0.0$ eV and 0.7 meV/atom $U_{2b} = U_{4d} = 1.5$ eV at Mn_{4d} site. Figure 4.1 shows anisotropy of the orbital magnetic moment and affirms that the Mn_{4d} atoms contribute significantly to the orbital magnetic moment and are the primary source of the high PMA. The orbital resolved MAE from Eq. (9) is shown in Fig.4.2 for Mn_{2b} and Mn_{4d} atoms in

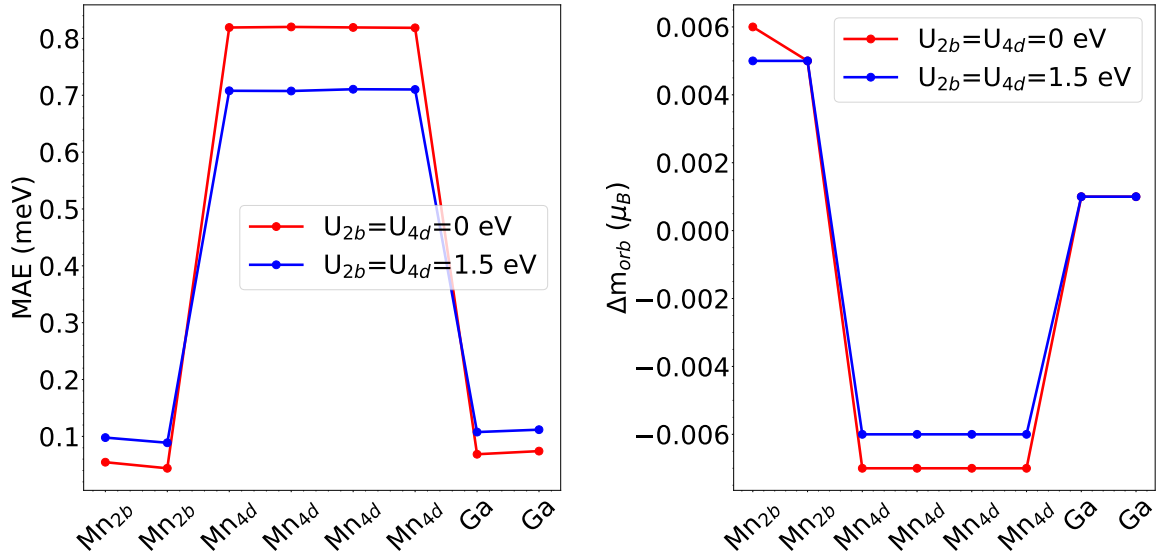


Figure 4.1: Atomic decomposition of magnetocrystalline anisotropy energy (MAE) in DO_{22} Mn_3Ga . (Left) Site-resolved MAE for Mn_{2b} , Mn_{4d} , and Ga sites. (Right) Corresponding site-resolved orbital magnetic moment anisotropy (Δm_{orb}). Results are shown for two Hubbard U parameter cases: $U_{2b} = U_{4d} = 1.5$ eV (red line) and $U_{2b} = U_{4d} = 0.0$ eV (blue line).

Mn_3Ga . For each site, Hubbard's correction impact on 3d orbitals was illustrated.

The Mn_{2b} atoms display in-plane anisotropy with large negative contribution to MAE from $d_{x^2-y^2}$ and d_{xy} orbitals, while the d_{z^2} and d_{yz} created favorably out-of-plane anisotropy with significantly larger positive MAE than other orbitals. Overall, the $d_{x^2-y^2}$, d_{xy} and d_{z^2} , d_{yz} orbitals contribution to MAE tend to cancel each other and this explains the reason why Mn_{2b} atoms didn't reveal a significant MAE contribution at calculated atom-resolved MAE (see Fig.4.1). The Mn_{4d} atoms have no negative MAE contribution as observed between $d_{x^2-y^2}$ and d_{xy} orbital of Mn_{2b} and between the others orbitals connection. On the contrary, $d_{x^2-y^2}$ and d_{xy} orbitals display a tendency for out-of-plane anisotropy with small positive energy contribution. The largest positive energy contribution is displayed by the connection between d_{z^2} and d_{yz} orbitals. In summary, the orbital contribution of Mn_{4d} in each matrix element reveals a positive contribution to MAE, and it explains the reason why Mn_{4d} atoms reveal a significant positive MAE contribution at calculated atom-resolved MAE (see Fig.4.1). The small reduction of MAE from 1.76 meV to 1.63 meV in the influence of Hubbard effective U parameter can be explained by the small diminishing energy between d_{xy} and $d_{x^2-y^2}$, d_{yz} and $d_{x^2-y^2}$ of Mn_{4d} . A similar MAE reduction was observed in Saha *et al.* [78] from

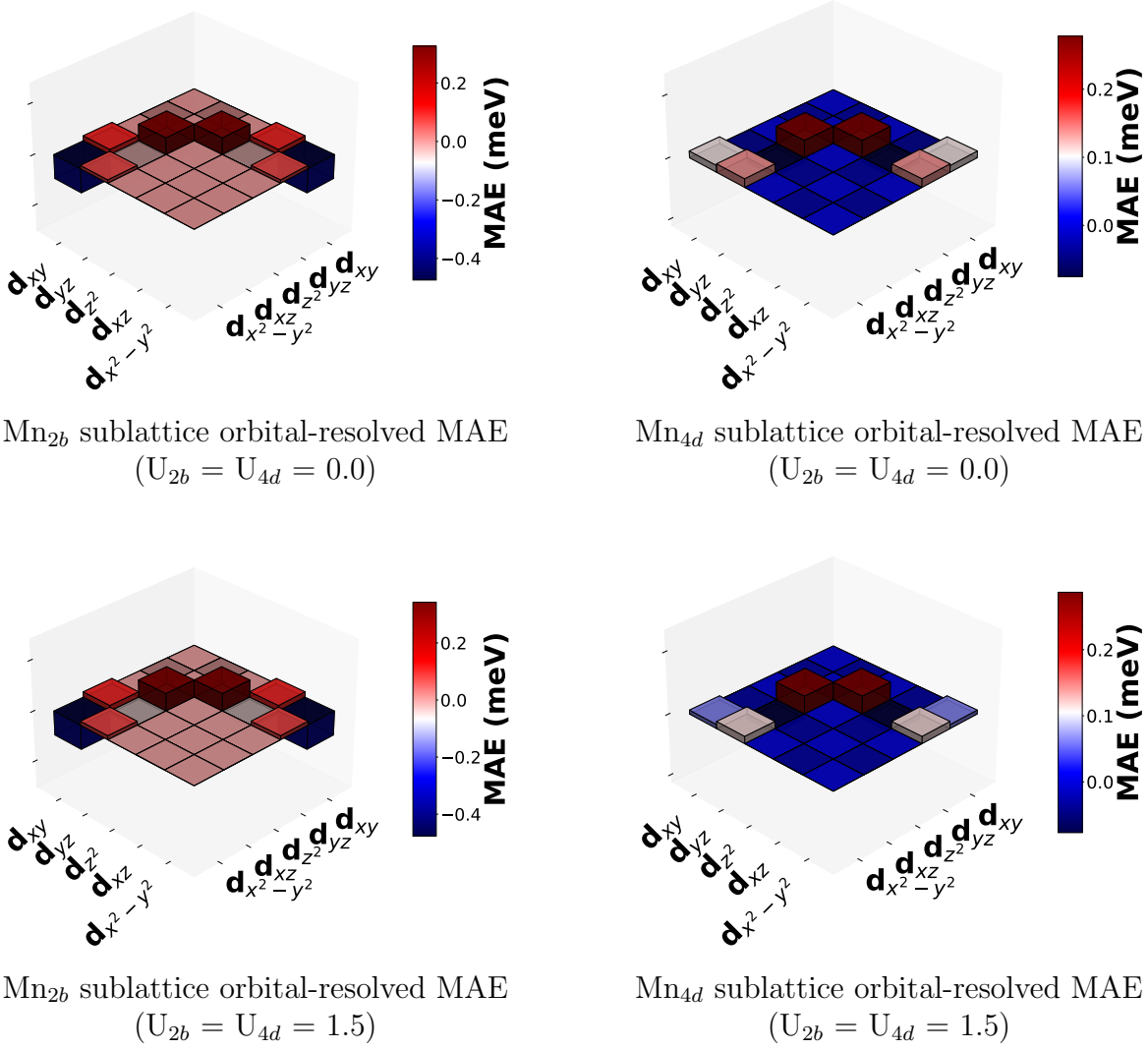


Figure 4.2: Orbital-resolved magnetocrystalline anisotropy energy (MAE) in in Mn₃Ga. The 3D plots show MAE (z-axis) as a function of d-orbital contributions (d_{xy} , d_{z^2} , etc. x-y axes)

1.76 meV (U_{2b}) to 1.41 meV (U_{2b}) when Hubbard U correction was applied. Details of the calculations: The calculations were performed under 500 eV cutoff energy for a plane-wave basis using the VASP code. The Brillouin zone integrations are done on a uniform Gamma-Centered $\mathbf{k}$ -point grid of 18x18x10.

The lattice constants were set $a = b = 3.77 \text{ \AA}$ and $c = 7.1 \text{ \AA}$ for $U_{2b} = U_{4d} = 0$. The lattice constants of optimized by GGAU ($U_{2b} = U_{4d} = 1.5$) are $a = b = 3.72 \text{ \AA}$ and $c = 7.06 \text{ \AA}$. Ionic positions are fully relaxed using the conjugate gradient algorithm until all inter-atomic forces are smaller than 0.01 eV/Å. The global break condition for the electronic self-consistent loop was set to 10^{-7} eV. An additional support grid was employed to evaluate the augmentation charges, enhancing the accuracy of MAE

calculations. The valance electron configuration of Mn and Ga in potential files are, respectively, $3d^6 4s^1$, and $3d^{10} 4s^2 4p^1$.

4.3 CrSb

In this section, we will undertake a similar MAE analysis of the hcp anti-ferromagnetic CrSb bulk. It exhibits strong anti-ferromagnetic ordering with a high Neel temperature (705 K), making it suitable for practical applications that need stable magnetism, such as on-chip applications [87]. The analysis carries on the same workflow as the previous section. The initial step of the analysis entailed calculating the perpendicular magnetic anisotropy energy of CrSb that found +1.09 meV by force theorem Eq. (4). Our calculated out-of-plane MAE result yielded a close agreement to +1.2 meV reported by Park *et al.* [88]. The next analysis phase was conducted to obtain an atom-resolved contribution to out-of-plane MAE. The atom-resolved calculation exhibits that the Sb atoms are the primary source of a large out-of-plane MAE with 1.4 meV/atom compared to 0.2 meV/atom contribution from Cr as shown in Fig.4.3. The final stage of MAE analysis was conducted to calculate orbital-resolved MAE to understand the physical source of high PMA energy from the Sb atom. Since the Cr-Sb electrons have a $p - d$ hybridization that directly contributes to enhancing MAE, the Sb's p -orbital and Cr's d -orbital resolved MAE matrix are calculated from Eq. (9), and the matrix elements contribution is displayed in Fig.4.3.

Calculation details: The calculations were performed under 500 eV cutoff energy for a plane-wave basis using the VASP code. The Brillouin zone integrations are done on a uniform Gamma-Centred $\mathbf{k}$ -point grid of 10x10x10. The lattice constants were set $a = b = 4.18 \text{ \AA}$ and $c = 5.35 \text{ \AA}$. Ionic positions are fully relaxed using the conjugate gradient algorithm until all inter-atomic forces are smaller than 0.01 eV/ $\text{\AA}$. The global break condition for the electronic self-consistent loop was set to 10^{-7} eV. An additional support grid was employed to evaluate the augmentation charges, enhancing the accuracy of MAE calculations. The valance electron configuration of Cr and Sb in potential files are, respectively, $3p^6 3d^5 4s^1$, and $5s^2 5p^3$.

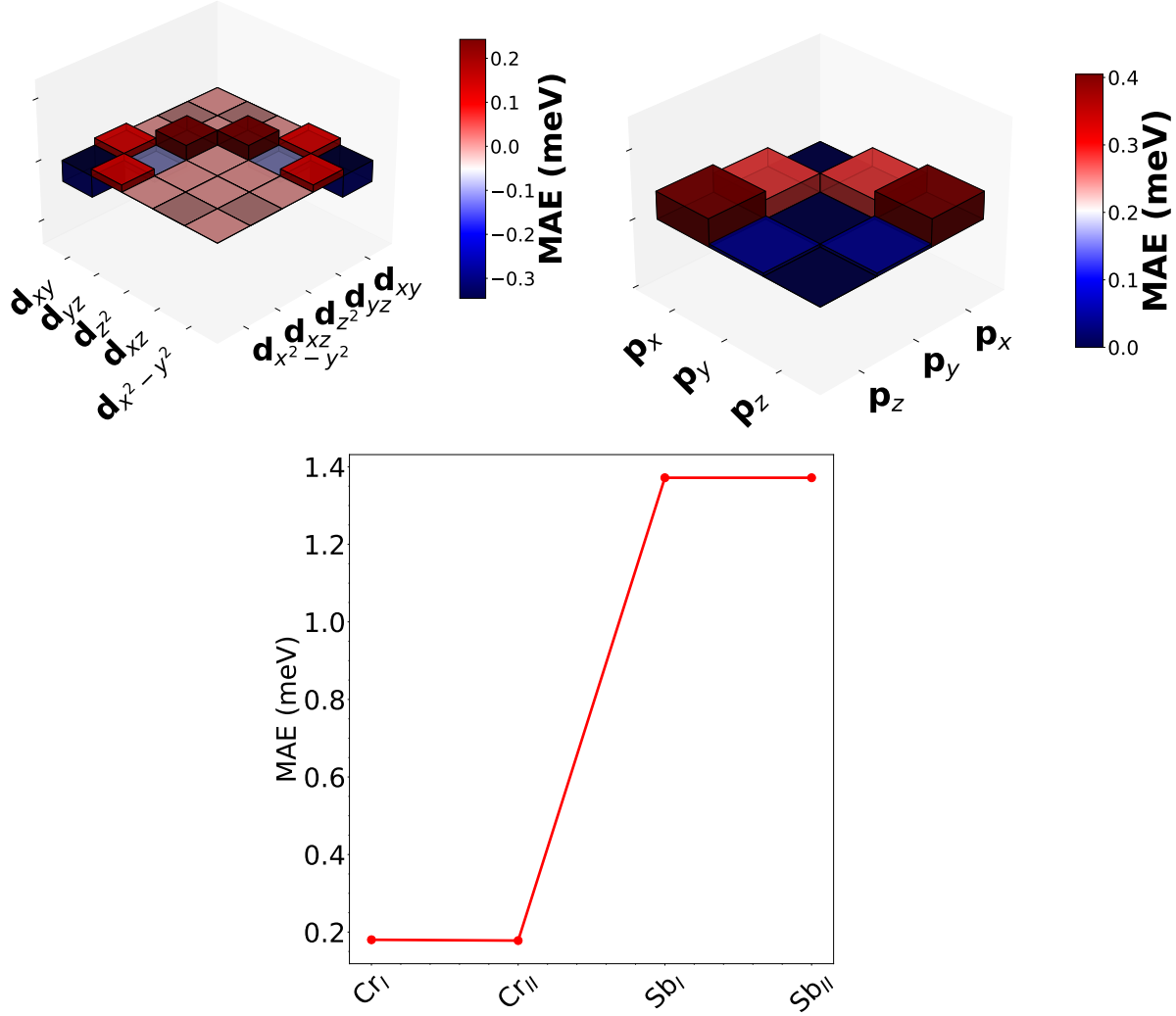


Figure 4.3: Magnetocrystalline anisotropy energy (MAE) analysis of CrSb. (Upper Left) 3D plot of Cr d-orbital-resolved MAE. (Upper Right) 3D plot of Sb p-orbital resolved MAE. (Below) Site-projected MAE for Cr and Sb atoms.

4.4 CuMnAs

In this section, we will perform the previously-described MAE analysis for the anti-ferromagnetic tetragonal CuMnAs using GGA and GGA+U ($U_{Mn} = 2.25eV$) exchange-correlation functional. CuMnAs with perpendicular magnetic anisotropy are proposed as an active material for anti-ferromagnetic memory. Moreover, CuMnAs exhibit multi-level switching characteristics due to current-induced Néel spin-orbit torques (SOTs). This faster spin dynamics can be used to reduce switching time in recording devices [89, 90].

The preliminary analysis was conducted through calculations of the MAE with

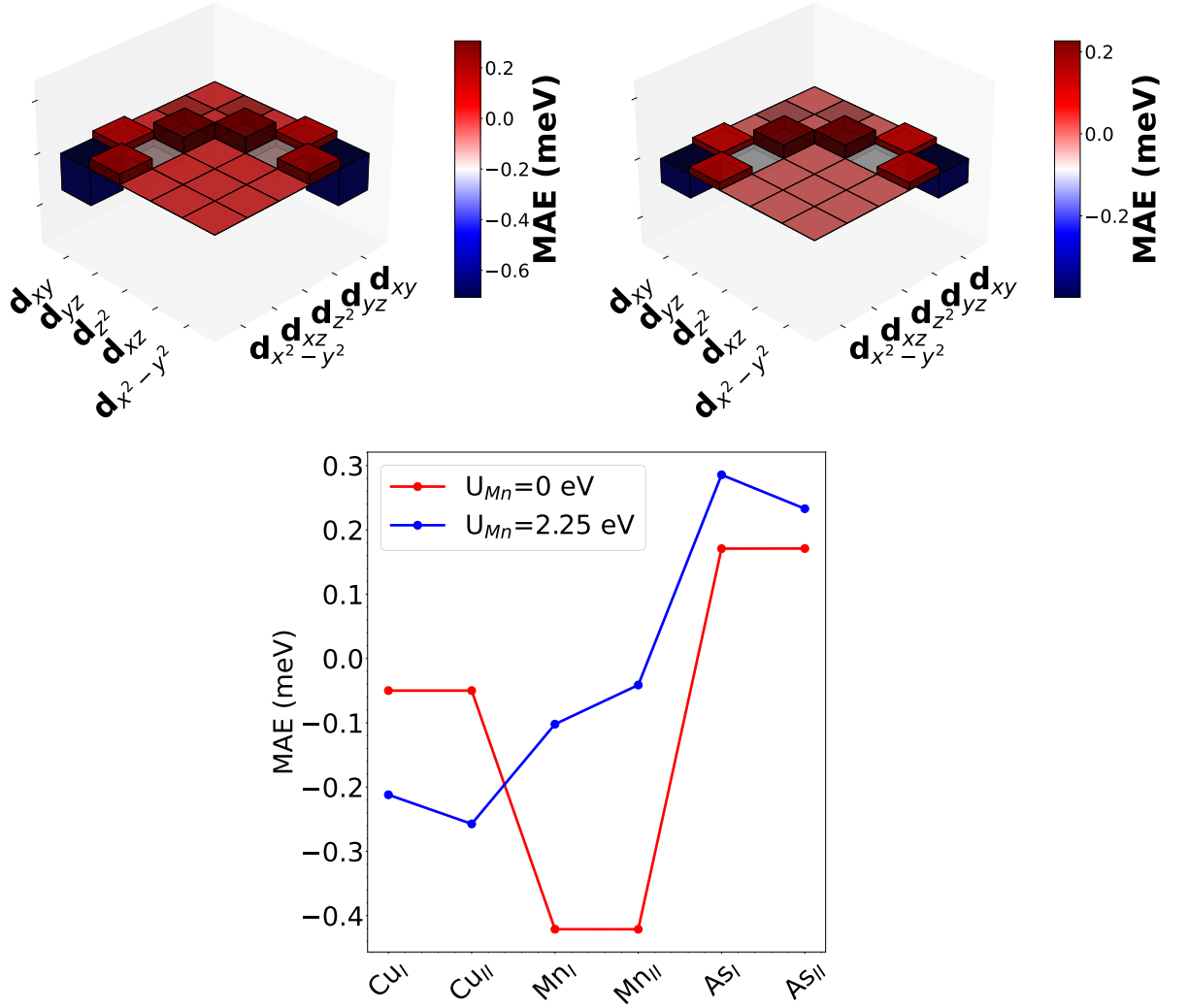


Figure 4.4: Magnetocrystalline anisotropy energy (MAE) analysis of CuMnAs. (Upper Left) Mn d-orbital-resolved MAE calculated with GGA functional. (Upper Right) Mn d-orbital-resolved MAE calculated with GGA+U ($U_{Mn} = 2.5$ eV). (Below) Site-projected MAE for Cu, Mn and As atoms comparing $U_{Mn} = 0$ eV (red line) and $U_{Mn} = 2.5$ eV (blue line).

GGA and GGA+U by force theorem (Eq. (4)), which is found to be -0.33 meV (-0.57 MJm⁻³) and -0.027 meV (-0.047 MJm⁻³) in order. The in-plane MAE calculated using the GGA+U method shows excellent agreement with the -0.09 meV (-0.0152 MJ m⁻³) value reported by Zhuravlev *et al.* [91]. The next analysis phase was conducted to obtain an atom-resolved contribution to in-plane MAE of GGA and GGA+U. The atom-resolved calculation shows that Hubbard U parameter on the Mn site is diminishing in-plane MAE; meanwhile, Cu site in-plane MAE contribution is increasing, but overall Hubbard U parameter suppresses MAE as shown in Fig.4.4. In the final stage of the MAE analysis, the *d*-orbital-resolved MAE was calculated for Mn atoms, the

primary contributors to magnetic interactions in CuMnAs, with Cu and As impacting the MAE through hybridization with Mn d -orbitals. As shown in Fig 4.4, the d_{xy} orbitals are the dominant source of in-plane MAE, and their contribution diminishes when Hubbard U term is applied on the Mn site.

Calculation Details: The calculations were performed under 500 eV cutoff energy for a plane-wave basis using VASP code. The Brillouin zone integrations are done on a uniform Gamma-Centered $\mathbf{k}$ -point grid of 10x10x10. The lattice constants were $a = b = 3.82$ Å and $c = 6.32$ Å. Ionic positions are fully relaxed using the conjugate gradient algorithm until all inter-atomic forces are smaller than 0.01 eV/Å. The global break condition for the electronic self-consistent loop was set to 10^{-7} eV. An additional support grid was employed to evaluate the augmentation charges, enhancing the accuracy of MAE calculations. The valance electron configuration of Cu, Mn, and As in potential files are, respectively, $3d^{10}4s^1$, $3d^64s^1$, and $4s^24p^3$.

5 — Spin-Waves and Exchange Interactions in 3d Ferromagnets and Heusler Compounds

In this Chapter, we will evaluate the performance of spin-spiral calculations using VASP. First, performance benchmark of spin-spiral calculations between self-consistent calculations and magnetic force theorem will be investigated. The next step is the magnon dispersion of 3d ferromagnet and Heusler alloys (Cu_2MnAl , Pd_2MnSn), which were calculated by magnetic force theorem and self-consistent field method to assess the applicability of spin-spiral calculations. Later, from our self-consistent spin-spiral method, the exchange parameters (J_{real}) of the ferromagnetic transition metals Fe, Co, and Ni and several Heusler alloys Cu_2MnAl , Pb_2MnSn , Ni_2MnGa , Ni_2MnSn , NiMnSb , NiMnSn and their Curie temperature will be calculated from mean field approximation (T_c^{MFA}) and random phase approximation (T_c^{RPA}) to compare with experimental T_C for evaluating self-consistent spin-spiral method results. Additionally, the spin-stiffness constant of 3d ferromagnets will be calculated to compare with experimental results.

5.1 Introduction to Magnetism and Magnetic Excitations

Understanding magnetic excitations in solids requires a distinction between different models of magnetism and an appreciation for the quantum-mechanical nature of spin dynamics. In this section, we provide a general introduction to the theoretical back-

ground necessary to analyze spin-wave excitations and their relationship to the underlying electronic and magnetic structure. The following will highlight the differences between localized and itinerant electron magnetism in terms of their description on magnetism in materials. Then, the role of the Heisenberg model will introduced for metals which provides a simple and accurate description of magnetism in these systems, and finalization of this section will underline the nature of elementary magnetic excitations such as magnons and Stoner modes.

5.1.1 Itinerant Electron Magnetism vs. Localized Electron Moments

Magnetism in solids arises from the collective behavior of electron spins. Depending on the degree of electron localization, two limiting pictures can be considered: the localized moment model and the itinerant electron model. Even though these two models are opposed each other, they are ensembling to narrate the intrinsic properties of magnetism.

In systems with well-localized electrons, such as insulators with partially filled d or f shells, magnetic moments are primarily associated with individual atomic sites. These local moments interact via exchange mechanisms, often leading to long-range magnetic order described by model spin Hamiltonian, most often the Heisenberg Hamiltonian [92].

$$H = - \sum_{i,j} J_{ij} \mathbf{S}_i \mathbf{S}_j \quad (1)$$

where J_{ij} is interatomic exchange interaction constant between all nearest neighbor pairs i and j which decrease by distant of pairs exponentially. The positive value of the constant ($J_{ij} > 0$) represent ferromagnetic interaction between the pairs, while negative values ($J_{ij} < 0$) are representing anti-ferromagnetic interaction. The Heisenberg model provide the fundamental theoretical framework to describe various magnetic ordering the materials such as ferromagnetism, helimagnetism by generalizing the sign and range of exchange interactions. Moreover, the Heisenberg Hamiltonian model provided microscopic basis for wave-like collective spin excitations. This theoretical leap

established spin waves as elementary excitations in magnetic materials.

In contrast, in metallic systems where electrons are delocalized, magnetism originates from the exchange splitting of energy bands. The itinerant electron model, often described within the framework of Stoner theory [93], accounts for the spontaneous polarization of a conduction band due to the competition between kinetic energy and exchange energy. This competition leads to the so called Stoner criterion for spontaneous magnetic order of a system of itinerant electrons,

$$ID(E_F) > 1, \quad (2)$$

where I is exchange integral and $D(E_F)$ is the density of states at Fermi level. The Stoner criterion is satisfied if either I or $D(E_F)$ is sufficiently large. Notably, $D(E_F)$ becomes large when the electron bandwidth is narrow, as is characteristic of localized $3d$ electrons. The Stoner model thus explains the emergence of ferromagnetism in certain transition elements (e.g., Fe, Co, Ni) and its absence in others, based on calculated values of I and $D(E_F)$ [94]. However, the Curie temperatures (T_c) of $3d$ ferromagnetic metals calculated within the Stoner model exceed experimental values by a factor of 3–5. This discrepancy arises because the model neglects collective spin excitations (e.g., spin waves), which are governed by the dynamical magnetic susceptibility. These excitations, naturally described within the Heisenberg model framework, are essential for accurately predicting T_c .

While these two models represent extremes, many materials—particularly transition-metal compounds—exhibit magnetic properties that fall between these regimes, necessitating theoretical frameworks that can bridge both localized and itinerant behaviors.

5.1.2 Classical Heisenberg Model for Itinerant Electrons

Despite the itinerant nature of electrons in $3d$ transition metals (e.g., Fe, Ni, Co), their thermodynamic behavior can be mapped onto an effective classical Heisenberg model because spin fluctuations in itinerant systems dynamically generate local moments at

thermodynamic scales [95]:

$$H_{eff} = - \sum_{i,j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j, \quad (3)$$

where J_{ij} are the exchange interaction parameters between spins at sites i and j , and $\mathbf{e}_i$ is the unit vector in the direction of the local magnetic moment at site i . In this context, J_{ij} can be derived from first-principles electronic structure methods and are interpreted as effective exchange parameters capturing the magnetic stiffness of the system.

5.1.3 Magnetic Excitations: Spin-Waves (Magnons) and Stoner Excitations

Magnetic excitations in solids manifest as collective or single-particle processes. At low temperature collective dynamics, spin-waves (or magnons), dominate while temperature is increasing Stoner excitations become more prominent.

Stoner excitations involve single-electron spin-flip transitions between majority and minority spin states. The minimum energy for the spin-flip transitions in ferromagnets with filled majority spin band equal to Stoner gap (Δ) as shown in Fig.5.1a. These are incoherent excitations that do not preserve phase coherence across atomic sites and typically dominate the high-energy excitation spectrum of itinerant ferromagnets with small exchange splitting like Ni.

In contrast, spin-waves are low-energy collective excitations in which magnetic moments precess coherently around the equilibrium magnetization direction. They begin with a parabolic energy dispersion at $\mathbf{q}=0$ and expand when they begin to overlap with single-electron excitations above the Stoner gap (Δ) as shown in Fig.5.1b. They are quantized as bosonic quasiparticles called magnons, and their dispersion relation $\omega(\mathbf{q})$ reveals information about the underlying exchange interactions.

The relative contributions of magnons and Stoner excitations depend on the material's electronic structure and magnetic ordering. A proper treatment of both requires a combination of band theory and many-body techniques.

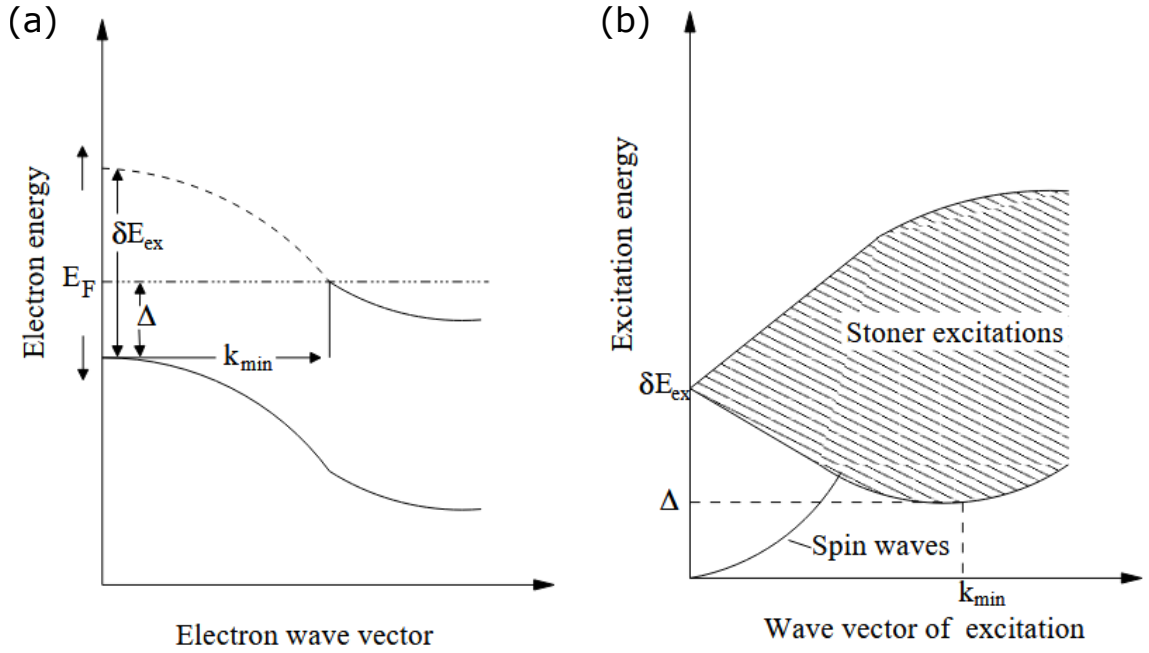


Figure 5.1: Magnetic excitations (a) Spin-split bands crossing the Fermi level in a strong ferromagnet. A spin flip can occur via a single electron excitation by lifting an electron from the majority band into the unoccupied part of the minority band (- - -). Such excitations require a minimum energy transfer equal to the Stoner gap Δ . (b) Schematic $E(\mathbf{q})$ diagram of magnetic excitations for strong and weak ferromagnets, respectively [2].

5.1.4 Adiabatic Approximation

The adiabatic approximation plays a central role in connecting ground-state electronic structure methods with spin dynamics. It assumes that spin degrees of freedom evolve much more slowly than electronic degrees of freedom, allowing the electronic system to remain in its instantaneous ground state as the spin configuration changes. From this physical picture, we can draw an adiabatic approximation for the systems that evolve from a certain magnetic moment configuration to another state with a different magnetic moment configuration with zero electron relaxation time. This evolution of magnetic moments can represent a series of snapshots of different magnetic moment configurations at fixed times, called a frozen magnon. The magnon energy ω_q is related to energy change by spirals [96],

$$\omega(\mathbf{q}) = \frac{4}{M} \lim_{\theta \rightarrow 0} \frac{\Delta E(\mathbf{q}, \theta)}{\sin^2(\theta)}. \quad (4)$$

This approximation enables the mapping of total energy variations due to long-

wavelength spin perturbations (such as spin spirals) onto a Heisenberg-like model, thereby extracting exchange parameters and magnon dispersions without explicitly solving the time-dependent Schrödinger equation.

While highly effective for systems with well-defined magnetic moments and low-energy excitations, the adiabatic approximation breaks down in cases with strong spin-flip scattering, low magnetic stiffness, or substantial entanglement of spin and charge degrees of freedom.

5.2 Spin-Spiral Method in VASP

The VASP implements an incommensurate spin spiral through the generalized Bloch Theorem where each spinor in plane waves are shifted by half of propagation vector of spin waves ($\mathbf{q}/2$):

$$\Psi_{\mathbf{k}}^{\uparrow}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{kG}}^{\uparrow} \exp i(\mathbf{k} + \mathbf{G} - \frac{\mathbf{q}}{2}) \cdot \mathbf{r} \quad (5)$$

$$\Psi_{\mathbf{k}}^{\downarrow}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{kG}}^{\downarrow} \exp i(\mathbf{k} + \mathbf{G} + \frac{\mathbf{q}}{2}) \cdot \mathbf{r}, \quad (6)$$

and the single-particle Hamiltonian matrix modify by shifted kinetic energy block $|\mathbf{k} + \mathbf{G} \pm \mathbf{q}/2|$, and the off-diagonal exchange-correlation potentials acquire the corresponding complex phase factors on the entire real-space grid,

$$\begin{pmatrix} H^{\uparrow\uparrow}[\rho] & V_{xc}^{\uparrow\downarrow}[\rho] \\ V_{xc}^{\downarrow\uparrow}[\rho] & H^{\downarrow\downarrow}[\rho] \end{pmatrix} \Rightarrow \begin{pmatrix} H^{\uparrow\uparrow}[\rho] & V_{xc}^{\uparrow\downarrow}[\rho] e^{-i\mathbf{q}\cdot\mathbf{r}} \\ V_{xc}^{\downarrow\uparrow}[\rho] e^{+i\mathbf{q}\cdot\mathbf{r}} & H^{\downarrow\downarrow}[\rho] \end{pmatrix}. \quad (7)$$

Spin-spiral energy calculations can be performed using two distinct approaches. The first is a fully self-consistent field (SCF) calculation, in which the spin-spiral propagation vector $\mathbf{q}$ modifies the exchange-correlation potential through its full feedback on the relaxed charge and magnetization densities $\rho(r)$ and $m(r)$, evaluated over the entire real-space grid. The second approach is a non-self-consistent field (NSCF) calculation, where the spiral twist alters only the band energies ϵ , while the charge and magnetization densities remain fixed to those from a prior self-consistent reference.

5.2.1 Magnetic Force Theorem and Spin-Wave Dispersion

The Magnetic Force Theorem (MFT) states that small rotations of the magnetic moment δm , treated as a small perturbation within the spin-spiral framework, will result in a change in the system's band energy δE_{band} . Within this framework, the mathematical relationship linking the perturbed system to variations in the band energy was derived (see Chapter 2). A simplified version of the equation, which represents a reduced-order model approximating the primary dependencies, is presented as,

$$\delta E = \delta E_{band} + O(\delta n^2, \delta m^2) \quad (8)$$

Here, $O(\delta n^2, \delta m^2)$ represents the second-order variations in band energy, accounting for double-counting terms. One well-known example for implementation of MFT in a simulation package was demonstrated by Lezaic *et al.* [7], showing that the perturbation caused by changes in spin-spiral states can be accurately captured using an exchange-correlation field rotation $\mathbf{B}_{xc}$. This approach effectively models the magnetic moment rotation corresponding to the spin-spiral state of atom i as determined from its self-consistent calculation.

$$B_{ni}^{xc} = B_i^{xc} \begin{pmatrix} \sin(\theta_i) \cos(\mathbf{q} \cdot \mathbf{R}_{ni}) \\ \sin(\theta_i) \sin(\mathbf{q} \cdot \mathbf{R}_{ni}) \\ \cos(\theta_i) \end{pmatrix} \quad (9)$$

where $B_i^{xc} = (V_{\uparrow i}^{xc} - V_{\downarrow i}^{xc})$ is the exchange-correlation field of the collinear magnetic system of atom i ($V_{\sigma i}^{xc}$ is the exchange-correlation potential dependent on spin $\sigma = \uparrow, \downarrow$). The rotation of the exchange-correlation field is applied inside the non-overlapping muffin-tin spheres while deliberately suppressing the magnetic part of the exchange-correlation potential ($\mathbf{B}^{xc} = 0$) in the interstitial region to zero during the non-self-consistent step.

Since there is no established scheme in VASP for calculating spin-spiral energies from magnetic force theorem, we established a following protocol that built within SCF and NSCF calculations steps:

1. A self-consistent calculation is performed to establish the charge density under the influence of the local magnetic moment at the desired spin precision (cone angle θ).
2. Spin-spiral propagation is performed (though the Bloch Theorem), driven by propagation (wave) vectors ($\mathbf{q}$), and non-self-consistent calculation is set up to restart using the charge density from the SCF step.

The spin-spiral energies obtained via the MFT may deviate from those computed self-consistently, particularly in VASP, due to the way the exchange–correlation potential is applied. In the MFT approach, the PAW-projected exchange–correlation field is rotated according to the spin-spiral phase across the entire real-space grid, while the underlying charge and magnetization densities remain frozen. This can lead to an overestimation of the spiral energy, especially when significant interstitial magnetization is present and cannot relax. Therefore, it is important to assess the validity of MFT within VASP by comparing non-self-consistent spin-spiral band energies with those obtained from fully self-consistent spin-spiral calculations. To this end, we performed test calculations on the $3d$ ferromagnet fcc Co (see Fig.5.2).

Figure 5.2a shows a spin-wave dispersion test carried out at a fixed cone angle of 30° , which was maintained throughout the analysis. The spin-wave energies computed via the magnetic force theorem (MFT, green line) begin to deviate noticeably from the fully self-consistent (SCF) spin-spiral results (red line) beyond the long-wavelength limit. This deviation is examined in greater detail in Fig.5.2 b and c, which present the dependence of the magnon energy on $\sin^2(\theta)$ for two propagation vectors: $\mathbf{q} = (0, 0, 1)\frac{2\pi}{a}$ (long wavelength, Fig.5.2b) $\mathbf{q} = (0, 0.0, 0.15)\frac{2\pi}{a}$ (short wavelength, Fig.5.2c). In the long-wavelength case (Fig.5.2b), the deviation between MFT and SCF energies increases smoothly with cone angle, becoming especially apparent around 30° . In contrast, for the short-wavelength case (Fig.5.2c), the deviation begins even at small cone angles ($\sim 10^\circ$) and continues to grow with increasing perturbation.

These results highlight a key limitation of the MFT as implemented in VASP: because the method relies on a one-shot, non-self-consistent band energy evaluation using a frozen charge and magnetization density, it cannot capture the relaxation of

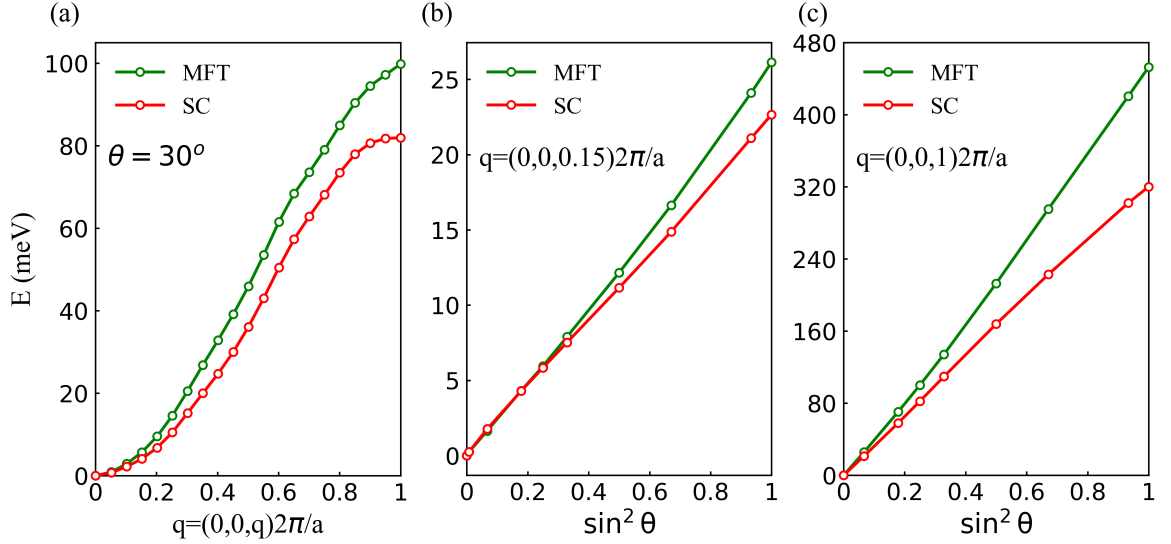


Figure 5.2: Comparison of the magnetic force theorem with self-consistent calculations for fcc Co. (a) dispersion curve of a spin spiral along the [001] direction for a cone angle $\theta = 30^\circ$. (b) Spin spiral energy vs $\sin^2 \theta$ for a long-wavelength spiral at the [0,0,0.15] direction. (c) Spin spiral energy vs $\sin^2 \theta$ for a short-wavelength spiral at the [0,0,1] direction.

the exchange–correlation potential in response to the spiral perturbation. As a result, MFT can significantly overestimate spin-spiral energies, particularly for large cone angles and short-wavelength spirals.

The relationship between the limitations of the magnetic force theorem (MFT) and the magnitude of the magnetic moment is illustrated in Figure 5.3 and Table 5.1. To examine this dependence, we calculated magnon dispersion curves for three materials with different magnetic moment sizes: fcc-Co ($m=1.65 \mu_B$), Cu_2MnAl ($m=3.55 \mu_B$), and Pd_2MnSn ($m=3.97 \mu_B$), using Eq. (4). These results help clarify the underlying cause of MFT overestimation in spin-spiral energies—namely, the lack of relaxation in the magnetization density due to the frozen charge approximation applied in the final, non-self-consistent step of the MFT calculation.

To benchmark the performance of our MFT-based spin-spiral energies, we compare them to reference magnon energies from the literature. For fcc-Co, reference values are taken from Halilov et al.’s tight-binding linear muffin-tin orbital (TB-LMTO) method [5], which combines computational efficiency with accuracy by transforming muffin-tin orbitals into a tight-binding basis. For Cu_2MnAl and Pd_2MnSn , we use values from Sasioglu et al.’s augmented spherical wave (ASW) method [4], a full-potential

Table 5.1: Magnetic moments (μ_B) of fcc Co, Cu_2MnAl , and Pd_2MnSn . The magnon energy difference $\Delta E = E_{\text{cal}} - E_{\text{ref}}$ (meV), and ratio $E_{\text{cal}}/E_{\text{ref}}$ between calculated magnon energies from MFT and reference magnon energies at high-symmetry point X. The reference magnon energies are taken from TB-LMTO [3] and ASW [4].

Compound	M (μ_B)	ΔE (meV)	$E_{\text{cal}}/E_{\text{ref}}$
fcc Co	1.65	387	1.5
Cu_2MnAl	3.55	382	4.3
Pd_2MnAl	3.97	388	7.4

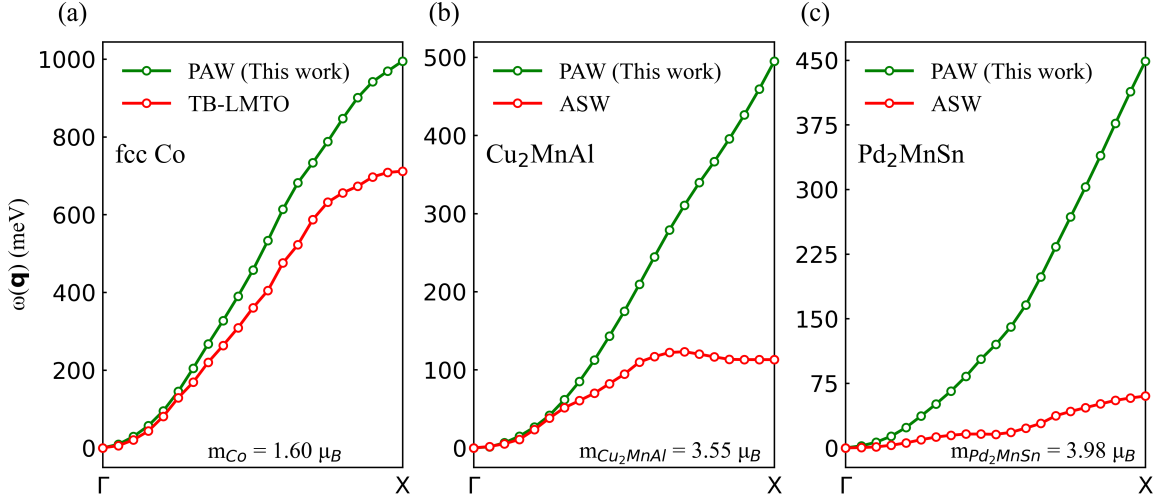


Figure 5.3: Magnon dispersion along Γ -X high-symmetry direction for (a) fcc Co, (b) Cu_2MnAl , and (c) Pd_2MnSn , calculated using the MFT (Green lines). The reference magnon energies (red lines) are taken from TB-LMTO [3] and ASW [4].

approach that treats both core and valence electrons self-consistently with a minimal basis set.

From Figure 5.3 and Table 5.1, we observe that systems with larger local magnetic moments tend to exhibit greater overestimation of magnon energies when computed using MFT. This behavior can be attributed to stronger interstitial magnetization in high-moment materials, which cannot relax within the frozen-density approximation, thus leading to increased discrepancies relative to MFT reference calculations.

5.2.2 Self-Consistent Calculations of Spin-spirals

The magnon energies (see Fig.5.3) calculated by MFT method in VASP gave unsatisfactory results, and the reasons were discussed in previous section (Sec.5.2.1). Then, we can conclude that by relaxing the charge density together with the imposed spin spiral

state only suitable way which can be achieved by *fully* self-consistent (SC) calculations.

The spin-spiral calculations can be performed within two characteristic spherical spirals: The *flat* spin-spiral structures are often used to study magnetic properties [97], but conical spin spirals provide a better representation of experimental magnon spectra and a better spin model mapping for extracting interaction parameters due to spin precession around an axis with a fixed out-of-plane component. This spin precession needs to be fixed during the SC calculation with an external magnetic field, which is imposed as a constraint on the local magnetic moment. The penalty energy accounts for forcing the local magnetic moments to the constrained ones during the search for the ground state with a fixed cone angle.

The local magnetic moment for each atomic site varies as functions of integration volumes, and their values depend on the choice of the Wigner-Seitz (WS) cell or the radius of the corresponding atomic sphere,

$$\mathbf{M}_i = \int_{\Omega_i^{ws}} \mathbf{m}(\mathbf{r}) d^3r, \quad (10)$$

where $\mathbf{m}(\mathbf{r})$ is the spatially varying magnetization density vector inside the WS sphere centered at atom i .

The magnetic moment is fixed within the WS sphere using a constrained total energy functional,

$$E = E_o + \sum_i \lambda_i (|\mathbf{M}_i^F| - \mathbf{e}_i \cdot \mathbf{M}_i^F), \quad (11)$$

where $\mathbf{M}_i^F$ is an alternative definition of the local magnetic moment in Eq. (10) with a trigonometric function contribution to create a monotonic converging to zero when the magnetization approaches the boundary of the WS sphere i . It is what is anticipated by the MCONSTRAINED in the input tag of VASP,

$$\mathbf{M}_i^F = \int_{\Omega_i^{ws}} \mathbf{m}(\mathbf{r}) F_i(|\mathbf{r} - \mathbf{r}_i|) d^3r. \quad (12)$$

In the Eq. (11) E_o is the DFT total energy of the material, and λ_i is the Lagrangian multiplier to create the penalty energy part for forcing the magnetic system to converge to a desirable magnetic directional configuration specified by $\mathbf{e}_i$ (unit vector). The

effective potential field is the main force for constraining the local magnetic moment inside the WS sphere,

$$V_i(\mathbf{r}) = -\mathbf{b}_p \cdot \boldsymbol{\sigma}_i, \quad (13)$$

where $\boldsymbol{\sigma}_i$ is the vector of Pauli matrices at site i atom, and the additional penalty field is

$$\mathbf{b}_p = -\frac{\delta E_p}{\delta \mathbf{m}(\mathbf{r})}. \quad (14)$$

From the derivation of Eq. (11) in terms of spatially varying magnetization density vector, the penalty field can be rewritten as,

$$\mathbf{b}_p = -\lambda_i \left(\frac{\mathbf{M}_i^F}{|\mathbf{M}_i^F|} - \mathbf{e}_i \right) F_i(|\mathbf{r} - \mathbf{r}_i|) d^3r. \quad (15)$$

The main trick is to obtain a balance between lambda λ_i and the desired local magnetic moment $\mathbf{M}_i$. The balance can be achieved with a suitable effective potential inside the WS sphere with an additional penalty field. It seems that the magnetic moment integrating inside the WS sphere for each atom can be tuned carefully with an assigned lambda value. It is advised that small lambda values tend to converge in a more stable magnetic moment for each atom type. Therefore, our strategy has been to stick with a small lambda and tune the constrained local magnetic moment inside the WS sphere to the desired magnetic moment at convergence. The drawback of the small lambda is that it introduces a bigger penalty energy.

The previous analysis of Ma *et al.* [98] conclude that in the limit where λ_i is large,

$$E_p \propto \frac{1}{\lambda_i}, \quad (16)$$

However, bigger lambda ($\lambda_i > 20$) tends to unstable SCF cycle for tested cases for spin-spiral calculations (bcc Fe, fcc Co etc.) which can get trapped in local minima. Our strategy of converging to our desired non-collinear magnetization is a straightforward mathematical calculation of Eq. (12) within the boundary of the WS sphere. The corresponding magnetic moment vector is then assigned in the MAGMOM tag, with a given WS radius (r_{ws}) where magnetization density is calculated. The crucial

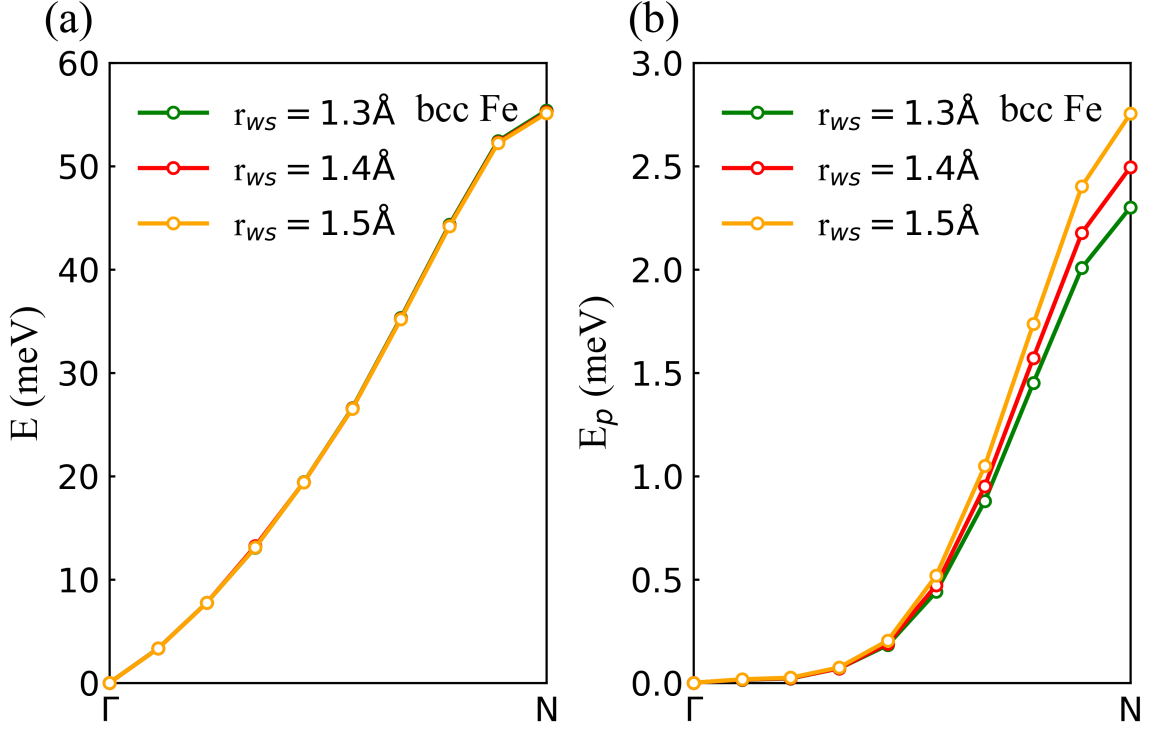


Figure 5.4: (a) Spin-spiral and (b) their penalty (E_p) energies along the high-symmetry direction for bcc Fe as a function of Wigner-Seitz Radius.

step is using magnetization density inside the integral definition of Eq. (10) with the smoothing function $F_I(\mathbf{r})$. Then the alternative definition of magnetization M_I^F can be calculated for the system, converging to the desirable magnetic moment M_I for atom I . These calculation steps can be performed by hand to converge numerical solutions with reasonable error margins. However, since $\mathbf{m}(\mathbf{r})$ is not constant, varying inside the volume of the sphere assigned by r_{ws} , using non-constrained SC cycle to calculate M_I^F within r_{ws} boundary will be numerically consistent. This method ensures the penalty energy will be significantly small, and the excitation state of the spin spiral does not suffer from high penalty energy.

A study of spin-wave energy changes as a function of the WS radius is essential because the constrained local magnetic moment is calculated inside the volume set by the WS radius, and these calculated moments enter the total energy under the penalty energy term. The study was conducted with bcc Fe and its atom radius specified to three different WS radius: 1.3 Å, 1.4 Å, and 1.5 Å, and their percentage of covering volume of cell was %78, %99, and %120 respectably. These radii were picked to include all possible scenarios: undercover, total cover, and overcover of the unit cell from the

atomic reference frame. The calculated spin-wave energies as a function of the WS radius are demonstrated as a spin-wave dispersion curve of bcc Fe in Fig.5.4a.

The spin-wave energies exhibited a small dependence on the WS radius changes along the high symmetry path of bcc Fe. Although, the non-monotonic relation between spin-wave energies is more noticeable at short wavelength ranges due to introduced penalty energy differences between WS spheres (as shown in Fig.b 5.4 but not significant in units of meV). The result of Fig.5.4 shows spin-spiral energies are not sensitive to WS sphere changes when magnetization density $[\mathbf{m}(\mathbf{r})]$ of the unit-cell are same.

5.2.2.1 Lambda benchmark: Validation of self-consistent spin spirals

After developing a robust technique to calculate the ground-state magnetic configuration within the WS radius of the atoms in the unit cell, we systematically investigated the effect of the Lagrangian parameter (λ) on both the local magnetic moment and energy change. These results are presented in Figures.5.5 for bcc Fe, providing a comprehensive benchmark for λ . Fig.5.5a displays spin-spiral energy differences with respect to $E(\mathbf{q}=0)$ along high-symmetry points in bcc Fe. In the long-wavelength limit, energy differences remain nearly identical for all the λ values; however, deviations for $\lambda = 1$ increase in the short-wavelength limit, particularly at the N symmetry point. Notably, $\lambda = 5$, $\lambda = 10$ and $\lambda = 15$ exhibit identical energy difference values throughout both wavelengths. As Eq. (16) demonstrates, the λ parameter exhibits an inverse relationship with penalty energy as shown in Fig.5.5b. Notably, $\lambda=1$ exhibits higher penalty energy which enters to total energy that are observed as energy deviation in Fig.5.5a

The local magnetic moment magnitude and cone angle changes for bcc Fe are displayed in Fig.5.5(c)-5.5(d). For each λ values, the local magnetic moment magnitude (less $0.05 \mu_B$) and cone angle experiences minor deviations (less than 1°). These findings highlight that lambda parameter is set a trade-off between spin-spiral energy and spin precision. Depend on material (e.g bcc Fe) and propagation wave-vector (e.g short or long wavelength limit), lambda values can adjust under that trade-off.

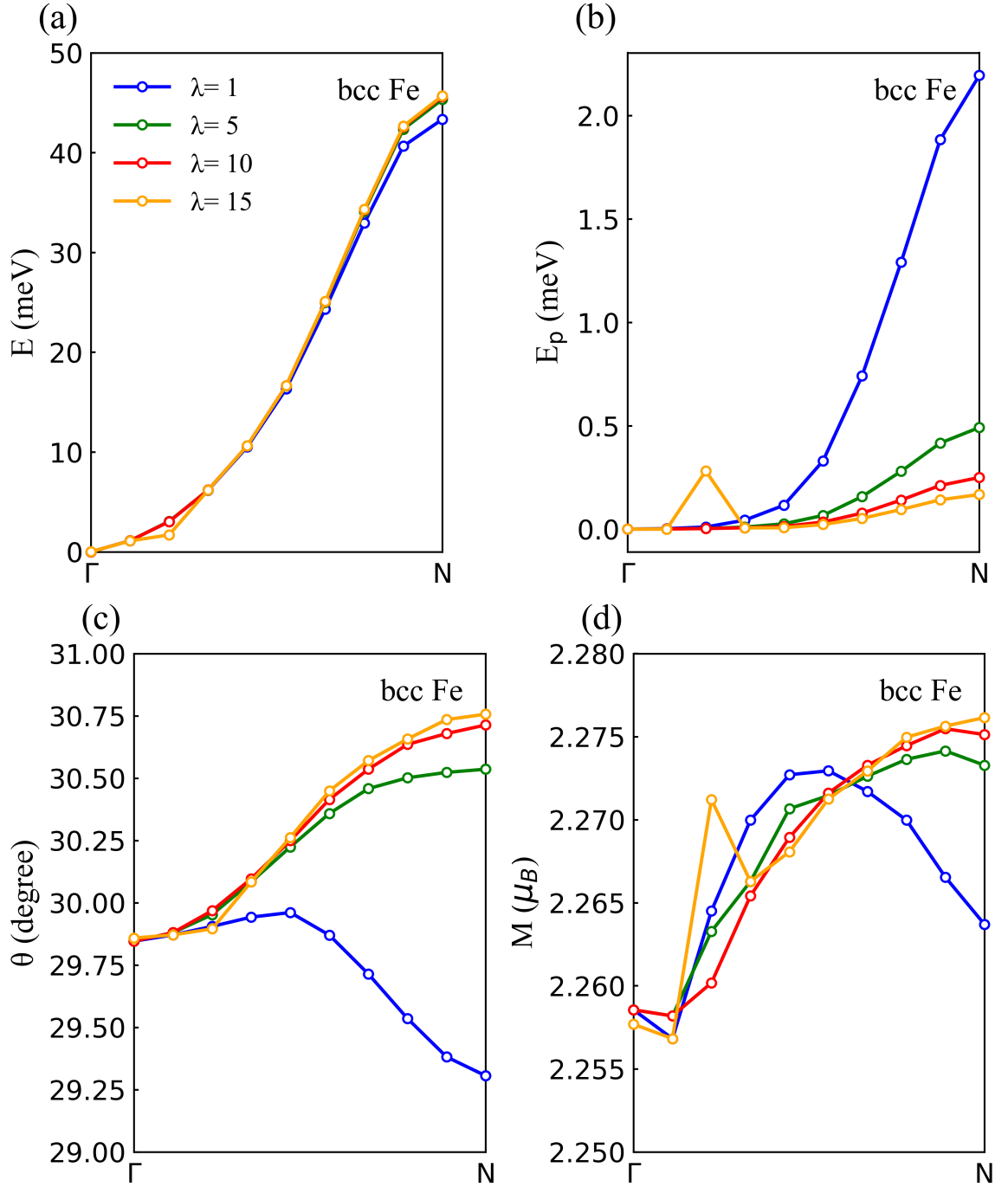


Figure 5.5: The Lagrangian parameter λ (λ) benchmark test for bcc Fe (a) Spin-Spiral energy differences as a function of (λ) along the high symmetry path. (b) The penalty energy of spin-wave dispersion curves as a function of (λ) along the high symmetry path. (c) The magnitude magnetic moment of spin-wave dispersion curves as a function of (λ) along the high symmetry path. (d) The cone-angle of magnetic moment as a function of (λ) along the high symmetry path.

5.2.2.2 Spin-wave dispersion from self-consistent calculations

In this section, the magnon dispersions of elemental 3d ferromagnets are calculated using the self-consistent field method described in the previous section to evaluate the performance of the constrained magnetic moment approach for spin-spiral calculations in VASP. We compare our results with magnon energies obtained from the spin-spiral calculations by Halilov et al. [5], based on the MFT and the adiabatic approximation. All magnon dispersion calculations were performed within the "safe" choice angle range (20° – 30°) [96] using the LDA exchange-correlation functional with $16 \times 16 \times 16$ $\mathbf{k}$ -mesh.

This comparison highlights the influence of self-consistency on the accuracy of magnon energies, particularly in itinerant systems like Co and Ni. reveals a material-dependent agreement. For bcc Fe-where a large exchange splitting suppresses Stoner-magnon coupling-our method (SS-SC) and Halilov's method (SS-MFT) approaches yield similar magnon energies as shown in Fig.5.6a. In the Halilov's calculations there are local minima features close to the H between Γ -H and H-N short wavelengths. However, they are not well-structured in our dispersions within 30° cone angle, but their potential location is still visible in the calculation. These local minima known as Kohn anomalies [99] occur due to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions [100, 101, 102] (See Appendix 4) observed in weak (itinerant) ferromagnets like Fe and have a crucial role in shaping the properties of spin-wave spectra. For fcc Co (see Fig.5.6b), our SS-SC method predicts slightly higher magnon energies compared to Halilov's results. This discrepancy is attributed to the smaller exchange splitting bringing the Stoner continuum closer to the collective spin wave excitations. Unlike Halilov's adiabatic spin approach, our SS-SC method rely on linear response, which is feedback from which is feedback from constrained spin configuration for SC, enabling a better representation of renormalization effects from spin wave excitations.

The fcc Ni magnon energies calculated by our SS-SC method (see Fig.5.6c) exhibits discrepancies from Halilov's magnon energies attributed to the smaller exchange splitting as fcc Co case but most importantly its related to the strong many-body effects in Ni cannot be accounted for by LDA exchange-correlation functional due to overestimating the exchange splitting energy by approximately a factor of two [103].

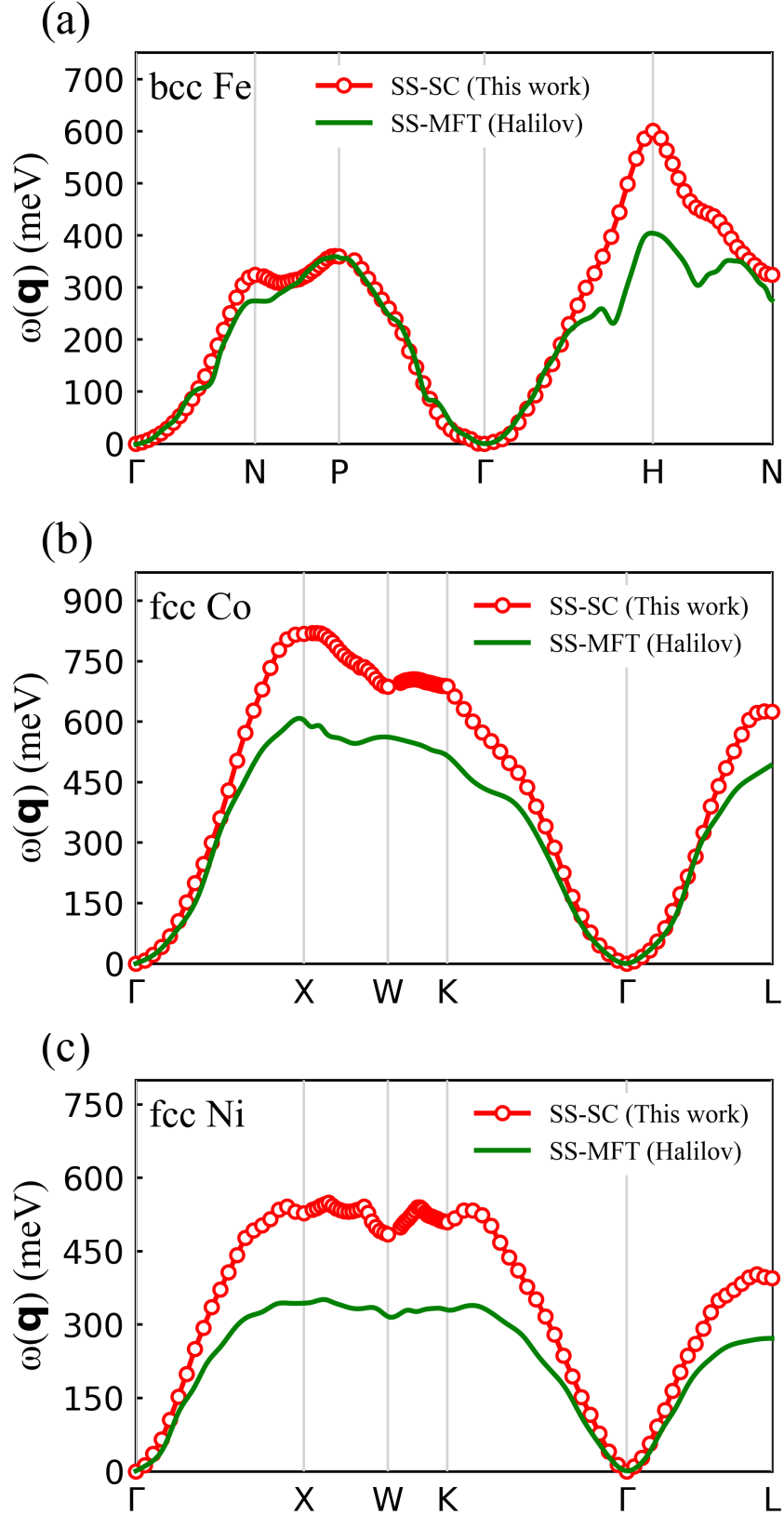


Figure 5.6: Magnon dispersion curves for (a) bcc Fe, (b) fcc Co, and (c) fcc Ni. Solid green lines denote results from the adiabatic spin-density-functional theory (SDFT) of Halilov et al.[5]. Red circle lines represent calculations using the constrained self-consistent spin-spiral (SS-SC) method from this work.

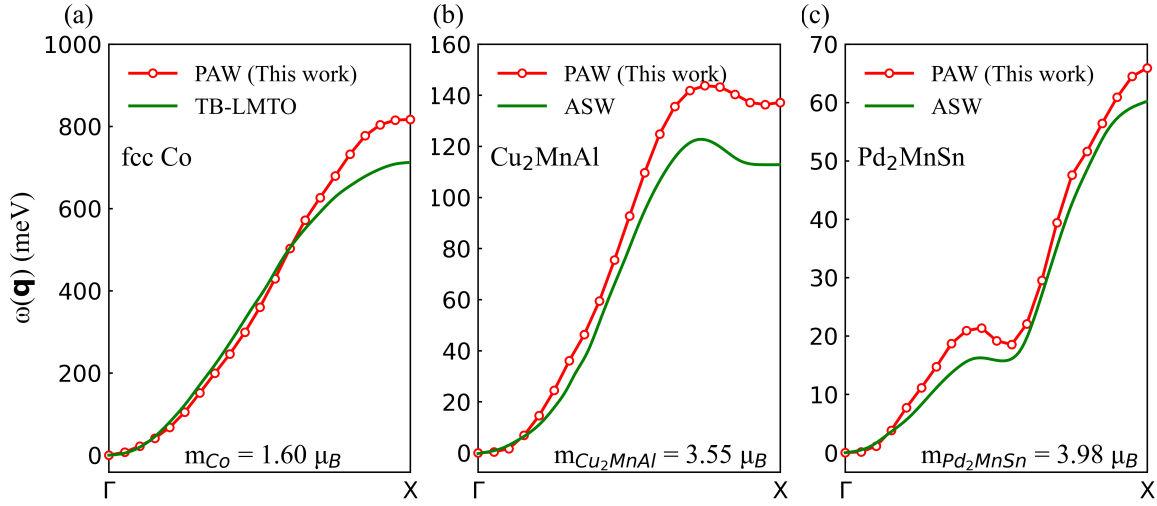


Figure 5.7: Magnon dispersion along Γ -X high-symmetry direction for (a) fcc Co, (b) Cu_2MnAl , and (c) Pd_2MnSn , calculated using the SS-SC (red lines). The reference magnon energies (red lines) are taken from TB-LMTO [3] and ASW [4].

Table 5.2: Magnetic moments (μ_B) of fcc Co, Cu_2MnAl , and Pd_2MnSn . The magnon energy difference $\Delta E = E_{\text{cal}} - E_{\text{ref}}$ (meV), and ratio $E_{\text{cal}}/E_{\text{ref}}$ between calculated magnon energies from MFT and reference magnon energies at high-symmetry point X. The reference magnon energies are taken from TB-LMTO [3] and ASW [4].

Compound	M (μ_B)	ΔE (meV)	$E_{\text{cal}}/E_{\text{ref}}$
fcc Co	1.65	134	1.2
Cu_2MnAl	3.55	24	1.2
Pd_2MnAl	3.97	5	1.1

The same investigation conducted for the MFT calculation method presented in Fig.5.3 was also performed for magnon energies calculated by our SS-SC method across fcc Co, Cu_2MnAl , and Pd_2MnSb compounds. As demonstrated in Fig.5.6 and Table.5.2, the discrepancy observed between the calculated magnon dispersion curve and the reference values was not significant as observed in MFT magnon energies. These findings further substantiate that relaxation of charge density is critical for achieving accurate spin-wave energies especially higher local magnetic moment systems.

5.2.2.3 Spin-Wave Stiffness Constant of 3d Ferromagnets

In the long-wavelength limit, spin-wave excitations are characterized by their energy, which is determined by the spin-wave stiffness constant D and it measures the resistance of an ordered spin system to a spatial variation of its spin orientations. A polynomial

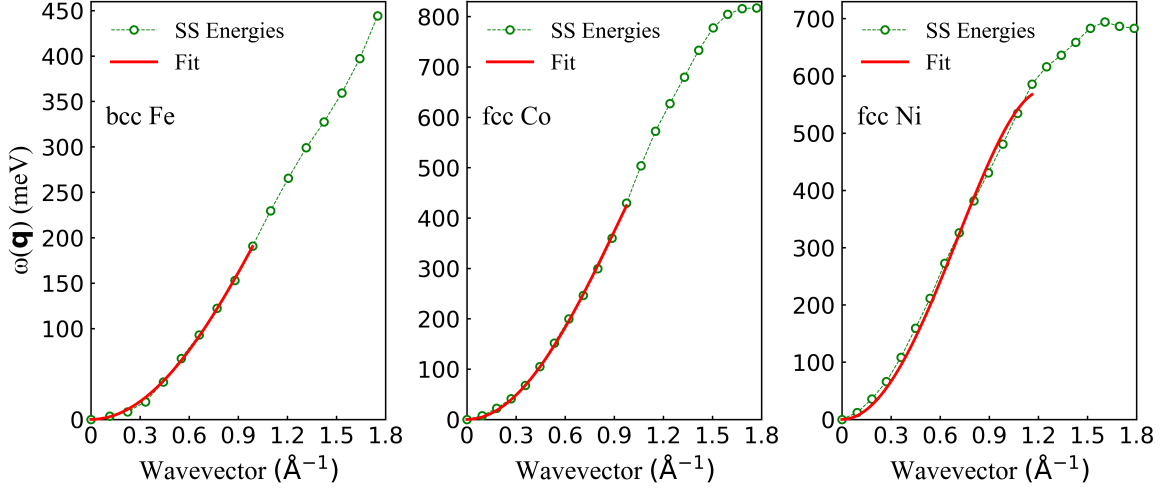


Figure 5.8: Spin-wave dispersion plots for bcc Fe, fcc Co, fcc Ni. Red circles show calculated spin-wave energies, while green curves represent $n = 2$ polynomial fits for calculating spin-wave stiffness constant (D) from spin-wave energies.

fit to magnon dispersion allows the extraction of the stiffness constant as the coefficient of the quadratic term in the spin-wave energy expansion. Consequently, the spin-wave energies for small $\mathbf{q}$ take on a specific form that reflects these properties.

$$w(\mathbf{q}) = D|\mathbf{q}^2|(1 - \beta|\mathbf{q}^2|), \quad (17)$$

where $w(\mathbf{q})$ is as derived in spin-wave energy. Based on Eq. (17), we utilize spin-wave dispersion calculations to extract the spin-wave stiffness constant for 3d-ferromagnets.

The Eq. (17) is analogous to polynomials representing the long-wave limit,

$$f_{2n}(\mathbf{q}) = \sum_{i=1}^n a_{2i}q^{2i}, \quad (18)$$

for $i = 2$, a quadratic term is obtained and it defines the spin-wave stiffness constant D ,

$$D = a_2. \quad (19)$$

The fitting interval must be centered around the Γ point ($\mathbf{q} = 0$) since the origin of the spin-wave stiffness constant lies in the static susceptibility at $\mathbf{q} = 0$. The choice of a narrow $\mathbf{q}$ -window ($\Delta\mathbf{q}$) ensures precision for capturing low-energy magnetic excitations where the spin-wave stiffness is highly sensitive to small changes in $\mathbf{q}$. By increasing the density of k-points, computational accuracy improves while preserving oscillatory

Table 5.3: Calculated and experimental spin stiffness constants D (meV/Å²) of bcc Fe, fcc Co and fcc Ni.

Compound	D_{cal}^1	D_{cal}^2	D_{cal}^3	D_{cal}^4	D_{exp}
bcc Fe	220	250	247	322, 313	314 ^a , 230 ^b , 280 ^c , 307 ^d
fcc Co	543	663	502	480, 520	510 ^e , 580 ^c
fcc Ni	757	756	739	541, 1796	422 ^c , 550 ^f

¹ Present calculation.

² Calculation from Ref. [3].

³ Calculation from Ref. [105].

⁴ Calculation from Ref. [106].

^a Taken from Ref. [107].

^b Taken from Ref. [108].

^c Taken from Ref. [109].

^d Taken from Ref. [110].

^e Taken from Ref. [111].

^f Taken from Ref. [112].

behavior characteristic of spin-wave dispersion curves, as demonstrated by Sipr *et al.* [104].

Following previous work by T.B *et al.* [113], we set the fitting range for bcc Fe to $|q| \in [0, 0.5, 0.0]$ (in units of $2\pi/a$), ensuring sufficient sampling around $q = 0$ while maintaining computational efficiency. The spin-stiffness constant was computed for bcc Fe using quadratic fourth-order polynomial fit over the selected $\mathbf{q}$ -range to ensure the stability of the fitting procedure. The fitting result is exhibited in Table 5.3 with several experimental results.

The fcc Co stiffness was calculated by fitting the spin-wave energies with polynomials of degree $n = 2$ to extract the quadratic term. Our choice of up to $n = 2$ for fcc Co was guided by the requirement to ensure numerical stability within the set $\mathbf{q}$ -range. The calculated spin-wave stiffness is documented in Table 5.3 with several experimental results.

The spin-wave stiffness of fcc Ni was calculated over a $\mathbf{q}$ -vector range between 0 and 1.2 Å^{-1} using a bi-quartic polynomial fit ($n = 2$). The spin-wave stiffness obtained from this calculation is 739 meV/Å^2 , which shows a significant deviation from its experimental value of 550 meV/Å^2 . Similar value of fcc Ni spin-wave stiffness

findings have been reported by T.B. and O. Sipr [104, 113]. The calculated value of the spin-stiffness constant differs in these studies due to the influence of LDA exchange-correlation limitations in fcc Ni calculation (see section.5.2.2.2).

5.3 Exchange Interactions and Estimation of Curie Temperature

5.3.1 Heisenberg Exchange Parameters

The Heisenberg exchange interaction parameters were calculated using equations derived in detail in the theory chapter (see Section 2). As a reminder, when there is a single magnetic atom in the unit cell, the Heisenberg exchange interaction parameters in the Brillouin zone are formulated (for magnetic moment treated as unit vector) as

$$J_i(\mathbf{q}) = -\frac{E_i(\mathbf{0}, 0) - E_i(\mathbf{q}, \theta_i)}{\sin^2 \theta_i}, \quad (20)$$

where $E_i(\mathbf{q}, \theta_i)$ is spin-spiral energy as a function of the wavevector and the cone angle of atom i .

For a unit cell containing multiple magnetic atoms (i.e., distinct magnetic sublattices), and considering only inter-site separations under the simplifying assumption $\theta_i = \theta_j = \theta$, the real part of the Heisenberg exchange parameters can be expressed as

$$\begin{aligned} \Re[J_{ij}(\mathbf{q})] &= \frac{E_{ij}(\mathbf{0}, \frac{\pi}{2}) - E_{ij}(\mathbf{q}, 0)}{2 \sin^2 \theta} \\ &+ \frac{E_i(\mathbf{q}, \theta) - E_i(\mathbf{0}, 0)}{2 \sin^2 \theta} + \frac{E_j(\mathbf{q}, \theta) - E_j(\mathbf{0}, 0)}{2 \sin^2 \theta}. \end{aligned} \quad (21)$$

The real-space Heisenberg interaction parameters were calculated using the inverse Fourier transform of $J(\mathbf{q})$ (see Chapter 2). These parameters will be used in the subsequent exchange coupling calculations of 3d-ferromagnets and Heusler compounds presented in this section.

5.3.2 Curie temperature: RPA and MFA Approaches

The Heisenberg exchange parameters can be used to determine the Curie temperature of $3d$ -ferromagnets and Heusler compounds. In this section, the two different approaches will be used to compute the Curie temperature. The first approach to calculate Curie temperature is the mean-field approximation (MFA) (for full derivation, see Kubler's book [96]). This approach is based on the assumption that each spin interacts with the same effective magnetic field created by all other spins. Due to its simplicity mean-field approximation is widely used. It usually yields qualitatively correct results, and provides insight into the nature of the magnetic phase transitions.

The starting point for calculating the Curie temperature within the MFA framework is the low-temperature regime, where the thermal excitation of magnons is described by quantizing the magnon spectrum and applying the Bose-Einstein distribution function to determine the mean magnon occupation number $\langle n_q \rangle$ for a magnon's energy ω_q ,

$$n_q(T) = \frac{1}{e^{(\hbar\omega_q/k_B T)} - 1}. \quad (22)$$

At low temperatures, magnons add up to the single magnon energies due to the assumption of no interaction between them,

$$E = \sum_q w_q \langle n_q \rangle. \quad (23)$$

The energy equation can be rewritten from the dispersion relation for spin-wave Eq. (4) taking a small angle approximation $\sin^2(\theta) \rightarrow \theta^2$,

$$\langle \theta_q^2 \rangle = \frac{4}{M} \langle n_q \rangle \quad (24)$$

The thermal reduction of the magnetization due to excited magnons (tilted by θ from equilibrium) at harmonic regime ($T \ll T_C$) become,

$$\Delta M(T) = M - M \sum_q \langle \cos \theta_q \rangle, \quad (25)$$

where $\langle \cos \theta_q \rangle$ is equal to $1 - \langle \theta_q \rangle / 2$ from small angle approximation and Eq. (24) can be rewritten from this approximation and Eq. (25) becomes,

$$\Delta M(T) = 2 \sum_q \langle n_q \rangle \quad (26)$$

At higher temperatures T_C , the magnon modes start to interact kinematically, and this leads to an inharmonic effect. The magnon propagation is replaced by a transverse spin fluctuations picture where the magnitude of the spin remains constant. In this regime, reduction of magnetization deals with semiclassical averaging schemes for the mean-field free energy [5] where Weiss field is acting on sublattice n introduced as,

$$B_{Weiss,n} = \sum_m 2J_{nm}^0 \langle M_m \rangle. \quad (27)$$

The thermal average of the magnetic moment at sublattice n ,

$$\langle M_n \rangle = M_n \coth\left(\frac{M_n B_{Weiss,n}}{k_B T}\right) - \frac{k_B T}{B_{Weiss,n}}. \quad (28)$$

At the Curie temperature T_C , the system magnetically disorders, and the Weiss field vanishes. The hyperbolic cotangent in the Langevin function at $T \approx T_C$ for small x can be approximated as:

$$\coth x \approx \frac{1}{x} + \frac{x}{3}. \quad (29)$$

From this expression, the thermal average of the magnetic moment can be rewritten as

$$\langle M_n \rangle \approx \frac{2M_n^2}{3k_B T} \sum_m J_{nm}^0 \langle M_m \rangle. \quad (30)$$

The homogeneous linear equation Eq. (30) represents eigenvalue matrix problem in the form,

$$\det\left(\frac{2M^2}{3k_B} - I\lambda_T\right) = 0. \quad (31)$$

The highest eigenvalue of this matrix is the Curie temperature for the multi-sublattice system. On the contrary, in the Bravais lattice, all site moments are identical $M_n = M$,

the exchange constant J_{nm}^0 simplifies to J^0 , and the expression of Eq. (31) become,

$$k_B T_C = \frac{2}{3} M^2 J^0. \quad (32)$$

The second approach for calculating the Curie temperature from exchange parameters is the random-phase approximation (RPA). This approach demonstrates better agreement with experimental T_C values. The formula was directly adapted from Pajda *et al.* [3],

$$\frac{1}{T_C^{RPA}} = \frac{6k_B}{M} \frac{1}{N_q} \sum_q \frac{1}{\omega(\mathbf{q})}. \quad (33)$$

Here, N_q is a number of $\mathbf{q}$ points in the Brillouin zone, and M is the local magnetic moment. The third method to calculate Curie temperature is the Monte Carlo method, which provides highly accurate T_C prediction. We discuss the method in Appendix E.

5.3.3 Use of Brillouin Zone Symmetries in The Calculation of Exchange Interactions

The main drawback of the SS-SC method for evaluating exchange parameters is that it is computationally expensive. Since calculating real space exchange parameters needs very dense k -mesh sampling. To overcome the expensive computational time, the number of k -vectors can be reduced by symmetry operations characterized by the Bravais lattice of the unit cell. The aim is to map some $\mathbf{q}$ -vectors to another one $S(\mathbf{q})$ in BZ,

$$S : \mathbf{q} \rightarrow R\mathbf{q} + \mathbf{T}, \quad (34)$$

where R is the rotation matrix and $\mathbf{T}$ is the translation vector, which is characteristic of the Bravais lattice symmetry. Two points $\mathbf{q}'$ and $\mathbf{q}$ are equivalent if symmetry operations of the Bravais lattice fulfill the relation,

$$\mathbf{q}' = R\mathbf{q} + \mathbf{T}. \quad (35)$$

For instance, the fcc symmetry group includes 48 space group operations where has 24 rotational symmetry elements with a combination of the 2-fold, 3-fold, and 4-fold

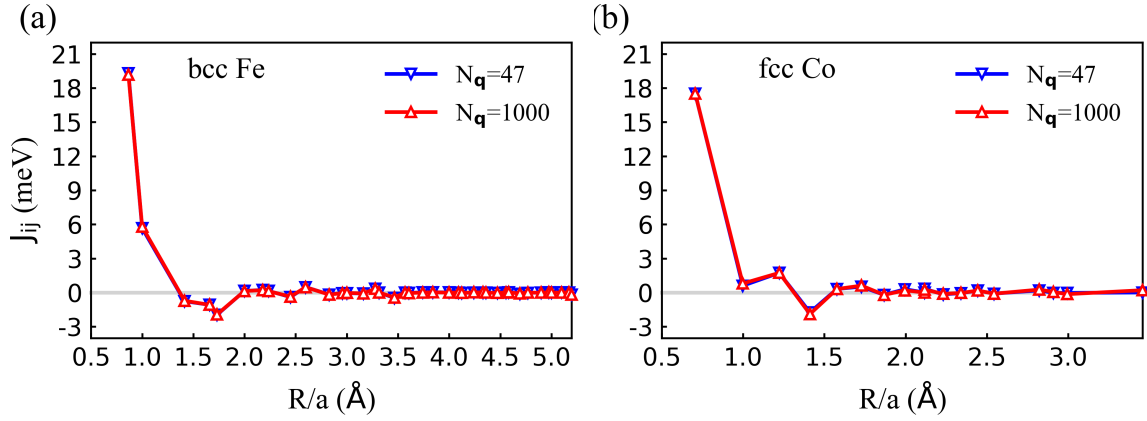


Figure 5.9: Heisenberg exchange parameters as function of the interatomic distance R (in units of the lattice constant a) for (a) bcc Fe and (b) fcc Co. Calculations employed 47 and 1000 q -vectors in the Brillouin zone. Positive (negative) values indicate ferromagnetic (antiferromagnetic) coupling.

Table 5.4: Calculated Curie temperature and computational time are shown for both dense (1000 q -points) and coarse (47 q -points) Brillouin zone samplings for bcc Fe and fcc Co.

Material	# of $\mathbf{q}$	T_c^{MFA} (K)	T_c^{RPA} (K)	CPU(per Node)	Time(Day)
bcc Fe	1000	1131	788	44	10
	47	1138	797	44	1/2
fcc Co	1000	1843	1538	44	10
	47	1841	1537	44	1/2

rotation axis and an inverse symmetry operation.

Thus, the number of 1000 $\mathbf{q}$ in the full Brillouin zone can be reduced to 47 unique propagation vectors ($\mathbf{q}'$) from where are located at the Irreducible Brillouin zone (IBZ),

$$N_{\mathbf{q}} = \frac{\mathbf{q}' \Rightarrow 1000}{S \Rightarrow 48} \approx \mathbf{q} \Rightarrow 47. \quad (36)$$

With this symmetry operation, the Heisenberg exchange parameters were calculated using 47 $\mathbf{q}$ vectors, as shown in Fig.5.9. These parameters exhibit an exact match with those obtained from calculations using 1000 propagation vectors, demonstrating the efficiency and accuracy of the reduced propagation vector approach.

The results for Curie temperature calculated by both MFA and RPA with two different $\mathbf{q}$ -vector sampling exhibit perfect agreement, and the precision of these symmetry operations in generating the irreducible set of points significantly reduces computational time, as demonstrated in Table 5.4.

The applicability of symmetry operations to reduce computational effort by decreasing the number of $\mathbf{q}$ -vector needed to calculate exchange coupling was tested for a bcc unit cell, which belongs to a cubic Bravais lattice system. While there are 48 total symmetry operations (S), applying these within the unique structure reduces the number of $\mathbf{q}$ -vector from 1000 in the Brillouin zone (BZ) to just 47 unique points. The use of symmetry not only maintains accuracy but significantly reduces computational time compared to using 1000 propagation vector mesh in BZ, as displayed in Table.5.4. After successfully implementing symmetry operations to reduce computational complexity by decreasing $\mathbf{q}$ -vectors from 1000 to 47 unique $\mathbf{q}$ -vectors in the Brillouin zone (IBZ), we proceed to validate their effectiveness for the first $3d$ -ferromagnet and then some Heusler compounds.

5.3.4 $3d$ -ferromagnets

The elemental $3d$ -ferromagnets are widely used in technological applications such as spintronics, magnetic storage devices, etc. Therefore, these fundamental materials have been well-studied ferromagnets from the Heisenberg exchange interaction framework, and we consider them as prototype systems for testing our Heisenberg exchange parameter recipe implemented into VASP and to serve as be a benchmark for its performance on itinerant magnets.

The LDA energy functional is used throughout these calculations. The calculations were performed on a $16 \times 16 \times 16$ $\mathbf{k}$ -point mesh with 47 $\mathbf{q}$ -vectors in the Brillouin zone. The local magnetic moment integrations were computed inside Wigner-Seitz spheres with radii of 1.94 Å, 1.38 Å, and 1.29 Å for bcc Fe, fcc Co, and fcc Ni, respectively. The exchange parameters were calculated using the formulation in Eq. (20) within spin-spiral self-consistent method (SS-SC). These results are compared with those obtained from three other established computational approaches: Pajda *et al.*'s Green-function-based magnetic force theorem (GF-MFT) using the TB-LMTO method [3], Lezaic *et al.*'s full-potential LAPW-based spin-spiral method combined with the magnetic force theorem (SS-MFT) [7], and Jacobsson *et al.*'s spin-spiral method incorporating constraining fields, referred to as the transverse-field (t-field) method [6].

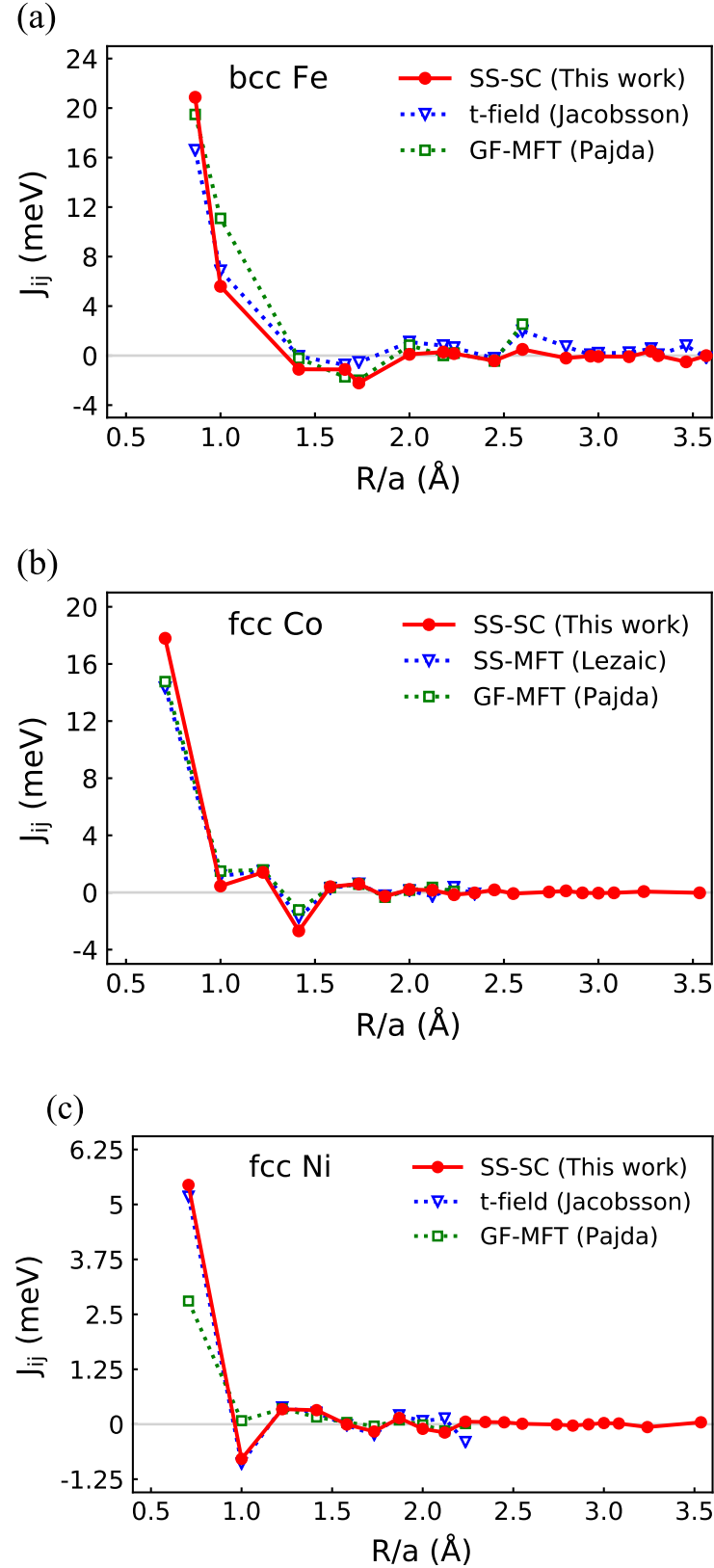


Figure 5.10: Heisenberg exchange parameters as function of the interatomic distance R (in units of the lattice constant a) for (a) bcc Fe, (b) fcc Co, and (c) fcc Ni. Results from our constrained self-consistent spin-spiral calculations (SS-SC) are compared with previous studies: Pajda *et al.* (MFT, real-space TB-LMTO) [3], Jacobsson *et al.* (T-field method, frozen magnons) [6], and Lezaic *et al.* (spin-spiral + magnetic force theorem) [7].

The Heisenberg exchange parameters of bcc Fe exhibit visible ferromagnetic interactions within the first two nearest neighbors in bcc Fe from the SS-SC method. The first nearest neighbors exchange parameter exhibits a similarity with the corresponding values derived from Pajda’s methodology, while it differs by a smaller margin compared to Jacobson’s calculations. Conversely, the second nearest neighbor exchange parameter aligns closely with Jacobson’s findings while displaying a notable difference relative to Pajda’s results. The interactions remain significant even at longer inter-atomic distances, particularly along the $[111]$ crystallographic direction at longer ranges, and from the third nearest neighbors interaction, the exchange parameters demonstrated a transition from ferromagnetic to anti-ferromagnetic but weaker compared to the ferromagnetic interactions within unit cell. This observation aligns with findings from both reference methodologies.

The calculated Curie temperature using the SS-SC approach within MFA closely matches Jacobsson’s computations, as illustrated in Table 5.5. Notably, this value is significantly lower than the estimate reported by Pajda’s method. The discrepancy arises primarily from differences in the number of atomic shell contribution within sum rule of MFA formula (see Eq. (32)). Specifically, for weak ferromagnet bcc Fe long range atomic shells distance is non-negligible due to oscillatory RKKY-type interactions contributions that partially cancel each other out and are weighted equally in the MFA summation. Consequently, our SS-SC and Jacobson’s methods yield internally consistent Curie temperature estimates from MFA summation that better align with experimental observations, whereas Pajda’s method results in notably higher Curie temperature estimates.

The fcc Co exchange parameters derived using the SC method exhibit a dominant ferromagnetic exchange interaction at the first nearest neighbor, which yields higher exchange energy compared to results obtained by Pajda and Leziac. Subsequently, the strength of exchange parameters from each calculation diminishes sharply at the second nearest neighbor, and the transition from ferromagnetic coupling to anti-ferromagnetic coupling occurs at the third nearest neighbor. Beyond this distance, the exchange parameters revert to ferromagnetic behavior at each calculation. Notably, subtle Kohn

Table 5.5: Lattice parameters, magnetic moments, Curie temperatures (T_C) for bcc Fe, fcc Co, and fcc Ni. Comparison includes values from this work, and experiment.

Material	a (Å)	m (μ_B)	T_c^{MFA} (K)	T_c^{RPA} (K)	T_c^{Exp} (K)
bcc Fe	2.87	2.25	1194 (1077 ^a , 1414 ^b)	820 (950 ^b)	1043
fcc Co	3.55	1.61	1711 (1645 ^b)	1383 (1311 ^b)	1388
fcc Ni	3.52	0.6	579 (579 ^a , 397 ^b)	530 (350 ^b)	627

^a Reference [6]

^b Reference [3]

anomalies in the magnon dispersion of fcc-Co due to almost strong ferromagnet nature expects less-pronounced RKKY-type character and faster decay of exchange interaction within R/a distance ratio. Despite the exchange interaction deviation between the SS-SC method and other reference methods at first nearest neighbor of fcc Co , the calculated Curie temperature using MFA and RPA aligns closely matches Pajda's results and the experimental value (see Table.5.5).

For fcc Ni, a system characterized by a dominant Stoner continuum, we observe that our SS-SC method yields results that closely align with those of Jacobson [6], while Pajda's calculation produces significantly lower first-nearest-neighbor exchange energies. The MFT method utilized by Pajda does not adequately account for renormalization effects, particularly in the context of small exchange splitting magnetic materials such as fcc Ni [114]. In contrast, both our SS-SC method and Jacobson's t-field method, which employ constrained self-consistent field calculations, successfully capture these renormalization effects, resulting in closer agreement with experimental Curie temperatures compared to Pajda's result (see Table.5.5).

5.3.5 Full Heusler Compounds

The L2₁-type full Heusler alloys of Cu₂MnAl has relatively a high Curie temperature (603 K), making it remain magnetic at the operating temperatures for spintronic devices where it have been experimentally studied by Tajima et al.[115]. The polarized

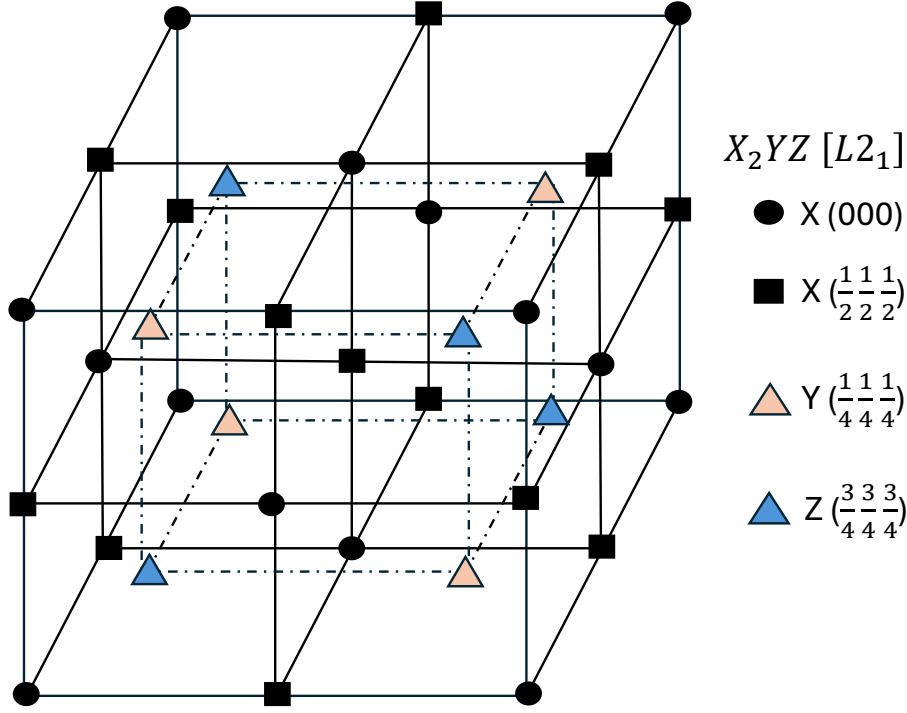


Figure 5.11: $L2_1$ structure adapted by the full-Heusler alloys. The lattice consists of 4 interpenetrating fcc lattices.

neutron diffraction study of $L2_1$ -type full Heusler alloys of Pd_2MnSn have been experimentally studied by Ishikawa et al. [116] for highlighting Pd's role in spin polarization due to Pd_2MnSn 's unique scattering properties, unresolved electronic behavior, and potential for neutron optics.

The Ni-based Full Heusler compounds are useful for spintronics applications due to high-quality epitaxial growth on widely employed semiconductors [117, 118, 119]. Additionally, Ni-based Heusler are magnetic shape memory alloys [20] and highly promising multi-caloric materials as they show large caloric effects [120, 121].

The unit cell of full Heusler alloys (X_2YZ) consists of four interpenetrating fcc sublattices with the positions (000) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for X, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ for Y and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ for Z atom (see fig.5.11).

The origin of ferromagnetic behavior in Heusler alloys emerged from the microscopic mechanism responsible for the formation of magnetic moments where exhibits localized magnetic moments that originate from Mn atoms. The localized character of the magnetic moment results from the fact that $3d$ electrons of Mn are partially delocalized due to hybridization with the majority spin d -states of the X atoms and the exclusion

of minority spin states that implies system has only one spin direction. This behavior leads to magnetic moments that are localized in character but formed from itinerant electrons, as originally discussed by Kübler *et al.* [122]. In their study, the X atoms were shown to primarily determine the lattice constant, while magnetic coupling between the widely separated Mn atoms is mediated via the Z atoms, specifically through Mn–Z *sp-d* hybridization.

The microscopic nature of exchange interactions in Heusler was thoroughly investigated by Şaşıoğlu *et al.* [123], who demonstrated that magnetic coupling in Mn-based Heusler alloys is highly sensitive to the number of conduction *sp*-electrons, their spin polarization, and the position of unoccupied Mn 3*d* states relative to the Fermi level. Their work identifies a competition between two indirect exchange mechanisms: (i) RKKY-type interaction, where the spin polarization and concentration of conduction electrons determine the strength and sign of the exchange, and (ii) superexchange, which arises from virtual electron hopping into unoccupied Mn *d*-states above the Fermi level.

Our calculations were performed on a 10 x 10 x 10 k-point mesh. Given that these materials' lattices consist of 4 interpenetrating fcc sublattices (see Fig.5.11), the same symmetry operations previously used for fcc ferromagnets were applied to reduce 1000 **q**-vectors to unique 47 **q**-vectors in the Brillouin zone. The local magnetic moments were computed inside WS spheres using the default WS radii extracted from their corresponding potential file. The exchange parameters of one magnetic sublattice case was calculated using the formulation in Eq. (20). Additionally, two magnetic sublattice case was calculated using the formulation in Eq. (21). The exchange-correlation functional was set to GGA since both the LSDA and GGA XC functional were stated to be suitable for investigating the magnetic properties of Heusler compounds [124]. The calculated Heisenberg exchange parameters J_{ij} from the SS-SC method for Cu₂MnAl, Pd₂MnSn and Ni₂MnGa, Ni₂MnSn are shown in fig.5.12. The results of Cu₂MnAl and Pd₂MnSn are compared with those obtained by Galanakis *et al.* [4], who employed the frozen magnon approach within the atomic sphere approximation (ASA) using the augmented spherical waves (ASW) method. In their approach, the magnetic interactions

are extracted from total energies of helical spin-spiral configurations, under the assumption of magnetism concentrated on Mn-side which was simplified to one magnetic sublattice systems. Both methods are grounded in the classical Heisenberg model but differ in how self-consistency and magnetic constraints are treated. The comparison allows us to assess the influence of self-consistent feedback and moment stabilization on the accuracy of short- and medium-range exchange interactions in local-moment ferromagnets. The results of Ni_2MnGa and Ni_2MnSn are compared with those obtained by Şaşıoğlu *et al.* [8], who extended the frozen magnon formalism to a multisublattice framework of Mn–Mn and Mn–Ni exchange interactions, providing insight into the role of intersublattice coupling in determining the magnetic behavior of these systems.

The exchange interaction in $\text{L2}_1\text{-Cu}_2\text{MnAl}$ calculated by our SS-SC method exhibit strong ferromagnetic coupling at nearest and next-nearest neighbor distances, with a tail behavior observed from third neighbors that show small fluctuations between ferromagnetic and anti-ferromagnetic tendencies (see fig.5.12a). These tail contributions are relatively minor compared to the dominant ferromagnetic interactions. The minimal impact of these tail contributions on magnetic properties suggests that the primary ferromagnetic coupling established by nearest- and next-nearest-neighbor exchange relations is sufficient for determining key magnetic behaviors in Cu_2MnAl . This implies that higher-order neighbor interactions, while present, do not significantly influence overall magnetic properties due to their relatively small magnitude. These observations closely align by Galanakis’s results and Curie temperature of Cu_2MnAl yielded with close agreement to experimental value as shown in table.5.6.

The exchange interaction in $\text{L2}_1\text{-Pd}_2\text{MnSn}$ calculated by our SS-SC method exhibit ferromagnetic behavior at the first, second, and third neighbor distances, but their magnitudes are much smaller compared to those observed in Cu_2MnAl (see fig.5.12b). However, a stronger anti-ferromagnetic interaction is present at the fourth neighbor distance. The presence of this anti-ferromagnetic characteristic and weaker ferromagnetic coupling in Pd_2MnSn results in overall less robust magnetic properties compared to Cu_2MnAl . This conclusion is supported by Curie temperature calculations, as demonstrated in Table 5.6, which show lower values for Pd_2MnSn due to the weaker ferro-

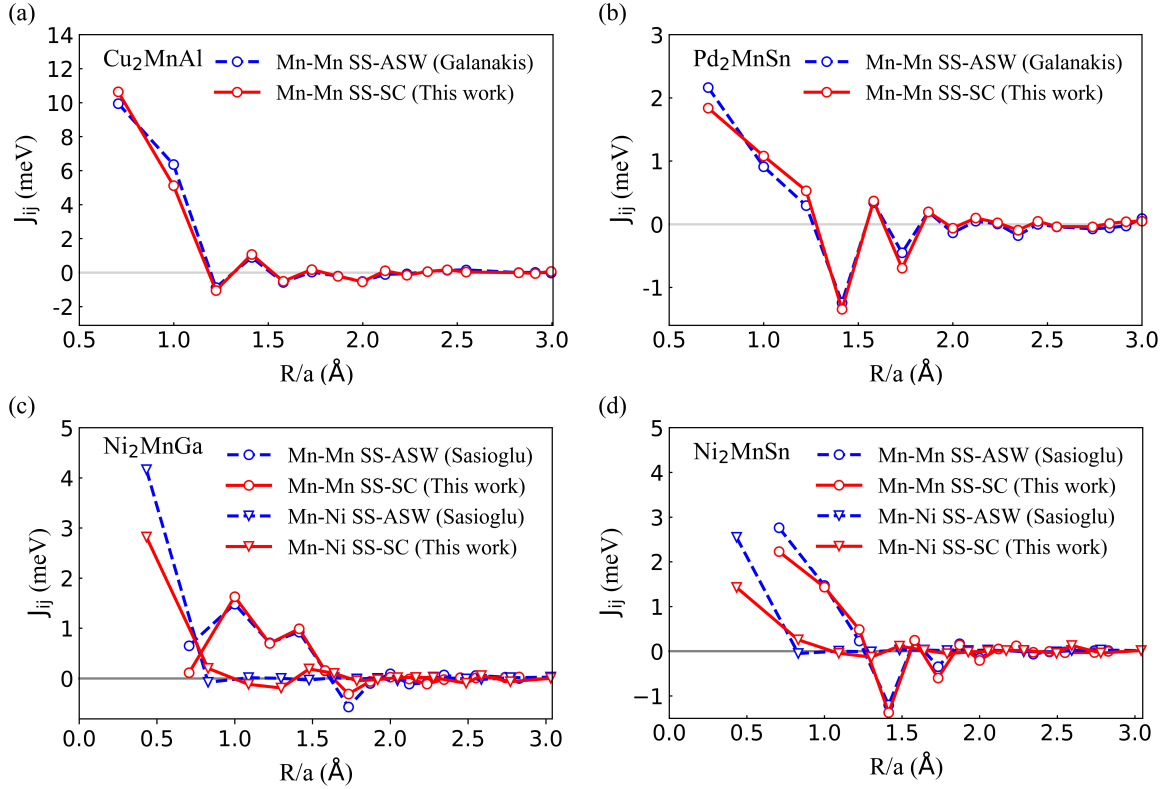


Figure 5.12: Heisenberg exchange parameters as function of the interatomic distance R (in units of the lattice constant a) for (a) Cu_2MnAl , (b) Pd_2MnSn , (c) Ni_2MnGa and (d) Ni_2MnSn . Results from our constrained self-consistent spin-spiral calculations (SS-SC) are compared with previous studies: Galanakis *et al.* (Spin-spiral with ASW) [4] and Şaşıoğlu *et al.* (Spin-spiral with ASW) [8].

magnetic coupling and the presence of anti-ferromagnetic interactions. In summary, while both materials exhibit significant exchange interactions at extending to multiple nearest neighbor distances, their differing magnitudes and types of interactions lead to distinct magnetic behaviors where arises from increased indirect interaction distance of Mn-Mn sublattices that leading to weaker exchange coupling (see table.5.6 lattice parameters).

Now, we will focus on the detailed analysis of the exchange interaction within two Heusler compounds Ni_2MnZ , where Z represents Ga or Sn as shown in fig.5.12c-d. We will investigate how the electronic structure differences between Ga and Sn affect the exchange interactions and the overall magnetic behavior of the materials. We found that the presence of element Z significantly affects the exchange interaction trends, particularly in both intra-sublattice (Mn-Mn) and inter-sublattice interactions. The intra-sublattice interaction becomes progressively weaker as the first neighbor interac-

Table 5.6: Lattice parameter a used in the calculations, atom-resolved and total spin magnetic moments, and both calculated and experimental Curie temperatures.

Material	a (Å)	m_X (μ_B)	m_Y (μ_B)	m_Z (μ_B)	m_{total} (μ_B)	T_C^{MFA} (K)	T_C^{RPA} (K)	T_C^{Exp} (K)
Cu ₂ MnAl	5.95	0.075 (0.02 ^b)	3.55 (3.67 ^b)	-0.09 (-0.11 ^b)	3.56 (3.60 ^b)	1008 (970 ^b)	713 (635 ^b)	603 ^a
Pd ₂ MnSn	6.38	0.07 (0.07 ^b)	3.97 (4.08 ^b)	-0.06 (-0.06 ^b)	4.11 (4.16 ^b)	275 (252 ^b)	242 (178 ^b)	189 ^c
Ni ₂ MnGa	5.85	0.33 (0.294 ^e)	3.44 (3.57 ^e)	-0.05 (-0.04 ^e)	4.03 (4.09 ^e)	382 (389 ^b)	-	380 ^d
Ni ₂ MnSn	5.99	0.23 (0.206 ^e)	3.53 (3.72 ^e)	-0.066 (-0.057 ^e)	3.92 (4.080 ^e)	345 (358 ^e)	-	360 ^d

^a Reference [125]

^b Reference [4]

^c Reference [115]

^d Reference [125]

^e Reference [126]

tion when we go from $Z = \text{Sn}$ to $Z = \text{Ga}$. In contrast, the inter-sublattice exchange interaction is short-ranged, limited to first-neighbor interactions, with its behavior exhibiting a slight oscillation that dies out as it transitions from Ga to Sn. These distinct patterns in exchange interactions are attributed to the electronic differences brought about by element Z , and our findings align well with those reported by Şaşıoğlu *et al.* [8] which further emphasizes the importance of the p -block elements (Ga and Sn) in determining these properties. The observed trends in exchange interaction behavior are consistent with their explanations of the underlying chemical influence of different types of Z atoms. Additionally, Curie temperature of Ni₂MnGa and Ni₂MnSn closely align with theoretical reference work and experimental value as shown in table.5.6.

5.3.6 Half Heusler Compounds

The successful application of our SS-SC method to calculate Heisenberg exchange parameters and Curie temperatures for 3d ferromagnets and full-Heusler compounds shows close agreement with both reference first-principles studies and experimental data. Building upon this validation, we extend our investigation to a newly proposed class of materials—spin-gapped metals (SGMs)—recently introduced by Şaşıoğlu *et*

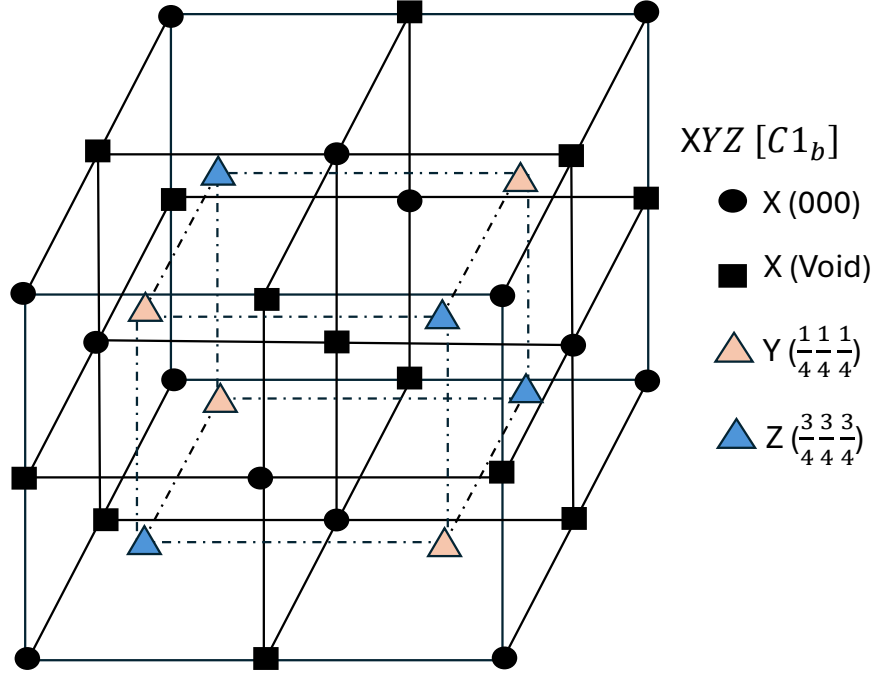


Figure 5.13: $C1_b$ structure adapted by the Half-Heusler alloys. The lattice consists of 3 interpenetrating fcc lattices.

al. [127]. SGMs are conceptually derived from the idea of cold (gapped) metals and represent a spin-polarized extension of such systems into magnetically ordered Heusler compounds. They are characterized by intrinsic spin-selective semiconducting behavior, where one spin channel exhibits metallic or narrow-band transport while the other remains gapped. Unlike dilute magnetic semiconductors, SGMs achieve spin polarization without extrinsic doping, and their stoichiometric and ordered structure minimizes band tailing, which typically degrades switching performance in traditional semiconductors. These characteristics make SGMs promising candidates for emerging device concepts such as semiconductor-free negative differential resistance (NDR) tunnel diodes, non-local giant magnetoresistance (GMR) devices, and steep-slope spin-FETs. Şasioğlu *et al.* [127] collected data from the Open Quantum Materials Database (OQMD) [128, 129] to identify spin-gapped metals. In this study, we selected NiVSb and NiVSn half-Heusler compounds (XYZ), which is one of the four fcc sublattices vacant (see Fig.5.13) to investigate their magnetic properties within the framework of Heisenberg exchange interactions and Curie temperature calculations.

The calculations were performed on a $10 \times 10 \times 10$ $\mathbf{k}$ -point mesh. The local mag-

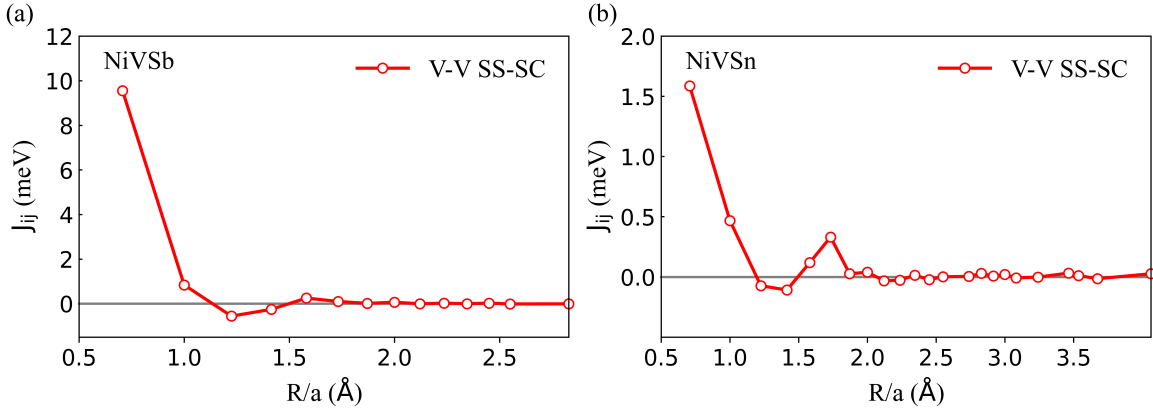


Figure 5.14: Heisenberg exchange parameters as function of the interatomic distance R (in units of the lattice constant a) for (a) NiVSb, (b) NiVSn.

netic moments were computed inside WS spheres with default WS radii extracted from their potential file. The exchange parameters were calculated using Eq. (20). The exchange-correlation functional was set to GGA. To investigate the magnetic stability and ordering in SGMs, we selected two representative compounds—NiVSb and NiVSn—from Table I of Şaşıoğlu et al. [127]. Both exhibit 100% spin polarization, an $n\text{-type}\uparrow/\text{SC}\downarrow$ spin-gap configuration, and a strong local magnetic moment on the V sublattice, indicating V–V exchange as the dominant magnetic interaction pathway. They also share a common electronic structure trait: a narrow majority-spin metallic band and a well-defined gap in the minority spin channel, making them ideal for probing the nature of spin-polarized magnetic exchange.

As shown in Fig.5.14, both compounds display dominant ferromagnetic exchange in the first and second nearest neighbor (NN) shells. Notably, NiVSb shows a stronger first NN exchange interaction compared to NiVSn. Additionally, an antiferromagnetic exchange emerges at the third NN, more prominently in NiVSn, whereas NiVSb retains a more coherent long-range ferromagnetic oscillation. The exchange profile in NiVSb exhibits RKKY-like behavior, with oscillations extending beyond the unit cell, while NiVSn shows a more localized magnetic interaction that decays more rapidly. These differences are reflected in the calculated Curie temperatures (Table 5.7), where NiVSb emerges as a stronger candidate for spintronic applications due to its higher T_C and robust ferromagnetism. The contrast in exchange behavior and magnetic ordering is likely rooted in the different d - p hybridization strengths between V and the Z-site

Table 5.7: Lattice parameter a used in the calculations, atom-resolved and total spin magnetic moments, and both calculated and experimental Curie temperatures.

Material	a (Å)	m_X (μ_B)	m_Y (μ_B)	m_Z (μ_B)	m_{total} (μ_B)	T_C^{MFA} (K)	T_C^{RPA} (K)
NiVSb	5.88	0.09 (0.03 ^a)	1.76 (2.12 ^a)	-0.07 -	2.00 (2.00 ^a)	890	716
NiVSn	5.87	0.03 (-0.03 ^a)	0.955 (1.15 ^a)	-0.065 -	1.00 (1 ^a)	196	182

^a Reference [127]

elements (Sb or Sn). This motivates further analysis of the density of states (DOS) and projected orbital contributions to better understand the microscopic origin of magnetic coupling in spin-gapped systems.

6 — Conclusion

In this work, we developed a practical computational protocol utilizing existing ab initio electronic structure implementations (based on Density Functional Theory—DFT) in commercial/academic software package (VASP) to evaluate key magnetic properties of materials considered for spintronic devices. The multi-parameter optimization technique was proposed as a means to address limitations of XC functionals in with standard density functional theory (DFT) in handling magnetic systems. Subsequently, we developed a comprehensive workflow to construct a spin Hamiltonian, which serves as the foundation for performing atomistic simulations aimed at elucidating the spintronic properties of various magnetic materials.

Firstly, we focused on developing a Hubbard correction scheme tailored for the complex magnetic system of $\text{DO}_{22}\text{Mn}_3\text{Ga}$. We introduced a multi-parameter optimization technique, which involves scanning over a wide range of potential lattice parameters and magnetic moments for each Mn site. This method systematically narrows down the most suitable Hubbard U parameters that align with experimental constraints on lattice parameters and total (local) magnetic moments. Through this approach, we successfully identified optimal Hubbard U corrections for each site within the experimental bounds. This multi-parameter optimization technique provides a reliable method for determining appropriate Hubbard U corrections for complex magnetic systems like Mn_3Ga . Our findings underscore the potential of systematic approaches in addressing computational challenges associated with Hubbard parameters and suggest that such techniques can significantly enhance our ability to model magnetic materials accurately.

We then investigated the impact of Hubbard U correction on the magnetic anisotropy energy (MAE) of Mn_3Ga and antiferromagnetic materials CrSb and CuMnAl . By an-

alyzing the orbital and atomic contributions of the Hubbard correction from each Mn site, d -orbital plays a critical role in determining the MAE. Similarly, for CrSb, the strong MAE origin was attributed to the s - p hybridization on the Sb site.

In finalizing our work, we successfully developed a new protocol for calculating Heisenberg exchange parameters using the Spin-Spiral approach within VASP. This protocol was first validated on elemental $3d$ -ferromagnets, ensuring the calculated properties matched well with established literature values. Subsequently, the protocol was applied to the Heusler compound, achieving results consistent with known data. Additionally, we incorporated symmetry operations and established benchmarks for constrained conditions, which significantly reduced computational time while maintaining accuracy. This advancement enhances the capabilities of VASP in handling a wide range of magnetic systems, providing valuable tools for future studies in adiabatic spin dynamics.

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A — Derivation of Spin Spiral Energy

In the following, we will demonstrate the derivation steps from the total energy per unit cell formula Eq. (70) to the spin spiral energy formula Eq. (72).

The local magnetic moment of atomic sites i , and j are formulated as,

$$\mathbf{M}_i = M_i[\cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i) \sin \theta_i \hat{x} + \sin(\mathbf{q} \cdot \mathbf{R}_i + \phi_i) \sin \theta_i \hat{y} + \cos \theta_i \hat{z}]. \quad (1)$$

$$\mathbf{M}_j = M_j[\cos(\mathbf{q} \cdot \mathbf{R}_j + \phi_j) \sin \theta_j \hat{x} + \sin(\mathbf{q} \cdot \mathbf{R}_j + \phi_j) \sin \theta_j \hat{y} + \cos \theta_j \hat{z}]. \quad (2)$$

To calculate the right-hand side (RHS) of the total energy per unit cell formula in Eq. 70, the dot product of Eq. 1 and Eq. 2 is performed,

$$\begin{aligned} \mathbf{M}_i \cdot \mathbf{M}_j = M_i M_j [\sin \theta_i \sin \theta_j (\cos \mathbf{q} \cdot \mathbf{R}_i) \cdot (\cos \mathbf{q} \cdot \mathbf{R}_j) + \\ \sin \theta_i \sin \theta_j (\sin \mathbf{q} \cdot \mathbf{R}_i) \cdot (\sin \mathbf{q} \cdot \mathbf{R}_j) + \cos \theta_i \cos \theta_j] \end{aligned} \quad (3)$$

Trigonometric identities were introduced to derive the right-hand side (RHS) of the dot product operation:

$$\begin{aligned} \cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i) \cos(\mathbf{q} \cdot \mathbf{R}_j + \phi_j) = \\ [\cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i + \mathbf{q} \cdot \mathbf{R}_j + \phi_j) + \cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i - \mathbf{q} \cdot \mathbf{R}_j - \phi_j)]/2 \end{aligned} \quad (4)$$

$$\sin(\mathbf{q} \cdot \mathbf{R}_i + \phi_i) \sin(\mathbf{q} \cdot \mathbf{R}_j + \phi_j) = [\cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i - \mathbf{q} \cdot \mathbf{R}_j - \phi_j) - \cos(\mathbf{q} \cdot \mathbf{R}_i + \phi_i + \mathbf{q} \cdot \mathbf{R}_j + \phi_j)]/2. \quad (5)$$

Eq. (3) become,

$$\mathbf{M}_i \cdot \mathbf{M}_j = M_i M_j [\sin \theta_i \sin \theta_j (\cos(\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j) + \phi_i - \phi_j)) + \cos \theta_i \cos \theta_j] \quad (6)$$

The final expression for the dot product of the local magnetic moments at atomic sites i and j is inserted into Eq. 70, leading to the derivation of the spin-spiral energy formula.

B — Imaginary Part of Heisenberg Exchange Parameter

In the following, we will demonstrate mathematical steps that lead to the imaginary part of the Heisenberg exchange The parameters ($\Im[J_{12}(\mathbf{q})]$).

The two initial condition was set to lead $[J_{12}(\mathbf{q})]$:

- $\mathbf{q} = \mathbf{q}$ and $\Delta = 0$
- $\mathbf{q} = \mathbf{q}$ and $\Delta = \frac{\pi}{2}$

From the first condition, the interaction between two atom ($i=1, j=2$) becomes,

$$E(\mathbf{q}, 0) = E_{11}(\mathbf{q}) + E_{22}(\mathbf{q}) + E_{12}(\mathbf{q}, 0) + E_{21}(\mathbf{q}, 0), \quad (1)$$

and from second condition becomes,

$$E(\mathbf{q}, \frac{\pi}{2}) = E_{11}(\mathbf{q}) + E_{22}(\mathbf{q}) + E_{12}(\mathbf{0}, \frac{\pi}{2}) + E_{21}(\mathbf{0}, \frac{\pi}{2}). \quad (2)$$

The spin spiral energy difference is defined as the difference between the energies of the spin configuration in phase 90° and phase 0° [$E(\mathbf{q}, \frac{\pi}{2}) - E(\mathbf{q}, 0)$],

$$\begin{aligned} E(\mathbf{q}, \frac{\pi}{2}) - E(\mathbf{q}, 0) &= E_{11}(\mathbf{0}) - E_{11}(\mathbf{q}) + E_{22}(\mathbf{0}) - E_{22}(\mathbf{q}) \\ &\quad + E_{12}(\mathbf{q}, \frac{\pi}{2}) - E_{12}(\mathbf{q}, 0) + E_{21}(\mathbf{q}, \frac{\pi}{2}) - E_{21}(\mathbf{q}, 0). \end{aligned} \quad (3)$$

The E_{12} and E_{21} become

- $E_{12}(\mathbf{q}, 0) = -M^2 \sin \theta \operatorname{Re}[J_{12}(\mathbf{q})] - M^2 J_{12}(\mathbf{q}) \cos^2 \theta$

- $E_{12}(\mathbf{q}, \frac{\pi}{2}) = -M^2 \sin \theta \frac{Re[J_{12}(\mathbf{q}) \exp(i\frac{\pi}{2})] = -\Im[J_{12}(\mathbf{q})]}{Re[J_{12}(\mathbf{q}) \exp(i\frac{\pi}{2})]} - M^2 J_{12}(\mathbf{0}) \cos^2 \theta$
- $E_{21}(\mathbf{q}, 0) = -M^2 \sin \theta Re[J_{21}(\mathbf{q})] - M^2 J_{12}(\mathbf{0}) \cos^2 \theta$
- $E_{21}(\mathbf{q}, \frac{\pi}{2}) = -M^2 \sin \theta \frac{Re[J_{21}(\mathbf{q}) \exp(-i\frac{\pi}{2})] = \Im[J_{21}(\mathbf{q})]}{Re[J_{21}(\mathbf{q}) \exp(-i\frac{\pi}{2})]} - M^2 J_{21}(\mathbf{0}) \cos^2 \theta$

with the help of first item of symmetry $J_{12}(\mathbf{q}) = J_{21}(-\mathbf{q})$, the expression of Eq. (3) becomes,

$$\begin{aligned}
E(\mathbf{q}, \frac{\pi}{2}) - E(\mathbf{q}, 0) &= E_{11}(\mathbf{q}) - E_{11}(\mathbf{0}) + E_{22}(\mathbf{q}) - E_{22}(\mathbf{0}) \\
&+ M^2 \sin^2 \theta \left(\Im[J_{21}(-\mathbf{q})] \right) + M^2 \sin^2 \theta \left(\Re[J_{21}(-\mathbf{q})] \right) \\
&- \cancel{M^2 J_{12}(\mathbf{0}) \cos^2 \theta} \\
&- M^2 \sin^2 \theta \left(\Im[J_{21}(\mathbf{q})] \right) + M^2 \sin^2 \theta \left(\Re[J_{21}(\mathbf{q})] \right) \\
&- \cancel{M^2 J_{21}(\mathbf{0}) \cos^2 \theta}
\end{aligned} \tag{4}$$

From relation $\Im[J_{12}(\mathbf{q})] = -\Im[J_{12}(-\mathbf{q})]$ and $\Re[J_{12}(\mathbf{q})] = \Re[J_{12}(-\mathbf{q})]$, the Eq. (4) becomes,

$$\begin{aligned}
&- M^2 \sin^2 \theta \left(\Re[J_{21}(\mathbf{q})] - \Im[J_{21}(\mathbf{q})] + \Re[J_{21}(\mathbf{q})] - \Im[J_{21}(\mathbf{q})] \right) \\
&= E(\mathbf{q}, \frac{\pi}{2}) - E(\mathbf{q}, 0) + E_{11}(\mathbf{0}) - E_{11}(\mathbf{q}) + E_{22}(\mathbf{0}) - E_{22}(\mathbf{q}).
\end{aligned} \tag{5}$$

After dividing both sides of the equation by $-2M^2 \sin^2 \theta$ and transferring the real part of the Heisenberg exchange parameter to the right-hand side (RHS), the final form of Eq. 5 yields the imaginary part of the Heisenberg exchange parameter, $\Im[J_{ij}(\mathbf{q})]$, on the left-hand side (LHS) of Eq. 5.

$$\begin{aligned}
\Im[J_{21}(\mathbf{q})] &= \frac{E(\mathbf{q}, \frac{\pi}{2}) - E(\mathbf{q}, 0)}{2M^2 \sin^2 \theta} + \frac{E_{11}(\mathbf{0}) - E_{11}(\mathbf{q})}{2M^2 \sin^2 \theta} \\
&+ \frac{E_{22}(\mathbf{0}) - E_{22}(\mathbf{q})}{2M^2 \sin^2 \theta} + \Re[J_{21}(\mathbf{q})].
\end{aligned} \tag{6}$$

C — Inverse Fourier Transform

In the following, we will demonstrate mathematical steps of inverse Fourier transform. The inverse Fourier transform of Eq. (73),

$$J_{ij}(\mathbf{r}_i, \mathbf{r}_i - \mathbf{R}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} J_{ij}(\mathbf{q}) \exp(i\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})) d^3q. \quad (1)$$

The reciprocal space Heisenberg exchange parameters include real (J_{ij}^R) and complex part (J_{ij}^i) of exchange values: $J_{ij}(\mathbf{q}) = J_{ij}^R(\mathbf{q}) + iJ_{ij}^i(\mathbf{q})$, then Eq. (1) become,

$$\begin{aligned} J_{ij}(\mathbf{r}_i, \mathbf{r}_i - \mathbf{R}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} & [J_{ij}^R(\mathbf{q}) \cos(\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})) + iJ_{ij}^R(\mathbf{q}) \sin(\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})) \\ & + iJ_{ij}^i(\mathbf{q}) \cos(\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})) - J_{ij}^i(\mathbf{q}) \sin(\mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}))] \end{aligned} \quad (2)$$

The integral interval can span between the negatively valued volume element in the Brillouin zone (V_{BZ-}) to 0 and from 0 to the positively valued volume element in the Brillouin zone (V_{BZ+}). The symmetry relations of the reciprocal space exchange parameters state the following conditions:

$$\Re[J_{ij}(\mathbf{q})] = \Re[J_{ij}(-\mathbf{q})], \quad \text{and} \quad \Im[J_{ij}(\mathbf{q})] = -\Im[J_{ij}(-\mathbf{q})].$$

Using these relations, Eq. 2 can be rewritten as:

$$\begin{aligned}
 J_{ij}(\mathbf{r}_i, \mathbf{r}_i - \mathbf{R}) = & \frac{1}{V_{BZ}} [\{ J_{ij}^R(\mathbf{q}) \cos \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}) - \cancel{i J_{ij}^R(\mathbf{q}) \sin \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})} \\
 & - \cancel{i J_{ij}^i(\mathbf{q}) \cos \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})} - J_{ij}^i(\mathbf{q}) \sin \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}) \}_{V_{BZ-}} + \\
 & \{ J_{ij}^R(\mathbf{q}) \cos \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}) + \cancel{i J_{ij}^R(\mathbf{q}) \sin \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})} \\
 & + \cancel{i J_{ij}^i(\mathbf{q}) \cos \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R})} - J_{ij}^i(\mathbf{q}) \sin \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}) \}_{V_{BZ+}}]. \quad (3)
 \end{aligned}$$

From the additivity rule, we can combine the integral of the same function over adjacent intervals,

$$J_{ij}(\mathbf{r}_i, \mathbf{r}_i - \mathbf{R}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} \{ \Re[J_{ij}(\mathbf{q})] \cos \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}) - \Im[J_{ij}(\mathbf{q})] \sin \mathbf{q} \cdot (\mathbf{r}_{ij} - \mathbf{R}) \} d^3 \mathbf{q}. \quad (4)$$

D — RKKY Exchange Interaction

The RKKY interactions describe indirect exchange interaction between d or f shell localized magnetic moments through conduction electrons in metal materials. These moments don't interact with each other directly. Instead, the localized magnetic moment interacts with a second localized magnetic moment at some distance by a long-ranged spin polarization effect. This interaction gives rise to an effective exchange coupling. The interaction is described by the exchange Hamiltonian,

$$H = J(|\mathbf{r}_i - \mathbf{R}_n|) \sum_i \sum_n \sigma_i \cdot \mathbf{S}_n. \quad (1)$$

Here $\mathbf{r}_i$ is electron i position, $\mathbf{R}_n$ is lattice position. The $\mathbf{S}_n$ is localized spin at lattice n . The σ_i is Pauli spin operator of the conduction electron i . Using the second-order perturbation theory, the exchange Hamiltonian between localized spin n , m becomes,

$$H = - \sum_n \sum_m J_{RKKY}(\mathbf{R}_{nm}) \mathbf{S}_n \cdot \mathbf{S}_m, \quad (2)$$

where $\mathbf{J}_{RKKY}$ is determined by conduction electron susceptibility [96, 130],

$$J_{RKKY}(R_{nm}) \propto J^2 \chi(\mathbf{q}) \quad (3)$$

The free-electron gas is the simplest case without geometry restriction to evaluate magnetic susceptibility (derivation details [96, 131]). Then, the RKKY exchange interaction between a magnetic moments distant R is expressed as,

$$J_{RKKY}(R) \sim \cos(2k_F R) / R^3, \quad (4)$$

where k_f is Fermi wave vector. The cosine term $[\cos(2k_F R)]$ states that the interaction oscillates between ferromagnetic and antiferromagnetic exchange coupling. The interaction distance term $(1/R^3)$ describes the 3rd power decay of interaction strength and leads to asymptotic behaviour.

E — Metropolis Monte Carlo of temperature phase transition

The magnetization of the system is caused by the average net magnetic moment of atoms in that system,

$$\mathbf{M} = \frac{1}{N} \sum_i^N \mathbf{m}_i \quad (1)$$

Under finite temperature and absence of the external magnetic field, a large ensemble average of possible magnetic moment configuration depends on the Boltzmann distribution and is weighted by the partition function,

$$Z = \sum_i^N \exp\left(-\frac{E(\mathbf{r}_i, \mathbf{m}_i)}{k_B T}\right). \quad (2)$$

Where $E(\mathbf{r}_i, \mathbf{m}_i)$ is energy for m_i configuration of atom at r_i position and k_B is Boltzmann constant. Then the mean magnetic moment become,

$$\langle M \rangle = \frac{1}{N} \sum_i^N \mathbf{M}_i \exp\left(-\frac{E(\mathbf{r}_i, \mathbf{m}_i)}{k_B T}\right). \quad (3)$$

The evaluation of atomic local magnetic moment configuration at various temperatures in Eq. (3) can be performed with the Metropolis Monte Carlo algorithm, which allows for spins (local magnetic moments) to flip with a probability based on Boltzmann distribution. To understand the underlying mechanics of the algorithm, Markov chains and its master equation will be discussed only briefly; for further information, we refer to the textbook of Landau and Binder [132] It starts with a state of a system denoted by X_t for a given time at t with discrete times in order t_1, t_2, t_3 , and so on. At the each time system X posses a possible state of S_i where i is assign by different configuration

of system's variable at finite time set. The conditional probability of the system of X_n is express,

$$P(X_{t_n} = S_{i_n} | X_{t_{n-1}} = S_{i_{n-1}}, X_{t_{n-2}} = S_{i_{n-2}}, \dots, X_{t_1} = S_{i_1}). \quad (4)$$

This process is crucial for expressing the change of spin-flip in the system because the previous state of spin configuration affects possible current spin configuration information. Such a process is called a Markov process, and the corresponding sequence of X_t is called a Markov chain, which will be the sequence of spin configuration in our MC model.

The translation rate (probability per unit time) of going from the previous state (S_i) to the current state (S_j),

$$W_{ij} = W(S_i \longrightarrow S_j) = P(X_{t_n} = S_j | X_{t_{n-1}} = S_i), \quad (5)$$

where translation rate requires equal and bigger than 0 and

$$\sum_j W_{ij} = 1. \quad (6)$$

The total probability of system X_{t_n} in-state S_j is

$$\begin{aligned} P(X_{t_n} = S_j) &= P(X_{t_n} = S_j | X_{t_{n-1}} = S_i) P(X_{t_{n-1}} = S_i) = \\ &= W_{ij} P(X_{t_{n-1}} = S_i). \end{aligned} \quad (7)$$

How the probability distribution of the state evolves with time is described by the master equation. The evaluation of the state in time is in continuous frame,

$$\frac{dP(S_j, t)}{dt} = \sum_i (W_{ji} P(S_j, t) - W_{ij} P(S_i, t)), \quad (8)$$

where W_{ij} is the lost term, all probability flows out of state i to state j , and W_{ji} is the gain term probability flows into state i from state j .

The Markov process (Eq. (8)) demonstrates that the information about a current state does not need memory from earlier times to determine the future time evolu-

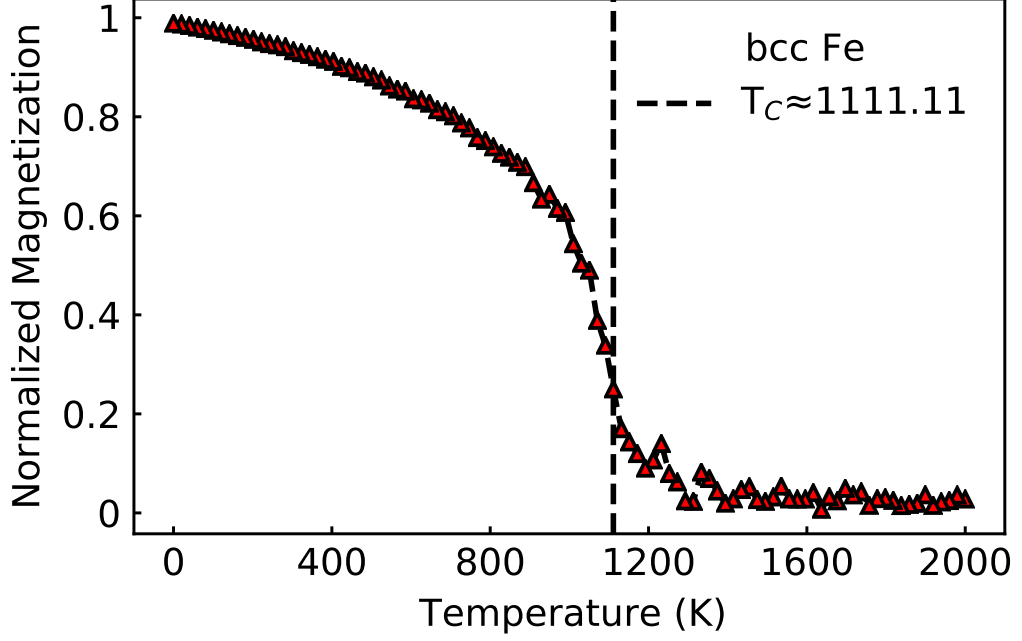


Figure E.1: Metropolis Monte Carlo Algorithm. Temperature versus normalized magnetization of bcc Fe.

tion of the current state. This important dynamics property is implemented into the Metropolis Monte Carlo algorithm with a particular translation rate choice that satisfies the system dynamics. In our case, the choice is Boltzmann's distribution of classical Heisenberg Hamiltonian,

$$w = \begin{cases} \exp(-\frac{\Delta E}{k_B T}) & \text{if } \Delta E > 0 \\ 1 & \text{otherwise.} \end{cases}$$

Where ΔE represents the differences in energy between two states. The master equation [Eq. (8)] reaches balance when the probability of the state reaches equilibrium,

$$\frac{dP_{eq}(S_j, t)}{dt} = 0, \quad (9)$$

which state that the loss and gain terms cancel each other $W_{ij}P_{eq}(S_i) = W_{ji}P_{eq}(S_j)$. The magnetization behavior as a function of temperature was obtained via statistical sampling of spin configurations using the Metropolis Monte Carlo algorithm. A code based on this algorithm was developed and initially tested with bcc Fe's Heisenberg exchange parameters calculated from our spin-spiral protocol for VASP.