Non-collinear spin in electronic structure calculations

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ABSTRACT
Non-collinear spin materials are an exciting class of materials that are of great interest from both a fundamental materials science point of view and also with their possible applications in energy-efficient technological devices. Here we introduce non-collinear magnetism, in particular how to describe the electronic structure of materials with non-collinear magnetically ordered spin structures giving insight as to why it happens. Additionally, the use of electronic structure calculations is ubiquitous in current materials science research, commonly used by both theoretical and experimental researchers; we therefore detail how non-collinear magnetism is incorporated into the most commonly used electronic structure method, density functional theory.

KEYWORDS
Magnetism, electronic structure, spintronics, density functional theory.

1. Introduction

1.1. Magnetism in materials

It has been known since ancient times that some materials exhibit magnetic properties, being influenced by external magnetic fields (such as a compass aligning to the Earth's magnetic field). Nowadays it is known that the source of magnetism in magnetic materials comes from the electrons in the atoms, and in particular unpaired electrons. This is because electrons can be thought of as having an intrinsic magnetic dipole, which when paired, shared or transferred between atoms such as in chemical bonding cancel and we're left without obvious magnetism. However in some atoms within materials such as those containing electrons in unfilled d or f atomic shells net magnetic moments are left over and we observe "magnetism".

Magnetism is a fundamental force of nature and it is responsible for the attractive or repulsive interactions between materials that possess magnetic properties. Describing the source of such interactions, even Richard Feynman could not do it justice [1]. However here we will describe how to calculate magnetic interactions using electronic structure methods and some of the consequences of it that lead to interesting and useful magnetic structures in materials at the atomic level.

The microscopic magnetic moments in materials interact with each other and cause their directions to correlate. In Fig. 1 a selection of some possible alignments of atomic

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magnetic moments[1] are shown where they align into a ferromagnet causing a macroscopic magnetic dipole; neighbours anti-align into an antiferromagnet; disordered such as at elevated temperatures forming a paramagnetic material; and of having complicated but still ordered structure. The latter two of these systems is what we regard as non-collinear magnetism (although ferro- and anti-ferromagnetism could be thought of as a special case) as the local magnetic moments are not parallel or anti-parallel with each other. With non-collinear spins, the extra degrees of freedom with respect to collinear spins gives the possibility of much more complex magnetic structures such as spin helices (Fig. 2) and skyrmions[2] (Fig. 3) which are magnetic topological objects that exhibit vortex-like spin configurations.

We can now see that the term magnetism encompasses a whole range of configurations of electron spins in a material, the most simple being ferromagnetism and antiferromagetism. Although ferromagnets have been a source of intrigue for thousands of years [3], antiferromagnets were discovered more recently by Néel in 1948 [4]. Since then, more exotic magnetic states have been the focus of research for decades, an example being the search for *spin ices* in the pyrochlores, culminating in the discovery of such a state in $Ho_2Ti_2O_7$ in 1998 [5, 6].

Here we present some insight into the properties of magnetic materials which are of both fundamental scientific and technological interest (for example, almost all computer storage being based on magnetism). In particular we will extend this discussion to materials with non-collinear spins, which are now also finding new important technological applications. For example, non-collinear systems can exhibit magnetoresistance which can be used to construct magnetic sensors, including read and write heads in hard disks. They will also be important in future spintronic device technologies where spin is used to process information rather than charge, for example in spin-transistors and spin-valves. A key benefit of non-collinear magnetic materials is that they have regions of stability and can be topologically protected and their structure can be manipulated with very low currents making fast and efficient devices.

Examining non-collinear spins in a little more detail, it can occur in systems with antiferromagnetic exchange interactions between magnetic ions where the crystal structure plays a role in how the magnetic moments can be arranged. For example, in a cubic crystal displaying antiferromagnetic exchange, it is possible for each ion to have the opposite spin of its neighbours. An issue occurs when the arrangement of ions forms an *incompatible* geometry with respect to spin, such as a triangular lattice in two dimensions. In that case it is impossible to satisfy all of the lowest-energy interactions since at least two of the ions will have the same spin as one neighbour. In three dimensions this effect is seen in tetrahedral lattices where two of the spin sites are unable to satisfy their interactions. This is known as geometric frustration in magnetism (Fig. 4) and can lead to a variety of exotic magnetic structures. Frustration is known to stabilise magnetic skyrmions as well as spin-ice states in pyrochlore materials. For example, in materials such as $YMnO_3$ the magnetic frustration may be overcome in a number of competing ways such as the possible magnetic alignments shown in Figure 5.

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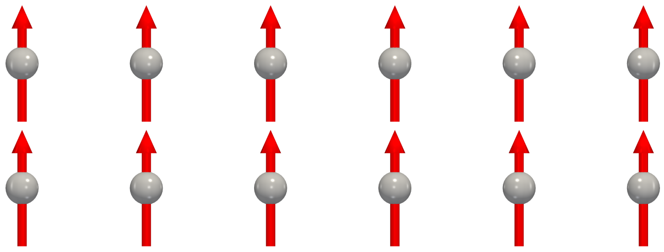
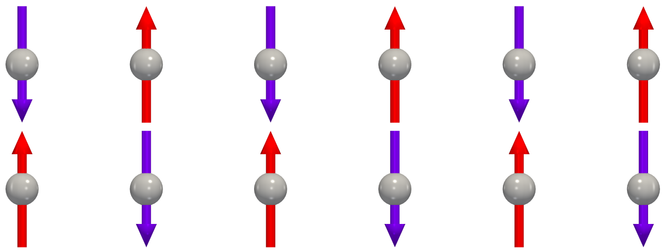
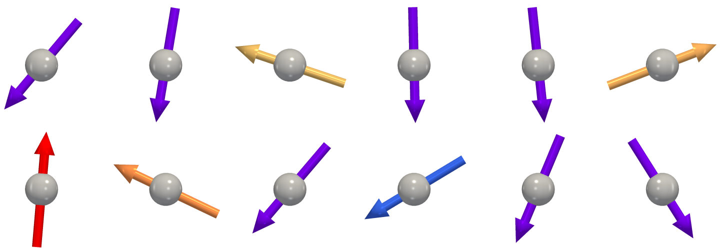
[1] Here we will consider atomic magnetic dipoles, although more granular analogues exist where, for example, crystallites of a ferromagnetic material may bound together forming domains which interact magnetically.



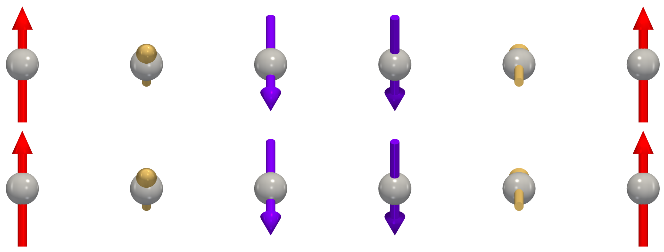
(a) FM



(b) AFM



(c) NCM



(d) Spin Wave

Figure 1. Schematic diagrams of some forms of magnetism are shown in terms of atomic molecular moments, (a) ferromagnetism, (b) anti-ferromagnetism, (c) unaligned non-collinear magnetism and (d) a magnetic spiral (spin wave).

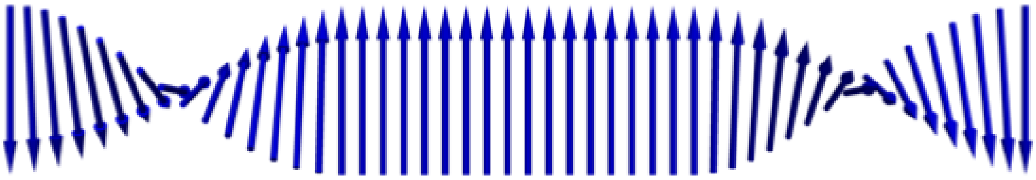


Figure 2. Schematic of a spin helix.

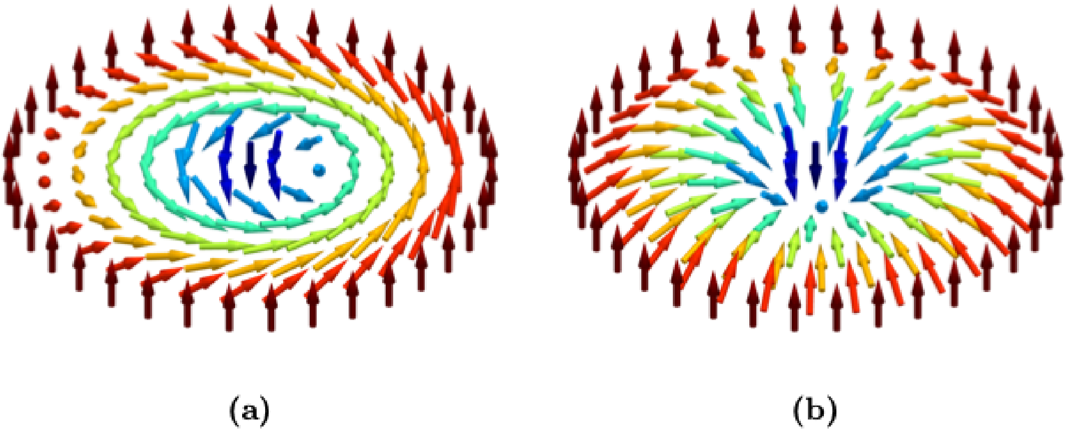


Figure 3. Illustrations of isolated magnetic skyrmions. Skyrmions are named by the type of domain wall created by a cut through the centre, the two types are (a) Bloch skyrmion and (b) a Néel skyrmion

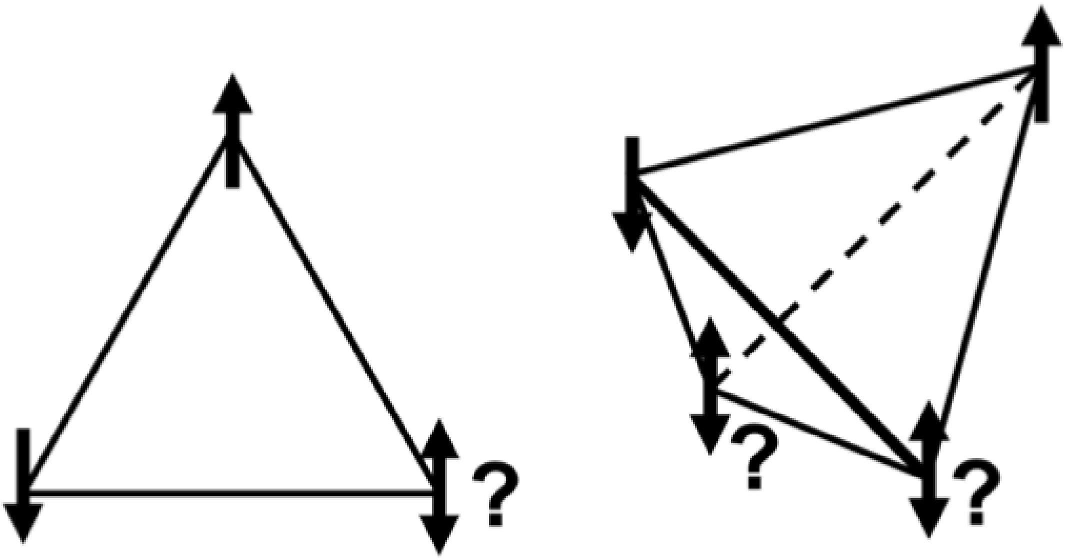


Figure 4. Geometrical frustration caused by antiferromagnetic exchange interactions in (a) a triangular lattice and (b) a tetrahedral lattice.

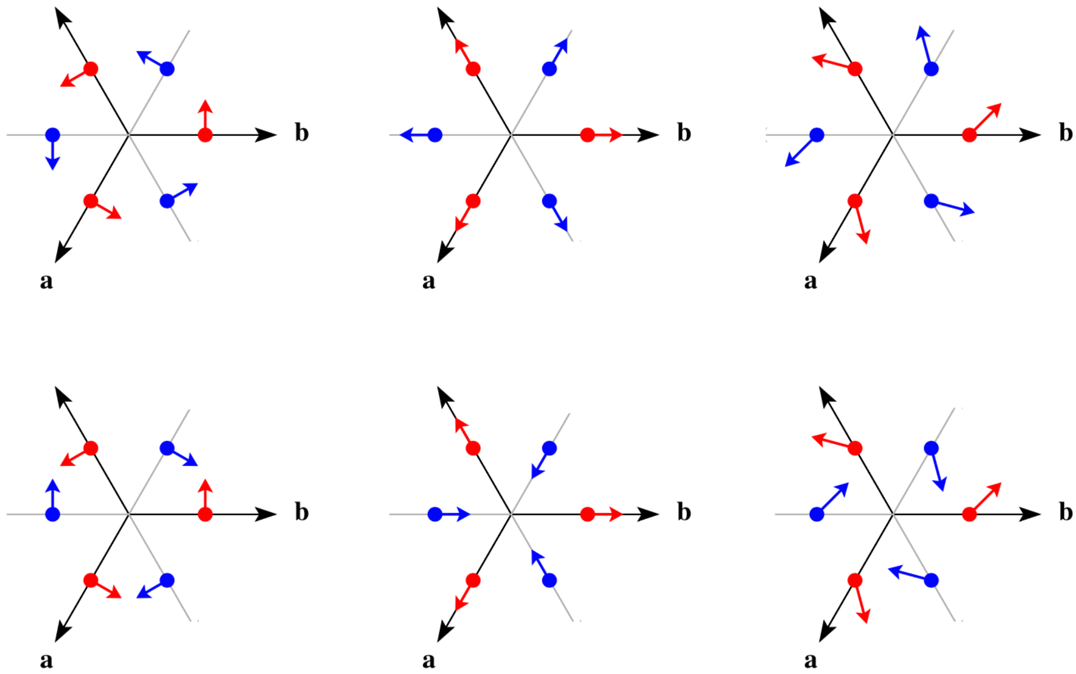


Figure 5. Some possible spin configurations on a triangular (hexagonal) lattice demonstrated in $YMnO_3$ are shown. The red and blue colour on the arrows show each of the two triangular lattices (one above the other) in the unit cell.

1.2. Quantum description of magnetism

The physical origin of magnetism is a purely quantum phenomenon. Niels Bohr and Hendrika van Leeuwen independently showed in their respective theses that, using classical physics, there can be no net magnetisation in a solid [7, 8, 9]. But afterwards quantum mechanics revolutionised the study of materials, allowing us to describe macroscopic magnetic phenomena in terms of interactions between the electrons and atomic nuclei. We threw away the old ideas of Newton, of point particles with well defined positions and momenta, and embrace the wavefunction and wave-mechanics [10].

But even at this point, considering the Schrodinger equation, intrinsic magnetism does not appear, it needs to be added as an extra variable. Electron spin is imposed in the Schrodinger equation where it is understood to be a separate quantum number with electrons having either up or down spin[2]. To include spin in the mathematical formalism of quantum mechanics the standard Schrödinger equation needs an extended description of particles with spin (such as electrons). It requires the use of matrices and spinors rather than ordinary wave functions to account for the effects of spin on the behavior of particles in the presence of magnetic fields and spin interactions. We will detail this below, but initially, if we let spin be denoted by σ (up or down) then we can add onto a Hamiltonian an extra term that includes spin and hence magnetism,

$$H_m = \sum_{\langle i,j\rangle} J_{i,j} \underline{\sigma}_i \cdot \underline{\sigma}_j, \tag{1}$$

where i and j label spins (lattice sites), and the sum is over all pairs of spins in the

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[2] spin $\hbar/2$ or spin $-\hbar/2$.

system. As the spin-spin interaction in equation (1) is short ranged (falling off as the cube of distance) it is common to include only nearest neighbours, indicated by the angled brackets. J is the magnetic coupling constant and can be negative or positive depending on whether aligned (ferromagnetic) or anti-aligned (antiferromagnetic) spins are more favourable. A dot product is maximised/minimised when vectors are aligned and hence it appears that collinear spins will stabilise the magnetic energy of a system with the energy being lower than magnetic systems with non-parallel spins.

Now we come to the crux of the matter for non-collinear spin systems. It is not until additional spin interactions are considered that we are able to find non-collinear magnetic systems which may be an energy minimum. The spin-orbit interaction is a relativistic interaction which couples the orbital and spin parts of the angular momentum, L and S. This gives rise to an extra term in a Hamiltonian proportional to the scalar product $L \cdot S$. In solids this splits the degeneracy in bands[3] and gives an off z-axis contribution to spin alignments. This is often realised in localised d and f electrons in heavier elements. This term, spin-orbit coupling, when added to a magnetic Hamiltonian is able to change the energy minima from spins that are collinear to cases where non-collinear spins form stable structures. We will return to this in more detail in section 2.6.

2. Electronic structure calculations

2.1. Background

Turning our attention to evaluating energies and hence the magnetic structure of solids, we now mention some electronic structure methods since these inform the type of Hamiltonian used. Reviews of these methods exist elsewhere and so here we only summarise enough to formulate non-collinear magnetism. The most widely used electronic structure method, density functional theory, has been around since the mid-1960s and then remaining fairly dormant until the first practical implementation of an exchange and correlation (XC) functional (the local density approximation) in 1981. Collinear magnetism was incorporated into that functional and realised several applications. It quickly followed from there attempts to incorporate non-collinear magnetism into the formalism.

Disordered magnetism was investigated[11] using electronic structure methods, for example, in an attempt to explain the magnetic structure of Mn and also spin spirals in iron[12] using a frozen spin approximation. However Kubler[13] made significant progress in formulating non-collinear spin within DFT and in particular the theoretical details of a self-consistent formalism. This included details of a practical implementation leading to insight into the ferromagnetism of $\gamma-$FeMn, the antiferromagnetic structure of Pt/RhMn$_3$. As noted above, spin-orbit coupling has a significant affect on the magnetic structure of materials and this is a relativistic property. The development of fully relativistic methods to account for such important interactions is necessary. There are various approximations to spin-orbit coupling but a fully relativistic approach is the gold standard. The robustness of the method was shown for the complex spin structure of USb and Yamagami[14] presented a fully relativistic formulation, with all electrons treated non-collinearly within the spin-polarised coupled Dirac equations and a mapping onto the density functional formalism.

The eloquent proof of Kohn and Sham[15] for DFT of non-magnetic systems in

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[3] Other effects also split degeneracies, but they are not core to this discussion.

principle applies to magnetic systems, although proof of the extension does not follow simply. Also, within the formalism, it took some time to finalise uniqueness theorems between density and spin potentials. For example, Gidopoulos[16] showed that the invertibility of the mapping between spin potentials and ground state spin densities was ensured for noncollinear magnetism. Additionally, physical magnetic structures form local minima in the electronic energy surface. Each local energy minimum corresponds to a particular spin configuration of the material and this often causes a "multi-minimum problem" in practical implementations. A calculation will fall into a particular local minimum (spin configuration) but it will be unknown if that is a global energy minimum.

After development of the spin-polarised DFT formalism, the main hindrance for practical use it for non-collinear magnetism is the accuracy of XC functionals. For example, the optimised effective potential (OEP)[17] has been shown to give good magnitudes of atomic magnetic moments and is a candidate method to extend the formalism DFT's XC to improve the description of non-collinear magnetism. Sharma[18] extended the spin-density formalism of non-collinear spin via the OEP. The importance of this is that it does not rely on the local collinearity of spins as required when applying standard XC functionals. They were able to demonstrate the reliability of their method for a monolayer of Cr obtaining a fully non-collinear magnetisation density. Eich[19] did similar for a Cr monolayer but within a local density-like approximation but with a spin-spiral-wave state of the uniform electron gas as reference system. Attempting to incorporate known exact conditions into an XC functional is also very advantageous. In moving from collinear spin systems to non-collinear, a simple reuse of standard XC functionals proves unsatisfactory because there are new degrees of freedom which are unconstrained but known exact conditions are available. Scalmani[20] and Bulik[21] introduced methods that would allow a non-vanishing local magnetic torque while being invariant with respect to spin rotations, demonstrating the ability to reproduce accurately the non-collinear spin states of the Cr clusters and monolayer.

Hybrid functionals, where there is mixing of (sometimes screened) non-local Hartree-Fock and semi-local XC functionals, have been used frequently to obtain good band structures and in particular accurate band gaps of materials. Therefore this method has also been extended to non-collinear magnetic systems. Bast[22] detailed this method, via time-dependent DFT, in particular for magnetic properties of excited states.

As XC functional development for non-collinear spin has yet to provide a general expression widely accepted to be accurate, other attempts such as constraining the spin to various configurations in a self-consistent manner have been investigated. For example, Ma[23] developed a constrained energy minimisation technique via a choice of Lagrange multipliers to explore non-collinear magnetic structures in materials, particularly in amorphous Fe where it allows magnetic moments to point in arbitrary directions.

2.2. Why DFT?

From a practical point of view, solving quantum mechanical equations to describe realistic systems is non-trivial. Finding ways to solve quantum systems is of such importance that the 1998 Nobel prize in Chemistry was shared by Walter Kohn for his involvement in the development of DFT. DFT has become a front-runner amongst methods for calculating properties of materials from quantum mechanics and has become the most used electronic structure method of solids, and so here we will demonstrate the use of DFT to probe materials which display the counter-intuitive property of magnetism.

The Thomas-Fermi model, developed not long after Schrödinger introduced his famous equation, framed the quantum problem in terms of the electron density [24, 25, 10]. This paved the way for Hohenberg and Kohn to lay out the mathematical foundation of DFT in 1964 [26] and for Kohn and Sham to devise an efficient scheme for calculations of electronic properties in 1965 [15]. We will take this DFT background as assumed knowledge and describe the extension to magnetic systems and in particular the use of DFT in non-collinear magnetism.

Here we want to describe how non-collinear spin can be incorporated into first principles electronic structure calculations. While DFT is often less accurate than other methods its speed allows one to compute with ease and reasonable[4] accuracy systems with many hundreds of electrons. DFT seeks to find approximations to the electronic density. This is done by seeking the electron density, bypassing the all-electron wavefunction via an equivalent potential, shown schematically in Fig. 6. Once the density is found, observables can be obtained in much the same way as from the wavefunction with the added benefit that the density is much simpler than the wavefunction.

With the addition of spin-density functional theory [27, 13], we are now in a position to calculate the electronic properties of materials that exhibit magnetic ordering. Spin-density functional theory is a common tool for studying systems displaying collinear magnetism, that is ferromagnetism or antiferromagnetism where the electron spins are parallel or antiparallel [28, 29, 30]. More recently, with the improvements in computing power and new computational methods, it is becoming increasingly possible to apply spin-density functional theory to systems displaying non-collinear magnetism. While calculations of materials hosting non-collinear magnetism are not yet common, it is certainly possible to use spin-density functional theory to examine their properties and magnetic states. In particular, with the inclusion of constrained minimisation techniques in some of the major DFT codes [23, 31] more advanced non-collinear magnetism structures can be realised with spin-density functional theory. In general these methods add a Lagrange multiplier (constraint) into a Hamiltonian which acts as an energy penalty, biasing the electronic minimisation to find a state with a particular spin configuration. An example study using such constraints can be found in Ref. [32] whereby constraints are used to realise a series of non-collinear magnetism states around a curved crystal. From these states the authors are able to use the total energy to extract anisotropy constants as a function of curvature. Spin-density functional theory has also proven useful at comparing the relative stability of non-collinear magnetism states and from that, for example, calculating Dzyaloshinskii-Moriya interaction (DMI) constants [33].

2.3. Spin-density functional theory

DFT is only concerned with the locations of the electrons through the electron density. It can predict the magnetic moments, magnetic ordering, and magnetic susceptibilities of molecules and solids, and is essential for understanding the electronic structure and magnetic properties of transition metal complexes which often have unpaired electrons with significant spin interactions. It has been crucial in the design and development

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[4] Although "reasonable" is subjective, the large number of DFT publications by both experts and non-experts in the field indicates it is often very reasonable.

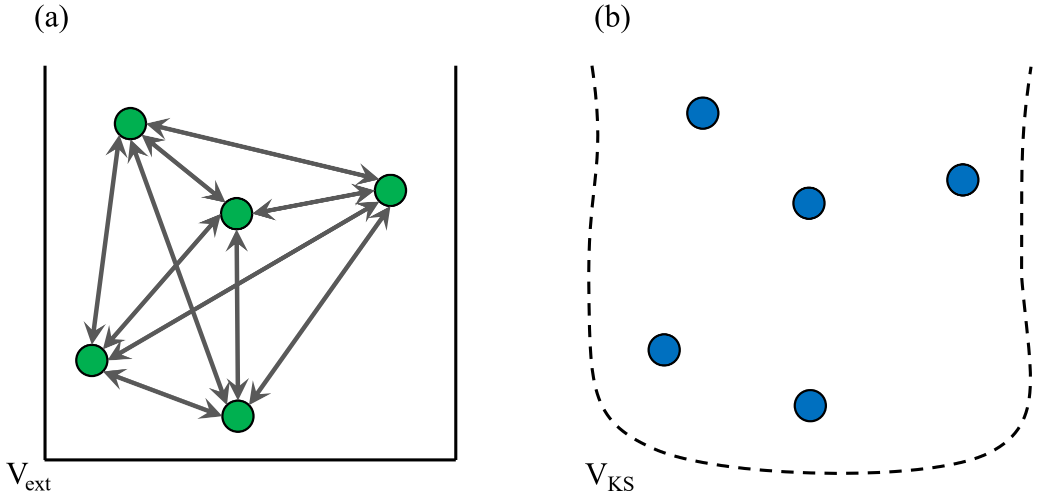


Figure 6. Schematic of the KS formalism, (a) shows a system of electrons (green) and their interaction sitting in an external potential, V_{ext}. (b) Shows the KS system with non-interacting]it quasi-electrons (blue) sitting in a KS effective potential. The effective potential includes all of the effects of the external potential and the electron-electron interactions. In principle the KS system is exact, however in practice approximations are made in constructing the KS potential.

of spintronic devices, which utilize the spin of electrons in addition to their charge for information processing and storage.

We have to make explicit reference to the fact that electrons carry angular momentum, both orbital and spin. Spin-DFT [27, 13] is a logical extension to DFT which introduces electron interactions with static magnetic fields. The magnetic fields are included in the Hamiltonian as a Zeeman-like term, and therefore is applicable to fields which interact with electron spins only rather than orbital momentum. Spin-DFT was developed with the intention of calculating the effects of external magnetic fields on the electronic structure, although many spin-DFT calculations are performed on materials in zero-field. While, in principle, DFT is able to handle open-shell systems (systems with unpaired electrons), spin-DFT is often the default choice when dealing with such systems. Spin-DFT is able to handle such things as spontaneous magnetisation arising in ferromagnetic materials as it allows for the number of spin-up and spin-down electrons to differ by more than one.

We now introduce the formalism so that we can then proceed to our main interest here, general systems with non-collinear magnetism, where no such constraint is applied.

2.4. Collinear spin-density functional theory

As a mechanism for defining some terms we will give a brief summary of the more familiar collinear DFT formalism which will form a base for expanding into non-collinear electronic structure. In addition to the usual electron charge density, spin-DFT is also concerned with the spin-density. In a collinear magnetism treatment the spins are treated as either spin-up or spin-down, typically aligned in the z-direction, although this choice is arbitrary. We can define a density associated with each of the spin-up and spin-down electrons, $n^{\uparrow}(\boldsymbol{r})$, $n^{\downarrow}(\boldsymbol{r})$, and the relation to the total density,

$$n(\boldsymbol{r}) = n^{\uparrow}(\boldsymbol{r}) + n^{\downarrow}(\boldsymbol{r}). \tag{2}$$

The total number of electrons in the system is fixed, although the number of spin-up and spin-down electrons is free to vary. We can also define the overall spin density,

$$s(\boldsymbol{r}) = n^{\uparrow}(\boldsymbol{r}) - n^{\downarrow}(\boldsymbol{r}). \tag{3}$$

By convention the magnetisation density is given by,

$$m_z(\boldsymbol{r}) = -\mu_{\mathrm{B}} s(\boldsymbol{r}), \tag{4}$$

where μ_{B} is the Bohr magneton [34]. In atomic units, $\mu_{\mathrm{B}} = 1/2$, however for clarity we will use the symbol rather than the numerical value.

The DFT (Kohn-Sham) approach introduces a set of auxiliary non-interacting electrons with fictitious one-electron wavefunctions, called Kohn-Sham orbitals. These fictitious electrons do not interact with each other, but they experience an effective potential, known as the Kohn-Sham potential (as illustrated above in Fig. 6). In DFT there is a one-to-one relation between density and potential, hence in spin-DFT the potential in DFT acquires a spin dependence, and so the orbitals also do. The KS orbitals become

$$\phi_i(\boldsymbol{r}) \rightarrow \phi_i^{\sigma}(\boldsymbol{r}),\ \sigma = \uparrow, \downarrow \tag{5}$$

and the KS functional becomes

$$\begin{aligned} E_{\mathrm{KS}}[n(\boldsymbol{r})] &\rightarrow E_{\mathrm{KS}}[n^{\uparrow}, n^{\downarrow}] \\ &= -\frac{1}{2}\sum_i \sum_{\sigma=\uparrow,\downarrow} f_i^{\sigma} \int \mathrm{d}\boldsymbol{r}\ \phi_i^{\sigma *}(\boldsymbol{r}) \boldsymbol{\nabla}^2 \phi_i^{\sigma}(\boldsymbol{r}) \\ &\quad + \frac{1}{2}\int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\ \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \int \mathrm{d}\boldsymbol{r}\ n(\boldsymbol{r}) V_{\mathrm{ext}}(\boldsymbol{r}) + E_{\mathrm{xc}}[n^{\uparrow}, n^{\downarrow}], \end{aligned} \tag{6}$$

where the XC functional (last term) depends explicitly on the spin-up and spin-down densities, and the kinetic energy (first term) now includes a sum over spin for the spin dependent KS orbitals. The other terms are the electron-electron Coulomb interaction called the Hartree term, V_H, and the next term is the interaction of electrons with their external environment, such as nuclei, often called the external potential, V_{ext}. The occupation number, f, of each orbital also picks up a dependence on spin. The electron-nuclear potential has been replaced by two more general external potentials,

$$\begin{aligned} V_{\mathrm{ext}}^{\uparrow}(\boldsymbol{r}) &= V_{\mathrm{en}}(\boldsymbol{r}) + \mu_{\mathrm{B}} B_z(\boldsymbol{r}) \\ V_{\mathrm{ext}}^{\downarrow}(\boldsymbol{r}) &= V_{\mathrm{en}}(\boldsymbol{r}) - \mu_{\mathrm{B}} B_z(\boldsymbol{r}), \end{aligned} \tag{7}$$

where $B_z(\boldsymbol{r})$ is an external magnetic field in the z-direction. The magnetic field acts differently on the spin-up and the spin-down electrons leading to a different expression for each.

We arrive now at a new set of KS equations taking into account spin,

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\mathrm{H}} + V_{\mathrm{ext}} + \frac{\delta E_{\mathrm{xc}}[n^\uparrow, n^\downarrow]}{\delta n^\sigma(\boldsymbol{r})} \right\} \phi_i^\sigma(\boldsymbol{r}) = \epsilon_i^\sigma \phi_i^\sigma(\boldsymbol{r}). \tag{8}$$

These equations are known as the *spin-unrestricted* KS equations [34]. While the Hartree and external potentials depend only on the total electronic density, the XC potential depends explicitly on the spin-densities. Any XC functionals should be constructed to account for both densities. Equations 8 must be solved self-consistently in the same way as the non-spin or *spin-restricted* KS equations. There is an added complication in the solving of the unrestricted equations in that the total number of each spin-up and spin-down electrons is not fixed. This means that when calculating occupancies one must also vary the number of electrons in each spin channel to find the minimum in energy. One common consequence of this is that a calculation will often not find the global minimum in energy if multiple possible magnetic states can exist in the material. An example of such an effect can be found in Fe which may be either non-magnetic, ferromagnetic or antiferromagnetic [35, 36]. Which state is realised will depend on the initialization of the trial orbitals. As highlighted above, we have a multi-minimum problem; each energy minimum corresponding to a particular arrangement of spins or magnetic state, but without an exhaustive search there is no guarantee that the global minimum energy (most stable spin configuration) will have been found.

2.5. Non-collinear spin-density functional theory

We have now enough detail in place to extend the above formalism to that of non-collinear spin. In the case of non-collinear spin-DFT there is no longer a restriction on the spin being aligned with a particular axis. At every point in space the electron spin may point in any local spin direction. Therefore the treatment of non-collinear magnetism is more complicated than collinear magnetism as the KS orbitals now becomes two-component spinors,

$$\phi_i(\boldsymbol{r}) = \begin{pmatrix} \varphi_i^\uparrow(\boldsymbol{r}) \\ \varphi_i^\downarrow(\boldsymbol{r}) \end{pmatrix}. \tag{9}$$

We can define a density matrix that is generated from the spinor-wavefunction,

$$\hat{n}(\boldsymbol{r}) = \sum_i f_i \left(\varphi_i^{\uparrow *}(\boldsymbol{r}), \varphi_i^{\downarrow *}(\boldsymbol{r}) \right) \begin{pmatrix} \varphi_i^\uparrow(\boldsymbol{r}) \\ \varphi_i^\downarrow(\boldsymbol{r}) \end{pmatrix} = \begin{pmatrix} n_{\uparrow\uparrow}(\boldsymbol{r}) & n_{\uparrow\downarrow}(\boldsymbol{r}) \\ n_{\downarrow\uparrow}(\boldsymbol{r}) & n_{\downarrow\downarrow}(\boldsymbol{r}) \end{pmatrix}. \tag{10}$$

It is more useful to describe the non-collinear density in terms of the charge density and the spin/magnetisation [16],

$$\begin{aligned} \hat{n}(\boldsymbol{r}) &= \frac{1}{2}\big(n(\boldsymbol{r})\mathrm{I}_{2\times 2} + \boldsymbol{\sigma} \cdot \boldsymbol{s}(\boldsymbol{r})\big) \\ &= \frac{1}{2}\left(n(\boldsymbol{r})\mathrm{I}_{2\times 2} - \frac{1}{\mu_{\mathrm{B}}}\boldsymbol{\sigma} \cdot \boldsymbol{m}(\boldsymbol{r})\right), \end{aligned} \tag{11}$$

where $\boldsymbol{s}(\boldsymbol{r})$ is the vector spin density, $\boldsymbol{m}(\boldsymbol{r})$ is the vector magnetisation density, $\mathrm{I}_{2\times2}$ is the identity matrix and $\boldsymbol{\sigma}$ is the vector formed of Pauli spin matrices given by components [9],

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \ \sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{12}$$

As the eigenvalues of the density matrix represent observable properties it is necessarily Hermitian, therefore $n_{\uparrow\downarrow} = n^*_{\downarrow\uparrow}$.

There are also a number of ways of expressing a non-collinear potential. In matrix form, analogous to the density, we have a spin-potential given by,

$$\hat{\mathcal{V}}(\boldsymbol{r}) = \begin{pmatrix} V_{\uparrow\uparrow}(\boldsymbol{r}) & V_{\uparrow\downarrow}(\boldsymbol{r}) \\ V_{\downarrow\uparrow}(\boldsymbol{r}) & V_{\downarrow\downarrow}(\boldsymbol{r}) \end{pmatrix}. \tag{13}$$

This matrix is also Hermitian. Using this matrix form for the spin-potential we can express the Hartree and external terms as

$$\hat{\mathcal{V}}_{\mathrm{H}}(\boldsymbol{r}) = \frac{1}{2} \begin{pmatrix} V_{\mathrm{H}}(\boldsymbol{r}) & 0 \\ 0 & V_{\mathrm{H}}(\boldsymbol{r}) \end{pmatrix} \tag{14}$$

and

$$\hat{\mathcal{V}}_{\mathrm{en}}(\boldsymbol{r}) = \frac{1}{2} \begin{pmatrix} V_{\mathrm{ext}}(\boldsymbol{r}) & 0 \\ 0 & V_{\mathrm{ext}}(\boldsymbol{r}) \end{pmatrix}. \tag{15}$$

Note that the spin-potentials in Eq. (14) and Eq. (15) are diagonal in spin space as there is no spin dependence on either potential.

We can also present the spin-potentials in terms of the contributions from a scalar potential $V(\boldsymbol{r})$ and a vector magnetic field $\boldsymbol{B}(\boldsymbol{r})$ [16],

$$\hat{\mathcal{V}}(\boldsymbol{r}) = V(\boldsymbol{r})\mathrm{I}_{2\times2} + \mu_{\mathrm{B}}\boldsymbol{\sigma} \cdot \boldsymbol{B}(\boldsymbol{r}). \tag{16}$$

If we constrain the $\boldsymbol{B}$-field to be along the z-axis, and take the trace of $\hat{\mathcal{V}}(\boldsymbol{r})$ then we recover the expression for a collinear potential in Eq. (7).

When we consider XC in non-collinear spin-DFT it becomes more complicated. Despite a wide range of XC-functionals that are available for non-magnetic and collinear-spin cases, at present there are no widely used XC-functionals specifically designed for non-collinear magnetism [37]. It is therefore common practice to make use of spin-dependent XC-functionals designed for the collinear case. As these are functionals of the collinear spin-up and spin-down densities we can perform a local rotation of the non-collinear density (Eq. 10) in spin space such that the density is locally collinear (diagonal) at each point $\boldsymbol{r}$ [13, 16],

$$\hat{n}(\boldsymbol{r}) \Rightarrow \begin{pmatrix} \tilde{n}_{\uparrow\uparrow}(\boldsymbol{r}) & 0 \\ 0 & \tilde{n}_{\downarrow\downarrow}(\boldsymbol{r}) \end{pmatrix}. \tag{17}$$

After this local rotation we are then able to calculate the xc-energy from the standard collinear functionals,

$$E_{\mathrm{xc}}(\boldsymbol{r}) = E_{\mathrm{xc}}[\tilde{n}_{\uparrow\uparrow}(\boldsymbol{r}), \tilde{n}_{\downarrow\downarrow}(\boldsymbol{r})]. \tag{18}$$

From the collinear XC-energy we can calculate the matrix elements of the locally collinear spin-potential as in Eq. (8),

$$\tilde{\mathcal{V}}_{\mathrm{xc}}(\boldsymbol{r}) = \begin{pmatrix} V_{\mathrm{xc}}^{\uparrow\uparrow}(\boldsymbol{r}) & 0 \\ 0 & V_{\mathrm{xc}}^{\downarrow\downarrow}(\boldsymbol{r}), \end{pmatrix} \tag{19}$$

where the matrix elements are given by,

$$\tilde{V}_{\mathrm{xc}}^{\tau}(\boldsymbol{r}) = \frac{\delta E_{\mathrm{xc}}[\tilde{n}_{\uparrow\uparrow}, \tilde{n}_{\downarrow\downarrow}]}{\delta \tilde{n}_{\tau}(\boldsymbol{r})},\ \tau = \uparrow\uparrow, \downarrow\downarrow . \tag{20}$$

Both $\tilde{n}$ and $\tilde{\mathcal{V}}_{\mathrm{xc}}$ are then transformed back into the locally unrotated frame by performing the inverse transform of Eq. (17).

A consequence of the potentials being 2 × 2 matrices is that the total energy for a non-collinear state is calculated in a different manner than the non-spin-polarised case (Eq. 6),

$$\begin{aligned} E_{\mathrm{KS}} = \sum_i f_i \epsilon_i + E_{\mathrm{H}}[n(\boldsymbol{r})] + E_{\mathrm{xc}}[\tilde{n}] \\ - \int \mathrm{d}\boldsymbol{r}\ [\mathrm{Tr}\{\mathcal{V}_{\mathrm{H}}(\boldsymbol{r})\}n(\boldsymbol{r}) + \mathrm{Tr}\{\mathcal{V}_{\mathrm{xc}}(\boldsymbol{r})\}n(\boldsymbol{r})]. \end{aligned} \tag{21}$$

Strictly it is not necessary to perform the rotation of $\mathcal{V}_{\mathrm{xc}}$ if one is only using it to calculate the total energy since the trace is invariant with respect to the choice of basis [38].

Note that, in the spirit of traditional DFT, for a spin-potential which is in general non-collinear, there is a direct one-to-one mapping of the spin-potential and the spin-density.

2.6. Spin-orbit interaction

To discuss more complex magnetic phenomena, we now cover some preliminaries about angular momentum. Electrons interacting with an atomic nucleus have orbital angular momentum as well as spin angular momentum which is an intrinsic property. The spin-orbit interaction, often denoted as SOC (spin-orbit coupling), is a fundamental quantum mechanical interaction that arises from the coupling between the intrinsic spin angular momentum (S) of electrons and their orbital angular momentum (L) as they move in an electric field created by atomic nuclei. The spin-orbit interaction arises from the relativistic effects experienced by electrons moving in the electric field of the atomic nucleus. Specifically, it results from the interaction between the magnetic moment associated with the electron's orbital motion (magnetic dipole moment) *seeing* a relativistic magnetic moment associated with the electron's intrinsic spin (spin magnetic moment). Therefore the energy of an electron depends not only on its orbital angular momentum but also on the orientation of its spin angular momentum relative to the orbital motion. It is this spin-orbit interaction that can influence the magnetic properties of materials, leading to phenomena like magnetic anisotropy.

Specifically, let an electron be in a localised state with orbital angular momentum $\boldsymbol{L}$ (with eigenvalues $L_z = 0, 1, 2, ...$ commonly referred to as s, p, d, ... orbitals). The electron has intrinsic spin $\boldsymbol{S}$ hence it has total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, and its square is $\boldsymbol{J}^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\boldsymbol{L} \cdot \boldsymbol{S}$. Rearrange to obtain the contribution $\boldsymbol{L} \cdot \boldsymbol{S} = 1/2(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)$.

At relativistic speeds, spin and orbital angular momentum are not necessarily individually conserved and can transfer from one to the other. Total angular momentum, $\boldsymbol{J}$, is always conserved. We can define a correction to the KS Hamiltonian which encompasses this effect known as the Thomas interaction, $\hat{\mathcal{H}}_{\mathrm{SO}} = \lambda \hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}}$, where λ is a material parameter [9, 39]. We can see that this effect is a function of the total vector spin, and therefore we must consider this in a non-collinear treatment as we require all components.

Additionally, in a crystal system, SOC can become important as it links the electron spin to the underlying lattice. Where there is a preferential spin direction with respect to the lattice, known as magnetocrystaline anisotropy, SOC provides that link. Of particular importance to long-range magnetic ordering in a material is the so-called DMI, or anti-symmetric exchange interaction [40, 41].

In magnetic materials, the DMI arises when there is a lack of inversion symmetry in the crystal structure. Because of broken inversion symmetry, the spatial variation of the spin-orbit coupling is not symmetric with respect to inversion, therefore the spin-orbit coupling leads to an antisymmetric exchange interaction between neighboring magnetic moments. Unlike the symmetric exchange interaction (Heisenberg exchange), which tends to align neighboring spins in parallel or antiparallel directions, the DMI introduces an antisymmetric term in the energy which depends on the vector cross product of neighboring spins. In systems where the DMI is significant, energy is found to be minimized when neighboring spins form non-collinear arrangements, such as spirals, helices, or chiral spin textures. This is in contrast to the Heisenberg exchange, which favors collinear spin alignments.

The form of DMI can be derived by applying second order perturbation theory to the SOC interaction [39, 42]. This interaction causes canting of spins and as a result, SOC is essential for the investigation of such magnetic states.

Here it is worth mentioning a technical point in practical applications of the SOC. A common form of electronic structure calculation of solids uses a plane-wave basis set and this necessitates the need of pseudopotentials, and SOC must be taken into account in the atomic core. The orbital contribution of the electron angular momentum comes from their interaction with atomic orbitals. Rather than directly including SOC in the Hamiltonian, it is more convenient to alter the pseudopotentials to include the effects. Instead of solving the Schrödinger equation for each atom, the Dirac equation (or some semi-relativistic approximtion) is used to account for relativistic effects of the electrons [43, 44]. For each atomic orbital, instead of simply evaluating the potential for the l quantum numbers, the j quantum numbers are required which include spin.

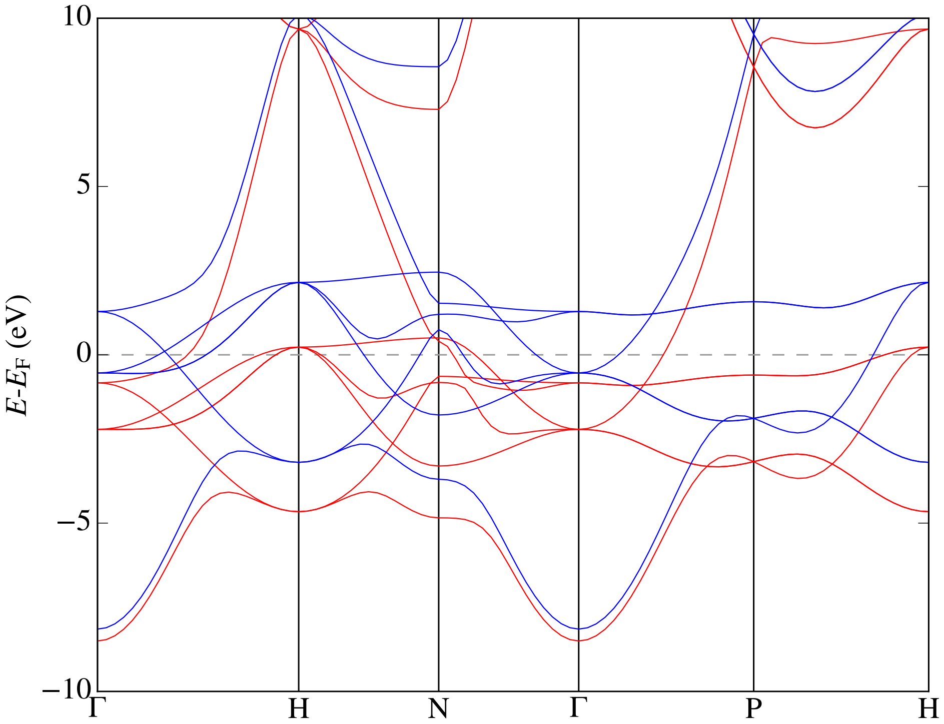


Figure 7. Spin polarised band structure of bcc Fe calculated under the LSDA. Spin-up and spin-down bands are shown in red and blue respectively. The splitting of the spin-up and spin-down bands shows there is a ferromagnetic moment. The Fermi level is shown by the dotted line.

3. Examples

3.1. Results background

Before describing the non-collinear case it will be useful to have a short reminder on spin-polarised band structures to then build upon. It is possible to calculate the band structure of a material using spin-DFT [45, 46]. For a collinear magnetic material, a band structure is a useful tool for identifying magnetic states. In a collinear treatment, we treat the spin-up and spin-down electrons separately through the coupled KS equations (Eq. 8), therefore we have a two sets of eigen-energies, $\epsilon_i^{\uparrow,\downarrow}$, associated with each spin. This allows us to effectively plot two band structures, one for each of the spins. Figure 7 shows a band structure of bcc Fe calculated using the LSDA. Just from the band structure we can see that bcc Fe has an overall magnetic moment as the spin-up and spin-down bands are non-degenerate. If, for example, a material had no overall magnetic moment, such as non-magnetic or antiferromagnetic, pairs of bands would be degenerate. Therefore it is possible to get a quick understanding of the magnetism of a material from its spin-polarised band structure.

Now turning to the more general case where the spin is treated as non-collinear, electrons are not categorised as purely spin-up and spin-down and we only have one eigen-energy related to each spinor wavefunction. In general there is not a unique magnetic quantisation axis and only one set of bands is presented from a non-collinear spin calculation.

If a calculation is done using spin-DFT, it is likely because the desired outcome includes some sort of magnetic state. There are many possible magnetic states in magnetic materials each corresponding to a local minimum on an energy surface spanned by the electrons. As such we are presented by a multi-minimum problem and the possibility of a search for a global minimum. It is not always likely that the desired spin structure will be realised in calculations without some clever initialisation. Instead of using a (for exmple) random initial density to seed a calculation, we can impose a spin projected onto some or all of the atoms. This initial spin can either be collinear or non-collinear. If the initialised spin configuration is not physical (falling into a local energy minimum commensurate with the initialised configuration), it will not be present in the solution.

3.2. FeAs

In some systems where the magnetic structure is incommensurate with the underlying crystal lattice, for example GdSi, Ho, Cr, there are many different magnetic phases. Iron arsenide (FeAs) is related to the iron arsenide superconductors[47], in which the correlated electrons form a coherent superconducting state. Although it is not superconducting, FeAs has been found to have a non-collinear incommensurate spin spiral structure[48]. The periodicity of this structure is also known to change with temperature[49], so FeSe forms a large number of different magnetic states often incommensurate with the underlying crystal lattice. It has been suggested that the magnetic structure originates as a result of frustration between different magnetic configurations[50], and so it may be possible that the change in the magnetic periodicity originates from changes in interactions between these competing configurations which can vary with temperature. In particular, FeSe is a material that displays an elliptic incommensurate helimagnetism, the structure of which is illustrated in Fig. 8 with the DFT magnetic structures in [51].

Unlike conventional ferromagnetic or antiferromagnetic systems, elliptic incommensurate helimagnetism is characterised by a complex magnetic structure with a helical twist that varies spatially, forming an elliptical pattern. The helical magnetic structure has two perpendicular modulation wave vectors, creating the elliptical shape, and the magnetic structure is incommensurate with the underlying crystal lattice.

3.3. Spin ice in $Dy_2Ti_2O_7$

Pyrochlore $Dy_2Ti_2O_7$ is a spin-ice which comprises corner sharing tetrahedrons of Dy^{3+} ions. These tetrahedrons are integral to the formation of the spin-ice state, whereby two spins point in and two spins point out along the local $\langle 111 \rangle$ axis. The spin-ice state in $Dy_2Ti_2O_7$ has been widely studied over the previous 30 years, although there have been limited first principles simulations of this state. A spin-ice is inherently non-collinear and highly degenerate, thus it provides a challenge for spin-DFT calculations.

Not only does the spin ice state in $Dy_2Ti_2O_7$ provide a way to investigate the residual entropy in water-ice, it is also well known for demonstrating magnetic monopoles. In 2008, quasi-particles resembling magnetic monopoles were discovered in $Dy_2Ti_2O_7$ by Castelnovo et al [52]. These are formed by creating defects in the two-in, two-out structure. By inducing a flip of one of the spins in a tetrahedron, the result is a three-in, one-out tetrahedron. But, as these are corner sharing tetrahedra, this causes the neighbouring tetrahedron to have a one-in, three-out spin configuration. For a typical

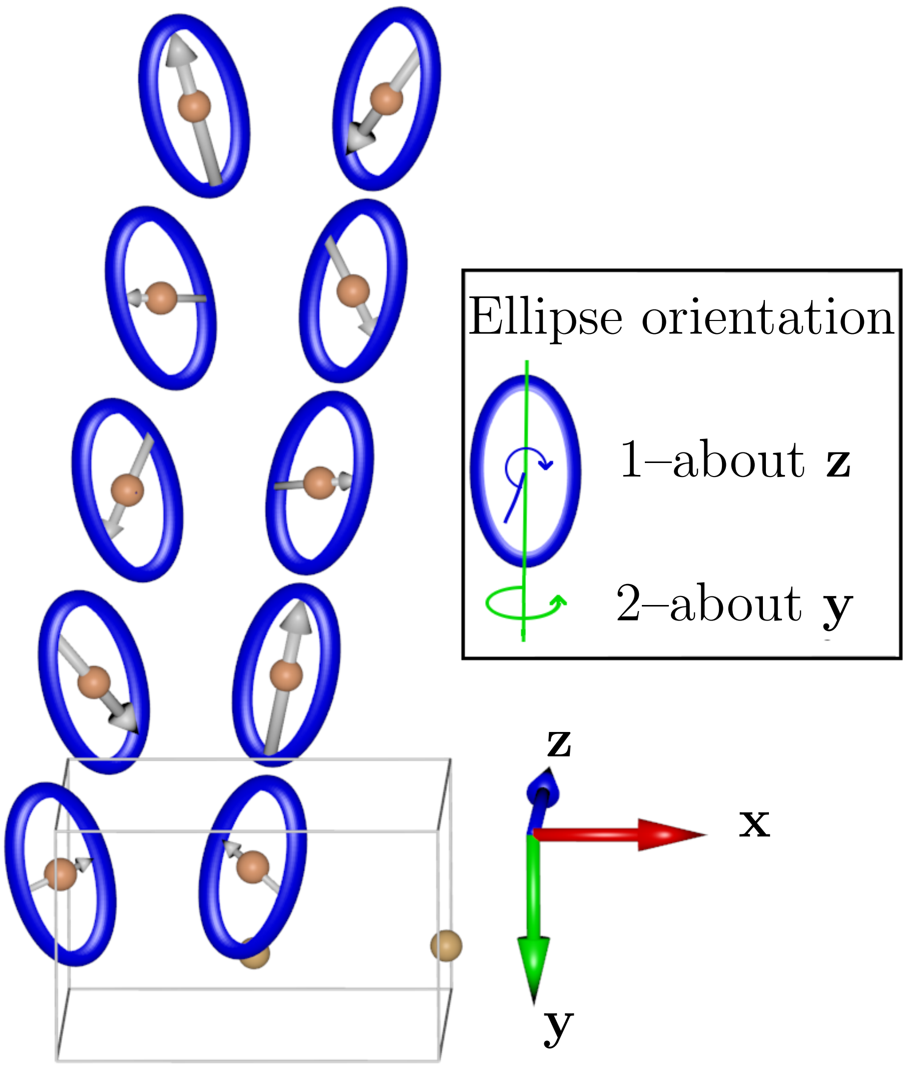


Figure 8. The FeAs spin spiral is illustrated[51].

tetrahedron, the divergence of the magnetisation is zero as there is equal amounts of spin flowing into the tetrahedron as flowing out. In the defect tetrahedron, there is more spin flowing in one direction than the other. Of course globally throughout the crystal the internal magnetic field is divergence-free, but locally a spin-ice tetrahedron with a defect appears like a magnetic monopole. By flipping one spin, one creates two tetrahedra with non-typical spin configurations. However by flipping a second spin in the second tetrahedron we can move this defect along through the crystal. Therefore, the two monopoles are free to exist independently in the crystal. $Dy_2Ti_2O_7$ is an important material for testing the fundamental properties of magnetism and it is important that first-principles studies of this material are able to capture the physics underpinning the spin-structure. The resulting spin structures are shown in Fig.9. It can be seen that magnetic moments which interact with each other and with the crystal lattice, results in a complex spin structure. Although there are approximations in the

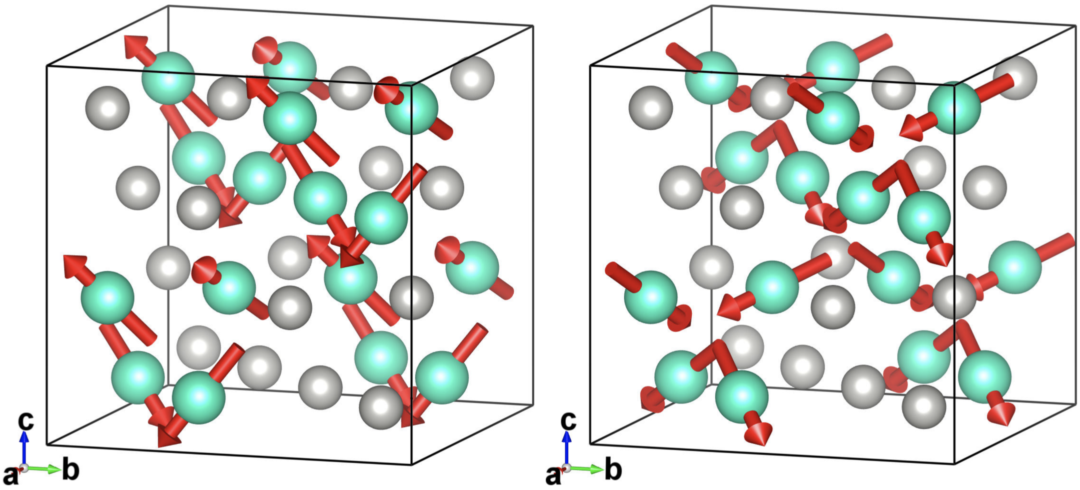


Figure 9. Example magnetic configurations of $Dy_2Ti_2O_7$ calculated using (left) LSDA and (right) a new source-free XC functional[53]. Structures are shown in the conventional unit cell. Dy ions and Ti ions are shown in green and silver respectively. The red arrows show the non-collinear spin density projected onto a local atomic basis for the Dy ions. Oxygen atoms are not shown for simplicity.

XC-functional used in DFT, it can still give a good description of the complex interplay of various factors, including the nature of the magnetic ions, their arrangement in the crystal lattice, the crystal symmetry, and external influences like magnetic fields. Understanding this spin structure is essential for studying the material's magnetic properties and its potential applications in areas of future technologies and condensed matter physics.

3.4. XC Functionals

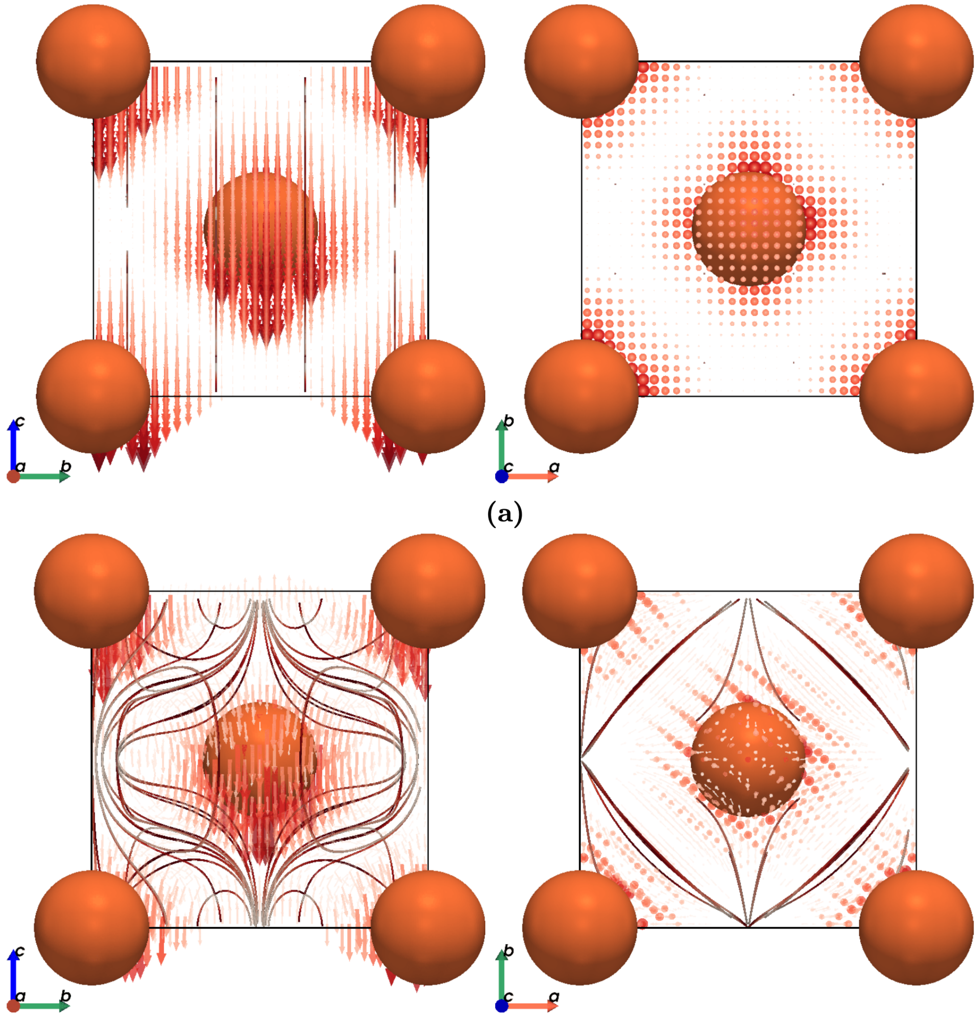
Earlier in this article a a short review of XC development for non-collinear spin was given. The accuracy of a DFT calculation depends heavily on the choice of XC functional. Whenever one performs a DFT calculation, one must choose from a vast selection of them. Different XC functionals capture different aspects of a physical system, and if comparison to experimental methods is sought, the XC functional will determine how accurately the calculations describe the physical quantity in question.

In particular some exact details are known about the nature of non-collinear XC functionals which should be constrained within the development. To give insight here we will present some details of one such functional, a magnetic source-corrected local spin density approximation[18]. We can express the XC spin potential in terms of this non-spin potential and a magnetic field

$$V_{xc}^{*}(r) \quad = \quad V_{xc}(r)I_2 + \mu_B \mathbf{B}_{xc}(r)\cdot\sigma \tag{22}$$

where $\mathbf{B}_{xc}$ is the magnetic field arising from the XC, σ is the vector of Pauli spin matrices, and I_2 is the identity matrix. From the Maxwell equations, for any arbitrary magnetic field the divergence of the field should be zero (zero magnetic sources) but this condition is not met for the most common functionals. But (in atomic units) one can remove sources via the Poission equation

$$\nabla^2\phi(r) \quad = \quad -4\pi\nabla\cdot\mathbf{B} \tag{23}$$



(a)

(b)

Figure 10. XC magnetic fields of Fe shown along the a (left) and c (right) crystal directions. (a) Fields calculated using standard LSDA functional and (b) fields calculated using source free LSDA[53].

giving a source-free magnetic field

$$\mathbf{B}^*(r) \quad = \quad \mathbf{B}(r) + \frac{1}{4\pi}\nabla\phi(r). \tag{24}$$

A useful way to visually test the effects of the correction to $\mathbf{B}^*(r)$ is to examine the magnetic field lines. It is easy to see from magnetic field lines if the source terms have been removed from the field. Using electric fields as an analogy, electric field lines emerge radially outwards from a point charge. However, to create a system which is source-free, we may add a second point charge of opposite sign. The field lines now will emerge from one charge and flow into the second charge, forming loops. Due to Maxwell's equations, we know that magnetic fields ought to follow this second scheme.

In Fig 10 we compare the field lines from a source-free functional to that of standard spin-LDA. We can see the field lines arising from the LSDA without the source correction. These lines are all parallel and flow only in the z-direction. As we have set a quantisaiton axis for these calculations along the z-direction, the spin density is all aligned along this axis. It is clear that these field lines for Fe are globally collinear with the magnetisation, one of the main issues with the LSDA highlighted by Sharma[18]. In a physical system, there is no requirement for the magnetic field and the magnetisation to be collinear at each point in space. This is one aspect of magnetic phenomena not captured by the LSDA. For the LSDA, the field lines are parallel throughout the entire infinite crystal, implying the presence of a magnetic source. If we instead study the field lines due to the source corrected functional we see that the field lines are distinctly different. The field lines form closed loops around the Fe ions, following similar patterns one sees by sprinkling Fe filings around a bar magnet. These field lines are continuous across the periodic boundaries. It is clear then that the field lines for B_{xc} are no longer constrained to be locally collinear with the magnetisation when the source terms are removed.

4. Summary

Non-collinear magnetism is a fascinating phenomenon in condensed matter physics that challenges our conventional understanding of magnetic order. Also, given the success of density functional theory as a powerful computational tool to investigate the electronic structure of materials, is it natural to extend it to the area of non-collinear magnetic structures. DFT has been used to uncover intricate magnetic structures, such as spiral, skyrmion, and chiral configurations, shedding light on the underlying physics of these phenomena.

Here we examined how DFT has been extended to non-collinear magnetic systems and its in understanding the stability of non-collinear magnetic states in exemplar materials. The energy can be made lower than the collinear case by the relativistic spin-orbit interaction, describing the energy change of electronic bands when electrons see the local magnetic field associated with the orbital angular momentum states. This interaction is now added to the Hamiltonian which can be applied to condensed matter systems within common electronic structure codes widely available. This allows a detailed insight into non-collinear magnetic properties at the atomic level, and the ability to calculate properties important for modeling low energy future technological devices. It also gives us insight into the fundamental physics in such materials, electron by electron, allowing us to build models of complex spin structures.

However the theoretical technology is still at a fairly early stage, for example the application of current XC functionals within density functional theory is still open to much improvement. The diverse applications of non-collinear magnetism, from spintronics and magnetic data storage to topological insulators and multiferroic materials, non-collinear magnetic systems have the potential to revolutionize various technological fields. Even though improvements in approximations are still required in electronic structure methods, DFT calculations currently provide invaluable insights into the electronic and magnetic properties of the materials, enabling the design of novel devices and materials with tailored magnetic functionalities.

Non-collinear magnetism, as investigated through density functional theory, represents both an interesting and technologically important area in condensed matter physics. DFT has proven to be an indispensable tool for unraveling the complexities materials and now is starting to be able to do that for non-collinear magnetic structures, investigating their stability, and their potential applications. As we continue to refine DFT methods and explore new materials, we can anticipate even more exciting discoveries in non-collinear magnetism, with far-reaching implications for both fundamental science and technological innovation.

5. Biographies

Stewart Clark is a Professor of Physics at Durham University, specialising in theoretical and computational condensed matter physics. His interests lie in developing new methods in electronic structure theory and implementing them computationally, particularly for use in high-performance supercomputers. He is an author of the Castep code (www.castep.org) which is widely used in academia and industry for materials science research based on first-principles electronic structure methods.

Zachary Hawkhead received his PhD in Physics from Durham University where he specialized in non-collinear magnetic properties. His PhD thesis focused on first-principles calculations of exotic magnetic materials, as well as implementation of new methods for non-collinear magnetism.

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