# ADVANCED MAGNETIC NANOSTRUCTURES

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# Edited by

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Advanced Magnetic Nanostructures

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## PREFACE

A key trend in modern science and technology is the exploitation of phenomena occurring on length scales between 1 nm and 1000 nm. This nanotechnology or nanoscience approach has lead to the emergence of fields such as nanobiology, nanoelectronics, and nanochemistry. An important and—in many respects—pivotal area is *nanomagnetism*. From early precursors in the first half of the 20th century to recent developments, magnetic nanostructures are interesting scientific objects with many present and emerging applications, including permanent magnets, soft magnets, magnetic recording media, sensors, and structures and materials for spin electronics. A key advantage of artifical magnetic nanostructures is their ability to surpass the performance of naturally occurring magnetic compounds. Examples are nanostructured permanent and soft magnets.

Magnetic nanostructures can be produced in a variety of geometries, such as nanoparticles, nanowires, dots and antidots, particulate thin films, nanotubes, nanojunctions, and nanorings. In addition, much progress has recently been made towards tuning the chemistry and crystallographic microstructure for a given geometry. For example, nanotubes can be produced as soft- and hard-magnetic structures.

A fascinating aspect of nanomagnetism is that the involved physics goes beyond a mixture of atomic-scale and macroscopic effects. The main competition between electrostatic interactions, such as exchange, and relativistic corrections, such as spin-orbit coupling, is organized on a length scale of a few nanometers. This gives rise to a variety of zero- and finite-temperature phenomena governing the static and dynamic behavior of the structures.

This book is devoted to the fabrication, characterization, experimental investigation, theoretical understanding, and utilization of advanced magnetic nanostructures. Focus is on various types of 'bottom-up' and 'top-down' artificial nanostructures, as contrasted to naturally occurring magnetic nanostructures, such as iron-oxide inclusions in magnetic rocks, and to structures such as perfect thin films.

Chapter 1 is an introduction into some basic concepts of interest to more than one chapter, such as the definitions of basic magnetic quantities. Chapters 2-4 are devoted to the theory of magnetic nanostructures, \$5 deals with the characterization of the structures, and \$6-10 are devoted to specific systems. Applications of advanced magnetic nanostructures are discussed in \$11-15 and, finally, the appendix lists and briefly discusses magnetic properties of typical starting materials.

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## Chapter 1

## **INTRODUCTION**

The nanostructures considered in this book are magnetic and characterized by *structural* length scales ranging from a few interatomic distances to about one micrometer. The basic length unit is the *nanometer* ( $1 \text{ nm} = 10^{-3} \text{ µm} = 10^{-9} \text{ m}$ ), corresponding to about four interatomic Fe-Fe distances. Magnetic nanostructures pose experimental challenges, exhibit interesting physical phenomena, and have many present or potential applications. An important aspect is that structural lengths affect, but only partly determine, the magnetic length scales encountered in the structures. Examples are domains in semihard nanoparticles, where both the domain size and the domain-wall thickness may be smaller than the particle size, and polycrystalline softmagnetic nanostructures, where the magnetic correlation length is much larger than the crystallite size.

Due to rapid progress in the fabrication and processing of nanostructures, it is now possible to realize a broad variety of geometries, crystalline textures, and chemistries. For a given geometry, the structures can be fabricated using a variety of magnetic materials (compounds), with different local magnetic properties and crystalline textures. The Appendix presents some magnetic materials of interest in nanomagnetism.

#### 1. BASIC DEFINITIONS AND UNITS

The magnetic moment **m** of the atoms in a nanostructure nearly exclusively originates from the electrons in the partially filled inner shells of transition or rare-earth metals. There are both spin (S) and orbital (L) contributions, but since L is much smaller than S in most iron-series transition-metal magnets, the magnetic moment is often equated with the spin polarization. The situation is similar to that encountered in bulk magnets, although both S and L may be modified at surfaces and interfaces (Ch. 2). As in infinite solids, nuclear moments are much smaller than electron moments and can be ignored safely for most applications.

The magnetic moment of an atom is created by intra-atomic or Hund'srules exchange, which favors parallel spin alignment on an atomic scale. In addition, ferromagnetism requires *inter*atomic exchange, to ensure parallel alignment of the moments of neighboring atoms. The resulting net moment gives rise to the magnetization  $\mathbf{M} = \mathbf{J}/\mu_0$  which is defined as the moment per unit volume. In bulk ferromagnets, the competition between interatomic exchange and thermal disorder leads to the vanishing of the spontaneous magnetization  $M_s = |\mathbf{M}(\mathbf{r})|$  at a well-defined sharp Curie temperature  $T_c$ . However, the existence of a Curie-point singularity is limited to infinite bodies, and in nanostructures, the concepts of magnetic phase transitions must be reevaluated (Ch. 3).

Spin-orbit coupling in combination with local crystal-field interactions gives rise to magnetic anisotropy. In the simplest case, magnetic anisotropy is of the uniaxial type and described by the lowest-order anisotropy constant  $K_1$ . This constant is equal to the energy density necessary to turn the magnetization from the easy to a hard magnetization axis. In addition, there are shape-anisotropy contributions of magnetostatic origin. In nanostructures, surface, interface, and shape anisotropy contributions are often important, particularly in cubic materials, where the lowest-order bulk anisotropy is zero.

An applied magnetic field **H** changes the magnetization by rotating the local moment. Since the magnetic anisotropy yields energy barriers between different magnetization states or spin configurations  $\mathbf{M}(\mathbf{r})$ , the field dependence of the net magnetization exhibits *hysteresis*. Important hysteretic properties are remanence  $M_r$ , defined as the zero-field magnetization after saturation in a strong magnetic field, and the coercivity  $H_c$ . The latter is defined as the reverse magnetic field at which the volume-averaged magnetization of an initially saturated magnet reaches zero. Some other hysteretic properties. For example, the coercivity of advanced magnetic nanostructures varies from about 1  $\mu$ T to several T. Analytical and numerical aspects of the hysteresis of magnetic nanostructures will be treated in Chs. 3 and 4, respectively.

The structural length scales of nanomagnets are intermediate between interatomic and macroscopic distances, but nanomagnetism cannot be reduced to a mixture of atomic-scale and macroscopic phenomena. For example, most extrinsic properties are realized on a nanoscale, and nanostructuring is used to produce optimized hard, soft, information-storage and sensor materials. A dynamic aspect of this interplay between atomic (or intrinsic) and hysteretic (or extrinsic) phenomena is that equilibration times vary from less than 1 ns to millions of years. This determines, for example, the magnetic switching time of spin-electronics structures and the lifetime of information stored in magnetic recording media. This is related to the thermal instability of the magnetization direction known as superparamagnetism (Bean and Livingston 1959). This effect occurs in very small particles and is strongly temperature dependent (Ch. 3).

In this book, the preferred *length unit* is 1 nm ( $10^{-9}$  m), but 1 Å = 0.1 and 1  $\mu$ m = 1000 nm are also used, particularly for submicron features having sizes of several 100 nm. Recording densities are also measured in bytes per square inch or bytes per square centimeter (1 in<sup>-2</sup> = 6.452 cm<sup>-2</sup>). Both SI and Gaussian units will be used for magnetic quantities, with explicit conversions occasionally included in square brackets. This also includes the parallel or alternate use of the SI unit tesla for coercivity and magnetization, as compared to the correct but cumbersome unit A/m. The latter corresponds to  $B = \mu_0(M + H)$ , and the former is obtained by incorporating  $\mu_0$  into M and H, so that one actually considers  $\mu_0 M$  and  $\mu_0 H$ . In the Gaussian system, multiplying the magnetization (emu/cm<sup>3</sup>) by the dimensionless number  $4\pi$  changes the unit to gauss. (This is similar to measuring the perimeter of an island in miles and its diameter in feet.) Some everyday numerical conversion rules are: (i) 1 T = 10 kOe  $\approx 0.8$  MA/m (coercivity), (ii) 1 emu/cm<sup>3</sup> = 1 kA/m and 1 T = 10 kG  $\approx$  0.8 MA/m (magnetization), (iii)  $1 T^2 = 100 MGOe \approx 800 kJ/m^3$  (energy product). Finally, an SI susceptibility of 1 corresponds to a Gaussian susceptibility of  $4\pi$ . In the above conversions, we have used the numerical relation that  $10/4\pi = 0.7958 \approx 0.8$ .



Figure 1. Typical nanostructure geometries: (a) chain of fine particles, (b) striped nanowire, (c) cylindrical nanowire, (d) nanodots, (e) nanojunction, (f) nanotube, (g) antidots, (h) vicinal surface step, (j) nanoring, and (k) patterned thin film. Note that the figures can consist of multilayered and granular nanocomposites.

#### 2. MAGNETIC NANOSTRUCTURES

Magnetic nanostructures can be produced in a wide range of geometries. Figure 1 shows some examples. In combination with specific choices of magnetic materials for the structures – or for parts of the structures – this versatility is a major reason for interest in magnetic nanostructures. Several chapters of this book deal with the fabrication, investigation, and application of individual geometries, such as nanowires and patterned thin films. The following paragraphs briefly characterize typical geometries, mention some systems of practical or scientific interest, and provide links to the individual chapters of this book. (For references, see the Chapters 2 to 15 and the further-reading section below.)

#### 2.1. Nanoparticles, Clusters, and Molecular Magnets

Small magnetic particles exist in nature or are produced artificially (Chs. 6 to 8). Nanoparticles have sizes ranging from a few nanometers to submicron dimensions (Ch. 7), whereas molecular magnets (Ch. 6) contain a few magnetic atoms in well-defined atomic environments. Clusters are intermediate structures, with less well-defined atomic environments but exhibiting atomic features such as facets (Ch. 8).

Examples of naturally occurring nanoparticles are magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles precipitated in bacteria, insects and higher animals, and magnetite and other oxide particles responsible for rock magnetism. Nanobiomagnetics is concerned not only with questions such as the role of magnetite particles for horizontal and vertical orientation of animals but also with important medical issues, such as local drug administration and cancer diagnosis (Ch. 15). The small remanent magnetization of magnetic rocks, first analyzed by Néel in the 1940's, is exploited, for example, in archeomagnetic dating and to monitor changes in the Earth's magnetic field. Small oxide particles, less than 10 nm in diameter, are observed in gels having the nominal composition  $FeO(OH) \cdot nH_2O$ . Fine particles are also encountered in meteorites.

Some artificially produced magnetic nanoparticle structures are Fe in  $Al_2O_3$  and so-called 'elongated single-domain particles'. Interesting applications of small particles are stable colloidal suspensions known as *ferrofluids*. A variety of materials can be used, such as Fe<sub>3</sub>O<sub>4</sub>, BaFe<sub>12</sub>O<sub>19</sub>, Fe, Co, and Ni, and a typical particle size is 10 nm. Most ferrofluids are based on hydrocarbons or other organic liquids, whereas water-based ferrofluids are more difficult to produce. They are used as liquids in bearings and to monitor magnetic fields and domain configurations.

#### 2.2. Granular Nanostructures

Embedded clusters, granular materials, and other bulk nanostructures are of great importance in nanoscience. The structural correlation lengths of typical nanocomposite materials range from about 1 nm in x-ray amorphous structures to several 100 nanometers in submicron structures. Magnetic glasses and atomic-scale defect structures are beyond the scope of nanomagnetics, but they are of indirect interest as limiting cases and because nanomagnetic phenomena have their quantum-mechanical origin in atomic-scale magnetism.

Depending on grain size and microchemistry, granular nanostructures are used for example as permanent magnets (Nd-Fe-B), soft magnets (Fe-Cu-Nb-Si-B), and magnetoresistive materials (Co-Ag). There are two types of exchange-coupled permanent magnets: isotropic magnets, which exhibit random anisotropy and remanence enhancement, and oriented hard-soft composites, which utilize exchange coupling of a soft phase with a high magnetization to a hard skeleton.

Closely related systems with many potential applications are magnetic clusters deposited in a matrix. For example, the narrow size distribution of 10-20% makes this material interesting as a granular media for magnetic recording. A well-known *soft-magnetic* nanocomposite is the 'Yoshizawa' alloy  $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ , which consists of DO<sub>3</sub>-structured Fe<sub>3</sub>Si grains embedded in an amorphous matrix.

#### 2.3. Particle Arrays and Functional Components

Two-dimensional arrays of nanoparticles are of interest as scientific model systems and have many present or future applications. For example, advanced magnetic recording media can be characterized as a complex array of magnetic particles, and interest in dot arrays has been sparked by the search for ever-increasing storage densities in magnetic recording. In very small dots, quantum-mechanical effects are no longer negligible, and there are phenomena such as quantum-well states. These effects are of interest in quantum computing and spin electronics.

Most easily produced and investigated are submicron dots made from iron-series transition metals, such as Ni, but it is also possible to use metallic alloys, such as Permalloy, and to reduce the dot size to less than 100 nm. The dots may form square or hexagonal arrays, or structures such as corrals. Among the investigated phenomena are the properties of individual dots and interdot interactions. A related class of nanostructures are *antidots*, that is, holes in a film rather than dots on a film. Potential applications include magnetic recording, sensors, magnetic and quantum computing, micron- and submicron-size mechanical devices, short-wavelength optics, and spin electronics. Other 'functional' building blocks are, for example, nanojunctions, spin valves, and tips for magnetic-force microscopy (MFM tips).

#### 2.4. Nanowires

There is a smooth transition from elongated dots and thin-film patches to nanowires. Magnetic nanowires have present or potential applications in many areas of advanced nanotechnology, including patterned magnetic media, magnetic devices, and materials for microwave technology. There a various methods to produce nanowires, such as deposition on vicinal surfaces and electrodeposition, including electrodeposition into porous alumina templates (Section 3).

Much of the early work on magnetic nanowire arrays was concerned with exploratory issues, such as establishing an easy axis for typical preparation conditions, the essential involvement of shape anisotropy, as opposed to magnetocrystalline anisotropy, and the description of magnetostatic inter-actions between wires. More recently, attention has shifted towards the understanding of magnetization processes, such as the transition from curling-type to quasi-coherent nucleation, the influence of depositiondependent polycrystallinity of typical transition-metal nanowires. Some other interesting phenomena are magnetic-mode localization, as evident *e.g.* from experimental activation volumes, spin-waves, and current-induced magnetization reversal.

#### 2.5. Magnetic Thin Films and Multilayers

Magnetic thin films and multilayers can be classified as magnetic nanostructures, too, but it is common to treat homogeneous thin films and multilayers as a separate branch of magnetism, intermediate between nanomagnetism and surface magnetism. However, many recently developed and investigated nanostructures are thin-film nanostructures. Examples are selfassembled thin-film nanostructures (Ch. 9), patterned nanomagnetic thin films (Ch. 10), hard-magnetic thin-film nanostructures and thin films for magnetic recording (Ch. 11).

Semihard thin films are used in magnetic recording media and have, more recently, attracted attention as tools for magnetic information processing. In addition, on a length scale of a few interatomic distances, there is a variety of interesting thin-film effects, such as vicinal and interface anisotropies, moment modifications at surfaces and interfaces, thicknessdependent domain-wall and coercive phenomena, interlayer exchangecoupling, and finite-temperature magnetic ordering. A specific example is the nanoscale exchange-coupling or 'exchange-spring' effects in multilayers.

#### 3. FABRICATION AND CHARACTERIZATION

The broad variety of magnetic nanostructures corresponds to a diverse range of processing methods. The suitability of individual methods depends on the length scale and geometry of the nanostructures. In addition, each method is usually restricted to a relatively narrow class of magnetic materials.

*Granular nanostructures* are produced by methods such as mechanical alloying and chemical reactions. A traditional though somewhat cumbersome method to fabricate *nanoscale particle arrays* of magnetic, dots, and wires on thin films is nanolithography. Other examples are molecular-beam epitaxy, the use of STMs, and chemical vapor deposition. The call for wellcharacterized large-area arrays of nanoparticles has stimulated the search for advanced production methods such as laser-interference lithography (LIL), where laser-intensity maxima effect a local transformation of a nonferromagnetic material into ferromagnetic islands. Another development is the use of focused ion-beam milling (FIB) to create small particles and particle arrays with well-defined properties.

Thin-film nanowires are comparatively easily obtained by depositing magnetic materials on vicinal surfaces and by exploiting structural anisotropies of the substrate. They can be produced with thicknesses down to one or two monolayers. Electrodeposition of magnetic materials into porous alumina may be used to produce regular wire arrays (see Sellmyer et al. 2001 and references therein). Other ways of fabricating cylindrical nanowires include deposition into molecular sieves, track-etched polymer membranes, and mica templates. By electrodeposition into porous anodic alumina it is now possible to produce hexagonal Fe, Co, and Ni nanowire arrays with diameters ranging from 4 to 200 nm, and lengths of up to about 1 µm, and variable center-to-center spacings of the order of 50 nm. The resulting materials are of interest as magnetic recording media, for optical and microwave applications, and as electroluminescent display devices. Aside from the above-mentioned iron-series transition-metal elements, there is interest in depositing alloys and multilayers, such as Fe/Pt, into porous templates.

The structural and magnetic characterization of magnetic nanostructures is the main focus of Ch. 5 and of various sections and subsections throughout the book. Structural correlation lengths can be probed for example by Xray diffraction, small-angle neutron scattering (SANS) and electron microscopy. Magnetic measurements are performed with the methods known from bulk and surface magnetism, although some techniques must be adjusted to the small signals from certain structures. Examples are vibrating sample magnetometry (VSM), magneto-optical Kerr effect (MOKE) measurements, and SQUID magnetometry. Some methods, such as magnetic-force magnetometry, are nanospecific and presently being applied to measure hysteresis loops of nanoscale magnetic particles.

#### 4. APPLICATIONS

Magnetic nanostructures are used in the form of traditional magnetic materials, such as hard and soft magnets, and in specific functional structures, such as sensors. Hard or *permanent magnets* are used, for example, in electromotors, hard-disk drives, loudspeakers, windshield wipers, locks, refrigerator magnets, and microphones. Some applications, such as toys, do not usually require high-performance magnets, but hard-disk drives and other high-tech applications require highly sophisticated rareearth permanent magnets with well-defined nanostructures (Ch. 12). Compared to the highly anisotropic hard magnets, *soft magnets* exhibit very low magnetic anisotropy. They are widely used for flux guidance in permanent-magnet and other systems, in transformer cores, and for high-frequency and microwave applications, and in recording heads. In advanced soft-magnetic materials, nanostructuring is used to reduce magnetic losses by controlling anisotropy, eddy-current losses, and other properties (Ch. 13).

A key application and driving force of magnetic nanotechnology is *magnetic recording media*. They are used not only for audio-visual technology, for example in audio and video tapes, but also in computer technology, for example in hard-disks (Ch. 11). A remarkable increase in areal density of many orders of magnitude in the last two decades has relied heavily on nanostructuring of media and read and write heads.

Artificial nanostructuring is a way of creating completely new technologies. One area is spin electronics, and various types of nanostructures, such as multilayers and nanojunctions, are being used or investigated in this context (Ch. 14). The magnetoresistance of metallic thin films, granular nanostructures and magnetic oxides are exploited in sensors, and a problem of current interest is spin injection into nonferromagnetic metals and magnetic semiconductors. Other recent developments are magnetic nanostructures for quantum computing, multiferroics (where nanoscale effects are exploited to synergize electric and magnetic degrees of freedom), and nanoparticle ferrofluids for cancer treatment, guided by a magnet and delivering high local doses of drugs or radiation. Nanoscale effects are also exploited in micro-electromechanical systems (MEMS) and magnetic-force nanotips made from CoPt.

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## Chapter 2

## SPIN-POLARIZED ELECTRONIC STRUCTURE

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Abstract This chapter is devoted to the electronic structure of nanoscale metallic magnets. After an introduction to methods of electronic structure calculations, we review how recent trends translate into the description of magnetic nanostructures. Among the considered structures are nanowires, small particles, surfaces and interfaces, and multilayers, and emphasis is on magnetic properties such as moment and magnetization, interatomic exchange, and anisotropy.

#### 1. INTRODUCTION

Nanostructures open new possibilities to tailor the mechanical, chemical, magnetic and electronic properties of materials and, at present, there is strong demand for basic understanding of new phenomena that nanostructures may exhibit. Nanomagnetic objects are different from both atoms and bulk materials, thereby providing an interface between physics, chemistry, material sciences, engineering and biology. For example, the length scale of typical nanostructures allows a direct use in many systems, including the human body. Some phenomena described by first principles are surface-and interface magnetic anisotropies, reduced or enhanced magnetic moments at particle or film surfaces, and optical properties, including magnetic dichroism. In addition, parameters obtained from firstprinciple calculations serve as an input in numerical micromagnetic simulations (Ch. 4).

Here we focus on iron-series transition-metal elements and their alloys. Magnetic oxides and rare-earth compounds can also be used in nanomagnets, but their magnetism goes beyond the scope of this review. For example, the large magnetocrystalline anisotropy of rare-earth transition-metal intermetallics, which are used in nanostructured permanent magnets, largely reflects the Hund's-rules ground state of tripositive rare-earth ions (Ch. 3).

Magnetic clusters containing a few atoms have been investigated for many decades, both theoretically and experimentally [1]. The electronic structure of atomic clusters was traditionally treated by real-space methods based on various approaches from tight-binding (TB) to density-functional methods [2, 3]. The methods of calculations of electronic structure of bulk materials use periodic boundary condition and k-space representation. They are very well developed and applied to broad variety of materials [4]. Nanostructures include 100-100000 atoms and do not exhibit periodicity, so that their first-principle study is a very challenging problem. Direct atomistic treatment of real nanodevices is very difficult due to the large number of atoms. The free-electron model, tight binding approaches and order O(N) density functional approach have all been applied to the nanoscale geometries to study their electronic properties. The choice of an approach depends on the degree of compromise between numerical and conceptual tractability on the one hand and quantitative accuracy on the other.

# 2. METHODS OF ELECTRONIC-STRUCTURE CALCULATIONS

Electronic structure methods for studies of nanostructures can be divided broadly into supercell methods and real-space methods. Supercell methods use standard k-space electronic structure techniques separating periodically repeated nanostructures by distances large enough to neglect their interactions. Direct space methods do not need to use periodic boundary conditions. Various electronic structure methods are developed and applied using both approaches. In this section we will shortly discuss few popular but powerful electronic structure methods: the pseudopotential method, linear muffin-tin orbital and related methods, and tight-binding methods.

#### 2.1. Linear Muffin-Tin Orbital and Related Methods

Basis-set methods may be divided into two categories, depending on whether they (i) use wave function expansions in some set of fixed basis functions like atomic orbitals, Gaussian and plane waves, or (ii) expand the wave function in a set of energy and potential dependent partial waves as done in Korringa-Kohn-Rostoker (KKR) and the augmented plane wave (APW) methods. The KKR and APW methods require computational efforts which, despite attempts to improve the efficiency, are barely feasible and limited to sp-like valence and conduction electrons. Computationally, this can be remedied by the addition of localized orbitals to the plane wave basis set. But such a hybrid scheme is neither elegant nor in accordance with the chemical and physical intuition based on the smooth trends observed through the periodic table. It is necessary to use the self-consistent methods for computing one electron eigenvalues and eigenvectors with speed and accuracy. The so-called linear methods of band theory satisfy the requirements rather well. This is true for the linear-muffin-tin-orbital method (LMTO) [5-8]. This method is linearized version of the KKR method. Almost identical with the solid state LMTO method is the augmented spherical wave (ASW) method of Williams et al. [9].

The LMTO has also been extended to treating crystalline impurities with the Green's function technique by Koeing *et al.* [10], and Gunnarson *et al.* [11] have used it for both metal and semiconductor hosts. Harris [12], Casula and Herman [13] and Springborg *et al.* [14, 15] have developed the LMTO method for clusters and molecules. For surfaces and thin films, LMTO techniques have been devised by Fuziwara [16] and Fernando *et al.* [17]. It was also discovered that the conventional solid-state LMTO basis set can be transformed exactly into orthogonal [6, 7], tight binding (TB) [6] and minimal [100] basis sets, which simplifies and generalizes the solid-state LMTO method considerably.

The use of the atomic-sphere approximation (ASA) [18], where the single-electron potential is modeled as a superposition of spherical potentials inside overlapping space-filling spheres, makes LMTO methods computationally very efficient. Where this approximation is applicable, the LMTO-ASA method is presumably the most efficient procedure available for solving the density functional equations to a reasonably high degree of accuracy. However, a full-potential treatment going beyond the ASA is needed for many systems, including surfaces and impurities, and for total-energy changes associated with phenomena such as phonon distortions and atomic relaxations etc. A number of full potential methods have been developed, namely, FPLAPW [19, 20], FPLMTO [21] and FPLO [22]. A real-space version of the full-potential approach was implemented by Beck [23].

#### 2.2. Plane-Wave Pseudopotential Methods

The pseudopotential method relies on the separation (in both energy and space) of electrons into core and valence electrons and implies that most physical and chemical properties of materials are determined by valence electrons in the interstitial region. One can therefore combine the full ionic potential with that of the core electrons to give an effective potential (called the pseudopotential), which acts on the valence electrons only. On top of this, one can also remove the rapid oscillations of the valence wavefunctions inside the core region such that the resulting wavefunction and potential are smooth.

Beyond a chosen cutoff radius, the all-electron and pseudofunctions (potential and wavefunction) are identical, while inside the core region both the pseudopotential and pseudowavefunction are smoothly varying. After the construction of these pseudofunctions for a single atom and ensuring that their scattering properties are almost identical to those of the all-electron functions, they can be used in any chemical environment.

The pseudopotential method has various advantages. Eliminating the core electrons from the problem reduces the number of particles that must be considered in the Kohn-Sham (KS) equations for the effective one-electron potential. For example, a pseudopotential calculation for bulk silicon (with 10 core and 4 valence electrons) requires the calculation of 4 occupied bands at each k-point, while an all-electron approach would require the calculation of 14 occupied bands. More importantly, the smooth spatial variation of the pseudopotential and pseudowavefunction allows the use of computationally convenient and unbiased basis, such as plane wave basis sets or grids in space.

The plane-wave pseudopotential method has proven to be an excellent computational tool for solving large scale electronic structure problems [24, 25]. Notable strengths of the method are the ability to use fast Fourier transform to update the Kohn-Sham equations, the lack of dependence on the basis on atom positions, and the clear control of convergence with the cutoff energy determined by the shortest wavelength mode. However, the method encounters difficulties in treating widely varying length scales. This issue is especially relevant for surfaces, clusters, and the hard pseudopotentials of first row elements or transition metals, which vary rapidly near the nucleus. A real-space version of the pseudopotential method was developed by Chelikowsky [26].

#### 2.3. Tight-Binding Methods

The traditional approach to obtain the electronic structure of a periodic solid with *ab initio* pseudopotentials has been to solve the Kohn-Sham (KS)

equations in momentum space using a plane-wave basis set. There are many advantages of plane-wave basis sets. For example, due to their completeness and orthonormality, they allow convenient and unbiased representation of the charge density and wavefunctions for calculating operator matrix elements. For non-periodic and localized systems, such as defects, surfaces, clusters, quantum dots, using a plane wave basis set requires an artificial periodicity in order to implement standard electronic structure algorithms. This artificial periodicity is introduced through the use of large unit cells called *supercells*.

While the supercell approach works well for localized systems, it is typically necessary to consider a very large supercell. This results in a planewave basis replicating not only the relevant electronic states but also vacuum regions imposed by the supercell. A much more efficient method to implement for investigating the electronic structures of localized systems is to use real space methods such as the recursion methods [27] and the moments methods [28]. These methods do not require symmetry and their cost grows linearly with the number of inequivalent atoms being considered. For these reasons, real space methods are very useful for a description of the electronic properties of complex systems, for which the usual k-space methods are either inapplicable or extremely costly.

Real-space methods are generally impractical, but they are extremely efficient when the system in consideration is well described by a tightbinding (TB) Hamiltonian. For a long time, parameterized TB Hamiltonians in conjunction with real space methods have been used to study the properties of complex transition metal alloys. In some cases, simple model TB Hamiltonians are very useful to stress the essential physics of the phenomenon in question and even to give the correct trends found in real systems. But in other cases, the effects are too subtle and the results obtained by the use of these parameterized Hamiltonians can be misleading. Even when trends can be well described, to obtain quantitative results a more exact Hamiltonians is usually needed. This has been a major problem regarding real-space electronic structure calculations. Usually, the involved parameters needed to build the TB Hamiltonian, such as hopping integrals, are obtained from a linear combination of atomic orbitals (LCAO) fit to more exact k-space calculations or are adjusted to fit experimental results [29].

When one considers complex systems, for which no exact results are available, parameters are usually obtained from a simple similar system and then transferred to the more complex system in question using the Slater-Koster rules [30] and some other empirical formulas which are known to be roughly obeyed. The results were often encouraging, but the lack of a solid theoretical background to justify the procedure left some fundamental questions unanswered. For example, how could one simulate the crystalfield splitting which depends on local environment and can not be transferred from one calculation to another, and how do we treat the wave function? The solution to these problems is not unique and several interesting points of view have developed. However, major progress towards obtaining a TB-Hamiltonian based on a solid theoretical understanding of the problem came in 1984 with the advent of the LMTO-ASA-TB formalism [31]. This gave rise to a new era regarding the quantitative description of the electronic structure of complex systems by using real-space methods.

#### 3. MAGNETIC PROPERTIES

In this chapter we describe how basic or 'intrinsic' magnetic properties are calculated from first principles. Technological applications, for example in magnetic recording, tend to require a large magnetization, thermal stability, and control over the coercivity. The reversal process is described usually by micromagnetic modeling which takes into account dipole-dipole interactions. The description of magnetization reversal is beyond the scope of our paper. For details of micromagnetic modeling, readers are referred to Chs. 3 and 4 and to the specialized literature [31].

Magnetic properties can be understood and fully described from microscopic considerations using ab-initio electronic-structure methods. The local magnetic moment in combination with intra-atomic exchange defines the magnetization, interatomic exchange describes the thermal stability, and the coercivity reflects the magnetic anisotropy of the system. These interactions have different energy scales. The intra-atomic exchange is of the order of 2 eV, interatomic exchange of the order of 10 meV, and anisotropy of the order of 1 meV. However, all of them are extremely important to describe the behavior of a magnet.

The description of nanomagnets requires new approaches. First, nanostructures are not periodic and tend to have large surface-to-volume ratios. Because of this the magnetization is not uniform across the nanostructure, local magnetic moments differ from site to site, exchange coupling varies throughout the nanostructure, and the anisotropy can be quite different from bulk or surface anisotropies. Second, it is hard to define properties in the similar fashion as in the bulk or as in case of molecules.

#### 3.1. Magnetic Moment

The magnetic moment is given by the difference between the filling of majority and minority spin bands, which is directly related to the ferromagnetic exchange splitting between the bands. There is also an orbital-moment contribution to the moment, but in 3d-based magnets, it is often small due to

quenching (Ch. 3). Total energy minimization over all occupied band states yields crystal structure and magnetic ordering. Magnetic coupling and magnetic moment are sensitive functions of the interatomic spacing and the atomic volume, respectively. Both are dominated by the Coulomb and by exchange interactions at small distances. The moment is determined primarily by intraatomic exchange interactions and the Curie temperature by the interatomic exchange interactions.

The most common approach to calculate the magnetization from first principles is to use the local density formalism, where the spin dependent part of the total energy is approximated by an expression derived for the electron gas [32]. The corresponding exchange-correlation potential depends only on the majority and minority spin densities. Different magnetic structures, such as paramagnetic, ferromagnetic and various antiferromagnetic configurations, exhibit different total energies, and the lowest energy configuration obtained by local density theory represents the observed magnetic state in most cases. Room-temperature ferromagnetism occurs in rather few elements, Fe, Co, Ni, Gd, and several other rare earths are ferromagnetic at low temperatures. However, many alloys are ferromagnetic. The stability of the ferromagnetism of itinerant magnets can be explained by the Stoner criterion, which takes the DOS at the Fermi level,  $D(E_{\rm F})$ , and an atomic exchange integral I as input [33-35]. The transition from paramagnetism to ferromagnetism is favourable for  $D(E_F)$  I > 1. Then the system can lower its energy by bringing enough majority spin electrons down in energy by opening up the ferromagnetic exchange splitting. The Stoner criterion explains why Fe, Co and Ni are singled out for ferromagnetism. Several other elements are close to fulfilling the criterion, for example Pd. Since the DOS is different for different atomic sites, nanostructures may exhibit different local moments and complicated magnetic transitions.

With increasing atomic volume, one approaches the free atom limit where Hund's first rule postulates maximum spin, so that the individual spins of the electrons in a shell are aligned parallel. More generally, Pauli's exclusion principle implies that electrons with parallel spins have different spatial wavefunctions, reduces the Coulomb repulsion and is seen as exchange interaction. When the atoms are squeezed into a solid, some of the electrons are forced into common spatial wavefunctions, with antiparallel spins and reduction of the overall magnetic moment. At surfaces and interfaces, the reduced coordination reverses this effect, and a part of the atomic moment is recovered.