Chapter 1

Introduction

Humanity has become highly dependent on information technology (IT). Parallel to the need for ever-increasing computational speed and data storage capacity, society is beginning to comprehend its need for a more energy-efficient IT. New technologies promise to solve both problems at the same time: While conventional computers rely entirely on the *charge* of the electron to carry information, the *spin* degree of freedom is so far only used in large ensembles for magnetic data storage. Two ideas of improvement are thus manifest: (i) if the spin could be used to process information, the transport of charge and the inevitable energy losses to ohmic resistance could be avoided. (ii) if single spins could be used for data storage, downsizing of the magnetic bits to the ultimate (atomic) limit would be possible. Once the controlled manipulation of individual spins is technologically feasible, another breakthrough comes within reach: Spin-based quantum computation, an inherently energy efficient, ultrafast data processing scheme that makes use of the quantum mechanical processes of interacting spins. Key ideas and advances of these emerging spin-based ITs are described in [1–4].

The *spin* of elementary particles, like the electron, is a fascinating but elusive concept. Pioneered by Pauli, Goudsmit and Uhlenbeck [5,6], it was found to be responsible for magnetism and is a central pillar of quantum physics. Therefore, the concept of spin is fundamental to our understanding of the physical world. The simplicity and elegance of its mathematical description illustrates that our difficulties in grasping quantum phenomena does not stem from a lack of mathematical skill, but from a lack of hands-on experience in the quantum world, which is governed by entirely different laws and concepts than the macroscopic world. However, in the quest to understand these foundations, physicists have developed ingenious experimental and theoretical tools to explore the quantum world. Moreover, great technological treasure has been discovered on its (sub-)nanometer length scale. Harnessing the po-

tential of this treasure is the goal of *nanotechnology*. The combination of spin-based IT described above and nanotechnology lead to the emerging field of *nano-spintronics*.

Future nano-spintronics applications require a solid understanding of magnetism on the atomic scale. Therefore, *fundamental research on model systems of nanomagnetism* is a crucial step towards the realization of these technological dreams. One general type of model system consists of one or more magnetic species (atoms or molecules), embedded in or adsorbed on a macroscopically sized substrate of nonmagnetic material. The open questions and challenges associated with this type of model system can be illustrated best by considering the phenomenological Hamiltonian that is often used to heuristically describe the energy of an ensemble of N spins or total angular momenta in a non-magnetic host environment:

$$\begin{aligned}\hat{H} = &\sum_{i=1}^{N} g\mu_{\mathrm{B}}\mathbf{B}\cdot\hat{\mathbf{S}}_i \\ &+ \sum_{i=1}^{N}\left(D_i\hat{S}_{i,z}^2 + E_i(\hat{S}_{i,x}^2 - \hat{S}_{i,y}^2)\right) \\ &+ \sum_{i=1}^{N}\sum_{j=i+1}^{N} J_{ij}(\mathbf{r}_{ij})\,\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j \end{aligned} \tag{1.1}$$

The first term in eq. (1.1) describes the Zeeman energy, i.e. the energy of each total angular momentum or spin $\hat{\mathbf{S}}_i$ in an externally applied magnetic field $\mathbf{B}$. μ_{B} is the Bohr magneton and g is the Landé g-factor. The second term describes the magnetic anisotropy energy [7]. This contribution stems from the spin-orbit interaction of each spin with the crystal field from the lattice of the substrate. In the form chosen here, where z points perpendicular to the sample surface, the D_i are called the magnetic out-of-plane anisotropy energies and the E_i are called the magnetic in-plane anisotropy energies. The third term describes the exchange interaction between the individual spins. For simplicity, a separation-dependent Heisenberg term was chosen, where the interaction strength J_{ij} between the ith and the jth spin depends only on the pair wise spatial separation $\mathbf{r}_{ij}$. In reality, the interaction can be more complex.

In writing down eq. (1.1), more questions are raised than answers given. The questions can be grouped into two categories: (i) Questions concerning the validity of the description given by eq. (1.1) itself and (ii) questions relating to the experimental accessibility and technological usability of the phenomena described by eq. (1.1). Of the first category, the most obvious question is

- What is the nature of the $\hat{\mathbf{S}}_i$?

First of all, the magnetic moment of an atom or molecule adsorbed on a surface comprises the spin and orbital angular momentum of the atom (molecule) itself and the spin and orbital angular momentum of the polarized substrate in the vicinity. Therefore, the $\hat{\mathbf{S}}_i$ have to be interpreted as the sum of all these angular momenta, i.e. as the total angular momentum. In most parts of this thesis, the word *atomic spin* is used as a synonym for this total angular momentum of the adatom. Moreover, the notation used here suggests that the magnetic atoms or molecules can be described by quantum mechanical spin operators. This is not a trivial claim at all. In fact, when the magnetic species interact with the substrate electrons, the quantum nature of their magnetic moments may be masked, leading to a situation where the $\hat{\mathbf{S}}_i$ have to be interpreted as classical vectors. Consequently, in the general form presented here, eq. (1.1) has to be understood as a purely heuristic expression. Mathematically well defined meaning has to be carefully assigned separately for each experimental situation. In most cases, this can only be achieved by making severe approximations to the true physical behavior. If questions of this nature are answered to some degree, questions of the second category can be investigated:

- Can the parameters g, D_i, E_i, J_{ij} be measured?
- Can the parameters be tuned?
- Can ensembles be constructed that perform some useful function?

To reach into the nanometer cosmos, an interface that connects to our macroscopic world is needed. The simplest yet most ingenious interface is a piece of material that is thick on one end, so our macroscopic equipment can connect to it, and atomically sharp on the other end, so it can feel the quantum effects that rule the nano world. This is the principal idea behind the probe tip of the Scanning Tunneling Microscope (STM). Invented by Binnig and Rohrer in 1981 [8], the STM has become the linchpin of nanotechnology. Its remarkable versatility enables it to not only image but also manipulate the nano world on the atomic scale [9] to build nanostructures that perform complex operations [10]. Even the controlled engineering of the electronic structure is possible [11]. The STM is thus ideally suited to advance many areas of nanotechnology. There have been three principal approaches to investigate nanomagnetism with STM: The Kondo effect, spin-polarized STM (SP-STM) and the detection of spin excitations via inelastic scanning tunneling spectroscopy (ISTS).

The Kondo effect is a specific form of spin-dependent scattering of the conduction electrons in a nonmagnetic host metal off the localized magnetic moments of magnetic impurities. It leads to a complete screening of the magnetic moment below the characteristic *Kondo temperature* T_{K}. This effect can be detected spectroscopically using STM as a narrow resonance at the Fermi energy whose shape has a characteristic temperature- and magnetic field dependence. The Kondo effect was exploited to study individual magnetic atoms [12–16] and molecules [17] as well as coupled atoms [18, 19] with STM. The disadvantage of Kondo systems is, that they are in principle non-magnetic and are thus not well suited for the technological applications discussed above.

A more direct way of investigating magnetic phenomena with STM is SP-STM, where a magnetic probe tip provides sensitivity to the spin degree of freedom of the sample [20–22]. The method is sensitive enough, that it can resolve the spin structure of the sample on the atomic scale [23]. The spin-polarized current from the magnetic tip can even be used to read out and write the spin states of magnetic nanoislands [24]. Most importantly in this context, the magnetization of individual atoms can be detected, as was shown for the first time in [25]. Single Co adatoms were deposited on the Pt(111) surface and the orientation of their magnetic moment was recorded as a function of an externally applied magnetic field, enabling the extraction of the magnitude of their magnetic moment. In this sense, the SP-STM technique represents the ultimate downscaling of magnetometry measurements like X-Ray Magnetic Circular Dichroism (XMCD) spectroscopy [26], which is usually performed on large ensembles of magnetic moments [27].

The SP-STM technique was advanced even further in [25, 28], where it was demonstrated that the magnetic exchange interactions of the Co atoms with a ferromagnetic Co nanowire and with other Co atoms can be measured directly. Pairs and triples of atoms with nanometer separations were investigated, showing that they are coupled by indirect magnetic exchange interactions which are mediated by the substrate conduction electrons. This interaction was shown to depend on the distance $|\mathbf{r}_{ij}|$ as well as the crystallographic direction along which two atoms are separated.

Yet another way to investigate single magnetic atoms or molecules with STM is to detect their spin-excitations using ISTS. Like a down-scaled version of the ensemble averaging Electron Spin Resonance (ESR) technique, this method can probe the excitation energies of individual magnetic species on nonmagnetic surfaces. The first observation of spin-flips of individual magnetic atoms with ISTS was reported in [29], where single Mn atoms were deposited on the NiAl(110) surface that was partially covered with double layer Al_2O_3 patches. These oxide layers were used to decouple the Mn atoms from the

conduction electrons to enable the observation of the excited spin states of the isolated quantum spin.

In [30], the concept of spin excitation ISTS of single magnetic atoms was extended to the class of magnetic nanostructures, constructed by atomic manipulation with the STM tip. Single Mn atoms and chains of up to 10 Mn atoms were constructed and investigated on decoupling monolayer patches of CuN on the Cu(100) surface. The development of spin excitation ISTS continued in [31], where spin excitations of single Mn and Fe atoms on the CuN/Cu(100) surface were analyzed in detail.

In addition to the experiments on thin insulating layers, ISTS measurements of single magnetic atoms on metallic surfaces were also reported [32,33], showing a strongly broadened excitation line width.

Spin excitation ISTS was also demonstrated on magnetic molecules [34], where the spin excitations of single Fe(II)-Phthalocyanine molecule could be observed when the molecule was adsorbed on the oxidized Cu(110) surface.

Finally, using the combination of SP-STS and ISTS, it has been demonstrated that the spin state of individual magnetic atoms cannot only be read out, but also controlled by the STM tip [35]. To this end, the spin polarized current from a tip that is terminated by a magnetic atom is passed through the target adsorbate. If the excitation rate is higher than the relaxation rate, the occupation distribution of the spin states will be driven away from thermal equilibrium. The spin dependence of ISTS was investigated in detail both theoretically and experimentally in [36]. The investigation of spin dynamics was developed further, when ISTS was combined with time resolved measurements in [37]. There, the spin relaxation times of individual atoms were measured by employing a pump-probe scheme of current pulses, detecting the relaxation of the shifted occupation distribution for varying delay times between the pump pulse and the probe pulse.

While far from complete, the above discussion gives a first overview of previous SP-STM and spin-excitation ISTS work on magnetic species. The objective of this thesis is to contribute to that work by filling some of the gaps and advancing our understanding towards future technological applications. In particular, this thesis has the following goals

- Investigation of individual magnetic atoms on a *semiconducting* substrate with spin-sensitive STM techniques.
- Comparison of the magnetic properties of one type of magnetic atom (Fe) for different metallic and semiconducting substrates.
- Investigation of the long range indirect exchange interactions of artificially constructed structures of two or more magnetic atoms.

- Construction of a magnetic nanostructure to serve as a proof-of-principle model for a spin-logic function.

Where possible, the experimental findings are complemented by simple model calculations performed by the author or more advanced calculations performed by collaborators. In detail, this thesis is organized as follows:

In the first part of **chapter 2**, the principle of STM as well as its different modes of operation and their spin-sensitive variants are introduced. With its emphasis on the methodology, this chapter is meant to prepare the ground for the description of the experiments in the subsequent chapters. In the second part, the low temperature, ultra-high vacuum STM facility with a superconducting magnet, that was used to obtain all data presented in this thesis, is introduced. The design and construction of a special purpose STM head is also described.

In the first part of **chapter 3**, model calculations of the spin excitations of isolated and coupled quantum spins, are described. These are used in the analysis of the experimental results obtained on the semiconducting substrate in chapter 4. In the second part, model calculations of exchange coupled ensembles of quasi-classical magnetic moments are presented. These are used in the analysis sections of chapters 5 and 6.

The spin excitations and the magnetization behavior of single Fe atoms on the InSb(110) surface are investigated in **chapter 4**. The Fe atoms are coupled to a two-dimensional electron system, which is induced at the sample surface by positively charged adsorbates. The Fe atoms are shown to behave like isolated quantum spins with spin quantum number $S = 1$, which are subject to substantial in-plane and out-of-plane magnetic anisotropy. Their behavior is described by model calculations. To complement the experiments, the results are compared to density functional calculations performed by S. Schuwalow and F. Lechermann.

In the first part of **chapter 5**, single atom magnetization curves are used to determine the statistical distribution of the effective magnetic moments of individual Fe atoms on the Cu(111) surface. In the second part, ISTS measurements of the spin excitations of Fe atoms on Cu(111) and Ag(111) are presented. The Landé g-factor and magnetic anisotropy of the localized magnetic moment as well as the energy dependent line width of its excited state are investigated. To complement the experiments, the results are compared to KKR and tight binding model calculations performed by S. Lounis, A.T. Costa and D. L. Mills.

The first part of **chapter 6** is devoted to the determination of the indirect exchange coupling strength in pairs of Fe atoms on Cu(111). Single atom magnetization curves are used to extract the coupling energies as a function

of separation. The results are compared to KKR calculations performed by S. Lounis. In the second part, larger magnetic nanostructures are constructed with the STM and their magnetization behavior is investigated. Making use of the pair couplings measured in the first part and the parameters for single atoms measured in chapter 5, their magnetization curves are compared to Ising model calculations. In the third part of **chapter 6**, the insight gained in the first and second part is used to construct a proof-of-principle spin-logic gate. Atomic manipulation is used to assemble the gate structure, which is based on the indirect exchange coupling between the atoms, as well as to ferromagnetic Co nanoislands. The magnetization of the nanoislands can be set by an external magnetic field so they can serve as stable inputs to the gate. For its operation, the structure uses transport of spin information along exchange coupled chains of magnetic atoms as well as spin frustration to act as a boolean OR gate. The experimental results are complemented by Ising model calculations.