Magnetism of a single atom

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Introduction

> *But I am not afraid to consider the final question as to whether, ultimately — in the great future — we can arrange the atoms the way we want; the very atoms, all the way down!*
>
> **R. P. Feynman**

Little could he know, when Feynman gave his classic lecture at the 1959 Annual Meeting of the American Physical Society [1], that this 'great future' was only just over 30 years away [2, 3]. And great it is. The two and a half decades following the Nobel Prize winning invention of the Scanning Tunneling Microscope [4] have not only witnessed the first demonstration of artificial atom arrangement (or atom *manipulation*, as it was eventually called), they also brought some of its incredible creations, including an atomic 'fence' for confining surface electrons [5] and an early dynamic molecular computer [6]. Having achieved such meticulous control over the atoms themselves it is only natural to ask the next question: can we also control the intrinsic properties of an atom? Here we will focus on one such property: the magnetism of a single atom.

Although magnetism, in the sense of a material property, has been around for technological purposes since medieval times (and even much longer than that as a topic of scholarly debate), its origin can be traced all the way down to the atomic scale. Whether a material is magnetic depends on whether each of its constituent atoms is magnetic. Further classifications such as ferro-, antiferro- or paramagnetism indeed do relate to the way the atoms interact and are oriented with respect to each other on a larger scale, but the overriding requirement for a material to be magnetic is that its atoms be magnetic.

Then, what makes an atom magnetic? In quantum-mechanical terms this is determined by the net amount of spin of its electrons. For a filled electronic shell this is zero, but partially filled shells should in principle always have a non-zero net spin according to Hund's rules. When the atom binds to other atoms – either through covalent bonds in a molecule or through metallic bonds in a lattice – in the case of s and p orbitals this net spin is often consumed by the formation of these bonds. Having more closely localized orbitals, many d and f materials are indeed found to be magnetic. This demonstrates the enormous significance of spin: while its algebra is so simple and elegant as to serve in numerous textbook examples of basic quantum mechanics, the electron spin is responsible for all solid-state magnetism and plays a crucial role in chemistry.

Apart from its fundamental relevance, spin draws much attention as it is proposed as a candidate for carrying information in many designs of future computation and data-storage devices [7, 8]. Therefore, many experiments in condensed matter are aimed at (1) isolating a single spin, (2) finding a way to determine its orientation, i.e. 'reading' it and (3) manipulating its orientation or 'writing' it. Each of these steps has been achieved separately in nanofabricated heterostructures, where individual electrons are confined on artificially crafted two-dimensional quantum dots – a field that has great potential for eventually harnessing the electron spin for technological purposes [9, 10].

Yet, in order to be able to study a spin in a more natural environment, e.g. as a magnetic impurity interacting with a metal, one would have to have access to individual magnetic atoms. A tool that is very well suited for this task is magnetic resonance. Although conventional Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR) – where one measures the absorbance of RF-radiation incident onto a sample – are only sensitive enough as to detect large ensembles of spins, some ingenious methods were developed that convert this technique into detecting a single spin. One of these methods is based on combining ESR with the Scanning Tunneling Microscope (STM) [11]. In this experiment a resonating spin, oscillating at the Larmor frequency, produces a specific AC-signal in the tunneling current. Another beautiful experiment exists by the name of Magnetic Resonance Force Microscopy (MRFM) [12], where the polarization of a spin is recognized by its effect on the oscillating frequency of a magnetic cantilever. In this configuration the spin can be 'written' by means of well-timed RF-pulses.

A fully electronic way of spin readout is provided by the field of spin-polarized STM, where magnetic tips are used to filter out one spin polarization from the tunneling electrons [13, 14]. Although single spin resolution has not yet been obtained with this technique, it has developed into a standard tool for investigating magnetism on the nanoscale.

In this thesis I present a study of atomic spins by means of the *excitations* that can be induced in them. For this purpose we use an adoptation of a technique named Inelastic Electron Tunneling Spectroscopy (IETS), which is known best for its strength in detecting vibrational modes in ensembles of molecules trapped within a planar junction [15]. Its principle is based on observing small changes in the conductance of the junction at those voltages where the tunneling electrons have just enough energy to perform specific inelastic (in this case vibrational) excitations. Single molecule resolution has been obtained in an STM configuration [16] and later by means of a Mechanically Controllable Break-junction (MCB) [17].

Only recently did similar spectroscopic analysis of inelastic excitations become accessible on atomic spins [18] and structures consisting of multiple atomic spins [19]. When used for these purposes we will refer to the technique as *Spin Excitation Spectroscopy* (SES). This tool forms the basis for many new experiments described throughout this thesis. The outline of the thesis is as follows.

In **chapter 1** we review the technical equipment needed for high energy resolution SES measurements: an STM cooled to liquid ^{3}He temperatures, capable of generating high magnetic fields. Specifically we will discuss one such experimental set-up located at the Leiden Kamerlingh Onnes Laboratory, in the development of which I have been involved for several years. Although nearing completion, this apparatus is not yet in a proper condition for performing SES. Experiments presented in subsequent chapters were all carried out in a different ^{3}He STM system based at the IBM Almaden Research Center.

Chapter 2 gives a detailed description of the experimental techniques used, as well as a characterization of the specific system of choice for our experiments: magnetic *d*-shell atoms evaporated onto a monolayer of copper-nitride (Cu_2N) on Cu(100). We will focus on the principles of SES and the possibilities of atom manipulation on this specific surface.

Chapter 3 is devoted to the magnetic anisotropy that an atomic spin experiences when it is placed onto a surface. Anisotropy is what makes a spin align (or *magnetize*) in a certain direction; a property that is of great importance for technological reasons such as non-volatile magnetic data storage. By placing manganese (Mn) and iron (Fe) atoms onto Cu_2N and following the evolution of their spin excitations as magnetic fields are applied in various directions, we find that this surface forms a strongly anisotropic environment for the spins of these atoms [20]. A comparison of the results to Density Functional Theory (DFT) calculations suggests that this may be explained in terms of the atoms being incorporated into a surface molecular network.

In **chapter 4** a third atom species is studied: cobalt (Co). In sharp contrast to both Mn and Fe, measurements performed on Co indicate the appearance of a remarkable resonance which we attribute to the Kondo effect: a many-body effect arising from the interaction of a localized spin with a bath of electrons. A brief introduction into this effect is given at the beginning of the chapter. Based on an analysis along the lines of chapter 3 we present an interpretation as to why this resonance occurs specifically on Co. We show that the magnetic anisotropy of the Cu_2N surface plays a crucial role in the question as to whether a spin becomes Kondo-screened or not. We conclude this chapter by investigating the effects of spin-coupling on the Kondo effect by placing other magnetic atoms close to the Co atom. An analytical model is presented, combining anisotropy, spin-coupling and the effect of a magnetic field, with which we can identify each excitation occurring on these structures with astounding precision.

Finally, **chapter 5** offers a future perspective. Several additional studies were initiated from which no clear conclusions can be drawn at this point. Yet a first step in their analysis is presented which may be useful in designing further experiments. These studies include an investigation into the physics behind the mechanism of spin-coupling on Cu_2N as well as a an attempt to create a spin-polarized tip by picking up a single magnetic atom.

Each of these experiments provides new insights into the physics of atomic scale magnetism that are of importance for scientific as well as technological reasons. But above all they are fun. Never before did we have such an incredible degree of control over individual atoms and their spins. It enables us to perform the most basic experiments that one could think of doing with atomic magnets, and almost all of the spin excitations encountered while doing them can be modelled extremely well by elementary quantum mechanics. Few experiments can be as suited to get a *feel* for the peculiar quantum mechanical property named 'spin' as the ones described here.