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Review article

Probing magnetic excitations and correlations in single and coupled spin systems with scanning tunneling spectroscopy

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ABSTRACT

Spectroscopic measurements with low-temperature scanning tunneling microscopes have been used very successfully for studying not only individual atomic or molecular spins on surfaces but also complexly designed coupled systems. The symmetry breaking of the supporting surface induces magnetic anisotropy which lead to characteristic fingerprints in the spectrum of the differential conductance and can be well understood with simple model Hamiltonians. Furthermore, correlated many-particle states can emerge due to the interaction with itinerant electrons of the electrodes, making these systems ideal prototypical quantum systems. In this manuscript more complex bipartite and spin-chains will be discussed additionally. Their spectra enable to determine precisely the nature of the interactions between the spins which can lead to the formation of new quantum states which emerge by interatomic entanglement.

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1. Introduction

The transfer of electrons between metallic leads separated by vacuum or an insulating gap is classically forbidden. However, it becomes possible if the size of the gap is reduced to the scale of a few Angstroms due to the tunneling effect. This entirely quantum mechanical effect, which allows the electrons to cross the forbidden region, was already discussed in the early days of quantum mechanics [1] and first observed in the 1960s on planar superconducting – oxide – normal conducting junctions [2,3].

In general, the electron transport in such tunnel junctions can be divided into two distinct classes: Elastic tunneling in which an applied bias drives electrons from the many states of one electrode to cross the junction without interaction with the local environment and inelastic tunneling, where the electrons interact with the junction environment and change their energy, phase, or angular momentum. These inelastic processes leave characteristic fingerprints in bias dependent conductance measurements. In particular, when discrete states are excited during tunneling and the tunneling electron looses partly its kinetic energy, a bias threshold voltage can be observed below which the inelastic process cannot occur (Fig. 1). In this sense inelastic tunneling spectroscopy (IETS) is complementary to far-field methods such as high resolution electron energy-loss (HREELS), infrared reflection adsorption (IRRAS), Raman spectroscopy, or inelastic neutron spectroscopy [4,5] and has been performed in planar tunnel junctions to detect vibrational excitation modes of molecules embedded in the junction for almost 50 years [6–11]. Remarkably, besides molecular vibrations, excitations due to the interaction of electrons with localized magnetic impurities have already been studied in these pioneering days leading to the discovery of anomalies in the density of states very close to the Fermi energy, which was shown to be due to the formation of a Kondo state and inelastic spin-flip excitations [12–16].

While planar tunnel junctions have the disadvantage of averaging over an ill-defined contact area, the development of the scanning tunneling microscope (STM) by Binning, Rohrer, Gerber, and Weibl in the early 1980s [18–20] opened a entirely new world for tunneling experiments. Very soon it became clear that the STM, with its capability to atomically resolve metallic and semiconducting surfaces, would become a powerful tool for the analysis of surfaces and nanoscale structures down to the single molecule or atom level. Its discovery was awarded with the Nobel prize in a surprisingly short time of only 4 years after its first successful demonstration.

In the early days of STM, collective vibrational excitations at the surface of graphite were detected [21], however, it was clear that the true capability of the STM would lie in combining its spectroscopic possibilities with its inherent atomic resolution. Nevertheless, it took about 15 years of technology development before the mechanical stability and electronic sensibility of the STM at cryogenic temperatures and in ultrahigh vacuum was high enough to make this dream reality.

The year 1998 brought two important experimental breakthroughs: The group around Wilson Ho at the Cornell University showed for the first time that IETS was possible on the single molecular level using the spatial resolution of the STM [22]. In their experiment they detected the vibrational excitations of an isolated acetylene (C_2H_2) molecule adsorbed on a Cu(100) surface. The detection of mechanical excitation in molecular systems, has since been applied to many quite different molecular systems ranging from diatomics like carbon monoxide [23,24], metal hydride molecules [25], and molecular hydrogen [26–28] to complex molecules like porphyrins [29] and C_{60} bucky balls [30]. However, importantly for the work discussed in this manuscript, inelastic excitations can also be observed on individual spin systems as discovered by Andreas Heinrich and co-workers at IBM Almaden first on Mn atoms adsorbed on patches of Al_2O_3 on a NiAl surface [31]. As we will discuss in the following, spin excitation spectroscopy gives unparalleled access to the quantum nature of individual and coupled spin systems enabling the determination and manipulation of their spin states, their magnetic anisotropy, and their coupling with the environment; properties which are actually mutually interdependent.

The second breakthrough was the detection of the spectroscopic signature of the correlated many-particle Kondo state of individual magnetic atoms adsorbed on non-magnetic metal substrates. This discovery was made almost simultaneously by the group around Wolf-Dieter Schneider at the University Lausanne [32][1] and the group around Michael Crommie at the University of Boston [38].

These two hallmarking observations are the foundation on which the work presented here is based. Both rely on the interaction of individual spins, i.e. atoms or molecules which have a magnetic moment, with the local environment as is schematically illustrated in Fig. 2. A paramagnetic atom with a total spin $S > 1/2$ has $2S + 1$ eigenstates which are indistinguishable in the gas phase when no external magnetic field is applied. Upon absorption on the surface this situation changes. When the atom is physisorbed, the out-of-plane direction forms a distinct axis, different from all other directions. This symmetry breaking is the origin of magnetic anisotropy which lifts the degeneracy and defines the stability of a spin in a preferred direction [41] (Fig. 2a). In the case the atom is chemisorbed onto the surface, that means it forms covalent chemical bonds and is rather incorporated into the surface, complex molecular networks might form, further reducing the system's symmetry. Additionally, spin–orbit coupling, charge transfer, and delocalized spin polarization in the substrate influences the effective magnetism of the atom [42].

The influence of the magnetic anisotropy on the tunneling spectra will be briefly discussed in Section 2. Here, we will additionally see how the strength of the direct exchange coupling between the localized magnetic moment and the itinerant electron bath of the substrate modifies the magnetic anisotropy via virtual coherences between the eigenstates [43,44].

[1] Note, that due to newer measurements which revealed that single Ce adatoms on Ag(111) are even at 5 K still very mobile [33–36], the original publications was presumably measured on a small Ce cluster, which can indeed show a Kondo state [37].