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Consequences of Kondo exchange on quantum spins

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ABSTRACT

When individual quantum spins are placed in close proximity to conducting substrates, the localized spin is coupled to the nearby itinerant conduction electrons via Kondo exchange. In the strong coupling limit this can result in the Kondo effect — the formation of a correlated, many body singlet state — and a resulting renormalization of the density of states near the Fermi energy. However, even when Kondo screening does not occur, Kondo exchange can give rise to a wide variety of other phenomena. In addition to the well known renormalization of the g factor and the finite spin decoherence and relaxation times, Kondo exchange has recently been found to give rise to a newly discovered effect: the renormalization of the single ion magnetic anisotropy. Here we put these apparently different phenomena on equal footing by treating the effect of Kondo exchange perturbatively. In this formalism, the central quantity is ρJ, the product of the density of states at the Fermi energy ρ and the Kondo exchange constant J. We show that perturbation theory correctly describes the experimentally observed exchange induced shifts of the single spin excitation energies, demonstrating that Kondo exchange can be used to tune the effective magnetic anisotropy of a single spin.

1. Introduction

The development of electron paramagnetic resonance made it possible to study the spin transitions of a variety of spin systems, such as paramagnetic molecules [1] and transition metal dopants in insulating hosts [2]. This led to the development of a single spin Hamiltonian, where the influence of both the Zeeman effect and magnetic anisotropy determine the energy spectrum and spin selection rules. Interestingly, the same type of Hamiltonian was successfully used to describe the quantum spin tunneling phenomenon [3] discovered in magnetic molecules with large spin.

Thanks to the tremendous progress in nano-fabrication and nano-manipulation, it is now possible to produce devices where an individual quantum spin can be probed. A single magnetic molecule can be placed in a nanoscale junction [4–7], on top of a carbon nanotube [8], or on a surface [9,10]. A particularly suitable instrument for studying spin systems at the atomic scale is a scanning tunneling microscope (STM) because it permits not only probing but also manipulation of the spin of individual magnetic atoms deposited on surfaces [11–13], which thereby takes us closer to the Feynman's dream of engineering matter at the atomic scale. Interestingly, magnetic adatoms can also be described with the same type of single ion Hamiltonian as magnetic dopants in insulating hosts and single-molecule magnets [14]. These systems have attracted significant attention because they represent the ultimate limit of magnetic objects where classical or quantum information can be stored [15,16].

Manipulation and readout of the information requires integration of these quantized spins (e.g. magnetic molecules, spin chains, or magnetic atoms) into a device. In the case of quantum spins in contact with a conducting electrode, found in many proposed device geometries [17], the question of how exchange interaction with the conduction electrons changes the spin dynamics of the quantized spin naturally arises. In the strong coupling regime, the Kondo effect is known to quench the magnetic moment of the quantum spin. This comes together with a strong renormalization of the states at the Fermi energy, which in STM measurements is revealed as a Fano lineshape in the low bias conductance [18,19].

More recently, the tunneling spectra of magnetic adatoms [20,21,14, 22–27] and molecules [28,29] have been found to display inelastic spin transitions, revealed as magnetic field-dependent steps in the differential conductance dI/dV (see Fig. 1). Fitting the energies of these steps to an effective spin Hamiltonian provides a quantitative understanding of the magnetic anisotropy [21,14,30,24,27]. The steps in dI/dV are equivalently peaks in d^2I/dV^2, whose half width at half maximum

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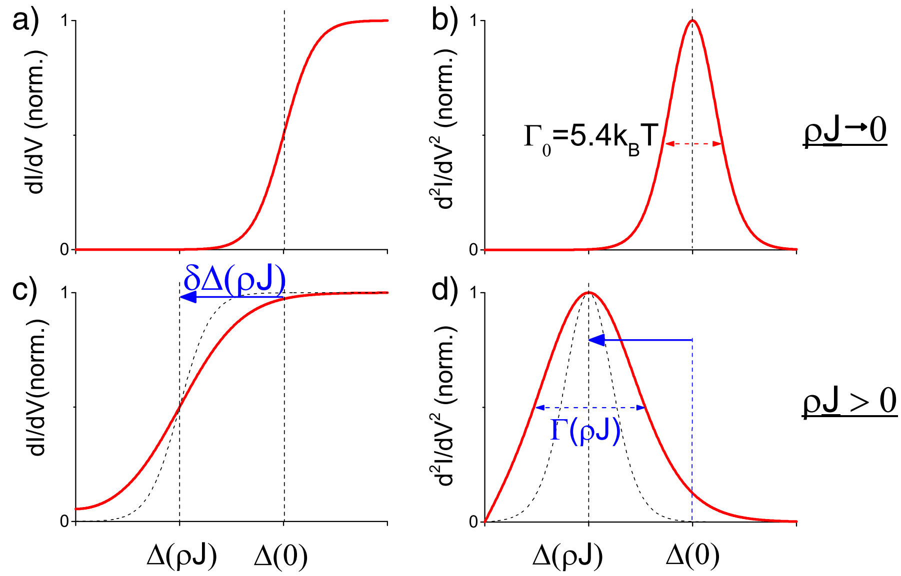

Fig. 1. Main effects of the Kondo coupling on the electronic transport. The inelastic spin-flip transitions are revealed as thermally broadened steps in the dI/dV [panels a) and c)], and peaks (or dips for negative voltage) in the d^2I/dV^2, panels b) and d). As the Kondo coupling grows (ρJ increases, lower panels), the inelastic step shifts to lower energies and it broadens. The black-dotted lines in panels c) and d) represent the shapes of the dI/dV and d^2I/dV^2 respectively considering only the shift $\delta\Delta(\rho J)$ in the transition energy and neglecting the change in the broadenings $\hbar\Gamma^{SS}_{n\rightarrow m}$, Eq. (12), while the new shapes appear in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

comes from thermal and instrumental smearing as well as the broadening of the transition due to the finite spin lifetime.

Importantly, Kondo exchange influences the quantum spins even in the absence of Kondo effect, i.e. when no Kondo feature is seen in the conductance spectrum. For instance, because of the Kondo exchange, the single-spin states acquire a finite lifetime [31,30]. In the case of magnetic adatoms, fast spin relaxation times of the order of 200 fs, have been estimated from the full width at half maximum of the d^2I/dV^2 peaks of Fe atoms on a metal [32], while direct STM measurements of the relaxation times of Fe on top of a Cu_2N substrate, possible using of pump and probe techniques [33], has demonstrated lifetimes up to 50 ns.

The Kondo exchange can actually arise from two different physical mechanisms. First, direct ferromagnetic exchange is possible between the itinerant electrons of the surface and the d or f levels of the atomic spin. This type of exchange is responsible, for instance, for the spin splitting of the conduction s-type band in diluted magnetic semiconductors [34]. Second, if the surface electrons hybridize with the localized d or f orbitals, the so called kinetic exchange [35] results in an antiferromagnetic Kondo coupling, in the limit where classical charge fluctuations of the atom are frozen. This second mechanism is almost ubiquitous and can coexist with the first, giving rise to a reduced total exchange due to their opposite signs.

In this work, we emphasize the central role of the Kondo exchange coupling in a vast variety of available experimental observations of magnetic adsorbates, and thus, we demonstrate that it is possible to quantify its effects. Table 1 shows a summary of physical quantities

Table 1
Physical quantities associated with the Kondo exchange coupling J between a magnetic impurity and conduction electron spins. All of them are determined by the product ρJ, with ρ as the substrate density of states at the Fermi level.

Quantity	Symbol	Equation	Reference
g factor	g^*	$g\left(1-\frac{g_e}{2g_A}\rho J\right)$	[39]
Spin relaxation	$\hbar T_1^{-1}$	$(\rho J)^2 S^2 \Delta$	[30]
Spin decoherence	$\hbar T_2^{-1}$	$(\rho J)^2 S^2 k_B T$	[16]
Indirect exchange	J_{RKKY}^{-1}	$(\rho J)^2$ F(r)	[36]
Exchange shift	$\delta\Delta$	$\propto(\rho J)^2 ln\frac{2W}{\pi k_B T}$	[37]
Kondo Temperature	$k_B T_K$	$We^{-1/(\rho J)^2}$	[38]

associated to the spins of a few magnetic impurities that are modified by the exchange coupling to the conduction electrons. Notice that all of them depend on the product of the electrode density of states at the Fermi level, ρ, and the Kondo exchange coupling J. The effect can be classified then according to the order in ρJ. To first order it leads to a modification of the effective g factor, an effect akin to the Knight-shift in metals. To second order, it leads to finite decoherence and lifetimes [30,16,32,33] or the indirect exchange due to the RKKY interaction [36]. In addition to these well known results, the Kondo exchange coupling also leads to another second order effect recently observed in magnetic atoms: the renormalization of the magnetic anisotropy [37]. Perturbation theory breaks down either when ρJ is not a small parameter, in the case of ferromagnetic J, or below the Kondo temperature [38], $k_B T_K = We^{-1/(\rho J)}$, in the case of antiferromagnetic J.

2. Theoretical approach

2.1. Hamiltonian model

Our starting point is the Hamiltonian [30,40,41]

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_{\rm surf} + \mathcal{V}_{\rm kondo}, \quad (1)$$

where $\mathcal{H}_S$ is a single spin Hamiltonian discussed below, and $\mathcal{H}_{\rm surf}$ describes the independent electrons of the surface

$$\mathcal{H}_{\rm surf} = \sum_{k,\sigma} \epsilon_{k,\sigma} c^\dagger_{k\sigma} c_{k\sigma}, \quad (2)$$

with $c^\dagger_{k\sigma}$ ($c_{k\sigma}$) the creation (annihilation) operator of an electron in the surface with momentum k, spin σ and single particle energy $\epsilon_{k\sigma}$. Except in Sec. 3, we consider non-magnetic surfaces where $\epsilon_{k,\sigma} = \epsilon_k$. Finally, $\mathcal{V}_{\rm kondo}$ describes the local exchange interaction between the surface electron density and the magnetic adatoms:

$$\mathcal{V}_{\rm kondo} = \frac{1}{2} \sum_{\vec{k},\vec{k}',\sigma,\sigma'} J_{\vec{k},\vec{k}'} \vec{S} \cdot \vec{\tau}_{\sigma,\sigma'} c^\dagger_{k\sigma} c_{k'\sigma'}, \quad (3)$$

with $\vec{\tau}$ as the vector of Pauli matrices (with ± 1 eigenvalues) and $J_{k,k'}$ as the s–d exchange interaction between the local spin $\vec{S}$ and the transport