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Pulling Apart Molecular Magnetism

A single molecule constitutes the ultimate nanoscale object through which electronic transport can take place. Being so small, molecules share many characteristics with atoms, such as discrete quantized energy spectra and angular momentum, yet at the same time are large enough to be mechanically deformed and chemically attached to metallic leads with which they can exchange electrons. Can we control these mechanical and exchange interactions and, if so, what new phenomena arise? On page XXX of this issue, Parks *et al.* (*1*) show how one can tune magnetism and quantum many body phenomena by precise mechanical manipulation of single molecule nanostructures at the sub-atomic scale.

Basic quantum mechanics states that electrons confined within a potential "box" can have only a discrete set of allowed energies. Such a discrete energy spectrum depends both on the strength of the confining potential and the boundary conditions imposed on the electron wave functions. For symmetric potentials, such as the Coulomb potential from a nucleus, the quantum energy states exhibit orbital degeneracies (the famous *s*, *p*, *d*, *f*,... atomic shells). Pauli's exclusion principle then dictates that at most two electrons, with total spin zero, can occupy a given energy state. But in the case of orbitally degenerate states, two or more electrons may be allowed to align their spins by occupying different states, minimizing their Coulomb repulsion. This phenomenon is exemplified by Hund's rule. Therefore orbital degeneracies are of fundamental importance for the existence of atoms with large magnetic moments (spin, $S \geq 1$) and play an important role in molecular magnetism.

Surrounding such magnetic atoms with other atoms and ligands to form a molecule alters the boundary conditions for the quantum box. This can lead to a splitting of the different orbital and spin states, depending on the symmetry properties of the atom's environment. This in turn results in a modification of the magnetic properties of the entire system. In their experiment, Parks *et al.* investigate the magnetic states of individual S=1 molecules placed in between two electrodes in a metal break junction. By stretching the electrodes, they explore the resulting symmetry breaking effects of this mechanical action on the conduction properties through the molecule. Their study focuses on the magnetic anisotropy of the molecules, that is, how the energy differences among the different S_Z states ($S_Z = 0$, ± 1) change for different degrees of stretching.

Now, getting to know the spin configuration of an individual molecule in a changing environment is not a trivial task, but here is where quantum many body physics comes to the rescue. A well-known correlated electronic transport phenomenon, called the Kondo effect (*2*), is exquisitely sensitive to the presence of spin and orbital degeneracies in quantum boxes. In its simplest incarnation — the spin-½ Kondo effect — an isolated spin ½ magnetic impurity is antiferromagnetically screened by the conduction electrons in a host metal. The net result is the formation

of an entangled singlet state (S=0) between the metallic leads and the magnetic impurity. In the case of quantum boxes connected to metallic leads, the Kondo effect results in a continuous exchange of spin up and down electrons between the leads and the box (*3, 4*). This exchange enables highly efficient electronic transport through the box at zero bias, i.e. a single conductance peak in *dI/dV at V=0* (see figure). This occurs in an otherwise insulating regime due to the Coulomb interaction between the incoming electrons and the existing electrons in the box (a phenomenon known as Coulomb blockade). The binding energy of this correlated state is characterized by a temperature scale called the Kondo temperature, T_K. Key to this process is that the spin ½ impurity state is two-fold degenerate (both $S_Z=\pm\frac{1}{2}$ spin orientations have the same energy). Creating an energy splitting between these spin states by, for example, applying a magnetic field, leads to a splitting of the Kondo resonance as soon as the splitting exceeds $\sim T_K$.

The Kondo effect becomes more interesting for larger spins. It turns out that, at zero temperature, a number 2S of channels in the leads are required to completely screen an isolated spin S (*5*). In the case of a spin ½ impurity, this means just one screening channel, which typically consists of linear combinations of conducting states in the two metallic leads to which the molecule is coupled. For larger spin, for example S=1, things get trickier. Each of the two screening channels (2S=2) will have in general a different coupling to the magnetic impurity. Since the Kondo temperature associated with each screening channel is an exponential function of the coupling strength, this means that there will be two Kondo temperatures, T_{K1} and T_{K2}, which can be very different. Therefore, in general there will be a temperature regime T_{K1} << T < T_{K2}, in which only one out of the two spin ½ degrees of freedom in the molecule will be screened. This results in the so-called underscreened Kondo effect. The S=1 underscreened Kondo effect has a very different temperature dependence and scaling laws than the ordinary S=½ Kondo effect (*6*), and can therefore be experimentally distinguished. The strategy then is: measure the differential conductance of your molecular device. If you see a Kondo peak, then its temperature dependence will tell you the spin of your molecule.

The theoretical predictions for this S=1 underscreened Kondo effect were very recently confirmed in a different experiment (*7*). Parks *et al.* provide an independent report. What is completely new in the Parks *et al.* study is that they can lift the degeneracy among the three triplet states by mechanically pulling apart the metal leads connected to the molecule. Such molecular stretching results, in this case, in a S_Z = 0 ground state, with the two other triplets ($S_Z = \pm 1$) being higher in energy by an amount called the magnetic anisotropy energy, *D* (see Figure). This anisotropy energy is tunable, because the stretching is controlled with an amazing sub-angstrom precision. Once the energy splitting is comparable to T_K, the degeneracy is broken significantly enough that the Kondo effect ceases to occur. Remarkably, Parks *et al.* observe a gradual splitting of the Kondo conductance peak as the distance between the electrodes is varied, in precise agreement with the prediction.

Other experiments had already used the Kondo effect as a spectroscopic tool to study magnetic anisotropy in magnetic atoms connected to an environment (*8*). However, in these previous studies the atoms had a half-integer spin (S=3/2), for which Kramers theorem guarantees partial spin degeneracy in the presence of time reversal symmetry, and therefore an unsplit Kondo peak at zero magnetic field. The new study by Parks *et al.* thus constitutes the first case where a Kondo effect associated with a magnetic atom can be dramatically tuned by purely mechanical means, resulting in a new degree of control to investigate Kondo resonances and splittings at zero magnetic field. Moreover, having two independent knobs to tune the energy spectrum — mechanical pulling for the anisotropy, and magnetic field for the Zeeman splitting — the authors were able to further confirm the theoretically expected behavior for the Kondo resonance peak splitting under simultaneous magnetic field and mechanical stretching.

The results by Parks *et al.* show that the Kondo effect, one of the most researched quantum many body phenomenona in strongly correlated physics, keeps surprising us in all its variations (spin, orbital, multichannel, and here underscreened, to name a few), and now too as a superb spectroscopic tool for non-trivial interrogations of the magnetic behavior of individual molecules. The possibility to mechanically tune the magnetic anisotropy of individual molecules opens the door to systematic investigations and detailed theoretical comparisons to quantum chemistry models, which will enormously broaden our knowledge of molecular magnetism. This has interest beyond the fundamental science level, and may play an important role in the use and manipulation of nanoscale magnets for spintronics and quantum information processing applications.

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9.   I acknowledge useful discussions with R.C. Ashoori and D. Goldhaber-Gordon.

Figure Caption:
Upper half: For the unstretched molecule, the three triplet states are degenerate, leading to a Kondo peak in the differential conductance, *dI/dV*, peak at zero source-drain voltage bias, *V*. Bottom half: mechanically stretching the molecule splits the triplet states degeneracy, thus leading to a split the Kondo peak.