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## Section number - Molecule on tip as a quantum sensor

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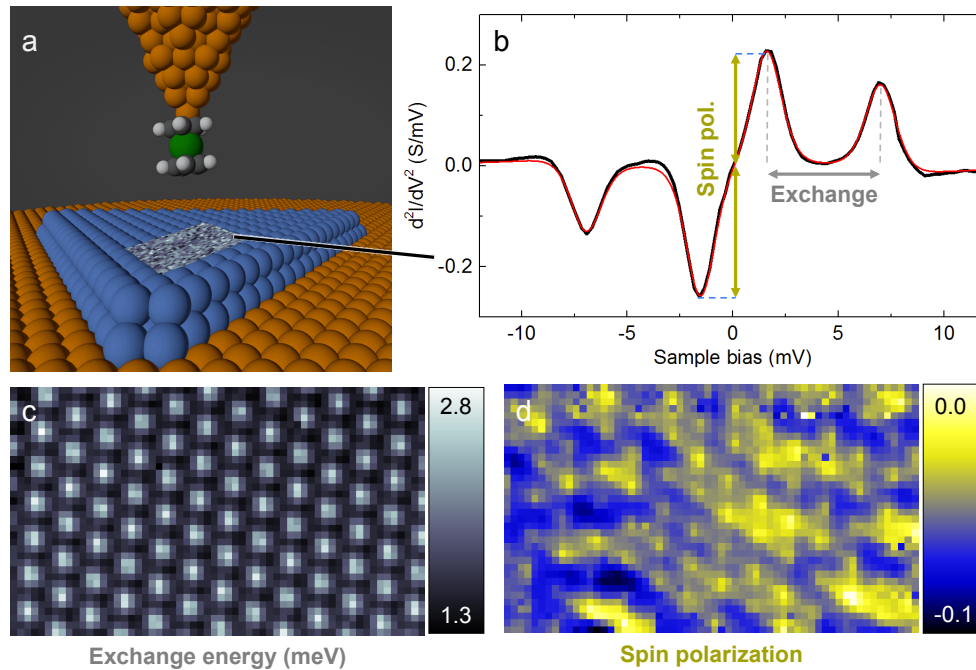
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### Status

The field of ultra-dense storage technology has driven the development of spin-sensitive techniques aimed at manipulating and addressing single spins within complex magnetic structures. Among these techniques, scanning tunneling microscopy (STM) stands out as the only method capable of detecting spins and imaging magnetic properties with atomic-scale precision. Enhancing spin sensitivity in STM is therefore pivotal for advancing research in this domain. The first atomic scale detection of a spin with STM dates back almost thirty years and involved observing zero-bias anomalies in the differential conductance of quantum magnetic impurities [1-3]. Concomitantly, spin-polarized STM (SP-STM) played a crucial role by using tunnel magnetoresistance to achieve spin contrast in images, enabling direct visualization and manipulation of surface magnetism with high spatial resolution [4].

In 2004, quantum spin sensing entered the realm of STM with spin excitation spectroscopy [5]. This technique utilizes electrically-driven spin excitations to probe and manipulate the spin states of quantum objects, such as single atoms or molecules. These objects can serve as sensitive quantum spin sensors due to their interactions with their local environment via mechanisms like exchange, superexchange, or Ruderman-Kittel-Kasuya-Yosida interactions. These interactions induce splitting and energy shifts in their spin states, which can be precisely tracked using spin excitation spectroscopy [6,7]. Once characterized, these objects can function as sensitive quantum spin sensors. However, several factors limit quantum sensing with STM. Atoms and molecules, with few exceptions for the latter, must be isolated from conducting surfaces using thin insulating buffers like MgO or Cu<sub>2</sub>N layers to preserve their intrinsic quantum properties and prevent the quenching of spin excitations. Consequently, studies are typically confined to these buffered surfaces. Additionally, spin sensitivity is affected by the temperature of the tunnel junction, which smears the spin-excited spectra and restricts detection to exchange fields of >1 T in conventional low-temperature STM setups. The sensor-to-target distance is crucial, often needing to be below 200 pm. The recent development of electron spin resonance in STM (ESR-STM) has significantly enhanced spin sensitivity and broadened the applicability of quantum spin sensing at the atomic scale [8]. ESR-STM “circumvents” temperature smearing, achieving a resolution of >10 mT and enabling detection of dipolar interactions at sensor-to-target distances above 1 nm [9].



**Figure 1** (a) Nickelocene-tip schematic. The energy landscape of a Nickelocene-tip is modeled using the spin Hamiltonian  $H=D S_z^2-J \mathbf{S} \cdot \mathbf{S}_{\text{sample}}$ , where  $J$  represents the Heisenberg interaction extending into the vacuum, coupling the spin  $\mathbf{S}$  of Nickelocene to the sample spin  $\mathbf{S}_{\text{sample}}$ . (b) Electrically-driven spin excitations associated with this Hamiltonian produce inelastic tunneling spectra in the form of  $d^2I/dV^2$  versus bias  $V$ , which can be analytically modeled (solid red line) [6,7] to extract magnetic information from the sample, including the exchange energy and the spin polarization of the tunnel junction. (c) and (d) Spatial maps of the exchange energy and spin polarization, respectively, are generated by acquiring a three-dimensional dataset, or voxel, in the form of  $d^2I/dV^2(x,y,V)$  at various tip positions  $(x,y)$  with a fixed distance from the sample. The exchange energy and junction spin polarization at each lateral tip position are then determined by fitting the spectra. Voxel imaging enables comprehensive extraction of magnetic information from measurements. It effectively distinguishes magnetic effects from electronic effects, ensuring clarity in experimental interpretation and facilitating theoretical comparisons.

### Current and Future Challenges

To broaden the applicability of quantum sensing with STM, it is essential to make it accessible to a wide range of systems, including magnetic surfaces. Recent studies have demonstrated that, unlike atoms, certain molecules can exhibit efficient spin excitations even when adsorbed on metal surfaces. Consequently, molecules are more suitable for spin sensing in STM than atoms. Moreover, a molecule can be attached to the tip apex of the STM and its status carefully monitored. Over the past decade, the decoration of metal probe tips with molecules intentionally picked up from a surface has proven to be a powerful method to enhance the measurement capabilities of STM. The degrees of freedom of the molecule introduce tip-surface interactions across the vacuum gap, endowing STM with enhanced submolecular resolution and providing new chemical insights. Recently, this approach has been extended [10] to spin sensing through the decoration of the tip apex with a single nickelocene molecule  $[\text{Ni}(\text{C}_5\text{H}_5)_2]$  (Fig. 1a). Nickelocene comprises a single Ni atom sandwiched between two cyclopentadienyl rings ( $\text{C}_5\text{H}_5$ ), resulting in a spin  $S=1$  molecule, where the spin is constrained to a plane parallel to the rings by a magnetic anisotropy of  $D=4.0$  meV. A nickelocene-decorated tip can freely access all surface locations and sense surface magnetism providing sensitivity to spin polarization and magnetization orientation [11]. Sub-angstrom precision in sample spin sensing is made possible by the exchange interaction occurring across the vacuum

between the nickelocene tip and the surface, which modifies the nickelocene spin states and, consequently, its spin excitations (Fig. 1b).

To date, nickelocene-decorated tips represent the only example of a molecular tip providing access to surface magnetism. The primary challenge for molecular-based spin sensors lies in precisely positioning the molecule at a specific location using a scanning probe tip while maintaining a weak connection to the tip to emulate the behavior of a free molecular spin with quantized spin states. However, this connection must also be chemically stable to produce a stable and reproducible molecular tip, allowing scanning at relatively short distances from the surface (typically below 200 pm) where the exchange interaction is active, with tunnel currents that can be as high as 20 nA. The technique is new and requires consolidation through the investigation of model spintronic systems if we wish to generalize its use for magnetic imaging. Improving the sensitivity to magnetic fields is also essential. A tantalizing goal is to use ESR-STM with a molecular tip, rather than spin excitation spectroscopy.

### **Advances in Science and Technology to Meet Challenges**

Advancements in this field necessitate further exploration in both tip engineering and data acquisition. Tip engineering is currently in its early stages. Spin-sensitive measurements predominantly focus on nickelocene, but they are also possible with another metallocene [12], cobaltocene [ $\text{Co}(\text{C}_5\text{H}_5)_2$ , spin  $S=1/2$ ]. Unlike nickelocene, which has its spin preferentially oriented due to magnetic anisotropy, cobaltocene requires an external magnetic field to fix its direction and extract information on sample spin orientation. A metallocene is attached to a non-magnetic tip, usually a W tip, coated with surface material such as a noble metal. The tip is mono-atomically sharp resulting in a stable chemical connection between the apex metal atom and the C-C bond of one cyclopentadienyl ring. Instead, different materials for the tip can be used. In Ref. 13 a superconducting molecular tip was pioneered leading to enhanced energy resolution in spectroscopic features. An appealing alternative would involve using a magnetic-coated tip. Exploiting the exchange coupling between the tip and the metallocene would potentially offer to control the orientation of the molecular spin and lock it in a given direction. A magnetic tip would also lift the degeneracy of the metallocene's spin states, enabling spin excitations that are 100% spin-polarized whether the Nc-tip is exchange-coupled or not to the sample, thus facilitating the visualization of a spin contrast. This approach calls for experimental and theoretical studies on how metallocenes interact with magnetic surfaces, clusters and atoms, including their ability to preserve their quantum spin states in these environments. Such work is still scarce [14], and should even be extended to the more straightforward case of non-magnetic surfaces, where spin preservation is already known to occur but not fully understood. Furthermore, this line of inquiry promises to advance knowledge in the chemical design of spin-sensitive molecules beyond metallocenes. It is also pertinent for potentially adapting the ESR technique to molecular tips [15], where both a quantum molecular spin and a magnetic tip are essential for detecting ESR signals [8]. Note, however, that for magnetic surfaces, ESR-STM will need to be operated with the molecular tip exchange-coupled to the surface to preserve atomic-scale spin sensitivity. Positioning the molecular tip further away would reduce spin sensitivity to that of dipolar coupling, making it also sensitive to spin centers beyond 1 nm from the tip position, thus blurring the magnetic information.

As for data acquisition with molecular probe-tips, there are technical aspects that can be improved. Generally speaking, magnetic imaging with STM is inferred from conductance measurements, often intertwining electronic and magnetic properties. This issue is particularly pronounced when using a nickelocene tip. The line shape of the spin-excitation spectrum is modified by the spin-polarized nature of the tunneling electrons and by the exchange interaction between the STM tip and sample (Fig. 1b). Additionally, the lifetime of the spin excitations can affect the line shape [7]. To address these complexities, a 3D data block (or voxel) imaging is proposed. This method involves recording the spin excitation spectrum at a position  $r$  and subsequently analyzing the line shape through post-treatment. The exchange interaction and spin polarization can then be mapped to  $r$  to produce a

spatial map (Figs. 1c-d). Remarkably, these maps correlate with spin density maps computed using density functional theory (DFT) [11], which describe the local magnetization  $m(\mathbf{r})$ . Further development of this approach aims to extend its application to another important voxel channel: spin polarization. Simultaneous acquisition of both exchange and spin polarization channels promises dual insights into spin texture and spintronic properties at atomic scale resolution. The technique is particularly well suited for investigating complex spin textures such as spin spirals, magnetic domain walls, antiferromagnets, nano-skyrmions lattices.

### Concluding Remarks

Nickelocene-decorated STM tips represent a pioneering approach in quantum spin sensing, enabling precise imaging of surface magnetism at the atomic scale. The method demonstrates robustness and reproducibility and will benefit from advancements in tip engineering and data acquisition techniques. Future research should focus on expanding the repertoire of spin-sensitive molecules beyond metallocenes, exploring interactions with magnetic-coated tips, and enhancing sensitivity to magnetic fields through techniques like ESR-STM. These efforts hold transformative potential for applications in spintronics, quantum information processing, and materials science. Interdisciplinary collaboration will be crucial for advancing molecular spin sensors and unlocking their full capabilities in atomic-scale magnetic imaging and manipulation.

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