ROADMAP • OPEN ACCESS

Roadmap on atomically-engineered quantum platforms

To cite this article: Soo-hyon Phark *et al* 2025 *Nano Futures* **9** 032001

NANO FUTURES

ROADMAP

Roadmap on atomically-engineered quantum platforms

Soo-hyon Phark[1,2,52,*], Bent Weber[3,52,*], Yasuo Yoshida[4,52,*], Patrick R Forrester[5], Robertus J G Elbertse[6,7], Joseph A Stroscio[7], Hao Wang[8,9], Kai Yang[8,9], Leo Gross[10], Shantanu Mishra[10,11], Fabian Paschke[10], Katharina Kaiser[12], Shadi Fatayer[13], Jascha Repp[14,17], Harry L Anderson[15], Diego Peña[16], Florian Albrecht[10], Franz J Giessibl[14,17], Roman Fasel[18,19], Joaquín Fernández-Rossier[20], Shigeki Kawai[21,22], Laurent Limot[23], Nicolás Lorente[24,25], Berthold Jäck[26], Haonan Huang[27], Joachim Ankerhold[28], Christian R Ast[29], Martina Trahms[30], Clemens B Winkelmann[31], Katharina J Franke[30], Martina O Soldini[32], Glenn Wagner[32,33], Titus Neupert[32], Felix Küster[34], Souvik Das[34], Stuart S P Parkin[34], Paolo Sessi[34], Zhenyu Wang[35], Vidya Madhavan[36], Rupert Huber[14], Gagandeep Singh[3], Fabio Donati[1,2], Stefano Rusponi[37], Harald Brune[37], Eufemio Moreno-Pineda[38,39,40], Mario Ruben[41,42,43], Wolfgang Wernsdorfer[40,42], Wantong Huang[40], Kwan Ho Au-Yeung[40], Philip Willke[40], Andreas J Heinrich[1,2], Susanne Baumann[44], Sebastian Loth[44], Lukas M Veldman[44], Sander Otte[45], Christoph Wolf[1,2], Lisanne Sellies[10,14], Steven R Schofield[46,47], Michael E Flatté[48,49], Joris G Keizer[50,51] and Michelle Y Simmons[50,51]

[1] Center for Quantum Nanoscience (QNS), Institute for Basic Science (IBS), Seoul 03760, Republic of Korea
[2] Department of Physics, Ewha Woman's University, Seoul 03760, Republic of Korea
[3] School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore
[4] Department of Physics, Kanazawa University, Kanazawa, Japan
[5] Department of Physics, Harvard University, Cambridge, MA 02138, United States of America
[6] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States of America
[7] Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States of America
[8] Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
[9] School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[10] IBM Research Europe – Zurich, 8803, Rüschlikon, Switzerland
[11] Department of Physics, Chalmers University of Technology, 412 96 Gothenburg, Sweden
[12] IV. Physical Institute—Solids and Nanostructures, Georg-August-Universität Göttingen, Göttingen 37077, Germany
[13] Applied Physics Program, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia
[14] Regensburg Center for Ultrafast Nanoscopy, University of Regensburg, 93040 Regensburg, Germany
[15] Department of Chemistry, Oxford University, Oxford OX1 3TA, United Kingdom
[16] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela; Oportunius, Galician Innovation Agency (GAIN), Santiago de Compostela, Spain
[17] Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany
[18] Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
[19] University of Bern, Bern, Switzerland
[20] International Iberian Nanotechnology Laboratory, Braga, Portugal
[21] Center for Basic Research on Materials, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[22] Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan
[23] Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France
[24] Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain
[25] Donostia International Physics Center (DIPC), 20018 Donostia-San Sebastián, Spain
[26] Hong-Kong University of Science and Technology, Hong Kong Special Administrative Region of China, People's Republic of China
[27] Department of Physics, Princeton University, Princeton, NJ, United States of America
[28] Institute for Complex Quantum Systems and IQST, Universität Ulm, Ulm, Germany
[29] Max-Planck-Institute for Solid State Research, Stuttgart, Germany
[30] Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany
[31] University Grenoble Alpes, CEA, Grenoble INP, IRIG/DEPHY/PHELIQS, 38000 Grenoble, France
[32] Department of Physics, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland
[33] Institute for Theoretical Physics, ETH Zurich, 8093 Zurich, Switzerland
[34] Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany
[35] Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
[36] Department of Physics and Materials Research Laboratory, University of Illinois Urbana-Champaign, Urbana, IL, United States of America
[37] Institute of Physics, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

OPEN ACCESS

RECEIVED
20 February 2025

REVISED
31 May 2025

ACCEPTED FOR PUBLICATION
20 June 2025

PUBLISHED
23 October 2025

[38] Facultad de Ciencias Naturales, Exactas y Tecnología, Departamento de Química-Física, Universidad de Panama, 0824 Panama, Panama
[39] Universidad de Panamá, Facultad de Ciencias Naturales, Exactas y Tecnología, Grupo de Investigación de Materiales, 0824 Panama, Panama
[40] Physikalisches Institut, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany
[41] Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[42] Institute for Quantum Materials and Technology (IQMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[43] Centre Européen de Sciences Quantiques (CESQ), Institut de Science et d'Ingénierie Supramoléculaires (ISIS), 8 allée Gaspard Monge, BP 70028, 67083 Strasbourg Cedex, France
[44] University of Stuttgart, Institute for Functional Matter and Quantum Technologies, 70569 Stuttgart, Germany
[45] Department of Quantum Nanoscience, Delft University of Technology, The Netherlands
[46] Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
[47] London Centre for Nanotechnology, University College London, London WC1H 0AH, United Kingdom
[48] Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa 52242, United States of America
[49] Department of Applied Physics and Science Education, Eindhoven University of Technology, Eindhoven 5612 AZ, The Netherlands
[50] University of New South Wales Sydney, Australia
[51] Silicon Quantum Computing, New South Wales, Sydney, Sydney, Australia
[52] Guest Editor of the roadmap.
* Authors to whom any correspondence should be addressed.

E-mail: phark@qns.science, b.weber@ntu.edu.sg and yyoshida@se.kanazawa-u.ac.jp

Keywords: quantum materials, quantum information, quantum sensors, topological quantum platforms, single spin quantum objects

Abstract

Matter at the atomic-scale is inherently governed by the laws of quantum mechanics. This makes charges and spins confined to individual atoms—and interactions among them—an invaluable resource for fundamental research and quantum technologies alike. However, harnessing the inherent 'quantumness' of atomic-scale objects requires that they can be precisely engineered and addressed at the individual atomic level. Since its invention in the 1980s, scanning tunnelling microscopy (STM) has repeatedly demonstrated the unrivalled ability to not only resolve but manipulate matter at atomic length scales. Over the past decades, this has enabled the design and investigation of bottom-up tailored nanostructures as reliable and reproducible platforms to study designer quantum physics and chemistry, band topology, and collective phenomena. The vast range of STM-based techniques and modes of operation, as well as their combination with electromagnetic fields from the infrared to microwave spectral range, has even allowed for the precise control of individual charge and spin degrees of freedom. This roadmap reviews the most recent developments in the field of atomically-engineered quantum platforms and explores their potential in future fundamental research and quantum technologies.

Contents

1. Leading-edge techniques for atomic-scale quantum platforms

1.1. The future of multimodal scanning probe instrumentation for quantum materials and quantum information platforms

Patrick R Forrester[1], *Robertus J G Elbertse*[2,3] *and Joseph A Stroscio*[3]
[1] Department of Physics, Harvard University, Cambridge, MA 02138, United States of America
[2] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, United States of America
[3] Physical Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, United States of America

Status

The advent of scanning tunnelling microscopy (STM) in 1981 [1] has evolved to the present day into a quantum workbench with measurements comprising a wide range of physical, chemical, and optical properties. Early breakthroughs in the 1980s already showed the ability of STM to measure quantum wavefunctions and electronic structures [2]. Today we have even more sophisticated capabilities to probe 2D quantum materials [3] and single atom qubit platforms [4] using scanning probe instruments that can operate routinely at mK temperatures, enabled by advances in reduced-noise dilution refrigeration [5]. Thus, with ever improving instruments the STM and its variants have become essential tools in studying exotic phases in 2D quantum materials and quantum coherence in solid-state quantum information platforms.

However, no single physical quantity, be it, for example the local density of states (DOS) measured by STM or local magnetic fields measured by scanning superconducting quantum interference devices (SQUIDs), is sufficient to uniquely decode the complex information contained in quantum systems. Frequently, understanding requires spanning multiple length scales from the macroscopic, to mesoscopic, to atomic scale. One example is the exotic physics recently discovered in 2D moiré systems [3]. Here, global electronic transport has identified superconducting and correlated insulating behaviour, which depends critically on both moiré and atomic scale strain as well as on twist angle inhomogeneity at the mesoscopic or microscopic scale. Therefore, combinations of measurements spanning length scales and physical observables, which can be obtained in the same instrument (and sometimes even simultaneously) is invaluable. Recently, we introduced a multimodal scanning probe instrument which can perform STM, atomic force microscopy (AFM), and electrical transport at mK temperatures and high magnetic fields in ultra-high vacuum [6]. This instrument is the state-of-the-art and can probe physics at various length scales with measurements of local DOS, atomic forces and local potentials, and global electrical conductance on the same sample or device platform [6, 7].

The adoption of scanning probe microscopy (SPM) has led to a host of expanding techniques, which range from measuring local DOS with STM, atomic forces with AFM, and magnetic fields with scanning SQUIDs, to measuring coherent spin dynamics with electron spin resonance (ESR) in a STM tunnel junction (ESR-STM). Table 1 summarizes a variety of these measurements, which can address the many facets of quantum materials and devices. It is of particular interest to apply ESR-STM to measure quantum coherent phenomena in solid-state systems. As this interest extends beyond the literal definition of ESR, we will use microwave (MW) STM to refer to general STM systems compatible with MW capabilities including both those using tips, antennae, strip lines, etc. for MW readout/excitation and those where the measured signal does not originate from ESR. The current challenge is how best to incorporate MW capabilities in general into a multimodal SPM instrumentation platform for future quantum research, and how to then further extend it to incorporate all the measurement modalities listed in table 1 in a general-purpose quantum workbench instrument.

Below, we describe the current status of ESR-STM. We then introduce circuit quantum electrodynamics (QED), from which we draw inspiration for improving the MW capabilities of multimodal scanning probe instruments, such as the one currently under development at the National Institute of Standards and Technology (NIST). We sketch several interesting experimental directions for MW-STM and discuss advances in instrumentation for realizing these experiments. Finally, we highlight the importance of combining all the measurement space spanned in table 1 into a single instrument using multimodal probes on chip (figure 1).

Current and future challenges

ESR-STM is a relatively new experimental paradigm that seeks to manipulate and read out quantum coherent systems using MWs to excite and tunnel electrons to transduce quantum states. ESR-STM occupies a valuable niche due to its ability to spatially manipulate and resolve matter at the subatomic scale with an energy resolution of tens of neV. Atomic manipulation allows for the *in-situ* tuning of qubit-qubit

Table 1. Various measurement techniques that can be combined in a scanning multimodal platform for application to quantum materials and information systems.

Modality-tunnelling	Modality-force	Modality-charge	Modality-photons
Technique: • Scanning tunnelling microscopy (STM) and spectroscopy (STS) • Spin polarized tunnelling spectroscopy (SPTS) • Inelastic tunnelling spectroscopy (IETS) • Pump–probe tunnelling spectroscopy (PPTS) • Electron spin resonance (ESR-STM) • Stochastic resonance spectroscopy (SRS)	**Technique:** • Atomic force microscopy (AFM) • Electrostatic force microscopy (EFM) • Kelvin probe force microscopy (KPFM) • Magnetic force microscopy (MFM) • Exchange force microscopy (ExFM) • Electron spin resonance (ESRAFM)	**Technique:** • Scanning single-electron transistor (scanning SET) • Scanning capacitance microscopy (SCM)	**Technique:** • Scanning microwave impedance microscopy (scanning MIM) • Scanning nitrogen vacancy centre (SNV) • Scanning superconductor resonator (SSR) **Description:** MIM measures local electrical conductivity and permittivity; SNV magnetic fields, SSR capacitance or inductance. **Spatial resolution:** ≈20-200 nm **Physical resolution:** MIM ≈ 0.2 zF, SNV ≈ 1 nT/√Hz, SSR ≈ 60 zF/√Hz
Description: Quantum tunnelling of carriers between a probe and a biased sample is used to measure the local density of states, spin polarization of magnetic materials, inelastic spectrum of excitations (phonons or spins), spin dynamics, and electron paramagnetic resonance of electron and nuclear spins.	**Description:** The static or dynamic motion of a cantilever is measured to determine the forces between a probe and surface. Forces can arise from electrostatic, magnetic, and exchange contributions. Spin sensing and dynamics can be determined from both charge and spin fluctuations.	**Description:** Electrostatic potential is measured by its effect on SET conductance. In certain configurations, one can extract thermodynamic quantities like chemical potential, electronic compressibility, entropy, etc. Scanning capacitance microscopy measures local capacitance between probe and sample.	
Spatial resolution: Atomic	**Spatial resolution:** Atomic to nm	**Spatial resolution:** SET ≈ 100 nm, SCM ≈ 10 nm	
Physical resolution: Energy resolution limited by thermal broadening of tunnelling carriers, can achieve μeV resolution in tunnelling at mK temperatures, and tens of neV in ESR-STM.	**Physical resolution:** Force resolution limited by detection method, can achieve aN sensitivity.	**Physical resolution:** SET ≈ 1 μe/√Hz, SCM ≈ 1 zF/√Hz	

Modality-magnetic flux
Technique: • Scanning superconducting quantum interference device (scanning SQUID)
Description: Magnetic flux threading SQUID loop is used to extract local magnetic fields.
Spatial resolution: ≈100 nm
Physical resolution: ≈5 nT/√Hz

interaction over large energy scales, ranging from strong exchange coupling to weak dipolar coupling using the same atomic species [11]. Moreover, qubits composed of single atoms and molecules on atomically clean surfaces can be made virtually identical. This is attractive for simulating Hamiltonians where small levels of disorder are relevant as well as for disentangling the contributions of varied decoherence sources that plague solid-state qubits. So far, the technique has investigated the quantum coherent properties of single atoms and molecules on surfaces and small ensembles thereof, increasing understanding of atoms/molecules on surfaces and the technique itself along the way (see related articles in this Roadmap series).

Circuit QED [12], like ESR-STM, aims to investigate and control quantum-coherent systems, in this case realized by quantized MW frequency electromagnetic radiation (photons) and qubits constructed from nonlinear superconducting circuits. Inspired by cavity QED, circuit QED originally focused on coupling photons with superconducting qubits via 2D cavities (superconducting resonators) in place of a 3D electromagnetic cavity. The demonstration of strong coupling between a single photon and a superconducting qubit in 2004 is generally agreed to mark the birth of the field [13]. In the past two decades, the field has developed extensive knowledge to coherently manipulate quantum systems and read out small signals with minimal perturbation, while simultaneously isolating these systems from intrinsic and environmental decoherence sources at very low temperatures and GHz frequencies. Advances in hardware

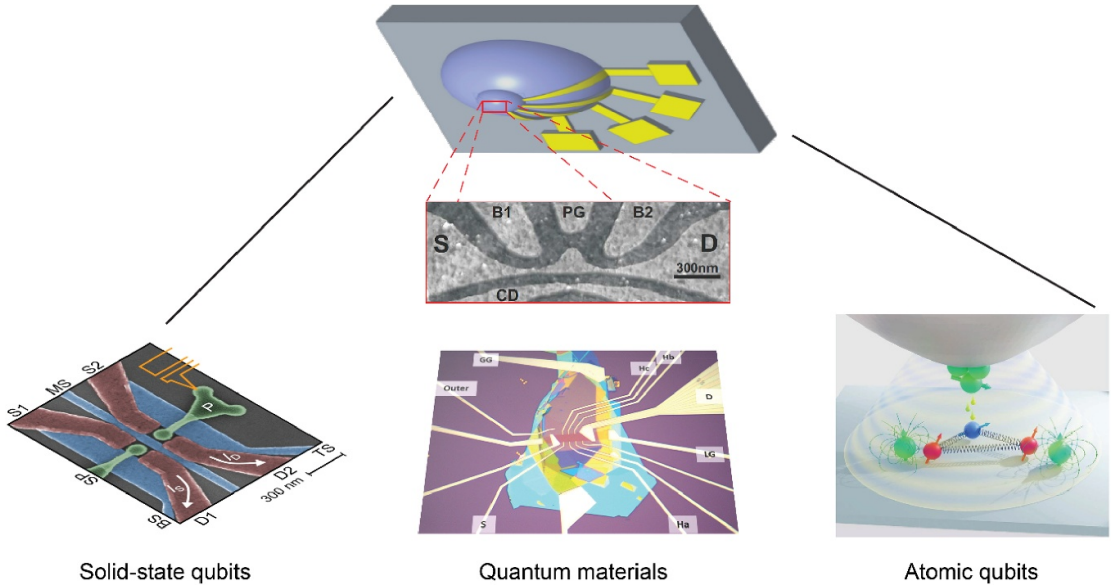

Figure 1. Proposed platform for multimodal probes for various scanning measurements described in table 1. Probes can use quantum materials, such as a graphene QD SET shown below the probe [8] (reprinted with the permission of AIP Publishing) or nanofabricated sensors on chip [9]. Moreover, probes may utilize solid-state qubits [10] (reproduced with the permission of AIP Publishing), quantum materials [7] (reproduced with permission from Springer Nature) or entangled atomic qubits [4] (reprinted with permission from AAAS).

and experimental design have proven key in facilitating many of these developments. Incorporating these advances into current MW/ESR-STM platforms represents a promising avenue to drastically enhance the experimental capabilities of these instruments. Below, we discuss several promising research directions for MW-STM, including those that have remained relatively unexplored with the technique thus far. We use this discussion to motivate the incorporation of useful techniques and hardware from the circuit QED community into the next generation of multimodal scanning probe instruments.

Beyond the atomic and molecular magnets on surfaces investigated by ESR-STM, a handful of other solid-state qubit platforms currently exist, with more under development. Mature platforms include those based on superconducting circuits or semiconductor quantum dots (QDs), while those based on non-abelian anyons in topological superconducting systems and 2D electron gasses remain under active exploration [14]. All suffer from obstacles related to decoherence, addressability, and scalability. As most of these platforms consist of mesoscale devices, little attention has been paid to their local, nanoscale properties and how these properties influence qubit performance. MW-STM is well-suited to answer these questions as it can measure at energy, time, and length scales [15] relevant to global qubit operation while addressing and manipulating atomic scale structures. As an example, we discuss the transmon qubit [16], a superconducting qubit, which, in a simplified picture, can be thought of as an LC oscillator with a Josephson junction constituting the inductive element. The non-linear inductance of the Josephson junction creates an anharmonic energy level spacing, allowing one to restrict the computational space to the two lowest energy levels. Transmons are a leading qubit platform, with coherence times exceeding 0.6 ms [17] and two-qubit gate fidelities exceeding 99.5% [14]. Nonetheless, decoherence still limits the capabilities of these systems and open questions remain. (I) Energy loss through coupling to fluctuating two-level systems (TLSs) has been identified as a significant decoherence source. Despite this, to date, there is little nanoscale data showing how or where this decoherence takes place. (II) Relatedly, Place *et al* [18] recently showed that transmons fabricated out of Ta significantly outperformed similarly fabricated Nb qubits (a leader in superconducting qubits). A comprehensive understanding of the relative contributions of intrinsic material properties, fabrication details, and surface and interface properties is largely absent. (III) While developing different material platforms for transmons has proved successful in improving qubit performance, almost all still rely on AlO_x tunnel junctions to provide the Josephson inductance. What nanoscale properties of these junctions make them so useful? How do they contribute to decoherence? Can better alternatives be engineered?

One could imagine experiments where MW-STM is used to identify, characterize, and manipulate nanoscale decoherence sources. This could be done using the atomically sharp tip as a direct current (DC) perturbation, by selectively driving local TLSs, by chemically or structurally modifying individual atoms or clusters of atoms, by engineering nanostructures that locally couple to circuit elements, etc. Notably, SPM

can easily tune how strongly a tip couples to a quantum system since tip-sample distance is an accessible tuning knob [19]. This increased understanding could then be used to rationally design more robust qubits. We have framed our discussion around the transmon for illustrative purposes, but this line of inquiry can be applied to many solid-state qubit platforms [20].

We now highlight an interesting and underexplored question: how can MW/ESR-STM be used to shed light on pressing contemporary problems in condensed matter physics? Identifying and controlling low-energy collective excitations has proven invaluable in understanding the ground states of the systems that host them. This has led to significant progress in diverse, fundamental topics ranging from superconductivity and magnetism to the integer and fractional quantum Hall (FQH) effects. However, most probes of collective excitations are global, and are thus typically insensitive to phenomena at very small length scales or in small samples. This problem is exasperated in 2D materials (even more so with moiré materials due to twist angle inhomogeneity) where homogenous sample volumes are exceedingly small, precluding characterization via established bulk measurement techniques. As an example, recently very fragile FQH [21] and Wigner crystal states [22] have been observed with STM in bilayer graphene, which also hosts families of newly discovered FQH states [23] whose order is still unknown. A MW-STM could play a role in exciting, detecting, and spatially resolving collective excitations in these systems, shedding light on their ground states [24]. This could be particularly exciting for recently discovered (fractional) Chern insulating states in several moiré systems, where both atomic and moiré lattice effects play a larger role [25]. This is just one example among many. Could a MW-STM couple to fluctuations near quantum critical points? Can reflectometry-type experiments be performed by an MW-STM as a means of probing the superfluid properties of superconductors, as has been recently demonstrated on the mesoscopic scale [26]?

In a recent work, it was shown that one may also use an ESR-active molecule attached to a tip whose resonance frequency depends on the local magnetic field as a magnetometer [27]. Such a system offers subatomic spatial resolution of magnetic fields, surpassing that of nitrogen vacancy (NV) centres in diamond and scanning SQUID. Applying such a probe to other condensed matter systems opens larger experimental phase spaces. In addition to measuring local magnetic moments and reconstructing charge carrier flow based on magnetic stray fields, this constitutes an attractive sensor for measuring both the coherent and incoherent finite-frequency magnetic signals mentioned in the previous paragraph up to tens of GHz (set by the ESR transition of the sensor). Combined with excitations either from the tip itself, a nearby antenna, or an on-chip strip line, ESR-active molecular scanning magnetometry could read out low-energy collective excitations in condensed matter systems with exquisite sensitivity.

Advances in science and technology to meet challenges

Exploring the above research directions with a general-purpose multimodal MW/ESR-STM based instrument demands technical improvements. First, a more controlled MW environment than those currently used in STM setups should be engineered to avoid destroying or obscuring the physics of interest. Second, measurement capabilities should be developed for sensing small signals, including but not limited to DC tunnel current, without unintentionally perturbing the sample. Much attention has been paid by the circuit QED community to engineer setups that meet these requirements. Using these advances as inspiration, we discuss their implementation into a MW/ESR-STM capable system.

Regarding a well-controlled MW environment, limiting the interaction between unwanted thermal photons and the sample under investigation is essential. For example, the ground and first excited state of a transmon correspond to the absence or presence of a single MW photon, respectively. Investigating such phenomena clearly requires the thermal photon occupation number to be well below $\langle n \rangle \ll 1$. To meet this requirement, the circuit QED community introduces cryogenic attenuators to MW ingress lines at various temperature stages of the cryostat (attenuation of $\approx$60 dB) [28], heavily attenuating thermal MW noise. To date ESR-STM MW lines are unattenuated (excluding the modest intrinsic losses in MW cabling of several dB m^{-1}). At NIST, our initial tests measuring tunnel conductance of superconducting Josephson junctions show significant broadening of the coherence peaks indicative of quasiparticle poisoning from thermal photons. These results highlight the need to attenuate MW lines similarly to circuit QED implementations. We anticipate similar problems for any experiment where thermal photons have sufficient energy, number, and coupling strength to unintentionally disrupt the state under investigation. However, heavily attenuating a STM tip signal line would make reasonable tip-sample bias voltages inaccessible. On the other hand, to achieve low electron temperatures for low-frequency/DC lines for STM, experimentalists heavily low-pass signals at low temperature, which is incompatible with MW signals. To meet the demand of low thermal photon noise for MW and low electron temperature for DC, attenuated MW signals and MW filtered low frequency signals must be combined at lower temperature stages, ideally at the mixing chamber of dilution units. This is implemented in the current NIST ESR-STM multimodal setup along with MW filtering of the low frequency lines at the mixing chamber using custom fabricated powder filters [6]. To further reduce

unwanted thermal photons, one should coat cryogenic radiation shields with highly infrared-absorptive materials, beyond traditional gold plating. This has been shown to increase qubit coherence [29] and resonator quality factors [30], with no obvious incompatibilities with scanning probe setups.

Environmental MW engineering is not limited to reducing the presence of thermal photons. The most pressing obstacle to a well-engineered MW environment centres around the tip itself. For STM, scanning gate microscopy, kelvin probe force microscopy, etc., the tip is biased relative to the sample, necessitating a DC galvanic coupling of the tip to some voltage source or ground. This constitutes a potential MW loss channel, which can allow a quantum system under study to decay, and may also act as an entry point for noise [31]. Tips should be made such that they do not perturb the system's MW environment too strongly. On the other hand, many of the aforementioned experiments would require the tip to sufficiently couple to samples for excitation, perturbation, or readout. These demands could conceivably be met by advances in 'smart tips' [32], which allow for the fabrication of circuitry directly on scanning probe tips using conventional cleanroom processes. These circuits could include on-tip Purcell filters [33] or tunable couplers [34], both of which have been employed by the circuit QED community for reducing unwanted decoherence from nearby MW loss channels. Further, one could implement on-tip circuitry to modify the tip-sample capacitances introduced in scanning experiments that could otherwise detrimentally affect the impedance experienced by devices under study. Taken together, these recommendations would facilitate a significantly improved MW environment for the next generation of multimodal MW/ESR-STMs.

We now discuss circuit QED-inspired technical improvements for minimally perturbative measurement of small signals. Many of the aforementioned phenomena are fragile to perturbations, necessitating low power MW drives. However, this results in weak, difficult to read, signals. Implementing advanced cryogenic hardware, developed for circuit QED, may prove useful for addressing these problems. Introducing state-of-the-art amplifiers (Josephson parametric amplifiers, travelling wave parametric amplifiers, high electron mobility transistor amplifiers, etc) at low temperature allows for quantum-limited signal amplification [35]. To achieve high-fidelity read-out, egress MW lines should not be attenuated before the first amplification stage and should be superconducting to avoid intrinsic cable losses. Cryogenic MW circulators/isolators should be used to block in-band thermal radiation, while out-of-band radiation should be rejected by wideband filters, in lieu of attenuators, which would degrade readout signals. With these hardware improvements, one can perform high signal-to-noise reflectometry experiments, opening the door to much more sensitive (and potentially non-destructive) measurements [12]. On-chip implementation can closely follow approaches used by others. Here the tip could be employed as a local perturbation, as an antenna to enhance effects directly under the tip, or to characterize and manipulate atomic scale structures. Performing MW-reflectometry measurements through the tip, in the spirit of MW impedance microscopy, may also be possible. However, this would require impedance matching circuits. These could be implemented with smart tips or elsewhere in the measurement chain. Despite these improvements, it is unclear if sufficient sensitivity could be achieved while maintaining the low power requirements we anticipate for many of the applications discussed. Such conditions may more easily be achieved with different scanning probe techniques, like scanning superconducting resonator microscopy, which highlights the need for multimodality.

Cryogenic hardware can also be used to flatten MW transfer functions and increase accessible frequencies via low temperature mixing [36]. Since the debut of ESR-STM, experimentalists have struggled with large, frequency dependent attenuation. To realize uniform MW power at the tip across a large frequency range, the input power is varied to compensate for frequency-dependent attenuation. Nonetheless, higher frequencies are often inaccessible. Moreover, measured transfer functions vary on experimentally relevant time scales, requiring frequent recalibration. Higher transmission, lower frequency tones could be combined at low temperature to furnish higher frequency signals with more efficient transmission. Similarly, difficult to measure high frequency signals can be down-converted to lower MW frequencies that are in the bandwidth of better performing, less costly, and more commercially available MW hardware. This would greatly enhance experimental phase spaces. The details of these strategies have already been thoroughly developed in the circuit QED community and in MW engineering at large [36].

Concluding remarks

In this article on the future of multimodal scanning probe instrumentation for quantum materials and quantum information platforms, we outlined the path forward to incorporate quantum coherent measurements with ESR/MW compatible STM and how to combine it with AFM and transport measurements as an extension of previous SPM instruments [6]. Moving forward, it is clear that the knowledge of the circuit QED community needs to be brought into the cryogenic ultra-high vacuum space that is occupied by SPM practitioners to successfully meet challenges in quantum science investigations. In particular, the future multimodal instruments should strive to incorporate all measurement modalities listed

in table 1 in a single instrument to actively unravel the fascinating physics in quantum systems and achieve significant impact. Currently the two columns in table 1 involving tunnelling and force transduction are conveniently combined with qPlus sensors [37] which can both perform simultaneous tunnelling and force measurements. We envision the solution to further bring columns 3 and 4 in table 1 with the fabrication of 'multimodal probes' on chip, which can contain all the modalities for incorporating tunnelling, force, charge, photons, and magnetic flux with integrated MW components for operation from DC to tens of GHz. These probes could be made from quantum materials such as a graphene QD single electron transistor (SET) (see table 1) [8], or various sensors could be fabricated using conventional nanofabrication processes on a suitable chip-based platform [9]. This would result in a powerful quantum workbench spanning from atomic, mesoscopic, and macroscopic scales, with high energy and temporal resolution. These ideas are currently under development in various laboratories around the world [9], and we expect the future of probing quantum materials and quantum information platforms to be exceedingly bright.

Acknowledgments

We thank Martin Gustafsson and Nick Poniatowski for stimulating comments and ideas and acknowledge funding from: University of Maryland and the National Institute of Standards and Technology (NIST) PREP program Grant No. 70NANB23H024 (RE) and the Office of Naval Research Grant No. N00014-23-1-2477. P R F acknowledges support from the National Science Foundation Graduate Research Fellowship under Grant Number DGE 1745303.

2. Designer quantum physics and chemistry

2.1. Quantum many body physics using tailored artificial atomic structures

Hao Wang[1,2] *and Kai Yang*[1,2]
[1] Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
[2] School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Status

The scientific community has long been interested in studying emerging quantum phenomena within spin networks. Artificial spin lattices are valuable tools for this purpose due to their high level of customization. Spin lattices constructed on surfaces (such as spin chains and arrays on Cu(111) [38], Cu_2N/Cu(100) [39], and Pt(111) [40]) has emerged as an attractive atomic-scale platform for quantum simulations of exotic phases of matter, and the complexity of these spin lattices varies from isotropic Heisenberg model to strongly anisotropic systems. These spin lattices have been probed using spin-polarized STM (SP-STM) and inelastic electron tunnelling spectroscopy in STM. In the past few years, ESR was combined with SP-STM to probe the many-body states of artificial spin structures on surfaces with highly improved energy resolution [11, 41–43]. During the ESR-STM measurement, a high-frequency voltage up to several tens of GHz is applied to the STM junction to drive the spin resonance. Titanium (Ti) atoms on MgO surfaces have been serving as important building blocks for constructing atomically-precise artificial spin networks with ESR-STM [11, 42, 43]. Interactions between two spin-1/2 Ti atoms are mapped over a range of distances extending from highly anisotropic dipole coupling to strong exchange coupling [11]. Furthermore, leveraging strong quantum fluctuations due to antiferromagnetic exchange interactions between neighboring Ti atoms, researchers have realized the resonating-valence-bond states in odd- and even-number spin chains and in spin plaquettes [42]. Recently, many-body topological states were realized in quantum Heisenberg spin lattices constructed with Ti atoms, including dimerized spin chains, and a two-dimensional dimerized spin array [43]. In addition to quantum simulation of many-body states, these surface spins have been employed for quantum computing applications [44], and a three-qubit spin structure has been constructed [4]. These advancements open a new avenue to design and explore quantum magnets at the atomic scale using spin-sensitive techniques for applications in spintronics and quantum simulations.

Current and future challenges

Artificial spin lattices constructed with ESR-STM has primarily focused on using Ti atoms on two-monolayer MgO, which serves as an insulating layer. The number of atoms in the spin lattice has been limited to 16 in previous works [43]. This limitation is mainly due to the low efficiency of atomic manipulation of 3*d* transition atoms on insulating MgO, which hinders the scalability of the spin networks. Currently, the movement of Ti on MgO is mainly through the lateral atom manipulation, which is more prone to defects on MgO than the vertical manipulation. Hence, achieving a high-quality, atomically flat MgO substrate is important for realizing larger spin networks.

Furthermore, the symmetry of the MgO lattice is C_{4v}. This means that it is easier to build square spin lattices on MgO than lattices with triangular geometry. This would pose a limitation to study certain interesting, frustrated lattices such as Kagome lattices.

As the size of the spin lattice grows larger, the ESR peaks resulted from denser energy levels should get closer in frequencies. This would require better energy resolution of ESR-STM, which is about 100 neV ($\sim$10 MHz) for Ti spins on two-monolayer MgO at the moment.

Advances in science and technology to meet challenges

As mentioned in the preceding section, achieving high-quality, large-scale, atomically flat MgO layers is vital for realizing large-scale spin networks. Addressing this challenge needs precise control over MgO growth parameters. Alternatively, one can explore the possibility to construct spin lattices on different decoupling substrates with different lattice symmetries than MgO such as the boron nitride substrate.

To enhance the energy resolution of ESR-STM, one approach is to extend the coherence time of surface spins. Since tunnelling current serves as the main source of spin decoherence, one strategy for increasing the coherence time of surface spins is to minimize the tunnelling current. Employing homodyne detection of the ESR signal at zero DC bias voltage is perhaps the most effective method to minimize the tunnelling current. Furthermore, the coupling between surface spins and the substrate also affects the spin coherence time. It was observed that as the MgO thickness increases, the energy lifetime of the spin system increases [45]. Therefore,

increasing the thickness of the insulating layer should reduce the coupling between the substrate and the spin network. While pervious ESR-STM experiments have focused on MgO, recent research has investigated spin states of molecules on the NaCl surfaces, suggesting a potential avenue for increasing the spin coherence time.

The dynamics of the spin lattices on MgO has barely been explored. With the advancement of the pulsed ESR-STM technique [4], we anticipate that the time evolution of interesting many-body spin states can be studied in the near future.

Concluding remarks

Atom-by-atom construction of spin lattices together with ESR-STM has yielded a series of exciting results. However, the field of quantum simulation with surface spins still confronts several challenges in its development. These include the limited applicability of ESR-STM to only a few substrates (such as MgO and NaCl) and the scalability to larger spin networks, which restricts its potential for exploring new many-body physics. Despite these challenges, the potential of the field remains largely untapped. The forthcoming years promise to be exciting as we witness the continued progress and development of quantum simulations with tailored artificial spin lattices.

Acknowledgments

This work is supported by the Beijing Natural Science Foundation (Z230005), the National Natural Science Foundation of China (12174433, 92476202), the National Key R&D Program of China (2022YFA1204100), and the CAS Project for Young Scientists in Basic Research (YSBR-003).

2.2. Tip-induced chemistry

Leo Gross[1], *Shantanu Mishra*[1,2], *Fabian Paschke*[1], *Katharina Kaiser*[3], *Shadi Fatayer*[4], *Jascha Repp*[5], *Harry L Anderson*[6], *Diego Peña*[7] *and Florian Albrecht*[1]
[1] IBM Research Europe – Zurich, 8803, Rüschlikon, Switzerland
[2] Department of Physics, Chalmers University of Technology, 412 96 Gothenburg, Sweden
[3] IV. Physical Institute—Solids and Nanostructures, Georg-August-Universität Göttingen, Göttingen 37077, Germany
[4] Applied Physics Program, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia
[5] Institute for Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany
[6] Department of Chemistry, Oxford University, Oxford OX1 3TA, United Kingdom
[7] Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela; Oportunius, Galician Innovation Agency (GAIN), Santiago de Compostela, Spain

Status

On-surface synthesis under ultra-high vacuum conditions has made remarkable progress over the last two decades. Two main strategies can be distinguished: On one side, using thermal activation (or global exposure to light) and on the other side, using atom manipulation. Both have strengths and weaknesses. With thermal activation, many product molecules are formed in parallel and with typically high yield [46, 47]. In contrast, atom manipulation [48], in the context of molecules called tip-induced chemistry [49, 50], requires each molecule to be generated individually. One advantage of this approach is the ability to form highly reactive and out-of-equilibrium products. Moreover, tip-induced chemistry potentially allows the creation of complex, individual and custom-designed nanostructures [51]. Both techniques can be efficiently combined by using tip-induced chemistry to modify structures that were synthesized by thermal activation.

In tip-induced chemistry, precursor molecules are deposited on a surface and transformed to the envisioned products by using the tip of a scanning probe microscope. To this end, masking groups can be dissociated, typically by applying voltage pulses [49–54]. In addition, further chemical reactions can be induced, such as intermolecular [50, 52, 53] and intramolecular [51, 53, 54] covalent bond formation and bond cleavage, which includes ring opening and closing reactions as well as skeletal rearrangements [51, 54]. Figure 2 shows a recent example [54], which demonstrates the selective generation of unprecedented molecules by means of a sequence of tip-induced reactions. Furthermore, the toolbox of atom manipulation allows control over the molecule's adsorption environment with atomic precision and preparation of molecules in charged [55] and excited states. An important asset of tip-induced chemistry is that novel and elusive molecules can be created, and their properties can be revealed directly at the atomic scale using high-resolution STM and AFM and their spectroscopy variants (see section 1 of this article). Tip functionalization, e.g. with CO molecules, increases the spatial resolution towards resolving covalent bonds even with bond-order discrimination, facilitating progress in tip-induced chemistry [51].

Current and future challenges

Figure 3 summarizes approaches and scientific objectives. Associated to the approaches are the challenges, which relate to improving, expanding, and advancing the current approaches. The synthesis of (elusive) molecules by tip-induced chemistry and the elucidation of their properties is one focus of current research. Examples of molecules with intriguing properties realized by tip-induced chemistry include polycyclic aromatic hydrocarbons with sublattice imbalance giving rise to high-spin ground states, such as triangulenes [51]; molecules with possible open-shell character such as long acenes and indenofluorenes; and molecular allotropes of carbon, such as cyclocarbons [53], the geometric and electronic structures of which were debated for decades. The study of such compounds is valuable for benchmarking theoretical approaches and for understanding reaction mechanisms and fundamental chemical concepts such as Jahn–Teller distortions [53, 54] and aromaticity [53]. There is a long wish list of intriguing conceivable molecules that are yet to be realized. For example, longer acenes, differently coupled/doped/modified triangulenes and other open-shell moieties, cyclic acenes, cyclocarbons and related carbon-rich molecules are goals to investigate highest occupied molecular orbital - lowest unoccupied molecular orbital gap oscillations predicted by theory, localization of excess charges, molecular magnetism, aromatic stabilization and the subtle balance between open- and closed-shell configurations. This challenge crucially involves the target-oriented design and synthesis of suitable precursor molecules.

The endeavour of deliberately synthesizing elusive molecular structures is intimately linked to advancing tip-induced chemistry, that is, to increase yield, selectivity and versatility in both intra- and inter-molecular

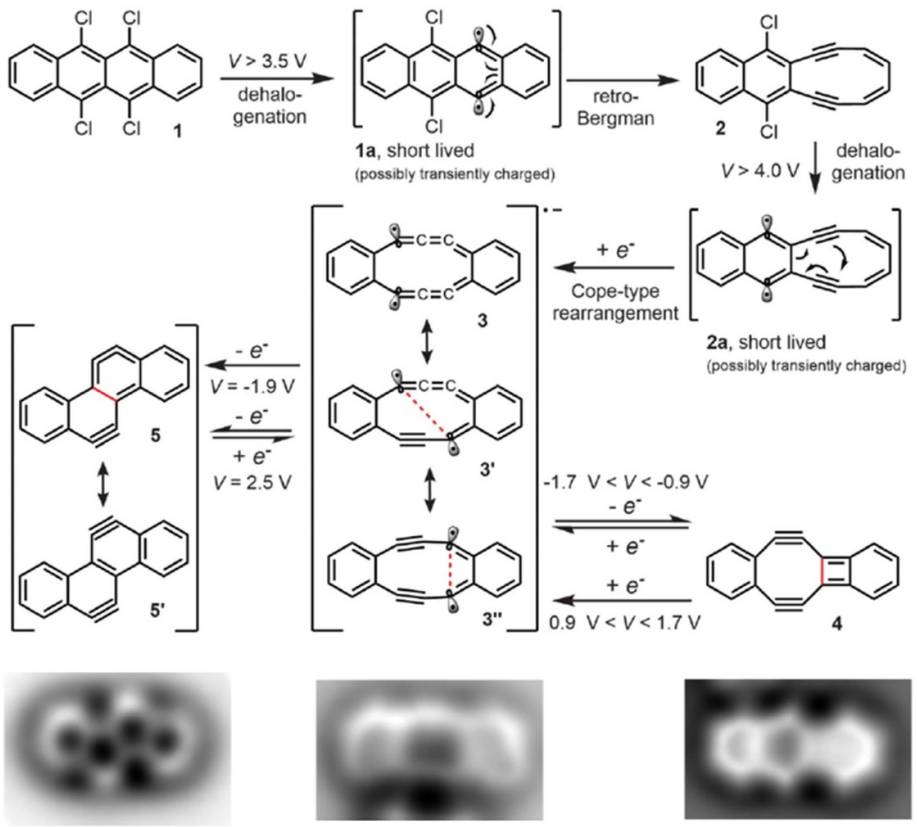

Figure 2. An example of tip-induced chemistry. Dissociation of four Cl atoms from the precursor **1** adsorbed on bilayer NaCl on Cu(111), results via **2** in the formation of three $C_{18}H_8$ structural isomers **3, 4** and **5**, which can be selectively and reversibly transformed into each other. All reactions are performed by tip-induced chemistry using voltage pulses, with the respective sample voltages V indicated. The lower row shows CO-tip AFM data of each product. From [54]. Reprinted with permission from AAAS.

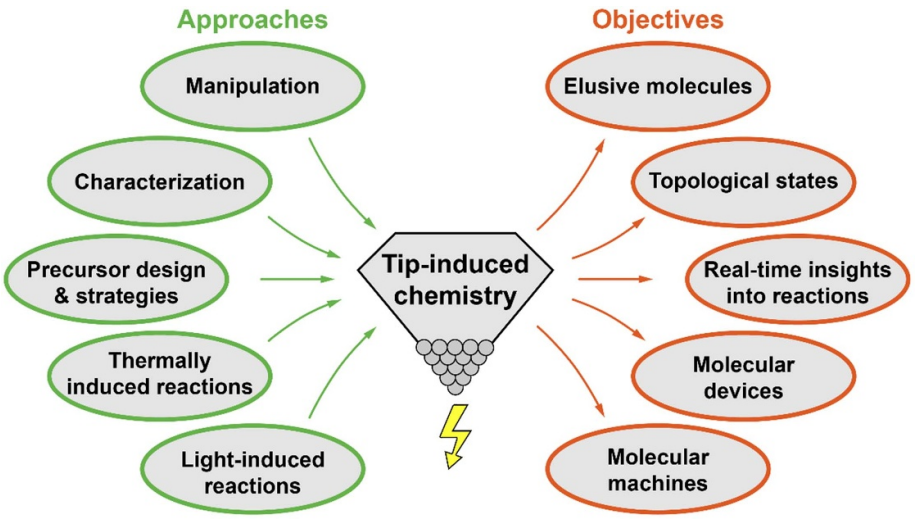

Figure 3. Approaches and objectives of tip-induced chemistry.

reactions. This is crucial for creating increasingly complex, custom-designed molecules and nanostructures with designed properties, such as hosting high-spin ground states or topologically non-trivial states and band structures. For the latter, structures made with on-surface synthesis by thermal activation might be modified by tip-induced chemistry on a local scale. This has recently been demonstrated even in the 3rd dimension by attaching atoms to an on-surface synthesised polymer, perpendicular to the surface [56] (see section 6). Alternatively, complex structures can be built up entirely by tip-induced chemistry by arranging and covalently fusing multiple molecules [52]. It will be important to advance the techniques of

tip-induced chemistry and explore new chemical reactions that can be controlled. Different reactions compared to conventional wet chemistry might be discovered [51, 54].

A related challenge is to obtain a better fundamental understanding of the processes involved in tip-induced chemistry, which will also foster its advancement. In this aspect, an appealing goal is to advance characterization methods towards resolving a tip-induced chemical reaction, e.g. bond formation or bond cleavage, on its intrinsic timescale and with atomic resolution. In combination with the ability to arrange the local environment with atomic precision, this could provide further important insights into heterogeneous catalysis.

Advances in science and technology to meet challenges

To improve tip-induced chemistry, in addition to optimizing voltage pulse parameters and precursor design, the use of tip functionalization for manipulation, or adsorbates such as single atom catalysts [57], might lead to improvements. Moreover, the use of different stimuli to drive reactions—in particular light—can be explored further. The confined electromagnetic near fields in a laser illuminated tip-sample junction can promote photochemical reactions with submolecular precision [58]. Fast laser pulses allow electronic excitations of molecules very far from equilibrium to initiate reactions. Moreover, advances in lightwave (LW)-driven STM (see section 12), might bring time resolution fast enough to follow atomic motion and orbital evolution in tip-induced chemical reactions. Recently, the feasibility of using terahertz (THz) pulses that provide femtosecond forces to control atom manipulation was demonstrated [59]. Directly resolving tip-induced reactions in space and time would break new grounds.

Moreover, tip-induced chemistry should be expanded to different substrates, importantly to truly insulating substrates. Although AFM can be used for characterization and manipulation on insulators, that task is challenging, because the use of STM is limited, and driving currents via the molecule to the substrate cannot be used for manipulation. At the same time, this enables other mechanisms to induce chemical reactions: reversible bond cleavages and formations are possible with electron yields on the order of unity, by attaching and detaching few (two) electrons to a molecule on a thick NaCl film using the tip of an AFM [60], indicating the feasibility of this approach. Advancing tip-induced chemistry on insulating substrates might be very rewarding. Because charges cannot tunnel to the substrate and are thus preserved in the adsorbates, single-electron transfer can effectively be studied and employed for functionality. Moreover, spins can be manipulated, and long coherence lifetimes are accessible using ESR-AFM [61] (see section 21). Bringing molecules to long-lived excited states and charged states [55], possible on insulators, might open new routes for tip-induced chemistry. Artificial molecular machines, logic devices and sensors that are driven and controlled by inter- and intra-molecular single-electron transfer might become possible.

Concluding remarks

Tip-induced chemistry is already an important tool for molecular synthesis and further progress is expected. Advances in tip-induced chemistry, molecular design and synthetic strategies for precursors, as well as on-surface chemistry by thermal activation will lead towards more complex molecules and designed nanostructures with tailored properties and novel functionalities resulting in novel artificial molecular machines and single-electron devices. The combination of tip-induced chemistry with LW-driven STM and taking advantage of tip-enhanced optical excitation might allow chemical reactions to be resolved on their intrinsic timescale with atomic resolution, providing a direct atomistic understanding of bond formation and dissociation.

Acknowledgments

Financial supported by the European Research Council Synergy Grant MolDAM (Grant No. 951519) is acknowledged. DP acknowledges financial support from the Spanish Agencia Estatal de Investigación (PID2022-140845OB-C62), the Xunta de Galicia (Centro de Investigación do Sistema Universitario de Galicia, 2023-2027, ED431G 2023/03), and the European Union (European Regional Development Fund_ERDF).

2.3. Chemical bonding properties of an artificial atom—revisiting the quantum corral of Crommie, Lutz and Eigler—an example of the utility of AFM in quantum physics at the atomic scale

Franz J Giessibl
Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany
Regensburg Center for Ultrafast Nanoscopy, University of Regensburg, 93040 Regensburg, Germany

Status

The quantum corral by Crommie *et al* [62], a ring of 48 Fe atoms that was arranged on a Cu(111) surface in 1993 became an icon of quantum nanoscience. The Cu(111) surface has a surface state that allows electrons to travel quasi freely on the surface with a Fermi wavelength of about 3 nm. The iron ring with its $r_C = 7.13$ nm radius confines the surface electrons and its influence on the surface electrons can be modelled as an infinitely high potential barrier, leading to confined electron states within the corral. The wavefunctions of these electrons can be split into factors with Bessel-type radial functions $y_{n,l}(r) \alpha J_l(r \rho_{0,n,l}/r_C)$, azimuthal parts $y_f(f) = \exp(ilf)$ and an exponentially decaying z—dependent part $\exp(-k z)$ where r is the radial distance, $\rho_{0,n,l}$ is the nth zero of Bessel function $J_l(\rho)$, l is the angular momentum and is the decay rate in vertical direction [63].

Thus, one can interpret the set of eigenstates $\Psi_{n,l}$ of the confined electrons as the electron shells of an artificial two-dimensional atom. The quantum number n denotes the number of radial nodes and l is the angular momentum number. A total of 102 electrons fits into the quantum corral with a radius of 7.13 nm, occupying quantum numbers from $n = 1$ to 5 and from $l = -10$ to 10. The decay rate k is equal for all corral states, and the states are spin degenerate (spin–orbit interaction should lift the degeneracy, but the width of the states is so large that this weak interaction cannot be observed). The states $\Psi_{2,-7}$, $\Psi_{4,-2}$, $\Psi_{5,0}$, $\Psi_{4,+2}$, $\Psi_{2,+7}$ are very close to the Fermi level and each hold 2 electrons (spin up/down), i.e. 10 of those 102 electrons have an energy close to the Fermi level and thus can be observed by STM. Advances in AFM and combined STM/AFM offer potential new insights into the fascinating quantum corral [63]. Experiments have shown, that the bonding energy between the tip of an AFM and this artificial atom is only on the order of 5 meV, a thousand times weaker than to a natural atom [63]. The bond was attractive to a metal AFM tip, and repulsive to a CO terminated tip. To probe if the interaction between a metal tip and the artificial 2D atom becomes repulsive at very small distances, we placed an atom inside the corral at a radial distance of 4.048 nm where the $\Psi_{2,7}$ state, a state with two radial nodes and an angular momentum of 7, has a high amplitude. The location of the azimuthal ripples in figure 4 show that the interaction is indeed repulsive at a close distance.

AFM is important because it often sheds new light on iconic results that have been studied extensively with STM. Further advances are also possible in insulating samples where STM cannot be applied.

Current and future challenges

In AFM, the spatial resolution typically exceeds the one of STM, and the proper tip termination is very important. The best resolution has been achieved when terminating a single-atom metal tip by a CO molecule. Gross *et al* [64] have shown that submolecular resolution on organic molecules is enabled by those tips. CO terminated tips interact primarily via Pauli repulsion forces on organic molecules [64].

Interestingly, the artificial 2D atom of figure 4 interacts with the AFM tip in a similar fashion as a natural atom—covalent bonding with a metal tip [63], and Pauli repulsion with a CO terminated tip (see figure 5(d)). A different high-resolution tip termination was suggested by Mönig *et al* [65]—again showing an oxygen atom as the tip apex, but attached to a copper tip (CuO*x*-tip). Both CO terminated tips and CuO*x* tips work in vacuum and at low temperatures. Finding a suitable tip with similar properties that works in ambient conditions would provide an enormous boost, but likely will require experimentation on a wider scales.

One key current and future challenge of reaching the full potential of AFM is the appropriate teaching of PhD students and Postdocs to enable them to operate AFMs at their full potential and the efforts of the manufacturers of AFMs to make them easier to use and highly reliable to operate. In the first years following the introduction of STM, many groups built their own STMs and therefore had a profound knowledge of the working of their instruments. Although commercial instruments are very sophisticated today, AFM is slightly more complex to operate and understand than STM and it is helpful for practioners to get first hand experience with the inner workings of their microscopes. Hopefully, the qPlus AFM for ambient conditions that we also used for electrochemistry [66] will become openly available in the future—its open architecture allows easy hands-on experience.

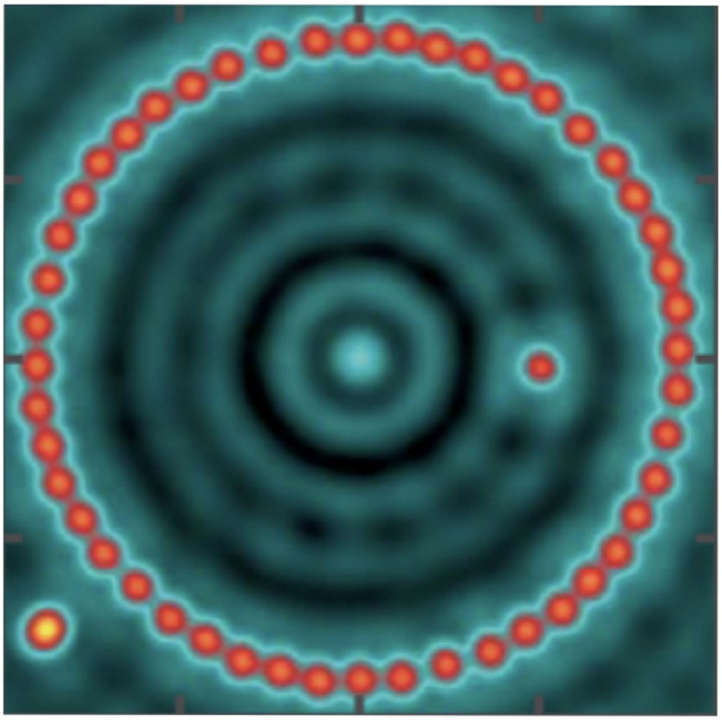

Figure 4. STM image of a copy of the original quantum corral [62] made of 48 Fe atoms on a Cu(111) surface. An additional adatom is placed at a distance of 4.048 nm from the centre—close to a radial maximum of the $\Psi_{2,7}$ state and lifting the degeneracy of the cos(7ϕ) and sin(7ϕ) states, leading to 14 azimuthal maxima according to $\sin^2(7\phi)$. From [63]. Reprinted with permission from AAAS.

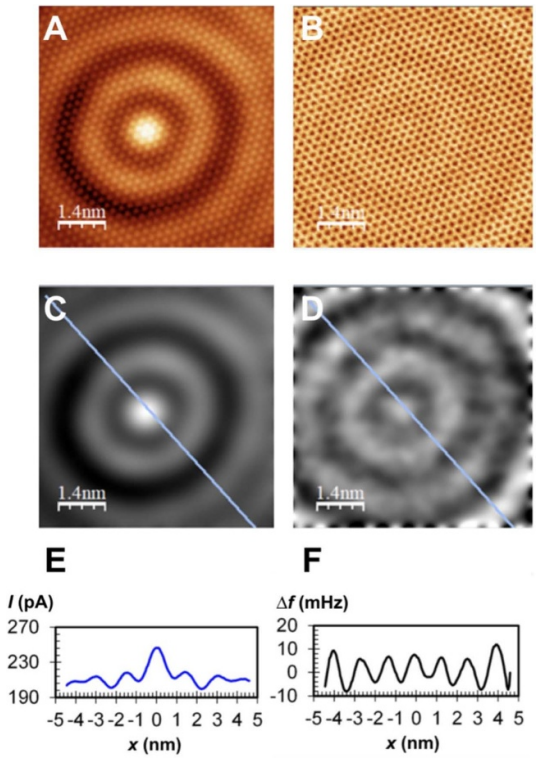

Figure 5. Central square (9 nm wide) within a 14 nm diameter quantum corral imaged at constant height by simultaneous STM (tunnelling current, left) and AFM (frequency shift, right). The data is recorded with a CO terminated tip, thus the atoms of the Cu(111) substrate appear as small maxima in A and as minima in B. C and D are low pass filtered versions of A and B, revealing the electronic states of the quantum corral. The STM data shows only the contribution of the electrons at the Fermi level, shown in blue in E. The AFM data shows the total charge density as plotted in F. From [63]. Reprinted with permission from AAAS.

Advances in science and technology to meet challenges

The introduction of the qPlus sensor [37] as a means to optimize spatial resolution and to simultaneously perform STM and AFM has brought many breakthroughs in recent years. The advances that led to these results were the creative identification of high impact scientific questions, the mastery of the experimental apparatus and the collaboration with outstanding theorists.

While this short contribution cannot cover the breadth of what has been achieved lately (see e.g. the references in [37]), latest breakthroughs include surface science on insulators [67], superlubricity of water [68], measuring the orbital states of molecules far from the Fermi level [69] or combined STM and AFM in electrochemical environments [66].

Concluding remarks

The AFM went on an exciting journey—starting with a lower resolution than the STM, however much wider applications as it can be used on samples that are insulating and 'dirty', i.e. not prepared with surface science standards. Today, AFM exceeds STM in spatial resolution and provides a powerful complement to STM. Its imaging principles rests on chemical bonding between natural or artificial atoms, and it can probe both the attractive as well as the repulsive parts in the interatomic interaction curve. Judging by recent developments, it is expected that new discoveries will be revealed in the near future by this powerful technique.

Acknowledgments

We gratefully acknowledge the support of our research by the German Science foundation under Contracts SFB689, SFB1277, GRK1570 and GRK2905.

2.4. Nanographenes as building blocks for artificial spin lattices

Roman Fasel[1,2] *and Joaquín Fernández-Rossier*[3]
[1] Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
[2] University of Bern, Bern, Switzerland
[3] International Iberian Nanotechnology Laboratory, Braga, Portugal

Status

Open-shell nanographenes, also known as π-electron radicals, have been known for more than a century. Notable examples include triangulene [70] and Clar's goblet [71] (figure 6). Their use as building blocks for artificial spin lattices has not been possible until very recently, for two main reasons. First, the stability of open-shell nanographenes is compromised by their high chemical reactivity. Second, the lack of magnetic probes for individual molecules. The development of on-surface synthesis [46] carried out in ultrahigh vacuum brought both a chemically stable environment for open-shell nanographenes and the possibility to probe their spins using STM inelastic electron tunnel spectroscopy (IETS). In this context, the report of the first on-surface synthesis and characterization of [46]-triangulene [72] (figure 6(b)) and Clar's goblet [73] (building block in figure 6(e)), the observation of zero-bias Kondo peaks in a nanographene [74], and the observation of finite-bias inelastic spin excitations [73, 74], associated to exchange-coupled spin dimers, have set the stage for the fabrication of nanographene spin lattices.

Artificial spin chains made with low spin ($S = 1/2,1$) nanographenes have been reported recently [75–78]. Their outstanding features make them ideal to explore quantum magnetism. First, intermolecular exchange, in the range of tens of meV, is orders of magnitude larger than magnetic anisotropy. Second, tip-controlled selective passivation and activation [76, 77] make it possible to control L, the number of active spin sites in the chains, enabling a systematic study of length dependent properties. Third, on-surface synthesis yields both chains and rings, making it possible to study the emergence of fractional edge spins [75, 76]. Fourth, STM-IETS can trace the amplitude modulations of spin excitations across different sites of the chain, that relates to the site-dependent spin spectral weight that can be computed almost exactly with density-matrix renormalization group calculations.

Outstanding examples include $S = 1$ triangulene chains [75] (figure 6(f)) that have made it possible to observe both the Haldane gap and edge spin excitations associated with $S = 1/2$ fractional spins. Chains made with Clar's goblets [76] (figure 6(e)) provide a realization of the $S = 1/2$ Heisenberg chain with alternating exchange, that also feature a gap and emergent edge spins. Chains made with $S = 1/2$ olympicene [77] (figure 6(c)) and phenalenyl [78] (figure 6(a)) realize the $S = 1/2$ Heisenberg model whose lowest energy excitations scale as $1/L$, becoming gapless in the thermodynamic limit.

Current and future challenges

An obvious next challenge for this field is to be able to grow two-dimensional lattices of open-shell nanographenes that realize two-dimensional (2D) spin lattices, thus going beyond 1D quantum spin models. For instance, 2D spin lattices can host quantum spin liquids and other exotic states, such as the 2D analog of Haldane spin chains, the AKLT model in the honeycomb lattice made with $S = 3/2$ spins with fine-tuned nonlinear exchange interactions, whose ground state is a universal resource for measurement based quantum computing. Therefore, the identification of $S = 3/2$ molecules that can form a honeycomb lattice and exhibit the right nonlinear exchange would be a major breakthrough in this field. A first step in this direction is the report of 2D lattices of $S = 3/2$ triangulenes [79].

The resolution of STM-IETS is limited both by temperature and by substrate induced broadening of the inelastic steps, which makes it difficult to resolve the different excited states because of their shrinking energy separation with increasing size of the artificial lattice. The ultimate origin of substrate broadening is the Kondo exchange interaction of the spin excitations with the underlying Fermi sea, that leads to a finite lifetime and broadening of the spin excitations. The same Kondo exchange is also screening the fractional edge spins in Haldane spin chains, preventing their use as singlet–triplet qubits and sensors. Even if surface broadening is completely eliminated, thermal broadening in SMT-IETS limits spectral resolution to 5.4 $k_B T$, making it impossible to resolve individual spin excitations in large spin lattices.

Most experiments so far have used benzenoid molecules. This brings both advantages and limitations. Both the spin of a benzenoid molecule, and the sign of intermolecular exchange, can be anticipated easily using the Lieb–Ovchinnikov rule, which relates the spin of the ground state of the bipartite graphs generated by benzenoid molecules to their sublattice imbalance. As a result, benzenoid molecules cannot form 2D lattices with frustrating interactions that promote quantum spin liquids. Both, non-benzenoid molecules as well as functionalized nanographenes, such as aza-nanographenes, are a way out of the bipartite paradigm.

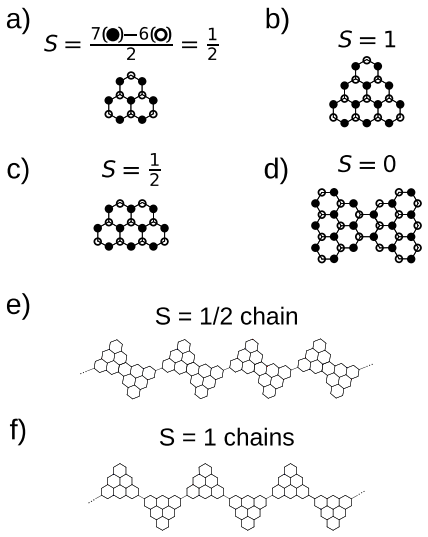

Figure 6. Top lines: the carbon atom backbones of phenalenyl, triangulene, olympicene and Clar's goblet, with the two sublattices represented with white and black circles. The spin of the ground state, shown on top of each molecule, is given by half the sublattice imbalance. Bottom: two examples of spin chains, made with Clar's goblet and triangulene.

Advances in science and technology to meet challenges

To fully realize the potential of nanographenes as building blocks for artificial spin lattices, breakthroughs are needed in on-surface synthesis, surface science and probing methods, and theoretical modeling. On the synthesis front, precise control over the fabrication of 2D spin lattices from both benzenoid and non-benzenoid nanographenes is crucial. Recent progress in alkali–metal and atomic hydrogen-assisted on-surface synthesis reactions shows promise, but the ability to engineer 2D open-shell nanographene lattices is still evolving.

The limitations posed by current STM-IETS approaches can be overcome in two ways. On the one hand, energy resolution can be improved by electronically decoupling the nanographenes from the typically used metal substrates by thin insulating layer(s), either by intercalation strategies or by STM tip manipulation. This also eliminates the Kondo screening of (fractional) edge spins and enables their study as singlet–triplet qubits. On the other hand, emerging techniques such as ESR STM provide new opportunities to explore spin dynamics and quantum coherence, which will be essential to fully understand the quantum phenomena occurring in large-scale artificial spin lattices. ESR-STM on open-shell nanographenes and their spin lattices will also allow exploration of the spin coherence timescales which are predicted to be long for carbon-based nanomaterials.

On the theory side, more sophisticated models are required to accurately describe the intermolecular exchange interactions, especially for non-benzenoid systems. Traditional density functional theory (DFT) often falls short when it comes to capturing the complex, highly correlated states that emerge in these systems. Multiconfigurational methods, beyond mean-field approaches, are needed to account for the entanglement between spins and to predict non-linear interactions in 2D lattices. These theoretical advancements will be vital for guiding experimental designs, especially in tailoring non-trivial spin interactions that could lead to the realization of 2D AKLT Hamiltonians with nanographenes.

Concluding remarks

In summary, the exploration of open-shell nanographenes as building blocks for artificial spin lattices presents a frontier in quantum magnetism with profound implications for future technologies. While significant strides have been made in synthesizing low-spin nanographenes and 1D chains and studying their properties, the transition to 2D spin lattices remains a critical challenge. The integration of advanced synthesis techniques, innovative probing methods, and sophisticated theoretical models will be essential to unlocking the full potential of these artificial quantum materials. We are confident that this will pave the way for novel quantum states and spintronic applications, thereby advancing our understanding of quantum materials and their potential in quantum technologies.

Acknowledgments

We acknowledge J C Henriques for help in preparing figure 6. This work was supported by the Swiss National Science Foundation (Grant Numbers 212875, 205987), the European Union (Grant FUNLAYERS-101079184), the Fundacao para a Ciencia e a Tecnologia (Grant No. PTDC/FIS-MAC/2045/2021), Generalitat Valenciana (Grants Nos. Prometeo2021/017, MFA/2022/04), MICIN-Spain (PID2022-141712NB-C22) and the Advanced Materials programme supported by MCIN with funding from European Union NextGenerationEU (PRTR-C17.I1). We also greatly appreciate financial support from the Werner Siemens Foundation (CarboQuant).

2.5. Memory bits using molecular networks

Shigeki Kawai
Center for Basic Research on Materials, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan

Status

Since the first systematic atomic manipulation of xenon atom on a nickel surface at low temperature using STM in 1990 [48], we have gained the capability to directly control surface structures. By moving and repositioning single atoms to specific atomic sites on surfaces, we can measure quantum phenomena such as quantum coral [62] and spin direction [80]. Single atom can also be regarded as bits in memory [39]. Given that atoms are the fundamental components of any material, controlled atom manipulation results in the fabrication of the smallest and highest-density storage systems. With the developments of the highly flexible digital SPM controllers and the automated manipulation protocol, the number of the manipulated atoms has rapidly increased [81].

Molecules can also be regarded as bits in the memory based on the position and states as well as the structure [82]. Particularly, recent developments in on-surface synthesis have enabled the creation of unique carbon nanostructures such as graphene nanoribbons through covalently linking small precursor molecules [46]. These nano structures can also be used as molecular network memories if the structures of each unit are precisely controlled. We recently demonstrated construction of dehydroazulene isomer and diradical units in three-dimensional organometallic compounds, which were initially obtained by debrominative homocoupling of Hexabromo-substituted trinaphtho[3.3.3]propellane molecules on Ag(111) (figure 7(A)). Controlled voltages pulses facilitated the formation of the diradical unit through the debromination, which subsequently transformed into dehydroazulene isomer units via the structural isomerization at 4.3 K [83]. The delicate balance of the reaction rates among the diradical and two stereoisomers, resulting from the in-line configuration of tip and molecular unit, allows for controlled directional azulene-to-azulene and azulene-to-diradical isomerization (figure 7(B)). These three states can be regarded ternary bits. Over successive tip-induced isomerization, text 'NIMS' was recorded (figure 7(C)).

Expanding the previous tip-induced local chemical reaction that synthesized unprecedented planar molecules at the single-molecule level, we are now capable of controlling the unit structures, which can be used for memory bits. This systematic isomerization, in addition to tip-induced stereoisomerization, would be crucial for advancing nanochemistry towards the fabrication of molecular memory systems on a molecule-by-molecule basis.

Current and future challenges

The size of molecular networks corresponds to the number of the memory bit. However, the number of the bits are limited by the yield of the on-surface reaction. The structure shown in figure 7 has a maximum length of 20 nm, which corresponds to 18 bits. Therefore, current and future challenges in this field involves addressing the length and size limitations of the molecular network. Considering factors such as size and thermal stability, organometallic bond compounds at the moment represent the best option. The repeated formation and rupture of organometallic bonds until equilibrium is reached generally results in the fabrication of extended structures. Covalently linked nanocarbon structures offer another promising option of the molecular network for memory bits. In this case, we can expect even higher thermal stability. However, despite rapid advancements in the field of on-surface synthesis, it is still challenging to achieve large-scale products without any defect due to the irreversible nature of coupling reactions. Thus, it is of central importance to develop new on-surface reaction that either have high reaction yields or possess process for defect correction.

Another major challenge relates to automatization. The writing and reading process of memory bits using molecular networks have relied on the STM technique, requiring a bit-by-bit approach with a tip. The scanning speed of the STM is inherently limited due to the measurement bandwidth. Therefore, it is of importance to improve the scanning speed. However, recognizing the memory sites and inducing the switches of the memory bits in the molecular network are more time-consuming, as these processes are currently performed by STM operators. Thus, current and future challenges in this field also involve automatization of the reading and writing processes. As the large-numbered atom manipulation has been demonstrated [81], the integration of the digital SPM controller with the manipulation algorithms has already been established. The next challenge is to achieve automated writing and reading processes of the bits

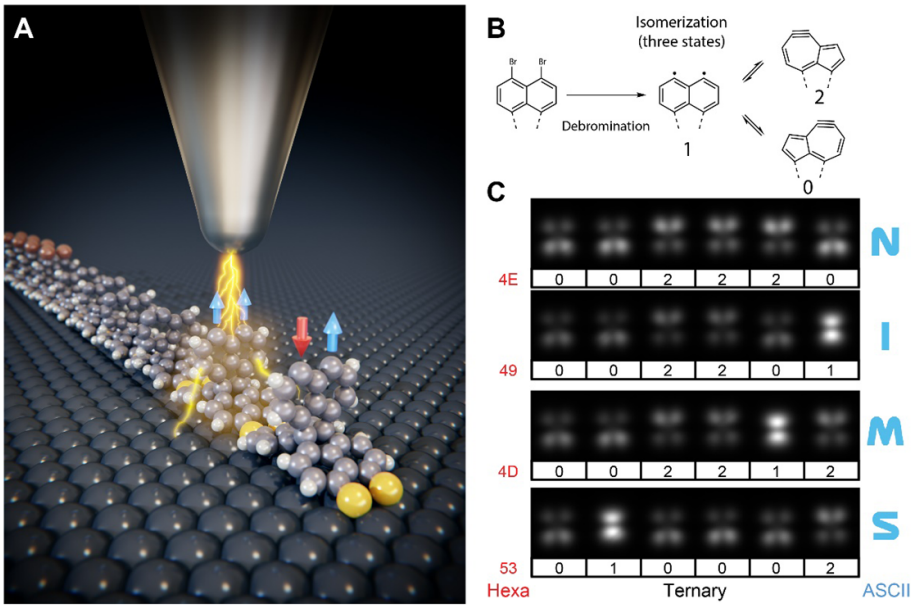

Figure 7. (A) Schematic drawing of memory bits using molecular networks under a tip of scanning tunnelling microscopy. (B) Example of three states isomerization. (C) Test recording with molecular bits in ternary cord. Reproduced from [83], with permission from Springer Nature.

in the molecular network based on the machine learning. This advancement would significantly improve the efficiency and precision of bit manipulation.

Advances in science and technology to meet challenges

The field of memory bits using molecular networks strongly relies on the advancements in STM/AFM and on-surface synthesis. These areas are steadily progressing with numerous efforts addressing various challenges from developing novel techniques to understanding on-chemistry. The main goal in the development of an efficient memory bits using molecular network would be to fully meet the technical requirements of the device such as scalability and reliability. To this end, state-of-the-art STM/AFM and on-surface chemistry are of central importance. Over the next decades, it is anticipated that the field of the on-surface synthesis will further develop. It will become possible to synthesize extended nanocarbon structures without any defects for memory bits using molecular networks. These structures should possess active sites that can be utilized for bit manipulation through structural isomerization, addition/elimination reactions [56], or a combination of these methods. A key factor that will relate to the individual and mutual development of SPM and on-surface chemistry would be the incorporation of machine learning as a recent successful example in this direction has reported [84].

In addition, there are many potential approaches in development of memory bits using molecular network. Currently, bit manipulations are based on the position and structures of molecule or molecular units, the so-called classical method. Recent advances in on-surface synthesis have enabled the fabrication of radical molecules and further linking each unit [75]. Thus, the entanglement of electronic spins between radical units in nanocarbon nanostructures represents another promising approach for realizing scalable, multifunctional system of memory bits using molecular networks. Ultimately, the concept of brain-inspired neuromorphic functions can be considered for dynamic memory systems. This brain-inspired memory must meet all requirement for scalability and reliability demanded in the memory bits using molecular networks. Achieving autonomous memory devices, that is capable of reading and writing large amounts of information, however, will undoubtedly require significant efforts.

Concluding remarks

Memory bits using molecular networks represent an exciting research field, driven by significant advancements of STM/AFM and on-surface synthesis. The demand for scalable and reliable devices, which can be achieved through classical, quantum, and neuromorphic approaches stimulates ongoing research in these areas. Efforts to explore physics and chemistry at the nanoscale will bring a number of novel possibilities for manipulating memory bits using molecular networks.

In summary, memory bits using molecular networks have a great potential to reduce energy consumption and enhance scalability, thereby improving current memory technology. In addition to technical innovation, these studies will contribute to the development of fundamental nanoscience, as demonstrated since the invention of STM and AFM.

Acknowledgments

This work was supported in part by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Numbers JP22H00285, JP24K21721 and JP25H00422.

2.6. Molecule on tip as a quantum sensor

Laurent Limot[1] *and Nicolás Lorente*[2,3]
[1] Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France
[2] Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain
[3] Donostia International Physics Center (DIPC), 20018 Donostia-San Sebastián, Spain

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, 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 [85–87]. Concomitantly, 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 [88].

In 2004, quantum spin sensing entered the realm of STM with spin excitation spectroscopy [89]. 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 [90, 91]. 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_2N 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 ESR-STM has significantly enhanced spin sensitivity and broadened the applicability of quantum spin sensing at the atomic scale [41]. 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 [19].

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 sub-molecular resolution and providing new chemical insights. Recently, this approach has been extended [92, 239] to spin sensing through the decoration of the tip apex with a single nickelocene molecule [$Ni(C_5H_5)_2$] (figure 8(a)). Nickelocene comprises a single Ni atom sandwiched between two cyclopentadienyl rings (C_5H_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 [93]. 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 (figure 8(b)).

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 behaviour 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

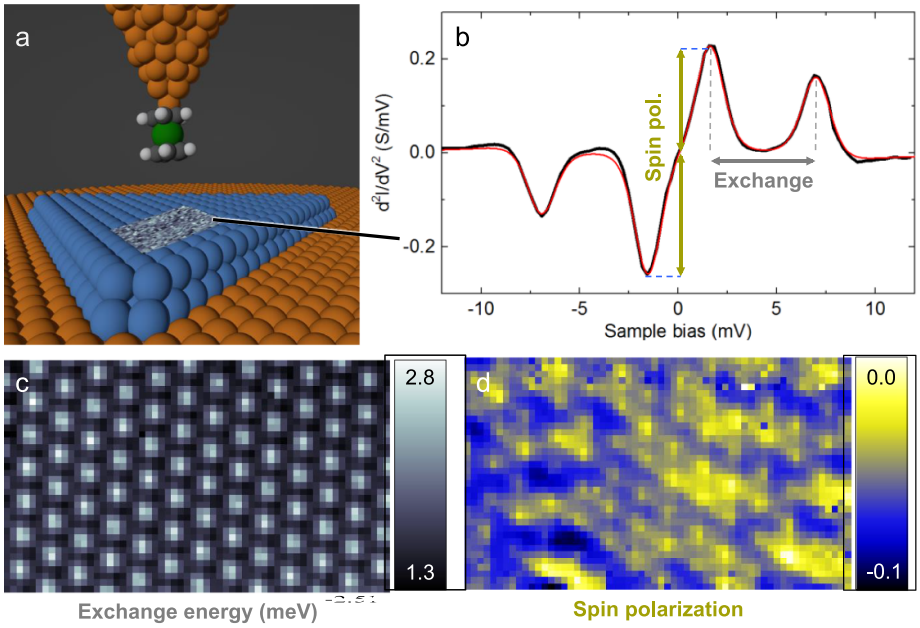

Figure 8. (a) Nickelocene-tip schematic. The energy landscape of a nickelocene-tip is modeled using the spin Hamiltonian $H = D S_z^2 - J\,\mathbf{S}\cdot\mathbf{S}_{\mathbf{sample}}$, where J represents the Heisenberg interaction extending into the vacuum, coupling the spin $\mathbf{S}$ of nickelocene to the sample spin $\mathbf{S}_{\mathbf{sample}}$. (b) Electrically-driven spin excitations associated with this Hamiltonian produce inelastic tunnelling spectra in the form of $\mathrm{d}^2I/\mathrm{d}V^2$ versus bias V, which can be analytically modelled (solid red line) [90, 91] 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 $\mathrm{d}^2I/\mathrm{d}V^2(x,y,V)$ 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.

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 [94], cobaltocene [$Co(C_5H_5)_2$, 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 Wallraff *et al* [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 [95], 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 [96], where both a quantum molecular spin and a magnetic tip are essential for detecting ESR signals [41]. 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 centres 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 tunnelling electrons and by the exchange interaction between the STM tip and sample (figure 8(b)). Additionally, the lifetime of the spin excitations can affect the line shape [91]. 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 analysing the line shape through post-treatment. The exchange interaction and spin polarization can then be mapped to **r** to produce a spatial map (figures 8(c) and (d)). Remarkably, these maps correlate with spin density maps computed using DFT [93], 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.

Acknowledgments

LL acknowledges support from the ANR (ANR-23-CE09-0036-01) and the International Center for Frontier Research in Chemistry (Strasbourg). NL acknowledges support from Projects PID2021-127917NB-I00 by MCIN/AEI/10.13039/501100011033, QUAN-000021-01 by Gipuzkoa Provincial Council, IT-1527-22 by Basque Government, 202260I187 by CSIC, ESiM Project 101046364 by EU. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the EU. Neither the EU nor the granting authority can be held responsible for them.

3. Topological quantum platforms crafted atom-by-atom

3.1. The Josephson effect in STM

Berthold Jäck[1], *Haonan Huang*[2], *Joachim Ankerhold*[3] *and Christian R Ast*[4]
[1] Hong-Kong University of Science and Technology, Hong Kong Special Administrative Region of China, People's Republic of China
[2] Department of Physics, Princeton University, Princeton, NJ, United States of America
[3] Institute for Complex Quantum Systems and IQST, Universität Ulm, Ulm, Germany
[4] Max-Planck-Institute for Solid State Research, Stuttgart, Germany

Status

Since its prediction by Brian Josephson in 1962 [97], the tunnelling of Cooper pairs, known as the Josephson effect or Josephson tunnelling, has been observed in various different devices and environments. More recently, the Josephson effect has also been employed as a versatile probe of emergent phenomena in unconventional and topological superconductors. Fundamentally, the Cooper pair tunnelling dynamics sensitively depend on the tunnel junction type (metallic or insulating barrier), the immediate junction environment (resistors, capacitors, or inductors in the vicinity), as well as on external parameters such as temperature and magnetic field. As a result, the experimental characteristics of current- and voltage-biased measurements of the Josephson effect operating in these different regimes require different types of theoretical models.

The most important distinction is whether the phase in the tunnel junction (i.e. the phase difference between the superconducting order parameters) can be effectively considered as a classical degree of freedom, or if a quantum mechanical treatment of the phase is necessary [98, 99]. While the well-known Josephson relations describing a dissipationless supercurrent are based on a classical phase picture with negligible fluctuations, the Josephson effect in STM is typically dominated by strong phase fluctuations [100]. These fluctuations can be mostly attributed to the few transport channels present in an STM tunnel junction leading to a small Josephson energy E_J as well as a high charging energy E_C due to the small junction capacitance [101]. When the thermal energy $k_B T$ is the leading energy scale the Josephson effect in the STM can be quantitatively described by the classical Ivanchenko–Zilberman model [102]. On the other hand, if the charging energy dominates, the tunnel junction resides in the dynamical Coulomb blockade regime where its dynamics are subjected to significant quantum fluctuations of the phase, as captured by the so-called P(E)-theory [103, 104], where details sensitively depend on the electromagnetic environment. For illustration, we have included a schematic in figure 9.

With this detailed quantitative understanding of the Josephson effect at hand, research has progressed from examining the Cooper pair tunnelling process itself to employing the Josephson tunnelling as a probe of emergent phenomena in quantum materials. Insights include the exchange of energy with the environment during Cooper pair tunnelling [105, 108], pair density waves [109], unconventional superconductivity [110]. Also, different mesoscopic devices exploiting the Josephson effect have been transferred to the atomic scale, such as an atomic scale SQUID [122] and a proposal for a superconducting diode [123]. In this sense, the Josephson effect in the STM has been established as an important local probe of various aspects of superconductivity for both bulk substrates and atomic scale structures (adatoms, molecules, etc). Future developments of the Josephson effect in the STM can benefit from further advances of both theory and experiment. The ability to extract the current-phase relation in a charge dominated environment, where the phase is not well defined, would, for example, greatly help understand local transport through Yu–Shiba–Rusinov (YSR) states and by extension Majorana bound states. Also, having only very few transport channels in an STM tunnel junction, an intimate interplay of Andreev processes with charge and phase noise emerges.

Current and future challenges

Due to dominating charge processes with sequential charge tunnelling in the STM tunnel junction, the phase in the tunnel junction is strongly fluctuating and not well defined. Accordingly, the classical picture of the phase dynamics in a washboard potential is washed out and Cooper pair tunnelling is strongly inelastic. As the Josephson effect is related to the smallest energy scales in scanning tunnelling spectroscopy (STS), its full potential can only be reached at lowest temperatures in the mK-regime. Also, extensive filtering has to be implemented for all signals going to and coming from the STM scan head to minimize voltage fluctuations and the pick-up of stray radiation. This is a rather technical challenge that is being addressed with an increasing level of sophistication. Ultimately achieving phase coherent Cooper pair tunnelling at low temperatures in an STM tunnel junction may be impossible due to the principal characteristics of the tunnel

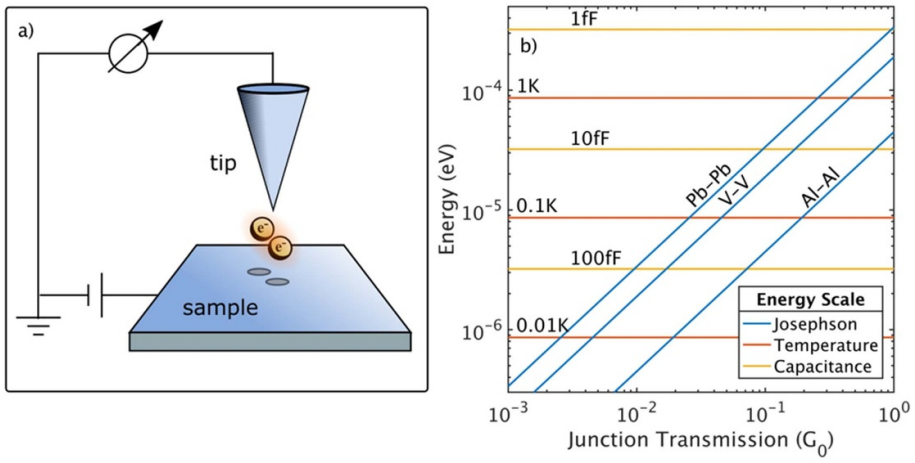

Figure 9. The Josephson effect in the STM: (a) schematic of the tunnel junction with a superconducting tip and a superconducting sample. The tunnelling of Cooper pairs is indicated. (b) Comparison of energy scales for the Josephson effect, the junction capacitance and temperature. The Josephson effect is visible in the spectra for junction conductance larger than about $0.03G_0$, where $G_0 = 2e^2/h$ is the conductance quantum. The Josephson energy (blue) depends linearly on the junction conductance [325] and is indicated for symmetric junctions of lead, vanadium and aluminum. At conductances approaching G_0, the Josephson energy may deviate from its linear evolution depending on the number of transport channels in the tunnel junction. The charging energy (yellow) of the junction capacitance is indicated for typical values between 1 fF and 100 fF. The thermal energy (red) is indicated for typical temperatures between 10 mK and 1 K.

junction ($E_J < E_C$). However, by making the tunnel junction more transparent, an emergent coherent coupling and a linear transmission dependence instead of a quadratic transmission dependence may be within experimental reach.

The properties of the materials forming the Josephson junction can have a significant influence on the behaviour of the Cooper pair tunnelling. However, in many cases, the underlying theoretical models assume a well-defined phase, which typically does not apply to the STM junction. Therefore, a comprehensive adaptation of the models assuming a well-defined phase to the charge dominated STM tunnel junction, would be greatly desirable and can help judge, what kind of information can be extracted from a Josephson junction and what not.

Advances in science and technology to meet challenges

There have been many advances in STM concerning Josephson junctions, both in the experimental observation as well as in the theoretical understanding in the past decades. Experimentally, the energy resolution and electronic temperature has dramatically improved over the past years not just due to experimental setups operating at lower and lower temperature, but also due to improved grounding and filtering concepts to reduce voltage noise in the tunnel junction. Still, the tunnel junction as well as the experimental environment may be exposed to high frequency radiation, such as thermal radiation ($1\ \mathrm{K} \approx 20\ \mathrm{GHz}$). This may be detrimental, if the tunnel junction is at base temperature, but is still exposed through a direct line of sight to components at higher temperature. Proper shielding and encapsulation of the STM scan head as well as filtering is desirable. Also, a number of interesting concepts have been developed in the mesoscopic Josephson community, which could be adapted for the STM, such as filtering and thermalization techniques [6, 106, 107].

The transformation from phase-coherent tunnelling in mesoscopic Josephson junctions to charge dominated sequential tunnelling in the STM is one of the primary differences that sets the Josephson tunnelling apart from mesoscopic junctions, which actually highlights the duality between these processes. As such, they can be related through a Fourier transform, such that the theoretical results for phase dominated tunnelling can readily be adapted to charge dominated tunnelling in a comprehensive way [108]. In this way, an adapted theory with a custom-tailored approach to the Josephson junction in an STM can provide more quantitative predictions for different measurements. Such measurements could go beyond the understanding of the Josephson junction itself and give more insight into the superconducting properties of the materials, such as the properties of their order parameter.

Concluding remarks

The Josephson effect has been established as the preeminent tool to examine tunnelling dynamics in the well-defined junction of the STM. It provides insight into the immediate surroundings through the

dynamical Coulomb blockade and P(E)-theory as well as a more thorough understanding of the materials and systems in the tunnel junction. Additionally, its use in studying unconventional superconductors has yielded valuable insights. We anticipate that extending Cooper pair tunnelling to topological superconductors and associated quasiparticle excitations, like Majorana zero modes [111–118], will further illuminate the nature of these states, though it still requires further development to reach its full potential. Advancing both theory methods and experimental conditions as discussed above would greatly improve the overall prospects of these research directions. Overall, the Josephson effect is a well-studied phenomenon whose many aspects have been in the focus of researchers for many decades. Therefore, the technique is in an advanced stage of refinement with many detailed questions to be addressed. It will be exciting to see how the Josephson effect in the STM further develops in the coming future.

3.2. YSR states at the single-atom scale and their effect in Josephson junctions

Martina Trahms[1], *Clemens B Winkelmann*[2] *and Katharina J Franke*[1]
[1] Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany
[2] University Grenoble Alpes, CEA, Grenoble INP, IRIG/DEPHY/PHELIQS, 38000 Grenoble, France

Status

Back in 1997, Yazdani and co-workers reported resonances within the superconducting energy gap of Pb(111) on single Mn and Gd atoms using STS [85]. They ascribed these signatures to YSR states, which had been predicted decades before as a result of a classical spin being exchange coupled to a superconducting condensate. Meanwhile, the theoretical description was expanded to quantum spins, where Kondo correlations were added as the competing energy scale to superconductivity (figure 10(a)). Lower operating temperatures of the STM and the use of superconducting tips have enabled the resolution of many more details pertaining to YSR states. Thus, it became possible to resolve YSR multiplets, originating from multiple scattering channels or anisotropy-split YSR states (for a review see [119]). Single-atom manipulation enabled the construction of nanostructures atom by atom while tracking hybridization and band formation originating from the YSR states. These nanostructures served particularly useful in two regards. First, the quantum spin nature could be identified by YSR states crossing the quantum phase transition, which separates screened and unscreened magnetic moments, when the atoms were in sufficiently close vicinity for substrate-mediated magnetic interactions [120]. Second, chains of magnetic adatoms were shown to be a promising platform for topological superconductivity including Majorana zero modes [111].

Both aspects—the quantum-spin nature and the possibility to construct topologically non-trivial states—still render the fundamental investigation of YSR states highly interesting. We note that these aspects are intimately linked to each other. While in many cases of magnetic adatom structures, the observations can be well explained within the classical-spin limit, it has been shown theoretically that the quantum-spin nature influences the topological phase diagram and reduces the phase space, where non-trivial states are to be expected [121]. Furthermore, competing energy scales originating from superconducting pairing, exchange coupling of the magnetic adsorbate to the substrate, and substrate-mediated exchange coupling may lead to intriguing magnetic spin textures and Kondo-lattice type behaviour in one- and two-dimensional adatom lattices. YSR states as building blocks of these structures thus remain a highly interesting research topic.

Current and future challenges

In addition to being regarded as building blocks for intriguing non-trivial states (which are discussed in separate sections), magnetic atoms on superconductors exhibit significant potential when inserted into Josephson junctions. Such junctions have been established by contacting the magnetic atom with a superconducting tip. In conventional voltage-biased Josephson junctions, a reduction of the zero-bias conductance peak—the hallmark of such junctions—was observed in comparison to non-magnetic junctions [105, 122].

However, as an applied voltage induces a time-dependent phase drop across the junction of the superconducting condensates in accordance with the Josephson relations, the full potential of the junctions can only be exploited in current-biased measurements. These types of measurements reveal information on the phase dynamics in the junction. Sufficiently small phase diffusion allows for the observation of a switching and retrapping current. The former marks the transition from the supercurrent-dominated phase to the resistive state upon an increase in the biasing current, while the latter marks the transition from the resistive state back to the superconducting state. The coexistence of phase diffusion and hysteresis in the switching/retrapping current indicates a frequency-dependent damping behaviour of the junction. Ideally, one would like to fully suppress phase diffusion. This, however, is very difficult to achieve as it is not sufficient to suppress thermal fluctuations. At very low temperatures, quantum fluctuations become dominant and cannot be avoided in atomic-scale junctions. Similarly, the control of damping properties is a challenge in the STM with the junction's impedance predominantly influenced by the interaction with the environment. The latter may be addressed by novel design schemes as discussed in the next paragraph.

Recent observations in Josephson junctions including YSR states further enhance the interest to gain full control of the interaction with the environment in an STM. Surprisingly, it was found that the retrapping current depended on the biasing direction of the junction [123]. Its origin was ascribed to broken electron–hole symmetry in the YSR states (figure 10(b)). The resulting direction-dependent damping is reminiscent of diode characteristics. The demonstration of an atomic-scale non-reciprocal Josephson junction is a promising avenue for miniature applications in quantum circuits.

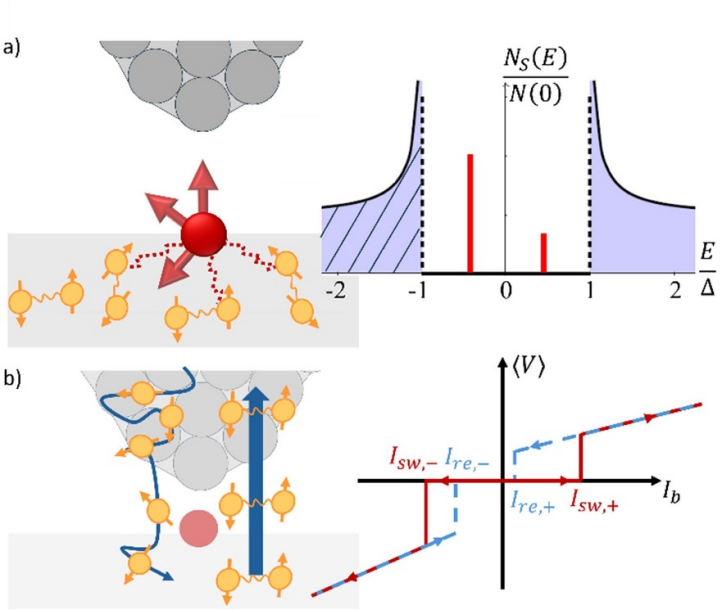

Figure 10. Spectroscopy of single magnetic adatoms. (a) YSR states are induced by the interaction of the magnetic adatom's unpaired spin with the superconducting condensate. The atom's magnetic moment does not have a preferential direction. YSR states are symmetric in energy and asymmetric in intensity due broken electron–hole symmetry by potential scattering. (b) In the Josephson regime, the damping of the Cooper-pair tunnelling events is influenced by the electron–hole asymmetry of the YSR states causing the retrapping currents to become asymmetric.

Advances in science and technology to meet challenges

Following the surprising discovery of Josephson-diode behaviour in a single-atom junction, the next challenge is to gain full control over the rectifying behaviour. First, one may envision to tune the rectification ratio by increasing electron–hole asymmetry possibly by variation of the adatom species or adsorption site. Second, technologically more relevant would be a non-reciprocity of the switching current of the junction. Indeed, other realizations of Josephson junctions exhibit non-reciprocal behaviour in the switching rather than the retrapping current, induced by broken time-reversal symmetry instead of broken electron–hole symmetry [124]. Broken time-reversal symmetry without application of an external magnetic field can be achieved by ferromagnetic structures [125]. The realization of such structures on the atomic scale is in sight [126].

Additionally, many interesting manifestations of Josephson physics are related to high-frequency properties. For instance, adding MWs to a dc-current-biased Josephson junction can lead to coherent phase dynamics which manifest as quantized (Shapiro) voltage steps. Irradiation by MWs is, thus, a method of choice for setting the quantum mechanical state of the junction. Vice versa, it may be used to investigate the current-phase relationship as well as out-of-equilibrium (relaxation) dynamics of the bound states carrying the supercurrent. Therefore, one of the next natural steps in the investigation of YSR states will consist in probing their ability to carry a supercurrent by high-frequency approaches.

One of the primary challenges in effectively coupling an STM junction to a MW drive or readout is the lack of precise control over the high-frequency properties of the STM junction environment [99, 105]. This lack of control leads to impedance mismatch and undesired losses, which are known to significantly influence the Josephson junction's dynamics. This is in contrast with on-chip quantum circuit experiments, which can be designed with a high degree of control of all relevant parameters, which is a necessary ingredient for preserving phase coherence.

Attempts in inserting MWs into STM junctions include simple antenna setups and MW strip lines, both mainly applied in single-atom spin-resonance measurements. Extending these approaches to magnetic atoms on superconductors and their Josephson junctions is a natural combination benefiting from the recent advances in the fields.

Concluding remarks

When they were theoretically predicted over 50 years ago, the potential of YSR states was not foreseeable. With the development of STM, their fascinating properties at the atomic scale were revealed, and yet, their interest still largely remained at a fundamental level. Only recently, it became clear that YSR states could also be of technological importance. These prospects include their implementation in Josephson diodes or as

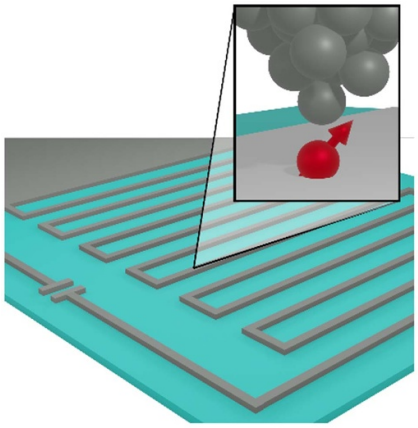

Figure 11. Atomic-scale STM experiments within a controlled electromagnetic environment as provided by carefully designed on-chip resonators may pave the way for new technological advances.

building blocks for topological superconductivity. When combined with high-frequency driving, these systems may provide further surprises. Theoretically, it has been proposed to use YSR states a qubits [127, 128]. However, to make YSR states integral parts of quantum technologies, many challenges are yet to be overcome, such as the control of electromagnetic environment on the atomic scale (figure 11). We believe that the progress could benefit from the knowledge of physical concepts and technologies routinely applied in quantum electronic transport community.

Acknowledgments

We thank L Farinacci, B W Heinrich, E Liebhaber, L Melischek, M Ruby, L M Rütten, H Schmid, J F Steiner, and F von Oppen for the fruitful collaborations over the past years. Financial support by Deutsche Forschungsgemeinschaft through Grant CRC 183 (Project C03) and through a joint DFG-ANR Grant (MagSta2D with DFG: FR2726/10 and ANR-22-CE92-0092-01) is gratefully acknowledged.

3.3. Engineering YSR nanostructures

Martina O Soldini[1], *Glenn Wagner*[1,2], *Titus Neupert*[1], *Felix Küster*[3], *Souvik Das*[3], *Stuart S P Parkin*[3] *and Paolo Sessi*[3]
[1] Department of Physics, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland
[2] Institute for Theoretical Physics, ETH Zurich, 8093 Zurich, Switzerland
[3] Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Status

Over the last decade, we have witnessed an increased interest in coupling magnetic nanostructures to superconducting condensates. An important motivation relates to the YSR localized states that are induced by the exchange interaction between the magnetic nanostructures and a superconducting condensate. The hybridization of these localized states can lead to the creation of YSR bands which, for carefully engineered structures, can drive the system into a topologically non-trivial superconducting state. It is predicted that this state can host Majorana modes (MMs) at the boundaries of the magnetic nanostructures. Early studies that revealed signatures compatible with Majorana modes focused on magnetic chains that are self-assembled on superconducting surfaces [111, 129]. More recently, STM techniques have been used to fabricate magnetic nanostructures atom-by-atom. These structures, typically in the form of spin-chains that are nominally disorder-free, have allowed for detailed studies of the formation of YSR bands in a variety of 1D and 2D spin chains coupled to superconductors. These studies have allowed for deep insights into the origin of the end-modes [130–133].

Studies on 2D YSR nanostructures have largely followed two distinct approaches: (i) molecular overlayers self-assembled on superconducting surfaces, and, (ii) molecular beam epitaxial growth of magnetic layers on superconducting substrates. By chemically programming the molecular building blocks, self-assembled YSR nanostructures form distinct 2D spin arrays, that are a result of a delicate balance between molecule–molecule and molecule–substrate interactions. STS studies showed that it is possible to tune the energy of the YSR states [134]. However, since the magnetic atom is generally embedded within an organic network, the distance between the YSR states is typically >1 nm and their hybridization is weak. On the other hand, magnetic layers deposited onto superconducting substrates, give rise to dispersive YSR bands that have been reported both for collinear ferromagnetic [135] as well as antiferromagnetic spin textures [136].

Recently, 2D YSR nanostructures crafted atom-by-atom have also been experimentally realized [137]. This strategy made possible the creation of YSR lattices that are characterized by distinct symmetries using the same building blocks, i.e. the same magnetic atoms and superconducting substrates, as illustrated in figure 12. Moreover, these lattices allowed for the design of distinct lattice terminations, thereby offering a control knob to directly test the bulk-boundary correspondence that characterizes topological states of matter (see figure 13). Moreover, this approach also offers the possibility to add desired defects, such as magnetic domain walls, in these structures. So far, the number of experimentally realized YSR nanostructures crafted atom-by-atom is rather limited. However, there are nearly an infinite number of possible combinations of different atoms and substrates. This great flexibility makes it possible to realize different classes of crystalline topological superconductors that are rare or absent in natural materials.

Current and future challenges

The biggest research issue currently faced by YSR nanostructures is to provide compelling experimental evidence for MMs. This difficulty arises from the possible existence of trivial excitations which can mimic or poison signatures of MMs. To rule out trivial mechanisms, putative MMs need to be linked to the topological properties of the bulk. In 1D, YSR bands could be measured by Fourier transform quasiparticle imaging on chains consisting of tens of atoms [130]. In the 2D realm, this number naturally scales up to hundreds of atoms. Beside stable tips for reliable atomic manipulation, large defect-free areas are needed to accomplish this task: for typical spacing between atoms, i.e. 0.3–1 nm, clean areas >10 nm^2 are required. Another related challenge is the simultaneous spectral and spatial isolation of MMs, which requires systems where no other YSR states exist near zero energy.

The platforms explored so far have mostly used elemental superconductors where the simultaneous optimization of relevant parameters, such as spin–orbit coupling (SOC) and superconducting energy gap, is a major obstacle towards the creation of MMs. Indeed, superconductors with large SOC are beneficial for the creation of large topological minigaps. However, elemental superconductors with strong SOC either exhibit a small superconducting gap (e.g. Ta and Re), that is an obstacle to disentangle YSR bands from temperature broadening effects, or have a small cohesive energy (e.g. Pb) that impedes atomic manipulation.

Furthermore, realizing specific 2D spin lattices is a formidable task. While the spin state can be controlled by varying the magnetic element, the magnetic anisotropy of single atoms strongly depends on their

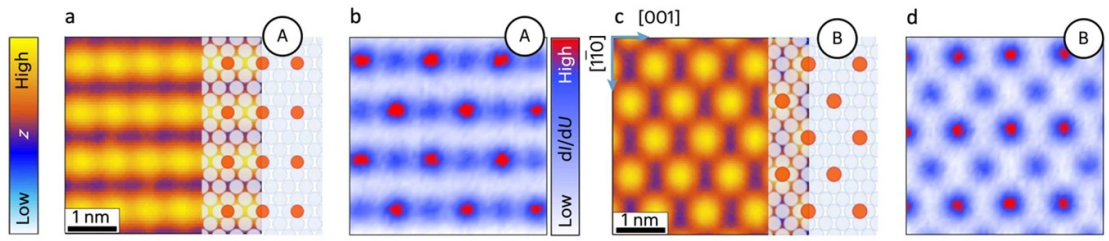

Figure 12. (a), (c) Topographic images of two distinct lattices assembled using Cr atoms coupled to the Nb(110) surface. System A corresponds to a rectangular lattice, whereas system B corresponds to a rhombic lattice. For each structure, a schematic illustration of the position of the atoms with respect to the underlying substrate is overlapped with the topographic image. (b), (d) dI/dU maps from STS acquired using a spin-polarized tip. The alternating contrast visible in both lattices reveals an antiferromagnetic ground state. Reproduced from [137], with permission from Springer Nature.

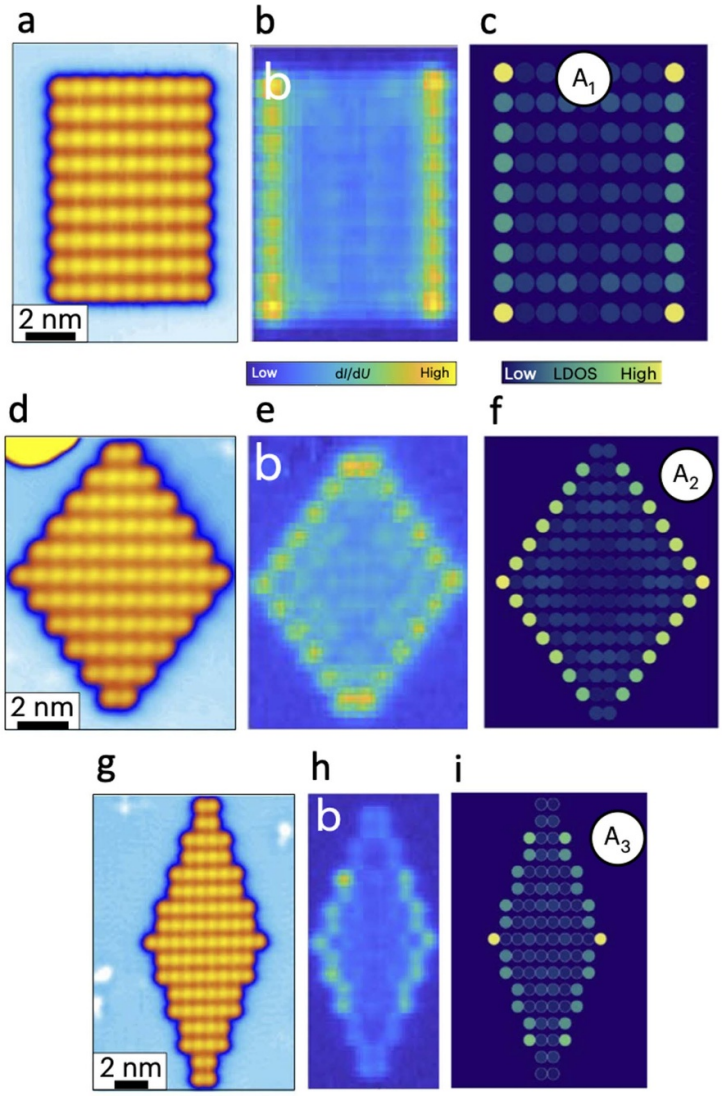

Figure 13. (a), (d), (g) Topographic images showing three different lattice terminations for the same rectangular structure assembled using Cr atoms coupled to the Nb(110) surface; (b), (e), (h) dI/dU maps showing the spatial distribution of the lowest energy boundary modes; (c), (f), (i) theoretically calculated local density of states at zero energy showing topological boundary modes. Reproduced from [137], with permission from Springer Nature.

interaction with the local environment. Moreover, various magnetic interactions, such as the Heisenberg exchange, the Ruderman–Kittel–Kasuya–Yosida and the Dzyaloshinskii–Moriya exchange interactions, are generally simultaneously at play, elevating the complexity of the physical systems substantially above those of conventionally studied toy models.

Finally, assembling YSR nanostructures atom-by-atom requires the development of STM tips which can simultaneously fulfil two conditions: they must allow for (i) low impedance operation (generally below 100 kΩ) for atomic manipulation, and, (ii) the imaging of the spin structure (necessary to define the spatiotemporal symmetries of the lattice). Conventional spin-polarized tips have major drawbacks: the most problematic one is that the tip apex might be easily modified by the high number of atomic manipulation sequences required to build the lattice, ultimately losing spin sensitivity.

Advances in science and technology to meet challenges

Building lattices consisting of hundreds of atoms is a tedious task and is prone to errors if carried out by hand. The reliability can be significantly enhanced by a combination of pathfinding algorithms with image recognition. Still, the need for large defect-free areas represents the main obstacle. This constraint can be mitigated by focusing on materials with strong SOC which, by enhancing the size of the YSR bands minigap, can increase the localization of MMs. The lack of the combination of the desired properties of elemental superconductors necessitates new approaches. A possible solution would be to proximitize heavy elements that have large SOC to superconducting substrates that host a large superconducting energy gap. First attempts with Bi [138] and Ir [139] layers coupled to Nb showed that sufficiently thin films largely preserve the superconducting energy gap of the substrate. Ultimately, solving this challenge requires the identification of materials that exhibit large superconducting gaps and strong SOC whilst having sufficiently high surface quality needed for precise atomic manipulation.

Overcoming the limitations of conventional spin-polarized tips requires the development of innovative spin-sensitive tips which can be controllably functionalized *in-situ*. One possible solution is the use of YSR tips prepared by attaching magnetic atoms deposited onto the surface at the apex of a superconducting cluster. Due to their strong spin-polarization, YSR states allow for the imaging of magnetic moments [140]. Furthermore, their spin quantization axis can be adjusted with relatively weak external magnetic fields [141]. However, the fabrication of YSR tips with predictable parameters remains challenging. Further advancements for deterministic control are required.

Another likely path forward is to consider additional mechanisms to form MMs at hybrid magnetic–superconductor interfaces. Promising approaches include, (i) designing skyrmionic textures, where the topological phase might be controlled by externally applied magnetic fields [142], and, (ii) embedding specific dislocation and disclination point defects inside the lattice which can be created and moved by atomic manipulation techniques [143]. In both cases, given the large variety of possible configurations, experimental progress can benefit tremendously from the development of predictive design strategies based on theoretical calculations.

Concluding remarks

Scanning tunneling microscopy and spectroscopy have proven to be powerful methods for imaging YSR nanostructures. However, significant progress is still needed to provide compelling experimental evidence for MMs. Among various approaches, the creation of YSR lattices crafted atom-by-atom has been proven to be highly promising due to the large number of possible lattices that can be created. By selecting appropriate building blocks, this approach has great flexibility for the generation of spin textures, symmetries, hopping amplitudes, as well as the design of atomically precise lattice terminations and defects. More generally, we envision that artificial spin lattices will open up new avenues for implementing and experimentally testing well defined model Hamiltonians.

Acknowledgments

TN and MOS acknowledge funding from the Swiss National Science Foundation (Project 200021E_198011) as part of the FOR 5249 (QUAST) lead by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) and through a Consolidator Grant (iTQC, TMCG-2_213805). GW acknowledges funding from the University of Zurich postdoc Grant FK-23-134 and is supported by the Swiss National Science Foundation (SNSF) via Ambizione grant number PZ00P2-216183.

3.4. Atomically-confined topological boundary modes

Zhenyu Wang[1] *and Vidya Madhavan*[2]
[1] Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
[2] Department of Physics and Materials Research Laboratory, University of Illinois Urbana-Champaign, Urbana, IL, United States of America

Status

A distinguishing feature of two-dimensional (2D) topological materials with a gap in their bulk single-particle spectra is that they host conducting edge modes on their 1D boundaries. The emergence of these boundary modes is enforced by bulk-boundary correspondence and thus topologically protected; importantly, the spin-momentum locking, at least in certain circumstances, protects these edge states from backing scattering, thus enabling electrical transport in a dissipationless manner. Since the discovery of the helical modes in semiconductor quantum walls [144], the investigation of topological boundary modes has been extended to systems where the quantum many-body interactions come into play, including Chern insulators hosting chiral edge modes, topological superconductors with Majorana edge modes and several exotic density wave phases (summarized in figure 14). This progress has not only pushed ahead our understanding of new quantum phases of matter, but also provides promising avenues towards energy-saving technology and topological quantum computation.

Because these topological boundary modes exhibit a strong 1D confinement to atomic length scales, experimental studies have largely focused on STM and ballistic transport signatures of these modes. Helical edge modes have, for example, been visualized in various time-reversal invariant 2D topological insulators where they spectroscopically manifest as uniformly distributed DOS at the boundaries, residing inside the bulk gap, and being immune to potential disorders or irregular boundary shapes. Material platforms include bismuthine on SiC [145], $Bi_{14}Rh_3I_9$ [146], monolayer transition metal dichalcogenides (TMDCs) [147, 148], $ZrTe_5$ [149] and bismuth halides [150]; and nearly quantized spin Hall conductance has been successfully observed for short edges in WTe_2 [151] and $TaIrTe_4$ devices [152]. Apart from 2D topological insulators, higher-order topological insulators (HOTIs) can also host topologically protected boundary modes as seen for example in thin films of Bi [153]. Towards practical application of these 1D helical modes, a sizeable topological band gap is needed to avoid detrimental contributions from thermal excitations of the bulk. So far, the bulk energy gap has reached hundreds of meV in bismuthine [145], while the edge channels have been shown to dominate electric transport up to 100 K in WTe_2 devices [151]. Interestingly, the 1D confinement of the helical boundary states may naturally lead to the formation of a Tomonaga–Luttinger liquid, resulting in a power-law suppression of the local DOS at E_F that encodes many-body correlations.

Current and future challenges

Chern insulators can host the quantum anomalous Hall effect (QAHE) at zero magnetic field with chiral boundary modes that carry dissipationless currents. However, the experimental realization of chiral boundary modes has proven to be difficult as it requires spontaneously broken time reversal symmetry due to global ferromagnetic ordering or valley polarization with strong electron–electron interactions. One symptom of this difficulty is that the quantization of Hall conductance as measured by transport is much more robust than that of the quantum spin Hall effect. In the archetypal Cr-doped topological insulators for example, electronic disorder induced by dopants drastically suppresses the minimum mass gap at the nanoscale [154], which has hampered the detection of possible boundary modes and limited the realization of QAHE to sub-kelvin temperatures. Until recently, chiral edge states have been observed by STM at the step edges in two kagome compounds, $TbMn_6Sn_6$ [155] and $Co_3Sn_2S_2$ [156]. These are both 3D magnetic materials in which 2D Chern insulating layers are stacked along the layer direction and separated by additional spacer layers. The intrinsic magnetization and spin–orbital coupling of the kagome layers can open a sizable Chern gap and produce linearly dispersing chiral boundary states within the gap. Although monolayer or few layers of these topological magnets hold promise for achieving QAHE at elevated temperatures, the synthesis of these 2D versions remains a great challenge.

Two-dimensional topological superconductors are a natural platform for hosting propagating 1D Majorana edge modes with linear dispersion. These much-coveted boundary modes are of fundamental interest and could be harnessed for quantum computing. Although such 1D Majorana modes are very rare in naturally occurring compounds, several intrinsic unconventional superconductors have shown promise, including heavy Fermion superconductor UTe_2 [157], iron-based superconductors [158, 159], the Weyl superconductor $MoTe_2$ [160] and TMDC 4Hb-TaS_2 [161]. However, elucidating the topological nature of these potential edge modes remains elusive, as it requires a detailed knowledge of the bulk superconducting

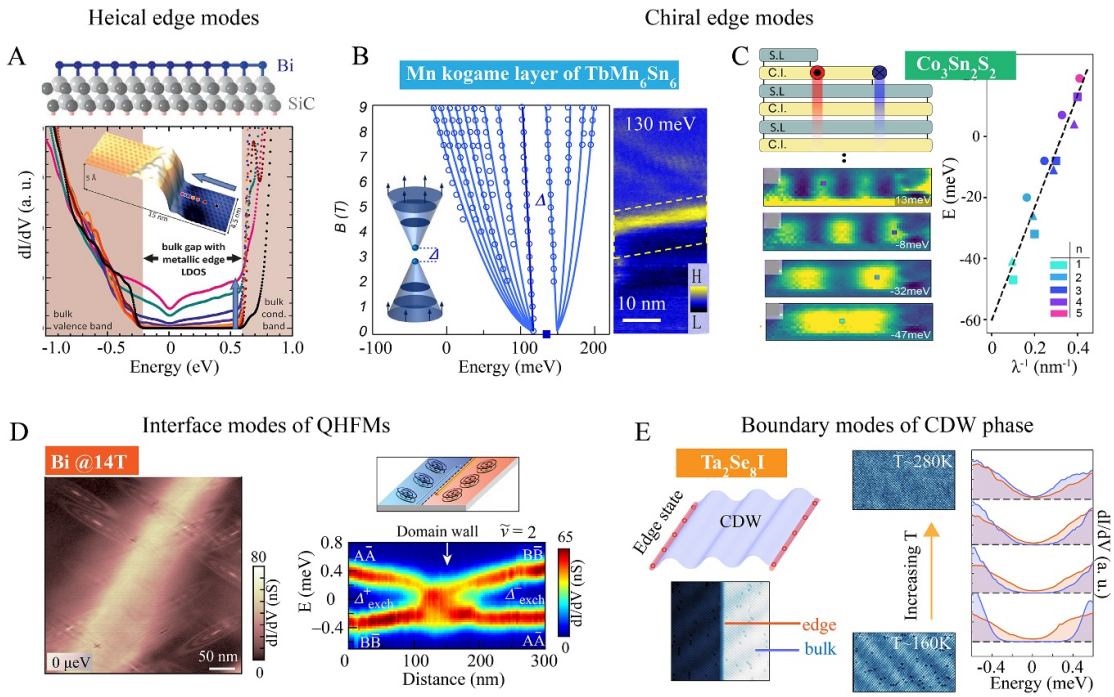

Figure 14. 1D atomically-confined boundary modes in various topological systems revealed by STM. (A) Helical edge modes in a time-reversal invariant 2D TI, bismuthine on SiC. From [145]. Reprinted with permission from AAAS. (B) and (C) Chiral edge states observed at the step edges of the Chern insulating layers in Kagome magnets $TbMn_6Sn_6$ and $Co_3Sn_2S_2$. (B) Reproduced from [155], with permission from Springer Nature. (C) Reproduced from [156], with permission from Springer Nature. (D) boundary modes at domain walls between two quantum Hall ferromagnetic (QHFM) phases with different valley polarization, on the surface of bismuth. Reproduced from [162], with permission from Springer Nature. (E) Topological boundary modes observed in the CDW phase of Ta_2Se_8I. Reproduced from [163], with permission from Springer Nature.

order parameter. An alternative approach is to construct 2D magnets, either with ferromagnetic order [116, 126, 135] or anti-ferromagnetic order [137, 136] on a superconducting surface, where topological superconductivity could emerge from the interplay between magnetism, SOC and superconductivity. A detailed summary can be found in other sections of this roadmap.

The exploration of topological boundary modes has been recently extended to more complex quantum materials. On the surface of bismuth, boundary modes have been directly visualized at domain walls between quantum Hall phases with different valley polarization [162]. STM studies have reported the demonstration of 1D boundary modes, possibly topologically protected, in the charge density wave phases of Ta_2Se_8I [163] and FeGe [164]. Very recently, an unexpected insulating state hosting quantized helical edge conductance emerges in monolayer $TaIrTe_4$ near the van Hove filling, hinting to an exotic charge density wave order therein [152]. These exciting observations call for in-deep theorical and experimental researches on the interplay between topology and correlations.

Advances in science and technology to meet challenges

One obvious obstacle in the study and application of 1D boundary modes lies in the complexity and uncertainty of achieving clean and stable thin sheets down to a single layer. Besides optimizing the material fabrication techniques, this problem may be overcome scientifically in the context of 'new bulk-boundary correspondence'. For instance, 3D topological crystalline insulators can exhibit robust gapless states at crystalline defects [165] and more remarkably, 1D metallic modes can be realized at special hinges of 3D HOTIs, which has been experimentally verified in Bi [166], BiSb alloys [153] and α-Bi_4Br_4 [167]. Interestingly, the higher-order topological invariant and the strong $\mathbb{Z}_2$ invariant might be simultaneously present in one compound, leading to a hybrid topological phase which hosts both topological surface states and 1D boundary modes at step edges [168]. Moreover, the concept of high Chern (spin Chern) number systems has been proposed to realize 3D quasi-quantized AHE by stacking Chern insulator layers together with very weak interlayer coupling.

The second issue is to obtain further spectroscopic insights into the topological boundary modes. These modes display extreme spatial confinement (within a few nm) to the boundaries, thus cannot be characterized by angle-resolved photoemission spectroscopy; moreover, the prohibited single-particle backscattering of these boundary modes makes the technique of quasiparticle interference imaging largely

invalid. Nonetheless, it has been shown that the spin-momentum locking, a hallmark of topological states, can be demonstrated by spin-selective tunnelling of the helical electrons using topological nanowires as the STM tip [169]. This finding encourages the fabrication of more quantum-material tips, for example bismuth halides and $K_2Cr_3As_3$, to reveal the topological nature of 1D boundary modes. Additionally, local shot noise spectroscopy, scanning MW impedance microscopy and nano-SQUID can be used to provide more comprehensive information for understanding these modes.

Finally, we highlight moiré superlattice systems as a superb platform for the investigation of topological boundary modes. In moiré materials, the convergence of topology and correlations produces new and unexpected correlated topological phases that are awaiting further experimental exploration [3]. The distinctive tunability of these materials also allows an electric control of the topological boundary states, and a recent example is the manipulation of chiral interface state at the boundary between two Chern domains in twisted monolayer–bilayer graphene [170].

Concluding remarks

To conclude, the study of 1D atomically-confined topological boundary modes represents a fascinating and fast developing field of research. With state-of-the-art scanning probes, the electronic properties of these boundary modes and the bulk insulating states associated with them can be concurrently revealed, enabling a comprehensive understanding of the bulk-boundary correspondence. The variety of material platforms, including heterostructures, moiré superlattices and artificial lattices crafted atom-by-atom, allow for a large landscape to be explored and optimized in the near future. We can expect new phenomena and new understanding in the study of 1D topological boundary modes, which has the potential to impact future technological applications.

Acknowledgments

Z W acknowledge the support from the National Natural Science Foundation of China (Grants No. 52261135638). V M acknowledges support from the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Materials Sciences and Engineering Division under Award No. DE-SC0022101, Gordon and Betty Moore Foundation's EPiQS initiative through Grant Number GBMF9465, and the Quantum Materials Program at CIFAR where she is a Fellow.

4. Light-matter interaction resolved at the atomic-level

4.1. Lightwave control of matter at the atomic scale

Rupert Huber and Jascha Repp
Regensburg Center for Ultrafast Nanoscopy, University of Regensburg, 93040 Regensburg, Germany

Status

Observing and controlling the intrinsic motion of single electrons and atoms in space and time may be regarded as the most direct way of engineering quantum platforms at the atomic scale. Efforts to combine femtosecond laser pulses with STM [171] have led to numerous ultrafast STM concepts. In 2013 Cocker *et al* reached subpicosecond time resolution in STM [172] following an unconventional strategy known as LW electronics [173–175]: They focused laser pulses in the THz spectral range into the tunnelling junction of an STM and employed the carrier electric field as a quasi-instantaneous transient bias voltage, driving tunnelling currents in narrow time windows. By elevating this method to low-temperature STM experiments, where state-selective tunnelling becomes possible, the sub-ångström spatial resolution of STM has been combined with femtosecond temporal resolution, see figure 15. This approach has allowed coherent THz vibrations of an individual molecule to be directly tracked in time in a pump-probe LW-STM experiment with sub-ångström precision [176]. Recently, the LW-driven analogue to STM conductance spectroscopy was demonstrated [177], adding energy resolution to the one in space and time.

While in these experiments both the pump and the probe pulse acted as bias-voltage transients driving electron tunnelling, the LW-STM concept can be generalized to various other modes of operation [174, 175, 178–180]. For example, the pump pulse can act as an ultrashort force transient due to its electric field, without requiring electron tunnelling [59]. In this spirit, in future LW-STM experiments very different types of pump pulses may be employed to cause excitations in the sample, while the LW concept is used for subsequent probing.

Finally, it has been demonstrated that LW-driven currents give rise to an oscillatory dipole moment, which can lead to the re-emission of light [181]. This allows LW-driven current transients to be detected optically, providing access to the entire time-resolved instantaneous current transients.

Current and future challenges

LW-STM can be applied to numerous material systems [174], [178], [182] ranging from single molecules [176], [179], [59], [183] to semi-[172], [180], [184] and superconductors to correlated-electron systems [185] and two-dimensional materials [177]. Spectroscopic methods and diffraction experiments rely on periodicity in time and space, respectively, but are insensitive to non-periodic phenomena. LW-STM represents as an ideal complement to address open research questions, exhibiting non-periodic atomic-scale variations and ultrafast transient dynamics in the time domain.

Knowing the exact near-field transient in the tunnelling junction is of paramount importance for any interpretation of LW-STM experiments. This goal has been achieved using hot-electron field emission and single-molecule voltage gauges for distinct geometries, but the general understanding of the conversion from the far to the near field needs to be improved further.

The achieved temporal resolution in THz-driven LW-STM of hundred femtoseconds marked a disruptive development in STM, yet, resolving intramolecular vibrations or optical phonons in solids calls for an even higher temporal resolution—by more than an order of magnitude. Obviously, this requires shorter laser pulses. Since the currently employed THz transients are already at the lower limit of sub-cycle pulses, LW-STM at higher carrier-wave frequencies towards infrared or even the visible will have to be developed.

The range of future experiments can be significantly widened by exploring different pump-probe variants. While past experiments employed THz pulses as pump and probe, pumping the system in the visible spectral range and probing it using the LW concept has the potential to study the transient electronic properties of optical excitations like excitons in semiconductors, defects and individual molecules. Following this idea, many other excitation and probing schemes can be envisioned.

Since the more than 40 years of existence, STM has lost none of its topicality; not least, because STM has undergone a constant development, for example, in combining it with differential-conductance spectroscopy, atomic manipulation, quasiparticle interference, spin-polarized tunnelling, inelastic electron tunnelling spectroscopy, tip-induced chemistry (section 2.2), luminescence, electron-spin resonance (ESR, see sections 5.3–5.7) and other techniques (see also section 1). Many of these combinations could analogously be fused with LW-STM [183] in future, advancing LW-STM to the next level. For example, spin-polarized LW-STM will allow to follow the transient dynamics of individual spins at the single-quantum limit. The combination of LW-STM with tip-induced chemistry (section 2.2) might enable following initial steps of a

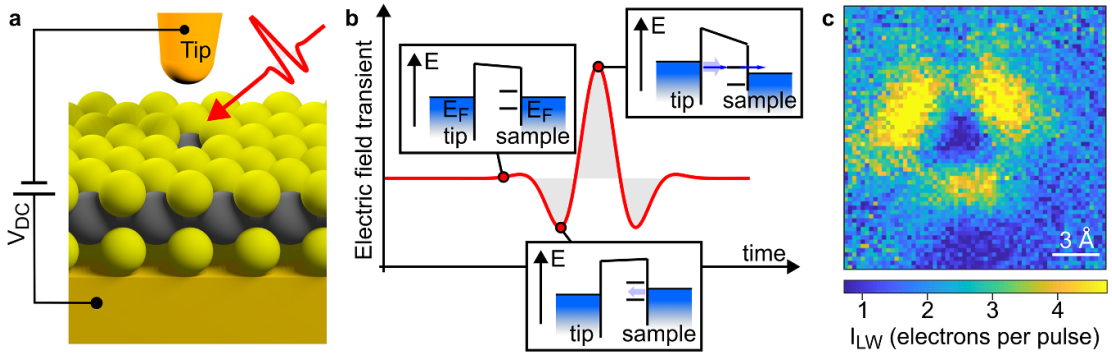

Figure 15. (a) Schematic of a lightwave scanning tunnelling microscope, where the transient electric field (red) of a laser acts as a quasi-instantaneous transient bias voltage adding to the constant bias voltage V_{DC} applied. (b) Thereby, the electric field transient (red) shifts the Fermi levels of tip and sample against each other (insets) on ultrafast timescales, driving the tunnelling of electrons (blue arrows). The presence of discrete electronic levels in the junction (black horizontal lines in the insets) may dominate the tunnelling current (dark, thin blue arrows) and thereby allows for ultrafast state-selective tunnelling. (c) Ultrafast stroboscopic LW-STM snapshot of an electronic defect level in a single vacancy in WSe_2. Panels (b) and (c) Reproduced from [177], license CC BY 4.0.

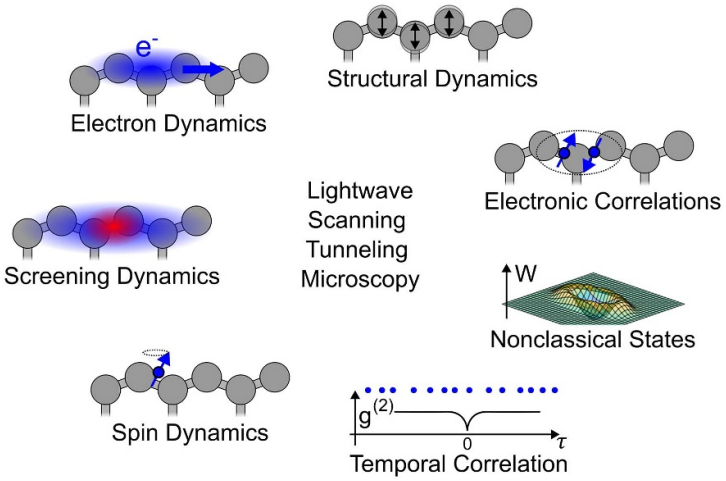

Figure 16. Schematic illustration of research opportunities, for which lightwave scanning tunnelling microscopy could provide unique real-space access in the time domain.

chemical reaction directly in space and time. In other words, employing LW-STM in the investigation of quantum materials can benefit from all the developments and extensive experience in conventional STM, but adding temporal resolution as the important variable that enables studying the nanoworld in motion.

Furthermore, the uniquely direct access of THz-STM to the quantum dynamics opens conceptually new opportunities, such as probing non-classical excitation states in matter, for example, squeezed states. Similarly, electronic quantum correlations in the tunnelling dynamics could become observable, see figure 16.

Finally, establishing an ultrafast variant of AFM would mark a milestone in combined atomic-scale and femtosecond spatiotemporal resolution. As AFM works on insulating samples and provides structural information, this combination would provide access to a range of materials and research questions that cannot be addressed by LW-STM. Here, the challenge is to extract the LW-induced forces from a large background of forces that will always be present also without biasing.

Advances in science and technology to meet challenges

As mentioned, an even higher temporal resolution will require laser pulses with larger carrier-wave frequencies. Such a development comes with several challenges. First, the concept of LW electronics implies that the laser transient acts classically as an electric field—a condition that was fulfilled well in past LW-STM employing THz radiation. Boosting the temporal resolution will inevitably require expanding the spectral range of the laser transients towards the infrared or even the visible spectrum. At these higher frequencies the photon regime of light will be entered, where the classical picture of the electric field, acting as an

instantaneous bias-voltage transient, breaks down. While this transition to the multi-photon regime is an interesting research topic on its own, it comes along with another challenge: higher frequencies of the carrier wave demand larger laser power to efficiently drive electron tunnelling. In addition, the absorption coefficients of metals typically also increase with frequency. Hence, with higher carrier-wave frequencies the problem of thermal effects becomes more prevalent. Every novel approach to LW-STM must therefore rigorously rule out artefactual effects. Disentangling thermal and other spurious effects from ultrafast LW-driven tunnelling is complex. To name only one example, laser pulses may not only heat up the tip at slow time scales, but may launch shock waves in the metallic tip, affecting the junction at much faster time scales than expected, while sub-ångström changes of the tunnelling gap can translate into large parasitic currents. To rule out this and other possible artefacts, commonly accepted strategies must be developed and established.

The classical pump-probe approach usually implies that the two pulses do not directly overlap to avoid (trivial) interference of their electric fields. In the near field the field transients usually exhibit trailing oscillations, such that this approach has the disadvantage of a dead time in the experiment. To resolve dynamics in the low femtosecond or even attosecond regime, the very conservative constraint of non-overlapping pulses is usually given up, at the expense of relying more heavily on modelling to interpret the results.

Many aspects discussed above illustrate that the future development of LW-STM is intimately linked to the availability of ever more sophisticated laser sources with advancing laser technology [326]. For example, the laser repetition rate directly limits the tunnelling current, if one is to stay in the limit of just one electron transferred per laser pulse. As discussed above, higher temporal resolution will require larger carrier frequencies and therefore large-bandwidth laser sources with a stable carrier-envelope phase and sufficient field strength to result into sufficient biasing. Avoiding thermal effects becomes more demanding with increasing frequencies, such that new concept will have to be developed to reach this goal.

Analytical models and numerical simulations of phenomena relevant in LW-STM face the challenge of vastly different length scales: the tunnelling occurs on ångström scales, while the near-field transient is influenced by light–matter interaction on the length scale comparable to the wavelength of light, being orders of magnitude larger than the dimension of tunnelling junction. To tackle this problem, hybrid models and simulations, merging different theories will have to be developed.

Concluding remarks

LW-STM offers an unparalleled access to study phenomena directly in real space and in the time domain. It thereby ideally complements other time-resolved techniques, such as time-resolved angle-resolved photoemission. We expect that in the coming years LW-STM will prove its potential in many different research topics on very diverse material platforms. The concept of LW-STM is still in an early phase of its development and has by no means evolved to its full potential. Method advancement for next-generation LW-STM will strive for even higher temporal resolution, different types of excitation schemes, increasing the signal by higher repetition rates and combinations with other extensions of STM such as spin-polarized currents, external magnetic fields, tip-induced chemistry and many more. The real-space access in the time domain of LW-STM leaves boundless uncharted territory to be explored in the years to come.

Acknowledgments

We gratefully acknowledge funding from the ERC Synergy Grant MolDAM (No. 951519) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through Project-ID, 314695032—SFB 1277 and the research Grants RE2669/8, HU1598/9, and HU1598/8.

4.2. Atomic point defects in 2D crystals as electronically and optically addressable spin systems

Gagandeep Singh and Bent Weber
School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Status

Charges and spins confined to atomic point defects in semiconductors and insulators are emerging as viable building blocks in quantum technologies. Lattice defects, for instance, such as vacancy centres [186–188] introduce highly-localized in-gap states and have been explored as electrically and optically addressable qubits [189], single photon sources [190] and quantum sensors [191]. Recently, two-dimensional (2D) semiconductors and insulators such as atomically thin crystals of hexagonal boron nitride (hBN) and the TMDCs have emerged as alternative materials platforms. What makes 2D semiconductors interesting from the perspective of single photon emission (SPE) [192] are large direct bandgaps in the visible to near-IR spectral range, and a circular optical dichroism, i.e. a chirality of emitted circularly polarized light depending on the crystal momentum ('valley' degree of freedom). As electron and hole spin are further locked to the valley by strong SOC, they constitute candidates for long lived (in terms of spin-valley lifetimes T_1) quantum bits, potentially allowing read-out and control via spin-selective optical transitions.

Several types of atomic defects in 2D crystals are being explored as SPE and qubit candidates. For example, carbon related defects (example C_2C_N trimer) in hBN have been associated with SPE at room temperature [193, 194]. Spin-active boron-vacancies in hBN have been demonstrated to enable optically detected magnetic resonance (ODMR) [195], promising applications in quantum sensing and development of a spin–photon interface. Defects in TMDCs such as chalcogen vacancies, introducing in-gap states with large SOC [190, 191], have been demonstrated to yield quantum emission [196, 197], and are being explored as potential qubit systems with proposed optical initialization, manipulation and read-out [198]. Regardless of the eventual choice of the 2D platform, the assignment of optical emission to specific defect types has often remained ambiguous. This motivates the development of spectroscopy techniques that provide atomic resolution of light–matter interaction, combined with highly-local structural and electronic information. Likewise, the addressability of SPE and qubits at the individual level will be paramount to their investigation and application in technology.

Uniquely, the atomic-thinness of 2D crystals allows to address individual atomic point defects by scanning probe-coupled optical spectroscopy. In this approach, Angstrom-scale resolution can be achieved (figure 17(a)) by exciting an emitter either electronically (scanning tunnelling luminescence-STL) or optically (tip-enhanced photoluminescence-TEPL) [199]. True atomic-resolution investigations of light–matter interaction in point defects and their eventual opto-electronic control, thus overcoming the diffraction limit imposed by conventional optical spectroscopy by more than two orders of magnitude, are now on the horizon.

Current and future challenges

Identification of individual optically active atomic defects will be critical for their successful integration into advanced quantum optoelectronic devices. The low formation energies of atomic defects (e.g. of the order of few eV in semiconducting TMDCs) pose a challenge to directly visualize them with scanning electron beam microscopies which employ high energy electrons (keV). STS, on the other hand, is a non-invasive probe which can provide insights into the local electronic structure of defects with Angstrom resolution. However, correlating this local electronic information (figure 17(b)) with the identification of optically active transitions towards the operation of quantum emitters is yet to be demonstrated.

A central challenge of ensemble-type measurements, common in conventional optical spectroscopy, is that the inhomogeneous distribution of the optical transition frequencies from different emitters within the excitation spot can adversely affect the indistinguishability of the emission. In STL, tunnelling charges can result in plasmonic or excitonic excitation (or a combination of the two) resulting in photon emission (figure 17(c)). Recently, coupling of STM with optical spectroscopy has allowed to capture plasmonic-emission from 2D TMDCs at the Angstrom scale (figure 17(d)) [199, 202]. However, quantum emission due to recombination of excitons bound to defect or strain potentials is yet to be observed. Observation of excitonic emission requires defect-emitters to be placed on atomically clean and flat surfaces that are electronically decoupled from underlying metallic counter-electrode/ substrate to supress non-radiative recombination. While such decoupling has been demonstrated for monolayer TMDCs decoupled using polymer contaminants (figure 17(e)) [202], an atomically smooth decoupling layer for atomic scale emitters in 2D crystals would be desired.

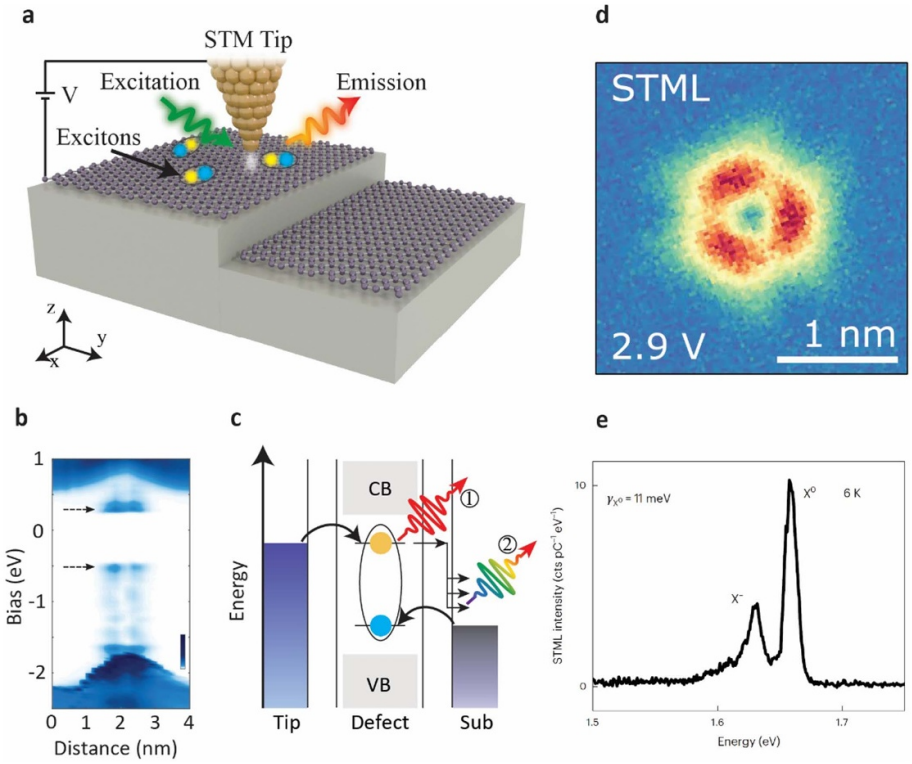

Figure 17. Atomic resolution optoelectronics of defect-based emitters in 2D crystals. (a) Excitation and detection of light at the tunnel junction of a STM. (b) STS across a sulfur vacancy in MoS_2 revealing its in-gap electronic structure. Reproduced from [200], with permission from Springer Nature. (c) Proposed mechanism of STL emission from atomic defects resulting in (1) narrowband photon emission as opposed to (2) broadband plasmonic emission. (d) Scanning tunnelling luminescence (STL) map of a single chalcogen vacancy in WS_2. From [201]. Reprinted with permission from AAAS. (e) STL spectra from $MoSe_2$ monolayer decoupled from underlying substrate. Reproduced from [202], with permission from Springer Nature.

Applications of emitters in quantum communication and quantum information require simultaneously maximized emission efficiency and the degree of indistinguishability towards unity. Presently, most experimental setups suffer from a low photon-collection efficiency at the STM tunnel junction. For example, assuming isotropic photon emission, the collection efficiency of most STL setups is limited to a low solid collection angle, only allowing about ∼10%–15% of photons to be captured. This poses a significant challenge for the characterization of quantum emitters as it takes extremely long acquisition time to build required photon statistics. Further, most STL studies have investigated the visible to near-infrared part of the electromagnetic spectrum (450–1000 nm). This is due to the large Purcell enhancement in Au or Ag substrate or tip, in this spectral range. Yet, applications of quantum emitters prefer photon energies in the centre of the low-loss C-band spectral window (1550 nm) of silica optical fibres, in which STL is yet to be demonstrated.

Advances in science and technology to meet challenges

Figure 18 shows recent efforts towards STM based optical spectroscopy of 2D crystals. While excitonic luminescence from TMDC crystals has been observed [197, 199, 201], atomically-resolved quantum emission due to defect-bound excitons is yet to be reported. Quantum emitters in TMDCs are optically active only at cryogenic temperatures ($T < 10$ K), adding further constraints to their atomic-scale detection. While recent work has mostly focused on TMDCs, quantum emitters in hBN few-layers crystals may potentially be technologically more relevant.

Another critical challenge that remains largely unsolved is the deterministic generation of defect arrays with atomic-scale spatial precision. Conventionally, techniques such as thermal annealing, ion irradiation, plasma treatment, and growth-phase doping have been extensively employed to stochastically introduce optically active defects, however, without control over the precise location of defects. Recent breakthroughs utilizing focused ion beams have demonstrated the creation of vacancy defects in MoS_2 and hBN, with nanometre-scale lateral resolution [206, 207]. Scanning probe lithography is emerging as an alternative approach for achieving atomically precise defect engineering in 2D materials, drawing direct parallels to its established success in realizing atomic-scale phosphorus dopant in silicon. For instance, defect-induced quantum states have been manipulated by atomic-scale dehydrogenation of impurities in WS_2 [208]. At the

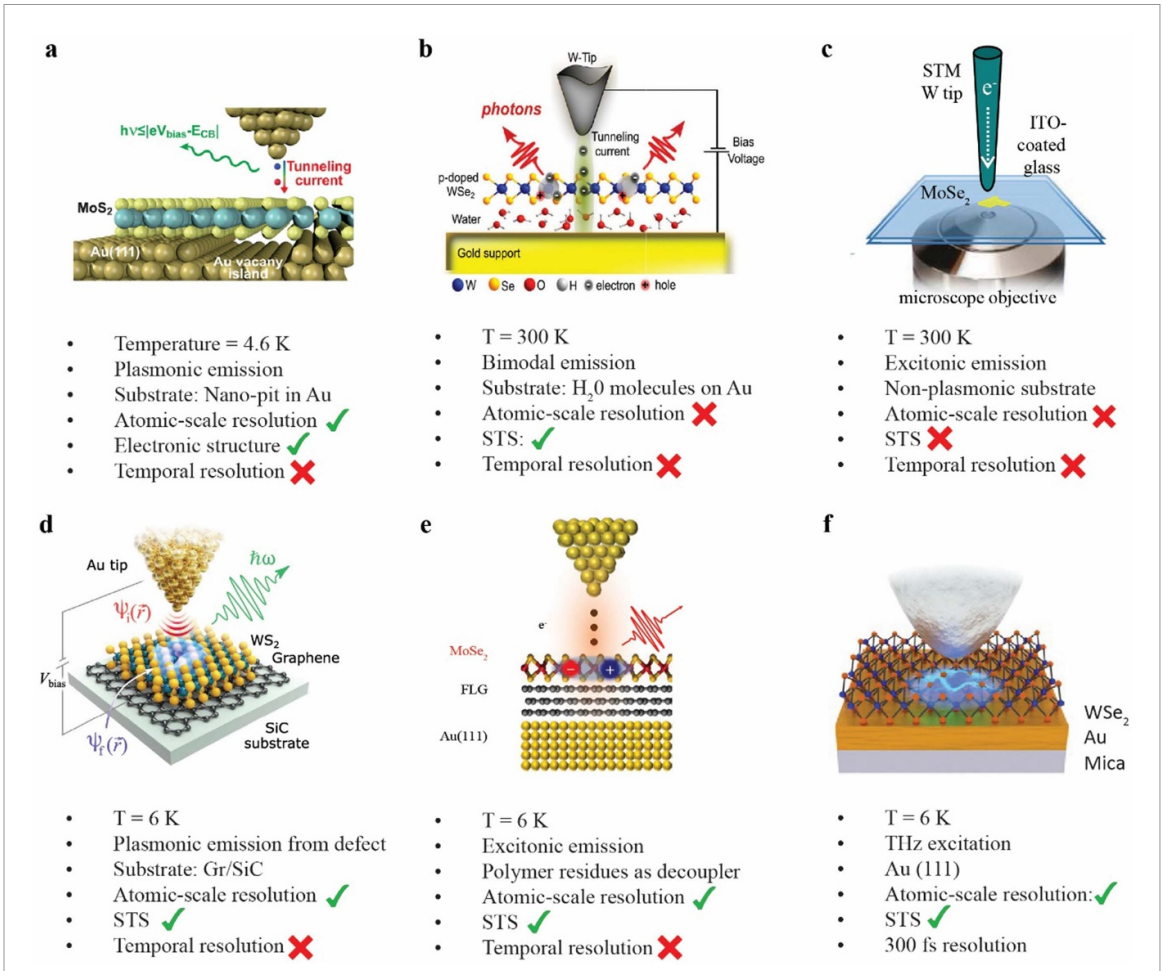

Figure 18. Recent works on STM coupled optical spectroscopy of atomically thin vdW crystals. (a) 1L MoS_2 on Au vacancy centre exhibit plasmonic STL emission [203]. (b) 1L WSe_2 on gold shows both excitonic and plasmonic STL emission due to mobile decoupling from underlying water molecules. Reproduced from [204] with permission from the Royal Society of Chemistry. (c) 1L $MoSe_2$ placed on a non-plasmonic substrate exhibit excitonic STL emission. Reprinted figure with permission from [205], Copyright (2019) by the American Physical Society. (d) A single chalcogen vacancy exhibits sub-nanometre resolved plasmonic emission. From [201]. Reprinted with permission from AAAS. (e) 1L $MoSe_2$ exhibits excitonic STL emission when decoupled via interlayer contaminants. Reproduced from [202], with permission from Springer Nature. (f) Terahertz radiation used to resolve spin–orbit split energy levels of a single selenium vacancy in WSe_2 [177].

more extreme limit, STM has been used on MoS_2 to controllably generate individual sulphur vacancy defects and even arrays thereof via field-evaporation from an STM-tip [209]. These demonstrations underscore STM's capability for atomically precise engineering, also in the context of quantum and optoelectronic properties of 2D materials.

Novel designs to enhance photon collection efficiency from STM tunnel junctions are currently being explored. For example, a recent paper has made use of a lithographically defined parabolic mirror in proximity of the STM tip for increased photon capture efficiency [203, 204]. Other works have explored directionality of photon emission from STM tunnel junction by engineering of either tip shape [210] or sample geometry [211]. In principle, transfer techniques of 2D crystals may be explored to integrate them with advanced on-chip optical elements such as waveguides or Bragg reflectors, which can direct the emitted photons towards collection optics.

TEPL—yet to be demonstrated with atomic resolution for vdW crystals—may allow the possibility of on-demand emission of a single photon from a single defect whereby the STM tip co-functions as an electrostatic gate [212]. Further, SP-STM combined with optical spectroscopy may allow to directly probe how heterogeneities such as atomic defects or strain in TMDC crystals reflect on the valleytronics at the Angstrom-scale. Finally, combining STM with time resolved optical spectroscopy experiments such as time-correlated single photon counting, second-order photon correlation and Hong–Ou–Mandel interference could provide access to dynamics of photon emission and may allow to confirm quantum emission from individual atomic defects.

Concluding remarks

STM coupled with optical spectroscopy is a promising technique towards the investigation of atomic scale emitters in 2D materials. The achievable Angstrom-scale resolution in light–matter interaction sets it apart from conventional optical techniques and provides direct access to combined electronic structure and optical signatures of individual emitters. This will allow for their identification and eventual engineering into advanced optoelectronic quantum devices. On a more fundamental level, light–matter interaction probed at such extreme length scales may provide new insights into optoelectronic processes in quantum emitters, promising unprecedented experimental opportunities, the ultimate dream of which would be the tip-based coherent optoelectronic control of a single atomically confined spin.

Acknowledgments

This research is supported by the Singapore Ministry of Education (MOE) Academic Research Fund Tier 3 Grant (MOE-MOET32023-0003) 'Quantum Geometric Advantage', the National Research Foundation (NRF) Singapore under the Competitive Research Program 'Towards On-Chip Topological Quantum Devices' (NRF-CRP21-2018-0001), and the Air Force Office of Scientific Research under Award Number FA2386-24-1-4064.

5. Single spin quantum objects

5.1. Single atom magnets (SAMs) on surfaces

Fabio Donati[1,2], *Stefano Rusponi*[3] *and Harald Brune*[3]
[1] Center for Quantum Nanoscience (QNS), Institute for Basic Science (IBS), Seoul 03760, Republic of Korea
[2] Department of Physics, Ewha Woman's University, Seoul 03760, Republic of Korea
[3] Institute of Physics, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Status

Magnetic information storage in the smallest unit of matter has been achieved in 2016 through the discovery of the first SAM, holmium (Ho) adsorbed on a few monolayers thin MgO films grown on Ag(100) [213]. The electron spin in individual Ho atoms exhibits remanence up to 40 K and coercivity exceeding 9 T. This remarkable stability is attributed to the well-localized nature of the 4*f* electrons, which remain largely decoupled from the environment, allowing them to retain their magnetization for extended periods exceeding thousands of seconds at cryogenic temperatures. This long retention time causes the non-equilibrium hysteretic behaviour observed in x-ray absorption spectroscopy (XAS) magnetization loops. After this discovery, other dysprosium (Dy)-based magnets with intriguing properties have been identified. Dy atoms on graphene/Ir(111) can be self-assembled into ordered arrays using the templating effect of the moiré pattern from the underlying graphene; thus, they represent the prototype of an ultra-high density magnetic recording media [214]. These atoms also possess open 5*d*6*s* shells, enhancing spin contrast in magnetic transport measurements conducted by STM [215]. Moreover, Dy atoms deposited on MgO exhibit the highest magnetic anisotropy observed to date for an individual surface adsorbed atom [216], promising longer spin stability at higher temperatures. Other recently discovered Dy-based single-atom magnets, such as Dy on $SrTiO_3$ [217] and Dy on BaO [218], offer new platforms for engineering the easy magnetization direction and for electric field control of the spin lifetime. Both Ho and Dy SAMs offer significant opportunities to explore magnetic storage at the atomic scale and the transition from classical to quantum dynamics of individual spins. Moreover, their potential use as local sources of magnetic fields [216] makes them attractive for integration into quantum logic devices, where they can fine-tune the resonance frequencies of qubits, advancing the development of atomic-scale quantum computing technologies.

Current and future challenges

The primary challenge in making further progress lies in increasing the maximum temperature until which magnetic remanence can be realized in a SAM. Thermal magnetization reversal arises from the interaction with surface phonons via localized vibrational modes [213]. To overcome this, it is crucial to find combinations of lanthanide species and substrates resulting in pure spin states that are protected from direct and thermally assisted quantum tunnelling of the magnetization (QTM) induced by phonon scattering. Compared to molecular magnets, individual adatoms face additional challenges, such as surface diffusion and subsequent aggregation into clusters, which become active above a few tens of Kelvin in all current systems [213, 214]. Identifying systems with stronger bonds could provide a more robust crystal field to separate spin states and enhance structural stability.

Moreover, spin state measurements currently require integration over a bandwidth of $>$100 ms due to limited signal-to-noise ratios (SNRs). Systems with open valence shells can increase the spin-polarized signal by an order of magnitude [215], enabling faster readout. Techniques that address inter-orbital coupling and spin polarization with orbital resolution are key to design more efficient SAMs. Presently, STM detects spin excitations between 4*f* and the outer 5*d*6*s* shell [215], while orbitally resolved XAS gives the occupation and magnetic properties of the individual orbitals [219].

Transforming QTM from a limitation into an opportunity is an intriguing challenge. While QTM can limit magnetic stability, it also allows the exploration of quantum phenomena, such as Landau–Zener tunnelling. This can be used to test the quantum properties of these atoms, including their potential to be set into a superposition state.

In this context, utilizing lanthanide atoms with tailored spin level structures, where the ground state doublet can be efficiently coupled to microwaves (MWs), could pave the way for lanthanide-based qubits. To this extent, a recent study pointed out that Er atoms on MgO/Ag(100) have the suitable ground state for quantum coherent manipulations [220]. These qubits could potentially offer much longer life- and coherence times compared to those based on 3*d* metal atoms, thereby significantly advancing the field of quantum computing.

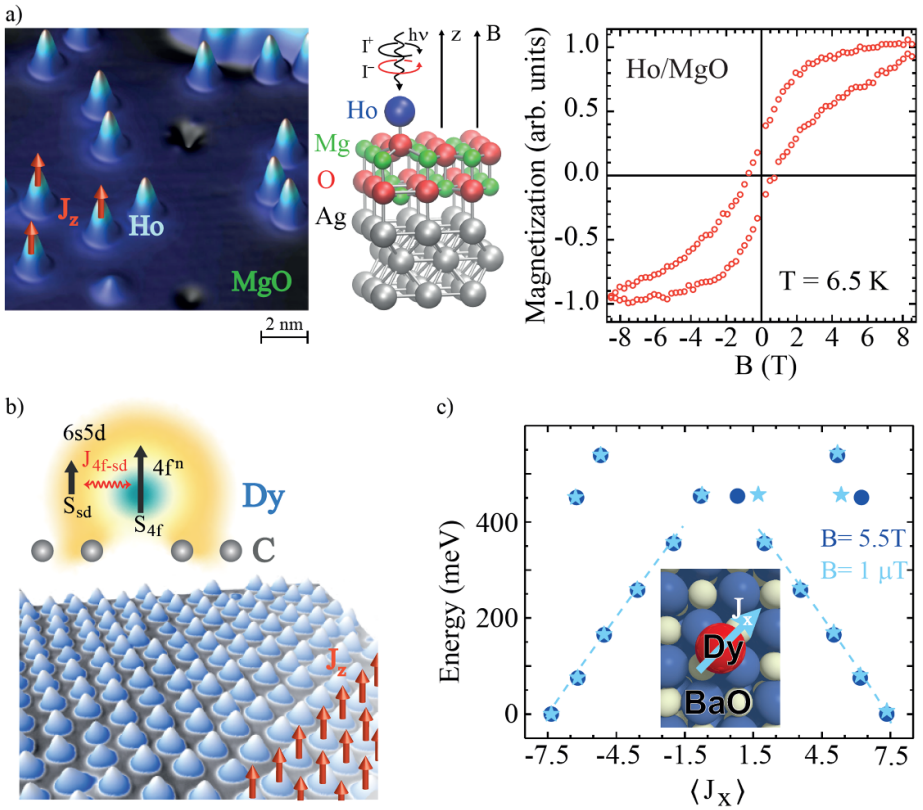

Figure 19. (a) Ho adatoms adsorbed on top of O on MgO/Ag(100) show out-of-plane easy magnetization axes and magnetic hysteresis beyond 9 T [213]. (b) Self assembled superlattice of Dy atoms on gr/Ir(111): electron transfer to the substrate creates spin-polarized 6*s*5*d* valence states [214, 215]. (c) Dy adatoms on bridge site of BaO are prototypes of SAMs with in-plane magnetization [218].

Advances in science and technology to meet challenges

Addressing the potential use of lanthanide atoms for magnetic storage systems involves tackling the magnetic recording trilemma, which encompasses three key design constraints: writability, readability with high SNR at high band-width, and thermal stability. Overcoming these challenges encompasses not only the right choice of materials but also engineering issues related to the addressability.

Currently, a single adatom can only be addressed with STM. Read-out speed is limited by the bandwidth of the current amplifier or feedback loop, depending on whether the magnetic state is detected in constant-current or constant-height mode. Writing speed is constrained by the time required for the tunnelling bias to rise to the switching threshold. In practice, both bandwidths lie between 1 kHz and 1 MHz. Another key factor limiting the read- and write-speed is the time needed to position the STM tip over a selected adatom. Shortening this latency—and turning the concept into an actual device—is primarily an engineering challenge. The physics of single-atom magnetic memory has been validated; once such memories are judged worth building, engineers can tackle the speed bottleneck with GHz-band current amplifiers, hybrid optical excitation, and related techniques.

In the presently best systems, the SNR can reach a factor of ∼100 with a bandwidth on the order of Hz [215]. Implementing more advanced amplification and feedback techniques could ensure faster readout and greater stability in the junction.

Enhancing the thermal stability of single-atom magnets requires stronger isolation of localized spins from conduction-electron and phonon scattering. In current Ho and Dy/MgO systems, this decoupling is provided by an ultrathin insulating spacer whose thickness is capped at a few monolayers to preserve STM conductance. Recent progress in spin detection with exchange-based AFM may enable reliable read-out through thicker insulators [61], combining greater electrical isolation with viable signal levels. In parallel, functionalized substrates—phononic superlattices or 2D materials with phonon band-gaps—can suppress spin–phonon coupling and thus push blocking temperatures beyond the present 40 K limit [213].

Recently, XAS on just one atom has been reported in a synchrotron x-ray STM [221]. This technique, combining the spatial resolution of STM with the ability of XAS to investigate the electronic (and potentially also the magnetic) properties for states far from the Fermi level, could provide critical information for the search of the optimum adatom-substrate combination.

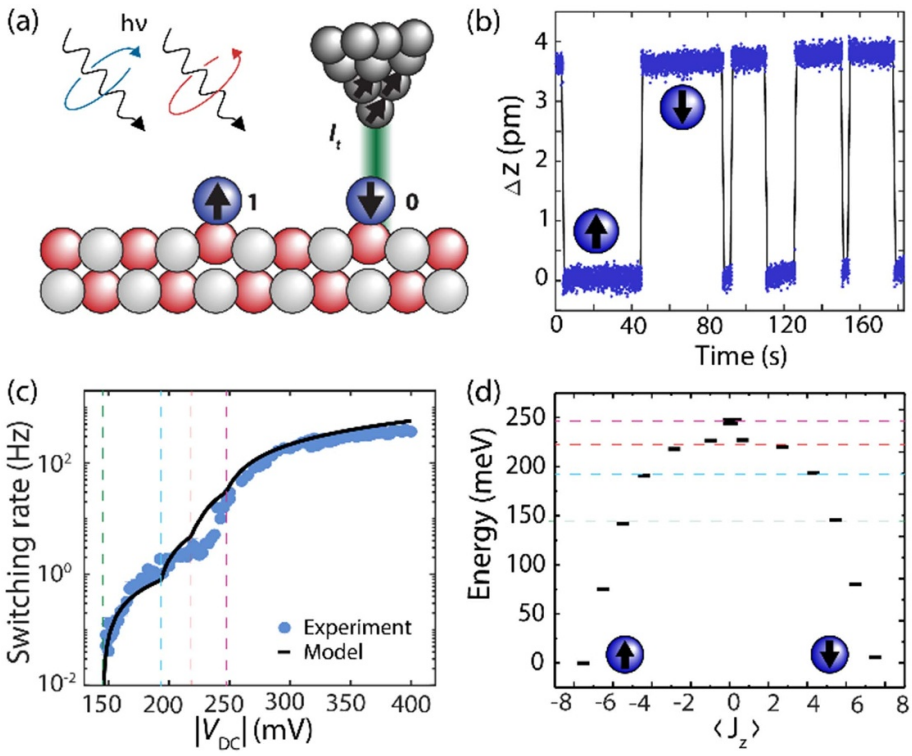

Figure 20. (a) Using spin-polarized STM it is possible to probe the orientation of the magnetic moments of the atoms. (b) Typical two-state signal from Dy atoms on MgO, showing fluctuation of the magnetic moment direction with characteristic time of tens of seconds. (c) The switching rate depends on the tip-sample voltage and reveals characteristic energy thresholds. A model based on atomic multiplet calculations allows to reproduce the data and (d) identify the quantum level scheme, together with the transition towards excited states inducing the reversal of the magnetization [216].

These advancements suggest that magnetic storage systems using single lanthanide atoms could become feasible with continued progress in materials science and instrumentation. Addressing the magnetic recording trilemma through innovative approaches such as MW or optical assistance, advanced amplification, and AFM techniques will be critical to realizing the full potential of lanthanide-based magnetic storage.

Concluding remarks

Single lanthanide atoms adsorbed onto surfaces are promising for ultra-high density magnetic information storage. Their mutual magnetic interactions are, e.g. for Dy/g/Ir(111), negligible down to distances of 1 nm enabling in principle densities up to 640 Tbit/in^2. The addressability with spin-polarized transport in an STM junction implies spin-polarized valence states that enable access to the otherwise well protected 4*f* electrons that carry most of the magnetic moment. Combining local detection with radiation-based techniques will be crucial to the full exploitation of lanthanide single atoms in future magnetic storage devices.

Acknowledgments

F D acknowledges support from the Institute for Basic Science (IBS-R027-D1). HB acknowledges support from the Swiss National Science Foundation (TMAG-2_209266).

5.2. Unlocking the quantum potential: the rise of molecular magnets as qudits

Eufemio Moreno-Pineda[1,2,3] *Mario Ruben*[4,5,6] *and Wolfgang Wernsdorfer*[3,5]
[1] Universidad de Panama, Facultad de Ciencias Naturales, Exactas y Tecnología, Departamento de Química-Física, 0824 Panama, Panama
[2] Universidad de Panama, Facultad de Ciencias Naturales, Exactas y Tecnología, Grupo de Investigación de Materiales, 0824 Panama, Panama
[3] Physikalisches Institut, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany
[4] Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany
[5] Institute for Quantum Materials and Technology (IQMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[6] Centre Européen de Sciences Quantiques (CESQ), Institut de Science et d'Ingénierie Supramoléculaires (ISIS), 8 allée Gaspard Monge, BP 70028, 67083, Strasbourg Cedex, France

Status

Molecular magnets (MMs) have emerged as pivotal players in advanced technology, promising revolutionary applications in quantum computing, quantum communication, and quantum sensing [222]. The discovery of magnetic bistability in Mn_{12} and later in $[TbPc_2]^-$ led to extensive research, revealing their potential for high-density storage and nanoscale quantum information devices. These molecules exhibit remarkable quantum effects, such as quantisation of the energy manifold, QTM, long quantum coherence, and Berry phases, positioning them as key components in quantum technologies. This has been exemplified by lanthanide complexes with record magnetic strength, high-temperature performance, outstanding sensing capabilities, and advanced quantum error correction protocols. Undoubtedly, MMs have the potential to lead to technological breakthroughs materialising the second quantum revolution, that is, the implementation of quantum effects in real-world applications.

In quantum computing, MMs are promising qu*d*it candidates (where $d = (2I + 1)^n$) [223]. Their tunable chemical properties enable the creation of qu*d*its using an isotopological [224] approach, offering higher-dimensional state spaces for denser information encoding by enhanced parallelism. Qu*d*its, unlike qubits, can exist in more than two states, allowing molecular qu*d*its to store and carry out quantum information processing in a single entity [225]. This higher dimensionality increases computational power and reduces circuit complexity, making quantum algorithms more efficient [226]. The feasibility of this approach was demonstrated with the quantum Grover algorithm using a single $[TbPc_2]^-$ ($I = 3/2$ with $d = 4$) [227] in a hybrid spin transistor and by executing quantum simulations using a (^{173}Yb(trensal)) ($I = 5/2$ with $d = 6$) electron-nuclear system [228].

Qu*d*its also offer enhanced error resistance, aiding in error correction and fault tolerance. This multilevel nature addresses one of quantum computing's major challenges. It has been proposed how antiferromagnetic coupling in ions creates resilient energy states. A heterometallic [ErCeEr] complex can protect qubits from errors using a three-qubit repetition code with controlled-NOT (CNOT) gates. Likewise, the Cr_7Ni–Cu system supports QEC, using Cr_7Ni's electronic state and Cu^{2+}'s nuclear state for quantum memory, allowing information processing during inactive periods and enhancing fault-tolerant quantum computing [229]. These advancements pave the way for robust quantum computer architectures using molecular qu*d*its as scaffolds.

Current and future challenges

MMs hold significant promise for quantum computing and advanced technologies due to their unique quantum properties. However, several challenges must be addressed to employ MMs as qu*d*its effectively. One primary challenge is maintaining quantum coherence, as MMs are highly susceptible to decoherence from environmental interactions, such as lattice vibrations (phonons) and magnetic interactions with nearby spins. Although relatively long coherences have been obtained in ensembles and single molecules, controlling these interactions to preserve long coherence times is crucial for their use in quantum computing. This is of utmost importance for the integration of these systems of hybrid devices, where interaction with leads or surfaces is deemed unavoidable.

Another important challenge in developing hybrid MM devices is integrating MMs into devices requiring precise surface deposition, especially for single-molecule architectures. Ensuring their magnetic properties are preserved during this process is significant and requires further action. Addressing this point requires the concerted work of chemists, producing the MMs, and physicists, incorporating the MMs into the hybrid structures. An alternative approach for employing MMs as qu*d*its involves coupling a molecular ensemble to on-chip resonators, requiring sufficiently strong coupling (G) between the ensemble and the resonator.

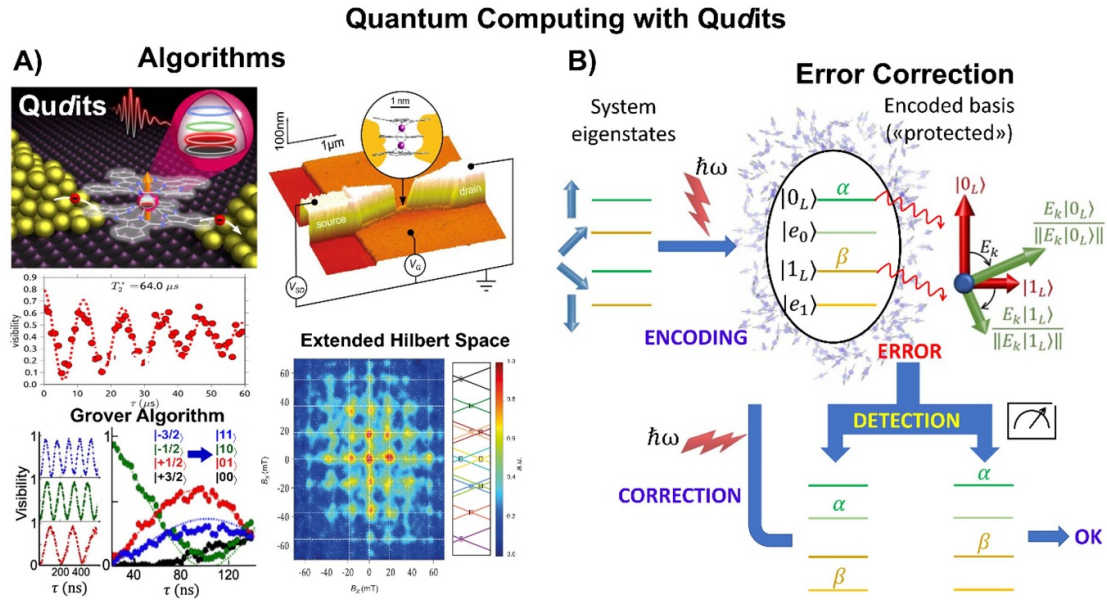

Figure 21. MMs acting as qu*d*its for quantum technologies: (A) single-molecule technologies employing a single MM unit. (B) The ancillary states offered by qu*d*its can allow the execution of complex algorithms and the realisation of Quantum Error correction protocols. Panel (A) is made up of figures from [230], reprinted with permission from AAAS, and reproduced from [231], with permission from Springer Nature, and a reprinted figure with permission from [227], Copyright (2017) by the American Physical Society. Panel (B) has been reproduced from [229]. © The Author(s). Published by IOP Publishing Ltd. CC BY 3.0.

However, conventional coplanar superconducting resonators typically achieve only a few Hz, well below the decoherence rates of MMs.

Another important challenge pertains to increasing the dimension of molecular qu*d*its to enhance the computational power. Although in principle a larger number of qu*d*its states would allow the execution of more complex algorithms, this approach faces technical challenges, such as 'frequency crowding' of the resonant transitions, making it spectroscopically difficult to address the qu*d*it's states. Proposals include switchable couplers within molecular structures or using molecular linkers to modify electronic structures. However, local control and wiring of individual molecular spins are necessary. Similarly, implementing error correction in quantum systems is inherently challenging. While qu*d*its offer advantages in error correction due to their multilevel nature, developing robust error correction protocols that can be practically implemented with MMs is still an ongoing research field.

Lastly, efficiently reading out and manipulating the quantum states of MMs is an important challenge. While the execution of the Grover's algorithm has been realised, faster and more precise read-out techniques must be developed for efficient computational tasks and information transport.

Advances in science and technology to meet challenges

The susceptibility to decoherence from environmental interactions, such as lattice vibrations (phonons) and magnetic interactions with nearby spins, is a major challenge for MMs. On the synthetic side, a thorough understanding of the aspects of governing relaxation can lead to noise-resilient systems. Theoretical and experimental works have shed some light on the key aspects governing relaxation in MMs, leading to important improvements. Advanced techniques are required to control these interactions and preserve long coherence times, including sophisticated cryogenic systems to minimize thermal noise and high-precision magnetic shielding to reduce external magnetic interference.

At a single molecular level, integrating MMs into practical devices necessitates precise deposition on surfaces while preserving their magnetic properties. Techniques like molecular beam epitaxy and chemical vapour deposition are being explored, ensuring that the MMs maintain their integrity and functionality when placed on surfaces or embedded in different environments. A chemical design with anchoring groups can also help to direct the MM into the desired location, for example, between the leads. Several devices can be envisioned for the hybrid architectures, such as spin transistors, spin valves, and spin resonator devices [232]. The sensing of the electronuclear characteristics of the MMs can be achieved through direct and indirect coupling. In such configurations, the reversal of the electronic magnetic moment, via QTM, or direct relaxation, would allow the initialisation and manipulation of the nuclear spin levels of the system. In

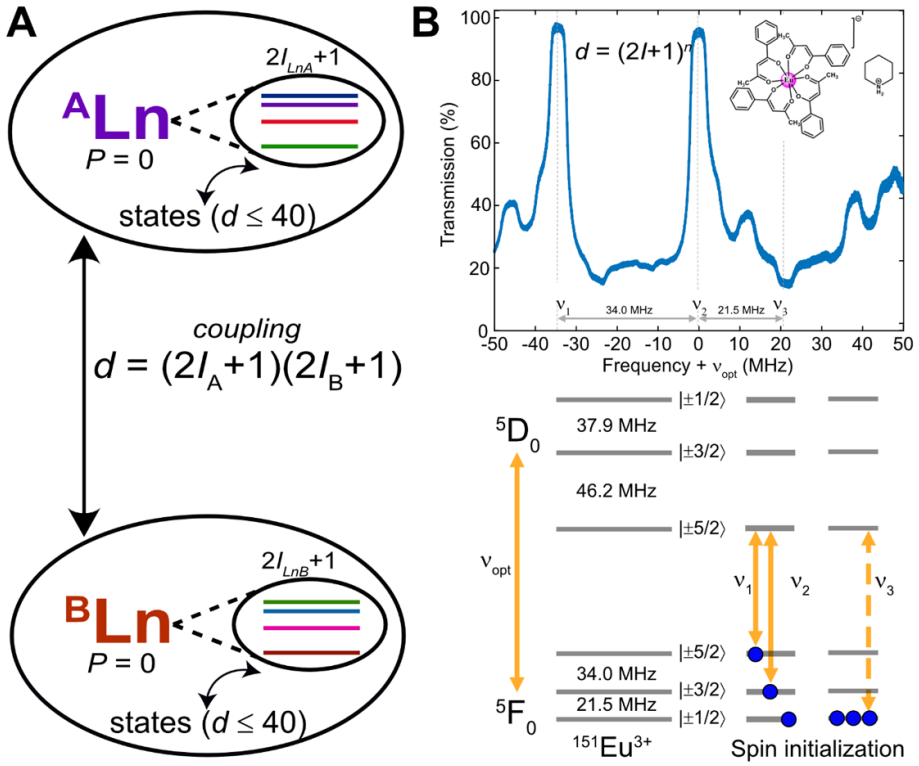

Figure 22. Future challenges—qu*d*its arrays and optical read-out: (A) schematic of qu*d*its arrays. (B) Optical readout of qu*d*its states. Panel (B) Reproduced from [232], with permission from Springer Nature.

the case of ensembles, the coupling strength (G) can be enhanced by reducing the gap between the circuit and the molecular ensemble. Reducing the inductor width to a few nanometres has been proven to increase (G) significantly. Another approach is using low inductance LC lumped-element resonators with high current densities. Combining these methods could bring (G) to tenths of MHz, enabling coherent coupling for single molecular spin qu*d*its if T_2 exceeds 10 μs. While the architecture's characteristics can vary depending on the targeted device, a universal requirement for the integration of the MM at a molecular level concerns the stability of the system upon deposition; hence, stable and robust MMs are sought. In the case of (small) ensemble architectures, molecular crystals are suitable [232].

Regarding the scalability of the Hilbert space, recent studies comparing the efficiency of qu*d*its and multiple qubits in noisy environments for quantum information processing suggest that the number of qu*d*it states should be maintained within certain limits ($d \leqslant 40$) [233]. Using the Lindblad formalism, a critical curve was identified that benchmarks gate efficiency relative to decoherence times. This curve helps determine conditions where qu*d*its offer competitive gate efficiencies compared to qubits. Numerical simulations support these findings, highlighting the potential of qu*d*its in near-term quantum computing applications, especially for platforms with lower dimensionality. Hence, inter-qu*d*it coupling is essential for creating and utilizing larger quantum algorithms.

An alternative method to read out the information from MMs is based on optical means. Ultra-narrow optical linewidths, enabling long-lived quantum states and fast readout, have been reported in Eu^{2+} molecular crystals with linewidths in the tens of kilohertz, much narrower than other molecular systems. This narrow linewidth allows for efficient optical spin initialization, coherent light storage using an atomic frequency comb, and optical control of ion–ion interactions [232]. These properties are crucial for implementing quantum gates, demonstrating the potential of molecular crystals as a versatile platform for photonic quantum technologies, combining highly coherent emitters with the flexibility of molecular materials.

Concluding remarks

MMs have been studied since the 1990s for their quantum effects and potential in quantum technologies. They can be engineered structurally and electronically, making them reproducible and suitable for new technologies. Significant advancements include systems operating above liquid nitrogen temperatures and systems with long coherence times. MMs are strong candidates for quantum sensors, communicators, and

simulators. They have shown high sensitivity in quantum sensing and can be used as qu*d*its for quantum computing, enabling quantum algorithms, gates, and error correction. Challenges remain in integrating MMs into hybrid devices, but strategies like tailored functions and molecular assemblies offer solutions. Continued research is essential to fully develop their potential in quantum technologies.

Acknowledgments

W W thanks the German Research Foundation (DFG) concerning the Gottfried Wilhelm Leibniz-Award, ZVN-2020_WE 4458–5. E M-P thanks the Alexander von Humboldt fellowship for experienced researchers for support.

5.3. Magnetic resonance imaging (MRI) at the atomic scale

Wantong Huang, Kwan Ho Au-Yeung and Philip Willke
Physikalisches Institut, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany

Status

MRI has emerged as an excellent technique for probing electron and nuclear spins in physics, chemistry, and life sciences. The first nanoscale MRI recorded by a scanning probe began with the idea of combining AFM and MRI: Following the invention of magnetic force microscopy (MFM) [234], magnetic resonance force microscopy was developed in 1995 which measures the force between the magnetic tip and resonantly excited spins [235]. Subsequently, rapid developments on magnetic sensing followed: For instance, single NV centres in diamond were shown to act as a moveable probe enabling high-sensitivity spin detection through ODMR. This allowed for instance for sensing of magnetic 2D materials with high spatial resolution [236], which however had not reached the atomic scale yet.

In 2015, the first demonstration of probing single magnetic atoms on surfaces utilizing ESR-STM was reported [41]. Here, the ESR signal is detected by the magnetoresistive tunnelling current in the STM junction, which depends on the spin alignment at the magnetic tip apex and on the surface. In this sense, ESR-STM can initialize, control, and read out spins through the tip, offering an excellent opportunity to spatially map individual spins.

Later on, the first nano-MRI revealed the magnetic fingerprint of single Ti and Fe atoms [237] when scanning across them (figures 23(a) and (b)): the spatial pattern arising from the interaction between the on-surface spin and the magnetic tip can be mapped at constant radiofrequency (RF) (figure 23(d)), instead of sweeping the frequency of the RF voltage (figure 23(c)). Also, alternating the vertical tip-sample distance, i.e. changing the effective strength of the tip magnetic field [19], resonant slices through the magnetic interaction potential can be obtained. Recently, this MRI approach was applied to the study of a single pentacene molecule [238] revealing the spatial dependence of the spin density. Furthermore, attaching a nickelocene ($NiCp_2$) spin sensor to the STM tip apex offers an alternative way to sense single magnetic atoms or molecules through exchange interaction [239], benefiting from a relatively straightforward tip preparation procedure. Ongoing and future developments focus for instance on improving the magnetic readout with the probe and a combination coherent control protocols.

Current and future challenges

To probe weak magnetic signals at the atomic scale, both achieving sub-nanometre spatial resolution and boosting sensitivity (e.g. detecting a magnetic field from a single proton) are critical challenges. For example, the NV centre in diamond is a well-known spin sensor that offers excellent magnetic sensitivity down to pT $Hz^{-1/2}$. When such a single spin centre is bound to a moveable tip, it enables a direct and quantitative measurement of stray magnetic fields emerging from a sample [236]. However, its spatial resolution is constrained to tens of nanometres due to the charge-state instability in the near-surface (shallow) NV centres [240].

In contrast, ESR-STM combines atomic-scale resolution down to sub-ångström length scales with high energy resolution in the MHz range. Since the tip is magnetic, shifting the ESR frequency while scanning it laterally over the surface spin enables MRI scanning capabilities. Figure 23 shows a nano-MRI of a single Ti atom on the oxygen site of 2 ML MgO/Ag(001), revealing the spatially resolved magnetic interaction potential between the tip and the surface spins. These interactions include exchange and dipolar contributions; however, this also means that the signal depends on the atomic species and the specific tip configuration, thus requiring a careful analysis about the complex tip–atom interaction. For the completeness, we provide a direct comparison of a few scanning probe-based magnetometry techniques in table 2.

Another challenge for improving MRI in an STM is mitigating sources of decoherence, which for on-surface spins mainly stem from the presence of the tip, including tunnelling current and tip-induced magnetic field variation [44]. This limits the energy resolution as well as the possibility for more complex pulse schemes for quantum sensing [241]. Although placing a sensor spin near the target spin which could promote indirect readout (i.e. without direct injection of tunnelling current) through their coupled exchange and dipolar interactions [4, 242], this approach is not effective for direct magnetic imaging.

An alternative approach is to create a mobile spin sensor on a tip by picking up a magnetic molecule. $NiCp_2$ has been found to retain its spin ($S = 1$) on the tip for imaging spin-exchange interaction in a qualitative way [239]. Recently, a perylenetetracarboxylic dianhydride (PTCDA; $S = 1/2$) molecule has also shown potential as an on-tip sensor for atomic-scale electric and magnetic fields by performing ESR on the molecule on the tip [27]. However, preparing a spin-polarized tip before transferring the molecule onto the tip apex is still necessary for readout and enabling the ESR driving mechanism. In short, developing a robust,

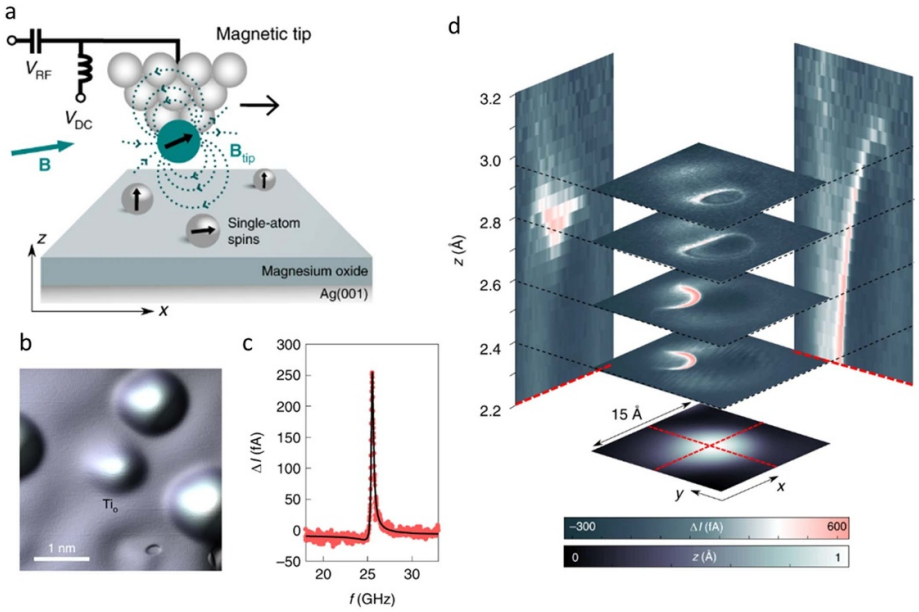

Figure 23. MRI in an STM. (a) Schematic set-up of ESR-STM setup. The STM tip with a magnetic tip apex is scanned across two-atomic layers of MgO on Ag(001) with single magnetic atoms atop. (b) Constant-current STM image of a Ti atom on MgO. (c) ESR spectrum taken on the centre of the atom in (b). (d) MRI scans in the same area with a magnetic tip showing a spatial pattern of resonance signals $\Delta I(x,y)$ at different tip–atom distances z. ($I = 5$–70 pA, $V_{DC} = 40$ mV, $V_{RF} = 40$–45 mV, $f = 23.65$ GHz, $B_x = 0.9$ T, $B_z = 0.1$ T, $T = 1.2$ K.). Reproduced from [237], with permission from Springer Nature.

Table 2. Nanoscale magnetic sensing techniques and their advantages and disadvantages.

Technique	Spatial resolution	Energy resolution	Operating conditions	Strengths	Limitations
MFM	∼10–100 nm	None	Ambient or vacuum	Simple setup, domain imaging	Low resolution, indirect and perturbative
NV centre magnetometry	∼10–100 nm	∼kHz (with pulsed protocols)	Ambient or cryogenic	Quantum sensing, operable in diverse conditions	Limited spatial resolution
Spin polarized-STM	Atomic to sub-Å	∼μeV–meV	UHV, cryogenic	Atomic resolution, magnetic texture imaging	Cannot resolve dynamics or weak magnetic couplings
ESR-STM	Atomic to sub-Å	Sub-μeV (MHz range)	UHV, cryogenic	Coherent spin control, high spatial and energy resolution	Complex setup, limited to specific spin systems

reliable and easy-to-implement spin sensor with long coherence times that allows for working in diverse environments is a major challenge for the field.

Advances in science and technology to meet challenges

The perfect spin sensor would combine high energy resolution of ESR spectroscopy (as demonstrated in scanning NV-magnetometry) with single-entity resolution and atomic-scale positioning of scanning probe methods. The latter is best realized with spin centres located on an STM or AFM tip. Here, we propose three practical criteria to guide the future steps:

1. **Selection of appropriate spin centres:**
   A suitable spin carrier that forms a TLS on the probe tip is required. This can be either an assembly of atoms or a single molecule, with $S = 1/2$ or $S = 1$, such as PTCDA [27] or $NiCp_2$ [239], capable of maintaining their spin properties on the tip. Ideally, the relaxation time (T_1) and coherence time (T_2) of the sensor spin should be long: The energy resolution is given by the ESR linewidth $\Gamma \approx \frac{1}{\pi T_2}$ for low RF powers. Experimentally, this remains still challenging due to e.g. contributions from tunnelling current electrons and tip magnetic field variation [44].

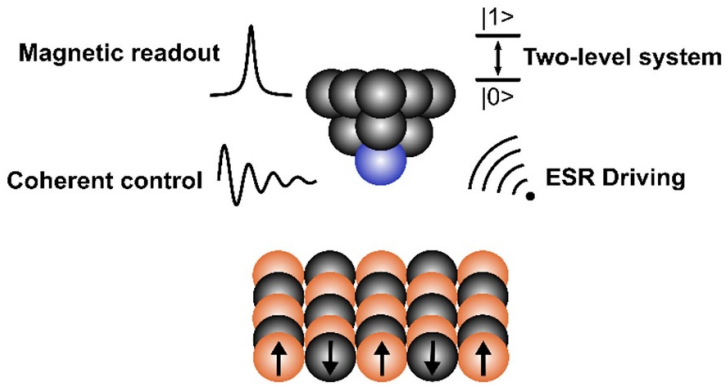

Figure 24. The criteria of constructing a moveable spin sensor at the atomic scale based on the scanning probe approaches: (1) optimization of magnetic readout (signal-to-noise ratio), (2) utilization of two-level system to reduce complexity, (3) integration of ESR driving and (4) enabling coherent control in the system.

2. **Reliable magnetic readout:**
   A reliable magnetic readout of the probe tip is crucial. In ESR-STM, creating a spin-polarized tip with individual magnetic atoms can be time-consuming and uncontrollable. An alternative method is to use an intrinsic spin-polarized tip, such as $Mn_{88}Ni_{12}$ [243], or explore molecules that lead to a spin-polarization of the tip. Alternatively, an optical readout might be employed, like for NV-centres.
3. **Advanced spin-driving techniques:**
   Driving spin transitions requires RF directly applied to the tip or a high-quality RF antenna capacitively coupled to the tip. In contrast to the conventional ESR-STM, one alternative scheme is to use strip lines as recently realized to perform ESR on individual pentacene molecules in non-contact AFM [61] (figure 24).

In contrast, the best energy resolution achieved in ESR-STM to date remains several MHz [41]. We envision that a spin sensor featuring improved T_1 and T_2, great versatility and robustness, can push the energy resolution into the kHz-regime. This would for instance enable the imaging of spin density in larger biomolecules as well as magnetic structures (including magnetic 2D materials, frustrated magnetism, spin density wave, artificial spin structures and magnetic vortices in superconductors).

Concluding remarks

Advanced scanning probe methods offer a promising route for detecting individual spins and their interaction with ultimate spatial resolution. Techniques like ESR-STM offer the latter, however still face challenges in tip preparation and energy resolution (10^6 Hz). Future advancements in atomic-scale MRI will focus on developing robust movable spin sensors, improving magnetic readout methods, and optimizing spin transition driving techniques. Addressing these challenges will pave the way for broader applications in materials science, biology, and quantum technologies, ultimately enabling the imaging of complex magnetic structures in solid state systems and of individual large biomolecules with unprecedented precision.

Acknowledgments

P W, W H and K A Y acknowledges funding from the Emmy Noether Programme of the DFG (WI5486/1-1) and financing from the Baden Württemberg Foundation Program on Quantum Technologies (Project AModiQuS).

5.4. Atomic-scale qubit platforms

Soo-hyon Phark[1,2] *and Andreas J Heinrich*[1,2]
[1] Center for Quantum Nanoscience (QNS), Institute for Basic Science (IBS), Seoul 03760, Republic of Korea
[2] Department of Physics, Ewha Woman's University, Seoul 03760, Republic of Korea

Status

A single electron spin represents a natural TLS with a splitting of its two eigenstates. Such a spin TLS carried in solid provides promising qubit platforms in the sense of an easiness of coherent control and versatility. By bringing the spins onto a surface, it can be spatially manipulated in a STM [48], which allows a bottom-up tailoring of spin arrays at the atomic scale [244]. The first coherent control of a single electron spin on surface was demonstrated in a STM combined with ESR [41, 44].

Utilization of spins on a surface as a quantum platform needs a simultaneous and selective driving and readout of the quantum states of multiple spins. A recent work by Phark *et al* demonstrated two-coupled qubits, implemented using two Ti atoms on a 2-monolayer (2-ML) MgO (figure 26(a)), one in the STM junction (*sensor*) and the other (*remote*) at ∼1 nm away, and double electron–electron resonance (DEER) technique (figure 26(b)) [245]. Coherent control of the remote spin is performed using *pulsed*-DEER (figure 26(b)): first, an RF pulse of its transition frequency (f_2) and duration τ is applied to the tunnel junction, which is immediately followed by a long RF pulse at a sensor spin's transition that measures the coherent rotation of the remote spin (see Rabi oscillations).

A qubit platform is established with a universal gate set by combining single and two qubit gates.

Single qubit quantum gate: To show a universal single qubit gate, it is sufficient to demonstrate full phase control of a quantum spin in a Bloch sphere, which can be achieved by adjusting the relative phase between two subsequent RF pulses, so called '2-axis control' (figure 25) [246]. This technique is also crucial to read out off-diagonal elements of the density matrix ρ, such as a measurement of entanglement, since STM probes only the diagonal elements (populations) of ρ.

Two-qubit quantum gate: Each of the four transitions in a two-qubit system (figure 26(b)) indeed corresponds to a coherent rotation of a spin controlled by the state of the other spin. The bottom right transition (f_2) of duration π flips the remote spin conditioned on the sensor spin being in the up (↑) state, which straightforwardly translates to a *controlled-NOT* gate (figure 26(c)). This can be extended to larger qubit systems, as *controlled-controlled-NOT* gates were demonstrated for a three-spin system [4].

Current and future challenges

As with any new architecture, on-surface spins face a series of challenges and open questions that are needed to be addressed, as outlined below.

Spins in tunnel junction: Readout of qubits in STM inevitably involves the tunnel current and temporal fluctuations of the tip's magnetic moment, giving rise to a considerable relaxation and decoherence of a spin in the junction ($T_2 = 10$–30 ns [44]). By using the remote spin approach, the influence of the tunnelling current has been largely mitigated, resulting in an enhanced T_2, e.g. ∼100 ns for a Ti spin on 2-ML of MgO on Ag [4]. Despite, indirect measurement scheme only via the sensor spin, inherent in the STM configuration, severely limits measurement fidelity of remote spins due to the tunnelling current-dominated poor coherence of the sensor spin.

ESR-based qubit control: A challenge for scaling up this platform is the added complexity from the increasing number of ESR transitions, which is ultimately limited from the frequency space given by the machine-specific RF transmission characteristics and natural line-width of each resonance. For a system of N qubits with non-degenerate eigenstates, $N{\cdot}2^{N-1}$ ESR transitions are available. Linewidth $\geqslant$ 10 MHz and band width = 40 GHz of a conventional ESR-STM limits the controllable number of qubits $N < 10$. Considering limited tunability of degeneracy and transition frequencies using magnetic fields and qubit-qubit interactions, the maximum total number of qubits will be even smaller.

Time-average measurement: The read-out of qubits using STM is currently achieved in a time-average method due to a poor time resolution of tunnelling current output ($\leqslant$1 kHz). However, for some quantum computing algorithms, it is highly desirable to perform a single-shot measurement [247], which requires a time resolution of 1 μs for spin qubits on 2-ML MgO.

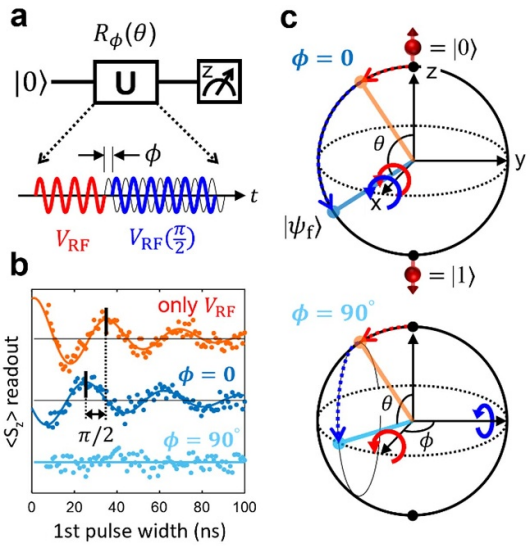

Figure 25. Single qubit gate: (a) A quantum logic gate using '2-axis control' scheme, driving a single qubit into a final state $|\psi_f\rangle$ of a superposition of $|0\rangle$ and $|1\rangle$. (b) and (c) 2-axis control applied to a Ti spin on MgO surface for phase delays $\phi = 0$ and $\phi = 90°$ of the second RF driving signal (blue) and corresponding rotations of the spin in a Bloch sphere. Reproduced from [246], with permission from Springer Nature.

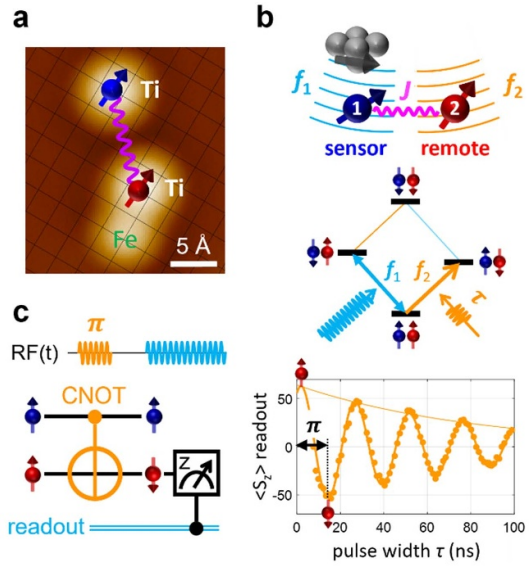

Figure 26. Two-qubit gate: (a) STM image of two-coupled spin qubits using Ti atoms on MgO surface [245]. A relatively long-lived single atom magnet, here an Fe atom, is paired with the remote spin (red) to provide a similar local source of magnetic field gradient [251], as the magnetic tip does to drive a spin in the STM junction [41]. (b) (top and middle) Scheme of coherent control f_2 (τ) of the remote qubit, the red Ti spin in (a), using double electron–electron resonance technique. (bottom) Rabi oscillations of the remote qubit, read out from an ESR transition of the sensor spin (f_1). (c) Scheme of controlled-NOT (CNOT) gate to the two qubits, performed using pulsed-ESR at f_2 and probed using CW-ESR at f_1.

State initialization via *thermalization*: In spite of the prototypicality of a Ti adsorbate on MgO ($S = 1/2$) as a TLS, it acts as a drawback in the state initialization that can be done by thermal relaxation. Thus, for an increasing T_1, read-out speed inverse-proportionally decreases.

Advances in science and technology to meet challenges

Decoupling substrate: Despite a remarkable enhancement of the figure of merit (ΩT_2) using a remote spin, by a factor of roughly 20 compared to a sensor [4], it is still severely limited by the electrons of the substrate [45]. Reducing this contribution might seem straightforward by: (i) increasing the thickness of the insulating layer, e.g. *3-ML* MgO on Ag. (ii) Using an atomic scale probe of no need for a metallic substrate [61]

Sensor's quantum coherence: For a given available frequency band, a straightforward approach to increase available number of qubits is to reduce the linewidth of each transition by enhancing the coherence of the sensor qubit. Implementing control of junction DC bias voltage with a ns resolution, hence the DC current, can minimize the tunnelling current-induced decoherence of the sensor.

Robust spins: It is desirable to explore atomic spins which are more robust against environmental decoherence: (i) Lanthanide elements are rising as promising candidates of electron spin qubits due to the localized nature of the 4f-orbitals. (ii) Nuclear spins have an ultimately long coherence. By exploiting the hyperfine interaction with electron spins, their spin states can be controlled by the electron tunnelling in the STM junction [248].

Scalability: System scaling can be readily addressed in two ways, provided that a large enough frequency space is given: (i) using N spin-1/2 qubits, resulting in a Hilbert space of dimension 2^N, is a straightforward way as long as physical design of tunable inter-qubit couplings around the sensor spin is allowed. (ii) A use of $S > 1/2$ units, generally referred to as *qudits*, is an efficient way to increase the Hilbert space with a smaller number of atoms. Hyperfine coupling with a nuclear spin of $S > 1/2$ provides a vast number of promising candidates for *qudits* on surface.

Single-shot measurement & *state initialization*: One option is to prepare a qubit of T_1 time enhanced beyond this limit. A straightforward example is recently given using a nuclear spin of ^{49}Ti ($I = 7/2$), revealing a T_1 of the order of seconds [248], while electron spins still need development of an advanced approach to effectively decouple environmental sources of the decoherence. A distinct approach could be to implement optical coupling to the qubit, similar to Λ-systems in trapped ion qubits [249], such that simultaneous control and probing of multiple qubits are available, independent of the single tip based tunnel junction as usual in an STM.

Concluding remarks

Combination of STM and ESR, together with implementation of pulsed RF technique with a nanosecond time resolution, has enabled on-surface atomic scale qubit platforms crafted atom-by-atom. Electron spins localized on surfaces already fulfill most of the criteria, established by Bennett and DiVincenzo [250]. Beside abovementioned challenges, to push this qubit system to the ranks of an advanced quantum platform, advances in experimental setups are also highly desired: (i) a dilution fridge equipped STM operating at a temperature $<$100 mK ensures the ground state population $>$0.99, with typical system parameters ($S = 1/2$, $g \approx 2$, $B_{\mathrm{ext}} \approx 0.6$ T), which would lead to a dramatic increase of gate fidelity. (ii) Careful design of RF circuits throughout the STM hardware can lead to a transmission window up to $\sim$100 GHz, which is highly desirable for scaling up the system.

Acknowledgments

The author acknowledges support by the Institute for Basic Science (IBS-R027-D1).

5.5. Stochastic resonance spectroscopy (SRS) of single atoms

Susanne Baumann and Sebastian Loth
University of Stuttgart, Institute for Functional Matter and Quantum Technologies, 70569 Stuttgart, Germany

Status

Stochastic dynamics play a fundamental role in the behaviour of matter at the atomic scale. One such example are the magnetization fluctuations of individual atoms or molecules on surfaces. At this length scale, the atoms' magnetic moments are quantized and can only change through quantum jumps, which inherently impart randomness. These quantum jumps are often too fast to be observed in real time, yet, their statistics contain detailed information about the coupling of the magnetic atoms to their environment and about the underlying scattering processes. This, in turn, can offer crucial insights for tuning the quantum properties of nanoscale systems and for the quest to boost coherence times of atomic or molecular spins on surfaces for quantum applications. To that end, a method that measures stochastic dynamics in particular at ultrafast timescales is necessary.

SRS is a novel technique that leverages the combination of STM and high frequency excitation of the tunnel junction, to directly measure these fluctuations over an extremely wide frequency range, from slow millisecond switching rates, that can also be observed in real time, to ultrafast processes at picosecond timescales that approach the intrinsic scattering rates of the atoms' environment [252–254] (see figure 27). The method builds on the phenomenon of stochastic resonance that manifests as a frequency-dependent synchronization of the stochastic switching of few-state systems to an external harmonic drive. This synchronization effect has been found in a large range of classical systems, among them electronic devices, lasers, nerve tissue and even the earth climate [255]. Its appearance in quantum systems was predicted in 1994 [256] and recently demonstrated for QDs [257] and individual atoms, where the stochastic resonance was discovered in the spin dynamics of individual magnetic atoms [253] and in the structural dynamics of an atomic orbital memory system [254] as well as of a molecule [258] (see figure 28).

The SRS method extends this concept to higher frequencies, i.e. much faster transition rates. It harnesses the synchronization between an external drive and the stochastic dynamics of the system (figure 27(A)) to induce fast oscillations of the state occupation (figure 27(B)), that are then measurable via homodyne detection (figure 27(C)). These fast oscillations would not be observable in the absence of synchronization. Previously established relaxometry methods such as pump-probe spectroscopy [259] or spin-echo measurements in ESR [44], typically resolve the relaxation dynamics of the undriven spin system. By contrast, SRS accesses the transition rates of driven open quantum systems and, due to its broadband nature, can simultaneously capture slow low-energy dynamics as well as fast excited state dynamics at the same time.

Current and future challenges

In fact, there are only two requirements to enable SRS in atomic-scale systems and they are remarkably simple: (i) the system must possess transition probabilities that can be modulated at different frequencies with an external control parameter, and (ii) there must be a measurable observable that detects the system's state. This simplicity indicates the broad applicability of SRS, yet, to fully realize the technique's potential, we identify three key challenges.

The first challenge lies in accessing even faster timescales. Stochastic resonance on atomic-scale systems has thus far been studied predominantly in settings where dynamics were relatively slow and amenable to real-time observation with the limited bandwidth of STM current amplifiers [253, 254] and have only recently been extended to the sub-nanosecond scale [252]. But many atomic-scale phenomena unfold at even faster timescales. For example, electron scattering and decay of quantum correlations in metals may be as fast as femtoseconds, exciton coherence in photoactive molecules evolves over picoseconds, and spin dynamics in low-dimensional magnetic systems appear in the tens of picoseconds range. Accessing these timescales is possible by homodyne detection that utilizes the synchronization effect of stochastic resonance, (figure 27(C)), but demands substantial advances in high-frequency driving capabilities while maintaining atomic-scale spatial resolution.

The second challenge emerges from systems exhibiting multiple dynamical processes that span different timescales, often ranging from slow changes in the system's low energy configuration to ultrafast excited state transitions. Established theoretical frameworks struggle to capture these processes as they are often interconnected and may not be treated as independent Markovian events. This ultrafast regime has been equally challenging to address with experimental methods, such as pump-probe spectroscopy, because the

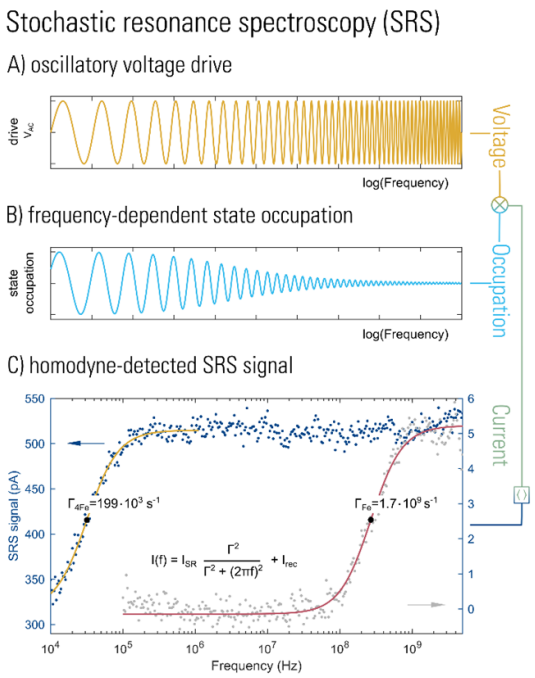

Figure 27. The method of stochastic resonance spectroscopy relies on the down mixing of an oscillatory drive (A) with the resulting frequency dependent state occupation of a driven system (B) in the tunnel junction (both of which are schematically depicted here), which leads to a frequency-dependent time-averaged current signal that has a step-like shape on a logarithmic frequency scale (C). Figure (C) is adapted from [252].

excited state signals suffer from low occupation probability and are therefore overwhelmed by the slow processes in the same system. SRS has the potential to disentangle these processes because it can reliably separate slow and fast processes by their characteristic switching frequencies.

The third challenge concerns limitations of bias voltage excitation and tunnel current detection of fast dynamics. While SRS has proven effective for magnetization dynamics and structural dynamics of atoms, other quantum phenomena of interest, such as electron-phonon coupling, entanglement transport or charge-neutral quasiparticles may not modulate with bias voltage, or they may involve changes in electronic states that are too subtle to alter the tunnelling probability sufficiently. We thus believe that exploring modulation of stochastic dynamics by other control parameters and harnessing alternative observables will realize the full potential of SRS as a universal probe of stochastic dynamics at the atomic scale.

Advances in science and technology to meet challenges

SRS has demonstrated its capacity to characterize stochastic processes on the atomic scale and it has been shown that the implementation of homodyne detection schemes (figure 27) extends the accessible frequency range far beyond the real-time bandwidth of the STM, which makes SRS a broadband technique that can capture stochastic dynamics ranging from milliseconds to picoseconds in one measurement.

The highest measurable frequency is, in principle, only limited by the implementation of the high-frequency modulation. Applying fast oscillatory voltage signals in a STM is nowadays routinely achieved up to approximately 40 GHz, as a consequence of the development of ESR of individual atoms on a surface (ESR-STM) [41]. Recent developments in antenna-based coupling have pushed this boundary up to 100 GHz [260] and ultrafast spectroscopy in the STM with subcycle THz pulses indicates that the STM is capable of frequencies up to several THz [261]. Hence, advances in MW generation, low-loss cryogenic waveguides and THz coupling could extend the frequency range of SRS substantially beyond the 5 GHz demonstrated so far (figure 27(C)), potentially enabling direct observation of higher order electron scattering processes and other ultrafast quantum phenomena such as quasiparticle dynamics that have thus far remained beyond reach.

Tackling the challenge of multi-state dynamics will become possible by harnessing the broadband capabilities of SRS in combination with advances in theoretical modelling of driven open quantum systems. By categorizing different switching pathways according to their characteristic frequencies, we can begin to understand intricate quantum jump dynamics between multiple states. This may elucidate the possibility for

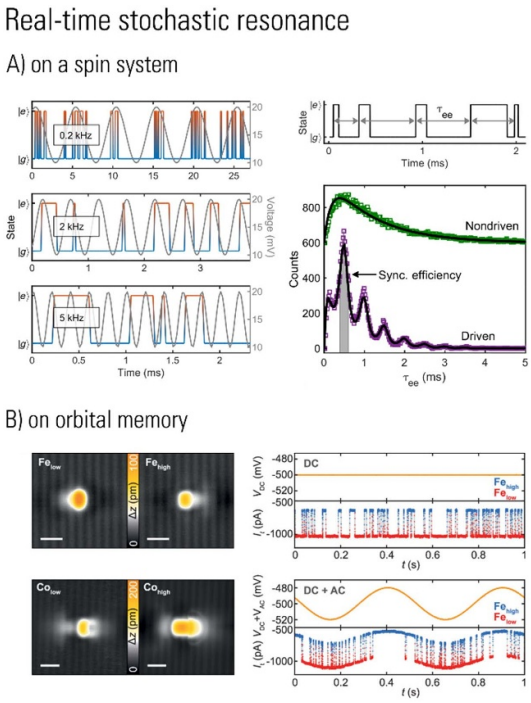

Figure 28. Real-time stochastic resonance has been observed on two different atomic-scale systems so far: (A) on an individual Fe atom on the N-binding site of a Cu_2N surface [253] and (B) on individual Fe atoms adsorbed on black phosphorous [254]. In both cases the authors were capable of showing how the switching statistics are indeed significantly influence by the frequency of the oscillatory voltage drive. (a) From [253]. Reprinted with permission from AAAS. (b) Reprinted with permission from [254]. Copyright (2024) American Chemical Society.

interference between switching pathways and potentially even detect non-Markovian processes and correlation effects in the system–environment coupling.

Finally, extending the applicability of SRS can be pursued for atomic-scale quantum systems in a STM in two complementary directions. First, by driving the quantum systems by other stimuli such as oscillating magnetic fields, tip-induced forces or photoexcitation. Second, detection schemes can be extended to other state-dependent observables. Particularly promising is luminescence detection that can resolve picosecond processes [262]. These alternative approaches will require fast synchronization of input and output signals and precise correction of frequency-dependent phase shifts, but promise an entirely new class of multi-messenger experiments of stochastic dynamics at the atomic scale.

Concluding remarks

SRS in STMs is a novel broadband method that measures the stochastic dynamics of atomic-scale systems. It features a large dynamic range that can span from milliseconds to picoseconds within one measurement.

This is particularly useful, because the stochastic dynamics of atomic-scale quantum systems often span large frequency ranges. Nevertheless, for probing ultrafast processes, such as excited state dynamics, it will be important to advance the high frequency capabilities of SPM to harness SRS even more effectively.

In addition, the ability to study driven and undriven dynamics will enable unprecedented insights into the physics of open quantum systems. It should become possible to distinguish specific switching pathways through different quantum states, or identify the emergence of non-Markovian dynamics due to built-up of correlations with the environment.

Since stochastic resonance is a universal phenomenon in stochastically switching, periodically driven systems, there are potential applications on the horizon for other open quantum systems such as QDs, colour centres, or dopants in semiconductors. For quantum dots, SRS could, for example, simultaneously probe both slow charge state dynamics and fast excited state transitions, providing a comprehensive picture of multi-level systems where conventional pump-probe techniques struggle with low occupation probabilities of excited states. In colour centres such as NV centres in diamond, SRS could quantify the switching rates of unstable impurities on the diamond surface, potentially elucidating previously hidden details of the environmental decoherence processes that limit electronic and nuclear spin dynamics. For dopants in

semiconductors, SRS may capture competing ionization and recombination processes that occur simultaneously but at different rates in a single broadband measurement.

Acknowledgments

S Baumann acknowledges support from the Volkswagen foundation (NEURAM, neuromorphic materials on the atomic scale). S Loth acknowledges support from the Integrated Quantum Science and Technology Center, Stuttgart and Ulm.

5.6. Hyperfine-mediated coherent control over individual nuclear spins

Lukas M Veldman[1] *and Sander Otte*[2]
[1] Institute for Functional Matter and Quantum Technologies, University of Stuttgart, Germany
[2] Department of Quantum Nanoscience, Delft University of Technology, The Netherlands

Status

Addressing individual spins in solid state materials has been of great interest to both fundamental nanoscience and quantum applications. Not only could single spin control be used for computational ends, it also offers a platform for studying the influence of the local microscopic environment on spins such as symmetry-induced magnetic anisotropies and decoherence processes. STM is a unique tool for this purpose that offers local control, spin sensitivity and manipulation down to the single atom scale. Nuclear spins in particular are of great interest because they are generally more protected from outside influence and therefore exhibit longer coherence times. This protection, however, also makes them more difficult to control and read out. Nonetheless, recent efforts combining STM with ESR [41] and pump-probe spectroscopy [259, 263] have improved energy and temporal resolution to the extent that access to the nuclear spins of individual atoms have come within reach.

The first hallmark work demonstrating the ability to address nuclear spins was the distinction of different isotopes of individual Ti atoms [264]. This was made possible by detecting the hyperfine splitting of the electron spin due to its coupling to the nuclear spin, if present, in ESR-STM measurements. Importantly, this is an indirect form of detection: the tunnelling electrons interact directly only with the electron spin of the atom, which in turn influences the nuclear spin via the hyperfine coupling.

Subsequently, the technique was extended to isotopes of Cu, which are characterized by a much stronger hyperfine interaction [265]. This work also demonstrated the possibility to 'pump' the system to a particular nuclear spin state. Here, the spin-polarized tunnelling current favours inelastic excitations of the atom's electronic spin in a particular direction. The resulting population imbalance of spin states is then transmitted to the nuclear spin via the hyperfine interaction (see figure 29).

For single Ti atoms on MgO, the hyperfine interaction was also shown to be highly anisotropic due to the influence of the surface symmetry [266, 267]. This allows for experimental control over the magnitude of the coupling between electron and nucleus by considering the atomic binding site as well as the direction of the external field. Most recently, hyperfine-mediated coherent dynamics were observed between electron and nucleus within a single atom, showing the potential for full coherent control of single nuclear spins using STM [268].

Current and future challenges

The study of individual nuclear spins using STM is a relatively young field with many open questions. One of the most intriguing and relevant examples is the actual relaxation and decoherence time scales of the nuclear spins of different atomic species. As mentioned before, the timescales of nuclear spins of atoms on a surface are expected to be orders of magnitude longer compared to their electronic counterparts based on previous experiments in systems like silicon spin qubits [269] and NV centres [270]. Direct measurement of these quantities using STM, however, has not been achieved yet. Reaching this milestone would quantify the potential capabilities of nuclear spins on surfaces for quantum applications as well as allow for the controlled study of the influence of binding site, electron-nucleus interactions and hyperfine coupling magnitude on the lifetime of the nuclear spin.

Another very promising direction is the direct driving of nuclear magnetic resonance (NMR) transitions in single atoms and molecules. This type of transition was already observed on both Cu and Ti atoms [265, 268] but it remains unclear if these transitions are driven through the mixing with the electron spin states or if there is any direct driving of the nuclear spin via a different mechanism observed in other systems, such as hyperfine Stark modulation [230] or nuclear quadrupole resonance [271]. Understanding the driving mechanism would signify a large step in full coherent control over the nuclear spin of single atoms and molecules on a surface.

Finally, we would like to point to the challenge of coupling individual nuclear spins. Achieving this would open the door to concrete applications like quantum computation and simulation. Usually, nuclear spins in insulators and semiconductors are coupled through their magnetic dipole fields [272]. It remains to be seen if this is also possible on a conducting surface or if a different coupling mechanism, e.g. mediated through the electron spins, is necessary. Building an experiment using multiple nuclei also raises the challenge of initializing multiple nuclear spins with the STM tip, possibly by temperature or spin pumping.

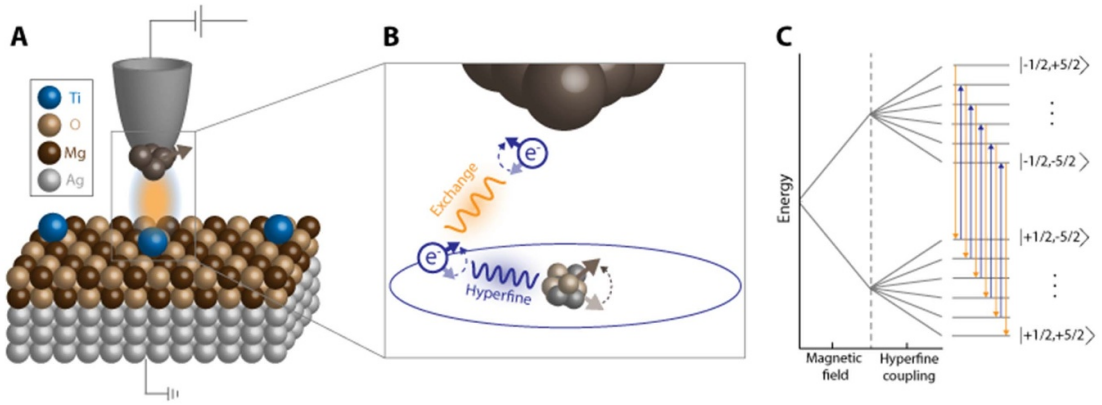

Figure 29. Measuring and controlling the nuclear spin of a single atom using scanning tunnelling microscopy. (A) Schematic picture of a typical STM experiment using single Ti atoms adsorbed on bilayer MgO grown on a Ag substrate. (B) Schematic image depicting the relevant interactions for the indirect measurement and manipulation of the nuclear spin. Tunnelling electrons interact with the single unpaired electron of the Ti atom via the Kondo exchange interaction. The nuclear spin and the orbiting electron interact via the hyperfine coupling. (C) Simplified level diagram for the electronic Zeeman energy and hyperfine coupling terms for a ^{47}Ti isotope ($S = \frac{1}{2}, I = \frac{5}{2}$). The external field splits the electron spin states while the hyperfine coupling splits the states further according to their nuclear spin state. Orange and blue arrows indicate spin pumping processes mediated by the exchange interaction and hyperfine flip–flop respectively.

Advances in science and technology to meet challenges

In the previous section, where we discussed a number of challenges for the control of nuclear spins using STM, we already pointed to possible directions to solve individual problems. Here, we would like to mention more general techniques that we think will be of importance to this research direction.

First, we would like to stress the importance of spin pumping in these systems and the need for more intricate combinations of RF and DC pulses in pulse schemes. Spin pumping through DC pulses was shown to be a very effective way to initialize spin states resulting in populations that can beat thermal distributions by two orders of magnitude [263, 265]. Additionally, DC pulses can be used to flip the direction of an electron spin within nanoseconds as well as probe the electron spin state with similar time resolution [268]. Combining this tool with coherent control via RF pulses will be a significant step towards answering the challenges mentioned above such as measuring nuclear spin lifetimes and measuring dynamics of coupled nuclear systems.

Recently, remote driving and detection was achieved for multiple electron spins in STM [4], showing the potential to expand control outside the atom located directly under the tip. Combining these techniques to drive remote nuclear spins would increase the possibilities for nuclear spins dramatically.

Lastly, we expect that a lot is to be gained by exploring new systems and substrates. Every atom has a nucleus and yet, as of the writing of this piece, the individual nuclear spins of only three species have been studied using STM: Cu, Fe and Ti on MgO. Other systems may be dominated by different phenomena such as the nuclear quadrupole moment or the direct interaction between an electron's unquenched orbital moment and the nuclear spin. Expanding our research to include these systems may enable the investigation of distinctly different physics and possibilities. The limit of which systems can be studied is set by the energy resolution that can be achieved by ESR-STM: a hyperfine splitting on the order of 10 MHz should be able to be resolved.

Concluding remarks

The study of individual nuclear spins using STM is still in its infancy and many avenues currently lie unexplored. Recent pioneering work has shown the possibility to distinguish different isotopes of individual atoms, control their nuclear spin state via spin pumping and NMR-type driving and resolve the coherent dynamics between electron and nucleus. We expect that greater control over individual nuclear spins can be gained by more intricate pulse sequences combining DC and RF pulses and remote driving schemes. Finally, we point towards the large set of unexplored species of atoms and molecules that in all likelihood harbour hyperfine physics that could be dominated by different interactions than what has been studied up to now.

Acknowledgments

LMV acknowledges funding by the Alexander von Humboldt Foundation. SO acknowledges funding from the European Research Council (ERC Advanced Grant 101095574 HYPSTER).

5.7. Open quantum systems study on multi-spin qubits on surfaces

Christoph Wolf
Center for Quantum Nanoscience (QNS), Institute for Basic Science (IBS), Seoul 03760, Republic of Korea
Department of Physics, Ewha Woman's University, Seoul 03760, Republic of Korea

Status

The discovery of quantum-coherent multi qubit control using a single tip in a STM combined with the pulsed ESR technique established spins on a surface as novel qubit platform [4]. In parallel to the experiment, accurate and predictive simulations are critical to understand existing experiments, optimize the systems under study and explore the limitations of this novel platform. Spins on surfaces are a challenging object for simulations as they are relatively strongly coupled with the environment. This requires the simulation of open quantum systems under the influence of the STM bias and current (figure 30(A)). The scattering of conduction electrons with the quantum spin was discovered to be the dominant decoherence source for a spin located in the STM junction, leading to a general limitation of the number of Rabi cycles Ω that can be achieved before a decoherence event T_2 so that $\Omega T_2 \approx 5$ in ideal driving conditions (figures 30(B) and (C)) in good agreement with experiments (figure 30(D)). Several methods exist that can accurately account for the interaction between spin qubit and environment either by ways of non-equilibrium Green's functions transport calculations and quantum master equations [273–275], or phenomenological Redfield or Lindblad master equations. The former approach has the advantage of a microscopic description of the STM junction which gives a direct physics-informed parametrization of the model whilst the latter is a well-established general method for open quantum systems where the interaction with the environment is constructed via more mathematical collapse operators. The latter method also has the advantage of being scalable to relatively large systems with moderate computational cost and has been applied to multi-qubit systems simulations [245, 276].

Current and future challenges

Current major challenges are threefold:

(i) Efficient scaling of simulations to systems with large Hilbert space
(ii) Predictive simulations based on first principles to aid the discovery of novel systems
(iii) Optimization of control fields to enhance the fidelity of quantum operations

Currently, simulations have focused on systems with generally less than 10 spin-1/2 particles aiming at the experimentally realized system size of 3 qubits. As system scaling is a crucial aspect of practical quantum systems with the goal to implement quantum algorithms also simulations must adapt to a growing number of physical qubits or growing Hilbert spaces from using larger qu*d*it building units. The second challenge is a more daunting one. Current simulations rely mostly on parameterization after the experiment, i.e. the parameters of the simulation are adjusted until they align with existing experiments. This still allows for additional insights in existing systems however it limits the exploration of novel systems that have not yet been experimentally studied. In particular, the search for spins on surfaces that allow to realize quantum TLS with an auxiliar third level used for temperature-independent initialization akin to λ-systems in ion trapped qubit is currently in the focus of *ab initio*-based search efforts after simulations have revealed that typical experimental temperatures are imposing a hard limit on the achievable degree of entanglement in a two-qubit system [277, 278].

Third, and last, is the question of optimized control of the driving fields in surface spin qubits. The challenge is here is itself twofold: on the one hand, the experimental control needs to be improved to reach the limits of the instrumentation. On the other hand, the quantum systems themselves have conceptual differences from some other existing systems, such as a permanent drift Hamiltonian due to the constant exchange coupling between qubits.

Advances in science and technology to meet challenges

To address scaling issues in the simulations efficient approaches need to be adapted from other fields to the open quantum system formalisms currently employed in quantum coherent surface spin system simulations. Promising pathways are available such as tensor networks, which allows for efficient description of large quantum systems. As supporting measure, existing codes should explore computational acceleration using modern accelerator hardware such as graphics processing unit-based computing.

To explore novel systems *ab initio*-based methods will become necessary to search the vast parameter space of substrate and adatom species, searching for systems beyond the tried and tested titanium atom

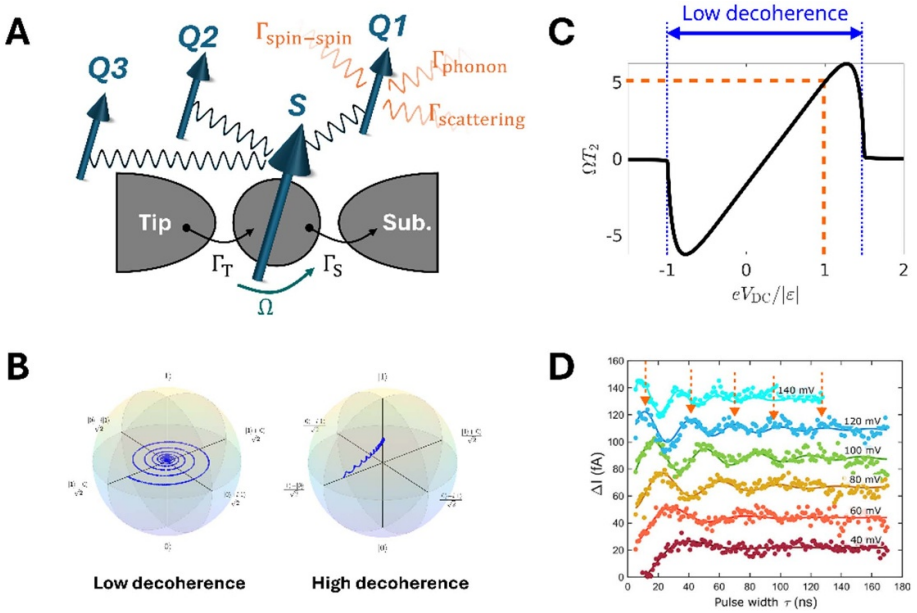

Figure 30. (A) Conceptual open quantum system realized by spins on surfaces. A sensor spin S is connected to two electrodes labelled as Tip and Substrate. A time-dependent spin-polarized current indicated by hopping operators $\Gamma_{T,S}$ through the electrodes will lead to Rabi oscillations on the spin with Rabi rate Ω. Additional qubits are exchange-coupled to the sensor as indicated by the lines. All qubits are subject to decoherence which can stem from scattering with conduction electrons, phonons or spin–spin interaction with individual rates as indicated. (B) The Bloch spheres show two cases: a slowly decohering quantum spin undergoing Rabi oscillations as well as a rapidly decohering spin which decoheres before undergoing a Rabi cycle. (C) The achievable figure of merit for quantum operations ΩT_2 is a function of the external bias V_{DC}. Within the slowly decohering regime (V_{DC} below the ionization energy ε) ΩT_2 can reach 5, i.e. 5 full Rabi cycles before the system decoheres (Reprinted figure with permission from [331], Copyright (2004) by the American Physical Society). This compares well with experimental data shown in (D) measured on an Fe(II)phthalocyanine molecule on 2 layers of MgO (Reprinted figure with permission from [332], Copyright (2023) by the American Physical Society).

adsorbed on thin layers of magnesium oxide. The combined requirement of treating large systems and transitions at very low energy poses a veritable challenge. Some guidance will be available from multi-scale approaches that treat large systems using computationally efficient mean-field methods and then treat a select subset of states at high precision using, for example, multi-orbital Hubbard models [279].

Lastly, several strategies are available going forward to optimize control conditions. Existing formalism such as quantum optimal control can already be applied relatively straightforwardly to existing model Hamiltonians of previously realized surface spin systems. A lot of improvements might be achievable by exploiting the constant drift Hamiltonian, i.e. the time-evolution of the system government by not directly controlled effects such as the Zeeman on-site energies of the qubits and the exchange coupling between the individual spins [280].

Concluding remarks

Surface spin systems are a new platform in quantum-coherent nanoscience. If the development towards quantum information processing and quantum computing is to be successful key metrics such as gate fidelity and entanglement must be demonstrated. Simulations of such qubit systems in the framework of open quantum systems have indicated that high gate fidelities and high degrees of entanglement are in principle possible. To experimentally achieve the same performance, novel physical systems should be explored, ideally supported by combining *ab initio* with open quantum systems simulations. Clearly, there is currently a strong demand and opportunity for predictive and quantitative open quantum systems simulations to advance the field of surface spin qubits.

Acknowledgments

The author acknowledges support by the Institute for Basic Science (IBS-R027-D1). I would like to thank Nicolas Lorente and Jose Reina-Galvez for extensive discussions.

5.8. Electron spin resonance-atomic force microscopy

Lisanne Sellies[1,2] *and Jascha Repp*[1]
[1] Institute for Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany
[2] IBM Research Europe—Zurich, 8803 Rüschlikon, Switzerland

Status

ESR is a spectroscopic technique, which is mainly used for the structural elucidation of species with unpaired electrons, but is also a promising tool to control qubits in quantum information processing. A drawback of conventional ESR is that a large number of spins is required to get a detectable signal. While the development of optical detection of an ESR signal enabled single molecule sensitivity in 1993 [281, 282], it remained a long-standing goal to combine single-molecule sensitivity in ESR with SPM. This dream was fueled by the prospect to combine local single-spin manipulation and detection with atomic manipulation, that is, the atomically precise placement of atoms and molecules on a surface to build artificial quantum structures. (section 5.7)

This vision became reality by the first demonstration of ESR with subångström spatial resolution using STM in 2015 [41]. Since then, this has developed into a vibrant research field with a very high pace of major breakthroughs, demonstrating the great potential of ESR-STM for quantum sensing and quantum engineering [4], see also sections 2.1, 5.3, 5.4, 5.6 and 5.7. While ESR-STM addresses numerous contemporary research questions, the achievable coherence times seem limited by the decoherence sources that are intrinsically present. Considering the nature of the decoherence sources, it became clear that if ESR was instead combined with AFM, these decoherence sources could be largely avoided.

Most approaches to develop ESR-AFM concentrate on exploiting dipole or exchange forces to detect the spin by means of AFM [283, 284], and a successful demonstration of this type of ESR-AFM with single-spin resolution and atomic-scale resolution would mark an important milestone. However, a different approach recently led to the first AFM-detected ESR spectra with atomic-scale spatial resolution: exploiting spin-to-charge conversion enabled zero-field triplet state ESR to be demonstrated for individual planar organic molecules [61]. The used pump-probe sequence relies on single-electron tunnelling for initialization (figure 31(a)) and read-out (figure 31(c)). In contrast, there is no electron tunnelling taking place during the ESR manipulations (see figure 31(b)). In these first current-free ESR-AFM experiments coherence times longer than ten microseconds could be demonstrated (see figure 31(d)).

Current and future challenges

ESR-AFM is in its infancy with only one ESR-AFM study reported. Hence, the next obvious steps are to extend the method to different sample systems and different operation conditions. For example, defect states in layered materials, dopant atoms or QDs in semiconductors could be characterized in the future. So far, ESR-AFM was performed in zero-magnetic field without a spin-polarized tip; ESR-AFM with such a field or tip could open new applications. A magnetic field will increase the coupling to the environment, including neighbouring atoms or molecules, useful for quantum sensing, see also section 2.6. A magnetic field would also energetically split spin states that are (nearly) degenerate otherwise, including nuclear spin states. Because of their long coherence times, it might be beneficial to use nuclear spins for quantum devices [286]. As in electron nuclear double resonance spectroscopy one may employ ESR-AFM to indirectly address nuclear spins via the electron spins for writing, processing, and reading [287], see also section 19. In such a setting one could use the external magnetic field for a tunable addressing of the nuclear spin states.

From a more general perspective, we see three categories for future ESR-AFM developments:

(a) The local ESR signal could complement usual AFM signals. This could include chemical and configurational fingerprinting of molecules, complementary to the bond-resolved AFM imaging. Potentially, the AFM tip could be used to perturb the molecule and thereby alter the ESR signal. Such perturbation is expected to spatially vary over the molecule, for example, for triplet-state ESR it might directly scale with the local triplet density. Hence, it might be possible to directly image the triplet density this way. Depending on which local modifications the ESR signals are sensitive to, other interesting scanning-gate-like experiments [288] are conceivable, such as the localization of isotopes inside a single molecule.
(b) The amazing spectral resolution of ESR-AFM together with the atomic-scale information provided by AFM could provide unprecedented insights into physical mechanisms. Imagine experiments, in which individual molecules are exposed to different atomically well-defined environments, while their ESR signatures, Rabi oscillations and coherence times are being measured. This would provide a robust

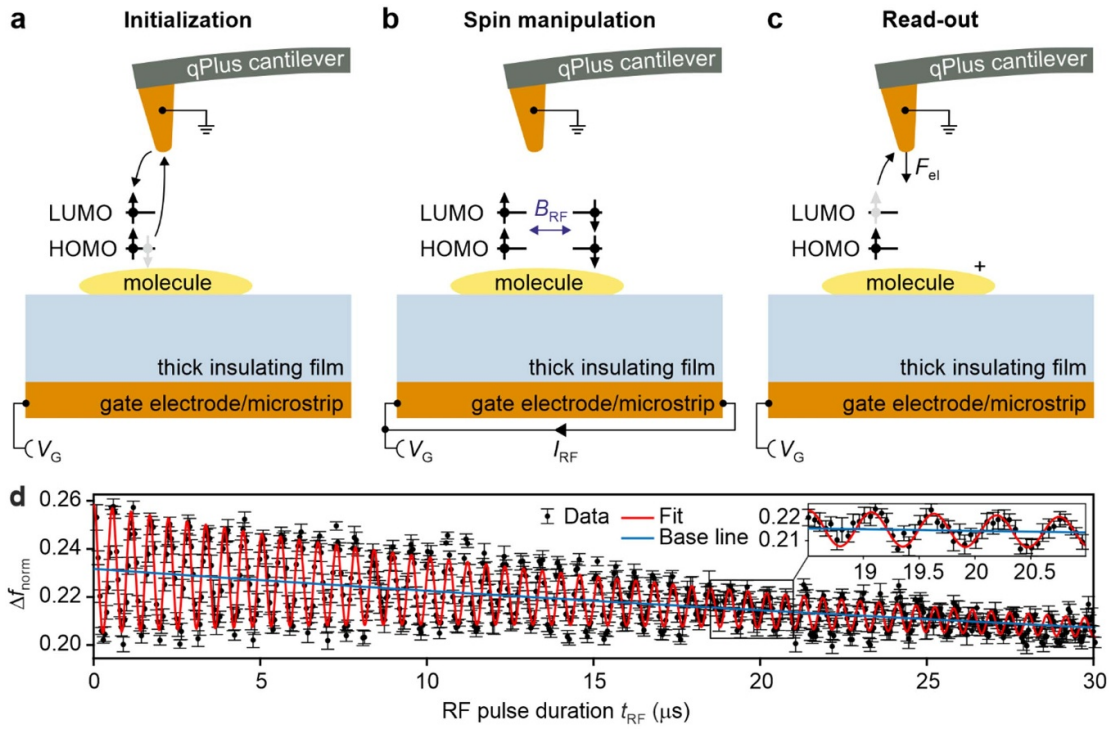

Figure 31. Principle of ESR-AFM based on spin-to-charge conversion and the measured Rabi oscillations. (a)–(c) Pump-probe sequence to measure zero-field triplet state ESR signals via qPlus [285] AFM. The molecule can be brought to its first excited triplet state by controlled electron tunnelling between tip and molecule (a). Owing to the different lifetimes of the triplet substates, a population difference will build up over time. Consequently, by driving transitions between the substates using an RF magnetic field, produced by running an RF current through a microstrip, forming the gate electrode (b), the triplet state population will be modified. This population can be determined by mapping the triplet and ground state onto two charge states (c), which can be discriminated in the AFM signal by the different electrostatic force. Since only a single molecule is being measured, many such pump-probe cycles are required to detect the triplet population and thereby the ESR signal. (d) Rabi oscillations measured using ESR-AFM on a perdeuterated pentacene molecule. Panel d reproduced from [61], license CC BY 4.0.

testbed for the atomistic theories on spin–spin-interactions, hyperfine coupling, spin–orbit interaction and their associated dephasing phenomena and scattering times—including non-Markovian relaxation.

(c) Atomically controlling the environment would also allow engineering quantum platforms at the atomic scale, similar to ESR-STM [4], while making use of the long coherence times observed in ESR-AFM. The insulating surface offers in addition a control of charge states in adsorbates [289], such that adsorbates can be deliberately switched between closed shell—without net spin—and other spin configurations. This would allow switching on and off mutual spin interactions, which is crucial for implementing possible functionality in spin-based quantum structures [290].

Advances in science and technology to meet challenges

We see two main challenges associated to the current implementation of ESR-AFM. The first challenge is the complexity of the measurements and the associated slow turnaround. Of course, working under ultra-high vacuum conditions and at cryogenic temperatures renders the technique demanding, but this applies to many conventional STM and AFM experiments. The ESR-AFM technique implemented so far relies on a pump-probe scheme (see figure 31) and the resulting signal is very weak. Consequently, a long data-acquisition time is required for every single spectrum, limiting the parameter space that can be explored in corresponding experiments. Spin-polarized tunnelling in ESR-AFM (see figure 32) could enhance the efficiency of spin-state preparation and read out. Further improvements may span from increasing the detection bandwidth of the AFM sensor to enhancing the signal strength by charge-sensitive tip-functionalization to optimizing the control protocols and the associated pump-probe sequence. While an increase in data-acquisition rate of an order of magnitude is well conceivable, speed is fundamentally limited by the duration of the desired coherent manipulation process and the stochastic readout in repeated single-molecule experiments. The second challenge is that the present implementation of ESR-AFM is not applicable to all sample systems; especially the requirement of an accessible long-lived triplet state is not always fulfilled. In this respect, chemical engineering of quantum-sensing molecules may tackle several of the molecular requirements at once.

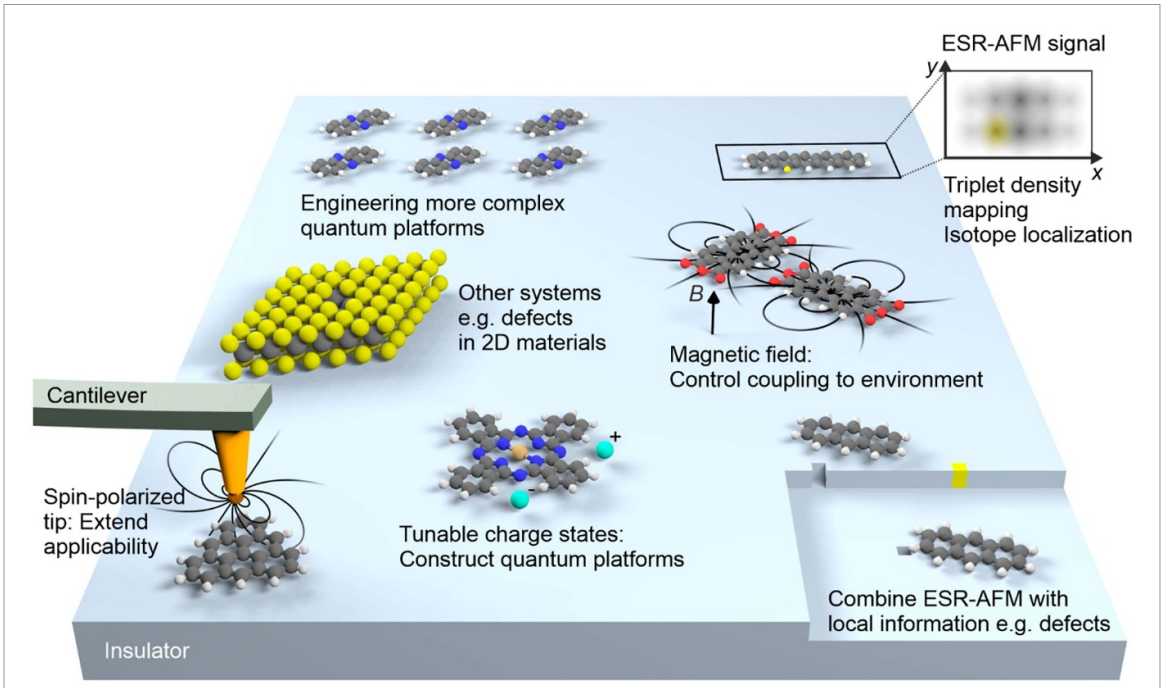

Figure 32. Schematic illustration of research opportunities in ESR-AFM.

Novel implementations of ESR-AFM could potentially solve both challenges. For instance, ESR-AFM with detection based on dipolar or exchange forces would be applicable to systems with a non-zero spin in the electronic ground state, thereby nicely complementing triplet-state ESR-AFM.

Furthermore, all aspects mentioned in the previous section will greatly benefit from atomic and molecular manipulation. Although it is established that the charge of single atoms or molecules can be deliberately changed on insulators [289], lateral and chemical manipulation of atoms and molecules on bulk insulators is much more challenging than on conducting surfaces [60, 291], see also section 2.2.

Concluding remarks

The first demonstration of single-molecule ESR by means of AFM provides a promising toolset for the engineering and characterization of quantum platforms at the atomic scale. ESR-AFM has demonstrated superior spectral resolution and coherence times, which is combined with atomic-scale spatial resolution. Next steps ahead include broadening the applicability of ESR-AFM to a wide range of molecules and materials. Improving the detection scheme or exploiting other detection mechanisms, such as magnetic exchange forces, might boost the applicability of ESR-AFM. Future directions to be explored range from atomic-scale scanning-gate-like experiments, over testbeds for fundamental atomistic quantum descriptions to engineered quantum platforms.

Acknowledgments

We thank Leo Gross for discussions. Funding from the ERC Synergy Grant MolDAM (No. 951519) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through RE2669/6-2 is gratefully acknowledged.

5.9. Quantum states of impurities in atomically engineered semiconductors

Steven R Schofield[1,2] *and Michael E Flatté*[3,4]
[1] Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
[2] London Centre for Nanotechnology, University College London, London WC1H 0AH, United Kingdom
[3] Department of Physics and Astronomy, University of Iowa, Iowa City, IA 52242, United States of America
[4] Department of Applied Physics and Science Education, Eindhoven University of Technology, Eindhoven 5612 AZ, The Netherlands

Status

Spin states in semiconductors offer one of the most stable and noise-resistant platforms for qubits, while also enabling integration with conventional semiconductor technologies [292]. Spins localised in nuclei or in the hydrogenic electron/hole states of substitutional impurities are particularly attractive, as they yield qubits that are intrinsically identical, setting them apart from many other qubit implementations. These substitutional impurities form donor or acceptor states with wave functions that extend well beyond the crystal lattice spacing. Their interactions are typically mediated by exchange coupling, making it essential to understand the structure and overlap of their hydrogenic wave functions. However, the extended nature of these states presents particular challenges, requiring close coordination between high-resolution experiments and advanced theoretical modelling.

The mapping of dopant wave functions with STM and conductance measurements was first pioneered in III–V semiconductors [293] due to the exceptional properties of the cleaved III–V (110) surface, laying the foundation for experimentally investigating dopant behaviour at the atomic scale for both donors and acceptors. The origin of the anisotropic shape of the acceptor wave function was identified as the cubic symmetry of the host valence bands, the binding energy of donors and acceptors was found to depend sensitively on their depth below the surface, and metastable switching behaviour was demonstrated for, e.g. Si dopants near the GaAs surface, in analogy with bulk DX^{-} centres.

Building on that pioneering work, it has since been demonstrated that hydrogenic states can also be observed in silicon. For instance, arsenic donors within the top 12 atomic layers (∼1.5 nm) were found to exhibit strongly modified states due to proximity to the surface [294]. At depths greater than 20 layers (∼2.5 nm), phosphorus and arsenic donors reveal more extended states with the expected hydrogenic envelope and valley-interference Bloch components of the donor ground states. Phosphorus donor pairs, identified opportunistically in STM experiments, show orientation-dependent variations in exchange and tunnel couplings, highlighting the importance of envelope anisotropy, crystal symmetry, and dopant position for evaluating exchange coupling predictions [295]. Most recently, the first STM images of acceptor states in silicon have been reported, revealing a strikingly anisotropic, square-like appearance that reflects the underlying crystal symmetry and electronic band structure (figure 33) [296].

Just as in the III–V semiconductors [297], understanding the physics of these states requires theoretical frameworks that bridge atomic and continuum scales. Effective mass theory has proven remarkably successful in reproducing the overall envelope of the donor and acceptor states. However, tight-binding theories additionally provide information about the registry of the dopant state to the underlying lattice and reveal the effects of local symmetry breaking on the dopant state structure. These features can also interact with near-surface properties to produce dopant features highly modified from those expected deep in the bulk material [298, 299].

Current and future challenges

A thorough understanding of dopant-dopant interactions requires the ability to position impurity atoms deterministically within the semiconductor lattice. SPM can achieve this level of control, for example by inserting cations directly into a III–V lattice through tip-induced substitution [300]. Such approaches are described elsewhere in this roadmap, yet directly repositioning atoms in silicon is challenging because of the strong covalent bonding. Instead, a lithographic technique has been developed: precursor molecules are chemically reacted on surfaces patterned to have reactive and inert regions. This was first demonstrated for phosphorus in silicon [301] using phosphine (PH_3) as a precursor and selectively desorbing hydrogen from a hydrogen-terminated Si(001) surface with the STM tip. The method has since been extended to arsenic in silicon and, to a lesser extent, other material systems [302]. Nonetheless, broadening this approach to acceptors (e.g. boron, gallium), deep-level/double donors (e.g. bismuth, selenium), and optically or magnetically active species (e.g. erbium, manganese) remains a significant opportunity. To illustrate the potential, bismuth, being electronically deeper than phosphorus, offers increased stability and the possibility of higher-temperature operation, while the spin states of a single antimony donor in silicon define a 16-dimensional Hilbert space, enabling the encoding of an error-correctable logical qubit within a single

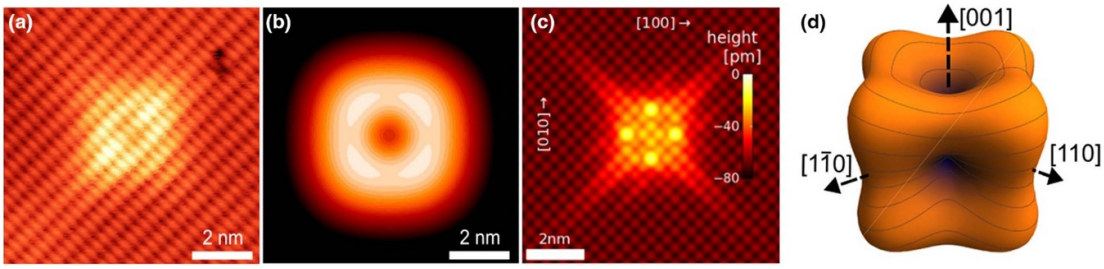

Figure 33. Subsurface acceptor states in silicon. (a) STM image a single acceptor located beneath the Si(001) surface, revealing characteristic spatial features of the bound hole state superimposed on the surface atomic lattice. (b), (d) Effective mass approximation calculations of an acceptor wave function in silicon; (b) shows the charge density evaluated for a plane 2.9 nm above the impurity layer along [001], while (d) shows a three-dimensional real-space iso-surface of the acceptor state wave function. (c) Tight-binding atomistic calculation of an acceptor wave function in silicon calculated for a depth of 0.81 nm. Reproduced from [296], with permission from ACS Publications.

atom [303]. Acceptor states, such as those provided by substitutional boron, offer a route to circumvent the exchange coupling oscillations inherent to donor systems, while enabling control via electric fields.

Achieving electrostatic gating and precise control of transport channels within *in-situ* STM experiments presents another major challenge. Creating in-plane circuitry at the atomic scale, where the dopant atom(s) to be studied are integrated alongside gates and leads, would open the door to studying correlated impurity states in an atomic-scale semiconductor system with direct access for the STM tip to act as a moveable gate or contact. The results of such experiments can enhance work toward scalable prototypes of atomically precise quantum devices. Progress here is likely to deepen our understanding of dopant–dopant interactions, spin-orbit coupling (SOC), and the influence and control of nearby reservoirs.

As the complexity of the experiments increases so do the challenges for theory. These include the effect of local symmetry breaking on the dopant electronic structure. These are most evident in the crystal field splittings of rare-earth dopants near the surface of a material; such features have been explored in the unique STM playground of MgO on silver especially for STM-ESR measurements [220].

Advances in science and technology to meet challenges

Progress in deterministic impurity placement depends on identifying suitable precursor molecules and understanding their surface chemistry. Phosphine is an ideal model: each molecule contains exactly one phosphorus atom, has a small dissociation footprint (six silicon surface atoms, or just under 1 nm^2), and contains only hydrogen as a by-product, which does not hinder subsequent process steps. The same is true of arsine. In contrast, no similarly simple hydrides exist for most other impurity species of interest, prompting exploration of alternatives such as metal-organics (e.g. trimethylaluminium, triphenylbismuth), which frequently leave carbon residues that are difficult to remove. Halide compounds such as aluminium trichloride, bismuth trichloride, and phosphorus tribromide have been attempted and offer a more promising route; boron trichloride has proven particularly effective, enabling the fabrication of p-type nanowires [304]. However, only phosphorus and arsenic can currently be positioned with nanometre precision. STM experiments combined with DFT calculations are crucial for identifying precursors and unravelling their dissociation pathways, as demonstrated for phosphine and arsine on Si(001) [305].

To address the broader challenge of understanding defect interactions generally, it is essential to extend these methods beyond silicon. Germanium, for example, is a particularly attractive platform for impurity-based quantum technologies: it exhibits three times larger Bohr radii compared to silicon, a stronger Stark effect, and is predicted to be less sensitive to exchange coupling oscillations in the technologically relevant (001) plane. Recently, arsenic has been shown to incorporate into germanium (001) from arsine (AsH_3) *at room temperature* (figure 34) a discovery with significant promise for the scale up to large qubit arrays.

In parallel, the development of lithographic resists and patterning methods must keep pace with new precursor chemistries. Halogen termination, for example, may be needed to control the adsorption of halides [302] and improve dopant placement fidelity. Further advances in patterning accuracy and the suppression of contaminants will also be vital as more complex devices are pursued. For scale up, it may be required to go beyond STM patterning; one such route now being explored is hydrogen desorption from silicon (001) using extreme ultraviolet photons [302].

Realising in-plane gating and electrical contacting within the STM environment will require several technological advances. Prefabricated gates and contacts formed by ion implantation have been

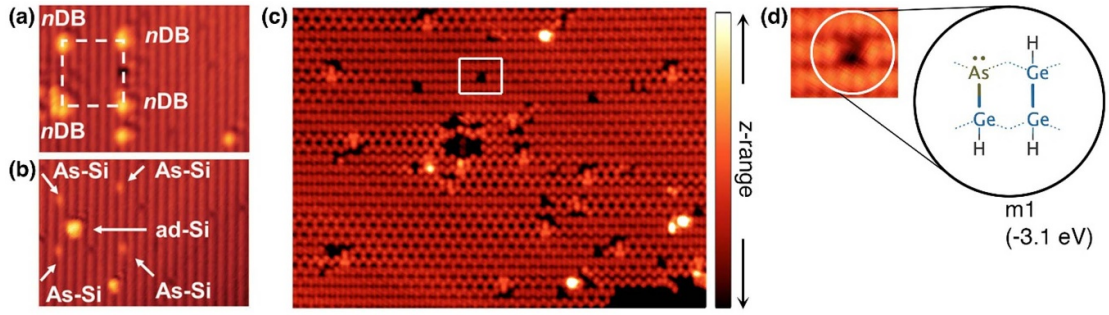

Figure 34. Arsine (AsH_3) as a precursor for the atomic placement of arsenic in silicon and gernamium. (a) A 2 × 2 array of dangling bond sites created on a hydrogen-terminated Si(001) surface. (b) The same area shown in (a) after exposure to arsine and subsequent thermal annealing (350 °C, 1 min) showing an incorporated arsenic atom at each of the four sites (As–Si) and ejected silicon on the surface (ad-Si). Adapted from Ref [306]. (c) Clean germanium (001) surface exposed to light dose of arsine. Unlike previously studied systems (PH_3 and AsH_3 on Si(001) or PH_3 on Ge(001)), arsenic incorporation occurs at room temperature on Ge(001), which is very promising for device scale-up in As/Ge. (d) Enlargement of an arsenic incorporated in Ge(001) from the adsorption of a single AsH_3 molecule; the site is marked by a rectangle in (b). This feature has one incorporated As atom and three adjacent adsorbed H atoms, as illustrated in the schematic. Reproduced from [307].

demonstrated, but not yet at the level of controlling single atoms [308]. Furthermore, conventional high-temperature processes can degrade these contacts, making low-temperature, in-UHV preparation methods necessary for preserving dopant integrity and enabling high-fidelity electrical measurements.

Extending theoretical models to address these device-scale configurations will be crucial for predicting and interpreting experiments on increasingly large-scale, multi-dopant quantum systems. Many similar features have been studied in other single-spin-coherent systems, such as nitrogen-vacancy centres in diamond or vacancy complexes in silicon carbide. The dynamical properties of intersystem crossings, dipoles (ground, excited, and transition) and dopant g tensors have proven to reveal highly sensitive features of the local charge and structural environments around the dopants.

Concluding remarks

With their exceptionally long quantum coherence times, intrinsic indistinguishability, and physical stability, the spin states of donors in isotopically purified semiconductors constitute near-ideal qubits. Yet despite these outstanding intrinsic properties, significant practical challenges remain. Chief among them is the need to position large numbers of impurity atoms with near-perfect precision. Single- and few-donor devices can now be fabricated reliably, but scaling to large, multi-qubit systems may require new material combinations, such as arsenic in silicon or germanium, or new approaches such as multi-donor qubits. A detailed understanding of the fabrication processes, dopant behaviour, and wave function interactions is steadily emerging, driven by high-resolution STM experiments and theoretical modelling. Together, these approaches are deepening our understanding of both fundamental physics and engineering pathways toward scalable quantum devices.

Acknowledgments

M E F acknowledges support from the US Department of Energy, Office of Science, Office of Basic Energy Sciences, through Award No. DE-SC0016379. S R S gratefully acknowledges funding from the Engineering & Physical Sciences Research Council (EP/M009564/1). We thank Julian Zanon for assistance with the preparation of figure 33d.

5.10. Atomic scale engineering of silicon qubits by STM

Joris G Keizer[1,2] *and Michelle Y Simmons*[1,2]
[1] University of New South Wales Sydney, Sydney, Australia
[2] Silicon Quantum Computing, New South Wales, Sydney, Australia

Status

Donors in silicon have a long history as a quantum platform that can be engineered at the atomic scale. Using STM to pattern a hydrogen resist in combination with gaseous precursor dosing and low-temperature molecular-beam epitaxy, dopant atoms can be placed with atomic precision inside a silicon matrix, see figure 35(a). Many atomic-scale electronic components, such as atomic-scale interconnects, single-electron transistors, single-lead charge sensors, charge sensing tunnel gaps, single-atom transistors, single-qubit gates, and two-qubit gates, have been demonstrated over the years. A key advantage of this platform over more traditional top-down approaches is that the qubits and their control and readout structures are all fabricated inside an isotopically pure and high-quality epitaxial silicon crystal. This environment acts as a 'semiconductor' vacuum where the dopant atoms are positioned away from noise inducing interfaces resulting in the lowest level of charge noise expired by qubits to date [309]. Importantly, the platform allows for three-dimensional manufacturing [310] by stacking multiple functional layers, which can be position on top of each other with nanometre precision in all dimensions, all within the same epitaxial silicon crystal. This three-dimensional manufacturing capability enables the realisation of a host of new or enhanced low-noise gating and control options, along with the possibility of all-epitaxial ESR and magnetic nuclear resonance (NMR) antennas, epitaxial noise shielding layers, and on-chip integrated logic. The ability to engineer multiple epitaxial device layers within a single crystal provides a pathway to realise scalable error-corrected universal quantum computing architectures. This is most evident in surface code-based architectures where the need to control and read out qubits synchronously and in parallel requires the formation of a two-dimensional array of qubits controlled by gates above and below the qubit layer [311]. Having demonstrated the capability to manufacture all the key components for an error-corrected and scalable universal quantum computer, the further development of this platform is now driven by the desire to increase qubit and gate performance. To this end, attention is now on qubits consisting of clusters of multiple dopant atoms where the qubit properties can be engineered by atomic precise placement of the constituents.

Current and future challenges

In Sydney we have pioneered atomic-precision manufacturing to realise nanoelectronic devices and reproducible, high-quality atom qubits in silicon. Recently, our work has progressed from single-electron qubits to multi-nuclear spin qubit registers consisting of multiple phosphorus atoms [312]. The-state-of-the art is currently a four-qubits silicon processor [313], combining 3 nuclear and 1 electron spin qubit, see figure 35(b), with every gate operation above the fault-tolerant threshold of 99%. This high fidelity, inherent to the atom-qubit platform, allowed for the execution of Grover's search algorithm with a 95% probability of finding the marked state, one of the most successful implementations in any qubit platform to date. The next step now is linking these multi-qubit processors together through the exchange interaction of the electrons. To this end, understanding and gaining control over key factors that affect the extent of the donor wave function, such as charging energies, valley-orbit splitting, Stark shift of the electron g-factor, nuclear hyperfine, and exchange coupling is of critical importance. The power of the atom-qubit platform is that it allows us to engineer all these properties, see figure 36 for an overview, through atomic-precise engineering. For example, we can directly engineer the wave function by adding atoms to the qubit, resulting in stronger electron confinement, and longer electron spin lifetimes ($\sim$30 s for a 3P register) [314]. Another controllable parameter is the separation between atoms within the register, where for distances larger than $\sim$8 nm the phosphorus atoms enter the molecular qubit regime, exhibiting excellent qubit properties that surpass those of single-atom qubits [315]. Similarly, we can control the angle of the atoms with respect to crystallographic axis of the silicon host. This is especially important for the exchange interaction as its strength is theoretically predicted to fluctuate due to valley interference depending on the angle. Positioning the atoms along the [110]-direction removes the valley interference, resulting in a well-defined exchange coupling [295]. Placement of the atoms along specific crystallographic directions also allows for engineering large hyperfine Stark coefficients ($\sim$70 MHz MV^{-1} m^{-1}) enabling fast and high-fidelity qubit operation ($\sim$99.99%) without affecting neighbouring qubits [316]. In terms of coupling, extremely fast (0.8 ns) $\sqrt{\text{SWAP}}$ gates have been demonstrated between qubit registers in natural silicon [317]. A key challenge moving forward is to limit charge noise, which causes unwanted fluctuations in the exchange coupling. Engineering a large magnetic field gradient, again by placing atoms in particular locations, can mitigate the effect of charge noise, promising CNOT gate fidelities of 99.98% [318].

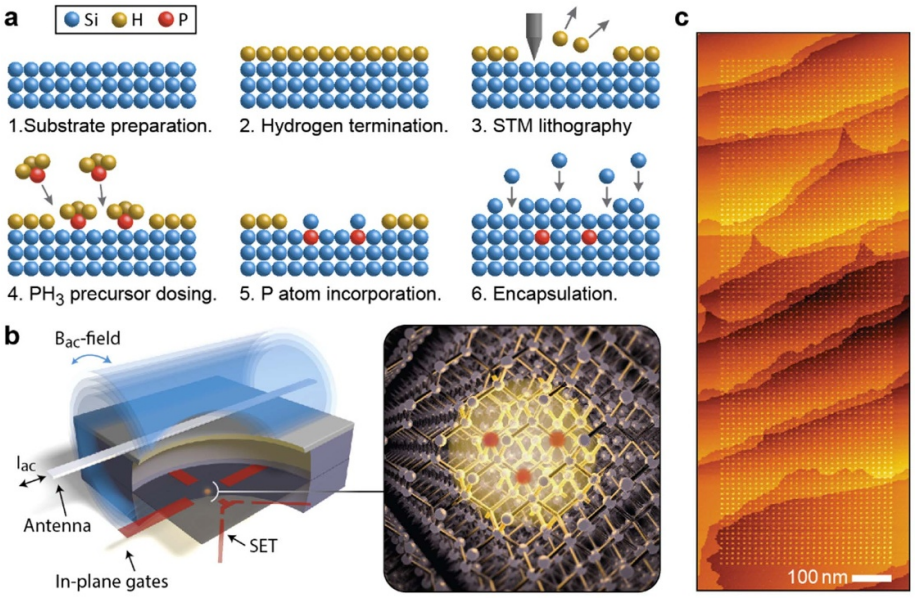

Figure 35. Atomic-precise engineering platform for atom-qubits in silicon. (a) Over the past 2 decades UNSW Sydney has pioneered a complete manufacturing process for atomically precise placement of atoms to realize fully crystalline integrated circuits and processors using only phosphorus and silicon. To achieve this (1) a silicon substrate is annealed to clean and flatten the surface, (2) followed by exposure to atomic hydrogen to form a monolayer resist. (3) The tip of a STM is used to locally remove H atoms leaving a lithographic imprint that exposes the bare silicon. (4) Next, upon exposure to the gaseous precursor PH_3 absorbs to the chemically active openings in the H mask. (5) The phosphorus atoms are then incorporated into the silicon surface by an incorporation anneal. (6) Finally, the patterned structures are overgrown with defect-free epitaxial silicon. (b) Using this process multi-qubit processors, in this example 3 nuclear (red dots) and 1 electron qubit (yellow cloud), and the readout and control structures can be fabricated within the silicon crystal. The qubits are operated by electron spin resonance (ESR) and nuclear spin resonance (NMR) fields applied through an antenna on the surface that is precisely aligned to the buried device. (c) A 3000-site array of QDs (ensembles of 10 s of donor atoms) spanning $\sim 0.5 \times 1.5$ μm showcasing the scalability of STM lithography.

Advances in science and technology to meet challenges

Achieving high fidelity multi-qubit processors and efficiently linking them together will ultimately require true atomic-precise control over phosphorus atom placement in the silicon host material. Tremendous progress has been made on this front since the early nanoelectronic components consisting of regions of many hundreds of atoms. Recent work on STM tip-assisted incorporation [319] has demonstrated that lattice-site accuracy is no longer a dream but possible in this platform. Whilst an important milestone, work needs to be done in terms of scalability as this approach is complex and time-consuming, requiring an exceptionally stable STM tip and limiting its application to low temperature ($<$77 K) lithography and few sites. Other more scalable approaches that aim to control the incorporation kinetics through precursor dosing pressures, times, and temperatures (150 °C or 77 K) are currently being developed in parallel. Results, across both different atom types and choice of material of the lithographic masks used, are promising with the first generation of devices fabricated in this manner to be expected soon. In terms of scalability of the STM lithography, progress has been made recently with large arrays of up to 15.000 QDs (ensembles of 10 s of donor atoms) demonstrated, see figure 35(c). Returning to the few donor multi-nuclear spin registers, figure 36 illustrates that the number of parameters and the combinations in which they can be used to engineer future multi-qubit processors is almost limitless. Whilst this is a blessing, as we have many options to achieve a particular outcome, at the same time it can make it challenging to achieve a particular outcome when adjusting multiple parameters at the same time. Here, a predictive tool in atomistic modelling is of high value. Historically, atomistic modelling has been focused on building an understanding of the physics of the devices realized by simulating and matching to experimental results. However, atomistic modelling has recently reached the level of sophistication where we use it as a predictive tool informing multi-qubit processor design [320]. This is not only the case for the small numbers of atoms within multi-qubit processors but extends to larger scale components such as charge sensors, tunnel gaps, electron reservoirs, and control gates. While these components have been used in nanoelectronic devices for many years and as such are well understood experimentally, their integration within large-scale architectures is still under development. Here, multi-scale modelling of full device structures [321], can assist in rapid development, not only for atom-based quantum computers but for novel transistor designs that leverage the ultra-sharp qubit confinement potentials offered in atom-scale devices.

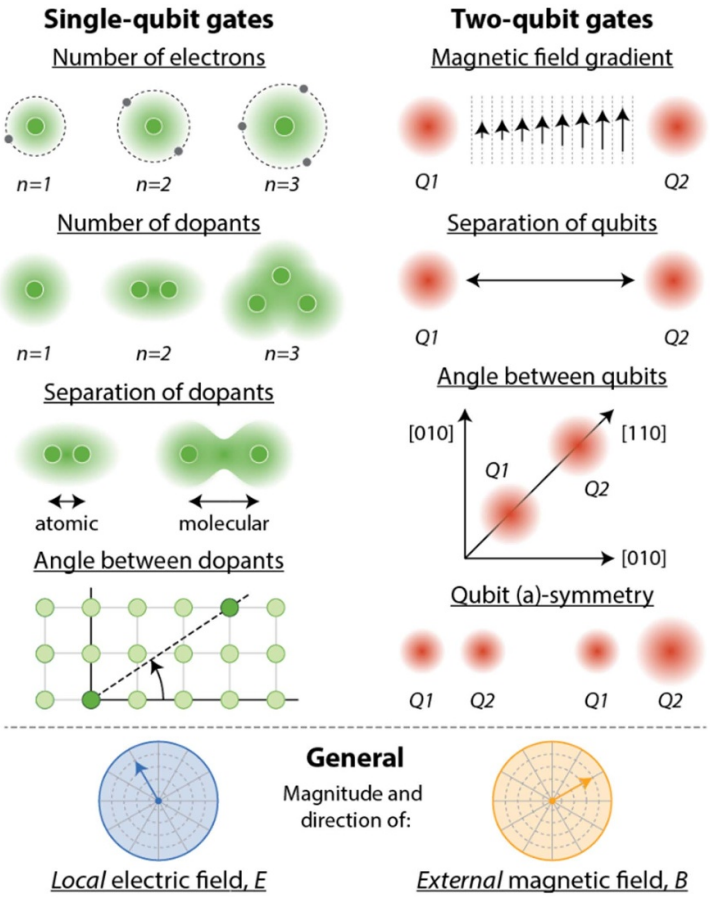

Figure 36. Precision engineering of single- and two-qubit gates for atom qubits in silicon. Both the number of electrons and number of phosphorus atoms determine the size of the electron wavefunction. Additionally, increasing the separation between phosphorus atoms changes the qubit from an atomic state to a molecular state, affecting T_1-relaxation and T_2-decoherence times. The angle between phosphorus atoms relative to both the crystal axis and the local electric field allows for engineering of both the hyperfine Stark coefficients and the spin–orbit interactions, which together with alignment to the external magnetic field can control the T_1-relaxation, T_2-decoherence, and T_2*-dephasing times. For two-qubit gates, engineering of the magnetic field gradient is possible through qubit composition affecting hyperfine strengths, while the tunnel coupling between qubits and therefore the exchange interaction can be tuned through their separation. Aligning the qubits along the [110]-direction negates fluctuations in the strength of the exchange interaction due to valley interference. The strength of the exchange interaction is high tuneable for asymmetric qubits (different electron occupation and/or number of dopants).

Concluding remarks

Atomically precise manufacturing of phosphorus atom processors has evolved from the first single-atom transistor in 2012 to the first integrated circuit made with atomic precision in 2022 [322] and now to multi-qubit processors in 2024 [313] with every gate operation above the fault-tolerant threshold. This is a remarkable achievement with focus now on engineering high-fidelity coupling between processors. Atomic modelling can inform the design of these multi-qubit processes, accelerating the speed of development of this platform for quantum computing. It has been shown that lattice-site placement of atoms is possible using tip-assisted incorporation, with scalable incorporation techniques currently under development. Manufacturing the large-scale integrated control and sensing components is achievable for multi-nuclear spin registers with qubit counts to ∼1000 with current processes. For larger qubit numbers, automated manufacturing will focus on tip stability, feedback control, precision lithography, automatization, and parallelization to ensure practical manufacturing times for large scale processors.

Acknowledgments

Since 2000 this work was undertaken in the Centre of Excellence for Quantum Computation and Communication Technology. Since 2017 the company Silicon Quantum Computing has been established to manufacture full-stack processors based on the excellent qubit properties achieved.

Data availability statement

No new data were created or analysed in this study.

ORCID iDs

Soo-hyon Phark 0000-0002-0541-5083
Bent Weber 0000-0001-8586-127X
Yasuo Yoshida 0000-0002-7311-555X
Patrick R Forrester 0000-0001-8882-9048
Robertus J G Elbertse 0000-0002-1429-1297
Kai Yang 0000-0002-5863-3666
Shantanu Mishra 0000-0002-2900-4203
Jascha Repp 0000-0003-2883-7083
Diego Peña 0000-0003-3814-589X
Florian Albrecht 0000-0002-7418-9155
Franz J Giessibl 0000-0002-5585-1326
Shigeki Kawai 0000-0003-2128-0120
Berthold Jäck 0000-0003-3826-0855
Haonan Huang 0000-0003-4059-0351
Joachim Ankerhold 0000-0002-6510-659X
Christian R Ast 0000-0002-7469-1188
Clemens B Winkelmann 0000-0003-4320-994X
Katharina J Franke 0000-0001-9416-023X
Titus Neupert 0000-0003-0604-041X
Zhenyu Wang 0000-0002-4857-7234
Rupert Huber 0000-0001-6617-9283
Gagandeep Singh 0000-0002-1884-6640
Fabio Donati 0000-0002-3932-2889
Wantong Huang 0000-0002-4081-3861
Kwan Ho Au-Yeung 0000-0003-2953-7955
Philip Willke 0000-0002-7215-8419
Susanne Baumann 0000-0002-3821-494X
Sebastian Loth 0000-0002-1587-3678
Lukas M Veldman 0000-0002-3854-0673
Christoph Wolf 0000-0002-9340-9782
Lisanne Sellies 0000-0001-6463-8642
Steven R Schofield 0000-0002-0727-3015
Michael E Flatté 0000-0001-5093-1549
Joris G Keizer 0000-0001-5341-4774
Michelle Y Simmons 0000-0002-6422-5888

References

[1] Binnig G, Rohrer H, Gerber C and Weibel E 1982 Surface studies by scanning tunneling microscopy *Phys. Rev. Lett.* **49** 57–61
[2] Stroscio J A, Feenstra R M and Fein A P 1986 Electronic structure of the Si(111)2 x 1 surface by scanning-tunneling microscopy *Phys. Rev. Lett.* **57** 2579–82
[3] Nuckolls K P and Yazdani A 2024 A microscopic perspective on moiré materials *Nat. Rev. Mater.* **9** 460–80
[4] Wang Y *et al* 2023 An atomic-scale multi-qubit platform *Science* **382** 87–92
[5] Song Y J, Otte A F, Shvarts V, Zhao Z, Kuk Y, Blankenship S R, Band A, Hess F M and Stroscio J A 2010 Invited review article: a 10 mK scanning probe microscopy facility *Rev. Sci. Instrum.* **81** 121101
[6] Schwenk J *et al* 2020 Achieving μeV tunneling resolution in an in-operando scanning tunneling microscopy, atomic force microscopy, and magnetotransport system for quantum materials research *Rev. Sci. Instrum.* **91** 071101
[7] Kim S *et al* 2021 Edge channels of broken-symmetry quantum Hall states in graphene visualized by atomic force microscopy *Nat. Commun.* **12** 2852
[8] Güttinger J, Stampfer C, Hellmüller S, Molitor F, Ihn T and Ensslin K 2008 Charge detection in graphene quantum dots *Appl. Phys. Lett.* **93** 212102
[9] Forrester P R *et al* 2024 Scanning multiprobe microscopy for mesoscopic devices and materials: part II *Bull. Am. Phys. Soc.* (available at: https://ui.adsabs.harvard.edu/abs/2024APS..MARZ12006F)
[10] Denisov A O, Fuchs G, Oh S W and Petta J R 2023 Dispersive readout of a silicon quantum device using an atomic force microscope-based rf gate sensor *Appl. Phys. Lett.* **123** 093502
[11] Yang K *et al* 2017 Engineering the eigenstates of coupled spin-1/2 atoms on a surface *Phys. Rev. Lett.* **119** 227206
[12] Blais A, Grimsmo A L, Girvin S M and Wallraff A 2021 Circuit quantum electrodynamics *Rev. Mod. Phys.* **93** 025005

[13] Wallraff A, Schuster D I, Blais A, Frunzio L, Huang R-S, Majer J, Kumar S, Girvin S M and Schoelkopf R J 2004 Strong coupling of a single photon to a superconducting qubit using circuit quantum electrodynamics *Nature* **431** 162–7
[14] de Leon N P, Itoh K M, Kim D, Mehta K K, Northup T E, Paik H, Palmer B S, Samarth N, Sangtawesin S and Steuerman D W 2021 Materials challenges and opportunities for quantum computing hardware *Science* **372** eabb2823
[15] Chen Y, Bae Y and Heinrich A J 2023 Harnessing the quantum behavior of spins on surfaces *Adv. Mater.* **35** 2107534
[16] Koch J *et al* 2007 Charge-insensitive qubit design derived from the Cooper pair box *Phys. Rev. A* **76** 042319
[17] Bal M *et al* 2024 Systematic improvements in transmon qubit coherence enabled by niobium surface encapsulation *npj Quantum Inf.* **10** 1–8
[18] Place A P M *et al* 2021 New material platform for superconducting transmon qubits with coherence times exceeding 0.3 milliseconds *Nat. Commun.* **12** 1779
[19] Yang K *et al* 2019 Tuning the exchange bias on a single atom from 1 mT to 10 T *Phys. Rev. Lett.* **122** 227203
[20] Denisov A O, Oh S W, Fuchs G, Mills A R, Chen P, Anderson C R, Gyure M F, Barnard A W and Petta J R 2022 Microwave-frequency scanning gate microscopy of a Si/SiGe double quantum dot *Nano Lett.* **22** 4807–13
[21] Hu Y *et al* 2025 High-resolution tunnelling spectroscopy of fractional quantum Hall states *Nat. Phys.* **21** 1–8
[22] Tsui Y-C, He M, Hu Y, Lake E, Wang T, Watanabe K, Taniguchi T, Zaletel M P and Yazdani A 2024 Direct observation of a magnetic-field-induced Wigner crystal *Nature* **628** 287–92
[23] Kumar R *et al* 2024 Quarter- and half-filled quantum Hall states and their competing interactions in bilayer graphene (arXiv:2405.19405)
[24] Kallin C and Halperin B I 1984 Excitations from a filled Landau level in the two-dimensional electron gas *Phys. Rev. B* **30** 5655–68
[25] Xie Y *et al* 2021 Fractional Chern insulators in magic-angle twisted bilayer graphene *Nature* **600** 439–43
[26] Bøttcher C G L *et al* 2024 Circuit quantum electrodynamics detection of induced two-fold anisotropic pairing in a hybrid superconductor–ferromagnet bilayer *Nat. Phys.* **20** 1–7
[27] Esat T *et al* 2024 A quantum sensor for atomic-scale electric and magnetic fields *Nat. Nanotechnol.* **19** 1–6
[28] Krinner S, Storz S, Kurpiers P, Magnard P, Heinsoo J, Keller R, Lütolf J, Eichler C and Wallraff A 2019 Engineering cryogenic setups for 100-qubit scale superconducting circuit systems *EPJ Quantum Technol.* **6** 1
[29] Barends R *et al* 2011 Minimizing quasiparticle generation from stray infrared light in superconducting quantum circuits *Appl. Phys. Lett.* **99** 113507
[30] Kreikebaum J M, Dove A, Livingston W, Kim E and Siddiqi I 2016 Optimization of infrared and magnetic shielding of superconducting TiN and Al coplanar microwave resonators *Supercond. Sci. Technol.* **29** 104002
[31] Purcell E M 1995 Spontaneous emission probabilities at radio frequencies *Confined Electrons and Photons: New Physics and Applications* ed E Burstein and C Weisbuch (Springer US) p 839
[32] Leeuwenhoek M, Norte R A, Bastiaans K M, Cho D, Battisti I, Blanter Y M, Gröblacher S and Allan M P 2019 Nanofabricated tips for device-based scanning tunneling microscopy *Nanotechnology* **30** 335702
[33] Reed M D, Johnson B R, Houck A A, DiCarlo L, Chow J M, Schuster D I, Frunzio L and Schoelkopf R J 2010 Fast reset and suppressing spontaneous emission of a superconducting qubit *Appl. Phys. Lett.* **96** 203110
[34] Sete E A, Galiautdinov A, Mlinar E, Martinis J M and Korotkov A N 2013 Catch-disperse-release readout for superconducting qubits *Phys. Rev. Lett.* **110** 210501
[35] Aumentado J 2020 Superconducting parametric amplifiers: the state of the art in Josephson parametric amplifiers *IEEE Microw. Mag.* **21** 45–59
[36] Pozar D M 2012 *Microwave Engineering* 4th edn (Wiley) (available at: https://search.library.wisc.edu/catalog/9910153599402121)
[37] Giessibl F J 2019 The qPlus sensor, a powerful core for the atomic force microscope *Rev. Sci. Instrum.* **90** 011101
[38] Khajetoorians A A, Wiebe J, Chilian B, Lounis S, Blügel S and Wiesendanger R 2012 *Nat. Phys.* **8** 497
[39] Loth S, Baumann S, Lutz C P, Eigler D M and Heinrich A J 2012 Bistability in atomic-scale antiferromagnets *Science* **335** 196–9
[40] Steinbrecher M, Rausch R, That K T, Hermenau J, Khajetoorians A A, Potthoff M, Wiesendanger R and Wiebe J 2018 *Nat. Commun.* **9** 2853
[41] Baumann S, Paul W, Choi T, Lutz C P, Ardavan A and Heinrich A J 2015 Electron paramagnetic resonance of individual atoms on a surface *Science* **350** 417
[42] Yang K, Phark S-H, Bae Y, Esat T, Willke P, Ardavan A, Heinrich A J and Lutz C P 2021 *Nat. Commun.* **12** 993
[43] Wang H, Fan P, Chen J, Jiang L, Gao H-J, Lado J L and Yang K 2024 *Nat. Nanotechnol.* **19** 1782–8
[44] Yang K, Paul W, Phark S-H, Willke P, Bae Y, Choi T, Esat T, Ardavan A, Heinrich A J and Lutz C P 2019 Coherent spin manipulation of individual atoms on a surface *Science* **366** 509
[45] Paul W, Yang K, Baumann S, Romming N, Choi T, Lutz C and Heinrich A 2017 Control of the millisecond spin lifetime of an electrically probed atom *Nat. Phys.* **13** 403
[46] Clair S and de Oteyza D G 2019 Controlling a chemical coupling reaction on a surface: tools and strategies for on-surface synthesis *Chem. Rev.* **119** 4717–76
[47] Grill L and Hecht S 2020 Covalent on-surface polymerization *Nat. Chem.* **12** 115–30
[48] Eigler D M and Schweizer E K 1990 Positioning single atoms with a scanning tunnelling microscope *Nature* **344** 524–6
[49] Stipe B, Rezaei M, Ho W, Gao S, Persson M and Lundqvist B 1997 Single-molecule dissociation by tunneling electrons *Phys. Rev. Lett.* **78** 4410–3
[50] Hla S-W, Bartels L, Meyer G and Rieder K-H 2000 Inducing all steps of a chemical reaction with the scanning tunneling microscope tip: towards single molecule engineering *Phys. Rev. Lett.* **85** 2777–80
[51] Pavliček N and Gross L 2017 Generation, manipulation and characterization of molecules by atomic force microscopy *Nat. Rev. Chem.* **1** 5
[52] Zhong Q, Ihle A, Ahles S, Wegner H A, Schirmeisen A and Ebeling D 2021 Constructing covalent organic nanoarchitectures molecule by molecule via scanning probe manipulation *Nat. Chem.* **13** 1133–9
[53] Kaiser K, Scriven L M, Schulz F, Gawel P, Gross L and Anderson H L 2019 An sp-hybridized molecular carbon allotrope, cyclo[18]carbon *Science* **365** 1299–301
[54] Albrecht F, Fatayer S, Pozo I, Tavernelli I, Repp J, Peña D and Gross L 2022 Selectivity in single-molecule reactions by tip-induced redox chemistry *Science* **377** 298–301
[55] Fatayer S, Albrecht F, Zhang Y, Urbonas D, Peña D, Moll N and Gross L 2019 Molecular structure elucidation with charge-state control *Science* **365** 142–5
[56] Kawai S, Krejčí O, Nishiuchi T, Sahara K, Kodama T, Pawlak R, Meyer E, Kubo T and Foster A S 2020 Three-dimensional graphene nanoribbons as a framework for molecular assembly and local probe chemistry *Sci. Adv.* **6** eaay8913

[57] Yang X-F, Wang A, Qiao B, Li J, Liu J and Zhang T 2013 Single-atom catalysts: a new frontier in heterogeneous catalysis *Acc. Chem. Res.* **46** 1740–8
[58] Rosławska A, Kaiser K, Romeo M, Devaux E, Scheurer F, Berciaud S, Neuman T and Schull G 2024 Submolecular-scale control of phototautomerization *Nat. Nanotechnol.* **19** 738–43
[59] Peller D, Kastner L Z, Buchner T, Roelcke C, Albrecht F, Moll N, Huber R and Repp J 2020 Sub-cycle atomic-scale forces coherently control a single-molecule switch *Nature* **585** 58–62
[60] Fatayer S, Moll N, Collazos S, Pérez D, Guitián E, Peña D, Gross L and Meyer G 2018 Controlled fragmentation of single molecules with atomic force microscopy by employing doubly charged states *Phys. Rev. Lett.* **121** 226101
[61] Sellies L, Spachtholz R, Bleher S, Eckrich J, Scheuerer P and Repp J 2023 Single-molecule electron spin resonance by means of atomic force microscopy *Nature* **624** 64–68
[62] Crommie M, Lutz C P and Eigler D M 1993 Confinement of electrons to quantum corrals on a metal surface *Science* **262** 218–20
[63] Stilp F, Bereczuk A, Berwanger J, Mundigl N, Richter K and Giessibl F J 2021 Very weak bonds to artificial atoms formed by quantum corrals *Science* **372** 1196–200
[64] Gross L, Mohn F, Moll N, Liljeroth P and Meyer G 2009 The chemical structure of a molecule resolved by atomic force microscopy *Science* **325** 1110–4
[65] Mönig H, Hermoso D R, Arado O D, Todorović M, Timmer A, Schüer S, Langewisch G, Pérez R and Fuchs H 2016 Submolecular imaging by noncontact atomic force microscopy with an oxygen atom rigidly connected to a metallic probe *ACS Nano* **10** 1201–9
[66] Auer A, Eder B and Giessibl F J 2023 Electrochemical AFM/STM with a qPlus sensor: a versatile tool to study solid-liquid interfaces *J. Chem. Phys.* **159** 174201
[67] Hütner J I, Conti A, Kugler D, Mittendorfer F, Kresse G, Schmid M, Diebold U and Balajka J 2024 Stoichiometric reconstruction of the Al_2O_3(0001) surface *Science* **385** 1241–4
[68] Wu D *et al* 2024 Probing structural superlubricity of two-dimensional water transport with atomic resolution *Science* **384** 1254–9
[69] Patera L L, Queck F, Scheuerer P and Repp J 2019 Mapping orbital changes upon electron transfer with tunnelling microscopy on insulators *Nature* **566** 245–8
[70] Clar E and Stewart D G 1953 Aromatic hydrocarbons. LXV. Triangulene derivatives *J. Am. Chem. Soc.* **75** 2667–72
[71] Clar E and Mackay C C 1972 Circobiphenyl and the attempted synthesis of 1:14, 3:4,7:8,10:11-tetrabenzoperopyrene *Tetrahedron* **28** 6041–7
[72] Pavliček N, Mistry A, Majzik Z, Moll N, Meyer G, Fox D J and Gross L 2017 Synthesis and characterization of triangulene *Nat. Nanotechnol.* **12** 308–11
[73] Mishra S *et al* 2020 Topological frustration induces unconventional magnetism in a nanographene *Nat. Nanotechnol.* **15** 22–28
[74] Li J, Sanz S, Corso M, Choi D J, Peña D, Frederiksen T and Pascual J I 2019 Single spin localization and manipulation in graphene open-shell nanostructures *Nat. Commun.* **10** 200
[75] Mishra S *et al* 2021 Observation of fractional edge excitations in nanographene spin chains *Nature* **598** 7880
[76] Zhao C *et al* Tunable topological phases in nanographene-based spin-1/2 alternating-exchange Heisenberg chains *Nat. Nano.* **19** 1789–95
[77] Zhao C *et al* Spin excitations in nanographene-based antiferromagnetic spin-1/2 Heisenberg chains *Nat. Mat.* **24** 722–7
[78] Yuan Z *et al* Atomic-scale imaging of fractional spinon quasiparticles in open-shell triangulene spin-1/2 chains (arXiv:2408.08612)
[79] Delgado A *et al* Evidence for excitonic insulator ground state in triangulene Kagome lattice (arXiv:2301.06171)
[80] Serrate D, Ferriani P, Yoshida Y, Hla S-W, Menzel M, von Bergmann K, Heinze S, Kubetzka A and Wiesendanger R 2010 Imaging and manipulating the spin direction of individual atoms *Nat. Nanotechnol.* **5** 350–3
[81] Kalff F E, Rebergen M P, Fahrenfort E, Girovsky J, Toskovic R, Lado J L, Fernández-Rossier J and Otte A F 2016 A kilobyte rewritable atomic memory *Nat. Nanotechnol.* **11** 926–9
[82] Heinrich A J, Lutz C P, Gupta J A and Eigler D M 2002 Molecule cascades *Science* **298** 1381–7
[83] Kawai S *et al* 2023 Local probe-induced structural isomerization in a one-dimensional molecular array *Nat. Commun.* **14** 7741
[84] Su J *et al* 2024 Intelligent synthesis of magnetic nanographenes via chemist-intuited atomic robotic probe *Nat. Synth.* **3** 466–76
[85] Yazdani A, Jones B A, Lutz C P, Crommie M F and Eigler D M 1997 Probing the local effects of magnetic impurities on superconductivity *Science* **275** 1767–70
[86] Li J, Schneider W-D, Berndt R and Delley B 1998 Kondo scattering observed at a single magnetic impurity *Phys. Rev. Lett.* **80** 2893–6
[87] Madhavan V, Chen W, Jamneala T, Crommie M F and N S Wingreen 1998 Tunneling into a single magnetic atom: spectroscopic evidence of the Kondo resonance *Science* **280** 567–9
[88] Heinze S, Bode M, Kubetzka A, Pietzsch O, Nie X, Blügel S and Wiesendanger R 2000 Real-space imaging of two-dimensional antiferromagnetism on the atomic scale *Science* **288** 1805–8
[89] Heinrich A J, Gupta J A, Lutz C P and Eigler D M 2004 Single-atom spin-flip spectroscopy *Science* **306** 466–9
[90] Loth S, Lutz C P and Heinrich A J 2010 Spin-polarized spin excitation spectroscopy *New J. Phys.* **12** 125021
[91] Ternes M 2015 Spin excitations and correlations in scanning tunneling spectroscopy *New J. Phys.* **17** 063016
[92] Verlhac B, Bachellier N, Garnier L, Ormaza M, Abufager P, Robles R, Bocquet M-L, Ternes M, Lorente N and Limot L 2019 Atomic-scale spin sensing with a single molecule at the apex of a scanning tunneling microscope *Science* **366** 623–7
[93] Fétida A, Bengone O, Romeo M, Scheurer F, Robles R, Lorente N and Limot L 2024 Single-spin sensing: a molecule-on-tip approach *ACS Nano* **18** 13829–35
[94] Garnier L, Verlhac B, Abufager P, Lorente N, Ormaza M and Limot L 2020 The Kondo effect of a molecular tip as a magnetic sensor *Nano Lett.* **20** 8193–9
[95] Bachellier N *et al* 2020 Vibron-assisted spin excitation in a magnetically anisotropic molecule *Nat. Commun.* **11** 1619
[96] Limot L 2018 Steering a single nuclear spin *Nat. Nanotechnol.* **13** 1093–4
[97] Josephson B D 1962 Possible new effects in superconductive tunnelling *Phys. Lett.* **1** 251
[98] Kimura H, Barber R P, Ono S, Ando Y and Dynes R C 2009 Josephson scanning tunneling microscopy: a local and direct probe of the superconducting order parameter *Phys. Rev. B* **80** 144506
[99] Jäck B, Eltschka M, Assig M, Etzkorn M, Ast C R and Kern K 2016 Critical Josephson current in the dynamical Coulomb blockade regime *Phys. Rev. B* **93** 020504
[100] Ast C R, Jäck B, Senkpiel J, Eltschka M, Etzkorn M, Ankerhold J and Kern K 2016 Sensing the quantum limit in scanning tunnelling spectroscopy *Nat. Commun.* **7** 13009
[101] Ingold G-L, Grabert H and Eberhardt U 1994 Cooper-pair current through ultrasmall Josephson junctions *Phys. Rev. B* **50** 395

[102] Ivanchenko Y M and Zilberman L A 1969 The Josephson effect in small tunnel contacts *Sov. Phys.—JETP* **28** 1272 (*Zh. Eksp. Teor. Fiz.**55**, 2395 (1968)*)
[103] Devoret M H, Esteve D, Grabert H, Ingold G-L, Pothier H and Urbina C 1990 Effect of the electromagnetic environment on the Coulomb blockade in ultrasmall tunnel junctions *Phys. Rev. Lett.* **64** 1824
[104] Averin D V and Yu Nazarov V 1990 Coulomb fingerprints on the I–V curves of the normal tunnel junctions *Physica B* **162** 309
[105] Randeria M T, Feldman B E, Drozdov I K and Yazdani A 2016 Scanning Josephson spectroscopy on the atomic scale *Phys. Rev. B* **93** 161115
[106] Assig M, Etzkorn M, Enders A, Stiepany W, Ast C R and Kern K 2013 A 10 mK scanning tunneling microscope operating in ultra high vacuum and high magnetic fields *Rev. Sci. Inst.* **84** 033903
[107] Fernández-Lomana M *et al* 2021 Millikelvin scanning tunneling microscope at 20/22 T with a graphite enabled stick–slip approach and an energy resolution below 8 μeV: application to conductance quantization at 20 T in single atom point contacts of Al and Au and to the charge density wave of 2H–$NbSe_2$ *Rev. Sci. Inst.* **92** 093701
[108] Senkpiel J *et al* 2020 Single channel Josephson effect in a high transmission atomic contact *Commun. Phys.* **3** 131
[109] Hamidian M H *et al* 2016 Detection of a Cooper-pair density wave in $Bi_2Sr_2CaCu_2O_{8+x}$ *Nature* **532** 343
[110] Smakov J, Martin I and Balatsky A V 2001 Josephson scanning tunnelling microscopy *Phys. Rev. B* **64** 212506
[111] Nadj-Perge S, Drozdov I K, Li J, Chen H, Jeon S, Seo J, MacDonald A H, Bernevig B A and Yazdani A 2014 Observation of Majorana fermions in ferromagnetic atomic chains on a superconductor *Science* **346** 602
[112] Jäck B, Xie Y, Li J, Jeon S, Bernevig B A and Yazdani A 2019 Observation of a Majorana zero mode in a topologically protected edge channel *Science* **364** 1255
[113] Xu J-P *et al* 2015 Experimental detection of a Majorana mode in the core of a magnetic vortex inside a topological insulator-superconductor Bi_2Te_3/$NbSe_2$ heterostructure *Phys. Rev. Lett.* **114** 017001
[114] Wang D *et al* 2018 Evidence for Majorana bound states in an iron-based superconductor *Science* **362** 333
[115] Jäck B, Xie Y and Yazdani A 2021 Detecting and distinguishing Majorana zero modes with the scanning tunneling microscope *Nat. Rev. Phys.* **3** 541
[116] Kezielebieke S, Huda M N, Vaňo V, Aapro M, Ganguli S C, Silveira O J, Głodzik S, Foster A S, Ojanen T and Liljeroth P 2020 Topological superconductivity in a van der Waals heterostructure *Nature* **588** 424
[117] Liu T *et al* 2024 Signatures of hybridization of multiple Majorana zero modes in a vortex *Nature* **633** 71
[118] Kong L *et al* 2021 Majorana zero modes in impurity-assisted vortex of LiFeAs superconductor *Nat. Commun.* **12** 4146
[119] Heinrich B W, Pascual J I and Franke K J 2018 Single magnetic adsorbates on s-wave superconductors *Prog. Surf. Sci.* **93** 1–19
[120] Liebhaber E, Ruetten L M, Reecht G, Steiner J F, Rohlf S, Rossnagel K, von Oppen F and Franke K J 2022 Quantum spins and hybridization in artificially-constructed chains of magnetic adatoms on a superconductor *Nat. Commun.* **13** 2160
[121] Steiner J F, Mora C, Franke K J and von Oppen F 2022 Quantum magnetism and topological superconductivity in Yu-Shiba-Rusinov chains *Phys. Rev. Lett.* **128** 036801
[122] Karan S *et al* 2022 Superconducting quantum interference at the atomic scale *Nat. Phys.* **18** 893
[123] Trahms M *et al* 2023 Diode effect in Josephson junctions with a single magnetic atom *Nature* **615** 628
[124] Steiner J F, Melischek L, Trahms M, Franke K J and von Oppen F 2023 Diode effects in current-biased Josephson junctions *Phys. Rev. Lett.* **130** 177002
[125] Wu H, Wang Y, Xu Y, Sivakumar P K, Pasco C, Filippozzi U, Parkin S S P, Zeng Y-J, McQueen T and Ali M N 2022 The field-free Josephson diode in a van der Waals heterostructure *Nature* **604** 653–6
[126] Ménard G C, Guissart S, Brun C, Leriche R T, Trif M, Debontridder F, Demaille D, Roditchev D, Simon P and Cren T 2017 Two-dimensional topological superconductivity in Pb/Co/Si(111) *Nat. Commun.* **8** 2040
[127] Mishra A, Simon P, Hyart T and Trif M 2021 Yu-Shiba-Rusinov qubit *PRX Quantum* **2** 040347
[128] Pavesic L and Zitko R 2022 Qubit based on spin-singlet Yu-Shiba-Rusinov states *Phys. Rev. B* **105** 075129
[129] Ruby M, Pientka F, Peng Y, von Oppen F, Heinrich B W and Franke K J 2015 End states and subgap structure in proximity-coupled chains of magnetic adatoms *Phys. Rev. Lett.* **115** 197204
[130] Schneider L, Beck P, Posske T, Crawford D, Mascot E, Rachel S, Wiesendanger R and Wiebe J 2021 Topological Shiba bands in artificial spin chains on superconductors *Nat. Phys.* **17** 943
[131] Schneider L, Beck P, Neuhaus-Steinmetz J, Rózsa L, Posske T, Wiebe J and Wiesendanger R 2022 Precursors of Majorana modes and their length-dependent energy oscillations probed at both ends of atomic Shiba chains *Nat. Nanotechnol.* **17** 384
[132] Küster F, Brinker S, Hess R, Loss D, Parkin S S P, Klinovaja J, Lounis S and Sessi P 2022 Non-Majorana modes in diluted spin chains proximitized to a superconductor *Proc. Natl Acad. Sci. USA* **119** e2210589119
[133] Schneider L, Beck P, Rózsa L, Posske T, Wiebe J and Wiesendanger R 2023 Probing the topologically trivial nature of end states in antiferromagnetic atomic chains on superconductors *Nat. Commun.* **14** 2742
[134] Franke K J, Schulze G and Pascual J I 2011 Competition of superconducting phenomena and Kondo screening at the nanoscale *Science* **332** 940
[135] Palacio-Morales A, Mascot E, Cocklin S, Kim H, Rachel S, Morr D K and Wiesendanger R 2019 Atomic-scale interface engineering of Majorana edge modes in a 2D magnet-superconductor hybrid system *Sci. Adv.* **5** eaav6600
[136] Bazarnik M, Lo Conte R, Mascot E, von Bergmann K, Morr D K and Wiesendanger R 2023 Antiferromagnetism-driven two-dimensional topological nodal-point superconductivity *Nat. Commun.* **14** 614
[137] Soldini M, Küster F, Wagner G, Das S, Aldarawsheh A, Thomale R, Lounis S, Parkin S S P, Sessi P and Neupert T 2023 Two-dimensional Shiba lattices as a possible platform for crystalline topological superconductivity *Nat. Phys.* **19** 1848
[138] Boshuis R, Odobesko A, Friedrich F, Jung J and Bode M 2021 Comparative growth study of ultrathin Bi films on clean and oxygen-reconstructed Nb(110) *Phys. Rev. Mater.* **5** 054801
[139] Beck P, Schneider L, Bachmann L, Wiebe J and Wiesendanger R 2022 Structural and superconducting properties of ultrathin Ir films on Nb(110) *Phys. Rev. Mater.* **6** 024801
[140] Schneider L, Beck P, Wiebe J and Wiesendanger R 2021 Atomic-scale spin-polarization maps using functionalized superconducting probes *Sci. Adv.* **7** eabd7302
[141] Küster F, Das S, Parkin S S P and Sessi P 2023 Yu-Shiba-Rusinov tips: imaging spins at the atomic scale with full magnetic sensitivity (arXiv:2307.09534)
[142] Mascot E, Bedow J, Graham M, Rachel S and Morr D K 2021 Topological superconductivity in skyrmion lattices *npj Quantum Mater.* **6** 6
[143] Teo C Y J and Hughes L T 2017 Topological defects in symmetry-protected topological phases *Annu. Rev. Condens. Matter Phys.* **8** 211

[144] König M, Wiedmann S, Brüne C, Roth A, Buhmann H, Molenkamp L, Qi X-L and Zhang S-C 2007 Quantum spin Hall insulator state in HgTe quantum wells *Science* **318** 766–70
[145] Reis F, Li G, Dudy L, Bauernfeind M, Glass S, Hanke W, Thomale R, Schäfer J and Claessen R 2017 Bismuthene on a SiC substrate: a candidate for a high-temperature quantum spin Hall material *Science* **357** 287–90
[146] Pauly C *et al* 2015 Subnanometre-wide electron channels protected by topology *Nat. Phys.* **11** 338–43
[147] Tang S *et al* 2017 Quantum spin Hall state in monolayer 1T'-WTe_2 *Nat. Phys.* **13** 683–7
[148] Ugeda M M *et al* 2018 Observation of topologically protected states at crystalline phase boundaries in single-layer WSe_2 *Nat. Commun.* **9** 3401
[149] Wu R *et al* 2016 Evidence for topological edge states in a large energy gap near the step edges on the surface of $ZrTe_5$ *Phys. Rev. X* **6** 021017
[150] Zhuang J, Li J, Liu Y, Mu D, Yang M, Liu Y, Zhou W, Hao W, Zhong J and Du Y 2021 Epitaxial growth of quasi-one-dimensional bismuth-halide chains with atomically sharp topological non-trivial edge states *ACS Nano* **15** 14850–7
[151] Wu S, Fatemi V, Gibson Q D, Watanabe K, Taniguchi T, Cava R J and Jarillo-Herrero P 2018 Observation of the quantum spin Hall effect up to 100 kelvin in a monolayer crystal *Science* **359** 76–79
[152] Tang J *et al* 2024 Dual quantum spin Hall insulator by density tuned correlations in $TaIrTe_4$ *Nature* **628** 515–21
[153] Aggarwal L, Zhu P, Hughes T L and Madhavan V 2021 Evidence for higher order topology in Bi and $Bi_{0.92}Sb_{0.08}$ *Nat. Commun.* **12** 4420
[154] Chong Y, Liu X, Sharma R, Kostin A, Gu G, Fujita K, Séamus Davis J C and Sprau P O 2020 Severe Dirac mass gap suppression in Sb_2Te_3-based quantum anomalous Hall materials *Nano Lett.* **20** 8001–7
[155] Yin J-X *et al* 2020 Quantum-limit Chern topological magnetism in $TbMn_6Sn_6$ *Nature* **583** 533–6
[156] Howard S *et al* 2021 Evidence for one-dimensional chiral edge states in a magnetic Weyl semimetal $Co_3Sn_2S_2$ *Nat. Commun.* **12** 4269
[157] Jiao L, Howard S, Ran S, Wang Z, Rodriguez J O, Sigrist M, Wang Z, Butch N and Madhavan V 2020 Chiral superconductivity in heavy-fermion metal UTe_2 *Nature* **579** 523–7
[158] Gray M J *et al* 2019 Evidence for helical hinge zero modes in an Fe-based superconductor *Nano Lett.* **19** 4890–6
[159] Wang Z, Rodriguez J O, Jiao L, Howard S, Graham M, Gu G D, Hughes T, Morr D K and Madhavan V 2020 Evidence for dispersing 1D Majorana channels in an iron-based superconductor *Science* **367** 104–8
[160] Wang W, Kim S, Liu M, Cevallos F A, Cava R J and Ong N P 2020 Evidence for an edge supercurrent in the Weyl superconductor $MoTe_2$ *Science* **368** 534–7
[161] Nayak A K *et al* 2021 Evidence of topological boundary modes with topological nodal-point superconductivity *Nat. Phys.* **17** 1413–9
[162] Randeria M T, Agarwal K, Feldman B E, Ding H, Ji H, Cava R J, Sondhi S L, Parameswaran S A and Yazdani A 2019 Interacting multi-channel topological boundary modes in a quantum Hall valley system *Nature* **566** 363–7
[163] Litskevich M *et al* 2024 Boundary modes of a charge density wave state in a topological material *Nat. Phys.* **20** 1253–61
[164] Yin J-X *et al* 2022 Discovery of charge order and corresponding edge state in kagome magnet FeGe *Phys. Rev. Lett.* **129** 166401
[165] Sessi P *et al* 2016 Robust spin-polarized midgap states at step edges of topological crystalline insulators *Science* **354** 1269–73
[166] Schindler F *et al* 2018 Higher-order topology in bismuth *Nat. Phys.* **14** 918–24
[167] Shumiya N *et al* 2022 Evidence of a room-temperature quantum spin Hall edge state in a higher-order topological insulator *Nat. Mater.* **21** 1111–5
[168] Hossain m *et al* 2024 A hybrid topological quantum state in an elemental *solid Nature* **628** 527–33
[169] Aishwarya A *et al* 2022 Spin-selective tunneling from nanowires of the candidate topological Kondo insulator SmB_6 *Science* **377** 1218–22
[170] Zhang C, Zhu T, Kahn S, Soejima T, Watanabe K, Taniguchi T, Zettl A, Wang F, Zaletel M P and Crommie M F 2024 Manipulation of chiral interface states in a moiré quantum anomalous Hall insulator *Nat. Phys.* **20** 951–6
[171] Bian K, Gerber C, Heinrich A J, Müller D J, Scheuring S and Jiang Y 2021 Scanning probe microscopy *Nat. Rev. Method Primers* **1** 36
[172] Cocker T L, Jelic V, Gupta M, Molesky S J, Burgess J A J, Reyes G D L, Titova L V, Tsui Y Y, Freeman M R and Hegmann F A 2013 An ultrafast terahertz scanning tunnelling microscope *Nat. Photon.* **7** 620
[173] Borsch M, Meierhofer M, Huber R and Kira M 2023 Lightwave electronics in condensed matter *Nat. Rev. Mater.* **8** 668
[174] Müller M 2024 Imaging surfaces at the space–time limit: new perspectives of time-resolved scanning tunneling microscopy for ultrafast surface science *Prog. Surf. Sci.* **99** 100727
[175] Bi L, Liang K, Czap G, Wang H, Yang K and Li S 2023 Recent progress in probing atomic and molecular quantum coherence with scanning tunneling microscopy *Prog. Surf. Sci.* **98** 100696
[176] Cocker T L, Peller D, Yu P, Repp J and Huber R 2016 Tracking the ultrafast motion of a single molecule by femtosecond orbital imaging *Nature* **539** 263
[177] Roelcke C, Kastner L, Graml M, Biereder A, Wilhelm J, Repp J, Huber R and Gerasimenko Y 2024 Ultrafast atomic-scale scanning tunnelling spectroscopy of a single vacancy in a monolayer crystal *Nat. Photon.* **18** 595–602
[178] Yoshioka K, Katayama I, Minami Y, Kitajima M, Yoshida S, Shigekawa H and Takeda J 2016 Real-space coherent manipulation of electrons in a single tunnel junction by single-cycle terahertz electric fields *Nat. Photon.* **10** 762
[179] Wang L, Xia Y and Ho W 2022 Atomic-scale quantum sensing based on the ultrafast coherence of an H_2 molecule in an STM cavity *Science* **376** 401
[180] Arashida Y, Mogi H, Ishikawa M, Igarashi I, Hatanaka A, Umeda N, Peng J, Yoshida S, Takeuchi O and Shigekawa H 2022 Subcycle mid-infrared electric-field-driven scanning tunneling microscopy with a time resolution higher than 30 fs *ACS Photonics* **9** 3156
[181] Siday T *et al* 2024 All-optical subcycle microscopy on atomic length scales *Nature* **629** 329
[182] Jelic V, Adams S, Hassan M, Cleland-Host K, Ammerman S E and Cocker T L 2024 Atomic-scale terahertz time-domain spectroscopy *Nat. Photon.* **18** 898–904
[183] Kimura K *et al* 2025 Ultrafast on-demand exciton formation in a single-molecule junction by tailored terahertz pulses *Science* **387** 1077
[184] Bobzien L, Allerbeck J, Ammerman S E, Torsi R, Robinson J A and Schuler B 2024 Ultrafast state-selective tunneling in two-dimensional semiconductors with a phase- and amplitude-controlled THz-scanning tunneling microscope special collection: ultrafast materials science: coherence and dynamics *APL Mater.* **12** 051110
[185] Sheng S, Abdo M, Rolf-Pissarczyk S, Lichtenberg K, Baumann S, Burgess J A J, Malavolti L and Loth S 2024 Terahertz spectroscopy of collective charge density wave dynamics at the atomic scale *Nat. Phys.* **20** 1603–8

[186] Kurtsiefer C, Mayer S, Zarda P and Weinfurter H 2000 Stable solid-state source of single photons *Phys. Rev. Lett.* **85** 290–3
[187] Rogers L J *et al* 2014 Multiple intrinsically identical single-photon emitters in the solid state *Nat. Commun.* **5** 4739
[188] Togan E *et al* 2010 Quantum entanglement between an optical photon and a solid-state spin qubit *Nature* **466** 730–4
[189] Fricke L, Hile S J, Kranz L, Chung Y, He Y, Pakkiam P, House M G, Keizer J G and Simmons M Y 2021 Coherent control of a donor-molecule electron spin qubit in silicon *Nat. Commun.* **12** 3323
[190] Castelletto S, Johnson B C, Ivády V, Stavrias N, Umeda T, Gali A and Ohshima T 2014 A silicon carbide room-temperature single-photon source *Nat. Mater.* **13** 151–6
[191] Boss J M, Chang K, Armijo J, Cujia K, Rosskopf T, Maze J and Degen C 2016 One- and two-dimensional nuclear magnetic resonance spectroscopy with a diamond quantum sensor *Phys. Rev. Lett.* **116** 197601
[192] Gupta S, Yang J-H and Yakobson B I 2019 Two-level quantum systems in two-dimensional materials for single photon emission *Nano Lett.* **19** 408–14
[193] Aharonovich I, Tetienne J-P and Toth M 2022 Quantum emitters in hexagonal boron nitride *Nano Lett.* **22** 9227–35
[194] Li K, Smart T J and Ping Y 2022 Carbon trimer as a 2 eV single-photon emitter candidate in hexagonal boron nitride: a first-principles study *Phys. Rev. Mater.* **6** L042201
[195] Gottscholl A, Diez M, Soltamov V, Kasper C, Sperlich A, Kianinia M, Bradac C, Aharonovich I and Dyakonov V 2021 Room temperature coherent control of spin defects in hexagonal boron nitride *Sci. Adv.* **7** eabf3630
[196] Zhu Y *et al* 2023 Room-temperature photoluminescence mediated by sulfur vacancies in 2D molybdenum disulfide *ACS Nano* **17** 13545–53
[197] Barthelmi K *et al* 2020 Atomistic defects as single-photon emitters in atomically thin MoS_2 *Appl. Phys. Lett.* **117** 070501
[198] Li S, Thiering G, Udvarhelyi P, Ivády V and Gali A 2022 Carbon defect qubit in two-dimensional WS_2 *Nat. Commun.* **13** 1210
[199] Kuhnke K, Große C, Merino P and Kern K 2017 Atomic-scale imaging and spectroscopy of electroluminescence at molecular interfaces *Chem. Rev.* **117** 5174–222
[200] Aliyar T *et al* 2024 Symmetry breaking and spin–orbit coupling for individual vacancy-induced in-gap states in MoS_2 monolayers *Nano Lett.* **24** 2142–8
[201] Schuler B, Cochrane K A, Kastl C, Barnard E S, Wong E, Borys N J, Schwartzberg A M, Ogletree D F, de Abajo F J G and Weber-Bargioni A 2020 Electrically driven photon emission from individual atomic defects in monolayer WS_2 *Sci. Adv.* **6** eabb5988
[202] López L E P, Rosławska A, Scheurer F, Berciaud S and Schull G 2023 Tip-induced excitonic luminescence nanoscopy of an atomically resolved van der Waals heterostructure *Nat. Mater.* **22** 482–8
[203] Krane N, Lotze C, Läger J M, Reecht G and Franke K J 2016 Electronic structure and luminescence of quasi-freestanding MoS_2 nanopatches on Au(111) *Nano Lett.* **16** 5163–8
[204] Peña Román R J, Auad Y, Grasso L, Alvarez F, Barcelos I D and Zagonel L F 2020 Tunneling-current-induced local excitonic luminescence in p-doped WSe_2 monolayers *Nanoscale* **12** 13460–70
[205] Pommier D, Bretel R, López L E P, Fabre F, Mayne A, Boer-Duchemin E, Dujardin G, Schull G, Berciaud S and Le Moal E 2019 Scanning tunneling microscope-induced excitonic luminescence of a two-dimensional semiconductor *Phys. Rev. Lett.* **123** 027402
[206] Mitterreiter E, Schuler B, Cochrane K A, Wurstbauer U, Weber-Bargioni A, Kastl C and Holleitner A W 2020 Atomistic positioning of defects in helium ion treated single-layer MoS_2 *Nano Lett.* **20** 4437–44
[207] Hennessey M, Whitefield B, Gale A, Kianinia M, Scott J A, Aharonovich I and Toth M 2025 Framework for engineering of spin defects in hexagonal boron nitride by focused ion beams *Adv. Quantum Technol.* **8** 2300459
[208] Cochrane K A *et al* 2021 Spin-dependent vibronic response of a carbon radical ion in two-dimensional WS_2 *Nat. Commun.* **12** 7287
[209] Hosoki S, Hosaka S and Hasegawa T 1992 Surface modification of MoS_2 using an STM *Appl. Surf. Sci.* **60–61** 643–7
[210] Cui S, Kim T-H and Ham U 2021 Influence of the tip shape on scanning tunneling luminescence spectra: implications for nanomaterial characterization *ACS Appl. Nano Mater.* **4** 29–32
[211] Mateos D, Jover O, Varea M, Lauwaet K, Granados D, Miranda R, Fernandez-Dominguez A I, Martin-Jimenez A and Otero R 2024 Directional picoantenna behavior of tunnel junctions formed by an atomic-scale surface defect *Sci. Adv.* **10** eadn2295
[212] Kaiser K, Jiang S, Romeo M, Scheurer F, Schull G and Rosławska A 2024 Gating single-molecule fluorescence with electrons *Phys. Rev. Lett.* **133** 156902
[213] Donati F *et al* 2016 Magnetic remanence in single atoms *Science* **352** 318–21
[214] Baltic R, Pivetta M, Donati F, Wäckerlin C, Singha A, Dreiser J, Rusponi S and Brune H 2016 Superlattice of single atom magnets on graphene *Nano Lett.* **16** 7610–5
[215] Pivetta M, Patthey F, Di Marco I, Subramonian A, Eriksson O, Rusponi S and Brune H 2020 Measuring the intra-atomic exchange energy in rare-earth adatoms *Phys. Rev. X* **10** 031054
[216] Singha A, Willke P, Bilgeri T, Zhang X, Brune H, Donati F, Heinrich A J and Choi T 2021 Engineering atomic-scale magnetic fields by dysprosium single atom magnets *Nat. Commun.* **12** 4179
[217] Bellini V *et al* 2022 Slow magnetic relaxation of Dy adatoms with in-plane magnetic anisotropy on a two-dimensional electron gas *ACS Nano* **16** 11182–93
[218] Sorokin B V, Pivetta M, Bellini V, Merk D, Reynaud S, Barla A, Brune H and Rusponi S 2023 The impact of lattice distortions on the magnetic stability of single atoms: Dy and Ho on BaO(100) *Adv. Funct. Mater.* **33** 2213951
[219] Singha A *et al* 2021 Mapping orbital-resolved magnetism in single lanthanide atoms *ACS Nano* **15** 16162–71
[220] Reale S, Hwang J, Oh J, Brune H, Heinrich A J, Donati F and Bae Y 2024 Electrically driven spin resonance of 4f electrons in a single atom on a surface *Nat. Commun.* **15** 5289
[221] Ajayi T M *et al* 2023 Characterization of just one atom using synchrotron x-rays *Nature* **618** 69–73
[222] Moreno-Pineda E and Wernsdorfer W 2024 *Magnetic Molecules as Building Blocks for Quantum Technologies* (Wiley) (https://doi.org/10.1002/qute.202300367)
[223] Moreno-Pineda E, Godfrin C, Balestro F, Wernsdorfer W and Ruben M 2018 Molecular spin qudits for quantum algorithms *Chem. Soc. Rev.* **47** 501–13
[224] Moreno-Pineda E, Damjanović M, Fuhr O, Wernsdorfer W and Ruben M 2017 Nuclear spin isomers: engineering a $Et_4N[DyPc_2]$ spin qudit *Angew. Chem., Int. Ed.* **56** 9915–9
[225] Yu X *et al* 2024 Creation and manipulation of Schr\"odinger cat states of a nuclear spin qudit in silicon (arXiv:2405.15494)
[226] Ringbauer M, Meth M, Postler L, Stricker R, Blatt R, Schindler P and Monz T 2022 A universal qudit quantum processor with trapped ions *Nat. Phys.* **18** 1053–7

[227] Godfrin C, Ferhat A, Ballou R, Klyatskaya S, Ruben M, Wernsdorfer W and Balestro F 2017 Operating quantum states in single magnetic molecules: implementation of Grover's quantum algorithm *Phys. Rev. Lett.* **119** 187702
[228] Hussain R, Allodi G, Chiesa A, Garlatti E, Mitcov D, Konstantatos A, Pedersen K S, De Renzi R, Piligkos S and Carretta S 2018 Coherent manipulation of a molecular Ln-based nuclear qudit coupled to an electron qubit *J. Am. Chem. Soc.* **140** 9814–8
[229] Chiesa A, Santini P, Garlatti E, Luis F and Carretta S 2024 Molecular nanomagnets: a viable path toward quantum information processing? *Rep. Prog. Phys.* **87** 034501
[230] Thiele S, Balestro F, Ballou R, Klyatskaya S, Ruben M and Wernsdorfer W 2014 Electrically driven nuclear spin resonance in single-molecule magnets *Science* **344** 1135–8
[231] Biard H, Moreno-Pineda E, Ruben M, Bonet E, Wernsdorfer W and Balestro F 2021 Increasing the Hilbert space dimension using a single coupled molecular spin *Nat. Commun.* **12** 4443
[232] Serrano D, Kuppusamy S K, Heinrich B, Fuhr O, Hunger D, Ruben M and Goldner P 2022 Ultra-narrow optical linewidths in rare-earth molecular crystals *Nature* **603** 241–6
[233] Janković D, Hartmann J-G, Ruben M and Hervieux P-A 2023 Noisy qudit vs multiple qubits : conditions on gate efficiency for enhancing fidelity *npj Quantum. Inf.* **10** 59
[234] Martin Y and Wickramasinghe H K 1987 Magnetic imaging by 'force microscopy' with 1000 Å resolution *Appl. Phys. Lett.* **50** 1455–7
[235] Sidles J A, Garbini J L, Bruland K J, Rugar D, Züger O, Hoen S and Yannoni C S 1995 Magnetic resonance force microscopy *Rev. Mod. Phys.* **67** 249–265
[236] Thiel L, Wang Z, Tschudin M A, Rohner D, Gutiérrez-Lezama I, Ubrig N, Gibertini M, Giannini E, Morpurgo A F and Maletinsky P 2019 Probing magnetism in 2D materials at the nanoscale with single-spin microscopy *Science* **364** 973–6
[237] Willke P, Yang K, Bae Y, Heinrich A J and Lutz C P 2019 Magnetic resonance imaging of single atoms on a surface *Nat. Phys.* **15** 1005–10
[238] Kovarik S, Schlitz R, Vishwakarma A, Ruckert D, Gambardella P and Stepanow S 2024 Spin torque–driven electron paramagnetic resonance of a single spin in a pentacene molecule *Science* **384** 1368–73
[239] Czap G, Wagner P J, Xue F, Gu L, Li J, Yao J, Wu R and Ho W 2019 Probing and imaging spin interactions with a magnetic single-molecule sensor *Science* **364** 670–3
[240] Neethirajan J N *et al* 2023 Controlled surface modification to revive shallow NV—centers *Nano Lett.* **23** 2563–9
[241] Degen C L, Reinhard F and Cappellaro P 2017 Quantum sensing *Rev. Mod. Phys.* **89** 035002
[242] Huang W *et al* Quantum spin-engineering in on-surface molecular ferrimagnets (arXiv:2410.18563)
[243] Forrester P R, Bilgeri T, Patthey F, Brune H and Natterer F D 2018 Antiferromagnetic MnNi tips for spin-polarized scanning probe microscopy *Rev. Sci. Instrum.* **89** 123706
[244] Yang K, Phark S, Bae Y, Esat T, Willke P, Ardavan A, Heinrich A J and Lutz C P 2021 Probing resonating valence bond states in artificial quantum magnets *Nat. Commun.* **12** 4–10
[245] Phark S H, Chen Y, Bui H T, Wang Y, Haze M, Kim J, Bae Y, Heinrich A J and Wolf C 2023 Double-resonance spectroscopy of coupled electron spins on a surface *ACS Nano* **17** 14144–51
[246] Wang Y, Haze M, Bui H T, Soe W H, Aubin H, Ardavan A, Heinrich A J and Phark S 2023 Universal quantum control of an atomic spin qubit on a surface *npj Quantum. Inf.* **9** 3–8
[247] Morello A *et al* 2010 Single-shot readout of an electron spin in silicon *Nature* **467** 687–91
[248] Stolte E W, Lee J, Vennema H G, Broekhoven R, Teng E, Katan A J, Veldman L M, Willke P and Otte S Single-shot readout of the nuclear spin of an on-surface atom (arXiv:2410.08704)
[249] Blatt R and Roos C F 2012 Quantum simulations with trapped ions *Nat. Phys.* **8** 277–84
[250] Bennett C H and DiVincenzo D P 2000 Quantum information and computation *Nature* **404** 247–55
[251] Phark S H, Bui H T, Ferrón A, Fernández-Rossier J, Reina-Gálvez J, Wolf C, Wang Y, Yang K, Heinrich A J and Lutz C P 2023 Electric-field-driven spin resonance by on-surface exchange coupling to a single-atom magnet *Adv. Sci.* **10** 1–8
[252] Betz N, McMurtrie G, Hänze M, Rajathilakam V K, Farinacci L, Coppesmith S N, Baumann S and Loth S 2024 Stochastic resonance spectroscopy: characterizing fast dynamics with slow measurements (arXiv:2412.12647)
[253] Hänze M, McMurtrie G, Baumann S, Malavolti L, Coppersmith S N and Loth S 2021 Quantum stochastic resonance in a single atom *Sci. Adv.* **7** eabg2616
[254] van Weerdenburg W M J, Osterhage H, Christianen R, Junghans K, Domínguez E, Kappen H J and Khajetoorians A A 2024 Stochastic syncing in sinusoidally driven atomic orbital memory *ACS Nano* **18** 4840–6
[255] Gammaitoni L, Hänggi P, Jung P and Marchesoni F 1998 Stochastic resonance *Rev. Mod. Phys.* **70** 223
[256] Löfstedt R and Coppersmith S N 1994 Quantum stochastic resonance *Phys. Rev. Lett.* **72** 1947–50
[257] Wagner T, Talkner P, Bayer J C, Rugeramigabo E P, Hänggi P and Haug R J 2019 Quantum stochastic resonance in an a.c.-driven single-electron quantum dot *Nat. Phys.* **15** 330–4
[258] Yao J, Chen S, Shi W and Ho W 2025 Quantum stochastic rectification in a single molecule *Phys. Rev. Lett.* **135** 026201
[259] Loth S, Etzkorn M, Lutz C P, Eigler D M and Heinrich A J 2010 Measurement of fast electron spin relaxation times with atomic resolution *Science* **329** 1628–30
[260] Drost R *et al* 2022 Combining electron spin resonance spectroscopy with scanning tunneling microscopy at high magnetic fields *Rev. Sci. Instrum.* **93** 043705
[261] Müller M, Martín-Sabanés N, Kampfrath T and Wolf M 2020 Phase-resolved detection and control of ultrabroadband THz pulses coupled to a scanning tunneling microscope junction *ACS Photonics* **7** 2046–55
[262] Doležal J, Sagwal A, de Campos Ferreira R C and Švec M 2024 Single-molecule time-resolved spectroscopy in a tunable STM nanocavity *Nano Lett.* **24** 1629–34
[263] Veldman L M, Farinacci L, Rejali R, Broekhoven R, Gobeil J, Coffey D, Ternes M and Otte A F 2021 Free coherent evolution of a coupled atomic spin system initialized by electron scattering *Science* **372** 964–8
[264] Willke P, Bae Y, Yang K, Lado J L, Ferrón A, Choi T, Ardavan A, Fernández-Rossier J, Heinrich A J and Lutz C P 2018 Hyperfine interaction of individual atoms on a surface *Science* **362** 336–9
[265] Yang K, Willke P, Bae Y, Ferrón A, Lado J L, Ardavan A, Fernández-Rossier J, Heinrich A J and Lutz C P 2018 Electrically controlled nuclear polarization of individual atoms *Nat. Nanotechnol.* **13** 1120–5
[266] Farinacci L, Veldman L M, Willke P and Otte S 2022 Experimental determination of a single atom ground state orbital through hyperfine anisotropy *Nano Lett.* **22** 8470–4
[267] Kim J, Noh K, Chen Y, Donati F, Heinrich A J, Wolf C and Bae Y 2022 Anisotropic hyperfine interaction of surface-adsorbed single atoms *Nano Lett.* **22** 9766–72

[268] Veldman L M, Stolte E W, Canavan M P, Broekhoven R, Willke P, Farinacci L and Otte S 2023 Coherent spin dynamics between electron and nucleus within a single atom (arXiv:2309.03749)
[269] Savytskyy R *et al* 2023 An electrically driven single-atom 'flip-flop' qubit *Sci. Adv.* **9** eadd9408
[270] Popa I, Gaebel T, Domhan M, Wittmann C, Jelezko F and Wrachtrup J 2004 Energy levels and decoherence properties of single electron and nuclear spins in a defect center in diamond *Phys. Rev. B* **70** 201203
[271] Smith J A S 1971 Nuclear quadrupole resonance spectroscopy. General principles *J. Chem. Educ.* **48** 39
[272] Childress L, Dutt M V G, Taylor J M, Zibrov A S, Jelezko F, Wrachtrup J, Hemmer P R and Lukin M D 2006 Coherent dynamics of coupled electron and nuclear spin qubits in diamond *Science* **314** 281–5
[273] Braun M, König J and Martinek J 2004 Theory of transport through quantum-dot spin valves in the weak-coupling regime *Phys. Rev. B* **70** 1–12
[274] Reina-Gálvez J, Wolf C and Lorente N 2023 Many-body nonequilibrium effects in all-electric electron spin resonance *Phys. Rev. B* **107** 235404
[275] Ast C R, Kot P, Ismail M, De-la-peña S, Fernández-Domínguez A I and Cuevas J C 2024 Theory of electron spin resonance in scanning tunneling microscopy *Phys. Rev. Res.* **6** 1–17
[276] Bui H T *et al* 2024 All-electrical driving and probing of dressed states in a single spin 1–23
[277] Broekhoven R, Lee C, Phark S, Otte S and Wolf C 2024 Protocol for certifying entanglement in surface spin systems using a scanning tunneling microscope **1** 1–9
[278] Switzer E D *et al* 2025 Unraveling spin entanglement using quantum gates with scanning tunneling microscopy-driven electron spin resonance (arXiv:2505.09428)
[279] Wolf C, Delgado F, Reina J and Lorente N 2020 Efficient ab initio multiplet calculations for magnetic adatoms on MgO *J. Phys. Chem. A* **124** 2318–27
[280] Teske J D, Cerfontaine P and Bluhm H 2022 Qopt: an experiment-oriented software package for qubit simulation and quantum optimal control *Phys. Rev. Appl.* **17** 034036
[281] Köhler J, Disselhorst J A J M, Donckers M C J M, Groenen E J J, Schmidt J and Moerner W E 1993 Magnetic resonance of a single molecular spin *Nature* **363** 242–4
[282] Wrachtrup J, Von Borczyskowski C, Bernard J, Orrit M and Brown R 1993 Optical detection of magnetic resonance in a single molecule *Nature* **363** 244–5
[283] Rugar D, Budakian R, Mamin H J and Chui B W 2004 Single spin detection by magnetic resonance force microscopy *Nature* **430** 329–32
[284] Kaiser U, Schwarz A and Wiesendanger R 2007 Magnetic exchange force microscopy with atomic resolution *Nature* **446** 522–5
[285] Giessibl F J 1998 High-speed force sensor for force microscopy and profilometry utilizing a quartz tuning fork *Appl. Phys. Lett.* **73** 3956–8
[286] Vincent R, Klyatskaya S, Ruben M, Wernsdorfer W and Balestro F 2012 Electronic read-out of a single nuclear spin using a molecular spin transistor *Nature* **488** 357–60
[287] Takui T, Berliner L and Hanson G (eds) 2016 *Electron Spin Resonance (ESR) Based Quantum Computing* (Springer) (https://doi.org/10.1007/978-1-4939-3658-8)
[288] Topinka M A, LeRoy B J, Shaw S E J, Heller E J, Westervelt R M, Maranowski K D and Gossard A C 2000 Imaging coherent electron flow from a quantum point contact *Science* **289** 2323–6
[289] Steurer W, Fatayer S, Gross L and Meyer G 2015 Probe-based measurement of lateral single-electron transfer between individual molecules *Nat. Commun.* **6** 8353
[290] Gaita-Ariño A, Luis F, Hill S and Coronado E 2019 Molecular spins for quantum computation *Nat. Chem.* **11** 301–9
[291] Kawai S, Foster A S, Canova F F, Onodera H, Kitamura S and Meyer E 2014 Atom manipulation on an insulating surface at room temperature *Nat. Commun.* **5** 4403
[292] Awschalom D D, Samarth N and Loss D (eds) 2002 *Semiconductor Spintronics and Quantum Computation* (Springer Verlag)
[293] Koenraad P M and Flatté M E 2011 *Nat. Mater.* **10** 91
[294] Brazdova V, Bowler D R, Sinthiptharakoon K, Studer P, Rahnejat A, Curson N J, Schofield S R and Fisher A J 2017 *Phys. Rev. B* **95** 075408
[295] Voisin B, Bocquel J, Tankasala A, Usman M, Salfi J, Rahman R, Simmons M Y, Hollenberg L C and Rogge S 2020 Valley interference and spin exchange at the atomic scale in silicon *Nat. Commun.* **11** 6124
[296] Siegl M, Zanon J, Sink J, da Cruz A R, Hedgeland H, Curson N J, Flatté M and Schofield S R 2025 *Nano Lett.* (in press) (https://doi.org/10.1021/acs.nanolett.5c02675)
[297] Yakunin A M, Silov A Y, Koenraad P M, Wolter J H, Van Roy W, De Boeck J, Tang J-M and Flatté M E 2004 *Phys. Rev. Lett.* **92** 216806
[298] Çelebi C, Garleff J K, Silov A Y, Yakunin A M, Koenraad P M, Van Roy W, Tang J-M and Flatté M E 2010 *Phys. Rev. Lett.* **104** 086404
[299] Mahani M R, Islam M F, Pertsova A and Canali C M 2014 *Phys. Rev. B* **89** 165408
[300] Kitchen D, Richardella A, Tang J-M, Flatt´e M E and Yazdani A 2006 *Nature* **442** 436
[301] Schofield S R, Curson N J, Simmons M Y, Ruess F J, Hallam T, Oberbeck L and Clark R G 2003 *Phys. Rev. Lett.* **91** 136104
[302] Schofield S R *et al* 2025 *Nano Futures* **9** 012001
[303] Fernández de Fuentes I *et al* 2024 Navigating the 16-dimensional Hilbert space of a high-spin donor qudit with electric and magnetic fields *Nat. Commun.* **15** 1380
[304] Dwyer K J, Baek S, Farzaneh A, Dreyer M, Williams J R and Butera R E 2021 *ACS Appl. Mater. Interfaces* **13** 41275
[305] Warschkow O, Curson N J, Schofield S R, Marks N A, Wilson H F, Radny M W, Smith P V, Reusch T C G, McKenzie D R and Simmons M Y 2016 *J. Chem. Phys.* **144** 014705
[306] Stock T J Z, Warschkow O, Constantinou P C, Bowler D R, Schofield S R and Curson N J 2024 *Adv. Mater.* **23** 12282
[307] Hofmann E V, Stock T J, Warschkow O, Conybeare R, Curson N J and Schofield S R 2023 Room temperature incorporation of arsenic atoms into the germanium (001) surface *Angew. Chem., Int. Ed.* **62** e202213982
[308] Voisin B, Salfi J and St Médar D D 2023 A solid-state quantum microscope for wavefunction control of an atom-based quantum dot device in silicon *Nat. Electron.* **6** 409–16
[309] Kranz L, Gorman S K, Thorgrimsson B, He Y, Keith D, Keizer J G and Simmons M Y 2020 Exploiting a single-crystal environment to minimize the charge noise on qubits in silicon *Adv. Mater.* **32** 2003361
[310] Koch M, Keizer J G, Pakkiam P, Keith D, House M G, Peretz E and Simmons M Y 2019 Spin read-out in atomic qubits in an all-epitaxial three-dimensional transistor *Nat. Nanotechnol.* **14** 137–40

[311] Hill C D, Peretz E, Hile S J, House M G, Fuechsle M, Rogge S, Simmons M Y and Hollenberg L C L 2015 Quantum computing: a surface code quantum computer in silicon *Sci. Adv.* **1** e1500707
[312] Reiner J *et al* 2024 High-fidelity initialization and control of electron and nuclear spins in a four-qubit register *Nat. Nanotechnol.* **19** 605–11
[313] Thorvaldson I *et al* 2024 Grover's algorithm in a four-qubit silicon processor above the fault-tolerant threshold *Nature Nano.* **20** 472–7
[314] Watson T F, Weber B, Hsueh Y L, Hollenberg L C L, Rahman R and Simmons M Y 2017 Atomically engineered electron spin lifetimes of 30 s in silicon *Sci. Adv.* **3**
[315] Kranz L, Osika E N, Monir S, Hsueh Y, Fricke L, Hile S J, Chung Y, Keizer J G, Rahman R and Simmons M Y 2023 Exploiting atomic control to show when atoms become molecules *Adv. Func. Mater.* **34** 2307285
[316] Jones M T *et al* 2023 Atomic engineering of molecular qubits for high-speed, high-fidelity single qubit gates *ACS Nano* **17** 22601–10
[317] He Y, Gorman S K, Keith D, Kranz L, Keizer J G and Simmons M Y 2019 A two-qubit gate between phosphorus donor electrons in silicon *Nature* **571** 371–5
[318] Kranz L, Roche S, Gorman S K, Keizer J G and Simmons M Y 2023 High-fidelity CNOT gate for donor electron spin qubits in silicon *Phys. Rev. Appl.* **19** 24068
[319] Wyrick J, Wang X, Namboodiri P, Kashid R V, Fei F, Fox J and Silver R 2022 Enhanced atomic precision fabrication by adsorption of phosphine into engineered dangling bonds on H-Si using STM and DFT *ACS Nano* **16** 19114–23
[320] Hsueh Y-L, Keith D, Chung Y, Gorman S K, Kranz L, Monir S, Kembrey Z, Keizer J G, Rahman R and Simmons M Y 2024 Engineering spin-orbit interactions in silicon qubits at the atomic-scale *Adv. Mater.* **36** 2312736
[321] Donnelly M B, Munia M M, Keizer J G, Chung Y, Huq A M S, Osika E N, Hsueh Y, Rahman R and Simmons M Y 2023 Multi-scale modeling of tunneling in nanoscale atomically precise Si:P tunnel junctions *Adv. Funct. Mater.* **33** 2214011
[322] Kiczynski M, Gorman S K, Geng H, Donnelly M B, Chung Y, Krauth F N, Jones M T, Keizer J G, He Y and Simmons M Y 2022 Experimental realisation of the single particle Su-Schrieffer-Heeger model in phosphorus doped silicon quantum dots *Nature* **606** 694
[323] Weiss M, Schelchshorn M, Stilp F, Weymouth A J and Giessibl F J 2024 Increasing the lifetime of confined electronic states in an artificial quantum structure *Phys. Rev. B* **109** 2354221–11
[324] Mier C, Verlhac B, Garnier L, Robles R, Limot L, Lorente N and Choi D-J 2021 Superconducting scanning tunneling microscope tip to reveal sub-millielectronvolt magnetic energy variations on surfaces *J. Phys. Chem. Lett.* **12** 2983–9
[325] Ambegaokar V and Baratoff A 1963 Tunneling between superconductors *Phys. Rev. Lett.* **10** 486
[326] Leitenstorfer A *et al* 2023 The 2023 terahertz science and technology roadmap *J. Appl. Phys.* **56** 223001
[327] Schuler B *et al* 2019 Large spin-orbit splitting of deep in-gap defect states of engineered sulfur vacancies in monolayer WS_2 *Phys. Rev. Lett.* **123** 076801
[328] Rai V, Balzer N, Derenbach G, Holzer C, Mayor M, Wulfhekel W, Gerhard L and Valášek M 2023 Hot luminescence from single-molecule chromophores electrically and mechanically self-decoupled by tripodal scaffolds *Nat. Commun.* **14** 8253
[329] Edelmann K, Gerhard L, Winkler M, Wilmes L, Rai V, Schumann M, Kern C, Meyer M, Wegener M and Wulfhekel W 2018 Light collection from a low-temperature scanning tunneling microscope using integrated mirror tips fabricated by direct laser writing *Rev. Sci. Instrum.* **89** 123107
[330] Lan Y, Klyatskaya S and Ruben M 2015 Bis(phthalocyaninato) lanthanide(III) complexes—from molecular magnetism to spintronic devices *Lanthanides and Actinides in Molecular Magnetism* ed R A Layfield and M Murugesu (Wiley-VCH) pp 223–92
[331] Reina-Galvez J, Nachtigall M, Lorente N, Martinek J and Wolf C 2025 Contrasting exchange-field and spin-transfer torque driving mechanisms in all-electric electron spin resonance (arXiv:2503.24046)
[332] Willke P, Bilgeri T, Zhang X, Wang Y, Wolf C, Aubin H, Heinrich A and Choi T 2021 Coherent spin control of single molecules on a surface *ACS Nano* **15** 17959–65