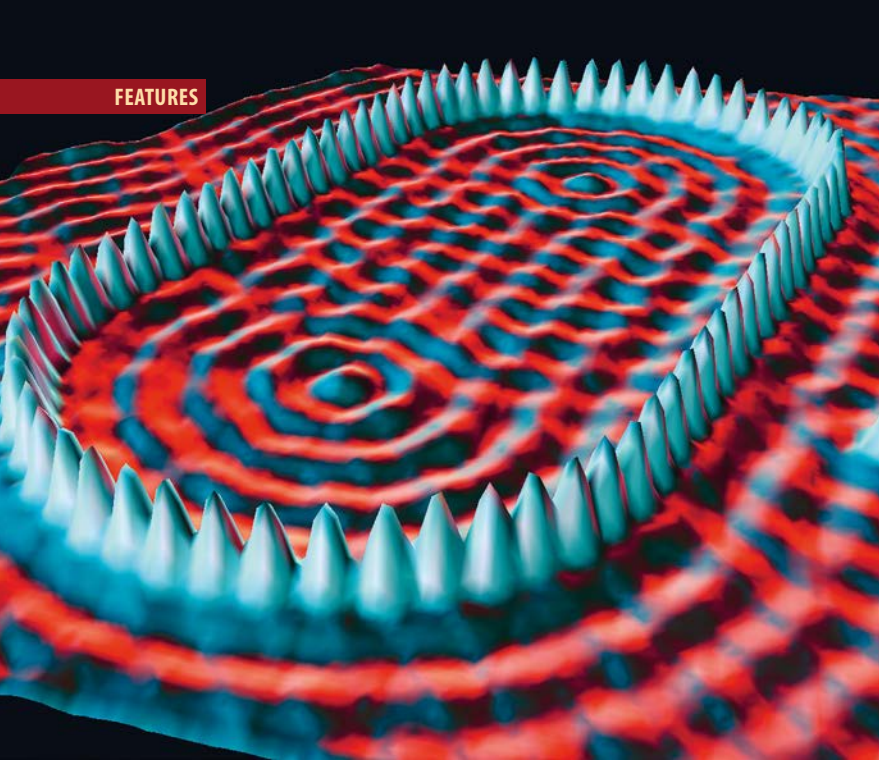

30 YEARS OF MOVING INDIVIDUAL ATOMS

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DOI: https://doi.org/10.1051/epn/2020205
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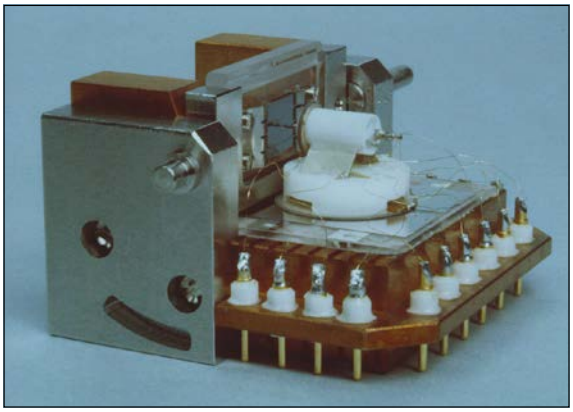
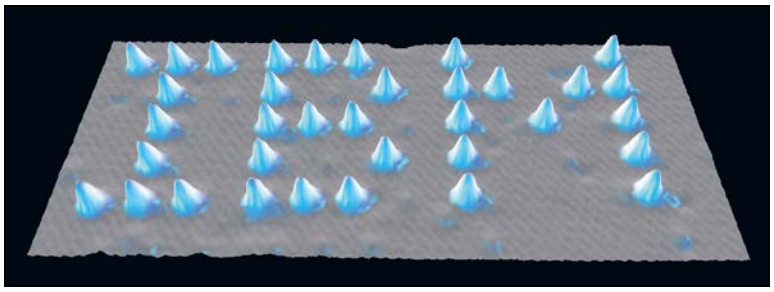
In the thirty years since atoms were first positioned individually, the atom-moving capability of scanning probe microscopes has grown to employ a wide variety of atoms and small molecules, yielding custom nanostructures that show unique electronic, magnetic and chemical properties.

This year marks the thirtieth anniversary of the publication by IBM researchers Don Eigler and Erhard Schweizer showing that individual atoms can be positioned precisely into chosen patterns [1]. Tapping the keyboard of a personal computer for 22 continuous hours, they controlled the movement of a sharp tungsten needle to pull 35 individual xenon atoms into place on a surface to spell the letters "IBM" (Figure 1). Eigler and Schweitzer's demonstration set in motion the use of a newly invented tool, called the scanning tunneling microscope (STM), as the workhorse for nanoscience research. But this achievement did even more than that: it changed the way we think of atoms. It led us to view them as building blocks that can be arranged the way we choose, no longer being limited by the feeling that atoms are inaccessibly small.

It is difficult to believe that only a hundred years ago, when quantum physics and relativity came into focus, the idea that atoms are real individual objects was still viewed with suspicion [2]. As late as 1952, Erwin Schrödinger wrote that "…we never experiment with just one electron or atom or (small) molecule. In thought-experiments we sometimes assume that we do; this invariably entails ridiculous consequences…" [3]. These consequences are not ridiculous, but are profoundly intriguing since many of the early speculations have become experimentally accessible in recent decades. For example, the atoms seen by Erwin Müller's field ion microscope in the 1950s [4], inspired many scientists, who marveled at the nested rings of individual atoms at the apex of the sharp metal tips. The atoms at the most exposed corners could be dislodged by voltage pulses, but could not yet be placed in predetermined arrangements. To achieve this, an invention that could sense and guide the atoms in a much gentler environment was required. This invention was the STM.



▲ **FIG. 2:** The STM that Don Eigler and coworkers used to position atoms. The tip is seen touching its reflection in the sample's surface. (Credit: IBM)



▼ **FIG. 1:** Thirty-five xenon atoms arranged on a nickel surface to spell IBM in letters 5 nm tall. (Credit: IBM)

A tool for imaging and moving atoms

In 1981, Gerd Binnig and Heinrich Rohrer, working at IBM's research laboratory in Zurich, created the first STM by raster scanning a sharp metal tip held just a few atomic diameters away from the surface [5]. They succeeded for the first time to image the atoms of a surface of silicon, an achievement that earned them the Nobel Prize in Physics in 1986. The principle of the STM is to control the narrow gap width between the tip and the surface by measuring the flow of electrons that quantum tunnel across this gap. Holding the current constant, the tip traces out contours that display the pattern of atoms. The key property that allows atomic resolution to be achieved is the exponential dependence of the tunnel current on the gap size. Indeed, if the tip is moved by one atomic diameter towards the surface, the current will increase by a factor 100. This extreme resolution opened the door to the nanoworld.

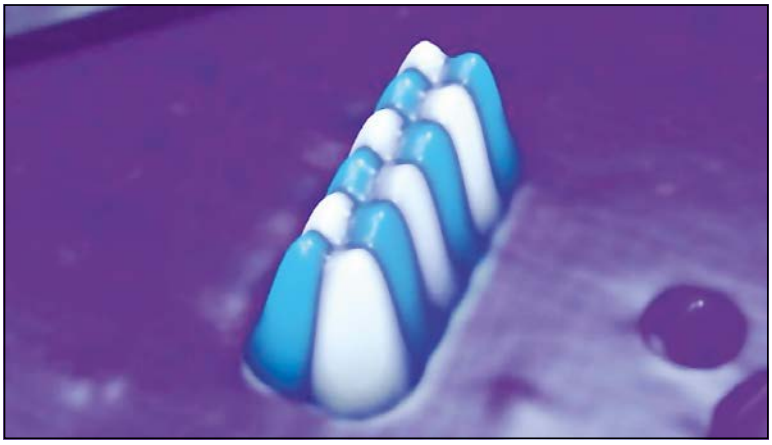
In the late 1980's Don Eigler constructed the first STM operating at liquid helium temperature (4 Kelvin) and under ultrahigh vacuum to keep the surface atomically clean. It was vibrationally isolated so that it had uncontrolled tip-sample motion of only 2 picometers (or 1/100th of a typical atomic diameter). The result was an instrument capable of positioning individual atoms. The whole table-sized STM apparatus is a vacuum chamber bristling with connectors. But the core of the STM – the scanner and sample holder – is small enough to hold in the palm (Figure 2). A sharpened tungsten wire serves as a tip, which is moved in three dimensions by piezoelectric actuators.

Eigler's STM can image individual atoms attached to a surface, even weakly bound elements like the xenon atoms used to write the IBM logo. The controlled motion of atoms depends on the right balance of forces: the atom must not desorb or move spontaneously on the surface while the tip must be able to pull it to a new location with large enough lateral forces. Due to the weak Van der Waals force to the surface, xenon atoms are moved easily by the tip. Other atomic elements require greater pulling forces, reached by bringing the tip in closer contact with the atom on the surface.

The atomic force microscope (AFM) is a sibling of the STM that relies on the force between sample and tip, rather than on the tunneling current. It was demonstrated in 1986 by researchers at IBM and Stanford [6]. The AFM has the advantage of being able to probe insulating surfaces and it provides complementary information to the STM. Nowadays many low-temperature tools measure force and current simultaneously, so they incorporate both AFM and STM capabilities, collectively called scanning probes.

Arranging atoms to control electrons

Controlled positioning of metal atoms has made it possible to construct large atomic arrangements such as the stadium-shaped "quantum corral" of introduction figure, which produces a standing wave pattern of electrons confined inside the corral [7]. Subsequently, various chemical elements were used to assemble a rich variety of structures having well-designed quantum states and band structures [8].

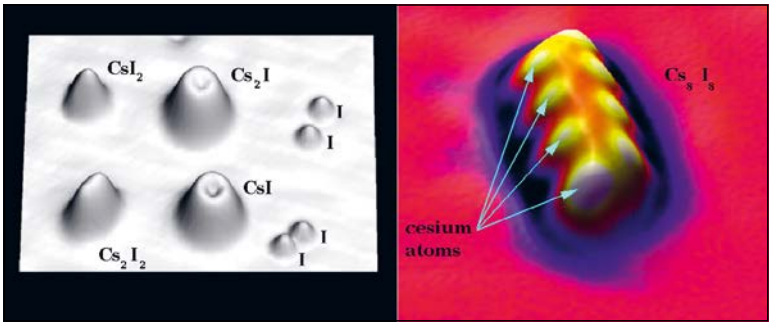


▲ **FIG. 3:** Bistable antiferromagnet made of 12 Fe atoms on an MgO film. Blue/white color shows the measured spin direction. (Credit: IBM)

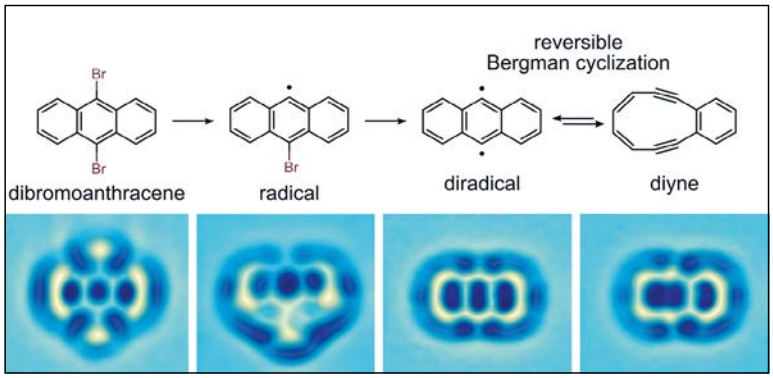
The STM has proven adept at constructing and imaging magnetic nanostructures. Atoms bound directly on the metal surface show many intriguing magnetic properties [8]. Placing them instead on a thin layer of insulating material, such as copper nitride or magnesium oxide (MgO), has yielded long-lived quantum magnetic states. Structures were assembled by transferring each magnetic atom onto the STM tip and back to the insulator, using voltage pulses for each transfer. An example is the antiferromagnet made of 12 iron atoms shown in Figure 3. This tiny magnet can be switched by flipping all the spins at once using a current pulse from the tip, making it a writable magnetic memory bit [9].

From atoms to molecules

A step toward building molecules using STM is to assemble ionic clusters made of alkali halides. Figure 4 shows how cesium (Cs) and iodine (I) atoms were manipulated to form precise molecule-like clusters [10]. The Cs atoms, stable only when attached to an I atom, were moved from one I atom to another by using an I-terminated tip in order to form clusters such as Cs_2I and Cs_2I_2. The Cs_2I_2 clusters were then pulled along the surface as a unit and attached together into polymer chains. Sodium iodide clusters were also obtained, suggesting that it will likely be possible to build a variety of alkali halide structures in the future.



▼ **FIG. 4:** Assembling planar ionic molecules from cesium and iodine atoms. Left: Small Cs- and I-based structures on a Cu(111) surface. Right: A Cs_8I_8 chain achieved by sliding four pre-assembled Cs_2I_2 units together. (Credit: IBM)



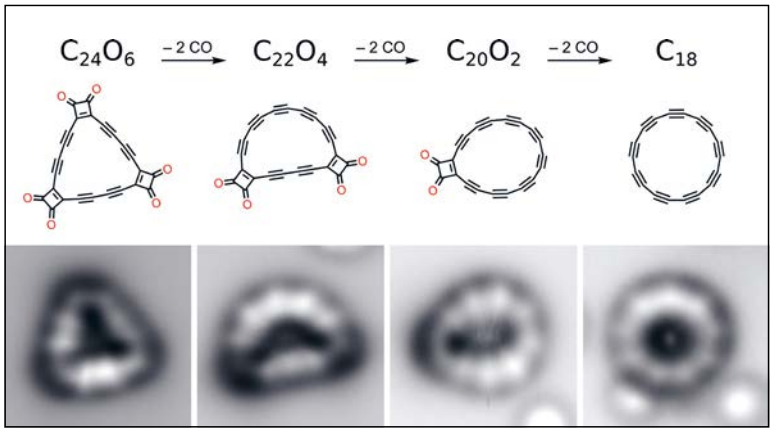
▲ **FIG. 5:** Breaking and forming covalent bonds by atom manipulation. Applying voltage pulses from the tip, two Br atoms are successively dissociated from a precursor molecule to generate a diradical. This diradical can be reversibly and repeatedly transformed into a diyne, breaking and forming covalent carbon-carbon bonds within the molecule. The AFM images are taken using a CO-functionalized tip. Adapted from ref [14], Springer Nature.

Atom manipulation can be used not only to move and place atoms and molecules on a surface, but also to break or form covalent bonds in molecules [11]. The synthesis of a molecule by atom manipulation was demonstrated by Saw-Wai Hla and coworkers in a landmark experiment in 2000, performing all steps of an Ullmann coupling reaction [12].

Recently, molecule and atom manipulation made great progress thanks to high-resolution AFM that uses CO terminated tips, revealing the internal structure and chemical bonds of molecules [13]. This approach permits chemical reactions to be followed step by step and to identify intermediate and final products with atomic resolution. On chemically inert surfaces such as NaCl or Xe monolayers, highly reactive molecules such as radicals and reaction intermediates can be generated, remaining stable enough to be studied. Figure 5 shows bromine (Br) dissociation followed by reversible carbon-carbon bond cleavage and bond formation in an individual molecule [14].

Exploiting the inert surface and the controlled influence of the scanning probe tip, elusive molecules can be generated that cannot be studied otherwise. For example, the cyclo[18]carbon C_{18}, a highly reactive allotrope of carbon, whose structure had been debated for years, was recently synthesized by atom manipulation [15].

▼ **FIG. 6:** Elusive molecules created by atom manipulation. The cyclic carbon C_{18} was formed by atom manipulation on a bilayer NaCl film on Cu(111). Here CO masking groups from the precursor $C_{24}O_6$ were dissociated by voltage pulses. In the AFM images (bottom row) the triple bonds appear with a characteristic bright contrast. Adapted from ref [15], AAAS.



The AFM images (Figure 6) settled a long-running debate by showing that the final structure is not cumulenic with only double bonds but polyynic, consisting of alternating single and triple bonds.

Prospering in the room at the bottom

Richard Feynman's 1959 essay "There's plenty of room at the bottom" looked into a future time when objects will be assembled atom-by-atom. As we strive to approach this ultimate level of miniaturization, we will benefit by making intentional use of every atom. In the last 30 years, scanning probes have led the way forward, and their versatility will surely keep them at the forefront of this exciting exploration. ■

About the Author

Christopher Lutz is a Senior Scientist at IBM Research – Almaden in San Jose, California. He joined the group of Don Eigler in 1990 and has led the group, now the atom manipulation and nanomagnetism project, since 2016.

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Acknowledgements

The authors acknowledge the careful proofreading of this article by their colleague Christophe Rossel at IBM Research – Zürich.

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