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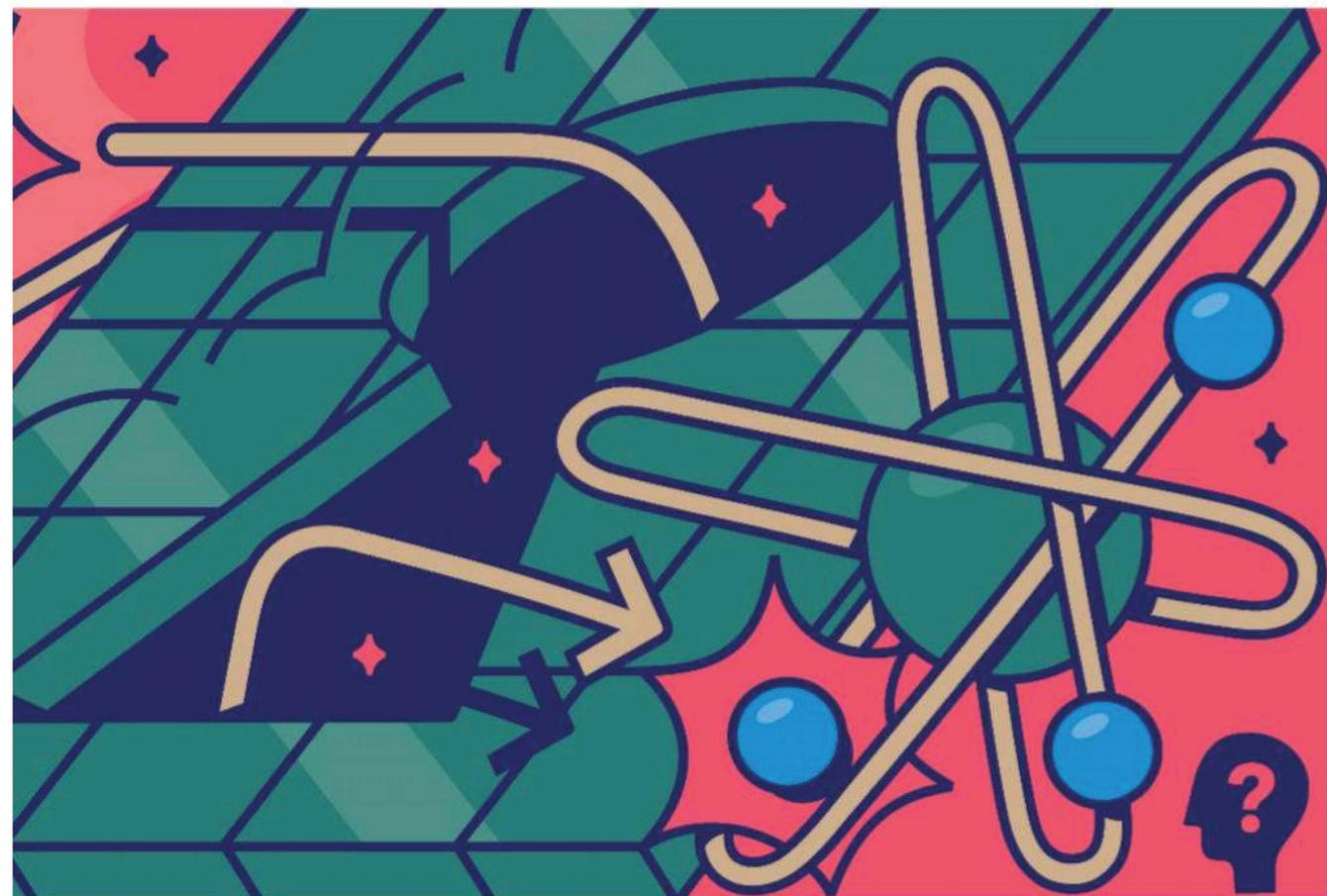
# Freaky bonding

Chemists are finding new and surprising ways that atoms can stick together – some of which could generate novel materials, finds **Philip Ball**

**N**O SCHOOL chemistry textbook is complete without a detailed enumeration of the basic types of chemical bond: covalent, ionic and metallic. And for good reason, because bonds are the glue that binds chemistry together. “We talk about chemical bonding because we want to understand and predict materials’ properties,” says Matthias Wuttig, a materials physicist at RWTH Aachen University, Germany.

That makes it all the more shocking that, a century and a half after the idea of chemical bonds was first floated, we are still a long way from a complete understanding of how atoms’ outermost electrons, the mediators of chemical bonds, form these links. Recent discoveries show that there are more types of bond than we thought, and that some of the familiar ones might not be quite as we had imagined. There are even bonds that, completely against chemical orthodoxy, involve no electrons at all.

We are still getting to grips with this new panoply of bonding varieties. Even so, it is



already clear that it can not only give us a better understanding of existing substances, but also unleash untapped potential in the elements, promising a whole new world of materials for applications that include solar cells, drugs, data storage and more besides.

As far back as the 1860s, scientists had begun writing out compounds in a distinctive format with sticks joining element symbols: H-H for the molecule ( $H_2$ ) made up of two hydrogen atoms, for example. By 1866, English chemist Edward Frankland had coined the term “bond” to describe the links that these sticks depicted.

At this point, the whole concept of the atom was still disputed. No one envisaged the picture of the atom that we have today: a structured nucleus surrounded by electrons. The idea that bonds between two atoms could arise from them sharing electrons, known as covalent bonding, was first put forward in the early 20th century. It wasn't until the 1920s that quantum theory showed how this might actually happen: atoms seek the lowest available energy state, and electron-sharing

gives the atoms a lower collective energy than they would have alone.

The terms we still use today to describe basic bonding types were laid out by Nobel-prizewinning chemist Linus Pauling in his seminal 1931 book *The Nature of the Chemical Bond*. As well as covering covalent bonds, Pauling showed that, in some unions, electrons hop from one atom onto another, producing positive and negative ions that stick together electrostatically: ionic bonds. Then there are metallic bonds, in which some electrons detach from their atoms and form a sort of electron sea that washes around and binds the positive ions they leave behind.

All of these are chemical bonds that share or poach electrons. But Pauling outlined a fourth type of bond: the hydrogen bond, which he described as an electrostatic attraction between hydrogen atoms and areas of high electron density in certain other elements, such as oxygen or nitrogen.

Even back then, it was clear that this simple classification was far from the whole story.

Take the van der Waals force, another staple of school chemistry textbooks. A weak force caused by fluctuations in the clouds of electrons surrounding the atomic nucleus, it can cause atoms to stick to one another even if they won't form regular chemical bonds. It helps inert gases like helium and argon liquefy at very low temperatures. It is also strong enough, on occasion, to lock atoms into well-defined unions – when two oxygen molecules ( $O_2$ ) join to form an  $O_4$  cluster, for example, or when gold atoms stick together in so-called aurophilic bonds. So are van der Waals bonds real bonds? No one has a definitive answer because there has never been a consensus about what bonding entails.

“Talking about chemical bonding does not increase the number of my friends,” says Wuttig. “It causes heated controversy because the concept of a chemical bond is not well defined.” Here are five instances where the prevailing wisdom about bonds is breaking down and what this could mean for future technology. ➤

# 1

## WANNABE METALS

Conventionally, covalent and metallic bonding are seen as mutually exclusive. Atoms can share electrons in a localised way to bind them tightly together, as in a covalent bond, or have free electrons floating about in a soupy glue, as with metallic bonds. But they can't do both.

It might not be that simple. In 2019, Wuttig and his colleagues argued that a whole class of materials lie in a no man's land between these traditional bonding types. They typically combine elements from the borderlands of metals and non-metals – “metalloids” such as tellurium and germanium – and elements at the far right-hand edge of the metallic region of the periodic table, like lead and tin.

It is as though these elements can't decide whether their unions should be covalent or metallic – and do something different from both. One way to look at it, says Wuttig, is that each bond is formed from fewer than two electrons. Yet like metallic bonds, these “metavalent” bonds are collective affairs that exist only in extended systems – in solid materials, not lone molecules. They have unique properties distinct from covalent or metallic materials: for example, whereas covalent bonds vibrate like simple springs, metavalent bonds wobble differently.

Wuttig calls the resulting compounds incipient metals: a kind of “wannabe” metal. Their soft bonds give them low heat conductivity (in contrast to normal metals), but they are nevertheless reasonable electrical conductors. What's more, collective vibrations of the soft bonds have a strong influence on how the electrons move through the material. This means that their electrical conductivity may be particularly sensitive to influences from their surroundings, such as heat, making some incipient metals useful as thermoelectric materials that scavenge waste heat from places like car exhausts, turning it into electricity. Thermoelectrics require almost contradictory properties, combining metal-style electrical conductivity with semiconducting behaviour and low heat conductivity – a weird blend of properties that incipient metals with the right combination of elements can offer. Incipient metals might also be attractive for use in solar

cells, because they absorb sunlight to mobilise electrons so that it can be harvested as electrical energy.

Incipient metals have some curious relatives called “strange metals”. These are more metallic than incipient metals, while still not quite going the whole hog. They are basically metallic, but with an electrical resistance that increases in direct proportion to temperature, rather than with the square of the temperature like a conventional metal. New kinds of superconductor, which have zero electrical resistance, might appear in these border regions between covalent and metallic bonds too, along with a host of other “odd metals”, such as “bad metals” and “chiral metals”.

# 2

## PHANTOM BONDS

Hydrogen bonds involve hydrogen atoms already covalently bound to atoms such as oxygen, nitrogen or fluorine – elements that tend to hog electrons, leaving the hydrogen with a slight positive charge. The hydrogen is therefore attracted to negatively charged regions of other molecules, or even parts of the same molecule, where electrons congregate – specifically, to “lone pairs” of electrons that don't take part in covalent bonding.

The extra stickiness caused by hydrogen bonds explains why water ( $H_2O$ ) holds together as a liquid rather than a gas under everyday conditions, and how water molecules link into a crystal lattice in ice. These bonds are

also a vital part of the glue that binds the molecular chains of protein molecules into their complicated shapes, and which zips up the double helix of DNA.

Yet it is still not entirely clear what hydrogen bonds are. As a simple model of hydrogen bonding, bifluoride ( $HF_2^-$ ) has been generally regarded as a covalently bonded hydrogen fluoride (HF) molecule H-bonded to a fluoride ion. But closer inspection has begun to confuse things. Andrei Tokmakoff at the University of Chicago and his colleagues have found that, as the bifluoride ion vibrates in water, the structure could vary between this picture and one in which the hydrogen atom is shared equally with both fluorines “at the tipping point where hydrogen bonding ends and chemical [covalent] bonding begins”.

Bonds generally aren't rigid, but bend and stretch as well as vibrating. This suggests that



**“It's as if these elements can't decide whether their unions should be covalent or metallic”**

# 3

## LOOPS AND LINKS

“While there are probably many thousands of new chemical compounds made every week in chemical laboratories around the world, it is only once in a blue moon that a new bond breaks upon the scene,” says Fraser Stoddart at Northwestern University in Illinois.

He should know: in the 1980s, Stoddart was one of the pioneers of molecular assemblies called rotaxanes and catenanes, mostly created in solution so far, that are permanently linked without using any electrons at all. Their “mechanical bonds” are formed by threading molecules together like links in a chain or a ring on a finger.

“Nature was using mechanical bonds long before we humans came on the scene,” says Stoddart. Indeed, they are found in many living systems – for example, they can help to hold the chain in RNA molecules in a particular functional shape. “Nature executes the chemistry of the mechanical bond with an elegance, complexity and beauty that will remain a source of inspiration to synthetic chemists for centuries to come,” he says.

That inspiration may pay dividends in molecular nanotechnology, where the loops and links of catenanes and other mechanically bonded molecules can be put to work as switches and rotors – the shape of rotaxanes can mimic an axle, for example. Potential applications include molecular information storage, where two switched states can encode binary data, and artificial molecular muscles, where switching causes a change in molecular length.

This field has exploded over recent years, and its achievements were recognised in the Nobel committee’s decision to award the 2016 chemistry prize for such work and its role in the design of molecular machines to Stoddart, alongside chemists Jean-Pierre Sauvage and Ben Feringa. One challenge now is to fix these molecular machines to solid supports so that they work in concert rather than in the random orientations they have in solution. For instance, a molecular muscle would only really pack a punch when many such units work together.

**“Nature was using mechanical bonds long before we humans came on the scene”**

# 4

## MUON GLUE

Some chemists have been exploring bonds that don’t occur in nature at all. The electron may be the classic bond-forming particle, but its heavy cousin, the muon, which has an identical negative charge, but a mass 207 times greater, can also unite atoms. Muons can be made in particle accelerators and can bump electrons out of atoms, taking their place before decaying in a fraction of a second.

That might not sound much use, but because they are heavier than electrons, muons create a stronger glue, pulling atomic nuclei closer together in molecules. Researchers have been trying to exploit this effect to bring hydrogen atoms closer for a split second so that they can fuse and release nuclear energy. In an H<sub>2</sub> molecule bound by a muon, the two nuclei are 196 times closer.

This effect – using heavy hydrogen isotopes deuterium and tritium, which fuse more readily – is the basis of muon-catalysed

to establish the presence of a bond, we need to evaluate not just whether atoms are stuck together, but for how long. A case in point is supercritical water: water heated past its “critical point” (374 °C at 218 atmospheres of pressure), where there is no longer any distinction between the liquid and gas states. Here it’s long been debated whether any hydrogen bonds persist. A better understanding of what’s going on would be great for the chemicals industry. Supercritical water can dissolve compounds that normal water can’t, making it a useful “green” alternative to solvents based on often toxic organic compounds such as benzene or toluene.

Theoretical chemists Dominik Marx and Philipp Schienbein at Ruhr-University Bochum in Germany recently sought to settle the debate by showing in simulations that hydrogen bonds in supercritical water break so fast that they don’t even have time to vibrate through a single oscillation. It is debatable whether this qualifies as a bond at all, says Marx, adding that with so many different ways to define bonds, “any bonding analysis will be subject to eternal discussion, excitement, and controversy”.

fusion, first demonstrated in 1957. However, the conventional approach requires cold, dense forms of hydrogen, which won't survive to sustain the reaction once fusion ignites. As a result, scientists have explored the possibility of fusion in gaseous fuel since the 1990s, but their ideas haven't yet advanced beyond the stage of theoretical proposals.

## 5

### BOUND BY DISORDER

Ultimately, chemical bonding is about atoms and electrons arranging themselves into lower energy states. The structure and order that can result is, however, potentially undermined by the influence of entropy, a thermodynamic quantity that is generally seen as promoting disorder and, according to the second law of thermodynamics, is always on the increase.

"Normally, people assume that energy and entropy are competing all the time," says chemical engineer Sharon Glotzer at the University of Michigan. "We think energy wants to order things, and entropy wants to disorder things." However, entropy alone can lead to a kind of order, and Glotzer has shown that this acts as a form of "entropic bonding".

Chemists can carefully tune the properties of a suspension of microscopic plastic spheres in a solvent so that the particles feel no significant interaction forces at all. It has been known for decades that, above a threshold density of particles in such a suspension, an orderly "colloidal crystal" will form. With no interaction energy until the particles actually touch and push back against each other, the only driving force for the ordering is entropy.

It isn't just a question of increased density forcing the particles to pack like oranges at a greengrocer's stall. Entropic crystals form well

before that point. The ordering happens when, bizarrely, the crystal state has a higher entropy than the liquid one.

For instance, Glotzer has engineered an entropic crystal of particles that assemble into an orderly cage-like framework that encapsulates other particles in the holes – an analogue of the chemically bonded materials known as clathrates. Here, all the disorder is focused on the captured "guest" particles, which "move like crazy, rotating around", she says, elevating the entropy so that the host framework is free to form an ordered structure. "If you stop the guests from spinning, the whole thing falls apart," says Glotzer. In fact, she says that she and her colleagues have yet to find a crystal structure formed by atoms or molecules bonding by covalent, ionic or metallic bonds that can't also be formed from entropic bonds of non-interacting particles.

But are these really "bonds"? Entropy, says

**"Surprisingly, entropy alone can lead to a kind of order"**



Glotzer, is a global state – it doesn't have any meaning for just two atoms, say. But she and her team have shown that it is possible to describe how their various entropically bonded arrangements come together in terms of a hypothetical force between pairs of particles that would bring them together in isolation in the same way as they come together under the entropic influence of their many neighbours in her colloidal system.

"I would like to make colloidal robots," Glotzer says, using the entropy to locally order and disorder the components. The relative weakness of the entropic bonds here is an advantage for making structures readily reconfigurable to suit different circumstances or functions. She also imagines a "periodic table of shapes" showing which particle shapes you need for a given material or structure to assemble entropically. Glotzer is convinced that future textbooks need to include something about entropic bonds. It certainly seems Pauling's original taxonomy is overdue an upgrade. ■



Philip Ball is a science writer. His latest book is *The Beauty of Chemistry* (MIT Press, 2021)