they require sophisticated methods capable of selectively probing only a few layers of water at the interface. Furthermore, the interpretation of vibrational spectra is complicated by coupling effects between vibrations in the water molecules themselves[7].

Water molecules at electrolyte–electrode interfaces undergo a reorientation when the surface charge on the electrode changes from positive to negative, or vice versa[8,9]. This reorientation is due to the interaction of electric dipoles of the molecules with the interfacial electric field that arises from the electrode surface charge, which is controlled by the electrode potential. At high potentials, positive or negative ions (cations or anions, respectively) in the electrolyte, whose charge is opposite to that of the net surface charge on the electrode, concentrate in the vicinity of the electrode. This increased concentration of ions is expected to affect the interfacial water structure. However, under potentials at which the electrocatalytic conversion of water to hydrogen occurs, the formation of bubbles of hydrogen gas interferes with spectroscopic measurements, making spectroscopy under reaction conditions highly challenging.

Wang *et al.* have neatly circumvented these difficulties by devising an innovative experimental approach in conjunction with Raman spectroscopy. They used a metal electrode comprising palladium atoms to act as a catalyst that dissociates water into molecular hydrogen (H_2) and hydroxide (OH^-; Fig. 1). As the electrode potential became more negative, they found that the water structure gradually shifted from a relatively disordered to a more ordered state.

The spectroscopic evidence indicates that this transition could be due to weakening of the hydrogen-bonding network, with a loss of water molecules that originally had four hydrogen-bonding partners and a concurrent gain of water molecules associated with sodium cations (Na^+) from the electrolyte; such water molecules form a 'hydration shell' around the ions. Hydrated sodium cations are electrostatically attracted to the negatively charged electrode surface and accumulate at the interface. Intriguingly, the authors found that the population of interfacial water molecules in the hydration shell of sodium ions tracks the rate of hydrogen formation across different single-crystal surfaces of palladium.

For a molecular picture of the more ordered state of interfacial water and its role in the rate of hydrogen formation, Wang *et al.* turned to *ab initio* molecular-dynamics modelling. They found that water in the hydration shell of the sodium ion can more closely approach the electrode surface than can other water molecules. This manifests in a more pronounced shift of the O–H stretching vibration of water associated with a sodium ion when the electrode potential decreases. Their theoretical modelling indicates that narrowing the physical gap between the hydration shell and the palladium surface aids electron transfer from the electrode to the water, enhancing the rate of water dissociation into molecular hydrogen and hydroxide ions.

The insights derived from this work are relevant to other technologically useful electrocatalytic processes that involve water dissociation, such as the hydrogenation of carbon dioxide to hydrocarbons or

"The authors have shown that the structure of interfacial water can be systematically tuned."

of nitrogen gas to ammonia. In those reactions, the dissociation of water needs to be carefully controlled to achieve the desired product selectivity. Wang *et al.* have shown that the structure of interfacial water, and, consequently, the dissociation of water, can be systematically tuned by appropriate choice of the electrode's crystal facet and the electrolyte's cation concentration and identity.

Inevitably, some questions remain. For example, how do the dynamics of interfacial water change with decreasing potential? These dynamics could be crucial in the formation of hydrogen and in electron transfer[10,11]. Investigations are now required to study the extent to which the dynamics of interfacial water at electrocatalytic interfaces can be altered with decreasing electrode potential.

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Mathematics

AI aids intuition in mathematical discovery

Christian Stump

Machine-learning tools have been used to assist the part of mathematical research that usually relies on human intuition and creativity — leading to two fundamental results in different areas of mathematics. **See p.70**

Mathematicians have been developing theories by studying examples throughout history. For instance, by looking at a cube and a pyramid, one might realize that the number of vertices, edges and faces are related. A mathematician recognizes such a pattern, extends it to more-general shapes, and then starts to think about why this relationship might hold. Parts of this process involve computations, for which mathematical software has been useful since it first became available in the 1960s. However, human creativity enables mathematicians to instinctively understand where to look for emerging patterns. On page 70, Davies *et al.* now describe a way of using artificial intelligence (AI) techniques to help with the creative core of the mathematical-research process[1].

The relationship between the properties of convex polyhedra (3D shapes with flat faces, straight edges and vertices that all point outwards) was found centuries ago, and the formula describing this relationship is named after the Swiss mathematician Leonhard Euler. Regardless of the shape, the number of vertices (V) minus the number of edges (E) plus the number of faces (F) is equal to two: $V - E + F = 2$ (Fig. 1). Can you arrive at this formula by studying a few examples of different shapes with a pen and paper? In this case, it's possible, but

mathematical ideas that are more complicated require more-extensive computations — for which a computer can be extremely useful.

Mathematical research based on finding and studying examples typically follows a cycle (Fig. 1). First, the researcher identifies a few relevant examples (a cube, a pyramid and perhaps a dodecahedron), then computes some of their properties and analyses the possible relationships between these properties. These relationships are then refined until a pattern emerges. The researcher continues by testing these relationships on more complicated examples (from icosahedra to huge, randomly shaped polyhedra) and discards any properties that aren't relevant. If the relationships do not hold, or the reasons why they hold remain unclear, the researcher redefines the criteria used to determine which examples are relevant. And the cycle continues.

All except one of the phases in this process require both human creativity and computation. For instance, analysing the properties of the examples chosen involves creativity in identifying which properties might be relevant and then computation to calculate them. The only phase without computational tasks is the refinement step, which could be considered the core of the creative process. This phase requires the researcher to extract general phenomena from concrete examples — based mainly on intuition. In the case of the polyhedra, this step might involve extending the pen-and-paper exercise above to different dimensions: does the pattern also hold for 2D shapes? And what about higher dimensions?

Although AI methods are not yet widespread in mathematical research, in the past few years, several groups have shown that machine-learning tools can, in principle, be used to find relevant examples in large data sets[2,3]. Others have used such tools to estimate the properties of mathematical objects with high accuracy in efforts to better understand these data sets[4]. Davies and co-workers have now shown that machine learning can be used to assist researchers in the refinement step of the research cycle, previously regarded as a task mainly based on human intuition. Their approach could, in principle, be used in many different areas of mathematics.

The idea is to identify two structures — perhaps lists of numbers or networks — from the properties of mathematical objects of a certain type. It is then possible to hypothesize that these structures are related in the sense that one structure can give us information about the other. Machine learning is ideally suited to this task for large data sets, because it can use one structure to guess details of the other with greater accuracy than would be expected on the basis of chance.

Euler's polyhedron formula offers a simple way of illustrating Davies and colleagues' approach. The first structure in this case would be a list of four numbers representing the number of vertices of the polyhedron, the number of edges, its surface area and its volume. The second structure would be the number of faces. Euler's formula can then be written as a simple linear relationship between these two structures. The process of arriving at the same formula also makes clear the fact that the volume and surface area are not relevant to this relationship. Applying this approach to Euler's formula is straightforward, but things become more complicated when the relationships aren't as simple to identify. In such cases, machine-learning techniques can help.

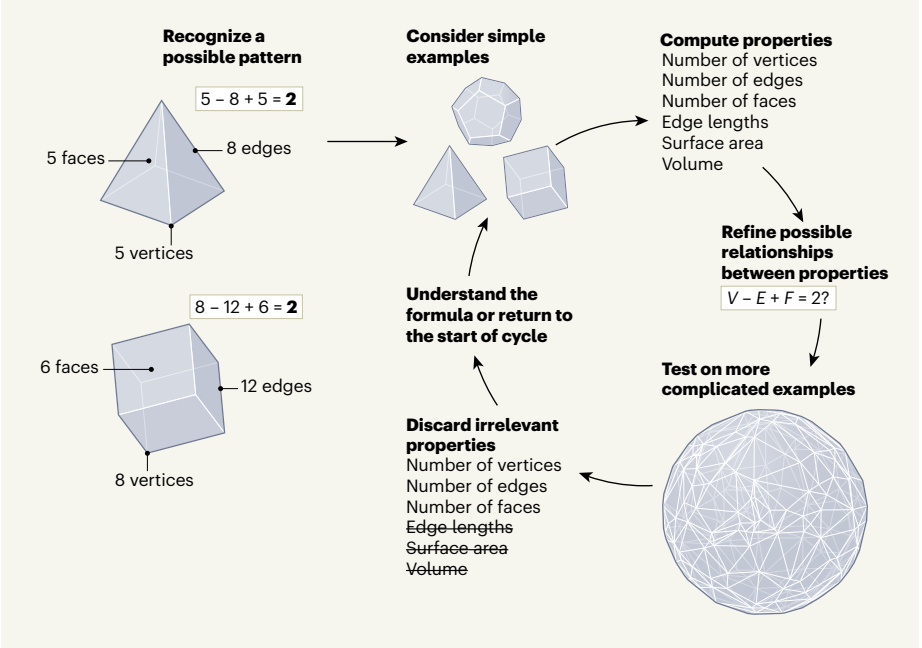

Figure 1 | The cycle of developing mathematical theories by studying examples. After recognizing a possible pattern in the properties of mathematical objects, such as convex polyhedra (3D shapes with flat faces, straight edges and vertices that all point outwards), mathematicians typically go through a cycle to understand this pattern. They first compute the properties of some simple examples and analyse the possible relationships between these properties. The researchers then refine these relationships. For example, they might come up with Euler's polyhedron formula, which posits that the number of vertices (V) minus the number of edges (E) plus the number of faces (F) of a convex polyhedron is always equal to two: $V - E + F = 2$. They then test this suggested relationship on more complicated examples, discard irrelevant properties and attempt to understand why the relationship holds. If it remains unclear, mathematicians then consider different examples and the cycle continues. Davies *et al.*[1] show that machine-learning techniques can help researchers with the refinement step, which usually relies strongly on human intuition.

"The real advance was demonstrated when the authors successfully applied their approach to two separate areas of mathematics."

The real advance was demonstrated when the authors successfully applied their approach to two separate areas of mathematics. They used it to identify previously unknown relationships in knot theory and in combinatorial representation theory. Neither result is necessarily out of reach for researchers in these areas, but both provide genuine insights that had not previously been found by specialists. The advance is therefore more than the outline of an abstract framework. Whether or not such an approach is widely applicable is yet to be determined, but Davies *et al.* provide a promising demonstration of how machine-learning tools can be used to support the creative process of mathematical research.

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