Electrons seen in orbit

Colin J. Humphreys

The classic textbook shape of electron orbitals has now been directly observed. As well as confirming the established theory, this work may be a first step to understanding high-temperature superconductivity.

The world-famous bongo drums player, Richard Feynman, who also won the Nobel Prize for Physics, once asked the following question: if you had only one sentence in which to pass on to the next generation the most important scientific knowledge we possess, what would that sentence be? Feynman's own answer was "everything is made of atoms". "But what is their size and shape," the next generation might reply, "and how do they stick together?"

"Well," Feynman might have said "most scientists think of an atom as a sphere, like a tiny orange, and if you magnify an orange to the size of our Earth then every atom in the orange is magnified to the size of the original orange. But in reality, many atoms are not spherical and the shape of atoms critically affects how they bond together."

On page 49 of this issue, Zuo *et al.*[1] use a combination of electron and X-ray diffraction to study the shape and bonding of oranges — in this case, copper atoms in copper oxide. For the first time the striking shape of some of the electron orbitals is revealed experimentally. These methods could be used to determine bonding in high-temperature copper oxide superconductors, the theory of which has eluded some of the world's best scientists for more than ten years.

What do we mean by the size and shape of an atom? In the simplest atom, hydrogen, a single electron at a distance r from the nucleus is attracted to the nuclear charge e^+ by a potential $V = -e^2/r$. Solving the quantum-mechanical Schrödinger equation for this potential tells us which electron states are allowed. Because V has spherical symmetry about the nucleus, the simplest solutions also have spherical symmetry. The lowest energy state, or ground state, is called the 1*s* orbital. So, the hydrogen atom in its ground state may be visualized as being a spherical charge distribution centred on the nucleus (Fig. 1a)[2].

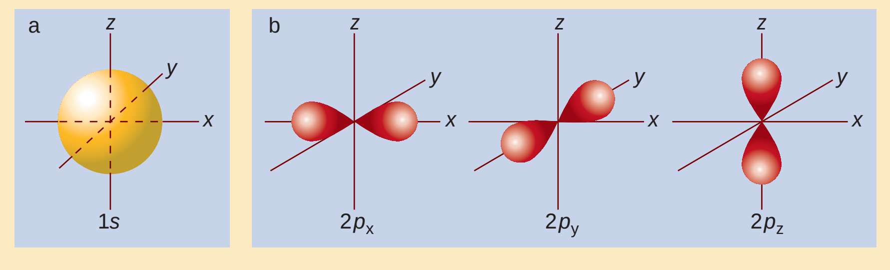

Figure 1 **Textbook examples of electron orbitals.** a, **The ground state of the hydrogen atom. The 1*s* orbital is represented by a sphere centred on the nucleus.** b, **The higher energy 2*p* orbitals. The $2p_x$, $2p_y$ and $2p_z$ orbitals all have the same energy, and the orbital direction is usually dictated by the environment, such as the position of neighbouring atoms in a crystal.**

There are also higher energy states, both spherically symmetrical and less symmetrical. The simplest states with lower symmetry are the 2*p* states, $2p_x$, $2p_y$ and $2p_z$, which all have the same energy and so we say they are degenerate (Fig. 1b). But if the three states are added together they make a spherically symmetric distribution. The next simplest degenerate states are the 3*d* states, of which there are five (Fig. 2). The 3*d* states are particularly important in transition elements, such as copper, because they are only partially filled, and hence a copper ion can exhibit a variety of charges. Whereas in an isolated hydrogen atom all the 3*d* states have the same energy, this degeneracy is removed in transition elements if they are in an environment which is not symmetrical, as is the case in many crystals. The shape and position of the 'lobes' of the 3*d* orbitals are crucial for understanding the directionality of bonding in transition-metal compounds.

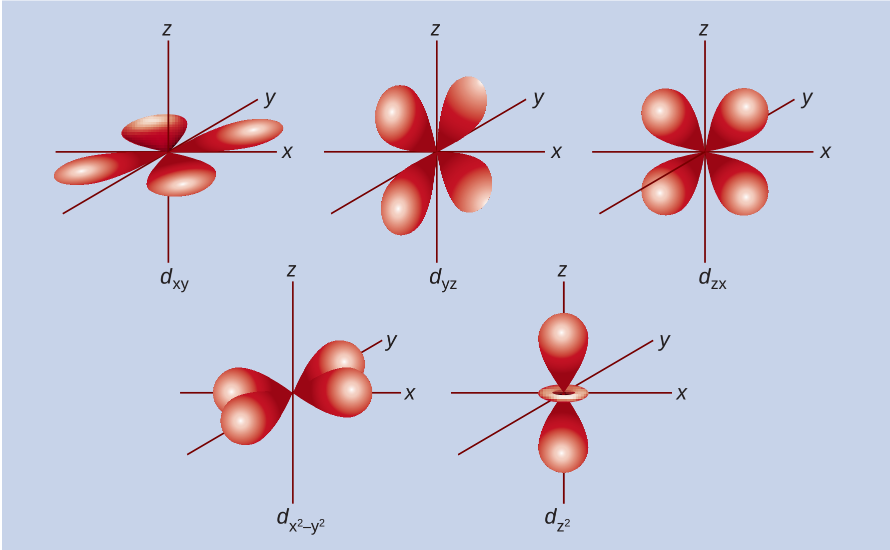

Figure 2 **The family of 3*d* orbitals. Despite appearances, the five orbitals are all equivalent, and when superimposed add up to a spherical distribution. Direct observation of the d_{z^2} orbital in a copper oxide by Zuo *et al.*[1] may help answer questions about bonding in the high-temperature copper oxide superconductors.**

The paper by Zuo *et al.*[1] is remarkable because the quality of their charge-density maps allows, for the first time, a direct experimental 'picture' to be taken of the complex shape of the d_{z^2} orbital (Fig. 2). The correspondence between the experimental charge-density map of Zuo *et al.* (see Fig. 3c on page 50) and the textbook d_{z^2} orbital is striking. In the past, charge-density maps from crystals have usually been measured using X-ray diffraction, which accurately reveals the main peaks of the charge density (that is, the atom positions). For example, Crick and Watson famously interpreted the X-ray diffraction results of Rosalind Franklin to obtain the double-helix structure of DNA.

Although X-ray diffraction reveals peak positions it is normally unable to give details about the shape of the charge distribution, in particular the shape of the bonds. The main reason for this is that crystals contain defects such as dislocations, and the X-ray scattering from such defects is greater than the scattering from bonding electrons. But using an electron microscope it is possible to image the crystal, select a perfect region between crystal defects, and form a diffraction pattern from this perfect region. Zuo *et al.*[1] use an electron beam focused to nanometre dimensions to find a region of the crystal where the perfect-crystal theory of diffraction applies. They also filtered the electrons transmitted by the specimen to remove inelastically scattered electrons and ease comparison with theory. Using these methods, very accurate charge-density maps can be made which reveal the shape of the electron bonds.

In metal oxides, the metal ions interact mainly with the oxygen atoms. But in many copper- and silver-oxide compounds the metal ions are found in close-packed crystal structures, leading to predictions of short-range metal–metal bonding. Such bonding would be covalent, and therefore require non-spherical orbitals, unlike the usual ionic bonding, which involves electrostatic interactions between spherical ions. The non-spherical charge density observed by Zuo *et al.* around Cu atoms in Cu_2O reveals unusual *d*-orbital holes (where the d_{z^2} orbital is unoccupied) and provides strong evidence for Cu–Cu bonding.

How does this work relate to high-temperature superconductivity? We now know that in the simple oxide Cu_2O there are *d*-orbital holes located on the Cu atoms. We also know that in the copper-oxide superconductors, which have CuO_2 (rather than Cu_2O) conducting planes, the charge carriers in the normal state are holes and in the superconducting state are hole pairs. In the CuO_2 superconductors, the available evidence suggests that the holes are on oxygen sites rather than on copper sites[3,4], whereas the work of Zuo *et al.* shows that for Cu_2O the holes are on copper sites. It would be of great interest to extend this approach to measuring charge densities to the more complex CuO_2 superconductors. Such an experiment should give us the following information about high-temperature superconductors: first, whether the holes are on copper or oxygen sites; second, how many holes there are per CuO_2 unit in the conduction planes and how many holes are elsewhere in the structure. Finally, we would like to know whether the distribution of holes in the conduction planes is actually periodic, as is usually assumed, or if there is an irregular two-phase charge density of holes as recently proposed[5]. Zuo *et al.*[1] have provided us with a tool to answer all these questions. ■

Colin J. Humphreys is in the Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK.
e-mail: cjh1001@hermes.cam.ac.uk

---

1. Zuo, J. M., Kim, M., O'Keeffe, M. & Spence, C. J. *Nature* **401,** 49–52 (1999).
2. Cottrell, A. *Introduction to the Modern Theory of Metals* (Institute of Metals, London, 1988).
3. Temmerman, W. M. *et al. J. Phys. C* **21,** L867–L874 (1988).
4. Nücker, N. *et al. Phys. Rev. B* **53,** 14761–14764 (1996).
5. Humphreys, C. J. *Acta Crystallogr. A* **55,** 228–233 (1999).

Ecology

Bite the mother, fight the daughter

Erkki Haukioja

Induced defences — which emerge or develop to full strength when activated by the presence of an enemy — are widespread in sedentary or slowly moving prey[1]. Such induced resistance, as opposed to constitutive resistance (which is present all the time), is profitable when defences are metabolically expensive, and when attack is unpredictable but recurrent[2]. Induced defensive traits are diverse. Water fleas, for example, form long, helmet-shaped spines on their necks, making it difficult for predators to handle them. Plants, on the other hand, can produce high levels of toxic compounds in their leaves. Much of the literature on induced plant defences contains reports of predators having a bad time of it if they try to target a plant that has already been attacked. However, these observations do not exclude the possibility that the poor quality of previously damaged plants is a fortuitous by-product of recovery from attack, not a sign of increased defence.

This is not the case for the organisms described by Agrawal *et al.*[3] on page 60 of this issue. These authors have used radish plants (*Raphanus raphanistrum*) and water fleas (*Daphnia cucullata*) to provide the best evidence yet that predator-activated responses help the victims to survive an attack[4]. Not only that, but they show that these defences can be transmitted from an organism to its offspring. Induced defence is known to be a form of genotypic plasticity — that is, the ability of a given gene sequence (genotype) to produce various traits (phenotypes) depending on environmental conditions. But it has never previously been reported to extend across generations.

Figure1 **Radish plant under attack by the butterfly larva *Pieris rapae*. The plant's defence response includes the production of bitter-tasting, toxic compounds, and the development of hairy trichomes.**

JACK KELLY CLARK

To be ready when needed, induced traits must develop quickly in the presence of a predator. This might be a real problem. Fortunately, it can be overcome if the target organism receives cues of the predator before the actual attack, or if the first attack is unlikely to be lethal. Although plant defences may be induced simply because herbivores are chewing the foliage, many organisms have sophisticated early-warning systems. Some plants, for example, switch on their defence mechanisms as soon as they detect volatile chemicals released by damaged plants close by[5]. Some of these volatiles also directly lure predators to attack plant-eating insects or mites[6]. But the first encounter with a predator is likely to be fatal for young water fleas, so they develop long neck spines in response to chemical cues emitted from their invertebrate predators. In the field, this causes water fleas to develop spiny, defensive helmets when living in a pond also inhabited by predators.

Agrawal and co-workers[3] now report that in both wild radish, which is a cruciferous plant (its petals are arranged in a cross shape), and the water flea, the risks of a young individual's first encounter with predators can be reduced by the experiences of their parents. In the case of the wild radish, the authors allowed butterfly larvae (*Pieris rapae*; Fig. 1) to attack the leaves in a controlled manner. The radish plants responded by a ten-fold increase in the concentration of glucosinolate, and they also developed more numerous hairy trichomes on their leaves. Glucosinolates are bitter-tasting, toxic compounds that reduce insect feeding; hairy trichomes on leaves have a similar effect. The authors then exposed seedlings produced by these plants to further larval predation. They found that the offspring of damaged mothers provided less suitable diets for larvae than seedlings from undamaged, control plants.

A similar thing happened when Agrawal *et al.* exposed water fleas (Fig. 2) to chemical cues called kairomones from two invertebrate predators — the water fleas developed long helmets. Furthermore, the offspring of kairomone-treated mothers produced longer helmets than offspring from control mothers, irrespective of the environment in which the offspring were raised. The authors saw the same effect in successive broods produced later by the kairomone-treated mothers in clean water. This result confirms that