

Photons⁵, atoms⁶, ions^{7–9} and also a menagerie of solid-state two-level systems^{10–12} have been used to carry elementary units of quantum information ('qubits'), which live in superpositions of two quantum states, 0 and 1. To translate Gleyzes and colleagues' experiment into the language of information processing, they have demonstrated that a stream of atomic qubits can be fully controlled by the qubit state of a trapped photon. In the next experimental steps, we can hope to see the electromagnetic field being prepared in a quantum superposition of one photon and no photon. In this case, the atoms in the stream leaving the box will all be in that same superposition state. Moreover, the properties of all the atoms will be 'entangled' such that it no longer makes any sense to consider them individually, even if they are spatially well separated.

As Nobel-prizewinning physicist Richard Feynman said, "We do not understand quantum

mechanics" — but, as Gleyzes and colleagues' achievement¹ shows, we do know increasingly well how to handle it in our experiments. ■

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THEORETICAL CHEMISTRY

The six-bond bound

Gernot Frenking and Ralf Tonner

What is the maximum number of covalent chemical bonds that two atoms can share? Six, according to the latest theoretical study — at least where just two atoms of the same element are concerned.

Every atom can make a small, integer number of covalent chemical bonds with neighbouring atoms. This number is usually not more than eight, although a precise statement is dangerous — in rare cases, atoms can have more than eight neighbours, but whether they are covalently bound is open to debate. By the nineteenth century, chemists had realized¹ that more than one bond may connect the same two atoms: most famously, adjacent carbon atoms can be bound twice or even three times. For many years, three seemed to be the limit. Then, in 1965, a salt compound was isolated with a fourfold rhenium–rhenium bond in its anion². Five bonds followed in 2005, when the synthesis³ of a complex organometallic compound was interpreted in terms of a quintuple bond between two chromium atoms^{4,5}. In a thorough theoretical study in *Angewandte Chemie International Edition*, Roos, Borin and Gagliardi⁶ use quantum chemistry to tackle the obvious question that arises — what is the maximum number of bonds that can bind two atoms?

Theoretical models of covalent bonding go back to 1916, when Gilbert Lewis⁷ introduced the idea of electron pairing between neighbouring atoms. Remarkably, this simple model is still the most widespread conceptual description of the covalent bond⁸. The first quantum-chemical study^{9,10}, however, struggled to reconcile the paired-electron idea with the delocalized nature of electron

wavefunctions, which are smeared over large areas of an atom in 'orbitals' (Box 1). Since then, the paired-electron bond has become chemistry's unicorn — although everyone seems to know what one looks like, no one has actually ever seen one¹¹.

Roos *et al.*⁶ simplify things by focusing

mainly on molecules made up of two atoms of the same elements, in which there are no further bonds to complicate the analysis. They considered all possible bonding and antibonding combinations of the two atoms' electron orbitals using 'multi-reference' wavefunctions. Here, the simple picture of molecular orbitals that are either empty or occupied by two electrons, one from each atom, does not apply. Instead, the authors calculated 'natural' molecular orbitals that retain the simple model, but have non-integer occupation numbers. By summing up the occupation numbers of all these orbitals (antibonding orbitals being negative in the sum), they could arrive at an overall, non-integer 'effective bond order' (EBO). To tie this in with the qualitative paired-electron bonding picture, the authors suggest that the true 'number' of bonds is the next integer larger than the molecules' EBO.

To find the molecules with the highest EBO, Roos *et al.* investigated the transition-metal dimers of chromium, molybdenum and tungsten, respectively Cr₂, Mo₂ and W₂. The atoms of these transition metals have six outer, or 'valence' orbitals, all of which are available for bonding (Fig. 1). (The availability of an orbital for bonding cannot be assumed: in dimers of atoms such as carbon, for instance, the antibonding combination of one pair of orbitals may be lower in energy than the bonding combination of another, effectively allowing a maximum of just three bonds to form.)

For Cr₂, however, the authors came up with an EBO of 3.5, which equates, following their method, to four paired-electron bonds, rather than the expected six for simple dimers. They explain this discrepancy with an imbalance between the optimal bond length for the outermost 4s and 3d orbital contributions to the Cr–Cr bond (Box 1). At the equilibrium bonding distance, 1.66 Å, the 4s component is already

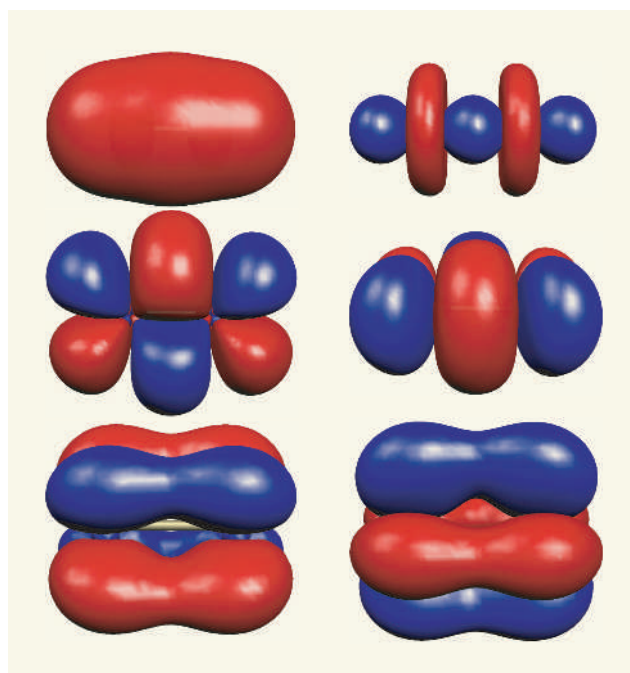


Figure 1 | Six bonds that bind. A depiction of the molecular orbitals of each bond in the sextuple bond between two transition-metal atoms, as investigated by Roos and colleagues⁶. Two bonds (σ bonds; top) each have a single component oriented along the bonding axis between the two atoms, which is horizontal here; two bonds (middle) have double components above and below, or to the sides of, the bonding axis (π bonds); two bonds (bottom) have four components around the axis (δ bonds).

Box 1 | Orbitals and electron counting rules

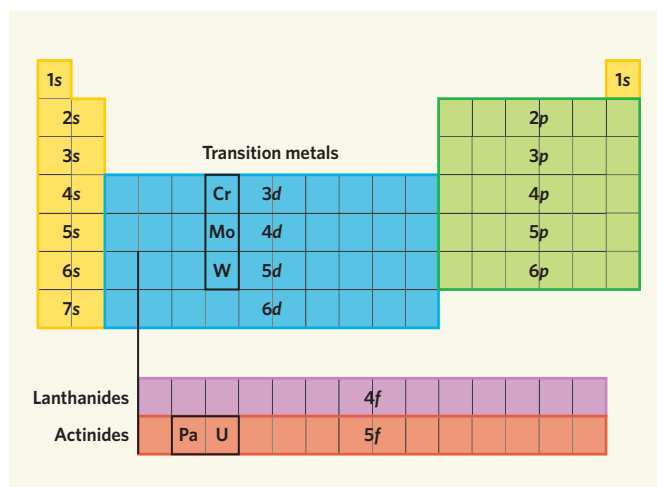
According to the view prevalent when Gilbert Lewis formulated his picture of covalent bonding⁷, electrons circle the atomic nucleus on prescribed orbits. The advent of quantum mechanics, with its probabilistic wavefunctions that smear an electron out over space, modified those classical orbits into quantum 'orbitals'. Each of these describes the spatial distribution of an electron in a particular allowed energy state of the atom.

Two quantum numbers, n and l , are generally sufficient to define an atomic orbital. (A third, m , distinguishes between similar orbitals oriented differently, and a fourth, s , defines the spin of the electron in the orbital.) The principal quantum number, n , depends roughly on the orbital's radial size, and is often thought of as indicating a 'shell' of electrons around the nucleus. The azimuthal quantum number, l , specifies the angular momentum and so the shape of the orbital. Each shell n contains 'subshells' with values of l from 0 to $n - 1$. These subshells are represented by letters, the lowest of them reflecting their appearance in

early spectroscopic investigations of the atom: s (sharp), p (principal), d (diffuse) and f (fundamental).

Taking into account the effects of magnetic field and electron spin, each subshell nl can contain $2(2l + 1)$ electrons. As the atomic number increases, electrons enter an orbital in order of ascending energy (the superscript numbers indicate the number of electrons the orbital can hold): $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}$. That is sufficient to fill the conventional periodic table (pictured), which is structured such that for the elements in the main group the most recently added (outermost) electrons are in the s and p orbitals. The d orbitals make their appearance with transition metals such as chromium (Cr), molybdenum (Mo) and tungsten (W), as investigated by Roos *et al.*⁶. The f orbitals appear only with the lanthanides and with actinides such as protactinium (Pa) and uranium (U)⁶.

The 8/18 electron counting rules that explain the stability of many molecules are a further consequence of this orbital order.



When elements combine to form compounds, their atomic orbitals combine to form molecular orbitals. Compounds of elements from the main group of the periodic table are particularly stable when they have eight electrons in their outermost shell, corresponding to fully occupied $(n)s^2(n)p^6$ orbitals. This octet rule was another landmark contribution by Lewis^{7,8}. A similar 18-electron rule that applies for transition-metal compounds with full $(n)s^2(n)p^6(n-1)d^{10}$

orbitals was formulated by Irving Langmuir¹⁶ in 1921.

Dognon *et al.*¹⁷ now tentatively extend this rule to 32 electrons. They investigated icosahedral compounds in which a metal atom is trapped inside an anionic structure of 12 lead atoms, Pb_{12}^{2-} . When the trapped metal atom was a plutonium ion, Pu^{2+} — with an overall completely filled $(n)s^2(n)p^6(n-1)d^{10}(n-1)f^{14}$ 32-electron system — a perfect match could be made. Time will tell how general this concept is. **G.F. & R.T.**

repulsive, whereas the $3d$ bonding has not yet reached its maximum strength. Significant repulsion between the outermost core electrons of the Cr atoms also occurs at this distance, weakening the bond still further. The dissociation energy needed to break the Cr–Cr bond, 1.65 electronvolts, is therefore low. But as Roos *et al.*⁶ point out, this dissociation energy depends on many factors besides the bond order. These include the interplay between attractive and repulsive electrostatic interactions between electrons and nuclei, and the quantum-mechanical Pauli repulsion between electrons that have the same spin¹².

The authors' calculations for Mo_2 and W_2 , which are heavier homologues of Cr_2 , give natural bond orders of 5.2, suggesting the presence of sextuple bonds⁵. In these dimers, the equilibrium bonding distance — 1.95 Å in Mo_2 , 2.01 Å in W_2 — is greater than in Cr_2 . The outermost orbitals ($5s$ and $4d$ in Mo_2 , $6s$ and $5d$ in W_2) are also better balanced and have a much larger radial extent¹³. The resulting more effective overlap of orbitals between the two atoms yields not only a higher bond order, but also much stronger bonds, with dissociation energies of 4.4 and 5.4 eV, respectively. This trend of bond strength increasing with higher atomic weight is quite general among the transition metals, where relativistic effects have an important role¹⁴; the trend for the elements in

the main group of the periodic table is usually the reverse.

Roos *et al.*⁶ also calculated the EBO of certain transition-metal compounds. For the archetypal $Re_2Cl_8^{2-}$ anion — that in which a quadruple bond was first identified² — their EBO of 3.2 supports the standard interpretation¹⁵. But analysis of an organometallic model compound structurally similar to that in which the quintuple Cr–Cr bond was thought to have been spotted³ yields an EBO of just 3.5.

Is it possible for a covalent bond to have an order greater than six? In principle, this should be possible for bonds between atoms such as the lanthanides and actinides. These each have seven atomic f orbitals that can yield seven f – f combinations. But the $4f$ orbitals in lanthanides are known to be much more contracted than the $6s$ and $5d$ orbitals that are the next lowest and highest in energy, respectively, meaning that they do not participate in chemical bonding. In actinides, Roos *et al.* do find a weak participation of the equivalent $5f$ orbitals in diatomic species M_2 , but the calculated EBOs — at most, 4.5 for a dimer of the rather exotic element protactinium (Pa), followed by 4.2 for uranium (U) — are far from those of a septuple bond.

The general conclusion thus seems to be that — at least as far as covalent bonds between equal atoms are concerned — six is the limit. As Roos and colleagues admit, however, a

measure of bond order between unequal atoms requires a more developed model that includes electrostatic interactions. Whether in these circumstances the upper limit remains bound at six is still open to question. ■

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