

IN RETROSPECT

Pauling's primer

Linus Pauling's book on bonding brought quantum mechanics into practical chemistry, finds **Philip Ball**.

Linus Pauling's *The Nature of the Chemical Bond* has, like Isaac Newton's *Principia* or Charles Darwin's *On the Origin of Species*, the kind of iconic status that, for some, removes any obligation to read it. Every chemist learns of Pauling's role in uniting the view of molecules as assemblies of atoms with the quantum-mechanical picture of atomic wave functions. But his book is long and mathematical, and more versatile approaches have emerged since it was published in 1939. Nevertheless, more than 70 years on, as we prepare for the International Year of Chemistry 2011, it remains a surprisingly good primer on chemical bonding that translates abstract quantum theory into the practical language of chemistry.

When Pauling's book was first published, some textbooks were still presenting an essentially nineteenth-century view of the bond. The term was introduced in 1866 by English chemist Edward Frankland, who regarded the chemical bond as a force akin to gravity. Jöns Jakob Berzelius suspected that the force was electrostatic, the attraction of oppositely charged ions. That view was encouraged by the discovery of the electron in 1897, as ions could result from an exchange of electrons between atoms.

But G. N. Lewis at the University of California, Berkeley, argued that bonding may result from sharing, not exchange, of electrons. Shared electrons give rise to what Irving Langmuir later called a covalent bond, which links neutral atoms. In 1916, Lewis suggested that atoms are stabilized by having a full 'octet' of electrons, which he saw as the corners of a cube; the octet may be completed by linking corners or edges with adjacent atoms. The model, which was popularized (or, in Lewis's bitter view, appropriated) by Langmuir, seemed vindicated when physicist Niels Bohr explained how the octets arise from quantum theory as discrete electron shells.

Yet because it considered only the individual atoms, this remained a rudimentary grafting of quantum theory on to the concepts that chemists used to rationalize molecular

formulae. Pauling, a supremely gifted young man from a poor family in Oregon who won a scholarship to the prestigious California Institute of Technology (Caltech) in 1922, was convinced that chemical bonding needed to be understood from quantum first principles. He wasn't alone — Richard Tolman at Caltech notably held the same view. But Pauling had a golden opportunity to develop it when, in 1926, he went to Europe on a Guggenheim fellowship to visit the architects of quantum theory: Bohr at Copenhagen, Arnold Sommerfeld at Munich and Erwin Schrödinger at Zurich. He also met Fritz London and his student Walter Heitler, who in 1927 published their quantum-mechanical description of the hydrogen molecule. They had found an approximate way to write the wave function of the molecule that, when inserted into the Schrödinger equation, allowed them to calculate a binding energy that was in reasonable agreement with experiment.

Pauling generalized this treatment into the valence-bond model, which considers chemical bonds to be formed by the overlap of single-atom electron orbitals. He put forward the idea of 'resonance' in molecules for which more than one valence-bond structure can be drawn; for example, in H_2^+ the single electron can be considered to reside on either hydrogen atom, and the molecule is said to resonate between the alternatives. In such cases, the mixed state has a lower energy than any of the contributing structures.

A NEW GEOMETRY

Pauling also proposed that 'hybrid' blends of atomic electron orbitals with new geometries may arise in some molecules. In methane, for example, the central carbon atom attaches to four hydrogen atoms in a tetrahedral shape; this configuration can be rationalized as the mathematical mixing of the atomic 2s and three 2p orbitals in carbon to give four tetrahedrally distributed sp^3 hybrid orbitals. These ideas on resonance and hybridization were published in a series of papers in 1928–31, which formed the core of *The Nature of the Chemical Bond*.

The book's scope is exhaustive. It brings

multiple covalent bonds and ionic, metallic and hydrogen bonds all within the valence-bond framework, and explains how the ideas fit with observations of bond lengths and ionic sizes in X-ray crystallography — the technique Pauling mastered at Caltech that led to his seminal work in the early 1950s on the structure of proteins and nucleic acids.

Pauling acknowledged that his treatment of chemical bonds is ultimately arbitrary — his resonating configurations of nuclei and electrons are conceptual fictions that allow us to estimate the molecule's energy. It is the wave function of the entire molecule that actually describes how the electrons are distributed in space. But he was resistant to recognizing alternative theories.

In particular, in the late 1920s, Robert Mulliken at the University of Chicago, Illinois, and Friedrich Hund at the University of Göttingen, Germany, approximated the electron wave functions in a different way to Pauling's valence-bond theory, giving rise to 'molecular orbitals' in which electrons are distributed over several nuclei. Their model offered a simpler account of the quantum energy levels as revealed by molecular electronic spectra. And it supplied a single description of some molecules for which the valence-bond approach had to invoke resonance between many structures. This was especially true for aromatic molecules such as benzene: the valence-bond model needed around 48 separate structures for naphthalene (two fused benzene rings), and no fewer than 560 for the organometallic compound ferrocene.

Although neither the valence-bond nor the molecular-orbital model could claim to be more correct than the other, the latter had practical advantages. This was known even by reviewers of Pauling's book — some criticized him for not mentioning the rival theory, and one reviewer suspected that the valence-bond method might triumph purely because of Pauling's superior presentation skills. By the 1970s, however, most chemists accepted that molecular-orbital theory was usually more convenient, although Pauling never did.

The significance of *The Nature of The Chemical Bond* was not so much that it pioneered the quantum-mechanical view of bonding, but that it made this a chemical theory: a description that chemists could understand and use, rather than a mathematical account of wave functions. It recognized that, if a model of physical phenomena is to be useful, it needs to accommodate itself to the intuitions and heuristics that enable scientists to talk coherently about the problem. Emerging from the forefront of physics, this was nevertheless a chemists' book. ■

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