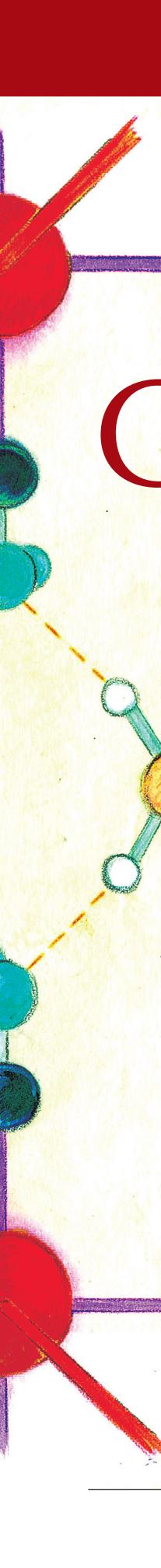


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CHEMICAL CONNECTIONS

Chemists have long pondered the nature of chemical bonding and continue to chase down their dreams of fully understanding it

STEPHEN K. RITTER, C&EN WASHINGTON

IN 1923, THE YEAR C&EN WAS BORN, Gilbert N. Lewis of the University of California, Berkeley, published a book titled “Valence and the Structure of Atoms and Molecules.” In the text, Lewis laid out the details of his general theory of chemical bonding, which is based on the concept that atoms form bonds in molecules by sharing pairs of electrons.

The world at the time was becoming more technologically sophisticated, with electricity, telephones, radios, automobiles, and airplanes. Scientists were coming to a better understanding that orchestrated chemical bonding is what makes life possible. And with rapid growth in chemical synthesis techniques, the chemical industry was cranking out dyes, fertilizers, natural and synthetic fibers, pharmaceuticals such as aspirin, and other products.

But one thing the world didn't have in 1923 was a good way to visualize the chemical bonds that led to these advances. Among Lewis' creative ideas was to use two dots, like a colon, as a symbol to represent the pairs of electrons forming bonds. It was a simple way to explain the experimentally determined chemical formulas of the majority of compounds known at the time.

In reality, there are no rope tethers, sets of hooks, or rigid rods that anyone could point to and say, “These are chemical bonds.” As quantum mechan-

ics and chemical bonding theories would soon show, atoms in molecules are held together by a balancing act of attractive and repulsive forces generated by Lewis' electron pair, an invisible entity felt but not seen. Although the abil-

ity to make, break, and control chemical bonds is what chemists do—it can be argued that chemistry doesn't exist without bonds—they are in fact not real objects and defy sets of criteria by which they can strictly be defined.

Even though the idea of a bond was fuzzy in the 1920s, writing out Lewis electron-dot structures enabled chemists to start reasoning more clearly about

the structure and properties of molecules and make predictions about reaction mechanisms. Instead of making chemicals and materials for producing consumer products based on observation and intuition, chemists could better tailor chemicals and materials by design. Lewis' work helped chemistry evolve from a mostly descriptive science into a predictive one, effectively relaunching the field.

Before Lewis came along, chemists knew that bonds were the product of some kind of force. They also knew that the periodic nature of the elements imbues them with an affinity, called valency, such that one atom can only make a certain number of connections with other atoms. They knew

FIVE IN ONE BLOW In 1982, Joel S. Miller of the University of Utah was part of a team that uncovered a single compound containing all five of the major types of chemical bonds (*J. Chem. Educ.* **1982**, 59, 361). In $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$, a highly conducting crystalline inorganic material, the O–H and C–N bonds are covalent, the bonds from the CN ligands to Pt are coordinate covalent, the K–Br and K–Pt(CN)₄ interactions are ionic, the links between multiple Pt atoms are metallic, and the water molecules hydrogen bond with CN and Br. (Pt is red, C is dark blue, N is light blue, Br is brown, K is green, O is yellow, and H is white.)

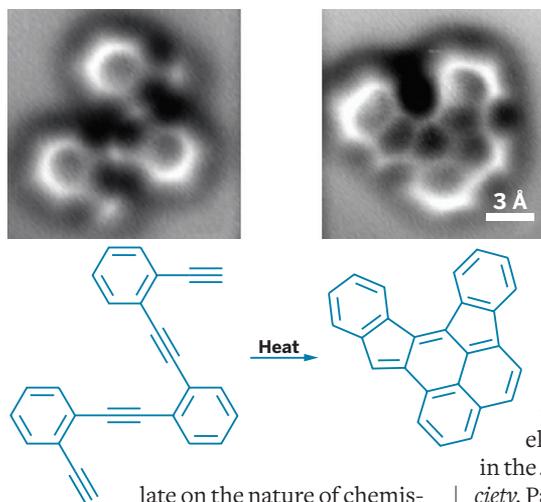
that bonding variations could produce molecules with right- and left-handed asymmetry, or chirality. They also knew about aromaticity, a mechanism that certain cyclic molecules use to share electrons across their entire molecular framework to improve their stability.

As early as the 1850s, chemists were using symbols and models—either on paper or made out of paper—to depict molecules. They were able to work out patterns of bonding for many chemical substances. But the models came with disclaimers: The chemists warned against interpreting the models as being representations of reality because they didn't have direct evidence for how molecules are constituted. For one thing, the electron had not been discovered.

That discovery came in 1897, when J. J. Thomson observed negatively charged particles streaming from the cathode in a discharge tube. Within a couple of years of Thomson's discovery, Lewis began tinkering with ideas about how electrons forge connections between atoms and how to draw representations of bonds. Thomson's discovery also unleashed scientists to begin proposing new theories to explain atomic structure.

ONE SUCH THEORY was put forward by Niels Bohr. This year marks the 100th anniversary of Bohr's famous paper "On the Constitution of Atoms and Molecules." Bohr took Ernest Rutherford's 1911 planetary model of an atom and coupled it with Max Planck's 1900 theory on quantization of radiation to provide a model of the atom in which negatively charged electrons circle around a positively charged nucleus in discrete energy levels, or orbitals. It took Erwin Schrödinger's wave equation in 1926, part of the then-new field of quantum mechanics, which describes the laws of motion of elementary particles, to work out the final details of how electrons behave in atoms.

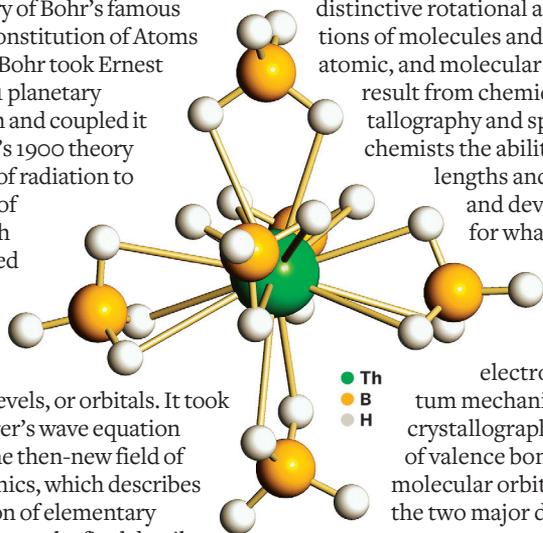
"The pace of chemical discovery has been significantly accelerated by computational investigations of Schrödinger's equation, the ultimate oracle of chemical knowledge," says theoretical chemist Frank A. Weinhold of the University of Wisconsin, Madison. "It was idle to specu-



late on the nature of chemistry and life processes until the discovery of quantum mechanics provided a rational basis for understanding chemical bond formation."

In 1913, the same year Bohr published his work, William L. Bragg and coworkers reported the first X-ray crystal structures of simple inorganic salts and of diamond. X-ray crystallography quickly became the most important source of information for structure and bonding. As more was known about molecular structure, scientists developed analytical instruments to measure spectroscopic signals stemming from the distinctive rotational and vibrational motions of molecules and myriad electronic, atomic, and molecular energy states that result from chemical bonds. Crystallography and spectroscopy gave chemists the ability to gauge bond lengths and bond strengths and develop loose cutoffs for what constitutes a bond.

By the late 1920s, the marriage of the electron pair and quantum mechanics supported by crystallography led to the birth of valence bond (VB) theory and molecular orbital (MO) theory, the two major descriptions of



PUSHING THE LIMITS University of Illinois, Urbana-Champaign, researchers Gregory S. Girolami and Andrew C. Dunbar earlier this year synthesized the first example of a 16-coordinate metal complex. The 16 bonds in the thorium hexa(borohydride) dianion shown, $\text{Th}(\text{BH}_4)_6^{2-}$, are the theoretical maximum for any element based on the number of atomic orbitals available for bonding.

VIEW TO A BOND Researchers using atomic force microscopy recently captured images at high enough resolution to see the electron density of covalent bonds in a molecule in the act of undergoing a heat-induced ring-closing reaction.

bonding that remain central guiding themes for chemists.

Linus C. Pauling of California Institute of Technology, the chief architect of VB theory, introduced its key concepts of hybridization of atomic orbitals, resonance, and electronegativity in a series of papers in the *Journal of the American Chemical Society*. Pauling's cumulative work led to his famous book, "The Nature of the Chemical Bond," which was dedicated to Lewis and first published in 1939.

Hybridization is the process of mathematically mixing atomic orbitals to form hybrid orbitals with different shapes and energies that are more suitable for bonding with other atoms. VB theory constructs bonds by overlapping hybrid orbitals so that a pair of atoms can share a pair of electrons. Molecules and reactions between them involve joining several of these VB structures.

As Pauling was building VB theory, Robert S. Mulliken, Friedrich Hund, Erich Hückel, and others developed MO theory, which helped make quantum mechanics applicable to large molecules. It has proved invaluable to organic chemists and structural biologists. The premise of MO theory is that the molecule's orbitals are not associated with particular bonds between two atoms, but rather that the electron pairs are distributed in sets of energy levels that encompass all of the atoms simultaneously. Reactions between molecules are viewed as arising from favorable interactions between electron donor and acceptor orbitals.

CHEMISTS SOON BEGAN to expand the understanding of the field from the atom connectivity concepts of Lewis and others to detailed information about chemical reactivity and the geometric arrangements of molecules. For instance, Henry Eyring, Michael Polanyi, and others in the 1930s used quantum mechanical principles to develop transition-state theory to explain chemical reaction rates. In the theory, chemists consider a reaction as a continuum along an axis upon which reactant molecules form intermediate or transition states and pass over energy

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Read what chemical bonding specialists say about bonds at <http://cenm.ag/bonding>. Join in with your comments.

barriers to reach isolable intermediates or final products.

In 1957, Ronald J. Gillespie and Ronald S. Nyholm refined ideas of how to correlate valency and molecular structure in the valence shell electron pair repulsion (VSEPR) theory. By knowing the molecular formula of a compound and the number of valence electrons available to each atom, chemists could use VSEPR to predict the geometric shape of a molecule, based on the Lewis connectivity of the bonds and the space occupied by any lone pairs of nonbonding electrons. This is a fun bit of chemistry, like working out a puzzle, and students today typically learn about VSEPR in their first chemistry course.

So long as electrons are localized on atoms, the VB and MO pictures of the chemical bond are essentially the same. Although VB theory can accommodate delocalization of electrons through resonance structures, MO theory is a more direct framework for treating delocalized electrons, such as those in aromatic compounds. As a result, by the mid-1950s MO theory came to the fore because it was more powerful for organic chemists studying the structure and bonding of carbocations and radicals, reaction mechanisms, and stereochemistry. MO theory further provided the underlying framework for much of today's computational chemistry.

In the early 1950s, Clemens C. J. Roothaan, George G. Hall, and others developed the first equations that enabled solving the Schrödinger equation on computers. To put their work in context, one might say that Lewis defined the basic concepts that chemists use to understand chemical bonding, whereas Roothaan, Hall, and others provided the recipes needed to put high-level numbers to these concepts.

In 1970, John Pople introduced the first of the Gaussian suite of computer programs, which have made it possible for anyone today to study chemical structure and bonding in a standardized way for any type of molecule, from H_2 to proteins. Because working out the math for complex molecules is computationally difficult, chemists have now devised simpler approaches that focus on the electron density of bonds rather than a complete solution of the Schrödinger equation for each electron involved in bonding. Combined with laser-based femtosecond spectroscopy,

molecular dynamics calculations now enable chemists to determine how chemical bonding changes occur during reactions and at what rates.

Even with advanced bonding theories and better-than-ever computer graphics

at their disposal, chemists still struggle to come up with an apt description of a chemical bond. They have some solace in knowing that there's a conceptual understanding of the force that holds atoms together. That is, pairs of electrons, with anti-symmetrical angular momentum derived from their spinning, are held in tow by the attraction of the positively charged nuclei

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“Any rigorous definition of a chemical bond is bound to be impoverishing.”

they are zipping around, even as their negative charges repel one another. The push-pull force stemming from this beehive of activity, adjusted so the molecule settles into the lowest possible energy state, is what we call a chemical bond. From the quantum mechanical perspective, a bond is a cold, hard mathematical function.

FOR THOSE SEEKING something tactile, a prescriptive definition of the chemical bond, based mostly on Pauling's words in “The Nature of the Chemical Bond,” is that a bond exists between two atoms or groups of atoms when the forces acting between them lead to an aggregation with sufficient stability to be considered an independent molecular species. This definition has been adopted in part by the International Union of Pure & Applied Chemistry.

The inanimate quantum mechanical view of a bond and the ambiguity of the dictionary definition of a bond have done little to placate chemists over the years. Even in the 1950s, theoretical chemist Charles A. Coulson of the University of Oxford, author of the classic textbook “Valence” and a Pauling contemporary, lamented over the inability to fully understand the nature of a chemical bond.

“Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it,” Coulson said. “Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination.”

But never say never. Coulson's prediction of never being able to see a bond is becoming frayed at the edges, thanks to the exquisite touch of the atomic force microscope (AFM). Earlier this year, C&EN reported on a research team that indirectly captured snapshots of the covalent bond structure of an aromatic molecule undergoing a heat-induced cyclization reaction (C&EN, June 3, page 7).

As the microscope's sharp vibrating tip, which is capped with a single atom, feels its way across

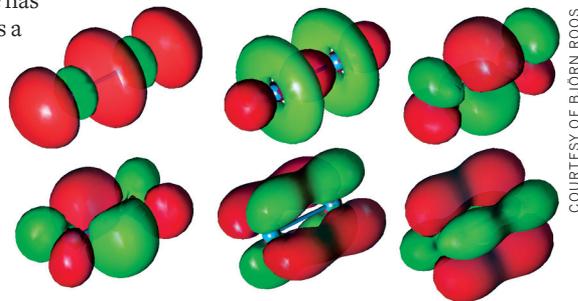


UC BERKELEY/LBNL

FOUNDING GRANDFATHER Lewis, a leading figure in the history of chemical bonding, shown in his UC Berkeley lab in the 1940s.

a sample, it senses and maps out individual atoms of the sample. The AFM pictures of the aromatic molecules are a little fuzzy, but sure enough the before-and-after outlines of the reactant and product molecules are there. You can see the shadows of electron density connecting the atoms.

These AFM images might be as close as we ever get to seeing a chemical bond. Or they may be a stepping stone to an era in which scientists will be able to



COURTESY OF BJORN ROOS

SIX PACK Tungsten, with no ligands to tie up bonding orbitals, has the distinction of being the most likely element to engage in a sextuple bond in an isolable compound—ditungsten, W_2 (six computed molecular orbitals shown). If prepared, W_2 's six bonds, which theoretically is the maximum number of bonds possible between two atoms, would surpass the quintuple metal-metal bonds of several chromium-based complexes, the first of which was prepared in 2005.



From C&EN Archives

Throughout its 90-year history, C&EN has explored new developments in chemical bonding and their impact on science, as these three examples reveal.

Aromatic Character

In 1965, to celebrate the 100th anniversary of August Kekulé's elucidation of the structure of benzene, C&EN published a special feature on aromaticity, complete with hand-drawn structures, written by Columbia University's Ronald Breslow, an authority on organic ring compounds and reaction mechanisms. In the review, Breslow notes that 100 years after Kekulé, "chemists are still trying to understand aromatic character. Modern techniques and the increasing application of quantum mechanics to organic chemistry have led to the preparation of many new aromatic systems and to a deeper understanding of conjugated systems generally" (C&EN, June 28, 1965, page 90).

Metals and Enzymes

"Multiple juxtapositional fixedness (MJF) is the tongue-in-cheek term that Dr. Daryle H. Busch has coined to describe the unusually strong bonding that occurs between metal ions and some ligands, and to account for certain aspects of metal-enzyme activity. Nevertheless, Dr. Busch notes that he was serious in his search for a phrase that would describe the principle of kinetic and thermodynamic stabilization that occurs whenever certain groups are so arranged in space that they can't undergo stepwise dissociation from a metal ion by the usual pathways. The Ohio State University professor of chemistry described the principle at the 25th annual Northwest Regional ACS Meeting in Seattle" (C&EN, June 29, 1970, page 9).

The Chemical Side of the Double Helix

"The double helix. That two-word phrase is so firmly planted in our scientific lexicon that even a good number of nonscientists recognize the reference to the structure of DNA. Many of us can't remember a time when DNA wasn't recognized as being the genetic material or as taking the form of two hydrogen-bonding complementary strands of base-pairing nucleotides wound around a single axis. Although the B-form DNA structure that James D. Watson and Francis H. C. Crick proposed in their April 25, 1953, letter to *Nature* made only a limited splash at the time, the subsequent ripples revolutionized biology—particularly genetics—turning it into a molecular science" (C&EN, March 10, 2003, page 49).

pluck out or insert electrons in bonds at will to control matter. Time will tell, but the important point for now is that probing chemical bonds has led to innumerable discoveries and bits of insight.

For example, chemists have unraveled the structure and bonding of molecular metal complexes and metal particles to design catalysts for making plastics that go into nearly every object we touch. Researchers have probed and dissected the structures of proteins and DNA, leading to a better understanding of human physiology and the mechanisms of disease to design more efficient medicines. And as scientists and engineers have come to better understand the bonding of chemical species on surfaces and self-assembly processes, they have refined ways of sculpting ultrathin features to speed up the operation of integrated circuits and lower the power consumption of electronic gadgets.

Mastering the chemical bond, the back-

bone of chemistry, has improved chemistry and in the process has helped turn biology and physics into molecular sciences that complement chemistry, even if ambiguity remains in what a bond might be.

"I think that any rigorous definition of a chemical bond is bound to be impoverishing," says theoretical chemist Roald Hoffmann of Cornell University. Hoffmann, who received the 1981 Nobel Prize in Chemistry for his work on predicting the mechanisms of organic reactions, prefers a more touchy-feely definition of the chemical bond.

"My advice is this," Hoffmann says. "Push the concept to its limits. Be aware of the different experimental and theoretical measures out there. Accept that at the limits a bond will be a bond by some criteria, maybe not others. Respect chemical tradition, relax, and instead of wringing your hands about how terrible it is that this concept cannot be unambiguously defined, have fun with the fuzzy richness of the idea." ■

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