

The Art of the Chemical Bond

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A look at the scientists who spend most of their time thinking about chemistry's most central concept.

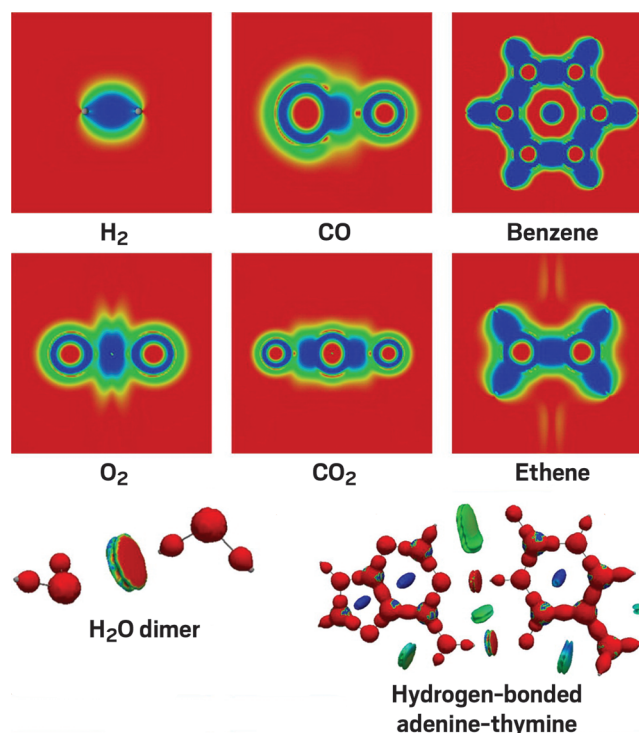
Chemical bonding enables scientists to take the 100-plus elements of the periodic table and combine them in myriad ways to form chemical compounds and materials. The success rate is pretty good, as more than 120 million chemical substances are currently registered by CAS, a division of the American Chemical Society.

But there are still hundreds of millions more waiting to be created. Researchers continue to find new ways to get atoms to interact and stick together. They also continue to evolve methods for breaking and re-forming bonds during chemical reactions to improve on the synthesis, properties, and performance of existing chemicals and materials.

For some, the work of scientists who spend most of their time thinking about chemical bonding—both the well-seasoned principles and newly discovered aspects—can seem mystifying. Taking a deeper look at what these scientists and engineers do and how they go about doing it, from thought experiments to developing their own computational software, can be illuminating.

“Chemical bonding is the language of logic for chemists,” according to [Anastassia N. Alexandrova](#), a theoretical and computational chemist at the University of California, Los Angeles. Some researchers spend their time developing bonding theories, and for that you need a strong background in quantum mechanics, Alexandrova says. They have little time to think about synthetic chemistry. In contrast, other researchers focus on computational methods and may spend a lot of time thinking about synthetic chemistry and not so much on quantum mechanics.

Experimentation is the essential leveling point between these two camps, Alexandrova says. “It is often the place to start and always the final goal.” She describes her research as being in the middle ground. “Our group uses existing observations to build knowledge and develop theory that allows us to make testable predictions,” Alexandrova says. “Along the way, we might develop new computational

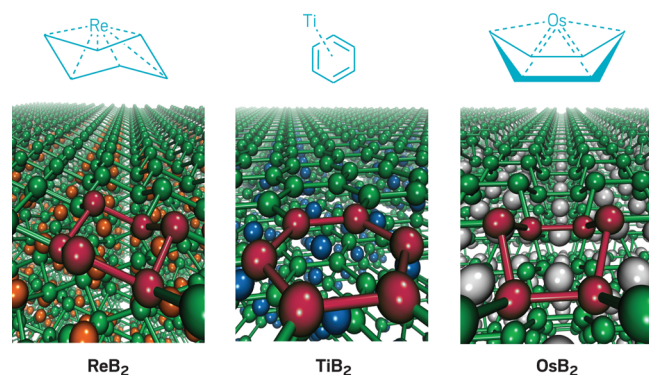


An electron-density-based computational tool called Density Overlap Regions Indicator, or DORI, developed by Clémence Corminboeuf and Piotr de Silva at the Swiss Federal Institute of Technology, Lausanne, allows researchers to simultaneously reveal types of bonding and noncovalent interactions in many types of molecular systems; blue and red indicate regions of high and low electron density overlap, respectively. Credit: Courtesy of Clémence Corminboeuf.

methods, but only as a by-product to assist the chemistry. Once we have sufficient understanding, we start manipulating the devised system, and this is the culminating moment, to see if we are getting somewhere new. This is where we provide a service to the rest of the chemistry community.”

In July, Alexandrova cohosted the [International Conference on Chemical Bonding \(ICCB\)](#) in Hawaii, an annual conference she cofounded and co-organizes with [Alexander I. Boldyrev](#) of Utah State University. The meetings bring together theorists, computational chemists, and experimentalists who probe new ways of manipulating bonds as they seek out means to improve on chemical synthesis, materials design, and property analysis.

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UCLA's Alexandrova and Robinson are introducing molecular-level bonding concepts (cyclohexane isomer and benzene structure models at top) to materials chemistry to explore the mechanical properties of new ultrahard materials and explain how different metal boride nanostructures are stitched together. In doing so, modeling and understanding the diverse bulk structures of ultrahard borides (bottom) become a small cluster problem (cluster units in red). Solving it reveals the ionic bonding of TiB₂ and different types of metal-ligand covalent back bonding for ReB₂ and OsB₂. Credit: Anastassia Alexandrova and Paul J. Robinson.

At ICCB 2016, Alexandrova and undergraduate student Paul J. Robinson discussed an example of the type of exploratory research she is talking about: studying the chemical bonding in metal borides to understand their mechanical properties. These ultrahard materials, such as TiB₂, ReB₂, and OsB₂, are being developed as potential lower-cost alternatives to diamond, carbides, and boron nitride that are traditionally used with cutting, drilling, and polishing tools.

Just performing computations on these materials often reproduces the experimental observations, Alexandrova says. But that doesn't teach researchers anything about the possible routes to designing new materials. "This is where chemical bonding becomes the key," she observes. "We need to find the critical elements in the electronic structure of the borides that explain the experimental results."

It turns out that the electron-deficient nature of boron lends itself to multiple B-B interactions, as well as to the previously unsuspected donation of s- or p-type electrons from the metal to the boron network, Alexandrova says. Her team is introducing molecular-level bonding concepts to materials chemistry to explain how the metal boride nanostructure is stitched together slightly differently for different metals and gives the material unprecedented strength.

"Now we can start thinking of new alloys that will enable even stronger metal-boron bonds," Alexandrova says. "The possibilities are immense, and most important, we now have a logical way to think about it, a kind of compass to point the way to where to dig for treasure."

"Chemical bonding does have a larger existence than what most people might normally think about," says George C. Schatz of Northwestern University, who is editor-in-chief of the *Journal of Physical Chemistry*. For example, Schatz says, if you imagine nanoparticles as atoms and biomolecules such as DNA, RNA, and peptides as bonds, these components can combine to form a crystalline lattice.

Schatz, who attended ICCB 2016, has been developing computational models for these nanoparticle–biomolecule frameworks to complement the synthetic work of his Northwestern colleague Chad A. Mirkin. With simulations, the team can see how these complex nanostructured materials form and which crystalline lattice will be produced for a given choice of nanoparticle diameter and DNA length.

"Simple rules can be formulated for determining crystal symmetry that are analogous to Pauling's rules of atomic crystallography," Schatz notes. In some cases, though, because the nanoparticles have different sizes than atoms, they can form crystal lattices that atoms cannot, he adds. Discovering these differences through exploratory theoretical and computational studies is proving valuable for uncovering interesting optical and mechanical properties that can be used to develop new types of chemical and biological sensors, Schatz says.

"We do have a real opportunity to use chemical bonding to our advantage when we want to optimize the performance of nanoscale materials," adds UCLA's Paul S. Weiss, who is editor-in-chief of the journal *ACS Nano*. For Weiss, that means not just constructing materials, but also finding precise ways to connect materials together and components together to make new devices, all while maintaining their sought-after chemical, physical, and electronic properties.

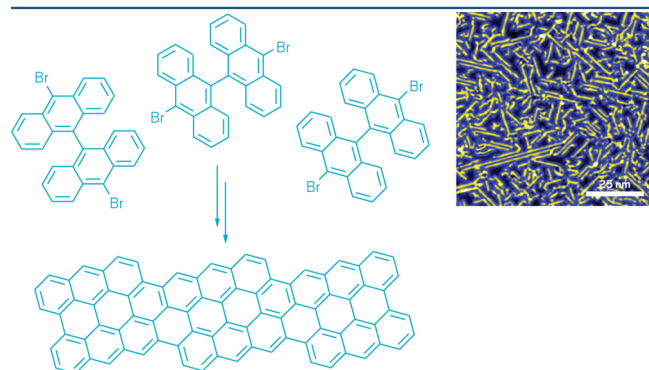
Graphene is one example of where this strategy can be applied, research that Weiss described at ICCB 2016. "Graphene is a material with perfect sp²-hybridized carbon atoms in two dimensions," he says. The question for scientists is how to make connections to it.

We could deposit a metal on it but destroy its extraordinary properties, Weiss says. Or we could oxidize it and then partially reduce it back with chemical reactions to make connections to it, he adds. But that disrupts its conjugation and properties. "Those are two terrible ideas," he emphasizes.

"Instead, we can leverage a century of organic chemistry to make precise bonds that retain sp² hybridization and optimize electronic band alignment, so that the contacts retain the properties of the material."

For instance, Weiss and his colleagues at Tohoku University have used a method called *surface-assisted molecular assembly* in which a copper substrate guides

brominated aromatic precursors to link together and form graphene nanoribbons. This approach goes further by enabling the ribbons to precisely connect end-to-end to create chiral nanoribbon strands.



UCLA's Weiss and coworkers use a method called surface-assisted molecular assembly in which a copper substrate guides brominated aromatic precursors to link together and form graphene nanoribbons. These segments are further connected end-to-end to create nanoribbon strands up to 50 nm long, as shown in this STM image, that can be attached to electrodes. Credit: *ACS Nano*.

Because precursors can be designed to form both the nanoribbons and connections to electrodes, they open up the possibility of producing simple, identical contacts that can reduce required operating voltages in devices and heat loss across connections. This technique could lead to new generations of more reliable and energy-efficient electronics, Weiss believes. "It all comes down to the contacts that control chemical, physical, and electronic interfaces at all scales, with precision."

Many bonding models have been developed or posed over the years, and they often help chemists such as Schatz, Mirkin, and Weiss explain or predict the outcomes of experiments and rationally design new molecules and new materials. But there are cases where the models run up against limitations or even fail. "Accuracy is not the main bottleneck most of the time, but rather the inability to provide understanding," points out [Célia Fonseca Guerra](#) of VU Amsterdam.

Like many chemical bonding specialists, Fonseca Guerra is out to improve the general understanding of chemical bonding, to not just make it more accurate, but also more insightful. "I not only want to know what happens, but why it happens," Fonseca Guerra says.

New research ideas that she explores are gleaned from coming across a peculiar statement in the literature that piques her interest or from asking probing questions of her experimental colleagues. The quantum chemical tools that Fonseca Guerra uses are often based on existing analysis

methods. But when those methods do not provide clear answers, she takes matters into her own hands and develops her own computational tools. And like her chemical bonding colleagues, Fonseca Guerra also draws inspiration from teaching, which is "a crucial ingredient for research," she says.

"In both undergraduate and graduate courses, we lay the foundation for the next generation of chemists," Fonseca Guerra explains. Teaching basic chemistry in undergraduate textbooks requires reading and rethinking textbook knowledge and comparing it with state-of-the-art results, not only from experiment, but especially from theory, she says. This often unexpectedly spawns research projects with the potential to lead to a paradigm shift.

At ICCB 2016, Fonseca Guerra presented an example of rethinking hydrogen bonding. The project involved using computational programs such as the Amsterdam Density Functional code, which she helps curate, to explore weak chemical interactions that facilitate self-assembly in biological and supramolecular systems. Her group is finding out how making [subtle structural changes in hydrogen-bonded base pairs](#) of DNA can impart different σ - and π -bonding influences in the hydrogen-bond donor and acceptor, which can affect the bond's distance and stability. The team's analyses of base pairs, DNA mismatches, and nucleic acid quadruplexes are contributing new insights into this realm of bonding for experimentalists, she believes.

Technology of course also comes into play when studying chemical bonding, with the biggest advance being the development and evolution of computers, according to [Klaus Ruedenberg](#) of Iowa State University. Ruedenberg, who is 96 years old, has some experience in the matter—he has witnessed practically the entire development of modern chemical bonding theory and practice.

"Vastly expanded computational capabilities have stimulated the development of new sophisticated mathematical and theoretical methods, and they have yielded new quantitative insights into many bonding patterns," Ruedenberg says. For example, the steadily increasing complexity of solutions to the Schrödinger equation has enabled a more rigorous and satisfying energy analysis of the equation's molecular wave functions, he notes. These developments have further benefited synthetic chemists who can now run their own bonding analyses using commercial software on a laptop computer.

At ICCB 2016, Ruedenberg discussed his theoretical analysis of multiple bonds in diatomic carbon, C_2 , a species that normally exists only as a high-temperature gas in electric arcs, flames, and stars. It is thought to be involved in forming nanotubes, fullerenes, and graphene. The standard view of

dicarbon is that there should be a double bond between the two carbons, Ruedenberg says, although some theorists have suggested quadruple bonding is at work. Ruedenberg has found with his latest modeling that three strong bonds are possible (two π bonds and one σ bond), and a weak fourth bond (an additional σ bond) could be invoked.

Among the advantages of being a theoretical or computational chemist is that it does provide researchers a certain level of freedom to jump in and explore new ideas such as C_2 bonding at the drop of a hat. For example, earlier this year, Chemical & Engineering News asked a few researchers to identify which molecule might be considered the smallest aromatic ring compound. The inquiry stemmed from reports by several research groups about the synthesis of three-membered aromatic boron ring compounds.

UCLA's Alexandrova, Utah State's Boldyrev, and graduate student Ivan A. Popov in Boldyrev's group quickly ran calculations on all plausible three-membered aromatic rings that could be made from the first few elements of the Periodic Table, from hydrogen to fluorine. The results, reported in *C&EN* (March 7, page 28), found that there are several answers, depending on the type of aromaticity, ring size, and whether the compound has already been synthesized or not. Spoiler alert: The littlest aromate turns out to be H_3^+ , a molecule observed in gas-phase lab experiments and in interstellar space—it's one of the most abundant molecular species in the universe.

Boldyrev says he is willing to make time for such detours because it not only satisfies a chemical curiosity but also invites an opportunity to help chemists broaden the scope and understanding of what they do. "I used to think aromaticity was a dead field, that after 150 years since Kekulé used it to describe the bonding in benzene that everything to know had been learned," Boldyrev says. "But then we started rethinking that when we were exploring the possibility of new planar boron and all-metal clusters."

It turns out aromaticity is crucial to describe the electronic structures of these new compounds. Boldyrev and others are showing that traditional π -electron delocalization involving p-orbital electrons as originally defined in molecules such as benzene is too restrictive. Aromaticity and antiaromaticity can be extended to also include σ -, δ -, and φ -types of bonding that can involve s, p, and/or d atomic orbitals, an idea he described at ICCB 2016. There's also the notion of multiple aromaticity, where two types of aromaticity, say σ and π , can be at work in the same molecule.

Not everyone agrees with the extended use of aromaticity. Some researchers have suggested keeping aromaticity as a term to describe just benzene and its derivatives, or to

describe just π systems and using some other description for all the other cases, Boldyrev says. Others have argued for abolishing aromaticity and just broadly adopting the idea of delocalized bonding. "Chemists tend to be too scientifically conservative and are resistant to change," Boldyrev states. "What is important is that we now have a zoo of aromaticity, and no matter which way you view it, we need to think about how we might use this new information."

Exploring these novel ways to describe chemical bonding and trying to make sense of them are why Alexandrova and Boldyrev started the ICCB series. "Chemists cannot talk to each other or say anything about structure, stability, or reactivity without chemical bonding," Boldyrev says. "Just think for a second: What if atoms could not form chemical bonds?"

"That is why we want to continue to bring researchers together from different disciplines of chemistry," he adds, "to help define or redefine chemical bonding, decide how we should investigate the concept, and determine how we should teach it."

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