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C&EN

CHEMICAL & ENGINEERING NEWS

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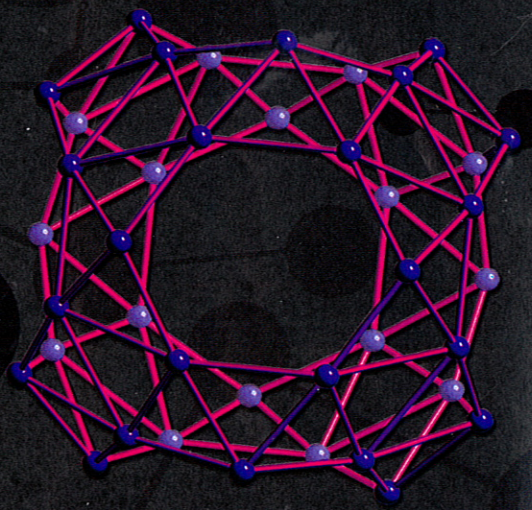
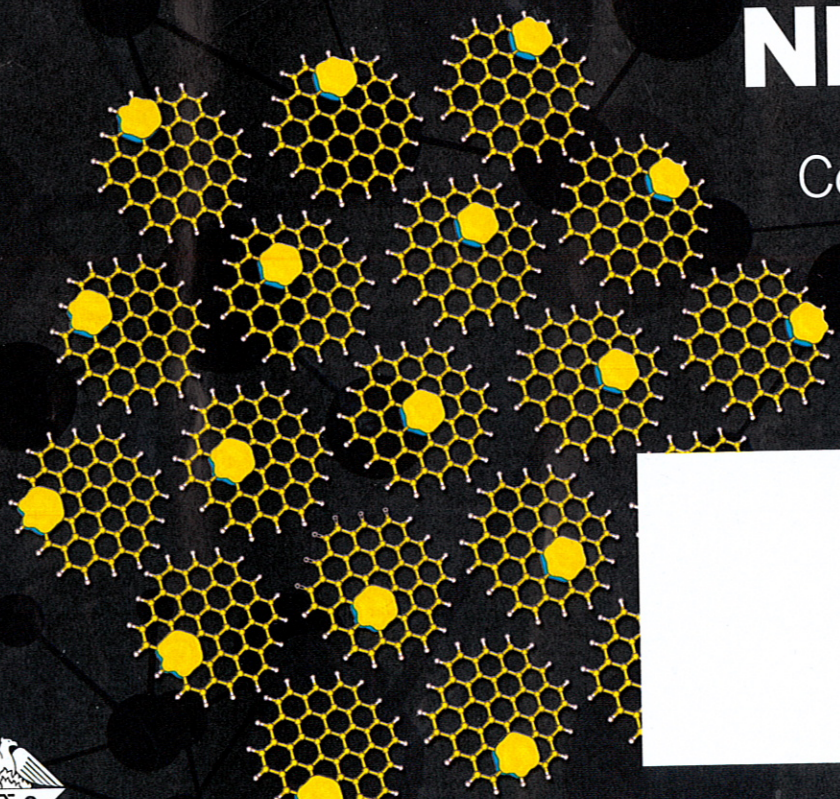


MAKING NEW BONDS

Computational models expand to broader applications **P.10**



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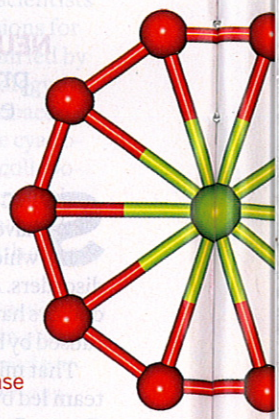
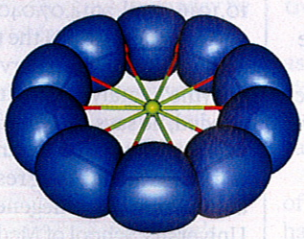
PUSHING THE LIMITS OF CHEMICAL BONDING

Conference highlights how computational and experimental chemists are applying **BONDING MODELS** to more complex systems

STEPHEN K. RITTER, C&EN WASHINGTON





NANOWHEEL Chemists used the AdNDP theoretical model to calculate the bonding orbitals for TaB_{10}^- (left), an observed gas-phase planar cluster.

COURTESY OF ALEXANDER BOLDYREV

CHEMICAL BONDING "is the heart of chemistry," according to Alexander I. Boldyrev, a chemistry professor at Utah State University who spends his time thinking about how molecules are put together. "But it is still not well-defined. We need to develop the breadth of the concept and make it as rigorous as we can, yet as simple as we can, so it is more powerful and more useful."

Boldyrev put that challenge to a group of some 50 of the world's leading experts on chemical bonding. The occasion was the opening session of the International Conference on Chemical Bonding, which was held on the Hawaiian island of Kauai during the final week of July. It's a meeting Boldyrev helped start last year to bring theoreticians, spectroscopists, and experimentalists together to forget business as usual and think about branching further out into underexplored fields in bonding such as biochemistry and materials science.

Chemists have developed many bonding models over the years in trying to comprehend the tussle between attractive and repulsive forces that hold atoms together in molecules. These models help researchers visualize changes in atomic and molecular orbitals that give rise to the many types of bonds.

Armed with knowledge of bond energies and other parameters, chemists can better orchestrate chemical reactions, determine how biomolecules respond to myriad chemical signals in the body, and monitor materials to see how they answer to external forces such as light or an applied current or magnetic field.

The end goal, Boldyrev emphasized, is the ability to better understand chemical behavior and advance the design and synthesis of chemicals and materials.

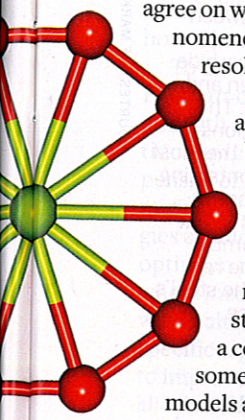
Wasting no time, Frank A. Weinhold of the University of Wisconsin, Madison, led off the conference by asking an often-repeated question: "What is a hydrogen bond?" It's a question fraught with controversy that Weinhold nevertheless feels compelled to pursue.

H-bonds give water its room-temperature liquid properties, lower or raise energy barriers and thus speed or slow reactions, and hold together the three-dimensional shapes of DNA, proteins, and synthetic materials such as some types of polymers. Better understanding of these weak interactions could enable chemists—in particular those in pharmaceutical research—to use H-bonding as a catalyst design tool or to design drugs for better interactions with their targets.

But current chemical bonding descriptions for H-bonds leave a lot to be desired, Weinhold believes. "The dipole-dipole concepts that fill current textbooks and are used for molecular dynamics simulations

& MORE ONLINE **How would you explain a bond?** Check out bonding specialists' descriptions at http://cenm.ag/explain.

of H-bonding are inadequate," he said. Still, just mentioning H-bonding raises the dander of many bonding specialists who can't agree on whether it is a true bonding phenomenon or not. Weinhold would like to resolve the issue once and for all.



An H-bond is typically described as a weak electrostatic attraction between an electronegative atom or a polar molecule and a hydrogen atom that is covalently bonded to an electronegative atom, typically oxygen or nitrogen. The interaction is not strong enough to be considered a conventional covalent bond, but some scientists contend that bonding models as well as spectroscopic evidence indicate that H-bonds must contain some covalent character. Others think it is purely an electrostatic interaction—and not a bond at all.

To address this disparity, in 2011 a committee of the International Union of Pure & Applied Chemistry proposed a broader definition of H-bonding along with a set of criteria that can be used as evidence for H-bonds. And last year, researchers used atomic force microscopy to capture stunning images of H-bonding for the first time. The wispy lines of electron density between 8-hydroxyquinoline molecules on a copper surface lend credence to a higher level of bonding.

For his part, Weinhold created a model for a surprising class of H-bonded complexes between ions of like charge, something so unthinkable that people haven't looked for them before. These anion-anion and cation-cation interactions exhibit the characteristics of H-bonding despite the powerful opposing electrostatic forces, Weinhold said. If H-bonds still occur in these complexes, he reasoned, there must be some type of covalent interaction involved.

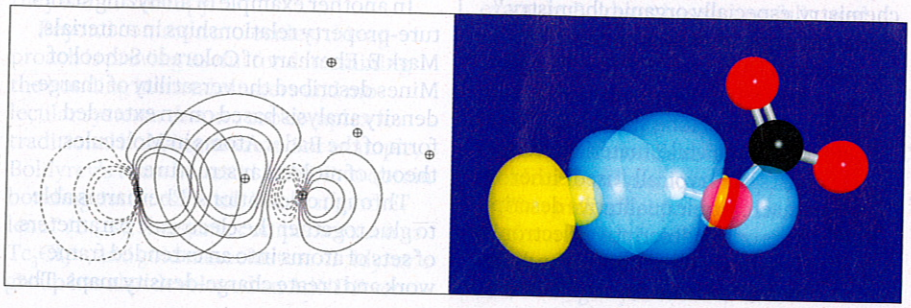
Weinhold used the Natural Bond Orbital analysis method he developed to analyze potential energy curves for the ion-ion interactions. Natural bond orbitals are designed orbitals with properties intermediate to the atomic orbital properties of atoms and the combined molecular orbitals of molecules. They are used to calculate the distribution of electron density and spot bonds in molecules.

To test his idea, Weinhold calculated the interactions between fluoride (F^-) and bicarbonate ($HOCO_2^-$). It seems improbable, he said, but short-range resonance-type covalent charge-transfer interactions between the anions overcome the long-range electrostatic opposition expected between ions of like charge. The small net bond energy observed signifies that there is a bonding interaction holding the atoms together. And the complex formed satisfies all the accepted criteria for authentic H-bonding, Weinhold said. Cation-cation H-bonded complexes, such as hydronium ion with protonated aminomethanol, are also feasible.

"THESE ANTIELECTROSTATIC H-bond complexes may finally put to rest the superficial quasiclassical conceptions of H-bonding and other resonance-type phenomena that have too long held sway in the molecular and supramolecular sciences," Weinhold concluded.

"Weinhold identifies, likely correctly, that H-bonds can exist between anions," noted Martin P. Head-Gordon of the University of California, Berkeley, who also studies H-bonding. The H-bonded dianion complexes are not the overall (global) energy minimum, which would represent infinitely separated anions, Head-Gordon noted. But they do represent a local energy minimum that is trapped from reaching complete dissociation by a large enough barrier so that the H-bonded complexes could possibly be observed experimentally.

But Head-Gordon took friendly



FRANK WEINHOLD

NEGATIVE H-BOND These calculated 2-D contour and 3-D overlap diagrams depict unexpected $F^-\cdots HOCO_2^-$ antielectrostatic hydrogen bonding.

BONDING NUGGETS

These digests highlight a selection of the research presented during the International Conference on Chemical Bonding.

C_2 Stays Single

Thom H. Dunning Jr.
Pacific Northwest National Laboratory

Dunning related how generalized valence bond theory, which draws on properties of both atomic orbitals and molecular orbitals, provides a simple yet richer description of bonding than molecular orbital theory alone for diatomic molecules such as C_2, N_2, and P_2 and hypervalent molecules such as PF_5 and SF_6. In C_2, for example, Dunning explained that bonding might best be viewed as only a single bond, rather than involving multiple bonding as previous models have suggested. The remaining six valence electrons reside in the leftover carbon orbitals in a high-spin coupled state.

B_{40} Fullerene

Lai-Sheng Wang
Brown University

B_{40} fullerene

LAI-SHENG WANG

Wang reviewed the progress his group has made using computational studies supported by photoelectron spectroscopy to analyze gas-phase all-boron clusters. Molecules with up to 24 boron atoms form planar species, after which larger molecules start forming 3-D structures. For example, Wang and his colleagues recently discovered B_{40}, an unprecedented all-boron fullerene-like cage molecule, which is a potential semiconducting material.

Two-Prong Analysis

Helmut Schwarz
Technical University of Berlin

By combining computational chemistry and mass spectrometry, Schwarz has been breaking new ground in understanding the activation sites of heterogeneous catalysts in gas-phase reactions. Mass spectrometry on isolated species provides a means of probing the energetics and kinetics of reactions in an unperturbed environment, which is typically not possible in solution-phase reactions. The approach allowed Schwarz to study the role of electron density in intermediates of metal-mediated C–C bond forma-

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BONDING NUGGETS CONTINUED

tion and oxygen-centered radicals in C–H activation.

Phase-Switch Bonding

Matthias Wuttig
RWTH Aachen University, Germany

Phase-change materials such as $Ge_2Sb_2Te_5$ rapidly switch between amorphous and crystalline states, changing their optical and electrical properties and making them useful for optical data storage. Wuttig showed that the crystalline state is characterized by resonant, directional covalent bonding rather than delocalized bonding as in the amorphous state. This information can be used to create phase diagram "treasure maps" for selecting alloy compositions in the design of new phase-change materials.

Sturdy Microalloys

William A. Goddard
California Institute of Technology

By studying the multicentered bonding in boron's many polymorphs, Goddard has been able to design boron alloys with carbon, oxygen, and other elements. For example, B_4C is a known material that is very hard. But it's also very brittle, which prevents its use in engineering applications. Goddard described how his team has used computational methods to explore the mechanism of the structural deformation that leads to B_4C's brittleness. The researchers are designing microalloys with improved properties by further adding hydrogen, silicon, or nitrogen atoms, with silicon looking the most promising.

What's the Highest Oxidation State?

Jun Li
Tsinghua University, China

Oxidation state is a central concept in chemistry, and the question of highest possible oxidation state has long been a controversial topic. For elements in neutral compounds, the highest state is thought to be 8+, which occurs in some transition-metal compounds, such as RuO_4. Li showed through new calculations that, despite their f electron shell, such high oxidation states are not stable in actinides. Because of mass-driven relativistic effects leading to contracted 5f electron

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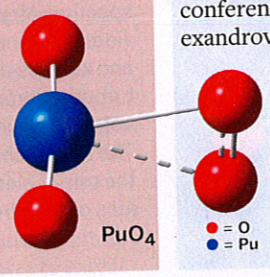


INORG. CHEM.

exception to Weinhold's argument that the possible existence of these ionic H-bonds shows "the essential irrelevance of electrostatic contributions to H-bonding." He also disagreed that Weinhold's results should lead to "skeptical reassessment" of energy decomposition analysis of H-bonding, a method Head-Gordon uses that offers partial support to the electrostatic view.

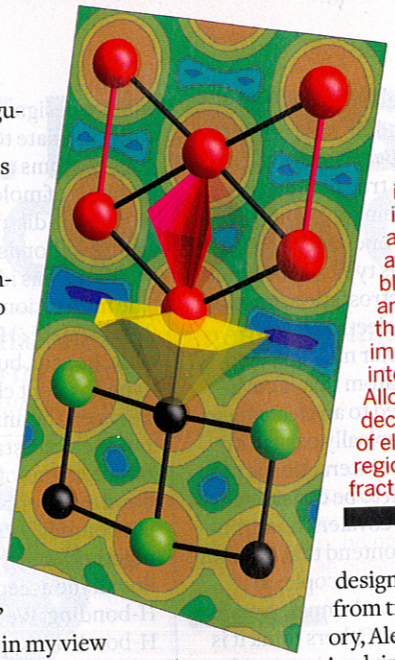
"The fact that like charges repel explains the overall minimum where there is no H-bond," Head-Gordon added. "But in my view it does not necessarily mean electrostatics are inessential." In fact, good energy decomposition analysis methods, which split complex bonding interactions up into permanent and induced electrostatics, dispersion, and charge-transfer contributions, can provide support for or contradict Weinhold's assertion about electrostatics, Head-Gordon told C&EN.

Weinhold's view that electrostatics are also not relevant for types of H-bonding beyond those found in ion-ion interactions is still open for debate, Head-Gordon suggested. On the basis of his own research, Head-Gordon thinks H-bonding typically has contributions from both charge transfer and electrostatics, with the relative importance of each varying, depending on details of the system. "It will be fascinating to see where this goes over the next few years," he said.

As debate about H-bonding continued off-line, other chemists took the floor to discuss advancing the synergy between electronic structure calculations and studying the properties of catalytic surfaces and solid-state materials.

"Chemical bonding theory traditionally has been in the realm of molecular chemistry, especially organic chemistry," conference cofounder Anastassia N. Alexandrova of UCLA told C&EN. "But that topic is perhaps considered archaic and long since done."

Meanwhile, materials scientists have typically used either macroscopic qualitative descriptors or nondescriptive electronic band structure concepts and not benefited from the rationale and design principles that arise from traditional bonding theory, Alexandrova explained.



BOND BUNDLES This charge-density map depicts a cross section of the interface between iron (red atoms) and a metal-carbide additive (green and black) in steel. The red and yellow regions in the middle are the most important in controlling interfacial strength. Alloying elements that decrease the number of electrons in the red region improve the steel's fracture resistance.

COURTESY OF MARK EBERHART

Applying bonding theory to solid-state materials has been underexplored. But even as capable models have become available, they are not garnering much attention. "Breaking this stagnation is one of the conference's goals," she said.

To set an example, Alexandrova's group is collaborating with Mark Saeys at Ghent University, in Belgium, to study the chemistry of unexpected square-planar carbon species that form on cobalt catalyst surfaces treated with synthesis gas. The tetracoordinated carbon takes on the square-planar geometry as opposed to the typical tetrahedral structure, and the aromaticity of Co_4C building blocks drives formation of nanocluster islands on the catalyst surface that facilitate the reaction.

In industrial reactions, catalyst surfaces often undergo massive reconstructions as the catalytic sites form and re-form via self-organization. Saeys and Alexandrova, in partnership with Shell, are now able to understand the unusual bonding leading to surface reconstruction of commercial cobalt catalysts. This bonding insight could lead to improved catalyst stability and selectivity in the Fischer-Tropsch synthesis of fuels and chemicals.

In another example of analyzing structure-property relationships in materials, Mark E. Eberhart of Colorado School of Mines described the versatility of charge-density analysis based on an extended form of the Bader Atoms in Molecules theory of molecular structure.

Through calculations, Eberhart is able to glue together the electronic parameters of sets of atoms into an extended framework and create charge-density maps. The

topology of these maps provides chemical information, with peaks (atoms), valleys (nonbonding areas), and ridges (bonding areas) illustrating where bonds exist and how reactive these bonds might be.

To demonstrate how the process works, Eberhart described an analysis of high-strength steel alloyed with dispersions of titanium carbide to determine the propensity of metal-carbide interfaces in the material to fracture and fail. The topologies enable Eberhart's team to determine optimum positions in the material's lattice where inserting other metals such as nickel would alter the number of electrons in specific regions and thereby allow them to improve the adhesive properties of the alloys. "This capability will be particularly beneficial in solids," Eberhart said, "where the nature of charge-density evolution associated with even simple processes, such as fracturing, is understudied."

YET ANOTHER bonding model discussed at the conference is Adaptive Natural Density Partitioning (AdNDP), which was developed by Utah State's Boldyrev and his colleagues. An extension of Weinhold's Natural Bond Orbital approach, AdNDP is geared toward preserving the classical Lewis two-center, two-electron bonding picture as much as possible. But it relies extensively on multicentered, two-electron delocalized bonding.

When analyzing a molecule, the researchers first localize electron pairs in two-center bonds or as lone pairs on single atoms. They then place the remaining electron pairs in multicentered bonds localized on the fewest atoms possible, which could be as many as all the atoms in the system. In doing so, the method invokes both σ and π aromatic and antiaromatic bonding.

"For me, a chemical bond is no longer an electron pair sitting between two atoms," Boldyrev said. "It is more simply a two-electron blob that can connect two, three, five, or more atoms. We allow the pairs to run over whatever part of the molecule they want to occupy."

Beyond common molecules, this approach is proving useful for determining the bonding in metal clusters and molecular systems that are too complex for traditional bonding models. For example, Boldyrev's team has used AdNDP to obtain bonding patterns in "all-boron naphthalene" (B_{16}^{2-}), inorganic complexes such as $Tc_3Cl_9^{2-}$, and gold nanoclusters. Boldyrev's group has also developed an AdNDP version for extended molecular structures in bulk materials and used it to analyze the bonding in graphene, all-boron planar sheets, MgB_2 with alternating magnesium and boron layers, and intercalated inorganic materials such as Na_8BaSn_6.

"I believe this is a method that eventually will enable us to draw structures of solids by hand based on their formula, as we do now for organic molecules," UCLA's Alexandrova speculated. "From there, we might eventually arrive to the intuitive interpretation of chemical reactivity and other properties of solid materials."

That is exactly where Boldyrev hopes the method will lead. "Like physicists who want a unified theory to explain all matter, we chemists would like a unified bonding theory that works seamlessly for solids, gases, and solutions and helps explain the behavior of organic and inorganic compounds, biomolecules, and nanomaterials," Boldyrev said.

Chemists currently must solve structural problems for different types of compounds by sifting through and choosing among different models, he explained. "The Lewis electron-pair model is simple, easy to understand, and teach," Boldyrev said. "However, it quickly runs into problems if we go beyond simple molecules. What is the Lewis structure for the tetrahedral Au_{20} cluster, the molecular TaB_{10}^- nanowheel, or the FeSMo cluster that serves as the cofactor of nitrogenase?"

Molecular orbitals can be obtained for any chemical compound, Boldyrev continued. But they are delocalized over the whole molecule, which is not always descriptive of the actual bonding, and get very complicated as the number of electrons in the system increases.

Weinhold's Natural Bond Orbital method, Bader's Atoms in Molecules approach, and the AdNDP model are all headed toward a unified model, Boldyrev thinks. For example, Boldyrev has successfully used AdNDP to decode the bonding in Au_{20} and TaB_{10}^-, though his group hasn't yet resolved the bonding in the nitrogenase cofactor. But it should only be a matter of time before bonding models evolve to tackle that problem as well as more complex ones.

That makes Boldyrev optimistic about the future of his field. "I don't think chemists are abandoning the concept of chemical bonding anytime soon." ■

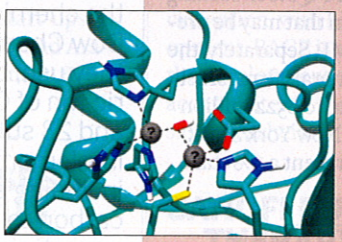
BONDING NUGGETS CONTINUED

shells, actinides such as plutonium tend to form superoxo (O_2^-) rather than oxo (O^{2-}) complexes and max out at an oxidation state of 5+, such as in PuO_4.

Enzyme Metal Mysteries

Crystal E. Valdez
University of California, Los Angeles

When it comes to designing catalysts, chemists often look to enzymes as models. But enzymes don't always work efficiently outside their cellular environment, so chemists often tweak enzymes to make artificial versions with the appropriate metal charge and size, coordination geometry, and redox potentials needed for chemical reactions. Valdez described using a new approach, quantum mechanics/discrete molecular dynamics (QM/DMD) simulations, to explore what makes a difference when switching one metal for another in metalloproteins. In two related natural amide hydrolases (one shown) different metals—zinc versus nickel—are used to catalyze similar reactions proceeding through identical mechanisms.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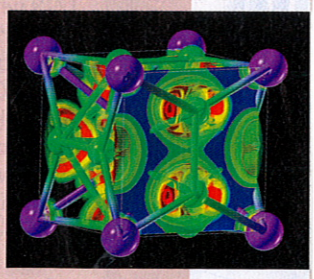
Predicting Crystal Structures

Artem R. Oganov
Stony Brook University, SUNY

Researchers have long wished for the ability to predict crystal structures of materials before they are synthesized, which could significantly accelerate chemical discoveries. Oganov described a computational tool he developed to fulfill that wish. Called USPEX, the method includes an evolutionary algorithm to search through multidimensional energy landscapes at different temperatures and pressures to find stable combinations of selected elements. Oganov's group has used USPEX to predict a new phase of boron (γ-B) and an insulating and optically transparent form of sodium, among other materials. The researchers have prepared some of the materials, including salt with unusual ratios of sodium and chloride, such as $NaCl_3$ shown.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