UCLA

UCLA Previously Published Works

Title

4th International Conference on Chemical Bonding.

Permalink

<https://escholarship.org/uc/item/7nk929b5>

Journal

The journal of physical chemistry. A, 120(47)

ISSN

1089-5639

Authors

Ugalde, Jesus M
Bultinck, Patrick
Bickelhaupt, F Matthias
et al.

Publication Date

2016-12-01

DOI

10.1021/acs.jpca.6b11179

Peer reviewed

4th International Conference on Chemical Bonding

The fourth International Conference on Chemical Bonding (ICCB) was held in Kauai Island, Hawaii, from July 14th to 26th, 2016. Sixty speakers from 15 different countries around the world gathered on this beautiful island for a multidisciplinary conference organized by Profs. Alexander Boldyrev and Anastassia Alexandrova, and sponsored by SCM - Software for Chemistry & Materials, *The Journal of Chemical Theory and Computation*, and the Chemistry & Biochemistry Departments of Utah State University and the University of California, Los Angeles. This brief viewpoint article summarizes the themes and objective of the ICCB Conference series. A full list of the presentations with their corresponding abstracts can be downloaded from the Conference web page: <http://www.chem.ucla.edu/~ana/ICCB2016.html>

The link between electronic structure and properties is, of course, central to chemistry. Nowadays it is possible to perform first principles calculations or electronic spectroscopy experiments on chemical systems, to probe their electronic structure and derive sound reasons for their observed properties. However, instead of doing this for each and every molecule we encounter, we instead generalize our observations into the language of chemical bonding, a set of qualitative concepts that allows chemists to converse efficiently with one another, teach students, and create and pass ideas quickly. It would take a good chemist only seconds to go from drawing a Lewis structure of a molecule to stating its properties with fair accuracy. The theory of chemical bonding ultimately gives chemists a huge advantage in understanding and designing matter. As an undisclosed UCLA fellow once said: “Without chemical bonding, we all still would be solving the Schrödinger equation for H_2 on cave walls; we would have no polymers, no modern drugs, and no detergents, to name a few”. Despite the apparent utility of the language of chemical bonding, it is incomplete: for many interesting systems, such as alloys, catalytic surfaces, nanoparticles, and clusters (including such long-known clusters as Fe–S and FeMoCo in biology) the theory is just not yet developed. In other words, we are not ready to draw an appropriate analogue of a Lewis structure, and from there, start speaking about properties. It is therefore of paramount interest to build this theory and start using it in the design of the cutting-edge materials for the future. This is why scientists gather on the Pacific island of Kauai, in addition to enjoying its legendary beauty.

The ICCB series is devoted to bringing together theorists and experimentalists, and to putting the fuzzy concept of the chemical bond onto firmer grounds. From the theoretical perspective, developing computational tools to make chemical bonds quantitatively accurate is the fundamental key to reach the ultimate objective of allowing the discovery of new molecules, functional materials, and homogeneous and heterogeneous catalysts and understanding and predicting their properties in an intuitive and quick manner. Experimentalists willing to take advantage of these tools come to unveil novel chemical bonding patterns and observable/measurable properties in all kinds of materials. An important observation

that could be made during the ICCB series is the synergy between the very diverse subdisciplines in the field of chemical bonding. One example, of the many fascinating contributions, is the bonding between nanoparticles that behave as very large atoms that are held together by DNA linkers playing the role of chemical bonds (Park, S. Y.; Lytton-Jean, A. K.; Lee, B.; Weigand, S.; Schatz, G. C.; Mirkin, C. A. DNA-programmable nanoparticle crystallization. *Nature* **2008**, 451, 553–556). This topic is relevant for designing functional molecular materials but it also provides opportunities to probe fundamental bonding concepts from the realm of small molecules composed of regular atoms, such as hypervalence.

Although the fundamental core of the meeting stays the same, the focus on different kinds of exciting systems shifts from year to year. In 2016, the prominent themes included chemical bonding at interfaces, in clusters, nanoparticles, 2D materials, and materials with outstanding mechanical properties. Here, we will highlight some of these themes.

FUNDAMENTALS

Chemical bonding lies at the heart of virtually every model used in chemistry to classify and even predict new compounds. Much of the classification relies on the analysis of the nature of the chemical bonds in these new compounds. However, given that the chemical bond is not a uniquely defined object from the perspective of quantum mechanics, its nature remains to some extent elusive especially in novel classes of compounds where the H_2 paradigm does not apply so easily anymore.

The key importance of a model for the nature of the chemical bond is clear from the attention devoted to such a model in several lectures. Three groups of methods that go back to the earliest days of quantum mechanical manifestations of the chemical bond, again played a major role in the 2016 conference. Miroslav Kohout (Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany) focused on the direct manifestation of chemical bonding in position space through sets of descriptors that can be used for the classification of bonding. Such an approach goes beyond the up-to-now more often used orbital approach and also beyond the simple depiction of electron densities. Clémence Corminboeuf (EPFL Lausanne, Switzerland) showcased the Density Overlap Region Indicator (DORI) as a position space based descriptor that reveals different types of bonding and noncovalent interactions.

In a second line of approaches, the focus lies on the energetic aspect of chemical bonding. Why does the energy lower when atoms link up on the basis of the variation principle? A series of presentations at ICCB2016 focused on energy decomposition analyses (EDA). A feature of these methods is that the difference between the energy of a structure and that of its composing fragments is decomposed in chemically relevant parts by stepwise releasing constraints going from the fragments to the final structure. Klaus Ruedenberg and Mark S. Gordon (Iowa State University, Ames, IA, USA) presented

Published: November 18, 2016

new EDA methods based on an unbiased and basis-set independent transformation of the molecular wave function in terms of configurations generated from “quasi atomic” orbitals whereas Célia Fonseca Guerra and Matthias Bickelhaupt (Vrije Universiteit Amsterdam, The Netherlands) gave new evidence of the suitability of their own chemically already very well tested scheme (Bickelhaupt, F. M.; Baerends, E. J. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15, pp 1–86) for chemical bonding analysis.

Third, there remains great promise in Valence Bond Theory (VBT) based analysis of the chemical bond. Yirong Mo (Western Michigan University, Kalamazoo, MI, USA) analyzed the nature of electron conjugation from a VBT perspective, and Alexander Sax (Karl-Franzens-Universität Graz, Austria) used orthogonal VBT to examine the role of spin in strong covalent bonding and weak noncovalent bonding.

Whereas chemical bonding is most often seen as an interaction between two or more atoms, aromaticity and its nature is still more elusive. Akin to the chemical bond departing from its H_2 paradigm, aromaticity is now a concept used far beyond benzene as its archetypal example. It is being used for compounds containing several cyclic systems and even for metallic systems. As benzene features many special properties, researchers now use (subsets of) these properties to classify supposedly aromatic molecules and—in some cases—to quantify a degree of aromaticity. Among the methods used at ICCB2016 are magnetically induced current density pathways, as discussed in detail by Dage Sundholm (University of Helsinki, Finland). Alternatively, some methods like adaptive natural density partitioning (AdNDP) as used by Alexander Boldyrev may be used for both chemical bonds as well as for more delocalized systems.

Patrick Bultinck (Ghent University, Belgium) urged double-checking the value of new bonding models using *ex absurdo* tests. Hamiltonians are used that force some trend in, e.g., specific observables and the accompanying energetic data are confronted with what the bonding model gives. If these sets of computed and expected data do not agree, the model needs further refining.

Some of the seemingly eternal applied questions were also raised at the meeting. For example, Jun Li (Tsinghua University, China) discussed the highest possible oxidation state of lanthanides. The highest known oxidation state in the Periodic Table is +VIII, as exemplified in tetra-oxides MO_4 ($M = Ru, Os, Ir, Xe$) and +IX in the IrO_4^+ cation. The chemistry of lanthanides ($Ln = La-Lu$) is dominated by the low-valent +III or +II oxidation state due to the chemical inertness of the valence 4f electrons. The highest known oxidation state of the whole lanthanide series is +IV for Ce, Pr, Nd, Tb, and Dy. The talk reported the finding of the first pentavalent lanthanide oxide species, PrO_4 and PrO_2^+ , featuring Pr(V) (Zhang, Q.-N.; Hu, S.-X.; Qu, H.; Su, J.; Wang, G.-J.; Lu, J.-B.; Chen, M.-H.; Zhou, M.-F.; Li, J. Pentavalent Lanthanide Compounds: Formation and Characterization of Praseodymium(V) Oxides. *Angew. Chem. Int. Ed.* **2016**, *55*, 6896–6900).

■ CLUSTERS AND NANOPARTICLES

Small clusters constitute a vast playground for chemical bonding pursuits. Indeed, a wealth of unprecedented bonding phenomena can be found in these species of size just below nanoparticles and of nonconventional stoichiometries. Boron clusters occupied a prominent stage at ICCB. Lai-Sheng Wang

(Brown University, Providence, RI, USA) gave an insightful overview of the propensity of boron to form (quasi)planar structures due to both σ - and π -electron delocalization. His group led the experimental part of the effort, namely, the photoelectron spectroscopy measurements. The planar B_{36} cluster, which features a hexagonal hole as a consequence of its intrinsic electron deficiency was shown, suggesting that boron sheets (with inner holes), named *borophenes*, could be viable. The B_{40} cluster is the biggest surprise: it features two nearly degenerate isomers, a quasiplanar one with two hexagonal holes, and a cage-like one. Remarkably, in the neutral cluster, the cage structure is the most stable isomer, being the first all-boron fullerene, named *borospherene*, ever observed (Zhai, H.-J.; Zhao, Y.-F.; Li, W.-L.; Chen, Q.; Bai, H.; Hu, H.-S.; Piazza, Z. A.; Tian, W.-J.; Lu, H.-G.; Wu, W.-B.; Mu, Y.-W.; Wei, G.-F.; Liu, Z.-P.; Li, J.; Li, S.-D.; Wang, L.-S. Observation of an all-boron fullerene. *Nat. Chem.* **2014**, *6*, 727–731). The remarkable bonding aspect of B_{40} is that, unlike in the carbon relative, C_{60} , there is not a single 2 center–2 electron B–B bond in this cage; all bonds are multicenter. The theme of borospherenes was continued by Si-Dian Li (University of Shanxi, China). The *in silico* examination of novel borospherenes, B_{36}^{4-} , B_{37}^{3-} , B_{38}^{2-} , B_{41}^+ , and B_{42}^{2+} , both naked and doped with two-electron donors, Li_2 and Ca, showed large structural fluctuations above room temperature for the clusters with an odd number of boron atoms, and higher stability of cages with an even number of borons.

Even the more traditional B-containing systems still hold surprises. Alexander Spokoyny (University of California, Los Angeles, USA) talked about icosahedral boron clusters as tunable building blocks for the interaction with light, and for creating chromophores and photosensitizers. Complexes where the B_{12} cluster replaces a transition metal can be photocatalytic, but surprisingly, instead of metal-to-ligand charge transfer, upon photoexcitation, the ligated B_{12} complex undergoes the ligand to boron charge transfer. The LUMO of B_{12} is delocalized over the entire cluster, and as a result the excited state of the system is stabilized. The hole left behind in the ligands matches the energy of the HOMO of an olefin, which then transfers an electron to the catalyst. Photoinduced polymerization is thus initiated (Messina, M.; Axtell, J.; Wang, Y.; Chong, P.; Wixtrom, A.; Kirlikovali, K.; Upton, B.; Hunter, B.; Shaafat, O.; Khan, S.; Winkler, J.; Gray, H.; Alexandrova, A. N.; Maynard, H. D.; Spokoyny, A. M. Visible Light-Induced Olefin Activation Using 3D Aromatic Boron-Rich Cluster Photooxidants. *J. Am. Chem. Soc.* **2016**, *138*, 6952–6955).

Jesus Ugalde (Euskal Herriko Unibertsitatea, Basque Country) discussed in-depth the electronic structure of ambiphilic, stoichiometric bimetallic AuAl hollow clusters, both naked and passivated. The possibility of encapsulating hydrogen was also investigated, and predicted to be very unlikely for Born–Oppenheimer molecular dynamics simulations predicted a very short lifetime (~ 11 ps) for the encapsulated species. Passivation, preserving the structure of the naked cluster, by ionic liquids was reported to be feasible.

Theodore Betley (Harvard University, Boston, MA, USA) in his provocative “reality check” talk, discussed the bonding interactions responsible for the stabilization, at room temperatures, of high-spin ground-states in a number of Fe–S clusters. He described how closely spaced the high-, low-, and in-between-spin states are, how single-molecule magnetic behavior in high symmetry clusters can be found, and how a unique

chemical reactivity arises from these electronic properties. Indeed, these clusters that resemble some of those found in biological systems are among the most relevant and hard-to-conquer frontiers, and have been found to be very challenging both for quantum chemistry, and for qualitative theories of bonding.

■ MATERIALS AND INTERFACES

Arguably, the realm of materials is one of the least established avenues for the theory of chemical bonding. Not only is it less conventional to discuss bonds in solids, the computational methodology is often inadequate to address functional materials of certain classes. Still with the advances being made, from one year to the next, the materials portion of ICCB grows.

One of the timeliest developments in the theory side of things is correlated electronic structure methods for treating materials. The working horse of computational materials chemistry is Density Functional Theory (DFT). However, it is well-known that DFT breaks down sooner or later for situations of strong static and dynamic electron correlation, or nonadiabatic electron–phonon coupling. Dominika Zgid (University of Michigan, Ann Arbor, MI, USA) presented her Green's function methods for treatment of strongly correlated solids. She then described an embedding framework for general multiscale methods free from empirical parameters. A strongly correlated subsystem is embedded into a many-body correlated field generated by weakly correlated electrons present in the system. With such a methodology, one can get the correct description of materials that are challenging for DFT but of interest to future device technologies, such as perovskite solar cells and batteries.

John Tse (University of Saskatchewan, Saskatoon, Canada) discussed chemical bonding in materials under high pressure. To avoid Pauli repulsions, the valence electrons in materials under pressure are “promoted” to diffuse unoccupied atomic orbitals that then participate in bonding of completely new types. For group I and II elements, there are more orbitals available, thus often resulting in 2D layer structures. In some cases, multicenter bonds are manifested as electrides. Tse illustrated this with examples of simple hydrides and halides, binary alloys, and amorphous-to-amorphous structural transformations in metallic glasses.

The promiscuous bonding nature of boron, as an element capable of localized and delocalized bonding, and also of covalent and ionic bonding, was brought up again in the materials sessions. Tadashi Ogitsu (Lawrence Livermore National Laboratory, USA) showed how this behavior results in the appearance of many allotropes of bulk boron. P. J. Robinson and Anastassia Alexandrova (University of California, Los Angeles, USA) showed how that plays out in bulk borides, which, due to the metal–boron bonding of various types, can exhibit such interesting properties as anisotropy of hardness and mixed valency.

An intermediate size regime of nanoparticles made a splash at ICCB-2016. Victor Klimov (Los Alamos National Laboratory, Los Alamos, NM, USA) reported on the photophysics of $\text{CuInSe}_x\text{S}_{2-x}$ (CISeS) quantum dots. These have emerged as a feasible, nontoxic alternative to the more familiar CdSe quantum dots. Klimov's spectroscopic studies of CISeS include magneto-optics, spectro-electrochemistry, and various time-resolved photoluminescence and transient absorption spectroscopies. He unveiled the vital role of the persistent intragap states that define the optical properties of CISeS quantum dots

and lead to famous carrier multiplication (Klimov, V. I.; Schaller, R. D. High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion. *Phys. Rev. Lett.* **2004**, *92*, 186601), with many cutting-edge applications becoming possible. This exciting field leaves us with more questions than answers when it comes to chemical bonding. What are those intragap states? Are they defects? Where are they located in the dot? How do defects couple to each other? How important is quantum confinement in the observed intragap photophysics? Attendees such as Klimov are very welcome at the conference, as they open additional fields for the ICCB community to plow.

■ BEYOND THE CONFERENCE ROOM

One avenue of immediate relevance to the development of theory of chemical bonding is university teaching. In fact, as new aspects of the theory of the chemical bond are being developed, some of us immediately apply the new language in undergraduate classrooms. However esoteric and shocking new concepts may sound to some (Ritter, S. K. Aromaticity For All. *Chem. Eng. News* **2015**, *93*, 37–38), the young minds absorb them readily and with ease. For example, for a long time aromaticity was restricted to π -aromaticity in hydrocarbons. However, the concept is broader, and now we think of σ - and δ -aromaticity as well, thanks to the seminal works (Mercero, J. M.; Boldyrev, A. I.; Merino, G.; Ugalde, J. M. Recent developments and Future Prospects of All-Metal Aromatic Compounds. *Chem. Soc. Rev.* **2015**, *44*, 6519–6534) of one of the ICCB organizers, Alex Boldyrev (Utah State University, USA). Indeed, aromaticity can be seen as simply a phenomenon when bonding in a cyclic system is too electron deficient to connect all participating atoms with 2 center–2 electron bonds, and thus it becomes delocalized; if then degenerate orbitals get evenly filled, high symmetry, special stability, and resonance emerge. It does not have to be constrained to π -systems of molecular orbitals, where atomic orbitals of all participating atoms use two lobes for the π -overlap. Indeed, it is just as natural for orbitals of the σ -type (where one lobe from each atomic orbital participates in the overlap), or the δ -type (where three lobes per atom overlap forming molecular orbitals) to exhibit this effect. Historically, we started from π -aromaticity, because the thinking began from C. If instead we would begin our exploration from Hf, we would find δ -aromaticity first, whereas if we would consider H_3^+ first, then σ -aromaticity would be the rightful predecessor of all other types of aromaticity. How bizarre would it be if today, of all the machines containing an engine we would accept only the Stanley Motor steam automobile? Though it is a metaphorical analogy, it nicely expresses that tradition can be a hindrance to progress. In contrast, students adapt quickly to new ideas and technologies. In General Chemistry classes of many Universities around the world the idea of aromaticity being σ -, π -, and δ - is accepted naturally, and it is immediately picked up and applied by students to predicting symmetries, stabilities, Jahn–Teller geometric distortions, etc. in systems beyond hydrocarbons. Although we may argue about the rightfulness of the concept, it is already running with its own momentum. We should not lag behind.

The success of ICCB stems from the friendly atmosphere set by the organizers that stimulates fresh exchange of ideas and the building of bold, long-standing friendship and mutual confidence among the participants that rather sooner than later crystallizes in various forms of fruitful collaborations.

The social events of the conference series constitute an essential part of each of the Conferences. They include an informal reception the night of the first Conference day, a BBQ at the beach, and a Hawaiian show and dinner (Luau) to close the Conference. Additionally, it has become a well-established tradition to have one free day in the middle of the conference, for the participants and their families to enjoy the Island's many beauties.

At ICCB, bonding concepts get communicated across fields, with the goal of driving progress with the power of chemistry. Altogether, the developments presented and discussed at ICCB testify of the unifying power of the physical concepts featuring in modern theories of chemical bonding. The field is thriving and many more exciting developments can be expected in the coming years. ICCB could not be timelier.

Jesus M. Ugalde^{*,†,Ⓜ}

Patrick Bultinck[‡]

F. Matthias Bickelhaupt^{§,||}

Anastassia N. Alexandrova^{⊥, #, Ⓜ}

[†]Kimika Fakultatea Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC), P. K. 1072, 20080 Donostia, Euskadi, Spain

[‡]Department of Inorganic and Physical Chemistry, Ghent University (UGent), Krijgslaan 281 (S-3), 9000 Ghent, Belgium

[§]Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

^{||}Institute of Molecules and Materials (IMM), Radboud University, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

[⊥]Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States

[#]California NanoSystems Institute, Los Angeles, California 90095, United States

■ AUTHOR INFORMATION

Corresponding Author

*J. M. Ugalde. E-mail: jesus.ugalde@ehu.es.

ORCID

Jesus M. Ugalde: 0000-0001-8980-9751

Anastassia N. Alexandrova: 0000-0002-3003-1911

Notes

The authors declare no competing financial interest.