International Conference on Chemical Bonding

Technical Program

Wednesday, July 23

Arrival and registration

Thursday, July 24

Morning: Tour the table *Presiding: Anastassia Alexandrova*

8:30 –9:00 am	Alex & Anastassia - Introductory remarks
9:00 –9:30 am	Frank Weinhold (University of Wisconsin, USA) *“What is a Hydrogen Bond?”*
9:30 – 10:00 am	Judy Wu (University of Georgia, USA) *“Tuning Hydrogen Bonds with Aromaticity”*
10:00 – 10:30 am	Thom Dunning (University of Washington, PNNL, USA) *“Insights into Chemical Bonding from Generalized Valence Bond Theory”*
10:30 – 11:00 am	Helmut Schwarz (TU Berlin, Germany) *“Ménage-à-Trois: Catalysis, Mass Spectrometry and Computational Chemistry”*
11:00 – 11:15 am	*Coffee Break*
11:15 – 11:45 am	Benoît Braida (Université Pierre et Marie Curie, France) *“A Classical Valence Bond Model for Electron-Rich Hypervalent Species. Application to XeF_2, SF_n (n = 1, 2, 4), PF_5 and ClF_3”*
11:45 – 12:15 am	Lai-Sheng Wang (Brown University, USA) *“From Planar Boron Clusters to Borophenes and All-Boron Fullerenes”*

Afternoon: Bonding in materials and surfaces *Presiding: Crystal Valdez*

3:00 – 3:30 pm	William Goddard (California Institute of Technology, USA) *“Bonding, deformations, and unique properties of elemental boron and boron rich alloys”*
3:30 – 4:00 pm	Alán Aspuru-Guzik (Harvard University, USA) *“The energy for tomorrow, needs to start today: A vision for high-throughput materials discovery”*
4:00 – 4:30 pm	Matthias Wuttig (Physikalisches Institut der RWTH Aachen, Germany) *“Phase Change Materials: From Optical Data Storage to Novel Electronic Memories”*
4:30 – 5:00 pm	Ralf Tonner (University of Marburg, Germany) *“The chemical bond in periodic systems – an energy-based method for surface-adsorbate complexes”*
5:00 – 5:15 pm	*Coffee Break*
5:15 – 5:45 pm	Mark Saeys (Ghent University, Belgium) and Anastassia Alexandrova (UCLA, USA) *“Formation of nanoclusters on catalytic surfaces driven by aromatic square planar carbon”*
5:45 – 6:15 pm	Peter Schwerdtfeger (Massey University, New Zealand) *“Why is Mercury a Liquid at Room Temperature?”*
6:15 – 6:45 pm	Artem Oganov (Stonybrook University, SUNY, USA) *“Computational Materials Discovery: New Developments and Surprising Discoveries”*
07.00 – 10:00 pm	*RECEPTION at Kauai Beach Resort*

Friday, July 25

Morning: Reactivity and catalysis

Presiding: Christine Isborn

9:00 – 9:30 am	Alexander M. Mebel (Florida International University, USA) *“Theoretical Studies of the Roaming Mechanism in Cl Radical Addition-Elimination Reactions with Alkenes”*
9:30 – 10:00 am	Clémence Corminboeuf (EPFL, Switzerland) *“New Tools to Visualize and Quantify Intra- and Intermolecular Phenomena”*
10:00 – 10:30 am	Dean Tantillo (UC Davis, USA) *“Weak Interactions in Biosynthetic and Organic Catalysts — C-H•••π, C-H•••O and S•••O Interactions as Selectivity Control Elements”*
10:30 – 11:00 am	Thomas Markland (Stanford University, USA) *“The interplay of nuclear and electronic quantum fluctuations in hydrogen bond networks”*
11:00 – 11:15 am	*Coffee Break*
11:15 – 11:45 am	Crystal Valdez (UCLA, USA) *“How the electronic structure of metals contribute, and impede, metalloenzyme structure and function”*
11:45 – 12:15 pm	Stefan Vajda (Argonne National Laboratory, USA) *“Tuning Catalyst Performance via Optimizing Cluster Size, Composition and Support: The Role of in situ Techniques in Catalyst Design”*
12:15 – 12:45 pm	Kit H. Bowen, Jr. (Johns Hopkins University, USA) *“Strong, Low Barrier Hydrogen Bonds may be Available to Enzymes”*

Afternoon: Exciting Frontiers

Presiding: Thomas Markland

3:00 – 3:30 pm	Jun Li (Tsinghua University, China) *“On the Highest Oxidation State of Actinide Compounds”*
3:30 – 4:00 pm	Robert Berger (University of Marburg, Germany) *“The chemical bond and its bonds to fundamental physics research”*
4:00 – 4:30 pm	Valeria Pershina (GSI, Germany) *“Relativistic Effects on the Electronic Structure and Bonding of the Heaviest Elements”*
4:30 – 5:00 pm	Peter Weber (Brown University, USA) *“Molecular Motions in Space and Time: Structural Views of Chemical Bonding”*
5:00 – 5:15 pm	*Coffee Break*

The simplest bonded thing

5:15 – 5:45 pm	John Herbert (Ohio State University, USA) *“Theoretical Studies of the Hydrated Electron in Clusters, Bulk Water, and the Air/Water Interface”*
5:45 – 6:15 pm	Dan Neumark (UC Berkeley, USA) *“Slow electron velocity-map imaging (SEVI) of cryogenically cooled anions”*
6:15 – 6:45 pm	Ryan Steele (University of Utah, USA) *“Vibrational Signatures of Electronic Motion in Oxidized Water”*

Saturday, July 26

8.50 - 5:30 p.m.	*TOUR DAY*

Sunday, July 27

Bonding in materials II

Presiding: Clémence Corminboeuf

9:00 – 9:30 am Oleg Prezhdo (University of Southern California, USA)
“Chemical bonding steers excited state dynamics in nanoscale materials”
9:30 – 10:00 am Boniface Fokwa (RWTH Aachen University, Germany)
“Tuning the Magnetic and Electronic Properties of $Ti_3Co_5B_2$-type Materials”
10:00 – 10:30 am Andrey Rogachev (Illinois Institute of Technology, USA)
“Sandwich-like Aggregates of Highly-reduced Corannulene: Theoretical Study of Their Formation and Electronic Structure”

10:45 – 11:00 am *Coffee Break*

11:00 – 11:30 am Mark Eberhart (Colorado School of Mines, USA)
“Structure and Bonding in Materials Science”
11:30 – 12:00 am Christine Isborn (UC Merced, USA)
“Optimum DFT Exchange for Computation of Properties of Large Scale Systems”
12:00 – 12:30 pm Li-Qiong Wang (Brown University, USA)
“Solid-State NMR Investigations of Structure Changes of Silicon Electrodes for Lithium-Ion Batteries”

Afternoon: Tools and fundamentals I

Presiding: Ryan Steele

3:00 – 3:30 pm Martin Head-Gordon (UC Berkeley, USA)
“Energy decomposition analysis for intermolecular interactions: Progress and problems, illustrated with applications”
3:30 – 4:00 pm Paul Ayers (McMaster University, Canada)
“How Reliable Is the Hard-Soft Acid-Base (HSAB) Principle?”
4:00 – 4:30 pm Philippe Hiberty (Université de Paris-Sud, France)
“V state of ethylene: a challenging test case that becomes so easy with valence bond theory”
4:30 – 5:00 pm Alexander Sax (University of Graz, Austria)
“Chemical Bonding: The Orthogonal Valence Bond View”

5:00 – 5:15 pm *Coffee Break*

5:15 – 5:45 pm Xiaosong Li (University of Washington, USA)
“Low-Scaling Approximations to the Equation of Motion Coupled-Cluster Singles and Doubles Equations”
5:45 – 6:15 pm Teresa Head-Gordon (UC Berkeley, USA)
“Advanced Potential Energy Surfaces for Condensed Phase Simulation”

Monday, July 28

Morning: Molecular design

Presiding: Andrey Rogachev

9:00 – 9:30 am Michael D. Morse (University of Utah, USA)
“Chemical Bonding in Diatomic Transition Metals”
9:30 – 10:00 am Jan Weigand (TU Dresden, Germany)
TBA
10:00 – 10:30 am Rainer Herges (Otto-Diels-Institut für Organische Chemie, Germany)
“Anisotropy of the Induced Current Density (ACID), a Tool to Visualize Electron

	Delocalization and the Synthesis of the First Triply Twisted Möbius Annulene"
10:30 – 11:00 am	Sotiris Xantheas (Pacific Northwest National Laboratory, USA) *"Analysis of bonding patterns in molecular systems exhibiting partial biradical character"*
11:00 – 11:15 am	*Coffee Break*
11:15 – 11:45 am	Juan Novoa (Universitat de Barcelona, Spain) *"Long bonds between radicals: covalent-like bonds at 3 Å"*
11:45 – 12:15 pm	Ingo Krossing (Freiburg University, Germany) *TBA*
12:15 – 12:45 pm	Alexander Boldyrev (Utah State University, USA) *"Multi-Center Bonding in 2D- and 3D- Periodic Systems"*

Afternoon: *Presiding: Ralf Tonner*

3:00 – 4:30 pm	Discussion (led by Lai-Sheng Wang and Philippe Hiberty)
5:00 – 9:00 pm	*BANQUET -LUAU at Smith Restaurants* *Hawaiian Show + Dinner* *Pick up at Kauai Beach Resort Lobby*

Abstracts

What is a Hydrogen Bond?

Frank Weinhold
Department of Chemistry, University of Wisconsin-Madison

Many lines of evidence indicate the inadequacy of the "dipole-dipole" conceptions that dominate current textbook definitions and MD simulations of hydrogen bonding. Following up on recent IUPAC initiatives, we describe progress in formulating more definitive operational and pedagogical answers to the title question based on the high correlations that are found between NBO/NRT-based measures of resonance-type "charge transfer" and well-established empirical signatures of H-bonding, as well as a variety of other evidence that challenges conventional "electrostatic" conceptions. We also describe how improved definition of H-bonding fits within a broader quantum mechanical conception of the "chemical bonding" phenomenon.

New Tools to Visualize and Quantify Intra- and Intermolecular Phenomena

Piotr de Silva, Antonio Prlj, Jerome F. Gonthier and Clémence Corminboeuf
Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Switzerland

We present a density dependent scalar field that can simultaneously reveal different types of intra- and intermolecular chemical interactions ranging from covalent bonds, and Pauli repulsion to van der Waals interactions.[1] We also exploit the introduced quantity to visualize and compare the "electronic compactness" of different quatertiophene-based crystals and demonstrate the existing correlation with field-effect mobility. Finally, we will provide an update on the remaining challenges associated with the development of our intramolecular variant of Symmetry adapted perturbation theory (SAPT).[2]

[1] de Silva, P.; Corminboeuf, C submitted.
[2] Gonthier, J. F.; Corminboeuf, C. *J. Chem. Phys.* **2014**, *140*, 154107

Insights into Chemical Bonding from Generalized Valence Bond Theory

Thom H. Dunning, Jr.
Northwest Institute for Advanced Computing, Pacific Northwest National Laboratory & University of Washington, University of Washington, Seattle, Washington 98195; Department of Chemistry, University of Washington, Seattle, Washington 98195; and Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Generalized Valence Bond (GVB) theory provides a compelling description of the electronic structure of molecules. The GVB wavefunction is more accurate than the Hartree-Fock (molecular orbital) wavefunction, including the non-dynamical correlation effects present in the valence complete active space self-consistent field (CASSCF) wavefunction. However, unlike wavefunctions with multiple spatial configurations, the GVB wave function – through the changes in the orbitals, spin couplings and overlaps – provides unparalleled insights into the bonding, structure, states, and energetics of molecules. We will discuss a number of examples that illustrate the power of the GVB approach, including bonding in simple diatomic molecules such as C_2, N_2 and P_2 as well as the bonding in hypervalent molecules such as PF_5, SF_4/SF_6, and ClF_3/ClF_5.

Ménage-à-Trois: Catalysis, Mass Spectrometry and Computational Chemistry

Helmut Schwarz, Nicolas Dietl and Maria Schlangen
Institut für Chemie, Technische Universität Berlin, 10623 Berlin, Germany

We shall present selected examples of gas-phase reactions which are of timely interest for the catalytic activation of small molecules. Due to the very nature of the experiments, detailed insight in the *active site* of catalysts is provided and – in combination with computational chemistry – mechanistic aspects of as well as the elementary steps involved in the making and breaking of chemical bonds are revealed.

Examples to be discussed include *inter alia*: (i) Metal-mediated carbon-carbon bond formation; (ii) low-temperature, catalytic oxidation of CO; (iii) oxygen-centered radicals as active sites in catalytic hydrocarbon activation, e.g. the oxidative coupling of methane 2CH4 à C2H6.

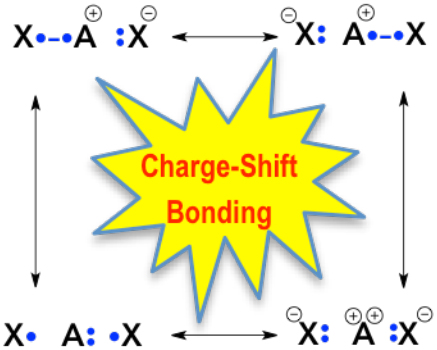
It will be shown that mass-spectrometry based studies on 'isolated' reactive species provide an ideal arena for probing experimentally the energetics and kinetics of a chemical reaction in an unperturbed environment at a strictly molecular level, and thus enable the characterization of crucial intermediates that have previously not been within the reach of conventional condensed-phase techniques. [1]

[1] (a) M. Schlangen, H. Schwarz, *Catal. Lett.* **2012**, *142*, 1265; (b) N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2012**, *51*, 5544; (c) H. Schwarz, *Angew. Chem. Int. Ed.* **2011**, *50*, 10096; D. K. Bohme, H. Schwarz, *Angew. Chem. Int. Ed.* **2005**, *44*, 2336.

A Classical Valence Bond Model for Electron-Rich Hypervalent Species. Application to XeF_2, SF_n (n = 1, 2, 4), PF_5 and ClF_3

Benoît Braida
Université Pierre et Marie Curie, France

Some typical hypervalent molecules, XeF_2, SF_4, PF_5, and ClF_3, as well as precursors SF ($^4S^-$ state) and SF_2 ($^3B_1$ state), are studied by means of the breathing-orbital valence bond (BOVB) method, chosen for its capability of combining compactness with accuracy of energetics. It comes out that the bonding mode of these hypervalent species and isoelectronic ones complies to Coulson's version of the Rundle-Pimentel model, i.e. a description in terms of 4 classical VB structures which all have significant weights, but assisted by charge-shift bonding which act as the "glue" that makes these electron-rich hypervalent molecules stable. This model directly emerges from high-level BOVB calculations, thus ensuring correctness of the interpretations. Conditions for hypervalence to take place can directly be stated from this model.



From Planar Boron Clusters to Borophenes and All-Boron Fullerenes

Lai-Sheng Wang
Department of Chemistry, Brown University, Providence, RI 02912

Photoelectron spectroscopy in combination with computational studies over the past decade has shown that boron clusters possess planar or quasi-planar structures [1-5], in contrast to that of bulk boron, which is dominated by three-dimensional cage-like building blocks. All planar or quasi-planar boron clusters are observed to consist of a monocyclic circumference with one or more interior atoms. The propensity for planarity has been found to be a result of both σ and π electron delocalization over the molecular plane, giving rise to concepts of σ and π multiple aromaticity. To date, boron clusters with up to 24 atoms have been found to be planar [6]. A question arises, to what size will boron clusters remain planar? An even more interesting question is if infinitely large planar boron clusters are possible, giving rise to atom-thin boron nanostructures analogous to graphene.

Boron is carbon's neighbor in the periodic table and has similar valence orbitals. However, boron cannot form graphene-like structures with a honeycomb hexagonal framework because of its electron deficiency. Computational studies suggested that extended boron sheets with partially filled hexagonal holes are stable, but there has been no experimental evidence for such atom-thin boron nanostructures. Recently, we have shown experimentally and theoretically that B36 is a highly stable quasiplanar boron cluster with a central hexagonal hole, providing the first experimental evidence that single-atom layer boron sheets with hexagonal vacancies are potentially viable. Photoelectron spectroscopy of B36– reveals a relatively simple spectrum, suggesting a symmetric cluster. Global-minimum searches for B36 – lead to a quasiplanar structure with a central hexagonal hole. Neutral B36 is the smallest boron cluster to have six-fold symmetry and a perfect hexagonal vacancy, and it can be viewed as a potential basis for extended two-dimensional boron sheets, which were named "borophene" [7]. Further studies suggest that hexagonal vacancies may be a defining feature for medium-sized boron clusters with more than 30 atoms [8]. Experimental evidence will also be presented, showing that allboron fullerenes are also possible [9].

[1] H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev, and L. S. Wang, *Angew. Chem. Int. Ed*. **42**, 6004-6008 (2003).
[2] H. J. Zhai, B. Kiran, J. Li, and L. S. Wang, *Nature Mater.* **2**, 827-833 (2003).
[3] A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, *Coord. Chem. Rev*. **250**, 2811-2866 (2006).

[4] W. Huang, A. P. Sergeeva, H. J. Zhai, B. B. Averkiev, L. S. Wang, and A. I. Boldyrev, *Nature Chem*. **2**, 202-206 (2010).
[5] A. P. Sergeeva, I. A. Popov, C. Romanescu, W. L. Li, A. A. Piazza, L. S. Wang, and A. I. Boldyrev, *Acc. Chem. Res*. **47**,1349-1358 (2014).
[6] I. A. Popov, Z. A. Piazza, W. L. Li, L. S. Wang, and A. I. Boldyrev, *J. Chem. Phys*. **139**, 144307 (2013).
[7] Z. A. Piazza, H. S. Hu, W. L. Li, Y. F. Zhao, J. Li, and L. S. Wang, *Nature Commun*. **5**, 3113 (2014).DOI: 10.1038/ncomms4113.
[8] W. L. Li, Y. F. Zhao, H. S. Hu, J. Li, and L. S. Wang, *Angew. Chem. Int. Ed*. **53**, 5540-5545 (2014).
[9] H. J. Zhai *et al*., to be published

Bonding, deformations, and unique properties of elemental boron and boron rich alloys

Qi An, William A. Goddard III, Tao Cheng, and Hai Xiao
Materials and Process Simulation Center, California Institute of Technology, Pasadena CA 91125

The ability of boron to form three very strong sp^2 covalent bonds, while leaving available the possibility of different character for forming a fourth bond plus the ability of an icosahedral shell of boron atoms to stabilize 13 strong multicenter intra-icosahedral bonds (Wade's rule) leads to an amazing pattern of structures, composed of 12-atom icosahedral clusters connected with each other through a combination of two-center and three-center bonds, leading to ~ 20 polymorphs of boron.

Moreover alloying the boron with carbon, oxygen, and other elements leads to families of new structures, such as boron carbide (B_4C), incorporating icosahedral structures with new types of interconnections. Although B_4C is very are hard, it is super brittle, fracturing though amorphous band formation, just beyond the elastic limit, which prevents their use for important engineering applications. We have used density functional methods to determine the mechanism of structural deformation and failure of these systems.

We find interesting phase transitions in which the icosahedra can play the role of a superatom with the inter-icosahedral bonds "walking" around the icosahedron. We predict that microalloying of hydrogen, silicon, and nitrogen into the boron carbide can dramatically change the mechanical properties, in some cases dramatic improvements. We will interpret these results in terms of the nature of the bonding within these systems.

The energy for tomorrow, needs to start today: A vision for high-throughput materials discovery

Alán Aspuru-Guzik
Department of Chemistry and Chemical Biology, Harvard University

With the present dangers of climate change and the urgent need of transitioning to a low-carbon economy, the world is in need of a new generation of materials for energy generation, energy efficiency, and storage. These materials are needed in the shortest timescale possible, developing these takes time. Therefore, efforts need to be increased today. In this talk, I focus on a simple and powerful idea to be able to meet this challenge: Materials genomics. The materials discovery cycle has to be transformed in such a way that literally tens of thousands of materials are calculated, synthesized and characterized in an advanced design cycle. Humanity has shown that it is possible to achieve great basic science and engineering discoveries in short amounts of time. One example is the Manhattan project for developing an atomic bomb. Scientists and engineers need to take a similar, focused approach to develop the energy of tomorrow. I will describe this general idea and illustrate it with a case study of the recent development of an inexpensive metal-free aqueous flow battery by my group and the groups of Michael Aziz and Roy Gordon at Harvard.

Phase Change Materials: From Optical Data Storage to Novel Electronic Memories

Matthias Wuttig
Physikalisches Institut der RWTH Aachen, Germany

Phase change media are among the most promising materials in information technology. These materials can be very rapidly switched between the amorphous and the crystalline state, indicative for peculiar crystallization behaviour. They are already employed in rewriteable optical data storage, where the pronounced difference of optical properties between the amorphous and crystalline state is used. This talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that the crystalline state of phase change materials is characterized by the occurrence of resonant bonding, a particular flavour of covalent bonding [1]. This insight is employed to predict systematic property trends [2]. Furthermore, it will be shown that phase change materials are characterized by a change in bonding mechanism upon crystallization. Phase change materials do not only provide exciting opportunities for applications including ‘greener’ storage devices, but also form a unique quantum state of matter as will be demonstrated by transport measurements [3,4].

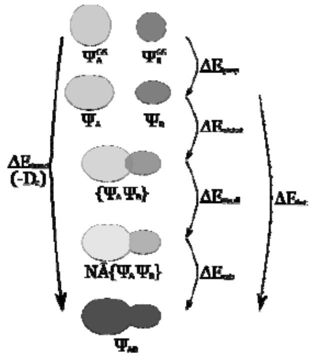
[1] K. Shportko et al., Nature Materials 7, 653 (2008)
[2] D. Lencer et al., Nature Materials 7, 972 (2008)
[3] T. Siegrist et al., Nature Materials 10, 202 (2011)
[4] W. Zhang et al., Nature Materials 11, 952 (2012)

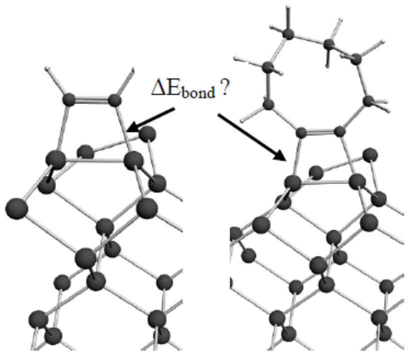
The chemical bond in periodic systems – an energy-based method for surface-adsorbate complexes

Ralf Tonner
Fachbereich Chemie and Materials Sciences Centre, Philipps-Universität Marburg, Hans-Meerwein Straße, 35032 Marburg

The chemical bond is one of the most fundamental concepts in chemistry. Classifications such as covalent, ionic or metallic bonding are central in discussing trends in different compounds and predicting new reactivity. Several very helpful concepts and methods were developed to understand the chemical bond at surfaces.[1] The question about energetic contributions to surface chemical bonds on the other hand did not receive great attention although energy changes are the ultimate driving force in bond formation. Starting from preliminary work by Philippsen and Baerends,[2] we implemented all terms of an Energy

Decomposition Analysis (EDA) to obtain quantitative data about energetic contributions to chemical bonding in periodic systems. This periodic EDA method was applied to questions of chemisorption of organic molecules at semiconductor surfaces where it can shed light on the nature of the surface-adsorbate bonds.[3]





Support by the Deutsche Forschungsgemeinschaft (TO 715/1-1) is gratefully acknowledged.

[1] a) A. Nilsson, L. G. M. Pettersson, J. Nørskov, *Chemical Bonding at Surfaces and Interfaces*, Elsevier, Amsterdam, **2007**; b) A. Groß, *Theoretical Surface Science*, Springer, Berlin, Heidelberg, **2009.**
[2] P. H. T. Philipsen, E. J. Baerends *J. Phys. Chem. B* **2006**, *110*, 12470.
[3] M. Raupach, R. Tonner, in preparation.

Formation of nanoclusters on catalytic surfaces driven by aromatic square planar carbon

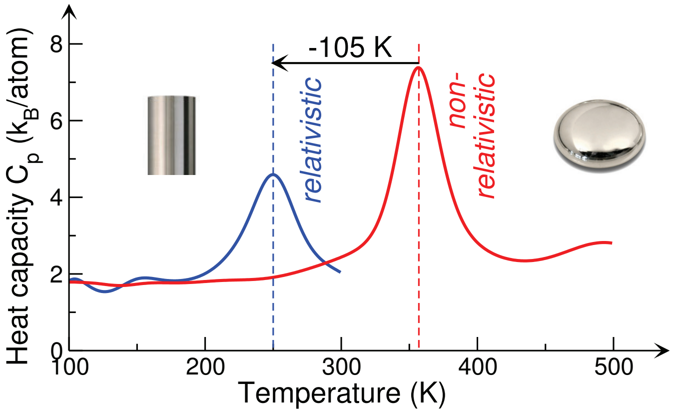
Mark Saeys[1] and Anastassia Alexandrova[2,3]
[1]Ghent University, Belgium.[2]University of California, Los Angeles, and [3]California NanoSystems Institute, USA

Catalytic surface often undergo massive reconstructions under reaction conditions and the catalytically active sites only form through self-organization during the reaction. Such massive reconstructions have been observed on cobalt and nickel catalysts used in steam reforming and Fischer-Tropsch synthesis, but their catalytic importance and driving force has not been understood. Our calculations show that the strong and attractive adsorption of CO and square planar carbon at step sites provides the driving force for this remarkable reconstruction. The formation and unique stability of square planar carbon bound to metal clusters is driven by the aromaticity of the cluster and is accompanied by the lack of the sp-hybridization on C. This unusual configuration of C is highly prominent on Co and Ni surfaces and can either promote the catalytic activity by driving a reconstruction, or poison the catalyst by forming extended structures. The local motifs containing square planar C in these extended systems also exhibit aromaticity, resulting in specific, thus rationalized reactivity. Furthermore, the limitation imposed by a proper electron count required for aromaticity is a predictor of the surface reconstruction and can lead to structures with well-defined vacancies which show high catalytic activity.

Why is Mercury a Liquid at Room Temperature?

Peter Schwerdtfeger
Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, Auckland, New Zealand.

It was long speculated that mercury is a liquid at room temperature because it is a chemically inert element and only Van der Waals forces are holding the mercury atoms together. Indeed, the Hg-Hg interaction is relatively weak in Hg_2 (400 cm^{-1}) and in the range of typical Van der Waals interactions such as Ar_2 (85 cm^{-1}), Kr_2 (127 cm^{-1}), or Xe_2 (186 cm^{-1}). However, the Hg-Hg bond distance shortens dramatically with increasing cluster size towards the bulk, indicating a fast transition from Van der Waals to covalent and metallic behaviour. But metals show rather high melting temperatures. So what is the reason for this unusual property of mercury? Only in the last two decades has it become clear that relativistic effects are responsible for the many anomalies observed in the chemistry and physics of mercury. One might speculate that such effects are responsible for the high superconducting transition temperature and low melting point of mercury. As we live in a relativistic world such speculations can only be proven by computation. However, the simulation of all three phases (solid, liquid and the gas phase) of mercury is a notoriously difficult problem in computational chemistry/physics, and the complex many-body interactions between the mercury atoms have eluded chemists and physicists for years to perform such calculations. It took our research group (together with Florent Calvo, Elke Pahl and Michael Wormit) 20 years of preparation to successfully model the melting behaviour, which we achieved just recently using the supercomputer system in Lyon.



Computational Materials Discovery: New Developments and Surprising Discoveries

Artem R. Oganov[1,2]
[1]*Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, NY 11794-2100,*
[2]*Department of Problems of Physics and Energetics, Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny city, Moscow Region, 141700, Russia*

Thanks to powerful evolutionary algorithms, in particular to the USPEX method [1-3], it is now possible to predict both the stable compounds and their crystal structures at arbitrary *P,T*-conditions, given just the set of chemical elements. Recent developments include the extension of this algorithm to molecular crystals [4] (which allowed large structures to be handled easily, leading to revision of high-pressure structures of $Mg(BH_4)_2$ [5], proving earlier proposed "experimental" structure to be incorrect) and a new technique called evolutionary metadynamics [6]. Some of the results that I will discuss include:

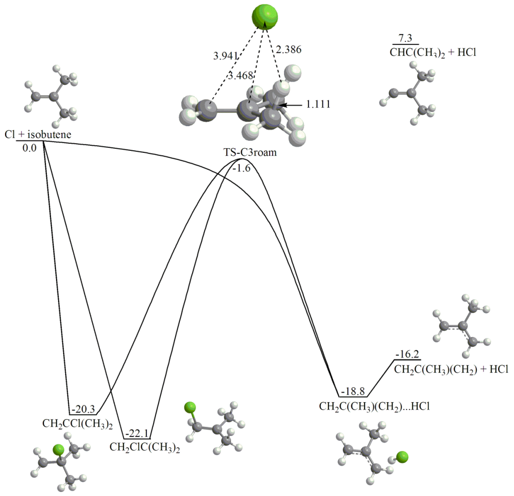
1. Theoretical and experimental evidence for a new stable high-pressure phase of boron, γ-B [7], showing superhardness and charge transfer between boron atoms.
2. New insulating and optically transparent, and experimentally confirmed, form of sodium [8].
3. Establishment of the structure of a carbon allotrope – M-carbon [1,9].
4. Predicted reactivity of noble gases under moderate pressures – Xe [10] and even He.
5. Predicted stability of "impossible" chemical compounds – such as Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, $NaCl_7$ [11], Mg_3O_2 and MgO_2 [12]. These compounds become stable under pressure and we already have compelling experimental evidence for some of them [11].

[1] Oganov A.R., Glass C.W., *J.Chem.Phys.* **124**, 244704 (2006).
[2] Oganov A.R., Lyakhov A.O., Valle M., *Acc. Chem. Res.* **44**, 227-237 (2011).
[3] Lyakhov A.O., Oganov A.R., Stokes H.T., Zhu Q., *Comp. Phys. Comm.* **184**, 1172-1182 (2013).
[4] Zhu Q., Oganov A.R., Glass C.W., Stokes H.T., *Acta Cryst.* **B68**, 215-226 (2012).
[5] Zhou X.-F., Oganov A.R., Qian G.R., Zhu Q., *Phys. Rev. Lett.* **109**, 245503 (2012).
[6] Zhu Q., Oganov A.R., Lyakhov A.O., *Cryst.Eng.Comm.* **14**, 3596-3601 (2012).
[7] Oganov A.R., Chen J., Gatti C., et al., *Nature* **457**, 863 (2009).
[8] Ma Y., Eremets M.I., Oganov A.R., et al., *Nature* **458**, 182 (2009).
[9] Boulfelfel S.E., Oganov A.R., Leoni S., *Scientific Reports* 2, art. 471 (2012).
[10] Zhu Q., Jung D.Y., Oganov A.R., et al., *Nature Chemistry* **5**, 61-65 (2013).
[11] Zhang W.W., Oganov A.R., Goncharov A.F., et al., *Science* **342**, 1502-1505 (2013).
[12] Zhu Q., Oganov A.R., Lyakhov A.O., *Phys. Chem. Chem. Phys.* **15**, 7796-7700 (2013).

Theoretical Studies of the Roaming Mechanism in Cl Radical Addition-Elimination Reactions with Alkenes

Baptiste Joalland,[1] Yuanyuan Shi,[1] Alexander Kamasah,[1] Arthur G. Suits[1] and Alexander M. Mebel[2],
[1]*Department of Chemistry, Wayne State University, Detroit, MI 48202, USA,* [2]*Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA*

Radical addition-elimination reactions are a major pathway for transformation of unsaturated hydrocarbons. In the gas-phase these reactions involve formation of a transient strongly-bound intermediate. However, the detailed mechanism and dynamics for these reactions remain unclear. The present studies address the reaction mechanism and dynamics of Cl radical with alkenes, such as structural isomers of C_4H_8 (1-butene, cis- and trans- 2-butenes, and isobutene) and isoprene (C_5H_8, 2-methyl-1,3-butadiene). Potential energy surfaces for these reactions have been studied by ab initio calculations at the CBS-QB3 levels and the theoretical results are compared with the experimental data obtained using the crossed-molecular-beam imaging techniques at the Wayne State University. The combination of the experimental and theoretical results show, for reaction of chlorine atoms with butenes, that the Cl addition – HCl elimination pathway is dominant and only occurs from an abstraction-like Cl-H-C geometry rather than a conventional 3-center or 4-center transition state. Furthermore, access to this geometry is attained by roaming excursions of the Cl atom from the initially-formed adduct. In effect, the alkene π cloud serves to capture the Cl atom and hold it, allowing many subsequent opportunities for the energized intermediate to find a suitable approach to the abstraction geometry. These bimolecular roaming reactions are closely related to the roaming radical dynamics recently discovered to play an important role in unimolecular reactions.



TBA

Graeme Henkelman
University of Texas, USA

Weak Interactions in Biosynthetic and Organic Catalysts — C-H•••π, C-H•••O and S•••O Interactions as Selectivity Control Elements

Dean Tantillo
Department of Chemistry. University of California, Davis

Theoretical studies on the magnitudes and origins of C-H•••π, C-H•••O and S•••O interactions found in biological and synthetic catalysts will be described. The roles of these weak interactions in controlling selectivity, and their associated utility as design elements, will be emphasized. Examples will include a terpene synthase catalyzed carbocation rearrangement, a phosphoric acid catalyzed sigmatropic shift and a nucleophile catalyzed Diels-Alder reaction.

The interplay of nuclear and electronic quantum fluctuations in hydrogen bond networks

Thomas E. Markland
Department of Chemistry, Stanford University

Ab initio molecular dynamics simulations, where the nuclei are evolved using the forces obtained by solving the electronic structure at each step, are typically performed assuming the nuclei behave classically. However, for processes involving light particles including nuclear quantum effects, such as zero point energy and tunneling, can dramatically alter their structure and dynamics. In this talk I will discuss our recent work showing how simulations incorporating both nuclear and electronic quantum effects give rise to significant changes in hydrogen bond networks ranging from water to enzyme active sites. I will also discuss our recent work developing approaches to treat nuclear quantum mechanical fluctuations in condensed phase systems and to calculate isotope effects at a cost barely more than the corresponding classical simulation. These advances allow the investigation of chemical systems where the inclusion of nuclear and electronic quantum effects is essential to obtain the correct result.

How the electronic structure of metals contribute, and impede, metalloenzyme structure and function

Crystal E. Valdez[1] and Anastassia N. Alexandrova[1,2]
[1]Department of Chemistry and Biochemistry, University of California, Los Angeles and [2]California NanoSystems Institute, University of California, Los Angeles, CA 90095

To design artificial enzymes for the catalysis of reactions that interest humankind, we must understand the principles by which Nature makes her own evolutionary choices. Examining metal choice in enzymes through the perspective of a chemist, we would often make different choices based solely on appropriate charge and size, coordination geometry, correct redox potentials, etc. However, in a cellular environment, there are more variables to consider then just pure catalysis, making the influence of metal choice in natural metalloenzymes interesting. This talk will showcase a few perplexing examples that illustrate the effects of metal replacement, and/or removal of non-catalytic metals in natural enzymes. (1) We will explain why the seemingly innocent replacement of Mg(II) with Ca(II) in catechol-O-methyl transferase (COMT) kills the activity of the enzyme.[1] (2) We will show why the replacement of Fe(II) with Ni(II) in the identical structure of acireductone dioxygenase (ARD) completely reroutes the catalytic mechanism.[2,3] (3) We will elaborate on the puzzling fact that two amide hydrolases, urease and β-lactamase, use different metals to catalyze similar reactions proceeding through identical mechanisms.[4] Also, we will introduce our new efficient dynamics method for modeling metalloproteins, QM/DMD, which made this research possible.[5] QM/DMD permits for fast and extensive sampling of metalloproteins done in conjunction with a quality ab initio description of the metal containing active site.

[1] Sparta, M.; Alexandrova, A. N. How metal substitution affects the enzymatic activity of COMT. 2012 PLoS ONE, 7, e47172.
[2] Sparta, M.; Valdez, C. E.; Alexandrova, A. N. Metal-dependent activity of Fe and Ni acireductone dioxygenases: how two electrons reroute the catalytic pathway. 2013 J. Mol. Biol., 245, 3007-3018.
[3] Valdez, C. E.; Gallup, N. M.; Alexandrova, A. N. Co^{2+} Acireductone Dioxygenase: Fe^{2+} Mechanism, Ni^{2+} Mechanism, or Something Else? 2014, Chem. Phys. Lett., 604, 77-82.
[4] Valdez, C. E.; Alexandrova, A. N. Why Urease is a di-Nickel Enzyme, whereas the CcrA beta-Lactamase is a di-Zinc Enzyme. 2012 J. Phys. Chem. B., 116, 10649-19656.
[5] Sparta, M.; Ding, F.; Shirvanyants, D.; Dokholyan, N. V.; Alexandrova, A. N. Hybrid dynamics simulation engine for metalloproteins. 2012 Biophys. J. 103, 767-776.

Tuning Catalyst Performance *via* Optimizing Cluster Size, Composition and Support: The Role of *in situ* Techniques in Catalyst Design

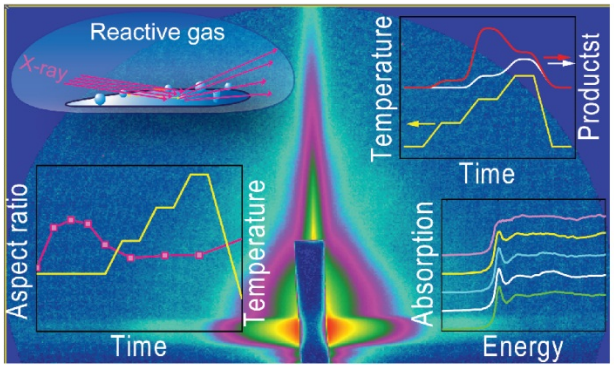
Stefan Vajda[1,2,3,4]
[1]Materials Science Division and [2]Nanoscience and Technology Division Argonne National Laboratory, Argonne, Illinois, USA, [3]Institute for Molecular Engineering, The University of Chicago, Chicago, Illinois, USA, [4]Department of Chemical and Environmental Engineering, School of Engineering & Applied Science, Yale University, New Haven, Connecticut, USA

The elucidation of the size, composition, shape, structure and function relationship, the effect of support along with the determination and control of the nature of the catalytic particles under reaction conditions are instrumental for addressing fundamental aspects of catalysis on the way to the design of new classes of catalytic materials. Highly uniform particles on technologically relevant supports are prerequisites for such studies.

Our experimental studies are based on 1) the use of technologically relevant oxide and carbon based supports, 2) size- selected cluster deposition with atomic precision control of cluster size and composition, 3) *ex situ* and *in situ* microscopies and 4) *in situ* synchrotron X-ray characterization of cluster size/shape and oxidation state under realistic working conditions, combined with mass spectroscopy analysis of the reaction products. The studies are complemented with *ex situ* and *in situ* microscopies and DFT calculations.

The first part of the lecture will focus on the understanding and optimization of catalyst function in oxidative reactions such as the dehydrogenation of propane and cyclic compounds and the selective partial oxidation of propylene on size-selected clusters and their assemblies.

As time shall allow, in the second part of the presentation the strongly size-dependent performance of sub-nanometer clusters in water splitting and Li-Air batteries will be discussed.



[1] S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood and P. Zapol, , *Nat. Mater.*, 2009, 8, 213
[2] Y. Lei, F. Mehmood, S. Lee, J. P. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. C. Curtiss, and S. Vajda, *Science*, 2010, 328, 224
[3] L. M. Molina, S. Lee, K. Sell, G. Barcaro, A. Fortunelli, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, M. J. Pellin, I. Barke, A. Kleibert, V. von Oeynhausen, Y. Lei, R. J. Meyer, J. A. Alonso, A. Fraile-Rodríguez, S. Giorgio, C. R. Henry, K.-H. Meiwes-Broer and S. Vajda, *Catal. Today* 160 (2011) 116
[4] S. Lee, M. Di Vece, B. Lee, S. Seifert, R. E. Winans and S. Vajda, *Chem. Cat. Chem.* 4 (2012) 1632

[5] G. Kwon, E. C. Tyo, C. Yin, G. A. Ferguson, J. DeBartolo, S. Seifert, R E. Winans, A. J. Kropf, C. J. Heard, R. L. Johnston, J. P. Greeley, L. A. Curtiss, M. J. Pellin, and S. Vajda, *ACS Nano* 7, (2013) 5808

Strong, Low Barrier Hydrogen Bonds may be Available to Enzymes

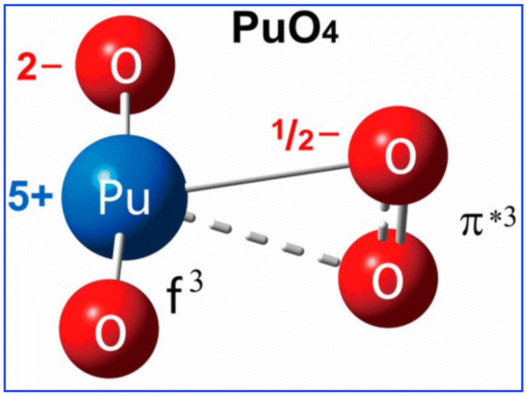
Jacob Graham, Allyson Buytendyk, Di Wang, Kim Collins, and Kit Bowen
Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218 USA

The ionic hydrogen bond strengths of three enzymatically-relevant model systems were measured in isolation (gas phase) by anion photoelectron spectroscopy and compared with the hydrogen bond strength of HF_2^-, which was also measured using the same technique during these experiments. These systems; the formate-formic acid, acetate-acetic acid, and imidazolide-imidazole anionic complexes, all exhibit hydrogen bond strengths that compare favorably with the hydrogen bifluoride anion, the strongest known hydrogen bond. According to numerous estimates, the values of these bond strengths are all easily more than enough to stabilize enzymatic intermediates. If there were to be enzyme active site environments that can facilitate the retention of even 1/3 of the strengths of these hydrogen bonded couples, then low barrier hydrogen bonding interactions might well play important roles in enzyme catalysis.

On the Highest Oxidation State of Actinide Compounds

Wei Huang, W. H. E. Schwarz and Jun Li
Theoretical Chemistry Center, Department of Chemistry, Tsinghua University, Beijing 100084, China

The oxidation state is a central concept in chemistry [1]. As an indication of the electronic state of atoms in a molecule, the "oxidation state" of an atom represents the number of valence electrons it has formally gained or lost when bonded with other atoms in a molecule [2]. The highest known oxidation state is +8, as exemplified in tetra-oxides MO_4 (M = Ru, Os, Xe) of group-VIII metal and less-inert noble gas. Despite claims of octavalent states of Pu and Cm in MO_4 compounds, whether or not such high oxidation state is stable for actinides is still unclear. We have investigated the electronic structures of PuO_4 and analogous complexes by using *ab initio* wavefunction theory and density functional theory [3]. It has been shown that the exotic low-spin high-oxidation state of Pu(VIII) is highly unstable against intramolecular electron transfer. The more common plutonyl(V)$^+$ unit may be loosely coupled to a superoxido O_2^- ligand, forming PuO_4 as a high-spin complex of lower oxidation state, $^5C_{2v}$-$(PuO_2)^+(O_2)^-$. The leading valence



configuration with open electron shells on plutonium, $(f^3)Pu^{5+}$, and superoxide dioxygen, $(\pi^{*3})O_2^-$, yields a highly correlated valence electronic system. We can thus conclude that the highest oxidation states of the actinides become more and more unlikely from uranium onward in the 5f actinoid series.

[1] P. Karen, P. McArdle, J. Takats, "Towards a Comprehensive Definition of Oxidation State (IUPAC Technical Report)", *Pure Appl. Chem*. **2014**, *86*, 1017-1081.
[2] H. Xiao, H.-S. Hu, W. H. E. Schwarz, J. Li, "Theoretical Investigations of Geometry, Electronic Structure and Stability of UO_6: Octahedral Uranium Hexoxide and Its Isomers", *J. Phys. Chem. A* **2010**, *114*, 8837–8844.
[3] W. Huang, W.-H. Xu, J. Su, W. H. E. Schwarz, J. Li, "Oxidation States, Geometries, and Electronic Structures of Plutonium Tetroxide PuO_4 Isomers: Is Octavalent Pu Viable?", *Inorg. Chem*. **2013**, *52*, 14237-14245.

The chemical bond and its bonds to fundamental physics research

Robert Berger
Fachbereich Chemie, Philipps-Universitaet Marburg, Hans-Meerwein-Str. 4, 35032 Marburg, Germany

Molecular electronic structure and chemical bonds play a crucial role in on-going attempts to study fundamental interactions of matter within the domain of molecular physics.

One promising route is to employ high-resolution spectroscopy of ultracold molecules that can be obtained from laser-based cooling schemes. Whereas several atoms can be cooled efficiently with lasers, molecules suffer usually from structural changes upon electronic transitions such that closed radiative cooling loops are difficult to maintain. Molecular candidates that are well suited for such cooling strategies require a special electronic bonding situation [1], which is discussed in this contribution.

Besides prospects for cooling, also possible effects that can reveal intriguing details of the underlying fundamental interactions depend crucially on the electronic bonding situation. Symmetry violating effects in open-shell diatomic molecules will be presented as an example and nuclear-charge dependent scaling laws along rows and columns of the periodic table will be discussed [2].

[1] T. A. Isaev, S. Hoekstra, R. Berger, Phys. Rev. A, 2010, 82, 052521.
[2] T. A. Isaev, R. Berger, J. Mol. Spectrosc., 2014, 300, 26-30.

Relativistic Effects on the Electronic Structure and Bonding of the Heaviest Elements

Valeria Pershina
GSI Helmholtzzentrum für Schwerionenforschung, D-64291 Darmstadt, Germany

Investigations of chemical properties of the heaviest elements (those with Z > 104) belong to the most fundamental and important areas of chemical science. Their purpose is to prove the placement of the new elements in the Periodic Table [1,2]. This is achieved by comparing the behaviour of the newly produced elements with that of their lighter homologs in the chemical groups. In this area, theoretical predictions play a particularly important role, because they serve as a guiding tool for expensive and sophisticated experiments with single atoms, as well as they help interpret experimental results [2,3].

It is now widely recognized that relativistic effects are of paramount importance for these very high Z numbers [3,4]. Their influence on the electron shells is so strong that deviations in properties and periodicities established for the lighter homologs in the chemical groups can occur.

In the presentation, examples of strong influence of relativistic effects on the electronic structure and bonding of atomic, molecular and cluster (solid state) systems of the heaviest elements in comparison with their lighter homologs in the chemical groups are considered. Particular attention is paid to elements 112 (Cn) and 114 (Fl), where relativistic effects are the strongest among the experimentally studied systems. Properties of atoms of elements 119 and 120, as future candidates for production, are also discussed. Peculiarities in periodicities of properties of different types of compounds in the Periodic Table are elucidated.

Theoretical results were obtained with the use of the most advanced relativistic methods and computational codes: DC(B) CC, 2*c*- and 4*c*-DFT, as well as the ADF (BAND) code.

[1] The Chemistry of Superheavy Elements, 2d Ed., Eds. M. Schädel and D. Shaughnessy, Springer, Heidelberg, 2014.
[2] A. Türler and V. Pershina, Chem. Rev. **113**, 1237 (2013).
[3] V. Pershina, In: Ref. 1, pp. 135-240.
[4] P. Schwerdtfeger and M. Seth, In: Encyclopedia on Calculational Chemistry, Vol. 1, pp. 2480-2499, Wiley, New York (1998).

Molecular Motions in Space and Time: Structural Views of Chemical Bonding

Peter M. Weber
Department of Chemistry, Brown University

The formation and destruction of chemical bonds is invariably associated with changes in the molecular structure. Two methods are presented to observe, on the femtoseconds time scale of molecular transformations, the structures of molecules.

Time-resolved Rydberg Fingerprint Spectroscopy (RFS) is a structural tool with unique capabilities. In the study presented here, we used RFS to explore the ultrafast structural motions associated with the movement of a (partial) charge in two diamine molecules, N,N′-Dimethylpiperazine (DMP) and *N, N, N′, N′*-tetramethylethylenediamine (TMEDA). Both molecules are excited to the 3p Rydberg states, from where they relax to the lower lying 3s state while injecting energy into the vibrational manifold. The structural dynamics is recorded by probing the binding energy of the Rydberg electron as a function of time. In both molecules, we find that immediately following the optical excitation in the UV, the charge of the molecular ion core is situated at a single nitrogen atom. The delocalization of the charge is accompanied by structural motions of the carbon skeleton, which are encoded in the binding energy spectrum. DFT with self-interaction correction properly describes the binding energy of the Rydberg electron and provides excellent agreement with the experimental results, allowing us to map the pathway of the molecular structure as the molecule internally converts from 3p to 3s and finds its way to the minimum energy where the charge is delocalized.

Time resolved x-ray diffraction has the potential to measure structure in the Fourier space of diffraction patterns. In ongoing studies, an ultrafast laser pulse at 267 nm and with 65 fs duration initiates the prototypical electrochemical ring-opening reaction of 1,3-cyclohexadiene by exciting the molecule to the 1B surface. The time-dependent molecular structure, which rapidly changes as the molecule descends a steep potential energy surface to approach a new chemical formula, is probed using intense x-ray pulses with 30 fs duration from the LCLS light source. Repetitive exposures involving some 10^5 laser/x-ray pulse pairs at many time delays should yield a molecular movie in the Fourier transform space of the diffraction signal. To derive the corresponding movie in the real space of molecular structure, we compute theoretical diffraction patterns of a swarm of molecules with slightly different starting conditions using the independent atom model. A statistical analysis of the match between the computed trajectories and the observed diffraction patterns should yield a time-dependent view of the structural evolution of the molecular reaction.

Theoretical Studies of the Hydrated Electron in Clusters, Bulk Water, and the Air/Water Interface

John Herbet

Department of Chemistry and Biochemistry, Ohio State University

The structure, spectroscopy, and reactivity of the hydrated electron continue to provoke interest more than half a century after the first measurements of this species' optical spectrum. Recently, the hydrated electron at the water/vapor interface has been suggested to have quite different properties from the aqueous electron in bulk water. This talk examines the extent to which this is true, based on ab initio molecular dynamics simulations, excited-state quantum chemistry, and one-electron pseudopotential models. Connections between the condensed-phase interfacial electron and its cluster analogues will also be explored.

Slow electron velocity-map imaging (SEVI) of cryogenically cooled anions

Daniel Neumark

Department of Chemistry, University of California, Berkeley

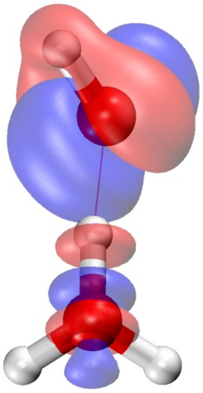
Slow electron velocity-map imaging of cryognecally cooled negative ions yields photoelectron spectra with sub-meV resolution for molecular anions, metal oxide clusters, and transition state precursors, representing a substantial improvement in resolution over conventional photoelectron spectroscopy. Examples will be presented with particular emphasis on transition metal oxides, where the high resolution of SEVI enables unambiguous assignments of ground state anion isomers.

Vibrational Signatures of Electronic Motion in Oxidized Water

Ryan P. Steele

Department of Chemistry, University of Utah

The splitting of water, as a means of chemically storing solar energy, offers as many promises for renewable energy as it does questions for the field of chemistry. This presentation will provide an explanation for the anomalous, experimental vibrational signatures of ionized water clusters. The resulting picture is an exquisite example of the strong coupling between electronic and nuclear motion. The role of this coupling in directing the post-ionization dynamics of oxidized water will also be discussed, including a size-dependent driving force toward ion-radical pair separation. If time permits, new methodological developments for the general simulation of anharmonic vibrational spectroscopy in large chemical systems will also be presented.



Chemical bonding steers excited state dynamics in nanoscale materials

Oleg V. Prezhdo
University of Southern California, Los Angeles

Our group's research focuses on modeling non-equilibrium processes in condensed phase systems explicitly in time-domain. We develop approaches for non-adiabatic molecular dynamics and time-domain density functional theory [1-4], and apply them to a variety of excited state electron-vibrational processes in nanoscale materials. The software to perform these simulations [5,6] are freely available at http://gdriv.es/pyxaid. A significant fraction of the efforts is motivated by photovoltaic and photo-catalytic applications. The talk will highlight the importance of chemical bonding in the excited state dynamics, including several, perhaps counter-intuitive, examples investigated recently both by pump-probe spectroscopies and theoretically in our group.

Various chromophores are used to sensitize TiO_2 to achieve photo-induced charge separation. Most chromophores have a significant band-gap to avoid rapid electron-hole recombination. Surprisingly, graphene – a metal (!) – can be used as a chromophore as well. The charge separation is faster than the electron-hole recombination due to chemical bonding between TiO_2 and graphene [7]. Long non-conjugated bridges between donor and acceptor species are viewed as insulators, slowing down electron transfer. A counter-intuitive observation, such bridge connecting a CdSe quantum dot and C_{60} accelerates charge separation. We rationalize this experimental fact by strong electron-phonon coupling mediated by the high-frequency vibrations of the bridge [8]. Bonding between metallic particles and TiO_2 enables direct plasmon-induced electron transfer, bypassing the intermediate step of plasmon dephasing into electron-hole pairs [9].

Surface defects are viewed as a negative attribute of quantum dots, and significant synthetic efforts are dedicated to eliminate them. Interestingly, Cd vacancies on CdS surface quench luminescence; however, S vacancies do not. We rationalize this by the ability of Cd-rich surfaces to "heal" defects much better compared to S-rich surfaces: excess non-metallic S is much more selective in creating chemical bonds than excess metallic Cd [10]. We also show that certain types of defects accelerate photo-induced charge separation in quantum-dot/molecular-chromophore systems, while maintaining slow charge recombination [11]. We demonstrate how the electron transfer mechanism changes from non-adiabatic to adiabatic as a result of chemical bonding induced by surface defects [12]. Finally, we will discuss a new type of electron transfer – Auger assisted electron transfer. It was discovered only this year [13], while it should be common in most nanoscale materials.

[1]C. F. Craig, W. R. Duncan, O. V. Prezhdo, *Phys. Rev. Lett.*, **95** 163001 (2005).
[2] **B. F. Habenicht, O. V. Prezhdo, *Phys. Rev. Lett.*, 100, 197402 (2008).**
[3] S. R. Fischer, B. F. Habenicht, A. B. Madrid, W. R. Duncan, O. V. Prezhdo, *J. Chem. Phys.*, **134**, 024102 (2011); chosen for Jan. 24, 2011 issue of Virt. J. Nanoscale Sci. & Tech.
[4] H. M. Jaeger, S. Fisher, O. V. Prezhdo *J. Chem. Phys*., **137**, 22A545 (2012).
[5] A. V. Akimov, O. V. Prezhdo, *J. Chem. Theor. Comp.*, **9**, 4959 (2013).
[6] A. V. Akimov, O. V. Prezhdo, *J. Chem. Theor. Comp.*, **10**, 789 (2014).
[7] R. Long, N. English, O. V. Prezhdo, *J. Am. Chem. Soc.*, **134**, 14238 (2012) ; chosen for *JACS* Spotlight.
[8] V. V. Chaban, V. V. Prezhdo, O. V. Prezhdo, *J. Chem. Phys. Lett.*, **4**, 1 (2013).
[9] R. Long, O. V. Prezhdo, *J. Am. Chem. Soc.*, **136**, 4343 (2014).
[10] H. Wei, C. M. Evans, B. D. Swartz, A. J. Neukirch, J. Young, O. V. Prezhdo, T. D. Krauss *Nano Lett.*, **12**, 4465 (2012) .
[11] R. Long, N. J. English, O. V. Prezhdo, *J. Am. Chem. Soc.*, **135**, 18892 (2013).
[12] D. N. Tafen, R. Long, O. V. Prezhdo, *Nano Lett.*, **14**, 1790 (2014).
[13] H. Zhu, Y. Yang, K. Hyeon-Deuk, M. Califano, N. Song, Y. Wang, W. Zhang, O. V. Prezhdo, T. Lian, *Nano Lett.*, in press.

Structure and Bonding in Materials Science

Mark Eberhart
Department of Chemistry and Geochemistry, Colorado School of Mines

One cannot overstate the importance of structure-property relationships to the field of materials science, and particularly to our ability to design materials. For the most part, these relationships have been discovered and refined through a taxonomic process where structures are observed and classified into groups with similar properties. For example, fine-grained metallic materials were observed to have greater strength than their course grained counterparts, leading metallurgists to postulate a relationship between grain size and strength. However, when it comes to uncovering the relationships mandated by density functional theory—between the charge density and properties—the process has proceeded down a much different path. Rather than infer the nature of these relationships through observation of the calculated or measured charge density, the emphasis has been placed on improving methods to calculate properties from first principles. The charge density is often considered as nothing more than a byproduct, and in some cases a worthless byproduct. At the very best the charge density is described and characterized in terms of inexact models of bonding whose origins date to a time before the advent of quantum mechanics.

In this presentation, I will explore the potential for discovering charge density-property relationships the traditional way—through observation and correlation. Such an approach demands that the charge density be described and quantified within a rigorous hierarchical framework. I will argue that treating the charge density as a topological space formed from "gluing together" a clearly delineated set of tetrahedra, i.e., by considering it as a simplicial complex, provides this framework. This approach leads to a nesting of structures that can be quantitatively described with a small number of parameters. Within this set of structures one finds a complex that possesses all the topological properties of the chemical bond, and in many instances recovers many of the conceptually fuzzy concepts of bonding such as bond order, directionality, and bond energy. I will show that this structure allows one to apply the powerful conceptual principles of chemistry, e.g., the Hammond postulate, functionality, *et cetera*, to design materials starting from first principles.

Sandwich-like Aggregates of Highly-reduced Corannulene: Theoretical Study of Their Formation and Electronic Structure

Andrey Yu. Rogachev
Department of Biological and Chemical Sciences, Illinois *Institute of Technology, Chicago, IL, 60616,*

Recent experimental achievements in chemistry of reduced corannulene ($C_{20}H_{10}$, the smallest buckybowl) revealed a tendency of highly reduced curved polyaromatic molecules to form sandwich-like aggregates. The latter contain alkali metals as "glue" between two bowls in their convex-convex orientation and show remarkable stability in solution. The electronic structure of these systems was investigated in detail in the present study with help of modern tools of quantum chemistry. First, we have studied the electronic structure and energetics of the simplest member of the series, in which five sites between two bowls (in-between 6-memered rings) are occupied by only lithium cations. The lithium cations carry almost unchanged positive charge +1, indicating non-participation in coupling with polyaromatic systems. The same was found for systems with other alkali metals. The influence of the metal center on the coupling between bowls as well as on the formation of sandwich-like structure was studied in detail.

Tuning the Magnetic and Electronic Properties of $Ti_3Co_5B_2$-type Materials

J. P. Scheifers, M. Hermus and Boniface P. T. Fokwa
Institute of Inorganic Chemistry, RWTH Aachen University, 52066 Aachen

In the last two decades phases with $Ti_3Co_5B_2$-type crystal structure have been intensely investigated both experimentally and theoretically, in particular with respect to itinerant magnetism [1, 2]. The presence of well separated one-dimensional chains of magnetic 3d atoms is the main reason for the observation of long range magnetic ordering in these phases.

Recently, the quinary members of the complex boride series $Sc_2FeRu_{5-x}Ir_xB_2$ were synthesized by arc melting the elements and characterized by powder and single-crystal X-ray diffraction as well as metallographic and energy-dispersive X-ray analyses. The use of a 4d/5d mixture allows distinguishing these elements with X-ray diffraction methods, thus enabling the study of site preference and its influence on the magnetic properties. Magnetic measurements reveal several changes of magnetic ordering within the series: from antiferromagnetism ($Sc_2FeRu_5B_2$) to ferromagnetism ($Sc_2FeRuIr_4B_2$) and finally to metamagnetism ($Sc_2FeIr_5B_2$). Within the quinary series, the magnetic moments continuously increase with increasing amounts of Ir in one (8j) of two possible Wyckoff sites. The members with x = 2 and 3 represent the first hard magnetic borides of transition metals. [3]

The magnetism of the new $Sc_2FeRu_{5-x}Ir_xB_2$ ($0 < x < 5$) series will be compared with the $Sc_2FeRu_{5-x}Rh_xB_2$ and $Ti_2FeRu_{5-x}Rh_xB_2$ series. Furthermore microscopic and resistivity measurements have been carried out for all members of the new series.

Also a new ternary ruthenium-rich member of the $Ti_3Co_5B_2$ structure type, $Nb_3Ru_5B_2$,[4] has been successfully synthesized recently and theoretical calculations predict, via the rigid band model, new ternary and quaternary synthetic targets. Many such ternary ruthenium-rich phases [5] which have been investigated experimentally and theoretically will be presented.

[1] B.P.T. Fokwa, *Eur. J. Inorg. Chem.* 2010, 3075.
[2] B.P.T. Fokwa, H. Lueken, R. Dronskowski, *Eur. J. Inorg. Chem.* 2011, 4877.
[3] M. Hermus, B.P.T. Fokwa, *Chem. Mater.*2014, *26*, 1967.
[4] M. Hermus, B.P.T. Fokwa, *Z. Anorg. Allg. Chem.*2012, *638*, 49.
[5] M. Hermus, B.P.T. Fokwa, *Eur. J. Inorg. Chem.* DOI:10.1002/ejic.201402206.

Optimum DFT Exchange for Computation of Properties of Large Scale Systems

Christine Isborn
School of Natural Sciences, University of California, Merced

I'll discuss recent results from our studies that examine the role of exact exchange vs DFT exchange in the computation of ionization potentials, excitation energies, and hyperpolarizabilties of large-scale systems, particularly in the context of tuning the range-separation parameter for long-range corrected functionals. We examine trends with increasing system size, and find that while it appears that the delocalization error of DFT improves with larger systems, computed properties of these larger systems are in poorer agreement with experimental results.

Solid-State NMR Investigations of Structure Changes of Silicon Electrodes for Lithium-Ion Batteries

L-Q. Wang[1], M. Song[1], S. P. V. Nadimpalli[2], P. R. Guduru[2], V. A. Sethuraman[2] and M. J. Chon[2]
[1]Department of Chemistry, Brown University, Providence, Rhode Island, USA, [2]School of Engineering, Brown University, Providence, Rhode Island, USA

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for probing local structures and chemical natures of a variety of materials, even in a disordered system because it is extremely sensitive to the local magnetic field around nuclei at an atomic scale. The incorporation of Li into the crystalline Si electrode leads to disintegration of the tetrahedral bonded Si network into small clusters of various shapes. Previous calculations showed that the charge transfer leads to weakening or breaking of Si-Si bonds with the growing splitting between

3s and 3p states, and consequently, Li-Si alloys soften with increasing Li content. Structural changes in amorphous Li_xSi were investigated as a function of Li flux density and total charge in the initial lithiation of single crystal (100) Si wafers using solid-state ^7Li nuclear magnetic resonance (NMR) spectroscopy. Solid-state ^7Li NMR spectra show that Li_xSi structures depend on the Li flux density during the initial lithiation. In addition, it was observed that under the same Li flux density, the Li concentration in Li_xSi stays constant regardless of total charges applied to the electrode. The ^7Li NMR results help better understand the chemical nature of Li_xSi clusters, the reaction mechanisms, and the kinetic modeling of chemical reactions at the reaction front during the initial lithiation of silicon electrodes.

Energy decomposition analysis for intermolecular interactions: Progress and problems, illustrated with applications

Martin Head-Gordon
Kenneth S. Pitzer Center for Theoretical Chemistry, and, Department of Chemistry, University of California, Berkeley, and, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720

Electronic structure methods today are able to accurately and relatively inexpensively calculate intermolecular interaction energies, such as arise in hydrogen-bonded systems ranging between relatively weak and very strong. While energy decomposition analysis (EDA) methods are quite well-known and widely used, there is still considerable scope for further development. I will discuss an EDA framework in which interaction energies are separated into separate contributions from permanent electrostatics and Pauli repulsions, polarization effects, and donor-acceptor charge transfer interactions. Separating the individual terms poses some interesting challenges, which will be discussed. Numerical results will be presented for conventional hydrogen bonds, as well as strong hydrogen bonds involving cationic radicals, to show how the nature of the interaction changes from being primarily electrostatic to being largely non-classical as the interacting partners change. Some other interesting and unusual intermolecular interactions will also be discussed, as progress and time permits.

How Reliable Is the Hard-Soft Acid-Base (HSAB) Principle?

Paul W. Ayers, Farnaz Heidar Zadeh, and Carlos Cárdenas
Department of Chemistry & Chemical Biology; McMaster University, Canada, Departamento de Física, Universidad de Chile, Chile

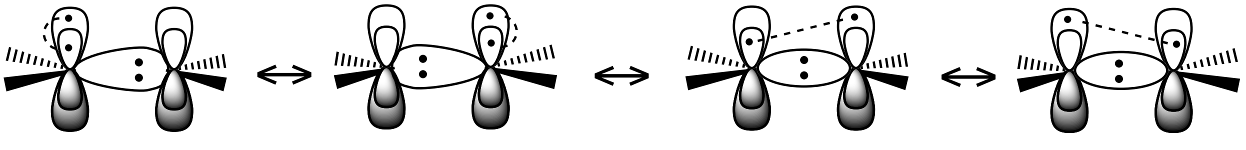
As the most fundamental rule of acid-base reactivity, the strong-weak acid-base (SWAB) principle states that, all other things being equal, strong acids displace weak acids and strong bases displace weak bases. However, when the strength of the acids and bases are similar, the hard-soft acid-base (HSAB) principle specifies the product of the reaction. Proposed by Pearson in the early 1960’s, the HSAB principle indicates that, all other things being equal, hard acids prefer binding to hard bases while soft acids prefer binding to soft bases. The “all other things being equal” caveat is never satisfied in practice, so there could be many exceptions to these rules. We assess the robustness of the HSAB principle when the strengths of acids and bases are not equal using the mathematical framework of conceptual density-functional theory (DFT), which quantifies the acid-base strength and chemical hardness through the first and second

derivatives of energy with respect to the number of electrons, at fixed molecular geometry. The reaction energies and electron-transfer energies of over four million double exchange reactions between diatomic species were computed using a complete basis set model chemistry (specifically, CBS-QB3). Following previous work, these reactions were classified into four cases, depending on the preference (reactants or products) and relative strengths of strong-weak and hard-soft driving forces. The resulting probability tables and graphs provide novel perspective on the predictive reliability of the SWAB and HSAB principles.

V state of ethylene: a challenging test case that becomes so easy with valence bond theory

Philippe C. Hiberty, Wei Wu, Huaiyu Zhang, Benoît Braida, Sason Shaik
Université de Paris-Sud

The first singlet excited state of ethylene (so-called the *V* state) is a notoriously difficult test case that has necessitated elaborate strategies and extensive configuration interaction in the molecular orbital (MO) framework. By contrast, the description of this electronic state and its transition energy from the ground state (so-called the *N* state), becomes very simple with valence bond methods. It is shown that extremely compact wave functions, made of three VB structures for the *N* state and four structures for the *V* state (**1**-**4** in the scheme below), provide an *N*®*V* transition energy of 8.01 eV, in good agreement with experiment (7.88 eV for the *N*®*V* transition energy estimated from experiments). Further improvement to 7.96/7.93 eV is achieved at the variational and diffusion Monte Carlo (MC) levels, using a Jastrow factor coupled with the same compact VB wave functions. Furthermore, the measure of the spatial extension of the *V* state wave function, 19.14 a_0^2, is in the range of accepted values obtained by large-scale state-of-the-art MO-based methods. The s response to the fluctuations of the p electrons in the *V* state, known to be a crucial feature of the *V* state, is taken into account using the breathing-orbital valence bond method (BOVB), which allows the VB structures to have different sets of orbitals, as is made apparent in **1** and **2**. Further valence bond calculations in a larger space of configurations confirm the results of the minimal structure-set, yielding an *N*®*V* transition energy of 7.97 eV and a spatial extension of 19.16 a_0^2 for the *V* state. Both types of valence bond calculations show that the *V* state of ethylene is not fully ionic as usually assumed, but involving also a symmetry-adapted combination of VB structures, **3** and **4**, each with asymmetric covalent p bonds. The latter VB structures have cumulated weights of at least 18-26%, and stabilize the *V* state by about 0.9 eV. It is further shown that these latter VB structures, rather than the commonly considered zwitterionic ones, are the ones responsible for the spatial extension of the *V* state, known to be ca. 50% larger than the *V* state.



1 **2** **3** **4**

Scheme — The compact VB representation of the *V* state of ethylene

Chemical Bonding: The Orthogonal Valence Bond View

Alexander F. Sax
Department of Chemistry, University of Graz, Austria

CASSCF wave functions are able to describe bond breaking and bond formation; the local processes, charge and spin reorganization, are however hidden by the delocalized molecular orbitals used. If the CASSCF molecular orbitals are localized by orthogonal transformations on predefined fragments,[1] the CASSCF wave function can be transformed into a VB-like wave functions that is a linear combination of orthogonal configuration state functions (CSF) made with orthogonal, localized fragment orbitals. This is called VB reading of CASSF wave functions. Some examples are given. Orthogonal VB CSFs and conventional VB CSFs, made with non-orthogonal atomic orbitals (or fragment orbitals), differ in several aspects, therefore, a short introduction into the OVB method is given. Angeli et al.[2] claim that the OVB CSFs for the hydrogen molecule have diabatic character; it will be shown, that for some test molecules our localized fragment orbitals have properties like Truhlar's diabatic molecular orbitals.[3] This corroborates the view that OVB CSFs have diabatic character. A speculative answer to the question: What kind of electrons are described by VB and OVB? is given.

[1] Alexander F Sax. Localization of molecular orbitals on fragments. J. Comp. Chem., 33(17):1495{1510, 2012.
[2] Celestino Angeli, Renzo Cimiraglia, and Jean-Paul Malrieu. Non-orthogonal and orthogonal valence bond wavefunctions in the hydrogen molecule: the diabatic view. Molecular Physics, 111(9-11):1069{1077, July 2013.
[3] Hisao Nakamura and Donald G. Truhlar. The direct calculation of diabatic states based on configurational uniformity. Journal of Chemical Physics, 115(22):10353, 2001.

Low-Scaling Approximations to the Equation of Motion Coupled-Cluster Singles and Doubles Equations

Xiaosong Li
Department of Chemistry, University of Washington

Methods for fast and reliable computation of electronic excitation energies are in short supply, and little is known about their systematic performance. This work reports new developments and assessment of several low-scaling approximations to the EOM-CCSD equations with other single reference methods for computing the vertical electronic transition energies of eleven small organic molecules. The methods, including EOM-MPBT2 and its partitioned variant, are compared to several valence and Rydberg singlet states for which accurate gas-phase experimental data is available. We find that the EOM-MBPT2 method was rarely more than a tenth of an eV from EOM-CCSD calculated energies, yet demonstrates a performance gain of nearly thirty percent. The partitioned equation-of-motion approach, P-EOM-MBPT2, which is an order of magnitude faster than EOM-CCSD, outperforms the CIS(D) and EOM-CC2 in the description of Rydberg states. The difference between the EOM-CC2 and P-EOM-MBPT2 can ultimately be traced back to how each method approximates EOM-CCSD. The result suggests that EOM-CC2 and P-EOM-MBPT2 are complementary: EOM-CC2 is best suited for the description of valence states while P-EOM-MBPT2 proves to be a superior O(N^5) method for the description of Rydberg states.

Advanced Potential Energy Surfaces for Condensed Phase Simulation

Teresa Head-Gordon
Departments of Chemistry, Bioengineering, and Chemical and Biomolecular Engineering University of California, Berkeley, CA 94720

Molecular simulation has realized broad adoption by academic researchers and industry scientists due in part to the tractability of the classical model assumption of pairwise additivity of molecular interactions. I will introduce new theoretical models and methods that include direct and mutual polarization based on the AMOEBA polarizable force field, and the Poisson Boltzmann Equation, their OpenMP/MPI implementation on multicores and high performance computing hardware platforms, that are now permitting more accurate study of larger and more complex condensed phase problems.

Chemical Bonding in Diatomic Transition Metals

Michael D. Morse
Department of Chemistry, University of Utah

The diatomic transition metals provide a fascinating and challenging group of molecules for understanding chemical bonding because of the wide variety of bonding mechanisms. Some, such as ScAu, offer the possibility of ionic bonding because of the low ionization energy of Sc and the high electron affinity of Au. Others possess what is best described as a single covalent bond, as in Cu_2 or Ag_2. In the center of the transition metal series we find species with bond orders that are nominally as large as 6 in species such as Cr_2, Mo_2, and W_2. In this talk I will present results on the chemical bonding of the multiply-bonded diatomic transition metals, examining how the bond length varies as charge is redistributed from one nucleus to the other. In the analogous main-group molecules, all of us consider N_2 to have a triple bond, and a triple bond is retained when a proton is shifted from one nucleus to the other to form CO. Shifting another proton forms BF, which has a much longer bond and is best considered to be singly bonded. With one more proton shift, we reach BeNe, with only a van der Waals bond. What happens when the nuclear charge asymmetry is introduced to the nominally sextuply bonded Cr_2? How does the bond length and ground state electronic symmetry change as we move to VMn, TiFe, ScCo, CaNi, KCu, and ArZn? What happens in the mixed 3d-4d dimer MoCr as we shift the nuclear charge to form NbMn, ZrFe, or YCo? These and related experimental results will be presented.

Chemical bonding in selected Compounds involving Group 15 Elements from the Perspective of an Experimentalist

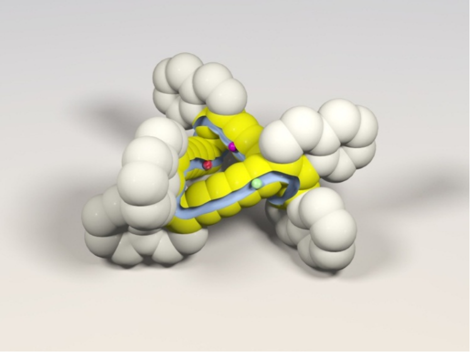
Jan Weigand
TU Dresden, Germany

TBA

Anisotropy of the Induced Current Density (ACID), a Tool to Visualize Electron Delocalization and the Synthesis of the First Triply Twisted Möbius Annulene

Rainer Herges
Otto-Diels Institute of Organic Chemistry, University of Kiel, Germany

The density of delocalized electrons is not an observable in quantum theory. Nevertheless, experimental chemists use this concept intensely in planning syntheses, designing reagents, elucidating mechanisms, and in predicting the properties of molecules. Magnetic properties have been successfully applied to quantify aromaticity (which is a special case of delocalization and also not an observable). We propose the anisotropy of the induced current density (ACID) to describe the more general concept of electron delocalization. ACID is defined in such a way that it meets the mathematical properties of an electron density (scalar field, invariant under unitary transformations, independent of the relative orientation of the molecule and the magnetic field, same symmetry as the total wave function, linear independent of the total electron density) and it does not include empirical parameters. ACID is implemented in Gaussian 09 Revision D.01. It can be applied to acyclic, cyclic, 3D delocalization of ground states, transition states, and excited states. In the second part of the talk the synthesis of the first triply twisted Möbius annulene is presented.



[1] R. Herges, in *The Nature of the Chemical Bond Revisited*: G. Frenking and S. Shaik Eds., Wiley in press
[2] D. Geuenich, K. Hess, F. Köhler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758-3772.
[3] G. R. Schaller, F. Topic, K. Rissanen, Y. Okamoto, J. Shen, R. Herges, *Nature Chem.* **2014** (doi:10.1038/nchem.1955)

Analysis of bonding patterns in molecular systems exhibiting partial biradical character

Sotiris S. Xantheas
Physical Sciences Division, Pacific Northwest National Laboratory, 902 Battelle Boulevard, P.O. Box 999, MS K1-83, Richland, WA 99352

A quantitative scale of the biradical charater ($0 \leq \beta \leq 1$) of a molecular system based on a Multi-Reference Configuration Interaction (MRCI) wavefunction is introduced and used to analyze its underlying electronic structure and bonding pattern. Triatomic ions in the FX_2^+ series, where X =

O, S, Se, Te and Po are the terminal atoms, were found to exhibit unusually high biradical characters ($0.76 < \beta < 0.92$), the largest among the homologous, 18 valence electron molecules CX_2^{2-}, NX_2^-, X_3 and OX_2 (X = O, S, Se, Te and Po). The concept of biradical character was further used to investigate the bonding mechanism in ozone (O_3) and its sulfur-substituted analogues, SO_2, OS_2, and S_3. We demonstrate that the binding in these molecules can be described by a mixture of a closed shell structure with one and a half bond between the central and terminal atoms and an open-shell structure with a single bond and two lone electrons on each terminal atom. The analysis provides a simple measure of the relative mixture of the two bonding scenarios, yielding a biradical character of 3.5% for OSO, 4.4% for SSO, 11% for S_3, 18% for O_3, 26% for SOO, and 35% for SOS. Our analysis further offers an explanation for the different O-O, S-O and S-S bond lengths and singlet-triplet splitting of these species, the stabilization of OSO and SSO over the SOO and SOS isomers as well as the (X-YZ) relative binding energies (X=S, O), all based on their different biradical character. Extensions of this approach to quantify the role of atmospherically important intermediates participating in ozonolysis and particle formation mechanisms are also introduced.

[1]V.-A. Glezakou, S. T. Elbert, S. S. Xantheas and K. Ruedenberg, *J. Phys. Chem. A* **114**, 8923 (2010).
[2] E. Miliordos, K. Ruedenberg and S. S. Xantheas, *Ang. Chem. Int. Ed.* **52**, 5736 (2013).
[3] E. Miliordos and S. S. Xantheas, *J. Amer. Chem. Soc.* **136**, 2808 (2014).

Long bonds between radicals: covalent-like bonds at 3 Å

Juan Novoa
Universitat de Barcelona, Spain

TBA

TBA

Ingo Krossing
Freiburg University, Germany

Multi-Center Bonding in 2D- and 3D- Periodic Systems

Alexander I. Boldyrev
Department of Chemistry and Biochemistry, Utah State University, Logan, UT, USA

Bonding considerations in extended 2D- and 3D- periodic systems depend on the community to which a researcher belongs. Solid-state physicists rationalize chemical bonding in periodic systems in terms of completely delocalized bands, while chemists in addition to that also consider bonding in terms of local bonds. The latter approach is important for understanding reactivities of solid-state compounds and their surfaces and for paving the road towards rational design of new materials. We recently developed the Adaptive Natural Density Partitioning (AdNDP) method,[1] which is an extension of the Natural Bond Orbital (NBO) analysis developed by Foster and Weinhold,[2] for revealing localized and multi-center bonding in finite systems in terms of 1c-2e, 2c-2e, 3c-2e, …, *n*c-2e bonds. This method has proven very successful for rationalization of chemical bonding in many molecules, clusters, complex compounds.[3-5] The

NBO method was recently extended to systems with periodic boundary conditions by Dunnington and Schmidt.[6] Based on this program, we in collaboration with Dunnington and Schmidt were able to extend our AdNDP method to Solid State Adaptive Naturally Partitioning (SSAdNDP) method, which takes into account translational symmetry.[7]

I will present results of application of the SSAdNDP method to 2D- (graphene, boron α-sheet, borane) and to 3D- (magnesium diboride, Na_8BaSn_6 Zintl phase, $CoAs_3$ skutterudite) systems. In all these cases, we were able to explain the chemical bonding from the localized and multi-center bonds perspective.

I believe that this new tool will help us to develop a systematic chemical bonding picture in 2D- and 3D- periodic systems and will help us to understand mechanisms of chemical reactions involving surfaces and bulk, as well as to rationally design of new materials.

[1] Zubarev, D. Y.; Boldyrev, A. I. Phys. Chem. Chem. Phys. **2008**, *10*, 5207–5217.
[2] Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.
[3] Galeev, T. R.; Boldyrev, A. I. *Annu. Rep. Prog. Chem., Sect. C*, 2011, 107, 124-147.
[4]Galeev, T. R.; Boldyrev, A. I. In *Comprehensive Inorganic Chemistry II (Second Edition),* Editors-in-Chief: Jan Reedijk and Kenneth Poeppelmeier, Amsterdam, 2013, pp 245-275.
[5] Popov, I. A.; Boldyrev, A. I. In *The Chemical Bonding: Chemical Bonding Across the Periodic Table*, *First Edtion*, Eds. Gernot Frenking, Sason Shaik, Wiley-VCH Verlag GmbH & Co. KGaA, of Boschstr. 12, 69469 Weinheim, Germany, Chapter 14, pp. 421-444.
[6] Dunnington, B. D.; Schmidt, J. R. *J. Chem. Theory Comput*. **2012**, *8*, 1902–1911.
[7] Galeev, T. R.; Dunnington, B. D.; Schmidt, J. R.; Boldyrev, A. I. *Phys. Chem. Chem. Phys*., **2013**, *15*, 5022-5029.