



International Conference on Chemical Bonding

*Lihue, Hawaii
July 14-18, 2016*

Sponsors:



International Conference on Chemical Bonding

Technical Program

Wednesday, July 13

Arrival and registration

Thursday, July 14

Morning: Tour de table

Presiding: Alexander Boldyrev

- 8:30 – 9:00 am Anastassia & Alex - Introductory remarks
9:00 – 9:30 am W. Carl Lineberger (University of Colorado, Boulder, CO, USA)
"Anion Photoelectron/Photodissociation Spectroscopy: Radical Thermochemistry and Solvation Dynamics"
9:30 – 10:00 am George C. Schatz (Northwestern University, USA)
"A New Direction in Chemical Bonding: Using Nanoparticles as Atoms and DNA as Linkers to Make Functional Materials"
10:00 – 10:30 am Lai-Sheng Wang (Brown University, USA)
"Photoelectron Spectroscopy of Size-Selected Boron and Doped-Boron Clusters: From Planar Structures to Borophenes, Metallo-Borophenes, and Borospherenes"
10:30 – 11:00 am Roberto Car (Princeton University, USA)
"TBA"
11:00 – 11:15 am *Coffee Break*
11:15 – 11:45 am Klaus Ruedenberg (Iowa State University, USA)
"Energy Decomposition Analysis of Molecular Wave Functions"
11:45 – 12:15 am Mark S. Gordon (Iowa State University, USA)
"Bonding Analyses for Novel Molecules"
12:15 – 12:45 am Victor I. Klimov (Los Alamos National Lab, USA)
"Mysteries of Photophysics of I-III-VI₂ Quantum Dots and the Role of "Native" Defects"

Afternoon: Fundamental aspects

Presiding: Dominika Zgid

- 3:00 – 3:30 pm Dage Sundholm (University of Helsinki, Finland)
"Calculation of Magnetically Induced Current Density Pathways in Annelated Molecular Rings"
3:30 – 4:00 pm Clémence Corminboeuf (EPFL, Switzerland)
"A Multifaceted Tool Built Upon (Non-)Covalent Interactions"
4:00 – 4:30 pm Alexander I. Boldyrev (Utah State University, USA)
"Aromaticity and Delocalized Bonding"
4:30 – 4:45 pm *Coffee Break*
4:45 – 5:15 pm Patrick Bultinck (Ghent University, Belgium)
"Constrained Quantum Chemistry: a Critical Analysis of Chemical Concepts"
5:15 – 5:45 pm F. Matthias Bickelhaupt (VU University Amsterdam, Netherlands)
"AROMATICITY. Molecular Orbital Picture of an Intuitive Concept"
5:45 – 6:15 pm Yanming Ma (Jilin University, China)
"CALYPSO: A Useful Tool for Discovery of Exotic Chemical Bonding"
07:00 – 10:00 pm **RECEPTION at Kauai Beach Resort**

Friday, July 15

Morning: Bonding at interfaces

Presiding: Anastassia Alexandrova

- 8:30 – 9:00 am Paul Weiss (UCLA, USA)
"Precise Chemical, Physical, and Electronic Nanoscale Contacts"
- 9:00 – 9:30 am Phillip Christopher (UC Riverside, USA)
"Relating Dynamic Structural and Performance Transformations on Heterogeneous Catalysts"
- 9:30 – 10:00 am Philippe Sautet (UCLA, USA)
"Molecular Bonding and Adsorption at Electrochemical Interfaces: an Approach From First Principles"
- 10:00 – 10:30 am Dmitri Kilin (North Dakota State University, USA)
"Dynamics of Electronic Excitations and Photocatalytic Reactions at Interfaces"
- 10:30 – 10:45 am *Coffee Break*

Fundamental aspects of bonding in materials

- 10:45 – 11:15 am Sergey Kalinin (Oak Ridge National Lab, USA)
"Big, Deep, and Smart Data in Materials Research: Atomic View on Chemical Bonding"
- 11:15 – 11:45 pm Ralf Tonner (University of Marburg, Germany)
"Discovering Molecular Chemistry Concepts in Functional Materials"
- 11:45 – 12:15 am Vidvuds Ozolins (UCLA, USA)
"Compressed Symmetry-Adapted Wannier Functions for Real-Space Electronic Structure Calculations"

Afternoon: Visiting different parts of the Periodic Table

Presiding: Svetlana Kilina

- 2:30 – 3:00 pm Eugen Schwarz (Universität Siegen, Germany)
"The Trend of Oxidation States Over the Periodic Table. The Case of Group 8 and the Actinides"
- 3:00 – 3:30 pm Andrei Sanov (University of Arizona, USA)
"Underemployed and Looking for Action: The Plight of Unpaired Electrons in Diradicals, Radicals, and Radical Anions"
- 3:30 – 4:00 pm Gabriel Merino (Cinvestav, Mexico)
"Nonclassical Carbocation Rearrangements"
- 4:00 – 4:15 pm *Coffee Break*
- 4:15 – 4:45 pm Jaroslav Burda (Univerzita Karlova v Praze, Česká Republika)
"Reduction Process of Tetraplatin in Presence of dGMP; Computational DFT Study"
- 4:45 – 5:15 pm Jun Li (Tsinghua University, China)
"TBA"
- 5:15 – 5:30 pm *Coffee Break*

Materials

- 5:30 – 6:00 pm Yuriy Mozharivskiy (McMaster University, Canada)
"Interplay Between the Sb/Bi Bonding and Charge Transport Properties in Rare-Earth Antimonide and Bismuthide Suboxides"
- 6:00 – 6:30 pm Sarbajit Banerjee (Texas A&M, USA)
"Mapping Phase Transitions in Ternary Vanadium Oxides: Small Polaron Formation and the Realization of "Purer" Mott Transitions"
- 6:30 – 7:00 pm Boniface Fokwa (UC Riverside, USA)
"Magnetic Ordering, Frustration and Possible Spin Liquid State from 1D Cr₃-Triangles in the TiCrIr_{2-x}Os_xB₂ Series"

Saturday, July 16

TOUR DAY

Sunday, July 17

Morning: Bonding facilitates materials' discovery

Presiding: Ivan A. Popov

- 9:00 – 9:30 am Michael Shatruk (Florida State University, USA)
"Activation of Red Phosphorus: Opening New Possibilities in the Main-Group Chemistry"
- 9:30 – 10:00 am Tadashi Ogitsu (Lawrence Livermore National Laboratory, USA)
"Stabilization Mechanisms of Boron Allotropes (and Compounds)"
- 10:00 – 10:30 am John S. Tse (University of Saskatchewan, Canada)
"Towards a Structural Principle for High Pressure Solids"
- 10:30 – 10:45 am *Coffee Break*
- 10:45 – 11:15 am Li-Ming Yang (Huazhong University of Science and Technology, China)
"The Chemical Bonding of Two Dimensional Layered Materials"
- 11:15 – 11:45 pm Aristides Zdetsis (University of Patras, Greece)
"Aromaticity and Related Properties of Graphene and Graphene-Based Materials: Traditional Methods New Understanding and Outlook"
- 11:45 – 12:15 am Eva Zurek (SUNY Buffalo, USA)
"Theoretical Predictions of Superconducting Hydrides Under Pressure"

Afternoon: Inorganic and homogeneous systems

Presiding: Clémence Corminboeuf

- 3:00 – 3:30 pm Alexander Spokoyny (UCLA, USA)
"Organomimetic Boron Cluster Chromophores and Photosensitizers"
- 3:30 – 4:00 pm Longjiu Cheng (USTC, China)
"Super Covalent Bond Model"
- 4:00 – 4:30 pm Theodore Betley (Harvard University, USA)
"High-Spin Electronic Structures in Cluster Design"
- 4:30 – 5:00 pm Matthew D. Woodrich (EPFL Lausanne, Switzerland)
"Volcano Plots as Tools for Screening Homogeneous Catalysts"
- 5:00 – 5:15 pm *Coffee Break*

Fundamentals

- 5:15 – 5:45 pm Cheuk-Yiu Ng (University of California, Davis, USA)
"A Quest to Identify a Quantum Chemical Procedure for Energetic Predictions of Transition-Metal-Containing Species with Chemical Accuracy"
- 5:45 – 6:15 pm Svetlana Kilina (North Dakota State University, USA)
"Bond Analysis and Electronic Properties of Functionalized Cyclosilanes"
- 6:15 – 6:45 pm Miroslav Kohout (Max Planck Institute, Germany)
"The Position Space Perspective of Chemical Bonding"

Monday, July 18

Morning: Clusters, molecules, and more

Presiding: Michael Shatruk

- 9:00 – 9:30 am Si-Dian Li (Shanxi University, China)
“Structures and Bonding of the B_n^q Borospherene Family ($q=n-40$, $n=36-42$)”
- 9:30 – 10:00 am Jesus Ugalde (University of the Basque Country, Spain)
“Structural and Optical Properties of the Naked and Passivated Al_5Au_5 Bimetallic Nanoluster”
- 10:00 – 10:30 am Xue-Bin Wang (Pacific Northwest National Lab, USA)
“Anion Specificity in Hydrated Clusters and Anion- π Complexes”
- 10:30 – 11:00 am Wojciech Grochala (University of Warsaw, Poland)
“Learning from Hydrogen and Hydrides: Opening the $1s^2$ Doublet”
- 11:00 – 11:15 am *Coffee Break*
- 11:15 – 11:45 pm Alexander Sax (Karl-Franzens-Universität Graz, Austria)
“The Role of Spin in Strong, Covalent and in Weak, Non-Covalent Bonding”
- 11:45 – 12:15 pm Célia Fonseca Guerra (VU University Amsterdam, Netherlands)
“Molecular Recognition in DNA: the Role of Aromaticity, Hybridization, Electrostatics and Covalency”
- 12:15 – 12:45 am Cina Forouta-Nejad (Masaryk University, Czech Republic)
“Modulating Inter-Molecular Interactions via an External Electric Field”

Afternoon: Fundamentals of bonding in materials

Presiding: Alexander Spokoyny

- 2:30 – 3:00 pm Ivan A. Popov (Utah State University, USA)
“Unique Cases of Chemical Bonding in Clusters and Solids: Localized and Delocalized Bonding Patterns”
- 3:00 – 3:30 pm Yirong Mo (Western Michigan University, USA)
“Intramolecular Multi-Bond Strain: The Unrecognized Side of the Dichotomy of Conjugated Systems”
- 3:30 – 4:00 pm Dominika Zgid (University of Michigan, USA)
“Green's Function Embedding Methods for Molecules and Solids”
- 4:00 – 4:30 pm Paul J. Robinson and Anastassia N. Alexandrova (UCLA, USA)
“Ultra-Hard Borides: Bonding, Hardness, Anisotropy, Mixed Valency”
- 5:00 – 9:00 pm **BANQUET -LUAU at Smith Restaurants**
Hawaiian Show + Dinner
- Pick up at Kauai Beach Resort Lobby*

Abstracts

Anion Photoelectron/Photodissociation Spectroscopy: Radical Thermochemistry and Solvation Dynamics

W. Carl Lineberger

JILA and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA

Anion photoelectron spectroscopy has proven to be a remarkably useful tool to obtain fundamental thermochemical and structural information for stable and transient species. This approach has proven especially useful when coupled with high-level theoretical analyses. I review briefly the experimental methodology and discuss several examples that illustrate both the opportunities and the essential need for collaboration between theorists and experimentalists. The anions described here all present large scale nuclear motion following electron photodetachment: methyl radical, hydroxymethoxyl radical ($\text{H}_2\text{C}(\text{OH})\text{O}^-$) and methylphenols.

Acknowledgements: Generously supported by the National Science Foundation and The Air Force Office of Scientific Research.

A New Direction in Chemical Bonding: Using Nanoparticles as Atoms and DNA as Linkers to Make Functional Materials

George C. Schatz

Department of Chemistry, Northwestern University, Evanston, IL, 60208, USA

In this talk I describe recent advances in experiment and theory in which crystalline lattices are synthesized in which nanoparticles serve as atoms and DNA linkers provide the “glue” that binds the nanoparticles into complex materials with novel functionality. This work has been a joint collaboration with Chad Mirkin, and it began in 2008 with the fabrication of superlattices composed of identical gold particles that could either be fcc or bcc depending on whether the DNA is self-complementary or not. Subsequent work has resulted in a couple dozen different lattice structures, with theory providing guiding principles for assembly based on the principle that the equilibrium crystal structure is determined by maximizing DNA hybridization. Structures based on particles other than gold, and on RNA linkers are also described. In addition to simple analytical models, we have developed the theory of these structures using both all-atom and coarse-grained models, and this has enabled us to describe structures that include anisotropic nanoparticles in addition to the spherical particles that are commonly considered. Applications of these superlattices in plasmonics is described to illustrate how these materials can be used to provide new functionality that is not available in more traditional atom-based materials.

Photoelectron Spectroscopy of Size-Selected Boron and Doped-Boron Clusters: From Planar Structures to Borophenes, Metallo-Borophenes, and Borospherenes

Lai-Sheng Wang

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Photoelectron spectroscopy in combination with computational chemistry over the past decade has shown that boron clusters possess planar or quasi-planar structures [1-3], in contrast to that of bulk boron, which is dominated by three-dimensional 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 double aromaticity.

Because of its electron deficiency, boron cannot form graphene-like structures with a honeycomb hexagonal framework. Computational studies suggested that extended boron sheets with partially filled hexagonal holes are stable. We have found that B_{36} is a highly stable planar boron cluster with a central hexagonal hole (Fig. 1). This finding provided the first indirect experimental evidence that single-atom layer boron-sheets with hexagonal vacancies, which we named “borophenes” [4], are potentially viable. We further found that the B_{35}^- cluster also possesses a hexagonal structure with two adjacent hexagonal holes and can be a more flexible motif for borophenes with different atomic arrangements [5]. More interestingly, our photoelectron spectroscopic studies revealed that the B_{40}^- cluster consisted of two nearly degenerate isomers competing for the global minimum: a quasi-planar isomer with two hexagonal holes and an unprecedented cage isomer (Fig. 2). In the neutral, the B_{40} cage is overwhelmingly the global minimum, which is the first all-boron fullerene to be observed and is named “borospherene” [6]. Further studies showed that the B_{39}^- cluster consisted of two nearly degenerate chiral cage structures [7], suggesting the possibility of a family of borospherenes. Finally, I will also discuss our recent progress to investigate transition metal doped boron clusters [8] and the possibility for metallo-borophenes [9].

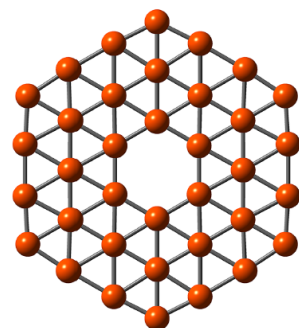


Fig. 1. The B_{36} cluster.

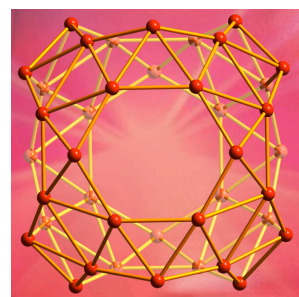


Fig. 2. The B_{40} cluster.

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TBA

Roberto Car
Princeton University, USA

Energy Decomposition Analysis of Molecular Wave Functions

Klaus Ruedenberg, Aaron C. West, Michael W. Schmidt, Mark S. Gordon
Department of Chemistry and Ames Laboratory USDOE, Iowa State University, Ames, Iowa 50011

The concepts that were developed in the 1930's to explain fundamental aspects of chemical bonding were aimed at sorting out the physical reasons for the energy lowering when atoms link up on the basis of the variation principle. While these qualitative elucidations were eminently successful, the development of a corresponding rigorous energy analysis of rigorous ab initio wave functions has proven difficult. In the present work, this analysis is obtained for strongly correlated molecular wave functions.

The basis of the analysis is the unbiased and basis-set-independent transformation of the molecular wave function into an expansion in terms of configurations generated from 'quasi-atomic' orbitals, i.e. orbitals in the molecular orbital space that are (i) as close to free atom orbitals as possible and (ii) 'hybridized' so as to be involved in individual bonds or no bonds. The existence of such quasi-atomic orbitals with strong atomic character, obtained through series of singular value decompositions and quartic optimizations has been established. The energy analysis is based on the expression of the first and second order density matrices in terms of these orbitals.

The major hurdle for any binding energy analysis is to account for the intra-atomic energy increases as well as the interatomic energy decreases. The problem is the rigorous identification of the atomic valence states that are embedded in a molecular wave function. The objective is accomplished by resolving the molecular wave function into three parts $\Psi = \Psi_v + \Psi_{sh} + \Psi_t$, where Ψ_v represents the juxtaposed valence states, Ψ_{sh} accounts for electron sharing without charge transfer, and Ψ_t accounts for the effect of interatomic charge transfer. From this resolution, atomic promotion energies, covalent binding energies and charge transfer energies are deduced. The energies are further resolved in terms of interference energies and coulombic energies

between the quasi-atomic orbitals on the atoms. The differences between the atomic valence states and ground states are resolved into orbital changes and configurational changes.

Applications of the analysis to specific molecules are discussed. In all molecules examined so far by this method, covalent bonding has been found to result from the kinetic energy lowering due to interatomic orbital interference between quasi-atomic orbitals. The sum total of the interatomic potential energy interactions has always been found to be antibonding. Accordingly, a simple approximate indicator for the comparison of covalent bond strengths, *viz.* the kinetic bond order, has been formulated.

Acknowledgements: Work is supported by the National Science Foundation

Bonding Analyses for Novel Molecules

Mark S. Gordon, Juan Duchimaza-Heredia, Michael W. Schmidt, Klaus Ruedenberg and Aaron West

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A mathematically rigorous and conceptually appealing analysis of the chemical bond has been developed by the authors. The analysis is applicable to the broad range of chemical environments. In this presentation, the bonding analysis will be applied to several interesting systems, including pyrogostic bonding, the bonding between rare gases and organic compounds, and water clusters.

Mysteries of Photophysics of I-III-VI₂ Quantum Dots and the Role of “Native” Defects

Nikolay Makarov, Addis Fuhr, Huidong Zang, Hongbo Li, Hyeong Jin Yun, and Victor I. Klimov

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The focus of this presentation is on photophysical properties of colloidal CuInSe_xS_{2-x} (CISeS) quantum dots (QDs) discussed in the context of their applications in light-emission and light-harvesting technologies. The CISeS QDs are close relatives of well-studied CdSe QDs, but with an important advantage of being free of toxic elements. This feature has motivated a significant amount of recent research into nanocrystals of CISeS and related compounds (*e.g.*, Ag-based) as a commercial-viable alternative to Cd-containing II-VI QDs. The CISeS semiconductors are good light absorbers and further have a band-gap, which is narrower than that of CdSe (as low as ~1 eV in the case of pure-phase CISe). These properties make them well-suited for harvesting sunlight, as was proven, for example, by our demonstration of the first certified sensitized photovoltaic (PV) cells based on CISeS QDs with efficiencies >5% (McDaniel *et al.*, *Nature Comm.* **4**, 2661, 2013). Recent follow-up efforts in this area have resulted in the development of CISeS QD devices with the record efficiencies (>10%) among the QD-PVs of all types. CISeS QDs are

also excellent emitters with photoluminescence (PL) quantum yields greater than 80% (L. Li *et al.*, *J. Am. Chem. Soc.* **133**, 1176, 2011). For this reason, these materials have been explored in the context of potential applications in light-emitting diodes and solid-state lighting.

Despite a large number of practical device demonstrations, the understanding of photophysics of CISES QDs is surprisingly poor, especially given a close similarity between I-III-VI₂ and II-VI semiconductors. Among the mysteries of these materials are very long radiative lifetimes (100 – 500 ns vs. ~20 ns in CdSe QDs), an extremely large Stokes shift between the PL band and the absorption onset (300-500 meV vs. <100 meV in CdSe QDs), and a strong PL broadening (>300 meV vs. <100 meV in CdSe QDs). To address these unusual properties, we have conducted a series of comprehensive spectroscopic studies using ensemble and single-dot techniques, methods of magneto-optics and spectro-electrochemistry, and various time-resolved PL and transient absorption spectroscopies. One outcome of these studies has been a strong indication that unusual PL properties of the CISES QDs originate from the involvement of one specific intra-gap defect, which is surprisingly persistent across all studied samples, suggesting that it is “native” to this material. Further, the similarity between optical properties of CISES QDs and II-VI QDs intentionally doped with Cu-ions suggests that this native defect is Cu-related (Rice *et al.*, *J. Phys. Chem. Lett.* **5**, 4105, 2014). Based on considerations of charge neutrality and defect-formation energies, we have identified several possible defect pairs (general structure: Cuⁿ⁺-Xⁿ⁻) that can explain our experimental observations. We have further concluded that the occurrence of these pairs depends on the initial position of the Fermi level in the system, which can be controlled by sample stoichiometry.

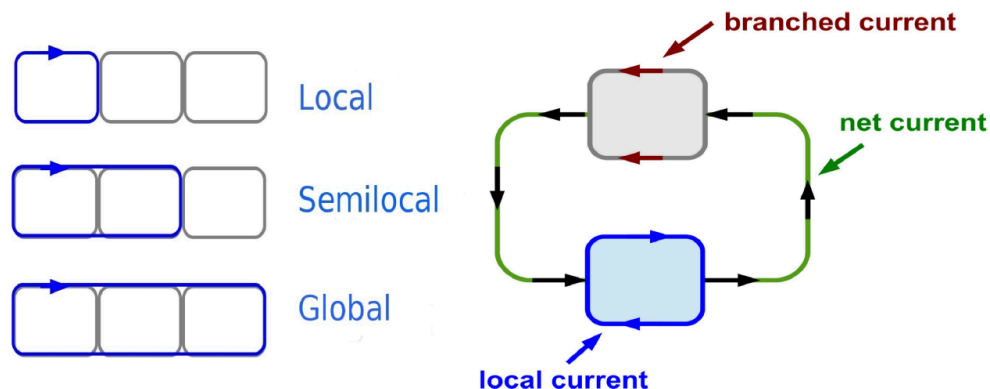
Calculation of Magnetically Induced Current Density Pathways in Annelated Molecular Rings

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Recent applications of the gauge-including magnetically induced currents (gimic) method are presented [1,2,3]. The method has been employed in aromaticity studies of porphyrinoids and related molecules. By using numerical integration approaches, we can assess global, semilocal and local aromatic properties of multiring molecules. Numerical integration of the current density combined with guiding visualization techniques of the current flow is shown to be a powerful tool for studies of the aromatic character of complicated molecular structures such as annelated aromatic and antiaromatic rings. The approach has been used for understanding current pathways in porphyrins and in bispentalene annelated naphthalene and benzene molecules [4,5]. GIMIC calculations and related approaches have recently been reviewed [6].



Local, semi-local, global, ring currents as well as bifurcated current pathways.

References:

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A Multifaceted Tool Built Upon (Non-)Covalent Interactions

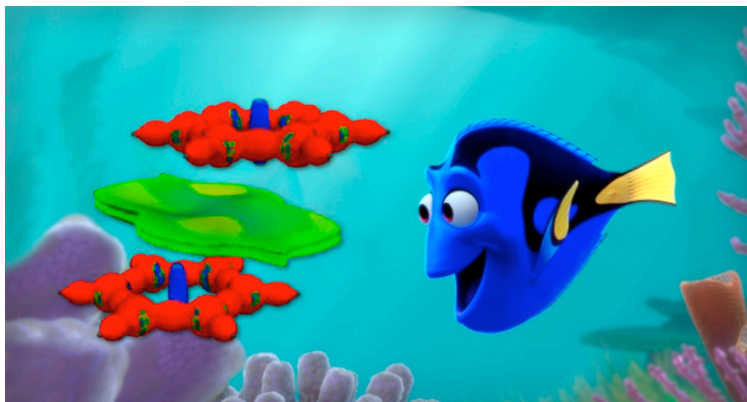
Clémence Corminboeuf^{a,*} Piotr de Silva,^{a,b} Laurent Vannay^a

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We will discuss the latest updates regarding a computational tool that simultaneously reveals different types of bonding and non-covalent interactions. The Density Overlap Region Indicator (DORI) [1] depends only on the density and its derivatives can distinguish between one-electron-like regions (e.g., core electrons and tails) from high-overlap bonding regions. The field of applicability capability of the descriptor will be illustrated through the analysis of visual and numerical DORI signatures associated with various chemical situations, ranging from identifying the nature of a bond to the design of compact one-dimensional organic nanowires [2]. It will also be shown that the attractive characteristics of this density overlap regions indicator (DORI) also make it a suitable ingredient of various types of density functionals [3].



References:

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Aromaticity and Delocalized Bonding

Alexander I. Boldyrev

Department of Chemistry and Biochemistry, Utah State University, Logan, USA

Kekulé introduced aromaticity 150 years ago in order to address low reactivity and high stability of unsaturated hydrocarbons such as benzene and its derivatives. However, reactivity is a difficult criterion to apply for molecules in order to find out if they are aromatic or not. Hückel was first who introduced an electronic criterion of aromaticity in 1931. According to Hückel, cyclic planar hydrocarbons are aromatic if they have $4n+2$ π -electrons. This is a qualitative criterion for aromaticity, which does not address the question on how aromatic a particular molecule is. Breslow proposed antiaromaticity, which explains higher than expected reactivity of cyclic molecules with $4n$ π -electrons. Since then many electronic criteria such as NICS index, MCI index, ring current, and other were introduced in chemistry in order to quantify aromaticity/antiaromaticity. Aromaticity and antiaromaticity were also extended into σ -, δ -, and ϕ -types of bonding. Also, multiple aromaticity, multiple antiaromaticity, and conflicting aromaticity based on σ -, δ -, π -, and ϕ -types of bonding were introduced in chemistry. All these new types made deciphering aromaticity to be very complicated. In 2008 we introduced a new method Adaptive Natural Density Natural Partitioning (AdNDP) [1] for molecules and clusters and in 2013 we developed Solid State Adaptive Natural Density Partitioning (SSAdNDP) [2] method for extended 1D-, 2D-, and 3D- systems with periodic boundary conditions. These methods allow us for the first time to partition bonding in complicated molecules, clusters and solids in localized bonding and delocalized bonding, and thus to look for aromaticity/antiaromaticity. If a molecule or a cluster has a globally delocalized bonding, then we believe we can assign such molecule as globally aromatic.

In my talk I will present examples of such systems. For such systems we can develop counting rules of aromaticity similar to Hückel's rules and I will present those rules for chemical

species with odd and even number of atoms in the ring. Similarly, counting rules can be developed for antiaromatic molecules. I will also present those rules for cyclic systems with odd and even number of atoms. It is interesting to note that globally antiaromatic σ -, δ -, π -, and ϕ -electron systems can be split into locally aromatic fragments. I will also show examples of aromatic systems with periodic boundary conditions. We believe that our way of analyzing aromaticity and antiaromaticity in complicated clusters, molecules, and 1D-, 2D-, and 3D-systems using our AdNDP and SSAdNDP methods could be a viable direction in deciphering aromaticity/antiaromaticity in chemistry. However, similar to Hückel's $4n+2$ rule for π -electrons, our conclusions should be considered as qualitative assignments.

Acknowledgements: This research was supported by the National Science Foundation (CHE-1361413).

References:

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Constrained Quantum Chemistry: a Critical Analysis of Chemical Concepts

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In DFT we write the energy alternatively as $E[\rho]$ or $E[N, v]$ where N is the number of electrons and v the external potential. However, one may also write it as $E[N_A, N_B, v]$ where in this example we have the diatomic AB and N_A is the number of electrons on A. This is a cornerstone of electronegativity equalisation methods [1] (EEM) where essentially one relies on the fact that in a molecule every subentity (atom, functional group, ...) has the same chemical potential as the whole molecule as otherwise no stable system would result. EEM methods require parameters (see e.g., [2]) obtained by regression although we have shown that they can be computed from constrained quantum chemistry [3-4].

Our ability to compute wave functions under a constraint in N_A and N_B opens the path to a new critical analysis of chemical concepts by widening the range of possible constraints by for example constraining N_{AB} , the number of shared electrons in the diatomic AB. What if we take for example $N \equiv N$ and compute wave functions where we intervene in the number of electron pairs in the bond? It is often assumed that if one would reduce the number of bonding pairs, one would also make the equilibrium distance longer. However, this assumption has never been tested in practice.

I will show how N_{AB} can be constrained using Mulliken's method. This method works in MO coefficient space and so can be implemented in a regular SCF procedure where one optimises the MO's. In SCF, the expectation value of a one-electron operator \hat{A} is:

$$\sum_i \langle i | \hat{A} | i \rangle \quad (1)$$

(Greek symbols refer to atom centred basis functions, $\phi_\mu \equiv |\mu\rangle$), Latin symbols refer to the MO basis. \mathbf{S} is the overlap matrix between the atom centred basis functions and \mathbf{C} is the matrix connecting the orthonormal basis functions and the atom centred basis functions: $|i\rangle = \sum_\mu C_{\mu i} |\mu\rangle$.

The Mulliken projection operator leads to atomic densities and is based on the attachment of the basis functions to atoms. The operator for atom A is given by:

$$\hat{\Pi} = \sum_{v \in A} \sum_\mu |v\rangle \langle S^{-1} \rangle_{v\mu} \langle \mu| \quad (2)$$

So by acting over the MO's, we get:

$$N_A = \sum_i \sum_{v \in A} \sum_\mu \langle i | v \rangle S_{v\mu}^{-1} \langle \mu | i \rangle \quad (3)$$

or using $|i\rangle = \sum_\sigma C_{\sigma i} |\sigma\rangle$ we get:

$$N_A = \sum_i \sum_{v \in A} \sum_\mu \sum_\sigma \sum_\lambda C_{\sigma i}^* S_{\sigma v} S_{v\mu}^{-1} S_{\mu\lambda} C_{\lambda i} \quad (4)$$

$$= \sum_i \sum_{v \in A} \sum_\mu (C^t S)_{iv} S_{v\mu}^{-1} (S C)_{\mu i} \quad (5)$$

We can now augment the Fock operator by simply adding a Lagrange term, and making sure the constraint is Hermitian.

In this presentation, I also show that many "assumptions" on how the energy or the wave function would change under a change in atomic charge, bond order, ... can not be validated. Moreover, application of this type of constraints at very long interatomic distances using Full CI calculations provide an alternative proof of the piecewise linear E versus N relationship compared to the ensemble based proof [5].

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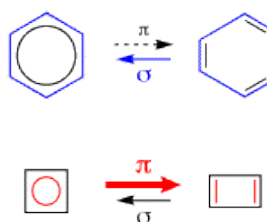
Aromaticity. Molecular Orbital Picture of an Intuitive Concept

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Geometry is one of the primary and most direct indicators of aromaticity and antiaromaticity: a regular structure with delocalized double bonds (e.g., benzene) is symptomatic of aromaticity whereas a distorted geometry with localized double bonds (e.g., 1,3-cyclobutadiene) is characteristic of antiaromaticity.



In my lecture, I present a MO model of aromaticity that explains, in terms of simple orbital-overlap arguments, why this is so. Our MO model is based on accurate Kohn-Sham DFT analyses of the bonding in benzene, 1,3-cyclobutadiene and various other cyclic molecules. In particular, I will show that the propensity of the π electrons is always, i.e., in both aromatic and antiaromatic molecules, to localize the double bonds, against the delocalizing force of the σ electrons. Interestingly, the π electrons nevertheless decide about the localization or delocalization of the double bonds (see illustration). I will point out the connection with larger aromatic ring systems, with aromatic transition states in pericyclic reactions, and with aliphatic ring systems.

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CALYPSO: A Useful Tool for Discovery of Exotic Chemical Bonding

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Knowledge of crystal structures is essential if the properties of materials are to be understood and exploited. Theoretical prediction of atomistic structures of materials with the only given

information of chemical compositions becomes crucially important, but it is extremely difficult as it basically involves in exploring a huge number of energy minima on the potential energy surface [1].

We have developed a CALYPSO approach [2-3] for structure prediction from “scratch” based on swarm algorithm by taking the advantage of swarm intelligence and structures smart learning. The method has been coded into CALYPSO software (<http://www.calypso.cn>, free for academic use), which has been widely applied into structure design on bulk materials, 2D layer materials, surface reconstruction, nanoclusters, etc [4].

In this presentation, I will give a short introduction to the CALYPSO method on why and how it can work efficiently on structure prediction, and then I shall focus on the application of CALYPSO into exploration of exotic chemical bondings formed in unusual stoichiometries of Fe₃Xe [5], N₆Xe [6], H₅Cl [7], AuLi₃ [8] and HgF₄ [9] under high pressures that are not accessible to ambient pressure.

Exotic chemical bondings will be reported: (i) Xe shows rich chemistry by reacting with Fe and N₂ [5-6]; (ii) Hg in HgF₄ compound transfers charge from its completely filled d orbitals to the F, thus Hg behaves as a real transition metal having a typical geometry for d⁸ metal centers [9]; (iii) Triangular H₃⁺ ions known in the interstellar medium have been stabilized for the first time in the crystalline structure of H₅Cl [7]; (IV) The high negative oxidation state (> -1) of Au has been achieved in AuLi₄ and AuLi₅, where Au acts as a 6p-element [8].

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Precise Chemical, Physical, and Electronic Nanoscale Contacts

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The chemical, physical, and electronic connections that materials make to one another and to the outside world are critical. Just as the properties and applications of conventional semiconductor devices depend on these contacts, so do nanomaterials, many nanoscale measurements, and devices of the future. We discuss the important role that chemistry can play in making and optimizing precise contacts that preserve key transport and other properties. Initial nanoscale connections and measurements guide the path to future opportunities and challenges ahead. Band alignment and minimally disruptive connections are both targets and can be characterized in both experiment and theory.

Relating Dynamic Structural and Performance Transformations on Heterogeneous Catalysts

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The use of heterogeneous catalysts for important chemical conversions often relies on the design of active sites consisting of metal nanoparticles supported on high surface area oxide materials. Key to design of these systems is the identification of active site geometries and compositions that are optimized for desired catalytic reactions. However, the exposure of oxide-supported metals to reactive environments can induce significant transformations in the structure of the metal, support, and interactions between the metal and support. The dynamic transformations in catalytic structures induced by exposure to reactions can cause significant changes in the reactivity of the structures, requiring detailed *in-situ* analysis to identify active site motifs.

I will highlight a few examples where we exploit quantitative and *in-situ* spectroscopy and microscopy to characterize heterogeneous catalysts at atomic scale and identify how reactive conditions modify active site structures and relate this to catalytic performance. The first example will focus on the identification of the most active configuration of Pt atoms for Al₂O₃ supported Pt nanoparticles in CO oxidation reaction conditions mimicking the catalytic convertor. We utilize quantitative *in-situ* IR spectroscopy to identify that reaction conditions reconstruct Pt surfaces, inducing surface faceting and minimizing the concentration of the active Pt sites, which are well-coordinated Pt atoms. In the second example, it will be shown that the selectivity of oxide-supported Rh catalysts in the reaction of CO₂ reduction by H₂ can be manipulated through a process where strongly bound HCO_x adsorbates on reducible supports dynamically induce the formation of discontinuous support overlayers on top of Rh nanoparticles. Mechanistic analysis using *in-situ* FTIR spectroscopy, transmission electron microscopy, electron energy loss spectroscopy and X-ray absorption spectroscopy provide insights into the formation and composition of the oxide overlayer on Rh and its resulting influence on Rh reactivity.

Molecular Bonding and Adsorption at Electrochemical Interfaces: an Approach from First Principles

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Electrified interfaces are central for electrocatalysis, batteries and molecular electronics. Experimental characterization of these complex interfaces with atomic resolution is highly challenging. First principles modeling could provide a link between the measurable quantities and an atomic scale understanding. However, such simulations are far from straightforward. Although approaches that include the effect of the potential and the electrolyte have been

proposed, detailed validation has been scarce and "indirect" since atomically resolved experimental studies of systems that can be convincingly simulated are scarce.

We introduce in this lecture the adsorption of pyridine on Au(111) as a convenient and relevant model: the adsorption mode of pyridine switches as a function of the electrochemical potential. We demonstrate that the primitive surface-charging model gives qualitatively correct results at a low cost. For quantitative agreement, however, the model needs to include a more realistic description of the electrical double layer. Approximating the latter through the linearized Poisson-Boltzmann equation leads to a quantitative improvement, lowering the error in the transition potential from 1 V to acceptable 0.3 V. Hence, we demonstrate the qualitative usefulness of the surface charging method and the excellent agreement that can be obtained by slightly more sophisticated electrolyte models.

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Dynamics of Electronic Excitations and Photocatalytic Reactions at Interfaces

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Atomistic modeling of broad range of excited state dynamics and charge transfer reactions at metal-to-semiconductor interfaces [1], supported metal clusters in aqueous environment [2], as well as in organic-inorganic lead-halide perovskites [3] and laser crystals[4] is performed by a range of methodologies including reduced density operator method, with nonadiabatic coupling being computed on-the-fly along nuclear trajectory [5]. A solution for non-equilibrium density of electrons is used for determining the dynamics of formation of surface charge transfer states, computing surface photo-voltage, and rates of energy and charge transfer [6]. An average over long *ab initio* molecular dynamics trajectories provides inhomogeneous broadening of spectral lines [7]. A modification of this methodology helps to evaluate distribution of products in photo-assisted reactions [8]. Atomistic modeling of photocatalytic reactions such as photo-electrochemical water splitting facilitated by metal catalysts at semiconductor support is represented with two subsequent phases, *photophysical* and *photochemical* ones. These phases are modeled independently as simultaneous description of them prohibitively increases numerical cost. Modeling of the *photophysical* phase demonstrates how the electronic structure features of metal and substrate determine optical absorption, direction of charge transfer, and amount of charge Q, injected to the metal catalyst [1],[2]. During the *photochemical* phase, the metal catalyst, enriched with certain amount of injected charge Q interfaces the thermal ensemble of reactant molecules, while the semiconductor substrate is removed from the explicit consideration. Charge transfer from metal catalyst to the reactants facilitates formation of the products, modeled by *ab-initio* molecular dynamics. The case study of a proton reduction half-

reaction at Pt and Pt nanocatalys allows to identify optimal ranges of reaction temperatures and amount of injected charge Q that maximizes product formation (hydrogen evolution) [9].

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Big, Deep, and Smart Data in Materials Research: Atomic View on Chemical Bonding

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The development of electron and scanning probe microscopies in the second half of XX century have produced spectacular images of internal structure and functionalities of matter with nanometer and now atomic resolution. Much of this progress since 80ies was enabled by computer-assisted methods for data acquisition and analysis that provided automated analogs of classical storage methods. However, the progress in imaging technologies since the beginning of XXI century has opened the veritable floodgates of high-veracity information on atomic positions and functionality, often in the form of multidimensional data sets containing partial or full information on atomic positions, bonding, electronic and magnetic functionalities, etc. In this presentation, I will discuss the imaging-enabled pathways to bridge imaging and theory via big data technologies to enable design of new materials with tailored functionalities. This goal will be achieved first through a big data approach – i.e., developing pathways for full information retrieval and exploring correlations in structural and functional imaging. In electron microscopy, the big data approaches are illustrated by full data acquisition in ptychography and real-space crystallographic mapping. In scanning probe microscopy, I will illustrate the examples of correlative data mining from structural images and structural-tunneling spectroscopic image pairs. These techniques can be further extended to develop structure property relationships on atomic levels, creating a library of atomic configurations and associated properties. I will further illustrate the creation of artificial non-equilibrium materials structures via controlled e-beam and He ion irradiation of materials with in-situ atomic resolution imaging. A deep data approach will allow merging this knowledge with physical models, providing input into the Materials Genome program and enabling a new paradigm for materials research based on theory-

experiment matching of microscopic degrees of freedom. Finally, a smart data approach will enable algorithms for data identification, expert assessment, and ultimately, control over matter.

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Discovering Molecular Chemistry Concepts in Functional Materials

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In molecular chemistry, quantum chemical methods reached a state where accuracy is comparable or even exceeds experimental approaches. Similarly, bonding and reactivity concepts based on various analysis methods are well established and very often complement experimental studies to aid interpretation or predict new chemistry. Surprisingly, this fruitful interplay of quantitative and qualitative theoretical approaches and experiment has barely been extended to surfaces and solids [1]. The increasing interest in materials designed for a specific purpose (functional materials) demands increasing efforts also in the theoretical description. Hence, an approach based on electronic structure theory will be presented that uses bonding and reactivity concepts from molecular chemistry for extended systems in surface and solid state sciences. Transferring a quantitative bonding analysis method from molecular systems to extended systems [2], in combination with other analysis methods and the application of density functional theory allows to describe both finite and extended systems equally well. Chemical and physical phenomena observed, e.g. in surface adsorption processes or interface structure formation can thus in many cases be understood in terms of molecular chemistry concepts. Examples from organic functionalization of semiconductors [3], surface chemistry in heteroepitaxy thin-film growth [4] or analysis of metal-organic interfaces [5], highlight the strength of this approach.

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Compressed Symmetry-Adapted Wannier Functions for Real-Space Electronic Structure Calculations

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Electronic states of periodic solids are usually discussed in terms of periodic Bloch waves with definite crystal momentum. Spatially localized Wannier functions (WFs) represent an alternative picture of electronic states in solids that has both conceptual and numerical advantages. Unfortunately, the calculation of exponentially localized Wannier functions is difficult for large systems. We propose a method for calculating WFs of periodic solids directly from a modified variational principle for the energy, without the need to obtain the Bloch eigenstates. Spatial localization is achieved by adding a weighted regularization term to the energy functional, chosen as the L_1 norm of the Wannier function. This approach results in "compressed" WFs with compact support (i.e., WFs are nonzero in a finite spatial region), and one parameter automatically controls the trade-off between the accuracy of the total energy and the localization of the WFs. In periodic solids, the WFs can be chosen as irreducible representations of the crystal symmetry group. Efficient numerical algorithms for the variational minimization problem are demonstrated. Applications to periodic systems, topological insulators and point defects in periodic solids are discussed to illustrate the advantages of this approach, and implementation within the density-functional theory is demonstrated.

The Trend of Oxidation States Over the Periodic Table. The Case of Group 8 and of the Actinides

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We have quantum-chemically investigated metal poly-oxide molecules of groups 6 [1-3], 7 [4], and 8 [5-8] at the correlated relativistic level, accompanied by highly accurate spectroscopic data from experimentalists. The later 3d and the earlier 5f6d elements are very special owing to their valence AOs of intermediate overlap capacity and their strong electron attracting power in high oxidation states. Besides O^{2-} ligands, also O^{1-} , O^{q-} and O_2^{2-} , O_2^{1-} , O_2^0 , O_3^- etc. ligands are common, O exhibiting various integer, rational and real oxidation numbers. We explain why it is often the O that yields the highest formal oxidation state of the metal, despite the higher electronegativity of F vs. O: Namely, formal F^I corresponds to physical F^{1-} , while formal O^{II} may correspond to physical O^{q-} , $q < 2$. We explain why sometimes not all valence electrons of the metal atoms can be oxidized. Further, we discuss how the atomic overlap and electronegativity properties may

support open-shell spin-singlet multi-configuration two-electron bonds instead of common closed-shell spin-singlet Lewis-type bonding.

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Underemployed and Looking for Action: The Plight of Unpaired Electrons in Diradicals, Radicals, and Radical Anions

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Elusive reactive intermediates and transient molecules are investigated by anion photoelectron imaging spectroscopy. We will present recent results focusing on the electronic structure and photochemistry of several radical and diradical systems, including the ethylenedione molecule OCCO and the related radical system involving the HOCCO and OHCCO species. Despite its apparent (and misleading) simplicity and the existence of the straightforward closed-shell Kekulé structure O=C=C=O, ethylenedione is in fact a transient diradical. Prior to this work, it possessed the reputation of a “mysterious” and even “hypothetical” molecule, which it had earned by eluding more than a century of efforts to synthesize and observe it. We report the first definitive spectroscopic observation of this controversial species and analyze the electronic and geometric structures of its low-lying electronic states using the photodetachment of the corresponding anion, OCCO⁻. The OCCO diradical is discussed in comparison to the HOCCO and OHCCO radicals, accessed and analyzed using the photodetachment of the corresponding anions. The comparative spectroscopy of these related species sheds light on the differential effects of a hydrogen bonded to different atoms within the OCCO diradical skeleton.

Nonclassical Carbocation Rearrangements

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Despite nonclassical carbocations have been extensively studied in organic chemistry, its behavior still holds a contemporary fascination. Particularly, the 2-norbornyl cation (**1**) is one of the most provocative nonclassical pentacoordinate carbocations. Quite recently, two contributions re-opened this controversial topic. The first one is the characterization of **1** by X-ray diffraction, confirming the presence of a pentacoordinate carbon atom [1], and the second one is the structural isomerization of **1** into the 1,3-dimethylcyclopentenyl cation in the gas phase [2]. Mosley et al. reported the infrared spectrum of $C_7H_{11}^+$, obtained by photodissociation of argon tagged species. The $C_7H_{11}^+$ ion was produced in a mixture of norbornene and H_2 in Ar, where H_3^+ serves as the protonating agent. Obviously, the expected species was **1**. However, the spectrum does not correspond to this species; it perfectly matches with the 1,3-dimethylcyclopentenyl cation. The question that immediately arises is: what is the mechanism of the isomerization of **1** into the 1,3-dimethylcyclopentenyl cation? In order to reply this “naive” question, we decided to run a series of Born-Oppenheimer Molecular Dynamics simulations to define a possible rearrangement pathway. The answer is very complicated; two options emerge as viable pathways and both are extremely complex [3]. Using the same methodology, we have delineated the rearrangements of three more cations: homocubyl [4], cubyl [5], and homododecahedryl [6], which will be discussed in detail in this talk.

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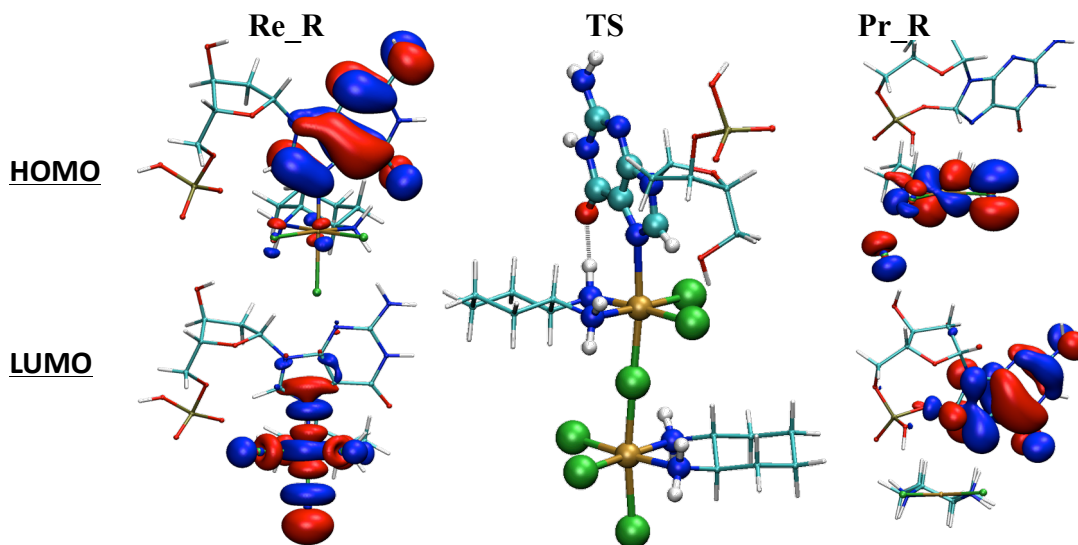
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Reduction Process of Tetraplatin in Presence of dGMP: Computational DFT Study

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This contribution focuses on a reduction mechanism of $\text{Pt}^{\text{IV}}(\text{DACH})\text{Cl}_4$ in the presence of dGMP. The first step represents a substitution reaction of a chloro-ligand by dGMP followed by a nucleophilic attack of phosphate or sugar oxygen to the C8 position of guanine. Subsequently, the reduction reaction occurs forming the $\text{Pt}^{\text{II}}(\text{DACH})\text{Cl}_2$ complex. The whole process is completed by a hydrolysis. Two different pathways for the substitution reaction were examined: direct associative and Basolo-Pearson autocatalytic mechanism. Activation barriers were used for estimation of the rate constants (according to Eyring's TST) and compared with experimental values. Structures were optimized at the B3LYP-D3/6-31G(d) level with COSMO solvation model and single-point energetics was evaluated at the B3LYP-GD3BJ/6-311++G(2df,2pd) level with IEF-PCM/scaled-UAKS solvent approach. The rate-determining step is the nucleophilic attack with a slightly faster performance in 3'-dGMP branch than in 5'-dGMP with the activation barrier of 21.1 and 20.4 kcal·mol⁻¹ (experimental values are 23.8 and 23.2 kcal·mol⁻¹, respectively). The reduction reaction is connected with the electron flow from guanine. The whole redox process (substitution, reduction and hydrolysis reactions) is exoergic by 34 and 28 kcal·mol⁻¹ for 5'-dGMP and 3'-dGMP, respectively.

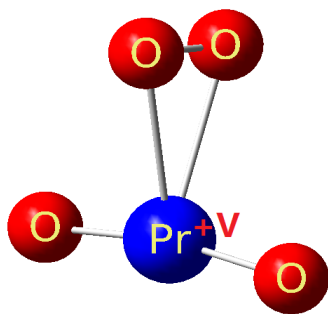


Pushing the Limit of the Highest Oxidation States of Lanthanides: Identification of the First Pentavalent Pr(V) Compound

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The oxidation state is a central concept in chemistry [1-3]. 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 IrO_4^+ cation [4]. 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 [5]. We have recently found the pentavalent lanthanide oxide species PrO_4 and PrO_2^+ complexes with the unprecedented Pr(+V) oxidation state, demonstrating that pentavalent state is viable for lanthanide elements under suitable coordination environment [6]. In this talk we will present an overview of the oxidation states of lanthanides, discuss the stability of pentavalent Pr(V), and summarize our understanding of the periodicity of oxidation states and its relationship with the electronic structures.

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Interplay between the Sb/Bi Bonding and Charge Transport Properties in Rare-Earth Antimonide and Bismuthide Suboxides

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The rare-earth antimonide and bismuthides suboxides with general formulas $RE_n(\text{Sb,Bi})_m\text{O}_n$ and $(RE,\text{Ca})_n\text{Sb}_m\text{O}_n$ were investigated as potential thermoelectric materials. These materials can be viewed to consist of the Sb/Bi and RE-O building blocks with different transport properties. The Sb/Bi substructure defines the density of states around the Fermi level and is responsible for the charge transport properties. The electronic properties of the Sb/Bi substructure can be finely tuned through the size of the RE atoms in the RE-O blocks. E.g. in the *anti*- ThCr_2Si_2 type $RE_2(\text{Sb,Bi})\text{O}_2$ phases, substitution of smaller RE atoms into the REO slabs or larger Bi atoms into the Sb layer yields different charge carrier activation mechanisms [1,2]. As a result, the electrical conductivity and Seebeck coefficient are improved simultaneously, while the number of charge carriers in the series remains constant. The charge transport properties can be explained within the framework of the Anderson/Mott-type localization.

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Mapping Phase Transitions in Ternary Vanadium Oxides: Small Polaron Formation and the Realization of “Purer” Mott Transitions

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The focus of this talk will be electron correlated mixed valence ternary vanadium oxides where closely linked lattice, orbital, and spin degrees of freedom give rise to pronounced structural and electronic instabilities. The binary vanadium oxides VO_2 and V_2O_3 have long been canonical examples of compounds showing pronounced electronic instabilities underpinned by the interplay of electron—phonon coupling and strong electron correlation. In recent work, we have explored the intriguing electronic phase diagrams of low-dimensional ternary vanadium oxides with the formula $\text{M}_x\text{V}_2\text{O}_5$ where M is an intercalating cation and x is its stoichiometry. Several of these compounds show colossal metal—insulator transitions and charge ordering phenomena. The talk will focus on mechanistic understanding of these transitions based on DFT+U calculations of electronic structure and synchrotron X-ray absorption/emission spectroscopy and imaging studies. The insulating phases of these compounds are characterized by the

stabilization of small polarons, which give rise to “mid-gap” states that reside intermediate in energy between the valence and conduction bands. The stabilization of polarons and their eventual melting to form a delocalized metallic phase has interesting implications for the design of cathode materials for intercalation batteries as well as for realizing Mott field-effect transistors. The discovery of a novel topochemical intercalation route has provided access to a wide variety of $M_xV_2O_5$ phases, thereby enabling tuning of correlation strengths and allowing for the partial decoupling of the lattice and electronic facets of the transitions. Finally, dimensional reduction of layered $M_xV_2O_5$ phases *via* ion exchange and exfoliation to few-layered nanosheets further allows for modulation of the correlation strengths and the bandgaps of these compounds as a result of the loss of 3D structural coherence.

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Magnetic Ordering, Frustration and Possible Spin Liquid State from 1D Cr₃-Triangles in the TiCrIr_{2-x}Os_xB₂ Series

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A new series of compounds $TiCrIr_{2-x}Os_xB_2$ ($x = 0 - 2$) was successfully synthesized and characterized using X-ray diffraction as well as energy-dispersive X-ray analysis. All members of the series crystallize in the hexagonal non-centrosymmetric $Ti_{1+x}Os_{2-x}RuB_2$ structure type (space group $P\bar{6}2m$, no. 189, Pearson symbol $hP18$). The structure contains trigonal planar B_4 units strongly interacting with triangles of magnetically active Cr atoms, which are stacked on each other to form isolated Cr_3 -chains along the c -axis. Magnetization measurements of $TiCrIr_2B_2$ (34 valence electrons, VE) reveal ferrimagnetic behavior below $T_C = 275$ K with a large, negative Weiss constant of -750 K. Density functional theory calculations demonstrate magnetic frustration due to indirect antiferromagnetic interactions within the Cr_3 triangles competing with direct ferromagnetic interactions. Tuning the valence electron count by replacing Ir with Os changes the magnetic behavior in the series. Magnetization measurements of $TiCrIrOsB_2$ (33 VE) and $TiCrOs_2B_2$ (32 VE) exhibit paramagnetic behavior with features reminiscent of the spin liquid state. Interestingly, the crystal orbital Hamilton population (COHP) of $TiCrIr_2B_2$ indicates Cr–Cr antibonding interactions above 32.9 VE, but part of the Cr–Cr antibonding region is

already occupied in $\text{TiCrOs}_2\text{B}_2$ even though it has 32 valence electrons. Therefore, the $\text{TiCrIr}_2\text{-}_x\text{Os}_x\text{B}_2$ ($x = 0 - 2$) series do not quite follow rigid band approximation.

Activation of Red Phosphorous: Opening New Possibilities in the Main-Group Chemistry

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The chemistry of polyphosphides, which represent small negatively charged cages of phosphorus atoms, has long been dominated by solid state reactions between metals and red phosphorus at elevated temperatures. A myriad of structurally diverse polyphosphides has been discovered through such reactions. In contrast, the solution chemistry of polyphosphides is underdeveloped, and the entry to such reactivity is typically achieved by using white phosphorus, a hazardous flammable molecular allotrope of the element. The red polymorph is characterized by oligomeric amorphous structure and generally considered to be a far more inert form of phosphorus. We have recently discovered unprecedented activation of red phosphorus with simple nucleophiles, such as potassium ethoxide, which allows solubilization of this allotrope in a number of organic solvents. Furthermore, the use of shelf-stable reactants allowed us to adapt this chemistry to a continuous-flow process that allowed a facile production of multi-gram quantities of polyphosphide salts. Consistent observation of the aromatic P_5^- anion in the reaction products indicates this fragment is the major building unit in the structure of red phosphorus.

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Stabilization Mechanisms of Boron Allotropes (and Compounds)

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Boron is known to have a rich family of allotropes like its neighbor in the periodic table, carbon, yet the underlying factors that lead to the diversity is significantly different. While carbon allotropes can be well rationalized within sp hybridization concept, boron allotropes tend to show much complex behaviors due to additional factors such as preference of 3-center-2-electron bond, metallic bond, ionicity, and their interplay leading to competing conditions in complex ways, or frustration [1-4].

At the presentation, I will first review what was learned from an investigation on beta-rhombohedral boron, where unbalanced ionicities of different building units leads to off stoichiometry between bonding electrons and orbitals, which in turn, introduces vacancies and interstitials in a correlated manner. These defects sites form a specific lattice structure, expanded kagome lattice, reflecting the space group of this material. As a consequence, geometrical frustration is realized.

Next, using the knowledge obtained from beta-boron study, I will attempt to categorically describe the stabilization mechanisms of boron allotropes including low dimensional ones as well as some boron compounds. I would also like to discuss about recent development in boron research for real world applications such as a boron compound as hydrogen storage material and/or a potential application for hydrogen production.

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Towards a Structural Principle for High Pressure Solids

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Recent experimental determination and theoretical predictions of solid structures at high pressure have revealed a myriad of complex, new and exotic structural types with some seeming defy the common concepts of structural chemistry. I will present a summary on our effort to develop a guiding principle to elucidate these structures and the chemical interactions in some of the unusual solids. In general, under pressure, in order to avoid Pauli repulsions, the valence electrons are “promoted” to diffuse unoccupied atomic orbitals and were utilized in “chemical bonding”. For group I and II elements, there are more available orbitals and thus often resulted in 2D layer structures and, in some cases, multicenter electron bonds are manifested as electrides. This concept is illustrated with examples on elemental solids, simple hydrides and halides, binary alloys and more recent studies on the devitrification and amorphous-to-amorphous structural transformations in metallic glasses.

The Chemical Bonding of Two Dimensional Layered Materials

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Unique geometry structures usually lead to the exotic chemical bonding, physicochemical properties and potential applications. The structures determine the properties, the properties determine the potential applications, following this line throughout we would like to show the exotic chemical bonding and interesting electronic properties of two-dimensional hypercoordinate sheets, by first principle calculations. Our results will stimulate the experimental and theoretical efforts for further pushing forward the relevant fields.

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Aromaticity and Related Properties of Graphene and Graphene-Based Materials: Traditional Methods New Understanding and Outlook

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Using real space nanographene models of various sizes and symmetries, we can generate the aromaticity pattern of infinite Graphene, which is a superposition of coronene (CO) and circumcoronene (CIRCO) type of aromaticity patterns by a process of “spatial” evolution [1]. Using the same process backwards we can obtain the uncoupled aromaticity patterns of finite graphene-based structures, like graphene dots, antidots, and graphene nanoribbons [2], and

nanotubes. For a given symmetry the primary Clar type CIRCO aromaticity pattern, which is associated with large bandgaps, appears periodically with varying size. For hexagonal samples the periodicity involves two members (CO, CIRCO); whereas for rectangular nanographens and nanoribbons we can distinguish three repeated patterns, with increasing size. The periodic variation of the aromaticity pattern, which is rooted in the primary aromaticity pattern of graphene, is responsible for the observed periodic bandgap variation in nanoribbons and nanotubes. On the basis of these periodicities we can rationalize the related bonding and banding electronic properties of such structures.

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Theoretical Predictions of Superconducting Hydrides Under Pressure

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The pressure variable opens the door towards the synthesis of materials with unique properties, i.e. superconductivity, hydrogen storage media, high-energy density and superhard materials, to name a few. Under pressure elements that would not normally combine may form stable compounds or may mix in novel proportions. As a result, we cannot use our chemical intuition developed at 1 atm to predict phases that become stable when they are compressed. To enable our search for novel BCS-type superconductors that can be synthesized under pressure we have developed *XtalOpt*, an open-source evolutionary algorithm for crystal structure prediction. *XtalOpt* has been employed to find the most stable structures of hydrides with unique stoichiometries that are superconducting under pressure. Herein, we describe our predictions of iodine polyhydrides (IH_n , $n > 1$) and hydrides of phosphorus (PH_n , $n = 1-5$). The electronic structure and bonding of the predicted phases is analysed by detailed first-principles calculations.

Organomimetic Boron Cluster Chromophores and Photosensitizers

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For a long time synthetic chemists have strived to develop a versatile toolbox of molecules and transformations, thereby assisting in providing solutions to pressing scientific and societal problems. We have been interested in expanding the currently available toolbox by moving beyond the “classical” realm of purely organic, inorganic and organometallic chemistry and identifying alternative chemical platforms best described as “organomimetic”.

This presentation will focus on our recent efforts in using organomimetic icosahedral boron clusters as tunable building blocks for molecules and materials capable of interacting with light. Importantly, I will highlight several extreme modalities that these clusters can serve in creating chromophores and photosensitizers that have no analogues in classical organic/organometallic chemistry.

Normally, unfunctionalized boron-rich clusters containing B-H bonds do not absorb light in the visible region and also cannot undergo well-defined redox processes. In the first part of this presentation I will focus on carboranes, which in their unfunctionalized form exhibit extremely large HOMO-LUMO gap (> 10 eV). This property recently allowed us to create a new class of chelating photophysically innocent ligand scaffolds providing a new avenue for rationally designing organic light-emitting diode (OLED) materials.

Perfunctionalization of B-H vertices can lead to a pronounced reduction in the HOMO-LUMO gap in the resulting cluster species producing unique photoredox properties. In the second half of this presentation, I will highlight our newly discovered visible light photoredox behavior of $B_{12}(OR)_{12}$ clusters which can interact with olefinic species and subsequently initiate their polymerization. Specifically, I will show that this process occurs across a wide array of both electron-rich and electron-deficient styrene monomers as well as isobutylene. Lastly, this presentation will highlight our most recent effort incorporating these clusters into solid-state materials resulting in unprecedented light-absorbing properties.

Super Covalent Bond Model

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Jellium model is widely used in studies of alkali-metal clusters. In this model, the valence electrons of a cluster are delocalized in the cluster volume and fill discrete energy levels. Based on the jellium model, atomic assemblings with magic number electrons can act as superatoms, and such a superatom concept has achieved great success in explaining the stability of pure metal clusters. Superatom concept for a cluster has been extended to mimic any atom, based on electronic states and reactivity.

Recently, we propose a new concept for bonding between superatoms—super valence bond (SVB), of which superatoms can share both valence pairs and nuclei for shell closure thus forming delocalized super bonding [1]. Using Li clusters as a test case, we theoretically find that metal clusters can mimic the behavior of simple molecules in electronic shells. It is found that Li_{14} , Li_{10} , and Li_8 clusters are analogues of F_2 , N_2 , and CH_4 molecules, respectively, in molecular orbital (MO) diagrams and bonding patterns. This new concept shows new insights in understanding the stability of clusters and designing the cluster-assembling materials, especially, ligand protected gold clusters, e.g., $Au_{38}(SR)_{24}$ and phosphine-protected Au_{20} nanoclusters [2,3]. Moreover, the Au_{20} pyramid can be viewed as a $Au_{16}Au_6$ superatomic molecule under the framework of SVB [4].

However, there are also some exceptions for some other thiolate-protected gold clusters ($\text{Au}_{18}(\text{SR})_{14}$, $\text{Au}_{20}(\text{SR})_{16}$ and $\text{Au}_{24}(\text{SR})_{20}$) in disagreement with the superatom model or SVB model. Thus, we propose a new concept of superatom-network (SAN) to understand the "magic" stability of the 4e compounds [4]. SAN model gives new physical insight into the chemical bonding of these 4e Au-SR compounds, which are viewed as "a network of two 2e-superatom gold cores" linked and stapled by four $[\text{Au}_n(\text{SR})_{n+1}]$ staple motifs.

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High-Spin Electronic Structures in Cluster Design

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In the pursuit of weak field cluster synthesis, we have discovered that thermally persistent high spin ground states can be stabilized to room temperature and beyond. The electronic exchange interaction is dominated by a direct exchange pathway governed by overlap of the cluster core valence orbitals. Redox reactions mediated by the clusters will reorganize the clusters to maximize this M-M bonding and, consequently, maximize the spin states observed. These results will be presented illustrating the emergence of single molecule magnet behavior in high symmetry clusters, as well as their attendant reactivity resulting from their high-spin ground electronic configurations.

Volcano Plots as Tools for Screening Homogeneous Catalysts

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Volcano plots are common tools used by the heterogeneous catalysis and electrochemistry communities to compare the thermodynamic profiles of different catalysts. These plots pictorially represent Sabatier's principle, which states that the interaction between a substrate and a catalyst should be neither too weak nor too strong [1]. Despite their inherent ability to identify attractive catalysts and to facilitate understanding of the roles that metal and ligand choice have on cycle energetics, volcano plots describing homogeneous catalysis remain unrealized. Recently, we created volcano plots examining the thermodynamics of Suzuki cross-coupling [2], a prototypical homogeneous catalytic reaction, that capably reproduced

experimental trends. However, homogeneous catalysts often contain bulky ligands that facilitate a desired chemical transformation, the resulting steric interactions of which are rarely reflected in thermodynamic profiles. This makes kinetic aspects of the catalytic cycle of paramount importance. Building on our previous work, we now create kinetic volcano plots [3] that provide essential information relevant to homogeneous catalysts extending beyond thermodynamic volcanoes. We also demonstrate how kinetic volcanoes derived from structure-activity relationships are able to estimate the transition state barriers associated with key steps of the catalytic cycle with minimal computational cost.

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A Quest to Identify a Quantum Chemical Procedure for Energetic Predictions of Transition-Metal-Containing Species with Chemical Accuracy

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We have developed a high-resolution VUV laser based experimental method for unimolecular dissociation study of state or energy-selected molecular ions by using the vacuum ultraviolet (VUV) laser pulsed field ionization (PFI)-photoion (PFI-PI) or mass analyzed threshold ion (MATI) technique. This method is generally applicable to small molecules, allowing the determination of accurate appearance energies (AE's) or dissociative photoionization thresholds of molecules with spectroscopic precision. As a demonstrate this method, we have determined the AE for the formation of CH_3^+ from CH_4 to be $\text{AE}(\text{CH}_3^+) = 14.32270 \pm 0.00014$ eV, (115520.3 ± 1.2 cm^{-1}). This AE value together with the known ionization energies (IE's) of CH_3 and CH_4 , has made possible the determination of the 0 K bond dissociation energies for CH_4^+ and CH_4 to be $D_0(\text{H}-\text{CH}_3^+) = 1.7070 \pm 0.0002$ eV (13767.9 ± 1.6 cm^{-1}) and $D_0(\text{H}-\text{CH}_3) = 4.4847 \pm 0.0004$ eV (36171.5 ± 3.2 cm^{-1}), respectively. A systematic effort is being made to measure the IE and D_0 values for 3d and 4d transition-metal-containing diatomic, and triatomic carbides, oxides, nitrides, and hydrides, including the FeC/FeC⁺, NiC/NiC⁺, CoC/CoC⁺, TiC/TiC⁺, VC/VC⁺, NbC/NbC⁺, TiO/TiO⁺, VO/VO⁺, NbO/NbO⁺, ZrO/ZrO⁺, MoO/MoO⁺, VN/VN⁺, TiO₂/TiO₂⁺, and VCH/VCH⁺ systems, for benchmarking energetic predictions of state-of-the-art *ab initio* quantum calculations. The comparison between the experimental IE and D_0 values and theoretical predictions obtained based on CCSDTQ/CBS calculations along with high-level corrections for selected transition-containing molecular systems will be presented.

Bond Analysis and Electronic Properties of Functionalized Cyclosilanes

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Relatively new compounds of cyclohexasilanes Si_6X_{12} and $[\text{SiX}_{12}\text{Y}_2]^{2-}$ with X and Y=Cl, Br, and I exhibit an unusual hypercoordination with two halides, Y, coordinated above and below the Si-ring and represent a novel area of silicon chemistry. Using density functional theory, we investigate the donor-acceptor coordination in Si_6X_{12} with various electron-rich groups at the Si-ring to better understand the nature of the bonds and predict properties of new complexes not yet synthesized. In particular, we compare structural stabilities between ring halides, including fluorine, and cyano and methoxy groups. While the Si-F bond is much stronger than Si-Si bond resulting in breaking the Si-ring, interactions of cyano and methoxy groups with the Si-ring are comparable to those in the stable $\text{Si}_6\text{Cl}_{12}$. Thus, alternatives to fluorinated cyclohexasilane, such as $\text{Si}_6(\text{OCH}_3)_{12}$, and $\text{Si}_6(\text{CN})_{12}$, with similar oxidation properties but weaker bond energies are predicted to be stable compounds with interesting electronic properties responsible for hypercoordination, which make them promising for various applications.

The Position Space Perspective of Chemical Bonding

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The analysis of the chemical bonding is nowadays an essential part of chemical investigation. In vast majority the chemical bonding is described by means of orbitals of different flavors (canonical, localized, natural, etc.). Such analysis has its strength in being closely connected to the methodology of quantum chemical calculations, its appealing visual representation and especially in the long experience with this approach. However, the orbitals are just mathematical objects included as a convenient (and today often necessary) ingredient to arrive at a particular solution of the energy equations.

In the last decades another perspective of chemical bonding was intensively investigated. It was the idea that the chemical bonding is expected to be directly manifested in the position space. Many descriptors emerged and were used for the classification of bonding. This effort is in full progress, as each of the descriptors is often suitable only to certain aspect of the bonding (which applies to the orbital viewpoint as well). The investigations go far beyond the description of the chemical bonding (as the chemical bond is not an observable anyway). Deeper knowledge of the rules and behavior of such position space descriptors could serve as an important ingredient by the solution of the energy equations.

Structures and Bonding of the B_n^q Borospherene Family ($q=n-40$, $n=36-42$)

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The experimental observation of the cubic-box-like borospherenes $D_{2d} B_{40}^{-/0}$ and $C_3/C_2 B_{39}^-$ (all-boron fullerenes) in 2014 marks the onset of borospherene chemistry [1,2]. Since then, based upon extensive global minima searches and first-principles calculations, our group has discovered a series of borospherene clusters B_n^q ($q=n-40$, $n=36-42$) including $T_h B_{36}^{4+}$, $C_s B_{37}^{3-}$, $C_s B_{38}^{2-}$, $C_3/C_2 B_{39}^-$, $D_{2d} B_{40}$, $C_1 B_{41}^+$, and $C_2 B_{42}^{2+}$ [1-7] (Fig. 1) which are all composed of interwoven boron double chains (BDCs) with twelve delocalized π bonds over a σ skeleton made of $n+8$ σ bonds (Fig. 2). Alkaline or alkaline earth metals prove to be effective dopants to stabilize $T_h B_{36}^{4+}$ in $Li_2[Ca@B_{36}]$, $C_s B_{37}^{3-}$ in $Ca@B_{37}^-$, $C_s B_{38}^{2-}$ in $Ca@B_{38}$, respectively. Molecular dynamics simulations indicate that the low-symmetry borospherenes or their metalloborospherenes with odd number of boron atoms exhibit structural fluctuations above room temperature, whereas those with even number of boron atoms remain dynamically stable at high temperatures. Borospherenes and their metal complexes which have unique electron-transportation and hydrogen-storage properties possess a rich chemistry and a wide range of possible applications.

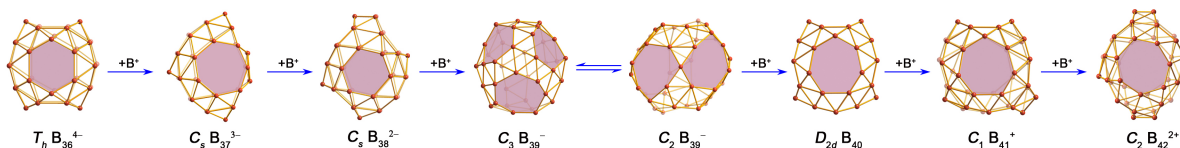


Fig. 1 The B_n^q borospherene family ($q=n-40$, $n=36-42$)

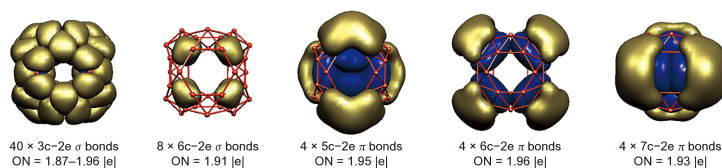


Fig. 2 The AdNDP bonding pattern of $D_{2d} B_{40}$

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Structural and Optical Properties of the Naked and Passivated Al₅Au₅ Bimetallic Nanocluster

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The structural and optical properties of both, the naked and passivated bimetallic Al₅Au₅ nanocluster have been studied based on data obtained from *ab initio* density functional theory and quantum molecular dynamics simulations. It has been found that the Al₅Au₅ nanocluster possesses a hollow shaped minimum energy structure with segregated layers of Al and Au domains, the former representing the electrophilic domain and the latter the nucleophilic domain. In particular, it has been shown that alkali metal cation attaches in the nucleophilic domain and hops from one Au site to the next one in the picosecond time scale. Simulating annealing studies are very suggestive of the proneness of the nanocluster towards coalescence into large cluster units, when the cluster is left unprotected by appropriate ligands. Further passivation studies with the NaF salt suggest, nonetheless, the possibility of the isolation of the Al₅Au₅ cluster in molten salts or ionic liquids.

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Anion Specificity in Hydrated Clusters and Anion- π Complexes

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In this talk, I will present our cluster approach using size-selected, low-temperature photoelectron spectroscopy and *ab initio* calculations to study a variety of complex anion solvation across the Hofmeister series. Pronounced anion specific effects and rich solute-solvent, solvent-solvent interactions have been discovered en-route to solvation evolution from molecular-like species to nano-sized droplets. Specific anion- π interactions and binding strength are found to exist in anion- π complexes as well. Thermodynamic advantage of organic acids in facilitating formation of bisulfate ion clusters, an important issue related to atmospheric chemistry and aerosol particle formation will also be discussed.

Learning from Hydrogen and Hydrides: Opening the $1s^2$ Doublet

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The core business of chemistry is about making and breaking bonds. Especially new types of chemical bonds are of interest, including chemical bonding to these elements, which show very little propensity to form them *i.e.* noble gases [1,2]. The lightest of noble gases, helium and neon, are particularly inert, and they do not form any distinct chemical compound (electrically neutral molecule).

Helium ($1s^2$) is isoelectronic to hydride anion, H^- , which is a constituent of many hydrogen storage materials. Thermal decomposition of any hydride-based hydrogen storage material is connected with the evolution of H_2 , and thus it constitutes a redox reaction. Great deal of knowledge exists about how to manipulate electron transfer reactions in hydrides [3,4] so that the “stable” two-electron shell of H^- is opened. This knowledge may be transferred to helium, with the scope of forcing it to form chemical bonds [5,6], and extended to other noble gases [7]. Thus, chemistry of helium may be within the reach of experimentalists.

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The Role of Spin in Strong, Covalent and in Weak, Non-Covalent Bonding

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The Fermion nature of electrons determines via the exclusion principle many more molecular properties than traditional teaching suggests. Not only bond angles of covalently bonded molecules [1,2] but also the angular structure of hydrogen bonded complexes are dominated by the exclusion principle. SAPT(DFT) results will show this for the water dimer and for the methanol/dimethyl ether complex.

Orthogonal valence bond theory (OVB) [3] is used to analyze symmetry allowed and symmetry forbidden reactions. It is shown that the origin of high reaction barriers in symmetry

forbidden reactions is related to local spin excitation, whereas symmetry reduction favors charge transfer processes and reduces barrier heights.

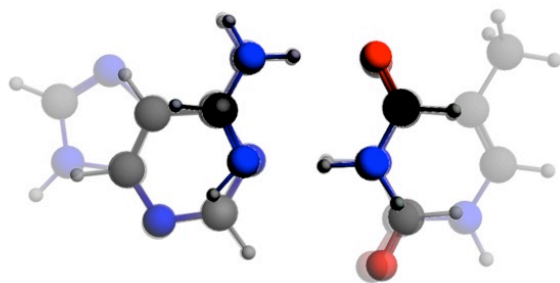
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Molecular Recognition in DNA: the Role of Aromaticity, Hybridization, Electrostatics and Covalency

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Quantum chemical studies show that neither aromaticity nor other π assistance are responsible for the enhanced stability of the hydrogen bonds in adenine-thymine (AT). This follows from extensive bonding analyses of AT and smaller analogs thereof, based on dispersion-corrected density functional theory. Removing the aromatic rings of either A or T has no effect on the Watson-Crick bond strength. Only when the smaller mimics become saturated, that is, when the hydrogen-bond acceptor and donor groups go from sp^2 to sp^3 , the stability of the resulting model complexes suddenly drops. Bonding analyses based on quantitative Kohn-Sham molecular orbital theory and a corresponding energy decomposition analyses (EDA) show that the stronger hydrogen bonds in the unsaturated model complexes and in AT stems from stronger electrostatic interaction as well as enhanced donor-acceptor interactions in the σ -electron system, with the covalency being responsible for shortening the hydrogen bonds in these dimers.

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Modulating Inter-Molecular Interactions via an External Electric Field

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Matter is all electric charge thus application of an external electric field (EEF) should be a straightforward way for influencing chemical phenomena. Indeed recent experimental and theoretical studies have demonstrated that an EEF can change the products of known chemical processes by influencing the potential energy surfaces (PES), [1] the nature of inter-/intra-molecular interactions [2-4], energies of the electronic states [5], and consequently the response properties of matter [6,7]. The potential of the EEF to affect the chemical bonds and molecular properties can be used for designing molecular machines [8,9], selective ion/molecule receptors [10], and catalysis [11].

In spite of vast application-based studies, the nature of chemical bonded interaction under the influence of an EEF is seldom discussed. In this lecture I describe the bond strengthening phenomenon in the presence of an EEF that was not known until recently [2]. Our efforts to understand the mechanism of bond strengthening phenomenon led us to a better understanding of the nature ion- π interactions and introduction of a novel concept, called multi-center covalency [12].

Aside from an introduction to the nature of bonding in the presence of an EEF, if time permits a novel molecular switch, operative in the presence of an EEF, will be introduced.

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Unique Cases of Chemical Bonding in Clusters and Solids: Localized and Delocalized Bonding Patterns

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While two-center-two-electron (2c-2e) classical bonds dominate organic chemistry and are also responsible for majority of bonding in inorganic chemistry, there are many compounds where multicenter (nc-2e, n>2) bonds are crucial to describe their electronic structures. The Adaptive Natural Density Partitioning (AdNDP) method [1], developed in Dr. Boldyrev's lab, allows us to express chemical bonding in terms of both localized (1c-2e and 2c-2e) and delocalized (nc-2e, n>2) bonding elements. It combines the compactness and intuitive simplicity of Lewis theory with the flexibility and generality of canonical molecular orbital theory. This method is a generalization of the Natural Bond Orbital (NBO) analysis and is based on the diagonalization of the blocks of the first-order density matrix in the basis of natural atomic orbitals. Recently developed solid-state version (SSAdNDP) [2] of the AdNDP method allows us to elucidate the bonding in bulk materials and interfaces in a natural, chemically intuitive fashion, yielding insight into the fundamental origins of their structure and properties. AdNDP and SSAdNDP provide a very efficient and visual approach to represent chemical bonding and could be used for research and for teaching chemistry. In my talk I will show the potentials of both methods for rationalization of chemical bonding in difficult cases of organic molecules, bare and embedded clusters, two-dimensional (2D-) sheets and magnetic materials. This will include the following species: (i) various organic molecules (hypervalent iodine compounds where the presence of I=O, I=N, and I=C double bonds is questionable) [3]; (ii) highly symmetric Ti₈O₁₂ cluster [4] (stabilized by d-orbital antiferromagnetic coupling); (iii) all-metal antiaromatic [Ln(η^4 -Sb₄)₃]³⁻ (Ln=La, Y, Ho, Er, Lu) anions [5] (the first locally π -antiaromatic all-metal systems in the solid state, stabilized by interactions of the three π -antiaromatic Sb₄ units with the central metal atom); (iv) Cu₂Si monolayer [6] featuring planar hexacoordinate copper and planar hexacoordinate silicon (delocalized bonding governs the planar geometry of the Cu₂Si sheet); (v) 2D antiferromagnetic boron [7] material composed of barrel-like B₂₀ cluster fragments in a hexagonal arrangement (first magnetic 2D form of elemental boron with unpaired electrons on the capping atoms of the B₂₀ units responsible for magnetism).

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Intramolecular Multi-Bond Strain: The Unrecognized Side of the Dichotomy of Conjugated Systems

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It has been well recognized that electron conjugation stabilizes conjugated systems. Thus, the recent findings and claims by Rogers et al. that there is no conjugation stabilization in 1,3-butadiyne and conjugation is even destabilizing in 2,3-butanedione and cyanogen are surprising, and have been refuted instantly by many researchers. By analyzing the literature, however, we found that there is an important factor missing in all sides, namely the direct repulsion among π bonds. In contrast, repulsion among adjacent σ bonds (such as in ethane) is widely accepted. In this talk, we will propose and validate a new concept, intramolecular multi-bond strain, which refers to the repulsion among π bonds. Using model systems B_4H_2 and B_2H_4 , we quantified the π - π repulsion (16.9 kcal/mol) as well as the σ - σ repulsion (7.7 kcal/mol) at the *ab initio* level, and showed that former is even stronger than the latter. Thus, this new concept successfully reconciles the discrepancy between experimental and theoretical versions of conjugation energy and settles the controversies over conjugation stabilization. This concept is also demonstrable in experimental findings such as the much longer carbon-nitrogen bond in nitrobenzene (1.486 Å) than in aniline (1.407 Å), and the remarkably stretched nitrogen-nitrogen bond in the weakly bound dinitrogen tetroxide (1.756 Å) compared with the single bond in hydrazine (1.47 Å), and the instability of long polyynes. However, we maintain that by definition, electron conjugation must be stabilizing.

Green's Function Embedding Methods for Molecules and Solids

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The experimental study of strongly correlated materials is among the most exciting and challenging areas of research in chemistry and materials science.

In strongly correlated materials, the motion of a single electron depends crucially on the motion of all the other electrons.

These systems reveal many fundamentally interesting and potentially very useful phenomena that can be harnessed into future devices such as highly efficient oxide perovskite solar cells and battery materials.

Currently, the numerical description of strongly correlated materials can be done either by studying model systems and employing methods of condensed matter physics or using realistic systems but employing methods such as density functional theory (DFT) common in chemistry.

Both of these approaches rely on empirical parametrizations. I will describe an embedding framework that we are developing in my group for general multiscale methods free from empirical parameters. In such methods a strongly correlated subsystem is embedded into a many-body correlated field generated by weakly correlated electrons present in the system. I will show results of such embedding as applied to molecules and discuss its possible generalization to solids.

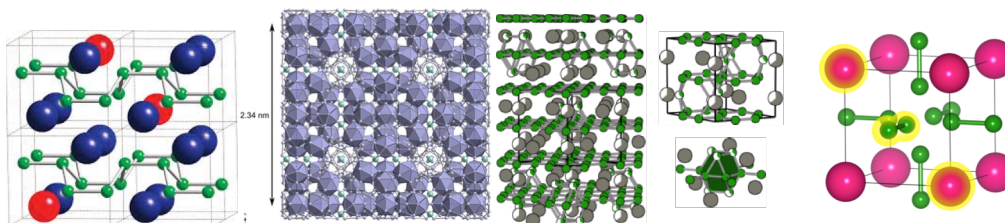
Ultra-Hard Borides: Bonding, Hardness, Anisotropy, Mixed Valency

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Since pre-historic times, there has been a need for ultra-hard materials to be used for tools. Until recently, mostly carbides were used as such materials, though they are not ultra-hard. The hardest materials known are diamond and cubic boron nitride, but they are very expensive. Also, diamond turns into carbides upon contact with ferrous metals at high T, making manufacturing of cutting tools problematic. Recently, it was discovered that borides of heavy transition metals are ultra-hard; they can scratch diamond in certain crystallographic orientations [1]. It is exceptionally exciting as it offers a new route to ultra-hardness that could be fundamentally free of the limitations of diamond-like materials. The understanding of ultra-hardness was in its rudimentary stage, however, and, as a result, many of their properties remained unexplained and unpredictable.

We will discuss several borides, WB_4 , ReB_2 , OsB_2 , SmB_6 . Our chemical bonding insight into these materials is local and cluster-based. We will show how hitherto unsuspected M-B bonding contributes to boride superhardness, and explains the counterintuitive anisotropy of the stiffness against shear stress of WB_4 [1]. We will explain why the $(B)_n$ sheets change from flat to extremely bent in the series: TiB_2 , ReB_2 , OsB_2 [2]. We note that in general, it is not understood why the geometries of the B-network within borides can be anything from chains to sheets to cages, depending on the metal. Finally, we will explain the outstanding question of mixed valency in SmB_6 [3]. In this solid, Sm exists in the oxidation states of +2 and +3 in a 50/50 mix. We show how that phenomenon emerges, without ever engaging in the change of the nature of the occupied electronic states. All presented results are new and unpublished.



Crystal structures of representative borides, left to right: OsB_2 , YB_{66} , WB_4 , SmB_6 .

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