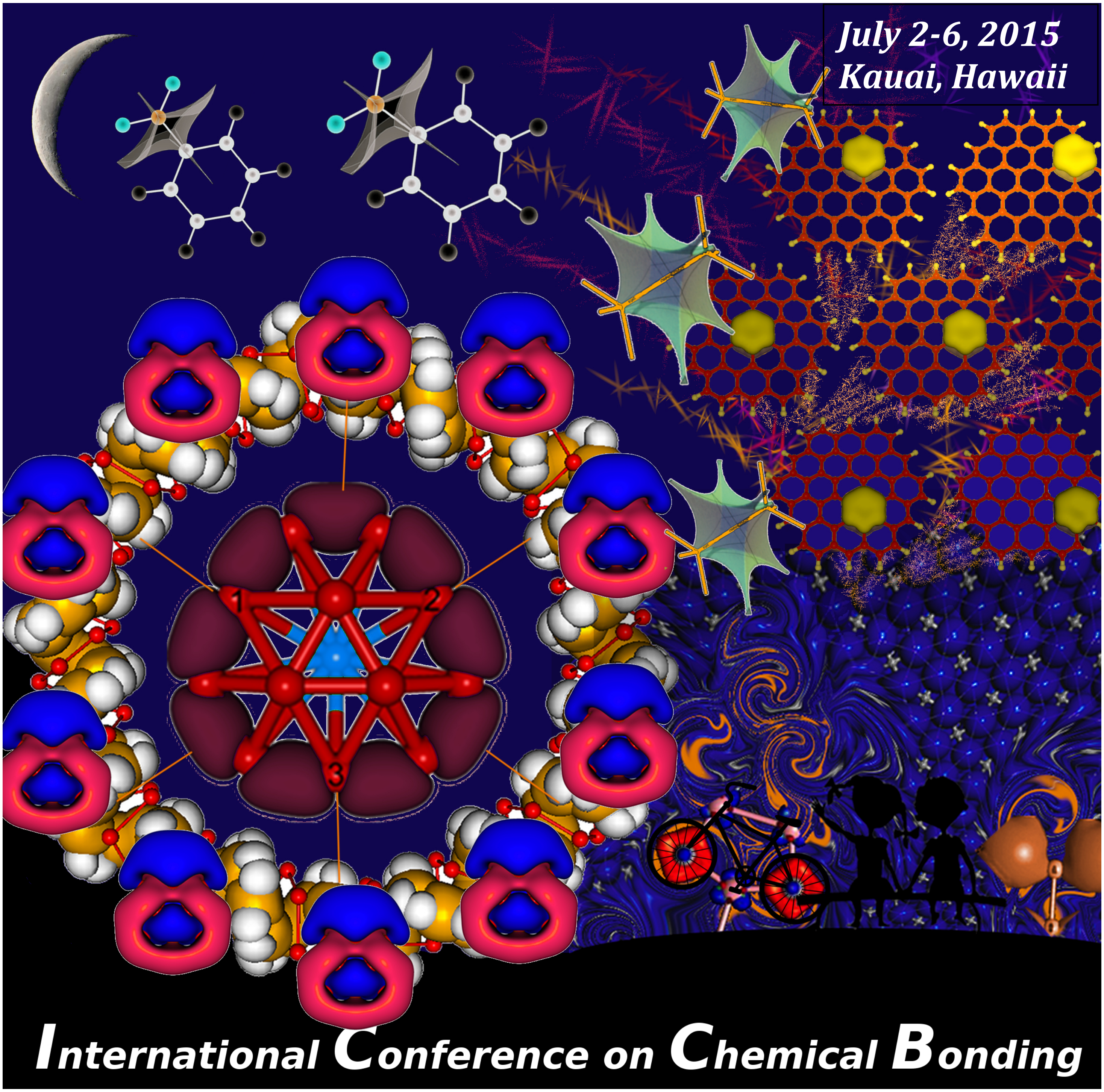

July 2-6, 2015
Kauai, Hawaii

International Conference on Chemical Bonding

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International Conference on Chemical Bonding

Technical Program

Wednesday, July 1

Arrival and registration

Thursday, July 2

<u>Morning</u>: Tour de table *Presiding: Anastassia Alexandrova*

8:30 – 9:00 am	Alex & Anastassia - Introductory remarks
9:00 – 9:30 am	Klaus Ruedenberg (Iowa State University, USA) *“A Quantitative Conceptual Analysis of Bond Patterns, Bond Breaking and Bond Forming through a Density and Energy Resolution in Terms of Oriented Quasi-Atomic Orbitals that are Intrinsic to Ab Initio Wave Functions”*
9:30 – 10:00 am	Lai-Sheng Wang (Brown University, USA) *“Planar Boron Clusters, Metal Doped-Boron Clusters, Borophenes, and Borospherenes”*
10:00 – 10:30 am	Clark Landis (University of Wisconsin, Madison, USA) *“Simple, Localized Bonding Concepts in the Quantum Era”*
10:30 – 11:00 am	Ben Janesko (Texas Christian University, USA) *“How Far Do Electrons Delocalize?”*
11:00 – 11:15 am	*Coffee Break*
11:15 – 11:45 am	Bruce Bursten (Worcester Polytechnic Institute, USA) *“Molecular Electronic Structure Theory Applied to Heavy-Element Chemistry: Some Past Accomplishments, Present Challenges, and Future Opportunities”*
11:45 – 12:15 am	Arne Lüchow (RWTH Aachen University, Germany) *““Insight into Chemical Bonding from $|\Psi|^2$ Analysis””*

<u>Afternoon</u>: Bonding in materials - I *Presiding: Ivan A. Popov*

3:00 – 3:30 pm	Eva Zurek (University at Buffalo, the State University of New York, USA) *“Chemical Bonding Under Pressure”*
3:30 – 4:00 pm	Xavier Roy (Columbia University, USA) *“Molecular Clusters Building Blocks in Solid-State Chemistry”*
4:00 – 4:30 pm	Qingsong Yu (University of Missouri, USA) *“Enhancement of Adhesive/Dentin Interface Bonding by Atmospheric Plasma Treatment”*
4:30 – 5:00 pm	Reinhold Tacke (Universität Würzburg, Germany) *“Donor-Stabilized Silylenes with Two Amidinato or Guanidinato Ligands: Synthesis and Reactivity”*
5:00 – 5:15 pm	*Coffee Break*
5:15 – 5:45 pm	Olexandr Isayev (UNC Chapel Hill, USA) *“A Genomic Approach to Charting Properties of All Inorganic Crystals”*
5:45 – 6:15 pm	Andrey Rogachev (Illinois Institute of Technology, USA) *“7Li-NMR of Corannulene Sandwich-like Aggregates: Playing with Records “*
07:00 – 10:00 pm	***RECEPTION at Kauai Beach Resort***

Friday, July 3

Morning: In the memory of Paul Schleyer *Presiding: Alex Boldyrev*

9:00 – 9:15 am	Intro by Alex Boldyrev
9:15 – 9:45 am	Judy Wu (University of Houston, USA) *"The Nature of Low Barrier H-Bonds in Enzyme Catalysis"*
9:45 – 10:15 am	Bruce King (University of Georgia, USA) *"The Quest for Higher Order Metal-Metal Multiple Bonds in Binuclear Metal Carbonyls and Cyclopentadienyls: Are Metal Quadruple and Quintuple Bonds Viable in 18-electron Transition Metal Complexes?"*
10:15 – 10:45 am	Gernot Frenking (University of Marburg, Germany) *"Unusual Bonds and Chemical Reactions – Research in the Spirit of Paul Schleyer"*
10:45 – 11:00 am	*Coffee Break*
11:00 – 11:30 am	Patrick Bultinck (Gent University, Belgium) *"Can NICS Values be Used to Extract Current Density Information?"*
11:30 – 12:00 am	Zhongfang Chen (University of Puerto Rico) *"Extending Professor Schleyer's Legacy to Nanomaterials Science"*

Afternoon: Solutions, proteins, and other "softies" *Presiding: Amanda Morgenstern*

3:00 – 3:30 pm	Edward Solomon (Stanford University, USA) *"Activating Metal Sites for Biological Electron Transfer"*
3:30 – 4:00 pm	Lyudmila Slipchenko (Purdue University, USA) *"Photochemistry of Solvated OH Radical"*
4:00 – 4:30 pm	Pavel Jungwirth (Academy of Sciences of the Czech Republic) *"Structure, Dynamics, and Reactivity of the Hydrated Electron"*
4:30 – 5:00 pm	Kasper Kepp (Technical University of Denmark) *"Fe-O_2"*
5:00 – 5:15 pm	*Coffee Break*

Smaller systems – big questions

5:15 – 5:45 pm	Jun Li (Tsinghua University, China) *"To Pair or Not to Pair, That Is the Question for F_3UAH (A = C - Fl) Molecules: Lewis Electron-Pair (LEP) Model Revisited"*
5:45 – 6:15 pm	Jesus Ugalde (Euskal Herriko Unibertsitatea and Donostia International Physics Center, Spain) *"Aromaticity in Small Inorganic Rings. A "stretch" or a "gizmo"?"*
6:15 – 6:45 pm	Holger Braunschweig (University of Wuerzburg, Germany) *"Boron-Boron-Bonds: Unexpected Results and New Insights"*

Saturday, July 4

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

Sunday, July 5

Morning: Bonding in catalysis

Presiding: Ben Janesko

9:00 – 9:30 am	Stefano Fabris (Istituto Officina dei Materiali, Trieste, Italy) *"Bonding and Reactivity at Catalytic Interfaces: Modelling Novel Fuel-Cell Electrodes from Ideal to Realistic Reaction Environments"*
9:30 – 10:00 am	Alexis Bell (University of California, Berkeley, USA) *"Applications of Theory to Understand the Role of Composition and Structure on the Activity of Zeolite Catalysts"*
10:00 – 10:30 am	Graeme Henkelman (University of Texas at Austin, USA) *"Some Recent Developments in Saddle Point Finding Methods: Gradient Squared Minimization; Solid State Transitions; and Temperature Accelerated Adaptive Kinetic Monte Carlo"*
10:30 – 11:00 am	Larry Curtiss (Argonne National Laboratory, USA) *"Catalytic Reactivity of Supported Subnanometer Clusters: A Computational Perspective"*
11:00 – 11:15 am	*Coffee Break*
11:15 – 11:45 am	Anastassia Alexandrova (University of California, Los Angeles, USA) *"Metalloenzyme Design"*
11:45 – 12:15 pm	Jamal Musaev (Emory University, USA) *"Key Mechanistic Details of the Transition Metal Catalyzed C-H Bond Functionalization"*
12:15 – 12:45 am	Matthias Bickelhaupt (VU University Amsterdam, Netherlands) *"Rational Design of Catalysts: New Concepts from the Activation Strain Model"*

Afternoon: Gold clusters and nanoparticles

Presiding: Lyudmila Slipchenko

3:00 – 3:30 pm	Katsuaki Konishi (Hokkaido University, Japan) *"Geometrical and Electronic Structures of Phosphine-coordinated Ultrasmall Gold Clusters"*
3:30 – 4:00 pm	De-en Jiang (University of California, Riverside, USA) *"New Paradigm for Monolayer-Protected Metal Nanoclusters: The Alkynyl Ligand"*
4:00 – 4:30 pm	Soichiro Kyushin (Gunma University, Japan) *"Unique Structures and Properties of Organosilicon Clusters"*
4:30 – 5:00 pm	Igor Koshevoy (University of Eastern Finland) *"Coinage Metal Clusters: Efficient Luminophores with Extensive Metallophilic Bonding"*
5:00 – 5:15 pm	*Coffee Break*

Fundamentals

5:15 – 5:45 pm	Paul Popelier (University of Manchester, UK) *"QCTFF: on the Construction of a Novel Protein Force Field"*
5:45 – 6:15 pm	Amanda Morgenstern (Colorado School of Mines, USA) *"Gradient Bundle Analysis: A Full Topological Approach to Chemical Bonding"*
6:15 – 6:45 pm	Richard Dronskowski (RWTH Aachem University, Germany) *"Chemical Bonding (in Solids) from Local Orbitals and Plane Waves"*

Monday, July 6

Morning: Bonding in materials - II

Presiding: Oleksandr Isayev

9:00 – 9:30 am	Qiang Zhu (SUNY-Stony Brook, USA) *"Evolutionary Structure Prediction of Organic crystals"*
9:30 – 10:00 am	Aurora Clark (Washington State University, USA) "*Topological Descriptors of Intermolecular Bonding in Solvents – Measuring Solvent Response to Unique Environments and Developing Predictive Capabilities*"
10:00 – 10:30 am	Ivan A. Popov (Utah State University, USA) *"Application of the AdNDP/SSAdNDP Methods for Understanding Chemical Bonding in Low-Dimensional Systems"*
10:30 – 11:00 am	Oleg Prezhdo (University of Southern California, USA) *"Chemical Bonding and Excited State Dynamics on Nanoscale"*
11:00 – 11:15 am	*Coffee Break*

Fundamentals

11:15 – 11:45 pm	Vincent Ortiz (Auburn University, USA) *"Ground and Excited States of Three-Dimensional Carbon and Boron Clusters from P3+ and NR2 Electron-Propagator Theory"*
11:45 – 12:15 pm	Toon Verstraelen (Ghent University, Belgium) *"Bridging the Gap Between Conceptual Density Functional Theory and Polarizable Force Fields"*

Afternoon: A few remaining puzzles

Presiding: Judy Wu

3:00 – 3:30 pm	Gabor Paragi (Free University of Amsterdam, Netherlands) *"Understanding Cooperativity in Halogen Bonds with Molecular Orbital Theory"*
3:30 – 4:00 pm	Alexander Boldyrev (Utah State University, USA) *"Multi-Center Bonding in Difficult Cases in Chemistry"*

5:00 – 9:00 pm	***BANQUET -LUAU at Smith Restaurants*** *Hawaiian Show + Dinner* *Pick up at Kauai Beach Resort Lobby*

Abstracts

A Quantitative Conceptual Analysis of Bond Patterns, Bond Breaking and Bond Forming through a Density and Energy Resolution in Terms of Oriented Quasi-Atomic Orbitals that are Intrinsic to Ab Initio 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

Through a basis-set-independent web of localizing orbital-transformations, strongly correlated molecular electronic wave functions are expressed in terms of *oriented quasi-atomic* orbitals. The molecular orbital space is resolved into a valence internal space, which has the minimal basis set dimension, and an external space. In the internal space, the oriented quasi-atomic orbitals are determined by singular value decompositions of overlap matrices between the molecular orbitals and highly accurate free atoms orbitals. These quasi-atomic molecular orbitals are found to have very large overlaps with corresponding orbitals on the free atoms. They separate into bonding and non-bonding orbitals. The resolution of the first and second order density matrices and of the molecular energy in terms of the quasi-atomic orbitals exhibits the bonding patterns between atoms in molecules and the changes of these patterns along reaction paths. The localized bonding and antibonding molecular orbitals derived from the bonding quasi-atomic orbitals are the rigorous ab initio HOMOs and LUMOs. The quasi-atomic orbitals obtained by this approach are essentially independent of the basis set in terms of which the original molecular orbitals are represented. In fact, the method has been used to extract quasi-atomic orbitals from DFT based plane wave functions of silicon crystals. The analysis is exemplified here for two chemical systems.

Applied to the urea molecule, the analysis identifies strong and weak covalent bonding interactions as well as intra-molecular charge transfers. It yields an unambiguous detailed elucidation of the bonding structure and provides a firm basis for establishing rigorous contact between ab initio theory and chemical concepts. It rules out some VB resonance structures.

The detailed analysis of the MCSCF wave functions that describe the dissociation of dioxetane into two formaldehydes yields quantitative conceptual insights into the changing bonding patterns during the reaction. The quasi-atomic orbitals persist throughout on the minimum energy path. The kinetic bond orders and the orbital populations of the quasi-atomic orbitals reveal the changes of the bonding interactions along the reaction path. At the transition state the OO-bond is broken, and the molecule becomes a biradical. After the transition state the reaction path bifurcates. The biradical structure persists on the minimum energy path, which gently descends from the transition state via a valley-ridge inflection point to a second saddle point. In close vicinity of this saddle point, the CC-bond breaks and the p-bonds of the formaldehyde fragments form. The changes of the interactions in this region are elucidated by the analysis of the rearrangements of the quasi-atomic orbitals. From the second saddle point, two new minimum energy paths lead to two equivalent very weakly bonded formaldehyde dimers.

Work supported by the National Science Foundation

Planar Boron Clusters, Metal Doped-Boron Clusters, Borophenes, and Borospherenes

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Using photoelectron spectroscopy and computational chemistry, we have found over the past decade that small boron clusters possess planar structures. The propensity for planarity is due to both σ and π electron delocalization over the molecular plane [1,2], giving rise to concepts of aromaticity and multiple aromaticity. The insights obtained about the chemical bonding of planar boron clusters have led to electronic design principles for metal-centered molecular wheels ($M©B_n^-$, n = 8−10), which have been produced experimentally and constitute a new class of doubly aromatic borometallic compounds [3]. In mid-sized boron clusters, B_{36} is found to possess a highly stable quasi-planar structure with a central hexagonal hole [4], providing the first indirect experimental evidence that single-atom layer boron sheets with hexagonal vacancies are potentially viable and they were named “borophenes”. More recent photoelectron and theoretical studies revealed that the B_{40}^- cluster consisted of two nearly-degenerate isomers competing for the global minimum: a quasiplanar isomer and an unprecedented cage isomer [5]. The neutral B_{40} cage is overwhelmingly the global minimum with a huge HOMO-LUMO gap; it is the first all-boron fullerene to be observed and is named “borospherene”. Very recent studies show that the B_{39}^- cluster consists of two nearly-degenerate chiral cage global minima [6]. Efforts and strategies to produce metal-doped borospherenes will also be discussed.

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[1] A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, Coord. Chem. Rev. 250, 2811 (2006).
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Simple, Localized Bonding Concepts in the Quantum Era

Clark Landis
University of Wisconsin, Madison, USA

Are Lewis structures consistent with high quality electronic structures? Natural Bond Orbital (NBO) analysis of molecules across the periodic table supports the primacy of Lewis-like structures in many small molecules. Deviations from Lewis-like structures are described by consistent and logical donor-acceptor concepts. Key to judging the validity of Lewis-like structures is the difference between the ab initio one-electron density matrix and that of the idealized Lewis structure. This metric-of-quality reveals that many concepts – Lewis structures, hybridization, electronegativity, resonance, etc. – originating from pre- and early quantum days, not only survive scrutiny but form the basis for new insights into the electronic structures of transition metal, and other, molecules. Do Lewis structures provide insight? Featured examples include hypervalency and "long-bond" motifs, open shell molecules and the Different Lewis Structures for Different Spins (DLDS) paradigm, applications to transition metal complexes, and insights provided by the NBO facilities for deletion of Fock matrix elements as expressed in the NBO basis set.

How Far Do Electrons Delocalize?

Ben Janesko
Texas Christian University, USA

Electron delocalization is fundamental to chemical bonding. Valence electrons are more delocalized than core electrons. Covalent bonds form when electrons delocalize between atoms. However, "delocalization" is a fundamentally non-classican and nonintuitive concept. Our electron delocalization range EDR(r;u) quantifies the extent to which an electron at point r in a calculated wavefunction delocalizes over length scale u. Applications of the EDR to delocalized solvated electrons show that it quantifies the "size" of the solvated electron, reproducing existing measures of delocalization and quantifying electron correlation effects. Applications to delocalized anions, aromatic systems, surface defects, metals, and bond dissociation provide a novel real-space illustration of delocalization's role in bonding and reactivity.

Molecular Electronic Structure Theory Applied to Heavy-Element Chemistry: Some Past Accomplishments, Present Challenges, and Future Opportunities

Bruce E. Bursten
Department of Chemistry and Biochemistry
Worcester Polytechnic Institute
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The author will present some perspectives concerning the past, present and future of theoretical contributions to the bonding in heavy-element chemistry and actinide science. The systems discussed will include large organometallic complexes that provide similarities and contrasts to analogous organotransition-metal complexes, small actinide-containing molecules formed experimentally by laser ablation and matrix isolation, and computational explorations of the chemistry of the super-heavy elements. The lecture will close with some thoughts on the future of bonding theory as applied to heavy-element complexes, including some of the grand challenges that this field might ultimately be able to address.

Insight into Chemical Bonding from Topological Analysis of the Many-Electron Probability $|\Psi|^2$

Arne Lüchow
RWTH Aachen University, Germany

It is demonstrated that a topological analysis of the many-electron probability density $|\Psi|^2$ is possible [1]. Stationary points can be visualized in ordinary space. An addition, basins or attractor domains are defined for the maxima of $|\Psi|^2$. The topological analysis is based on sampling of $|\Psi|^2$ with quantum Monte Carlo methods. It yields surprisingly comprehensive first-principles insight into chemical bonding and structure. In comparison to the topological analysis of the density or related one-electron distributions the many-body character of chemical bonding can be analyzed. With a number of examples it is shown how electron pairs, lone pairs, and their distributions can be obtained and visualized. We show how electron paths along a reaction coordinate can be determined in a quantum mechanically sound way. Finally, we demonstrate the analysis of spin couplings in position space and their importance to chemical bonding.

[1] A. Lüchow, J. Comp. Chem. 35, 854 (2014)

Chemical Bonding Under Pressure

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The pressure variable opens the door towards the synthesis of materials with unique properties, ie. 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 polar intermetallics and hydrides with unique stoichiometries under pressure. Herein, we describe our predictions of novel superconducting systems: $BaGe_3$ phases that can be quenched to 1 atm, as well as iodine polyhydrides (IH_n, $n > 1$). The electronic structure and bonding of the predicted phases is analyzed by detailed first-principles calculations. The results of our computational experiments are helping to build chemical and physical intuition for compressed solids.

Molecular Clusters Building Blocks in Solid-State Chemistry

Xavier Roy
Department of Chemistry, Columbia University, New York, NY 10027

Traditional solid-state compounds are infinite crystalline arrays of densely packed atoms, whose interactions lead to cooperative physical properties. In this work, we describe analogous multi-component solids in which the "atomic" building blocks are independently prepared, electronically and structurally complementary molecular clusters rather than simply atoms. The underlying focus of this work is to explore how the interplay between charge, structure, inter-cluster coupling and magnetism in cluster-based crystals can be exploited to fabricate materials with multiple, predictable functions. From a fundamental perspective, we want to understand how the isolated characteristics of superatoms can couple across the crystalline lattice to produce long-range cooperative properties and bulk emergent behaviors. The individual clusters (superatoms) that we discuss are fully tunable and their assembly generates atomically precise solids in which the molecular cluster superatoms can communicate electronically and magnetically, akin to atoms in conventional solid-state compounds. Our compounds exhibit collective materials properties such as activated electrical transport, low thermal conductivity and bulk ferromagnetic ordering. We demonstrate that we can tailor the materials properties of these solids in predictable ways by varying the isolated attributes of the individual clusters.

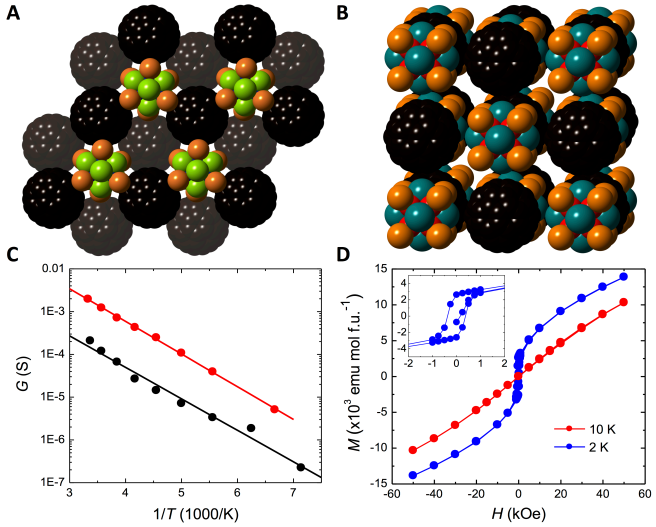

Figure 1. Crystal structure of (**A**) $[Co_6Se_8(PEt_3)_6][C_{60}]_2$ and of (**B**) $[Ni_9Te_6(PEt_3)_8][C_{60}]$. Carbon, black; nickel, red; cobalt, blue; phosphorus, orange; tellurium, teal; selenium, green. The ethyl groups on the phosphines were removed to clarify the views. (**C**) Plot of the four probes conductance (G) vs. $1/T$ for $[Co_6Se_8(PEt_3)_6][C_{60}]_2$. Black = single crystal; red = pressed pellet. (**D**) Magnetization (M) as a function of applied field (H) at 10 K and 2 K for $[Ni_9Te_6(PEt_3)_8][C_{60}]$. The inset shows the enlarged magnetic hysteresis at 2 K.

Enhancement of Adhesive/Dentin Interface Bonding by Atmospheric Plasma Treatment

Xiaoqing Dong[a], Hao Li[a], Meng Chen[b], Yong Wang[c], Qingsong Yu[a,*]

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Acrylic resins have received widespread clinical acceptance in dentistry, including dental restoration, treatment of caries, and orthodontic procedures, etc. Dental bonding of these acrylic resins is the most crucial factor for the success of these dental procedures. This study is to evaluate plasma treatment effects on dentin surfaces for improving adhesive/dentin interface bonding and therefore for potential clinical applications. Extracted unerupted human third molars were used after crown removal to expose the dentin surface. One half of dentin surface was treated with a non-thermal argon plasma brush, while another half was covered and used as untreated same tooth control. Dental adhesives including total etch and self-etch adhesives and dental composite were applied to the dentin surfaces as directed by manufacturers' instructions. Adhesive/dentin bonding strength was evaluated by micro-tensile bond strength (μTBS) test. μTBS test results showed that, for total etch adhesive, the bonding strength was increased over 30% as compared with the untreated controls. For self-etch adhesive, the bonding strength was improved over 22% than the untreated controls. SEM examination of the adhesive/dentin interfaces did show thicker hybrid layer and longer resin tags were formed with plasma treated dentin. The results obtained in this study show the great promise of atmospheric plasma technology in clinical dental restoration applications. This study was supported in part by US National Institute of Health (NIH) with grant numbers of 5R44DE019041 and 1R01DE021431.

Keywords: bonding strength, plasma treatment, dentin, dental adhesives

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Donor-Stabilized Silylenes with Two Amidinato or Guanidinato Ligands: Syntrhesis and Reactivity

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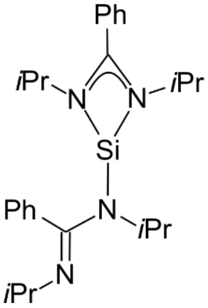
The bis(amidinato)silicon(ii) complex **1** [1,2] and the related bis(guanidinato)silicon(ii) complex **2** [3] were synthesized and structurally characterized. Silylene **1** is three-coordinate in the solid state and four-coordinate in solution (**1'**), whereas silylene **2** is three-coordinate in both phases.



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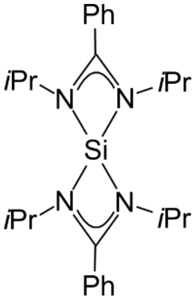

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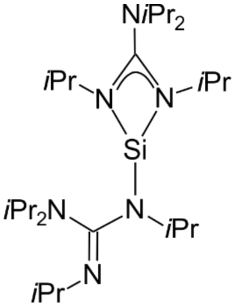

2

Compounds **1** and **2** were studied for their reactivity in oxidative addition, nucleophilic substitution, and Lewis acid/base reactions (in this context, see also refs. [4–10]).
In this contribution, the reactivities of the amidinato/guanidinato analogues **1** and **2** will be compared.

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^{7}Li-NMR for Corannulene Sandwich-like Aggregates: Playing with Records

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Recent experimental achievements in chemistry of reduced corannulene ($C_{20}H_{10}$, the smallest buckybowl or fullerene fragment) revealed a tendency of highly reduced curved polyaromatic molecules to form sandwich-like aggregates. The latter contain five or six alkali metals as positive “electrostatic glue” between two negatively charged bowls in their convex-convex orientation and show remarkable stability in solution. Then, it was found that step-by-step replacement of small lithium by potassium or larger alkali metals leads to so-called “clamshell” effect resulting in occupation by lithium cation of the last available site – the space between two 5-membered rings. Subsequent theoretical investigations revealed that this lithium center shows unprecedentedly large chemical shift of ~-25ppm. The detailed theoretical study of the electronic structure with special focus on shielding tensors was performed. Analysis of components of shielding tensor (including MO-by-MO analysis) revealed that the electronic coupling between two bowl-shaped fragments, which forms electronic cocoon around central lithium, is the main reason for such dramatic chemical shift. The trend between size of alkali metals (from Li to Cs) and chemical shift of the central lithium was established. Surprisingly, in the system, where two lithium cations are replaced by two Rb-cations, the one site between 6-membered rings remained open as revealed by X-ray structural analysis. Instead, the sixth lithium is attached to the border of the sandwich-like aggregate. Our calculations clearly point at this lithium center as showing another record chemical shift of ~+10ppm. The dramatic deficiency of the electronic density around this cation was found to be the main reason.

A Genomic Approach to Charting Properties of All Inorganic Crystals

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The Materials Genome Initiative is transforming Materials Science into a data-rich discipline. These developments open exciting opportunities for knowledge discovery in materials databases using informatics approaches to inform the rational design of novel materials with the desired physical and chemical properties. Statistical and data mining approaches have been successfully employed in both chemistry and biology leading to the development of cheminformatics and bioinformatics, respectively. However, until recently their application in materials science has been limited due to the lack of sufficient body of data. In this work we showcase a pilot materials informatics applications capable of (i) instantaneously query and retrieve the necessary material information in the desired form, (ii) identify, visualize and study important data patterns, and (iii) generate experimentally-testable hypotheses by building predictive Machine Learning (ML) models based on materials’ characteristics. Specifically, we posit that materials with similar structural, topological, and electronic characteristics are expected to have similar physical chemical properties irrespective of their formal composition. To enable uniform comparison of materials by their intrinsic properties, w*e will represent all materials uniquely by multiple numerical descriptors, or fingerprints. This representation will enable the use of classical cheminformatics and ML approaches to mine, visualize, and model any set of materials as we demonstrated in our recent pioneering studies on Materials Cartography [1].*

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The Nature of Low Barrier H-Bonds in Enzyme Catalysis

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Low-barrier H-bonds (LBHBs), which form between donors and acceptors with matching pKa values, can be strengthened additionally (by up to 8-18 kcal/mol) if such interactions also polarize the π-system of the H-bond donor and increase their π-electron delocalization energies. This cooperative effect explains why weak acids like imidazole and phenol can act as the general acid catalyst for many enzymatic reactions. These effects are separate from electrostatic interactions and persist even in polar environments. H-bond donors that are saturated or are linked to the H-bond acceptor through a common π-conjugation unit do not exhibit such cooperativity.

The Quest for Higher Order Metal-Metal Multiple Bonds in Binuclear Metal Carbonyls and Cyclopentadienyls: Are Metal Quadruple and Quintuple Bonds Viable in 18-electron Transition Metal Complexes?

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The first example of a metal-metal quadruple bond was found by Cotton and Harris in 1965 in the octachlorodirhenate(III) anion $Re_2Cl_8^{2-}$ [1]. Forty years later in 2005 the discovery by Power and coworkers of the first metal-metal quintuple bond in a stable binuclear chromium(I) aryl, ArylCrCrAryl, [2]. has revived considerable interest in higher order metal-metal multiple bonds. However, neither $Re_2Cl_8^{2-}$ nor ArylCrCrAryl have the 18-electron configuration for the central transition metals that is favored in transition metal carbonyl and cyclopentadienyl chemistry. We have now used density functional theory, including analyses of the frontier molecular orbitals, to explore possibilities for high order metal-metal multiple bonds in the following metal carbonyl and metal cyclopentadienyl systems, typically with the favored 18-electron configuration for the transition metal:

(1) The binuclear niobium carbonyls $Nb_2(CO)_n$ (n = 9, 8) [3]: The 18-electron rule suggests that $Nb_2(CO)_9$ and $Nb_2(CO)_8$ are candidates for binary metal carbonyls containing metal-metal quadruple and quintuple bonds, respectively. Density functional theory (MPW1PW91 and BP86) indeed predicts structures having very short Nb-Nb distances of ~2.5 Å for $Nb_2(CO)_9$ and ~2.4 Å for $Nb_2(CO)_8$ as well as relatively large Nb-Nb Wiberg bond indices supporting these high formal Nb-Nb bond orders. However, analysis of the frontier molecular orbitals of these unbridged structures suggests formal Nb≡Nb triple bonds and 16-electron metal configurations. It appears that the d electrons needed for increasing the Nb-Nb bond order from three to four or five are instead used for $d\pi \rightarrow p\pi^*$ back-bonding to the CO groups. In addition, these $Nb_2(CO)_n$ (n = 9, 8) structures are higher energy structures than isomeric structures with four-electron donor bridging η^2-μ-CO groups and lower order niobium-niobium bonds.

(2) The dimetallocenes Cp_2M_2 ($Cp = \eta^5$-C_5H_5; M = Ir, Os, Re, W, Ta) with terminal Cp ligands [4]: Analysis of the frontier bonding molecular orbitals indicates a formal Os-Os quintuple bond ($\sigma + 2\pi + 2\delta$) in singlet Cp_2Os_2 and a formal Re-Re sextuple bond ($2\sigma + 2\pi + 2\delta$) in singlet Cp_2Re_2, thereby giving the metals in both molecules the favored 18-electron metal configurations. Predicted low-energy triplet structures for Cp_2M_2 (M = Os, Re) have formal quintuple bonds but with only two δ one-electron "half" bonds (M = Os) or a single δ two-electron bond (M = Re) and a second σ component derived from overlap of $d(z^2)$ orbitals. A quintuple bond similar to that found in triplet Cp_2Re_2 is found in singlet Cp_2W_2, giving both tungsten atoms a 16-electron configuration. The iridium derivative Cp_2Ir_2 has a formal $2\sigma + 2\pi$ formal Ir-Ir quadruple bond that is different from the $\sigma + 2\pi + \delta$ quadruple bond in $Re_2Cl_8^{2-}$. However, all of these structures are found to lie at significantly higher energies than isomeric structures with bridging Cp rings.

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Unusual Bonds and Chemical Reactions – Research in the Spirit of Paul Schleyer

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If time permits, I will present and discuss results of four different topics:
- Reaction mechanism of the formally symmetry forbidden [2+2] addition of ethylene and acetylene to Ph_2N-EE-NPh_2, (E = Ge, Sn)
- Chemical bonding in the boron dicarbonyl anion $[B(CO)_2]^-$
- Bond order and chemical bonding in C_2
- Carbon Monoxide Bonding with BeO and $BeCO_3$: Surprisingly High CO Stretching Frequency of $OCBeCO_3$

Can NICS Values be Used to Extract Current Density Information ?

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In 1937, London [1] established that molecules like benzene sustain a ring current when exposed to an external magnetic field. The presence of a ring current soon seemed typical for molecules with a highly delocalized system with aromatic systems characterized by a clear diatropic current.

For a long time, the calculation of so-called magnetic indices of aromaticity was rather non-trivial, especially the calculation of the current density itself. Most calculations are limited to single determinant levels of theory although it can be expected that for most (organic) molecules, such Hartree-Fock currents are not likely to differ very much from those of higher level theories (pending that the single determinant is a sufficiently good reference). While calculated ring current density plots are available thanks to the work of some authors [2], a rather different approach has appeared where aromaticity is gauged from chemical shifts computed at certain specific points in the molecule. The so-called Nucleus Independent Chemical Shifts (NICS) method [3] has for many become the method of choice to assign a degree of aromaticity to a molecule, implicitly assuming that there is a direct connection between NICS and the ring current pattern.

The desired direct connection referred to indeed exists through the law of Biot-Savart. The ring current immediately, ignoring numerical issues in the integration, leads to NICS values at a grid of points. However, can one derive from an integrated quantity the integrand? Can one truly extract a ring current pattern, and thus degree of aromaticity, from a limited set of points with associated NICS values or is one confronted with the well-known rank problems that also plague ESP derived charges ? [4] In this presentation we examine these issues with emphasis on the algebra behind the problem.

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Extending Professor Schleyer's Legacy to Nanomaterials Science

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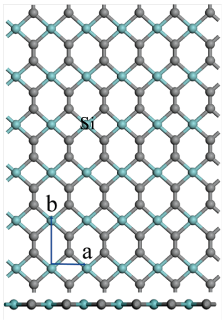
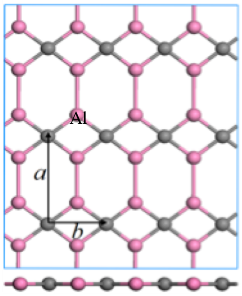
Rule-breaking molecules not only enrich chemical bonding theory, gain us deeper chemical insights, but also often lead to discoveries of exceptional materials with novel properties. Molecules with planar hypercoordinate carbon, a favorite topic of Professor Schleyer, are seminal examples.

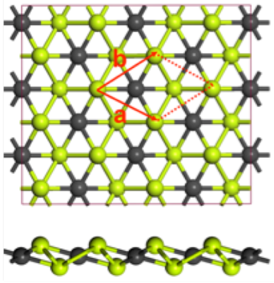
Paul's legacy is far from physical organic chemistry and computational chemistry, it is also in nanomaterials science. Here by means of density functional theory (DFT) computations, we extend the planar hypercoodinate carbon from molecules to nanomaterials. Our predicted SiC_2, Al_2C and Be_2C monolayers have rather unusual chemical bonding: the Si/C atoms in SiC_2/Al_2C adopt planar tetracoordinate configuration, while Be_2C contains planar hexacoordinate carbon moieties. Besides the unique bonding character, these rule-breaking systems also hold great promise for applications in nanoelectronics and optoelectronics. The high stabilities of these systems strongly suggest the feasibility for their experimental realizations. We are calling for more efforts on nanomaterials with novel chemical bonding, especially on the rule-breaking systems.



SiC_2 monolayer



Al_2C monolayer



Be_2C monolayer

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Activating Metal Sites for Biological Electron Transfer

Edward I. Solomon
Stanford University

Metal sites in proteins often exhibit unique spectral features relative to small molecular inorganic complexes. These reflect novel geometric and electronic structures, in particular, highly covalent ligand-metal bonds, that activate the metal center's reactivity. This presentation will mostly focus on the Blue copper active site and emphasize experimental spectroscopic methods that enable quantification of ligand-metal bonding.

Photochemistry of solvated OH radical

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The hydroxyl radical (**OH**) is one of the most important atmospheric oxidants. In this talk we will discuss our recent work on understanding photochemical activity of the solvated OH radical. Specifically, we explore formation of the charge-transfer states in small OH-water clusters, as well as in bulk water and at the air-water interface, by employing a combination of EOM-IP-CC methods, Koopmans' theorem, and hybrid QM/MM techniques based on the polarizable effective fragment potential (EFP) method. We show that the charge transfer to the hydroxyl radical preferentially happens from the interfacial water molecules whose lone pairs are not involved in H-bonding with other waters. These long-range (as far as 7 Å) charge-transfer transitions occur within the UV range present in the atmosphere and might lead to intriguing implications such as increased acidity of water surface and ionization of atmospheric aerosols.

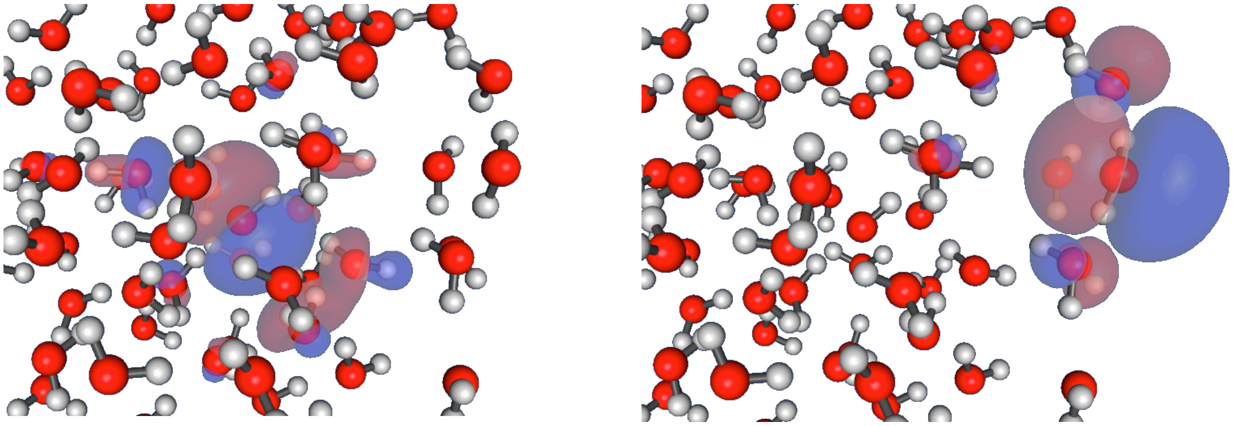

Figure 1. Left: HOMO of OH radical; right: lone pair orbital of surface water contributing electron to the OH radical.

Structure, Dynamics, and Reactivity of the Hydrated Electron

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Interaction of water with ionizing radiation is, in addition to direct DNA damage, causing radiation damage in living organisms and it is also important for nuclear waste treatment. Upon photoionization in water an electron and a cationic hole are formed, and we have followed the fate of both. In the talk, I focus on the structure, dynamics, and reactivity of the hydrated electron which, despite its key role in radiative processes in water, has remained elusive. The traditional cavity model has been questioned recently, but the newly suggested picture of an electron delocalized over a region of enhanced water density is controversial. Here, we present results from ab initio molecular dynamics simulations, where not only the excess electron but also the valence electrons of the surrounding water molecules are described quantum mechanically. Unlike in previous one-electron pseudopotential calculations, many-electron interactions are explicitly accounted for. The present approach allows for partitioning of the electron solvated in liquid water into contributions from an inner cavity, neighboring water molecules, and a diffuse tail. We demonstrate that all three of these contributions are sizable and, consequently, important, which underlines the complex nature of the hydrated electron and warns against oversimplified interpretations based on pseudopotential models. We also investigate the electron solvated at the water surface. The present results clearly demonstrate that the surface electron is mostly buried in the interfacial water layer, with only about ten percent of its density protruding into the vapor phase. Consequently, it has structure which is very similar to that of an electron solvated in the aqueous bulk. Finally, we show how to follow solvated electrons upon dissolving sodium in water (yes, it is explosive!).

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Fe-O$_2$

Kasper Planeta Kepp
Technical University of Denmark

The chemical bond is the fundamental unit of chemistry, yet we still cannot accurately compute the strength and dissociation of chemical bonds, in particular when situated within more realistic, large chemical systems. This talk describes the nature of one of the most important chemical bonds, the Fe-O$_2$ bond, and how its reversible formation forms the basis of life processes. Recent efforts to understand this bond electronically, and how the surrounding ligand fields in porphyrins evolved over millions of years form the basis of organism-level O$_2$ transport, are discussed.

Key words: Heme, O$_2$, DFT, spin inversion, reversible binding, ligand field

To Pair or Not to Pair, That Is the Question for F_3UAH (A = C - Fl) Molecules: Lewis Electron-Pair (LEP) Model Revisited

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Lewis electron pair (LEP) model has established electron pair as one of the most useful concepts in chemistry in the 20th century.[1] The importance of this model can hardly be overstated because of the role it plays in chemistry in interpreting structures and bonding of chemical compounds, although it was established prior to the finding of quantum mechanics. In the Periodic Table, each period row corresponds to the filling of electrons in quantized shells. The elements in the same group column usually have similar properties due to the same electron configuration in their valence shell. However, heavier p-block main-group elements tend to have more or less different chemical bonding from those of 2p elements partly due to *quantum primogenic effect*.[2] Here we discuss the U-A (A = C, Si, Ge, Sn, Pb, Fl) chemical bondings of F_3UAH complexes based on quantum chemical analyses. The calculations were performed using density functional theory (DFT) and *ab initio* wavefunction theory (WFT) at the levels of CASSCF, CASPT2, and CCSD(T) methods. We have shown that while U-C maintains perfect multiple bonds in F_3UCH,[3-6] the naively anticipated "Lewis electron pairs" between U-A in F_3UAH (A = Si, Ge, Sn, Pb, Fl) were broken, leading to a multi-radical bonding scenario.[7] The implication of this finding to chemical bonding in heavy-elements will be discussed.

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Aromaticity in Small Inorganic Rings. A "stretch" or a "gizmo"?

Rafael Grande-Aztazi, Eduard Matito, Jose M. Mercero and Jesus M. Ugalde
Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU) and Donostia International Physics Center (DIPC); P. K. 1072; 20080 Donostia; Euskadi (Spain).

Extension of the aromaticity concept to small inorganic ring compounds has raised considerable controversy recently. Two (irreconcilable) groups have emerged, the former group claims that aromaticity should be associated with electron delocalization in consonance with Huckel's view, and the latter group claims that aromaticity is more than this, for it should cover, as organic aromatic species do, additional features like thermodynamic stability, kinetic persistence and unique reactivity associated to the concept, in line with Kekule's view, which are normally not met by most inorganic ring compounds.

Three inorganic molecules for which their stability has been claimed under the guise of aromaticity will be revisited, namely, the three-membered Al_3^-, Cr_3^{2+} rings, and the $[X(m\text{-}YH)]_2$, X,Y=N, P, As, four-membered rings. The first two species lack the thermodynamic stability and kinetic persistence attributable to classical organic aromatic species, but analysis of their electron wavefunctions reveals that they posses a set of fully delocalized electrons. Conversely, the latter constitutes the structural motif of a highly stable both, thermodynamically and kinetically, class of small inorganic ring compounds, but does not posses delocalized electrons.

Perhaps the time has arrived to discuss the value of “stretching” the meaning of aromaticity beyond the narrow scope given to it by Kekule, and give aromaticity the chance, in line with Huckel's view, to be used as a new “gizmo” to ease the description of the electronic structure and increase the understanding of the novel features of the chemical bonding in electron-deficient metal-containing inorganic ring compounds.

Boron-Boron-Bonds: Unexpected Results and New Insights

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Due to its inherent electron deficiency, boron prefers non-classical bonding regimes when combined to molecules with itself - in other words, boron forms polyhedral boranes, made up of multicenter bonds, rather than chains or rings with electron-precise boron-boron bonds. In the case of the latter, only very few well-defined examples have been published over the past decades, which all suffer from low-yielding, non-selective syntheses that solely rely on reductive coupling of amino(halo)boranes. Consequently, the area of classical boron-boron single and multiple bonds is relatively undeveloped.

Over the past few years we have put significant effort into the development of new synthetic strategies to overcome this seemingly element-specific deficiency. Here, results on the following topics will be presented:

- Single Bonds - Recent Developments: Dehydrocoupling, Catenation and Hydroboration
- Double Bonds - Recent Developments: Base-free Diborenes @ Platinum
- Triple Bonds – Recent Developments: Stabilization of B2 with CAACs:

A different Class of Molecules

- Reactivity Studies

Bonding and reactivity at catalytic interfaces: Modelling novel fuel-cell electrodes from ideal to realistic reaction environments

Bonding and Reactivity at Catalytic Interfaces: Modelling Novel Fuel-Cell Electrodes from Ideal to Realistic Reaction Environments

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CNR-IOM DEMOCRITOS & SISSA

Platinum-group metals supported and dispersed on highly reducible oxides are common active catalysts for the industrial synthesis of chemical products and for renewable-energy applications such as fuel cells or artificial photosynthesis. Due to the high price of Pt, the sustainable development of these technologies requires new materials that reduces the content of precious metal without affecting the device efficiency. I will discuss the challenges opened by these systems to electronic-structure simulations and will present a case study in the context of fuel-cell electrodes, i.e. novel non-conventional CeO_2-based catalyst with ultra-low metal loading. We combine DFT simulations with ab-initio molecular dynamics, atomistic thermodynamics, metadynamics, and other enhanced-sampling methods to reveal the new surface chemistry opened by these systems. The calculations are used to characterize the chemical bonding and the reactivity at the electrode active sites in a wide range of compositions and environments, ranging from model surfaces at T=0K in vacuum conditions to realistic wet electrodes at finite temperatures, i.e. chemical reactions at complex solid-liquid interfaces comprising nano-structured surfaces in contact with a solution. The calculated results allow for rationalizing the available experimental data and identify correlations among the reaction mechanisms, thermodynamic efficiency, and local structure of the active sites, thus shedding light on the origins of the amplified reactivity and stability of these novel electrodes.
Acknowledgement: FP7-NMP-2012 project chipCAT under Contract No. 310191

Applications of Theory to Understand the Role of Composition and Structure on the Activity of Zeolite Catalysts

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Zeolites, crystalline, microporous aluminosilicates, are used extensively as catalyst for the conversion of petroleum to fuels, the synthesis of commodity and specialty chemicals, and the abatement of pollutant in automotive exhaust. The catalytically active centers in zeolites take several forms – Brønsted acidic protons, metal cations, metal oxo species, and framework metal atoms other than Al. The activity of such centers is affected not only by the composition of the center but also by the size and shape of the pores and channels in the zeolite framework. In recent years, advances in electronic structure calculations together with statistical mechanics have enabled exploration of the influence of these variables on the activity and selectivity of zeolite-based catalysts. The ability to carry out such investigations has come as a consequence of advances in density functionals for performing electronic structure calculations by DFT,

advances in methods for carrying out QM/MM calculations on systems involving hundreds of atoms, efficient algorithms for determining transition state for complex systems, and development of new algorithms for estimating entropies of activation for elementary reactions. This talk will present a brief overview of the methods now available for carrying out theoretical analyses of elementary reactions occurring in zeolites and will illustrate their application to a number of reactions systems. The latter will include the cracking and dehydrogenation of alkanes, the oligomerization of alkenes, the carbonylation of dimethoxymethane, the isomerization of glucose to fructose, and the decomposition of nitrous oxide.

Some Recent Developments in Saddle Point Finding Methods: Gradient Squared Minimization; Solid State Transitions; and Temperature Accelerated Adaptive Kinetic Monte Carlo

Graeme Helkelman
University of Texas at Austin, USA

Some recent developments in saddle point finding and long time scale dynamics methods will be presented, including biased gradient squared optimization; the kappa-dimer method; solid state phase transitions; and basin-constrained molecular dynamics saddle-search based adaptive kinetic Monte Carlo.

Catalytic Reactivity of Supported Subnanometer Clusters: A Computational Perspective

Larry Curtiss
Argonne National Laboratory, USA

Supported metal clusters are known to possess reactivity not observed in their bulk analogs, which makes them attractive for catalysis. The distinct catalytic properties of small clusters are hypothesized to result from the unique geometric and electronic characteristics of the clusters such as under-coordinated surface atoms and modified inter-atom spacings. Subnanometer clusters have a much larger fraction of highly under-coordinated atoms compared to larger nanoclusters, which is expected to give them new capabilities for bond activation in catalytic reactions. Materials based on subnanometer clusters are also attractive for catalysis because their activity can provide valuable insights into catalytic mechanisms and calculations can be done at sufficient accuracy to allow guidance for improvement. Size-selected clusters have exhibited superior selectivity and unmatched activity for several key catalytic reactions, such as the oxidative dehydrogenation of propane and selective oxidation of propylene. Recently, subnanometer cluster have been found to have unique electrocatalytic properties for reactions such as water oxidation, CO2 reduction, and in lithium oxygen electrochemistry. In this talk I will focus on computational studies used to help understand the catalytic properties of supported subnanometer clusters for these reactions.

Metalloenzyme Design

Crystal Valdez, Manuel Sparta, Michael Nechay, Amanda Morgenstern, Anastassia Alexandrova
Department of Chemistry and Biochemistry, University of California, Los Angeles

Enzymes are highly dexterous catalysis, operating at mild conditions, requiring only water for the solvent, and basically 100% enantio-selective – to name just a few attractive features. Metalloenzymes in particular can catalyze most remarkable transformations in a single step, by virtue of electronic effects at the metal. We are pursuing design of metalloenzymes to catalyze processes that interest human kind, using non-physiological (toxic or scares) metals of the highest catalytic potency. We will discuss a few enzyme systems illustrating the complexity and multi-scale nature of the problem. We will introduce our new tools for metalloenzymes modeling and design. We will show our first results on the redesign of natural metalloenzymes, for operating on modified substrates, and designs of enzymes based on non-physiological metals.

Key Mechanistic Details of the Transition Metal Catalyzed C-H Bond Functionalization

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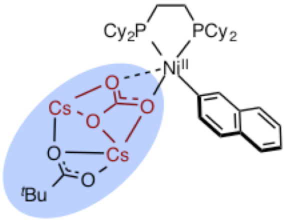
Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta GA, U.S.A. 30322

The understanding of key mechanistic details of the transition metal catalyzed CH bond functionalization is vital for designing better and environmentally friendly processes for formation of new C-C, C-N and C-heteroatom bonds. Our extensive studies have revealed certain complexity, as well as key factors controlling reactivity and selectivity of these reactions. Namely, we have demonstrated unprecedented roles of base, auxiliary ligands and directing groups in the transition metal catalyzed C-H bond alkylation and amination. For example, it was shown that addition of Cs_2CO_3 base to the reaction of Ni-dcype catalyzed C–H/C–O coupling of benzoxazole and naphthalen-2-yl pivalate, forms the Ni(dcype)(Naph)[PivOCs·$CsCO_3$] cluster complex. Coordination of azole to the resulting cluster complex leads to an intermediate with a weak Cs-N(azole) bond, the existence of which increases acidity of the activated C–H bond and reduces C–H activation barrier. This emerging mechanistic knowledge was validated experimentally. Based on these findings we proposed the modified catalytic cycle for the Ni(cod)(dcype)-catalyzed C–H/C–O biaryl coupling of benzoxazole and naphthalen-2-yl pivalate.



Rational Design of Catalysts: New Concepts from the Activation Strain Model

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The aim of this work is to understand [1] the factors that determine the activity and selectivity of transition-metal catalysts in oxidative-addition steps that occur in bond activation and cross-coupling reactions. We studied the effect of varying the metal M along the d^{10} metals of groups 9, 10 and 11, in combination with varying the number as well as the type of ligands, using relativistic density functional theory (DFT) [2] and the activation strain model (ASM) [1].

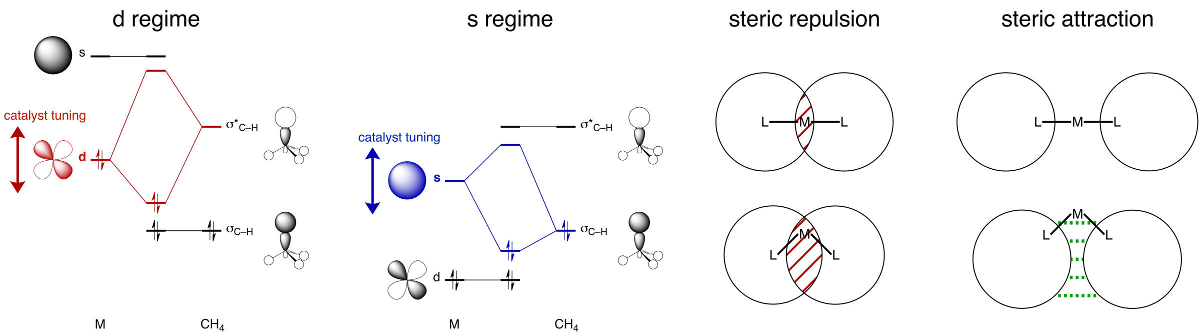

Figure 1. Schematic illustration of concepts presented in this lecture.

Three concepts for tuning a catalyst's activity emerge: (i) d-regime catalysts; (ii) s-regime catalysts; and (iii) bite-angle flexibility (see Figure 1, left). These concepts explain why the effect of one and the same ligand on a catalyst's activity can be completely different, even opposite, for catalysts from different electronic regimes. Furthermore, I will point out why not the bite angle itself, but its flexibility is decisive for the catalyst's activity. Finally, I show how the latter is influenced not only by steric repulsion but also by what we designate "steric attraction" (see Figure 1, right).

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Geometrical and Electronic Structures of Phosphine-Coordinated Ultrasmall Gold Clusters

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It is well known that colloidal metal compounds with a diameter of several nanometers or above are characterized by their size-dependent properties, which have been widely exploited in diverse applications. However, when the object's size approaches 1 nm (metal number ~100), colloidal characters disappear and molecule-like features associated with discrete electronic structures emerge instead. In this talk, I will show that the properties of such metal species in the subnanometer regime do not only arise from their size (nuclearity), but also critically depend on the inorganic microstructures and surface environments in the case of molecular gold clusters stabilized by phosphine ligands.

Phosphine-ligated gold clusters with defined nuclearity have a long history of studies to offer a library" of 'Tiny Goldworks' with diverse geometrical and electronic structures. During the recent studies on diphosphine-ligated clusters, we have recently found some exceptional diphosphine-coordinated Au_6, Au_7, Au_8, Au_{11} clusters with non-spherical geometries, which were unambiguously determined by single-crystal X-ray crystallography [1,2]. Unlike conventional sphere-like Au_9, Au_{11} and Au_{13} clusters, these non-spherical clusters exhibit isolated absorption bands in the visible region to show various colors which are strictly dependent on the geometrical structures. We also show that the surface organic units are usable to switch the electronic (optical) properties of the inorganic cores, which allows to offer nice opportunities to design selective guest-responsive functions applicable to chemical sensors [3].

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New Paradigm for Monolayer-Protected Metal Nanoclusters: The Alkynyl Ligand

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The thiolate group has been the dominant ligand for making monolayer-protectd gold nanoclusters. Tremendous progress has been made in this area in the past 10 years. Is there another ligand that can approach or even replace the leading status of the thiolate group as a ligand of choice in making atomically precise monolayer-protected gold nanoclusters? In this talk, I will show that the answer is yes according to the latest experimental and computational advances. This new paradigm ligand is the alkynyl group, especially phenyethynyl. I will show the similarity and difference between thiolate and alkynyl groups in terms of the ligand-Au interface, bonding energitics, and gemoetry and electronic structure of some newly crystallized phenyethynyl-Au nanoclusters. The conclusion is clear: More Au clusters with the alkynyl ligand will be discovered and their structure diversity could rival those of the thiolate ligand.

Unique Structures and Properties of Organosilicon Clusters

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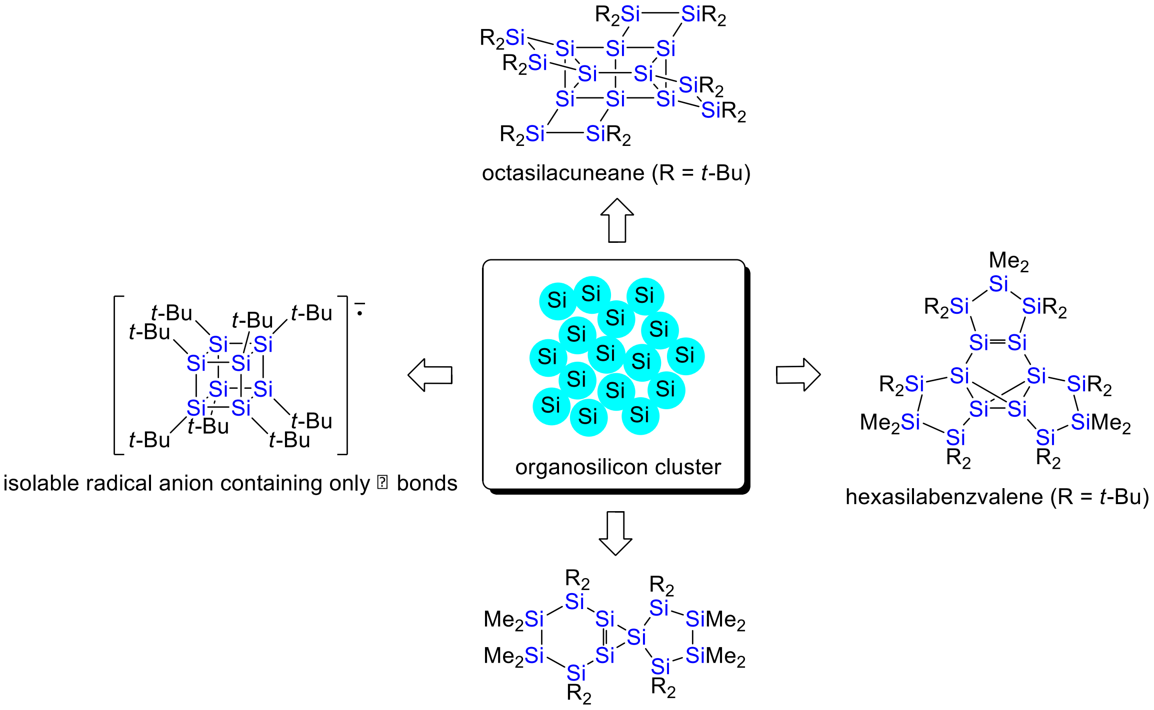
Organosilicon compounds and silicon semiconductors belong to completely different classes of substances. Organosilicon clusters can be regarded as an intermediate between both classes of substances and are expected to show different properties from both substances. However, their research has not yet developed because of synthetic difficulty. I report herein the following recent progress in the studies on organosilicon clusters.
a) New synthetic methodology for the synthesis of organosilicon clusters.[1-3]
b) Structures and properties of cyclotetrasilane-fused octasilacuneane, cyclopentasilane-fused hexasilabenzvalene, and tetrasilane-bridged bicyclo[4.1.0]heptasil-1(6)-ene[1-3]
c) Structure of an isolable radical anion containing only σ bonds.[4]



octasilacuneane (R = *t*-Bu)

isolable radical anion containing only ▯ bonds

hexasilabenzvalene (R = *t*-Bu)

bicyclo[4.1.0]heptasil-1(6)-ene (R = *t*-Bu)

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Coinage Metal Clusters: Efficient Luminophores with Extensive Metallophilic Bonding

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The complexes of d^{10} coinage metals represent a fascinating field of organometallic chemistry. A large variety of Cu, Ag and Au species have been designed for catalysis and development of functional materials with unusual physical characteristics. An intrinsic feature of the closed-shell d^{10} compounds is a strong tendency to form extended networks of metallophilic bonds, which facilitate the assembly of multinuclear metal cores (clusters).[1] The variation of the ligand environment and the nature of the constituting metal centers determines an impressive structural diversity of cluster frameworks, reported during the last decade. Additionally, the metal-metal interactions are often responsible for a dramatic change or emergence of efficient photoluminescence that significantly stimulates preparative efforts in this topical area. In our work dedicated to the coinage metal compounds we have been investigating metallophilicity-driven self-assembly processes of alkynyl M(I) species (M = Cu, Ag and Au). Chosing a suitable selection of ancillary phosphine ligands, we synthesized series of homo- and heterometallic clusters of variable nuclearity, showing attractive photophysical properties (Φ_{em} up to 100% and a wide color range).[2] From the viewpoint of practical use, the gold cluster was employed in the fabrication of an organic electroluminescent device (OLED).[3] Furthermore, a relative weakness of the metal-metal bonds, that stands behind the easiness of their modulation, opens a way to the dynamic systems, which exhibit stimuli-dependent variations of the photophysical characteristics leading to vapo-, mechano- or thermochromic luminescence[4] that forms a basis for selective luminescent chemo- or ratiometric sensing. Another potential application of these highly efficient luminophores is development of phosphorescence dyes suited for one- and/or two-photon imaging. Their employment as bioimaging agents calls for the synthesis of the cluster derivatives with improved water solubility, biocompatibility and affinity to targeted tissues and cells.[5]

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QCTFF: on the Construction of a Novel Protein Force Field

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We explain the strategy behind QCTFF, the current name for a novel atomistic protein force field. The atoms are constructed using Quantum Chemical Topology (QCT). These topological atoms determine how a system's energy is partitioned. We give a brief account of the results hitherto obtained, and a glimpse of unpublished results. Combining this QCT partitioning with the universal quantum expression of energy, leads to four types of fundamental energy contributions. The first of these is intra-atomic and the remaining three inter-atomic: (i) atomic self-energy, (ii) Coulomb energy, (iii) exchange energy and (iv) correlation energy. All structural and dynamic effects emerge from the interplay of these contributions. The machine learning method kriging captures well how they change in response to a change in nuclear configuration. Secondly, the Coulomb energy is represented by a converging multipolar series expansion when the nuclei are sufficiently far apart.

Gradient Bundle Analysis: A Full Topological Approach to Chemical Bonding

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The chemical bond has meanings that change with context. In some instances a bond is viewed as a physical connection between atoms while in others it is described as an energy lowering “bonding interaction''. Which of these two connotations should be attached to the chemical bond has fostered considerable debate. For example, the Quantum Theory of Atoms in Molecules (QTAIM) describes bonds as 1D ridges of charge density running between bound nuclei. While this definition provides an unambiguous definition of a bond as a physical link, it has been argued that these connections are not always energy lowering and hence do not correspond to bonding interactions [1]. We have extended QTAIM by describing bonds more fully as 3D objects, called bond bundles, which are bounded by zero-flux surfaces in the gradient of the charge density. This definition retains the topological elegance of a bond as an observable link between atoms, while also allowing one to associate with the bond bundle well defined properties, such as energy. It is possible to further decompose bond bundles into infinitesimal volumes, also bounded by zero-flux surfaces, and hence recover a property distribution of a bond bundle [2]. We are able to locate bonding and lone pair regions in small molecules from the bond bundle electron density and kinetic energy distributions in smaller gradient bundle. Bond bundles have been used to understand bonding interactions in small molecules [3], solid-state materials [4], and most recently, enzymes.

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Chemical Bonding (in Solids) from Local Orbitals and Plane Waves

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Population analysis holds a prominent place in quantum chemistry, in particular for the solid state where periodic bonding indicators such as Crystal Orbital Overlap Population (COOP) and Crystal Orbital Hamilton Population (COHP) have been helpful tools for chemical understanding using local-basis approaches such as extended Hückel or tight-binding LMTO-ASA. While plane-wave pseudopotential/PAW packages offer other computational advantages, however, they lack *locality*, so the aforementioned concepts were so far unavailable. Nonetheless, local information can be reconstructed to yield projected COOPs and COHPs, and one may also generate an analytical framework to transfer PAW functions to a localized basis built from Slater-type orbitals. Thus, the projected analogues to the density-of-states (DOS), COOP and COHP are readily available, and they have been implemented in the computer program LOBSTER (www.cohp.de) to derive all of the aforementioned chemical-bonding quantities from PAW calculations. By doing so, not only close-packed solids but also nano-objects, surfaces, amorphous matter, (H-bonded) molecules etc. can be analyzed using the same framework.

Evolutionary Structure Prediction of Organic Crystals

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Recently, evolutionary algorithm (EA) has proved to be an efficient tool that enables accurate and reliable structure prediction for inorganic crystals. Here we illustrate its application to organic crystal structure prediction. We designed a constrained EA, which treats each motif as a building block with internal coordinates. It significantly speeds up the structural search together with the evolutionary variation operators. This method can be applied to study the crystal packing of a wide range of systems (including small molecules, pharmaceuticals, explosives, polymers and even inorganic complexes containing distinct molecular blocks). Some of the recent results will be discussed as well.

Topological Descriptors of Intermolecular Bonding in Solvents – Measuring Solvent Response to Unique Environments and Developing Predictive Capabilities

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The structure and dynamics of solvents are often quantified in terms of correlation functions that map the relationships between specific variables or species. Here we present an alternative approach, Intermolecular Network Theory (INT), that borrows from graph theoretical methods used in data science. By converting all of the intermolecular interactions in the liquid into a network defined by molecular nodes and edges of intermolecular interactions, a broad variety of data-mining techniques can be used – from the PageRank algorithm of Google, to the routing algorithms of Mapquest. These topological descriptors of the network can help to understand both the structure, dynamics, and thermodynamics of liquids, including miscibility, the properties of phase boundaries, and chemical reactivity of solutes.

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Application of the AdNDP/SSAdNDP Methods for Understanding Chemical Bonding in Low-Dimensional Systems

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The adaptive natural density partitioning (AdNDP) algorithm combines the compactness and intuitive simplicity of Lewis theory with the flexibility and generality of canonical molecular orbital theory. The objects of chemical bonding in this method are n-center 2-electron bonds, where n goes from one (lone-pair) to the maximum number of atoms in the system (completely delocalized bonding). The algorithm is a generalization of the natural bonding 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. Our extension of AdNDP to periodic systems via SSAdNDP 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. In my talk, I will demonstrate the versatility of both methods by applying them to several systems featuring both localized and many-center chemical bonding, and varying in structural complexity: from clusters (0D) to chain-like species (1D) and various atomic-scale lattices (2D). The following systems will be discussed: 0D - alkane-like structures of $Li_2Al_2H_6$ and $Li_3Al_3H_8$ as well as the experimentally observed $Li_2Al_3H_8^-$ anion; 1D - extended nonmetal atom chains of M_nF_{4n+2} (M=S and Se); 2D - graphene, coronene, isocoronene, circumcoronene, BC_3 honeycomb epitaxial sheet, C_4F fluorinated graphene sheet, and Cu_2Si monolayer featuring planar hexacoordinate Cu and Si.

Acknowledgements
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Chemical Bonding and Excited State Dynamics on Nanoscale

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

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

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

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Ground and Excited States of Three-Dimensional Carbon and Boron Clusters from P3+ and NR2 Electron-Propagator Theory

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Tests on the predictive ability and computational efficiency of a variety of electron-propagator methods disclose their advantages in determining electron binding energies of various kinds, including ionization energies of large organic molecules and carbon clusters, electron detachment energies of anions and electron affinities of organic acceptors. The extrapolation of basis-set trends and employment of explicitly correlated techniques for estimating the effects of basis-set incompleteness reveal the favorable intrinsic characteristics of several, highly efficient approximations which deserve more widespread use. Among these approximations are the diagonal second-order, partial third order, renormalized partial third order (P3+) and non-diagonal renormalized second-order (NR2) methods. Composite models in which basis-set and self-energy corrections are estimated in a sequence of calculations and schemes for the correction of spin-contamination in calculations based on unrestricted spin-orbitals facilitate reliable predictions of electron binding energies for large anionic clusters of carbon and boron. For carbon fullerenes, several anionic states with diffuse or valence character are bound with respect to the uncharged cluster. Photoelectron spectra of anionic boron clusters with cage structures also have been successfully assigned.

Bridging the Gap Between Conceptual Density Functional Theory and Polarizable Force Fields

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In conceptual Density Functional Theory (CDFT), insights from Density Functional Theory (DFT) are used to understand the reactivity and chemical bonding of compounds from the ground state of the reactants and the derivatives of its energy toward the number of particles, the density and the external potential [1]. This description is remarkably close to the purpose of a polarizable force field, where the interactions between monomers (molecular fragments) are modeled through the response of the monomer energy and electron density to perturbations in the external field. Recently, both fields started growing closer as the CDFT community now also started using the (non-interacting) response kernel to understand chemical bonding [2] and new types of polarizable force fields build on the same quantities [3]. In this talk, this connection between CDFT and polarizable force fields will be explored in the light of recent developments in both fields.

A brief overview will be presented of modern variants of the Hirshfeld partitioning method. Such methods allow one to define atoms-in-molecules (AIM) operators that will be used in the remainder of the talk to condense kernels into pairwise atomic properties, as to facilitate their visualization and interpretation.

In the first part of the talk, I will summarize the findings in the literature on the condensed linear response kernel for molecular systems with different types of chemical bonds [2] and I will extend these results with additional compounds that exhibit non-trivial chemical bonding patterns. These results will be compared to the delocalization index (DI) for the same compounds. Although Unsöld's approximation connects the DI with the non-interacting response kernel [4], this linear relation breaks down in several examples, showing that the response kernel allows one to look at chemical bonding from a different angle.

In the second half of the talk, a new type of polarizable force field will be presented: "Atom Condensed Kohn-Sham approximated to 2nd order" (ACKS2) [3]. In this polarizable force field, the non-interacting response kernel is explicitly incorporated. In order to use it for extended atomistic simulations (millions of atoms) over extended timescales (many nanoseconds), the structure of the response kernel must be understood in terms of molecular geometry or topology. This was first explored in the BOP/SQE model, where a one-to-one relation between the DI and linear response was intuitively assumed [5]. The examples from the first half of the talk clearly illustrate that one must go beyond such simple assumptions. This raises new challenges that will have to be addressed in the development of polarizable force fields.

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Understanding Cooperativity in Halogen Bonds with Molecular Orbital Theory

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Understanding cooperativity in halogen bonds with molecular orbital theory.
We present here a detailed analysis of the nature of halogen bonds, how they resemble and also how they differ from the better understood hydrogen bonds.[1] An accurate physical model of the halogen bond follows from quantitative Kohn–Sham molecular orbital (MO) theory, energy decomposition analyses (EDA) and Voronoi deformation density (VDD) analyses of the charge distribution. It appears that the halogen bond arises not only from classical electrostatic attraction but also receives substantial stabilization from HOMO–LUMO interactions just as in the case of hydrogen bonds.

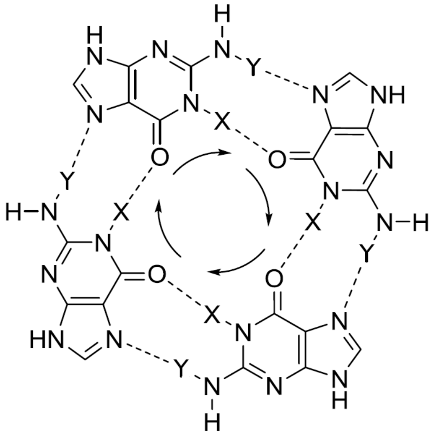

Figure. G-tetrad analogue. (X, Y = H, Cl, Br, I)

In this presentation, we focus in particular on the resonance-assisted hydrogen and halogen bonding mechanism (RAHB and RAXB) in quadruplexes of G-DNA[2] and in the corresponding *N*-halo-base quartets, respectively (see Figure). Similar to RAHB, the RAXB arise not only from classical electrostatic interaction but also receive substantial strengthening from donor–acceptor interactions within the σ-electron system. There is also a small stabilization by π-electron delocalization. Our analyses prove that the observed cooperativity in *N*-halo-guanine quartets and natural guanine quartets both originate from the charge separation that occurs with donor–acceptor orbital interactions in the σ-electron system.[3,4]

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Multi-Center Bonding in Difficult Cases in Chemistry

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Canonical Molecular Orbitals (CMO) obtained by either the Hartree-Fock method or by Density Functional Theory are completely delocalized over the whole chemical system. When systems are getting larger it is hard to interpret CMOs. Chemist on the other side prefer to use localized bonding based on Lewis model, which operates with lone pairs (1c-2e) and two-center two-electron (2c-2e) bonds. When Lewis model works, interpretation of chemical bonding is simple. However, many new chemical systems cannot be represented by Lewis model. The resonance description may be used in those cases, but it becomes very challenging for structurally complex chemical species. We recently introduced two new theoretical methods Adaptive Natural Density Partitioning (AdNDP)[1] and Solid State Adaptive Natural Density Partitioning (SAdNDP)[2], which allow to express chemical bonding in terms of localized (1c-2e and 2c-2e) and delocalized (multi-center nc-2e) bonds. We initially search for all lone pairs, core electrons and 2c-2e bonds with good occupation numbers. In the ideal Lewis model occupation numbers correspond to 2 (an electron pair). After that we look for multicenter bonds still trying to use as small number of centers as possible, though in principle delocalized bonds can be delocalized over the whole chemical system. In my talk I will show how AdNDP and SSAdNDP methods allow us to use both localized and delocalized bonding elements for rationalization of chemical bonding in difficult cases of organic molecules, bare and embedded clusters, two-dimensional sheets and solids. AdNDP and SSAdNDP provide a very efficient and visual approach to represent chemical bonding and could be used for research and for teaching chemistry.

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