International Conference on Chemical Bonding

July 13 – 17, 2018
Lihue, Hawaii

Sponsors:

UtahStateUniversity

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ACS NANO

International Conference on Chemical Bonding

Technical Program

Thursday, July 12

Arrival and registration

Friday, July 13

<u>Morning</u>: Opening. Bonding appetizer plate. *Presiding: Anastassia Alexandrova*

8:30 – 8:45 am	Alex, Anastassia, Lai-Sheng - Introductory remarks
8:45 – 9:15 am	Frank Weinhold (University of Wisconsin, Madison, USA) *"What's New in NBO Theory?"*
9:15 – 9:45 am	Mark Hersam (Northwestern University, USA) *"Surface and Interface Engineering of Van der Waals Heterostructures"*
9:45 – 10:15 am	Masaichi Saito (Saitama University, Japan) *"A Bench-stable Compound Possessing (σ+π) Double Aromaticity"*
10:15 – 10:45 am	Susan Kauzlarich (UC Davis, USA) *"Zintl Phases for High and Mid Temperature Thermoelectric Applications"*
10:45 – 11:00 am	*Coffee Break*
11:00 – 11:30 am	Mark Eberhart (Colorado School of Mines, USA) *"The Chemical Bond: A Deviant's View"*
11:30 – 12:00 am	Giovanni Maestri (Università di Parma, Italy) *"Expanding the chemistry of stable trinuclear all-metal aromatics"*
12:00 – 12:30 am	Angela Wilson (Michigan State University, USA) *"Computational Strategies Towards Potential Energy Surfaces in Vibrational Calculations"*

<u>Afternoon</u>: Materials, Interfaces, Functionality - I *Presiding: Alexander Boldyrev*

3:00 – 3:30 pm	Volker Blum (Duke University, USA) *"Efficient, Accurate All-Electron Theory of Materials for Energy and Electronics with Numeric Atom-Centered Basis Sets"*
3:30 – 4:00 pm	Paul Weiss (UCLA, USA) *"TBA"*
4:00 – 4:30 pm	Gang-yu Liu (UC Davis, USA) *"Guiding Chemical Bond Formation and Breakage towards Building 3D Nanostructures"*
4:30 – 4:45 pm	*Coffee Break*
4:45 – 5:15 pm	J. Nathan Hohman (Molecular Foundry, LBNL, USA) *"Engineering Dimensionality in Excitonic Low-Dimensional Silver MOCHAs (Metal-organic Chalcogenolate Assemblies)"*
5:15 – 5:45 pm	Jin Z. Zhang (UC Santa Cruz, USA) *"Surface Chemistry Approach to Stabilizing Organo-metal Halide Perovskite Quantum Dots And Bulk Films"*
07:00 – 10:00 pm	***RECEPTION***

Saturday, July 14

Morning: Catalysis *Presiding: De-en Jiang*

8:30 – 9:00 am	Jean-Sabin McEwen (Washington State University, USA) *"Elucidating the Roles of Electric Fields in Catalysis"*
9:00 – 9:30 am	Philippe Sautet (UCLA, USA; CNRS, France) *"TBA"*
9:30 – 10:00 am	Sergey Kozlov (KAUST, Saudi Arbia) *"Reactivity of Alloy and Supported Nanoparticles"*
10:00 – 10:30 am	Roger Rousseau (PNNL, USA) *"Understand the role of solvent effects in the thermal and electrochemical hydrogenation of Organic Compounds"*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Vassiliki-Alexandra Glezakou (PNNL, USA) *"Chemical Bonding and Entropy Effects under Confinement: Ethanol Adsorption, Dehydration and Oligomerization in Zeolites"*
11:15 – 11:45 am	Daniel Ess (Brigham Young University, USA) *"Examining Bonding Assumptions in Transition-Metal C-H and H-H Bond Activation Reactions and Metal-Heteroatom Bond Energies"*
11:45 – 12:15 pm	Boniface Fokwa (UC Riverside, USA) *"Designing Earth-Abundant Boron-based Materials for Hydrogen Production"*
12:15 – 12:45 pm	Rex Skodje (Colorado University, Boulder, USA) *"Sum Over Histories Representation for Chemical Kinetics"*

Afternoon: Small and Fundamental - I *Presiding: Giovanni Maestri*

3:00 – 3:30 pm	Jose Goicoechea (University of Oxford, UK) *"From Chemical Curiosities to Versatile Reagents: Heavy Analogues of the Cyanate Ion"*
3:30 – 4:00 pm	Stefanie Dehnen (Philipps-Universität Marburg, Germany) *"Structures and Bonding in Multimetallic Cluster Anions"*
4:00 – 4:30 pm	Alexander Boldyrev (USU, USA) *"Delocalized Bonding in Inorganic Compounds"*
4:30 – 4:45 pm	*Coffee Break*
4:40 – 5:15 pm	Kieron Burke (UC Irvine, USA) *"Density-corrected density functional theory"*
5:15 – 5:45 pm	Michael Morse (University of Utah, USA) *"Predissociation Measurements of Bond Dissociation Energies"*
5:45 – 6:15 pm	Michael Duncan (University of Georgia, USA) *"Structure and Bonding in Metal Ion-Acetylene Complexes via Infrared Spectroscopy and Photofragment Imaging"*
6:15 – 6:45 pm	De-en Jiang (UC Riverside, USA) *"Hydrogen in Nanometal"*

Sunday, July 15

TOUR DAY

Monday, July 16

Morning: Boron, Lanthanides, Actinides, and the Unexpected *Presiding: Lai-Sheng Wang*

8:30 – 9:00 am	Holger Braunschweig (Julius-Maximilians-Universität Würzburg, Germany) *“Borametallomimetics – Activation of Small Molecules by Low-valent Boron Species”*
9:00 – 9:30 am	Emmanuel Lacôte (University of Lyon, France) *“NHC-Boryl Radicals: new Synthetically useful Boron-Based Reactive Intermediates”*
9:30 – 10:00 am	Jean-François Halet (University of Rennes, CNRS, France) *“Zero-, one-, and two-dimensional boron-carbon frameworks in solid-state rare earth boride carbides”*
10:00 – 10:30 am	Anastassia Alexandrova (UCLA, USA) *“Covalency, Ionicity, promiscuity, and bizarre properties of late element borides”*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Thomas Albrecht-Schmitt (Florida State University, USA) *“Origin of Covalency in Late Actinides”*
11:15 – 11:45 am	Enrique Batista (Los Alamos National Laboratory, USA) *“Covalency of Actinides (An^{III}, An^{IV})) with Chelating Agents Across the Actinide Series (An = Th to Es)”*
11:45 – 12:15 pm	Eluvathingal D. Jemmis (Indian Institute of Science, Bangalore, India) *“Nature Plays Dice with Boron: Inevitability of Uncertainties”*
12:15 – 12:45 pm	Xuenian Chen (Henan Normal University, China) *“Nucleophilic Behaviors of the B–H Bond in Borane Complexes”*

Afternoon: Materials, Interfaces, Functionality - II *Presiding: Nate Hohman*

3:00 – 3:30 pm	Sarah Tolbert (UCLA, USA) *“TBA”*
3:30 – 4:00 pm	John Tse (University of Saskatchewan, Canada) *“Structure, structural evolution and Superconductivity of high pressure hydrogen-rich alloys”*
4:00 – 4:30 pm	Tomas Base (The Czech Academy of Sciences, Czech Republic) *“Carborane Cages in 2D Self-Assemblies”*
4:30 – 4:45 pm	*Coffee Break*
4:45 – 5:15 pm	Yuan Ping (University of California, Santa Cruz, USA) *“Charged Defects in Two-dimensional Materials from Many Body Perturbation Theory”*
5:15 – 5:45 pm	T. Pradeep (Indian Institute of Technology Madras, India) *“Reactions between noble metal clusters”*
5:45 – 6:15 pm	Gereon Niedner-Schatteburg (Technische Universität Kaiserslautern, Germany) *“Many Electron High Spin States: Structures and Stability of Transition Metal Clusters: Non Haber-Bosch Iron?”*

Tuesday, July 17

Morning: Small and Fundamental - II

Presiding: Sergey Kozlov

8:30 – 9:00 am	Benjamin Schwartz (UCLA, USA) *"Solvents Can Alter the Identity of Solute Chemical Bonds"*
9:00 – 9:30 am	Marco Nascimento (Universidade Federal do Rio de Janeiro, Brazil) *"The chemical bond as a manifestation of quantum mechanical interference"*
9:30 – 10:00 am	Robert Continetti (University of California, San Diego, USA) *"Chemical Bonding and Dynamics in Tetra-atomic Anions and Transient Neutrals"*
10:00 – 10:30 am	James Lisy (UIUC, USA, and Tokyo Institute of Technology, Japan) *"Ion-peptide interactions between alkali metal ions and AcYNHMe (termini-protected GYG); Modeling the GYG selectivity filter in K^+ channels"*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Yuxiang Mo (Tsinghua University, China) *"Photodissociation dynamics of H_2, $H_2 \rightarrow H(1s)+H(2s,2p)$"*
11:15 – 11:45 am	Bing Zhang (Wuhan Institute of Physics and Mathematics, CAS, China) *"Visualizing the evolution of coherent vibrational wavepacket"*
11:45 – 12:15 pm	Richard Mabbs (Washington University in St. Louis, USA) *"Interactions of Electrons With Molecules: Probing Excited Anion States"*

Afternoon: Desert

Presiding: Anastassia Alexandrova

3:00 – 3:30 pm	Jared Olson (Utah State University, USA) *"Electronic Transmutation (ET): recent theoretical and experimental developments and applications of ET"*
3:30 – 4:00 pm	Evangelos Miliordos (Auburn University, Auburn, USA) *"Metal-ammonia complexes disclose a secret periodic table of solvated electron precursors"*
4:00 – 4:30 pm	Lai-Sheng Wang (Brown University, USA) *"Recent Progress in the Investigation of Size-Selected Boron Clusters: From Borophenes to Metallo-Borophenes"*

Abstracts

What's New in NBO Theory?

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We preview a variety of new features in the forthcoming ***NBO 7.0*** program, focused on (i) comparisons with alternative analysis methods, (ii) improved description of resonance-structural and electronic correlation effects, and (iii) improved visualization of reactive processes. New features to be briefly described include:

- `NEDA` for Gaussian
- Natural Poly-Electron Population Analysis (`NPEPA`)
- `$WF` keylist input for CAS/CI-type wave functions
- 2nd-order reduced density matrix and cumulant elements (`RDM2`)
- Resonance NBOs (`RNBO`)
- Convex-solver `NRT`

As time allows, we'll also preview the new ***NBOPro@Jmol*** program that integrates the powerful ***Jmol*** 3D molecular viewer with the ***NBOPro*** "plugin" of four interactive modules (and supporting suite of ***NBO****7*-level programs)

- *MODEL*: molecular design editor and file-conversion utility;
- *RUN*: ***GenNBO*** wavefunction analysis
- *VIEW*: ***NBOView*** orbital viewer (still/animated)
- *SEARCH*: interactive data-mining utility

to provide the ideal pedagogical and research-level tool for "file-free" NBO applications.

Surface and Interface Engineering of Van der Waals Heterostructures

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Two-dimensional materials have emerged as promising candidates for next-generation electronic and optoelectronic applications [1]. With electronic properties spanning the spectrum from insulating (e.g., hexagonal boron nitride and montmorillonite) to semiconducting (e.g., transition metal dichalcogenides and phosphorene) to conducting (e.g., graphene and borophene), nearly any electronic device can be fabricated by stacking two-dimensional materials into heterostructures [2]. However, in the atomically thin limit, the influence of surface chemistry, defects, interfaces, and the surrounding environment play an important if not dominant role, especially in comparison to bulk materials [3]. Consequently, methods for controlling and characterizing heterostructure interfaces with atomic precision are critical steps in the realization of the full technological potential of two-dimensional materials [4]. Towards this end, this talk will outline the latest efforts in our laboratory to engineer surfaces and interfaces in two-dimensional heterostructures. For example, rotationally commensurate growth of MoS_2 has been realized on epitaxial graphene on SiC substrates [5], which allows deterministic control over MoS_2 grain boundary orientation [6] with implications for gate-tunable memristive charge transport properties [7]. For chemically reactive 2D materials (e.g., phosphorene), encapsulation with atomic layer deposition [8] and passivation with covalently tethered organic adlayers [9] minimize ambient degradation and provide charge transfer doping. Finally, this talk will describe emerging efforts concerning the growth [10,11] and chemical functionalization [12] of synthetic two-dimensional materials (e.g., borophene) that do not exist as layered materials in the bulk.

References

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A Bench-stable Compound Possessing (σ+π) Double Aromaticity

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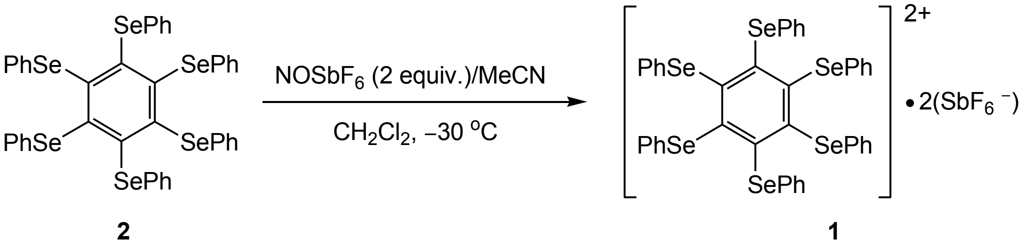
Since benzene was discovered and subsequently the properties of benzene were investigated, aromaticity has become one of the most fundamental principles in chemistry. Aromaticity was considered to emerge exclusively out of π-orbital interactions; however, it is now expanded to interactions arising from σ-,[1] δ-[2] and φ-symmetric orbitals.[3] As a novel pattern of aromaticity, double aromaticity arising from σ- and π-orbital interactions was first proposed by Schleyer,[4] and subsequent experimental studies exhibited double aromaticity of a salt of hexaiodobenzene dication.[5] However, the formation of the dication salt itself is still controversial,[6] and accordingly, the preparation of a bench-stable double aromatic compound remains elusive.

We independently designed a hexaselanylbenzene dication as a potential (σ+π) double aromatic compound[7] and succeeded in the full characterization of salt of hexakis(phenylselanyl)benzene dication **1**[8] prepared by the two-electron oxidation of hexakis(phenylselanyl)benzene **2**[9] (Scheme 1). We concluded that the dication salt **1** possesses (σ+π) double aromatic character, based on the conventional definition of aromaticity.



Scheme 1 Preparation of salt of hexakis(phenylselanyl)benzene dication **1**.

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Zintl Phases for High and Mid Temperature Thermoelectric Applications

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In order to have an efficient thermoelectric generator, it is necessary to have a high zT across a wide temperature range. The Zintl phases $Yb_{14-x}Ce_xMnSb_{11}$ and $Yb_{2-x}A_xCdSb_2$ (A = Eu, Ca, Sr, Na) are compatible Zintl phases that could be used in the next generation of segmented thermoelectric generators operating over the temperature range of 1000 – 100 °C. Both phases are p-type semiconductors. In the case of $Yb_{14}MnSb_{11}$, it is stable at temperatures as high as 1200 °C; however, sublimation is an issue. Alloying with Ce^{3+} allows for high temperatures while minimizing the sublimation problems. Both compounds have extremely low thermal conductivity and high Seebeck coefficients. These two phases can be prepared as single crystals via flux growth or high purity single phase by mixing of the elements on-stoichiometry and subsequent heat treatment. The structure and properties of these two phases will be presented.

The Chemical Bond: A Deviant's View

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The Quantum Theory of Atoms in Molecules[1] (QTAIM) extracts chemical significance from the charge density's gradient field, $\boldsymbol{\nabla\rho}$. However, the charge density's Hessian field, $\mathcal{H}\rho$, is also central to QTAIM. By way of illustration: i) The zeros of the gradient field serve to locate critical points (CPs). Yet, the signs of the eigenvalues of $\mathcal{H}\rho$ determine their type—ring, cage, bond, or nuclear. ii) The bond path requires that two eigenvectors of $\mathcal{H}\rho$ be normal to the gradient vector at all points along the bond path. iii) While atomic basins are bounded by zero flux surfaces (ZFS) in $\boldsymbol{\nabla\rho}$, they are simultaneously surfaces where one eigenvalue of $\mathcal{H}\rho$ is normal to the surface.

Apparently, the chemical significance of QTAIM structures derives from a relationship between $\boldsymbol{\nabla\rho}$ and $\mathcal{H}\rho$; a relationship that may be quantified in terms of the deviation between the Hessian and the gradient coordinate frames.

The coordinate frame of $\mathcal{H}\rho$ is given by its eigenvectors. A natural coordinate system to represent the gradient field is its Frenet frame, an orthogonal reference system in which one direction is that of the gradient vector and the mutually orthogonal directions are given by the normal ($\boldsymbol{n}$) and binormal ($\boldsymbol{b}$) vectors. From another perspective, these vectors provide information regarding the shape of the charge density isosurface at a point, $\boldsymbol{\nabla\rho}$ is of course normal to the isosurface and $\boldsymbol{b}$ and $\boldsymbol{n}$ give the directions in which the isosurface is most and least curved. Because chemically meaningful structures are recognized where these frames align or partially align, it seems reasonable to seek a measure giving the degree of "misalignment" between these two reference systems.

Two orthogonal coordinate systems can be aligned through a rotation of one of the systems by an angle θ about an axis given by a unit vector $\boldsymbol{v} = \{v_1, v_2, v_3\}$ together forming a four vector, $\{\theta, v_1, v_2, v_3\}$. Such four vectors are elements of the quaternion space and well-known as a convenient mathematical notation for representing orientations and rotations of objects in three dimensions. A quaternion has a "length" designated by its norm. We define the charge density deviation, or more simply the deviation ($\mathcal{D}$) as the norm of the quaternion representing the rotation aligning the charge density's Fernet frame with its Hessian frame. This scalar field provides a new way to quantify the structure of the charge density and differs in a meaningful way from other scalar fields used to interpret the charge density, *e.g.* the electron localization functions (ELF). In particular, $\mathcal{D}$ vanishes near a nucleus and over the entirety of an isolated atom. Its magnitude will be maximal in the regions we associate with bonding and its integrated value over an atom in a molecule will be smaller for weakly bound as opposed to covalently bound systems. We take $\mathcal{D}$ as a field that has the characteristics we would expect as representative of the chemical bond and in this presentation, we will explore the characteristics of this field

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Expanding the chemistry of stable trinuclear all-metal aromatics

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All-metal aromatics are cyclic molecules that parallel their carbon-based peers by presenting a similarly delocalized bonding network. However, in most cases their limited stability prevented any broad experimental application. A straightforward synthetic route[1] delivers a family of bench-stable M_3^+ (M = Pd, Pt) complexes that are the noble-metal analogues of the cyclopropenyl cation.[2] This enabled to study the effect of their unusual bonding on reactivity. The Pd_3^+ cluster can semi-reduce alkynes with complete selectivity.[3] These prototypical subnanometric metal surfaces can trigger unique C-C bond forming cascades too.[4] The delocalized metal-metal bonding of these *cations* makes them *donor ligands* that bind Lewis acids.[5]

Recent developments that are currently ongoing include the possibility to incorporate Ruthenium nuclei in the trinuclear kernel, giving rise to heterobimetallic and heterotrimetallic species that retain an equilateral core. The talk will also present preliminary hits on the reactivity of Pt_3^+ complexes towards polyunsaturated substrates, which is complementary to that of Pd_3^+ ones.

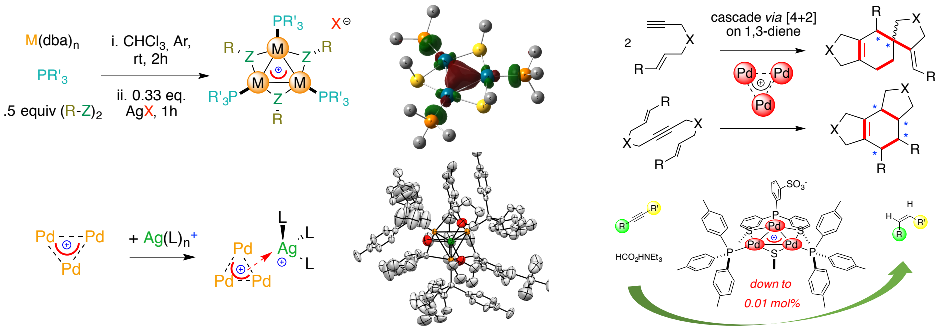

Figure 1. Structure, bonding and reactivity of all-metal aromatic Pd_3^+ complexes

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Computational Strategies Towards Potential Energy Surfaces in Vibrational Calculations

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Intermolecular interactions govern molecular structure and dynamic properties such as reaction pathways and vibrational motion. While the former can be obtained by using standard optimization methods, an analysis of dynamic properties within the Born-Oppenheimer approximation requires the knowledge of a potential energy surface (PES). By carrying out many electronic structure calculations, such PESs can be generated. However, often high-level methods are computationally too demanding, while using approximate theories for the PES directly impacts the accuracy of the dynamics calculations.

Vibrational spectroscopy is critical for characterizing structural and dynamical properties of polyatomic molecules. Theoretical methods are often restricted to the harmonic approximation, and computationally costly (memory, disk space, CPU time) *ab initio* methods are required to attain quantitative accuracy for vibrational and electronic properties of molecules. While it is common practice to use scaled harmonic frequencies to avoid the costly computation of the PES which is required in an anharmonic treatment, there is no guarantee that the predicted spectra will be correct. In particular, for a differentiation of different conformers and solvation modes, anharmonic vibrational calculations are indispensable, as the harmonic approximation does not provide sufficient detail about the local topology. The correlation consistent Composite Approach (ccCA) has been used to generate potential energy surfaces (PES) for diatomic and small polyatomic molecules. Structural and vibrational properties such as frequencies, dipole moments, and infrared absorbance intensities are predicted in tandem with vibrational self-consistent field (VSCF) and post-VSCF theory. The combination of ccCA and post-VSCF theory aims to reduce the computational cost associated with generating accurate PESs for anharmonic mode-mode couplings as well as calculating contributions from anharmonic corrections to the potential. The ccCA method proves to be a very accurate, robust, reliable and efficient approach for the prediction of vibrational properties.

Efficient, Accurate All-Electron Theory of Materials for Energy and Electronics with Numeric Atom-Centered Basis Sets

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Light harvesting, light emission, electronic levels and their character are phenomena that all inherently arise at the atomic scale, closely linked to the structure and excitation properties of the underlying materials. This talk focuses on accurate, scalable computational techniques for these phenomena based on high-accuracy numeric atom-centered orbital basis sets in the FHIaims code [1], suitable for non-periodic and periodic simulations across the periodic table, including large hybrid nanostructured systems and applicable on current highest-performance computer architectures [2,3,4]. The main approaches covered are semilocal and hybrid density-functional theory for structure and alignment of frontier energy levels, as well as many-body approaches such as *GW* and the Bethe-Salpeter Equation for electronic excitations. We show how these developments enable us to predict the electronic character of new layered organic-inorganic hybrid perovskite based materials with complex organic functionality [5], a class of three-dimensional crystalline semiconductor materials with tunable electronic and optical properties based on refining both the inorganic and the organic components. We finally discuss ongoing developments to further extend the reach of the underlying approaches include an efficient, scalable GPU implementation (currently for semilocal DFT), as well as the broader, open-source electronic structure infrastructure "ELSI" [4] for large-scale applicable electronic structure theory across a community including different electronic structure codes and solvers.

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TBA

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Guiding Chemical Bond Formation and Breakage towards Building 3D Nanostructures

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Controlling chemical bond formation and breakage is the Holy Grail in surface and materials science. Towards this goal, this presentation introduces a high resolution and local approach to guide bond breakage and formation using examples in surface chemistry. Using scanning probe microscopy, the weakest bonds can be broken under contact, e.g. chemisorption at interface, or mechanophores within individual polymer chains.[1] The force and contact area dictate the outcomes of the breakages, including the number and locations. Complex structures can be formed following custom design, and with high spatial precision. Building up into 3D could be achieved *via* surface reactions if the exposed termini carry reactive functionality, or by adding materials *via* scanning probes layer-by-layer, as shown in Figure 1.[2, 3] The current advances in building 3D nanostructures will be reported in conjunction with new insights into surface chemistry.[1-5]

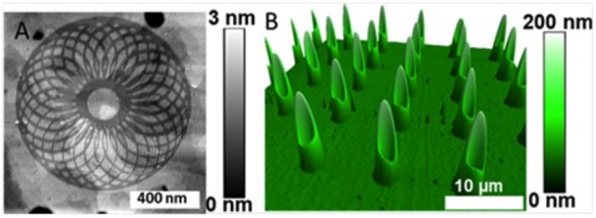

Figure 1. (A) AFM topographic image of a spirograph pattern produced by nanografting octanethiol inlaid in a (5-(hexadecyloxy)-1,3-phenylene) dimethanethiol monolayer. (B) 3D display of AFM topographic image of an array of bamboo shaped structures of star [PS_{34}-$PDMAEMA_{40}]_{39}$ on glass.

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Engineering Dimensionality in Excitonic Low-Dimensional Silver MOCHAs (Metal-organic Chalcogenolate Assemblies)

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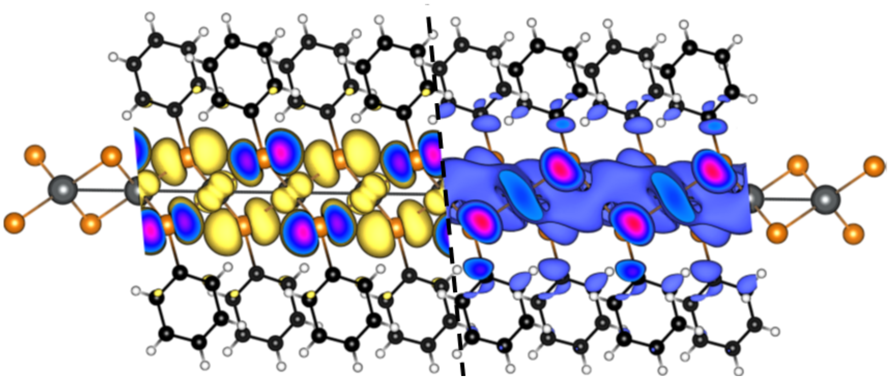
A semiconductor's bandgap can be manipulated my controlling its dimensions at the lengthscale of the Bohr radius of the excitons (1-5 nm). Abstracting single monolayers from lamellar van der Waals solids like graphene or the transition metal dichalcogenides (TMDCs) has been a straightforward route towards preparing freestanding materials with high confinement of electronic carriers at such short dimensions. Strongly bound excitons and tunable properties in TMDCs have recently attracted considerable interest for ultra-lightweight photovoltaics, electrocatalysts, and spintronic materials. However, most 2D materials reported to date are either elemental or binary semiconductor phases, limiting the discovery to materials that can be exfoliated from bulk crystals or prepared in thin films on support substrates. Recently, crystalline hybrid materials like metal-halide perovskites and metal organic chalcogenide assemblies (MOCHAs) have been reported that combine the structural and electronic properties of inorganic monolayer materials with chemically configurable ligands. The inclusion of organic moieties incorporated in self-assembling, three-dimensional arrays present an opportunity to leverage chemistry to build new categories of materials having inorganic nanostructures are isolated from one another, physically and electronically, by the supramolecular lattice composed of the organic ligands. Here, we consider the structure and organization of silver benzeneselenolate, a self-assembling layered hybrid structure, and examine its optoelectronic properties in the context of a 2D-like material. We found that its optical response is dominated by tightly bound exciton states and observed large exciton binding energy comparable to the monolayer TMDCs. Synthetic manipulation of dimensionality and topology is used to prepare a family of related crystalline polymer systems, and the role of intermolecular forces and molecular geometry on the inorganic phases are considered in the context of transitions between 1D, 2D, and 3D coordination polymer systems.



Partial charge densities at the valence (left) and conduction band (right) of silver benzeneselenolate, an electronically 2D self-assembling metal organic chalcogenolate assembly (MOCHA).

Surface Chemistry Approach to Stabilizing Organo-metal Halide Perovskite Quantum Dots And Bulk Films

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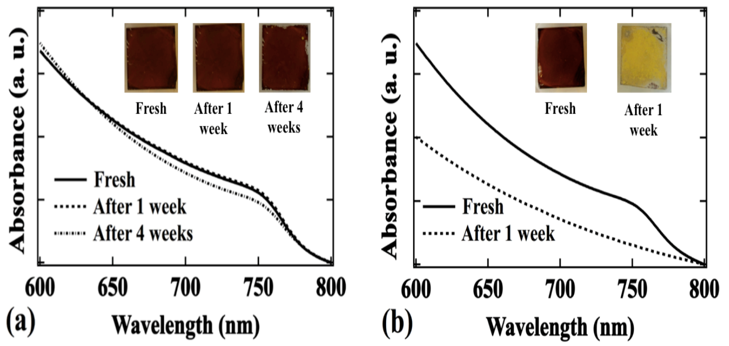
Organo-metal halide perovskites (OMHP), such as $CH_3NH_3PbI_3$, exhibit novel electronic, optical and magnetic properties that are promising for various applications including photovoltaics. However, instability due to factors such as UV light, water, oxygen, and temperature limits their applications. The surface of the perovskites strongly affects stability, especially in terms of environmental factors such as solvent and oxygen. We have developed different surface passivation strategies to stabilize perovskite quantum dots (PQDs) and bulk films using surface chemistry approaches based on molecular ligands [1-4]. The detailed molecular structures of the ligands make a major difference in their effectiveness of passivation for PQDs vs bulk films, *e.g.* steric hindrance between ligand molecules. For instance, while cone-shaped ligands are effective for PQDs but not for bulk, linear ligands are better for bulk films and not for PQDs. As an example, oleic acid (OA), essentially a linear molecule, does not passivate PQDs effectively but is highly effective for bulk films. Another important finding is that ammonium ions ($-NH_3^+$) and carboxylate groups ($-COO^-$) have synergistic effects in surface passivation, attributed to simultaneous passivation of both anions (X^-) and cations (Pb^{2+} or $CH_3NH_3^+$) on the surface. As support to this finding, bifunctional peptide-like molecules are highly effective as bidentate ligands for surface passivation. Our studies demonstrate that surface chemistry approaches are promising for stabilizing OMHP, which is significant for many emerging applications.



$CH_3NH_3PbI_3$ film with (left) and without (right) passivation using oleic acid (OA).

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Elucidating the Roles of Electric Fields in Catalysis

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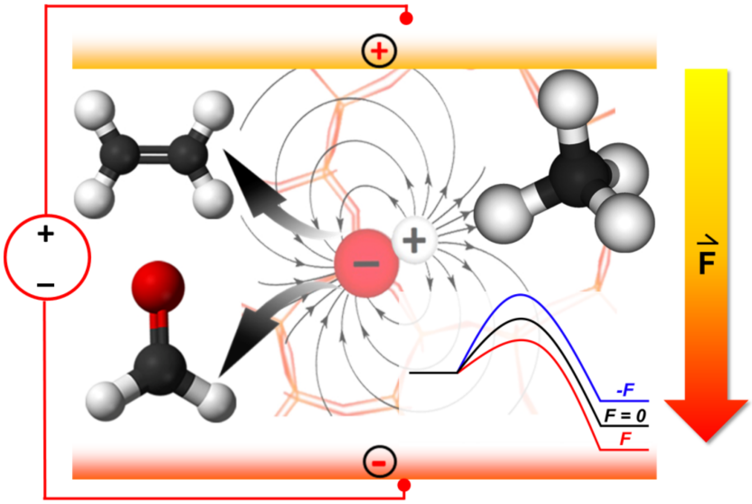
In this talk, we will illustrate how the presence of internal and external electric fields can affect catalytic activity and selectivity, with a focus on heterogeneous catalysts. We will show how the electric field, whether externally applied or intrinsically present, can affect the behavior of a wide number of materials relevant to catalysis [1]. We review some of the theoretical methods that have been used to elucidate the influence of external electric fields on catalytic reactions, as well as the application of such methods to selective methane activation. In doing so, we illustrate the breadth of possibilities in field-assisted catalysis.



Examples of chemical reactions involving direct activation of methane to produce alkenes and oxygenates in which the impact of local and external electric fields are largely unexploited.

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TBA

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Reactivity of Alloy and Supported Nanoparticles

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Although typical heterogeneous catalysts consist of transition metal or alloy nanoparticles on high surface area oxide supports, they are often modelled by single-crystal surfaces. More sophisticated models are needed to study the effects of alloy nanostructuring and metal-support interactions on the properties of nanostructured materials. Herein, I will discuss recent advances in the development of such models.

In particular, density functional (DFT) simulations of ~1.5 nm large Pt particles on $CeO_2(111)$ and Pd particles on MgO(100) and $ZrO_2(111)$ will be presented. Electron transfer across Pt interface with reducible ceria support is found to significantly affect the reactivity of Pt clusters [1], which may have implications for fuel cell technologies. In turn, the effect of irreducible MgO and ZrO_2 supports on CO oxidation on Pd nanoparticles is more subtle, but it extends over entire µm-large aggregates [2].

For realistic modelling of nanoalloys, a new method to determine chemical ordering in alloy nanocrystallites based on DFT results was developed [3]. This method yields realistic models of ~2 nm bimetallic particles with essentially the accuracy of the employed DFT method. Moreover, the obtained results can be extrapolated to the nanoparticles of ~6 nm with more than 3000 atoms, which can be directly compared to the experimentally observed particles. The robustness and the power of this method were demonstrated for mixed (CuPd, PtSn, NiCo), core-shell (AuPd, AgPd, PtCo), intermetallic (Pd-Zn) and phase-separated (Cu-Ni) alloy particles.

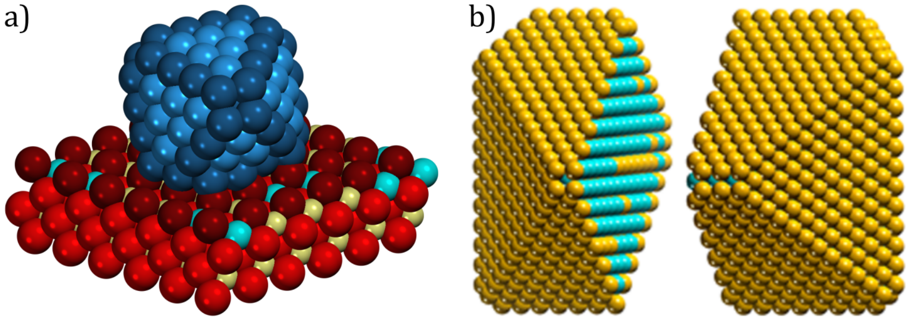

Figure 1. a) electron transfer from Pt_{122} to $CeO_2(111)$ reduces some Ce^{4+} (ivory) to Ce^{3+} (cyan), b) the lowest energy configuration of ~5 nm fcc $Pd_{1382}Au_{1382}$ particle.

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Understand the role of solvent effects in the thermal and electrochemical hydrogenation of Organic Compounds

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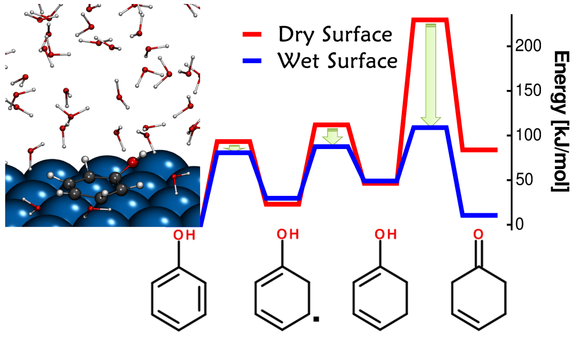
organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydro/lypo helicity of the support. In this talk. we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab into molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in the double layer as well as its orientation with respect to the electrode surface. While both examples included have been drawn from the upgrading of bio-oil *ex* pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.



Ab initio molecular dynamics simulations show critical differences between catalytic pathways in the vapor and liquid phase.

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Chemical Bonding and Entropy Effects under Confinement: Ethanol Adsorption, Dehydration and Oligomerization in Zeolites.

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Zeolites are extremely promising materials for selective conversions of biomass-derived alcohols into fuels and value-added chemicals. With their well-defined Brønsted acid sites (BAS), they constitute ideal substrates for rigorous studies where the acid strength, solvation environment and confinement have subtle but drastic effects on the free energetics, mechanisms and reaction rates. Molecular simulations are inherently equipped with the ability to follow and changes occurring at the atomic scale. Confinement and solvent effects are the primary sources of entropic drivers and represent major computational challenges for their description. We will discuss computational protocols that allow us to estimate free energetics from molecular dynamics trajectories, using as examples ethanol adsorption, dehydration and oligomerization in zeolitic materials [1]. Our studies are able to quantitatively distinguish the chemistry occurring at external or internal BAS sites that in spite of having similar reaction enthalpies, they present significantly different reaction entropies and overall mechanisms due to confinement.

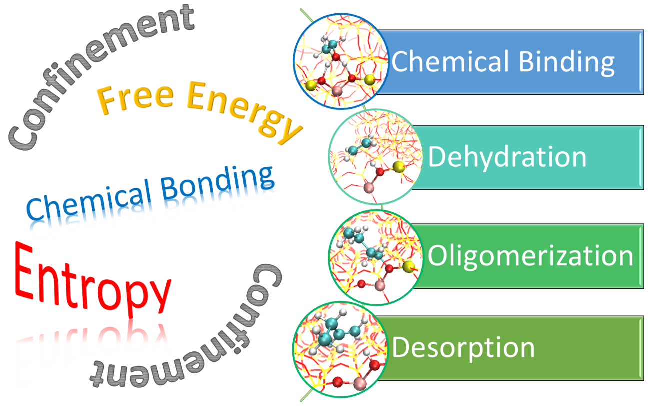

Figure 1. Atomistic simulations shed light on reactivity under confinement.

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Examining Bonding Assumptions in Transition-Metal C-H and H-H Bond Activation Reactions and Metal-Heteroatom Bond Energies

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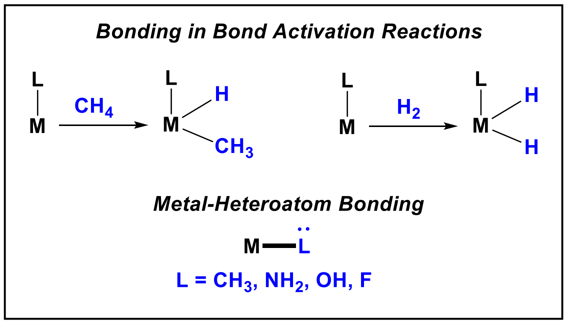
I will discuss our computational studies that have explored the following chemical bonding assumptions: #1) In transition metal oxidative addition C-H bond activation reactions the metal center becomes more electron deficient.[1] #2) Forward-bonding and back-bonding orbital interactions determine the ground and transition state structures in H_2 activation reactions by transition metals.[2] #3) Repulsive d_π-p_π interactions determine bond strengths for transition-metal-heteroatom bonds (alkoxo, amido, and fluoro).[3] #4) Hydrogen and alkyl halide bond strengths are determined by orbital overlap.[4]



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Designing Earth-Abundant Boron-based Materials for Hydrogen Production

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The electrolysis of water is considered as a clean mean for large scale hydrogen gas production. [1] However, this large-scale production is still hindered by the high cost and scarcity of noble metal catalysts such as Pt. Recently, non-noble metal materials have emerged as highly active electrocatalysts for the hydrogen evolution reaction (HER) to produce hydrogen. Our recent research found that MoB_2 exhibits high activity and chemical stability. [2] In addition, density functional theory (DFT) calculations show that several surfaces of MoB_2 are active and the optimum evolution of H_2 occurs on the graphene-like B-terminated {001} surface. It was recently also found that FeB2 is highly active for overall water splitting in basic solution. [3] However, TiB_2 is not as active as MoB2 and FeB_2 for HER reaction. To examine the distinct activities of metal diboride as HER catalysts and how the metals could affect the graphene-like boron layer, DFT was applied to investigate the H-surface adsorption process on MB_2 (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W). Our results indicate that the H-surface binding energy decreases as the electronegativity of the metal increases. Therefore, the electron transfer between metal and boron is one of the key parameters to control the HER activity of MB_2. In addition, VB_2 behaves similarly to MoB_2, thus it is predicted to be a highly active HER catalyst candidate. We have also probed the activity of MgB_2 and AlB_2, both are found to be poor HER catalyst. Hence, the type of chemical bonding (covalent, ionic, metallic) in these compounds also plays an essential role on their catalytic activity. Using a recently developed synthesis, [4] we were able to synthesize most of the above-mentioned diborides at the nanoscale. Our experimental HER results show that the activity can be significantly improved if compared to the bulk. [5]

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[5] unpublished results.

Sum Over Histories Representation for Chemical Kinetics

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A new representation for chemical kinetics is introduced which is based on the idea of a sum over histories employing chemical pathways defined at a molecular level.[1-3] The time evolution of a chemically reactive system is described by enumerating the most important pathways followed by a chemical moeity. This approach is inspired by the path integral representation of quantum mechanics introduced by Feynman. An explicit formula for the pathway probabilities is derived and takes the form of an integral over a time-ordered product. When evaluating long pathways, the time-ordered product has a simple Monte Carlo representation that is computationally efficient. Graph theoretical methods can be used to generate select important paths that contribute to the chemistry. The method was applied to a realistic propane combustion problem and is shown to yield accurate results. The Sum Over Histories Representation proved useful for interpreting the results of sensitivity analysis for combustion and surface catalytic reaction mechanisms. The standard differential equation approach to mass action kinetics can be replaced by the Sum over Histories Representation if the pathway probabilities are computed using a self-consistent iteration.

The work described resulted from collaborations with Shirong Bai, Dingyu Zhou, and Michael J. Davis. The research is supported by the National Science Foundation.

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From Chemical Curiosities to Versatile Reagents: Heavy Analogues of the Cyanate Ion

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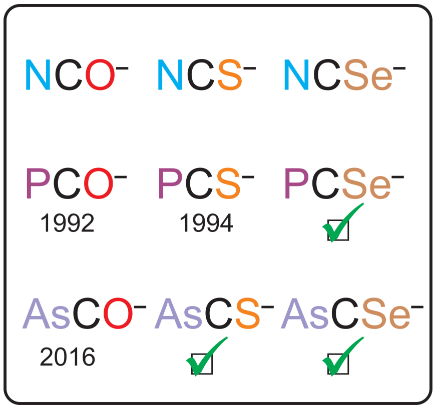
The 2-phosphaethynolate anion (PCO^-; the phosphorus-containing analogue of cyanate) was first isolated by Becker and co-workers as a lithium salt in 1992.[1] Due to difficulties associated with its manipulation, the chemistry of this remarkable species laid dormant for decades. The report of a high yielding, multi-gram synthesis of $[Na(dioxane)_x][PCO]$ in 2014 rekindled the interest in this fundamental ion.[2] Since then, the reactivity of PCO^- and its use in decarbonylative and deoxygenative processes has been extensively explored.[3]

Following Becker’s original report on the isolation of PCO^-, heavier analogues have also become synthetically accessible ($PnCCh^-$ where Pn = P, As; Ch = O, S, Se).[4, 5] These ions are rare insomuch as they contain highly reactive pnictogen–carbon multiple bonds, yet can be manipulated with ease due to their negative charges, which preclude common decomposition pathways (e.g. oligomerization), associated with neutral valence-isoelectronic species. This talk will survey recent studies on this family of anions paying particular attention to their structure and bonding and their use in the synthesis of novel molecular compounds, clusters and materials.



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Structures and Bonding in Multimetallic Cluster Anions

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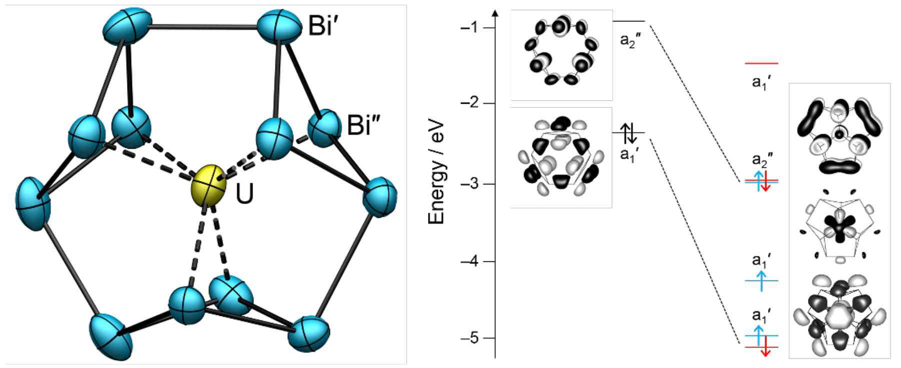
Multinary, non-oxidic metalates as well as metalides have been actively investigated by many research groups over the past decades regarding basic properties as well as their potential use as innovative materials.[1-3] Recently, binary main group element aggregates proved to be useful synthetic tools for the access of multinary transition metal-main group (semi-)metal clusters.[4-9] Reactions of chalcogenidotetrelate ions $[E^{14}{}_{x}E^{16}{}_{y}]^{q-}$ (E^{14} = Ge, Sn, Pb; E^{16} = S, Se, Te) or the inversely polarized pnictogentrielide/tetrelide ions $[E^{13}/{}^{14}{}_{x}E^{15}{}_{y}]^{q-}$ ($E^{13/14}$ = Ga, In, Tl; Ge, Sn, Pb; E^{15} = As, Sb, Bi) with transition metal (M) compounds lead to the formation of unprecedented cluster anions like $[Rh_3(CN)_2(PPh_3)_4(\mu_3\text{-}Se)_2(\mu\text{-}PbSe)]^{3-}$, $\{[CuSn_5Sb_3]^{2-}\}_2$, or $[U@Bi_{12}]^{3-}$ (see figure) with unusual geometric and electronic structures.[10-12]



Molecular structure and frontier orbital scheme of the intermetalloid cluster $[U@Bi_{12}]^{3-}$.

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Delocalized Bonding in Inorganic Compounds

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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 simultaneously in localized bonding and delocalized bonding. In this presentation I will discuss applications of these methods to inorganic compounds. We begin with the analysis of chemical bonding in the Na_8BaPb_6, Na_8BaSn_6, and Na_8EuSn_6 Zintl Phases. Todorov and Sevov proposed that these compounds contain Pb_5^{6-} or Sn_5^{6-} **π**-aromatic building blocks, which are valence isoelectronic to the organic cyclopentadienyl anion. Our SSAdNDP analyses reviled that such multiply charged anions indeed contain 6 π-electrons delocalized over five atoms of the five-membered rings. Sun's family of all-metal antiaromatic complexes, $[Ln(\mathbf{h}^4\text{-}Sb_4)_3]^{3-}$ (Ln=La, Y, Ho, Er, Lu), have been identified by the AdNDP as the first examples of antiaromtic species, where the Ln^{3+} ions facially coordinated by three cyclo-Sb_4 units containing 4 delocalized π-electrons. We then discuss the presence of **σ**-aromaticity in Fisher's clusters $[Zn_3]^+$ and $[Zn_2Cu]$. The AdNDP method shows that these triatomic building blocks indeed possess delocalized 3c-2e bonds, making them **σ**-aromatic. Sun's complex $[Au_2Sb_{16}]^{4-}$ containing two quasi-planar $AuSb_4$ moieties are examples of **σ**-aromatic species with 6 **σ**-electrons due to the interaction of the Au atom with four neighboring Sb atoms in a delocalized manner. Thus, the $[Au_2Sb_{16}]^{4-}$ anion is the first solid-state all-metal **σ**-aromatic cluster featuring six delocalized **σ**-electrons. Other examples of delocalized bonding will be also discussed, including 3c-2e bonds in supertetrahedral aluminum − a new allotropic ultralight crystalline form of aluminum, 4c-2e bonds in the $MoZn_{10}$ building block, 8c-2e bonds in sodium vacancies in the high-pressure Na_2He compound, 6c-2e and 5c-2e bonds in oxygen vacancies in the bulk and on the surface of MgO crystal. We believe that both AdNDP and SSAdNDP methods present powerful tools for deciphering chemical bonding in new inorganic compounds.

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Density-corrected density functional theory

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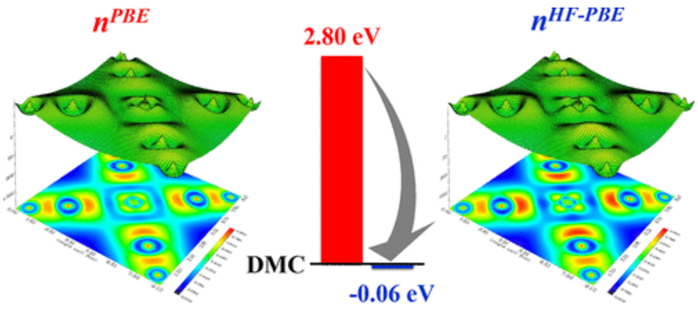
I will review the concepts of density-corrected DFT and the successes of HF-DFT, i.e., DFT energy on HF density, in dealing with many examples of delocalization errors including anions, barrier heights, and stretched bonds.[1,2] I will focus on our latest triumph, spin energy differences in small Fe(II) octahedral complexes.[3] I may also address the deficiencies of the recent analysis of densities within DFT.[4]



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Predissociation Measurements of Bond Dissociation Energies

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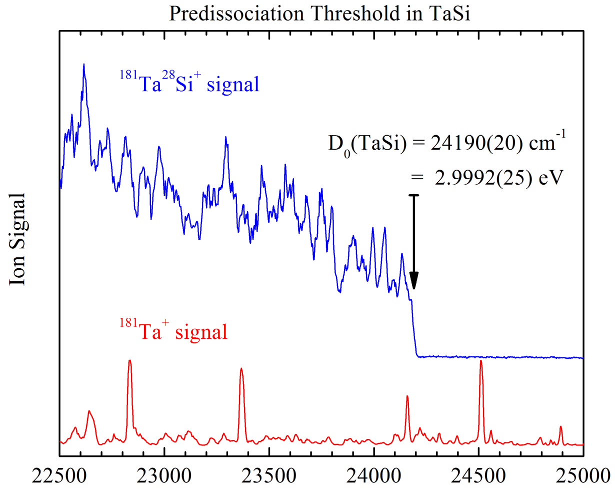
Diatomic transition metal molecules formed from open *d*-subshell metals typically have a high density of electronic states that becomes so high near the ground separated atom limit that electronic spectra appear to be continuous. We have previously shown that when two open d-subshell metal atoms are present, a sharp predissociation threshold is found that may be identified as the bond dissociation energy (BDE).[1-3] In the past 3 years, we have extended this technique to the investigation of transition metals bonded to main group elements, including diatomic metal carbides, nitrides, silicides, sulfides, selenides, and one chloride. Sharp predissociation thresholds are nearly always found, allowing high-precision measurements of BDEs. To date, we have used this method to measure the BDEs of 48 MX species (26 published thus far),[4-8] thereby providing important data for the calibration of quantum chemical methods and for the development of a qualitative understanding of chemical bonding in these species.



Bond dissociation energy measurement for diatomic TaSi. The abrupt drop in resonant two-photon ionization signal at 24,190 ± 20 cm^{-1} shows that the molecule falls apart at this energy. This determines the bond energy as D_0(TaSi) = 2.9992(25) eV. Ta atomic spectra were simultaneously recorded for calibration purposes.

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Structure and Bonding in Metal Ion-Acetylene Complexes via Infrared Spectroscopy and Photofragment Imaging

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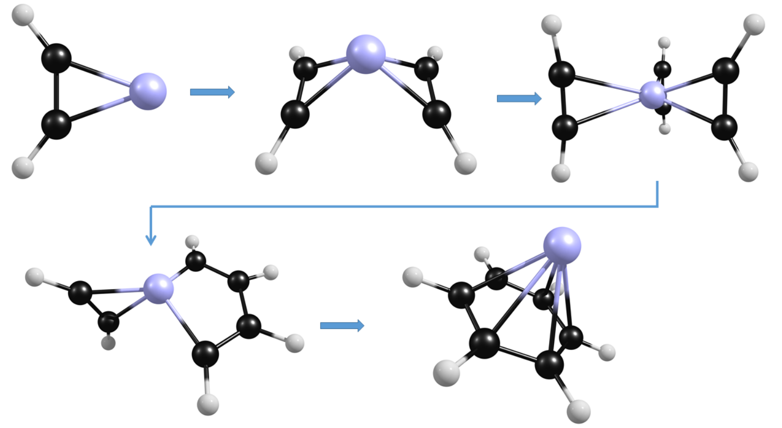
Transition metal ion-acetylene complexes are produced by laser vaporization in a supersonic expansion. Complexes with a specific number of acetylene ligands are mass-selected and studied with infrared laser photodissociation spectroscopy and the method of rare gas atom tagging in the C–H stretching region. Spectra patterns compared to those predicted by computational chemistry (DFT/B3LYP) make it possible to identify structural motifs and coordination numbers for complexes containing different transition metals. Cation-π bonding is common for many transition metals (e.g., copper, gold, cobalt) with coordination numbers of two, three or four ligands. Vanadium cation complexes form three- and five-membered metallacycles, and with additional acetylene, mediate the cyclo-trimerization to form benzene. Zinc complexes bind preferentially to a single carbon of acetylene, forming M-C-C moieties. Additional experiments using UV-laser induced photodissociation detect metal-to-ligand charge transfer processes. Acetylene cation elimination proceeds with substantial kinetic energy release, which is measured with photofragment velocity-map imaging. Analysis of such images probes the metal-ligand bonding energetics.



Intermediates detected in the cyclo-trimerization of acetylene to benzene mediated by vanadium cations.

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Hydrogen in Nanometal

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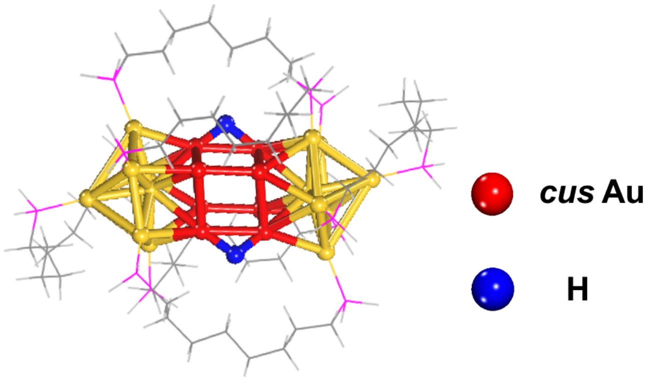
Hydrogen in metals underpins many key technologies in energy storage and conversion such as hydrogen storage and metal-hydride batteries, but little is known about hydrogen in many nanosystems such as gold nanoclusters. In this talk, I will discuss our recent computational efforts to elucidate the role of hydrogen in metal nanoclusters and the relevant catalytic impact. Especially, we focus on the energetics of H-metal interaction and how it changes the electronic structure of the nanosystems. In addition, the catalytic impact of such interaction will be demonstrated by some examples as well, including hydrogen evolution reaction and CO_2 reduction.



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Borametallomimetics – Activation of Small Molecules by Low-valent Boron Species

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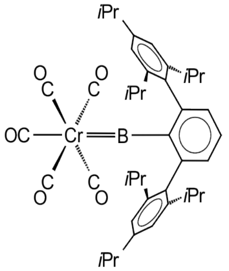
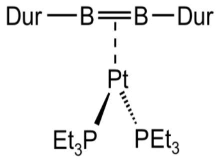
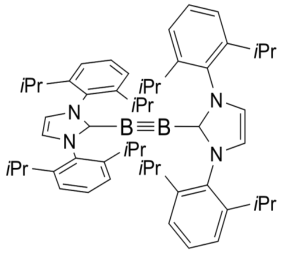
The activation of small molecules is generally associated with transition metals (TM) and constitutes the basis of catalysis. It was believed that TM catalysts are required to facilitate processes such as the activation of H_2 and other unreactive substrates. However, recent years have witnessed exciting developments in main group element chemistry, and the discovery of carbenes, FLPs and heavy main group species that are capable of TM-like activation reactions.[1]
Our ongoing studies on borylenes, diborenes, and diborynes have shown that these low-valent species exhibit a very rich chemistry, which is distinctly different from that of common compounds deriving from boron in oxidation state +3. Particularly interesting is the metal-like behavior of some borylenes and diborynes, which form CO complexes analogous to TMs, bind H_2 and unsaturated organic substrates under mild conditions and even activate N_2.[2]



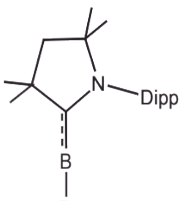
metal-bound borylene



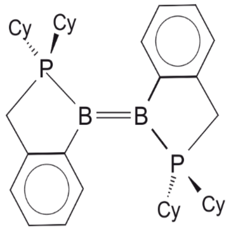
metal-bound diborene



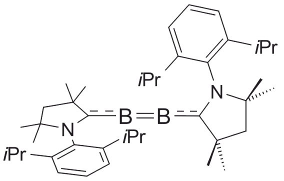
stabilized diboryne



transient borylene



phosphine-stabilized diborene



CAAC-stabilized cumulene

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NHC-Boryl Radicals: new Synthetically useful Boron-Based Reactive Intermediates

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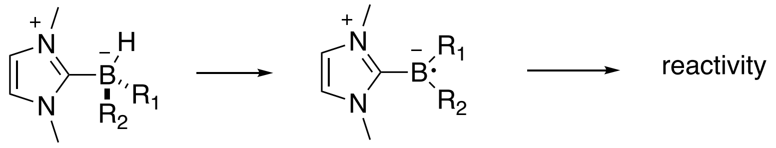
We are interested in exploring how the interaction between organic Lewis bases and inorganic small molecules activates bonds, in particular B–H ones. In this talk we will discuss how the complexation of boranes with N-Heterocyclic carbenes stabilizes radicals at boron, making them planar π-type radicals and how this can be applied to radical reactions and photopolymerizations. The talk will focus first on the formation and characterization of transient NHC-boryl radicals and the factors governing their reactivity[1] and then move to the application of NHC-boranes as initiators for photopolymerization using UV[2] then visible[3] photons, and from bulk polymerizations to emulsion processes,[4] detailing how the reactivity is affected by the photopolymerization conditions.

NHC-Boryl radicals: new reactive intermediates



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Zero-, one-, and two-dimensional boron-carbon frameworks in solid-state rare earth boride carbides

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Though boron and carbon, neighbors on the periodic table, have some conspicuous electronic differences, they behave rather similarly when combined together in a more or less equal content with rare earth metals, leading to the formation of ternary boride carbide (generally called *borocarbide*) compounds $R_xB_yC_z$ (R = rare earth element - R refers not only to lanthanide elements but also to Sc, Y, and actinide elements). Borocarbide chemistry has blossomed over the last fifty years or so, offering today a broad diversity of original topologies and physical properties, most of them unique, especially due to the size of rare earth atoms and the peculiar bonding within the nonmetal atom frameworks [1-4]. Indeed, boron and carbon have a particular affinity with rare earth elements. The latter supply electrons to stabilize zero-, one- or two-dimensional (Figure 1) boron-carbon frameworks whereas its *d* or *f*-electron shell affords attractive properties like electric conduction or magnetism for instance. A survey of these rare earth borocarbides discussing their structural arrangements and bonding properties, and, where relevant, their comparison with all-boron or all-carbon compounds will be presented.

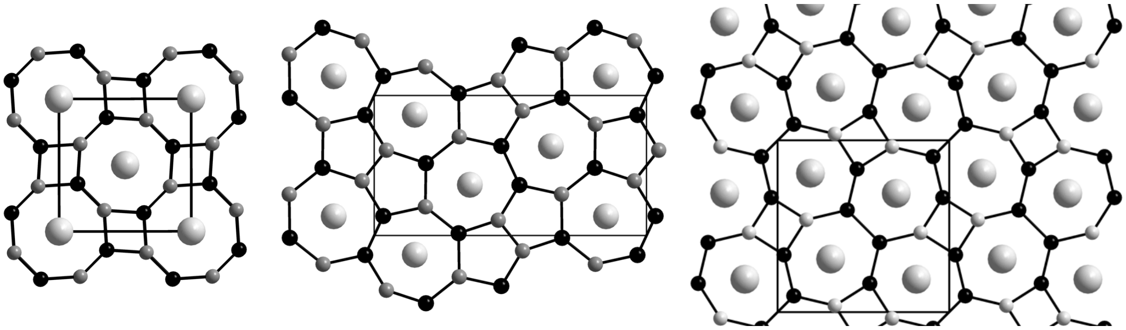

Figure 1. Some examples of 2D boron-carbon networks encountered in $R_xB_yC_z$ compounds (large grey, small black and small grey spheres represent R, B and C atoms, respectively).

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Covalency, Ionicity, Promiscuity, and Bizarre Properties of Late Element Borides

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Late borides can be exceptionally hard, nearly competing diamond in hardness, and as such ignite interest of materials design. They also present a number of mysteries, e.g. they can be topological and Kondo insulators, have anomalous spectra, magnetic phase transitions, and mixed valency of unclear origin. By dividing these borides onto chemically meaningful small cluster motifs, then constructing and even simpler phenomenological model of the solid representing the essential physics, we reconstruct the bonding picture for the solid such that the anomalous behavior is fully explained. Importantly, small cluster models not only give information in the language of chemistry, but also permit treating the solid at levels of theory at extremes of static and dynamic electron correlation, unattainable for solid state. We consider bonding both at equilibrium, and as evolving away from equilibrium, in way characteristic of what the material undergoes in conditions of its function. Thus, the view on bonding is dynamic rather than static.

Of a particular interest is SmB_6, whose magnetic phase transitions, mixed valency, anomalous behavior of entropy as a function of temperature, symmetry forbidden spectral features, all can be explained by Sm and B having access to first covalent and then ionic bonding within the phonon motion in the solid.

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Origin of Covalency in Late Actinides

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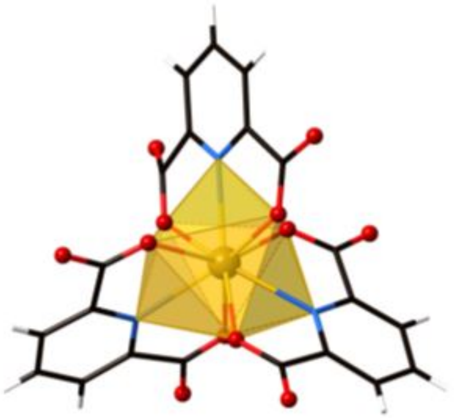
Actinides beyond plutonium have long been predicted to have metal-ligand interactions that are more ionic than found earlier in the series. These predictions are born out in the large volume expansion of the unit cell from plutonium to americium and the concomitant localization of 5*f* electrons at americium. Moreover, the 5*f* orbitals undergo a contraction similar to that of the lanthanides. When taken together, one would predict that actinides beyond curium would possess bonding where covalency can be entirely neglected. The opposite has proven to be true however. Instead of diminished involvement of frontier orbitals in bonding in the post-curium elements, berkelium and californium, it appears to be enhanced. The evidence for this lies in overly contracted An-L bonds, reduced magnetic moments, vibronically-coupled charge-transfer photoluminescence, and other spectroscopic features that all tell the same tale of increasing covalency in the late actinides. Very recent results from Dirac-Fock calculations will be presented that describe the possible origin of these effects.



View of a berkelium coordination complex exhibiting aspects of increased covalency where it is unexpected.

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Covalency of Actinides (An^{III}, An^{IV})) with Chelating Agents Across the Actinide Series (An = Th to Es)

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Actinide-ligand bonding has a long history of investigation due to its importance to the nuclear fuel cycle, environmental remediation, nuclear medicine, and other concerns. Early actinides (up to plutonium) generally mimic some aspects of transition metal chemistry, including the formation of covalent An-ligand bonds through the 6d orbitals. Whereas the early actinides have seen extensive study, studies on the actinides heavier than plutonium are sparse. As the actinide series is traversed, the contraction of the 5f orbitals stabilizes the trivalent oxidation state, potentially limiting covalent interactions and enforcing lanthanide-like behavior. It is generally thought, therefore, that the heavier actinides do not form significant covalent interactions, though some evidence suggests this is not the case.

Our team recently investigated interactions across the actinide series as function of chelating agents using three model systems: the biological decorporation ligand 3,4,3-LI(1,2-HOPO), a classic metal chelator diethylene-triaminepentaacetate (DTPA), and a strongly donating hydroxylamine ligand, N-tert-butyl N(pyridine-2-yl)-hydroxylamine (pyNO$^-$). Our investigation of changes in covalent interactions across the actinide series in both An(III) and An(IV) ions (An = Th to Es) offer new insights into the complexation of the late actinides in comparison to early actinides and guiding principles for the design of new chelating ligands.

Despite the contraction of the 5f orbitals across the actinide series, actinide-ligand interactions rely more upon the 5f and less upon the 6d orbitals as the series is traversed from thorium (Th) to einsteinium (Es). Fig 2 shows increased electron donation into the actinide 5f orbitals by the 3,4,3-LI(1,2-HOPO) ligand. In complexes with formal An(IV) ions (right panel of Fig 2), 5f orbitals actually accept more electron density than the 6d orbitals for Cm, Cf, and Es compared to early actinides, including plutonium. Whereas counter to the common consensus on bonding in the later actinides described above, these finding are consistent with further electronic structure calculations, EXAFS and thermodynamic measurements on the DTPA system. We further extended the study to the strong-donating hydroxylamine ligand pyNO$^-$ and a similar phenomenon was observed. The covalent interactions of the early actinides, with electron density primarily donated into the 6d orbitals, change across the series. An(IV) ions are shown to form stronger bonds with the ligands than An(III) ions, correlating with the increased participation of the 5f orbitals.

The results clearly indicate the importance of the 5f orbitals in covalent actinide-ligand interactions across the actinide series. The changing nature of these covalent interactions as the series is traversed provides new insights into the complexation of the actinides and will offer guiding principles for the design of new chelating ligands for this part of the periodic table.

Nature Plays Dice with Boron: Inevitability of Uncertainties

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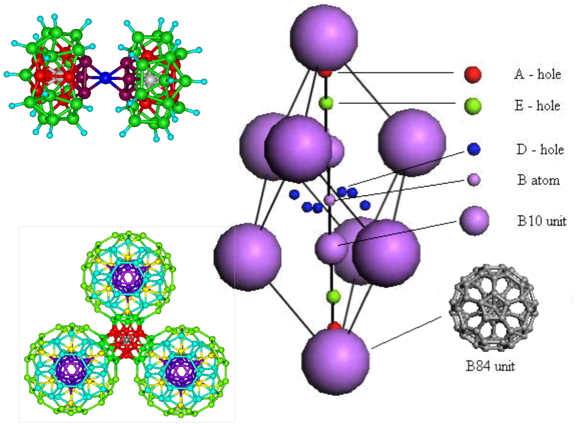
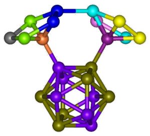
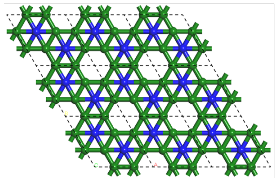
Chemists have nearly mastered bonding in diborane, polyhedral boranes, condensed polyhedral boranes, boron clusters and the like which are shown to be electron sufficient for their structures. The certainty with which the structures of graphene and diamond can be ascertained experimentally and computationally, makes us feel that this should be possible for elemental boron allotropes as well. However, nature continues to play dice with boron: structures of its 3D allotropes, boron-rich metal borides, and doped structures are not known with the certainty we desire.[1] These are not necessarily due to the limitations of the measurement, but inherent in the nature of the electronic structure which results in "one" set of position of atoms in one experiment/(part of the crystal) and "another" set of position in another experiment/(part of the crystal).[2-5] Have we reached the limit of understanding? The uncertainty appears for 2D allotropes of boron in a different way.[6,7]

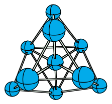
Beta-Rhombohedral Boron,
Thermodynamically most stable allotrope





Borophene, 2D allotrope





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Nucleophilic Behaviors of the B−H Bond in Borane Complexes

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Boron and boron containing compounds are well-known their electrophilic property but much less known are their nucleophilic properties. However, the slightly lower electronegativity of boron (2.0 in the Pauling scale) compared to that of hydrogen (2.1) makes a hydrogen atom bonding to boron slightly negative so it was called hydride ($B^{\delta+}$−$H^{\delta-}$). Thus, the partially negatively-charged hydrogen atoms in boron hydrides possess Lewis base properties. It is the Lewis base property of the B−H bond that enables R″BH_3 (R″ = H^-, NH_2^-, THF, and NH_3) to be a nucleophilic reagent in nucleophilic substitution reactions. In this type of reactions, the role of the bonding pair electrons in the B−H bond is similar to that of the lone pair electrons in classical nucleophiles. In a few known examples of nucleophilic substitution reactions involving the B−H bond as a nucleophilic reagent, the hydride on the B−H bond usually attacks another boron atom to form an unsupported B−H−B 3c-2e bond. The newly formed unsupported B−H−B bond by the B−H bond nucleophilic substitution is unstable which can cause further reactions. With this important property of the B−H bond, new boron chemistry has been developed recently.[1]

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TBA

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Structure, structural evolution and Superconductivity of high pressure hydrogen-rich alloys

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Pressure has an enormous effect in altering the structure, physical and chemical properties of matters. In general, for elemental metals, compression led to loosely bound valence electrons redistributed into the interstitial vacancies and often resulted in novel open 2-D and 3D structures. Incidentally, when mixed with H_2, which has an electronegativity similar to group 13 and 14 elements, charge transfer Zintl-Klemen type compounds can be formed. This phenomenon helps to explain the structural trend in hydrogen-rich alloys predicted by First Principle methods. Under suitable conditions, these alloys may even become superconductors and, in some cases, with very high critical temperature (T_c). Analysis of the functional derivative of Eliashberg spectral functions show that efficient electron-phonon coupling over the entire vibrational spectrum can be achieved on crystal structures when the stretch and bend vibrations of weakly linked hydrogen network atoms are strongly mixed. The development of unprecedently high superconductivity critical temperature recently observed in highly compressed H_2S molecular solid was traced using metadynamics calculations. A novel incommensurate structure composed of molecular H_3S^+ and meandering $(SH)^-$ chains is suggested to be the superconducting phase.

Carborane Cages in 2D Self-Assemblies

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Carborane cages with their rigid molecular structures and rich isomeric forms (see the Fig.) enable to investigate particular physical properties of their 2-D assemblies while keeping the surface pattern either identical or very similar. The respective self-organized monolayers have many advantages such as low total numbers and fewer types of surface defects compared to other systems, partly as a consequence of their low conformational freedom. In our laboratories we have been using these molecules and their isomeric forms to unveil some most fundamental self-assembly principles and intermolecular interactions which lead to a certain supramolecular structure and function. This talk will introduce the unique molecular system and will focus on the relations between the inherent properties of individual molecular isomers and the respective self-assembled monolayers.

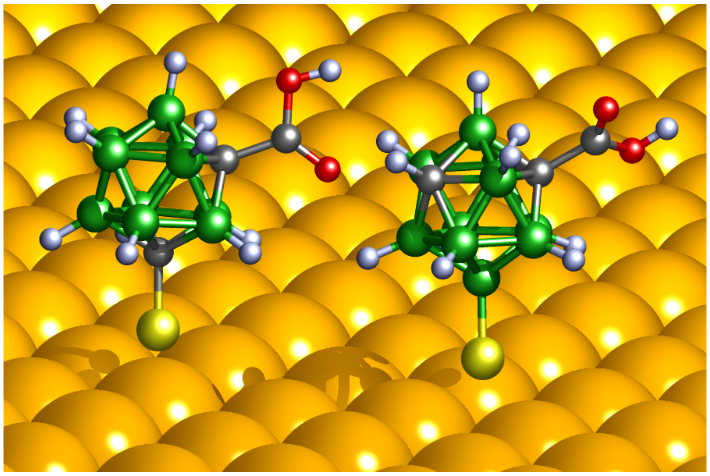

Fig. Find the Differences!

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Charged Defects in Two-dimensional Materials from Many Body Perturbation Theory

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Recently, defects in 2D materials such as ultrathin h-BN have been found to be promising single-photon emitters with polarized and ultrabright single-photon emission at room temperature. This opens up possibilities for emerging applications in nanophotonics and quantum information, with potentially much better scalability than the long-studied nitrogen vacancy (NV^-) in diamond. Despite of promising properties experimentally demonstrated so far, first-principles prediction of accurate defect properties in 2D materials remains challenging, mainly because of the highly anisotropic dielectric screening in 2D materials and strong many body interactions including electron-hole, electron-phonon and defect-exciton interactions, which could not be treated by standard density functional theory (DFT) codes.

The talk will discuss how we solved the numerical convergence issues for charged defect properties in 2D materials at both the DFT and MBPT levels, and how we will tackle the complex many body interactions for the excited state properties of defective 2D materials and heterojunctions.[1] In particular, we resolved the long-standing issues of dealing with charged defects in 2D materials from first-principles, which necessitates proper treatment of electrostatic potentials of charges near a 2D plane and of the screened Coulomb interaction in the MBPT.[2] With our methods, we will design promising quantum defects that have deep defect levels, high spin states, bright optical excitations between defect states, long excited state lifetime and high photoluminescence efficiency.

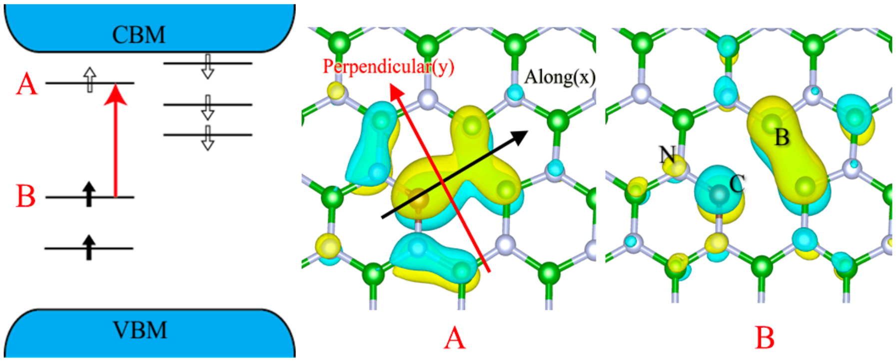

Figure 1. Defect in hexagonal boron nitride (h-BN) with promise for quantum emitter applications: nitrogen vacancy adjacent to boron substituted by carbon 'C_BV_N'. The left panel shows this defect has three deep defect levels, a triplet ground state (black thick filled arrows are occupied state), and a bright optical excitation between two defect states A and B. The right panel shows the wavefunctions of defect states A and B. Only the "perpendicular" direction has allowed optical transition (red arrow) as shown in the left and right panels. Reproduced from Ref. [1]

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Reactions between noble metal clusters

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Research in the recent past has shown that ligand protected atomically precise clusters of noble metals are indeed molecules. This is shown most elegantly by atom and structure conserving chemical reactions between such nanoparticles. Several clusters, which are archetypal nanoparticles, $Ag_{25}(SR)_{18}$ and $Au_{25}(SR)_{18}$ (-SR = alkyl/aryl thiolate) have been used for such reactions. Despite their geometric robustness and electronic stability, reactions between them in solution at room temperature produce alloys $Ag_{m}Au_{n}(SR)_{18}$ (m+n = 25), keeping their $M_{25}(SR)_{18}$ composition, structure and topology intact. We captured one of the earliest events of the process, namely the formation of the dianionic adduct, $[Ag_{25}Au_{25}(SR)_{36}]^{2-}$, by electrospray ionization mass spectrometry. Molecular docking simulations and density functional theory (DFT) calculations also suggest that metal atom exchanges could occur through the formation of adducts. Such isomorphous transformations between nanoparticles imply that microscopic pieces of matter can be transformed completely to chemically different entities, preserving their structures, at least in the nanometric regime. Intercluster interactions can also produce cluster dimers and unusual, well-defined alloys. They reflect the shell structure of certain reactants. Atom exchanges suggest interesting dynamics in solution, early results of these investigations will be presented. New experiments in this subject area confirm the fascinating chemical diversity possible in such systems.

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Many Electron High Spin States: Structures and Stability of Transition Metal Clusters: Non Haber-Bosch Iron?

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Iron is generally accepted as an efficient catalyst for reductive nitrogen activation, and it is efficiently applied in ammonia synthesis. While the optimized protocol (by Mittasch et al.) invokes promotors such as potassium, naked Iron is an active catalyst in itself. We are investigating the surface morphology and adsorbate bonding properties of naked transition metal clusters under cryo conditions, and we have conducted a series of spectroscopic and kinetic studies of the nitrogen adsorption onto size selected Cobalt and Nickel clusters [1-4], as well as a case study of Nitrogen N_2 and Hydrogen H_2 co-adsorption onto a selected Ruthenium cluster [5]. In the course of these studies we chose to investigate Iron clusters and Iron-Rhodium nanoalloys as well. We found some Iron clusters reluctant to attach neither Nitrogen N_2 nor Hydrogen H_2. Careful consistency checks confirm these findings. Hypothetical interpretations are up for evaluation. This presentation puts the current level of understanding to the stage and presents all unpublished work.

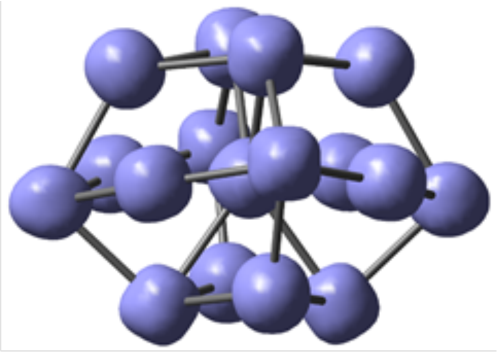

Figure 1: "Exploratory" DFT calculations (PBE0/cc-pVDZ) of Fe_{17}^+ suggest a geometry with an almost smooth cluster surface and an electronic 51tet high spin state.

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Solvents Can Alter the Identity of Solute Chemical Bonds

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In this work, we combine several recent theoretical advances to better understand the nature of chemical bonds in condensed phases. We take advantage of new methods for developing coordinate-dependent pseudopotentials,[3] new ways of solving the Schrodinger equation at the CISD level with a 10^8 plane-wave basis set in a time fast enough to allow for molecular dynamics,[4] and a new method for performing umbrella sampling with quantum objects[5] to explore the behavior of the Na_2 molecule in different environments. In liquid Ar, we find that the bond shortens and its frequency blue-shifts as a result of compression of the bonding electrons by collisions with the nearby solvent atoms. These collisions also induce a large instantaneous dipole since the bonding electrons are pushed off-center, giving rise to an IR absorption.[6] When Na_2 is placed in liquid THF, in contrast, the average vibrational frequency is strongly red-shifted and the molecule has a much larger average dipole moment and more intense IR spectrum than in liquid Ar.[7] The reason for this is chelation: the ether solvent chelates both ends of the molecule, pushing the electron density off of the bond axis. The dative bonds formed between the THF oxygen atoms and the Na^+ cores are about the same strength as an H-bond in water. As a result, the PMF for chelation of the dimer along a chelation coordination number order parameter shows that each chelated state occupies a local free energy minimum, with barriers of 6 to 8 k_BT separating the different chelation states. As a result, each chelation state represents a distinct molecule with its own vibrational frequency, IR and electronic absorption spectrum. Thus, the mere presence of local specific interactions with solvent that are on the same order as an H-bond turns what had been a single Na_2 molecule into multiple different molecular species with different properties in equilibrium. Clearly, solvents not only modulate chemical properties, but also play a direct role in solute chemical identity.

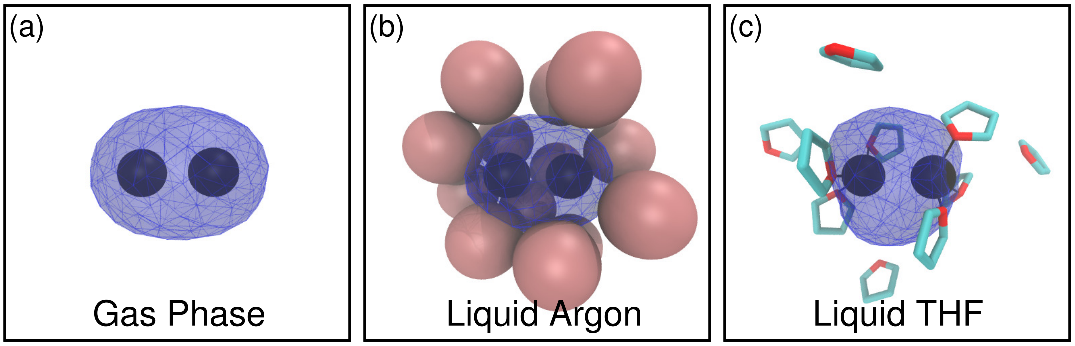

Figure 1: Representative snapshots of the Na_2 molecule in different environments. The Na^+ cores are shown as black spheres, and the blue mesh contour shows the bonding valence electron density calculated with CISD. The gas-phase result (a) matches CCSD(T) calculations. In liquid Ar, (b), the bond is shortened and its frequency is raised due to Pauli repulsion forces from the solvent. In liquid THF, (c), dative bonding interactions between the solvent and Na^+ cores lengthen the bond and lower the frequency, changing the identity of the molecule.

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The chemical bond as a manifestation of quantum mechanical interference.

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The nature of the chemical bond is perhaps the central subject in theoretical chemistry. Our understanding of the behavior of molecules developed amazingly in the last century, mostly with the rise of quantum mechanics (QM) and with QM-based theories such as valence bond and molecular orbital. Such theories are very successful in describing molecular properties, but they are not able to explain the origin of the chemical bond. This problem was first addressed by Ruedenberg [1], who showed that covalent bonds result from quantum interference between one-electron states. The generality of this result and its quantification for a large variety of molecules was made possible through the recent development of the Generalized Product Function Energy Partitioning method (GPF-EP) [2], which allows the partition of the electronic density and energy in their interference and quasi-classical (non-interference) contributions for each bond of a molecule, separately. This Interference Energy Analysis (IEA) has been applied to a large variety of molecules with single, double and triple bonds, with different degrees of polarity, linear or branched, cyclic or not, conjugated and aromatics, to verify the role played by quantum interference. In all cases, the conclusion was **exactly the same**: for each bond of the molecules considered the main contribution to its stability comes from the interference term. One-electron two-center (2c1e) bonds are the simplest kind of chemical bonds. Yet they are often viewed as odd or unconventional cases of bonding. ***But, are they any different from the conventional (2c2e) bonds***? If so, what differences can we expect on the nature of (2c1e) relative to electron-pair bonds? More recently the GPF-EP method was extended [3] to describe bonds involving N electrons in M orbitals (N<M), and applied to several (2c1e) bonds and the results compared with the respective analogous molecules exhibiting the "conventional" two-electron bond. For all cases the GPF results show that interference is the dominant effect for the one-electron bonds and, therefore, (2c1e) bonds should not be considered as special, since they also result from quantum interference. These results together with the ones already obtained for (2c,2e) bonds normally classified as pure covalent, polar or ionic, clearly indicate that there is no conceptual difference among them and that quantum interference provides a way for the unification of the chemical bond concept (CNPq, FAPERJ, CAPES).

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Chemical Bonding and Dynamics in Tetra-atomic Anions and Transient Neutrals

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Tetra-atomic anions are frequently more strongly bound than the corresponding neutral species as a result of charge-resonance and covalent interactions. A number of these systems have been studied over the last 25 years using photoelectron-photofragment coincidence (PPC) spectroscopy. PPC spectroscopy provides a kinematically complete measure of the reaction dynamics of simple systems by measuring the momenta of ejected electrons in coincidence with either stable neutrals or the momenta of neutral photofragments. Examples of the insights gained into the O_4^-/O_4 and $N_2O_2^-/N_2O_2$ systems will be reviewed, as well as the reassignment of the $C_2O_2^-$ photoelectron spectrum and the reported discovery of the lowest-lying triplet state of C_2O_2.[1,2] Using the multiplexed measurement capability of PPC spectroscopy, direct dissociative photodetachment, ionic photodissociation pathways and ionic photodissociation followed by autodetachment can all be identified, as well as the identification of stable and long-lived neutral products. Electronic structure calculations in these systems remain challenging, and there have been no theoretical studies for the dissociation dynamics on the neutral states, so this remains an area ripe for further exploration. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-FG03-98ER14879 and the US-Israel Bi-National Science Foundation under award number BSF-2014071.

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Ion-peptide interactions between alkali metal ions and AcYNHMe (termini-protected GYG); Modeling the GYG selectivity filter in K^+ channels

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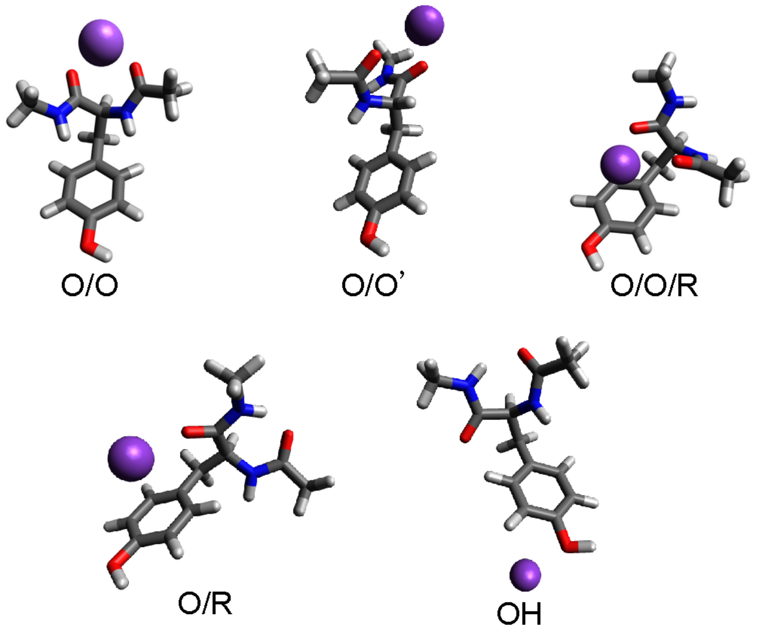
The structures of sodium and potassium ions complexed to AcYHNMe, a termini-protected peptide sequence to model the GYG portion of the selectivity filter of a K^+ channel, have been determined from infrared laser spectroscopy and supporting ab initio calculations. AcYNHMe contains two carbonyl groups, representative of the S_1 and S_2 binding sites of the selectivity filter. Using a cryogenic ion trap, H_2-tagged clusters of mass-selected Na^+AcYHNMe and K^+AcYHNMe are photodissociated, monitoring loss of H_2 molecules. Three conformations have been identified for both ions by laser IR-IR double resonance methods. Two conformations have the ion bound to the two C=O groups. The third conformation has, in addition, a cation-pi interaction with the aromatic ring of tyrosine, i.e. tridentate binding. The relative contributions of the three conformers are approximately the same for K^+AcYHNMe, while the tridentate conformer is preferred for Na^+AcYHNMe. These differences will be discussed in context of ion mobility and selectivity.



Stable structures of M+AcYNHMe complexes. The O/O, O/O', and O/O/R conformers, the three lowest in energy, have been observed.

Photodissociation dynamics of H_2, $H_2 \rightarrow H(1s)+H(2s,2p)$

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The H_2 molecule, the simplest and the most abundant species in the universe, serves as a benchmark to study the electronic structure and dynamics of molecular systems. The first dissociation limit of H_2, however, correlates to the triplet states that is dipole transition forbidden. The threshold for the second dissociation limit, $H(2s/2p)+H(1s)$, is about 14.3 eV, which is so high that not so much experimental studies have been performed. Recently, using XUV laser generated by four wave mixing, velocity map images to measure the angular distribution of the photofragments, and delay-time-curves to measure the H(2*s*)/H(2*p*) branching ratios, we have studied the direct dissociation and predissociation of H_2, D_2 and HD. Some of the interesting results are:

(1) For predissociations, the angular distributions of fragments are strongly dependent on the excitation photon energies, which are due to interference between the two perturbed states.

(2) For direct dissociations, the branching ratios D(2*s*)/(D(2*s)*+D(2*p*) oscillate with the wave vectors of the fragments, which can be explained by the interference of two vibrational continua of the electronic states.

(3) For the HD predissociations, it is found that the g/u symmetry is broken in the state distribution of the fragments H(2*s*,2*p*) and D(2*s*,2*p*), however, the angular distributions of the fragments and absorption line profiles by detecting the state-resolved fragments are *u*-symmetry conserved.

(4) If the angular-resolved fragment are detected, the Fano-profiles describing by coupling between the perturbed states are dependent on recoil angles of the fragments.

Visualizing the evolution of coherent vibrational wavepacket

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The energy flow induced by the coherent nuclear wavepacket motion, which is created by coherent excitation of the neighboring vibrational eigenstates, is manifested as quantum beat-modulated decays. The beats arise from quantum interferences among the superposition eigenstates.

The nuclear motion of the coherent vibrational wavepacket in photoexcited 2,4-difluorophenol and its resulting energy flow are visualized by time-resolved ion yield (TR-IY) spectroscopy combined with photoelectron imaging. The wave packets around the planar geometry are ionized exclusively by careful selection of probe wavelengths combined with the geometry change upon photoionization, exhibiting the pronounced quantum beats superimposed on the parent ion transients. The time dependences of the photoelectron peaks originated from the planar geometry exhibit the clear beats with similar periodicities but a phase shift of π rad with those from the nonplanar geometry, providing an unambiguous picture of the oscillating nuclear motion between the planar geometry and the nonplanar minimum.

The butterfy vibration in electronically excited *o*-fuorophenol has been visualized in real time by femtosecond time-resolved ion yield spectroscopy coupled with time-resolved photoelectron imaging technique. As the C–F bond vibrates with respect to the aromatic ring, the nuclear geometry varies periodically, leading to the corresponding variation in the photoionization channel. By virtue of the more favorable ionization probability from the nonplanar minimum via resonance with the Rydberg states, the evolution of the vibrational wave packet is manifested as a superimposed beat in the parent-ion transient. Moreover, time-resolved photoelectron spectra offer a direct mapping of the oscillating butterfly vibration between the planar geometry and nonplanar minimum.

The vibrational energy flow between 6a1□□□6b2 Fermi resonances in the S1 state of pyrimidine has been directly tracked by the femtosecond time-resolved photoelectron imaging. A coherent superposition of two Fermi resonance components of 6a1 and 6b2 is prepared by the femtosecond pump pulse, resulting in a localized vibrational wave packet. The temporal evolution of the coherent wave packet is directly visualized by the quantum beat superimposed on the parent ion transient. The photoelectron spectra originated from the 6a1 and 6b2 vibrational states exhibit a clear quantum beat with the similar periodicity but a phase shift of π rad, offering a physical picture of vibrational energy flow between a Fermi resonance pair.

Interactions of Electrons With Molecules: Probing Excited Anion States.

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The wavelength dependence of photoelectron spectra and photoelectron angular distributions are illustrated using detachment from CH_2CN^- and CuF_2^- as specific examples. Allowed direct transitions to the continuum reveal details of parent anion orbital structure (through the angular distributions) and anion/neutral vibronic levels (through the transition energies). In the presence of an intermediate metastable excited anion state, auto-detachment (electronic or vibrational) leads to the appearance of forbidden transitions in the photoelectron spectra. These transitions allow access to a greater range of internal energy states of the neutral species. The metastable anion states themselves are akin to electron scattering resonances and hence represent strong interactions of unbound electrons with molecules, doorway states for electron capture and reduction chemistry. The intensities of the indirect detachment transitions are highly dependent on the excitation energy and the action spectra probe the internal levels of the resonances, reveal details of vibrational and vibronic coupling and provide important tests of theoretical methods designed to treat such situations.

Electronic Transmutation (ET): recent theoretical and experimental developments and applications of ET.

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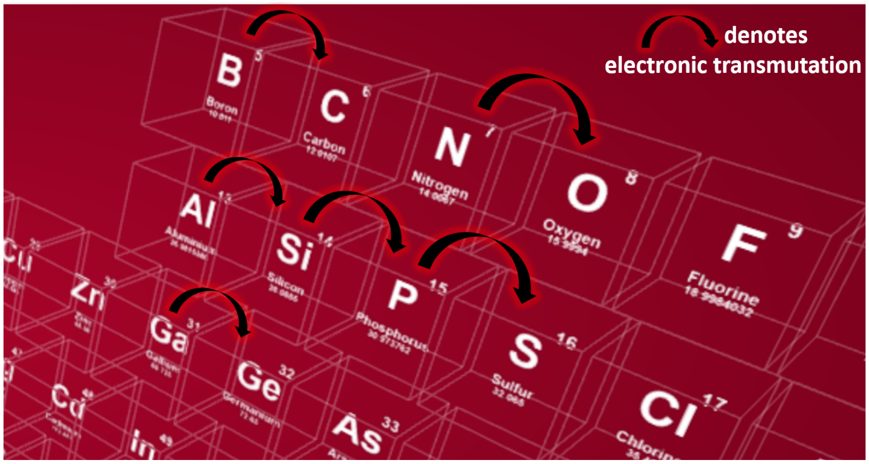
According to the concept of electronic transmutation (ET), elements, by acquiring an extra electron, begin to have the chemical bonding and geometric structure properties of compounds composed of neighboring elements. In 2011 we demonstrated that boron, by acquiring an extra electron in boron-hydrogen compounds, forms molecular analogs of those of saturated hydrocarbons.[1] This talk will summarize the recent developments and applications of ET on both the theoretical and experimental fronts. Examples of ET of Group 13 elements into Group 14 elements, Group 14 into Group 15 elements, and Group 15 into Group 16 elements will be discussed. The concept of double electronic transmutation (DET), which depicts the process that by acquiring two extra electrons, an element with the atomic number Z begins to form chemical bonds and geometric structures of compounds composed of Z+2 elements, will also be discussed.[2] We believe that the ET concept may have a significant effect on predicting new chemical compounds and the rationalization of experimental observations arising from electronically transmutated elements.



ET: elements, by acquiring an extra electron, begin to have the chemical bonding and geometric structure properties of compounds composed of neighboring elements.

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Metal-ammonia complexes disclose a secret periodic table of solvated electron precursors

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Metal-ammonia complexes, $[M(NH_3)_4]^{0,\pm}$, are shown theoretically to have a $M(NH_3)_4{}^{x+}$ positively charged core with one, two, or three outer electrons orbiting in its periphery. Our results reveal a new class of molecular entities (solvated electron precursors) which host several electronic shells resembling atoms. The observed electronic shell model (1s, 1p, 1d, 2s, 1f, 2p, 2d) differs from that of the hydrogen-like model and resembles the jellium or nuclear shell model. Selected orbitals are shown in Figure 1. This fact is attributed to the different effective electrostatic potential experienced by the outer electrons [1]. Multi-reference and propagator approaches combined with diffuse basis sets are employed to calculate accurate geometries, ionization energies, electron affinities and vertical excitation energies.

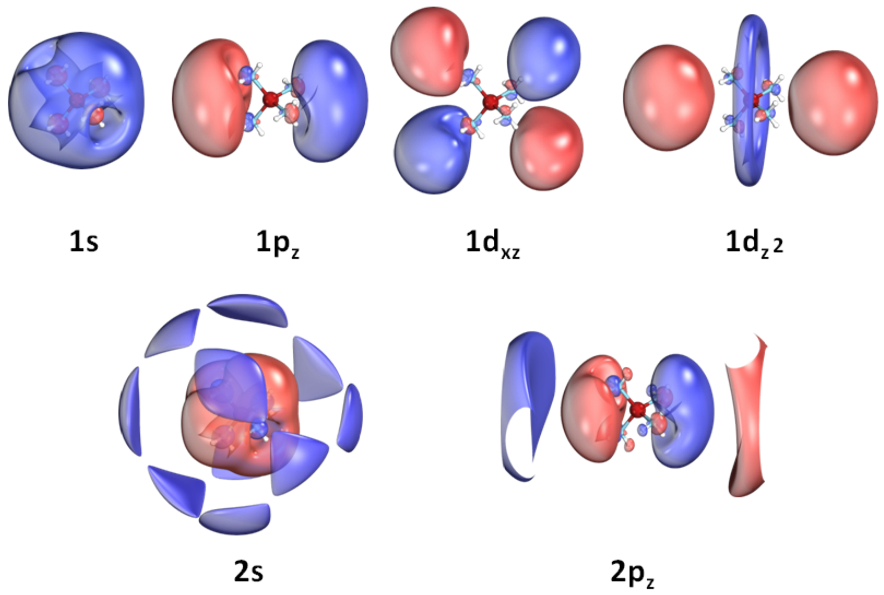

Figure 1. Selected super-atomic orbitals of $Li(NH_3)_4$.

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Recent Progress in the Investigation of Size-Selected Boron Clusters: From Borophenes to Metallo-Borophenes

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Photoelectron spectroscopy in combination with computational studies has shown that small boron clusters possess planar structures, in contrast to that of bulk boron, which is dominated by three-dimensional polyhedral building blocks. The propensity for planarity has been found to be a result of both s and p electron delocalization over the molecular plane, giving rise to concepts of s and p multiple 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 vacancies are stable. We found that the B_{36} cluster

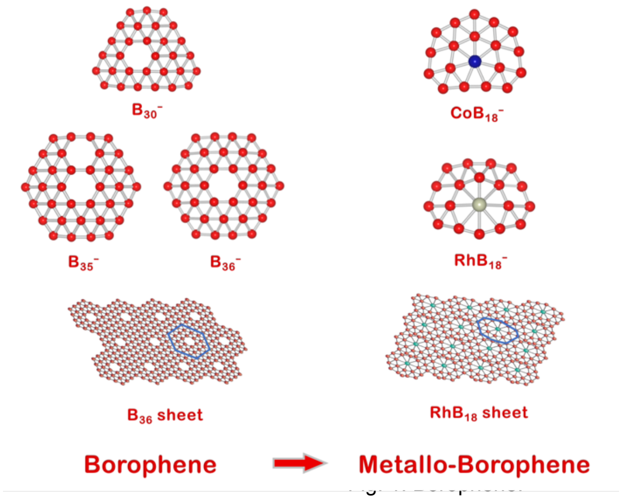

Fig. 1. From borospherenes to metallo-borophenes.

has a highly stable quasi-planar structure with a central hexagonal vacancy, providing the first experimental evidence that single-atom boron-sheets with hexagonal vacancies, or borophenes, are viable [1]. Borophenes have since been synthesized on Ag(111) surfaces, forming a new class of 2D materials [2]. Recent studies of metal-doped boron clusters have shown that transition metals can be doped into the plane of boron clusters [3,4], suggesting the possibility of metallo-borophenes (Fig. 1) [5]. Finally, I will also discuss recent progresses in the investigation on the structures and bonding of lanthanide-doped boron clusters [6].

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