# International Conference on Chemical Bonding

**August 11-16, 2022**
**Lihue, Hawaii**

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# International Conference on Chemical Bonding

## Technical Program

### Thursday, August 11

*Arrival and registration*

### Friday, August 12

**Morning: Opening. Bonding appetizer plate.** *Presiding: Alexander Boldyrev*

| | |
|---|---|
| 8:30 – 8:40 am | Alex, Anastassia, Lai-Sheng - Introductory remarks |
| 8:40 – 9:15 am | Sergei Tretiak (Los Alamos National Laboratory, USA)<br>*"Chemical bonds on the surface and quantum photon emission from carbon nanotubes"* |
| 9:15 – 9:50 am | Benjamin Schwartz (UCLA, USA)<br>*"When does photodissociation become photoisomerization? When solvents become part of solute chemical identity"* |
| 9:50 – 10:25 am | Lai-Sheng Wang (Brown University, USA)<br>*"Nanoclusters of Boron and Metal Boride: From Aromaticity to Metal-Boron Multiple Bonding"* |
| *10:25 – 10:40 am* | *Coffee Break* |
| 10:40 – 11:15 am | Brenda Rubenstein (Brown University, USA)<br>*"Resolving Bonding and Magnetism in 2D Materials via Quantum Monte Carlo"* |
| 11:15 – 11:50 am | Peter Gill (University of Sydney, Australia)<br>*"A Different Lens on Bonding via Highly Localized MOs"* |
| 11:50 – 12:25 pm | Mark Eberhart (Colorado School of Mines, USA)<br>*"At the Bond's Edge"* |

**Afternoon: Materials and Nanostructures** *Presiding: Alex Ivanov*

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|---|---|
| 3:00 – 3:35 pm | Denis Usvyat (Humboldt University of Berlin, Germany)<br>*"Embedded-fragment quantum chemical treatment of periodic systems"* |
| 3:35 – 4:10 pm | Addis Fuhr (Oak Ridge National Laboratory, USA)<br>*"Bridging Theory with Experiment — Digital Twin & Deep Learning Enabled Image Segmentation of Defects in Monolayer $MX_2$ Phases"* |
| 4:10 – 4:45 pm | Sarah Tolbert (UCLA, USA)<br>*"Controlling the Properties of Bulk and Nanostructured Superhard Metal Borides"* |
| *4:45 – 5:00 pm* | *Coffee Break* |
| 5:00 – 5:35 pm | Oleg Prezhdo (University of Southern California, USA)<br>*"Chemical bonding steers excited state dynamics in nanoscale systems"* |
| 5:35 – 6:10 pm | Yang Ping (Los Alamos National Laboratory, USA)<br>*"Structure, Stability, and Chemistry of Actinide Nanocrystals – Insights from Quantum Simulations"* |
| *07:00 – 10:00 pm* | ***RECEPTION*** |

## Saturday, August 13

**Morning: Materials, Interfaces, Functionality** *Presiding: Maksim Kulichenko*

| | |
|---|---|
| 8:30 – 9:05 am | Elisa Jimenez-Izal (DIPC, Basque Country, Spain)<br>*"Understanding novel catalysts through chemical bonding analysis"* |
| 9:05 – 9:40 am | Philippe Sautet (UCLA, USA)<br>*"Molecule – metal surface interaction: is DFT accurate enough?"* |
| 9:40 – 10:15 am | Cristina Diaz (Universidad Complutense de Madrid, Spain)<br>*"Bond formation on and in graphene-based materials"* |
| *10:15 – 10:30 am* | *Coffee Break* |
| 10:30 – 11:05 am | Anastassia Alexandrova (UCLA, USA)<br>*"Chemical bonding at electrified interfaces"* |
| 11:05 – 11:40 am | J. Nathan Hohman (University of Connecticut, USA)<br>*"Engineering Topology in Metal-organic Chalcogenolates by Systematic Ligand Selection"* |
| 11:40 – 12:15 pm | Kenneth Jordan (University of Pittsburgh, USA)<br>*"Non-valence Correlation-bound Anions of Polycyclic Aromatic Hydrocarbons and the Approach to the Image Potential States of Graphene"* |

**12:20 pm CONFERENCE PHOTO**

**Afternoon: Molecular Reactivity** *Presiding: Ivan Popov*

| | |
|---|---|
| 3:00 – 3:35 pm | Chong Liu (UCLA, USA)<br>*"Electrochemical ambient activation of light alkanes"* |
| 3:35 – 4:10 pm | Michal Straka (Czech Academy of Sciences, Czech Republic)<br>*"Fullerene cage as a nanolab for exotic chemical bonds"* |
| 4:10 – 4:45 pm | Theodore Betley (Harvard University, USA)<br>*"Stretching bonding to its limits: stabilizing radical ligands"* |
| *4:45 – 5:00 pm* | *Coffee Break* |
| 5:00 – 5:35 pm | Olexandr Isayev (Carnegie Mellon University, USA)<br>*"Learning chemical reactivity with neural networks"* |
| 5:35 – 6:10 pm | Benjamin Nebgen (Los Alamos National Laboratory, USA)<br>*"Intuitive Machine Learning for Chemical Properties"* |

## Sunday, August 14

*TOUR DAY*

## Monday, August 15

### **Morning**: Bonding for Quantum Technology

*Presiding: Nikita Fedik*

| | |
|---|---|
| 8:30 – 9:05 am | Wesley Campbell (UCLA, USA)<br>*" Properties and performance of molecules for quantum information applications"* |
| 9:05 – 9:40 am | Vladimiro Mujica (Arizona State University, USA; DIPC, Spain)<br>*"Generalized Spin-dependent Dispersion Intermolecular Forces"* |
| 9:40 – 10:15 am | Michael Heaven (Emory University, USA)<br>*"Spectroscopy for molecules that might be laser-cooled"* |
| *10:15 – 10:30 am* | *Coffee Break* |
| 10:30 – 11:05 am | Lan Cheng (Johns Hopkins University, USA)<br>*"Approaching Heavy-Element Spectroscopy Using the Spinor Representation"* |
| 11:05 – 11:40 am | Xiaosong Li (University of Washington, USA)<br>*"Study Covalency in Rare-Earth and Heavy-Element Complexes with Relativistic Electronic Structure Methods"* |
| 11:40 – 12:15 pm | Michael Morse (University of Utah, USA)<br>*"Bond Dissociation Energies and Electronic Structure of d- and f-Block Molecules"* |
| 12:15 – 12:50 pm | Chérif Matta (Mount Saint Vincent University, Canada)<br>*"Non-Nuclear Maxima and the Universality of Bright Wilson's Justification of the First Hohenberg-Kohn Theorem"* |

### **Afternoon**: Small and Fundamental

*Presiding: Alina Sergeeva*

| | |
|---|---|
| 3:00 – 3:35 pm | Brett VanVeller (Iowa State University, USA)<br>*"Surfing the excited-state energy landscape to understand reactivity and improve fluorescent probe design"* |
| 3:35 – 4:10 pm | Alvaro Muñoz-Castro (Universidad Autónoma de Chile)<br>*"Unifying Planar and Spherical Aromatics. Shielding Cone as Common Characteristic Across Periodic Table Clusters"* |
| 4:10 – 4:45 pm | Martin Rahm (Chalmers University of Technology, Sweden)<br>*"A Different Take on Atomic Charge, Energy and Electronegativity"* |
| *4:45 – 5:00 pm* | *Coffee Break* |
| 5:00 – 5:35 pm | Christopher Johnson (Stony Brook University, USA)<br>*"Precision Probes and Rationalization of Gold Nanocluster Electronic Structure"* |
| 5:35 – 6:10 pm | Ivan Černušák (Comenius University in Bratislava, Slovakia)<br>*"Cyclo[N]carbon rings and catenanes from different perspective. Disentangling molecular thread"* |

## Tuesday, August 16

### **Morning**: Boldyrev's Jubilee Session *Presiding: Anastassia Alexandrova*

| | |
|---|---|
| 8:30 – 9:05 am | Ivan Popov (The University of Akron, USA)<br>*"Multi-nodal "in-plane" interactions in actinide compounds"* |
| 9:05 – 9:40 am | Pavel Rublev (Utah State University, USA)<br>*"Revealing of $NdCl_3$ speciation in aqueous solutions by QM/MM molecular dynamics simulations"* |
| 9:40 – 10:15 am | Nikolay Tkachenko (Utah State University, USA)<br>*"Simulating Electronic Structure on Quantum Computers with PermVQE and QDavidson algorithms"* |
| *10:15 – 10:30 am* | *Coffee Break* |
| 10:30 – 11:05 am | Alina Sergeeva (Columbia University, USA)<br>*"Free energy perturbation calculations of mutation effects on SARS-CoV-2 RBD::ACE2 binding affinity"* |
| 11:05 – 11:40 am | Nikita Fedik (Los Alamos National Laboratory, USA)<br>*"From Organics to Organometallics: Transfer Learning Interatomic Potentials"* |
| 11:40 – 12:15 pm | Maksim Kulichenko (Los Alamos National Laboratory, USA)<br>*"Accelerating Data Generation for Machine Learning Potentials by Biasing Towards Regions of Uncertainty"* |
| 12:15 – 12:50 pm | Boris Averkiev (Kansas State University, USA)<br>*"Crystal structures of new materials containing structure-directing halogen and chalcogen bonds"* |

### **Afternoon**: Boldyrev's Jubilee Session *Presiding: Lai-Sheng Wang*

| | |
|---|---|
| 3:00 – 3:35 pm | Alex Ivanov (Oak Ridge National Laboratory, USA)<br>*"What do we mean by the structure of high-temperature liquids?"* |
| 3:35 – 4:10 pm | Dmitry Zubarev (IBM Almaden Research Center, USA)<br>*"Neuro-symbolic reinforcement learning for polymer discovery"* |
| 4:10 – 4:45 pm | Alexander Boldyrev (Utah State University, USA)<br>*"Spherical Aromaticity"* |

### Adjourn

**5:00 pm Bus departing to Luau**

## Wednesday, August 17

Informal discussions and collaborations

# Abstracts

## Friday, August 12

## Morning:

**Chemical bonds on the surface and quantum photon emission from carbon nanotubes**

Sergei Tretiak
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An intentional introduction of quantum defects to the carbon nanotube surface leads to unique photoluminescence properties that may be useful for a wide range of optoelectronic, sensing, imaging and quantum communication applications. Quantum-chemical modeling have shown how chemical surface adducts locally alter the pi-conjugated network of the nanotube surface that leads to a spatial confinement of the electronically excited wavefunctions. Engineering of chemical bonds and interfacial surface structures of single-chirality nanotube materials with dopant-induced defects then allowed us for accurate control over energy transfer and luminescence properties. These results suggest that covalent doping chemistry is a powerful route toward harnessing dynamics of excitons and charges in carbon nanotubes leading to new enhanced optical behaviors.

A. Saha, B. J. Gifford, X. He, G. Ao, M. Zheng, H. Kataura, H. Htoon, S. Kilina, S. Tretiak, S. K. Doorn *"Chemical Selection of Emission State Configuration in a Quantum Light Emitter"* Nature Chem, **10**, 1089 – 1095 (2018).
B. J. Gifford, S. Kilina, A. Saha, X. He, Y. Kim, H. Htoon, S. K. Doorn, and S. Tretiak, *"Controlling Defect-State Emission in Covalently Functionalized Single-Walled Carbon Nanotubes"* Acc. Chem. Res., **53**, 1791 – 1801 (2020).
Y. Zheng, B. M. Weight, A. C. Jones, V. Chandrasekaran, B. J. Gifford, S. Tretiak, S. K. Doorn, H. Htoon *"Photoluminescence Dynamics Defined by Exciton Trapping Potential of Coupled Defect-States in DNA-Functionalized Carbon Nanotubes"* ACS Nano, **15**, 923 – 933 (2021).
Y. Zheng, Y. Han, B. M. Weight, Z. Lin, B. J. Gifford, M. Zheng, D. Kilin, S. Kilina, S. K. Doorn, H. Htoon and S. Tretiak, *"Photochemical Spin-State Control of Binding Configuration for Tailoring Organic Color Center Emission in Carbon Nanotubes,"* Nature Comm. (2022, in press).

**When does photodissociation become photoisomerization? When solvents become part of solute chemical identity**

Benjamin Schwartz
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For simple solution-phase chemical reactions, such as the photodissociation of a diatomic molecule, is it appropriate to assume that the potentials energy surfaces of the molecule are the same in solution as in the gas phase? If not, what modifications need to be made because of the solute-solvent interactions? In this talk, we explore what happens where there are relatively modest local specific interactions between a solute and solvent, with strengths on the order of that of an H-bond. By performing quantum simulations of the $Na_2$ and $Na_2^+$ molecules in a variety of liquids, we find that the solvent not only controls the bond dynamics of the solute, but that the solvent actually becomes part of the chemical identity of the solute. For different coordination states of the solute by the solvent, there are entirely different bond lengths, vibrational spectra and electronic structure. We show that once in the solvent, photoexcitation of $Na_2^+$ actually leads to a photoisomerization reaction rather than photodissociation, as in the gas phase. We also show the chemical identity of the solute can change during the reaction, exemplifying the complexity of chemical reactivity in solution. See, e.g., *Nature Chem*. **10**, 910 (2018); *J. Phys. Chem. Lett.* **11**, 9230 (2020)

**Nanoclusters of Boron and Metal Boride: From Aromaticity to Metal-Boron Multiple Bonding**

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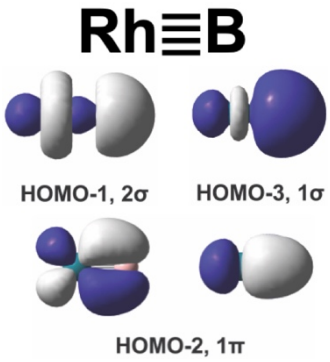
Combined photoelectron spectroscopy and computational chemistry studies have shown that small boron clusters possess planar structures,[1-3] in contrast to that of bulk boron, which is dominated by three-dimensional polyhedral building blocks. The propensity for planarity has been found to be a result of both σ and π electron delocalization over the molecular plane. It was found that the $B_{36}$ cluster possesses a highly stable planar structure with a central hexagonal vacancy, providing the experimental evidence that single-atom boron-sheets with hexagonal vacancies, a.k.a. borophenes,[4] are viable. Borophenes have since been synthesized and characterized on inert substrates and are becoming a new class of synthetic 2D materials.[5,6] Recently the $B_{48}$ cluster is shown to have a bilayer structure,[7] suggesting the feasibility of bilayer borophenes, which have been indeed synthesized.[8,9] Aromaticity has been found in planar transition metal doped boron clusters.[10] A recent study has revealed that the pentagonal $ReB_4^-$ cluster with four p electrons exhibits Möbius aromaticity.[11] Finally, I will also discuss our recent discovery of a metal-boron quadruple bond (left).[12]

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11. Cheung, L. F.; Kocheril, G. S.; Czekner, J.; Wang, L. S. *J. Am. Chem. Soc*. **2020**, *142*, 3356-3360.
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**Resolving Bonding and Magnetism in 2D Materials via Quantum Monte Carlo**

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In recent years, 2D materials have garnered a wealth of interest because of their unique low-dimensional physics, exotic magnetism, and the relative ease with which their properties can be tuned via doping, crinkling, strain, and stacking. Nonetheless, 2D materials can be challenging to characterize because of their limited thickness and the impact of substrates on their properties. In this talk, I will describe how quantum Monte Carlo methods can be used to resolve the detailed structure, bonding, and magnetism within 2D materials and thus serve as useful complements to spectroscopies. In particular, I will focus on how a combination of quantum Monte Carlo methods and a novel surrogate Hessian line search optimization technique were used to uncover the geometries and magnetism of two of the first discovered monolayer ferromagnets, $CrI_3$ and $NiPS_3$, with an unprecedented level of accuracy. I will then end with a discussion of the prospects for these methods for studying the emergent properties of multilayer heterostructures and topology.

**A Different Lens on Bonding via Highly Localized MOs**

P.M.W. Gill[1,*], T.C. You Lee [1] and A.T.B. Gilbert[2]
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In most quantum chemical calculations, all of the molecular orbitals (MOs) are expanded in a large set of basis functions, typically contracted gaussians that are centred on the nuclei [1]. However, we contend that this is computationally inefficient and conceptually unhelpful, and we argue that it is preferable to expand each MO in a small set of relevant functions [2]. In order to accomplish this in the context of Hartree-Fock theory [3], one needs to abandon the traditional Roothaan-Hall energy formula [4] and avoid diagonalization in the self-consistent field procedure [5]. A disadvantage of this approach is that it usually gives a higher energy than that obtained from the full basis set. The twin advantages are: (1) the HF calculations are much faster (2) they yield localized MOs [6,7] with clear chemical interpretations.

A selection of results for various molecules and basis sets will be presented.

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**At the Bond's Edge**

Mark Eberhart
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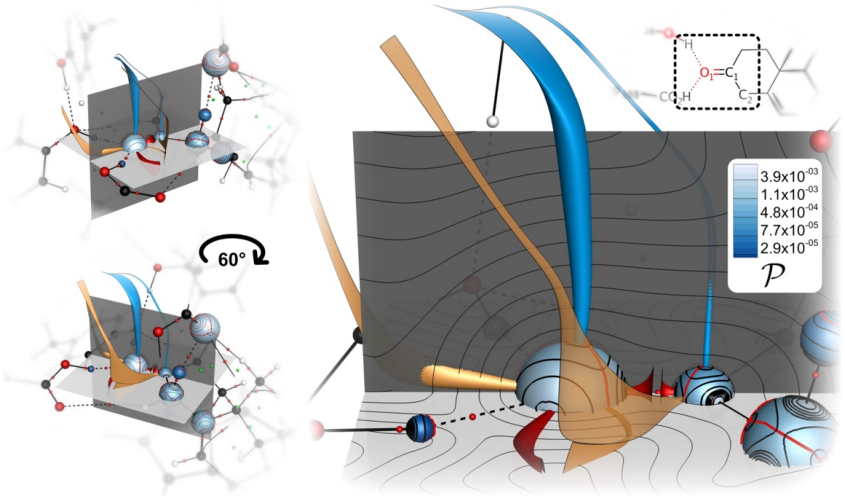
I will review developments in Gradient Bundle Analysis—an extension of the Quantum Theory of Atoms in Molecules that, among other things, provides a real space representation of chemical bonds called "bond bundles." Bond bundles are characterized by well-defined energies and occupy volumes bounded by unambiguous surfaces. Bond breaking, then, must be accompanied by the movement of bond bundle surfaces followed by the ultimate collapse of the bond bundle. Thus, the evolution of the charge density associated with a chemical reaction or other process is intimately tied to the motion of bond bundle surfaces.

Drawing from metallic, organic, and enzymatic systems, the motion of bond bundle surfaces due to chemical and physical perturbations will be explored. I will argue that the intrinsic and extrinsic geometry of the charge density is ultimately a predictor of bond bundle surface motion and therefore a predictor of chemical reactivity.



## Afternoon:

**Embedded-fragment quantum chemical treatment of periodic systems**

Denis Usvyat
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High-level quantum chemical treatment of periodic systems has become an essential tool in solid state applications. It generally allows for a systematic control of error and a higher quantitative accuracy than density functional theory. However, due to a substantial computational cost, quantum chemical models usually require special techniques and approximations to be feasible in practical applications to periodic systems. One of such approaches is the embedded-fragment method [1,2,3], where a group of localized occupied and virtual orbitals, corresponding to a periodic HF calculation, are subjected to a high-level quantum chemical treatment. This method is especially effective for point defects in solids and on surfaces. We provide an overview on the current developments and applications of the embedded-fragment approach.

[1] O. Masur, M. Schütz, L. Maschio, D. Usvyat, J. Chem. Theory Comput., 12, 5145 (2016)
[2] T. Mullan, L. Maschio, P. Saalfrank, D. Usvyat, J. Chem. Phys., 156, 074109 (2022)
[3] E. Christlmaier, D. Kats, A. Alavi, D. Usvyat, J. Chem. Phys., 156, 154107 (2022)

**Bridging Theory with Experiment — Digital Twin & Deep Learning Enabled Image Segmentation of Defects in Monolayer $MX_2$ Phases**

Addis S. Fuhr, Rama Vasudevan, Panchapakesan Ganesh, Bobby Sumpter
*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, USA*
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The physical properties of 2D monolayer $MX_2$ materials such as transition metal dichalcogenides can be significantly altered by point defects. It is therefore essential to gain a clear understanding of defect-induced changes in structure-property relationships, and eventually precise control of defect formation in order to use 2D monolayer $MX_2$ materials in applications ranging from quantum information to catalysis. Characterizing defects remains a challenge though. Recent progress in scanning transmission electron microscopy (STEM) has enabled direct atomic-level visualization of chemical bonding, and corresponding classification of defects. However, automation and image segmentation algorithms are required to gain a complete statistical description of chemical bonding (e.g. classification and quantification of all defect types in the material). This is particularly a challenge given that image resolution of defects is dependent on electron dose, and high doses can artificially create new defects or cause existing defects to migrate. Here, we use *ab initio* computational chemistry to create a digital twin STEM image database for defective 2D monolayer $MX_2$ phases, benchmark several deep learning architectures for segmentation of atomic defects, and develop methods to improve STEM resolution via generative machine learning models trained on digital twins. Our approach benefits from a large diversity of defects (~600 monolayer $MX_2$ materials with vacancies, adatoms, anti-sites, or other defects), and highly reliable ground truths. Specifically, the identity and position of each defect is known *a priori* from density functional theory (DFT) calculations, and our multislice STEM image simulations use DFT-optimized structures without considering beam-induced reactions. Hence, this enables direct comparison of different deep learning segmentation and generative modeling architectures for a large variety of defects under varied electron dose conditions without worry of mislabeling, artificially creating, or moving defects due to beam-matter interactions.

**Controlling the Properties of Bulk and Nanostructured Superhard Metal Borides**

Sarah H. Tolbert
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In this talk, we will examine a family of super-hard materials based on late transition metal borides. These materials are exciting because, unlike diamond, they can be synthesized at atmospheric pressure. The materials were initially constructed using three very simple molecular design rules: 1) use late transition metals to create high electron density so that the materials are incompressible; 2) add boron to build strong covalent bond to prevent slip and generate hard materials; 3) use solid-solution effects to further tune materials properties. While these ideas are quite simple, they have also proven to be very effective. In this talk, we will thus use a combination of materials synthesis, indentation measurements, and high-pressure diffraction to gain an understanding of how the hardness in this family of materials can be tuned based on chemical composition and bonding motifs. We will specifically take advantage of non-hydrostatic high pressure X-ray diffraction methods to directly probe both elastic lattice deformations and the onset of plastic deformation in a wide range of materials in a lattice specific manner. To gain a global understanding of the family of materials we will move from metal (M) rich MB phases, to more conventional $MB_2$ and $MB_4$ type materials, and finally to very high boron content $MB_{12}$ type materials. In all cases, the goal will be to correlate structure and bonding with hardness. Finally, we will end with some new studies on nanoscale versions of these materials, where nanoscale architecture is combined with bonding constraints to further improve hardness.

**Chemical bonding steers excited state dynamics in nanoscale systems**

Oleg V. Prezhdo
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Our group's research focuses on modeling quantum dynamics in condensed phase systems, by combining non-adiabatic molecular dynamics and real-time time-dependent density functional theory [1-5]. The talk will highlight the importance of chemical bonding in such dynamics.

Most chromophores used to sensitize $TiO_2$ to achieve photo-induced charge separation have a significant band-gap to avoid rapid charge relaxation. Surprisingly, graphene, a metal, can be used as a chromophore as well. The charge separation is faster than the recombination due to chemical bonding between $TiO_2$ and graphene [6].

Similarly, plasmonic excitations of metallic particles induce charge transfer to a $TiO_2$ substrate. In the traditional mechanism, plasmons rapidly dephase into electron-hole pairs, and then an electron is transferred. Why don't electron-hole pairs recombine in the metals? We showed that charge separated states can form immediately during plasmon excitation [7]. The prediction was confirmed experimentally a year later [8]. This mechanism relies on strong interaction between metallic particles and charge acceptor. In comparison, the traditional mechanism operates for metals on $MoS_2$, because the interaction is weak [9].

Plasmonic particles can act as efficient photo-catalysts. Is it simply because of their strong light absorption and rapid local heating, or do excited electronic states play a role? Using a machine learning force-field we demonstrated that slow, 50 ps oscillations of atoms at particle corners and edges can lead to longer-lived excited states, which can induce photo-chemical event [10].

Defects due to broken or misplaced chemical bonds deteriorate efficiency of optoelectronic devices. Gentler chemical vapor deposition produces less detrimental defects in transition metal dichalcogenides that cruder physical vapor deposition [11]. Broken bonds create strong electron-vibrational interactions that outcompete electrostatic electron-hole interactions, which otherwise play key roles driving Auger processes [12].

Chemical bonding between molecules and semiconductor quantum dots create strong electronic coupling and allows a new type of charge transfer mechanism, Auger assisted electron transfer [13]. It eliminates the Marcus inverted region and accelerates photon-induced charge separation.

Metal halide perovskites are a very different kind of semiconductor, combining features of inorganic, organic and even liquid matter. In contrast to inorganic semiconductors, bonds in perovskites depend critically on oxidation state [14,15]. Bonds can break and form on 100 ps timescales [16], and atoms can flow slowly [17], having a strong influence on excited state dynamics. Edge states in perovskites help separate photo-generated excitons into electrons and holes. Edges formed by non-metals, e.g. iodines, play a more important role than metallic edges, e.g. Pb, because they create more localized states [18].
Similarly, the type of chemical bonding, covalent vs metallic, on surfaces of semiconductor quantum dots determine their optical properties. E.g., Cd vacancies on CdS surface quench luminescence; however, S vacancies do not. This is because Cd-rich surfaces can heal defects much better than S-rich surfaces, due to more flexible metallic bonding, compared to directional covalent bonding [19,20].


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**Structure, Stability, and Chemistry of Actinide Nanocrystals – Insights from Quantum Simulations**


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Nanoscale materials bearing heavy elements have a wide range of applications from the nuclear fuel cycle to environment and health. Nanocrystals (NCs) with size and shape dependent properties are a thriving research field and remarkable progress has been made in the controlled synthesis and characterization of NCs composed of stable elements in the past three decades. In this context, interfacial chemistry of nano-sized materials is critical for controlling the morphology that drives their unique associated chemical and physical properties. The understanding of NCs containing f-elements is comparatively limited due to difficulties in handling them both experimentally and theoretically. In this talk, I will share some recent progress in understanding the interplay between surface energy, surfactant ligands, and the chemistry in determining the morphology of 5f-element nanoparticles. Quantum simulations provide a molecular-level picture of the relevant driving forces and dynamic properties. To push for larger lengthscale, we recently developed the density functional theory tight-binding (DFTB) parameters for actinide systems, that enabled the microsecond quantum MD simulations of actinide nanoparticle systems.


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## Saturday, August 13

**Morning:**

### Understanding novel catalysts through chemical bonding analysis

Andoni Ugartemendia,[1,2] Jose M. Mercero,[1,2] Jesus M. Ugalde,[1,2] Aran Garcia-Lekue,[2,3] Elisa Jimenez-Izal[1,2,3,*]
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[2]*Donostia International Physics Center (DIPC), Donostia, Euskadi (Spain)*
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Today, over 90% of all chemical manufacturing processes make use of heterogeneous catalysis, having an enormous impact on the world's economy. Catalysis is not only important for the production of chemicals, materials and food, but it is also essential for pollution control and medical applications, and it is at the heart of the development of sustainable energy solutions. Therefore, suggesting means to extend the useful life of these substances as well as finding novel catalysts is perentory. In the first part of this talk I will show how PtGe catalysts with a roughly 1:1 atomic ratio exhibit an outstanding resistance toward CO poisoning, a major drawback for the current commercialization of fuel cells [1,2]. The uniqueness of the PtGe equimolar clusters is traced down to the electronic effects. The strong covalency and electrostatic stabilization arising from the advantageous Pt-Ge mixing, make the equimolar clusters highly resistant towards CO poisoning and therefore, more durable. Importantly, the novel catalysts are not only more resistant to deactivation, but they remain catalytically active towards hydrogen oxidation. In the second part of the talk, I will show a potential catalyst made of carbon and oxygen, two of the most earth-abundant elements. The system consists of a quasi-planar tricoordinated oxygen atom embedded in an extended $sp^2$-bonded carbon matrix [3,4]. The exotic arrangement of this species will be deciphered using the chemical bonding analysis. Understanding this atypical compound could pave the way for a new class of environmentally friendly catalysts.

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### Molecule – metal surface interaction: is DFT accurate enough?

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E-mail: sautet@ucla.edu

Describing the interaction and bonding between molecules or their fragments and metal surfaces is key for our understanding of heterogeneous catalysis. Most calculations in the literature are performed in the framework of density functional theory (DFT). There are however evidences showing that that exchange correlation functional of DFT might not be accurate enough for adsorbates as CO and its derivatives, which is an important class of substrates.

Here we compare several DFT functionals (GGA, hybrid, with non-local correlation) with random phase approximation (RPA), a post-Hartree−Fock method based on many-body perturbation theory. We find that RPA appears to be the only method giving correct site preference, diffusion barrier, adsorption enthalpy, and surface energy for CO and its derivatives on Cu(100). For all of the other methods, at least one of these properties is not correctly captured. Applications concern CO adsorption and diffusion on Cu(100) [1] and the reaction pathway and mechanism for $CO_2$ electrochemical reduction on Cu(100), for which RPA provides qualitative differences in the potential determining step [2]. For electrochemical reactions we develop an original workflow combining the grand canonical treatment of electrons with RPA. This approach provides

the correct on-top Cu geometry for CO at reducing potential, and significantly improves the match with experimental results, compared to the functionals at the generalized gradient approximation level. Our results suggest that it is important to use more accurate methods like RPA when modeling reactions involving CO and related species like the $CO_2$ reduction reaction.


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2. Ziyang Wei and Philippe Sautet, Towards More Accurate Modelling of $CO_2$ Electroreduction Mechanism with Many-body Perturbation Theory, submitted **2022**.
3. Ziyang Wei, Florian Göltl, Stephan N. Steinmann, and Philippe Sautet, Modeling Electrochemical Processes with Grand Canonical Treatment of Many-Body Perturbation Theory, *The Journal of Physical Chemistry Letters* **2022** *13* (26), 6079-6084


**Bond formation on and in graphene-based materials**


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Graphitic carbon particles deposited on transition metals (TM) have been along studied as poisons of TM catalysts due to their chemical inertness and physical blocking of the active sites [1]. However, a *complete* graphene (Gr) layer adsorbed on a TM substrate behaves very different from this poisoning carbon deposits, boosting new chemical mechanisms. Among the different Gr/TM systems, Gr/Ru(0001) is especially relevant because, due to its moiré structure [2], it is a very versatile template for the formation of new organic molecule structures and the promotion of chemical processes involving organic molecules [3]. Among these phenomena, here we discuss the reversible formation of a C-C bonds [4] between cyanomethylene groups (-$CH_2CN$), anchored covalently at specific positions on the graphene surface, and 7,78,8-tetracyano-p-quinodimethane (TCNQ), able to diffuse at room temperature.

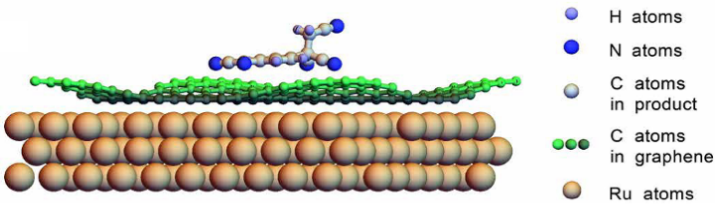

Fig1: The resulting molecule when a cyanomethyne group is bounded to one of the exocyclic alkanes of TCNQ on Gr/Ru(0001)

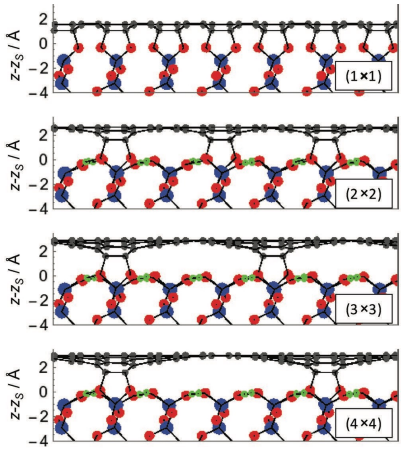

Fig 2: Graphene bonded to $SiO_2$

Another interesting phenomenon associated to graphene bond formation is the appearance of covalent bonds between graphene and an underlying $SiO_2$ substrate upon application of ultrahigh pressure [5]. The possibility of inducing bond formation in Gr/$SiO_2$ in a controlled and selective way allows a fine adjustment of graphene effective doping and opens the possibility of selectively modifying graphene areas, for example, to improve their electrical contact with metal electrodes. In a more general context, this phenomenon opens a convenient avenue to tuning the electronics of 2D materials through pressure with nanometer resolution.


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**Chemical bonding at electrified interfaces**

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*University of California, Los Angles, USA*

When an electrocatalytic interface is held under an applied electric potential, it may undergo the change of the charge state during the catalyzed reaction. I will discuss electrochemical interfaces that exhibit substantial reconstruction, and/or relentless dynamics resulting from the applied potential, the presence of solvent, and adsorbate binding under electrocatalytic conditions. In case of electrodes decorated with transition metal clusters, the geometric and stoichiometric fluxionality leads to the constant change of the nature of the active site, throughout the reaction, as every cluster isomer has a different response of the free energy to the change of charge. This leads to breakdown of scaling relations and opens opportunity for catalyst design, where fluxionality is strategically used rather than avoided. In another example, the Cu electrode in conditions of electroreduction undergoes a potential-dependent Cu row-shifting reconstruction accompanied by embedding of hydrogen into the surface, driven by the formation of surface hydride. This fundamentally changes the nature of Cu sites available for electroreduction catalysis. The simulated STM images of the calculated reconstructed structures agree with experimental in situ STM images, but also exposes a challenge for theory: Reconstruction of electrocatalysts can be kinetically driven, upsetting the already complex thermodynamic picture. Statistical models can be devised to address this effect, and more work is required in this direction.

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**Engineering Topology in Metal-organic Chalcogenolates by Systematic Ligand Selection**

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Hybrid materials, those that contain inorganic and organic structural elements, have developed a large variety of structural features because of the infinite variability of the organic constituent. The ready availability of single crystal x-ray diffraction has led to a wealth of new materials characterized each year. However, known material structures are biased towards those that are easily crystallized and hybrid materials in particular trend towards crystals too small or otherwise pathological to be used for traditional characterization techniques. Here, we used a new technique of serial femtosecond chemical crystallography (SFCX) that uses the high brightness of an X-ray free-electron laser to acquire diffraction from crystals in the 1-5 micron range. Graph theory is used to index those snapshots, enabling determination of crystal structure. We used this technique to explore the ligand environment with variables of steric hinderance, functional group, and intermolecular forces, each addressed by selecting different ligand shapes and configurations. We find dramatic differences in the connectivity, topology, and dimensionality of the resulting silver organothiolates. Of particular note is the nature of the Ag-Ag interactions, which appear to be an important component of the fine structure of the silver systems, and compare and contrast the Ag-Ag networks with the supramolecular ordering of each example system.

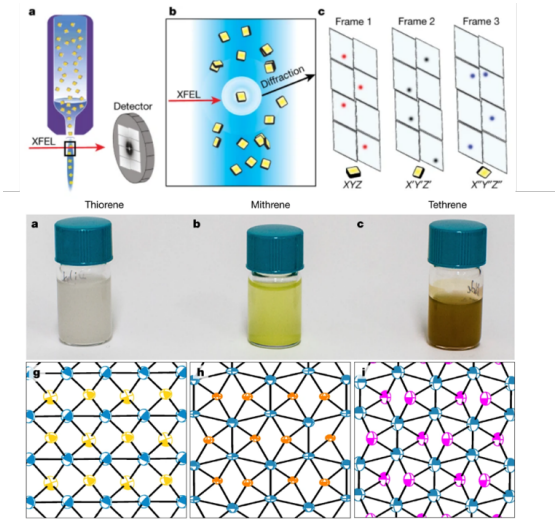


Figure: (*top*) Serial femtosecond crystallography utilizes a bright x-ray pulse and a jet of microcrystals to yield partial diffraction patterns. (*middle*) Examples of three microcrystal suspensions: thiorene [AgSPh], mithrene [AgSePh], tethrene [AgTePh]. (*bottom*) The mithrene and tethrene are structural homologs with 2D Ag-Ag networks, and the thiorene exhibits a new 1D Ag-Ag network and loses the optical properties of the other members.

**Non-valence Correlation-bound Anions of Polycyclic Aromatic Hydrocarbons and the Approach to the Image Potential States of Graphene**

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Molecules and clusters can possess non-valence anions where the electron binding is a consequence of long-range electrostatics and/or correlation effects. Two limiting cases are dipole-bound anions and non-valence correlation-bound (NVCB) anions. In this talk I focus on NVCB anions of hexagonal polycyclic aromatic hydrocarbons (PAHs) as well as their dehydrogenated analogues with an interest in elucidating how the NVCB anion states of these species evolve into the image potential states of graphene with increasing number of carbon atoms. A model Hamiltonian approach that allows us to extend the calculations to thousands of atoms is described. The evolution of the polarizability with increasing system size is also considered.

## Afternoon:

**Electrochemical ambient activation of light alkanes**

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An ambient conversion of light alkanes into other commodity chemicals is both fundamentally significant and potentially applicable for commercial implementation. We sort to discover new electrocatalytic systems for ambient conversion of light alkanes. In this talk, we would like to discuss a few new electrocatalysis that we have discovered and their different underlying mechanisms. The mechanistic insights provide the guidance for future design of electrocatalysis for not only light alkanes but also for other industrially relevant chemical transformation.

**Fullerene cage as a nanolab for exotic chemical bonds**

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Only a few experimental systems with An–An bonds have been observed so far, in particular the multiple bonds in $U_2$ and $Th_2$, single Th–Th bond in $Th_2@C_{80}$ and multiple one-electron two-center bonds in $U_2@C_{80}$ and possibly in $U_2@C_{78}$.[1–2] We have investigated theoretically (DFT BP86) An–An bonds inside various fullerene cages ($C_{70}$, $C_{80}$, $C_{90}$) across the Ac-Cm actinide series and showed that systems form cage-dependent An–An bonds, mostly OETC ones.[3–4] The bonding interactions were predicted even between two Pu atoms separated by 5.9 Å. Our most fresh investigations, however, unravel a strong dependence of the An–An bond orders, expressed, e.g. via the delocalization index from QTAIM analysis, or Mayers bond orders, on the method used. Pure DFT functionals predict stronger bonding interaction, i.e. more electron density between the actinide atoms, while hybrid and range-separated functionals predict weaker interactions, ca 3x smaller. A calibration study using CASPT2 and MC-pDFT calculations on the DFT optimized structures show that pure functionals predict better molecular structures, while the range-separated DFT functionals provide the most reliable description of An–An bonding. Thus, combination of different functionals for optimization and bonding analysis should be considered in the future studies of An–An bonding.[5]

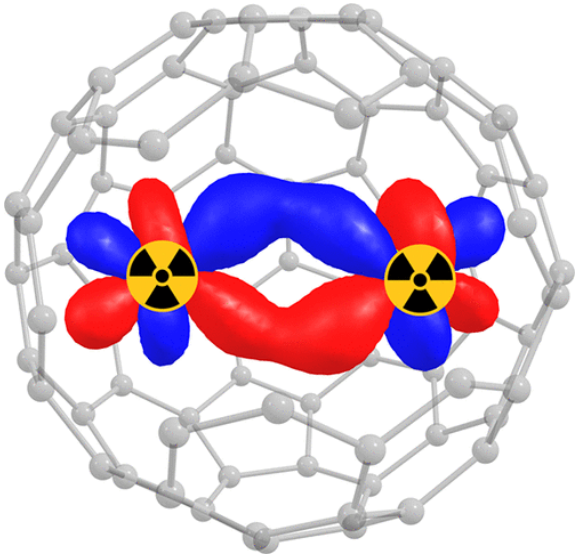

**Fig.1:** Example of a Pu–Pu OETC bond.

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[5] Manuscript in preparation.
**Acknowledgments:** Czech Science Foundation, grant 21-17806S.

**Stretching bonding to its limits: stabilizing radical ligands**

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Metal-ligand mulitple bonds are critical reactive intermediates in both small molecule activation processes as well as atom- and group transfer catalysis. We have shown how the covalency of the primary redox pair (functional group ligand and the metal to which it is bound) is altered as the transition metal ion is changed. For example, dianionic imido ligands are observed for both trivalent iron and cobalt, imidyl radicals are observed on divalent nickel, whereas copper supports ligation of diradical nitrene moieties. We will present how these bonding formalisms are determined, how they affect catalysis in C-H bond functionalization, and methods for stabilizing the primary redox pair to stretch the bonding association to its limits.

**Learning chemical reactivity with neural networks**

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Interatomic potentials derived with Machine Learning (ML) algorithms such as Deep-Neural Networks (DNNs), achieve the accuracy of high-fidelity quantum mechanical (QM) methods in areas traditionally dominated by empirical force fields and allow performing massive simulations. Most DNN potentials were parameterized for neutral molecules or closed-shell ions due to architectural limitations. In this work, we propose an improved machine learning framework for simulating molecules in arbitrary states. We introduce the AIMNet-NSE (Neural Spin Equilibration) architecture, which can predict molecular energies for an arbitrary combination of molecular charge and spin multiplicity with errors of about 2–3 kcal/mol and spin-charges with error errors ~0.01e for small and medium-sized organic molecules, compared to the reference QM simulations. The AIMNet-NSE model allows to fully bypass QM calculations and derive the ionization potential, electron affinity, and conceptual Density Functional Theory quantities like electronegativity, hardness, and condensed Fukui functions. We show that these descriptors, along with learned atomic representations, could be used to model chemical reactivity and outcomes of chemical reactions. AIMNet-NSE brings ML and physics-based models one step closer by offering a discrete, physically correct dependence of system energy with respect to a total molecular charge and spin states.

**Intuitive Machine Learning for Chemical Properties**

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Modern Machine Learning (ML) methods have made theoretical chemistry more relevant than ever. ML methods trained to replicate properties predicted by expensive quantum simulations have enabled significantly faster, larger, and more accurate simulations than previously possible. These methods are quickly gaining traction and have been recognized by notable awards such as the 2020 Gordon Bell Prize in Computing. Despite this progress, ML methods relevant to chemistry have many major drawbacks compared to traditional quantum simulations. ML methods are still largely black box preventing the development of intuitive explanations for physical phenomena that are satisfying to theoretical chemists. Further, some delocalized properties, such as those that arise from electronic excitations, are difficult to predict with traditional ML methods.

In this presentation a variety of physics aware ML models will be explored that seek to overcome the limitations of traditional ML approaches. The Hierarchical Interacting Particle Neural Network (HIPNN) has been trained to predict quantities such as atomic charges, molecular dipoles, singlet-triplet energy gaps and inter-atomic bond orders. Utilizing these non-traditional models as a stepping-stone, we will present two Hamiltonian based models where HIPNN dynamically adjusts atomic parameters based on the local atomic configuration. The first model utilizes the Extended Hückel framework and accurate predictions of molecular orbital shapes and energies will be illustrated. The second model extends PM3 and shows improved accuracy and extensibility when compared to both traditional semi-empirical methods and neural networks. In both models, intermediary Hamiltonian parameters will be examined and connections made to traditional views of chemical bonding. Overall, the presentation will aim to illustrate a wide range of applications of ML and advocate for wider adoption in the theoretical chemistry community.

## Monday, August 15

## Morning:

**Properties and performance of molecules for quantum information applications**

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A list of features required for a system to be useful as a programmable quantum processor was provided by DiVincenzo in 2000 [1]. Of the five DiVincenzo criteria, two involve non-unitary operations in which information (entropy) is exchanged between the processor and its environment. For these two, spontaneously emitted photons serve nicely, and I will discuss principles for designing large, organic molecules that can produce repeated spontaneous emission [2] and share experimental results of some of these species [3].

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[3] Zhu, G.-Z. *et al.*, arXiv:2202.01881 **2022** DOI: 10.48550/arXiv.2202.01881. Mitra, D. et al., arXiv:2022.01685 **2022** DOI: 10.48550/arXiv.2202.01685

**Generalized Spin-dependent Dispersion Intermolecular Forces.**

Vladimiro Mujica[1,2], Jesus Ugalde[2] and Rafael Gutierrez[3],
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[2] *Euskal Herriko Unibertsitatea, and Donostia International Physics Center (DIPC), Euskadi, Spain.*
*Dresden University of Technology, Germany*
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Intermolecular London dispersion forces are due to induced-electric dipole induced-electric dipole interaction. In this contribution, we will analyze how the Chirality-Induced Spin Selectivity (CISS) effect causes important changes in the expression for van der Waals interactions between chiral molecules. In particular, we will discuss how the CISS effect induces a spin-dependent molecular response resulting from fluctuations in the magnetic moment, analogous to the fluctuation in the dipole moment responsible for dispersion forces. the interaction between the molecule and the field. The above-mentioned effect, induces a hitherto ignored mechanism for chiral discrimination, which plays a fundamental role in molecular recognition of bio-molecules.
The underlying physical mechanism is related to chirality-induced space inversion symmetry breaking, which couples the electric and magnetic molecular susceptibilities to electromagnetic fields. The outgoing propagating field carries information about the molecular chirality in its circularly polarized components, which become different in magnitude due to the interaction with the chiral molecule. The analysis of these two phenomena can lead to a unified description of the CISS effect and molecular chiro-optical properties, a theoretical problem we are currently exploring.

**Spectroscopy for molecules that might be laser-cooled**

Thomas D. Persinger[1], Jiande Han[1], Anh Le[2], Timothy Steimle[3] and Michael C. Heaven[1]
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[2] *Georgia Institute of Technology, USA*
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Laser-cooling of molecules to temperatures that are sub milli-Kelvin allows for precision measurements of phenomena that are not encompassed by the standard model of particle physics. Manifestations of charge-parity and time-reversal symmetry violations such as the electron electric dipole moment are the targets of several ongoing investigations that require ultra-cold molecules.

Laser-cooling of molecules is challenging because the cooling transition must scatter $10^4$ photons or greater before losing population to levels that are outside of the cooling cycle. This requires electronic transitions that are highly diagonal in terms of their Franck-Condon factors (very high propensity for Dv=0). Molecules that meet this condition are rare, and it is typical to find that optical re-pumping using axillary lasers is needed to return population into the cooling cycle. Electronic structure calculations have been used in attempts to identify suitable molecules, but the currently available computational methods do not have the stringent accuracy needed for these predictions to be reliable. Hence, spectroscopic measurements are needed to evaluate the true potential of candidate species. As part of the effort to obtain these data, we have carried out spectroscopic studies of the molecules BeLi, MgLi, YbF, YbOH and $YbOCH_3$. Cooling and trapping of ions is also of interest, and the cations $BeLi^+$, $MgLi^+$ and $YbF^+$ have been characterized using two-photon ionization techniques. A survey of these results and their relevance to laser cooling will be presented.

**Approaching Heavy-Element Spectroscopy Using the Spinor Representation**

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It is a major challenge for quantum chemistry to accurately treat strongly correlated f-electrons in lanthanide- and actinide-containing molecules because of the complex interplay among relativistic effects, spin-orbit coupling, ligand field, and electron correlation. This presentation is devoted to an alternative approach based on the relativistic spinor representation, i.e., the representation of the wave functions with spin-orbit coupling included in the orbitals. The use of spinors is shown to feature compact representation of wave functions for many highly open-shell lanthanide- and actinide-containing molecules. Calculations of example lanthanide- and actinide-containing small molecules with more than two open-shell f-electrons including NdO, SmO, UO, and $UO_2$ are presented to demonstrate the applicability of spinor-based relativistic coupled-cluster methods to study of heavy-element spectroscopy.

**Study Covalency in Rare-Earth and Heavy-Element Complexes with Relativistic Electronic Structure Methods**

Xiaosong Li
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The computational modeling of rare-earthy and heavy-element complexes requires an accurate treatment of spin-orbit and electron correlation effects to fully understand the physical underpinnings of their chemical properties. Our recent studies using many-body multireference methods suggest that there is a significant

correlation effect of inner-valence electrons in rare-earth and heavy-element complexes. Ignoring this effect could lead to inaccurate descriptions of molecular properties, such as covalency, bonding, and spectroscopic response. In this talk, we will examine how the correlation effect of inner-valence electrons is manifested in molecular properties with a focus on the covalency in rare-earth and heavy-element complexes.

**Bond Dissociation Energies and Electronic Structure of *d*- and *f*-Block Molecules**

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Over the past 6 years, we have recognized that small *d*- and *f*-block molecules exhibit a dazzling density of electronic and vibronic states in the energetic vicinity of their lowest separated atom limit, and that spin-orbit and nonadiabatic couplings among these states allow the molecule to find a path to dissociation as soon as its lowest separated atom limit is exceeded in energy. By measuring this onset of predissociation using resonant two-photon ionization spectroscopy, it is possible to measure the bond dissociation energies (BDEs) of these molecules to high precision. This provides benchmarks of unprecedented accuracy for comparison with quantum chemistry. In this talk I will present evidence that predissociation sets in as soon as it is energetically possible by comparison of predissociation threshold results with velocity map imaging results on the molecules CrO, MoO, and VO. Next, I will present data concerning the late transition metal borides and show how the widely varying BDEs can be explained by considering the diabatic dissociation limits of these species. Data on the lanthanide sulfides and selenides will also be presented and it will be shown that the wide variations can be likewise understood when the appropriate diabatic dissociation limits are considered. Finally, the extension of the predissociation method to measure the BDEs of the triatomic transition metal borides ($ScB_2$, $TiB_2$, $VB_2$, $YB_2$, and $MoB_2$) will be presented along with computational results that demonstrate a radically different chemical bonding mechanism than in the more commonly encountered Dewar-Chatt-Duncanson model.

**Non-Nuclear Maxima and the Universality of Bright Wilson's Justification of the First Hohenberg-Kohn Theorem**

Chérif F. Matta[1], James S. M. Anderson[2], Aldo de Jesús Mortera-Carbonell[2], Lou Massa[3]
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[3]*Hunter College & City University of New York, USA*.

The neglect of the finite nuclear size is an excellent approximation for much of chemistry and is at the origin of the appearance of cusps (singularities) at the positions of the nuclei. The Kato cusp condition relates the nuclear electric charge to the derivative of the spherically-averaged electron density around a given atomic nucleus with respect to distance from that given nucleus (which we call the "Kato ratio") weighted by the electron density at this point nucleus. This "Kato ratio" is shown, analytically, to vanish at all points of the electron density, and of the external potential, which are devoid of singularities *including the position of non-nuclear maxima/attractors* (NNMs/NNAs) since these are true maxima and not cusps. These analytical results are confirmed numerically using prototypical test cases. This result, while simply demonstrated and, possibly, tacitly known and expected, could not be found in the literature to the best of the authors' efforts. Since the Kato ratio is zero at a NNM/NNA, this saves the DFT plausibility argument of E. Bright Wilson – since the non-nuclear maximum occurs at a position that has zero nuclear charge. The extension of these ideas to excited electronic states will also be discussed.

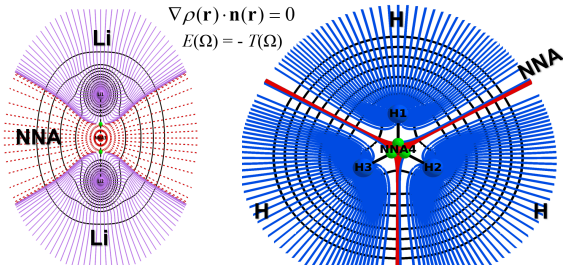


Figure: Two prototypical examples of NNAs and their associated pseudo-atomic basins: $Li_2$ and $H_3^+$


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## Afternoon:

**Surfing the excited-state energy landscape to understand reactivity and improve fluorescent probe design**


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Initially motivated by the development of tools to identify risk factors associated with dementia and cardiovascular disease, we sought to understand the driving force behind excited-state intramolecular proton transfer (ESIPT) fluorescence. This work demonstrates the first application of Baird's rule to rationalize previously unexplained experimental behavior of the singlet state. Further, we propose a complementarity to Baird's rule: greater aromaticity in the ground state leads to greater antiaromaticity in the excited state and vice versa. These findings have immediate application in the design of functional ESIPT fluorophores and, more generally, for photochemical reactions that are driven by the relief of antiaromaticity in the excited state. Notably, a tenet of traditional chromophore design states that expansion of conjugation generally leads to a red-shift in absorbance and emission wavelengths. The results of this study show that ESIPT fluorophores run contrary to those conventional design principles and this behavior can only be rationalized by considering Baird's rule.

**Unifying Planar and Spherical Aromatics. Shielding Cone as Common Characteristic Across Periodic Table Clusters**


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After one and half century since Kekule´s seminal work on the rationalization of benzene structure, this molecule continues to delight attracting interest of chemist communities.[1] This small cyclic hydrocarbon is indubitable one of the more relevant example of a prototypical planar aromatic molecule, displaying a characteristic induced magnetic field opposing or shielding the external field, resulting in long-ranged shielding cone.[2] A relevant extension of the concept of *aromaticity* is the realization of three-dimensional

aromatic systems, involving a *spherical aromatic* behavior. Here we unravel a common property linking planar and spherical aromaticity, among other species, by showing their characteristic shielding cones (Figure 1)[3,4] across clusters along with periodic table elements.[5] It is found that for planar aromatics, the cone is reserved only for a perpendicularly applied field, whereas for spherical aromatic compounds, it remains similar under different orientation of the external field. Thus, we expose the shielding cone property as a useful descriptor for aromaticity, despite of the very different structural diversity, composition, and nuclearity.

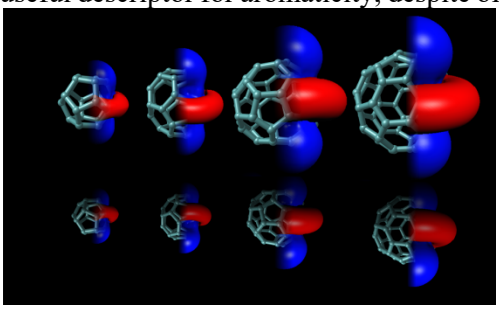

**Figure 1**. The shielding cone in spherical aromatic fullerenes.

**Acknowledgments:** Authors acknowledge FONDECYT 1221676 for financial support.

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**A Different Take on Atomic Charge, Energy and Electronegativity**

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This presentation outlines a theoretical framework that aims to connect Molecular Orbital Theory, Quantum Chemical Topology and Energy Decomposition Analysis. In this theory, electronegativity is defined as the average energy of valence electrons. This definition runs counter to the electronegativity equalization postulate of Sanderson and allows a perspective in which electronegativities of bonded atoms need not be equal. As chemical potentials equalize in this framework, electronegativities equilibrate. Complementarity and comparison with Conceptual Density Functional Theory is discussed. A practical definition of what constitutes an atom in a molecule is introduced, which allows for the quantification of charge, energy and electronegativity in a new way. Utility is demonstrated, with in situ electronegativity shown to be a potent indicator for pKa.

**Precision Probes and Rationalization of Gold Nanocluster Electronic Structure**

Christopher Johnson
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Nanostructured particles hold much promise as "designer materials," but full realization of this promise requires an understanding of the interplay between composition, geometric structure, and electronic structure that drives their behavior. A subset of these particles, often called nanoclusters and with sizes below 2 nm, can be synthesized monodispersely and crystallized to determine their exact geometric structures, but

no similarly powerful technique exists for the determination of their electronic structures and computational efforts to the same are challenging. We have extended gas phase spectroscopy techniques to small these nanoclusters. These experiments reveal dramatically more information, near the limit of spectroscopic resolution, than do typical UV/Vis spectra in solution, allowing us to probe electronic structure with precision similar to that routinely found for molecules or coordination complexes and yielding ideal benchmarks for theoretical study. For instance, we find that subtle functionalization of the protecting ligands has a drastic impact on the cluster electronic structure, even for transitions between two nominally metal-based states, suggesting a route to control critical features of their electronic structure such as the HOMO-LUMO gap. Very subtle environmental effects, such as complexation with He or N2, yield notable shifts to the spectra, suggesting state-specific surface chemistry effects. Finally, we can benchmark current density functional theory techniques and show that explicit evaluation of atomistic particle-in-a-box models can provide a quick, intuitive, and semiquantitative alternative to these laborious calculations. Taken together, these studies provide detailed experimental windows guiding the use of classic coordination-chemistry-type methods to tune the electronic properties of these clusters for chemical and technological applications.

**Cyclo[N]carbon rings and catenanes from different perspective. Disentangling molecular thread**

Ivan Černušák, Silvia Kozáková, Nissrin Alharzali
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E-mail: cernusak@fns.uniba.sk

Chemical modelling of all-carbon ring molecules of different size is reviewed. Recently, cyclo[N]carbon rings have been studied both experimentally and theoretically revealing interesting properties of these systems[1-4]. The rings are considered to be aromatic/antiaromatic depending on the value of N, where N = 4n + 2 or N = 4n (n being the number of π-electrons). Interesting feature of these systems is the presence of two mutually orthogonal sets of π-orbitals as revealed by the AdNDP method[5]. We will analyse the bonding and present the aromaticity/antiaromaticity analysis of series of cyclo[N]carbon rings (6 – 46) in terms of various molecular properties calculated within the density functional ωB97X-D model. We will also report the results of DFT computational experiments with the interlocked cyclo[N]carbon rings of various size that represent the model of molecular threads.

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## Tuesday, August 16

## Morning:

**Multi-nodal "in-plane" interactions in actinide compounds**

Ivan A. Popov
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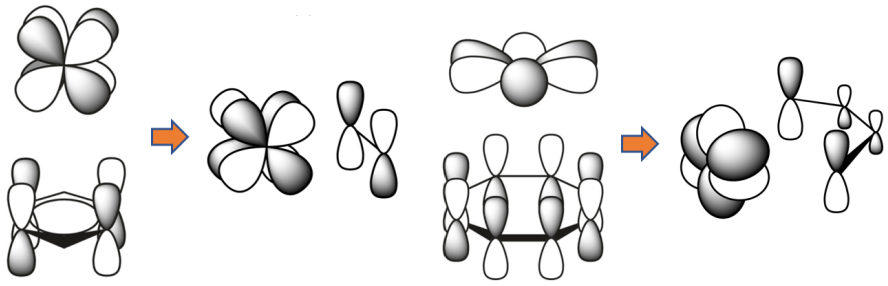
Separating heavy elements from one another is one of the biggest challenges of nuclear waste management. Because actinide (An) atomic radii get smaller when moving from left to right across the An series, metal-ligand bond lengths usually decrease with increasing atomic number. In addition to the ligand-to-metal charge

transfer, there could also be additional interactions, *i.e.* from metal back to ligand (back-donation) that could also affect the An–L strength and impact the An contraction trend. In this talk, we will show various types of the An–L interactions of an actinide center with a varying number of carbon atoms constituting the ligand that lead to unique chemical bonding motifs. Specifically, we will demonstrate how multi-nodal back-bonding ($\delta$ and $\varphi$)[1,2] may be invoked that can promote enhanced An–L covalent interactions in molecular actinide compounds, which hold potential implication in nuclear separation chemistry.



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**Revealing of $NdCl_3$ speciation in aqueous solutions by QM/MM molecular dynamics simulations**

Pavel Rublev[1,2], Pavel A. Dub[2], Sergei Tretiak[2], Ben Nebgen[2], Alexander I. Boldyrev[1], Artaches Migdissov[2] and Alexander Gysi[3]
*[1]Utah State University, [2]Los Alamos National Laboratory, [3]New Mexico Institute of Mining and Technology, USA*

Materials based on Rare Earth Elements (REE) are truly fantastic and can be applied to various fields: luminescent materials with narrow bands with constant positions and long lifetimes, renewable energy sources (such as wind turbines, solar panels), and advanced ecological energy storages. Hydrothermal fluids play a significant and, in some cases, even dominant role in the formation of REE ore deposits, and for better extraction it is necessary to understand the nature of REE ores speciation in hydrothermal solutions at a very wide range of temperatures and pressures. By the way, not all processes can be investigated experimentally, and here quantum chemical simulations start to play.

Universal modern technique - Ab initio molecular dynamics (AIMD) - provides accurate and essential approach to understand the processes occurring in aqueous solutions under different conditions. However, due to the polynomial numerical scaling with respect to the number of atoms, off-the-shelf AIMD methods are currently limited to ~500 atoms and picosecond timescale simulations, which significantly limits phase-space sampling capabilities and thus, drastically decrease accuracy of statistic-based calculations. Additional challenge is employed by open-shell nature of Neodymium cation.

In this talk we will discuss quantum mechanics/molecular mechanics molecular dynamics (QM/MM MD) simulations as a decent variant to overcome scalability problem. Preliminary results will be presented for $NdCl_3$ system in aqueous solutions by means of QM/MM. Additionally, process of Nd-Cl bond cleavage and solvent reorganization will be analyzed from Path Integral QM/MM perspective.

**Simulating Electronic Structure on Quantum Computers with PermVQE and QDavidson algorithms**

Nikolay V. Tkachenko,[1,2] Yu Zhang,[3] Lukasz Cincio,[3] Alexander I. Boldyrev,[2] Sergei Tretiak,[3] Pavel A. Dub[1]
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[2]*Department of Chemistry and Biochemistry, Utah State University, Logan, UT, USA*
[3]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, USA*
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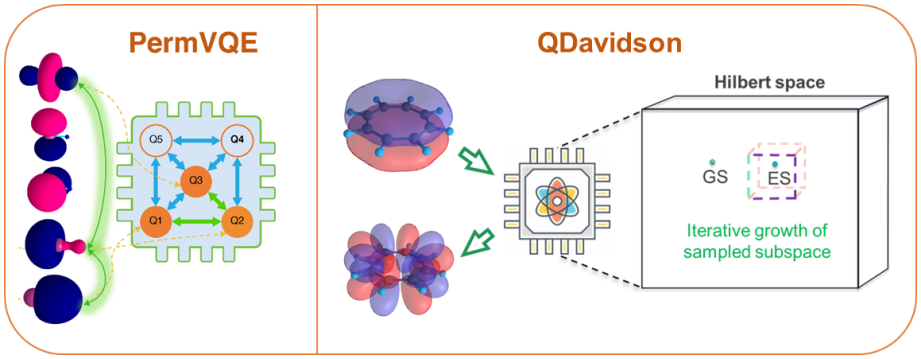
Quantum computing is expected to modernize computational chemistry by achieving polynomial scaling in both the number of quantum particles and the completeness of the wave function approximation of the system (i.e., the number of basis functions). Though the ideal noiseless quantum devices could bring an exponential speedup to quantum chemistry calculations, currently only noisy intermediate-scale quantum (NISQ) devices are available for researchers. For the past several years, huge progress has been made to effectively calculate the ground electronic state on NISQ devices. The leading algorithm for that is variational quantum eigen solver (VQE). This algorithm was successfully tested on real NISQ devices, however the growing circuit depth with problem size can cause trainability and noise issues. Much less effort has been done in the area of excited states calculations on NISQ devices. Developing algorithms for efficient computation of excited states is an open challenge in modern quantum chemistry.

During my talk, I will cover two novel algorithms that were developed in our group: PermVQE and QDavidson algorithms. The former algorithm is proposed to improve the VQE procedure by decreasing the number of required circuit layers to solve the electronic-structure problem. The latter algorithm inherits the main idea of the classical Davidson algorithm, trying to project the Hamiltonian onto the most meaningful Hilbert subspace that is smaller than the full space of the problem. As a result, low-lying excited state energies can be reproduced. We believe that the proposed methods will facilitate the simulation of larger molecular systems with NISQ devices and contribute to the demonstration of chemical advantage.




**Free energy perturbation calculations of mutation effects on SARS-CoV-2 RBD::ACE2 binding affinity**

Alina P. Sergeeva
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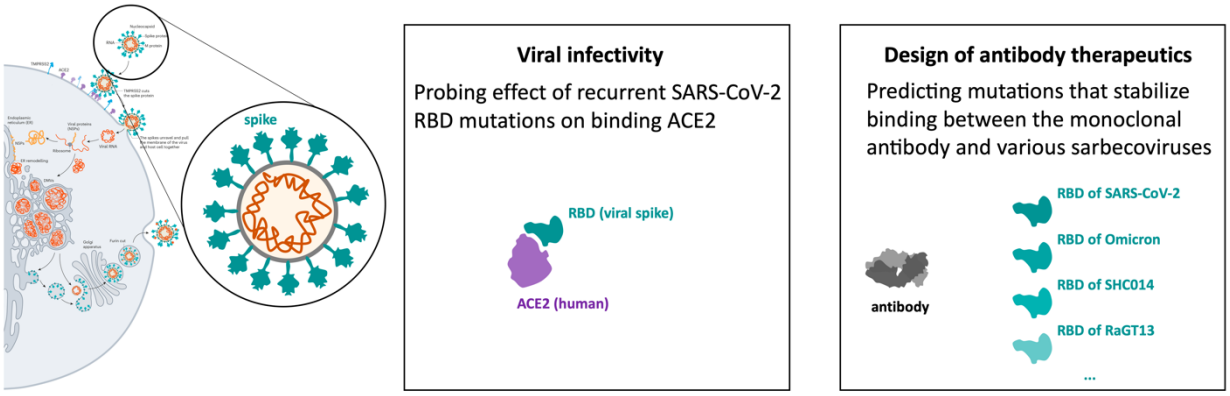
The strength of binding between human angiotensin converting enzyme 2 (ACE2) and the receptor binding domain (RBD) of viral spike protein plays a role in the transmissibility of the SARS-CoV-2 virus. We focus on a subset of RBD mutations that have been frequently observed in sequenced samples from infected individuals and probe binding affinity changes to ACE2 using surface plasmon resonance (SPR) measurements and free energy perturbation (FEP) calculations. We find that FEP performance is significantly better than that of other computational approaches, in part due to its ability to account for protein structure relaxation resulting from the mutation of interfacial residues. Moreover, analysis of FEP trajectories offers physical insights not available from other methods. Notably, FEP calculations successfully predict the

observed cooperative stabilization of binding by the Q498R N501Y double mutant present in the Omicron variant and offer a physical explanation for the underlying mechanism. Our results furthermore suggest a strategy as to how to effectively deploy FEP methods in the optimization of neutralizing antibodies.




**From Organics to Organometallics: Transfer Learning Interatomic Potentials**

Nikita Fedik, Benjamin Nebgen, Nicholas Lubbers, Sergei Tretiak
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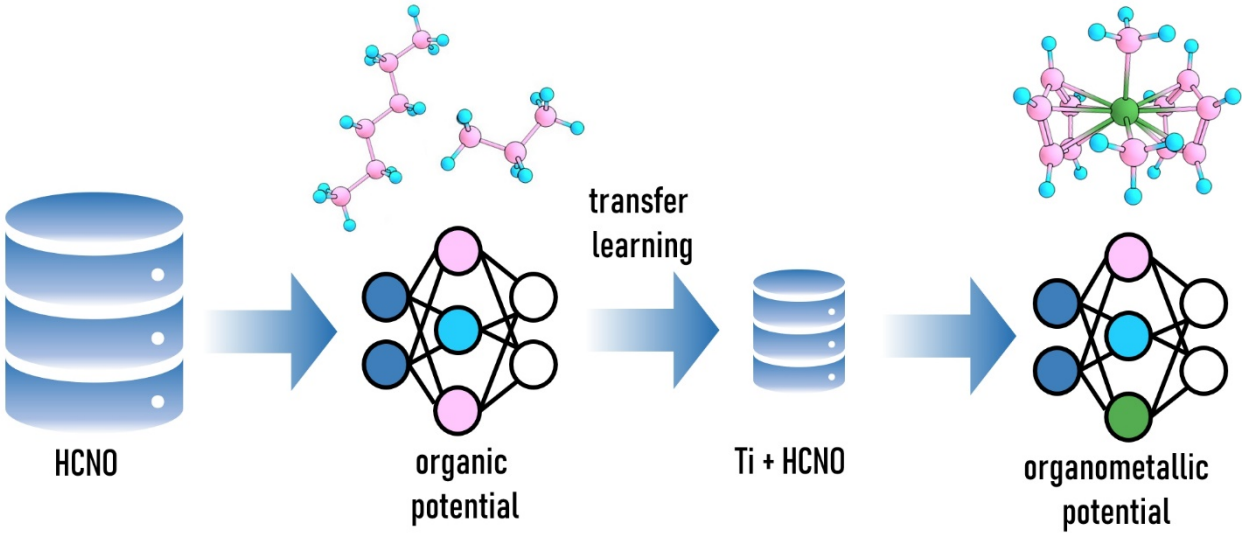
Machine Learning (ML) interatomic potentials are becoming essential and popular research tools for chemical discovery. Highly flexible ML algorithms are capable to establish the relationship between chemical structure and its properties. Properly trained ML potentials can be almost as accurate as reference quantum-mechanical data (from DFT to coupled-cluster) only at a fraction of cost which is comparable to molecular mechanics.

Traditionally, ML potentials are only applicable to the systems comprising the same types of atoms as in the training data. This limitation implies that extension of the ML model to new chemical species would require full expensive retraining of the model. Our guess is that organic interatomic potential trained to HCNO molecules has already near-optimal parameters for HCNO-ligands in organometallic complexes. In our work we explore the possibility of extending the interatomic potentials to new chemical species via transfer learning (TL). In general, TL shows excellent performance for image-recognition when the models pre-trained on one visual dataset can be transferred to another set of images by a short training procedure. It greatly reduces number of training iterations and can save weeks of computational time while often providing better accuracy than models trained from scratch.

We apply TL technique to achieve an accurate model of organometallic Ti complexes using purely organic pretrained interatomic potential. Along with greatly reduced computational cost of TL compared to full training, we achieve reasonable accuracy using only a small dataset of ~17000 Ti complexes while "from scratch" trained models require millions of structures. TL techniques paves the way to fast and robust extension of accurate pre-trained interatomic potentials to new domains of chemical species. This advancement will allow broader community of researchers to easily tune ML interatomic potentials to their own highly specific chemical problems and datasets.




**Accelerating Data Generation for Machine Learning Potentials by Biasing Towards Regions of Uncertainty**

Maksim Kulichenko
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Neural Networks (NN) can model atomic-scale interactions with the accuracy of quantum mechanics methods at a fraction of their computational cost. In order to produce reliable simulations, NN-based interatomic potentials need high-quality training data, spanning a diverse and chemically meaningful phase space. Uncertainty Quantification methods help detect atomic configurations where an ensemble of NN-potentials exhibits high prediction deviation and, thus, poor performance. Uncertainty Quantification combined with Active Learning (AL) helps iteratively improve training data. However, structural samplers, such as molecular dynamics, can take a long time to reach high-uncertainty space or are unable to reach some phase regions at specific thermodynamic conditions.

In this work, the uncertainty of ensemble predictions is used to construct the bias potential. The resulting potential acts as an energy function of uncertainty and modifies the potential energy landscape to make atomistic systems move toward high-uncertainty regions, underrepresented in the training data. The proposed approach can be seen as a generalized case of metadynamics without the need of manual selection of collective variables. As a result, uncertainty-based bias potential helps accelerate data sampling compared to unbiased Active Learning. Moreover, it enables efficient exploration of chemically important space inaccessible by regular approach at low temperature conditions.

**Crystal structures of new materials containing structure-directing halogen and chalcogen bonds.**

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It is well-known that many properties of solid-state materials depend not only on molecular structure but also on crystal structure. Properties such as non-linear optical, electroconductivity, liquid crystallinity, and pharmaceutical bioavailability, dramatically depend on molecular mutual orientation and intermolecular

contacts. Hence, it is critical to understand the principles of intermolecular bonding in crystals in order to develop some practical guidelines that allow us to 'predict' the most likely intermolecular bonds simply from knowing molecular structure. Using these rules, one can then modify molecules to design materials with specific structure and desirable and tunable properties.

While hydrogen bonding is the most studied example of intermolecular contacts, specific interactions involving halogen, chalcogen, and pnictogen bonds are currently attracting much interest for more advanced and versatile methodologies. Polarizable halogen atoms can form strong and directional intermolecular interactions, and the same is true for chalcogen and pnictogen atoms. The modification of the molecules with electron-withdrawing group results in the charge redistribution in the molecules, which, in turn, leads in different bonding pattern. In this work, we present the systematic study of series of compounds that contain halogens and chalcogen atoms. We explore how changing halogen atoms and the addition of various electron-withdrawing groups result in precise changes of bonding pattern in crystals structures. These data are obtained experimentally by single-crystal X-ray analysis.

## Afternoon:

**What do we mean by the structure of high-temperature liquids?**

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In liquids the timescales of the structure, diffusion and phonon are all similar, of the order of a pico-second. This not only makes characterization difficult, but also renders it highly questionable whether the terminologies typically used for solids could be applied to condensed matter. The concept of the structure is particularly problematic because liquid is inherently dynamic, where the motions of atoms are locally strongly correlated, and the many-body nature of dynamic interactions results in emergent unpredictable behavior. Our research seeks to provide atomic-level insights into the ionic correlations in high-temperature molten ionic fluids by applying synchrotron X-ray and neutron scattering coupled with our new approach to describe the locally correlated atomic dynamics of liquid in real-space and time through the Van Hove function. A thorough analysis paints a more complex picture than previously understood, with the formation of ionic chains even at the high temperatures and surprising similarities with aqueous solutions, suggesting a possible universal connection between local configurational changes and macroscopic viscosity of liquids despite the drastically different types of bonding.

**Neuro-symbolic reinforcement learning for polymer discovery**

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We present the first application of neuro-symbolic reinforcement learning (NS RL) in materials discovery domain. Deep RL requires excessively large volume of training data, and the learned policies lack explainability. As a result, practical application of deep RL in material discovery is problematic. We explore Neuro-Symbolic approaches to deep RL that combine the strengths of data-driven AI with the capabilities of human-like symbolic knowledge and reasoning. Neuro-Symbolic approaches are anticipated to enable co-creation of models/policy with subject matter experts (SMEs) by capturing new domain knowledge in symbolic form. We investigate Logical Neural Networks (LNNs) where each neuron has an explicit meaning

as a part of a formula in a weighted real-valued logic. In addition, the model is differentiable, and learning helps in learning new facts and make the network resilient against contradicting facts.

In the presented study we use Logical Optimal Actions (LOA), an NS RL framework based on LNN, to train RL agents to select experimental conditions for the synthesis of spin-on-glass (SOG) given target values of experimental outcomes. The SOG is based on tetraethyl orthosilicate as the precursor and co-precursors such as phenyltriethoxysilane. Experimental degrees of freedom include temperature, reaction time, precursor/co-precursor ratio, total co-/precursor concentration, water/-precursor ratio, and catalyst-/precursor ratio. We explicitly pursue training of generalizable agents that learn to navigate abstract space of experiments relevant to SOG synthesis to find reaction conditions that yield materials with desired properties. We introduce a data-augmentation strategy to meet data requirements of NS RL while maintaining affordable volume of experimental data – under 300 experimental data points. NS RL experiments show that the LOA in combination with logical action-aware features noticeably improves agent's performance in the search for the experiments targeting specific molecular weight and polydispersity index of the produced SOG. Furthermore, the agent learns to avoid experimental conditions that produce undesirable outcomes: for example, the agent avoids synthesis conditions leading to gelation of the reaction mixture of cross-linked SOG. Finally, we validate and benchmark the proposed NS RL approach by running spin-on-glass synthesis in the lab following AI agent predictions.

**Spherical Aromaticity**

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Aromaticity is one of the most controversial concepts in chemistry. Spherical aromaticity is even more controversial. Yet, in recent years this concept is getting popularity in inorganic chemistry in deciphering chemical bonding in complicated compounds [1]. In this talk I will present our results, where we used the spherical aromaticity to a series of inorganic compounds. We will follow the $2(N+1)^2$ Hirsch formula for the delocalized electrons and the Adaptive Natural Density Partitioning (AdNDP) method for visualizing delocalized bonds. Delocalized bonds in the spherical aromaticity are looking like superatomic orbitals, s, p, d, etc. and therefore people use also a concept of superatom for interpreting chemical bonding in such chemical species. Which approach is correct?

In my talk I will discuss in details a few compounds corresponding to different N. For N=0, the number of delocalized electrons is 2 and the delocalized bond should look like s-AO orbital. An example of such compound is $\{[(^t\mathrm{Bu})_3\mathrm{PAu}]_4\}^{2+}$. At the center of this compound there is a $Au_4$ tetrahedron, which contains a s-AO like multicenter bond. For N=1, the number of delocalized electrons is 8, and those four multicenter bonds look like s, $p_x$, $p_y$, and $p_z$.

There are few examples of such compounds in chemistry: $[Sb@In_8Sb_{12}]^{3-}$, $[Bi@In_8Bi_{12}]^{3-}$, $[Sn@Cu_{12}@Sn_{20}]^{12-}$ and others. I also will discuss examples for d-like and f-like delocalized bonds. One can see, that those delocalized bonds are indeed reminds the superatomic orbitals. Thus, we believe that these two concepts spherical aromaticity and superatoms can be used as interchangeably.

[1] Maksim Kulichenko, Nikita Fedik, Nikolay V. Tkachenko, Alvaro Munoz-Castro, Zhong-Ming Sun, Alexander I. Boldyrev In *Aromaticity: Modern Computational Methods and Applications*, Ed. Israel Fernandez, Elsevier 2021, ISBN: 9780128227237, pp. 447-488.