International Conference on Chemical Bonding

Technical Program

Wednesday, July 3

Arrival and registration

Thursday, July 4

Morning: Fundamentals *Presiding: Anastassia Alexandrova*

8:45 –9:00 am	*Alex & Anastassia - Introductory remarks*
9:00 –9:30 am	Kenneth Jordan *Correlation-bound Anion States of Molecules and Clusters*
9:30 – 10:00 am	Gernot Frenking *Main Group Complexes with Unusual Donor-Acceptor Bonds*
10:00 – 10:30 am	Alexander Sax *Chemical Bonding: Calculation versus Interpretation*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Artur Izmaylov *Conical Intersections and Topological Insulating State of Molecules*
11:15 – 11:45 am	Mark Tuckerman *Understanding and Exploiting Chemical Bonding Patterns in the Design of Hybrid Organic-Semiconductor Structures*
11:45 – 12:15 pm	Mingfei Zhou *Infrared Photodissociation Spectroscopy of Mass-Selected Cluster Ions in the Gas Phase*
12:15 – 12:45 pm	Gabriel Merino *A Planar Tetracoordinate Carbon Zoo*

Afternoon: Fundamentals *Presiding: Gabriel Merino*

4:00 – 4:30 pm	Anastassia Alexandrova *What is There to Battle and Conquer Aromaticity?*
4:30 – 5:00 pm	William Hase *Study of Condensed Phase Post-Transition State and Microsolvation Dynamics by Direct Dynamics Simulations*
5:00 – 5:30 pm	Alexandre Tkatchenko *(Un)Chemical Bonding: Surprises in Non-Covalent Interactions in Molecular Systems*
5:30 – 5:45 pm	*Coffee Break*
5:45 – 6:15 pm	Artëm Masunov *Two Bonds with One Photon as Reported by Solid State Dual Fluorescence*
6:15 – 6:45 pm	Dmitry Zubarev *Cyber-Enabled Discovery of Reaction Mechanisms*
07.00 – 10:00 pm	*RECEPTION at Kauai Beach Resort*

Friday, July 5

Morning: Methods

Presiding: Kirill Kovnir

9:00 – 9:30 am	Frank Weinhold *What's New in Natural Bond Orbital Theory*
9:30 – 10:00 am	Sharon Hammes-Schiffer *Avoiding the Born-Oppenheimer Separation between Electrons and Protons: Explicitly Correlated Wavefunctions and Multicomponent Density Functional Theory*
10:00 – 10:30 am	Clémence Corminboeuf *Modern Computational Approaches for Quantifying Inter- and Intramolecular Interactions*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Dage Sundholm *Applications of the Gauge-Including Magnetically-Induced Current (GIMIC) Method*
11:15 – 11:45 am	Patrick Bultinck *Characterizing Chemical Bonds and Aromaticity from a Density Matrix Perspective*
11:45 – 12:15 pm	Jin Zhang *Modeling Surface-Deposited Sub-Nano Catalysts with Explicit Solvent*

Afternoon: Bonding and Reactivity

Presiding: Louis Bouchard

4:00 – 4:30 pm	Scott Anderson *Metal-Surface, and Adsorbate-Metal Bonding in Supported, Size-Selected Model Catalysts*
4:30 – 5:00 pm	Mark Saeys *Orbital Analysis, a Powerful Tool to Guide the Design of Catalysts*
5:00 - 5:30 pm	Alexander Mebel *Photochemically Induced Cold Synthesis of Complex Organic Molecules on Titan and in the Interstellar Medium: A View from Ab Initio/RRKM Calculations*
5:30 – 5:45 pm	*Coffee Break*
5:45 – 6:15 pm	Dorian Parker *On the Formation of Interstellar Organo Silicon Molecules*
6:15 – 6:45 pm	Henrik Ottosson *On Excited State Aromaticity in Various Forms: a Focus on Aromatic Chameleons*

Saturday, July 6

8.50 - 5:30 p.m.	*BUS TOUR to* *Waimea Canyon, Kalalau Lookout, Spouting Horn Blowhole,* *Lunch at Poipu Beach (1.5 h), Opaeka'a Falls.* *Pick up at Kauai Beach Resort Lobby*

Sunday, July 7

Morning: Materials *Presiding: Artur Izmaylov*

9:00 – 9:30 am	Louis Bouchard *Solid State Studies of Electronic and Magnetic Properties in Topological Insulators*
9:30 – 10:00 am	Boris Yakobson *Topological Mis-Bonding in Dislocations and Grain Boundaries of 2D Materials: Graphene, h-BN, Metal-Disulfides*
10:00 – 10:30 am	Kirill Kovnir *Barium Polyphosphides for Thermoelectric Energy Conversion: Synthesis, Structure, and Bonding*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Mathias Weber *Solvent-Driven Reductive Activation of CO_2 by Gold and Silver Anions*
11:15 – 11:45 am	Lai-Sheng Wang *Covalent Gold*
11:45 – 12:15 pm	Boniface Fokwa *Itinerant Magnetic Borides Containing Planar B_6 Rings: Experiment and Theory*

Afternoon: Bonding and Reactivity *Presiding: Dmitry Zubarev*

4:00 – 4:30 pm	Edward Solomon *Geometric and Electronic Structural Contributions to Fe/O_2 Reactivity*
4:30 – 5:00 pm	Kenneth Merz *Blurring to Bring Binding Free Energies into Focus*
5:00 – 5:30 pm	Darrin York *Molecular Mechanisms of RNA Catalysis*
5:30 – 5:45 pm	*Coffee Break*
5:45 – 6:15 pm	Cynthia Burrows *Redox-Active Ribonucleotides Connect DNA Repair and the RNA World*
6:15 – 6:45 pm	Steven Wheeler *Understanding Non-Covalent Interactions with Aromatic Rings*

Monday, July 8

Morning: Clusters and Molecules *Presiding: Clémence Corminboeuf*

9:00 – 9:30 am	Thomas Heine *Structure and Fluxionality of Decorated and Bare Boron Clusters in the Gas Phase*
9:30 – 10:00 am	Steve Scheiner *The Noncovalent Bond. Is it a Contradiction in Terms?*
10:00 – 10:30 am	Miquel Solà *Aromaticity in Fullerenes and Endohedral Metallofullerenes. Effects on Electronic Structure, Molecular structure, and Reactivity*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:15 am	Ivan Černušák *Photoelectron Spectroscopy and Ab Initio Study of* La_n^- *(n = 1-3)*
11:15 – 11:45 pm	Jack Simons *A Few Examples of Unusual Bonding*
11:45 – 12:15 pm	Vladimír Špirko *Localised Quantum States of Atomic and Molecular Particles Physisorbed on Carbon-Based Nanoparticles*

Afternoon: The Last Frontiers *Presiding: Jin Zhang*

3:00 – 3:30 pm	Daniel Singleton *Dynamics and the Limited Implications of Weak Bonding in Organic Transition States*
3:30 – 4:00 pm	Viktor Zhdankin *Hypervalent Bonding: Structure and Reactivity of Organohypervalent Iodine Compounds*
4:00 – 4:30 pm	Alexander Boldyrev *Deciphering Delocalized Bonding in Molecules, Clusters and Solids*

4:45 – 9:00 pm	*BANQUET -LUAU at Smith Restaurants* *Hawaiian Show + Dinner* *Pick up at Kauai Beach Resort Lobby*

International Conference on Chemical Bonding

Abstracts

Correlation-bound Anion States of Molecules and Clusters

Kenneth D. Jordan and Vamsee Voora

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

In addition to valence-bound and dipole-bound anions, some molecules and clusters can possess so-called correlation-bound anions. In these species, the excess electron is unbound in the Hartree-Fock approximation, and the binding is dominated by dispersion-like correlation effects. When using the flexible basis sets needed to describe such anions, the Hartree-Fock wave function collapses onto an approximate continuum solution, and, as a result, methods such as MP2 or CCSD(T) that are built on a Hartree-Fock reference fail to bind the excess electron. A proper theoretical treatment of correlation-bound anions requires the use of theoretical methods that do not depend on the suitability of the Hartree-Fock approximation in providing a good starting point. Using such methods we demonstrate the existence of correlation-bound anions of selected water clusters, C_{60}, and C_6F_6. The importance of allowing for orbital relaxation in response to correlation effects is discussed, and simple one-electron models that capture the key interactions are introduced. For some challenging systems, we present results of quantum Monte Carlo calculations of the electron binding energies.

Main Group Complexes with Unusual Donor-Acceptor Bonds

Gernot Frenking

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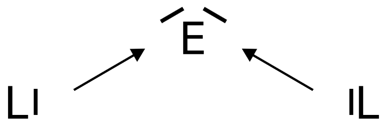
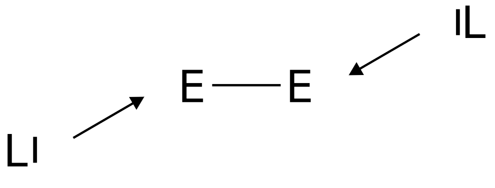
The lecture focuses on donor-acceptor complexes of main-group elements where two strong σ donor ligands bind to a single center E in L→E←L[1] or to a diatomic species E_2 in $L \rightarrow E_2 \leftarrow L$.





E = C, BH, N^+, Si

E = Group 13, 14, 15 atoms

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[1] (a) G. Frenking, R. Tonner, Pure Appl. Chem. **81**, 597 (2009). (b) K.C. Mondal, H. W. Roesky, F. Klinke, M. C. Schwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, Angew. Chem. **125**, 3036 (2013) (c) G. Frenking, N. Holzmann, Science **336**, 1394 (2012).

Chemical Bonding: Calculation versus Interpretation

Alexander F. Sax

Institute of Chemistry, University Graz, Graz, Austria

Chemical bonding is a special form of interaction between subsystems in a molecular system, the quantitative aspect of an interaction is its strength, the qualitative aspect is its origin. Strength of interaction can be measured with various scalar quantities, like energy differences, the absolute value of forces, force constants etc. , the most popular measure is the difference in the total energy. According to this measure chemical bonds are often classified as strong or weak; covalent bonds are examples of strong bonds, hydrogen bonds are examples of weak bonds.

Modern electron structure methods are successful in the quantitative description of strong chemical bonds, but they are not very useful for their interpretation, because the processes of spin rearrangements or charge transfer behind covalent bonding are local processes involving mostly 2 to 3 atoms, but such processes are frequently disguised when the electron structure methods are based on delocalized orbitals. Valence bond methods are much better suited for the interpretation than for quantitative calculation. Powerful methods for the calculation of bond strength should be supplemented by interpretative tools (VB like) that allow a better description of local effects.

Weak intermolecular interaction is the general term for the following four interactions: (i) Coulomb interaction of permanent multipoles, (ii) Coulomb interaction of induced multipoles, (iii) exchange and (iv) dispersion. The first two are classical electrostatic interactions, when the interacting subsystems have permanent dipoles caused by polar bonds the origin of the first long-range interaction can be localized on few atoms. Exchange and dispersion are of quantum origin, dispersion is caused by long range correlations of the electron distributions of the interacting subsystems; both quantum interactions are effective even in systems with homogenous charge distributions. Hydrogen bonds are traditionally attributed to a special arrangement of two electronegative atoms with a hydrogen atom in between: R1-X-H…Y-R2 where X-H is the hydrogen donor group, Y the acceptor atom and R1 and R2 are substituents. Although it is known that the dispersion interaction energy increases with the number of atoms in sufficiently short distance, the influence of the substituents on the hydrogen bonding interaction is mostly ignored and hydrogen bonding is regarded as an intrinsic property of the X-H…Y group.

Conical Intersections and Topological Insulating State of Molecules

Artur Izmaylov

Department of Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Ontario M1C 1A4, Canada; and Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

A conical intersection (CI) of several electronic states is one of the most common structural motives in molecules where the Born-Oppenheimer approximation breaks down. Besides possible inter-electronic transitions in nuclear dynamics, CIs also change the topology of the individual electronic surfaces, so that a nuclear wave-packet confined to a particular electronic surface must change the sign after encircling a locus of CI. This is a manifestation of the geometric phase associated with the parametric dependence of electronic wavefunctions on nuclear coordinates. We investigated influence of the geometric phase associated with CI on nuclear and electronic dynamics in series of two dimensional models. It was found that topological changes associated with the geometric phase can freeze transitions between coupled electronic states in a certain parameter range, and thus, give rise to an insulating phase. These results are highly relevant to nuclear dynamics in real molecules with Jahn-Teller distortion and open possibilities to design new molecular switches based on the topologically induced insulating state.

Understanding and Exploiting Chemical Bonding Patterns in the Design of Hybrid Organic-Semiconductor Structures

Mark E. Tuckerman

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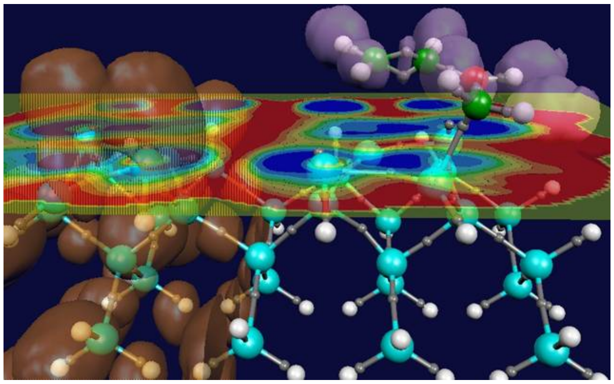
First-principle molecular dynamics (FPMD), the technique in which the interatomic forces in a molecular dynamics calculations are computed "on the fly" from electronic structure calculation, is employed to study the mechanism and suggest methods to control the addition of conjugated dienes to semiconductor surfaces in the creation hybrid organic-semiconductor structures. In particular, I will consider the addition of 1,3-butadiene and 1,3-cyclohexadiene to the Si(100)-2x1, 3C-SiC(001)-3x2, and SiC(100)-c(2x2) surfaces. FPMD calculations reveal both the product distributions, which can be compared to STM measurements, and the free energy profiles for the addition reactions on each of the surfaces. Moreover, using FPMD, I will show how specific modifications to the organic molecules and the choice of the surface can be made in order to control the reactions in such a way as to suggest a route to the creation of ordered layers on a semiconductor surface.



Infrared Photodissociation Spectroscopy of Mass-Selected Cluster Ions in the Gas Phase

Mingfei Zhou

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Fudan University, Shanghai, 200433, China

Infrared photodissociation spectroscopy is used to investigate the infrared spectra of cluster ions in the gas phase. The cluster ions are produced via a laser vaporization supersonic cluster source. The ions of interest are each mass-selected and their infrared spectra are measured via infrared photodissociation spectroscopy using a collinear tandem time-of-flight mass spectrometer. The structures of the ions are established by comparison of the experimental spectra with simulated spectra derived from density functional theory calculations. Recent results on transition metal carbonyl cluster cations and anions as well as transition metal oxide/dioxygen complexes will be presented. The results provide new insight into the structure and bonding of transition metal-containing cluster ions.

A Planar Tetracoordinate Carbon Zoo

Gabriel Merino

Departamento de Física Aplicada. Centro de Investigación y de Estudios Avanzados

Organic Chemistry would be very different if CH_4 was flat. The tetravalence of carbon, the stereochemistry or hetero-substituted C centers, and importance of the tetrahedral conformation to the properties of saturated carbon compounds is an inexhaustible source of intrigue for Organic Chemists. Now, the chemical literature is saturated with beautiful examples of unstable, strained, distorted, sterically hindered, bent, and battered organic structures. These atypical molecules have fascinated the chemical imagination, not only for the challenge of devising and synthesizing them, but also because they are often chemically feasible geometries with the promise of unusual patterns in their chemical bonding. The question of planar tetracoordinate carbon chemistry was opened in 1970 by Hoffmann, Alder, and Wilcox who proposed some rules for stabilizing ptCs in various molecular frameworks. While the number of ptC systems experimentally synthesized or detected is still quite low, several ptC molecules have been identified and proposed in silico. There are currently more than 20 millions organic compounds that follow the classical expectations for the tetrahedral and related bonding patterns for C compounds. So, the number of the ptC species that have actually been proposed computationally and identified experimentally is perhaps disappointingly small. However, to paraphrase Schleyer, each new ptC example is a landmark, not just in validating theory, but in establishing the limits of such seemingly outlandish structures.

In 1991, Schleyer and Boldyrev proposed a series of stable structures with planar tetracoordinate atoms (Al_4O, Al_4N^-, Al_3SiN, *cis*-$A1_2Si_2C$, *trans*-$A1_2Si_2C$) that were investigated at the *ab initio* MP4SDTW/6-311+G*//MP2/6-31G* level. Years later, Boldyrev and Simons identified general characteristics of planar tetracoordinate pentaatomic species composed of a first-row central atom and four second- or third-row atoms: such species have 17 or 18 valence electrons. A question that remains to be addressed at this stage, however is universality of the apparent 18 electron valence electron rule for the stability of ptC molecules in simple pentatomic molecules (not to be confused with the 18e- rule for organometallic compounds). We report herein a comprehensive analysis of 18-electron pentatomic neutral, cationic, and anionic, systems spanning the set of main group elements in the periodic table. This systematic investigation of the potential energy surfaces of these molecules has been undertaken to determine the population of a potentially massive family of 18 valence electrons pentaatomic clusters for which the global minima contains a ptC center. We imposed two basic restrictions on our set: we required that (1) all the atoms in the clusters are main group elements, and (2) the charge of the clusters are in the range of [+2,-2]. Within those constraints we uncover a veritable zoo of 600 candidates structures of which some 200 clusters are global minima containing a ptC! This outcome appears to at least double the number the ptC systems reported in the literature to date.

What is There to Battle and Conquer Aromaticity?

Anastassia N. Alexandrova

and UCLA Chem 126/226 Classes of Winters 2012 and 2013:
Mioy T. Huynh, Michael J. Nayhouse, Jonathan L. Kuo, Arek V. Melkonian, Gerardo Chavez, Nina M. Hernando, Mathew D. Kowal, Chi-Ping Liu, Lilit Gabrielyan, Derek Urwin, Daniel P. Buchan, Ivan P. Kostirkin, Yunshi Tan, Alex J. Yeh, Paul M. Abukhalil, Brian R. Lydon, Michael R. Nechay

Department of Chemistry and Biochemistry, University of California, Los Angeles, USA

There has been an avalanche of observations of aromaticity in small inorganic clusters. However, though prominent, it is an intrinsically weak bonding effect. We show how aromaticity can be overruled by partial covalency, even in all-metal clusters. Covalency and aromaticity appear to be opposing each other in defining cluster structures. We will demonstrate how the two bonding effects can be used as two knobs of rational cluster design.

Study of Condensed Phase Post-Transition State and Microsolvation Dynamics by Direct Dynamics Simulations

William L. Hase

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX USA 79409

An important question in chemical kinetics is the manner in which solvent molecules affect the reaction dynamics. This question is being probed by direct dynamics simulations of the post-transition state dynamics for the BH_3 + propene hydroboration reaction and for the bimolecular dynamics for the $OH^-(H_2O)_n$ + CH_3I reaction. The solvent has only a minor effect for the former, but a substantial effect for the latter. The solvent may affect the reaction dynamics by altering the potential energy surface and/or by removing energy from the reactive system.

(Un)Chemical Bonding: Surprises in Non-Covalent Interactions in Molecular Systems

Alexandre Tkatchenko

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Non-covalent van der Waals (vdW) interactions are ubiquitous in molecules and condensed matter, and play a crucial role in determining the structure, stability, and function for a wide variety of systems. The accurate prediction of these interactions from first principles is a substantial challenge because they are inherently quantum mechanical phenomena that arise from correlations between many electrons within a given system. We discuss the recently developed efficient method [1,2] that combines quantum and classical electrodynamics and accurately describes the nonadditive many-body vdW energy contributions arising from interactions that cannot be modeled by an effective pairwise approach. It is demonstrated that such contributions can significantly affect the behavior of biological (DNA), chemical (molecular crystals), and condensed (bulk, hybrid interfaces) systems. In most of these cases it is found that collective vdW interactions play a noticeable, if not crucial role, not just for quantitative values but also for the qualitative behavior [3,4,5].

[1] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).
[2] A. Tkatchenko, R. A. DiStasio Jr., R. Car, and M. Scheffler, Phys. Rev. Lett. 108, 236402 (2012).
[3] R. A. DiStasio Jr., O. A. von Lilienfeld, and A. Tkatchenko, Proc. Natl. Acad. Sci. USA 109, 14791 (2012).
[4] N. Marom et al., Angew. Chem. (2013); doi: 10.1021/jz400226x.
[5] V. V. Gobre and A. Tkatchenko, Nat. Comm., to be published (2013).

Two Bonds with One Photon as Reported by Solid State Dual Fluorescence

Artëm E. Masunov

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The emission spectrum of the crystalline phase of two organic (isonaphthalene imide and pyridine-2-aldoxime) and two coordination compounds (with pyridine-2-aldoxime as chelating ligand) demonstrate dual fluorescence, with short and long wavelength components. The geometrical and electronic structure of the ground and excited states of the isolated molecules and their aggregates is investigated using Density Functional Theory (DFT) methods. The simulations indicate that dual fluorescence can be explained by coexistence of the excited states of ππ* and *n*π* nature. While specific C=N π-bond is broken in the ππ* state (which is consequently twisted out of molecular plane), the coordination N:→Zn bond is broken in *n*π* state. Both states, therefore, relax into very different geometries, so that they live long enough to emit before their interconversion. The simulations also indicate, that unconstrained relaxation of the isolated molecules in solution opens a pathway to radiativeless relaxation, while environmental confinement in the crystalline state prevents it. As a result, dual fluorescence is only observed in the solid state, and not in solution.

Cyber-Enabled Discovery of Reaction Mechanisms

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One of the chemically relevant tasks that can be delegated to scientific cyber-structure is prediction of viable transformations of a given set of molecules. A possible solution to the problem is to construct a network of thermodynamically and kinetically viable local transitions on respective potential energy surface. A computational framework that is being developed for this purpose relies on combinatorial and quantum chemistry. This combination facilitates affordable production of knowledge in contrast to pure data-mining. Current results of the investigation of formose reaction and possible extensions are discussed.

What's New in Natural Bond Orbital Theory

Frank Weinhold

Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

We provide an overview of recent developments in Natural Bond Orbital (NBO) theory and applications, including structural program changes, new analysis options, and generalized search and labeling conventions of the recently released *NBO 6.0* program version. Particular attention is drawn to a fundamentally new type of 2c/2e chemical bonding phenomenon (metallic $\hat{\sigma}$-type "long-bonding") which these changes now make routinely accessible to analysis.

Avoiding the Born-Oppenheimer Separation between Electrons and Protons: Explicitly Correlated Wavefunctions and Multicomponent Density Functional Theory

Sharon Hammes-Schiffer

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Recent advances in the development of the nuclear-electronic orbital (NEO) approach will be presented. In this approach, selected nuclei are treated quantum mechanically on the same level as the electrons with molecular orbital or density functional techniques. For hydrogen transfer and hydrogen bonding systems, typically the hydrogen nuclei and all electrons are treated quantum mechanically. Electron-proton dynamical correlation is highly significant because of the attractive electrostatic interaction between the electron and the proton. An explicitly correlated Hartree-Fock scheme has been formulated to incorporate explicit electron-proton correlation directly into the variational self-consistent-field framework with Gaussian-type geminal functions. A multicomponent density functional theory has also been formulated, and electron-proton functionals have been developed based on the explicitly correlated electron-proton pair density. Initial applications to hydrogen-containing systems illustrate that these new methods enhance the accuracy of calculated molecular properties, such as geometries and frequencies, and provide insight into the coupling between electronic and nuclear motions. This approach is particularly useful for applications to proton-coupled electron transfer reactions, where electron-proton nonadiabatic effects are significant. Furthermore, recent applications to positronic systems illustrate that this approach provides accurate electronic, postitronic, and electron-positron contact densities, as well as annihilation rates.

(1) S. P. Webb, T. Iordanov, and S. Hammes-Schiffer, "Multiconfigurational nuclear-electronic orbital approach: Incorporation of nuclear quantum effects in electronic structure calculations," *J. Chem. Phys.* **117**, 4106-4118 (2002).
(2) M. V. Pak and S. Hammes-Schiffer, "Electron-proton correlation for hydrogen tunneling systems," *Phys. Rev. Lett.* **92**, 103002 (2004).
(3) C. Swalina, M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, "Explicit electron-proton correlation in the nuclear-electronic orbital framework," *J. Phys. Chem. A* **110**, 9983-9987 (2006).
(4) A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, "Development of electron-proton density functionals for multicomponent density functional theory," *Phys. Rev. Lett.* **101**, 153001 (2008).
(5) C. Swalina, M. V. Pak, and S. Hammes-Schiffer, "Analysis of electron-positron wavefunctions in the nuclear-electronic orbital framework," *J. Chem. Phys.* **136**, 164105 (2012).
(6) A. Sirjoosingh, M. V. Pak, and S. Hammes-Schiffer, "Multicomponent density functional theory study of the interplay between electron-electron and electron-proton correlation," *J. Chem. Phys.* **136**, 174114 (2012).

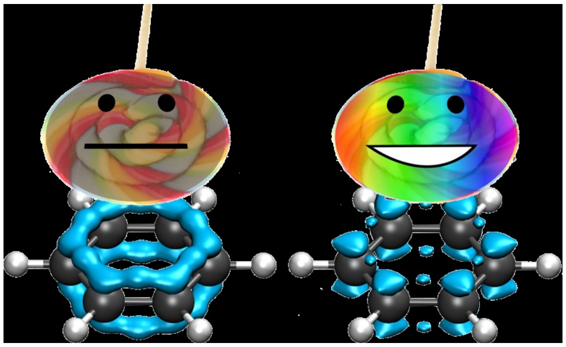
Modern Computational Approaches for Quantifying Inter- and Intramolecular Interactions

Jerome F. Gonthier and Clémence Corminboeuf

Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Intra- and intermolecular van der Waals interactions govern a variety of structural and energetic phenomena such as self-assembly processes, protein–drug interactions, crystal packing of organic molecules and isomer energy differences. We here discuss two approaches that enhance our understanding of both intra- and intermolecular interactions.

We first introduce the LOLIPOP criterion as a visual and quantitative tool to detect π-conjugated frameworks presenting enhanced π-stacking ability.[1] The utility of LOLIPOP is illustrated by identifying tailored chemosensors for caffeine and TNT.



Analyses of intramolecular interactions are, on the other hand, scarcer and theoretically more challenging. Among the various existing decomposition schemes, Symmetry-Adapted Perturbation Theory (SAPT) [2] may be considered as the most successful, as it naturally decomposes the interaction energy into physical and intuitive terms such as electrostatics, exchange, dispersion. However, there is no such energy decomposition scheme available for intramolecular interactions. Our second approach attempts to fill the gap by obtaining a zeroth-order wavefunction and energy for an intramolecular variant of the SAPT formalism. Challenges associated with the scheme will be discussed based on numerical applications on the illustrative protobranching interaction.

[1] Gonthier, J. F.; Steinmann, S. N.; Roch, L.; Ruggi, A.; Luisier, N.; Severin, K.; Corminboeuf, C. *Chem. Commun.,* **2012**, 48, 9239.
[2] Jeziorski, B.; Moszynski, R.; Szalewicz, K., *Chem. Rev.* **1994**, *94*, 1887.

Applications of the Gauge-Including Magnetically-Induced Current (GIMIC) Method

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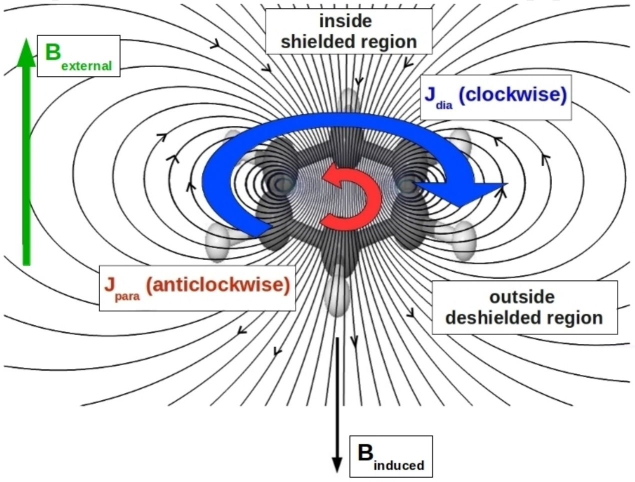
The GIMIC method is used to calculate magnetically induced current densities in molecules [1,2,3]. GIMIC calculations provide detailed information about electron delocalization, aromatic character, and current pathways in molecules [4,5]. An overview of applications of the gauge including magnetically induced current method (GIMIC) is presented. The GIMIC method has recently been extended rendering magnetic-field-direction independent calculations of gauge-independent current densities feasible [6].



Magnetically induced current density in molecular rings.

The applications of the GIMIC method include current-density calculations on hydrocarbons, complex multi-ring organic nanorings [7,8], porphyrins [9], Möbius twisted molecules [10,11,12], inorganic and all-metal molecular rings [13], and openshell species [2]. Recent studies on hydrogen-bonded molecules indicate that GIMIC can also be used to estimate hydrogen-bond strengths without fragmentation of the system [14]. Results obtained using magnetic-field-direction independent GIMIC calculations will also be presented.

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[2] S. Taubert, J. Jusélius, D. Sundholm, J. Chem. Phys. 134 (2011) 054123
[3] H. Fliegl, S. Taubert, O. Lehtonen, D. Sundholm, Phys. Chem. Chem. Phys. 13 (2011) 20500
[4] H. Fliegl, D. Sundholm, S. Taubert, J. Jusélius, W. Klopper, J. Phys. Chem. A 113 (2009) 8668
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Characterizing Chemical Bonds and Aromaticity from a Density Matrix Perspective

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The chemical bond is central to chemistry but is plagued by the fact that it has no formal quantum mechanical definition. This renders it, much like atoms in molecules, a subject of hot debate.

Based on the Hirshfeld-I model for atoms and bonds [1], it will be shown how a coherent theory encompassing atoms, bonds and aromaticity can be derived to describe both with respect to the electron density function but also chemical reactivity. Multicenter indices, as one of the more successful aromaticity delocalization indices [2-3], will be derived from a density matrix perspective [4].

It will be shown how Fukui functions can be derived for chemical bonds to aid in understanding bond reactivity and a Fukui matrix background of the Fukui function will be given [5], including proper treatment of electron correlation and degeneracy [6].

Finally, constrained quantum chemistry is presented as a way to go from a posteriori analysis of chemical bonds to evaluation of wave functions that produce a desired atom in the molecule [7] or chemical bond.

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Modeling Surface-Deposited Sub-Nano Catalysts with Explicit Solvent

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To model the catalytic reactions in realistic conditions (high temperature / high pressure), we developed a QM/MM based Monte Carlo sampling method for computing the free energy perturbation (FEP) of a reaction catalyzed via sub-nano clusters with solvent molecules treated explicitly. We developed an algorithm that combines sequential Markov-chain Monte Carlo method with particle filter algorithms from artificial intelligence to address the vast phase space exploration problem.

Metal-Surface, and Adsorbate-Metal Bonding in Supported, Size-Selected Model Catalysts

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Supported catalysts typically contain metal clusters or nanoparticles in various oxidation states, dispersed on the surface of a support material. The activity of such materials is controlled by a balancing act in which the binding of reactants to the catalytic active site(s) must be strong enough to destabilize the bonds that need to break or be attacked, but not so strong that the active sites become poisoned by adsorbates that bind stably at the operating temperature. The geometry and electronic structure of the active site are important factors in tuning activity, and both factors can be tuned by varying the catalytic metal cluster size, or by changing or modifying the support material. Real catalysts are structurally complex heterogeneous materials, and are therefore quite difficult to study in any detail. As a result, there are very few examples of supported catalysts where the exact nature of the active sites is known. Our approach to this problem is to reduce the heterogeneity by studying model catalysts, prepared by depositing pre-formed, size-selected metal clusters onto planar (single crystal or thin film) supports, to create samples where, at least as deposited, the active sites should be reasonably homogeneous. This capability allows us to probe the chemistry using area-averaging surface spectroscopy and chemistry tools.

Results will be presented for several systems, including CO oxidation over $Pd_n/TiO_2(110)$ and Pd_n/alumina films grown on several single crystal supports, and electro-catalysis over Pt_n/glassy carbon and Pt/ITO. One common feature, observably only by doing size-selected studies, is that activity appears to be anti-correlated with metal core level binding energies. We also examine the valence electronic structure, and here the correlations are not so obvious.

Orbital Analysis, a Powerful Tool to Guide the Design of Catalysts

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The design of catalysts and the construction of kinetic models often start from molecular-scale hypotheses about the reaction mechanism, the structure of the active sites and the nature of the rate and selectivity determining steps. Such molecular-scale hypotheses are difficult to test experimentally. First-principle modelling on the other hand is ideally suited to evaluate such molecular-scale concepts and ideas.

In this presentation, I will discuss how molecular modelling and analysis of the orbitals involved in bond forming and bond breaking steps has guided the design of both heterogeneous and homogeneous catalysts in my group, such as the first Pd-based aryl-fluorination catalyst [1], highly active catalysts for C-O and C-S coupling [2], as well as the design of heterogeneous Co-based catalysts with greatly improved stability for the production of clean fuels [3].

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Photochemically Induced Cold Synthesis of Complex Organic Molecules on Titan and in the Interstellar Medium: A View from Ab Initio/RRKM Calculations

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The presentation will overview results of high-level ab initio quantum chemical calculations of potential energy surfaces, combined with statistical theory calculations of reaction rate constants and product branching ratios, carried out in order to unravel the growth mechanisms of complex organic molecules, including polyacetylenes, cyanopolyacetylenes (nitriles), cyclic (aromatic) hydrocarbon molecules, polycyclic aromatic hydrocarbons (PAHs), and nitrogen-containing polycyclic aromatic compounds (N-PACs) under low-temperature conditions of Titan's atmosphere or in the interstellar medium (ISM). These reactions include additions of the ethynyl (C_2H) and cyano (CN) radicals to various unsaturated hydrocarbons, as well as reactions of the phenyl radical (C_6H_5) with vinylacetylene and 1,3-butadiene. The reactions exhibit no entrance barrier and have their intermediates, transition states and products lying lower in energy than the initial reactants. This makes the ethynyl and CN addition mechanisms of the molecular growth attainable even at very low temperatures characteristic for reducing atmospheres of outer planets and moons in the Solar System and for the ISM. Therefore, the proposed mechanisms can drive the molecular growth if C_2H and CN radicals are abundant from the photolysis of acetylene and HCN, respectively, and their reaction counterparts are also present.

The results of the ab initio/statistical calculations are compared with recent experimental studies of these reactions performed in crossed molecular beams under single-collision conditions.

On the Formation of Interstellar Organo Silicon Molecules

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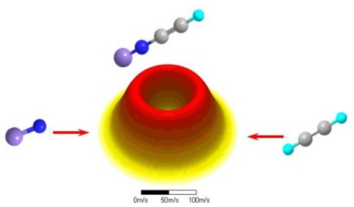
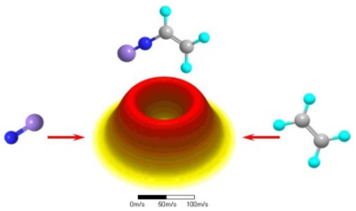
During the last decade, the molecular processes involved in the formation of organosilicon molecules have received considerable attention from the astrochemistry community. This is due to the key role of silicon-bearing molecules in the formation of silicon carbide dust grains in the outflow of circumstellar envelopes of carbon rich Asymptotic Giant Branch (AGB) stars like IRC+10216, where temperatures can rise up to a few 1,000 K close to the photosphere of the central star. IRC+10216 acts as a natural laboratory to understand the synthesis of organosilicon molecules and their connection to dust formation. However, the basic molecular processes, which link the circumstellar silicon and carbon chemistries, are far from being understood.

For the first time small organosilicon molecules silaisocyanoacetylene ($SiNC_2H$) silaisocyanoethylene ($SiNC_2H_3$) and silacyclopropenylidene (c-SiC_2H_2) have been synthesised in the gas phase through the reaction of silicon nitride radicals ($SiN(X^2\Sigma^+)$) with acetylene ($C_2H_2(X^1\Sigma_g^+)$) and ethylene ($C_2H_4(X^1A_g)$), and D1-silylidyne radicals ($SiD(X^2\Pi)$) with acetylene (C_2H_2), respectively. Here, we investigate the reaction dynamics via single collision condition cross beam experiments coupled with *ab initio* calculations. The reactions are found to undergo a radical-hydrogen atom exchange mechanism through the formation of long-lived reaction intermediates in overall exoergic reactions that are mainly barrierless. We find the size and diffuse orbitals of the silicon atom play a significant role in the structure of the reaction products formed. In the silicon nitride ($SiN(X^2\Sigma^+)$) reactions the nitrogen atom is preferentially bound to the π-electron denisty of the hydrocarbon reactant, which is in direct contrast to the isoelectronic reactions of cyano ($CN(X^2\Sigma^+)$) radicals with acetylene ($C_2H_2(X^1\Sigma_g^+)$) and ethylene ($C_2H_4(X^1A_g)$) where the carbon atom preferentially binds to the hydrocarbon reactant. In the D1-siliydyne reaction with acetylene ($C_2H_2(X^1\Sigma_g^+)$) we find that the diffuse orbital nature of the silicon atom prefers a tricyclic arrangement reinforcing the notion that silicon compounds prefer low order bonds. In comparison, methylidyne ($CH(X^2\Pi)$) reactions with acetylene ($C_2H_2(X^1\Sigma_g^+)$) show that carbon preferentially forms non-cyclic molecules (C_3H_2) with higher order bonds. Despite the isoelectronicity between silicon and carbon bearing radicals they form markedly different compounds in comparable environments such as the interstellar environment.





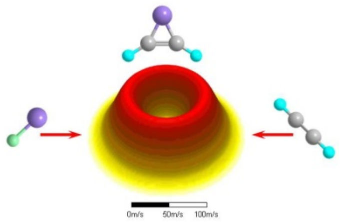


Fig. 1: Center-of-mass velocity contour flux maps for the reactions of silicon nitride radicals with acetylene (left) and ethylene (center) and D1-silylidyne radical with acetylene at collision energies of 35.7 $kJmol^{-1}$, 35.9 kJ mol^{-1} and 41.2 kJ mol^{-1} forming silaisocyanoacetylene ($SiNC_2H$), silaisocyanoethylene ($SiNC_2H_3$) and silacyclopropenylidene ($c\text{-}SiC_2H_2$) molecules, respectively, plus a hydrogen atom.

On Excited State Aromaticity in Various Forms: a Focus on Aromatic Chameleons

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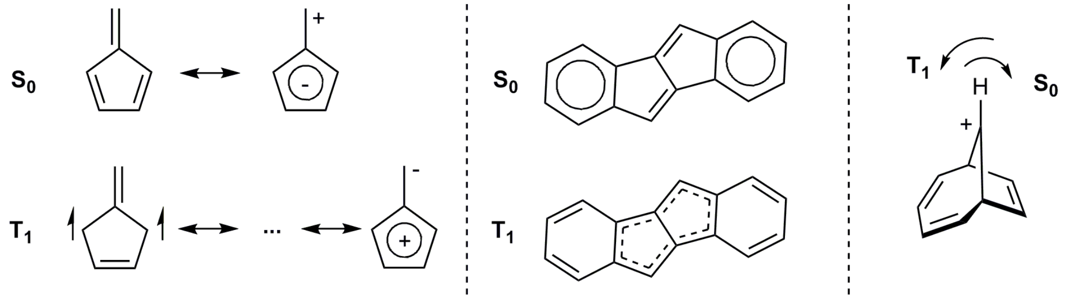
Four decades ago Colin Baird used perturbation molecular orbital (PMO) theory to show that annulenes with $4n$ π-electrons are aromatic while those with $4n+2$ are antiaromatic in their lowest ππ* excited triplet states (T_1).[1,2] During the last years, a series of high-level quantum chemical investigations have solidly confirmed the validity of Baird's rule,[3] and it has been shown that it is also applicable to the lowest singlet excited state (S_1).[4,5] Yet, even though the Dewar-Zimmerman approach for analysis of the allowedness *vs.* forbiddeness of pericyclic reactions (both thermal and photochemical) in terms of transition state aromaticity/antiaromaticity is known by organic chemists, Baird's rule has found no widespread support within the experimental community, despite that it can be highly useful for the rationalization of earlier reported photophysical and photochemical properties and processes.[6]

We earlier coined the term "aromatic chameleons" to describe compounds that can adapt some aromatic character in several electronic states by shifting the electron density so as to obey to the different aromaticity rules.[7] In these studies we focused on fulvenes and fulvalenes as dipolar aromatic chameleons as they are influenced dipolar Hückel- *vs.* Baird-aromatic resonance structures in S_0 and T_1/Qu_1, respectively. However, aromatic chameleon behavior of similar type can be found in a number of other compound classes as will now be discussed. Biphenylene, dibenzopentalene and similar compounds with both $(4n+2)$π- and $4n$π-electron paths are examples of compounds that may be called nonpolar aromatic chameleons. And nonclassical carbocations in which a bridging cationic carbon can participate in either the formation of a 2π-electron or in a 4π-electron cycle may be termed homoaromatic chameleons.



polar aromatic chameleons | nonpolar aromatic chameleons | homoaromatic chameleons

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Solid State Studies of Electronic and Magnetic Properties in Topological Insulators

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In recent years the emergence of gapless topologically protected edge states in the solid state has led to searches for new phases of condensed matter in new and existing materials. For example, certain thermoelectrics and Kondo insulators have been shown to be topological insulators. The protected edge states in topological insulators are due to the combination of spin-orbit coupling and time-reversal invariance. Examples of exotic phenomena include the quantum anomalous Hall effect, fractional quantum anomalous Hall effect, fractional time-reversal invariance, topological Kondo insulator, topological crystalline insulator and the topological magneto-electric effect. However, the interesting properties of topological materials are found at edges and interfaces, making them challenging to study from the experimental standpoint. In this talk, we will review recent advances in experimental techniques to study the electronic and magnetic properties of such topological materials. Among the novel techniques, we shall discuss radioactive ion beam spectroscopy, electrically-detected electron spin resonance and nuclear magnetic resonance.

Our group has been carrying out experiments at TRIUMF using low energy spin-polarized muon and lithium ion beams to resolve properties as function of depth, with nanoscale resolution. Studies of material defects in the bulk will also be discussed. Results from these ongoing experiments as well as other experiments will be discussed. Ultimately, the development of new experimental methods is expected to lead to not only insight for improving material properties but may also enable the development of composite materials with optimized properties.

Topological Mis-Bonding in Dislocations and Grain Boundaries of 2D Materials: Graphene, h-BN, Metal-Disulfides

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“Dislocation”, “defect”, “disorder” are familiar terms in medicine and carry no good news. In materials, these things are also often detrimental to the properties, reducing mechanical strength, conductivity, stability [1]. In our theoretical studies of grain boundaries, dislocations and edges in 2D nitrides [2] and disulfides [3] we find a few examples where such defects and theiraffected chemical bonds can bring about useful functionality, serving as electrically conducting imbedded nanowires [3]or evenmagnetic elements, forming at certain conditions semi-metallic spin channels [4].

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Barium Polyphosphides for Thermoelectric Energy Conversion: Synthesis, Structure, and Bonding

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Development of the novel materials where charge and heat transport are partially de-coupled is a key factor for the next generation of thermoelectric materials. New compounds with high density of states near Fermi level and low thermal conductivity are required for efficient thermoelectrics. In this report we present barium-transition metal polyphosphides as a base for new thermoelectric materials. Electron balance in these compounds is achieved in a way similar to classical Zintl phases assuming closed shell d^{10} configuration of the transition metal. Structural and bonding diversity of the barium polyphosphides will be illustrated by examples of BaP_3 and BaM_2P_4 polymorphs (M = Cu, Au). Influence of the local atomic coordination of the gold atoms in $Ba_8Au_{16}P_{30}$ on the heat transfer in solids will be discussed. In the latter compound, a tendency for gold to relax from the tetrahedral coordination by phosphorus atoms leads to formation of highly coherent twinning and intergrowths defects as well as anti-phase boundaries as evidenced by high resolution and high angle annular dark field scanning transmission electron microscopy. Such interfaces are “invisible” for the charge carriers but serve as efficient scattering centers for the heat carrying phonons. This results in unprecedented low value of the room temperature lattice thermal conductivity ($0.18\ Wm^{-1}K^{-1}$).

Solvent-Driven Reductive Activation of CO_2 by Gold and Silver Anions

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Catalytic activation and electrochemical reduction of CO_2 for the formation of chemically usable feedstock and fuel are central goals for establishing a carbon neutral fuel cycle. The role of solvent molecules in catalytic processes is little understood, although solvent-solute interactions can strongly influence activated intermediate species. We use vibrational spectroscopy of mass-selected $M(CO_2)_n^-$ (M = Au, Ag) cluster ions to probe the solvation of MCO_2^- as a model for a reactive intermediate in the reductive activation of a CO_2 ligand by a single-atom catalyst. We highlight effects of solvation at the partially reduced CO_2 moiety vs. solvation of the metal atom, discuss reductive activation as a function of the number of solvent molecules, and compare the results for Au with those for Ag.

Covalent Gold

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Gold is known to be the noblest of all metals because of the relativistic stabilization of its outer 6s orbital. The relativistic effects also lead to destabilization of the 5d orbitals, reducing the 6s-5d energy gap and enhancing s-d hybridization. Therefore, in contrast to its lighter congeners, gold exhibits significant covalent bonding characters and a remarkable repertoire of chemistry, which are increasingly being exploited in catalysis and nanotechnology. This talk presents a brief account of recent experimental efforts in our laboratory using photoelectron spectroscopy that lead to the observation of covalent bonding in several relatively simple Au compounds [1]: Au oxides (AuO^- and AuO_2^-), sulfides (AuS^- and AuS_2^-) [2], and the well-known $Au(CN)_2^-$ complex [3]. In a series of Au-Si and Au-B mixed clusters, it has also been found that gold atoms behave like H atoms, forming auro-silicon [4,5] and auro-boron clusters [6,7] with strong covalent bonding, analogous to the corresponding silicon and boron hydrides, such as the tetrahedral auro-silane ($SiAu_4$) versus silane (SiH_4). In very recent studies, we have found unusually strong bonds between gold and alkynyl ligands, which may provide valuable insight into the mechanisms of alkylnyl activation in homogeneous gold catalyses [8].

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Itinerant Magnetic Borides Containing Planar B6 Rings: Experiment and Theory

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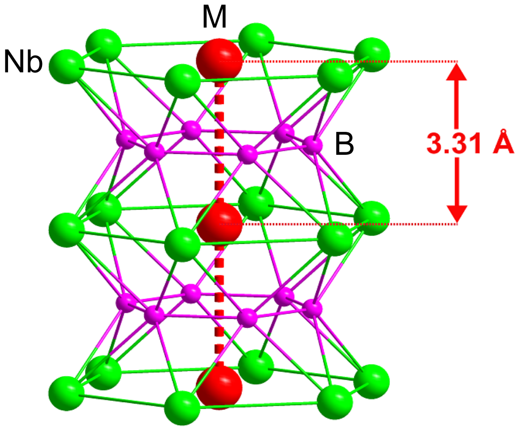
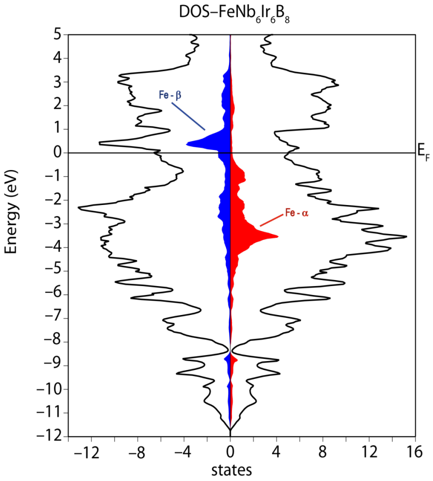
We have recently reported on a novel compound, $Ti_7Rh_4Ir_2B_8$, containing in its structure the first planar B_6 ring found in the solid state. [1] The occurrence of such a planar B_6 ring, also found in the gas phase [2], in metal borides may have been expected because it can be considered the starting motif to generate the boron layer in the AlB_2-type structure. Other isostructural borides were also published recently. [3] In recent years we have been able to substitute Ti (or Nb)-chains by chains of magnetically active elements (Cr, Mn, Co, Fe, Ni) to produce new itinerant magnets (antiferro-, ferri- and ferromagnets).[4] Now, we have transferred this synthetic strategy to the ternary phase $Nb_7Ir_6B_8$ and obtain new quaternary phases containing one dimensional sandwich-like MB_6 (M = Cr, Mn, Co, Fe, Ni) substructures (Figure 1, left). [5] Theoretical DFT investigations predict various magnetic characteristics including Pauli paramagnetism as well as ferromagnetism (Figure 1, right) among the series. The predicted magnetic properties have been confirmed experimentally. It is found that the chemical bonding around the magnetically active elements play a significant role in the occurrence of these magnetic properties.





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Geometric and Electronic Structural Contributions to Fe/O_2 Reactivity

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Non-heme iron enzymes either activate substrate using a ferric center or dioxygen using a ferrous site. The latter has been extremely difficult to study. Thus we have developed new spectroscopic methodologies that provide geometric and electronic structural insight into the ferrous center, its interaction with cosubstrates for activation of dioxygen, and the nature of the Fe(III)-OOH and Fe(IV)=O intermediates generated in this reaction.

Blurring to Bring Binding Free Energies into Focus

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Docking calculations coupled with binding free energy estimates (scoring) are a mainstay of structure-based drug design. This talk addresses how to use ensemble principles to estimate and reduce uncertainty of computed binding free energies. In particular, we analytically demonstrate that sampling reduces computed binding free energy uncertainties and we will highlight two methods that incorporate these concepts. The first approach incorporates sampling by “blurring” a ligand in a given binding pocket and then using statistical mechanical concepts to estimate the binding free energy. This method is brute force in its construction in that the phase space of the protein-ligand complex has to be systematically delineated leading to significant computational expense. The second approach, which we call the moving type method, employs a more elegant approach to generate the protein-ligand ensemble by using a “binned” pairwise knowledge-based potential combined with atom pair probabilities extracted from known protein-ligand complexes. This allows us to compute binding free energies rapidly, accurately and yields molecular poses at a minimal computational cost.

Molecular Mechanisms of RNA Catalysis

Darrin York

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A multiscale modeling approach is taken to study the molecular mechanisms of RNA catalysis. These include the use of new quantum chemical models, sampling techniques, and methods to estimate the free energy and predict experimental observables such as mutational, thio/rescue and kinetic isotope effects. Recent advances in the development of linear-scaling quantum methods for molecular simulations of biocatalysis will be presented. Applications will focus on phosphodiester bond cleavage catalyzed by several small self-cleaving ribozymes, and the mechanisms compared with those of protein enzyme analogues and non-enzymatic reactions in solution.

Redox-Active Ribonucleotides Connect DNA Repair and the RNA World

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Present-day organisms are under constant environmental stress that damages bases in DNA leading to mutations, such that the error rate would be catastrophic were it not for the action of DNA repair processes. How did early RNA genomes protect themselves from chemical damage, particularly UV photochemistry that would have hampered non-enzymatic replication and led to a mutation rate too high to pass on accurate sequence information from one generation to the next? We describe an analysis of simple derivatives of guanosine and other bases that show two prerequisites for flavin-like photolyase activity: a significantly lowered one-electron reduction potential and a red-shifted adsorption spectrum such that they are capable of excited-state electron transfer in a window of the spectrum that does not form cyclobutane pyrimidine dimers. Computational studies (Jack Simons, U of U) help explain some of the behavior of the excited states of purines in duplex DNA.

Understanding Non-Covalent Interactions with Aromatic Rings

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Substituents and heteroatoms can be used to tune the strength and geometry of non-covalent interactions, which can provide a means of controlling many supramolecular assembly phenomena. We will discuss recent progress understanding the influence of substituents and heteroatoms on π-stacking and other non-covalent interactions involving aromatic rings. Traditional models of substituent effects in π-stacking interactions, for example, are cast in terms of substituent-induced changes in the π-system of the substituted ring. We provide an alternative model based on direct, local interactions between the substituents and the proximal vertex of the other ring. The origin of anion/π interactions will also be discussed.

Structure and Fluxionality of Decorated and Bare Boron Clusters in the Gas Phase

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It has been shown by electrospray ionization–ion-trap mass spectrometry that $B_{12}I_{12}^{2-}$ converts to an intact B_{12} cluster as a result of successive stripping of single iodine radicals or ions. We report the structure and stability of all intermediate $B_{12}I_n^-$ species (n = 11 to 1) determined by means of first-principles calculations. The initial predominant loss of an iodine radical occurs most probably via the triplet state of $B_{12}I_{12}^{2-}$, and the reaction path for loss of an iodide ion from the singlet state crosses that from the triplet state. Experimentally, the boron clusters resulting from $B_{12}I_{12}^{2-}$ through loss of either iodide or iodine occur at the same excitation energy in the ion trap. It is shown that the icosahedral B_{12} unit commonly observed in dodecaborate compounds is destabilized while losing iodine. The boron framework opens to nonicosahedral structures with five to seven iodine atoms left. The temperature of the ions has a considerable influence on the relative stability near the opening of the clusters. The most stable structures with five to seven iodine atoms are neither planar nor icosahedral.

In the same experiment, a gas-phase dimerization of the $B_{12}I_n^-$ (n = 9, 8) anions to $B_{24}I_{2n}^{2-}$ dianions was observed. We have studied this intriguing phenomenon by means of density functional theory calculations. The dimerization process is found to be thermodynamically favorable, and the stability of the lowest-energy structures is substantiated by molecular dynamics simulations. The calculations imply that the experimentally observed $B_{24}I_{18}^{2-}$ and the hypothetical $B_{24}I_{16}^{2-}$ species are formed through dimerization of the respective $B_{12}I_n^-$ (n = 9, 8) monomers, rather than through loss of two I radicals from $B_{24}I_{2n+2}^{2-}$ dimers. Electronic properties such as natural charges, vertical detachment energies (VDEs), frontier molecular orbitals (FMOs), and HOMO–LUMO gaps are computed and analyzed in detail for all monomers and dimers. The analysis shows that the most stable $B_{24}I_{2n}^{2-}$ dimers are formed through two 2c-2e B–B and two 3c-2e B–I–B bridges between the parent $B_{12}I_n^-$ (n = 9, 8) monomers. These new bridging bonds engage the deiodinated (bare) faces of the two B_{12} icosahedra, as well as one (per monomer) of the nearest boron neighbors and its iodine substituent.

Finally, we address the issue of fluxionality in planar boron clusters. We find that a variety of $B_n^{(k)}$ clusters (n >10) contain fluxional units, and that fluxionality is promoted by certain structural patterns, while others create stiff structures.

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The Noncovalent Bond. Is it a Contradiction in Terms?

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When thinking about a chemical bond, most thoughts turn to the standard (2e-2c) covalent bond where an electron pair is shared between two atoms, with a bond strength on the order of 100 kcal/mol or more. Noncovalent bonds typically occur between a pair of molecules, and are much weaker, usually less than 10 kcal/mol. Perhaps the most famous of this category is the H-bond, wherein a lone pair of electrons from the proton acceptor molecule involves the bridging H in a second, weaker, bond. More correctly, this electron pair migrates partially over to the donor molecule, largely bypassing the proton that lies between the two molecules, forming a (2e-3c) noncovalent bond. Recent years have brought increasing attention to analogs of this interaction, in which the role of the bridging proton is played by a halogen, chalcogen, or pnicogen atom. Calculations, bolstered by some experimental data, have suggested that the latter interactions are comparable in binding strength to the better known H-bonds. There are fundamental questions as to the ultimate source of the attraction in these bonds, and their degree of similarity to H-bonds. Various perspectives on this issue will be discussed, including energy decomposition, measures of charge transfer, the forces that lead to the equilibrium orientation, internal geometry changes caused by the interaction, angular distortion energies, and electron density redistributions.

Aromaticity in Fullerenes and Endohedral Metallofullerenes. Effects on Electronic Structure, Molecular Structure, and Reactivity

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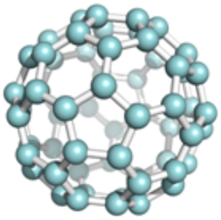
After the discovery of fullerenes in 1985, it was initially assumed that these molecules exhibited extremely stable aromatic character. However, this initial hypothesis was soon rejected in the light of the numerous chemical reactions undergone by fullerenes. Now, it is considered that these species have an ambiguous aromatic character, with certain properties being characteristic of aromatic compounds while others not. In general, aromaticity is not considered an essential factor when analyzing the molecular and electronic structure of fullerenes or their reactivity. In this work, we aim to change this assumption by showing several cases in which aromaticity plays a central role to explain the properties and chemical behavior of fullerenes.



Our first example is related to the electronic structure of fullerenes and refers to the open-shell spherical aromaticity rule. This rule is the extension of the 4N Baird's rule of aromaticity in annulenes to spherical compounds having a same-spin half-filled last energy level. This situation is reached in spherical systems for a number of electrons equal to $2N^2+2N+1$ and with a spin of N+1/2. We prove this rule by showing that open-shell icosahedral fullerenes following the $2N^2+2N+1$ rule are aromatic.[1] This $2N^2+2N+1$ rule for spherical systems is related to the 4N

Baird's rule for annulenes in the same way the $2(N+1)^2$ Hirsch's rule for spherical compounds is the analog of the $4N+2$ Hückel's rule.

The second example involves the molecular structure of fullerenes. Endohedral metallofullerenes (EMFs) are carbon cages incarcerating metal clusters. These clusters are encapsulated in cages that in most cases are far from being the most stable isomer in the corresponding hollow fullerenes. In large metal clusters the election of the fullerenic cage is mainly driven by the need to reduce strain. For the not so large metal clusters, it is usually said that the cage is chosen to minimize the electrostatic repulsion between charged five-membered rings, but our results clearly show that this is not the case and that it is the Maximum ARomaticity Criterion (MARC) that determines the most suitable hosting cages.[2]

The last two examples concern the chemical reactivity of fullerenes and EMFs. First, we show that the regioselectivity of the Diels-Alder cycloaddition to C_{60} changes from the usual [6,6] addition in neutral species to the [5,6] attack when the number of electrons added to the fullerenic cage increases. This important regioselectivity change is explained by the variation of the aromaticity of five- and six-membered rings of C_{60} during the reduction process.[3] And second, we show that the regioselectivity of the Bingel-Hirsch reaction is governed by the additive local aromaticity of the final adducts and not by the bond lengths or pyramidalization angles of the attacked C atoms.[4]

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Photoelectron Spectroscopy and *ab initio* Study of La_n^- (*n*=1-3)

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Lanthanum is the transition metal having plethora of applications (optical fibres – ZBLAN fluoride glasses, catalysts, studio lighting and projection, ignition elements, electron cathodes, scintillators). Lanthanum chemistry is also a challenging task for theoreticians because opening of the 5*d* shell offers a complicated electronic structure and bonding in molecules and clusters, flavoured with multi-configuration nature and relativistic effects. Clusters - the transition between microscopic structure and bulk - are an attractive area of experimental and theoretical research. Neutral and anionic La clusters have not been studied before experimentally. One of the favourite experimental techniques to study transition metal clusters is the anionic photoelectron spectroscopy (APE). Combining the APE spectroscopy with *ab initio* calculations is the goal of this contribution. CASSCF/CASPT2 and RASSCF/RASPT2 methods used with the ANO-RCC basis set [1] are a suitable tool for assisting in the interpretation of APE spectra. Due to large number of electrons and active orbitals the proper choice of the active orbitals and the maximum level of excitations allowed in the CAS/RAS is the matter of delicate balance between computational tractability and reasonable accuracy. So far, only density functional calculations (DFT) of La clusters (omitting their multi-configuration nature) have been published [2-5].

We report the photoelectron spectra of La_n/La_n^- (n up to 7), electron affinities of La and La_2, spectroscopic constants for La_2/La_2^- as well as the structures and electron affinities for La_3/La_3^-. Both DFT and wave function based methods were used. In the latter set of calculations (RASSCF/RASPT2) we adopted equilateral triangle as a simplified model for all structures. Correspondence between the La_3/La_3^- spectrum and manifold of states calculated at the RASPT2 level is discussed.

Acknowledgement

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A Few Examples of Unusual Bonding

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In this presentation, I will overview the nature of bonding in
a. H_2 and H_2^+
b. He_2
c. Alkali dimers and their ions
d. Rydberg dimers
e. Tetracyanoethylene anion dimers
f. Dipole bonds
g. Planar tetracoordinate tetrabonded carbon

Emphasis will be placed on examining what may be surprising in such systems, hoping this will inspire others to consider such bonding paradigms in their own research endeavors.

Localised Quantum States of Atomic and Molecular Particles Physisorbed on Carbon-Based Nanoparticles

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The vibrational states of atomic and molecular particles adsorbed on finite nanographenes are described using reliable theoretical potentials and appropriate vibrational (lateral) Hamiltonians. Although they rigorously obey the Bloch theorem only for the infinite nanographenes, the energy patterns of the probed states resemble closely the usual Bloch bands and gaps. In addition, for any finite nanographene, these patterns are enriched by the presence of ”solitary” energy levels. While the band states are profoundly delocalized, due to a fast tunnelling of the adsorbed particle, the ”solitary” states exhibit strong dynamical localization, similar to the behaviour of the states of the Wannier-Stark ladders in optical and semiconductor superlattices. The present study of the localised states of the physisorbed particles on the finite nanographenes is focused on theoretically predicting their behaviour. As a matter of fact, the actual calculations have suggested not only their existence, but also the reasons causing this existence: Obviously, the gradual increase of the potential energy at the edges of the probed nanographenes plays the same role as the electric field applied to periodic semiconductor superlattices or the chirping of the frequency difference of the counterpropagating laser standing waves in optical lattices, being thus responsible for the same localisation effects as those ones faced in the superlattices. In other words, the localised states predicted in this study can be viewed as bound analogs of the famous Wannier-Stark ladder resonances. It is thus not unthinkable to view the probed nanographenes as nanoscopic/mesoscopic variants of the macroscopic semiconductor and optical lattices and, consequently, as possible candidates for formation of a novel kind of the Wannier-Stark-effect (WSE) based devices, for instance formation of nanoscopic analogs of the macroscopic electro-optical modulators. As these modulators can be operated at both low optical and low electrical powers, they appear attractive especially for optical computing.

Dynamics and the Limited Implications of Weak Bonding in Organic Transition States

Daniel Singleton

Texas A&M University

In barrierless association reactions, a weak attractive interaction between reactants on the potential energy surface does not by itself commit the reactants to product formation. Rather, it is only when the attractive energetic interaction outweighs the entropic cost of bringing the reactants closer together, so that the free-energy surface become attractive, that product formation becomes likely. This idea is well understood and has been routinely applied in simple reactions, but its implications toward the mechanism of complex organic reactions have been largely ignored. Many organic transition states involve very weak interactions between pairs of atoms that are fully bonded in the ultimate product. If an IRC then leads to bond formation between the atoms, standard analyses implicitly assume that the transition state leads directly to the bond formation. This ignores the entropic cost of bond formation.

This talk will discuss our experimental, computational, and dynamic trajectory studies of organic reactions where entropic and related free-energy costs of bond formation lead to more complicated mechanisms than would be expected from the potential energy surface. In the solvolysis of diazonium ions, the transition state that is supported by isotope effects has the appearance of being a concerted displacement. However, the transition state is very loose, and in dynamic trajectories the water molecule apparently carrying out the displacement may move away from the incipient aryl cation, leading to long-lived aryl cations. In [2,3]-sigmatropic rearrangements, the apparent transition states for the concerted rearrangement tend to be "loose," and dynamic trajectories may lead to dissociation. This phenomenon can account for the common co-observation of [2,3]- and [1,2]-rearrangements. In asynchronous cycloadditions, the "second" bond formation may face an entropic barrier. As a result, trajectories passing through the apparent single transition state may face a hidden free-energy barrier that is higher than that for the first barrier. In between the two barriers there is an unusual intermediate that might be described as "bonded" in potential energy but is held back from full bonding by the entropic cost. The implications of these observations to what defines bonding in transition states and intermediates will be discussed.

Hypervalent Bonding: Structure and Reactivity of Organohypervalent Iodine Compounds

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Iodine is the heaviest non-radioactive element in the Periodic Table classified as a non-metal, and it is the largest, the least electronegative, and the most polarizable of the halogens. It formally belongs to the main group, p-block elements; however, because of the large atom size, the bonding description in iodine compounds differs from the light main-group elements. In particular, the interatomic π-bonding, typical of the compounds of light p-block elements with double and triple bonds, is not observed in the compounds of polyvalent iodine. Instead, a different type of bonding occurs due to the overlap of the 5p orbital on iodine atom with the appropriate orbitals on the two ligands (L) forming a linear L—I—L bond. Such a three-center-four-electron (3c - 4e) bond is commonly referred to as a "hypervalent bond".[1] The hypervalent bond is highly polarized and is longer and weaker compared to a regular covalent bond, and the presence of hypervalent bonding leads to special structural features and reactivity pattern characteristic of polyvalent iodine compounds. The reactivity pattern of hypervalent iodine in many aspects is similar to the reactivity of transition metals, and the reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination, and ligand coupling, which are typical of the transition metal chemistry. Exploration and practical utilization of these similarities may lead to the development of new useful methodologies for modern organic synthesis.

Our research on the development of new organoiodine(III) and (V) oxidants, reagents for aziridination and amidation, highly soluble carbene precursors, and catalytic systems based on organoiodine compounds will be overviewed.[2-5] Preparation, structural studies, and reactivity of numerous new organic derivatives of polyvalent iodine will be presented.

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Deciphering Delocalized Bonding in Molecules, Clusters and Solids

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Chemists usually view chemistry through a single classical structure with chemical bonding represented by lone pairs and two-electron two-center (2c-2e) bonds, the so called Lewis bonding model. However, this model could not properly describe bonding in aromatic molecules. Thus, chemists introduced the concept of resonance of a few classical structures. Chemical bonding in benzene can be represented by a resonance of two Kekulé structures. This resonance is simply another way to say that π-bonding in benzene is delocalized. Of course, canonical molecular orbitals, which are always available from Hartee-Fock or density functional calculations, are delocalized over the whole molecule and thus could be used to describe delocalized bonding in aromatic molecules. However, chemists believe that σ-bonding in organic aromatic molecules is localized. Thus, we have a dilemma which description to choose: localized bonding with resonance or completely delocalized bonding with canonical MOs.

Recently, we proposed a new method, called Adaptive Natural Density Partitioning (AdNDP), which allows us for the first time to reconcile localized bonding with delocalized bonding in one molecular model. The AdNDP method is an extension of the Natural Bond Orbital (NBO) analysis developed by Weinhold. In the AdNDP analysis, the search is initially performed for localized 1c-2e (lone pairs) and 2c-2e bonding elements similar to the NBO analysis. The electron density responsible for localized bonding is removed. Then the search is performed for delocalized bonding elements (*n*c-2e bonds with *n* ranging from 3 to the total number of atoms in the system). Bonding elements recovered by AdNDP always correspond to the point group symmetry of the system (after these bonding elements are superimposed onto the molecular frame). Similar to NBO, all the bonding elements are chosen to have occupation numbers (ON) close to 2.00 |e|. Because of that, Lewis idea of an electron pair as the essential element of chemical bonding is preserved. I will show how our method helped to rationalize bolding in aromatic organic molecules, remarkable sandwich complex $[Pd_4(\mu_4\text{-}C_9H_9)(\mu_4\text{-}C_8H_8)][BAr^f_4]_2$, and the nano-molecular wheel, TaB_{10}^-, with the highest coordination number 10 in two dimensional compounds. In all these cases, delocalized bonding is essential for understanding structure, stability and some unusual properties of these new chemical species.

A new tool to elucidate chemical bonding in bulk solids, surfaces and nanostructures has been developed. Solid State Adaptive Natural Density Partitioning (SSAdNDP) is an extension of the AdNDP method to systems with periodic boundary conditions. It is a method to interpret chemical bonding in solids, two-dimensional materials, and surfaces in terms of classical lone pairs and two-center bonds, as well as multi-center delocalized bonds. We demonstrate the versatility of the method by applying it to the Na_8BaSn_6 Zintl phase featuring both localized and multi-center chemical bonding.

Acknowledgements

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