Structure and Dimensionality Affecting Physical and Chemical Properties of Supported, Suspended and Interfacial Clusters

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Gaining insights into the nature of physical and chemical systems of highly reduced sizes, and developing experimental and theoretical methodologies aimed at probing, manipulating and controlling them on the atomic and molecular level, are among the major challenges of current basic interdisciplinary research. Emergent physical and chemical phenomena at the nanoscale regime and the use of atomistic simulations as tools of discovery in this area [1] will be discussed and demonstrated through studies focusing on systems involving: (i) surface-supported nanoclusters, (ii) suspended clusters (in the form of interfacial nanowires), and (iii) quantum electron and boson clusters in 2D dots and cold-atom traps.

(i) Nanocatalysis by small gold clusters [2(a-c)]; Structure, dimensionality and chemical reactivity of surface-supported gold clusters; Control of the physical and chemical properties of supported clusters through the selection of support thickness [2(d-f)] and via the use of external electric fields [2(g)].

(ii) Nanowire formation mechanisms; Structural (atomic and electronic) properties, Mechanical response; Shuttling wire-suspended nanoclusters; Quantized electric conductance; Metal-insulator transition and local magnetic moments in oxygenated gold nanowires [1, 3 ].

(iii) Symmetry breaking phenomena resulting in formation of electron Wigner crystallites and rotating electron molecules in 2D quantum dots, and in the appearance of crystalline arrangements and rotating vortex clusters in atomic traps [4].


Clustering and self-organization in Bio-Nano systems

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There is an increasing interest towards understanding of the principles of structure formation, clustering and self-organization dynamics in Bio-Nano systems, as well as towards numerous applications of this knowledge in bio-, nanotechnology and medicine [1].

In this context there will be discussed self-organization processes in a number of Bio-Nanosystems, which have the characteristic features of nanoscale phase transitions [2]. The nanoscale phase transitions is a common physical phenomenon manifesting itself in many nanoscale systems of both biological and nonbiological nature. Particular attention in the discussion will be paid to the protein folding process [3] and the fullerene fragmentation-reassembly dynamics [4].

Another important aspect of clustering and self-organization concerns the aggregation dynamics in various complex manybody systems. Here the diffusion process of single atoms or nanoparticles plays the central role leading to the formation of various structures like nanofractals [5], bio-nano supperlattices [6], nanowires [7], nanotubes [8] etc. This aspect of clustering and self-organization in Bio-Nano systems will be thoroughly addressed in the talk and a number of characteristic examples will be given.

Finally, the problem of monitoring, controlling and governing the Bio-Nano systems dynamics, their selforganization and growth with the use of various accessible parameters will be discussed. Here we address the idea of atomic confinement [9], use of atomic impurities [10], plasmons excitations [11], nuclear magnetic resonance observables [12], quantum and geometrical shell effects.
[13], single molecule manipulations by means of atomic force field microscopy and optical tweezers [14].

Abstract

In the first part of the presentation an overview about the recently developed auxiliary density functional theory (ADFT) [1,2] is given. The use of ADFT in Born-Oppenheimer molecular dynamics (BOMD) simulations and related property calculations is discussed. BOMD trajectories of simple metal clusters are analyzed [3] and compared with experimental results. It is shown that certain mismatches between experiment and theory can be resolved by these studies.

Modelling and simulation of materials have been one of the important areas of research which face the major challenge of a proper handling of the hierarchical nature of the length scales inherent in all materials. Depending on the concerned interest and application, an appropriate length scale needs to be chosen for a theoretical description of the structure and properties of materials. One of the concepts that has played a major role in the conceptual as well as computational developments covering all the length scales of interest in a number of areas of chemistry, physics and materials science is the concept of single-particle density.

In the microscopic length scale, it is the electron density that has played a major role in providing a deeper understanding of chemical binding in atoms, molecules, clusters and solids. In the intermediate mesoscopic length scale, an appropriate picture of the equilibrium and dynamical processes has been obtained through the single particle number density of the constituent atoms or molecules. A wide class of problems involving nano-scale materials, molecular assemblies and soft condensed matter has been addressed using the density based theoretical formalism as well as atomistic simulation in this regime. In the macroscopic length scale, however, a continuum description using various property density functions has often been found to be appropriate.
In spite of the differences in the nature of the density variables used in all these descriptions, the corresponding theoretical frameworks have been found to possess an underlying unified structure. Besides attempting to project the many-particle picture to a single particle one, this density functional theory based description provides a unified theoretical framework for quantum as well as classical systems encompassing the diverse length scales involved in materials modelling. The basic features and some recent developments of this description with emphasis to modeling of molecules, clusters and materials at the nano-scale, and applications to molecular hydrogen adsorption in doped carbon based nanomaterials, form the subject matter of the lecture.
For Li nanoclusters, I will discuss our recent variational and diffusion Quantum Monte Carlo (QMC) simulations of the ground state using resonating valence bond (RVB) guiding wave functions, comparing the results to those of standard Jastrow-Slater (JS) wave functions.[1] Our results show a systematic improvement in the cohesive energy with the RVB ansatz. The RVB nature of the ground state is revealed by a significant transfer of electrons from s- to p-like character, constituting a possible explanation of the breakdown of the Fermi liquid picture observed in high resolution Compton scattering measurements of electron momentum density in bulk Li as well as Li impurities in Al.[2,3] Turning to CdSe, I will discuss the interpretation of positron annihilation spectra from CdSe nanodots ranging in diameters from 2.5 nm to 6 nm in terms of the related computations of the relevant electron-positron momentum density[4]. Here we show that positrons are trapped at the surface of CdSe nanocrystals. They annihilate mostly with Se electrons and thus provide a powerful tool for monitoring changes in the composition and structure of the surface of the nanodot with little influence of the ligand molecules. I will also comment on our results for an exactly solvable model Hamiltonian for describing the interacting electron gas in a quantum dot and the interplay between confinement and correlation effects so revealed on momentum density in nanosystems.[5] Work supported by the US Department of Energy.


[3] J. Kwiatkowska, B. Barbiellini, S. Kaprzyk, A. Bansil, H. Kawata and N. Shiotani,


Controlling Magnetic and Superconducting Properties at Extreme Scales

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In the first part of my talk I will discuss our recent results on a magnetic nanostructure. We have used electrochemical process to grow templates with 60 nanometer sized pores. The template with pores is used to grow nanostructures of Cobalt. Detailed structural characterization studies have revealed crystalline nanowire morphology of Co within the nanopores. Our aim was to play with the ever present competition between shape-anisotropy and magneto-crystalline anisotropy effects in the magnetic nanostructures. From detailed magnetization measurement we show the predominance of magneto-crystalline effects, and discuss the origin of this in our nanostructure\textsuperscript{1}. The results I will discuss have interesting application potential for the magnetic data storage industry.

In the second part of my talk, I will focus on some interesting properties in superconducting nanostructures we have patterned in our lab. We have generated a hexagonal periodic array of nanometer sized holes with diameter 170 nm and spacing of 350 nm. The interest in these structures is due to the fact that the spacing between the adjacent holes is close the superconducting magnetic penetration length ($\lambda$) of the patterned material (NbSe$_2$). We find significant magnetic field sweep rate dependent metastable magnetization response develops in our patterned sample. Our results are explained on the basis of a unique collective action of the patterned structures which creates a barrier against vortex redistribution inside the superconductor. We propose that this barrier leads to a phase separation creating distinct population of vortices in the patterned superconductor\textsuperscript{2}.

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Designing Nanostructures for Hydrogen Storage

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Designing a suitable material for Hydrogen storage is a challenging task, as it has to satisfy several criteria viz. high storage capacity, satisfactory kinetics, optimal thermodynamics. Complex light metal hydrides such as alanates and imides involving light elements have been intensely studied [1]. However, the recent trend is to explore various kinds of nanostructured complexes involving light elements such as Carbon, Boron and Silicon, that satisfy many of the above mentioned criteria. We have investigated metal decorated Si$_{60}$H$_{60}$ fullerenes [2], as well as nanotubes [3] and graphene-like sheets of BC$_4$N composite [4], as possible hydrogen storage materials. There are several outstanding issues, e.g. metal clustering on the surface, problem of barrier crossing in exohedral versus endohedral storage, controlling the Hydrogen desorption temperature etc. First-principles calculations have been carried out on these confined systems, to investigate their structural, electronic and thermodynamic properties, and to ensure that H$_2$ molecules can be attached with binding energy intermediate between physisorption and chemisorption. In this talk, we shall discuss the various issues and challenges involved in designing such novel nanomaterials for effective storage of hydrogen in molecular form.

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S. Bhattacharya, C. Majumder and G.P. Das, to be published
Gas-phase Catalysis by Atomic and Cluster Metal Ions:

The Ultimate Single-Site Catalysts

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Gas-phase experiments, employing state-of-the-art techniques of mass spectrometry, provide detailed insights into numerous elementary processes. The focus of this review will be on elementary reactions of ions that achieve complete catalytic cycles at thermal energies. The examples chosen cover aspects of catalysis pertinent to areas as diverse as atmospheric chemistry and surface chemistry. We will describe how oxygen-atom transfer, bond-activation and fragment-coupling processes can be mediated by atomic or cluster metal ions. In some instances truly unexpected analogies of the idealized gas-phase ion catalysis can be drawn with related chemical transformations in solution or the solid state and so improve our understanding of the intrinsic operation of a practical catalyst at a strictly molecular level.
Catalysts accelerate and boost thousands of different chemical reactions, and thereby form the basis for the multibillion dollar chemical industry worldwide and indispensable environmental protective technologies. Research in nanotechnology and nanoscience is expected to have a great impact on the development of new catalysts. Thus, a detailed understanding of chemistry of nanostructures and the ability to control materials on the nanometer scale will ensure a rational and cost-efficient development of new and more capable catalysts for chemical production.

This presentation will cover two catalytic applications of nanoclusters: (i) the CO oxidation of Fe encapsulated boron nitride nanoclusters and (ii) and the hydrogen energy storage efficiency of Mg based nano clusters. These studies have been carried out using the density functional theory formalisms under the plane wave – pseudo potential approach. The primary focus of these studies is to predict advanced nano-catalyst materials which show faster kinetics as well as cost effectiveness for industrial applications.
Structure, Reactivity and Catalytic Behaviour of Metal Oxide Cluster Ions

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The potential of certain metal clusters to weaken or even break the oxygen bond plays an important role in catalysis. The process strongly depends on composition, size, structure, charge and environment. Thus, we investigated the inherent structures, stabilities and reactivity of metal oxide cluster ions in the gas phase.

The positively and negatively charged metal oxide cluster ions were produced by a laser vaporisation source or a sputter arrangement. For selecting and characterizing their sizes, the cluster ions were injected into a tandem quadrupole mass spectrometer, with a temperature-controlled radio frequency ion trap (T>10K) inserted in-between, in which the experiments were performed. Also neutral buffer and reactant gases could be introduced at variable pressure (<10^{-2} mbar) into the ion trap. Various view ports allowed for the spectroscopic characterizations and photo-reactivity studies of the trapped ions.

The cold environment of the trap allowed the attachment of He or Ar messenger atoms to the trapped cluster ions. When irradiating them with the resonant IR-light from a tuneable IR laser (e.g. the free electron laser FELIX) the weakly
bound messenger atoms were re-detached. The technique allowed to record the vibrational spectra of various cluster ions and their reaction products, allowing to affirm their structures by comparison with DFT calculations. Namely, on the system \( V_nO_m^{+/-} \) we systematically studied cluster structures for different sizes [1], and we were even able to distinguish the spectral features of different isomers. At a cluster size of \( V_8O_{20}^- \) spectral fingerprints of charge localisation appeared indicating an onset of bulk behaviour [2]. Vanadium oxide clusters are often used as model systems for the active site of a catalyst. Different types and structures of the metal oxide substrate can - on the other hand - be modelled by \( Ti_nO_m \) and \( Al_nO_m \) clusters [3]. So a smart assembly of active site and substrate allows to compose complete model catalyst systems that can be studied in the gas phase. Furthermore, we investigated the reactivity behaviour of vanadium oxide cluster ions as active site model systems [4].

References:
Clusters: Order- disorder -order cycle in evolutionary trends, local order in disordered clusters and finite temperature properties.

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We have examined ground state and about 100 isomers of all the clusters of Nan (10 < n < 148) using ab initio methods. We bring out a cyclic pattern of order - disorder - order in the evolution. It turns out that the growth is characterized by emergence of multicenters having local icosahedral order. The global icosahedral order gets established rather suddenly by addition of one or two atoms. The relationship between these features and finite temperature properties is discussed.
Size-Dependent "Stiffness" of Clusters and Its Consequences

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We have performed density functional theory (DFT) and density functional perturbation theory (DFPT) calculations to obtain the structure and interatomic force constant tensors for small clusters of Si, Sn and Pb. We find that bond lengths, bond stiffness and average vibrational frequency vary quite smoothly as a function of size, though mean squared amplitudes of vibration and the Lindemann melting temperature show large and non-monotonic variations. As a result, clusters can melt either above or below the bulk melting temperature. We suggest that coordination number is the key to understanding many of these phenomena. We also find evidence of some rather surprising scaling relations.
First-Principles Study of Boron Nanostructures: Sheets and Nanotubes

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Understanding of the structural stability, electronic properties and chemical bonding of boron nanostructures can be set as a baseline for the evolutionary changes from carbon to hybrid C_xB_yN_z to BN nanostructures. In this talk, we will explore structural stability, electronic properties and chemical bonding of boron nanostructures including clusters, sheets and nanotubes using first principles periodic approach. The results on the thermodynamic stability together with the vibrational spectrum of several structural motifs of the pristine 2D boron sheet will be reported. A hybrid of triangular and hexagonal configuration is found to be the most stable configuration. A boron sheet composed of either perfect triangular or perfect hexagonal motifs is unlikely to be synthesized. It appears that the nature of the chemical bonding, rather than thermal effects appear to be the prime factor in determining the stability of atomic monolayers of boron.

For the single-walled (SW) boron nanotube, the calculated results predict a ballistic transport, with a relatively lower resistance of 7 kΩ as compared to that of single-walled carbon nanotubes which is calculated to be about 20 kΩ. It may be attributed to the electron-deficient nature of boron. It is expected that the present study will initiate further theoretical and experimental studies on boron nanostructures, which will be helpful in understanding, designing and realizing boron-based nanoscale devices.

(in collaboration with Kah Chun lau and Roberto Orlando)

References:

First-principles Simulations of Carbon, Boron and Nitrogen based Nano-structures

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Abstract:

We present first-principles theoretical analysis of structure, electronic and thermal properties of carbon, boron and nitrogen based nano-structures such as nano-tubes and graphene. In complement to experimental synthesis of BC$_4$N nano-tubes [1], we determine chemical ordering of B and N substituted for carbon in these nano-tubes that is responsible for their stability and semi-conducting electronic structure. Our work leads to a prediction of stable junction between boron nitride and carbon nano-tubes, which can be used in applications such as high-frequency resonant tunneling diodes. We predict a new class of carbon nano-tubes that are made from graphene with a line defect and can be described with fractional indices of helicity [2], and determine their electronic and vibrational properties. Finally, we determine effects of electrostatic and chemical doping on the vibrational properties of graphene [3, 4], and uncover various contributions through comparison with experimental results.
Growth of semiconductor nanocrystals

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As the size of materials is decreased and one enters into the regime of dimensions in nanometers, one finds significantly different properties than in the bulk. The strong dependence of physical properties on size, found especially in semiconductors, has significant technological implications and this, coupled with the ease of fabrication and processing makes this class of materials promising building blocks for materials with designed functions. An access to a control of the properties requires an ability to control the uniformity of size, shape, composition, crystal structure and surface properties. In this talk I will present results in which we theoretically examine two limiting scenarios of nanoparticle growth and determine the extent of control that can be achieved on the surface structure and the consequences.

The work is done in collaboration with Roby Cherian.
Size-selected rare earth and palladium nanoparticles for hydrogenation applications

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A continuous and reversible ‘structural, optical and electronic’ transition between reflecting metallic dihydride and transparent semiconducting trihydride states in rare earth (RE) metals on hydrogenation make these materials suitable for switchable mirror, sensing and other technologically important applications. In our laboratory, ‘nanoparticle route’ has been used for achieving an ‘all-round’ improvement in the switching characteristics of a ‘new generation’ of Gd and Pr nanoparticle based switchable mirrors in comparison to previously reported thin film, RE-Mg alloys and multilayers. It has been shown that the observed improvements in color neutrality, response time, optical and electrical contrasts are a direct consequence of quantum confinement and coordination reduction effects at nanodimensions. The changes in electrical and optical properties have been observed to be directly linked to the H/RE ratio and H concentration profiles. RE nanoparticle structures have been used for measuring the catalytic properties of Pd nanoparticles and monitoring two-way transport of hydrogen through ion induced nanotacks. A dual-deposition set up comprising of size selected nanoparticle synthesis, thin film deposition and on line measurements of particle size distribution. The dual-deposition set up can be used for growing nanoparticles dispersed in thin films, thin films capped by nanoparticle layers, and nanoparticle layer-thin film multiplayer structures. Hydrogenation properties of Pd thin films, nanocrystalline layers, size-selected nanoparticle and nanorod structures have been studied. By controlling the nanoparticle size and separation, geometrical effects due to lattice expansion during hydride formation and electronic effects due to H incorporation can be controlled and separated. These results sets the foundation for a new type of H sensor having a pulse like response.
Metals such as Cu and Nb have a positive enthalpy of mixing, due to which solid state alloying between them is not permitted under equilibrium conditions. However, far from equilibrium processing techniques, such as vapor deposition may, in some cases, produce amorphous “alloys” of such immiscible elements. Using the powerful technique of 3D Atom Probe Tomography, we have shown that the apparently amorphous Cu-Nb “alloy” is actually a phase separated system consisting of 2-3 nm size, interpenetrating amorphous clusters of Cu and Nb. A more detailed study of the local structure, performed using the EXAFS technique, shows that there are subtle but important differences in the local atomic coordinates of Cu and Nb. We have also studied the effect of annealing on the structural evolution as well as transport properties of the as-deposited nano-amorphous Cu-Nb system.

In the second part of my talk, I would summarize some of our work on the geometry, stability and electronic structure of negatively charged \( C_n \) \((n<11)\) clusters produced by Cs-sputtering followed by magnetic separation. We also investigate the interaction of such negatively charged \( C_n \) clusters with single atoms of H, N etc.
Production of Atomic Clusters with a Heated Wire and Size Classification at Normal Pressure

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If atomic clusters were produced and suspended in an inert gas at normal pressure, they would basically be available for experimental studies on chemical reactivity, coalescence and thermal stability for a long time. If size classification took place at the same pressure, this would avoid losses associated with pressure drops, and much more size selected material could be collected in view of cluster assembled materials compared to state-of-the-art methods. Moreover, normal pressure set-ups are feasible at much lower cost than the vacuum devices conventionally used for atomic cluster research.

As an important step in this direction, it is shown that an electrically heated metal wire can produce a variety of atomic clusters and nanoparticles under normal pressure conditions. They obtain an electric charge from the same wire, and electrical mobility classification allows efficient selection and separation of variable sizes. For high temperatures, the charge is determined by thermoemission of electrons, and impurities with low ionization threshold dominate particle charging at low temperatures. On the example of silver it is shown that traces of K in the wire lead to $\text{K}^+$ ions, which attach to the clusters and provide the charge necessary for electrostatic separation. $\text{Ag}_n\text{K}^+$ clusters are obtained. First principles calculations reveal that $\text{Ag}_n\text{K}^+$ cluster properties show little change in terms of energetic and electronic stability and cluster structure with respect to the neutral $\text{Ag}_n$ clusters. The relative abundance of the clusters obtained from the wire was explainable by the stability of the neutral clusters and $\text{K}^+$ attachment energy, supporting both the model and the interpretation of the mobility distribution.
Aromaticity in Metal Clusters

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All metal aromatic compounds like $\text{Al}_4^{2-}$ and all-metal antiaromatic compounds like $\text{Al}_4^{4-}$ and their complexes have been studied using various conceptual density functional theory based descriptors as well as the nucleus independent chemical shift values. Aromaticity and antiaromaticity in cyclic alkali clusters like $\text{Na}_6$ and $\text{K}_6$, polyacene analogues of inorganic ring compounds, multivalent superatoms, triangular cyclic $\pi$-bonded dianions like $\text{Be}_3^{2-}$ and $\text{Mg}_3^{2-}$ as well as their different sandwich and multi-deck complexes have been analyzed through various reactivity descriptors and the associated electronic structure principles.

Selected references

Nanostructures of Mo-S: Clusters, Platelets, Nanowires, and Their Assemblies

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Currently, there is a growing interest on understanding nanostructures of metal chalcogenide compounds as they are currently used for sulfur removal in petroleum industries, solid state lubricants in space technology, and Pt-free fuel cell research activities. Nanostructures of MoS\textsubscript{1+x} such as triangular platelets, nanowires and their assemblies have been synthesized and studied by experiment as well as theoretical calculations. However, structural stability of MoS\textsubscript{1+x} nanostructures and their physical-chemical properties have not been understood clearly. In the present work, we study the MoCS nanoclusters, nanowires and their assemblies, and the triangular nanoplatelet by first principles density functional calculations. Mo-S compound clusters stabilize the Mo polyhedral structures and sulfurs atoms capped on such metal polyhedron. This structure has strong structural stability as it maintains the strong Mo-Mo and Mo-S bonding. Some of polyhedral clusters are having the non-zero magnetic moment due to presence of partially occupied electron in Mo atoms. Among polyhedral Mo-S clusters, Mo\textsubscript{6}S\textsubscript{8} octahedral cluster has ultra-high stability in the sub-nanometer sized clusters. Mo\textsubscript{6}S\textsubscript{8} clusters could be further condensed and resulted to formation of Mo-S nanowire or nanorod. The nanowires of Mo-S are interesting electronic conductors and could play an important role in miniature devices. Assembly of nanowires stabilizes the hexagonal structure and there is existence of trigonal void space due to weak vdW interaction between the sulfur atoms. Li ions can be inserted into this void space and Li-Mo-S compound can be potential used for Li-ion battery applications. Further, the structural stability and electronic structure of Mo-S triangular platelets are discussed in this present work.
Superatom Assemblies: Towards Novel Nano-Materials with Precise Control over Properties

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A promising development in the field of clusters and nanoscience is the possibility of synthesizing nanoscale materials where size specific clusters serve as the elementary molecular building blocks. As the physical, chemical, electronic, and magnetic properties of clusters can be tuned by size and composition, this may provide an unprecedented ability to design customized materials. The cluster materials, in addition, possess intra-cluster and inter-cluster length scales leading to novel functionalities not available in conventional materials. While this thought has existed for more than two decades, its realization has been delayed by the reality that clusters are usually metastable and coalesce when assembled. Indeed, the only working example is the alkali-doped-fullerides where fullerenes marked by directional C-C bonds serve as the primary unit. Extending the fullerene experience to other metal and semiconducting systems is likely to emerge as an important frontier in the nanoscience. The talk will focus on our recent efforts in this direction. I will first talk about the possibility of forming cluster motifs, based on metals, that are fairly stable and maintain their identity upon further growth. A class of these can be classified as superatoms forming a new dimension to the periodic table [1-4]. I
will then present a new three step protocol that combines (1) gas phase investigations to examine feasible units, (2) theoretical investigations of energy landscapes and geometrical shapes of feasible units to identify potential motifs, and (3) synthetic chemical approaches to synthesize and structurally characterize such cluster assemblies in the solid state. Through this approach we have established selected arsenic-alkali cluster as a potential building block via gas phase molecular beam experiments. Employing the idea that the particular species identified in the gas phase is a uniquely stable Zintl entity that could effect self-assembly, we report success in synthesizing several assemblies of As$_7^{3-}$ clusters with alkali metal counter-cations and those linked with covalent linkers. I will present our recent striking finding combining optical measurements and first principles theory that indicate that the band gaps in assemblies based on the same polyvalent anion can vary over a wide range. Theoretical studies reveal that the variations in the band gap are linked to the energy levels of the counter-cation, the degree of charge transfer, with additional tuning through covalent linkers. The findings offer a novel protocol for synthesis of nanoassemblies with tunable electronics.

REFERENCES


Designer magnetic superatoms

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One of the key discoveries in cluster science is that some clusters mimic chemical behavior of elements in the periodic table, opening avenues for building materials with designer properties. These clusters have been termed superatoms. Superatom behavior is closely related to the stability of the clusters. So far as metal clusters are concerned, their stability can be understood in terms of various shell models for the valence electrons [1]. Electronic energy levels occur in close lying bunches, known as shells. A filled electronic shell leads to enhanced stability. Therefore, clusters having one more or one less electron than a filled shell configuration may behave like alkali or halogen superatoms. Indeed, Al\(_{13}\), being one electron short of a filled shell configuration, is found to behave like a `superhalogen' [2]. Enhanced stability as a consequence of filled shell electronic configuration precludes the possibility of having superatoms that are magnetic. However, if atomic orbitals of the valence pool in a cluster have localized as well as diffuse sub-spaces, new possibilities open up. Clusters having a filled shell configuration in the diffuse sub-space may acquire enhanced stability, while the localized electrons produce magnetic moment.

Through first-principles density functional calculations we demonstrate for the first time that a concrete realization of this possibility can be 3d transition metal (TM) doped alkali clusters. Due their peculiar chemistry, many of the TMA\(_n\) (TM=Sc, Ti, V; A=Na, K, Cs) clusters posses magnetic moments that are larger than those on the isolated TM atoms [3]. TMA\(_n\) (TM=Cr-Ni) clusters, on the other hand, retain atomic
moments on the TM atoms [4]. More intriguingly, as a consequence of this peculiar chemistry, a VCs₈ cluster mimics select magnetic behavior of a Mn atom. Possibilities of building new class of cluster-assembled materials using such magnetic superatoms will be discussed.

References
Ab initio Study of Binary $Au_nPd_m$ Clusters ($n,m \, 1-5$)

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Ab initio method based on density-functional theory has been used to investigate the $Au_nPd_m$ ($n,m \, 1–5$) clusters in their neutral, anionic and cationic forms. The lowest stable geometrical configurations with their electronic states are determined, and verified through a vibrational analysis. The energy gaps between the HOMO and LUMO of the ground states, the EAs, VDEs and ADEs as well as their IPs are investigated. Our results show that the one excess electron is strong enough to modify the known growth pattern of the neutral $Au_nPd_m$ clusters in some cases, and in those cases it is found that (1) an electron promotion occurs from 4d to 5s orbital in the Pd atom, and that (2) the bond of Au–Pd is formed through an overlap between 6s of Au and 5s of Pd. (3) The calculated electron affinities (EAs) and vertical detachment energies (VDEs) are in good agreement with experimental evidence where they exist. (4) IPs have also been calculated and compared when available. (5) An odd-even oscillation in HOMO-LUMO gaps and in the electron affinities, is observed. The latter is in agreement with photoemission experiments of Koyasu et. al. The atomic structure and stability of these clusters are discussed. It is believed that the present calculations will be useful to understand the enhanced catalytic activity and selectivity gained by using palladium-doped gold catalyst.
Large Cluster Applications with Density Functional Theory

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Calculations on large clusters like giant fullerenes and cluster models of zeolites have been performed using the density functional theory (DFT) deMon2k code [1]. Fullerences containing up to 540 atoms as well as cluster models of mordenite-type zeolites containing up to more than 400 atoms have been considered [2]. The calculations were of all-electron type and local and gradient corrected functionals have been employed. The fullerene structures were fully optimized without symmetry constrains. The analysis of the obtained structures as well as a study on the evolution of the bond lengths and binding energies will be discussed. For the zeolite systems [3] the only restriction that the position of the hydrogens atoms terminating the zeolites models are kept fixed was introduced. Optimized geometries, energetic parameters and molecular electrostatic potential maps will be presented.

Cage, endohedral and exohedral clusters of metals

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Most metals in bulk have close-packed atomic structures and the absence of periodicity in clusters often makes the densest icosahedral packing to be energetically most favorable. However, some clusters of metals such as Au$_{32}$, Pt$_{22}$ [1] and Pb$_{12}$ surprisingly show cage structures to be most favorable. From studies on clusters of different metals using ab initio calculations, we find cage structures to be of lowest energy for clusters of some other metals such as Rh [2] and Ta [3]. The tendency to form a cage or open structure is found to be enhanced as one goes down in a column in the periodic table. In this talk I shall present results of these studies as well as the effects of endohedral doping of the cage, the superatom behavior, and the magnetic properties. Endohedral doping is also used to produce superatoms of metal clusters though a cage structure may not be favorable for the undoped cluster. Further, exohedral interaction with atoms such as oxygen has been studied [3] to explore the stability and the superatom behavior while a nanocoating has been used to produce a novel compound fullerene of metals [4].

[3] V. Kumar, to be published.
Ground state structures and optical properties of small hydrogenated silicon clusters

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In order to understand the effects of hydrogenation of silicon clusters we present calculation of ground state structures and optical properties of small hydrogenated clusters using the first-principles pseudopotential method. The ground state structures have been obtained using the Car-Parrinello method and simulated annealing. These structures have been used to calculate photo-absorption cross section using the time-dependent density functional theory (TD-DFT). We find that although the addition of a single hydrogen atom does not change the structure of a silicon cluster, further hydrogenation can significantly change it. This is also seen in the photo-absorption cross section which changes if the underlying silicon cluster changes. In general, we find that the hydrogenation shifts the photo-absorption spectrum to higher energies.
II-VI semiconductor clusters display unusual structural and electronic properties. The HOMO-LUMO gap for these clusters can be tuned by changing the shape and size of the cluster and by varying the type of doping impurities and their percentage. Larger clusters or quantum dots also constitute important materials from device application point of view viz. LEDs, sensors etc. To render the surface of a quantum dot inert, passivation is essential. Passivation of the clusters using fictitious "hydrogen"-like pseudo atoms removes the states in the HOMO-LUMO gap region and results in widening of the gap. Passivation also locks the symmetry for three-dimensional structures but the smaller clusters like Cd$_n$Te$_n$ (1 ≤ n ≤ 6), which are planar, attain higher symmetry structures on passivation. We also observe ‘self-healing’ mechanism viz. opening of optical gap on relaxation without the aid of passivating ligand. However, we note that ‘self-healing’ is a stoichiometry dependent phenomenon. Passivation also prevents diffusion of vacancy in the cluster while in unpassivated clusters, the vacancy is annealed out. Attempts to have semiconductor clusters with extrinsic carriers will be discussed.

The smallest stable stoichiometric cage-like structure Cd$_9$S$_9$ of Cd$_n$S$_n$ is found to have enough space to dope atoms endohedrally. Single Mn doped cage is formed with a magnetic moment of 5 $\mu_B$ but bidoped endohedral cage is unstable. These doped clusters constitute useful building blocks for designing new diluted magnetic semiconductor materials. Semiconductor nanostructures used in devices need metal electrodes, as nanoleads, for conduction of electrons. Towards the end of my talk I will discuss some interesting results on
Cadmium selenide nanorods connected to gold electrodes as a prototype nanodumbbell. A short rod is fully metalized by metal-induced gap states whereas a gap similar to that in bare cadmium selenide nanorods is observed near the nanodumbbell center with sub-gap structure emerging near the metal-semiconductor nanocontact for comparatively larger nanorods.