| | |
|---|---|
| cecam Centre Européen de Calcul Atomique et Moléculaire | **Workshop Scientific Report**<br>Please do not repeat the program (unless there were last-minute changes) or the initial description - we already have this material. |
| **Title** | Theoretical Challenges in Electronic Structure of Clusters and Nanoparticles |
| **Organizers** | Vijay Kumar (VKF, India),<br>Angel Rubio (UPV/EHU, Spain),<br>P, Jena (VCU, USA) |

**Scope of the workshop** (one-two paragraphs)

The 3 day Workshop was attended by 37 people (2 organizers, 18 speakers, and 17 participants) from 13 countries (US, IN, ES, IL, DE, FI, CH, SE, JP, IT, FR, KR, UK). One of the organizers Prof. Angel Rubio could not come. There were 12 sessions with 20 invited talks each of 45 minutes and 5 oral presentations of 20 minutes as well as one poster session in which 14 posters were presented. The 12 sessions covered different aspects of research on clusters and nanoparticles including atomic structure and magnetic properties, electronic structure, ligated and supported clusters, clusters assembled materials, weak interactions and hybrid functional in DFT, energy harvesting and large scale systems, electron and ion dynamics, and reactivity. Though the focus of the Workshop was on recent developments in computational studies of clusters and nanoparticles and the challenging problems, there were a few experimental talks to have synergy between theory and experiments and they constituted as important component of the Workshop and for the future development of the field. The conference started with a welcome by Prof. V. Kumar and Prof. W. Andreoni, Director CECAM and ended with a summary by Prof. P. Jena. The program of the Workshop proceeded as planned except for one participant from Turkey who could not come due to visa problem. Also one invited speaker Prof. Kandalam cancelled at the last minute due to his movement to another institution. However, the main contents of his talk were covered by his collaborator Prof. Bowen. The talks were followed by lively discussions. A report on the scientific contents is given below.

Main **outcomes** of key presentations (one page)

The atomic structure of clusters and nanoparticules are often quite different from bulk and are size dependent. As the properties depend on atomic structure, it is very important to develop knowledge of the atomic structure for different systems and cluster sizes. Often it is difficult to determine atomic structure directly from experiments and therefore a synergy between theory and experiment is very desirable. The Workshop started with two experimental talks. The first talk by Andre Fielicke focussed on structure determination of free metal clusters via far-infrared vibrational spectroscopy using free electron laser. Comparing experimental results with calculations, the problem of the treatment of exchange-correlation in clusters of transition metals and the relativistic effects in clusters of heavy elements was highlighted. In the second talk, Tobias Lau presented very recent developments of measuring spin and orbital contributions to the magnetic moments in free transition metal clusters using X-ray magnetic circular dichroism. Understanding of the quenching of orbital magnetic moments in going from atom to bulk is of importance to understand magnetism in clusters and nanoparticles. It has been a challenge to both theory and experiments as total magnetic moments have been obtained from Stern-Gerlach experiments about two decades ago. These experiments would help to develop proper theoretical tools to understand the orbital contribution which has so far been generally neglected. Following these talks, Kumar presented theoretical developments in the understanding of the atomic structures. The successes of DFT based formalisms have made it possible to make predictions and design new species. One such prediction was of silicon fullerene and other polyhedral forms that were later realized in laboratory. Kumar discussed how doping of an atom in clusters of semiconductors and metals could lead to new species that may also lead to the development of novel cluster assembled materials. Comparing calculated results with now available experimental data, new growth behaviour of metal doped silicon clusters was highlighted. Further possibilities of developing magnetic nanogold by doping Gd as well as doping of magnetic atoms such as Mn or rare earths in nanoclusters of II-VI and III-V compound semiconductors and oxides were discussed that could lead to new routes to develop dilute magnetic semiconductors and optical materials. Also some results on nanoparticles of Pd-Au were presented. Nakajima followed the theme of metal doped semiconductor clusters and presented many results on electronic properties of Si, Ge, and Sn clusters containing transition or lanthanide metal atom of group 3, 4, and 5 using photoelectron spectroscopy as well as their reactivity to $H_2O$ adsorption to identify encapsulation of metal atom.

Bowen presented results on photoelectron spectroscopy (PES) of rare-gas solvated nucleobase anions in order to understand the interaction of electrons with nucleobases and their electron affinity. There are findings that even very low energy electrons could initiate single and even double strand breaks in DNA. From PES spectrum dipole bound as well as valence features were reported to coexist depending upon the number of rare gas atoms. Theoretical work on these systems is yet to be done. Bowen also discussed the results of baby crystals – a talk planned to be given by Kandalam. Gantefor described new developments on using sources with photon energies between 10 eV and several keV for the study of the electronic structure of size selected clusters. This would enable study of the whole valence band spectrum as well as to probe the deeper lying sigma bonded states e.g. in carbon systems. So far the highest photon energy used in such studies has been limited to 7.9 eV. Chelikowsky discussed algorithms appropriate for computing the response of molecules and clusters to external fields using pseudopotentials and a real space method. Applications of this method to vibrational Stark shift in molecules and for the photoemission spectra of titania clusters were presented. Umari presented GW calculations of electronic quasi-particle levels on large molecules and nanostructures. Applications to DNA bases, porphyrin-derivatives, and carbon nanostructures were discussed. For systems with d- and f- electrons GW approach requires explicit treatment of valence s and p orbitals. Using examples of zinc-phthalocyanine and gold, it was demonstrated how this could reduce calculational effort.

Hakkinen presented the developments on thiolate-protected gold clusters, their self-assembled monolayers and molecular junctions. These systems are excellent examples where the notion of magic clusters with shell closing in a jellium model is beautifully realized. These systems demonstrate how the concept of cluster assembly could be realized on one hand and at the same time these systems are relevant for understanding the interface at the nanoscale for potential

applications in labelling and sensing, drug delivery, and medical therapy.

Harbich discussed catalytic activity of Pt clusters deposited or grown on a TiO2 surface as a function of cluster size for CO oxidation. It was shown that the surface oxygen vacancies have a very strong effect on the catalytic activity. STM measurements after the catalytic activity showed that the cluster size distribution changes considerably and converges to an average of 12 Pt atoms per cluster size for all deposited size. Jellinek presented results of extensive DFT studies on structural, electronic and chemical reactivity properties of pure Pt and Mo as well as mixed Pt/Mo clusters. Besides the results on distribution of Pt and Mo atoms and their effect on catalysis, interaction with CO and intermediates involved in glycerol reforming were reported.

Starting with the idea of clusters as building blocks of novel materials, mimicking the chemistry of atoms, Jena discussed a class of clusters called superhalogens whose electron affinity far exceeds that of a chlorine atom (the highest in the periodic table). These superhalogens could be used to synthesize unconventional salts with applications as high energy density materials. Also hyperhalogens with electron affinities even higher than those of superhalogens were presented. Experimental data supporting theoretical results were also presented.

Bromley reviewed progress on silicate clusters. Silicate is one of the prime constituents of the universe and silicate clusters are of importance in understanding the dissolution as well as nucleation in terrestrial geology and formation of dust around stars. He presented results on pure silica clusters as well as on clusters of MgO and mixed (MgO)/(SiO2)m, (SiO2)/(MgO)m, and (SiO2)/(MgO)m(H2O)n clusters and highlighted their relevance to physical/chemical/astronomical phenomena in the universe.

Lundqvist discussed the developments on treating van der Waals interactions within DFT and applications to adsorption of small molecules as well as clusters and nanoparticles on metals. Weak interactions arising from dispersion forces are very important in a variety of systems including interactions between molecules, molecules and another system, superatom - superatom interactions as well as in biological systems in which nanoparticles are also playing increasingly important role. There have been several attempts to incorporate vdW interactions in DFT. It was shown from some test calculations that vdW-DF2 functional gives potential energy curves, levels, and differences in corrugation close to experimental data and stronger performance compared with DFT-D3 and TS-vdW corrections to traditional DFT formulations due to more adequate account of surface polarization. Baer described a first principles approach to overcome some of the problems (failures) of DFT methods and showed many examples including charge transfer excitations, water ionization, occupied orbital energies, and ionization potentials, HOMO-LUMO gaps, fundamental gap, Rydberg excitations, barrier, etc.

Rozzi presented theoretical and experimental results on light harvesting property of supramolecular systems. Experiments using pump-probe spectroscopy with 10 femtosecond time resolution and calculations using TD-DFT method showed that calculations are able to describe the key quantities controlling the dynamics of the light harvesting process. The driving mechanism of the charge separation process was shown to be a correlated wavelike motion of electrons and nuclei on a time scale of about 100 femto seconds. Wöste discussed dynamic processes in metal clusters from experiments as well as theory on pure, mixed as well as oxide clusters with specific mass and charge. Further “cluster on cluster” architecture mimicking active sites on a surface were reported. Controlled collisions experiments with non-reactive and reactive gases revealed information about geometric structure and reactive behaviour. IR absorption experiments were found to be the best ways to reaffirm cluster structures along with theoretical predictions. The evolution of wave packet dynamics, vibronic coupling, geometric rearrangement, and fragmentation as a function of cluster size from pump-probe experiments were reported. Optimally shaped white light pulses to maximize yield of multiphotonic charge reversal processes could open a new perspective for photochemistry. Suraud discussed the non adiabatic dynamical response to laser irradiation of clusters and small molecules in contact with an environment such as a substrate or matrix. Results of the modelling of processes such as electron ionization and variation of laser frequencies in studying the properties of clusters were presented.

**Report** on selected discussions (one page)
eg. Were there interesting hints for new research? for new developments? for collaborations?

Electrical contacts constitute the basic building blocks of nanoscale devices and their characterization as well as understanding is challenging. Schneider reported low-temperature scanning tunnelling spectroscopy results on conductance of nanocontacts between flat Pb islands and their supporting substrate such as Si(111)7x7, HOPG, BN/Ni(111), NaCl/Ag(111) and on Cu(111) as well as the effects of dynamical Coulomb blockade. These studies are important for the future nanostructures in relation to superconductivity, magnetism, and catalysis.

The absorption of electromagnetic radiation in metal nanoparticles depends upon the excitability of surface plasmons and a new field of plasmonics has emerged. The surface plasmon frequency depends on size, shape and environment of nanoparticles. Stella discussed the main computational features of the real time TDDFT+jellium approach as applied to nanoparticles and a novel application to a pair of nanopillars. One can successfully describe the strong dependence of surface plasmon frequency on both electric field direction and the distance between the pillars. He further discussed possible multiscale approach for optical response of large plasmonic nanostructures.

Among five oral presentations, Tangney discussed distribution of charge in polar nanostructures such as those of GaAs, CdSe, and ZnO. The non uniform distribution could lead to large internal and external fields. It was shown that the spontaneous polarization of wurtzite lattice plays a subordinate role in surface chemistry and that a mechanism analogous to Fermi-level pinning at semiconductor interfaces could stabilize large dipole moments in naorods. Samanta presented ways to stabilize Zn in a +3 oxidation state by studying its interaction with F, BO2, and AuF6, leading to possibilities of synthesis of unusual compounds using strong oxidizing property of superhalogens. Bester presented development of effective atomic pseudopotentials for large scale electronic structure calculations that are suitable for band edge states involved in electronic excitations. These pseudopotentials are material dependent. Varga discussed electron and nuclear dynamics induced by interaction of strong laser pulses and nanoparticles using TDDFT. Examples of laser enhanced field emission, Coulomb explosion, laser assisted H desorption from silicon clusters and graphene flakes were given. Jackson discussed the dielectric properties of single component and binary clusters using site specific polarizabilities.

Fourteen poster presentations were devoted to topics of van der Waals non local correlation effects on properties of clusters, stability and spectroscopic properties of doubly charged anions, structure and optical properties of gallium oxide clusters, rare earth doped GaN nanoparticles, growth behaviour of Y and Sc doped Si anion clusters, Gd doped magnetic gold clusters, description of van der Waals interaction between imidazole analogues of an anti-cancer drug with DNA base pairs, Mn doped magnetic II-VI quantum dots, boron derivatives as a new class of super and hyperhalogens, structural transitions in 13-atom Ag/Au nanoalloys, optical absorption of Al clusters from large scale CI calculations, surface plasmons and optical properties of Ag-Au nanoalloys from TDDFT, and electronic properties of Au nanoclusters from GW calculations.

To what extent were the **objectives** of the workshop achieved (strong points, weak points)? (one paragraph at least)

Judging from the feedback from several participants as well as from our own assessment Workshop was very successful in achieving its objectives. There was ample scope for discussions and most of the talks were followed by lively discussions that indeed continued in lunch and coffee breaks. The combination of experimental and theoretical talks is most likely to lead to new collaborations and that would be a very welcome outcome. Some of the challenges of proper description of exchange correlation effects particularly in transition metals and f electron systems remain and we are likely to see important development in this direction in the near future and this would help to understand better these technologically important materials. It is now possible to do GW calculations on large systems and this would help better understanding of the excitations in nanoparticles. Important developments in treating van der Waals interactions would lead to many phenomena in nanoparticles, clusters, catalysis and biological systems to be understood well and we hope to see much activity in the near future. Significant developments in describing dynamical aspects both electron and ions would lead to better understanding of real life phenomena and energy materials.

**Do you have suggestions** for new workshops/tutorials/conferences on the topic?