Research Networking Programmes

Science Meeting – Scientific Report

"Stabilized Noble Metal Nanoparticles, recent advances and present challenges"

Application Reference N° 4579

1) Summary

The aim of the workshop was to bring together leading scientists in the emerging research field of quantum simulation of metal nanoparticles weakly interacting with organic matter. Key scientists in closely related fields were invited to frame the discussion of present challenges around the most recent advances in theory and algorithmic tools. With the participation of experimentalists, we focused on the mechanisms at the heart of the most promising applications. The following main subjects were discussed in the sessions:
-- Optical absorption, emission and enhancement
-- Non adiabatic dynamics
-- Catalysis
– Ab initio simulation of polymers and biomolecules

The workshop was initially oversubscribed showing the high interest in the computational community for this particular challenging system. The total number of participants was slightly increased to 43 out of the 40 initially planed. There were 18 invited speakers and 8 contributed speakers. Out of the invited speakers, a percentage of 28 % were women, comparable to the 32% reached in one of the best conferences in clusters, the Gordon Research Conference on Noble Metal Nanoparticles 2012. The format of 30 minutes talks with a 10 minutes for discussion prove to be adequate for the mixture of communities that was present. All the sessions were fully attended, including the poster session. Feedback from the participants was very high. It was expressed during the talk's discussions and personally to the organizers. It is expected this workshop will increase the number of computational scientists doing research in these systems, strengthen the theoretical community and therefore will boost the scientific developments in this very complex research direction.

2) Description of the scientific content of and discussions at the event

Assembling nanosystems with organic matter, and understanding their electronic and dynamic properties is a challenge that combines both nanosciences and soft matter physics. Though these two fields have different paradigms, such as different length scales and type of research questions, these systems can have complementary properties in the form of nanocomposites. Studying nanocomposites will open the way to new, very stable, tunable materials with a wide range of applications in biosensing, imaging, and catalysis.

The workshop focused on quantum computational approaches for modelling metal nanoparticles stabilized by organic matter. There is a large, growing interest of such systems due to achievements in recent experiments. The ab-initio computational studies are, however, scattered. Interacting organic-metal composites are a particular type of a hard-soft system, and presently an extremely challenging system to simulate. The workshop addressed current challenges and successful methods to study the electronic properties of stabilized metal nanoparticles. To reach this aim, we brought together leading scientists working both on ground and excited state electronic properties of organic stabilized metal nanoparticles. We framed the discussion around the particular difficulties that are relevant for a deep understanding of state-of-the-art experiments. For this purpose, key experimentalists were invited to give review talks. Additionally, leading scientists from close fields that share common challenges were invited to give overview talks on their recent advances. The mixture of relevant communities provided an exciting opportunity for discussing recent advances and addressable challenges.

Talks and generated discussions

The opening talk was given by one of the organizers, Olga Lopez-Acevedo (Aalto University). She presented the goals of the workshop and an overview of general problems and particular methods theoretical methods and experimental results that were going to be discussed during the workshop. An overview of the different systems that were going to be discussed was presented in the form of a “survival guide”. To help to solve communication difficulties, in the opening also was discussed the difference between the terms cluster and nanoparticle and also the difference between the terms protected and stabilized. The distinction turned out to be important for several participants and it was continued in the discussions following other talks and during the

breaks. As it is used in this report, a metal nanoparticle is an aggregations of metal atoms with a metallic bond with a nanometric length scale. A metal cluster is then used to emphasize that a nanoparticle has a size below 1nm. Concerning the interaction of the metal and organic components, stabilized and protected are distinct by the strength of such interaction energy. A ligand-protected system has strong binding energy between the metal and the organic component (for example in thiol protected metal clusters, the typical Au-SR bond is higher than 1 eV) while a stabilized system has a lower binding energy allowing the system to visit different conformations by thermal agitation. This is typical of soft matter systems and is is at the origin of the difficulties in simulating these stabilized systems.

There are several important questions that the workshop focused on in the talks and the discussions. For example: What are the addressable systems that can be reached with present computational resources? Which are the state-of-the-art algorithms that the community could more widely adopt to deal with the difficulties encountered? From experiments, what type of properties are most interesting when considering technological applications? How to test experimentally the resulting models?

The tutorials reviewed very important concepts and topics: when and how to use van der Waals (vdW) DFT functionals, the state-of-the-art many body techniques and the current model to describe a metallic bonding.

In the following subsections, a summary of the main points given in the talks that are related to the previous questions is going to be presented. Name and affiliation of the authors is also indicated.

State-of-the-art computational methods

To deal with the multi-scale lengths stabilized nanoparticles systems have, several available methods were discussed. For example, when studying optical properties Lasse Jensen (Pennsylvania State University) discussed the difficulties studying the effect of plasmon molecular enhancement. The difficulties are based on the optical properties of an electronically delocalized system (nanoparticle) and an electronically localized system (molecule). He showed recent achievements developing hybrid classical-quantum electrodynamics methods that accurately simulate the plasmon-molecule interaction. Christine Peter (Konstanz University), reviewed key obstacles for classical methods in multi-scale algorithms, specifically she discussed the representability and transferability problems in coarse-grained multi-scale methods. Karen Johnston (Max Planck Institute for Polymer Research) presented quantum derived classical potentials for multi-scale simulations of weakly interacting polystyrene – gold-surfaces. She showed how crucial for accuracy it is the inclusion of the vdW functionals in the quantum level used for the classical potential derivation. Volker Blum (Max Planck – Fritz Haber Institute) showed different level of consecutive methods (ending in replica exchange) to efficiently search in conformational space when studying biomolecules, starting from classical and ending with quantum methods. From purely quantum methods, Leonardo Espinosa in Olga Lopez-Acevedo's group (Aalto University) showed the effect of Au and Ag metal atoms have in optical properties when binding to DNA in different places like gluing basis pairs or attaching to DNA backbone. Also from quantum methods Alexander Kulesza (Creative Quantum GmBh) showed how quantum calculations can be used for characterizing interacting metal-biomolecule systems when the size the of the system is still in an attainable range.

Some of the important state-of-the-art methods in electronic simulation aim at including the coupling of the electron and nucleus simultaneous time evolution, known as a nonadiabatic dynamics. Jens Petersen from Roland Mitric's group, introduced the Field Induced Surface Hopping nonadiabatic dynamics that predict the behaviour of excited state relaxation under the influence of a laser field. Comparison with time-resolved photoelectron spectroscopy experiments showed that under the stimulated emission condition the implementation is extremely successful in reproducing experimental data of clusters and biomolecules. Ari Ojanperä in a joint work between Olga Lopez-Acevedo and Martti Puska's group (Aalto University), showed the use of Ehrenfest dynamics with TDDFT for a small member of the protected gold clusters where deformation of the core and charge evolution was followed after an excitation simulated with Delta Self-consistent Field method.

Finally, some talks where focused on related systems like protected clusters, and gold and copper surfaces interacting with polymers and molecules. Using the chirality mechanism proposed few years ago for the cluster Au38SR24, Lauri Lehtovaara from Hannu Häkkinen's group (Jyväskylä University) showed a proposition for a Au40 thiol protected cluster. Gana Natarajan from Thalappil Pradeep's group (Indian Institute of Technology Madras) showed DFT modelling of a supramolecular ligand-protected system. In the catalysis session, Karolina Honkala (University of Jyväskylä) talked about a recent implementation of Kinetic Montecarlo and its applications to surface catalysis simulation. David Willock discussed the interaction between Au particles and the catalyst support and finally Javier Montoya (Universidad de Cartagena) discussed high pressure DFT calculations were clusters can potentiate catalytic reactions. In the final session, Bengt Lundqvist and Kristian Berland (Chalmers University) showed how the use of vdW functionals are crucial when considering physisorption of molecules on Cu(111) surfaces.

From the talks and the discussion it is concluded that there exists a rich variety of computational tools currently available to study the different aspects of stabilized systems. Most importantly these state-of-the-art methods are in its majority being publicly available by the effort of the speakers and their respective communities working in the most used DFT codes (like ADF, GPAW, FHI-AIMS).

State-of-the-art experiments

Experimental talks showed a great variety of high interest applications. These were presented in a pedagogical way for the theoretical-experimental audience that was present. For example, Francesco Stellacci (Ecole Polytechnique Federale de Lausanne) showed how the role of the organic ligands can lead to applications to molecular recognition and ion capturing. Thalappil Pradeep (Indian Institute of Technology Madras) discussed recent experiments building supramolecular structures benefiting from particular choices of ligands. Robin Ras (Aalto University) overviewed the properties of fluorescent polymer stabilized silver nanoclusters. Among the topics he reviewed the solvatochromic effect was pointed as a particular challenge for simulation. The advantages of these systems are a high 30% quantum yield, nontoxicity and photostability. Elisabeth Gwinn (University of California Santa Barbara) presented her recently published breakthrough, where using size selection experiments techniques, the DNA-Ag cluster composition was determined (ex. relation between charge and size, existence of single, double and triple strands). Peter Liljeroth (Aalto University) reviewed electrochemical and optical experiments performed on protected clusters, including an unexplained fine structure in the emission spectrum of the Au38SR24 cluster. Cristopher Ackerson (Colorado State University) discussed his recent experiments testing the superatom model predictions in thermal stability using calorimetry experiments.

Extension of such tests to consider magnetic properties were also presented. Finally, Noelia Vilar-Vidal from Arturo Lopez-Quintela group (Santiago de Compostela University) presented an interesting application of electrochemically synthesized copper clusters in solution to photocatalytic applications, including a promising route to metal ion sensing.

Tutorials

Patrick Rinke (Fritz Haber Insitute of the Max Planck Society), discussed the most prominent failures of DFT semilocal functionals and state of the art results on Green's functions and advanced DFT functionals to correct them. Elsebeth Schröder (Chalmers University) started by discussing the correct interpretation of vdW functionals as a term missing in current DFT functionals (the universal functional would not need such extra term), presented the most common vdW functionals and practical guide on how they perform. Pekka Pyykkö summarized decades of work on the metallophilic attraction, how it has been characterized as a type of dispersion interaction and the current computational methods available to study it. All the tutorials were highly appreciated for the high-quality and pedagogical effort the speakers made.

3) Assessment of the results and impact of the event on the future directions of the field

In the workshop all the sessions were attended by the majority of all participants showing the interest the talks created. All the speakers made an effort to be pedagogical yet technical enough and it was clear they had succeeded by the mixture of general and particular questions they created in the audience. In the discussions, both theoretical and experimental researchers participated actively making the related objective fulfilled. The impact on the computational modelling of quantum properties of stabilized metal nanoparticles is expected to be important. Several research groups will include projects in this direction and a strengthen of the theoretical community has been created. A follow-up workshop in few years would support the development of this community in this very challenging research direction.

4) Annexes 4a) and 4b): Programme of the meeting and full list of speakers and participants