Computational Nanoscience at
Laboratory for Simulation and Modeling of Materials

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Abstract

The computational infrastructure improvement, as well as the theoretical treatment of materials, has enabled extensive calculations on a variety of physical and chemical systems, with a striking effect also on biological and materials science applications. At Departamento de Investigación en Física, computational resources permitted the raising of Computational Nanoscience as a manner to understand the unique, and sometimes amazing, properties of nanoscale matter. It is presented in this document the development of Computational Nanoscience as a research area developed at Laboratory for Simulation and Modeling of Materials, outlining the main results obtained to date by using high performance computers, and giving future research perspectives.

1. Origin of Computational Nanoscience at Universidad de Sonora

The intense computational work in physics, chemistry and materials science worldwide, stimulated a very competitive research activity since the mid 1950's, with computers playing a main role for understanding a plethora of basic phenomena governing materials, ranging from nanoscale materials to the bulk. Currently, computer simulation is recognized as a research activity bridging experimental and theoretical approaches. In silico experiments prevent expending time and economic resources, providing fanciful outcomes that give original clues into the knowledge of real materials. Validation of theory through experiments is the icing on the cake, though.
In the 1980’s, when personal computers became popular, computational work was eventually incorporated at the Centro de Investigación en Física. The first theoretical/numerical results on the calculation of the ground and first excited state energy shifts and optical transition energy for a surface F center, appeared on the Revista Mexicana de Física, in 1981.\(^1\) Professor Angelina Uribe-Araujo, a mathematician working at Departamento de Física, assisted the authors, professors Alejandro Clark-Bayón, Marcelino Barboza-Flores, Ricardo Rodríguez-Mijangos and Carlos Ruíz-Mejía, in performing the model codification and numerical calculations. Since then, computer simulation and calculation of electronic properties have been carried out intensively at Universidad de Sonora, and in particular at the Departamento de Investigación en Física. The approval of funds by CONACYT to the project *Computer Simulation of Binary Metallic Systems*, which evolved into the study of homo- and heteroatomic nanoparticles, promoted research activities on simulation and modeling of materials.

The first article on metal nanoparticles where one of the co-authors was working for Universidad de Sonora was published in 1993.\(^2\) Vibrational properties of nickel nanoparticles were studied through a combination of theoretical and computational techniques. In 1996, a series of papers dealing with nickel and gold clusters as well as liquid and amorphous nickel were published\(^3\)-\(^5\) as part of a doctoral research related to computer simulation of materials. In 1997 it was proposed the first research project on computer simulation to get funds from CONACYT, being accepted and obtaining the assigned funds in 2000. This funding was used, in part, to acquire the first high performance computer used to carry out calculations on both, computer simulation of liquid metals and electronic properties calculation of H-doped Si crystal.\(^6\),\(^7\)

2. **Evolution of Research Lines**

It was in 2003 when the *Laboratory for Simulation and Modeling of Materials* was proposed by Dr. Alvaro Posada-Amarillas to the former Head of the Department, Dr. Germán Campoy Güereña, being leaded since then by Dr. Posada-Amarillas, who has received Bachelor and Graduate students and Postdocs wishing to acquire additional
research experience. The current research lines are related to fundamental research on the study of nanoscale systems, particularly devoted to the search of novel structures by using global and local optimization methods, and to the understanding of nanomaterials by quantum chemistry methods. Additionally, this laboratory has facilitated local and external collaborations, existing at present many active collaborators.

The following is a list of current and past senior scientist collaborators:

* Abraham F. Jalbout, Departamento de Investigación en Física, UNISON
* Dora J. Borbón-González, Departamento de Matemáticas, UNISON
* Ignacio L. Garzón, Instituto de Física, UNAM
* Donald H. Galván-Martínez, CNyN, UNAM-Ensenada
* Andreas M. Köster, Departamento de Química, CINVESTAV
* José M. Cabrera-Trujillo, Facultad de Ciencias, UASLP
* Juan M. Montejano-Carrizalez, Instituto de Física, UASLP
* Roy L. Johnston, School of Chemistry, University of Birmingham, U.K.
* J. Christian Schön, Max Planck Institute for Solid State Research, Germany
* Alessandro Fortunelli, Consiglio Nazionale delle Ricerche, Italy

And Postdocs:

* Roberto Núñez-González, currently at Departamento de Matemáticas, UNISON
* Rafael Pacheco-Contreras, currently at Universidad de la Sierra

International collaboration through a research network aimed at the study of nanoalloys, the COST Action "Nanolloys as Advanced Materials" funded by the European Union, has underpinned the scientific growth by increasing the research impact of the investigations developed in this area and providing the means for students and scientists exchange to work within top level international groups. From this, a significant expansion
of skills and work methods has been obtained which, to a great extent, have increased scientific production also making possible the publishing on higher impact factor journals. This may be regarded as a crucial step in the area growth.

Modified version of a photographic composition representing a section of LSMM and the high performance computer, Faraday, which has 136 cores shared out as follow: 16 quad core processors (64 cores) and 12 six core processors (72 cores), all of which are distributed in several nodes. Additionally, the laboratory has 4 iMac computers each having 1 quad core processor and 8 GB in RAM. Faraday was acquired through grants obtained by doctors Felipe Ramos-Mendieta, Jorge A. Gaspar-Armenta and Alvaro Posada-Amarillas.

It should be mentioned that Faraday is a high performance computer also accessed by students working for doctors Ramos-Mendieta and Gaspar-Armenta. Some of them are: Jesús Pablo Lauterio (M.Sc.), Luis Mayoral (M.Sc. and currently a Ph.D. student), Hugo Borbón (Ph.D. student) and José Manuel Nápoles (Postdoc). They have developed software for their research or have run installed packages such as Quantum Espresso, for the calculation of optical properties of relevant materials.
3. Achievements

Nowadays the Computational Nanoscience area goals contemplate scientific research, and developing and training of human resources. A number of scientific articles on mono- and bimetallic nanoparticles have been published; some of them are shown below:


A number of novel structures have been found using a basin hopping code designed to search for minimum energy structures through the global exploration of the potential energy hypersurface (atomic bonding model), some of which are part of Ph. D. thesis results by Maribel Dessens-Félix, from the Programa de Posgrado en Ciencias de Materiales, Universidad de Sonora. The next figure exhibits a few of the lowest energy structures each having different chemical composition.

Figure 1. Four representative lowest energy structures of clusters Pt\textsubscript{x}Au\textsubscript{101-x} obtained by varying chemical composition.

Another global search strategy, the threshold energy method, provided us with a deeper understanding of isomeric spiral and biplanar structures. A major contributor on these findings was Dr. Rafael Pacheco-Contreras, currently at Universidad de la Sierra. In this study we found chirality as a fingerprint of these structures. Chirality is a geometric structural characteristic which means that the structure is not super-imposable to its mirror image by means of pure translations and/or rotations only. Figure 2 shows part of these spiral and biplanar chiral isomers.

Figure 2. Typical spiral and biplanar structures obtained through the threshold method. BP stands for biplanar.
Finally, to emphasize the role played by composition and number of atoms, Dr. Dora J. Borbón-González suggested the existence of Pt-based dodecahedral clusters. A vast search over several bimetallic clusters was performed, succeeding in finding these platonic solid clusters after using a set of parameters for Pt-Cu clusters investigated by Josafat Guerrero-Jordan in his M. Sc. in Physics thesis. Figure 3 shows one of these structures. It is worth mentioning that dodecahedral structures have recently been experimentally obtained as core structures in thiolated nanoparticles.

![Dodecahedral core-shell cluster](image)

**Figure 3.** A dodecahedral cluster obtained by optimizing an empirical model potential.

Density Functional theory (DFT) has also been utilized in our laboratory. A theoretical calculation of the structural properties of a neutral Pt$_1$Pd$_{12}$ cluster was performed by Maribel Dessens-Félix as part of her M.Sc. thesis on Materials Science, using DFT to search for the minimum energy structure. The structural reoptimization and frequency analysis were performed within the generalized gradient approximation (GGA) employing the PBE exchange-correlation functional. Structural distortion of the reoptimized cluster was attributed to a Jahn-Teller effect.

![Figure 4: Local distortion is produced as an effect of electron correlation, as well as an increase of cluster size. Initial structure was obtained from a genetic algorithm (GA).](image)
Recently, copper sulfide clusters were studied by Octavio J. Juárez-Sánchez, a Ph. D. student at Programa de Posgrado en Ciencias de Materiales, Universidad de Sonora, using a combined Empirical Potential-DFT approach to locate ground state structures, focusing on those structures behaving as semiconducting nanoparticles. Our theoretical results are expected to drive experiments in the tailoring of novel, promising nanomaterials for producing energy by taking advantage of photocatalysis. A 12-atom copper sulfide cluster is shown below.

![Figure 5](image.png)

Figure 5. Most stable structure of a copper sulfide cluster. The calculated HOMO-LUMO gap indicates that this nanoparticle is a semiconductor.

3. Available Computational Tools

3.1 Molecular Dynamics

The Newton’s equations of motion are solved using any available numerical integration algorithm with a time step which assures total energy conservation. The initial values of the system's atomic coordinates are provided and the initial momenta are chosen from a Maxwell-Boltzmann distribution of velocities according to the initial simulation temperature. The simulation proceeds through a time loop until the total simulation time is reached. Initialization, equilibration and production are the 3 typical simulation stages needed to unravel structural and dynamical properties of physical systems. It is necessary a model empirical potential from which forces are obtained, thus the integration scheme provides values of acceleration, velocity and coordinates at each time-step. Sometimes a local optimization method is needed to eliminate the thermal motion effect, obtaining a set of typical 3-D structures characterizing the energy landscape of the system's
thermodynamic phase. This dynamical approach allows us to change the thermal state simply by a velocity-scaling procedure.

\[ \text{3.2 Genetic Algorithm}\]

This is a global search strategy based on evolutionary principles to find the optimal individual. When applied to the structural determination of the lowest energy nanoparticle, the configuration of the individual, a nanoparticle, is expressed by atomic coordinates. Many of these configurations are randomly generated to form a generation which evolves according to natural selection rules. In the Darwinian approach, energy is evaluated and compared after performing local optimizations over each cluster. Those having the lowest energy are singled out for mating to build a new generation with optimal individuals. This procedure is repeated until the pre-defined number of generations is reached or the energy convergence criterion has been met. Fitness is defined in terms of an empirical potential function modeling interatomic bonding.

\[ \text{3.3 Basin Hopping}\]

The basin hopping algorithm has been extensively utilized since the pioneering work by J. P. K. Doye and D. Wales as a stochastic search strategy to explore hypersurfaces of cluster systems, and applied to atomic clusters with manageable interaction potential models. Despite its simplicity, this method has proven to be an effective strategy to study several systems described by empirical potentials. It is based on a mathematical transformation of the function that models the potential energy to be explored, which is transformed into a collection of interpenetrating staircases. For each nanoparticle's chemical composition optimizations can be started from random configurations, increasing the likelihood of unveiling their structural complexity by generating a vast number of initial configurations. The basin hopping method requires assigning a definite number of Monte Carlo steps.
3.4 The Threshold Energy Method

This is a Monte Carlo based approach which makes use of random walks below a sequence of prescribed energy lids combined with stochastic quenches. This method requires a low-energy configuration usually obtained from other optimization techniques as initial input. Starting from the global or a local minimum, random walks are carried out through the configurational space, under the constraint that a given energy threshold is not exceeded accepting all moves that fulfill this criterion. After a certain number of steps the system is relaxed into one neighboring minimum. Several stochastic quenches are usually carried out from the same point in order to determine whether the walker is inside a basin or in a transition region. By performing several Monte Carlo runs at different energy lid values, energy barriers separating the accepted global minimum from other minimum energy structures can be estimated. Such a set of runs is repeated starting from many local minima on the landscape to carefully explore the potential energy surface landscape.

3.5 Density Functional Theory

This methodology has evolved since the 1960's, when Hohenberg and Kohn, and later Kohn and Sham, established the mathematical basis for studying quantum systems through the use of electron density functionals. A set of Kohn-Sham equations is obtained by applying the variational theorem to minimize the energy functional, which is solved using exchange-correlation functionals to appropriate model the physical system under study. After a self-consistent procedure leading to obtain the electron density which minimizes the energy, energy eigenvalues and Kohn-Sham orbitals are obtained from which physical or chemical properties are calculated by using computer packages.

4. Theses on Atomic Clusters and Crystals

4.1 Concluded

"Propiedades estructurales y estabilidad en cúmulos de oro, plata y cobre", Johann Omar Zazueta Sánchez, Licenciatura en Física, June 2005.

"Estudio Teórico-Experimental de la densidad de estados electrónicos en la vecindad de la banda de conducción en cristales de KCl:Cu⁺ y KCl:In⁺⁺", Margarita Franco Ortiz, Maestría en Ciencias (Física), April 2006.

“Estudio de propiedades electrónicas y estructurales mediante método Kohn-Sham DFT para nanoaleaciones de 13 átomos de Pdₙ₋ₘPtₘ", Maribel Dessens Félix, Maestría en Ciencias de Materiales, November 2009.


"Cálculo de propiedades estructurales y dinámicas de metales líquidos por medio de simulación computacional", Efrain Urrutia Bañuelos, Doctorado en Ciencias (Física). June 2003.

"Determinación de los mecanismos de formación de nanopartículas de plata sintetizadas en etilén glicol utilizando caracterización teórica y experimental de la banda del plasmón", Ángel Slistan Grijalva, Doctorado en Ciencias de Materiales, April 2005.

“Paisaje de energía de nanopartículas bimetálicas”, Rafael Pacheco Contreras, Doctorado en Ciencias (Física), June 2010.

4.2 Underway*


*All dates are tentative.

5. Future Work

With the available resources at LSMM, it is possible to give a suitable response to the new questions posed by the technological necessity of new (nano) materials. The threshold method can be used to study thermal stability of medium-size mono- and
bimetallic nanoparticles; basin hopping and genetic algorithms might aid in providing new candidate structures to be used in more advanced theoretical schemes; and DFT strategies can be used to explore additional chemical properties of more complex bi- and multimetallic structures. Also, new strategies are feasible to implement with the aim of elucidating new and fascinating basic phenomena leading to the computational design of nanomaterials by means of state-of-the-art methodologies. Nobel Prize in Chemistry 2013 has highlighted the important role played by computer simulation and modeling of materials. New discoveries on nanoscale materials are now made possible by modern computers.

References


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