IX Workshop on Novel Methods for Electronic Structure Calculations

November 10 -19, 2021
La Plata, Buenos Aires
Argentina

Universidad Nacional de La Plata

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Dear friends and colleagues, again this year as we have done every odd year since 2005 we are organizing the Workshop on Novel Methods for Electronic Structure Calculations, this time will be their 8th edition.
The workshop will be dedicated to providing an up to date with the different mechanisms of calculation on materials, as well as the study of different materials. In general, during the workshop an intense exchange is targeted between speakers and participants.

Always the relaxed atmosphere that has been generated at the meeting has allowed communication between speakers and participants, generating ideas for new lines of work, participation in projects, etc. As in the past it will be a great pleasure that you can participate in the workshop and a great joy that we can meet again or visit us first time.

The workhsop will be held in the city of La Plata (Argentina), in the National University of La Plata, between the days 10th and 19th November.

Previous editions

- 2005: Seminar on ab-initio solid state calculations, La Plata – Argentina.
- 2007: Workshop on novel methods for electronic structure calculations and 6th FPLO hand-on, La Plata – Argentina.
- 2009: Workshop on novel methods for electronic structure calculations, La Plata – Argentina.
- 2011: 4th Workshop on novel methods for electronic structure calculations, and first southamerican congress on materials, La Plata – Argentina.
- 2013: V Workshop on novel methods for electronic structure calculations, Montevideo – Uruguay.
- 2015: VI Workshop on novel methods for electronic structure calculations, La Plata – Argentina.
- 2017: VII Workshop on novel methods for electronic structure calculations, Santiago de Chile – Chile.
- 2019: VIII Workshop on novel methods for electronic structure calculations, La Plata – Argentina.

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	Wednesday 10	**Friday 12**	**Wednesday 17**	**Friday 19**
09:00	**Opening talk (9:45)**	**Jorge Kohanoff**	**Claudia Draxl**	**Helena Petrilli**
10:00	**Eduardo Menéndez Proupin**	**Peter Blaha**	**Manuel Richter**	**Sandro Scandolo**
11:00	**Stefaan Cottenier**	**Alejandro Goñi**		**Verónica Ganduglia Pirovano**
13:00	**BREAK**			
14:00	**César Proetto**	**Ricardo Faccio**	**Pablo Lustemberg**	**Verónica Vildosola**
15:00	**Álvaro Mombrú**	**Jorge Sofo**	**Alfredo Juan**	

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Oral talks

IX Workshop on Novel Methods for Electronic Structure Calculations
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Memory Function Representation for the Electrical Conductivity of Solids

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We derive an approximate expression for the electrical conductivity of solids that includes relaxation, dissipation, and quantum coherence effects. The derivation is based on the Kubo expression with a Mori memory function approach to include dissipation effects at all orders relaxation interaction. The expression obtained provides a clear understanding of the evolution of the Drude peak and the broadening of optical transitions for all possible perturbation strength. At the same time offers a practical form of evaluating this important transport coefficient with electronic-structure codes without the complications and limitations of supercell calculations or assumptions about the lost of coherence.

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Understanding the Temperature & Pressure Dependence of Hybrid Perovskite Band Gaps

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Hybrid lead halide perovskites exhibit an atypical temperature dependence of the fundamental gap for the phases stable at ambient conditions: it decreases in energy with decreasing temperature. Reports ascribe this behavior to a strong electron-phonon renormalization, neglecting contributions from thermal expansion. However, high pressure experiments performed on the archetypal perovskite $MAPbI_3$ (MA stands for methylammonium) yield a negative pressure coefficient for the gap of the tetragonal room- temperature phase [1], which speaks against the assumption of negligible thermal expansion effects. I will show that for $MAPbI_3$ the temperature-induced gap renormalization due to thermal expansion is as important as that caused by electron-phonon coupling [2]. This result holds also for phases, stable at ambient conditions, of most halide perovskite counterparts. As an example, results obtained for a series of $FA_xMA_{1-x}PbI_3$ solid solutions, where FA stands for formamidinium [3], will be also presented. Strikingly, the temperature dependence of the gap of a presumably tetragonal but disordered phase, which is stable in a wide range of intermediate compositions and temperatures lower than ca. 250 K, exhibits a quadratic *bowing* of the gap with temperature. This is again interpreted in terms of the combined effects of thermal expansion and electron-phonon interaction. Ab-initio band-structure and lattice-dynamics calculations provide crucial insights into this intriguing behavior of the gap with temperature.

[1]. A. Francisco-López et al., J. Phys. Chem. C **122** (2018) 22073-2208.

[2]. A. Francisco-López et al., J. Phys. Chem. Lett. **10** (2019) 2971-2977.

[3]. A. Francisco-López et al., J. Phys. Chem. C **124** (2020) 3448-3458.

Mixed Ionic-Electronic Transport for Crystalline poly(3-hexylthiophene) with both Explicit Lithium bis(trifluoromethanesulfonyl) imide Dopant and dimethoxyethane Additive Assessment Using ab-initio Molecular Dynamics

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Here, we present *ab-initio* molecular dynamics (AIMD) calculations on the mixed ionic-electronic transport for crystalline poly(3-hexylthiophene) (P3HT) using explicit lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) dopant and dimethoxyethane (DME) additive. Up to now, and to the best of our knowledge, AIMD calculations dealing with mixed ionic-electronic transport in a P3HT crystalline supercell including the use of explicit dopants remain unexplored.

Our ionic and electronic conductivities estimations show good correlation with experimental reports of similar mixed ionic-electronic conductors. The use of less artifacts in our calculations allowed us to reveal some interesting behavior due to the presence of explicit dopant on the most relevant parameters associated to mixed ionic-electronic transport in a wide temperature range.

For the electronic transport, our transfer integral (J) and reorientation energies (λ) values showed an increment respect to typical unexplicit-doped calculations. Furthermore, we also introduce the role of the explicit dopant on the inter-chain, intra-chain, "effective" doping and charge-transfer complex bonding distances and their associated static and dynamic disorder effects on the electronic transport.

The Nature of the Active Sites on Ni/CeO_2 Catalysts for Methane Conversions: When Theory and Experiment go Hand in Hand

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Methane (CH_4) is difficult to convert to upgraded fuels or chemicals because of the strength of the C-H bonds. Its activation and reforming with CO_2 to syngas or with H_2O to produce hydrogen, as well as its direct oxidation to methanol, is increasingly important because CH_4 is a potent greenhouse gas. Ni at low loadings on CeO_2 are active for CH_4 activation at room-temperature and for these methane conversion reactions [1-3]. Revealing the nature of the active sites in such systems is paramount to a rational design of improved catalysts. Here we show that the most active sites are Ni atoms in clusters at step edges on the CeO_2 surface, with a small size. We show that the size and morphology of the supported nanoparticles together with strong Ni-support bonding and charge transfer at the step edge are key to the high catalytic activity towards methane activation, allowing much better activity than expected from earlier linear scaling relations [4-6]. The emphasis is here put on theoretical studies in combination with experiments using ambient pressure X-ray photoelectron spectroscopy, adsorption calorimetry and surface analysis measurements.

We thank Zhongtian Mao and Charles T. Campbell (UW) as well as the experimental group led by José A. Rodriguez and Sanjaya Senanayake (BNL) for their cooperative work. The collaboration of Agustín Salcedo and Beatriz Irigoyen (ITHES, CONICET-UBA, Argentina) is acknowledged.

[1]. Z. Liu, D. C. Grinter, P. G. Lustemberg, T. Nguyen-Phan, Y. Zhou, S. Luo, I. Waluyo, E. J. Crumlin, D.J. Stacchiola, J. Zhou, J. Carrasco, H. F. Busnengo, M. V. Ganduglia-Pirovano, S. D. Senanayake, and J.A. Rodriguez, Angew. Chem. Int. Ed. **55** (2016) 7455-7459.

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[3]. P. G. Lustemberg, R. M. Palomino, R. A. Gutiérrez, D. C. Grinter, M. Vorokhta, Z. Liu, P. J. Ramírez, V. Matolín, M. V. Ganduglia-Pirovano, S. D. Senanayake, and J. A. Rodriguez, J. Am. Chem. Soc. **140** (2018) 7681-7687.

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[6]. P. G. Lustemberg, Z. Mao, A. Salcedo, B. Irigoyen, M. V. Ganduglia-Pirovano, C. T. Campbell, ACS Catal. **11** (2021) 510604-10613.

DFT study of ethanol and formic acid adsorption on CaO(001)

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Ethanol and formic adsorption on CaO (0 0 1) surface at low coverage is studied using Density Functional Theory (DFT) calculations with van der Waals corrections. We investigated the CaO surface in its rock salt structure. The more favorable sites for C_2H_5OH adsorption are on one (or two) Ca cations bonding the O atom from ethanol. H form (OH group) bond to surface oxygens with an adsorption energy of -1.12 (-1.14) eV. The distance of ethanol to surface is in the range of 2.3 - 2.5$\AA$. The molecule presents a strong elongation of the adsorbed O-H group being 53% (51%) larger that its molecular distance. Bond order analysis shows that distances and BO are similar for Ca-O molecule and Ca-O surface. A charge transfer occurs from O atom of the 2nd layer to Ca ions at 1st layer and the molecular O atom gain some charge, while H loses charge towards surface oxygen and from this to the rest of the surface. In the case of H-COOH we found two possible adsorption sites with -2.38 and -2.07 eV, again the O-H bond is elongated with respect to the molecular states. DOS and bonding analysis are performed in both cases.

Breaking Simple Scaling Relations Through Metal-Oxide Interactions: Activation of Methane on M-CeO$_2$ (M= Pt, Ni or Co) Interfaces

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Methane (CH_4) -a greenhouse gas (GHG)- is difficult to convert to upgraded fuels or chemicals because of the high C-H bond strength in the molecule and its non-polar nature. Enabling low-temperature activation of CH_4 is a major technological objective. Descriptors and scaling relations for the first dehydrogenation of CH_4 provide guidelines for comparing and predicting the performance of potential new catalysts [1]. In this work, we investigate how to use metalsupport interactions to enhance chemical reactivity for methane activation, breaking existing scaling relations [1]. In this talk, results obtained using computational models of Pt/ceria systems will be discussed, which are consistent with those of experimental model [2] as well as powder [3] catalysts, and thus help to bridge the materials gap between them. The experimental AP-XPS data indicates that methane dissociates on the Pt/CeO$_2$(111) surface and a Pt/CeO$_2$ powder at temperatures between 25 and 427 °C. When compared to other low-loaded M/CeO$_2$(111) (M = Cu, Ni or Co) systems [4,5], Pt nanoparticles supported on ceria produce the largest amount of CH_x, and is the most active for the conversion of carbon dioxide and methane. The theoretical results for a number of low-loaded metal/ceria systems show that the proposed linear scaling relation,[1] does not generally hold for ceria-supported metal nanoparticles, for which smaller C-H bond activation energy barriers than predicted are found, by up to ∼1 eV. Strong interactions between the small metal particles in direct contact with the ceria support lead to the stabilization of both the CH_4 molecule and the CH_3+H dissociation product, producing active and stable catalysts for methane activation. Our findings should be useful in the rational design of catalysts for reactions involving C-H bond dissociation [2].

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IX Workshop on Novel Methods for Electronic Structure Calculations

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Systematic Studies of Graphenic Systems in the Search of Applications

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Graphene is a material with very exceptional properties which has encouraged very intense research worldwide. However, these properties should be improved through controlled modifications for the application to be feasible.

We undertook a research of graphenic materials -graphene and graphene quantum dots- where DFT simulations were carried out in systems where defects systematically distributed were included.

We used the complementary figure to implement the systematic study and to extract useful conclusions -i.e. the figure formed by the carbon atoms removed to build a vacancy. The occurrence of magnetism, distortions and rippling are features that take part of this study and that help to make useful description to guide the controlled synthesis to be carried out.

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Simulation of Hybrid Metal Halide Perovskites

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Hybrid metal halide perovskites with organic A-site cations have made a great impact in solar cell research, as well as other areas. Here, I present some fundamental aspects of the simulation of these materials using density functional theory, together with our research. These studies include several aspects of single phase $MAPbI_3$ ($MA=CH_3NH_3$), ferroelectric-like grain boundaries, and interfaces with a hole transport material. Also, I present a model of a solid solution of $FAPbI_3$ with $MAPbBr_3$, where $FA=HC(NH_2)_2$.

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Calculating 4f Crystal-Field States by Density Functional Theory

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This lecture provides an overview of existing methods to determine the parameters of a 4f single-ion model by meansof density functional theory (DFT). The standard model of 4f magnetism is introduced, justified, and explained. The ingredients to evaluate its parameters (exchange field and crystal field) are the radial 4f wave function, constructed under observation of the localized character of 4f states, and an appropriately constrained Kohn-Sham potential. Three different implementations of crystal-field parameters from DFT are presented and discussed, and four methods beyond the single-ion model are evaluated.

Electron-Phonon Coupling from Exact Factorization

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The electron-phonon coupling (EPC) is one of the cornerstones concepts in condensed matter physics. Its first-principles derivation is on the other side a long-standing open issue. Aimed at filling this gap, a rigorous approach to the EPC has been attempted, starting from the exact factorization (EF) theorem. Two main questions to be discussed in the talk are as follows: i) how to extract the EPC from the time-independent EF electronic and nuclear equations; and ii) how to proceed with the practical evaluation of the EPC within an ab-initio framework?

DFT Contributions to the Understanding of Li-O_2 Battery Operation

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The Li-O_2 battery is a promising energy storage system that has generated much interest in the scientific community owing to its high theoretical energy density in view of the potential use in electric cars. In the last years, it has been intensively studied with the aim of finding solutions to the limitations that are preventing its practical implementation. The origin of the poor performance is mainly related to the insulating nature of the main discharge product, the lithium peroxide (Li_2O_2), which passivates the cathode during the discharge, limiting the capacity. On the other hand, it demands a high charging potential during the recharge that reduces its efficiency.

A profound knowledge of the electronic and transport properties of Li_2O_2, both in bulk and at the surface, is crucial to understanding battery operation and to propose new routes and strategies to circumvent the above mentioned difficulties.

In this talk, I will describe some of the DFT contributions on this matter.

Standard local DFT functionals induce spurious metallic states in the insulating Li_2O_2 upon lithium vacancy formation or at its non-stoichiometric surfaces. These metallic states have been interpreted as beneficial to the battery because a metallic behaviour of the Li_2O_2 surface could mitigate the electrical passivation of the cathode. I will comment on the crucial role of the intrinsic defects such as polarons and lithium vacancies in the physical properties of Li_2O_2 and I will show the importance of using the correct functionals for the exchange and correlation potential in the DFT calculations.

I will finally describe the effect of doping in the Li_2O_2 decomposition that takes place during the recharge, showing that Na-doping decreases the energy barrier of the limiting step in the electrochemical decomposition reaction, reducing the charging overpotential, in line with the experimental observations.

Carbon at extreme conditions

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The pressure-induced transformation of graphite into diamond, first reproduced in the laboratory in 1955, is now an industrial process with a global market worth $20 billions. In the graphite-diamond transformation pressure is used as an external force to induce the sp^2-sp^3 hybridization change. Extreme conditions of pressure and temperature such as those found in the interiors of planets can nowadays be reproduced routinely in the lab and can be used to explore novel chemical changes in carbon. Understanding such changes has far ranging implications in materials science, chemistry, planetary sciences, and geophysics. In this context, atomistic simulations based on density-functional theory play an important role [1]. I will present some recent updates on the phase diagram of carbon at TPa pressure [2] and discuss the mechanical stability of diamond under hydrostatic and strongly uniaxial compression [3]. I will also illustrate how extreme conditions affect the chemistry of carbon-bearing compounds such as CO_2 and CH_4. Specifically, I will describe the pressure-induced collapse of molecular CO_2 into extended covalently-bonded polymorphs [4] and the solvation, ionization, and full dissociation of methane in water under planetary conditions [5, 6].

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DFT as a tool for electronic structure calculations for solids

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Density functional theory has become the de facto standard for electronic structure simulations in materials science. However, the accuracy and predictability of DFT calculations still depend on the approximate functional in use and unfortunately different material classes and even different properties like formation energies or band gaps may require different approximations. It is thus very advantageous to know for which material class certain DFT functionals perform well and what accuracy/errors one can expect. Even using the most advanced meta-GGAs like the famous SCAN functional, particular challenging are systems with transition metal atoms because of possible strong d-d correlations or van der Waals systems with very weak, but still essential interactions. For testing new functionals an accurate all-electron method like the APW-lo method as embodied in the WIEN2k code provides unbiased results. I'll also demonstrate that the power of DFT nowadays also extends to finite temperature properties and discuss temperature induced phase transitions in $BaTiO_3$ or the effect of phononson the B-K edge spectrum ofhexagnal BN.

Simulation of electron dynamics with real-time TDDFT: Application to electronic stopping

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In this talk I will briefly review ground state DFT and its use in ab initio molecular dynamics simulations, comparing Born-Oppenheimer (BOMD) and Car-Parrinello (CPMD) approaches. Then I will introduce time-dependent DFT (TDDFT) to describe electronic excitations and will discuss its properties, advantages, and limitations as well as similarities and differences with CPMD. I will then focus on the use of TDDFT in its real-time version for the simulation of electronic stopping in materials, showing results for a variety of systems that span from crystalline solids to disordered molecular systems. I will pay special attention to the case of water, which is frequently used as a model medium to describe the irradiation of biological systems. I will also show some recent results of the irradiation of DNA in the presence and absence of the aqueous medium. I will use the example of water to illustrate statistical sampling aspects in the determination of the stopping power, and also to investigate empirical models that are customarily used to compute stopping power of compounds from that of the elementary constituents, e.g. the Bragg additivity rule.

exciting NEWS

Claudia Draxl and the exciting developers team [a]
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Linearized augmented planewave (LAPW) methods are known to be the gold standard for solving the Kohn-Sham equations of density-functional theory (DFT). The all-electron full-potential computer package exciting [1] implements LAPW basis sets that allow for reaching microhartree precision in DFT calculations [2] and providing benchmark results also in many-body perturbation theory (MBPT). The latter comprise, in particular, the GW approach for obtaining the quasi-particle band structure [3] and the Bethe-Salpeter equation for treating optical [4] and core-level spectra [5]. I will provide a review of this method, discussing benefits and challenges, and will introduce the latest developments and implementations. They concern, for example, resonant inelastic x-ray scattering (RIXS) [6], real-time TDDFT [7], various hybrid functionals [8], Ehrenfest molecular dynamics [9], and many others.

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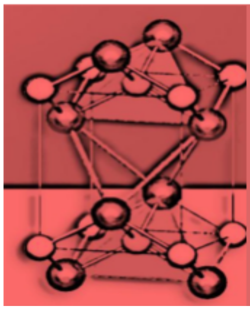

Computer simulations of materials through ab-initio electronic structure calculations performed at IF-USP

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Some examples of the research actually performed in our group at IF-USP using ab initio electronic structure calculations in the framework of the Density Functional Theory in the Kohn-Sham scheme will be shown. We also use these ab-initio results as input to multiscale approaches to model and understand properties of advanced materials. Currently under study are electronic, magnetic, hyperfine and spectroscopic properties of materials with focus on nanomagnetism, hybrid improper ferroelectrics and systems with Nano-biotechnological applications.

IX Workshop on Novel Methods for Electronic Structure Calculations

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Virtual oxides as a test bed for DFT methods and codes

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Some years ago, a community-wide benchmarking effort of +40 DFT methods and codes demonstrated that modern mainstream DFT codes are in good agreement with one another [1]. 71 elements of the periodic table were represented in this test, each as an elemental crystal. A next step in the process is to study all elements (Z=1 to Z=95, no gaps) in a series of very different environments. These environments are provided by 6 binary oxides for every element, chosen in such a way that the element under consideration is forced in 6 different formal oxidation states. This represents a strong transferability test for pseudopotentials. When compared with all-electron results, cases can be found which passed the simpler test but fail on the oxides. We will have a look at preliminary conclusions from this exercise, and I will formulate some caveats on the extent to which DFT codes can be meaningfully compared to each other.

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POSTERS

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Coke-free methane steam reforming on Ni-Ceria catalysts: Active sites and reaction pathway

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Methane steam reforming (MSR, $CH_4 + H_2O \rightleftarrows 3H_2 + CO$) plays a key role in the production of syngas and hydrogen from natural gas. Environmental concerns about air pollution and greenhouse gases have renewed the interest in using hydrogen as a clean energy carrier for automotive applications, through its electrochemical conversion in fuel cell systems. Industrially, MSR involves severe operation conditions such as high temperature and pressure, which are prohibitive for fuel cell applications. The current challenge is to develop novel catalysts capable of carrying out the MSR reaction with high conversion at milder conditions. Ni-based catalysts are promising because of their high activity and low cost, but coke formation generally poses a severe problem[1].

In this work, we present a density functional theory (DFT) study of the MSR reaction over ceria-supported well-dispersed small Ni nanoparticles. Calculations performed for a Ni_{13} cluster deposited on the $CeO_2(111)$ surface predict the complete dehydrogenation of methane over the Ni particle with relatively low activation barriers between 0.3–0.7 eV [2,3]. Water activation occurs preferentially at the Ni-CeO_2 interface with no energy barrier. Different pathways for the oxidation of carbonaceous species were investigated, including their reaction with lattice oxygen or with chemisorbed oxygen resulting from full water dissociation over Ni, as well as with OH groups. The study reveals that neither CH_4 nor H_2O activation are rate-determining steps on this catalyst. We find that the interaction between Ni and the ceria support as well as the low Ni loading are crucial for the reaction to proceed in a coke-free and efficient way through a pathway with barriers below 1 eV that would enable reduced operating temperatures[3].

Ambient-pressure X-ray photoelectron spectroscopy measurements confirm the DFT predicted pathway. These results could pave the way for further advances in the design of stable and highly active Ni-based catalysts for hydrogen production.

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Theoretical-computational study of $CsGeX_3$ (X=I, Br, Cl) perovskites and their applications for solar cells

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All-inorganic perovskite-based solar cells are a new alternative for the more efficient development of solar energy storage technology and industry. Among these materials are the inorganic halide perovskites $CsPbI_xBr_{3-x}$, where the band-gap range varies from 1.72 eV to 2.31 eV for the cases of $CsPbI_3$ and $CsPbBr_3$, respectively. However, these materials contain Pb, which is a polluting material to the environment with a high toxicity, both manufacturing and disposal of devices. Due to this, Pb-free compounds have been proposed such as $CsGeI_3$, $CsGeBr_3$ and $CsGeCl_3$.
In this work, first-principle methods based on Density Functional Theory (DFT) were used in order to study the structural stability, electronic structure and the band-gap of the $CsGeI_3$, $CsGeBr_3$ and $CsGeCl_3$. Additionally, analysis of the differences and similarities of the physical properties between the three Pb-free compounds and the Pb-containing perovskites $CsPbI_3$ and $CsPbBr_3$ was carried out. All calculations were performed with the Full-Potential Augmented Plane Wave method using ELK code. The results obtained from the ab-initio calculations will allow us to perform numerical simulations to optimize the efficiency of solar cells based on these Pb-free compounds, for which the SCAPS-1D software will be used.

Theoretical analysis of the Burstein-Moss shift for n-type semiconductors and the influence of ligand binding

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Based on first-principles calculations within the time-dependent density functional theory, we investigate the main effects of charge carrier concentrations and ligand binding to ZnO nanoparticle surfaces on electronic and optical properties. In this work, we explore the impact of the chemical nature and number of ligands on the Burstein-Moss shift (BM), which is an increase in the optical bandgap with increasing charge carrier concentration. We describe the BM effect as an outcome of the renormalization of the optical bandgap by increasing the charge carrier concentrations, rather than the rigid shift of the Fermi level and absorption edge as established by the current paradigm. Furthermore, our results show the presence of intraband transitions in the crystalline conduction band (CCB) indicating that the free carriers that enable the conductivity can absorb light. These transitions as well as the electronic structure of the CCB are controlled by surface modification with different ligands.

H_2 adsorption and storage on Ni_4 cluster embedded in multivacancy defected graphene. A DFT and thermodynamic study

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Carbon materials such as graphene can efficiently storage hydrogen only at cryogenic temperatures since hydrogen molecules weakly physisorb on the surface [1]. Decorating graphene with transition metals trapped by defects increases considerably the storage capacity reinforcing the bonding and also by the spillover process [2,3].

In the present work, calculations based on density functional theory were performed to study the hydrogen adsorption and storage on Ni_4 cluster embedded in defected graphene with three, four and six vacancies (D_{2h} and D_{6h} symmetry). The Gibbs free energy change with temperature was obtained according to statistical mechanics through a canonical ensemble approach.

Based on the adsorption energies and bond distances, the first H_2 molecule dissociates in all the systems except $H_2/Ni_4@V_4$. Energy absorption of a second and a third H_2 molecule ranges between -0.3 and -0.7 eV with a 0.8-0.9 Å H-H bond distance, corresponding to a physico-chemical mechanism. The 4th molecule adsorbed has a purely physical interaction with the surface (0.1 eV). The stability analysis with the temperature suggests that the second molecule for $H_2/Ni_4@V_3$ and $H_2/Ni_4@V_6\_D_{2h}$ systems can be desorbed at temperatures close to 298 K, suitable for hydrogen reversible adsorption-desorption at ambient conditions. A stable dissociative adsorption up to more than 600 K promises a hydrogen storage efficiency improvement by spillover, which occurs at lower temperatures.

In addition, the analysis of the electronic structure and charge distribution were performed. Besides, the study of the bonds through state density curves, Bader's method, overlap population calculations and bond orders were carried out.

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Theoretical investigation of the interaction between small molecules (H_2X) and an Al_2C monolayer. Potential applications in heterogeneous catalysis and sensors

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Density functional theory (PBE), has been applied to study the adsorption of H_2X molecules on the Al_2C monolayer, with X = O, S, Se, Te. In this work, the potential use of the Al_2C monolayer as a sensor of the small molecules H_2S, H_2Se and H_2Te is studied. These molecules are toxic to humans and have an electronic structure similar to the water molecule (H_2O), which is not toxic and it is difficult (or impossible) to remove under ambient conditions. Adsorption and dissociation energies are calculated. The density of states (DOS) of the pristine Al_2C surface and the Al_2C surface with adsorbed H_2O is also calculated.

A 2 × 2 unit cell is used with lattice constants of 6.019 and 10.14 Å, calculated using the hybrid functional HSE06. The optimized bond length between aluminum atoms is 2.61 Å, while the carbon-aluminum bond length is 1.94 Å.

In Figure 1, a sphere model of the adsorption of the H_2S molecule is shown. The H_2O molecule was adsorbed in the same area, but with each hydrogen pointing towards a carbon atom. The calculated adsorption energies are -0.1575 eV and -0.5096 eV for H_2S and H_2O respectively, in these preliminary results. In Figure 1, a sphere model of the dissociation of the H_2Se molecule is, also, shown. The H_2Te molecule was dissociated in a similar way. Preliminary results show the calculated energies are -1.869 eV and -1.9019 eV for H_2Te and H_2Se, respectively, for both dissociative adsorption configurations.

H_2S and H_2O molecules adsorption sites are similar, while H_2Te and H_2Se molecules differ with respect to the two previous molecules, since H_2Te and H_2Se prefer dissociative adsorption rather than molecular adsorption. On the other hand, the dissociation energies of the H_2O and H_2S molecules were calculated, bringing one of the hydrogen atoms closer to a carbon atom. These energies turned out to be -1.42 eV for H_2O and -1.69 eV for H_2S.

We can observe, from these preliminary results for all cases, that the dissociative adsorption of the H_2X molecules have the lowest energy. However, for H_2S and H_2O, this dissociation must be forced, because H_2O and H_2S interact with the Al_2C surface through molecular adsorption and not direct dissociation. The activation energies required for the dissociation processes $H_2X \rightarrow HX + H$ and $HX \rightarrow H + X$ will be calculated, using the NEB (Nudged Elastic Band) and cNEB (Climbing NEB) methodology. In this way, it will be possible to know how much energy must be supplied to the system, surface with the H_2O or H_2S adsorbed, to obtain the dissociation of H_2S and H_2O molecules. Finally, it was calculated the density of states of the pristine surface and the surface in which the H_2O molecule is adsorbed, based on HSE06 functional. The energy gaps found are 1.08 and 1.4 eV for the pristine surface and the surface with H_2O adsorbed, respectively, which represents a variation of 30% if the two systems, Al_2C and Al_2C-H_2O, are compared, as in Figure 2.

To conclude this presentation, following these preliminary theoretical results, we can say they show that the Al_2C surface has a potential use in catalysis and as a sensor of the studied molecules: H_2O, H_2S, H_2Se and H_2Te.

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Fluorination of goethite (α-FeOOH) at natural concentrations enhances the heterogeneous photocatalytic and photo-Fenton processes towards organic pollutants abatement: degradation pathway and DFT calculations.

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Effect of simultaneous presence of fluorine (0.15-1.2 mg L^{-1}), bicarbonates (83.6-596 mg L^{-1}), and synthesized goethite (α-FeOOH) (0.3 mg L^{-1}) at typical concentrations often found in natural groundwater samples was evaluated on the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) at pH 6.9 under simulated sunlight irradiation (300 W m^{-2}) and H_2O_2 concentrations of 10 mg L^{-1}.2,4-D removal was strongly enhanced by the presence of fluoride. XPS measurements of goethite separated from the aqueous solution after the reaction, confirm the presence of fluoride on goethite surfaces (1.2 % At) and a high resolution F 1s spectrum revealed the presence of two signals at 684.7 eV and 689.5 eV often linked to the presence of adsorbed fluoride on iron (hydr)oxides and Fe-F bonds. This together with the bicarbonate species could benefits the formation of free ﬄOH radicals, producing upward band bending reducing the electron-hole recombination and enhancing the electron transfer to H_2O_2. In this context, the possible modifications of goethite surface were clarified by quantum chemical computation using periodic density functional theory (DFT-periodic) implemented in VASP 6.1. The adsorption of fluoride and bicarbonate ions (F^- and HCO_{3^-}) onto a goethite are simulated in slab models build from (001), (010) and (100) surface. The adsorption energies, density of state (DOS), and optical properties were obtained, giving light to understanding the enhance of the photocatalytic performance.

Probing intercalated transition metal dichalcogenides from ab initio statistical thermodynamic models

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Transition metal dichalcogenides are a large and widely studied class of materials that exhibit a plethora of unique electronic, elastic, thermodynamic and topological properties. They are formed by weakly bound MX_2 stacking-ordered layers, where M is a transition metal and X is a chalcogen, either S, Se, or Te. Chemically stable thin layers of TMDs can be easily obtained via graphene-like mechanical exfoliation from bulk high-quality single crystals due to their weak interlayer van der Waals interactions. Especially, the pristine CdI_2-type structure is a friendly environment for tweaking and fine-tuning the electronic structure through intercalation of other atomic species and complexes in the region between adjacent chalcogen planes. Although CdI_2-type TMDs have proven to be a fertile soil attracting research efforts worldwide with the promising to pave the road for a wide range of both technological applications and high-standard fundamental research, there is a dearth of novel systematic, comprehensive studies regarding the effects of different intercalated species on their electronic ground state and thermodynamic stability. In this vein, we have explored the stability, structural, electronic, and bonding properties of $ZrTe_2$ intercalated with several transition metals by combining statistical thermodynamic models with first-principles electronic-structure calculations. Therefore, we intend to demonstrate with our preliminary results how the use of the generalized quasichemical theory within cluster expansion method can be used successfully in describing these systems in a robust, efficient way, with particular focus in probing the superconducting ground state.

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Decomposition of Li_2S in explicit solvent

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The specific storage capacity of current rechargeable lithium batteries represents a serious limitation for their use in applications such as electric vehicles. One of the most promising technologies for *the next generation* of Li batteries is rechargeable lithium-sulfur (Li-S) batteries [1-5]. These are based on a cathode of a sulfur composite, an organic electrolyte and metallic lithium as the active material for the anode. However, the implementation of Li-S batteries in everyday applications still presents several technical drawbacks that must yet be overcome.

One possible solution with great potential is the use of lithium sulfide (Li_2S) as the cathode material, since it is possible to couple it to Li-free anodes, such as graphite, Si or Sn. However, Li_2S like S_8 are electronic and ionic insulators, with a high activation potential for their initial oxidation step. To overcome this problem, different strategies have been explored, such as the use of catalytic surfaces [6,7]. In a previous work in our group, the effect of the dielectric constant on the activation barrier for the decomposition of Li_2S, was studied by means of DFT calculations on different reactive surfaces, such as graphene and transition metal sulphides [8]. It was observed that an increase in the value of the dielectric constant produces a dramatic reduction in the activation barrier of the reaction.

However, it has been suggested that another important factor that governs the reactions in organic solvents is the so called ”donor number” (DN), which is a measure of the ability of the solvent to form complexes with ions in solution. This implies that to improve the description of the effect of the solvent in the decomposition reaction of Li_2S, it is necessary to include explicit solvent molecules to properly describe the first sphere of solvation of the species along the reaction pathway.

In the present work, we determined, by means of DFT calculations, the barriers for the decomposition of isolated Li_2S (ie. in the absence of a catalytic surface) and where the effect of the solvent is modeled with the introduction of explicit DOL (1,3-dioxolane), DME (dimethyl ether) and DMF (dimethylformamide) molecules, in combination with an implicit description, in which the system is embedded in a continuous dielectric.

DFT computational calculations were performed using Quantum Espresso (QE). The decomposition barrier energy for isolated Li_2S was done using the climbing image elastic band method (CI-NEB). The solvent effect is introduced as a continuous polarizable dielectric, as implemented in the Environ library.

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Tuning the hydrogen adsorption on hydroxyl functionalized graphene with titanium

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Fossil fuels are the main source of energy for the world economy, but they are non-renewable and polluting. Therefore, it is necessary to develop new knowledge and technologies in order to implement the use of other energy sources. The use of hydrogen as a fuel is a good alternative due to its high energy density (3 times higher than gasoline) and low pollution: It only releases water vapor during use in fuel cells. However, the development of a hydrogen-based economy demands an efficient medium for its storage. Storage in gaseous or liquid form does not meet the requirements of the US Department of Energy. So the best option is solid-state storage. Carbon-based materials such as activated carbon, carbon nanotubes, carbon nanofibers, and graphene are attractive for hydrogen storage because of their low density, high porosity, and high surface area[1]. However, only at cryogenic temperatures, they are able to achieve efficient storage due to the low physisorption energy. There are several strategies to improve the adsorption capacity, such as decorating with atoms or clusters of alkali and transition metals, generating vacancies and pores, doping with nitrogen and boron, applying stresses, hydrostatic pressures, and electric field, etc[2]. Following some of these strategies, we investigate, using DFT, the interaction of titanium with the graphene functionalized with hydroxyl group. We describe structural properties, evaluate the hydrogen adsorption mechanisms and energies.

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Water adsorption on β-PbO$_2$: A surface orientation study

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Lead acid batteries (LABs) are one of the main technological innovations in 20th century energy storage. However, to this day, LABs dominate the global battery market, due to their high efficiency, safety, recyclability, and low cost. Lead acid batteries have different disadvantages, such as corrosion in the current collector, sulphation in the electrodes, degradation of the active material and water loss, the latter being one of the most important [1]. The loss of water in LABs can be studied through the interaction of the active material and the H2O molecules. The active material is made up of a mixture of spongy Pb, α-PbO$_2$, and β-PbO$_2$, the latter being in a higher percentage. β-PbO$_2$ has a tetragonal crystalline phase, with surfaces (110) and (101) being the most stable and reactive [2], [3]. In this work, the density functional theory (DFT), implemented in the Quantum Espresso software, is used to calculate the adsorption energy of a molecule of H_2O on two different surfaces, (110) and (101), of β-PbO$_2$, and β-PbO$_2$-OX (with reticular oxygen). The results indicate higher stability of the (110) and (101) surfaces, and the strong influence of the reticular oxygen on the adsorption energy, achieving mechanisms of physisorption and chemisorption.

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Evaluation of the potentiality of phosphorus doped carbon nitride as protective layer of metallic lithium-sulfur batteries

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The growing energy demand and the high environmental impact generated by the use of conventional fuels are the main driving force in the search for alternative methods that are environmentally friendly. In the last decade, special attention has been paid to high-performance energy storage and conversion devices [1-3]. In this regard, lithium-ion batteries are currently the dominant technology as the power source in mobile devices. Notwithstanding the increasing improvements achieved in the last decade, this technology has almost reached its theoretical limit, and does not meet the requirements of new storage systems to be used in, for instance, electric vehicles [4]. There is currently great interest in the development of new materials that provide higher energy density for the *next generation lithium batteries*. Among these, lithium - sulfur (Li-S) and lithium - air (or Li-air) are two of the most promising technologies in this regard. However, there are still numerous problems that must be overcome before these new technologies can become a competitive product in the market. In both types of batteries metallic lithium is used as the active material for the anode. Although this material is ideal for rechargeable batteries due to its high specific theoretical capacity, low specific density and because it has the lowest negative electrochemical potential, there are two main problems that prevent its development: One is the excessive growth of dendrites during the cycles of charge / discharge, and the other is the low coulombic efficiency of the process due the instability of the solid electrolyte interface (SEI). One of the many strategies being explored to tackle these problems is to protect the lithium anode using polymers or laminar materials that modify its surface.

In this work we explore, through DFT calculations, the potential of using 2D sheets of graphitic carbon nitrides (g-C_3N_4) with different degrees of phosphorus doping, to protect lithium metal anodes. We studied the electronic properties of different structures obtained by substituting both nitrogen and carbon atoms in the pristine material. We also analyzed how this influences the adsorption and surface diffusion of lithium.

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High-throughput search of multiferroic materials within different families of ferroelectrics

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Multiferroics materials displaying ferroelectricity and ferromagnetism have technological applications of great interest for electronic devices. Recently, Smidt et al.[1] identified 200 high- quality ferroelectric candidates from the Materials Project database, where 100 of them correspond to new ferroelectrics. Motivated by these results, in this work, we integrate high-throughput screening of materials databases with first-principles density functional theory-based calculations to predict new hypothetical multiferroics materials. We will discuss preliminary result and future directions.

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DFT modelling of hybrid 2D materials for lithium protection in lithium-sulfur batteries

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In the field of lithium batteries there are great challenges to be met. Among them, one of the most important is the one that involves improving energy density in current devices due to the fact that it is very low to be implemented in applications that require high energy demand, such as electric vehicles [1]. In this way, "next generation batteries" can be found, like the lithium–sulphur ones and the lithium–air ones which noticeably improve the previously mentioned aspect [2,3]. However, these batteries in their design have metallic lithium as anode which is very reactive and involves a huge technological challenge for the mass production of these devices. Thus, different alternatives that concern the design of 2D materials which can be used as a protective layer of the anode are studied. The material of this previously mentioned layer must have the characteristics that allow the absorption and quick diffusion of the lithium ions to prevent the dendrites from growing.

In this work we present the computational study of the 2D material with g-C_3N_4, structure. The modelling was made through the Quantum Espresso (QE) that implement the Density-Functional Theory (DFT) and uses periodic plane waves as a base. We mostly analyse the efficacy in this type of material to be implemented as a protective layer of the lithium anode. For this, we carried out a characterization according to the descriptors based on the electronic nature while evaluating as well the effect of the doping with elements like P, O, S and B. Below, we studied the thermodynamic adsorption in different sites and the lithium diffusion as well as the kinetic barriers for its diffusion through the nudged elastic band (NEB) method.

Our results show that the material doping increases the energy of the lithium adsorption over the surface and that it is possible to correlate this phenomenon with the electronic properties of the material.

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Ab initio study of thermophysical and mechanical properties of Ni-X (X=In,Sn) intermetallic compounds

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There is long-standing interest in the study of intermetallic phases (IPs) of the Ni-In and Ni-Sn systems in relation to the In-Sn alloys and their use in lead free micro-soldering processes, considering Ni as the contact material. In this work we investigate by ab initio density functional theory calculations the cohesive, elastic and thermodynamic properties of different intermetallic phases (IP) of the Ni-In and Ni-Sn systems. In particular, we are interested in extending the ab initio database previously developed by the present authors at zero-kelvin [1] to include finite temperature properties. To this end we have performed density functional theory calculations in combination with the quasi-harmonic approximation (QHA) to predict the vibrational density of states, the frequency moments and related Debye temperatures, the Gibbs energy and the heat capacities. Specifically, the $T = 0$ K energy-volume relations determined by VASP [2] were combined with phonon calculation using the PHONOPY code [3] to develop a QHA account of the vibrational thermal properties of various Ni-In and Ni-Sn IPs [4]. In the present work the electronic contribution to the heat capacities and other thermal properties of the low temperature Ni3X (X =In,Sn) hP8 phase stable, the high pressure cP4 phase and the elements Ni, In and Sn are determined. We also analyze trends on the composition dependence of these properties and compare with available experimental data.

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Substitutional iron (Fe) in 2:1 clays

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Environmental pollution is a present day concern. In particular. water pollution has become one of the most important issues due to its direct impact on life. Some widely used remediation technologies are based on the process of sorption of pollutants. Among the sorbent materials, clay minerals such as montmorillonite (MMT) are well qualified [1]. Recently, efforts are being made to design remediation materials that possess permanent magnetism. This allows to manipulate them by external magnetic fields, thus reducing the potential health risks associated with direct manipulation methods [2].

The present work summarizes the preliminary results of a theoretical-experimental study of the influence of substitutional Fe on Na-MMT, $Na_{0.41}[(MgAl_3O_8(OH)_4(Si_8O_{12})]_2 \cdot n(H_2O)$. The present results will allow further studies on magnetically modified clays.

The modelling of Fe-containing clays was performed within the Density Functional Theory framework. Pseudopotential and plane-wave method (Quantum Espresso Code [3]) was used for the ab-initio calculations, with the GGA-PBE approximation for the exchange- correlation term [4]. The starting structure was the pristine phase Na-MMT [5]. First, the magnesium (Mg) atom was replaced by Fe in the unit cell, and then the dilution was decreased by means of $2 \times 1 \times 1$ and $2 \times 2 \times 1$ supercells, by replacing one Mg atom by one Fe. The electric field gradient in the different atoms and the hyperfine parameters for Fe were determined using the GIPAW code (6), and then compared with the experimental results obtained by Mössbauer spectroscopy. Also, the d_{001} of the different proposed structures was calculated to compare with those obtained by XRD for Na-MMT. It was observed that the replacement of Mg by Fe in all the units cells considered decreases d_{001}.

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CO adsorbed on the reduced $Pt_{13}/TiO_2(110)$ catalyst

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Platinum subnanometer clusters adsorbed on oxides like $TiO_2(110)$ are known to play an important role as catalysts for the oxidation process of CO to form CO_2. The CO adsorption by a Pt_{13} cluster deposited on the reduced rutile $TiO_2(110)$ surface is here investigated by means of density functional theory calculations (DFT), using the VASP [1] code and including the Hubbard term "U" to correct the coulombic interactions in the oxide support. The aim is to provide relevant structural and energetic information of this CO/cluster/substrate system.

Previous studies using this methodology let us determine the equilibrium configurations of isolated $Pt_1 3$ clusters; we find that layered clusters are more stable than the more compact and symmetrical cubeoctahedral (Oh) and icosahedral (Ih) isomers. However, when these compact isomers are adsorbed on the oxide rutile surface they experience a strong restructuration, with the Pt cluster getting oxidated and adopting a more layered structure which increases the interaction with the substrate, leading to a high adsorption energy [2,3]. A recent experimental study based on fast dynamic scanning transmission electron microscopy (STEM) performed for Pt clusters deposited on carbon, showed a strong trend for these clusters to exhibit the fcc bulk structure with cuboidal geometries. In particular, for Pt13, the cuboidal structure consists of a basic fcc cube, with a Pt atom missing at one corner [4]. In this work, we first analyze the stability of this new cuboid configuration for the isolated cluster, to evaluate its relative stability as compared to the layered and Oh structures, previously studied by us. Then, we characterize the cluster/substrate interaction for these isomers deposited on the reduced surface: TiO_2 (110) plus an oxygen vacancy (TiO_2+Vo), and compare with the Pt_4-rutile system [5]. The last step is to study the adsorption of CO over the Pt_{13} cluster/substrate system, for the different Pt_{13} cluster geometries considered, and investigating the more favorable sites of adsorption of this molecule. We determine the equilibrium geometries, energies of adsorption, charge transfer effects and the electronic density of states, and discuss these results in connection with the possible oxidation of CO by an oxygen of the substrate.

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