X Workshop on Novel Methods for Electronic Structure Calculation

X WNMESC

December 04 – 06, 2023
La Plata, Buenos Aires
Argentina

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 10th 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 days 4th and 6th December 2023.

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.

↪ 2021: IX Workshop on novel methods for electronic structure calculations, La Plata – Argentina.

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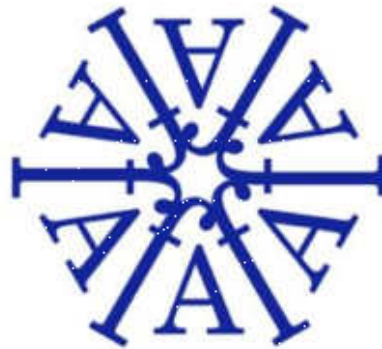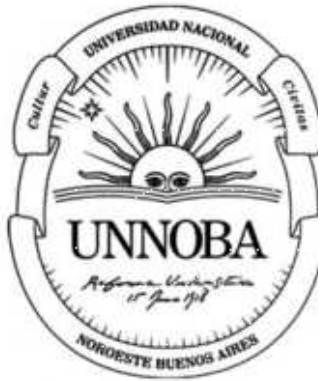
PROGRAM

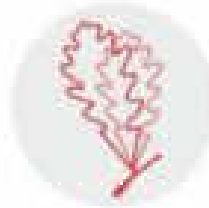|	Monday 4	Tuesday 5	Wednesday 6
09:00 - 09:50	Opening talk	P. Gianozzi (virtual)	S. Cottenier (virtual)
09:50 - 10:30	A. Juan	A.M. Llois	I. Miranda
	BREAK		
11:00 - 11:50	H. Petrilli (virtual)	A. Valencia	J. Kohanoff
11:50 - 12:30	M. Zoloff-Michoff	L. Fernández	D. Mombrú
	L U N C H		
14:00 - 14:50	G. Scuceria	R. Pérez	J. Sofo
14:50 - 15:40	M.V. Ganduglia Pirovano	D. Estrín	A. Saúl
	BREAK		
16:10 - 16:50	A. Bonivardi		S. Koval
16:50 - 17:30	J.M. Oliva-Enrich	Posters + Coffe	I. Arellano Ramírez
17:30 - 18:00	Posters		Closing remarks

LIST OF SPEAKERS

↪ **Jorge Kohanoff**
Instituto de Fusión Nuclear "Guillermo Velarde", Universidad Politécnica de Madrid, Spain.

↪ **Dominique Mombrú**
Área Física, Facultad de Química, Universidad de La República, Uruguay.

↪ **Jorge Sofo**
Department of Physics, Department of Materials Science and Engineering, and Materials Research Institute, The Pennsylvania State University, Penn State, USA.

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Instituto de Física, Universidade de São Paulo, Brazil.

↪ **Luciana Fernández**
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↪ **Dario Estrín**
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↪ **Iván Miranda**
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ORAL TALKS
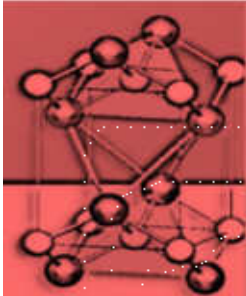
Trends in software for electronic structure calculations

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First-principle calculations have become an exceedingly successful tool for the study of materials properties. Much attention is dedicated on the one hand to the application of old theories and the development of new ones; on the other hand, to the computed physical results. Less attention is paid to what stands in the middle, allowing to translate theory into materials properties: electronic-structure software.

In this talk I will provide my personal point of view on the state of the art and perspectives of electronic-structure software, notably in the framework of density-functional theory. I will briefly describe old and new problems in software development, posed by requirements of

↪ correctness and reproducibility,

↪ maintainability and interoperability,

↪ performance in both serial and parallel execution,

↪ portability on all kinds of hardware, and known solutions (or lack thereof).

Finally I will describe particular some recent improvements of the popular open-source Quantum ESPRESSO distribution, aiming towards "performance portability", that is: the ability to run with excellent performances on all modern computer architectures, in particular hybrid, GPU-accelerated ones that require extensive, architecture-dependent reorganization of codes. Performance portability is one of the main goals of the EU Horizon-2020 project MaX (Materials Design at the Exascale) whose main objective is to provide the community with high-quality, maintainable software that can be used for ambitious scientific goals on forthcoming "exascale" (capable of 10^{18} flops) machines.

[1]. "Quantum ESPRESSO: one further step towards the exascale",
I. Carnimeo, F. Affinito, S. Baroni, O. Baseggio, L. Bellentani, R. Bertossa, P. Davide Delugas, F. Ferrari Ruffino, S. Orlandini, F. Spiga, and P. Giannozzi,
Special Issue on "Software for Electronic Structure Based Simulations in Chemistry and Materials", J. Chem. Theory Comput. (2023), doi: 10.1021/acs.jctc.3c00249
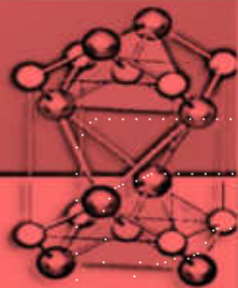
QM-MM simulations using the ANI machine learning potential: assessment of embedding schemes

J.S. Grassano [a, b], J.A. Semelak [a,b], M.C. Gonzalez Lebrero [a,b], A. Roitberg [c], D.A. Estrin [a, b],

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Introduction: Multiscale quantum (QM-MM) schemes, which consist of describing one portion of the system with quantum mechanics and the other using classical force fields, are ideal tools to describe chemical processes in complex environments, such as proteins or solutions. The computational cost of performing QM-MM simulations is mainly determined by the computational cost of the QM calculation and the extent of sampling necessary to describe the system. This makes QM-MM simulations very demanding from a computational point of view. For alleviating this issue, in this work we present a scheme in which the QM region is described by using the ANI machine learning approach developed in the University of Florida in A. Roitberg's group, which provides results of QM quality at a much lower computational cost.

The key issue of the implementation consists in modeling the coupling QM-MM contribution. This interaction is typically computed using an electrostatic embedding approach in which the QM density is calculated in the presence of the MM electrical field. In order to be able to use the ANI approximation to the QM energy, a simpler mechanical embedding scheme is proposed, in which the QM-MM coupling energy is computed by using a set of point charges on the QM(ANI) region. In addition, we propose a correction that includes the polarizability of the QM subsystem by the presence of the field generated by the MM subsystem.

Results : For validating the scheme, we employed a set of molecules, structural isomers of 18 amino acid species, which were extracted from the ANI-1x database. The species were solvated with 4000 water molecules and 100 ps long classical molecular dynamics simulations were performed to relax the solvent and generate representative solvated structures.

The results suggest that, in general terms, the mechanical embedding approach succeeds in reproducing the benchmark term given by an electrostatic embedding scheme using DFT. The quality of the approximation depends strongly on the charge partitioning scheme used. A substantial improvement was demonstrated by implementing the correction for atomic polarizability. The QM(ANI)-MM scheme was tested by performing MD simulations of several small species in different solvents, and computing the IR spectrum using the Fourier transform of the dipole autocorrelation function.

[1]. Smith, J. S., et al, Chemical Science, 2017, 8(4) 3192-3203.

[2]. Smith, J. S., et al., Scientific Data, 2020, 7(1)1-10.
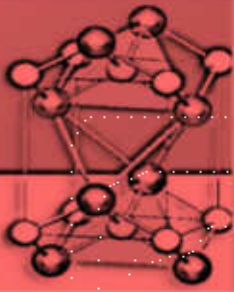
Dependence of the formation energy with the Kohn-Sham solution method and exchange-correlation functional for the XN (X=Al, Ga, In) semiconductors

I.D. Arellano Ramírez [a, b], A.V. Gil Rebaza [c,d]

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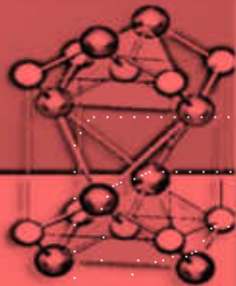[b] *Universidad Nacional de Colombia, sede Manizales, Colombia.*
[c] *Departamento de Física, Facultad de Ciencias Exactas de la Universidad Nacional de La Plata UNLP, La Plata, Argentina.*
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Theoretical and computational studies of materials through Density Functional Theory (DFT) are widely used in solid-state physics to characterize, describe, and predict the properties of diverse and new compounds. One of the parameters to consider is the formation energy of the compound, which gives an idea of its energetic stability. In this study, the formation energies (Ef) of the binary AlN, GaN, and InN semiconductors are reported, and its dependence on the method used to solve the self-consistent Kohn-Sham equations is investigated. The methods used are the Full Potential Augmented Plane Wave (FP-LAPW) method, implemented in the Wien2k code, and the Pseudopotential and Plane Wave (PP-PW) method, implemented in the Quantum Espresso code.
For the PP-PW method, NormConserving, Ultrasoft, and PAW type pseudopotentials are considered. In addition, the dependence of Ef on the exchange-correlation part (XC) is analyzed, where the Local Density Approximation (LDA) is considered with the PW91 parametrization, and the Generalized Gradient Approximation (GGA) with the parametrizations PBE, PBEsol, and WC.
The results show that the formation energies of AlN, GaN, and InN are found to be sensitive to both, the method used to solve the Kohn-Sham's equations, and the XC functional.

Testing the hell out of DFT codes with virtual oxides

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If you use DFT to predict a property of a crystal, how confident can you be that the prediction is computed in a bug-free way? And if your DFT-code uses pseudopotentials, can you trust that the pseudopotential does not modify your predictions? Answering such questions has been the goal of a study a few years ago, in which 71 unary crystals were examined in exactly the same way by 40 different DFT methods and codes [1]. In a next step, a consortium of 45 scientists has done a similar exercise for a much larger pool of crystals: all elements of the periodic table up to Z=96, each in 10 different crystal structures, most of them being (virtual) oxides that sample a range of chemical bond types [2]. In this presentation, I will discuss the reasons to choose these crystals, the different quality criteria by which results can be compared, and we will demonstrate how this exercise leads to more precise and more trustworthy pseudopotential libraries.

[1]. https://doi.org/10.1126/science.aad3000
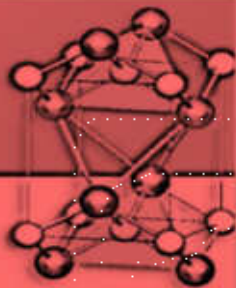
[2]. https://arxiv.org/abs/2305.17274

Low dimensional structures derived from $A_2Ti_nO_{2n+1}$ (n=1-9, A=alkali metal or H) layered titanates and titanium oxides

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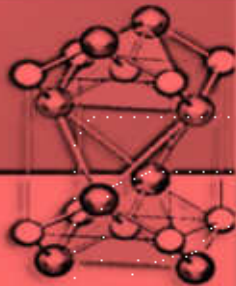
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Since first synthesized by Kasuga et al [1], titania and titanate nanostructures have been extensively investigated given their novel properties and potential applications. They have been characterized in terms of ion-exchange properties, proton conductivity, photocatalytic properties, lithium transport and photovoltaic behavior, showing promising results. Particularly given their high surface area and electronic structure, they are interesting for preparing photoelectrodes to dye sensitized solar cell applications (DSSC).

Despite numerous efforts regarding the synthesis and characterization of titanium dioxide and titanates nanotubes and nanostructures, there is still an open debate about their composition and structural characterization, which are crucial to understand their physical properties and surface reactivity. The aim of our line of research is to contribute to the elucidation of crystal structure (building blocks), geometrical parameters and physical properties of high aspect to ratio titanate nanostructures by looking for experimental- theoretical correlation.

We propose modified bulk phases and two-dimensional models derived from titanium dioxide consistent with experimentally observed nanosheets [2], which can also be a first level of approximation of the walls of larger nanotubes. It is in progress the modeling of this type of structures for the case of lamellar titanates of hydrogen, sodium, and lithium; evaluating structure, reactivity, and optical properties, for which an important volume of experimental results has already been obtained by our group [3-7].

Also, from the fundamental point of view, we model one-dimensional structures such as nanowires with a few angstroms in radius, for which there is experimental evidence. In this type of structures, most of the atoms are found on the surfaces and therefore the superficial and quantum confinement effects that generate important changes in the physical and chemical properties are enhanced. It is intended to deepen the study of these systems [8, 9].

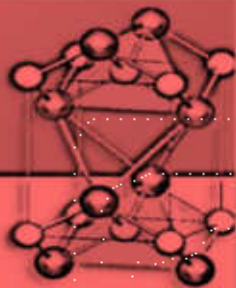In summary, we will show the application of Density Functional Theory for proposing new crystalline phases with different aspect to ratio characteristics. Through the study of its electronic structure, it will be discussed structural properties, vibrational properties (phonons), surface reactivity and optical properties. All of these with the aim to predict and to explain experimental results on layered titanates and titanium oxides.

[1]. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Langmuir 1998, 14, 3160–3163.

[2]. L. Fernández-Werner, R. Faccio, A. Juan, H. Pardo, B. Montenegro, A. W. Mombrú, Appl. Surf. Sci., 2014, 290, 180-187.

[3]. L. Fernández-Werner, F. Pignanelli, B. Montenegro, M. Romero; H. Pardo, R. Faccio and A.W. Mombrú, J Energy Storage 2017, 12, 66–77.

[4]. F. Pignanelli, L. Fernández-Werner, M. Romero, D. Mombrú, M. A. Tumelero, A. A. Pasa, E. Germán, R. Faccio and A. W. Mombrú, Mater. Res. Bull. 2018, 106, 40-48.

[5]. M. Esteves, L. Fernández-Werner, F. Pignanelli, B. Montenegro, M. Belluzzi, M. Pistón, M. Rodríguez Chialanza, R. Faccio, A. W. Mombrú, Ceram. Int. 2019, 45, 1, 708-717.

[6]. M. Esteves, L. Fernández-Werner, F. Pignanelli, M. Romero, M. Rodríguez Chialanza, R. Faccio, A. W. Mombrú, Ceram. Int. 2020, 46, 3, 2877-2886.

[7]. M. Esteves, L. Fernández-Werner, C. Campos Plá Cid, S. Pelegrini, A. A. Pasa, R. Faccio; A. W. Mombrú, Appl. Surf. Sci. 2021, 552, 149534.

[8]. L. Fernandez-Werner, E. A. Gonzalez, R. Faccio, A. W. Mombru, J. Phys. Chem. C 2018, 122, 33633370.

[9]. M. Esteves, L. Fernández-Werner, P. Bechthold, R. Faccio, A. W. Mombrú, ChemestrySelect 2022, 7, 29.

Unraveling Reaction Mechanisms in Heterogeneous Catalysis by Oxides: The Dynamic Duo of Infrared Spectroscopy and Density Functional Theory

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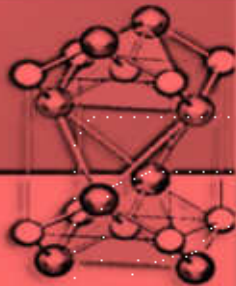
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A comprehensive understanding of reaction mechanisms is essential for the rational design of catalysts to enhance their catalytic performance. To achieve this goal, the use of in situ and operando infrared (IR) measurements combined with density functional theory (DFT) calculations is crucial. In the context of real industrial processes, various key intermediate species have been postulated following this approach:

↪ Formate species are proposed as primary intermediates in the synthesis of methanol from CO_2 hydrogenation on palladium-gallium catalysts and in the water gas shift reaction on ceria-based catalysts,

↪ doping ceria with gallia facilitates hydride formation, significantly impacting the activity for selective hydrogenation of acetylene,

↪ ethoxy configurations and their transformation on CeO_2 nanocubes and nanooctahedra have a profound effect on selectivity during ethanol steam reforming (similar effects are observed in ceria-gallia and Co-based catalysts), and

↪ geminal dicarbonyl species on $Cu^{\delta+}$, with $0 < \delta < 1$, appear to be responsible for the heightened activity of reduced $CuGaO_2$ delafossite compared to the oxidized catalyst, specifically under CO oxidation conditions.

These examples underscore the power of the combined IR+DFT perspective in elucidating rational reaction mechanisms.

Assessment of Density Functional Approximations for correlated oxides surface chemistry: The case of CO bound to CeO$_2$ surfaces

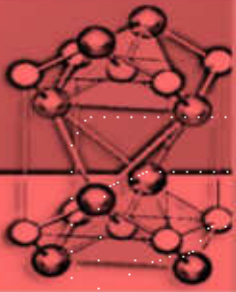M. Verónica Ganduglia-Pirovano [a], Pablo G. Lustemberg [a]

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This presentation comprehensively reviews the facet-dependent adsorption of CO on all three low-index oxidized and reduced CeO$_2$ surfaces. The primary focus is on investigating how CO coverage affects the IR vibrational modes and evaluating the performance of state-of-the-art quantum-mechanical methods in describing these phenomena.

To provide valuable insights, a meticulous comparison is made with a high-resolution IR spectroscopy study conducted on single crystal samples, which aids in assigning distinct CO vibrational bands observed on all three low-index ceria surfaces (see Figure). In contrast to the commonly applied DFT(PBE)+U method, our hybrid-DFT approach, employing the HSE06 functional and saturation coverage, exhibits excellent agreement and reliability in determining CO vibrational frequencies. We attribute the failure of conventional density-functional theory (DFT) to its inadequacy in accurately describing the facet- and configuration-specific donation and backdonation effects. The study convincingly demonstrates that the structure of cerium oxide surfaces and the presence of oxygen vacancies significantly influence CO behavior. The findings are pivotal in revealing the nature of the exposed facets of ceria nanoparticles.

[1]. P. G. Lustemberg, P. N. Plessow, Y. Wang, C. Yang, A. Nefedov, F. Studt, C. Wöll, M. V. Ganduglia-Pirovano, Phys. Rev. Lett. 125, 256101 (2020).

[2]. P. G. Lustemberg, C. Yang, Y. Wang, C. Yang, C. Wöll, M. V. Ganduglia-Pirovano, J. Chem. Phys. 159, 034704 (2023).

Electronic stopping in liquid water, water vapor, and ice

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[b] Department of Physics, Nanjing University of Information Science and Technology, Nanjing 210044, China.

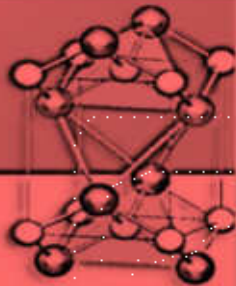[c] Theory of Condensed Matter, Cavendish Laboratory, University of Cambridge, CB3 0HE, United Kingdom.

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Time-dependent density-functional-theory (TDDFT) is a valuable tool to describe electronic excitations, in particular the energy loss to electrons and the electronic stopping power (S_e) in a material due to ion irradiation. TDDFT is implemented in two ways: linear response calculations (LR-TDDFT), and real-time electron dynamics simulation (RT-TDDFT). LR-TDDFT is used to compute the dielectric function and, from there, differential cross sections, energy loss function, and stopping power. Its main limitation is that electrons should respond linearly to the interaction with the external agent. This is valid at high velocities but becomes questionable as the velocity of the projectile decreases. RT-TDDFT, instead, is valid in any velocity regime and, while stopping power can be readily calculated, access to quantities like differential cross sections is far from obvious. Since the seminal work of Pruneda et al. 15 years ago [1], RT-TDDFT has been increasingly used to calculate electronic stopping power in a variety of materials including metals, semiconductors and insulators, 2D-materials, molecular systems, water and biological matter. The usual setup of these simulations is that the projectile crosses the sample at constant velocity and direction, exciting electrons along its way. Since the energy loss depends on the electronic density, which is non-uniform through the system, being this a crystal or a disordered medium, it is important to consider sufficiently many trajectories to obtain a meaningful average S_e that can be compared to observation. At low velocities the projectile is likely to get deflected from its path, and hence constant velocity is not meaningful any longer. Instead, Ehrenfest dynamics where the projectile (and the other atoms in the system) are allowed to move with the forces arising from the time-dependent density.

For disordered systems we recently proposed a trajectory pre-sampling method based on a geometric criterion, which proved very efficient for liquid water [2]. We will first summarize this methodology and discuss results for liquid water. Then, we will address the issue of additivity in stopping power of compounds in terms of their components, focusing on water vapor [2], comparing our RT-TDDFT curves to experimental and SRIM data and use them to validate Bragg's Additivity Rule (BAR) and the Core and Bond model for stopping in compounds [3]. For hexagonal ice we used a different sampling method using a grid of trajectories parallel to the hexagonal channels and studied it via Ehrenfest dynamics. This allowed us to unveil an interesting new effect by which low impact-

parameter projectiles deposit energy into the target nuclei through the modification of the electronic density. Unlike standard nuclear stopping, this effect is maximum at the electronic Bragg peak, and explains an isotope effect between light and heavy water so far ignored [4].

Protons generate low-energy electrons that can also go on and interact with water, exciting other electrons. Simulating the irradiation with electrons is much more complicated than with protons for several reasons. Firstly, they due to their small mass, constant velocity is not a meaningful option, and one must use Ehrenfest dynamics. Secondly, in principle they can exchange with the other electrons in the sample. Thirdly, at low velocities their quantum character cannot be ignored. At high velocities one can approximate this with classical electrons, but at low velocities this is not meaningful. The crossover is estimated to be at around 1 keV. The simulations with classical electrons are in progress, but in the meanwhile we have calculated the electronic stopping power for electrons using LR-TDDFT [5] and found that the effect of the mass is quite important, reducing S_e significantly relative to protons. This reduction was traced back to energy and momentum conservation rules [6]. The location of the Bragg peak, however, is not reproduced well in linear response, while RT-TDDFT simulations are closer to experiment in this respect.

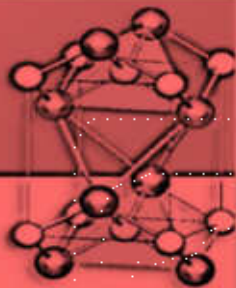[1]. J. M. Pruneda et al., Phys. Rev. Lett. 99, 235501 (2007) https://doi.org/10.1103/PhysRevLett.99.235501

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A theoretical study of ethyl formate adsorption on CaO (001)

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Ethyl formate adsorption on CaO (001) is analyzed using Density Functional Theory (DFT) with Van der Waals corrections, implemented through the Vienna ab Initio Simulation Package (VASP). Our calculations reveals a posible adsorption sites at low coverage with adsorption energies of -1.21 eV, that is more stable than ethanol and less stable than formic acid. Both molecular oxygens bond to two Ca atoms and C methyl bonds to a surface oxygen. The analysis of the electronic structure and bonding show a stabilization of ethyl formate as a result of a shift in their states to lower energies, with respect to the gas phase. A relaxed molecular geometry is obtained after adsorption with no dissociation detected. There is a charge transfer ($0.20\ e^-$) from the adsorbate to the surface. At the same time, H-C (formate) experiment a charge decrease of $0.16\ e^-$. The Ca-O in the surface shows mostly a decrease in BO after adsorption. In this presentation, we also compare ethyl formate adsorption with previous studies considering formic acid and ethanol in the context of biodisel production.
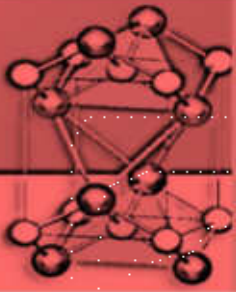
Ab initio molecular dynamics and path integral Monte Carlo simulations of the ferroelectric phase transition in KDP

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The prototype of the H-bonded ferroelectrics KH_2PO_4 (KDP) was comprehensively studied in the past, although the explanation of its ferroelectric-paraelectric (FE-PE) phase transition and the associated huge isotope effect still remains elusive. We have carried out ab initio molecular dynamics (AIMD) and path integral Monte Carlo (PIMC) calculations to shed light in the nature of the FE phase transition. We included nonlocal dispersion corrections with the van der Waals functional vdW-DF, which are, together with nuclei quantum corrections, necessary to describe properly the H-bond geometry and the proton transfer energy barriers of the system. A first insight in the transition is achieved by AIMD simulations for classical nuclei with the lattice fixed to that for KDP and to the expanded one for the deuterated case (DKDP). The results for the DKDP lattice show a large increase in T_c, about $\sim 70K$, compared to the KDP case, in qualitative agreement with experiments. We also show that neighboring proton jumps, driving the disorder phase, are correlated at the transition, fulfilling the so called ice rules. In order to study nuclear quantum effects, we developed a 1D model with potential parameters adjusted to the ab initio results, which considers the bilinear proton-proton interaction in mean-field. PIMC simulations for this model show a huge isotope effect in the critical temperature originated in a strong feedback between tunneling and geometrical modifications of the H-bond, which is in very good agreement with experiments. By applying pressure we found a linear correlation between T_c and the proton/deuteron distance to the center of the O-H-O bond which agrees with neutron diffraction data. Our results show the relevance of the geometrical effects in the FE phase transition and the existence of a quantum paraelectric phase at a large critical pressure.
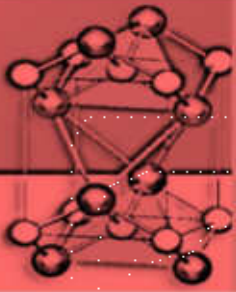
Spin-lattice couplings and Gilbert damping with *ab-initio* accuracy

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In the field of ultrafast magnetization dynamics, understanding the interplay between lattice, spin, and electronic degrees of freedom is a necessary step to the description of its origin. The microscopic picture can be initially draw based on the angular momentum and energy flows between those three main actors in play, which can, in turn, be characterized by their respective couplings. For systems with magnetic order, where a collective motion of spins exists, both magnetic moments and lattice degrees of freedom are coupled via the electronic medium, which can influence, for instance, both magnon and phonon spectrum and lifetimes.

Although a formalism to describe the magnetization dynamics accounting for the spin-lattice coupling (SLC) is known from many years ago [1], there is still a gap in the literature regarding the parameters for real materials, obtained with ab-initio accuracy. On the other hand, the coupling between the spins degree of freedom and the electronic system is related to the Gilbert damping (GD) parameter, which regulates the rate of energy dissipation from the former. I'll discuss the new theoretical developments to calculate both SLC and GD quantities from first principles, in the framework of a real-space linear muffin-tin orbital (LMTO) method.

The formulations are derived to provide input parameters for the phenomenological Landau-Lifshitz-Gilbert dynamics, in the atomistic description. Results and implications for elemental ferromagnetic materials (e.g., Fe, Co, Ni) will be also presented and examined.

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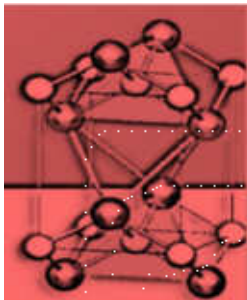
X Workshop on Novel Methods for Electronic Structure Calculations
04th – 06th December 2023
La Plata – Argentina

Molecular identification with high-resolution AFM images, DFT simulations and deep learning

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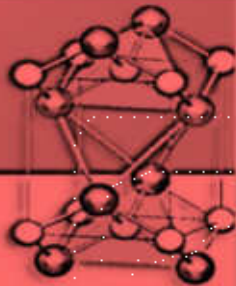
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High resolution non-contact atomic force microscopy (HR-AFM) with CO-functionalized metal tips reveals the internal structure of adsorbed organic molecules with unprecedented resolution. resolving intermolecular features, determining bond orders, and characterizing intermediates and final products generated in on-surface reactions [1]. Recent advances in the interpretation using DFT-based methods [2] of the AFM contrast observed in porphycenes [3] and on self-assembled molecular layers driven by either halogen [4] or hydrogen bonds [5], shows that there are clear connections between fundamental chemical properties of the molecules and key features imprinted in HR-AFM images with submolecular resolution.

Inspired by these results, we address the problem of the complete identification (structure and composition) of molecular systems solely based on AFM images exploiting deep learning (DL) techniques. In a first step, we restrict ourselves to a small set of 60 flat molecules and demonstrate the automatic classification of AFM experimental images by a DL model trained essentially with a theoretically generated data set [6]. We analyze the limitations of two standard models for pattern recognition when applied to AFM image classification and develop a model with the optimal depth to provide accurate results and to retain the ability to generalize. We show that a variational autoencoder (VAE) provides a very efficient way to incorporate into the training set, from very few experimental images, characteristic features that assure a high accuracy in the classification of both theoretical and experimental images.

Learning from the successes and the limitations of this proof-of-concept, we have developed QUAM-AFM, the largest data set of simulated AFM images generated from a selection of 685,513 molecules that span the most relevant bonding structures and chemical species in organic chemistry [7]. QUAM-AFM contains, for each molecule, 24 3D image stacks, each consisting of constant-height images simulated for 10 tip–sample distances with a different combination of AFM operational parameters, resulting in a total of 165 million images. The data provided for each molecule includes, besides a set of AFM images, ball-and-stick depictions, IUPAC names, chemical formulas, atomic coordinates, and map of atom heights. In order to simplify the use of the collection as a source of information, we have developed a graphical user interface that allows the search for structures by CID number, IUPAC name, or chemical formula. Using QUAM-AFM, we have designed and trained different deep learning models to go beyond the classification of limited groups of molecules and achieve the complete identification of an arbitrarily complex, unknown molecule, including multimodal recurrent networks (M-RNNs) [8] and Conditional Generative Adversarial Networks (CGANs) [9].
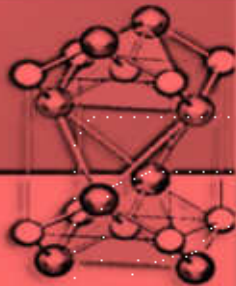
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# Studies of doped systems of poly(3-hexylthiophene) (P3HT)

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Here, we present a combined experimental and theoretical study on the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) doping mechanism of regioregular poly(3-hexylthiophene) (P3HT). First, we focus on the effects of LiTFSI doping in both crystalline and amorphous structures of P3HT by performing a complete structural analysis supported by classical molecular dynamics (MD) calculations. Then, we study the effects of LiTFSI doping on electronic properties such as charge transfer and charge transport by performing Raman and impedance spectroscopy, in both cases supported by density of functionals theory (DFT) calculations using periodic boundary conditions. Our structural analysis suggests that the LiTFSI dopant is mainly located in the amorphous region and only a small fraction is located in the crystalline region. In addition, our DFT calculations also suggest that the LiTFSI dopant can effectively act as an electronic acceptor only when it is located in the vicinity of and is accessible to the thiophene rings of P3HT due to the formation of a $\pi \cdots \text{Li}$ chemical bond as an anchoring mechanism, permitting the electronic charge loss of thiophene rings through the sulfonyl groups.

We also made ab initio molecular dynamics calculations dealing with mixed ionic-electronic transport in a poly(3-hexylthiophene) crystalline supercell, including the use of full explicit lithium-based dopants and additives. Up to now and to the best of our knowledge, the use of full explicit dopants and additives for both ionic and electronic transport calculations has remained practically unexplored due to their high computational cost. The use of fewer artifacts and other common assumptions in our calculations allowed us to reveal some interesting behavior associated with the presence of LiTFSI dopant and dimethoxyethane (DME) additives on the mixed ionic-electronic transport in a wide temperature range. Our ionic and electronic conductivity calculations show a good correlation with the experimental reports of similar mixed ionic-electronic conductors in the very recent literature. We also introduce the role of the explicit dopant in the interchain, interchain "effective" doping, and charge-transfer complex bonding distances, and their associated static and dynamic disorder effects on the electronic transport. A thorough understanding of the LiTFSI doping mechanism of poly(alkyl thiophenes) (P3HT in this particular case) is crucial to elucidating not only the electronic but also the eventual mixed ionic-electronic transport mechanism and its promising properties, particularly as electrodes for lithium ion battery applications.
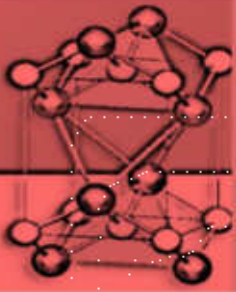
Interfacial interdiffusion and formation of skyrmions: Pd/Co/Pd as a test case

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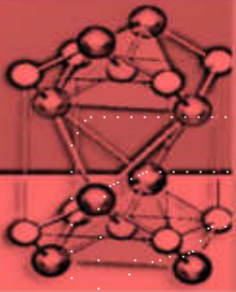
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Skyrmions are magnetic nanostructures which have promising applications in the design of new technologies, especially in storage devices. One of the main interactions known to be responsible for its stabilization is the Dzyaloshinskii-Moriya interaction (DMI), which arises in the presence of broken inversion symmetry and its strength is related to a large spin-orbit coupling (SOC). Asymmetric interfaces, which combine magnetic and heavy elements, attracted the main attention in the search for skyrmions. But curiously, recent experimental works have placed symmetrical interfaces in perspective as candidates to host topological magnetic nanostructures, with the observation of room temperature skyrmions in Pd/Co/Pd multilayers [1]. The origin of a non-null DMI in these symmetrical stackings is still controversial. Here, using a Real-Space [2] method to perform electronic structure calculations in the framework of the Density Functional Theory (DFT) in combination with Atomistic Spin Dynamics simulations [3], we investigate Pd/Co/Pd multilayers, focusing on correlating interfacial atomic intermixing and the formation of skyrmionic phases. As an important result [4], we show that the DMI strength is strongly enhanced by the presence of defects, due to a local symmetry breaking induced in the system.

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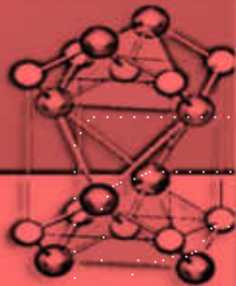[4]. P.C.Carvalho et al, Nano Lett. 23, 4854(2023).

Generalized Quantum Langevin Equation for Transport: The Case for Interband Coherences in the Electrical Conductivity

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Decoherence, dissipation, and thermalization are key ingredients for a quantum theory of transport processes. To go beyond the semiclassical description given by the quantum Boltzmann equation, we explore the use of the generalized, quantum Langevin equation. A single memory-function approximation, appropriate for the hydrodynamical regime, allows the inclusion of interband coherences that are neglected in the semiclassical description. These interband coherences are relevant even in the limit of weak scattering, where the Boltzmann description is deemed appropriate. As an example, we discuss the case of narrow band gap semiconductors at low doping that are commonly used in thermoelectric applications. In these materials, Boltzmann wrongly predicts zero conductivity at zero temperature, while we obtain a finite residual conductivity. This improvement in the description of transport coefficients is achieved without extra computational cost and can be easily implemented in current electronic structure codes and is already implemented in Exciting and PAOFLOW. The memory-function approach to quantum dynamics has a long history of development. I will review the basics of this approach and provide a perspective on possible applications in the description of decoherence and dissipation in materials.
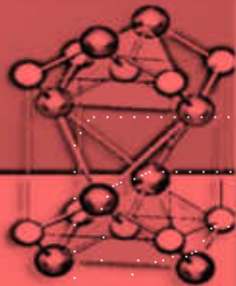
Methods for Strong Electron Correlation

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email:

Quantum Chemistry is a mature field. Progress in the last 50 years has been fantastic. The weak electron correlation problem has been conquered by coupled cluster theory, but strong correlation remains pervasive and problematic. Many practical applications are hindered by this obstacle. Of course, it is not surprising that after almost 100 years of Schrodinger equation, only the most difficult problems are left. In the past decade, my research group has focused on strong correlation, and in this talk, I will discuss our recent effortsto tackle it. Our current approach centers around the hope that a noncanonical duality may convert strongly correlated electrons into weakly correlated ones. Many-body string operators, whose matrix elements can be obtained with polynomial cost, play a central role in our approach. I will present proof of principle applications to model systems where the interaction strength can be tuned.
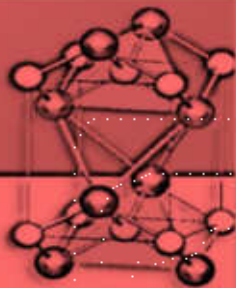
Optical properties of perfluorotetracene (PFT) crystal polymorphs and Perfluoropentacene (PFP) co-crystals

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The family of perfluorinated acenes is gaining popularity among organic materials for optoelectronics. Since the electronic and optical properties of molecular solids are crucially dependent on their packing motifs, it is crucial to consider crystalline phases in the simulations to understand the structure-property relationships of these materials, especially regarding electronic correlations and excitations. Here, we investigate from first principles by means of density functional theory and many-body perturbation theory the electronic structure and the optical excitations of two crystal polymorphs of perfluorotetracene, considering for comparison tetracene and the corresponding isolated molecules. In addiction to that the triclinic pentacene:perfluoropentacene co-crystal is including in our study. This way, we can assess the effects of fluorination as well as of the crystal periodicity. In the polymorphs crystals we find that the absorption spectra are only mildly influenced by the packing motif. However, our analysis gives insight into the exciton binding energies as well as the spatial distribution of the excitons. We inspect not only the first excitations but also the higher-energy ones, thus providing an all-around understanding of the optical excitations in these materials. Interesting in the case of molecule co-crystal, we demonstrate that the nature of optical excitations cannot be reproduced by a molecular cluster model where the first excitation is unambiguously polarized along the short molecular axis.

"In Silico" Design of Novel Materials for the Next Generation of Lithium Batteries

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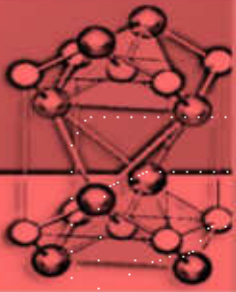email: martin.zoloff@unc.edu.ar

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 are 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.

Most notably, the so-called "shuttle effect", originated by the migration of Li_2S_x (x = 2, 4, 6, 8) species on the side of the cathode; the generation of lithium dendrites on the side of the anode, are only two of the most prominent problems that have not yet met a definite solution.

One possible solution for both of these problems is the use of laminar 2D materials, such functionalized graphene sheets, or doped graphitic carbon nitride [6].

In this work, we show how ab initio computational modeling at the DFT level can be used as a very useful tool to guide the design of tailored-made surfaces with specific electronic properties to address on one hand the adsorption and electrocatalysis of lithium polysulfides in the cathode, and on the other hand, to provide multiple sites for lithium nucleation and low diffusion barriers for a more homogeneous patting process in the anode.

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Magnetic order, magnetic excitations and magnetoelastic interactions in a two-dimensional van-der Waals system

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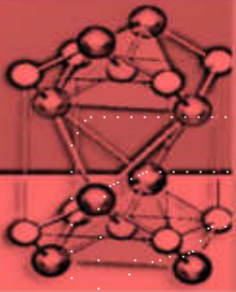
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The discovery of graphene, followed by the development of exfoliation techniques of other van der Waals (vdW) systems, has motivated a great interest to study the unique properties of quasi two-dimensional (2D) compounds. Interestingly, many vdW compounds are magnetic and antiferromagnetic (AFM) order is very often observed in semiconductors with relatively large effective interactions resulting on intermediate transition temperatures (75 - 210 K) and AFM resonances in the THz range close to the optical phonon's frequencies. The van der Waals antiferromagnetic systems thus represent an extremely rich playground for studying non-trivial interactions between electronic, magnetic, and vibrational properties with potential applications.

In this work, we are interested in $MnPS_3$, a member of the metal phosphorus tri-chalcogenides family MPX_3 (M = Fe, Co, Ni, M and X = S, Se). The magnetic centers in $MnPS_3$ are the Mn^{2+} ions. They form a distorted honeycomb lattice showing AFM Néel order below 78 K with magnetic moments perpendicular to the planes.

In the first part of the talk, I will discuss the magnetic order and the physical origin of the magnetic anisotropy taking into account that one expects a negligible spin-orbit coupling associated to the 3d5 electronic configuration of the Mn^{2+} ions. I will compare single ion and magnetic dipolar contributions to available magnon band and magnetic spin resonance measurements.

In the second part, I will show Raman scattering measurements as a function of temperature where some of the modes show a blue shift when the temperature is raised and cross the AFM-paramagnetic transition. I will present density functional theory (DFT) calculations of the effective exchange interactions and Raman active phonon modes which show that the peculiar behavior with temperature of the low energy phonon modes can be explained by the symmetry of their corresponding normal coordinates which involve the virtual modification of the super-exchange angles associated with the leading antiferromagnetic (AFM) interactions.

Xth edition of "Novel Methods for Electronic Structure Calculations": What have we done in these nearly two decades?

Ana M. Llois [a]

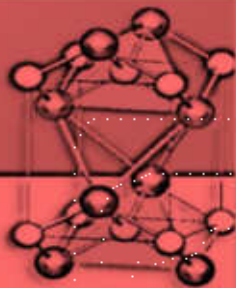*a Instituto de Nanociencia y Nanotecnología (INN) CNEA-CONICET
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It has been nearly two decades since the first edition of the Workshops "Novel methods for electronic structure calculations", marking a significant passage of time.

Throughout these years, our group has dedicated itself to exploring various types of materials and studying diverse properties. A wide range of low dimensional systems, complex surfaces and interfaces as well as 2D materials have been visited using ab initio techniques. We have gone from LMTO to Wien2k, from Wien2k to VASP. FLEUR, SIESTA, and Quantum Espresso have also been and are being used.

In this presentation, I will provide a concise historical overview of the research conducted within our group using ab initio techniques. Additionally, I will offer some insight into the current state of the field.

A new 2D chemistry of Boron?

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[f] *CONICET-Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Buenos Aires 1428, Argentina.*
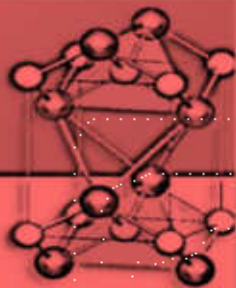[g] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Universidad Nacional de La Plata, CONICET, La Plata 1900, Argentina.*
[h] *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Bilbao E-48080, Spain.*

email:

The isolation of a 2D hexagonal borane layer $(BH)_1$ – borophane – from superconducting MgB_2 [1] and the 2D hexagonal pure boron layer β_{12}-borophene [2,3] calls for the possibility of developing a new 2D boron chemistry.
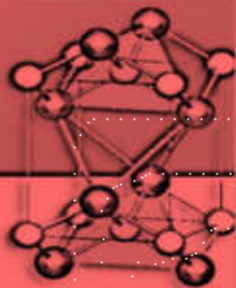
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[8]. J.M. OlivaEnrich et al, Chem. Phys. Chem. 2020, 21, 2460 - 2467

POSTERS

Theoretical study of Fe_3O_4 (111) and (001) surfaces and their reactivity towards H_2O_2

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Fe_3O_4-based nanozymes are nanomaterials that have the inherent ability to mimic the catalytic activity of peroxidase-like enzymes[1]. These materials are being increasingly used for generating or scavenging reactive oxygen species through catalytic reactions for industrial or therapeutic applications. Fe_3O_4 is a mixed-valence compound that consists of both Fe^{2+} and Fe^{3+} ions which promotes the transfer of electrons between the two ions, resulting in a unique catalytic behaviour [2]. The most stable Fe_3O_4 terminations are the (111) and (001) facets [3].

In this work, density functional theory (DFT) was used to study the Fe_3O_4 (111) and (001) surfaces, the latter one considering the observed $(\sqrt{2} \times \sqrt{2})R45°$ surface reconstruction [4]. We consider the adsorption and dissociation of H_2O and H_2O_2 on these Fe_3O_4 surfaces as a first step towards understanding the peroxidase-like catalytic mechanism on the surfaces of Fe_3O_4 nanozymes.

[1]. L. Z. Gao et al., Nat. Nanotechnol. 2, 577 - 583 (2007).

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A theoretical study about structural phases of nanostructured sodium titanates under different synthesis conditions

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[b] Department of Material Science and Engineering, Saarland University, Germany.
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Sodium-based titanates nanostructures are promising materials for energy storage and photo-electronic applications. These structures can be obtained by the hydrothermal method developed by Kasuga [1,2]. Hydrothermal synthesis conditions, such as temperature, time and pH, can modify the internal structure and morphology of nanostructures obtaining: nanoparticles, nanotubes and nanorods. As it was presented in [2, 3], temperature, time and pH conditions of hydrothermal treatment influence the morphology, structural, electrical, and optical properties of these compounds. This work proposes a theoretical study based on residual structural phases resulting from high-temperature heating of a selection of the samples presented in [2,3]. After this calcination process, an X-ray diffraction scan reveals that the samples show the coexistence (in different proportions) of hexa- and tri-titanates of sodium. Due to the high annealing temperatures applied, only sodium phases appear, but it cannot be ruled out that it initially phases incorporates H^+. As it suggested in literature [4, 5], it is inferred that before the annealing process both hexa- ($Na_xH_{2x}Ti_6O_{13}$) and tri-($Na_xH_{2x}Ti_3O_7$) titanates of hydrogen and sodium phases may be presented. To study this possibilities we simulate the mentioned phases with x = 0, 1, 2. Calculations were made on these structures based on first principles in the bulk material. The results obtained from the theoretical calculations attempt to explain the properties measured as X-ray diffraction, Raman spectroscopy and optical measurements of nanostructures experimentally obtained. Furthermore, we explore the use of both single (PBE) and hybrid (HSE06) functionals for calculating bandgap energies. Surprisingly, contrary to what might be expected for other types of structures, the hybrid functional does not demonstrate any improvement in the gap values [6].

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[6]. Amy,L.; Favre,S.; Campo Schneider, L.; Faccio, R. (2023). Structural phases of sodium titanate nanotubes obtained in diferent synthesis conditions: A theoretical study. MRS Advances
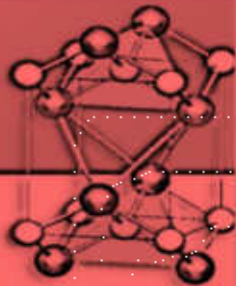
Density Functional Theory for the study of the physical properties of Fe_3O_4 and $CoFe_2O_4$
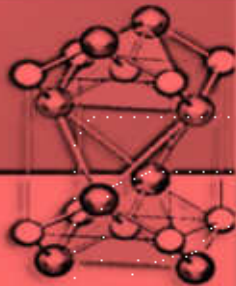
C.A. Portilla Liberato [a], A.V. Gil Rebaza [b,c], S.R. Jauregui Rosas [a]

[a] *Grupo de Investigación en la Nanociencia y Nanotecnología (GMIN-UNT), Universidad Nacional de Trujillo, Trujillo - Perú.*

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We present a computational study based on the Density Functional Theory (DFT) of the magnetic properties and density of states (DoS) of Fe_3O_4 and $CoFe_2O_4$. Using ab initio calculations, the electronic structure and the optical transitions have been analyzed and the structural and magnetic ground states were obtained. In addition, in order to understand the distribution of electronic states in the valence range energy and describe the orbital hybridization between the atoms, the DoS has been investigate. Finally, we performed a phonon calculation using a finite difference method to obtain the normal vibrational modes of the compounds.

A new 2D chemistry of Boron?

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[a] Instituto de Química-Física "Blas Cabrera" (CSIC), Madrid E-28006, Spain.

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[f] CONICET-Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Buenos Aires 1428, Argentina.
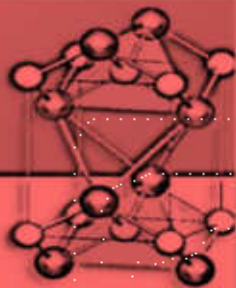
[g] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Universidad Nacional de La Plata, CONICET, La Plata 1900, Argentina.

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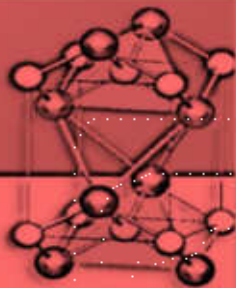
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Core-shell nanohybrids (Au/Graphene): Spontaneous synthesis, characterization and potential application in biosensors
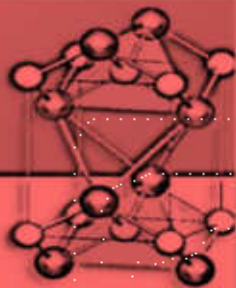
J. Ventre [a], S.D. Barrionuevo [a], A. Renna [a], D.M. Arboleda [b], M.G. Bellino [c], F.J. Ibañez [a]

[a] *Instituto de Investigaciones Fisicoquímicas, Teóricas y Aplicadas (INIFTA), Universidad Nacional de La Plata - CONICET, Sucursal 4 Casilla de Correo 16 (1900), La Plata, Argentina.*
[b] *Centro de Investigaciones Ópticas (CIOp), (CONICET-CIC-UNLP), Camino Centenario y 506, Gonnet, 1897, La Plata, Argentina.*
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In recent years, research on hybrid nanomaterials based on graphene has intensified because of their outstanding optical, electronic, and catalytic properties. It has been reported that the assembly of materials based on Au and C improves their properties for applications related to optoelectronics, biosensors or molecule sensing of glucose, among others. In this work we demonstrate that the mixture of HAuCl4 with graphene quantum dots (GQDs) at room temperature and pH 6-7 leads to the spontaneous formation of core- shell type Nanohybrids (NHs). The product obtained was characterized by high resolution transmission electron microscopy (HRTEM) where gold nanoparticles coated by a graphene shell of 1 nm (3-4 layers) with an average size of 8.6 nm, monodisperse and without agglomerations, were observed. The chemical composition of the core and the shell was determined by electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS). Optical characterizations were also performed by UV-vis and fluorescence spectroscopy, where the presence of the typical surface plasmon resonance of gold nanoparticles around 520 nm and the characteristic $\pi - \pi^*$ transitions of the GQDs were observed. In addition, different experimental conditions were studied by modifying temperature, reaction time and ratio between Au+3 and GQDs concentrations to obtain Au/graphene NHs of different sizes and geometries. We demonstrate that these NHs can be used as a platform to electrochemically sense glucose. To make a thin film of NHs on conductive electrodes we used the electrophoresis technique (EPD). The electrode with NHs was then subjected to an oxidation/reduction cycle using glucose as a redox intermediate. We found that the current maintains a linear relationship in the concentration range of 0.1 mM to 10 mM, allowing for the determination of glucose concentrations within this range.

Computational design of graphene-based materials for green hydrogen storage: Overcoming the technical challenges of its implementation

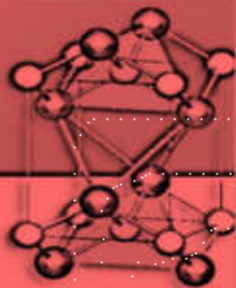A. Cipollone [a, b], G. Soldano [a, b], M. Mariscal [a, b]

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[b] *Departamento de Química Teórica y Computacional (DQTC), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, CONICET, Haya de la Torre esq. Medina Allende (Ciudad Universitaria), Córdoba, Argentina.*

In a world affected by the energy crisis and global warming, the need for renewable and clean energy sources is pressing. Green hydrogen emerges as a promising solution to address these challenges [1]. However, its implementation faces technical and scientific hurdles. This work focuses on two-dimensional graphene materials doped with transition metals for hydrogen storage [2]. Issues such as degradation in the presence of oxygen [3] and metal agglomeration [4] are addressed through a computational approach. The immobilization of metal centers on graphene is proposed using vacancies and boron and nitrogen co-dopants, as previously reported in the synthesis [5,6]. Through theoretical chemistry tools and advanced computational resources, the stability of nanostructures that prevent the agglomeration of metal centers is investigated, revealing 17 outstanding catalytic candidates. These findings have the potential to facilitate the experimental synthesis of materials, promoting the development of viable and catalytically active hydrogen storage systems, which, in turn, accelerates the transition to more sustainable energy sources.

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Atomistic Simulations in Surface Science by using Neural Networks

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[b] Facultad de Ciencias Exactas, Ingeniería y Agrimensura, Universidad, Nacional de Rosario, Av. Pellegrini 250, S2000 Rosario, Argentina
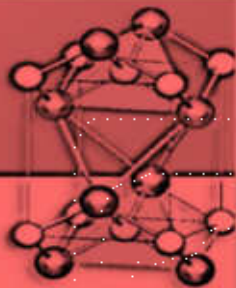
[c] Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain

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We present a study at the intersection of surface science and artificial intelligence. Our research is based on ab initio calculations using Density Functional Theory (DFT) and the use of neural networks to parameterize force fields, enabling molecular dynamics simulations of adsorbates on surfaces. The primary aim is to investigate microscopic processes that occur between adsorbates and surfaces. In this way, we calculate physicochemical observables that can be experimentally measured, such as: adsorption probability; activation energies for diffusion, reaction, and dissociation; diffusion coefficients; frequencies and life-times of excited vibrational states of adsorbates on surfaces. Additionally, we study dynamic effects out of thermodynamic equilibrium, such as those generated by laser irradiation and molecular beams on surfaces.

To validate our simulations, we compare the computational results with previous theoretical calculations and with experimental data. In this context, we focus our attention on two specific systems: hydrogen (H) on Pt(211) and carbon monoxide (CO) on Cu(110). These systems are used as case studies with the purpose of contributing to the microscopic understanding of physicochemical processes that take place on metallic surfaces. Our research not only focuses on the fundamental understanding of interactions between adsorbates and surfaces but also highlights the potential of combining machine learning methods, such as neural networks, with ab initio calculations to enhance the capability to simulate and comprehend complex physical phenomena.

Half-projection of doubly-occupied configuration interaction wave function

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[c] *Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Física and CONICET, Instituto de Física de Buenos Aires (IFIBA), Ciudad Universitaria, 1428 Buenos Aires, Argentina.*

[d] *Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain.*

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The doubly-occupied configuration interaction (DOCI) method expresses the N-electron system wave function in terms of doubly occupied Slater determinant basis sets [1]. It has been proven that the DOCI method captures most of the static correlation and, consequently, it has been proposed as an alternative to excitation-based truncations of the full configuration interaction (FCI) treatment. The energies of the DOCI Hamiltonian depend on the single-particle basis set employed, and therefore a minimization with respect to orbital rotations is required. If this optimization is carried out by performing the same transformation on the - and - orbitals (restricted DOCI, or RDOCI), one obtains a good description of molecules near equilibrium distances, but the dissociation products are not predicted correctly. On the other hand, if the optimization is performed by allowing the $\alpha-$ and $\beta-$ orbitals to be different (unrestricted DOCI, or UDOCI), the description of molecular dissociation, in general, is correct but at the cost of global spin contamination [2, 3].
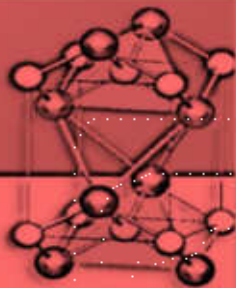
The half-projection method consists in projecting the odd or even spin quantum number components out of a wave- function by combining it linearly with its spin conjugate [4]. For singlet states, this projection usually leads to a better wavefunction since the spin contamination from triplet contributions, which is usually the most relevant, is removed. In the present work we aim to correct the spin contamination of UDOCI wave functions by means of this method, by performing the half-projection both before and after orbital optimization. We employ as a test case scenario the dissociation curves of several H_4 clusters, and show that, for these systems, spin contamination is almost removed, while the energies are improved.

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[2]. D. R. Alcoba, A. Torre, L. Lain, G. E. Massaccesi, O. B. O na, and E. R ıos, J. Chem. Phys. 150, 164106 (2019).

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Theoretical study of the adsorption and effect of explicit micro solvation of Li_2S for next generation batteries

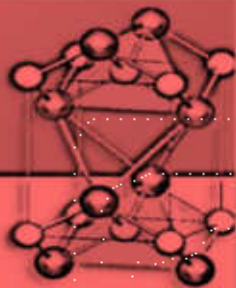V.V. Costello [a], M.B. López [a], M.E. Zoloff Michoff [b]

[a] *Centro de Investigaciones Fisicoquímicas Teóricas y Aplicadas (CIFTA), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Catamarca, Catamarca, Argentina.*

[b] *Instituto de investigaciones en Fisicoquímica de Córdoba (INFIQC), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina.*

One of the most promising technologies for the next generation of Li batteries is rechargeable lithium-sulfur (Li-S) batteries [1-3]. However, its implementation in daily life applications still presents several drawbacks. A possible solution with great potential is the use of lithium sulfide as a cathode material since it is possible to couple it to Li-free anodes, such as graphite, Si or Sn. However, both lithium sulfide and sulfur 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 [4,5].

To computationally model these reactions, it is crucial to consider the effect of the solvent [6]. In the present work, the interaction of Dimethyl ether (DME) and Dimethylformamide (DMF) with Li_2S, both in vacuum and adsorbed on a graphene sheet, was studied and characterized by DFT calculations. Using ab initio molecular dynamics, the optimal number of molecules for the first solvation sphere of Li_2S was determined for both solvents. Subsequently, the fragmentation of one of the Li-S bonds was studied, both for Li_2S isolated and adsorbed on the carbonaceous material.

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PVA/PEDOT:PSS conducting hydrogels as channel materials for organic electrochemical transistors
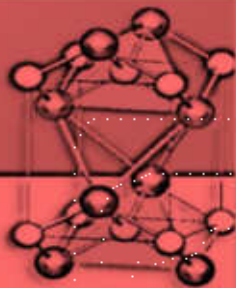
T. Gregorio [a], D. Mombrú [a], M. Romero [a], R. Faccio [a], A. Mombrú [a]

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Organic electrochemical transistors (OECTs) are being studied for different applications in the field of biosensors and bioelectronics. To fulfill the requirements of such applications, the device fabrication process must be compatible with flexible and scalable digital techniques.

To the best of our knowledge, here we report for the first time the preparation and evaluation of PVA/PEDOT:PSS conducting hydrogels working as channel materials for OECT applications. Our PVA/PEDOT:PSS conducting hydrogels were characterized using X-ray diffraction, FT-IR, Raman spectroscopy, scanning electron microscopy, swelling and chronoamperometry studies. In addition, we have performed in-operando Raman spectroscopy in the OECT devices evidencing the doping/de-doping processes under applied gate voltages. First Principles calculations, based on DFT simulations were carried out using the Gaussian 16 code modeling a PEDOT:PSS system interacting with explicit water molecules, chloride and potassium ions. After full structual optimization local minima analysis and corresponding IR and Raman spectra were obtained.

Finally, although lower channel current values were observed compared to typical OECT channel materials based on PEDOT:PSS thin films, our PVA/PEDOT:PSS conducting hydrogels exhibited excellent linear response with applied gate voltages making them promising candidates to be further considered for sensing devices.
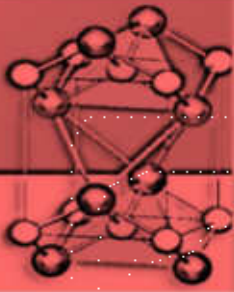
Adsorción y difusión de litio sobre g-C$_3$N$_4$ dopado con fósforo para su aplicación en ánodos en baterías de la próxima generación

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Las baterías secundarias de la próxima generación de Li-Azufre (Li-S) y Li-aire, son tecnologías prometedoras para el almacenamiento de energía. Tienen como material anódico activo Li metálico, que presenta algunas problemáticas a resolver antes de ser comercializadas: Uno es el crecimiento desmedido de dendritas durante los ciclos de carga/descarga y el otro es la baja eficiencia coulómbica del proceso debido a una interfase sólida del electrolito (SEI) inestable. Nuestro trabajo se centra en analizar, utilizando la Teoría del Funcional de la Densidad (DFT), el potencial uso de láminas 2D de nitruros de carbono grafítico (g-C$_3$N$_4$) con diferentes grados de dopaje con fósforo, con el objeto de ser utilizados como lámina protectora del litio metálico anódico. para ello se calcularon las energías de dopaje en diferentes sitios de la lámina. Posteriormente se determinaron las energías de adsorción para un átomo de litio sobre las estructuras más estables, para luego simular los procesos de difusión de Li entre sitios de la lámina y a través de la misma mediante el método de banda elástica c-NEB. Nuestras determinaciones, nos permiten concluir que el dopaje se produce sustituyendo preferentemente átomos de C de la lámina de g-C$_3$N$_4$ y que la difusión de Li, se da más fácilmente en estos mismos sistemas.

DFT study of the structural and magnetic ground state of the chromites $CdCr_2O_4$, $HgCr_2O_4$, $ZnCr_2O_4$

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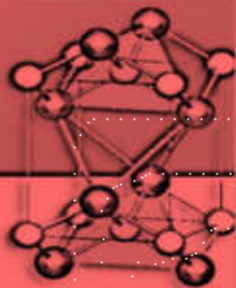
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Chromites like ACr_2O_4, where A=Zn, Cd, Hg, exhibit a wide variety of magnetic behaviors [1] and also shown an interest as materials with potential applications in spintronics and magneto-optical devices [2,3].

In this work, the magnetic and structural properties of chromites has been studied from a theoretical-computational perspective, in the framework of the Density Functional Theory (DFT). Both normal and inverse crystal structures has been considered, as well as, different magnetic configurations between Cr atoms were explored, such as ferromagnetic and many antiferromagnetic states, with the aim of find the structural and magnetical ground state.

Furthermore, DFT+U calculations were performed in order get a better description of the electronic structure, analyzing the variation in Fermi energy, magnetic moment, and the band gap respect to U value . For all calculations, we have considered PBE parametrization of the Generalized Gradient Approximation (GGA) to describe the exchange-correlation term. Ours result are in great agreement with experimental data reported in the literature.

[1]. A.N. Yaresko. Electronic band structure and exchange coupling constants in ACr_2O_4 (A=Zn, Cd, Hg; X=O, S, Se) spinels. Physical Review B 77, (2008), 115106.

[2]. A.P. Ramirez et al. Nature, 286, (1997), 156.

[3]. J. Hemberger et al. Nature, 434, (2005), 364.

[4]. J.P. Perdew, K. Burke, M. Ernzerhof, Physical Review Letters, 77 (1996), 3865.

Determination of quadrupole moment and isomeric shift for ^{119}Sn. Comparison of different methods based on DFT calculations

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Hyperfine techniques in general, and Mossbauer spectroscopy (MS) in particular, have been extensively employed for the structural, electronic, and magnetic characterization of materials. What makes these techniques particularly interesting is their ability to measure properties related to chemical state, charge symmetry (the electric field gradient tensor, EFG), and spin polarization and currents (hyperfine magnetic fields, BHF) at the site of a core probe. In the case of EM, one of the isotopes of Fe (^{57}Fe) and Sn (^{119}Sn) are the most commonly employed probes, making this technique particularly suitable for studying a very broad set of materials of both basic and applied interest. The use of MS allows information related to the electronic and magnetic configuration at the core-probe site and its immediate surroundings to be obtained on a nanoscopic scale. The experiment-theory combination allows us to extract all the information contained in the experimental results. To achieve this, different structural and electronic scenarios will be proposed for the system under study, and from the theory-experiment comparison, it will be determined which one best reproduces the experiments.

In particular, three hyperfine parameters are determined via MS: the isomeric shift (IS), the quadrupole splitting (QS), and the hyperfine field (BHF). In this paper, we focus on the first two. The IS is an observable that provides information about the local chemical bonding of the probe- atom, and the QS is a fingerprint of the charge symmetry around the probe nucleus. The information contained in these parameters is the product of a nuclear quantity (specific to the core- probe) and one that depends on the crystalline environment where the probe is located. In the case of IS, the nuclear parameter is the constant α (which depends on the nuclear radii involved in the Mossbauer transition), and the material property is the electron density at the core site (obtained from DFT calculations). In the case of QS, the nuclear property is the quadrupole momentum Q, and the electronic property is the GCE (obtained from the DFT calculation). It is clear then that a precise and accurate knowledge of and Q is fundamental to be able to translate; from calculated to experimentally determined quantities and thus to compare theory with experiment.
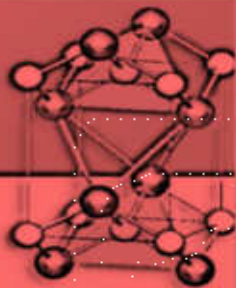
In the present work, a wide variety of Sn-based compounds have been considered to calculate the GCE and electron density at the probe core site in order to correlate the results obtained by DFT with the experimental values, thus allowing and Q to be obtained. The Full Potential Augmented Plane Waves (FP-LAPW) method, which is a well-established method for electronic structure calculations, and the Gauge-Including Projected Augmented Waves (GIPAW) method implemented in
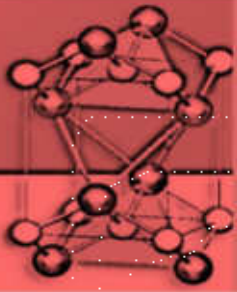
the Quantum Espresso plane+pseudopotential wave code was used for the calculations, in order to establish the capability of this method for the calculation of hyperfine properties. In the case of IS, calculations were also performed using the full-potential local-orbital (FPLO) method, which, unlike FP-LAPW, does not use the point core hypothesis.

Assessment of embedding schemes for QM/MM machine learning approaches

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Machine Learning (ML) methods have reached high accuracy levels for the prediction of in vacuo molecular properties. However, the simulation of large systems through solely ML methods (like those based on neural network potentials) is still a challenge. In this context, one of the most promising frameworks for integrating ML schemes in the simulation of complex molecular systems are the so-called ML/MM methods. These multiscale approaches combine ML methods with classical force fields (MM), in the same spirit as the successful hybrid quantum mechanics-molecular mechanics methods (QM/MM).

The key issue for such ML/MM methods is the adequate description of the coupling between the region of the system described by ML and the region described at the MM level. In the context of QM/MM schemes, the main ingredient of the interaction is electrostatic, and the state of the art is the so-called electrostatic-embedding. In this study, we analyze the quality of simpler mechanical embedding-based approaches, specifically focusing on their application within a ML/MM framework utilizing atomic partial charges derived in vacuo. Taking as reference electrostatic embedding calculations performed at a QM(DFT)/MM level, we explore different atomic charge schemes, as well as a polarization correction computed using atomic polarizabilities. Our benchmark data set comprises a set of about 80k small organic structures from the ANI-1x database, solvated in water. The results suggest that the MBIS atomic charges yield the best agreement with the reference coupling energy. Remarkable enhancements are achieved by including a polarization correction.
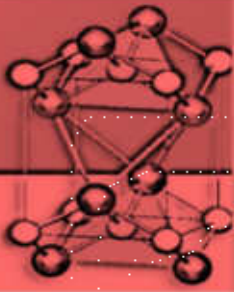
Exploration of the structural, electronic and magnetic properties of the new perovskite semiconductor material $CaCo_{0.5}Zr_{0.5}O_3$

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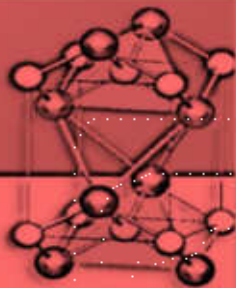
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The study delves into the structural, electronic, and magnetic characteristics of the newly discovered perovskite semiconductor, $CaCo_{0.5}Zr_{0.5}O_3$. The material was synthesized using the standard solid-state reaction method, and its crystal structure was analyzed via Rietveld refinement of the X-ray diffraction pattern, revealing an orthorhombic structure within the *Pcmn* space group. To obtain a comprehensive understanding of its properties, morphological and compositional analyses were conducted using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). These analyses confirmed an average grain size of $1.19 \pm 0.02\,\mu m$ and underscored the material's minimal impurity content as per the EDX results. Thorough exploration of the electronic and magnetic properties was carried out through Ab-initio calculations.

The Density of States (DOS) and band structure analyses provided critical insights: the material displays characteristics of a ferromagnetic semiconductor, featuring an average gap of 0.89 eV and a net magnetic moment of $2.0\mu_B$. This in-depth analysis illuminates the distinct properties of $CaCo_{0.5}Zr_{0.5}O_3$, laying a foundational understanding for its potential applications in semiconductor technology.

Kaolinite: A study of the first steps on the dehydroxylation process

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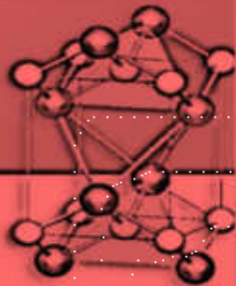
Kaolin is a natural clay with kaolinite as the main crystallographic phase. The importance of this clay is related to its influence in ceramics, materials science, and mineralogy. The industrial use of kaolinite requires thermal treatments, so it is interesting to understand how metakaolin is formed during the thermal activation of this clay and also to know what are the physics and chemistry mechanisms behind its production [1]. These mechanisms are complex and according to the literature there is not a general agreement on which is the rate-controlling step in the reaction, and on the atomic arrangement of metakaolinite [2].

In this work it is studied the beginning of the dehydroxylation process using calculation methods based in Density Functional Theory. Four systems that combine vacancies of an OH group and a H atom in the kaolinite unit cell were proposed, considering each one as a possible first step in the reaction. Using the open source package Quantum ESPRESSO [3], the structure of each system was optimized and its energy was analyzed after the optimization. The results were compared between them and with the literature. After that, one system was chosen as the most compatible with the physical process, and its properties were analyzed. The X-ray diffraction pattern, the vibrational normal modes, and the electronic density of states were also studied and compared with those calculated for kaolinite.

The predicted properties were also compared to experimental data, obtained from a well-crystallized kaolinite (KGa-1) and a national one (Sur de Río Blanco).

The obtained results help to elucidate the beginning of the metakaolin production process and also help to understand the differences between the four proposed systems. The promising results encourage further analyses using the same theoretical-experimental methodology in order to continue the study of the transformation of kaolinite towards its dehydroxylated form.

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[2]. Bellotto, M., Gualtieri, A., Artioli, G., and Clark, S. M. (1995) 'Kinetic study of the kaolinite-mullite reaction sequence. Part I: kaolinite dehydroxylation', Physics and Chemistry of Minerals, vol. 22, pp. 207-217..

[3]. Giannozzi, P., Andreussi, O., Brumme, T., Bunau, O., Buongiorno Nardelli, M., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Cococcioni, M., Colonna, N., Carnimeo, I., Dal Corso, a., de Gironcoli, S., Delugas, P., DiStasio Jr., R. A., Ferretti, A., Floris, A., Fratesi, G., Fugallo, G., Gebauer, R., Gerstmann, U., Giustino, F., Gorni, T., Jia, J., Kawamura, M., Ko, H.-Y., Kokalj, A., Küçükbenli, E., Lazzeri, M., Marsili, M., Marzari, N., Mauri, F., Nguyen, N. L., Nguyen, H.-V., Otero-de-la-Roza, A., Paulatto, L., Poncé, S., Rocca, D., Sabatini, R., Santra, B., Schlipf, M., Seitsonen, A. P., Smogunov, A., Timrov, I., Thonhauser, T., Umari, P., Vast, N., Wu, X., and Baroni, S. (2017) 'Advanced capabilities for materials modelling with Quantum ESPRESSO', Journal of Physics: Condensed Matter, vol. 29, no. 46, pp. 465901.

Density Functional Calculation of H_2O molecules adsorption on AgI (001) surface

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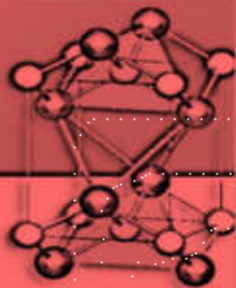[a] *Instituto de Física La Plata IFLP, CCT La Plata - CONICET, 1900 La Plata, Argentina.*

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The research of such systems is of significant interest, particularly in industries like viticulture, which includes the growing of grapes for wine production. In viticulture, the economic implications of both public and private "anti-hail" programs are substantial. This is especially relevant in the province of Mendoza-Argentina, where cloud seeding measures are employed to safeguard crops from being damaged by hail. Consequently, the study of systems like AgI-H_2O contributes to our understanding of high-impact materials relevant to these agricultural practices.

In the present study, we conducted a series of ab initio calculations within the framework of Density Functional Theory (DFT) to investigate the adsorption of H_2O molecules on the (001) AgI surface. We solved the Kohn-Sham self-consistent equation using the plane-wave and pseudopotential method, specifically the QuantumEspresso software. The exchange-correlation part of our calculations was described using the PBE parametrization of the General Gradient Approximation (PBE-GGA).

We determined the preferential site for adsorption, as well as the adsorption energy and lateral interaction energy between H_2O molecules at different coverage levels. These parameters are essential for studying dynamic processes such as Thermal Programmed Desorption (TPD) using kinetic Monte Carlo simulations.

Theoretical-experimental study of the structural, magnetic and electronic properties of the material $LaFe_{0.5}V_{0.5}O_3$

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The extensive range of applications for materials structured in the perovskite formation (ABO_3) propels an ongoing exploration to alter their properties using varied synthesis techniques and cationic substitutions within the A and B positions. The diversity inherent in these structures emerges from their structural flexibility, a consequence of octahedral rotations and potential cationic displacements. This study involved the synthesis of polycrystalline $LaFe_{0.5}V_{0.5}O_3$ samples through the gel-assisted combustion synthesis method. Structural analysis via X-ray diffraction (XRD) and Rietveld refinement indicated that the material crystallizes within a primitive orthorhombic structure, falling under the *Pnma* space group (#62). The material's magnetic response was assessed through DC magnetic susceptibility measurements across a temperature range of 50 K to 350 K, as well as magnetization concerning the magnetic field. These analyses revealed an antiferromagnetic behavior, potentially accompanied by a small ferrimagnetic phase, which was attributed to shape anisotropies occurring during the material's synthesis. Furthermore, the electronic properties were explored via Density Functional Theory (DFT). The analysis demonstrated the material's conductive nature and identified the antiferromagnetic phase, specifically in the T-AFM configuration, as the most stable. Finally, the observed coexistence of a minor ferrimagnetic phase aligned with the experimental findings.
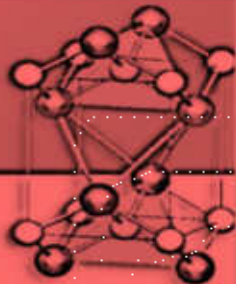
Direct variational determination of two-particle reduced density matrices corresponding to zero seniority number wave functions: Generalization of the seniority number concept and brealing of spin and time-reversal symmetries

T.R. Ayala [a], E.D. Ríos [b], D.A. Corvalán [a], D.R. Alcoba [a, c], G.E. Massaccesi [d, e]
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The variational approach is a widely used method for approximating two-particle reduced density matrices (2-RDM) corresponding to fermionic systems. In this technique, the elements of the matrices are optimized by imposing constraints that guarantee the N-representability of the solution found [1]. Recently, satisfactory results have been described in strongly correlated systems, applying the variational method under the so-called p-positivity conditions to approximate the 2-RDMs corresponding to wave functions belonging to the interaction space of doubly occupied configurations of zero seniority number [2]. The optimization has been carried out by means of a conventional semidefinite program (SDP). In this work, a generalization of the concept of seniority number is proposed. An improved reformulation of the method is presented, which allows the elimination of spin and time-reversal symmetry constraints, leading to the breaking of such symmetries in the solutions found. The projection of the reduced Hamiltonian of the treated system onto the space of generalized zero seniority number allows the resulting SDP to be implemented using existing algorithms and exploiting the sparse character of the associated matrix structures. Energies and density matrices of strongly correlated many-body systems are calculated, comparing the results obtained using the new technique with those obtained from exact calculations. It is shown that the breaking of the above mentioned symmetries significantly improves over previously obtained solutions at affordable computational cost.

[1]. W. Poelmans, M. Van Raemdonck, B. Verstichel, S. De Baerdemacker, A. Torre, L. Lain, G.E. Massaccesi, D.R. Alcoba, P. Bultinck, D. Van Neck, J. Chem. Theory Comput. 11, 4064 (2015).
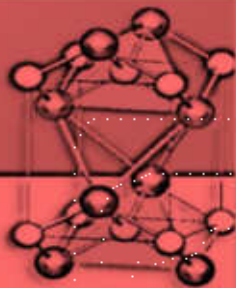
[2]. D.R. Alcoba, A. Torre, L. Lain, G.E. Massaccesi, O.B. Oña, E.M. Honoré, W. Poelmans, D. Van Neck, P. Bultinck, S. De Baerdemacker, J. Chem. Phys. 148, 024105 (2018); D.R. Alcoba, P. Capuzzi, A. Rubio-García, J. Dukelsky, G.E. Massaccesi, O.B.
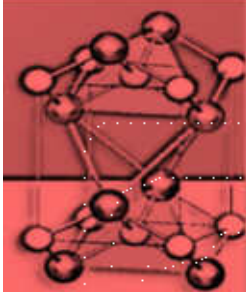
Oña, A. Torre, and L. Lain, J. Chem. Phys. 149, 194105 (2018); A. Rubio-García, J. Dukelsky, D.R. Alcoba, P. Capuzzi, O.B. Oña, E. Ríos, A. Torre, and L. Lain, J. Chem. Phys. 151, 154104 (2019); D.R. Alcoba, O.B. Oña, L. Lain, A. Torre, P. Capuzzi, G.E. Massaccesi, A. Rubio-Garcia, and J. Dukelsky, J. Chem. Phys. 154, 224104 (2021).

Structural, vibrational and optical properties of TiO_2 nanoparticles and sodium titanate nanotubes $Na_2Ti_2O_5.H_2O$ doped with transition metals. A theoretical-experimental study.

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This work presents the synthesis, structural characterization and optical properties of anatase nanoparticles and anatase nanoparticles doped with transition metals (Fe, Cu, Ni) obtained by modified sol gel methods, and their comparison with titanate nanotubes [1]. $Na_2Ti_2O_5.H_2O$ phase sodium dititanate [2] obtained from the aforementioned precursor nanoparticles. A structural model for one-dimensional nanostructures is presented based on first principles and that manages to account for the complex diffraction patterns of the system. On the other hand, their optical properties were studied, in particular the bandgap energies and the Urbach tails, to complete the model used to describe the absorption edge of the materials.

As main results, it is mentioned that experimentally no significant changes are observed for the anatase nanoparticles in the band gaps and that a moderate red shift is observed for the indirect bandgap energies of the nanotubes. The doped samples in all cases present higher Urbach energies than the pristine ones, consistent with the addition of impurity electronic states in the band gap. Furthermore, greater optical activation is observed, understood at higher Urbach energies in sodium dititanate systems with respect to anatase nanoparticles and consistent with our electronic and optical DFT calculations [3,4]. These phenomena can be interpreted in terms of the hybridization characteristics of the impurity states that were added to the electronic gap.

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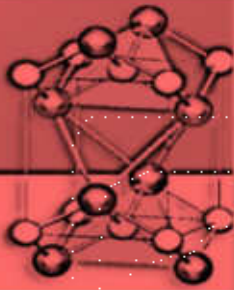
hP8-to-cP4 Structural Transition in Ni$_3$In: Ab Initio Study of Compression and Phase Stability
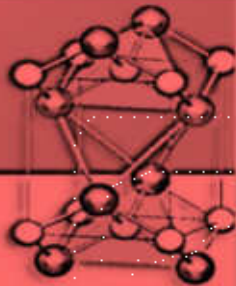
D.S. Bertoldi [a], S.B. Ramos [b], A.F. Guillermet [c]

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According to Webb et al. (1986) by heating the Ni3In-hP8 compound at 800 - 1200 °C under a pressure (P) of 6.5 GPa, a cP4 phase was formed, which reverted to hP8 when annealed at low pressure. A striking X-ray result is that the atomic volume (V) of cP4 was higher than that of hP8. To clarify such "volume anomaly" Webb et al. determined the V versus P relations in samples quenched to room temperature. They reported that the compressibility of the cP4 phase was significantly larger than that of the hP8 phase and invoke this finding to explain the "volume anomaly". These various findings have been theoretically analyzed in the current work by using ab initio DFT calculations, including an account of the vibrational and electronic contributions to the thermodynamic properties. Calculations of the V versus P relations are used to reassess the compressibility relation between the cP4 and hP8 phases, and Gibbs energy calculations to characterize the relative stability of these structures. In particular, detailed comparisons are reported with the only information available on the thermal properties of the hP8 phase, viz., the Gibbs energy estimates obtained in CALPHAD-type phenomenological modeling of the Ni-In equilibrium diagram. The key qualitative result of the current work is that cP4 should be considered as a high-temperature phase, which might be stabilized by heating to the temperature chosen to anneal the hP8 material under pressure. On this basis it is suggested that the "volume anomaly" problem discussed by Webb et al. might be a consequence of considering only the effect of pressure on the cP4/hP8 relative phase stability.

Shape-dependent CO chemisorption on Pt_{13} cluster supported on reduced $TiO_2(110)$

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Transition metal clusters supported on TiO_2 have attracted significant attention due to their remarkable catalytic activity in chemical reactions associated with pressing global issues such as increasing energy demands and environmental pollution. The presence of defects in the oxide support, such as oxygen vacancies (Vo), has been shown to enhance the catalytic activity of these systems. In this work, we focus on the impact of cluster shape on the reactivity of Pt13 nanocatalysts supported on reduced $TiO_2(110)$ concerning CO chemisorption and its oxidation to CO_2. Clusters with the same number of Pt atoms but different shapes exhibit varying reactivity to CO adsorption, indicating that catalytic properties can be controlled through shape-selective synthesis. The particular cluster size here chosen is motivated by scanning transmission electron microscopy observations [1] which detected prominent cuboid structures for Pt_{13} deposited over carbon.

We consider various Pt_{13} cluster geometries (cuboid, Oh, and DT-double triangle) [2] to elucidate the shape effect when deposited on reduced $TiO_2(110)$, modeled as $TiO_2(110)+Vo$. This understanding of the interfacial and CO chemisorption properties is achieved through DFT+U calculations that include a Hubbard coefficient for modeling the oxide.

The calculated formation and adsorption energies are correlated with the electronic properties of the system and the oxidation states of the Pt atoms involved in the process. By analyzing the band shifting that occurs when Pt clusters are deposited onto the oxide and comparing the maximum of the conduction band with measured redox potentials for a CO to CO_2 reaction, we predict about the system's oxidation capability for this reaction. Our findings suggest that the Oh and cuboid supported Pt_{13} clusters are favorable for catalyzing the CO to CO_2 reaction. We compare these findings with recent experimental reports on the oxidation of CO activity for $Pt_{13}/TiO_2(110)+Vo$ [3].

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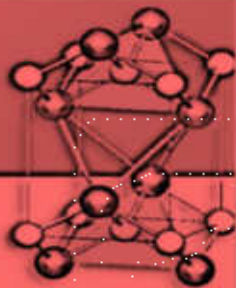
Adsorption of Fe_3O_4 nano clusters on montmorillonite

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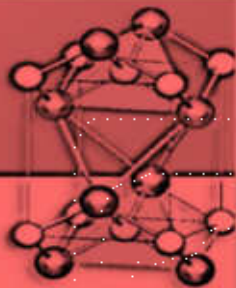
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Industrialization has a great impact on environmental health, potentially contributing to an increament in pollution, which is critical for water reservoirs since it affects the whole life on the planet. Many of the methods used for remediation technologies are based on the sorption process. Clay minerals such as montmorillonite (MMT) are among the materials used [1]. Moreover, providing magnetic properties to materials suitable for remediation would allow their manipulation using external magnetic fields for recovery, thus reducing potential health risks in the process [2].

The aim of this work is to study the modelling of the adsorption of magnetic nano-particles (MNP) on different MMT surfaces and sites. Thus, preliminary results of magnetite (Fe_3O_4) nano-clusters adsorption modelling on different surfaces of $Na_{0.41}[(MgAl_3O_8(OH)_4(Si_8O_{12})]_2.4(H_2O)$ (Na-MMT) are presented. Quantum mechanics calculations were performed within the Density Functional Theory. Surfaces structures were build starting from the pristine structure of MMT for different crystal orientations, and using two layers of MMT and a vacuum separation layer with $25\mathring{A}$ width. The surfaces as well as the clusters were optimized prior to the construction of the composite system MNP-MMT. The formation energy for the 001 surface was the lower obtained for the different directions analysed. On this surface, the Fe_3O_4 cluster was located on different possible sorption sites. This process was studied by descending it in steps of $2\mathring{A}$ from an initial position of $8\mathring{A}$ until reaching the selected sites [3], allowing the complete relaxation of the system at each step. Them by total energy analysisit was established that the most probable adsorption sites are basal oxygen's (O), which constitute the outer layer of the surface 001.

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Electronic structure calculation of the structural and magnetic properties of the MgFe$_2$O$_4$. From bulk to surface

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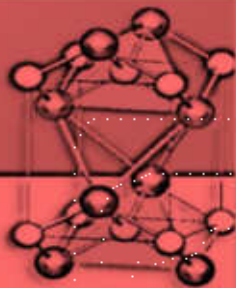[b] Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), CP 1900 La Plata, Argentina.

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Spinel ferrites of AFe$_2$O$_4$ (A = Ni, Cu, Mn, Mg, Co or Zn, etc.) have remained one of the most interesting functional materials in recent decades, because of their unparalleled magnetic, electric and dielectric properties. These electrical and magnetic properties have a wide range of applications in high and very high frequency radio frequency circuits, transformer cores, data storage devices, high read/write speed, among others.

Among different spinel ferrites, magnesium ferrite (MgFe$_2$O$_4$), a soft magnetic n-type semiconducting material possessing inverse spinel structure is one of the most prominent. In this work, an ab initio study of the structural, electronic, magnetic and hyperfine properties of MgFe$_2$O$_4$ was carried out within the framework of Density Functional Theory (DFT) using the FP-LAPW+LO and Pseudopotential methods, employing the Generalized Gradient Approximation (GGA) and the GGA+U for the potential term and exchange. The calculations show that the equilibrium structure corresponds to an inverted and antiferromagnetic configuration, in which the magnetic moments of the Fe atoms in the A sites are ordered ferromagnetically with each other and antiferromagnetically with respect to the Fe in the sub-network of B sites, while the Magnesium atoms do not polarize.

The excellent agreement between theoretical calculations and experimental results reported in the literature supports the cation distribution and the lowest energy magnetic configuration obtained for MgFe$_2$O$_4$. From these results, the stability of the different surfaces of this ferrite began to be studied considering different surface finishes, taking into account structural reconstructions in all cases. The results we present predict that the most stable surface is inverted, exposing Fe, Mg, and O atoms. This surface presents a net magnetic moment, giving rise to a ferrimagnetic system.

A DFT study of Li in $H_2Ti_3O_7$ bulk: intercalation and thermodynamic properties

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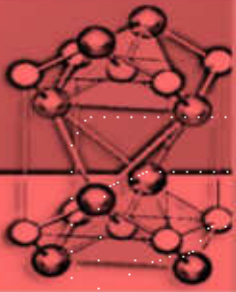
A Li intercalated in $H_2Ti_3O_7$ bulk theoretical study was performed. The electronic, thermodynamic and diffusion properties of the doped and pure systems were performed. The Density Functional Theory (DFT) based calculations were performed with the VASP software [1]. The Hubbard parameter was included in order to take into account the Ti transition metal effect. Three different intercalation sites were tested, and the stability of each site was studied. Afterwards, the densities of states were calculated, and showed a shift of the doped systems and the presence of a magnetic moment. The Bader [2] method was applied to study the charge transfer, finding a transfer of the electron to the titanate. Moreover, vibrational calculations were performed in order to obtain the phononic densities of states and the thermodynamic properties with the implementation of Phonopy [3]. In order to do this, we checked that no extra imaginary frequency vibrational mode was present, which also showed the stability of the studied systems. Thermodynamically, the doped systems presented to be more stable. MLFF-AIMD calculations were performed to confirm the stability of the systems with temperature. The NEB [4] methodology was applied to find the energetic barriers of the Li intercalated system. A direction of preference for diffusion was found, with an energy barrier of 0.33 eV, which is more favorable than the second barrier, which was 1.75 eV. Therefore, these results show promising aspects of this candidate material as an anode, which can be studied more in future theoretical and experimental studies.

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Relevance of DFT+U formalism to treat strongly correlated d electrons of Ta acting as an isolated impurity-probe in oxides. TDPAC and ab initio study

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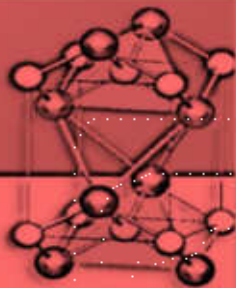
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To study the influence of doping impurities in condensed matter and the development of new functional materials, nowadays it is crucial to perform a combined experimental and theoretical study, with an accurate description of the electronic density $\rho(\mathbf{r})$ of the impurity-host system.

Here we present an ab initio all-electron density functional theory (DFT) electronic structure calculations study, contributing to answer the general question of when it is relevant and necessary the inclusion of the Hubbard U parameter used in the DFT formalism (DFT+U) to correctly describe strongly correlated orbitals of diluted probe-atoms, in particular $5d$ orbitals of Ta doping semiconductors oxides. We selected for this purpose to study Ta-doped α-Al_2O_3, a semiconducting wide band-gap oxide with native cations that present the advantage of not having strongly correlated electrons. These calculations were compared with a precise experimental determination of the electric-field gradient (EFG) tensor at (^{181}Hf$\rightarrow$)^{181}Ta probe-atoms suitably localized at substitutional free of defects cation sites, essential for the above-mentioned purposes since enables to compare experimental results with theoretical predictions of the same physical situation.

We studied theoretically the influence of the inclusion of the U parameter in the structural, electronic, and hyperfine properties of the impurity-host system, showing that the use of the DFT+U formalism does not introduce relevant structural changes with respect to DFT, evidencing that the anomalous large difference in the predictions of the EFG's magnitude between both formalisms comes only from the modification of the electronic structure description.

Based in the new insight gained in the present study, and the further comparison between DFT and the DFT+U predictions performed in ^{181}Ta-doped rutile TiO_2 and SnO_2 we propose that the inclusion of the U parameter to treat the Ta-$5d$ states when it behaves as a diluted impurity probe-atom would be only necessary when the donor level introduced is very localized in energy and space.

SpecPy: A python library for the calculation of electronic and vibrational spectra using a wave packet formulation

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We present here a python library implementation of Heller's wavepacket formulation of resonant Raman scattering, which expresses the Raman amplitude in terms of Fourier transforms of an overlap that involves propagating a wavepacket. This methodology presents some advantages over traditional sum-over-states approach. It is much more scalable and errors are usually easier to track. The library is also capable of computing UV-Vis and Fluorescence vibronic spectra using the same approach. We present some examples and compare to experiment.

The role of doping and vacancies in the structural and electronic properties of TeGeX (X=Sb, Sn, and vacancies) alloys: A first-principles study

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Te-based chalcogenide materials have been found to exhibit very outstanding characteristics for use in thermoelectric [1] and phase-change memories [2] applications. For this reason, many efforts have been made to the chemical composition and the electronic properties of these compounds.

In this work we study the structural, electronic, and thermoelectric properties of TeGeX (X: Sb, Sn) and the role played by the Ge vacancies in the origin of these properties by means of Density Functional Theory [3] based first principles methods. Calculations were performed using the full-potential linearized augmented plane waves method (FP-LAPW) method [4] considering different vacancy and dopant distributions and concentrations. Theoretical modelling shows that Sn replaces Ge atoms and that Ge vacancies formed. There is no preferential distribution of dopants or vacancies in the Ge sublattice. The obtained results obtained for the structural and electronic properties and the hyperfine parameters at the Sn sites are compared with experimental results obtained by X-ray diffraction, ^{119}Sn Mössbauer spectroscopy and other characterization techniques to achieve a better characterization of the system under study.

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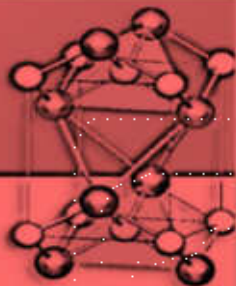
Theoretical Study of Electrochemical Promotion of Oxygen migration on Cu/ZnO Catalysts

M. Patrignani [a], J. Wang [b], M.G. Sandoval [a], E.A. Baranova [b], P.V. Jasen [a]

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[b] Department of Chemical and Biological Engineering, Centre for Catalysis Research and Innovation (CCRI), Nexus for Quantum Technologies (NexQT), University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada.
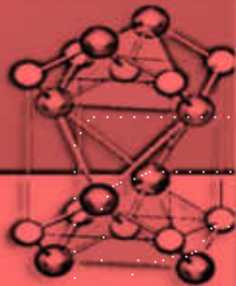
A Density Functional Theory (DFT) model, using VASP code [1], is developed to study the largest measured relative electrochemical surface areas (ECSAs) enable the easiest O^{2-} migration via the most oxygen vacancies provided by the ZnO phase, as indicating by the ECSAs of the catalysts shown to be positively correlated with the magnitude of the electrochemical promotion of catalysis (EPOC) effects. PBE-GGA spin polarized calculations were performed taking into account the Hubbard correction for the Zn transition metal effect. Also, DFT-D2 Grimme was included to consider Van der Waals interaction [2]. Pristine and defective ZnO(101) surfaces were simulated. All possible adsorption sites for Cu-atom were studied in all systems. In the most stable Cu-systems the Oxygen adsorption was taken into account in all Cu surrounding adsorption sites. Our results show that Oxygen vacancies in ZnO are the easiest to be formed. Also, Cu adsorption is a favorable process in all cases. Once the Oxygen adsorption is considered in Cu-systems, the binding energies show that after the Oxygen vacancy formation, the binding energy gap is around ~1 eV lower when compared with the system without vacancy. This could indicate that the Oxygen migration is preferable from the surface rather than a surrounding O_2, in good agreement with the experimental results. Electronic structure, Bader charge analysis [3] and Bond Order [4] were also computed for a better understanding of this effect.

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Electronic structure properties of zig-zag graphene nanoribbons adsorbed with single atoms
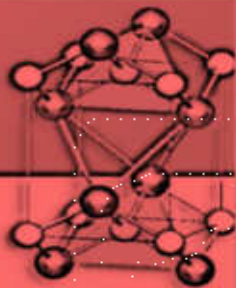
S. Piriz [a], L. Fernández-Werner [b], H. Pardo [b], A.W. Mombrú [b], R. Faccio [b]

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Lamellar carbon materials, such as graphene, have received significant attention for its promising technological application due to its particular electronic structure. Among these materials, graphene nanoribbons have been a topic of interest because they offer a model to study electronics correlations due to its small size, as well as its potential use in spintronics since they can function as perfect spin filters and in addition, its production has allowed important advances.

In this work different configurations for the adsorption of B, N and O interacting with zigzag edge nanoribbons (ZGNR) were evaluated. The most stable structural configurations were identified and the most relevant electronic properties will be shown. The most important result is that edge adsorption is always the most favorable situation. The semiconductor or metallic character is closely linked/related to the magnetic coupling of the edges of the nanoribbon. Whenever the magnetic order changes from AFM, as a consequence of adsorption, metallic systems will be obtained; while if the AFM order is maintained, the systems will be semiconductors. An exception to the above is the one in which an oxygen adsorption on ZGNR conducts to a half-metal solution where one spin is semiconductor and the other is metallic.

Electronic band structure calculation of all-inorganic perovskites CsAB$_3$, with A: Pb, Sn, or Ge, and B: I, Br, or Cl

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In the quest for next-generation solar cells, perovskite-based technologies have gained considerable attention [1-2] from the industry due to their cost-effectiveness in comparison to the Silicon-based ones, and increasing solar-to-electricity conversion efficiency over the past decade. While perovskite configurations like Methylammonium-based organic cells $CH_3NH_3PbI_3$ (MAPI) [3] and fully inorganic lead-based $CsPbI_3$ perovskites [4] have shown promise, this research aims to substitute Sn or Ge for A (typically lead, Pb) in order to reduce the proportion of lead, with B representing halide ions: Iodine (I), Bromine (Br), or Chlorine (Cl). The research primarily analyzes the electronic band structure of these inorganic perovskites to identify the most suitable configurations for subsequent solar cell device simulations. The band gap of the material is a critical factor determining energy conversion efficiency, and it must lie within the energy range of 1.7 eV and 2.3 eV [5]. First-principles calculations based on Density Functional Theory (DFT), where Khon-Sham's self-consistent equations were solved using the Planewave and pseudopotentials method (VASP) [6], the exchange-correlation part was described using PBE-GGA and SCAN parametrizations. This allowed us to determine physical parameters such as lattice parameters, energies, band gaps, and density of states for the band structure analysis. The results obtained from the ab initio calculations will allow us to perform numerical simulations, for which the SCAPS-1D software will be used.

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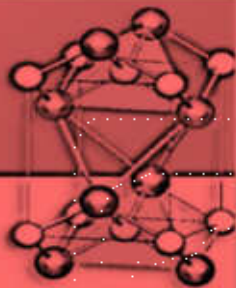
Delafossite CuGaO₂ surfaces: study of CO adsorption on Cu⁺ reactive sites

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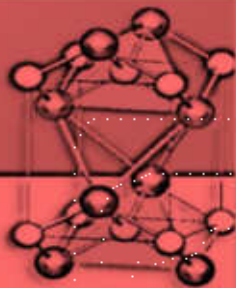[d] *Facultad de Ingeniería Química, UNL, Santiago del Estero 2829, 3000 Santa Fe, Argentina.*
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Noble metal catalysts are highly effective for oxidation reactions but are expensive, driving research into more affordable alternatives like Cu^+. However, stabilizing Cu^+ on surfaces is challenging, limiting its application in catalytic materials. Delafossite $CuGaO_2$ is a promising alternative due to its stable Cu^+ cations, but remains unexplored as a catalyst. In this study, we present experimental and theoretical analyses of $CuGa_2$ surfaces, CO adsorption at various active sites, CO oxidation performance, and the impact of oxygen vacancies on these properties. By employing DFT within the PBE+U and HSE06 approximations, $CuGaO_2$ surfaces were modeled alongside CO adsorption and vibrational spectra of adsorbed CO. The findings were subsequently analyzed and compared to experimental results obtained through HRTEM, XRD, XPS, and FTIR techniques.

Porous $CuGaO_2$ (111) nanoplates terminated with Ga were obtained via microwave-assisted hydrothermal synthesis. The edges of these plates are fundamental for the reactivity due to the presence of exposed Cu^+ sites and due to their large surface area (greater than the (111) face). DFT calculations of surface energy explained the Ga termination of the (111) faces and attributed the (110) termination to the edges of the nanoplates. CO adsorption on $CuGaO_2$, followed by FTIR and simulated via DFT, mainly occurs on Cu^+ sites forming mostly carbonyl (t-Cu^+), and also geminal dicarbonyl species (two CO molecules bound to the same Cu^+, g-Cu^+). In presence of oxygen vacancies, two types of copper are obtained (Cu^+ and $Cu^{+\delta}$, where $0 < \delta < 1$), and the CO adsorption energy significantly increases. Furthermore, CO adsorbed on reduced $CuGaO_2$ forms mainly g-$Cu^{\delta+}$ dicarbonyl, and less frequently, t-$Cu^{\delta+}$ and t-Cu^+ species.

Under reducing conditions, the CO oxidation performance is also considerably enhanced. Our findings on $CuGaO_2$ should be useful in the study of reactions activated by Cu^+ and also to propose the development of new technological catalysts.

X Workshop on Novel Methods for Electronic Structure Calculations
04th – 06th December 2023
La Plata – Argentina

Systematic theoretical evaluation of 2D/bidimensional ZnO nanostructures as potential anodes for lithium-ion batteries

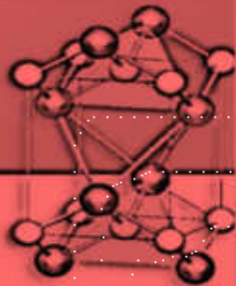F. Pignanelli [a], M. Romero [a], R. Faccio [a], A.W. Mombrú [a]

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Graphite has been a widely used material in batteries, particularly prominent in lithium-ion type. However, its low theoretical capacity limits its application in the storage of high energy densities. On the other hand, metallic lithium or sodium are prone to oxidation during system assembly, posing a hazard as well as a problem for electrochemical performance. Therefore, the development of alternative high-performance anodes for lithium-ion batteries.

Zinc oxide (ZnO) has been considered an effective material due to several interesting features, such as high theoretical capacity, ease of synthesis, low environmental impact, and moderate cost [1]. In addition to its many advantages, it suffers from two main problems: first, its low electrical conductivity, and second, its volume expansion during electrochemical charging and discharging. To overcome these problems, the scientific community has put a lot of effort into different approaches, such as nano-structuring (which helps reduce the stress caused by volumetric change) and the formation of composites with materials that improve electrical conductivity, such as carbonaceous derivatives, polymers, etc [2].
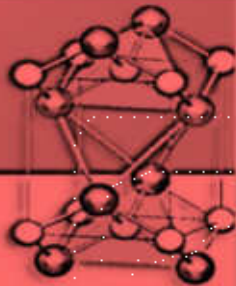
In order to achieve a comprehensive understanding of the structure and properties of this materials, as well as its potential application as an anode for lithium-ion batteries, here we present the modeling of three two-dimensional ZnO nanostructures, using ab initio computational methods (Density Functional Theory). Particularly, we are interesting to model the lithiation processes that occur on the surface of the proposed ZnO nanostructures during the battery operation, with the objective of carrying out a systematic comparison of the proposed systems performance.

[1]. Bhatt, M. D.; Lee, J. Y. (2019). High-capacity conversion anodes in Li-ion batteries: A review. International Journal of Hydrogen Energy, 44(21), 10852-10905.

[2]. Bui, V. K. H., Pham, T. N., Hur, J.; Lee, Y. C. (2021). Review of ZnO Binary and Ternary Composite Anodes for Lithium-I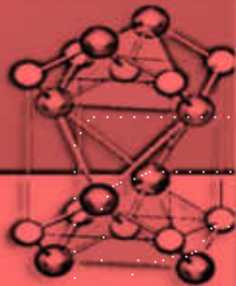on Batteries. Nanomaterials, 11(8), 2001.