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Viewpoint

The essential synergy between experiments and theory in applied surface science

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Viewpoints

I want to begin this contribution by briefly relating a personal story to the reader. My basic training during my PhD was in experimental catalysis, particularly in Ru-Mo bimetallics for synthesising alcohols from syngas. Later collaborated on experimental and theoretical work related to Ziegler-Natta catalysts for propylene synthesis [1]. The need to explain my experimental results led me to theoretical studies in Ru clusters [2] and $TiCl_4/MgCl_2$ surfaces [3], but I always maintained my communication with my experimental colleagues. I believe that this migration and kind of mutation has been a great "catalyst" in the application of Density Functional Theory (DFT) methods in applied surface science.

The question that has guided me since then is how to contribute from theoretical methods to the resolution of applied problems and to what extent one can help. A repeated situation occurs like this: a colleague who works in heterogeneous catalysis tells me: will it be possible to calculate the heat of adsorption, an isotherm or the IR spectrum of my system? Another colleague from metallurgy asked me to correlate dislocations and grain boundaries with mechanical properties in an alloy. The question itself is almost impossible to answer yes or no, mainly due to a problem of understanding and concepts.

The difficult communication between two worlds, catalytic and theoretical, repeats (and expands) the communication difficulties between physicists and chemists. While the former talk about the band gap, the latter understand better if they refer to HOMO-LUMO. Citing Roald Hoffmann's complaint about physicists, sometimes they take a reductionist approach toward chemistry and fail to understand its essence [4]. From the book *"The Same and Not the Same*": "*For a chemist, concepts like aromaticity, acid-base behavior, functional groups and substituent effects wilt at the edges when they are defined too closely. They cannot be mathematicalized, they cannot be defined unambiguously, yet they are of fantastic utility to our science* ".

Just starting this viewpoint, imagine now how difficult communication is when on the experimental side we start from reaction kinetics, activity and selectivity graphs, the effect of temperature and pressure on the kinetic constants, X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (IR) and so many acronyms for Ultra- High Vacuum (UHV) techniques in surface science and on the other side a theorist trying to computationally solve the Kohn & Sham equations with the best precision [5–8]. Here it is important to warn the experimental group, that computational calculations can provide some of the answers, not all of them and they will always be those provided by a model. At the beginning of the conversation, the theorist will ask what the exposed surface plane is. Are IR or Electron Energy Loss Spectroscopy (EELS) data available for adsorbate frequencies or Low Energy Electron Diffraction (LEED) to know the surface geometry? In most of the cases that have dealt with my research group, my colleagues do not have this data or the information is partial. In catalysis, polycrystalline materials are usually used, sometimes with low BET areas or with loads of supported metals below the detection limits of techniques such as Transmission Electron Microscopy (TEM) or XRD.

When working in teams, experimentalists and theoreticians must find a intermediary to cooperate. The computational cost, for instance, of calculating enormous systems at the DFT level demands a high computational power that is non-existent for the majority of scientists. However, making a model together, smaller fundamental sites of interest in the systems can be studied comprehensively by DFT and give results on fundamental interactions. Numerous works correlate macroscopic data, catalytic activity and selectivity based on chemical or physical concepts (acidity-basicity, the width of the d-band, support metal interaction, and formation of bimetallic particles, among others). Those basic concepts of introductory chemistry or solid physics are still valid and are useful to guide the definition of a calculation model. It is then the model to use that defines the game. My experience as a reader, editor or reviewer indicates that many times the proposed model is so simple that it represents nothing. Of course, these are always questions about polycrystalline samples and reactions at high T and pressures close to atmospheric. Sometimes (in my case) and many others, single crystal data are not available, with molecule adsorption data in

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conditions of very low coverage at UHV and on very clean and defined surfaces. STM or Atomic Force Microscopy (AFM) images are sometimes available. In these cases, the closeness between a model and the experiments is very simple. However, it is also challenging because it demands maximum theoretical precision. A very nice example shows how a simulated STM image matches the experimental data in the case of 1D tungsten oxide nanostructures on a Cu(110) surface [9].

Today it is very common to be able to perform periodic DFT theoretical calculations, that is, using a slab to represent the surface with a finite thickness and infinite 2D dimensions. There are excellent open-source computational packages for this, such as Quantum Expresso or SIESTA, to name a few [10-14]. It is not my intention here to go into details of the theory of DFT, there is an excellent bibliography that deals with the subject [15-18]. Beyond calculation methods based on DFT, there are more precise formulations, but more computationally demanding [19].

Cluster models, very useful several decades ago when computing power was very limited, no longer represent real surfaces. There are effects of non-periodicity, among others edge effects, or balance of charges, that cannot be ignored if what we want is to address surface science problems seriously.

The construction of the calculation model requires the definition of a specific plane where the adsorption or catalytic phenomenon will be simulated. At this point, surface science data on defined surfaces at very low coverage are very valuable. In the first approximation, the most prominent planes are selected from XRD data and those with the lowest Miller index because they have the lowest surface energy. The low coverage allows adsorption energies to be calculated without lateral interactions, which makes subsequent analysis easier. Once the surface is defined, it is important to know the geometry of the molecule to be adsorbed. Sometimes they are very simple molecules such as CO, NO or methanol, others are more complex such as polyethylene terephthalate (PET) [20-22]. It is possible to know molecular geometry data from literature or obtain data from molecular calculations. There are numerous free distribution packages for academic uses, very useful for this purpose, such as ORCA, Avogadro, and Dalton, among others [23-25]. Once the model is defined, it is extremely important in DFT to properly choose the correlation and exchange terms (Local-Density Approximation (LDA), Generalized Gradient Approximation (GGA), hybrids, among others), the density of K points for sampling, the convergence limits for optimization and the energy of cut-off. These parameters cannot always be obtained directly from the literature, it is important to test them and compare them with available data to avoid gross errors. For example, incorrect sampling of K points will cause the Silicon to have or not have a band gap. Incorrect use of GGA or LDA or the non-use of spin polarization will not correctly represent a material with magnetic characteristics [26].

We all use computers, but this does not mean that anyone can perform computational calculations in surface science in seconds. Just to give a comparison, no one would think of using UHV equipment whose cost exceeds a million dollars if they do not have prior training, and even more so the interpretation of results, both experimental and theoretical, requires significant expertise.

Previous reasoning and the use of chemical intuition are also extremely important, to avoid redundant calculations, i.e. situations that are impossible due to symmetry, even if there is access to a supercluster with millions of cores. You also have to pay for CPU time. For example, the adsorption of formic acid on calcium oxide, it is evident that at the bottom it is an acid-base reaction and that the -COOH functional group will most likely be oriented with its Oxigens to surface Ca^{2+} ions [27]. This is at least initially extrapolable to the adsorption of acids such as CH_3—COOH, it does not seem logical to attempt adsorption by the -CH_3 group. As almost always, brute force is not a good advisor when performing DFT calculations on surfaces.

The calculation model must initially reproduce the bulk properties of the metals involved, among them the lattice parameter and the elastic module. The thickness of the slab should be such that the intermediate layer approximates the bulk electronic states in a 3D solid and the upper layers are allowed to relax to be representative. For example, in a surface represented by a five-layer slab, the first two layers are allowed to relax and the other three are left fixed. The third should represent the solid. If this does not occur, more layers must be required, of course with this the computational cost increases considerably, especially when it comes to transition metals. Some important parameters are difficult to reproduce in pure DFT, such as the band gap. It is well known that the calculation provides lower values than the experimental ones, in several cases the error can be corrected (or at least mitigated) through DFT+U calculations, that is, using the Hubbard parameter [28]. Once we achieve the parameter and geometric optimization of a given surface and the adsorbate, we will have the adsorption energy at the site of the highest stability. Current calculation packages also allow the study of system stability at different temperatures, this is called Ab Initio Molecular Dynamics (AIMD), and in many cases, they benefit from improvements based on machine learning [29]. At this point, a very important process begins, the post-processing of the results. These consist of obtaining the electronic structure of the system by plotting the Density Of States (DOS); the charge density difference and charge analysis to have a map of charge transfer in the system and to quantify this transfer, respectively. This can be done for instance by studying the charge transfer of an alkali metal and the surface of a material that is candidate for batteries anodes [30]. The electronic structure and the contribution of the different orbitals to the surface bond are analyzed using the DOS technique. The different projections give us information about what are the greatest changes before and after absorption, band shifts, and changes in the width of the d-band or the band gap. It is a detective task that allows us to shed light on the most relevant molecular interactions [31]. It is also possible to calculate the vibration frequencies and these can often be compared with IR spectra and literature data. Comparison with spectroscopic data of systems formed by a single atom is often useful, this facilitates the rationalization of results [32].

Another parameter frequently required by experimentalists is the electric charge in the system and its transfer. This issue is problematic since the charge is not an observable in Quantum Mechanics, but it can be obtained by various methods from the integration of the electronic density. In particular, the most useful for me is the so-called Bader's charges analysis [33,34]. Charge transfers can be compared with XPS data [35].

Studies on the nature of the chemical bond are possible through Cristal Orbital Overlap Population (COOP) and Cristal Orbital Hamiltonian Population (COHP) techniques [31,36,37], the determination of the Bond Order (BO) [38], or the plot of Electron Localized Functions (ELF) [39], all can be computed from DFT calculations output. The first allows you to visualize which atoms or orbitals are bonding or antibonding in the energy range and the second gives a specific number that measures how a bond is strengthened or weakened after adsorption. Here it is important to note that both the adsorbed species modifies its chemical bond and the surface itself.

Furthermore, Nudged-Elastic-Band (NEB) methodology is also commonly used to obtain energy activation barriers of the movement of the metals (or any adsorbate) in these systems, which is vital to know for processes to occur [40]. AIMD in different ensemble calculations can also be performed to test the stability of the system with temperature to have more realistic conditions [41]. Moreover, for batteries, Open-Circuit-Voltages can be calculated by varying the amount of alkali metal atoms on the surface until obtaining its limiting capacity [42].

Although DFT calculations indeed provide results at 0 K, it is possible to analyze the effect of temperature through entropic variations and thus obtain values for $\Delta G(P,T)$. Finally, a detailed analysis of the normal modes of vibration in the solid can be performed using the free code Phonopy [43].

To exemplify the construction of a model and the interaction with experimental groups, I will comment on the case of the synthesis of biodiesel over CaO catalysts. Waste eggshell was investigated in triglyceride transesterification to determine its viability as a solid catalyst for use in biodiesel synthesis. The CaO catalyst obtained from this source achieves 97 % activity [44]. The bulk solid CaO is then modelled and the results are compared with previous experimental and theoretical calculations [45]. The experimental group of Prof. Marchetti at the Norwegian University of Life Sciences (NMBU), Norway and João Gomes at Instituto Superior de Engenharia de Lisboa (ISEL), Portugal, provide us data about the possible surface to be modelled. That was the CaO(001), as one of the most frequently detected in fresh and used catalysts [46]. Of course, the XRD also indicates the presence of other phases from $Ca(OH)_2$ and other unknown peaks, but building a first as a model, we need to simplify. Jasen and Marchetti have shown that when working with some solid catalysts the adsorption of the alcohol is the limiting reaction step [47]. Following this result, we decided to model the adsorption of ethanol. The results of our modelling were the presence of an ethoxy species Et-O bonded to a Ca^{2+} ion on the surface and the H (from –OH) group ending at a surface O^{2-}. We found an elongation in the Et-OH group. The O—H distance in the alcohol increased by about 54 % (from 0.97 to 1.49 Å) and its BO decreased by 71 %. At the same time the surface Ca-O BO decreases 57 % with a bond elongation of about 10 %. The electron density difference plots show an O—H broken bond in the alcohol. It is worth mentioning that the calculations are coincident with those predicted from kinetic consideration by Idriss and Seebauer [48]. These authors elucidates that upon adsorption, the -OH bond of ethanol dissociates heterolytically to yield an ethoxide and hydrogen linked to a negatively charged surface. One question from a reviewer gave us an idea for future studies. Our CaO (100) was stoichiometric, what would happen if it had Ca^{2+} or O^{2-} defects? How does temperature affect surface bonding? How does ethanol coverage affect adsorption energies? What is the role of surface hydroxyls in adsorption"?. As can be seen, an initial model does not cover all aspects, it gives clues, and indications and allows the construction of future steps and new ideas for experiments.

Two recent events show an interest in theoretical-experimental cooperation. During the International Conference on Applied Surface Science (ICASS) a workshop called "Theoretical Modeling for Experimentalists" was held by B. Han, I. Shuttleworth, H. Urbassek and myself [49] and a preface of Lee et al. emphasizes the novel aspects of Theoretical and Computational Surface Science [50].

Of course, it was not my intention to cover all aspects of theoretical or computational methods in this overview, at least three major aspects deserve your attention, those methods based on Monte Carlo simulation [51], Molecular Dynamics [52] and others with a growing role of Artificial Intelligence [53,54]. I recommend to the reader these recent articles on the application of these methodologies.

I would like to emphasize the situation today is quite different from that of metallic surfaces where the so-called "Surface Science Approach" has gained a comprehensive understanding [55]. Already in the case of oxide surfaces, the acquired knowledge is much lower than in the case of metals and is initially achieved for single-crystal model substrates such as TiO_2, ZnO or CeO_2. A recent publication of Wiesener et al. mentioned that the structures of metal oxide surfaces and inherent defects are vital for a variety of applications in materials science and chemistry [56]. In this article, a nice combination of AFM and extensive theoretical modeling is described. Other surfaces, such as those made of natural and synthetic polymers, are a current challenge, both experimental and modeling, for surface science applications. As an example, Oranli et al. presented a complete study focused on the application of sand blasting process for investigating the wettability of polymeric materials to produce hydrophobic behavior [57].

From an economic perspective, the impact of DFT modelling is difficult to measure, the estimate is that for each U$S invested in simulations, between 3 and 9 are recovered, that is, the investment is very good and a theoretician should be part of a team [58].

It is often said that the final word lies with the experiment, however many times the data are confusing, the processes extremely fast or impossible to measure, or simply excessively complex. In these cases, DFT (and other theoretical methodologies) allows processes to be decoupled and helps to rationalize and understand.

As a closing statement, I must say that it is not easy to interact with experimental groups and answer their questions using DFT calculations, but on the other hand, in my personal experience, they have ended up being the most cited articles of my career. In short, not an easy way, but with excellent results.

CRediT authorship contribution statement

Alfredo Juan: Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Alfredo Juan reports financial support was provided by European Union. I am an Editor of Applied Surface Science Advances If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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