

UNIVERSIDAD COMPLUTENSE DE MADRID
FACULTAD DE CIENCIAS QUÍMICAS



TESIS DOCTORAL

Estrategias computacionales de alto
rendimiento para descubrir catalizadores en la
Economía de Hidrógeno incluyendo ingeniería
de deformaciones elásticas

High-throughput computational strategies to
discover new catalysts for the Hydrogen Economy
including elastic strain engineering

MEMORIA PARA OPTAR AL GRADO DE DOCTORA

PRESENTADA POR

Carmen Martínez Alonso

DIRECTOR

Francisco Javier Llorca Martínez



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Facultad de Ciencias Químicas

INSTITUTO IMDEA MATERIALES

Doctorado en Química Avanzada

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Carmen Martínez Alonso

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Madrid, 2024



UNIVERSIDAD
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D./Dña. CARMEN MARTÍNEZ ALONSO,
estudiante en el Programa de Doctorado QUÍMICA AVANZADA,
de la Facultad de Ciencias Químicas de la Universidad Complutense de
Madrid, como autor/a de la tesis presentada para la obtención del título de Doctor y
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*A todas las mujeres científicas que fueron, son, serán y no pudieron ser, tan importantes en
nuestra historia.*

"Solo hay que pintar las rosas de rojo."
Lewis Carrol.

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Glossary

Acronym	Definition
AEC	Alkaline Electrolyzer Cell
AFC	Alkaline Fuel Cell
ASE	Atomic Simulation Environment
bcc	Body Centered Cubic
DMFC	Direct Methanol Fuel Cell
DFT	Density Functional Theory
ESE	Elastic Strain Engineering
fcc	Face Centered Cubic
GCN	Generalized Coordination Number
GGA	Generalized Gradient Approximation
GPR	Gaussian Process Regressor
hcp	Hexagonal Close Packed
HER	Hydrogen Evolution Reaction
HOR	Hydrogen Oxidation Reaction
LDA	Local Density Approximation
MAD	Median Absolute Deviation
MAE	Mean Absolute Error
MCFC	Molten Carbonate Fuel Cell
MEP	Minimum Energy Path
ML	Machine Learning
ML	Monolayer
NEB	Nudged Elastic Band

Table 1: Recurrent acronyms used throughout this thesis. From A to N.

Acronym	Definition
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PAFC	Phosphoric Acid Fuel Cell
PBE	Perdew–Burke–Ernzerhof functional
PCA	Principal Components Analysis
PEMEC	Proton Exchange Membrane Electrolyzer Cell
PEFC	Polymer Exchange Membrane Fuel Cell
PDOS	Projected Density of States
PW91	Perdew–Wang functional
RF	Random Forest
RMSE	Root Mean Squared Error
SAD	Superposition of Atomic Densities
SAP	Superposition of Atomic Potentials
SOEC	Solid Oxide Electrolyzer Cell
SOFC	Solid Oxide Fuel Cell
WAR	Weighted Atomic Radius
WEN	Weighted Electronegativity
WIE	Weighted first Ionization Energy
WOE	Weighted Outer Electrons

Table 2: Recurrent acronyms used throughout this thesis. From O to Z.

Abstract

The hydrogen economy stands as one of the most promising alternatives to generate green energy and slow down carbonization. This technology is based on two main processes: the generation of hydrogen (limited by the HER and the OER) in electrolyzer cells, and the production of energy (limited by the ORR and the HOR) in fuel cells. These reactions need the use of a heterogeneous catalyst, usually a precious metal, such as platinum. The high cost and the low availability of this material hinder the widespread use of this technology, boosting the search for new catalysts and techniques to improve the catalytic activity of these reactions. Four techniques are commonly used to tune the active surface of the so-called heterogeneous catalysts: the introduction of different facets, alloying, the addition of defects, and the application of elastic strains.

Within this framework, this thesis analyzes, from a computational point of view, the catalytic activity of pure metals and multimetallic materials in two of the main reactions in the Hydrogen Economy: the Hydrogen Evolution Reaction (HER) and the Oxygen Reduction Reaction (ORR). Additionally, the effect of elastic strains is also considered. To this end, Density Functional Theory calculations were performed for different pure metals, binary, and ternary intermetallic compounds in order to calculate the adsorption energy of the three main adsorbates present in the reactions: H, O, and OH, with and without the application of elastic strains. The effect of different types of strains -biaxial, uniaxial, and shear- at different adsorption positions was analyzed in depth. These calculated adsorption energies were used as estimators of the catalytic activity, following the Bell-Evans-Polanyi principle [53] and the *d*-band theory proposed by J. K. Norskov [92, 94, 182].

Complimentary, all the DFT calculations with and without the application of strains for pure metals and intermetallic compounds were used to generate a Machine Learning database and train a Random Forest Regressor Model that was able to predict the hydrogen, oxygen, and hydroxyl adsorption energies of many multimetallic materials. The obtained predictions for binary intermetallic compounds had very low errors in the case of H (MAE=0.07eV) and O/OH (MAE=0.18 eV) models. The model was able to predict the effect of elastic strains in the adsorption energy and was used to propose new intermetallic compounds that can replace noble metals for the HER and the ORR.

This work represents a high-throughput computational strategy to discover new catalysts for the Hydrogen Economy including Elastic Strain Engineering.

Resumen

La Economía del Hidrógeno representa una de las más prometedoras alternativas para la generación de energía verde y la descarbonización del sector energético. Esta tecnología se fundamenta en dos procesos principales: la generación de hidrógeno (limitada por la HER y la OER) en celdas electrolíticas, y la producción de energía (limitada por la ORR y la HOR) en pilas de combustible. Estas reacciones requieren el uso de un catalizador heterogéneo, siendo este generalmente un metal precioso, como el platino. El alto costo y la baja abundancia de este material obstaculizan el uso generalizado y el avance de esta tecnología, e impulsan la búsqueda de nuevos catalizadores y de técnicas para mejorar su actividad catalítica. Existen cuatro técnicas comúnmente utilizadas para modificar la superficie activa de los catalizadores heterogéneos: el estudio de diferentes planos de adsorción, el diseño de aleaciones, la inclusión de defectos en la superficie y la aplicación de deformaciones elásticas.

El objetivo principal de esta tesis es analizar, desde un punto de vista computacional, la actividad catalítica de diferentes metales puros y materiales multimetálicos en dos de las principales reacciones en la Economía del Hidrógeno: la Reacción de Evolución de Hidrógeno (HER) y la Reacción de Reducción de Oxígeno (ORR). Paralelamente, el efecto de las deformaciones elásticas en la superficie del catalizador -Ingeniería de deformaciones elásticas- en materiales metálicos se estudió en profundidad. Para ello, se realizaron cálculos de Teoría del Funcional de la Densidad para diferentes metales puros y compuestos intermetálicos binarios y ternarios con el fin de calcular la energía de adsorción de los tres adsorbatos principales presentes en las reacciones: H, O y OH, con y sin la aplicación de deformaciones elásticas. Se analizó en detalle el efecto de diferentes tipos de deformaciones -biaxiales, uniaxiales y de cizalla- en distintos sitios de adsorción. Estas energías calculadas se utilizaron para estimar la actividad catalítica, siguiendo el principio de Bell-Evans-Polanyi [53] y la teoría de las bandas d propuesta por J. K. Norskov [92, 94, 182].

A su vez, las simulaciones de DFT con y sin la aplicación de deformaciones elásticas para metales puros y compuestos intermetálicos se utilizaron para generar una base de datos de Aprendizaje Automático y entrenar un modelo de Regresión de Bosques Aleatorios para predecir las energías de adsorción de hidrógeno, oxígeno e hidroxilo en materiales metálicos y multimetálicos. Las predicciones obtenidas en los compuestos bimetálicos presentaron errores muy bajos en el caso de H (MAE=0.07 eV) y O/OH (MAE=0.18 eV). El modelo diseñado fue capaz de predecir también el efecto de las deformaciones elásticas en la energía de adsorción y se extendió a compuestos intermetálicos ternarios con la adición de un solo descriptor.

En su conjunto, este trabajo contiene estrategias computacionales de alto rendimiento para descubrir nuevos catalizadores en la Economía de Hidrógeno incluyendo la ingeniería de deformaciones elásticas.

The main results of this thesis have been published in

C. Martínez-Alonso, JM. Guevara-Vela, J. LLorca,
The effect of elastic strains on the adsorption energy of H, O, and OH in
transition metals,
Phys. Chem. Chem. Phys. **23**, 21295-21306 (2021)

C. Martínez-Alonso, JM. Guevara-Vela, J. LLorca,
Understanding the effect of mechanical strains on the catalytic activity
of transition metals,
Phys. Chem. Chem. Phys. **24**, 4832-4842 (2022)

C. Martínez-Alonso, J. LLorca,
Applicability of the *d*-band model to predict the influence of elastic
strains on the adsorption energy of different adsorbates onto Pt and PtO₂
surfaces,
ACS Omega, Advance Article (2024)

C. Martínez-Alonso, V. Vassilev-Galindo, B. M. Comer, F. Abild-Pedersen,
K. T. Winther, J. LLorca,
Application of machine learning to discover new intermetallic catalysts
for the hydrogen evolution and the oxygen reduction reactions,
Catal. Sci. Technol. **14**, 3784 (2024)

The complete adsorption energies database and the code for the Machine
Learning Model are openly available at:

<https://zenodo.org/doi/10.5281/zenodo.10364546>

<https://www.catalysis-hub.org/publications/AlonsoStrain2023>

1.1 Hydrogen economy

The 7th sustainable development goal of the United Nations Organization is to ensure access to affordable, reliable, sustainable, and modern energy for all, while the 13th goal is to take urgent action to combat climate change. Both objectives are closely linked to the use of clean and renewable energy sources for addressing the world's rising energy needs while limiting environmental effects. Currently, renewable energy (solar, wind, and hydropower) generates 28% of the world's electricity [3]. While hydropower accounts for 62% of this generation, its expansion is limited due to resource availability and environmental impact. Meanwhile, solar and wind are projected to account for > 70% of renewal energy generation by 2050 [3]. However, further expansion is limited because power provided by solar and wind energy (as opposed to coal, natural gas, and nuclear) is intermittent and has to be associated with large energy storage capabilities.

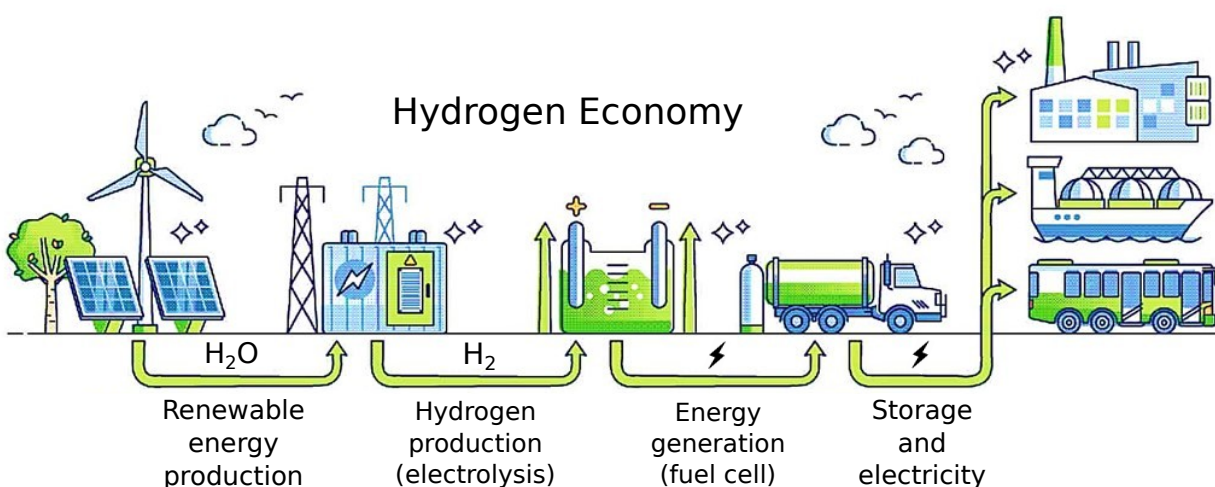


Figure 1.1: General scheme of the Hydrogen Economy roadmap. Figure based in [115].

The most relevant large energy storage capabilities are pumping water uphill (pumped-

storage hydroelectricity), batteries, and hydrogen storage. While pumped-storage hydroelectricity and batteries have high efficiency, they do not scale to the energy storage needs of large grids powered by intermittent renewable energy due to land restrictions or cost, respectively [365]. On the contrary, hydrogen energy storage offers a unique combination of scalability, long-term storage, and portability, leading to the so-called hydrogen economy (Figure 1.1). In this model, renewable energy sources are used to split water into hydrogen and oxygen. The hydrogen is stored for later use in fuel cells or gas-fired turbines to generate electricity without the emission of pollutants. Storing large-scale reserves of hydrogen is feasible underground using depleted gas reservoirs [4] and is portable. It can be compressed and transported in pipes similar to natural gas for local electricity generation or use. Although hydrogen is less efficient than fossil fuels in terms of energy stored per volume is more efficient in terms of mass. This means that hydrogen is not only suitable for surface transport but also for aircraft.

As shown in Figure 1.2, there are many types/colors of hydrogen. The majority of the H_2 currently consumed in the world is Grey. It has its origin in fossil fuels and can be obtained from natural gas through methanol steam reforming, producing CO_2 emissions [263]. These emissions can be lowered by Carbon Capture and Storage, in the alleged Blue hydrogen [110]. Green hydrogen is one of the pillars of sustainable development. It is produced through water electrolysis powered by renewable energies and offers the potential to leverage clean and plentiful water resources [5]. Although it is still in the early stages of development, Turquoise hydrogen presents a low-emissions source of hydrogen. It is produced through methane pyrolysis and generates solid carbon as a by-product [289]. Brown hydrogen is fabricated from coal gasification releasing CO_2 in the process and contributing to greenhouse emissions [145]. Finally, both Pink and Yellow hydrogen are produced by electrolysis using nuclear power energy, and a mixture of solar energy and natural gas, respectively [12].

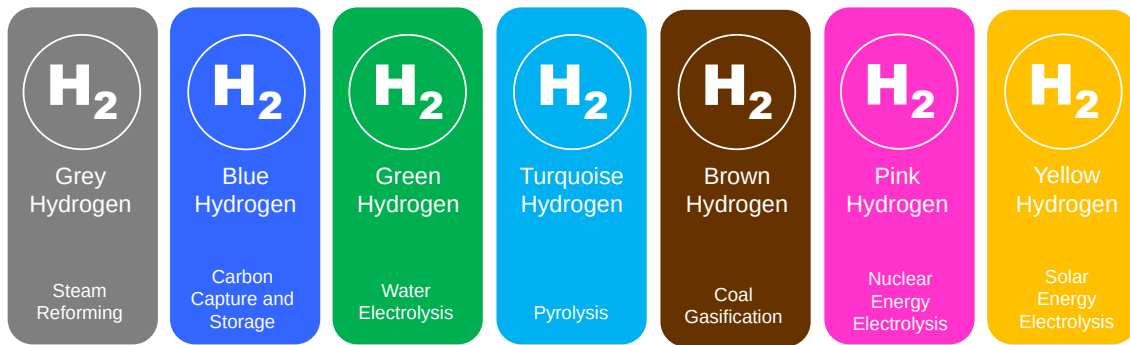


Figure 1.2: Types/colors of hydrogen and their energy source. Figure based in [54].

The notion of "Hydrogen economy" was introduced by John Bockris in the 1970s [25]. He envisioned the idea of producing hydrogen via water electrolysis, which would be converted back to electricity through on-site fuel cells. This approach corresponds to the definition of Green hydrogen and requires the use and design of two types of devices: electrolyzer and fuel cells.

1.1.1 Electrolyzer cells

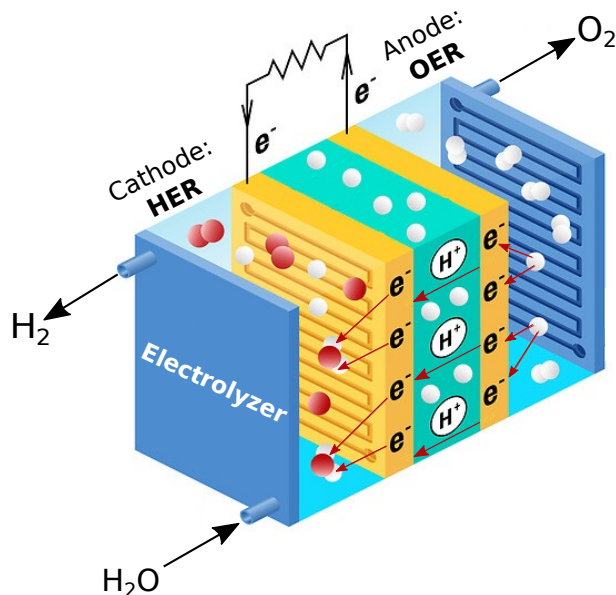


Figure 1.3: Scheme of an electrolyzer cell. Figure based in [67].

Electrolyzer cells (Figure 1.3) are devices designed for the splitting of water into molecules of hydrogen (H_2) and oxygen (O_2) through the supply of electrical power, and consequently, they are used in the production of Green hydrogen. Several types of electrolyzer cells have been developed in recent years: Solid Oxide Electrolyzer Cells (SOEC), Alkaline Electrolyzer Cells (AEC), and Proton Exchange Membrane Electrolyzer Cells (PEMEC), among others. The global reaction that occurs in Electrolyzer cells can be separated into two half-reactions: the Hydrogen Evolution Reaction (HER), which takes place in the cathode, and the Oxygen Evolution Reaction (OER), which happens in the anode. One of the major obstacles that impede this process from being efficient in the industry is the slow rate and the high overpotentials of the HER and the OER [275, 309], and efficient and cheap catalysts are necessary to overcome these limitations.

OER

In the anode of electrolyzer cells (water splitting process), the Oxygen Evolution Reaction (OER) takes place. The OER is a four electron-proton coupled reaction that requires high energies to overcome the associated kinetic barriers [275]. This reaction is highly affected by the pH of the electrolyzer cell, and one can distinguish between the global reaction and the proposed mechanism in acidic and alkaline media, shown in Table 1.1

HER

The Hydrogen Evolution Reaction (HER) is the cathodic reaction in the process of water splitting (electrolyzer cell) and plays a key role in the production of hydrogen by dissocia-

OER	Acidic media	Alkaline media
Reaction	$2 \text{H}_2\text{O} \longrightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$	$4 \text{OH}^- \longrightarrow 2 \text{H}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^-$
Mechanism	$* + \text{H}_2\text{O} \longrightarrow \text{HO}^* + \text{H}^+ + \text{e}^-$ $\text{HO}^* + \text{OH}^- \longrightarrow \text{O}^* + \text{H}_2\text{O} + \text{e}^-$ $2 \text{O}^* \longrightarrow 2 * + \text{O}_2$ $\text{O}^* + \text{H}_2\text{O} \longrightarrow \text{HOO}^* + \text{H}^+ + \text{e}^-$ $\text{HOO}^* + \text{H}_2\text{O} \longrightarrow * + \text{O}_2 + \text{H}^+ + \text{e}^-$	$* + \text{OH}^- \longrightarrow \text{HO}^* + \text{e}^-$ $\text{HO}^* + \text{OH}^- \longrightarrow \text{O}^* + \text{H}_2\text{O} + \text{e}^-$ $2 \text{O}^* \longrightarrow 2 * + \text{O}_2$ $\text{O}^* + \text{OH}^- \longrightarrow \text{HOO}^* + \text{e}^-$ $\text{HOO}^* + \text{OH}^- \longrightarrow * + \text{O}_2 + \text{H}_2\text{O} + \text{e}^-$

Table 1.1: OER global reaction and proposed mechanisms in acidic and alkaline media. * represents a site on the surface of the catalyst and HO*, O*, and HOO* the atoms adsorbed.

HER	Acidic media	Alkaline media
Reaction	$\text{H}^+ + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2$	$\text{H}_2\text{O} + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2 + \text{OH}^-$
Mechanism	$\text{H}^+ + * + \text{e}^- \longrightarrow \text{H}^*$ $\text{H}^* + \text{H}^+ + \text{e}^- \longrightarrow * + \text{H}_2$ $2 \text{H}^* \longrightarrow 2 * + \text{H}_2$	$\text{H}_2\text{O} + \text{e}^- + * \longrightarrow \text{H}^* + \text{OH}^-$ $\text{H}_2\text{O} + \text{e}^- + \text{H}^* \longrightarrow \text{H}_2 + \text{OH}^- + *$ $2 \text{H}^* \longrightarrow \text{H}_2 + 2 *$

Table 1.2: HER global reaction and proposed mechanism in acidic and alkaline media. * represents a site on the surface of the catalyst and H* the atom adsorbed.

tion of the water molecule. It is a classic example of a reaction with a transference of two electrons through the Volmer-Heyrovsky or Volmer-Tafel mechanisms [123]. The kinetics of the reaction is limited by the adsorption of hydrogen on the surface for acidic solutions. The adsorption process (Volmer) limits the kinetics if hydrogen binds weakly on the catalyst surface, while desorption (Heyrovsky/Tafel) is the limiting process otherwise (Figure 1.4 a).

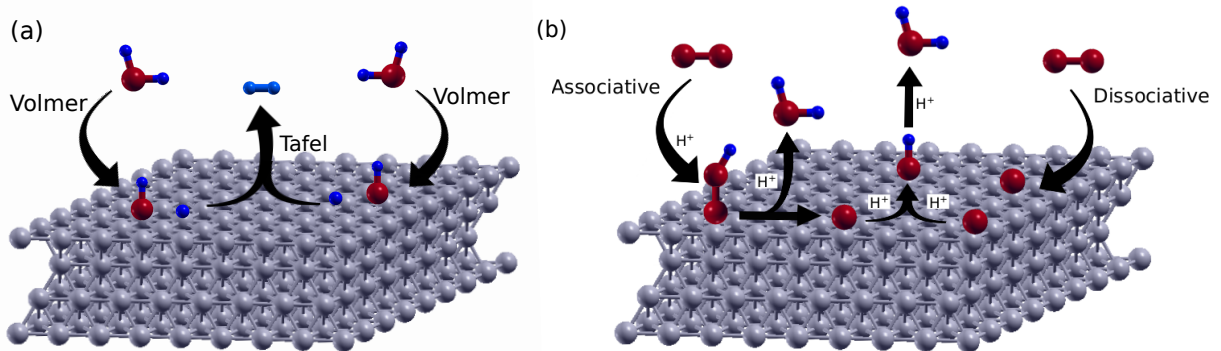


Figure 1.4: (a) Schematic of the mechanisms for the (a) HER and the (b) ORR, in a Pt fcc(111) surface and acidic media. Red, blue, and grey atoms represent oxygen, hydrogen, and platinum, respectively.

The global process and the proposed mechanisms are shown in Table 1.2 in acidic and

alkaline media. The mechanism involves first the electrochemical hydrogen adsorption (Volmer reaction) followed by the electrochemical (Heyrovsky reaction) and/or chemical (Tafel reaction) hydrogen desorption reactions. The reaction path for the HER is shown in Figure 1.4a.

1.1.2 Fuel cells

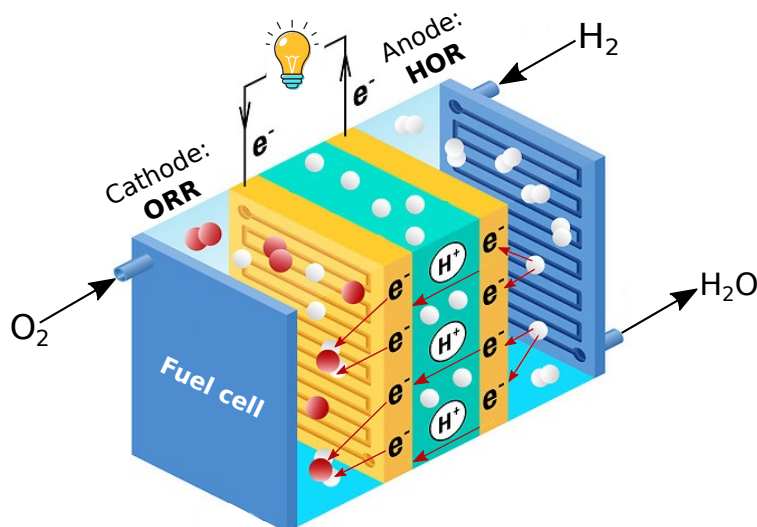


Figure 1.5: Scheme of a fuel cell. Figure based in [67].

The second type of devices crucial in the Hydrogen Economy are fuel cells (Figure 1.5). In this device, hydrogen, which has been previously produced in electrolyzers, and oxygen are used to generate electricity, with molecules of water as the only by-products. This type of power generation prevents CO₂ emissions, reduces pollution, and contributes to the decarbonization of energy [216]. Depending on the materials and the support, there are many different types of fuel cells, namely Direct Methanol Fuel Cells (DMFC), Polymer Exchange Membrane Fuel Cells (PEMFC), Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Solid Oxide Fuel Cells (SOFC). Analogously to electrolyzer cells, two half-reactions occur on each of the electrodes: the Oxygen Reduction Reaction (ORR) that happens in the cathode, and the Hydrogen Oxidation Reaction (HOR), which takes place in the anode.

HOR

The Hydrogen Oxidation Reaction (HOR) is the anodic process occurring at the anode of Fuel cells. It represents the reversible reaction to the HER which can be written in acidic and alkaline media as shown in Table 1.3. As well as the HER, the mechanism of the HOR consists of three main steps: the Volmer, the Heyrovsky, and the Tafel reactions, which occur in reverse order in comparison with the HER.

HOR	Acidic media	Alkaline media
Reaction	$\frac{1}{2} \text{H}_2 \longrightarrow \text{H}^+ + \text{e}^-$	$\frac{1}{2} \text{H}_2 + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{e}^-$
Mechanism	$2 * + \text{H}_2 \longrightarrow 2 \text{H}^*$ $* + \text{H}_2 \longrightarrow \text{H}^* + \text{H}^+ + \text{e}^-$ $\text{H}^* \longrightarrow \text{H}^+ + * + \text{e}^-$	$\text{H}_2 + 2 * \longrightarrow 2 \text{H}^*$ $\text{H}_2 + \text{OH}^- + * \longrightarrow \text{H}_2\text{O} + \text{e}^- + \text{H}^*$ $\text{H}^* + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{e}^- + *$

Table 1.3: HOR global reaction and proposed mechanisms in acidic and alkaline media. * represents a site on the surface of the catalyst and H^* the atom adsorbed.

ORR

The ORR is the critical reaction for the generation of energy from hydrogen in fuel cells and represents the reversible process of the OER. Currently, the kinetics of the ORR is limited by the low rate of the reduction reaction of oxygen which can be enhanced by the use of a catalyst. The ORR in a PEMFC is carried out through the transfer of 4e⁻ through either a dissociative or associative pathway [232]. The molecule of O_2 dissociates before it is hydrogenated in the former, whereas hydrogenation happens previously to the dissociation in the latter (Figure 1.4b). The steps of both mechanisms and the global reactions are shown in Table 1.4.

ORR	Acidic media	Alkaline media
Reaction	$\text{O}_2 + 4 (\text{H}^+ + \text{e}^-) \longrightarrow 2 \text{H}_2\text{O}$	$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \longrightarrow 4 \text{OH}^-$
Mechanism	Dissociative: $\frac{1}{2} \text{O}_2 + * \longrightarrow \text{O}^*$ $\text{O}^* + \text{H}^+ + \text{e}^- \longrightarrow \text{HO}^*$ $\text{HO}^* + \text{H}^+ + \text{e}^- \longrightarrow \text{H}_2\text{O} + *$ Associative: $\text{O}_2 + * \longrightarrow \text{O}_2^*$ $\text{O}_2^* + \text{H}^+ + \text{e}^- \longrightarrow \text{HOO}^*$ $\text{HOO}^* + \text{H}^+ + \text{e}^- \longrightarrow \text{H}_2\text{O} + \text{O}^*$ $\text{O}^* + \text{H}^+ + \text{e}^- \longrightarrow \text{HO}^*$ $\text{HO}^* + \text{H}^+ + \text{e}^- \longrightarrow \text{H}_2\text{O} + *$	Dissociative: $\frac{1}{2} \text{O}_2 + * \longrightarrow \text{O}^*$ $\text{O}^* + \text{H}_2\text{O} + \text{e}^- \longrightarrow \text{HO}^* + \text{OH}^-$ $\text{HO}^* + \text{e}^- \longrightarrow \text{OH}^- + *$ Associative: $\text{O}_2 + * \longrightarrow \text{O}_2^*$ $\text{O}_2^* + \text{H}_2\text{O} + \text{e}^- \longrightarrow \text{HOO}^* + \text{OH}^-$ $\text{HOO}^* + \text{e}^- \longrightarrow \text{OH}^- + \text{O}^*$ $\text{O}^* + \text{H}_2\text{O} + \text{e}^- \longrightarrow \text{HO}^* + \text{OH}^-$ $\text{HO}^* + \text{e}^- \longrightarrow \text{OH}^- + *$

Table 1.4: ORR global reaction and proposed mechanisms in acidic and alkaline media. * represents a site on the surface of the catalyst and HO^* , O^* , O_2^* , and HOO^* the atoms adsorbed.

Although each mechanism presents different reactions, the reaction rate is independent of the mechanism [129] and the analysis in this thesis will be based on the dissociative mechanism, which is simpler. Two different adsorbed species have to be considered in this case, O^* and HO^* (notice the difference with the HER, where the only intermediate adsorbate is H^*). The reaction path for the dissociative mechanism is depicted in Figure 1.4b).

One limiting factor for the widespread use of hydrogen is the 35% efficiency of the round trip process (water electrolysis plus energy generation in fuel cells), which is much smaller than that achieved with hydropower (70-80%) or batteries (80-95%) [365]. Thus, the use of catalysts is crucial to overcome the sluggish kinetics of both the HER/OER in electrolyzers and HOR/ORR in fuel cells. Currently, Pt-based (or Pt-group metals) catalysts are used in both electrolyzers and fuel cells to ensure the H_2 production and energy generation from H_2 at considerably low temperatures and pressures. However, capital costs will begin to dominate H_2 production and energy generation from H_2 as the cost of electricity produced from renewable sources (wind, sun) decreases. These capital costs are heavily dependent on the Pt-based catalysts used both for water splitting and fuel cells. In fact, the percentage of capital costs related to platinum for fuel cells jumps to over 40% when taking into consideration the entire cost of the electrocatalyst, which includes support structures that are needed to increase the power density of Pt [51]. Thus, the search for efficient and affordable catalysts for the HER and ORR is a critical priority to ensure the success of the hydrogen economy

1.2 Heterogeneous Catalysis

The development of efficient and selective catalysts has been one of the keystones of technological progress in the last century [10]. Currently, most fossil fuels used in transportation are refined using catalytic processes [146, 147, 222], while a substantial fraction of chemical products are manufactured through technologies based on catalysis [30, 120, 279]. Additionally, catalysis is critical for the electrochemical processes necessary to generate clean energy and/or to produce clean fuels, such as hydrogen [140, 197]. It is known that the rate-limiting steps for these reactions are associated with the adsorption of the intermediate species (H, O, OH, and OOH) onto the surface of the catalyst [49, 198]. These adsorption energies must follow Sabatier's principle [238] in order to find an efficient catalyst.

1.2.1 Sabatier's principle

The variation of the adsorption energy can be used to modulate the activity of a catalyst following Sabatier's principle [238]. It states that the adsorption energy should be neither too high nor too low for reactions passing through an adsorbed intermediate. If the energy is too high (endothermic), adsorption is slow and limits the overall rate, whereas the catalyst surface becomes poisoned and desorption is limited if the adsorption energy is too low (exothermic). In terms of hydrogen and oxygen electrocatalysis, this principle leads to the conclusion that the free energy of adsorption should be close to zero at the equilibrium potential [301, 328]. If Sabatier's principle is the only factor that governs the catalytic process, the plot of the reaction rate *vs.* the energy of adsorption of the intermediate species leads to a volcano-shaped curve [195, 198] as illustrated in Figure 1.6.

Starting from a low, negative (exergonic) energy of adsorption, the catalytic activity initially rises, leading to the ascending branch of the volcano. The rate passes through a

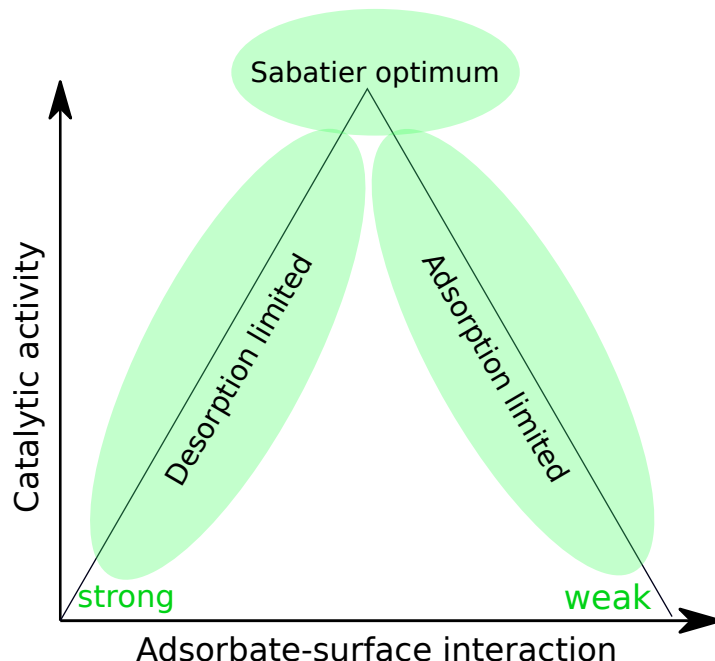


Figure 1.6: Volcano-shaped plot illustrating Sabatier's principle.

maximum around null adsorption energies and then starts to decrease as it becomes more endergonic in the descending branch of the volcano. The magnitude of the adsorption energy can be used to determine the overall rate of the reaction. In other words, optimal catalysis occurs when interactions between catalyst and substrate are of intermediary strength [128], and an equilibrium between adsorption of the reactants and desorption of the products should be attained to get the maximum activity. These adsorption processes are controlled by the electronic structure of the catalysts, which can be modified using different techniques (Figure 1.7) in order to reach the cusp of the volcano. The most relevant strategies to modify the electronic structure of the catalysts are facet Engineering [52, 65], defect Engineering [349], alloying [71, 166, 236, 287], and elastic strain engineering (ESE) [258, 259].

1.2.2 Strategies to design new catalysts

Facet engineering

The selection of different facets is a general strategy to change the catalytic activity of the heterogeneous catalysts in the Hydrogen Economy. Their reactivity is highly related to the exposed facets as the adsorption and desorption strength of the intermediate species varies on the different surfaces [211]. In essence, the influence of facets can be divided into two separate effects: the different energy barriers of the facets, which present dissimilar activation energies, and the densities of active sites that are also peculiar for each facet. These two effects can be exploited in order to get the maximum catalytic activity. Qiao et al. [224] presented an overview of the state-of-the-art of Cu single crystal and their

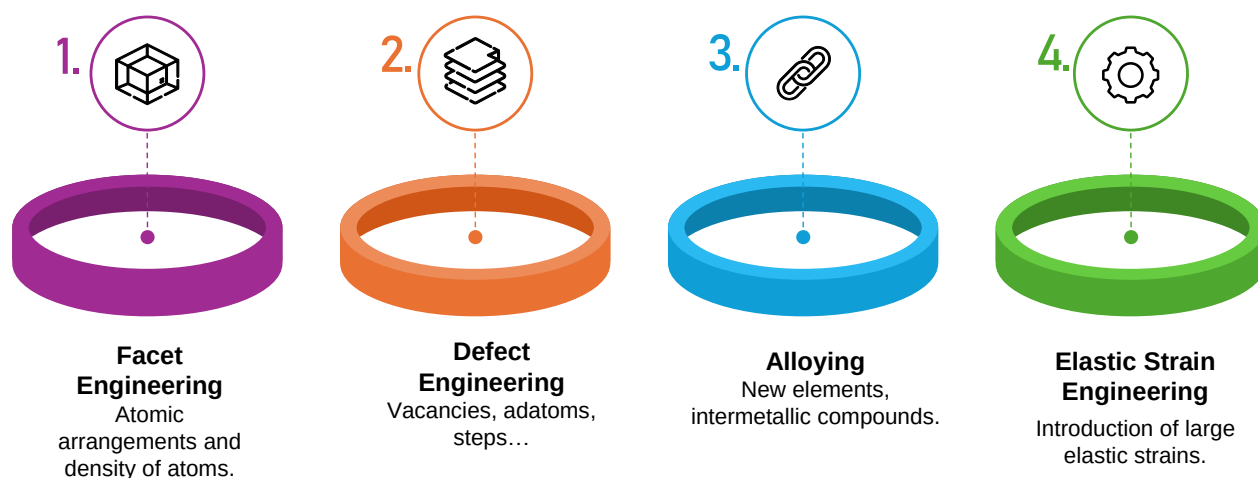


Figure 1.7: Four different strategies to modify the electronic structure (and catalytic activity) of the catalyst surface.

facet dependency in electrochemical CO_2 reduction and showed that the performance of the reactions involved in the process is highly dependent on the surface geometry of the Cu catalysts [109]. Guo et al. [90] analyzed the Ag/CeO₂ catalyst in the oxidation of N, N-dimethylformamide, depending on the crystal facets exposed. After testing different exposed crystal facets such as nanorods (110) and (100), nanocubes (100), and nanooctahedrons (111) as support, they found more than 80% yield in those orientations with more Ag-O-Ce interfaces.

In the field of Hydrogen Economy, there are also studies that show the application of facet engineering. For example, Li et al. [154] compared the ORR activities for Pt and Cu on (100) surfaces with those on (111) surfaces. The differences in adsorption energy for each step at both facets resulted in a higher catalytic activity at the (111) facets. Similarly, Duan et al. [48] compared the activities of nickel (100) and (111) surfaces in the ORR. They observed that intermediates have stronger binding at (100) surfaces, which hinders the protonation steps and produces –at least– an activity reduction of 13.4% when compared to the (111) surfaces. These authors attribute this phenomenon to the different atomic arrangement and the density of atoms, which is larger in (111) surfaces. Rodriguez et al. [167] reported that the (001) crystal facet of Ni₂P has the highest HER activity compared to the (111) crystal face of Ni. This is due to the lower potential barrier for the Heyrovsky or Tafel step (H^* desorption).

Defect engineering

The introduction of defects in the surface of the catalyst directly affects the number of active sites and the surface area, which consequently changes the catalytic activity [65, 349]. Numerous studies have been carried out to understand the effect of the different types of defects (e.g. vacancies, adatoms, steps, kinks, etc.) on the catalytic activity. For instance, Zhang et al. [352] utilized this strategy on CeVO₄ catalysts for the reduction of organic dyes and heavy metal pollutants in the dark. Cao [35] created defects in ultrathin

C_3N_4 catalyst, which resulted to be efficient active sites in the photocatalytic conversion of lignin into aromatic monomers via the C-C bond cleavage. Shi et al. [254] used an electric field to create vacancies that boost the selective CO_2 photoreduction. These oxygen vacancies, are also found by Wang et al. [316] to be efficient in the catalysis of single-crystal VO_2 for aqueous zinc ion battery cathodes.

Regarding the reactions involved in the production of hydrogen and the generation of green energy, there are many studies in the literature that utilize defect engineering. Callejas et al. [34] studied the ORR performance of different Pt alloys depending on the vacancies, which were found to directly affect the adsorption energies of O and OH. Another common approach to insert defects in the surface of the catalyst is de-alloying [176, 271, 339]. Fortunelli et al. [62] worked on the ORR activity of de-alloyed Pt_xNi_y alloys and observed that the rate-limiting step, which was the oxygen hydrogenation in all cases, became more favorable in surface slabs with defects. The adsorption at the step edges of metal surfaces can also change the preference of atomic adsorbates. Feibelman et al. [60] studied the O/Pt(111) system and evidenced that the lower coordination of the surface at the step edge results in energetically higher d-bands and higher reactivity. Fan et al. [58] performed oxygen defect engineering on low-crystalline Fe(III) oxyhydroxide as an electrocatalyst for water oxidation. They observed a reduction from 1.65 eV to 1.91 eV in the activation barriers of the OER process.

Alloying

Another effective method to change the surface reactivity is alloying. The integration of different elements at the catalyst surface increases the number of binding geometries and changes the electronic structure of the adsorption sites. Commonly, one of the elements of the alloy segregates to the surface and generates a strain due to the difference in lattice parameters between the alloy and the individual alloying elements. For example, Yuan et al. [348] found that alloying Co with Ni, improves methane cracking and promotes the CO_2 activation and the reduction of graphitization of carbon deposits. Wang [307] and Chen [41] verified that Ni-Ru and Pd-Cu alloys act as robust and efficient catalysts for the electroreduction of nitride to ammonia (NO_2RR), respectively. Li [156] designed a stable Cu-Ni alloy catalyst with ordered microchannels using 3D printing which boosted the reverse water-gas shift reaction by the enhancement of mass and heat transfer.

Many Pt-based alloys have been studied for the HER and the ORR in the last decades: Pt-Fe [150], Pt-Au [255], Pt-Ag [166], Pt-Cu [47], Pt-Co [160], Pt-Ni [285], Pt-Pd [345], Pt-Cr [39], etc. Some alloys showed better electrocatalytic performance for the HER and the ORR than pure Pt, while the opposite was found in other cases. Stamenkovic et al. [269] ordered the catalytic activities of some alloys for the ORR: $Pt_3Fe > Pt_3Ni > Pt_3V > Pt_3Ti > Pt$. Duan et al. [48] analyzed the catalytic performance of PtM (M: Fe, Co, and Ni) alloys for the ORR. They found that the adsorption energies of the adsorbates for all the alloys were weaker than those for pure Pt, which resulted in a reduction of the activation energies of the protonation steps and an increase in the dissociation energies. Considering the rate-limiting step for each of the alloys, it was found that the activation energy barriers considerably decreased, leading to an enhancement of the catalytic performance. Ou et

al. [203] evidenced the greater catalytic activity of Pt-Cu, Pt-W, Pt-Sn, and Pt-Al in the ORR compared with pure Pt. Escudero et al. [52] measured the catalytic activity of eight Pt-lanthanide and Pt-alkaline electrodes, Pt_5M (M: La, Ce, Sm, Gd, Tb, Dy, Tm, and Ca) in the ORR, which presented an activity enhancement by a factor of 3 to 6 over pure Pt.

Elastic Strain Engineering

High-pressure physics has demonstrated how elastic deformations significantly impact material properties. For instance, Na in its solid state transforms into an electrical insulator and becomes transparent to visible light under hydrostatic compressive stresses of 200 GPa [173]. The impact of elastic deformations on the physical and chemical properties of the catalyst becomes significant when elastic strains reach or exceed 1-2% [152]. Such levels of elastic deformation are typically attained only under hydrostatic pressure conditions in bulk materials because tensile or shear elastic deformations are relieved for values less than 1% due to defect nucleation (such as dislocations or fractures). Nevertheless, significant elastic deformations in tension or shear (which can approach the theoretical limit of 10%) can be attained in various types of nanomaterials (such as nanowires and two-dimensional materials), thin sheets, or bulk materials with a nanostructured microstructure [168, 362]. These deformations may arise from the inherent structure of the material (such as epitaxial deformations in a thin sheet) or the application of external loads. This approach offers a novel avenue for altering the catalyst properties (electronic, optical, magnetic, catalytic, etc.) by methodically adjusting the six components of the elastic strain tensor. It opens up a vast realm for the development of new functional catalysts with tailored properties for specific applications through the utilization of elastic deformations. Different instances illustrating the impact of elastic deformations on the reactivity of metal surfaces and oxides, ionic conductivity, electrocatalysis, and chemical reactivity are documented in [153]. Additionally, [18] provides a comprehensive account of the utilization of elastic deformations to enhance the mobility of electrons and holes in semiconductors, a classic example within this domain.

As mentioned before, alloying can lead to the development of strains on the surface of the catalyst due to the mismatch in the lattice parameters of the different alloying elements. However, the direct application of strain to pure elements and alloys has not yet been fully explored. Regarding catalysis, Xia [324] explained how strain engineering can improve the catalytic performance of Cu-Ag bimetallic electrodes in CO_2 electroreduction. Gao et al. [69] activated the catalytic activity in-plane of MoS_2 through the combination of metal heteroatom doping and a small compressive strain. Zhao et al. [356] analyzed the synergy between defect and elastic strain engineering in Pd and Au for CO oxidation. Wang [309] proved the effects of in-plane uniaxial and biaxial strains on the electronic and photocatalytic activity of WS_2 /BlueP which affect the band gap, band edge arrangement, band type, and the electron transition type. All the authors mentioned above agree that Elastic Strain Engineering (ESE) is a very efficient methodology for tuning the catalytic activity of metals and intermetallic compounds.

Accounting for the application of ESE in the field of Hydrogen Economy, Shuttleworth [258–261] analyzed the adsorption of H, O, and OH in different transition metals and Pt-

Ni alloys. In particular, his work was focused on the changes in the preferred adsorption site with the application of strains. Although many researchers have worked on the variations of the adsorption energies of H, O, and OH with strains [190, 209, 227, 251, 298], the application of the observed trends in the actual catalysis of the HER and the ORR is still slightly explored. Some authors have measured experimentally the variations of the catalytic activity with strain, but the number of metals that can be tested is limited due to the lack of time and resources. As an example, Yan et al. [333] experimentally evaluated the variation of the catalytic activity of strained Ni, Cu, and Pt for the HER. Compressive strains led to an increase of the catalytic activity of the metals and tensile strain had the opposite effect. In addition, Escudero-Escribano et al. have recently shown that the activity of Pt catalysts can be increased by a factor of between 3 and 6 (concerning pure Pt) by alloying them with lanthanides. The ORR activity in these alloys is related to the lattice parameter of the crystal structure and the maximum values are reached when the lattice parameter is reduced by 3%, from 0.55 nm for Pt to 0.525-0.530 nm for Pt₅Tb, Pt₅Gd or Pt₅Sm [52].

Despite being a demonstrated powerful technique to enhance the catalytic activity of these processes, ESE has been scarcely applied in the Hydrogen Economy. Miaou et al. [188] explain that the constraints on the advancement of strain engineering in catalysis could stem from: i) limitations in the methodologies for implementing strain engineering in catalysts; ii) constraints in characterization techniques; and iii) gaps in theoretical frameworks. In this last regard, one can see numerous advances in the last years based on the postulated *d*-band model.

d-band model

B. Hammer and J. K. Nørskov postulated the *d*-band center model to explain how the application of strains could affect the catalytic activity of different transition metals [92, 94, 182]. The basis of the model is that the adsorption energy of an adsorbate to a transition metal surface depends to a large extent on the electronic structure of the surface itself [234]. For instance, in the adsorption of a hydrogen molecule in the gaseous state to a platinum slab, the σ orbital of the adsorbate hybridizes with the *d*-band of the metal forming two states: bonding ($d - \sigma$) and antibonding ($d - \sigma$)* states. Whilst the bonding state is full, the filling of the antibonding state depends on the electronic structure of the metal, reflected on the surface projected density of states, PDOS. In other words, the larger the filling of the ($d - \sigma$)* state, the weaker the binding adsorbate-metal due to the electronic destabilization. They discovered a parameter -experimentally and theoretically determinable- to correlate the filling of the ($d - \sigma$)* state with the adsorption process: the *d*-band center, ϵ_d [92]. Metals with a higher ϵ_d with respect to the Fermi energy correspond with less filled ($d - \sigma$)* states and less destabilized systems, which translate into stronger adsorbate-metal adsorptions. They observed that the overlap of the *d*-states of the surface at neighboring sites will either decrease or increase when a surface is subjected to tensile or compressive strains, respectively, and so will the *d*-bandwidths [94]. The *d*-band center shifts up or down when applying tensile or compressive strains, respectively, in order to maintain a constant filling. This tendency is shown in Figure 1.8. As a general rule, the applica-

tion of tensile strains in metals with more than half-filled d -bands reduced the d -orbital overlap due to a sharpening of the d -band and moved ϵ_d towards higher energies. This produced a strengthening of the adsorption process (more negative adsorption energies). The opposite phenomenon would occur for metals with less than half-filled d -bands [182]. Although ϵ_d can be used to rationalize the catalytic reactions, there is no model to directly predict the adsorption energies as a function of the applied strain using the d -band center.

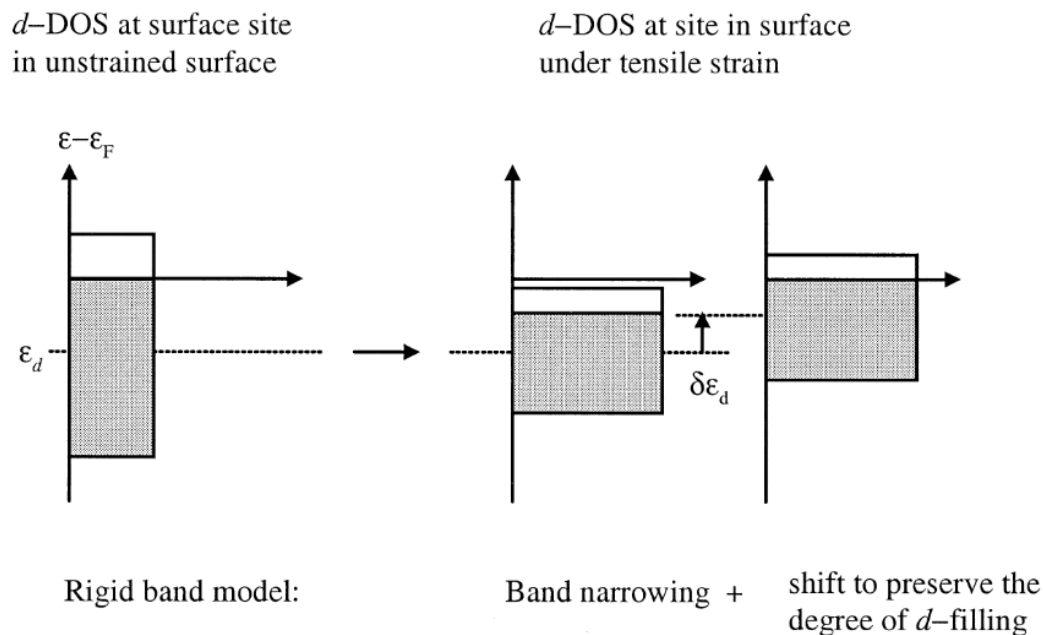


Figure 1.8: Illustration of the effect of strains on the d -band center and the binding energy according to the d -band model. From [94, 130].

It should be noted that the exploration of the different strategies indicated above to design and discover new catalysts is limited by the experimental cost associated with the synthesis, characterization, and determination of the catalytic activity of each compound. Moreover, the combination of all these variables gives rise to endless possibilities that cannot be explored experimentally without high-performance tools to guide research towards more promising materials and structures in the catalysis of the OER/HER and the HOR/ORR processes.

1.3 Catalysts for the Hydrogen Economy

Nowadays, Pt stands as the best catalyst for the Hydrogen Economy, as it is the most efficient and stable option for the rate-limiting reactions in the production of hydrogen and the generation of clean energy: the Hydrogen Evolution Reaction (HER) and the Oxygen Reduction Reaction (ORR) [250, 300]. Nonetheless, its high cost and limited availability hinder the industrial application of this technology, leading to a search for cheaper and more widely available metallic catalysts [100]. As explained in the previous sections,

there are many different approaches in the design of new catalysts, however, efficient candidates to replace this noble metal are still missing.

1.3.1 Catalysts for the HER/HOR

Pt is by far the best-known catalyst for HER/HOR and requires very small overpotentials even at high reaction rates in acidic and alkaline solutions [246]. Two main lines of research have been created to find new catalysts that can replace Pt: HER/HOR electrocatalysts based on noble metals and those based on non-noble metals. Within the realm of noble-metal-based electrocatalysts, with a focus on Pt-based catalysts, ongoing efforts aim to enhance HER/HOR performance while simultaneously reducing the cost of electrocatalysts. Strategies include alloying Pt with economically viable transition metals to optimize Pt utilization [112, 217, 323] and leveraging the synergistic effects of alloys to modify electronic environments and improve activity [225, 332]. Another approach involves coupling Pt with water dissociation promoters, a crucial strategy for enhancing alkaline HER/HOR activities with practical implications for industrial applications [9, 282]. On the non-noble metal front, significant attention is directed towards developing HER/HOR electrocatalysts including transition metal carbides [114, 280, 284], transition metal phosphides [220, 308, 354, 359], and transition metal chalcogenides [165], that have undergone significant progress in the last years.

Acidic media

Catalyst	Tafel Slope (mVdec ⁻¹)	Stability	Ref.
AuMoS ₂	69	-	[311]
Mo ₂ C-R	58	2000 cycle	[326]
Mo ₂ C-GNR	63	3000 cycles	[163]
N/P graphene	91	-	[359]
Ni ₂ P/Ti	46	500 cycles	[220]
NiCo ₂ P _x	59.6	5000 cycles	[354]
Defect rich MoS ₂	50	10000 s	[329]
Cu ₃ P@NPPC-650	76	-	[308]
CoS ₂ NW	51.6	3 h	[57]
CoS ₂ MW	58	41 h	[57]
Oxygenated MoS ₂	55	3000 cycles	[329]
PtMoS ₂	52	-	[231]
PtSnS ₂	69	-	[165]
RuC ₃ N ₄	57	-	[212]
WS ₂ nanosheets	60	-	[302]

Table 1.5: Summary of the HER/HOR performance for electrocatalysts in acidic electrolytes (H₂SO₄ 0.5M). From [309].

Among the most common catalysts for the HER and the HOR in acidic media, transition

metal carbides have taken considerable attention as non-noble metal-based electrocatalysts. Beyond their robust electrical conductivity, these materials possess favorable hydrogen adsorption properties and a d -band electronic density state close to that of Pt. As an example, Hu et al. [303] confirmed that commercial Mo_2C showed good HER/HOR catalytic activity in acidic media. Transition metal phosphides also represent one of the developing electrocatalysts with high catalytic activity and stability in acid HER/HOR. Zhang et al. [354] developed bimetallic NiCo_2P_x , which showed excellent durability and long-term stability both in acidic and alkaline media. Similarly, transition metal chalcogenides (sulfides and selenides) are also among the favorite candidates to replace Pt. Chorkendorff et al. [119] identified MoS_2 as a promising electrocatalyst due to the free energy of atomic hydrogen bonding, which was very close to that of Pt. They found that the presence of edge sites at the surface (most active sites) was linearly dependent on the HER/HOR activity. A summary of some of the most common electrocatalysts used in acidic HER and HOR is shown in Table 1.5.

Alkaline media

Catalyst	Tafel Slope (mVdec^{-1})	Stability	Ref.
C_3N_4	120	-	[121]
CoP@BCN	52	-	[252]
$\text{Co}_9\text{S}_8\text{@NOSC}$	105	-	[113]
FeCoP/Ti	75	-	[281]
PtNiNi NA/CC	42	90 h	[330]
PtNiO/C	78.8	10 h	[358]
PtNi(N) NW	29	10 h	[331]
PtSm	169	-	[239]
PtCe	114	-	[239]
$\text{Mo}_2\text{C-R}$	45	2000 cycle	[326]
$\text{Mo}_2\text{C-GNR}$	64	3000 cycles	[163]
MoP	48	-	[326]
Ni nanoparticles	111	-	[1]
NiCo_2P_x	34.3	5000 cycles	[354]
$\text{Ru@C}_2\text{N}$	38	-	[242]
$\text{RuO}_2/\text{Co}_3\text{O}_4$	91	-	[165]

Table 1.6: Summary of the HER/HOR performance for electrocatalysts in alkaline electrolytes (KOH and NaOH, 0.1M and 1M). From [309].

As a reference point for Pt electrocatalysts, the HER/HOR activity in alkaline media typically lags behind that in acidic media [361]. This discrepancy arises from the inefficiency of water dissociation on the Pt surface, leading to reduced activity. Consequently, a widely employed strategy to enhance alkaline HER/HOR activities involves pairing Pt with water dissociation promoters [331]. Markovic et al. [273] deposited onto de Pt electrode nanometer Ni(OH)_2 clusters and observed a factor of 8 in the enhancement of HER/HOR

activity vs. the state-of-the-art Pt. Huang et al. [358] tested PtNiO nanoparticles which in alkaline media transformed to $\text{Ni(OH)}_2/\text{Pt(111)}$ interfaces giving catalytic activities close to pure Pt. Sun et al. [330] produced ultrafine PtNi nanoparticles on carbon cloth with very low contents of Pt (below 8%) with better activities than Pt/C (20%) and long-term durability. All in all, Durovic et al. [50] concluded that the state-of-the-art design in new catalysts for the HER/HOR in alkaline media was focused on pure precious metals, precious metal alloys, and metal sulfides, selenides, nitrides, carbides, and phosphides. Some of the best candidates found in the current literature are shown in Table 1.6.

1.3.2 Catalysts for the OER/ORR

Over the past few decades, significant attention has been dedicated to the electrocatalytic OER/ORR, with numerous catalyst designs aimed at enhancing electrode kinetics and stability across diverse electrolytic conditions. For instance, rutile-type RuO_2 has demonstrated remarkable catalytic activity in both acidic and alkaline electrolytes [64, 149]. However, RuO_2 exhibits high instability in such electrolytes under elevated anodic potentials, leading to oxidation and dissolution into RuO_4 [141]. Another commonly employed OER/ORR catalyst, IrO_2 , also exhibits promising performance. Nonetheless, it faces a similar challenge, as it is prone to oxidation and dissolution, forming IrO_3 [11].

Acidic media

A diverse range of nanostructures utilizing Pt, Ir, and Ru have been created to enhance oxygen evolution and reduction reactions efficiency under acidic conditions. In addition to the valuable Pt, Ir, and Ru nanostructures, alternative catalysts based on non-precious metals and carbon-doped with heteroatoms have also been documented. In Table 1.7, a summary of the OER/ORR electrocatalysts in acidic electrolytes is shown. As observed, the design of new catalysts for these reactions in acidic media is focused on nanostructures and materials doped with carbon, in order to increase the active surfaces. But as of now, IrO_2 and RuO_2 stand as the leading electrocatalysts for acidic OER/ORR, consequently undergoing thorough investigation over the past few decades.

Alkaline media

Despite the favorable kinetics and the availability of a wide range of catalysts for alkaline OER and ORR, acidic OER/ORR are preferred over alkaline OER/ORR due to the diverse advantages offered by proton exchange membrane water electrolyzers compared to alkaline water electrolyzers [230, 253]. Among the best catalysts for the OER and the ORR in alkaline media, the precious metals Pt, Au, Ag, and Pd are still at the top due to their stability and outstanding efficiency [102, 314]. Au (100) and Ag (110) are extremely active for the OER and the ORR in alkaline media, albeit being poor catalysts in acidic media [89, 193]. Non-metal doped carbon and carbon transition metal hybrids are also good catalysts for these reactions in basic media because of their high electronic conductivity and large surface area [342, 357]. Complementary, transition metals oxides such as spinel structures (AB_2O_4), perovskites (ABO_3), and other oxides like CoO_x and MnO_x present

Catalyst	Tafel Slope (mVdec ⁻¹)	Stability	Ref.
3D Ir superstructure	40.8	8 h at 10 mA cm ⁻²	[219]
Ir wavy nanowires	30.1	25 000 s at 10 mA cm ⁻²	[66]
Ir ₆ Ag ₉ nanotubes	61.1	6 h at 5 mA cm ⁻²	[361]
IrCoNi PHNCs	53.8	–	[61]
IrNi nanoflowers	47.3	4 h at 20 mA cm ⁻²	[171]
P-IrCu _{1.4}	53.9	10 h at 10 mA cm ⁻²	[218]
Ir ₄₄ Pd ₁₀ nanocages	53.9	15 h at 10 mA cm ⁻²	[361]
IrNiCu DNF	–	2500 cycles	[207]
Amorphous IrO _x	34	24 h at 1 mA cm ⁻²	[264]
Mesoporous Ir nanosheets	49	8 h at 10 mA cm ⁻²	[122]
Amorphous Ir nanosheets	40	8 h at 255 mV	[321]
Ru nanosheets	54	2 h at 10 mA cm ⁻²	[139]
a-RuTe ₂ PNRs	47	24 h at ≈7 mA cm ⁻²	[308]
RuCu nanosheets	40.4	12 h at 10 mA cm ⁻²	[340]
CoRuIr nanocrystals	66.9	25 h at 10 mA cm ⁻²	[248]
RuIr nanocrystals	111.5	Decay continuously	[248]
RuIrO _x nano-netcages	42	3000 cycles	[364]
Cu-doped RuO ₂	43.96	8 h at 10 mA cm ⁻²	[272]
P-PNRO/C	52	2000 cycles	[200]
Ru@IrO _x core/shell	69.1	24 h at 1.55 V vs RHE	[248]
Ultrafine defective RuO ₂	36.9	20 h at 10 mA cm ⁻²	[74]
Branched PdRu	61	≈ 2 h at 250 mV	[82]
Cr _{0.6} Ru _{0.4} O ₂ solid solution	58	10 h at 10 mA cm ⁻²	[161]
MnRuO ₂	42.94	5000 cycles	[43]
NaRuO ₂ nanosheets	38	6 h at 1 mA cm ⁻²	[143]
CaCu ₃ Ru ₄ O ₁₂	40	24 h at 10 mA cm ⁻²	[187]
Ir _{0.6} Cr _{0.4} O _x nanowires	69	25 h at 10 mA cm ⁻²	[85]
single-layer IrOOH nanosheets	58	14 h at 10 mA cm ⁻²	[318]
IrO _x /SrIrO ₃	–	30 h at 10 mA cm ⁻²	[247]
Co-doped 6HSrIrO ₃	51.8	20 h at 10 mA cm ⁻²	[335]
IrSTO	–	20 h at 10 mA cm ⁻²	[158]
IrSA@Fe@NCNT	58.2	11.5 h at 10 mA cm ⁻²	[170]
Y ₂ Ir ₂ O ₇	51.8	24 h at 10 mA cm ⁻²	[256]
Pr ₂ Ir ₂ O ₇	–	10 000 s at 10 mA cm ⁻²	[249]
Co ₃ O ₄ @C	82	86.8 h at 100 mA cm ⁻²	[338]
Co ₂ TiO ₄	320	–	[8]
amino-HNC	96	100 h at 1.5 V vs RHE	[356]
N-doped graphite/carbon black	226	–	[363]
C ₆₀ SWCNTs	46.7	5 h at 1.7 V vs RHE	[70]

Table 1.7: Summary of the OER/ORR performance for electrocatalysts in acidic electrolytes (HClO₄, H₂SO₄, and H₂SO₄, 0.1M and 0.5M). From [155].

high turnover frequencies because of their unique structures [42, 132, 150, 292]. In Table 1.8, a summary of the most commonly used catalyst for the ORR and the OER in alkaline media is shown.

Catalyst	Tafel Slope (mVdec ⁻¹)	Stability	Ref.
Pt/CaMnO ₃	65	95% at 0.8V for 27.8 h	[98]
Au (1.8 nm)/rGO	-	84% at 0.78V for 11.1 h	[344]
PdP	-	58% at 0.8V for 8.3 h	[44]
Ag@Pd/MWCNTs	-	50% at 0.82V for 0.5 h	[277]
N-doped porous carbon	-	75% at 0.60V for 7 h	[353]
N-doped graphene	-	72% at 0.61V for 5.6h	[204]
N/B-doped nanodiamond	-	95% at 0.81V for 13.9 h	[266]
P/N-doped biocarbon	-	95% at 0.71V for 10 h	[336]
Fe/Fe ₃ C/N/C	-	62% at 0.81V for 5.6 h	[149]
Pt (20 wt.%)/C	57	-	[215]
Au(36 at.%)/Ag	67	-	[111]
Co ₃ O ₄ /N-rmGO	42	-	[159]
Co ₃ O ₄ /rGO	101	96% at 0.41V for 1.7h	[350]
Co@Co ₃ O ₄ /NCNT	83	78% at 0.47V for 5.6 h	[325]
FeS/Fe ₃ C/Fe ₂ C/N/C	-	97% at 0.57V for 5 h	[334]
Co/N/rGO	-	80% at 0.66V for 6 h	[359]
Mn ₃ O ₄ /N/C	-	94% at 0.57V for 4.2 h	[72]
Fe ₃ O ₄ /Co ₃ O ₄	-	44% at 0.76V for 1 h	[341]
NiCo ₂ O ₄	-	70% at 0.67V for 100 h	[327]
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	64	-	[56]
NiCo ₂ O ₄ /NrGO	-	87% at 0.71V for 2 h	[116]
Mn _{0.4} Co _{2.6} O ₄ /C	-	86% at 0.47V for 2.8 h	[148]
FeN/Fe ₂ N/NGR	-	91% at 0.71V for 5.6 h	[343]
B- and N-doped CNT	-	90% at 0.71V for 13.9 h	[310]
N-rich porous carbon	-	99% at 0.71V for 1.1 h	[346]
Ag(110)	80	-	[22]
Pd	65	-	[268]
Pt@Pd	-	80% at 0.13V for 1000 cycles	[98]
Ag@Pd/MWCNTs	-	50% at 0.82V for 0.5 h	[277]
F-doped carbon	-	99% at 1.31V for 1200 cycles	[351]

Table 1.8: Summary of the OER/ORR performance electrocatalysts in alkaline electrolytes. From [75].

All things considered, despite the diverse possibilities that have been studied to replace platinum catalysts for Hydrogen Economy reactions, the effect of the application of external elastic deformations (Elastic Strain Engineering) in these catalytic processes has not been explored either computationally or experimentally.

1.4 Computational design of catalysts

The extraordinary progress of *ab initio* calculation methods based on Density Functional Theory (DFT) to calculate the electronic structure has opened the door for the virtual design of catalysts from computer simulations [196]. In particular, calculation codes and the speed of computers allow today to simulate large enough systems and calculate the interaction energies of atoms or molecules with surfaces with sufficient precision to discover trends in adsorption or recombination processes.

There are examples in the scientific literature in which the entire kinetics of a catalytic reaction (including the determination of the activation states as well as the activation and reaction energies and the corresponding entropic contributions) have been determined from DFT calculations and Monte Carlo simulations [108, 126, 232], but it is necessary to recognize that the evaluation by first principles of the kinetics of all the reactions in a catalytic process is - in most cases - an impossible task. Therefore, the discovery of new catalysts through simulations is usually carried out based on the rational definition of different descriptors related to various stages of the catalytic process that allow determining the stages that control the kinetics of said reaction. The identification of these descriptors can be simplified because the activation energies of the elemental reactions on the catalyst surface are proportional to the adsorption energies according to the Bell-Evans-Polanyi principle [53], explained in section 1.4.1.

1.4.1 Density Functional Theory

Norskov et al. were among the first to use Density Functional Theory calculations to predict the catalytic properties of different transition metals for the HER and the ORR [195, 198]. They developed a model to relate the adsorption energy of all the intermediates of the reactions (calculated by DFT) with the catalytic activity of any transition metal. These results are shown in Figure 1.9, which depicts the experimental (Top) and the DFT calculated (Bottom) values of the catalytic activity (as given by the exchange current density) for the HER as a function of the free energy of hydrogen adsorption, with considerable good agreement for most of the transition metals. DFT was proven not only to give accurate predictions of the catalytic activity of metals but also good estimations of the effect of ESE on the catalyst surface. The accuracy associated with DFT in the calculation of adsorption energies is in the range of 0.1 eV [26] and this strategy has been used in the OER/HER and the HOR/ORR reactions with good agreement between theoretical and experimental results [94, 196].

Bell-Evans-Polanyi principle

The Bell-Evans-Polanyi principle [53] states that the adsorption enthalpy energy can be directly related to the activation energy of the reactions as shown in Figure 1.10. Therefore, this principle can be used to establish a linear relationship between the activation energy of the reaction and the adsorption energy following the expression

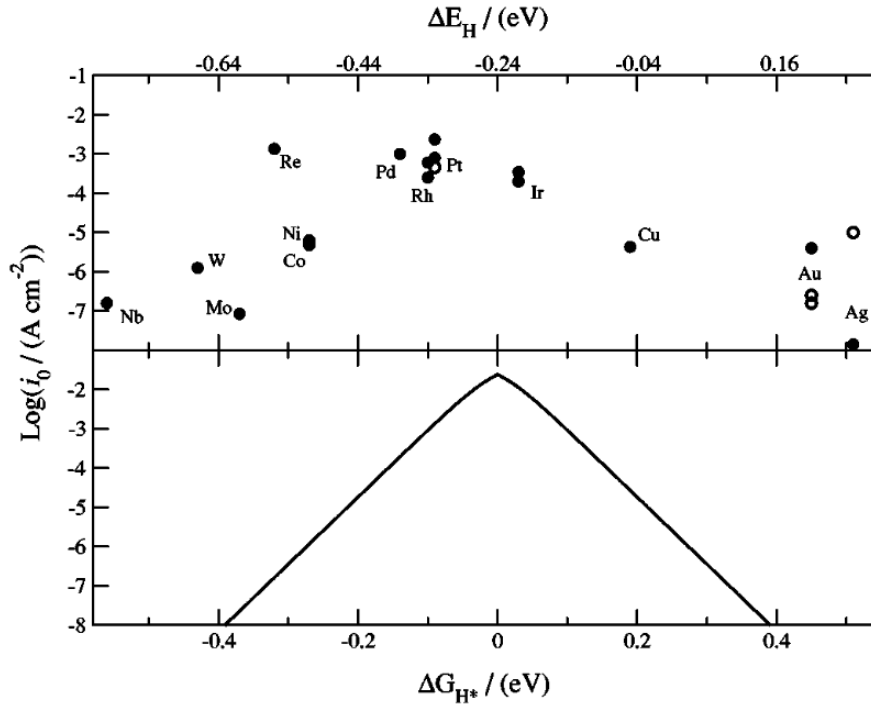


Figure 1.9: (Top) Experimentally measured exchange current density ($\log i_0$) for the hydrogen evolution reaction over different metal surfaces as a function of the calculated hydrogen chemisorption energy per atom. (Bottom) The results of the kinetic model as a function of the free energy for hydrogen adsorption. From [195].

$$E_a = E_a^0 + \alpha \Delta H \quad (1.1)$$

where E_a represents the energy of activation, E_a^0 is a constant, α is a measure of how far a reaction has proceeded along the reaction coordinate when the transition state is reached, and ΔH is the enthalpy of reaction.

This well-known principle has been proved computationally [184, 235] and validated experimentally [144, 175], and consequently used in many catalytic studies. As an example, Quinghui [184] based his study on this principle, successfully determining the kinetic parameters of catalytic reactions in biodiesel combustion. Abdulsattar et al. [2] applied it in the catalysis of acetone by Rh-doped SnO_2 clusters, and Jo [124] justify his study of CO adsorption on bimetallic Cu/M with it.

Transferring this principle to the specific field of study of this work, the adsorption energy of the intermediates present in Hydrogen Economy (H, O, OH, and OOH), calculated by means of Density Functional Theory, can be used as a direct predictor of the catalytic activity for the different surfaces in the OER/HER and the HOR/ORR.

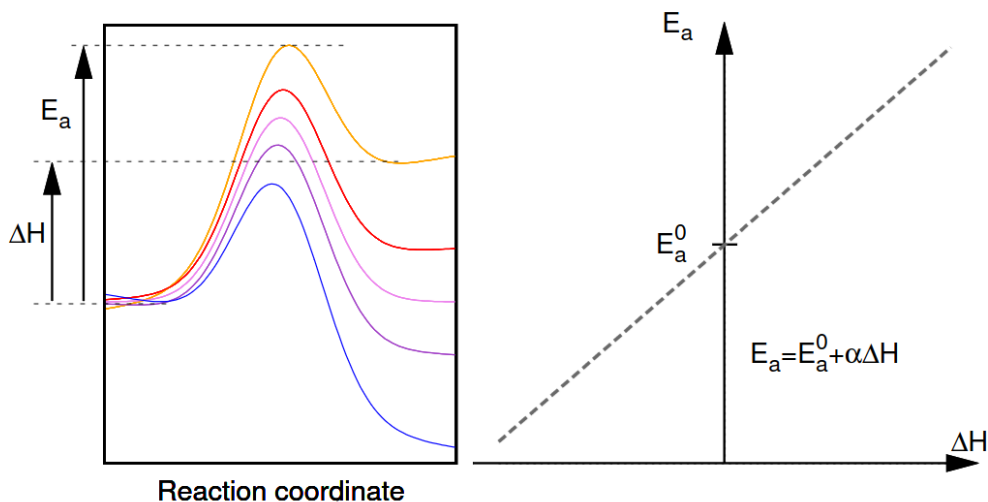


Figure 1.10: Illustration of the Bell-Evans-Polanyi principle: enthalpy profile along a reaction coordinate for similar processes (left), evolution of the activation energy (or barrier height) as a function of the reaction enthalpy (right) [106].

1.4.2 Machine Learning

However, the computational cost of DFT -scales as $O(n^3)$, with n being the number of electrons in the system [245]- prevents a detailed exploration of the chemical compound space spanned by all possible pure metals and intermetallic materials [237]. This limitation has encouraged the use of strategies based on artificial intelligence, namely Machine Learning (ML), in the prediction of new materials in different fields, including catalysis [31, 96, 192, 304, 319]. Three main ingredients are needed to build an ML model able to predict the catalytic activity of different materials: a large enough database, a proper set of features/descriptors, and a mathematical algorithm able to describe the phenomena. The database must be as large and diverse as possible and has to contain enough information to expand the predictions to different catalyst surfaces and reactions. There are two common ways of constructing a database: with experimental and computational data. As an example, Catalysis-Hub.org [320] is a repository of computational DFT adsorption energies of many intermediates for different surfaces. The set of descriptors refers to the different variables that the model must take into account when predicting new cases. When applying ML to a catalysis problem, the features must describe all the factors that are relevant for the reaction, such as the electronegativity, the d -electrons, the size of the unit cell... Finally, the algorithm is the most obvious part. Usually, different mathematical methods can give solutions to the same problem, so the discrimination between one algorithm and another, will be based in terms of accuracy, yield, efficiency, and size of the database.

The application of ML in the field of catalysis is still limited but there are a few studies where it is employed to predict the adsorption energy of different reaction intermediates. For instance, Wang et al. [313] used k-nearest neighbors in Mg binary alloys to investigate the corrosion properties of binary Mg alloys, using as descriptors the band gap, the formation enthalpy, the Miller indices, the energy above hull, the atomic radius, or the

electronegativity. Hansen, Lamoreux, and Fung [68, 101, 243] reported various strategies to predict adsorption energies in different catalytic processes. They used neural networks, Gaussian processes, and extra tree regression algorithms, and features such as: the surface atoms' positions, the neighboring atoms, the coordination numbers, the *d*-band center, the bulk formation energies, etc. Toyao et al. [290] discovered that by utilizing twelve readily available descriptors coupled with extra tree regression, they could effectively forecast adsorption energies of methane-related intermediates on Cu-based alloys, achieving a mean RMSE of 0.26 eV. They utilized their discoveries to pinpoint dopants that enhance the stability of CH₃ over CH₂, aiming to enhance the efficiency of methane utilization for both methanol synthesis and oxidative coupling of methane. Noh et al. [194] integrated kernel ridge regression with an active learning approach. They selected *d*-band width and the geometric mean of electronegativity as descriptors, representing non-first-principle input features. This methodology enabled them to predict CO* adsorption energies with a root mean square error of 0.05 eV and pinpoint Cu₃YCu as a potent electrochemical catalyst for CO₂ to CO reduction, exhibiting low overpotential. Ma et al. [172] and Li et al. [157] employed artificial neural networks trained on DFT-calculated adsorption energies and electronic structure fingerprints. Utilizing these neural networks, they successfully forecasted adsorption energies of catalytic intermediates on multimetallic surfaces, achieving RMSEs ranging from 0.1 eV to 0.2 eV.

However, the application of ML tools to assess catalytic processes involving hydrogen is scarcely explored [133, 205] due to three main limitations: the first one is the lack of large and robust databases that can be used to train ML algorithms that can deal with different geometries, stoichiometries, and surfaces [37, 320]. Winther et al. [320] elaborated an open repository for chemical reactions on catalytic surfaces called Catalysis-hub.org. This database contains more than 100,000 chemisorption and reaction energies obtained from DFT calculations. However, it contains neither data with the application of elastic strains nor intermetallic compounds with rare earths on their structure. Similarly, Chanussot et al. [37] developed the Open Catalyst dataset, consisting of 1,281,040 DFT relaxations across different materials, surfaces, and adsorbates but it only considers nitrogen, carbon, and oxygen as adsorbates. Moreover, the analysis of different types of strains, namely uniaxial, biaxial, or shear, is not included in this database.

The second limitation is the lack of accuracy of the ML model predictions, which provide mean absolute errors (MAEs) equal to or higher than 0.16 eV for H [291], and 0.23 eV for O and OH adsorption energies [174], too large to predict the catalytic activity. Tran et al. [291] performed a screening of alloys of 32 different elements. In their study, they encompassed 50% of the *d*-block elements to identify 258 surfaces across 102 alloys for HER, nevertheless, the errors of the Gaussian Process Regressor were not small enough (Mean Absolute Error: > 0.25 eV and Root Mean Square Error: > 0.35 eV). Mamun et al. [174] based their screening on scaling relations for hydrogenated species. They extended the single-descriptor linear scaling relation to a multi-descriptor linear regression model and used Bayesian Information Criteria to select the best model. Nevertheless, predictions based solely on a singular descriptor disregard model uncertainty, resulting in less-than-optimal forecasts of chemisorption energy.

Finally, information about the influence of elastic strains on the catalytic activity of ML models to predict adsorption energies is missing.

1.5 Objectives

The main limitations that hinder the development of sustainable development based on the Hydrogen Economy are the low efficiency of the processes for hydrogen generation by electrolysis and energy production from hydrogen in fuel cells and the cost of the Pt (or other Pt-group metals) that are used as catalysts. In fact, approximately 40% of the cost of a hydrogen fuel cell is represented by the catalyst [183] because Pt is among the 10 most expensive materials in the world [267].

Thus, there is a huge driving force to find new catalysts as efficient as Pt but cheaper and more abundant. Particularly, they should reduce the working temperatures and allow high current/power densities in the case of PEMEC and PEMFC [36, 95]. In these devices, the catalytic activity of Pt decreases with increasing pH, which makes the acidic conditions very favorable [164]. Out of the four reactions, the cathodic reactions in both electrolyzer and fuel cells in acidic media are: the Hydrogen Evolution Reaction and the Oxygen Reduction Reaction. In these rate-limiting reactions, the presence of Pt is essential to make the whole process favorable both from the kinetic and thermodynamic viewpoints, which makes finding a substitute for Pt in the HER and the ORR the main focus of the Hydrogen Economy and of this thesis.

As indicated above, the experimental search for new catalysts - following the traditional trial-and-error approach - is a hopeless task unless it is guided by high-performance computational tools to focus the research toward the most promising materials. The main objective of this thesis is to provide an example of the application of high-throughput computational strategies to discover new intermetallic catalysts for the Hydrogen Economy, in particular for the HER and ORR. The high-throughput strategy will include the effects of alloying and elastic strain engineering.

The specific goals of this thesis are listed below:

1. The first objective of this thesis is to establish a computational framework based on DFT calculations and the Bell-Evans-Polanyi principle [53] to reasonably predict the catalytic activity of metals and intermetallic compounds. These predictions do not need to be extremely accurate but have to establish the catalytic behavior compared to Pt, which would be set as the reference. The methodology should be validated with experimental results and be useful to determine the catalytic activity of different materials both on a general scope and in the HER and the ORR.
2. The second objective is to evaluate the effect of the Elastic Strain Engineering tool to tune the catalytic activity of different metallic materials in the HER and the ORR. To this end, different types and levels of strain will be applied to the surfaces and the associated effect in the adsorption energy (and catalytic activity) will be analyzed. The information provided by these results will allow to determine the potential of ESE in the design of new metallic catalysts for the Hydrogen economy.

3. The last objective is to design a high-throughput methodology to screen a huge number of intermetallic compounds as potential catalysts for the HER and the ORR. With Machine Learning tools, the DFT calculations can be collected on a database big and varied enough, and used to train a model that predicts the catalytic activity of different materials. The idea is to build a model that is able to predict the effect of the strain applied on the catalyst surface as well.

The global objective of this thesis is to find a cheap and abundant Pt substitute as the catalyst for the HER and the ORR, lowering the cost of the Hydrogen Economy process and making a source of green energy affordable for everyone. A scheme of the main goals of this thesis is shown in Figure 1.11.

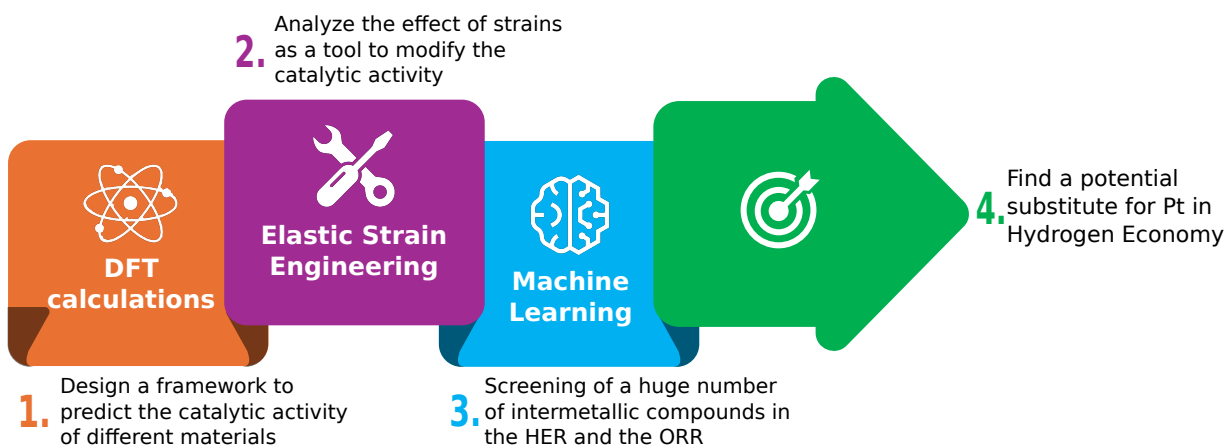


Figure 1.11: Scheme of the main goals of this thesis.

This thesis is structured as follows. After the Introduction and the Objectives in Chapter 1, all the computational methods utilized throughout the document are specified in Chapter 2. A DFT study of the H, O, and OH adsorption energies in pure metals is presented in Chapter 3, and their corresponding catalytic activity for the HER and the ORR with and without the application of strains is explained in Chapter 4. Chapter 5 is an in-depth study of the adsorption phenomena and the two main contributions (electronic and mechanical) that conform the process. All previous methodology is applied to binary intermetallic compounds in Chapter 6. In Chapter 7 the DFT calculated adsorption energies are utilized to train a Machine Learning model able to predict other binary surfaces. Finally, the main conclusions and the future work are summarized in Chapter 8. Appendices and Bibliography are displayed afterward.

2.1 Density Functional Theory Simulations

2.1.1 Quantum chemistry background

DFT simulations have dominated the panorama of computational solid-state physics and chemistry since the 1970s [26]. This method, rooted in quantum mechanics, enables the calculation of the electronic structure of solids, molecules, and atoms [17], yielding precise quantitative estimations of material properties.

In the domain of quantum mechanics, the state of a system is given by the Schrödinger equation [16]. Its nonrelativistic, time-independent form can be expressed as:

$$\hat{H}\Psi = E\Psi \quad (2.1)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ the wave function, and E the total energy [244].

The Hamiltonian $\hat{H}$ assembles every energy component within the system, including the kinetic energy of individual electrons and nuclei, as well as the potential energy. This potential energy can be categorized into electron-electron, nuclei-electron, and nuclei-nuclei interaction energies. Despite this, the positions of the nuclei are commonly assumed to be fixed. This assumption, referred to as the Born–Oppenheimer approximation [27], involves neglecting the motion of the nuclei and treating their spatial positions as constant. Consequently, the Hamiltonian of an N-electron system can be simplified as:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(\mathbf{r}_i) + \sum_{i=1}^N \sum_{j<i}^N U(\mathbf{r}_i, \mathbf{r}_j) \quad (2.2)$$

where the three different terms of the sum represent the kinetic energy of the electrons, the potential energy due to the interaction between each electron and the nuclei (V), and the electron-electron interaction energy (U), respectively. m , $\hbar$, ∇_i^2 , and $\mathbf{r}_i$ stand for the elec-

tron mass, the reduced Planck constant, the Laplacian operator, and the spatial positions of the i -th electron, respectively.

The quantum state of the system is represented by the electronic wave function Ψ , denoted as $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$, where $\mathbf{r}_i$ represents the electron coordinates (3N coordinates in total). This function is complex-valued and is not directly observable. Instead, it must be obtained through the solution of the Schrödinger equation. Additionally, Ψ serves as an eigenfunction, and its eigenvalues are encompassed in the final term, E , representing the energy of the system.

Hence, both the wave function, Ψ , and the system's energy, E , should be obtained through the solution of the Schrödinger equation to characterize the system under investigation. Despite simplifying assumptions – such as time independence, non-relativistic conditions, and the Born–Oppenheimer approximation – the challenge remains to find the 3N dimensional function. Consequently, numerous methods were devised in the twentieth century to streamline the resolution of this problem and the post-Hartree-Fock methods and Density Functional Theory (DFT) have emerged as the most common approaches.

The electron density

Density Functional Theory (DFT) employs the electron density, denoted as $n(\mathbf{r})$, as the key element for approximating the solution to the Schrödinger equation. Although the electron wave function Ψ is inherently a function of the coordinates of all electrons, it can be approximated by expressing it as the product of individual electron wave functions, $\Psi = \Psi_1(\mathbf{r}_1), \Psi_2(\mathbf{r}_2), \dots, \Psi_n(\mathbf{r}_n)$, commonly referred to as the Hartree product [257]. The electron density $n(\mathbf{r})$ can then be derived from these one-electron wave functions $\Psi_i(\mathbf{r})$:

$$n(\mathbf{r}) = \sum_i |\Psi_i(\mathbf{r})|^2 \quad (2.3)$$

where $|\Psi_i(\mathbf{r})|^2$ represents the probability of finding an individual electron wave function $\Psi_i(\mathbf{r})$ at an specific position, denoted as $\mathbf{r}$. This function is dependent on only three coordinates. Building upon this notion of electron density $n(\mathbf{r})$, Kohn and Hohenberg formulated two crucial mathematical theorems in the 1960s [107]. These theorems are the fundamental principles of DFT.

The first theorem asserts that the ground-state energy, as derived from Schrödinger's equation, is a distinctive functional of the electron density. This functional yields a singular energy value based on the electron density function $n(\mathbf{r})$, expressed as $E[n(\mathbf{r})]$. Additionally, a one-to-one correlation between the wave function Ψ and the electron density $n(\mathbf{r})$ exists at the ground state. Consequently, the electron density at the ground state uniquely determines all properties of the lowest energy configuration of the electrons, as described by the wave function Ψ . This simplifies the task of determining the ground-state energy to finding its electron density $n(\mathbf{r})$, which involves three spatial variables as opposed to the 3N variables in the wave function Ψ .

The second Hohenberg–Kohn theorem offers crucial insights into the functional described

in the first theorem. It asserts that the electron density minimizing the energy of the overall functional is the authentic electron density corresponding to the precise solution of the Schrödinger equation. However, the exact formulation of this comprehensive functional remains elusive. As a result, the energy function can be expressed as a combination of one known term and one unknown term

$$E[\Psi_i] = E_{known}[\Psi_i] + E_{XC}[\Psi_i] \quad (2.4)$$

where $E_{XC}[\Psi_i]$ is the exchange-correlation functional which includes all the quantum mechanical effects that cannot be analytically described. $E_{known}[\Psi_i]$ includes the electron kinetic energies, the Coulomb interactions involving electrons and nuclei, the interactions between pairs of electrons, and the interactions between pairs of nuclei. It can be expressed as

$$E_{known}[\Psi_i] = -\frac{\hbar^2}{m} \sum_i \int \Psi_i^* \nabla^2 \Psi_i d^3r + \frac{e^2}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{ion} \quad (2.5)$$

The Kohn-Sham equations

Following the outcomes of the two Hohenberg-Kohn theorems, Kohn and Sham formulated a set of equations for the single-electron wave functions $\Psi_i(\mathbf{r})$. These equations, referred to as the Kohn-Sham equations, rely solely on the three spatial variable functions and can be articulated as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}) \quad (2.6)$$

where ϵ_i represents the orbital energy, and V , V_H , and V_{XC} are three potentials [135]. V represents the potential energy arising from the interaction between each electron and the nuclei, as previously introduced in equation (2.2). V_H is the Hartree potential, responsible for capturing the Coulombic repulsive interaction among electrons, as outlined in the subsequent equation

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \quad (2.7)$$

Lastly, the contribution from the exchange-correlation potential V_{XC} encompasses the remaining interactions. It is characterized as the derivative of the exchange-correlation energy concerning the electron density $n(\mathbf{r})$

$$V_{XC}(\mathbf{r}) = \frac{\partial E_{XC}(\mathbf{r})}{\partial n(\mathbf{r})} \quad (2.8)$$

Hence, it is necessary to define the exchange-correlation energy functional, and various approximations can be employed for this purpose.

Exchange-correlation energy functionals

To address the solution of the Schrödinger equation, an approximation for the exchange-correlation functional is necessary. The fundamental methods are the local density approximation (LDA), which relies on the electron density $n(\mathbf{r})$ at individual points, and the exchange–correlation functional derived from the model of the homogeneous electron gas. Notably, this exchange-correlation functional is the only one that can be precisely derived [40].

A more complicated technique is the generalized gradient approximation (GGA) [136]. This method follows a similar approach to LDA but introduces the local gradient in the electron density. However, there are various approaches to incorporate the contributions of the local gradient, leading to diverse GGA exchange-correlation functionals. As a result, one can choose from different GGA exchange-correlation functionals. Among them, the most widely employed functionals are the Perdew–Burke–Ernzerhof functional (PBE) and the Perdew–Wang functional (PW91) [213, 214].

Apart from GGA approximations, more precise methods are available that approximate the exchange-correlation functional by incorporating additional physical insights. Meta-GGA functionals, for example, involve the local Laplacian in the electron density, while hyper-GGA functionals utilize contributions from the exact exchange energy [257].

Self-consistent field method

The exchange-correlation energy functional is employed to calculate the exchange-correlation potential. However, the electron density $n(\mathbf{r})$ is necessary to define this potential and the Hartree potential. This function can be derived from the single-electron wave functions $\Psi_i(\mathbf{r})$ using equation (2.3). Yet, the Kohn–Sham equations should be solved simultaneously to obtain these functions. This process involves computing the Hartree and exchange-correlation potential and, therefore, an iterative method becomes necessary to find the solution. The widely used approach for addressing this challenge is the self-consistent field method.

The self-consistent field method, outlined in Figure 2.1, is an iterative technique employed to determine the electron density $n(\mathbf{r})$ of a system. To compute the potential energy contributions, an initial estimate of the electron density is introduced. Various options are available for this initial guess, with the most prevalent ones being the extended Hückel method, the superposition of atomic densities (SAD), and the superposition of atomic potentials (SAP).

The Kohn–Sham equations from expression (2.6) are then solved to determine the single-electron wave functions $\Psi_i(\mathbf{r})$. Utilizing equation (2.3), a new electron density $n(\mathbf{r})$ is calculated and compared with the initial trial. This process is iteratively repeated until convergence is achieved, indicating that the difference between the previous and current electron density falls below a specified convergence limit. This iterative procedure yields an approximate value for the true electron density.

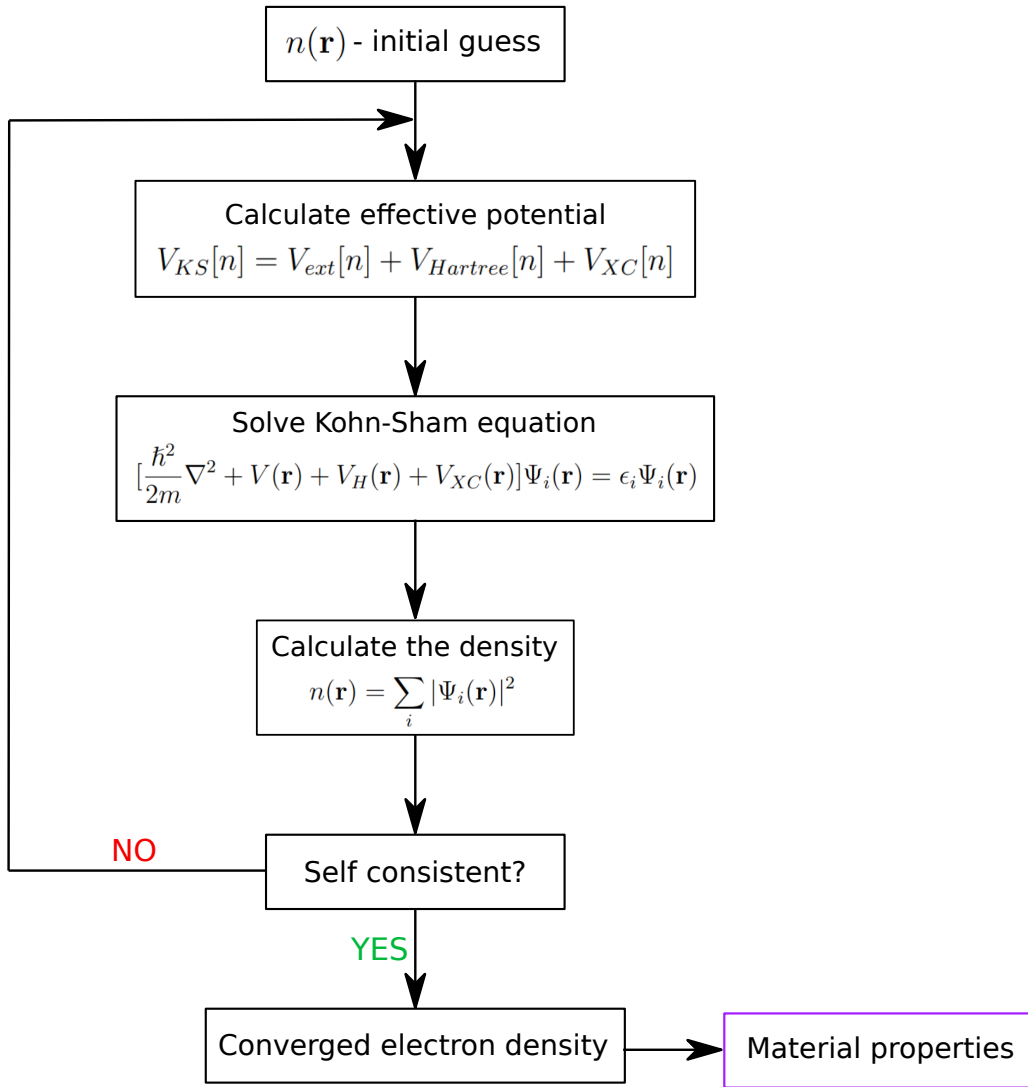


Figure 2.1: Flow chart of the self-consistent method for DFT calculations. Adapted from [257].

2.1.2 DFT simulations of crystalline solids: real and reciprocal spaces

Solids frequently show long-range ordering in their stable states. The characterization of these well-ordered materials, known as crystals, involves symmetric patterns that repeat along the principal directions of three-dimensional space [257]. This feature is employed to apply DFT methods for exploring the properties of crystalline solids.

The organized structure can be elucidated by the repetition of a set of atoms across space. The smallest assembly forming this recurring pattern in the crystal is called the unit cell. This unit cell faithfully mirrors the symmetry and configuration of the entire crystal, reproduced through its repetitive translation along the principal axes. The dimensions of the

unit cell axes and the angles between them are denoted as lattice constants, also known as cell parameters. The translation processes are defined by translation vectors, outlining points in three-dimensional space to create the Bravais lattices.

Many different unit cells exist for a given crystalline structure. The smallest possible are the primitive cells, which contain only one lattice point. When the lattice point resides at the center of the cell, it is termed a Wigner-Seitz cell [202]. This particular primitive cell is distinct for each crystal lattice. Additionally, the translation vector of a primitive cell $\mathbf{r}$ is expressed as a function of the primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ as:

$$\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad (2.9)$$

for any integers n_1 , n_2 , and n_3 . Additionally, the particular position of an atom j can be represented as a function of the primitive translation vectors $\mathbf{a}_i$ as

$$\mathbf{r}_j = \sum_{j=1}^3 f_{j,i} a_j \quad (2.10)$$

where f , j , and i are the fractional coordinates of an atom defined between [0,1]. For instance (1/2, 1/3, 2/3).

Additionally, within a crystal lattice, one can identify different atomic planes. These planes are usually denoted using the Miller index notation, represented by three values [189]. In this notation, a set of parallel planes is characterized as (h, k, l), where the indices h, k, and l indicate the reciprocal of the intersection points of the planes with the x, y, and z axes. Moreover, in certain crystal structure simulations, a repeated pattern involving a larger cluster of atoms, known as a supercell, might be necessary. While creating a supercell demands more computational time, it becomes essential for describing specific phenomena.

As indicated above, a crystalline solid can be characterized using a primitive cell that repeats regularly in space. Its properties can be ascertained by solving the Schrödinger equation following Bloch's theorem [23]. This theorem asserts that the solutions to the Schrödinger equation can be represented as a combination of functions called Bloch functions. These functions can be expressed in relation to the crystal translation vector $\mathbf{r}$ as:

$$\Phi_k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_k(\mathbf{r}) \quad (2.11)$$

The components in the $\exp(i\mathbf{k} \cdot \mathbf{r})$ equation are referred to as plane-waves, where $\mathbf{k}$ stand for the crystal momentum wave-vector, i the imaginary unit, and u_k functions with cell periodicity. Consequently, the Schrödinger equation can be solved with the vectors $\mathbf{k}$. To discover solutions in this vector space, calculations involving plane waves are carried out. It is noteworthy that while the vector space of $\mathbf{r}$ belongs to the real space, the vector space of $\mathbf{k}$ is defined in the reciprocal space.

The lattice formed in reciprocal space is termed the reciprocal lattice. It comes from the Fourier transform of the lattice in real space, also referred to as the direct or real lattice [257]. Similar to the real lattice, three reciprocal lattice vectors — $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ — can be established based on the primitive lattice vectors, according to:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}, \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} \quad (2.12)$$

The conversion of the real lattice into the reciprocal lattice is illustrated in Figure 2.2 for the face-centered cubic (fcc) structure. The lengths of the reciprocal lattice vectors, denoted as b_i , are inversely proportional to the lengths of the primitive translation vectors, represented as a_i .

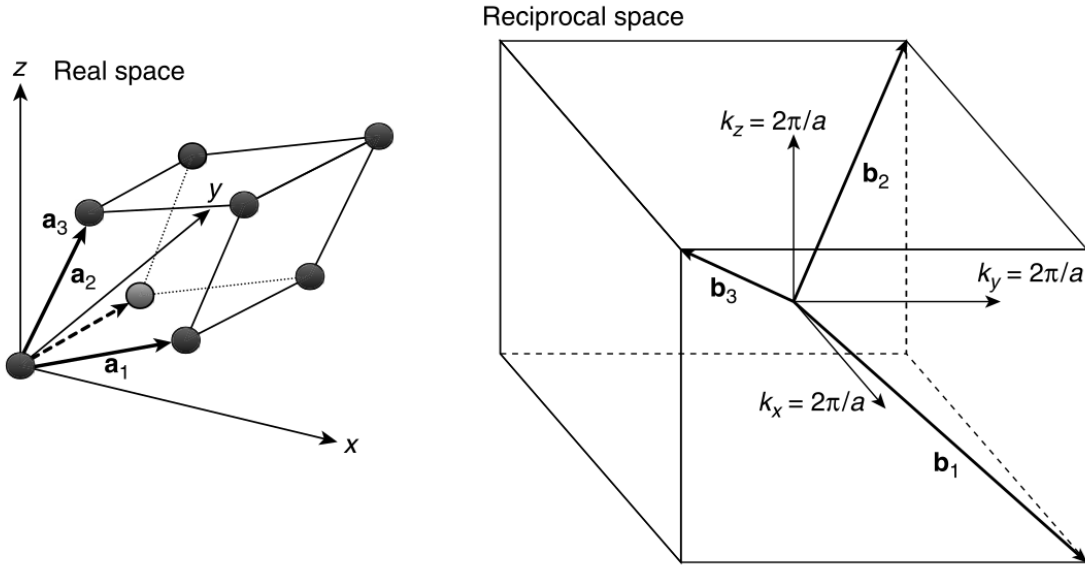


Figure 2.2: View of the real space and reciprocal space lattice vectors for the fcc primitive cell. Circles represent atoms in the real space representation. In the reciprocal space representation, the basis vectors are shown inside a cube with side length $4\pi/a$ centered at the origin. From [257].

Moreover, the Wigner–Seitz cell of the real lattice is represented by the Brillouin zone (BZ) within reciprocal space [29]. This zone is delineated by distinct points referred to as critical points. For example, the central point of the Brillouin zone, corresponding to $\mathbf{k}=0$, is identified as the Γ point.

k points

A considerable portion of the computational time needed for plane-wave calculations arises from assessing integrals across potential $\mathbf{k}$ values within the Brillouin zone (BZ), formulated as

$$g = \frac{V_{cell}}{(2\pi)^3} \int_{BZ} g(\mathbf{k}) d\mathbf{k} \quad (2.13)$$

The most common approach for computing these integrals was proposed by Monkhorst and Pack [191]. This method involves choosing a specific number of k points along the three reciprocal lattice vectors, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$. Typically denoted as $(N \times M \times O)$, where N , M , and O are integers determining the quantity of k points in each of the reciprocal directions.

Hence, preliminary calculations are essential to assess the convergence of the Density Functional Theory (DFT) method concerning the number of k points employed for the system. A greater number of k points generally enhances accuracy but increases the computational time. Therefore, a balance must be found between the quantity of k points and the computational effort. The required number of k points depends on the supercell volume and symmetry.

The symmetry of the supercell is critical to determining the appropriate number of k points because symmetries can effectively narrow down the region for evaluating integrals in reciprocal space. Consequently, computations can be confined to the irreducible Brillouin zone (IBZ) rather than the entire Brillouin zone (BZ) [257]. As a result, systems with higher symmetry demand less computational time to achieve convergence. Interestingly, the computational effort tends to be similar for consecutive odd and even values of k points (e.g., N and $N+1$, with N being an even number). This characteristic arises because the Monkhorst–Pack method incorporates k points on the boundaries of the IBZ for odd values, while even integers encompass points only within the IBZ. Therefore, even values of k points often lead to improved convergence in calculations.

Electron smearing

The solutions derived from solving the Schrödinger equation through plane-wave calculations need the determination of the number of k points within the system's Brillouin zone (BZ) in the reciprocal space. In the context of metals, the BZ can be partitioned into two regions: occupied and unoccupied by electrons. Consequently, the functions integrated into reciprocal space exhibit discontinuities, transitioning from zero to non-zero values [257]. Achieving convergence under these circumstances requires the use of a large number of k points, resulting in large computational costs. This gradual convergence can be addressed through various approaches, with the tetrahedron method and the smearing method being the most popular ones [166].

The first method involves interpolating the integrands by defining a set of tetrahedra in reciprocal space. The second approach focuses on mitigating the discontinuities of the integrands. Various methods can accomplish this, with commonly used ones including ordinary Gaussian spreading [125], the Fermi-Dirac function [117], the Methfessel-Paxton method [186], and the Marzari-Vanderbit-DeVita-Payne cold smearing [180]. In the first two methods, straightforward analytic functions are employed to approximate the discontinuities. The Methfessel-Paxton method introduces a fictitious electronic temperature,

thereby incorporating a fictitious entropic contribution to the total energy of the system [241]. The Marzari-Vanderbit-DeVita-Payne cold smearing method employs a similar technique but additionally ensures the total free energy of the system remains independent of the smearing temperature, at least up to the second order.

Energy cutoffs

The solutions to the Schrödinger equation can be represented as a combination of Bloch functions. Within these functions, as in eq. (2.11), the periodic functions $u_k(\mathbf{r})$ of Bloch functions need to be specified. These functions can be expressed in relation to plane waves as follows

$$u_k(\mathbf{r}) = \sum_G c_G \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (2.14)$$

where c_G represent coefficients, and $\mathbf{G}$ stands for a set of vectors defined as $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$, where m_i are integer values. Consequently, an infinite set of possible values for $\mathbf{G}$ exist. However, this infinite sum is constrained to a finite sum in DFT calculations, comprising solutions with low-energy values. The selection of physically representative solutions is determined by a specified energy cutoff, defined as

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}^2 \quad (2.15)$$

The solutions to the Schrödinger equation can be then expressed, following Bloch's theorem as:

$$\Phi_k(\mathbf{r}) = \sum_{|\mathbf{G}+\mathbf{k}| < G_{cut}} c_{\mathbf{G}+\mathbf{k}} \exp[i(\mathbf{G} + \mathbf{k})\mathbf{r}]. \quad (2.16)$$

Establishing the energy cutoff is another crucial parameter in the DFT simulations. Typically, an energy cutoff is assigned for each element. In scenarios involving systems with multiple elements, the highest cutoff energy is selected for the entire supercell. Additionally, it is essential to ensure that energies across different systems are compared using consistent energy cutoffs [257].

Pseudopotentials

The inner core electrons typically have a minimal influence on bonding. Consequently, the simulations to solve the Schrödinger equation are often streamlined by approximating the electron density of these electrons. These approximations, known as pseudopotentials, enable a reduction in the necessary number of plane-wave functions for DFT simulations. Pseudopotentials are defined for most elements in the periodic table and need the application of a minimum energy cutoff. Hard pseudopotentials demand high cutoff energies, whereas soft pseudopotentials require lower values.

The common types of pseudopotentials include ultrasoft pseudopotentials (USPPs) [142], projector augmented-wave (PAW) pseudopotentials [296], and norm-conserving pseudopotentials [91]. In the norm-conserving pseudopotentials, the all-electron wavefunction is approximated using pseudo-wavefunctions for the valence electrons with equal norms. This condition is relaxed for USPPs, accepting the use of a lower energy cutoff. Additionally, PAWs offer potentially more accurate calculations by reconstructing the exact valence wavefunction.

2.1.3 Software and methodology

All the adsorption energies on pure metals and intermetallic surfaces presented in this thesis were determined from DFT plane wave simulations using the CPU and the GPU-accelerated version of Quantum Espresso [79]. Most calculations were performed on GPUs NVIDIA V100-16GB, NVIDIA A100-PCIE-40GB, M2090 NVIDIA GPU-24GB, and K80 NVIDIA GPU-120GB.

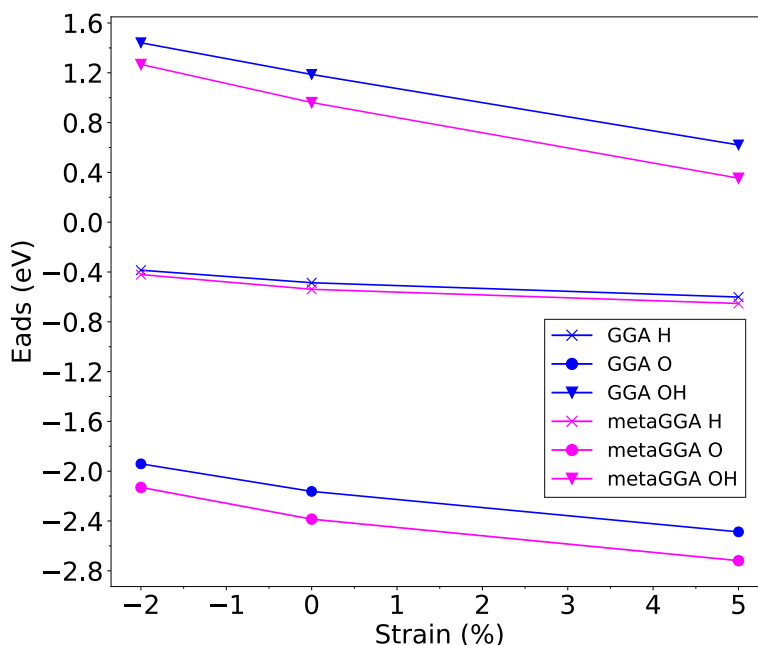


Figure 2.3: Adsorption energy of H, O, and OH in a Pt(111) slab as a function of biaxial strain. Blue curves represent the calculations performed with a GGA functional (PBE [213]) and magenta curves represent the calculations performed with a metaGGA functional (SCAN [278]).

The electron exchange-correlation was described using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [213] and the calculations were carried out using ultrasoft pseudopotentials [296]. The metaGGA functional SCAN [278] was also considered, as it is known to provide accurate values of the adsorption energies at a significantly higher computational cost. In

the case of Pt, the differences in E_{ads_H} between the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional and the metaGGA SCAN functional were only 0.03 eV but they increased to 0.24 eV in the case of Cu. Thus, the predictions of the adsorption energy for Cu seem to be particularly sensitive to the selection of the functional. In addition, the effect of biaxial elastic strains in the adsorption energy of H, O, and OH on a Pt(111) slab is plotted in Figure 2.3 for GGA-PBE and metaGGA-SCAN functionals. Although there are some differences in adsorption energy between both functionals, the trends with strain are identical. Additionally, GGA functionals have been proven accurate for metal and intermetallic surfaces in the bibliography [221, 229]. That moves us to conclude that the utilization of a GGA functional is sufficient for the aim of this work.

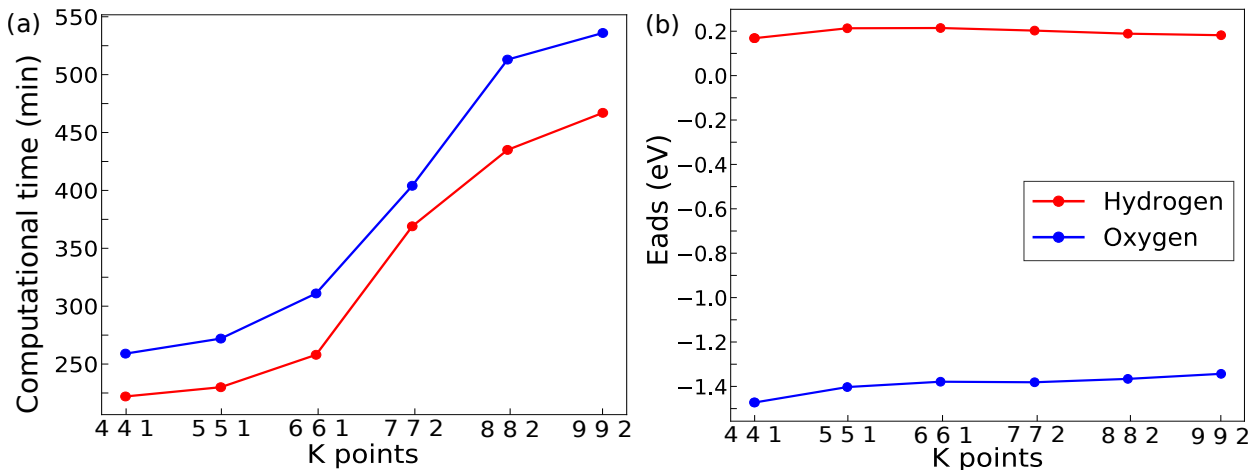


Figure 2.4: Example of a convergence test performed for an Ag_3In fcc(111) surface at FCC AAA adsorption position. (a) k-points vs, computational time. (b) k-points vs. E_{ads} . Red curves represent the H adsorption and blue curves represent the O adsorption.

The experimental value of lattice constant a for Pt is 3.94 Å [118]. The lattice parameters and adsorption energies (E_{ads_H}) of H on top fcc(111) Pt obtained with various DFT functionals and pseudopotentials are depicted in Table 2.1. Moreover, simulations of H adsorption on Pt (111) surfaces carried with ultrasoft pseudopotentials were compared with those obtained using the projector augmented-wave method (PAW), which provides more accurate results [24, 59, 99, 138, 221] with higher computational cost. The differences in adsorption energies between both simulations were negligible. Thus, it was concluded that the combination of the PBE functional with an ultrasoft pseudopotential offered the best balance between accuracy and computational time.

Brillouin zone calculations were performed using a Marzari-Vanderbit-DeVita-Payne cold smearing of 0.015 Ry [180]. The plane-wave basis was expanded to a cutoff energy of 80 Ry, and the Monkhorst-Pack k-points were sized $(20 \times 20 \times 20)$ for the unit cells of all metals, $(4 \times 4 \times 1)$ for the pure metallic supercells, $(6 \times 6 \times 1)$ for all the binary intermetallic compounds with the exception of A_2B stoichiometry in which $(8 \times 8 \times 1)$ was used due to the higher number of atoms involved, and $(8 \times 8 \times 1)$ for the tests with ternary intermetallic

Functional	Pseudopotential	Lattice parameter a (Å)	E_{ads_H} (eV)	Calculation time
PBEsol	ultrasoft	3.91	-0.52	5 h 39 min
revPBE	ultrasoft	3.98	-0.39	4 h 05 min
PBE	ultrasoft	3.96	-0.49	3 h 44 min
PBE	PAW	3.97	-0.48	5 h 10 min

Table 2.1: Lattice parameters and adsorption energies of H onto fcc(111) platinum at FCC position with different DFT functionals and pseudopotentials.

compounds. An example of the convergence test performed for the binary intermetallic compound Ag_3In is shown in Figure 2.4.

2.1.4 Adsorption energy calculations

The adsorption of H, O, and OH -the three intermediates in the HER and the ORR- was modeled on four-layer slabs. The surface plane for each material was selected for being the lowest surface energy and, thus, stands as the most stable one for each lattice [118]. The (2x2) slab supercells with four layers of atoms perpendicular to the the surface were generated with the Atomic Simulation Environment (ASE) [14] from the equilibrium lattice parameters.

The lattice parameters were calculated by DFT for pure metals (Tables 2.2 and 2.3) in bulk calculations. However, only a few candidates with all the stoichiometries were computed in the case of intermetallic compounds. The differences between the calculated and the values obtained from the Materials Project Database [118] of the lattice parameters were negligible in all cases and can be found in Table 2.4. For that reason, the supercell slabs simulated for binary intermetallic compounds were constructed from these database lattice parameters.

	Ni	Cu	Pd	Ag	Pt	Au	Rh	Ir
a (Å)	3.52	3.63	3.94	4.09	3.96	4.16	3.77	3.87

Table 2.2: Lattice parameter a for fcc metals. Values are referred in Å.

	Zn	Cd	Co
a (Å)	2.63	3.01	2.49
c (Å)	5.13	5.84	4.04

Table 2.3: Lattice parameters a and c for hcp metals. Values are referred in Å.

The periodic slabs were separated by 10 Å of vacuum (Figure 2.5) in the direction perpendicular to the surface. Adsorption energies were calculated for each chemical species assuming a coverage of 1/4 monolayers. All metal atoms in the top two layers of the slab

Stoichiometry	Material	Calculated by DFT		Materials Project	
		a (Å)	c (Å)	a (Å)	c (Å)
A	Pt	3.96	3.96	3.94	3.94
	Ag	4.09	4.09	4.10	4.10
	Au	4.16	4.16	4.17	4.17
	Ir	3.87	3.87	3.85	3.85
	Pd	3.94	3.94	3.92	3.92
	Co	2.49	4.04	2.47	4.03
AB	AlFe	2.86	2.86	2.85	2.85
	AlNi	2.89	2.89	2.86	2.86
	AlRu	3.00	3.00	2.98	2.98
	CuPd	3.02	3.02	2.98	2.98
	DyIn	3.74	3.74	3.74	3.74
	FeRh	3.00	3.00	2.99	2.99
	HfRu	3.23	3.23	3.23	3.23
	MgSc	3.58	3.58	3.60	3.60
	NdZn	3.67	3.67	3.67	3.67
	RuV	3.00	3.00	3.00	3.00
	TiRe	3.12	3.12	3.11	3.11
A ₂ B	Fe ₂ Zr	5.22	16.66	5.02	16.43
	Os ₂ Y	5.21	8.98	5.28	8.93
	Re ₂ Sm	5.24	8.98	5.45	8.93
	Ru ₂ Sm	5.15	8.80	5.27	9.06
A ₃ B	Al ₃ Li	4.02	4.02	4.00	4.00
	Co ₃ Ti	3.60	3.60	3.59	3.59
	In ₃ Sc	4.53	4.53	4.50	4.50
	In ₃ Y	4.65	4.65	4.63	4.63
	Ir ₃ Ti	3.87	3.87	3.86	3.86
	Ir ₃ Zr	3.98	3.98	3.96	3.96
	Pd ₃ Y	4.13	4.13	4.10	4.10
	Pt ₃ In	4.05	4.05	4.02	4.02
	Zn ₃ Mn	3.82	3.82	3.81	3.81
	Zn ₃ Nb	3.94	3.94	3.91	3.91
	Zr ₃ Al	4.38	4.38	4.38	4.38

Table 2.4: Equilibrium lattice parameters (a and c) in Å. Displayed values calculated by DFT and obtained from Materials Project Database [118] for all the different stoichiometries.

and all adsorbed H, O, and OH were fully relaxed, while the positions of metal atoms in the bottom two layers were fixed to simulate the bulk. The adsorption energies of H in the case of Pt (111) surfaces were evaluated for slabs including 3, 4, and 5 atomic layers perpendicular to the surface and the results obtained with 4 and 5 layers were very close,

indicating that 4 layers were enough to reach convergence.

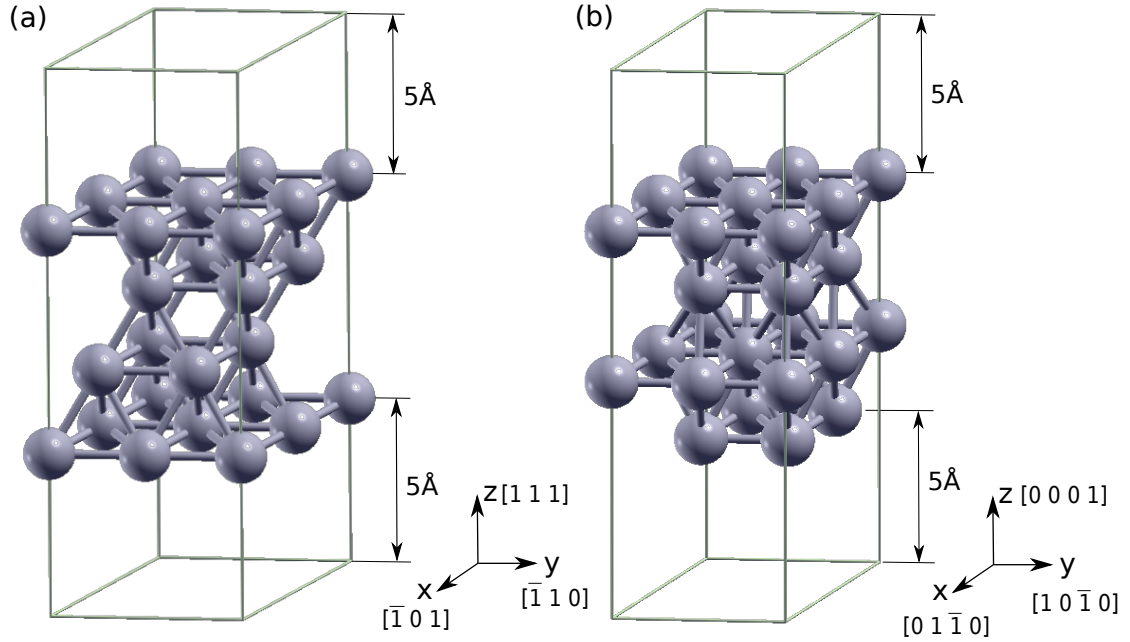


Figure 2.5: (a) Four-layer slab supercell of a (111) fcc surface. (b) *Idem* for a four-layer slab supercell of a (0001) hcp surface. The surfaces in the supercells are separated by 10 Å of vacuum.

The adsorption energy of each different adsorbate X was defined as

$$E_{\text{ads}_X} = E_{\text{slab}+X} - (E_{\text{slab}} + E_{X_{\text{gas}}}) \quad (2.17)$$

where E_{slab} and $E_{\text{slab}+X}$ stand for the total energies of the slab without and with the adsorbate X. $E_{X_{\text{gas}}}$ accounts for the total energy of the molecules in the gaseous state. The specific equations for each of the adsorbates can be written as

$$E_{\text{ads}_H} = E_{\text{slab}+H} - (E_{\text{slab}} + \frac{1}{2}E_{H_2}) \quad (2.18)$$

$$E_{\text{ads}_O} = E_{\text{slab}+O} - (E_{\text{slab}} + \frac{1}{2}E_{O_2}) \quad (2.19)$$

$$E_{\text{ads}_N} = E_{\text{slab}+N} - (E_{\text{slab}} + \frac{1}{2}E_{N_2}) \quad (2.20)$$

$$E_{\text{ads}_\text{C}} = E_{\text{slab}+\text{C}} - (E_{\text{slab}} + E_{\text{CH}_4} - 2E_{\text{H}_2}) \quad (2.21)$$

$$E_{\text{ads}_{\text{OH}}} = E_{\text{slab}+\text{OH}} - (E_{\text{slab}} + (E_{\text{H}_2\text{O}} - \frac{1}{2}E_{\text{H}_2})) \quad (2.22)$$

$$E_{\text{ads}_{\text{NO}}} = E_{\text{slab}+\text{NO}} - (E_{\text{slab}} + E_{\text{NO}}) \quad (2.23)$$

$$E_{\text{ads}_{\text{CO}}} = E_{\text{slab}+\text{CO}} - (E_{\text{slab}} + E_{\text{CO}}) \quad (2.24)$$

Adsorption sites

Adsorption is a very localized process since the adsorption energy depends on the local atomic environment of the adsorption site. Therefore, all possible adsorption sites for both the pure metals and binary intermetallic compounds were explored (Fig. 2.6). The main adsorption sites for pure metals (Figs. 2.6 a, b, c, d, and e) are FCC, HCP, ONTOP, and BRIDGE. At FCC and HCP positions, the adsorbate is placed on a hole between three atoms. There is no atom in the second layer below at FCC, while, a metal atom is present right under the adsorbate at HCP. ONTOP refers to the adsorption above an atom of the first layer, and BRIDGE describes the adsorption at the bond between two atoms. For bcc(100) surfaces, SHORTBRIDGE and LONGBRIDGE sites should be discriminated, as there are two different bond distances on the surface. HOLLOW refers to the adsorption site in the hole between four atoms.

For the binary intermetallic compounds (Figs. 2.6 f, g, h, i, and j), the number of possible adsorption sites was bigger, as it was necessary to discriminate between A and B atoms on the surface. Here, different FCC and HCP possibilities were analyzed depending on the three atoms around the hole -AAA, AAB, or ABB-. Similarly, the ONTOP positions could occur above an atom A or an atom B, and BRIDGE sites between two atoms AA, BB, or AB. In AB bcc(101) samples, an extra position appeared: THREEFOLD. It stands for a hole between three atoms where the atom in the second layer below is at an intermediate position between FCC and HCP. In all cases, the most favorable binding site would be that with lower values of adsorption energy.

In the case of ternary intermetallic compounds (Figs. 2.7 a, b, c, and d) the surfaces studied were: A3BC fcc(111), ABC hcp(0001), A2BC hcp(0001), and A3BC hcp(0001). Here, the adsorption sites are equivalent to binaries but they contain atom C. Hence, positions ONTOP C, FCC ABC, and BRIDGE BC arise.

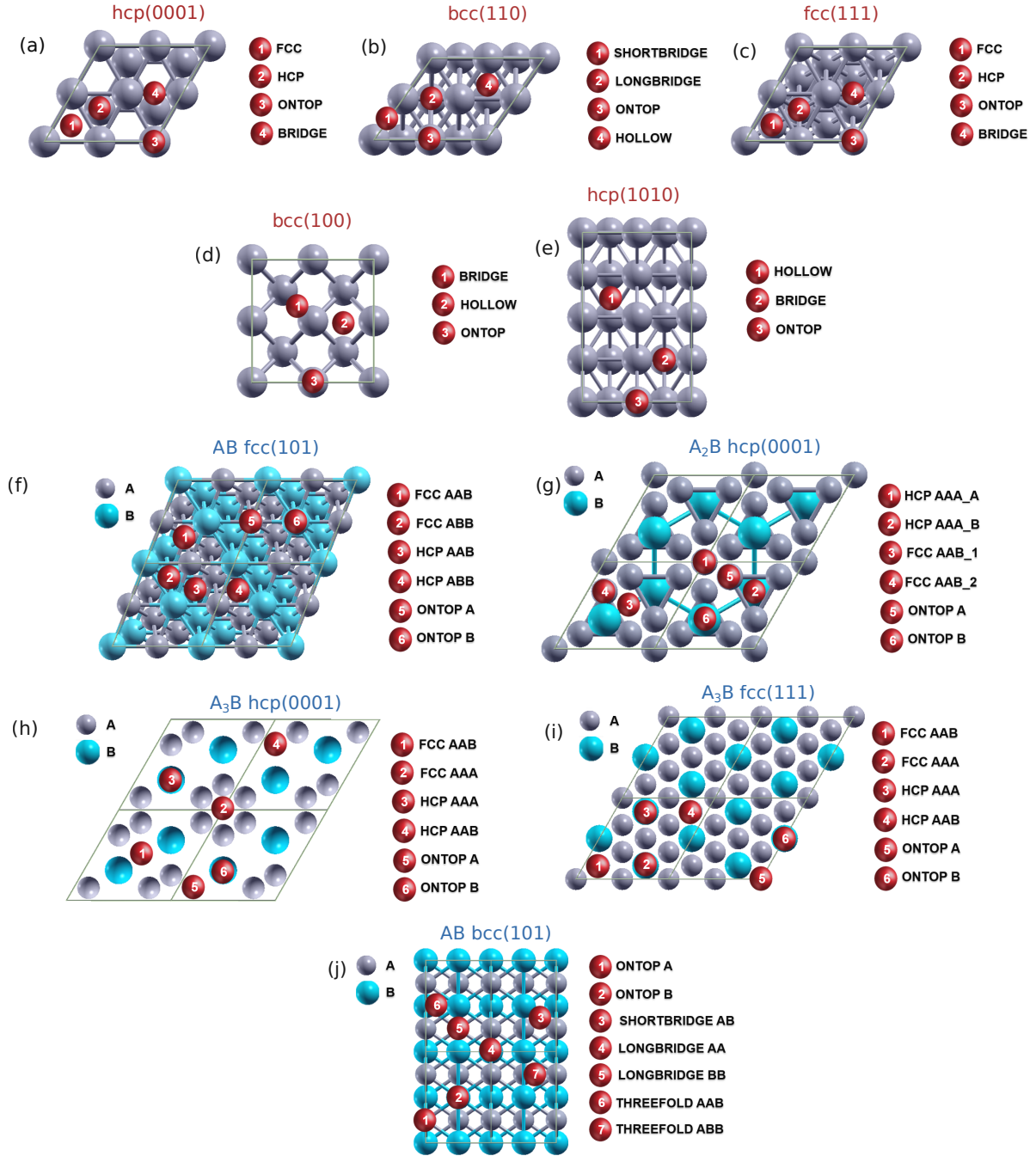


Figure 2.6: Possible adsorption sites explored on the surface of pure metals (a, b, c, d, and e) and binary intermetallic compounds (f, g, h, i, and j) with different stoichiometries and geometries: a) hcp(0001), b) bcc(110), c) fcc(111), d) bcc(100), e) hcp(1010), f) AB fcc(101), g) A₂B hcp(0001), h) A₃B hcp(0001), i) A₃B fcc(111), and j) AB bcc(101).

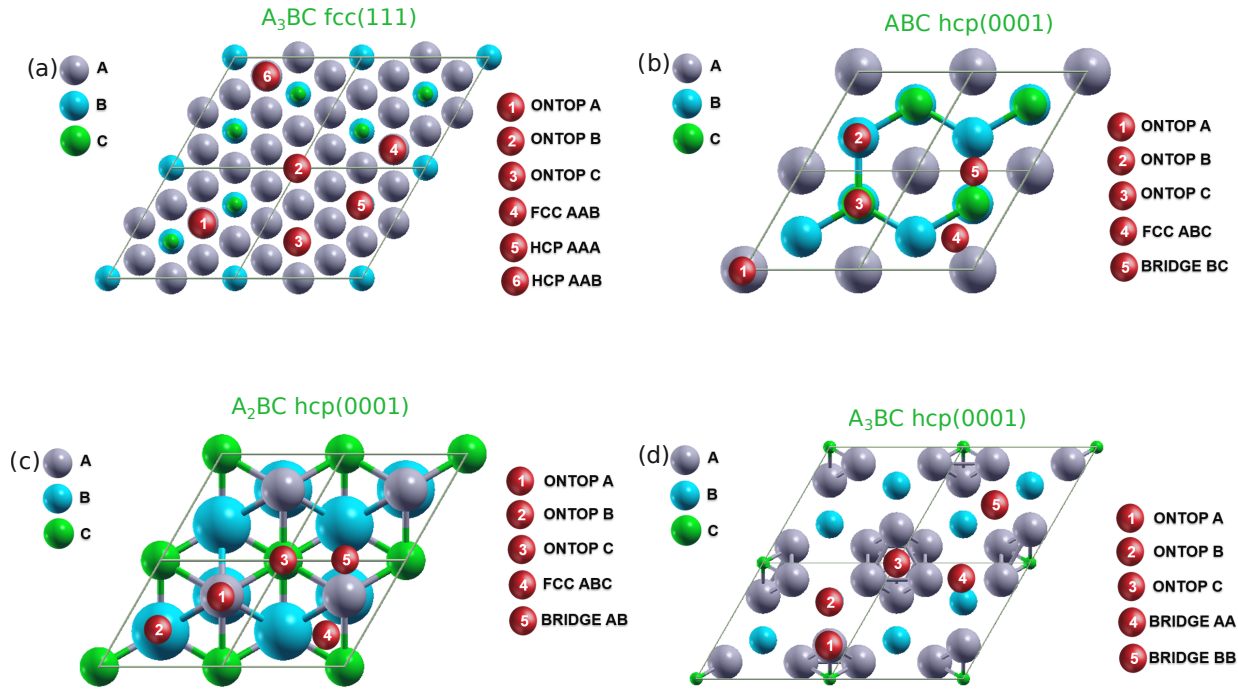


Figure 2.7: Possible adsorption sites explored on the surface of ternary intermetallic compounds with different stoichiometries and geometries: a) A_3BC fcc(111), b) ABC hcp(0001), c) A_2BC hcp(0001), d) A_3BC hcp(0001).

2.1.5 Catalytic activity calculations

As explained in section 1.4.1, the adsorption energy can be used to estimate the activity of a catalyst following Sabatier's principle [238]. The magnitude of E_{ads} - obtained from DFT simulations - can be employed to determine the overall rate of the reaction according to

$$G_{ads} = E_{ads} + E_{ZPE} - T\Delta S \quad (2.25)$$

where G_{ads} , E_{ads} , E_{ZPE} , and ΔS stand for the variation of the free and adsorption energies, the zero point energy and the entropy, respectively, during the adsorption of the intermediate species, and T is the absolute temperature [198]. This relationship should be evaluated for each intermediate species that appear in the catalytic process (only H in the HER reaction and O and OH in the ORR), taking into account that the process with the highest free energy barrier will limit the rate of the reaction.

2.1.6 HER

The reaction path for the HER that is shown in Figure 2.8 a and equation (2.25) can be used to compute the free energy associated with the adsorption process, G_{ads} , including the differences in zero-point energies between products and reactants, ΔE_{ZPE} . These zero-point energies were calculated for the adsorption of H on Cu(111) and on Pt(111) and their

values were 0.04 eV in both cases, in agreement with the one previously reported in the literature for the adsorption of H on Cu(111) [195]. The same value of ΔE_{ZPE} was used for all the pure metals and intermetallics compounds analyzed in this thesis. The difference in zero-point energies (ΔE_{ZPE}) for the Hydrogen Evolution Reaction (HER) is calculated as

$$\Delta E_{ZPE} = E_{ZPE_{H^*}} - \frac{1}{2} E_{ZPE_{H_2}} - E_{ZPE_{*}} \quad (2.26)$$

where $E_{ZPE_{H^*}}$, $E_{ZPE_{H_2}}$, and $E_{ZPE_{*}}$ stand for the zero-point energies of the H atom and the metallic slab, the hydrogen molecule, and the metallic slab, respectively. They were computed with the Phonopy3 program [288] together with the Quantum Espresso package [78, 80, 81].

The vibrational entropy is determined by the contribution of $0.5H_2$

$$\Delta S = -\frac{1}{2} S_{H_2}^0 \quad (2.27)$$

where $S_{H_2}^0 = 130.68 \text{ J/mol}\cdot\text{K}$ [38] is the entropy of H_2 in the gas phase at standard conditions (300K and 1 bar). Thus, G_{ads} at $T = 300 \text{ K}$ can be expressed as

$$G_{ads_H} = E_{ads_H} + 0.24 \text{ eV} \quad (2.28)$$

G_{ads_H} depends only on the energy of adsorption of hydrogen according to equation (2.28) and the catalytic activity of the HER can be measured by the exchange current density, i_0 . This parameter describes the electron transfer between the electrode (which in our case would be the catalyst) and the solution and can be calculated following the strategy developed by Norskov *et al.* [195]. If $G_{ads_H} < 0$, the proton transfer is an exothermic process and the exchange current density can be expressed as

$$i_0 = -e k_0 \frac{1}{1 + \exp(-G_{ads_H}/kT)} \quad (2.29)$$

where e is the electron charge and $k_0 = 200 \text{ s}^{-1} \text{ site}^{-1}$ [198] is a constant independent of the metal that includes all the effects related to the reorganization of the solvent during the transfer of protons to the surface. kT stands for the Boltzmann constant and the absolute temperature, respectively.

On the contrary, if $G_{ads_H} > 0$, the proton transfer is endothermic, and the exchange current density is given by

$$i_0 = -e k_0 \frac{1}{1 + \exp(-G_{ads_H}/kT)} \exp(-G_{ads_H}/kT) \quad (2.30)$$

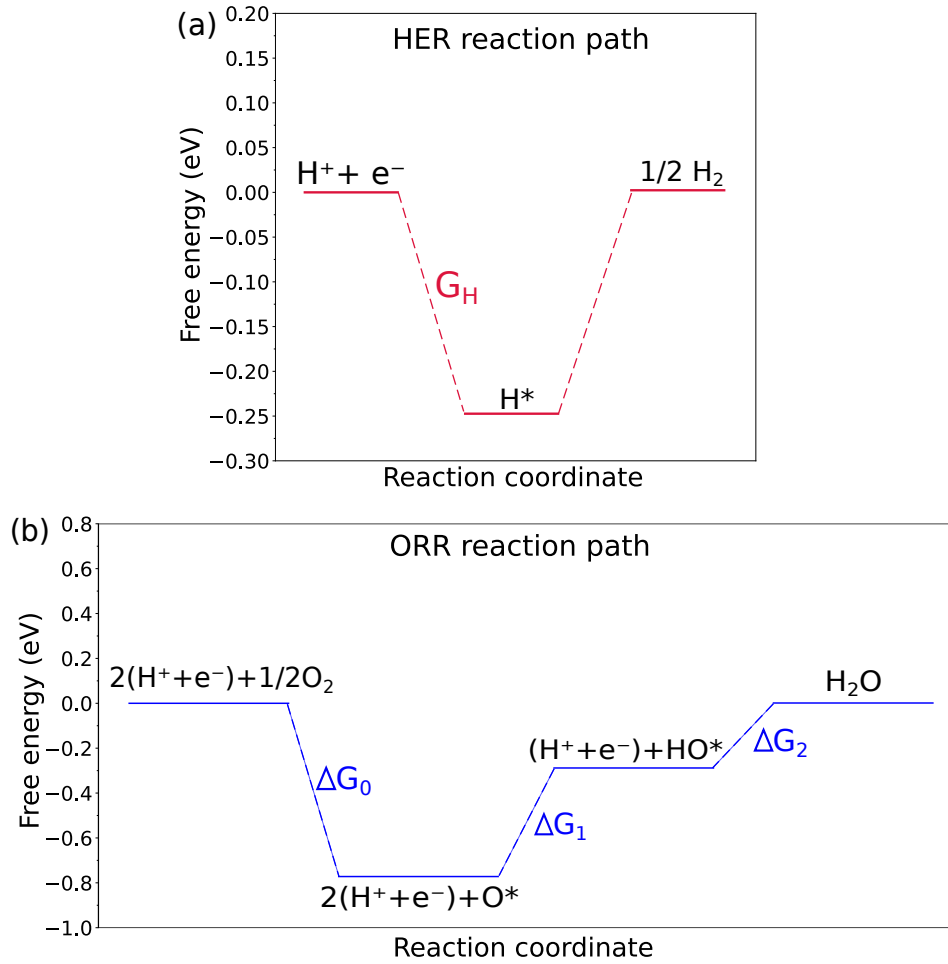


Figure 2.8: Reactions paths and different steps for the (a) HER and the (b) ORR in acidic media.

2.1.7 ORR

Two different adsorbed species have to be considered in this case, O^* and HO^* (notice the difference with the HER, where the only intermediate adsorbate is H^*). The reaction path for the dissociative mechanism is depicted in Figure 2.8 b. Three different free energies, G_0 , G_1 , and G_2 , that correspond to the three steps of the dissociative mechanism shown in Table 1.4, are involved in the process. The free energies (G) for these steps can be expressed as

$$G_0 = G_{O^*+H_2} - G_{H_2O+*} \quad (2.31)$$

$$G_1 = G_{HO^*+\frac{1}{2}H_2} - G_{O^*+H_2} \quad (2.32)$$

$$G_2 = G_{\text{H}_2\text{O}^*} - G_{\text{HO}^* + \frac{1}{2}\text{H}_2} \quad (2.33)$$

which leads to

$$G_0 = [E_{\text{O}^*} + E_{\text{H}_2} + E_{\text{ZPE}(\text{O}^* + \text{H}_2)} - T\Delta S_{(\text{O}^* + \text{H}_2)}] - [E_{\text{H}_2\text{O}} + E_* + E_{\text{ZPE}(\text{H}_2\text{O}^*)} - T\Delta S_{(\text{H}_2\text{O}^*)}] \quad (2.34)$$

$$G_1 = [E_{\text{HO}^*} + \frac{1}{2}E_{\text{H}_2} + E_{\text{ZPE}(\text{HO}^* + \frac{1}{2}\text{H}_2)} - T\Delta S_{(\text{HO}^* + \frac{1}{2}\text{H}_2)}] - [E_{\text{O}^*} + E_{\text{H}_2} + E_{\text{ZPE}(\text{O}^* + \text{H}_2)} - T\Delta S_{(\text{O}^* + \text{H}_2)}] \quad (2.35)$$

$$G_2 = [E_{\text{H}_2\text{O}} + E_* + E_{\text{ZPE}(\text{H}_2\text{O}^*)} - T\Delta S_{(\text{H}_2\text{O}^*)}] - [E_{\text{HO}^*} + \frac{1}{2}E_{\text{H}_2} + E_{\text{ZPE}(\text{HO}^* + \frac{1}{2}\text{H}_2)} - T\Delta S_{(\text{HO}^* + \frac{1}{2}\text{H}_2)}] \quad (2.36)$$

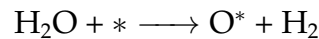
where E_{ZPE} and ΔS stand for the zero point energy for each species and the change in entropy for each reaction and can be found in Table 3 of [198]. At $T = 300\text{K}$, the final expressions can be reduced to

$$G_0 = G_{\text{O}^* + \text{H}_2} - G_{\text{H}_2\text{O}^*} = E_{\text{adsO}'} + 0.01 \text{ eV} \quad (2.37)$$

$$G_1 = G_{\text{HO}^* + \frac{1}{2}\text{H}_2} - G_{\text{O}^* + \text{H}_2} = E_{\text{adsOH}} - E_{\text{adsO}'} - 0.26 \text{ eV} \quad (2.38)$$

$$G_2 = G_{\text{H}_2\text{O}^*} - G_{\text{HO}^* + \frac{1}{2}\text{H}_2} = -E_{\text{adsOH}} + 0.25 \text{ eV} \quad (2.39)$$

where $E_{\text{adsO}'}$ is defined below and it is assumed that $T = 300 \text{ K}$. G_0 and G_2 depend only on the adsorption energy of O and OH, respectively, whereas G_1 depends on the difference. Note that in order to calculate the catalytic activity, $E_{\text{adsO}'}$ must be considered instead of E_{adsO} . This adsorption energy, $E_{\text{adsO}'}$, takes into account that the adsorbed oxygen comes from water in the catalytic process from the reaction:



and it is expressed as

$$E_{\text{adsO}'} = E_{\text{O}^*} + E_{\text{H}_2} - E_{\text{H}_2\text{O}} - E_* = E_{\text{adsO}} + E_{\text{H}_2} - E_{\text{H}_2\text{O}} + \frac{1}{2}E_{\text{O}_2} \quad (2.40)$$

where E_{H_2} , E_{O_2} , and $E_{\text{H}_2\text{O}}$ account for the total energy of the hydrogen, oxygen, and water molecules in the gaseous state, respectively.

Additionally, the effect of the potential in the cell has to be taken into account because it is an electron transfer process. The free energy at pH = 0, atmospheric pressure of 1 bar, and 300 K of temperature, with electrode potential corrections, is given by

$$G(U) = G + neU \quad (2.41)$$

where U is the cell potential, n the number of electrons that flow from the media to the electrode (if the electrons move in the opposite direction, n must be multiplied by -1), and e the elementary charge carried by a single electron, -1. At equilibrium, U would be the equilibrium potential $U_0=1.23$ V [198]. Considering the electrons that flow in each of the three steps, the corresponding free energies at equilibrium potential, atmospheric pressure, and 300 K are

$$G_0(U_0) = E_{\text{adsO}'} + 0.01\text{eV} - 2U_0 = E_{\text{adsO}'} - 2.45\text{ eV} \quad (2.42)$$

$$G_1(U_0) = E_{\text{adsOH}} - E_{\text{adsO}'} - 0.26\text{eV} + U_0 = E_{\text{adsOH}} - E_{\text{adsO}'} + 0.97\text{ eV} \quad (2.43)$$

$$G_2(U_0) = -E_{\text{adsOH}} + 0.25\text{eV} + U_0 = -E_{\text{adsOH}} + 1.48\text{ eV} \quad (2.44)$$

The catalytic activity, A , can be expressed [198]

$$A = kT \log \left[\exp(-G(U_0)/kT) \right] \quad (2.45)$$

where $G(U_0) = \max\{G_0(U_0), G_1(U_0), G_2(U_0)\}$ and corresponds to the activation energy of the process that limits the catalytic reaction.

2.1.8 Application of elastic strains

The metallic surfaces were subjected to normal and shear elastic strains in the surface plane. Mixed boundary conditions are imposed to solve the elastic problem in the DFT simulations. They include imposed strains in the slab plane and zero stresses on the free surface. The deformation gradient $\mathbf{F}$ applied to the supercells was

$$\mathbf{F} = \begin{pmatrix} 1 + \epsilon_1 & \gamma \\ 0 & 1 + \epsilon_2 \end{pmatrix} \quad (2.46)$$

where ϵ_1 and ϵ_2 stand for the normal strains along x and y directions while γ for the shear distortion in the xy plane. Uniaxial deformation was applied when $\epsilon = \epsilon_1$ and $\epsilon_2 = \gamma = 0$, while $\epsilon = \epsilon_1 = \epsilon_2$ and $\gamma = 0$ for biaxial deformation.

In addition, the mechanical stability of surface slab supercells under strain was analyzed from the harmonic phonon spectrum using the Phonopy code [288]. To calculate the phonon spectrum, the atomic forces after perturbing slightly the atomic positions from the equilibrium positions were calculated for different strains in large slab supercells. They were obtained by repeating the basic slab supercells in Figure 2.5 by 2 times in the x direction and two times in the y direction, leading to supercells with 64 atoms. The number of perturbations to obtain the phonon spectrum depends on the symmetries of the supercell which in turn depend on the applied strain and can vary from 4 (no strain applied) to 24 (15% biaxial deformation). It should be noted that the phonon calculations are computationally very expensive and they were used to assess the maximum strain levels that should be explored in the adsorption calculations under normal and shear strains because mechanical instabilities are likely to appear well before these limits.

2.2 Machine Learning

2.2.1 Theory background

Machine learning (ML) is a subset of artificial intelligence (AI) and computer science that revolves around leveraging data and algorithms to replicate the human learning process, enhancing its accuracy over time. Usually, authors break out this learning process into three main parts:

1. A Decision Process: Typically, machine learning algorithms are employed for making predictions or classifications. Using input data, whether labeled or unlabeled, the algorithm generates an estimation concerning a pattern within the data.
2. An Error Function: The role of this function is to assess the model's predictions.
3. An Optimization Process: If the model can better align with the data points in the training set, adjustments are made to the weights to minimize the disparity between the known example and the model estimate. The algorithm iteratively engages in an "evaluate and optimize" process, autonomously updating weights until a specified accuracy threshold is reached.

In order to perform this learning process, three main ingredients must be considered and chosen adequately: a proper database, a set of features/descriptors, and an algorithm.

Database

A database in ML is the systematic collection of data that the model is going to use as a starting point to learn and elaborate predictions. The success of ML models relies significantly on the quality and accessibility of the database, ensuring their accuracy and utility. Hence, researchers need to employ techniques such as data cleaning and normalization

to guarantee the consistency and accuracy of the data. Apart from being diverse and big enough, it should contain a representative amount of data within the range we aim to predict. The total amount of entries in the database must be divided into training and test sets. The training set constitutes the dataset employed for model learning, forming a substantial portion of the available data and serving as the basis for estimating model parameters. It should encompass all potential inputs that the model is capable of processing. The test set, distinct from the training phase, consists of a subset of data held back. It serves as an impartial benchmark to assess the model's performance post-training. This set replicates real-world data the model may encounter in production, allowing us to evaluate its ability to generalize and accurately predict new, unseen data by analyzing its performance on previously unseen examples.

Features

The features, also called descriptors, are the quantifiable properties of a data sample utilized as input for training and serving in a machine-learning model. It is essential for a feature to possess predictive capability relevant to the model it is applied to as they are the variables or attributes which describe the entries present in the database. There are three common types of descriptors: categorical (ordinal or nominal), numerical (interval or ratio), and array types (lists or embeddings). Categorical features refer to characteristics with a finite set of values that offer valuable insights into data patterns and relationships. They pose specific challenges for machine learning models as they must be preprocessed before employing them in most models. This preprocessing entails converting them into numerical counterparts that can be effectively processed by machine learning algorithms. Numerical features can be measured on a scale as they are continuous values, and array descriptors are sets of variables that can be grouped to train the model.

Algorithm

Finally, the ML algorithm constitutes the set of rules or processes used for the model to uncover new insights and patterns in the data or to predict output values based on a specific set of input variables. Although there are many types and branches in which ML diverges, generally two main types of ML algorithms arise: supervised and unsupervised machine learning algorithms.

Supervised ML

Supervised machine learning algorithms are those in which the connection between input and output is known. The inputs, often called x-variables, correspond to the output, typically termed the targets or y-variables. The dataset encompasses both x and y variables and is known as labeled data. There are a number of common supervised ML algorithms [55]. For instance, Linear classifiers utilize linear (hyperplane) decision boundaries to separate input vectors into classes creating groups with similar features [299]. Logistic regressions use a classification multinomial function with a single estimator [7]. Naive Bayesian (NB) Networks consist of directed acyclic graphs featuring a sole parent (representing the unobserved node) and multiple children (associated with observed nodes), under the strong assumption of independence among child nodes concerning their parent

in the given context [134]. Multi-layer Perceptrons, determine the weights of the network through solving a quadratic programming problem with linear constraints [201]. Support Vector Machines are centered on the concept of a "margin" that involves the space on either side of a hyperplane and distinguishes between two data classes [46]. K means, that follows a straightforward way to classify a data set through a number of clusters fixed a priori [127]. Decision Trees that classify instances by sorting them based on feature values [46]. And Bayesian Networks, which serves as a graphical model illustrating the probability relationships among a set of variables, commonly referred to as features [127].

Unsupervised ML

By contrast, unsupervised learning employs algorithms to categorize unlabeled datasets into subsets known as clusters. These algorithms unveil patterns or groupings within the data without human intervention. This approach's capability to discern similarities and differences in information makes it well-suited for tasks such as exploratory data analysis, devising cross-selling strategies, customer segmentation, as well as image and pattern recognition. Additionally, unsupervised learning is utilized to streamline models by reducing the number of features, a process known as dimensionality reduction. Principal Component Analysis and Singular Value Decomposition are common methods for this purpose. One of the most used unsupervised algorithms are: Neural Networks, which consist of layers of nodes: input, hidden, and output, that connect to others with their own weights and thresholds [297]. K means clustering, which partitions into k clusters the n observation with the nearest mean [270]. And Probabilistic clustering methods, based on hidden categories over the data space, which are parameterized with a probability density function [276].

2.2.2 Model details

Different types of Machine Learning models have been used to describe the adsorption phenomena that occur in heterogeneous catalysis. They include Support Vector Regression (SVR) [177], K-nearest neighbors (KNN) [313], Convolutional Neural Network [68], and Gaussian Process Regression [101]. Among all, the state-of-the-art MAE of ML model predictions for the adsorption energy is in the range of 0.16-0.3 eV [174, 291].

In this thesis, Random Forest (RF) regressor models were built separately for the prediction of E_{ads_H} and $E_{ads_O}/E_{ads_{OH}}$. RF is a part of a family of methods known as ensemble methods. Ensemble methods combine the predictions of different base estimators. In RF models, the ensemble consists of a collection of decision trees that are trained independently using random subsets of both features and training data. Each decision tree predicts the target variable by learning simple decision rules inferred from the features. In regression tasks, the final prediction of an RF model is the average of the predictions made by each tree in the forest.

RF models are generally robust to overfitting, can handle outliers, and provide information about the importance of each feature in the descriptor, which can be useful for feature selection and for elucidating the model's behavior. RFs are known to be versatile to different datasets without requiring an expensive hyperparameter tuning. We chose an RF

regressor as the algorithm for this work due to the size of our database (useful with small-hundred- or medium-sized -thousand- databases), the quick training, and the good accuracy obtained. Under the same conditions, our databases were trained with a Gaussian Process Regressor algorithm, but the MAE was 0.2 eV higher on average. Graph Neural Networks were not considered due to the diversity and size of our databases. Usually, the rule of 10 is used for an initial estimation of the amount of data required to train a neural network. It states that the amount of training entries needed is 10 times the number of parameters in the model. [84] Although in the case of O and OH, we fulfill this rule, bigger databases are needed in order to find better predictions than with a Random Forest Regressor. In our RF model, the training set was 85% of the data and the remaining 15% conformed the test set. The hyperparameters were optimized with a k-fold Grid-search cross-validation (K=5) and they can be found in Table 2.5. For that, we constructed a parameters grid and optimized it with the GridSearchCV routine as implemented in the Scikit-learn library [210].

Hyperparameter	Eads _H	Eads _{O/OH}
n_estimators	1000	1000
max_features	9	10
min_samples_split	4	3
min_samples_leaf	1	1
max_depth	600	300

Table 2.5: Optimized hyperparameters for the Random Forest Regressor model in the prediction of the adsorption energy of hydrogen, oxygen, and hydroxyl.

The algorithm selected was ExtraTreesRegressor and was constructed and analyzed using the Scikit-learn library [210]. The accuracy of the model was analyzed with the coefficient of determination R^2 , the Mean Absolute Error (MAE), the Root Mean Squared Error (RMSE), and the Median Absolute Deviation (MAD) which can be defined as

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y})^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (2.47)$$

$$MAE = \frac{1}{N} \sum_{i=1}^N |y_i - \hat{y}| \quad (2.48)$$

$$RMSE = \sqrt{MSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_i - \hat{y})^2} \quad (2.49)$$

$$MAD = \frac{1}{N} \sum_{i=1}^N |y_i - \bar{y}| \quad (2.50)$$

where N is the number of entries, and $\hat{y}$ and $\bar{y}$ are the predicted and the mean values of y , respectively.

Adsorption energy in pure metals

Pure metals have always been in the top three types of effective catalysts in the Hydrogen Economy (specifically in the HER and the ORR). As a first approach to solve the problem of finding substitutes to replace Pt, we aim to predict the catalytic activity of different pure metals by calculating the adsorption energy of the adsorbates involved in the reactions (Bell-Evans–Polanyi principle, section 1.4.1). Complimentary, the effect of Elastic Strain Engineering on those surfaces is also illustrated in this chapter.

3.1 Adsorption energies of H, O, and OH

As explained in section 1.5, the three adsorbates present in the HER and the ORR at acidic media, are H, O, and OH. DFT calculations (following the methodology explained in Chapter 2) were performed in 11 transition metals from the groups 9th to 12th in the periodic table with either fcc (Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au) or hcp (Co, Zn, Cd) structure. The corresponding equilibrium bulk lattice constants are shown in Tables 2.2 and 2.3 for fcc and hcp metals, respectively.

The adsorption of H, O, and OH was modeled on four-layer slabs with the (111) surface facet in the fcc metals and the (0001) surface facet in the hcp metals. These surfaces were chosen because they have the minimum surface energy and stand for the most stable surfaces for each lattice [118]. The (2x2) slab supercells with four layers of atoms perpendicular to the surface were generated with the Atomic Simulation Environment (ASE) from the equilibrium lattice parameters. The periodic slabs were separated by 10 Å of vacuum (Figure 2.5) in the direction perpendicular to the surface. Adsorption energies were calculated for each chemical species assuming a coverage of 1/4 monolayers.

Firstly, adsorption energies were computed in the absence of applied strains in all the available positions for all studied metals. The four possible positions in which H, O, and OH can be adsorbed onto the (111) fcc and the (0001) hcp surfaces are shown in figure 3.1 a-b and c-d, respectively. They are labeled H, F, O, and B in the figure and stand for the HCP, FCC, ONTOP, and BRIGDE positions on the surfaces, respectively. It was found

System	F	H	O	System	F	H	O	System	F	H	O
H/Ni	-0.52	-0.50	0.06	O/Ni	-3.13	-3.03	-1.29	OH/Ni	0.03	0.57	1.04
H/Cu	-0.25	-0.23	0.39	O/Cu	-2.68	-2.54	-0.82	OH/Cu	0.14	0.18	1.05
H/Pd	-0.54	-0.51	-0.01	O/Pd	-2.16	-1.99	-0.58	OH/Pd	0.71	0.85	1.64
H/Ag	0.17	0.18	0.73	O/Ag	-1.38	-1.27	0.13	OH/Ag	0.72	0.75	1.57
H/Pt	-0.49	-0.43	-0.42	O/Pt	-2.16	-1.75	-0.73	OH/Pt	1.19	1.50	1.91
H/Au	0.09	0.14	0.39	O/Au	-0.98	-0.72	0.50	OH/Au	1.52	1.58	2.22
H/Rh	-0.53	-0.53	-0.25	O/Rh	-2.96	-2.84	-1.55	OH/Rh	0.27	0.45	1.15
H/Ir	-0.39	-0.36	-0.47	O/Ir	-2.62	-2.40	-1.52	OH/Ir	0.76	0.98	1.29
H/Co	-0.54	-0.51	0.11	O/Co	-3.34	-3.42	-1.97	OH/Co	-0.13	-0.2	0.55
H/Zn	0.70	0.67	0.81	O/Zn	-2.53	-2.62	-2.59	OH/Zn	0.46	0.37	—
H/Cd	0.80	0.81	0.79	O/Cd	-2.19	-2.24	-2.22	OH/Cd	0.36	0.31	—

Table 3.1: Adsorption energies of H, O, and OH on FCC (F), HCP (H), and ONTOP (O) sites for all the metals. The adsorption surface of the fcc metals (Ni, Cu, Pd, Ag, Pt, Au, Rh, and Ir) was the (111) plane, whereas adsorption occurred at the (0001) plane in the hcp metals (Zn, Cd, and Co). The adsorption energies for OH in Zn and Cd in the ONTOP position are not indicated because the molecule moves towards the BRIDGE position. The energy values are expressed in eV.

that adsorbates at BRIDGE position diffused towards more favorable positions and they were omitted from this study. In the case of OH adsorption, the molecule was placed perpendicularly to the adsorption plane with the O atom closer to the surface.

The adsorption energies for H, O, and OH onto the surfaces, calculated following the equations in section 2.1.4, are shown in Table 3.1 for the different adsorption sites. There are very large differences between the strongest (FCC) and the weakest (ONTOP) adsorption sites in many cases. For instance, the adsorption of O onto Ni is associated with an energy of -3.13 eV in the FCC position but is reduced to -1.20 eV on the ONTOP site. On the contrary, the differences in adsorption energies between the FCC and HCP positions are much smaller. These trends are in agreement with previous experimental and theoretical results [169, 195, 198, 206]. For instance, the difference with the calculated adsorption energy of H/Co in [195] was only 0.03 eV and 0.23 eV in the case of OH/Cu adsorption [198]. Moreover, the FCC position was found to be the most favorable adsorption site (most negative energy) in the fcc metals while the FCC and HCP positions had very similar adsorption energies in the hcp metals. The ONTOP site presented the least favorable adsorption energy in all cases, except for Ir.

Regarding the different adsorbates, the adsorption process of O is always exothermic for the FCC and HCP positions whereas the adsorption of OH is an endothermic process in most cases (with the exception of Co) with positive adsorption energies. The adsorption energies for H are, in general, smaller in absolute values and can be endothermic or exothermic depending on the transition metal.

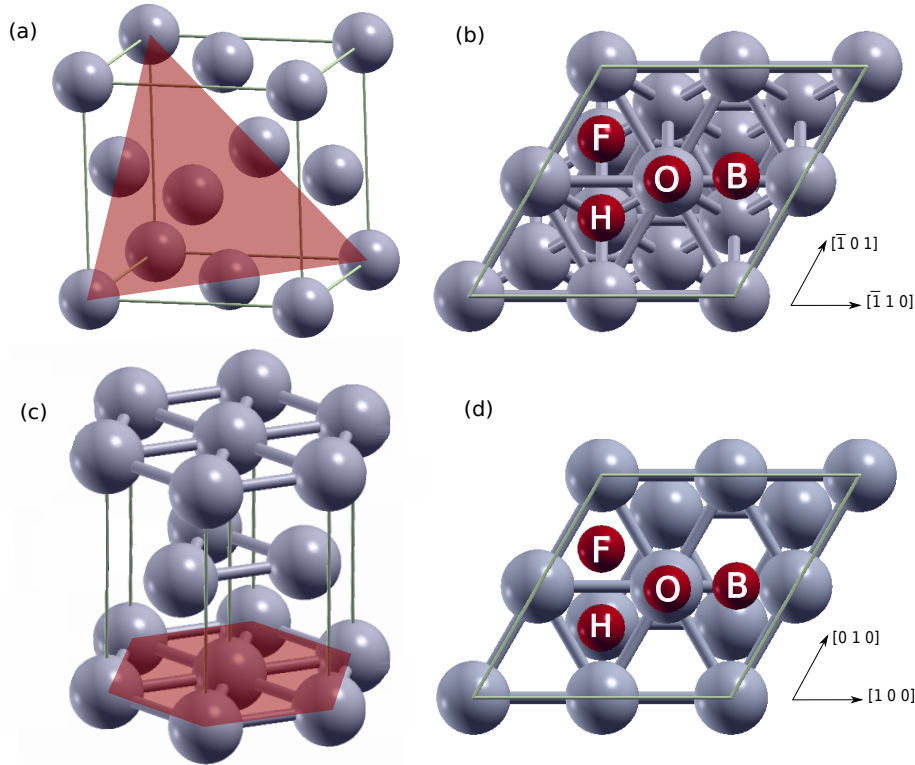


Figure 3.1: (a) fcc unit cell. The (111) plane is shadowed in red. (b) Perpendicular view to the (111) plane of the fcc lattice showing the binding sites for adsorbates. (c) hcp unit cell. The (0001) plane is shadowed in red. (d) Perpendicular view to the (0001) plane of the hcp lattice showing the binding sites for adsorbates. The red circles in (b) and (d) denote the binding sites and the labels 'H', 'F', 'O', and 'B' represent the HCP, FCC, ONTOP, and BRIDGE positions, respectively.

3.2 Effect of elastic strain on the adsorption energy

3.2.1 Stability limits

The mechanical stability limits of fcc Cu and Pt slabs under biaxial tension and compression as well as pure shear were determined from the harmonic phonon spectra (Figures 3.3 and 3.4). Calculations were limited to 5%, 10%, and 15% biaxial strains in tension, -5% and -10% biaxial strains in compression, and 10% strain in shear because of the high computational cost. The phonon density of states showed negative frequencies in the fcc slabs subjected to 15% biaxial tension in Pt and to 10% biaxial tension in Cu. Similarly, negative frequencies appeared in both metal surfaces at -10% biaxial compression or shear. In the case of the (0001) slabs of the hcp metals, it was found that the order in the supercell was lost for smaller strains, indicating that the mechanical instabilities triggered by compressive or shear strains in (0001) hcp slabs develop sooner than in (111) fcc slabs.

Taking into account the theoretical values of the stability limits obtained with the phonon calculations, it was decided to explore the effect of elastic strains on the adsorption ener-

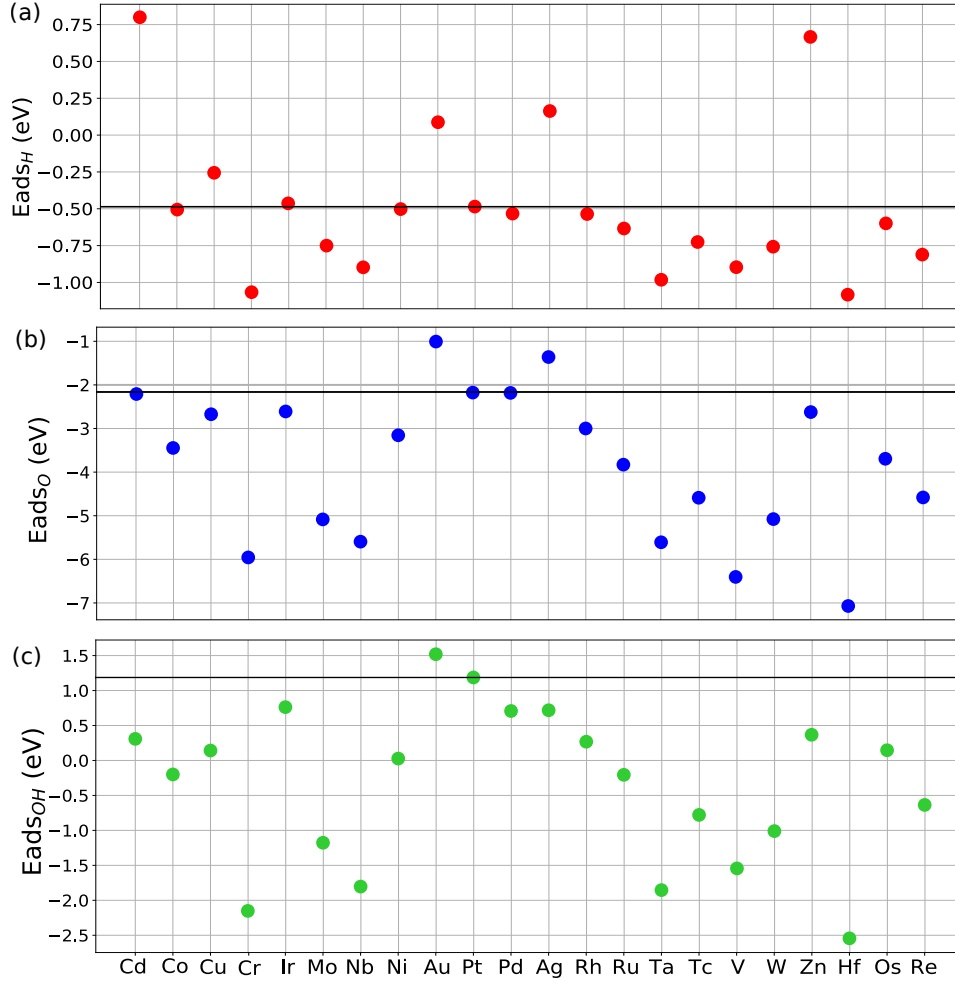


Figure 3.2: Adsorption energies for (a) H, (b) O, and (c) OH in different transition metals at the most favorable adsorption site. The horizontal black line represents the adsorption energy in Pt (111) at FCC position.

gies in the (111) fcc slabs up to 8% tensile strain, -5% compressive strain, and 4% shear strain. In the case of (0001) hcp slabs, only the effect of tensile strains (and of small compressive strains in particular cases) on the adsorption energy was analyzed.

3.2.2 Influence of strains on the optimum adsorption site

The effect of mechanical strains (either uniaxial, biaxial, or shear) on the adsorption energies of H and O onto the different adsorption sites (FCC, HCP, ONTOP) were determined by DFT calculations in Pt. The results are plotted in Figure 3.5 for either uniaxial ($\epsilon = \epsilon_1$, $\epsilon_2 = \gamma = 0$) or biaxial ($\epsilon = \epsilon_1 = \epsilon_2$, $\gamma = 0$) deformations in the range -3% up to 8%, and for shear strains γ in the range 0% to 4% ($\epsilon_1 = \epsilon_2 = 0$), in agreement with the limits indicated above.

The same behavior can be observed for all the adsorption sites and adsorbates: compres-

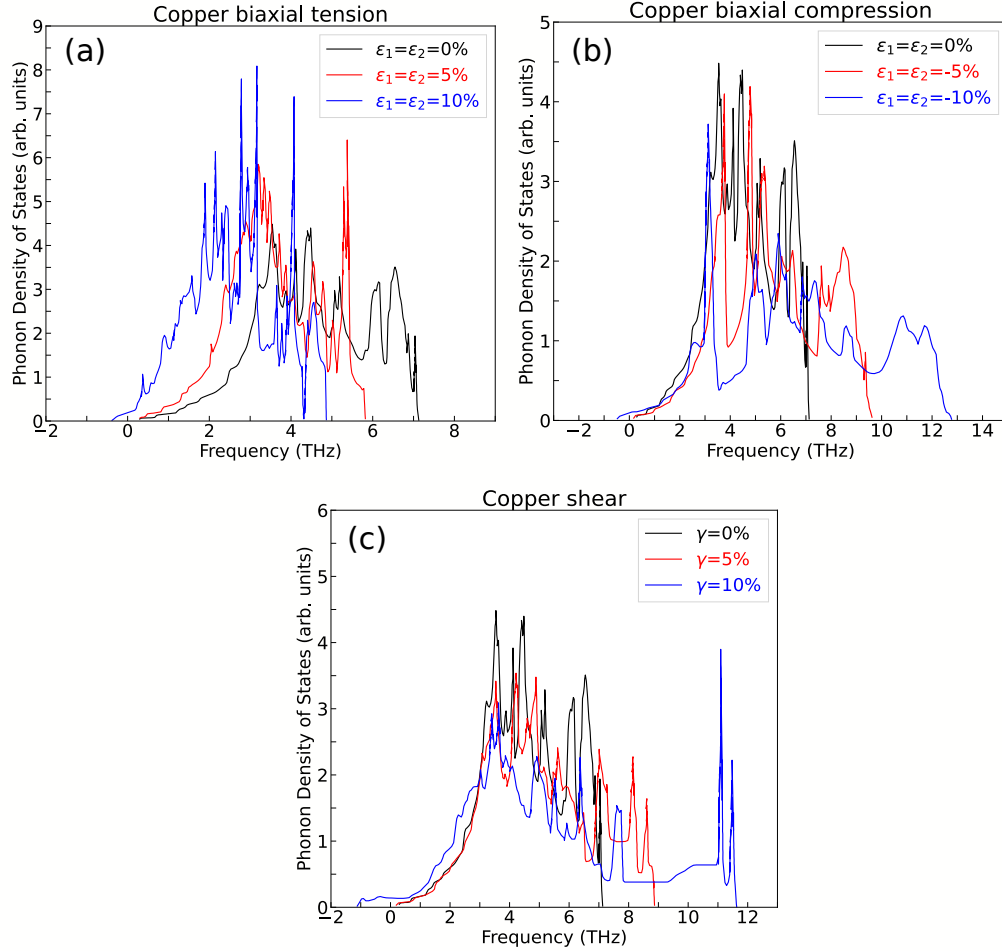


Figure 3.3: Phonon density of states for the (111) fcc Cu slab subjected to: (a) biaxial tensile strains. (b) biaxial compressive strains. (c) Shear strains.

sive strains increase the adsorption energy (less negative and, therefore, adsorption is less favorable) while tensile strains lead to the opposite behavior. Moreover, the variation in adsorption energy with strain is always higher in the case of biaxial deformation. In addition, shear deformations behave as compressive deformations and increase the adsorption energy. The only exception to these trends is found in the adsorption energy of H onto the ONTOP position subjected to very large biaxial tensile strains ($> 5\%$), which lead to a slight increase in the adsorption energy. This difference may be caused by the proximity to the instability limits of the slab at this strain.

The effect of mechanical strains on the adsorption energy of O is higher than that of H but it should be noted that the absolute values of the adsorption energies are also much higher in the former. In addition, the effect of mechanical strains is similar for all the adsorption sites for a given adsorbate. Thus, the application of mechanical strains does not change the most favorable adsorption site for H and O in Pt, which is always FCC. Similar results were obtained for the (111) surfaces of other fcc metals, while the optimum adsorption site for (0001) surfaces of hcp metals is the HCP and it is also independent of the strain state.

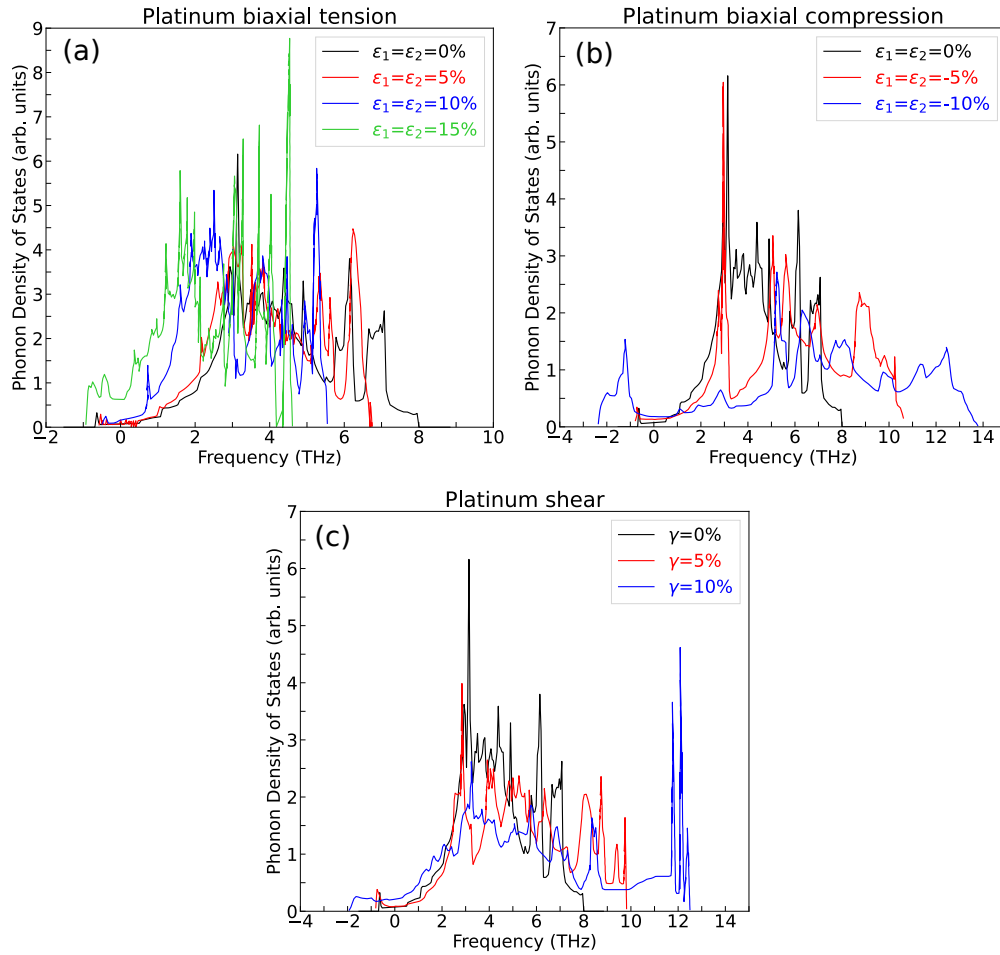


Figure 3.4: Phonon density of states for the (111) fcc Pt slab subjected to: (a) biaxial tensile strains. (b) biaxial compressive strains. (c) Shear strains.

3.2.3 Influence of strains on the adsorption energy

The analysis of the influence of mechanical strains on the adsorption energy of H, O, and OH was focused on the FCC sites of (111) fcc surfaces and on the HCP sites of the (0001) hcp surfaces, which are the most favorable locations for adsorption.

The effect of mechanical strain (either uniaxial, biaxial, or shear) on the adsorption energies of H, O, and OH on the FCC sites of the (111) surfaces of eight fcc transition metals (Cu, Pt, Ni, Au, Ir, Rh, Pd, and Ag) is plotted in Figure 3.6. The corresponding results on the HCP sites of the (0001) surfaces are plotted for Co, Zn, and Cd in Figure 3.7. As indicated above, the application of compressive and shear strains was restricted in hcp metals because of the development of instabilities in the supercell.

The highest (less favorable) adsorption energies are always found for OH while the lowest (more favorable) are reported for O. Adsorption energies for H are smaller (in absolute values) than those calculated for O and OH in all metals, following the trends reported

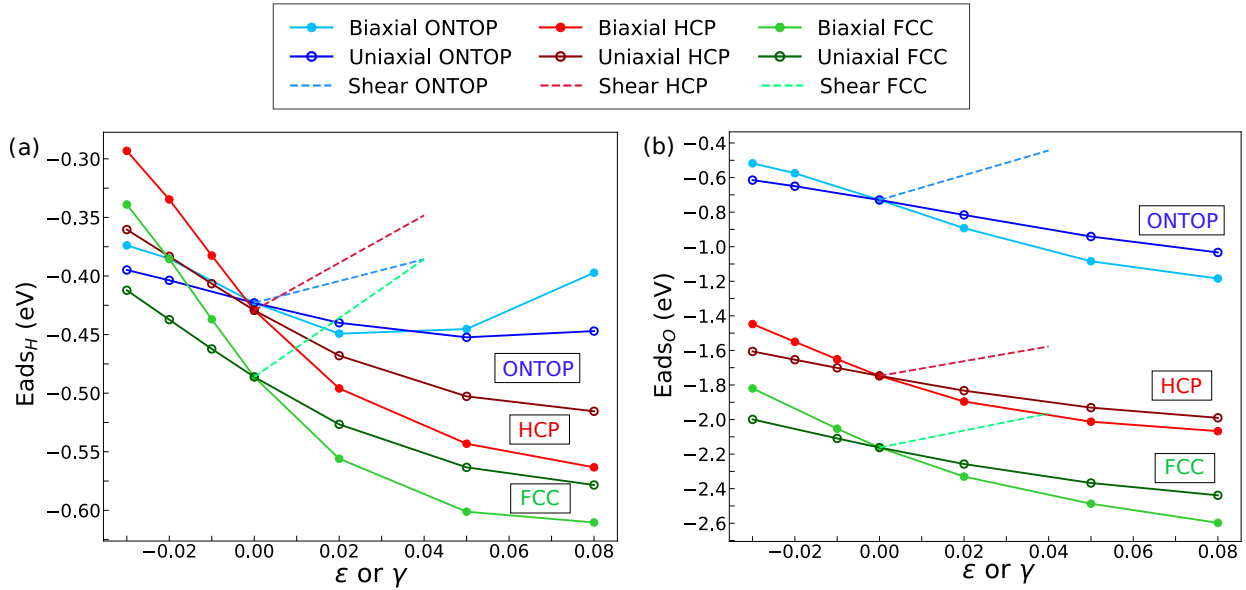


Figure 3.5: Effect of strains (either uniaxial, biaxial, or shear) on the adsorption energy of (a) H, E_{ads_H} and (b) O, E_{ads_O} onto different sites of (111) Pt surfaces.

above for Pt. In addition, the adsorption energies increase (become less negative) with compressive strains and decrease (become more negative) with tensile strains, while biaxial deformations have a stronger influence than uniaxial deformation on the adsorption energy for the same strain. Shear strains increase slightly the adsorption energies in all cases. For a given metal, the effect of mechanical strains on the adsorption energy of O and OH is quite similar, very likely because adsorption is dominated by the larger O atom.

The variation in adsorption of energy of O and OH with strain is significantly higher than that of H and these differences can be attributed to the larger atomic radius of the O atom. The additional p -orbitals increase the size of the electronic environment and, therefore, the overlap with the d -band structure of the metals. The presence of p -electrons further apart from the nucleus favors the interaction with the d -electrons of the surfaces.

Indeed, the effect of mechanical strains on the adsorption energies depends on the metal. Noble metals, such as Au and Pt, show the highest sensitivity to the strain while Ni shows much lower sensitivity. It is also worth noting that the adsorption of H onto Co is not affected by either uniaxial or biaxial strains in the range - 5% to 8% but the largest changes in the adsorption energy of O and OH (> 0.5 eV) are found in Co for the same strain range.

The trends observed for the adsorption energies in this work are in agreement with the predictions of the d -band model (section 1.2.2). This theory states that the more favorable adsorption energies related to tensile and the less favorable ones corresponding to compressive and shear strains can be explained in terms of displacements in the d -band center [93, 94, 182, 206]. Indeed, the d -band theory indicates that tensile strains shift the d -band center towards higher energies for transition metals with more than half-filled d -bands. A higher d -band center results in stronger bonding and leads to more favorable adsorption energies, while compression and shear strains produce a shift towards a lower d -band

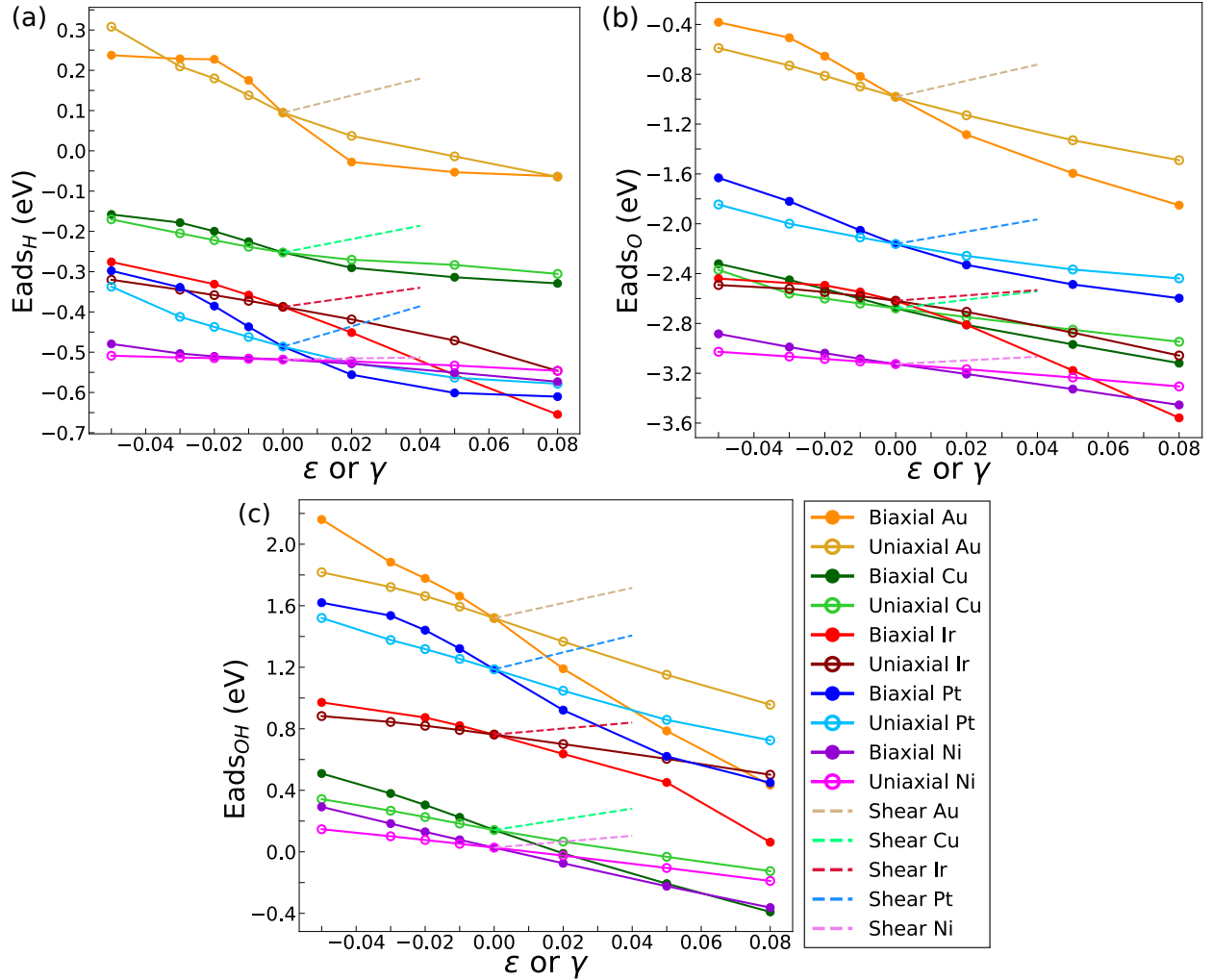


Figure 3.6: Effect of strain (either uniaxial, biaxial, or shear) on the adsorption energy of (a) H, E_{ads_H} ; (b) O, E_{ads_O} , and (c) OH, $E_{ads_{OH}}$ onto the FCC sites of (111) surfaces of fcc transition metals. Curves for Ag, Pd, and Rh are omitted because they overlap with the curves for Au, Pt, and Ni, respectively.

center and lead to less favorable interactions.

Separate curves for all metals with strain can be found in the Appendix Chapter A for H (Figures A. 8.3 and A. 8.4), O (Figures A. 8.5 and A. 8.6), and OH (Figures A. 8.7 and A. 8.8).

3.2.4 Influence of strains on the distance metal-adsorbate

A study of the variation of the distance metal-adsorbate with strain was carried out to understand the adsorption process for H and O atoms in more detail. In accordance with previous studies [317], the distance Metal-H at equilibrium was found to be 1.86 Å, 1.71 Å, and 1.73 Å for Pt, Ni, and Cu, respectively. Ni is a 3d metal, in the same row as Cu; this

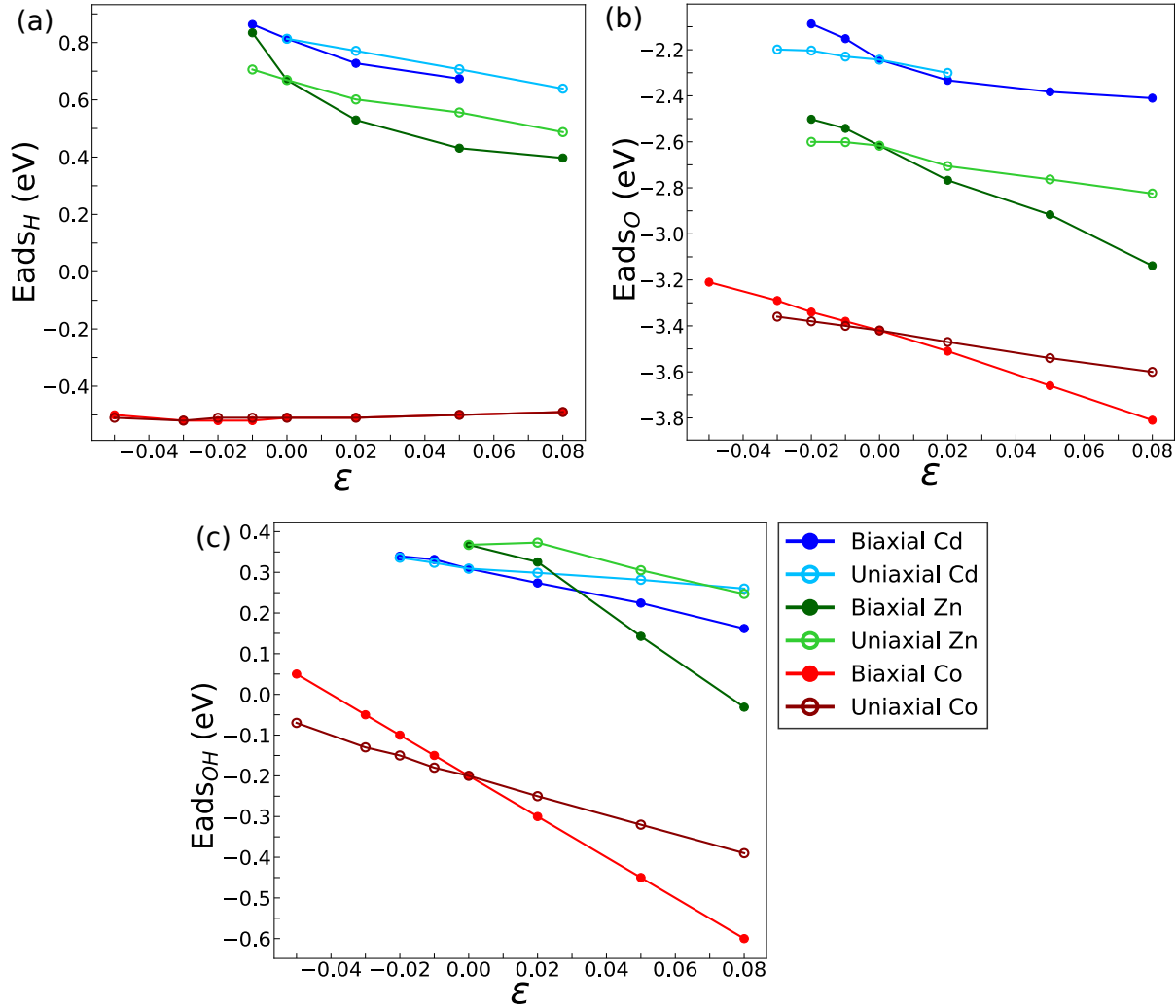


Figure 3.7: Effect of strains (either uniaxial or biaxial) on the adsorption energy of (a) H, E_{ads_H} ; (b) O, E_{ads_O} and (c) OH, $E_{ads_{OH}}$ onto the HCP sites of (0001) surfaces of hcp transition metals.

entails that its orbitals are compact, and the interaction with the H atom falls off rapidly with distance [240] even though the adsorption energy is quite favorable (see Table 3.1). Pt, by contrast, belongs to the fifth-row transition metals with more diffuse d -orbitals. This allows the interaction with the adsorbates at larger distances.

Figure 3.8 illustrates how the application of strains affects not only the variation of the adsorption energy but also to the interaction metal-adsorbate with distance. The adsorption energy for hydrogen was calculated by placing the adsorbate at 8 different fixed positions starting from the surface and incrementing by 0.05 Å the H-metal distance. A more negative adsorption energy corresponds to a more energetically favorable situation. As the lattice constant decreases, the equilibrium position moves slightly towards larger metal-H distances, whereas the interaction is reduced to shorter distances with tension, in agreement with previous observations [32, 130, 228, 322, 355]. In other words, the optimum

distance of H adsorption varies with the application of strain. The increase in the interaction strength with tensile strain makes the stretched slab considerably more reactive towards H and O atoms [182].

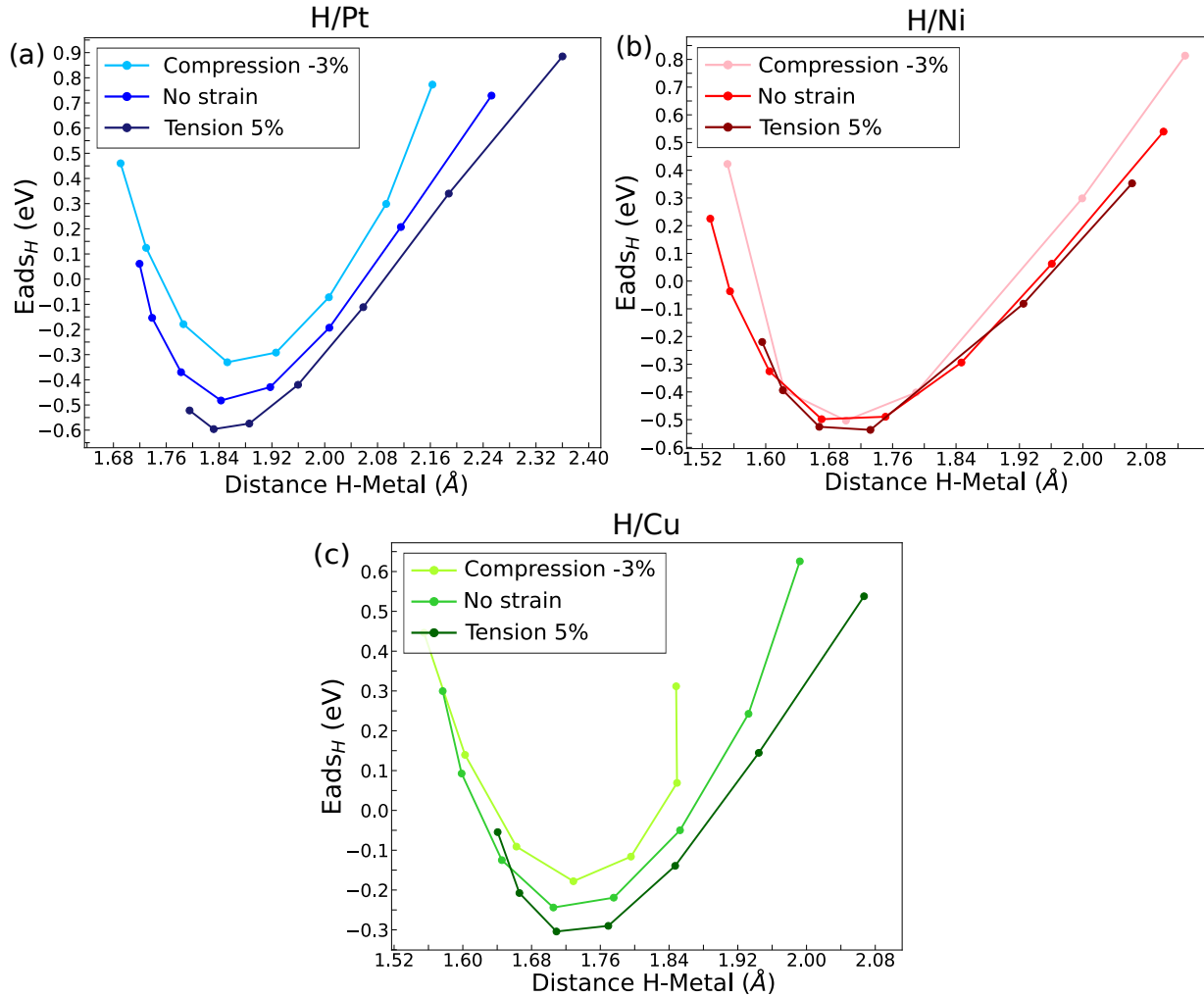


Figure 3.8: Hydrogen adsorption energy as a function of the metal-adsorbate distance for (a) Pt, (b) Ni, and (c) Cu under biaxial 3% compression and 5% tension.

3.2.5 Relationship between adsorption energy and hole area

While the *d*-band model provides a qualitative explanation of the trends reported in Figures 3.6 and 3.7, models that are able to quantify the effect of mechanical strains on the adsorption energy are lacking. In this respect, the adsorption energies of H, O, and OH in the fcc and hcp transition metals are plotted in Figures 3.9 and 3.10, respectively, as a function of the area of hole (either FCC or HCP) at which adsorption takes place. The area of the hole was calculated from the length of the sides of the triangle which conform the FCC and the HCP adsorption sites (Figure 3.1 b and d), which depends on the deformation gradient F applied to the supercell. After relaxation, the area of the hole was

measured again using the code XCrysDen [137] and it was found that the differences in the hole area between the unrelaxed and relaxed structure were negligible.

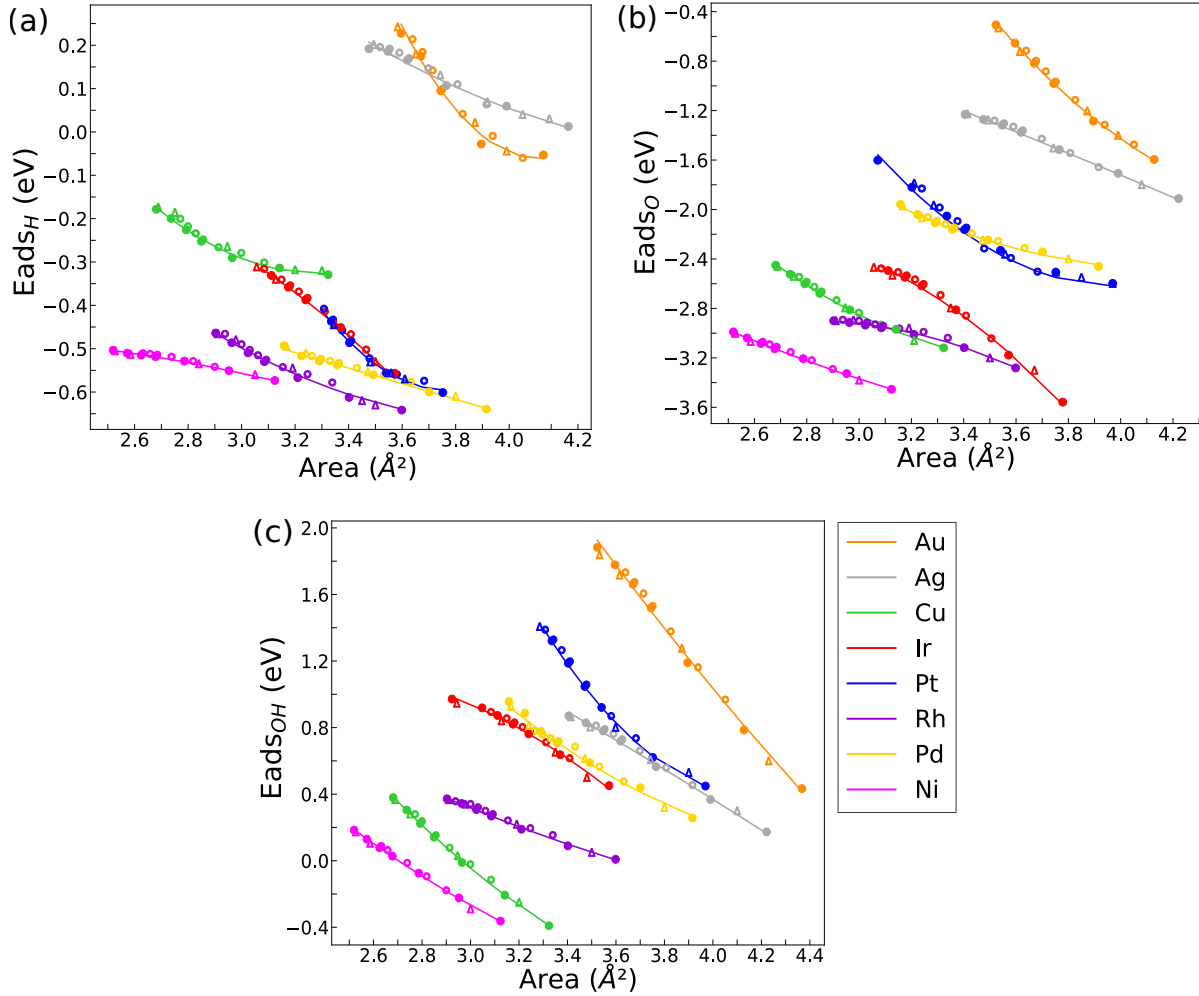


Figure 3.9: Adsorption energies as a function of the area of the adsorption hole that is a function of the applied deformation gradient. (a) H adsorption at FCC positions of (111) surfaces of fcc transition metals. (b) O adsorption at FCC positions of (111) surfaces of fcc transition metals. (c) OH adsorption at FCC positions of (111) surfaces of fcc transition metals. Solid and open circles stand for the adsorption energies calculated under biaxial and uniaxial strains, respectively, while open triangles refer to adsorption energies under shear strains or a combination of shear and axial strains. The lines show the best fit to the DFT results in the strain ranges indicated in Figure 3.6.

The adsorption energies under biaxial strains (solid circles), uniaxial strains (open circles), and a combination of shear and axial strains (open triangles) are plotted for each metal in these figures. They show that the actual adsorption energy only depends on the area of the hole and that the effect of different strains can be superposed, i.e. different combinations of normal and shear strains that lead to the same hole area have the same effect of the adsorption energy. Moreover, the relationship between the adsorption energy and the

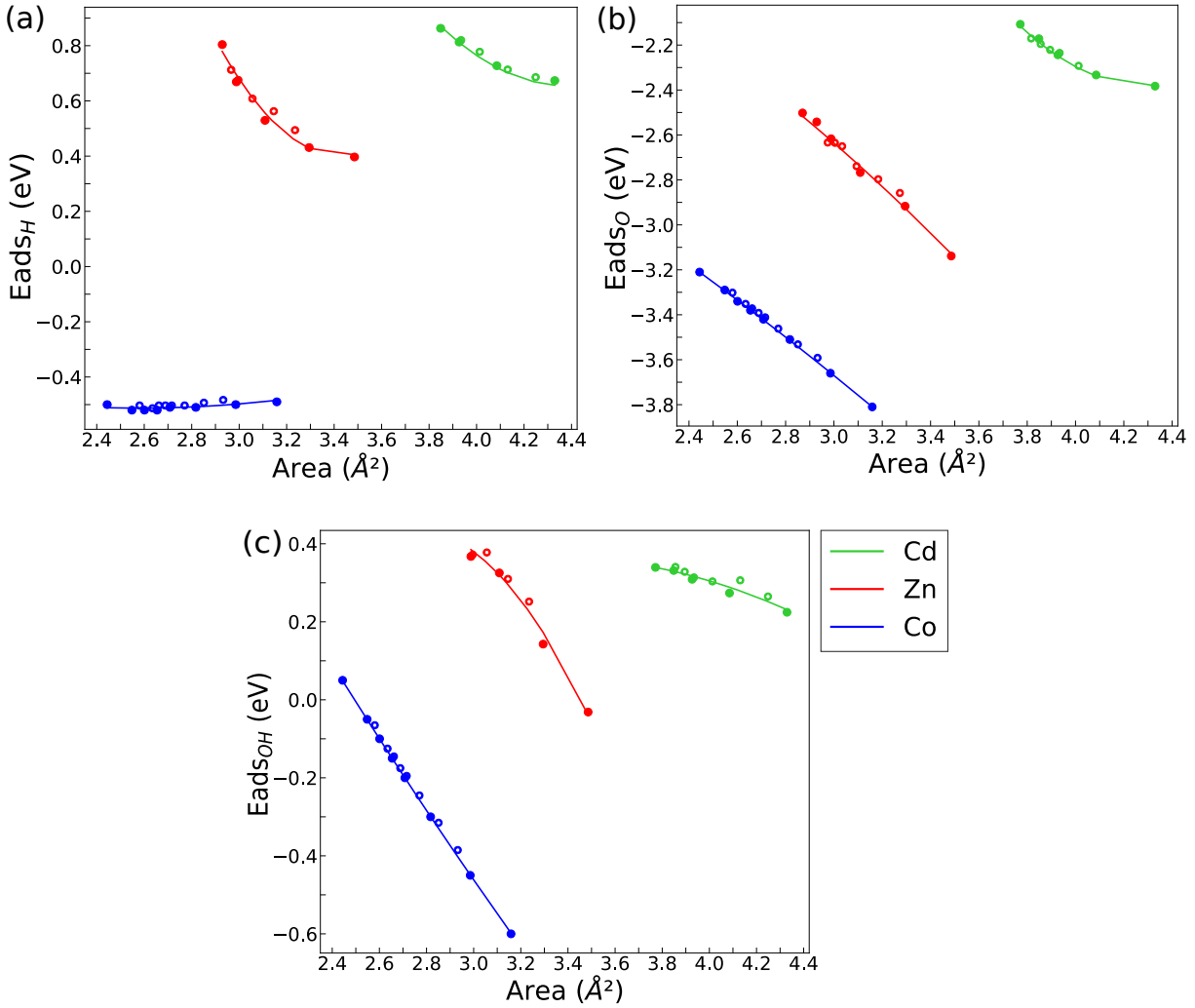


Figure 3.10: Adsorption energies as a function of the area of the adsorption hole that is a function of the applied deformation gradient. (a) H adsorption at HCP positions at (0001) surfaces of hcp transition metals. (b) O adsorption at HCP positions at (0001) surfaces of hcp transition metals. (c) OH adsorption at HCP positions at (0001) surfaces of hcp transition metals. Solid and open circles stand for the adsorption energies calculated under biaxial and uniaxial strains, respectively, and lines show the best fit to the DFT results in the strain ranges indicated in Figure 3.7.

hole area is fairly linear in most cases (although the DFT results are better approximated by a parabola in several cases). Finally, the data in Figures 3.9 and 3.10 allow to make a fast and accurate estimation of the effect of mechanical strains on the adsorption energies of H, O, and OH for any of these transition metals from the geometrical analysis of the change in either FCC or HCP hole area under the application of a deformation gradient $\mathbf{F}$. Because the hole area does not change during relaxation, it is not necessary to perform the DFT simulations to determine the adsorption energy.

The curves corresponding to the 1st-row transition metals (Cu, Ni, Zn, and Co) in Figures 3.9 and 3.10 are located in the region with smaller hole areas because of the smaller size of these atoms. In addition, Ni and Co also show very low adsorption energies, while the adsorption energies of Cu and Zn are much higher for similar hole areas. The curves corresponding to the 2nd and 3rd-row transition metals (Au, Ag, Ir, Pt, Rh, Pd, and Cd) are spread towards the right in Figures 3.9 and 3.10 as a result of the larger atomic radius. In general, the adsorption energies become more positive (less favorable) when going from left to right in the periodic table periods. This tendency is related to the electronic density of the metals, whose d -bands become more populated as the atomic number of the metal increases in a period. Thus, as a general rule, the adsorption process is favored by a reduction in the number of valence electrons in the metal.

In most cases, the relationship between the adsorption energy and the hole area is linear, although a parabola is more appropriate in several cases. Moreover, the slope of the linear fit is similar for most transition metals and large differences are only found in the case of H adsorption on Ni, which is almost insensitive to the applied strains. These results indicate that the mechanisms that control the adsorption of H, O, and OH are very similar and the differences that appear in these figures are ultimately related to the particularities of d -orbitals of each metal and/or to magnetic effects.

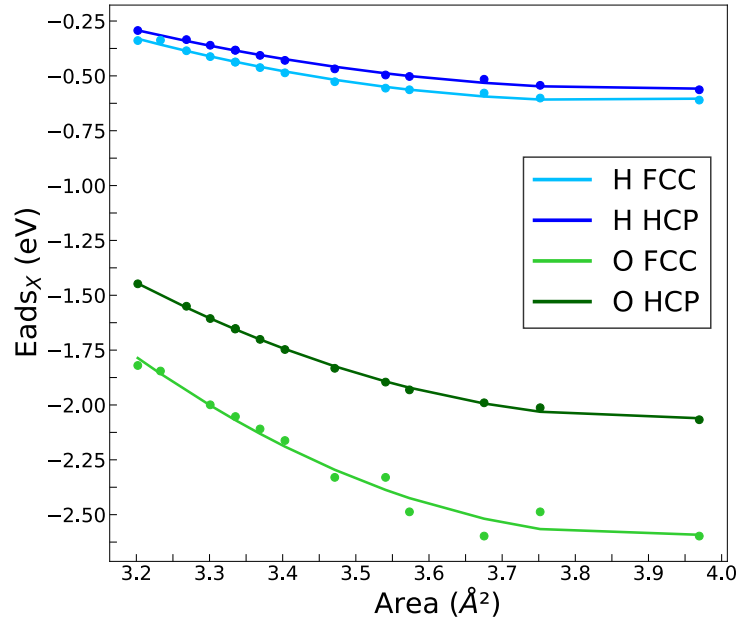


Figure 3.11: Adsorption energy of H and O in Pt as a function of the area of the FCC and the HCP sites from 5% compression to 8% tension.

Finally, the adsorption energies of H and O onto the HCP position of (111) Pt surfaces were determined for different magnitudes of axial strains to check whether the relationship between adsorption energy and hole area could be extrapolated to other adsorption sites. They are plotted in Figure 3.11 together with the adsorption energies onto the FCC positions of (111) Pt surfaces. As observed, the variation of E_{ads} with the area of the adsorption site follows the same tendency for both the FCC and the HCP positions in H and

O adsorption. This supports the previous findings: for a given adsorption site, the effect of mechanical strains on the adsorption energy of transition metals only depends on the area of the adsorption hole.

3.3 Electronic structure

It is known that changes in the surface geometry are accompanied by changes in the surface electronic structure [94]. To quantify these effects, the projected density of the states (PDOS) on the d -band onto the surface of all metals and adsorbates was analyzed to explore the electronic origin of the adsorption energy-hole area relationship. The PDOS corresponding to the (111) fcc Pt slab subjected to biaxial tensile ($\epsilon = 2\%$ and 8%) or compressive ($\epsilon = -2\%$) strains are plotted in Figure 3.12 a and compared with the PDOS at $\epsilon = 0$. The overlap of metal d -states at neighboring sites will either increase or decrease when a surface undergoes compressive or tensile strains, and so will the d -bandwidths in order to maintain a constant filling. Thus, compressive or tensile strains lead to downshifts or upshifts of the d -band centers, respectively [130], as shown in figure 3.12 a. The variations of E_{ads_H} and the d -band center with strain for a Pt fcc(111) surface is shown in the Appendix Chapter A Figure A. 8.2.

The PDOS onto the 5d orbitals of a (111) fcc Pt surface after the adsorption of a H atom onto the FCC site and the ONTOP site are plotted in Figure 3.12b, together with the PDOS of a hydrogen molecule and of the clean (111) fcc Pt slab. The adsorption of an H atom on the ONTOP position generates strong electronic changes, which in turn are reflected in the PDOS. In contrast, the PDOS when adsorption takes place onto the FCC site remains practically identical to the one corresponding to the clean (111) Pt slab, with the only difference being a small shoulder at -2 eV. This variation in the PDOS can be considered negligible, as compared with the electronic changes produced by the application of strain, and, therefore, allows to establish a direct link between the adsorption energy with the geometrical changes induced at the FCC adsorption site by the application of strain. The PDOS of a (111) fcc Pt surface after the adsorption of an O atom onto the FCC site and the ONTOP site together with the PDOS of an oxygen molecule, and of the clean (111) fcc Pt slab are plotted in Figure 3.12c and very similar trends are observed. The PDOS is localized in a single peak on the left after the adsorption of the O atom on the ONTOP position, whereas the PDOS becomes broader but maintains its original shape after the adsorption of the O atom onto the FCC position. Similarly, the PDOS of a (111) fcc Pt surface after the adsorption of OH onto the FCC site and the ONTOP site are plotted in Figure 3.12d together with the PDOS of a hydrogen and a water molecule, and of the clean (111) fcc Pt slab. The trends are equivalent to those observed in Figs. 3.12b and c. While the adsorption of OH at ONTOP position produces significant changes in the PDOS, the adsorption of OH at FCC position leads to negligible changes in the PDOS as compared with that of the clean (111) Pt slab. The above results suggest that the analysis of the electronic structure of the clean surface slabs may be enough to determine the effect of strain on the adsorption energy of H, O, and OH in the transition metals studied in this investigation. Moreover, the application of strain does not modify the shape of the PDOS curves but only leads to a shift of the energy levels (Figure 3.12a). Thus, the Fermi level

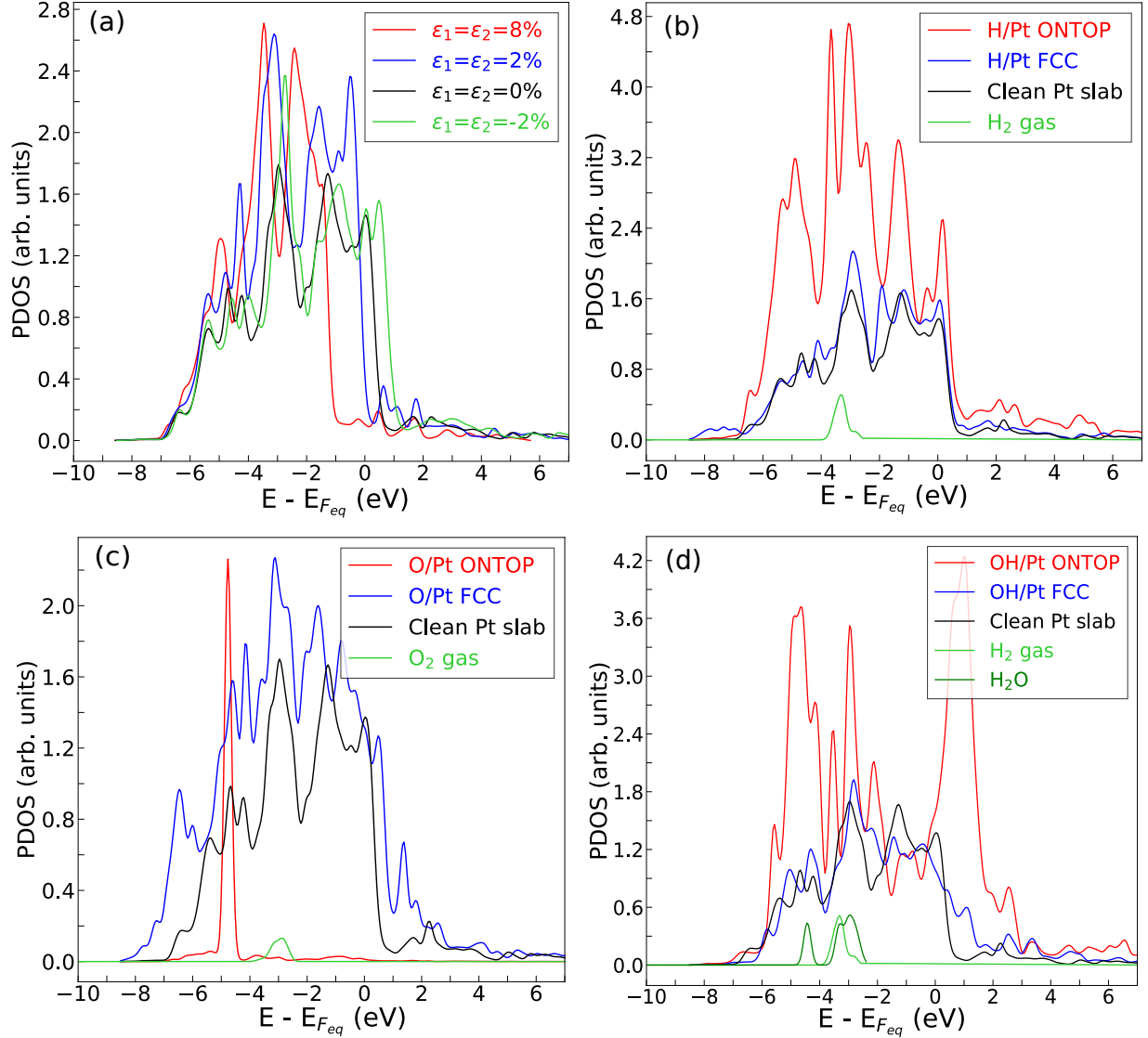


Figure 3.12: (a) PDOS onto the 5d orbitals of the (111) fcc Pt surface slab subjected to biaxial strain states characterized by $\epsilon = -2\%$, 0% , 2% , and 8% . (b), (c), and (d) PDOS of the 5d orbitals of the (111) fcc Pt surface with H, O, and OH, respectively, adsorbed at FCC and ONTOP positions. The corresponding PDOS of the 5d orbitals of the clean (111) fcc Pt slab, the H_2 molecule, the O_2 molecule, and the H_2O molecule at gaseous state are also included for comparison. The energy values are referenced to the Fermi level of the (111) Pt slab when $\epsilon = 0$ ($E_{F_{eq}} = 3.5668$ eV).

could be used as a metric of the electronic changes in the slabs upon the application of mechanical strains and, eventually, of the adsorption energies.

This hypothesis is supported by the results in Figures 3.13a, b, and c in which the adsorption energies as a function of the mechanical strains are plotted as a function of the Fermi level of the clean, strained surface slabs for H, O, and OH adsorbates, respectively. The

	H		O		OH	
	m	b	m	b	m	b
Ni	0.06	-0.64	0.37	-3.93	0.45	-0.94
Cu	0.14	-0.49	0.59	-3.71	0.67	-1.04
Pd	0.12	-0.68	0.41	-2.64	0.57	0.02
Ag	0.18	-0.12	0.45	-2.08	0.52	-0.08
Pt	0.19	-1.14	0.43	-3.67	0.63	-1.08
Au	0.27	-0.35	0.96	-2.65	0.91	-0.10
Rh	0.10	-0.94	0.15	-3.61	0.21	-0.61
Ir	0.18	-1.18	0.52	-4.93	0.32	-0.67
Co	-0.05	-0.50	0.82	-3.69	0.85	-0.48
Zn	0.30	-0.05	0.46	-3.72	0.40	-0.54
Cd	0.28	0.26	0.20	-2.65	0.15	0.03

Table 3.2: Values of coefficients m and b in eq. (3.1) for each transition metal and adsorbate (either H, O, or OH). Data correspond to the best fittings of Figure 3.13.

linear correlation between both magnitudes is obvious for all metals and adsorbates and can be represented by

$$E_{ads_X} = b + mE_F \quad (3.1)$$

where $X = \text{H, O or OH}$ and the coefficients b and m for each pair of adsorbate and transition metal can be found in Table 3.2. It should be noted that E_F in eq. (3.1) stands for the Fermi energy of the clean, strained slab. Obviously, these similarities indicate that the underlying adsorption processes are governed by the same physical mechanisms.

The last step to link the adsorption energy with the area of the adsorption site is to find the relationship between the latter and the Fermi energy. The values of both magnitudes were obtained by DFT calculations on clean, strained slabs of the 11 transition metals plotted in Figure 3.14. The straight lines in this figure are given by

$$E_F = 7.4 - 7.37A + E_F(A_0) \quad (3.2)$$

where E_F is the Fermi energy (in eV), and A is the area of the adsorption site in the surface subjected to a given strain state. $E_F(A_0)$ is the Fermi energy of the surface corresponding to the undeformed state, which is given in Table 3.3 for each transition metal. This equation captures the independent contribution of the metal-ligand (expressed by $E_F(A_0)$) and of the mechanical strain (given by A) to the Fermi energy and, thus, through eq. (3.1) to the adsorption energy for each adsorbate. It should be noted the excellent agreement of this simple linear equation with the DFT calculations for most transition metals indicates that changes in the local electronic environment as a result of strain are better represented by the area of the hole than by the distance between one atom and the different neighbors.

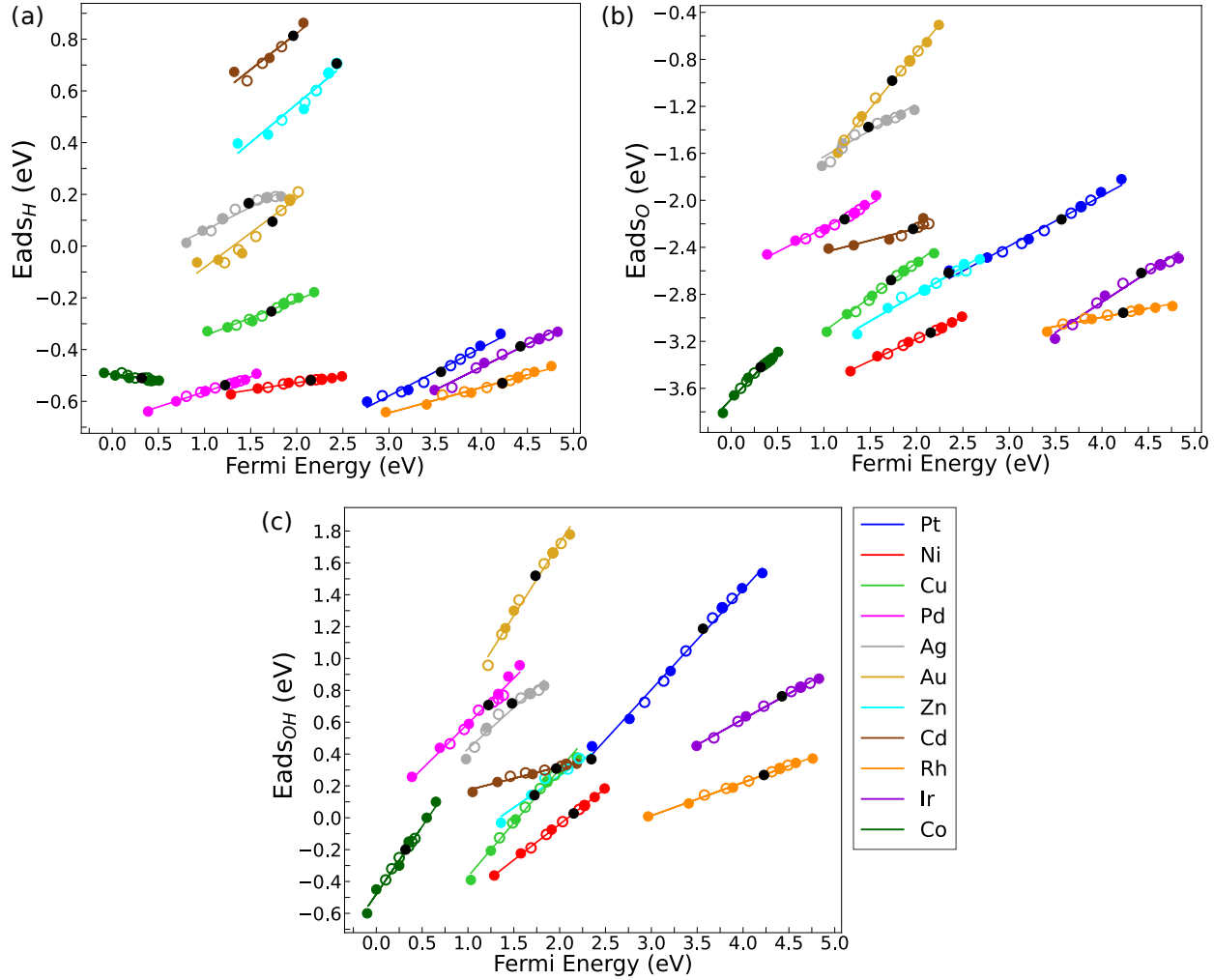


Figure 3.13: Adsorption energies of strained slabs as a function of the Fermi level in the clean, strained slab for all metals. (a) H adsorption. (b) O adsorption. (c) OH adsorption. The adsorption energies were calculated onto the FCC sites on (111) fcc slabs and onto HCP sites of (0001) hcp slabs. Values in both axes are expressed in eV. Solid and open circles represent the biaxial and uniaxial DFT calculations, respectively. The solid lines stand for the fit of the DFT results with equation (3.1). Black circles indicate the adsorption energy without strain.

Moreover, eq. (3.2) provides the explanation of the link between the adsorption energy and the area of the adsorption site in Figures 3.9 and 3.10. The different behavior of Co -that does not follow equation (3.2) -may be due to the magnetic properties of this metal but further research is needed to clarify this point. Moreover, it should be noted that preliminary studies on (110) bcc Cr and (100) bcc V surfaces did not find a clear relationship between adsorption energy, Fermi energies, and the area of the adsorption site. These differences may be attributed to the nature of the *d*-orbitals in these metals, which are less than half or half-filled in metals on the left side of the periodic table. Thus, further research is needed to reach a full understanding of the effect of mechanical strains on the

adsorption properties of transition metals.

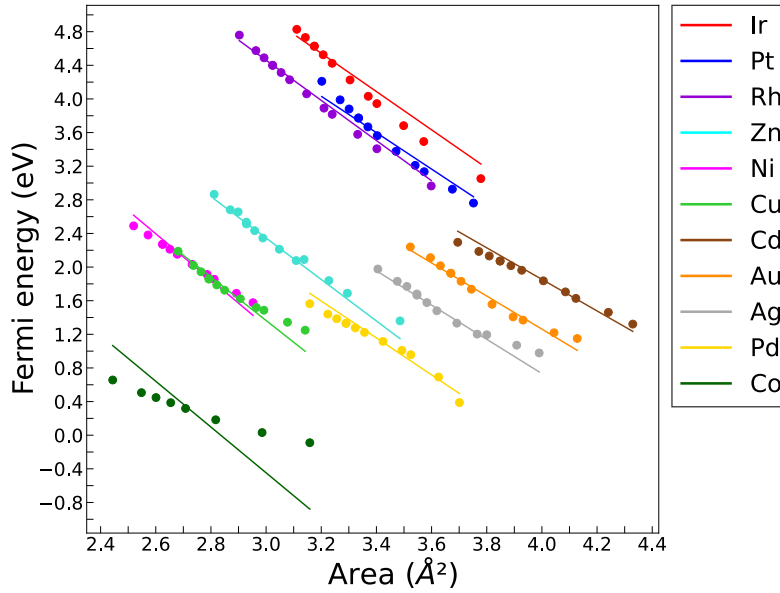


Figure 3.14: Evolution of the Fermi energy, E_F , at the surface of the different transition metals as a function of the area of the adsorption site, A . Circles stand for the results of the Fermi levels corresponding to the clean, deformed slabs obtained by DFT and the straight lines stand for the predictions of equation (3.2).

Metal	Ni	Cu	Pd	Ag	Pt	Au	Rh	Ir	Co	Zn	Cd
$E_F(A_0)$	2.15	1.73	1.22	1.48	3.57	1.74	4.23	4.42	0.32	2.47	1.96

Table 3.3: Fermi energies of clean, undeformed metallic slabs. Values of energy are referred in eV.

3.4 Coverage

In real applications, both the Hydrogen Evolution Reaction (HER) and the Oxygen Reduction Reaction (ORR) typically take place in a saturated environment. Consequently, various adsorbates coexist within electrolyzer cells for hydrogen production and fuel cells for energy generation. Therefore, it is relevant to assess the effect of the ratio of adsorbates to catalyst atoms on the adsorption energy. This ratio, often referred to as coverage, has been shown in numerous studies to significantly impact the adsorption and desorption processes of diverse molecules on metallic surfaces [257, 274].

Additionally, studies indicate that including elastic strains on the catalyst surface has an impact on the coverage of adsorbates [103, 283]. For instance, He et al. [103] studied the strain-induced decrease in the H/Pt adsorption energy as a function of the CO coverage.

They found that tensile strains can shift the H adsorption energy more positive at CO-saturated surfaces rather than at clean surfaces. Temmel et al. [283] performed cyclic voltammetry experiments for CO oxidation in Pt under elastic strains. They observed how the application of strains reduced the OH coverage and increased the specific ORR activity, as more active sites were available.

Following the definition provided by the International Union of Pure and Applied Chemistry (IUPAC), surface coverage, denoted as θ , represents the ratio of adsorbed molecules on a surface to the molecules in a complete monolayer on that surface. Thus, the coverage on the surface of a supercell can be defined as follows:

$$\theta = \frac{\text{Number of adsorbates}}{\text{Number of surface atoms}} \quad (3.3)$$

where the surface atoms are those occupying the top surface layer in the supercell. The coverage (θ) is quantified in monolayers (ML). For instance, a coverage of 0.25 ML stands for one adsorbate for every four catalyst atoms.

The influence of surface coverage on adsorption was investigated for three adsorbates (H, O and OH) on the (2x2) supercell slab of the Au fcc(111) surface. Au was selected because the application of strains produces significant changes in the adsorption energy of H, O, and OH (Figure 3.6). The number of adsorbates was increased from 1 to 4 leading to coverages ranging from 0.25 monolayers (ML) to 1 ML. It should be noted that as the results presented above considered only 0.25 ML of coverage.

3.4.1 Effect of coverage on the adsorption energy

Without strain

Three distinct coverage monolayers (ML) were examined: 1 ML, 0.5 ML, and 0.25 ML. Correspondingly, the number of adsorbates for each case on the (2x2) slab are 4, 2, and 1, respectively. Only the optimal adsorption sites determined for each adsorbate with a coverage of 0.25 ML were considered in this analysis. The Au(111) surfaces featuring the three different surface coverages at the FCC position for H adsorption are depicted in Figure 3.15.

The adsorption energy taking into account the coverage is calculated by dividing the total energy by the number of adsorbates, n . In the case of the adsorption of H and O, this is expressed as

$$E_{\text{adsX}} = \frac{E_{\text{slab+X}_n} - (E_{\text{slab}} + \frac{1}{2}nE_{\text{X}_2})}{n} \quad (3.4)$$

where X is the adsorbate (H or O), and E_{X_2} is the energy of the molecule X_2 in the gas phase. Analogously, the energy for the adsorption of the OH molecule is calculated as

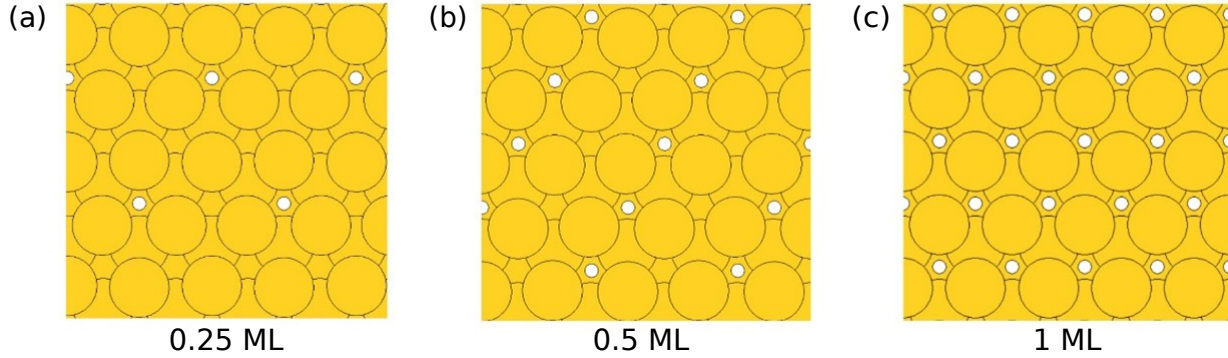


Figure 3.15: Au fcc(111) surface with different surface coverages: (a) 0.25 ML, (b) 0.5 ML, and (c) 1 ML, at the FCC position for the H adsorption.

$$E_{\text{adsOH}} = \frac{E_{\text{slab+OH}_n} - (E_{\text{slab}} + nE_{\text{H}_2\text{O}} - \frac{1}{2}nE_{\text{H}_2})}{n} \quad (3.5)$$

The adsorption energies for the three adsorbates H, O, and OH were only computed for their respective optimum sites. The adsorbates are placed in the FCC position in the case of H and O, and in the BRIDGE site for OH. The adsorption energies in eV for each case are listed in Table 3.4. In the case of H and O, the adsorption energy increases with the surface coverage. This increase is more significant, approximately double, between 0.5 ML and 1 ML than between 0.25 ML and 0.5 ML. This behavior can be explained by the repulsion between the closest adsorbate atoms. In the case of 0.5 ML, this repulsion is larger as the distance between the closest adsorbates is half the one of the adsorbates for 0.25 ML (i.e. 2.94 Å for 0.5 ML and 5.89 Å for 0.25 ML for H). In the case of 1 ML, this distance is not further reduced but the number of adsorbates doubles and the repulsion between adsorbates consequently increases. The adsorption process of H and O is thus less favorable when the coverage increases.

In the case of the OH molecule, the lowest adsorption energy is observed for 0.5 ML of coverage. The adsorption energy is reduced by around 0.2 eV with respect to 0.25 ML, and approximately 0.3 eV compared to the 1 ML configuration. Relevant geometrical differences were observed, as depicted in Figure 3.16. In the three cases, the H atom is tilted towards the FCC position with an angle of around 65° normal to the surface, similar to 0.25 ML of coverage. Nonetheless, in the case of 0.5 ML, the H atoms are oriented in the in-plane direction towards the closest O atom of other OH molecules. The distance between the H and O atoms of distinct OH groups is 2.15 Å. This distance is in the range of strong hydrogen bonds O-H...O [20]. These bonds, absent with 0.25 ML of coverage (O-H...O distances of 5.16 Å), can explain the reduction in the adsorption energy for 0.5 ML with respect to 0.25 ML. In the 1 ML configuration, all the bridge positions are occupied. The H atom of each OH molecule is tilted toward the FCC site like in the case of 0.25 ML. It thus presents two equidistant neighbor O atoms of other OH molecules. O-H...O distances are 2.23 Å so hydrogen bonds could be formed. However, the repulsion between

the now closer O atoms leads to an increase in the adsorption energy. Unlike the case of H and O, a surface coverage of 0.5 ML leads to the lowest adsorption energy of OH onto the Au fcc(111) surface.

	0.25 ML	0.5 ML	1 ML
E_{ads_H}	0.09	0.14	0.26
E_{ads_O}	-0.88	-0.54	0.41
$E_{ads_{OH}}$	1.35	1.16	1.48

Table 3.4: Adsorption energy (in eV) of H, O, and OH on the optimum adsorption site for Au fcc(111) surface at different monolayers (ML). The lowest adsorption energies for each surface coverage are highlighted in bold font.

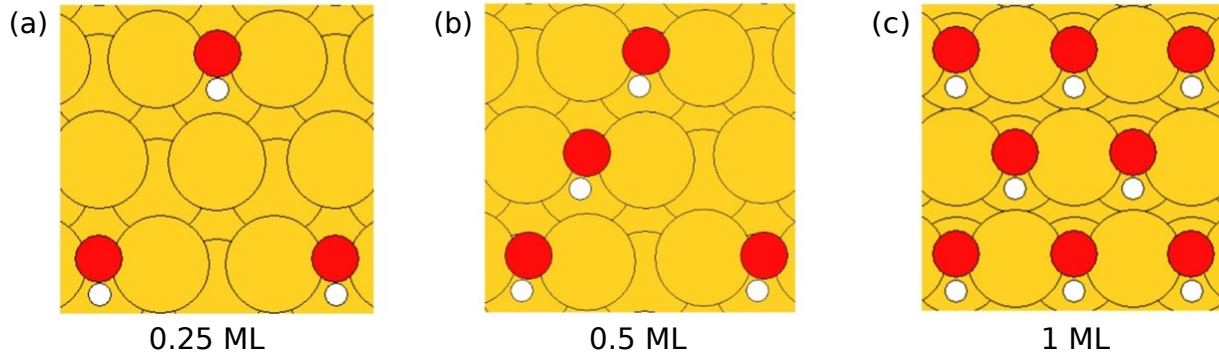


Figure 3.16: OH adsorption at Au fcc(111) BRIDGE position for (a) 0.25 ML, (b) 0.5 ML, and (c) 1 ML of surface coverage in the absence of strain. Au is depicted in yellow, O in red, and H in white.

With applied strain

The impact of biaxial elastic strains on the adsorption of H, O, and OH was examined for various surface coverages (0.25 ML, 0.5 ML, and 1 ML) on Au(111) surfaces. Deformations were applied to the Au supercell while the adsorbates were positioned at the FCC adsorption site in the case of H and O because this was the position with the lowest adsorption energy at 0.25 ML. Meanwhile, the BRIDGE position was used for OH adsorbates, except in the case of 5% and -5% biaxial strains at 0.25 ML, where the molecule migrates at the FCC site.

The adsorption energy of H, O, and OH vs. the applied biaxial strain for the three surface coverage monolayers is plotted in Figure 3.17. The trends observed for the unstrained slab are maintained for the three adsorbates. Specifically, the adsorption energy increases with surface coverage in the case of H and O. Thus, the configuration with a surface coverage of 0.25 ML exhibits the lowest adsorption energy.

The change of the adsorption energy of H due to coverage for a given biaxial strain is more important when the slab is subjected to compressive strains than when it is subject

to tensile strains (Figure 3.17 a). This behavior can be explained because the repulsion between the H adsorbates is reduced when the in-plane distances are augmented by the application of tensile strains. The opposite effect is observed under compressive strains although. Simulations with 5% biaxial compressive strain and 1 ML coverage led to the development of structural instabilities in the slab, which were probably triggered by the interactions between H adsorbates.

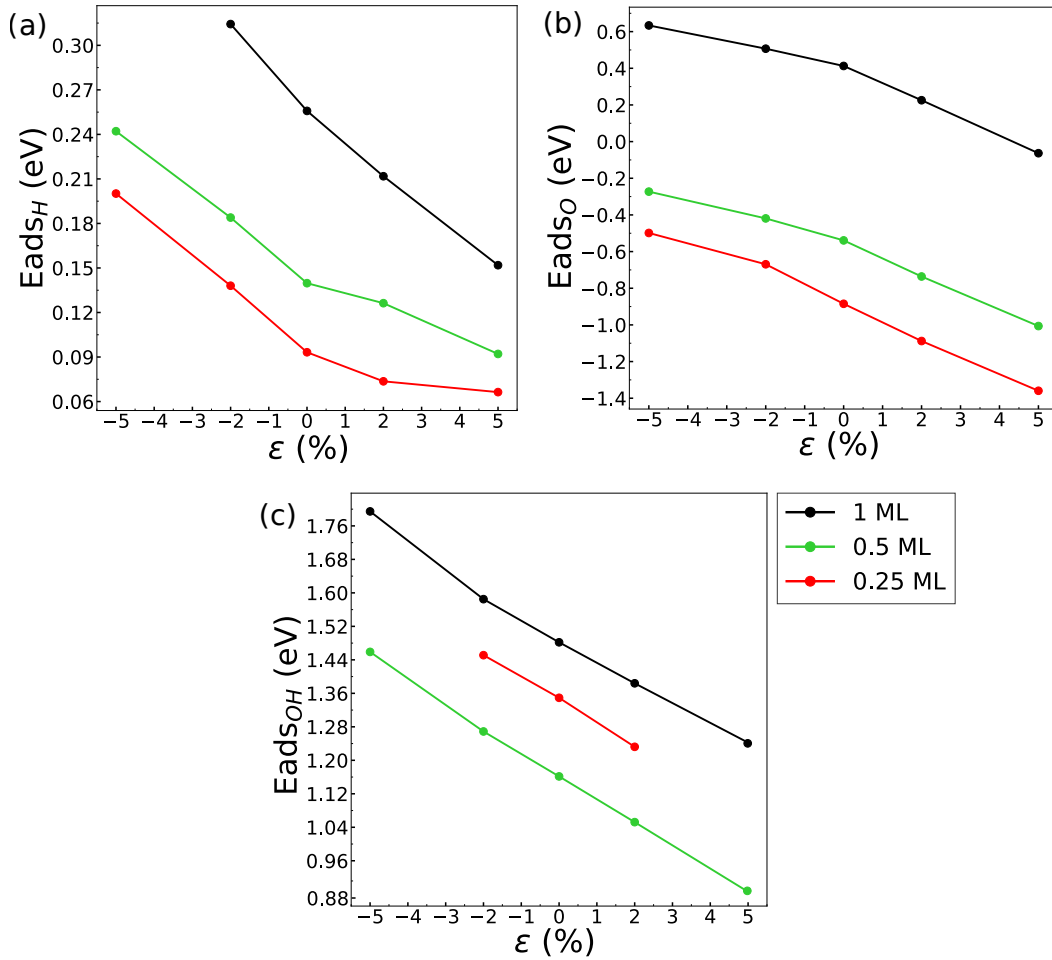


Figure 3.17: Adsorption energy as a function of the applied biaxial strain with different surface coverage monolayers (ML) for (a) H, (b) O, and (c) OH at the most favorable adsorption sites (FCC for H and O, and BRIDGE for OH). In the OH curve, the adsorption site moved from the BRIDGE to the FCC site when the slab was subjected to 5% of either tensile or compressive biaxial and the corresponding adsorption energies were not included.

On the contrary, the differences in adsorption energies between 0.25 ML, 0.5 ML and 1 ML are practically independent of the applied biaxial strain in the case of O adsorption (Figure 3.17 b). These results suggest that the application of strains does not alter the repulsion between O atoms when coverage increases. Under tensile strains, the higher lattice distances (i.e. 0.15 Å larger for 5%) enhance the adsorption while the opposite

behavior is observed for compressive strains, (i.e. 0.15 Å smaller for 5%). Hence, the effect of repulsion between the neighbor O atoms and the influence of elastic strains on the adsorption energies are independent.

In the case of OH, the minimum adsorption energy is observed at 0.5 ML of coverage for biaxial compressive strains and for tensile strains up to 5% (i.e. 0.89 eV for 5% tension). The adsorption process is more favorable than in the case of 0.25 ML and 1 ML. Similar to the case of O, the variation in the adsorption energies between the different surface coverages is approximatively constant, around -0.18 eV between 0.25 ML and 0.5 ML, and also higher between 0.5 ML and 1 ML, around 0.33 eV. The trend of the three curves of Figure 3.17 c reflects a similar change of the adsorption energy as a function of the applied biaxial strain. However, the adsorbate moves towards an FCC site in the case of 0.25 ML coverage at strains higher than 2% and lower than -2%, and the adsorption energy with coverage cannot be compared to that at BRIDGE. For that reason, it was omitted from the graph.

Charge transfer

In order to provide an explanation of the curves shown in Figure 3.17, the charge transfer from/to the adsorbate to/from the surface was computed using the Bader program, developed by Yu and Trinkle [347] which uses the Bader definition of an atom [13] to predict the electronic density. A negative charge transfer stands for a loss of electronic density whereas a positive charge transfer represents a gain of electronic density.

The charge transfer of OH in an Au fcc(111) surface at BRIDGE position is shown for the three different coverages (0.25 ML, 0.5 ML, and 1 ML) in Figure 3.18. In all cases, the adsorbate gets charge from the surface, while the surface Au atoms lose electronic density. It is remarkable how the amount of charge gained by the adsorbates is the same for both 0.25 ML and 0.5 ML. However, the origin of this charge (-0.43e) is different. In the case of 0.25 ML, most of that charge is donated from the H atom in the adsorbate, while more charge is donated from the surface in 0.5 ML. This results explain why the adsorption energy is minimum for 0.5 ML (see Figure 3.17 c): more charge is donated from the surface to the adsorbate, which makes the adsorption process more favorable.

The amount of charge received by the adsorbate in the case of 1 ML is lower (-0.38e), shifting the adsorption energies up and making the adsorption process less favorable (Figure 3.17 c). The hydrogen bonds are represented in black dash lines in the Figure, and they explain why the amount of charge on each of the O and H atoms of the different adsorbates varies. No H-bonds are formed at 0.25 ML coverage but one H-bond is formed between the H atom of Ads1 and the O atom of Ads2 in the case of 0.5 ML. This explains why those atoms have lost/gained more charge than the others, respectively.

The effect of strains in the OH adsorption energies with coverage follows the usual behavior (Appendix A Table A. 8.1): biaxial compressive strains increase the adsorbate-surface distance and, therefore, the amount of charge transfer decreases. These phenomena produce a consequent shift up of the adsorption energy. Conversely, the application of tensile strains decreases the distance between the OH and the Au surface and thus increases the

System	Au1 (e)	Au2 (e)	Au3 (e)	Au4 (e)	Adsorbate (e)	
OH/Au(0.25ML)	0.17	0.17	0.02	-0.02	-1.01 (O)	-0.43 (Ads1)
					0.58 (H)	
OH/Au(0.5ML)	0.18	0.20	0.21	0.18	-1.13 (O)	-0.43 (Ads1)
					0.70 (H)	
					-1.08 (O)	-0.43 (Ads2)
					0.65 (H)	
OH/Au(1ML)	0.37	0.36	0.36	0.36	-1.13(O)	-0.38 (Ads1)
					0.75 (H)	
					-1.00 (O)	-0.38(Ads2)
					0.62 (H)	
					-1.18 (O)	-0.38 (Ads3)
					0.80 (H)	
					-1.38 (O)	-0.38 (Ads4)
					1.00 (H)	

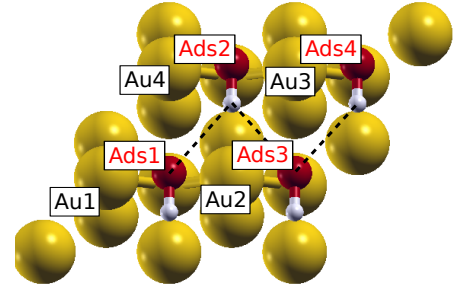


Figure 3.18: Charge transfer for OH in an Au fcc(111) surface in the BRIDGE position at zero strain for the 3 different coverages (0.25 ML, 0.5 ML and 1 ML). The Au1, Au2, Au3, and Au4 positions and the four different adsorbates are shown in the schematic at the side of the table. Hydrogen bonds are represented with dash black lines. All values are expressed in elemental units where $e = -1$. A positive value expresses a gain of negative charge, whereas a negative value expresses a loss of negative charge.

amount of charge transferred. With all this, the adsorption energy becomes more negative, favoring the process. The aforementioned trend is fulfilled for the three coverages and the application of -2% compressive strains and of 2% tensile strains, leads to a change of ± 0.1 eV in the adsorption energy in all cases.

Conclusions

The influence of elastic strains on the adsorption of H, O, and OH on the (111) surfaces of 8 fcc (Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir) and on the (0001) surfaces of 3 hcp (Co, Zn, Cd) transition metals was analyzed by means of DFT calculations. The surface slabs were subjected to different strain states (uniaxial, biaxial, shear, and a combination of them) up to strains dictated by the mechanical stability limits indicated by the phonon calculations. It was found that tensile strains favored the adsorption of the three adsorbates while compressive and shear strains increased the adsorption energy (less negative) and, thus, hindered the adsorption, in agreement with the *d*-band theory. Adsorption energies for H were smaller in absolute values than those calculated for O and OH in all cases. Moreover, the optimum adsorption (lowest energy) of the three species was found on the FCC sites of the (111) fcc surfaces and on the HCP sites of the (0001) hcp surfaces and did not change with strain. The distance metal-adsorbate increased with compression strain and decreased under tensile deformations.

It was found that the variation of the adsorption energy in all metals due to the application of mechanical strains was only a function of the change in the area of the adsorption site and the relationship between both magnitudes was fairly linear in most cases. Thus, different combinations of normal and shear strains that lead to the same change in the

area of the adsorption site have identical effects on the adsorption energy. This general behavior indicated that the physical mechanisms of adsorption were equivalent in all metals. The analysis of the electronic structure showed that the application of strains did not modify the shape of PDOS of the *d*-orbitals of the transition metals but only led to a shift in the energy levels. Moreover, the adsorption of H and O on the surfaces led to negligible changes in the PDOS. Thus, the adsorption energies of all adsorbates in all metals were a function of the Fermi energy which in turn was associated with the change of the area of the adsorption through linear law that was valid for all metals.

As the change in the area of the adsorption site due to the application of strain can be accurately determined by purely geometrical considerations, the information in this chapter allows the immediate and accurate estimation of the effect of any elastic strain on the adsorption energies of H, O, and OH on 11 transition metals with more than half-filled *d*-orbitals. This information can be used to predict the activation free energies of the different intermediates in the HER and ORR (as well as in other catalytic reactions) as a function of the applied strain for different transition metals with very limited computational cost, indicating the optimum combination of material and strain to enhance the catalytic activity. Moreover, the results in this chapter can spur the search for correlations between geometrical descriptors of the elastic deformation and adsorption energies that can be used to make accurate predictions of the latter with minimum computational cost for other compounds and adsorbates.

Finally, a study of coverage on a surface of Au fcc(111) was performed. 0.25 ML coverage was found to be preferred in the H and O adsorption at all strain levels. However, the adsorption of OH at 0.5 ML was favored due to the formation of hydrogen bonds O-H...O between the different adsorbates and the amount of charge transferred from/to the adsorbate to/from the surface.

Catalytic activity in pure metals

This chapter aims to go one step forward in the study of pure metals as potential catalysts for the Hydrogen Economy under the application of elastic strains. The adsorption energies for H, O, and OH, calculated and analyzed in Chapter 3, are utilized to obtain the catalytic activity of these materials in the HER and the ORR. Within this context, the present chapter analyzes the effect of mechanical strains onto the catalytic properties of 8 fcc (Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir) and 5 hcp (Co, Zn, Cd, Ru, Os) transition metals for the HER and the ORR. Thus, the results in this chapter rationalize the mechanisms that determine the influence of mechanical strains on the catalytic activity of transition metals and provide a framework to explore their effect on other materials.

4.1 Fulfillment of Bell-Evans-Polanyi principle

As explained in Chapter 1 Section 1.4.1, the Bell-Evans-Polanyi principle [53], states that the adsorption enthalpy energy can be directly related to the activation energy of the HER and the ORR, and correspondingly to the catalytic activity. This linear relationship between the activation energy of the reaction and the adsorption energy is well known and has been reported in pure metals [6, 21, 295], Nudged Elastic Band calculations were performed for the hydrogen adsorption in pure Ag to corroborate the fulfillment of the Bell-Evans-Polanyi principle under the application of tensile and compressive strains.

The Nudged Elastic Band (NEB) technique is utilized to locate saddle points and the minimum energy paths (MEP) connecting known reactants and products. This approach involves optimizing multiple intermediate states along the reaction pathway. Each state is adjusted to minimize energy while preserving uniform spacing with adjacent states. This optimization process is achieved by incorporating spring forces between states along the band and by eliminating the force component perpendicular to the band caused by the potential. This technique is extensively employed in determining the reaction pathways of atomic-scale phenomena within chemical and materials systems [105].

In the study of the hydrogen adsorption in pure Ag, the initial state was defined by H

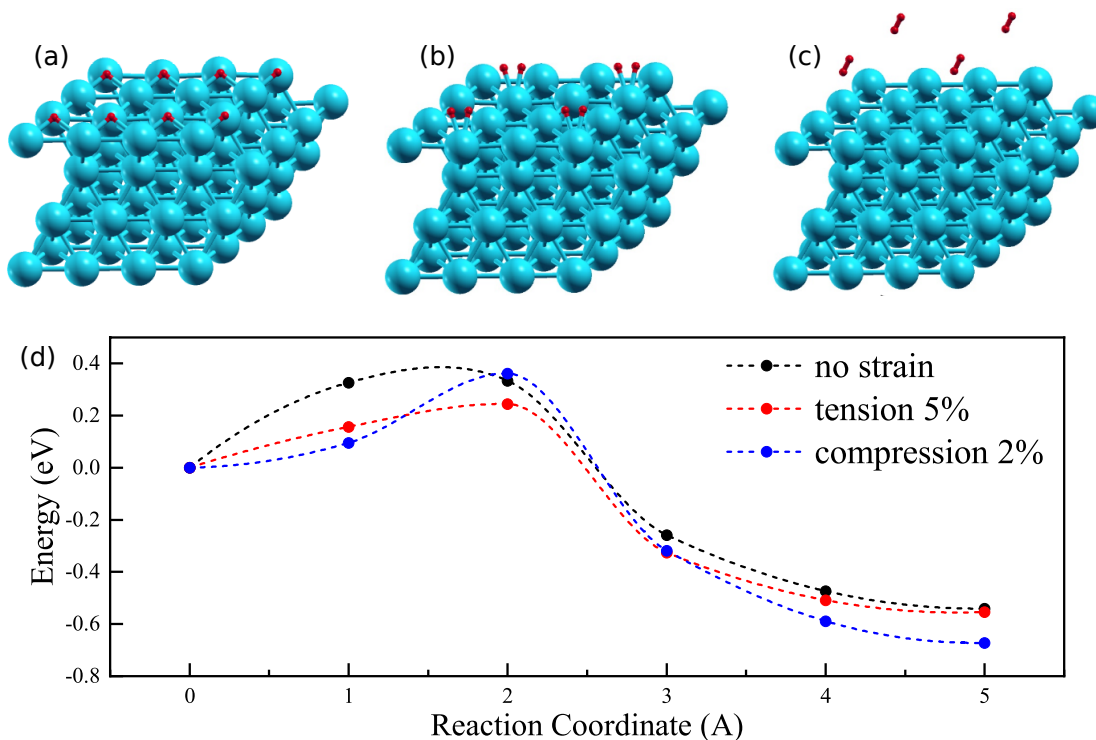


Figure 4.1: (a) Initial, (b) intermediate, and (c) final states in the NEB calculation for the hydrogen adsorption onto Ag fcc(111) at FCC site. (d) MEP without strain (black), with 5% biaxial tension (red), and with 2% biaxial compression (blue). Each dot represents the total energy of the six images obtained in the NEB calculation.

atoms adsorbed in FCC position at Ag fcc(111), and the final state by a H₂ molecule desorbed and apart from the clean Ag fcc(111) surface (Figure 4.1 a and c). Complimentary, an intermediate image was defined to help the algorithm in the search for the MEP (Figure 4.1 b). Quantum Espresso [78, 80, 81] was used for these calculations with 6 images, a Marzari-Vanderbit-DeVita-Payne cold smearing of 0.015 Ry [180], a cutoff energy of 80 Ry, and a Monkhorst-Pack k-mesh of $6 \times 6 \times 1$. As shown in Figure 4.1 d, the Minimum Energy Paths (MEP) were computed for the Ag fcc(111) slab without the application of biaxial strain and under 5% tension and 2% compression. In the three cases, the image with the highest energy, which dictates the activation barrier and conforms the transition state, is the third. Here, both H atoms get closer to each other on top of a silver atom to form a covalent bond and desorb as an H₂ molecule.

As expected, the energy barrier increases as the lattice of the supercell decreases. It changes from 0.36 eV, 0.33 eV, and 0.24 eV, when comparing 2% compression, no strain, and 5% tension, respectively. The corroboration of the Bell-Evans-Polanyi principle is shown in Figure 4.2 for the H/Ag(111) system. The relationship between the reaction energy (adsorption energy of H) and the activation energy is almost linear. Compressive strains increase the adsorption energy of H onto Au and lead to higher activation energies, while tensile strains decrease the adsorption energy and reduce the activation energy. The real-

ization of the Bell-Evans-Polanyi principle allows the prediction of the catalytic activity of the calculated metals, based on their adsorption energies, with and without the application of elastic strains.

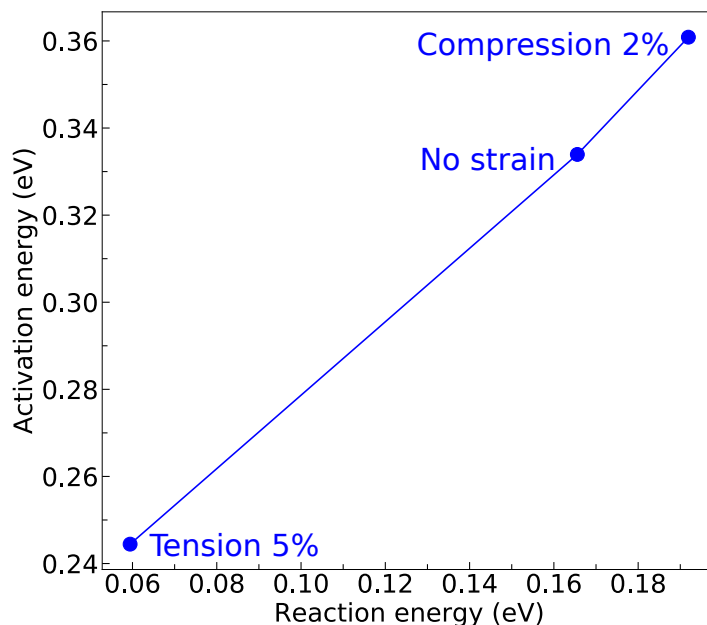


Figure 4.2: Fulfillment of Bell-Evans-Polanyi principle with strain for the hydrogen adsorption on Ag fcc(111).

4.2 Volcano plots

Gerischer [76] and Parsons [208] were the first ones to find out that certain models for the activity of the HER resulted in a volcano-like curve. Nonetheless, it was Trasatti [293] who collected experimental data and represented the first volcano plot for the HER. Since then, many authors have represented the exchange current density as a function of the free energy for hydrogen adsorption for the HER and the catalytic activity against the adsorption energy of O for the ORR [87, 195, 226, 315]. These plots provide a very intuitive and visual representation of the catalytic performance of transition metals. The peak of the volcano corresponds to the optimum catalytic properties, the ascending branch corresponds to metals in which the reactions are limited by the desorption of the products and the descending branch represents the processes that are limited by the adsorption of the reactants. According to Sabatier's principle [238], an equilibrium between adsorption of the reactants and desorption of the products should be attained to get the maximum activity.

4.2.1 Volcano plots at mechanical equilibrium

The adsorption energy of hydrogen at equilibrium in the most favorable adsorption site, E_{ads_H} , is given in Table 4.1. This information can be used to calculate the free energy and the corresponding exchange current density according to eqs. (2.29) and (2.30), which are also included in Table 4.1. Volcano plots at the mechanical equilibrium of 23 transition metals for the HER obtained from the DFT calculations are plotted in Figure 4.3 a. Complementary, a detailed comparison between the experimental data from the literature and the calculated exchange current densities as a function of free energy of adsorption of H is shown in Figure 4.4. These results are in good agreement with the ones found in the literature [87, 195, 226, 315] with the exceptions of Cu and Ir, whose experimental activity is lower than that computed according to Figure 4.3 a. In particular, the G_{ads_H} calculated for Cu is around 0.2 eV lower than what has been previously stated, which places Cu on the cusp of the volcano plot.

Metal	E_{ads_H} (eV)	G_{ads_H} (eV)	$\log i_0$ (A cm ⁻²)
Pt	-0.49	-0.25	-5.52
Au	0.09	0.33	-7.06
Cu	-0.25	-0.01	-1.52
Ag	0.17	0.41	-8.27
Pd	-0.54	-0.30	-6.40
Ni	-0.52	-0.28	-6.07
Ir	-0.39	-0.15	-3.83
Rh	-0.53	-0.29	-6.27
Cd	0.81	1.05	-19.39
Zn	0.67	0.91	-16.92
Co	-0.51	-0.27	-5.97
Nb	-0.89	-0.65	-12.46
Mo	-0.74	-0.50	-9.92
W	-0.75	-0.51	-10.09
Re	-0.80	-0.56	-10.97
Ru	-0.64	-0.40	-8.08
Fe	-0.59	-0.35	-7.26
Os	-0.59	-0.35	-7.29
Hf	-1.08	-0.84	-15.77
Ta	-0.99	-0.75	-14.11
V	-0.90	-0.66	-12.53
Cr	-1.06	-0.82	-15.35
Tc	-0.72	-0.48	-9.58

Table 4.1: Adsorption energy of hydrogen at equilibrium in the most favorable adsorption site, E_{ads_H} , for different transition metals. The free energy of adsorption, G_{ads_H} , at 300 K and the logarithm of the exchange current density, $\log i_0$, for the HER according to eqs. (2.29) and (2.30) are also included.

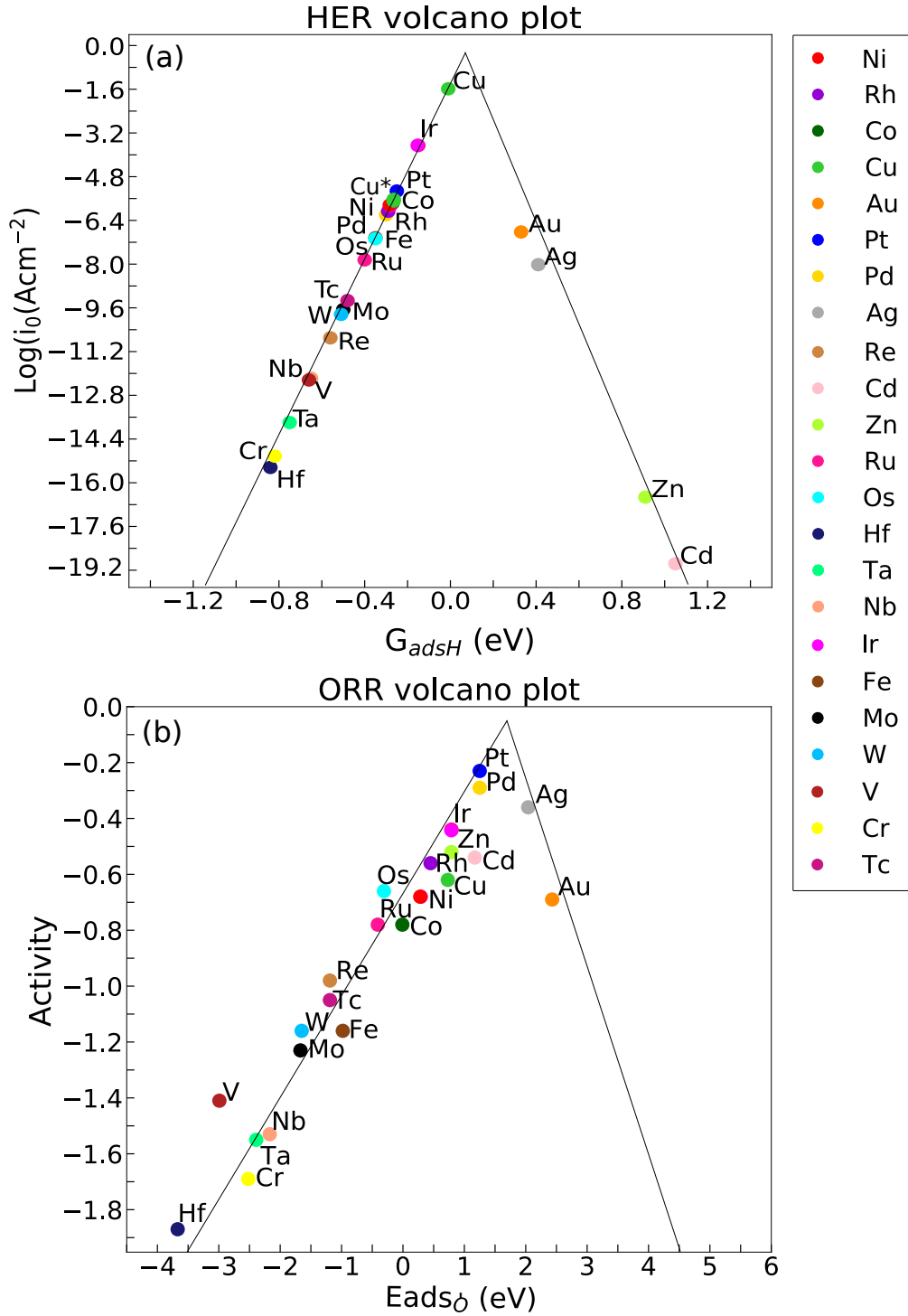


Figure 4.3: Volcano plots at mechanical equilibrium for (a) the HER as a function of G_{adsH} and (b) the ORR as a function of E_{adsO} . Cu* in the HER volcano plot corresponds to the free energy obtained from the adsorption energy calculated with the DFT functional SCAN[278].

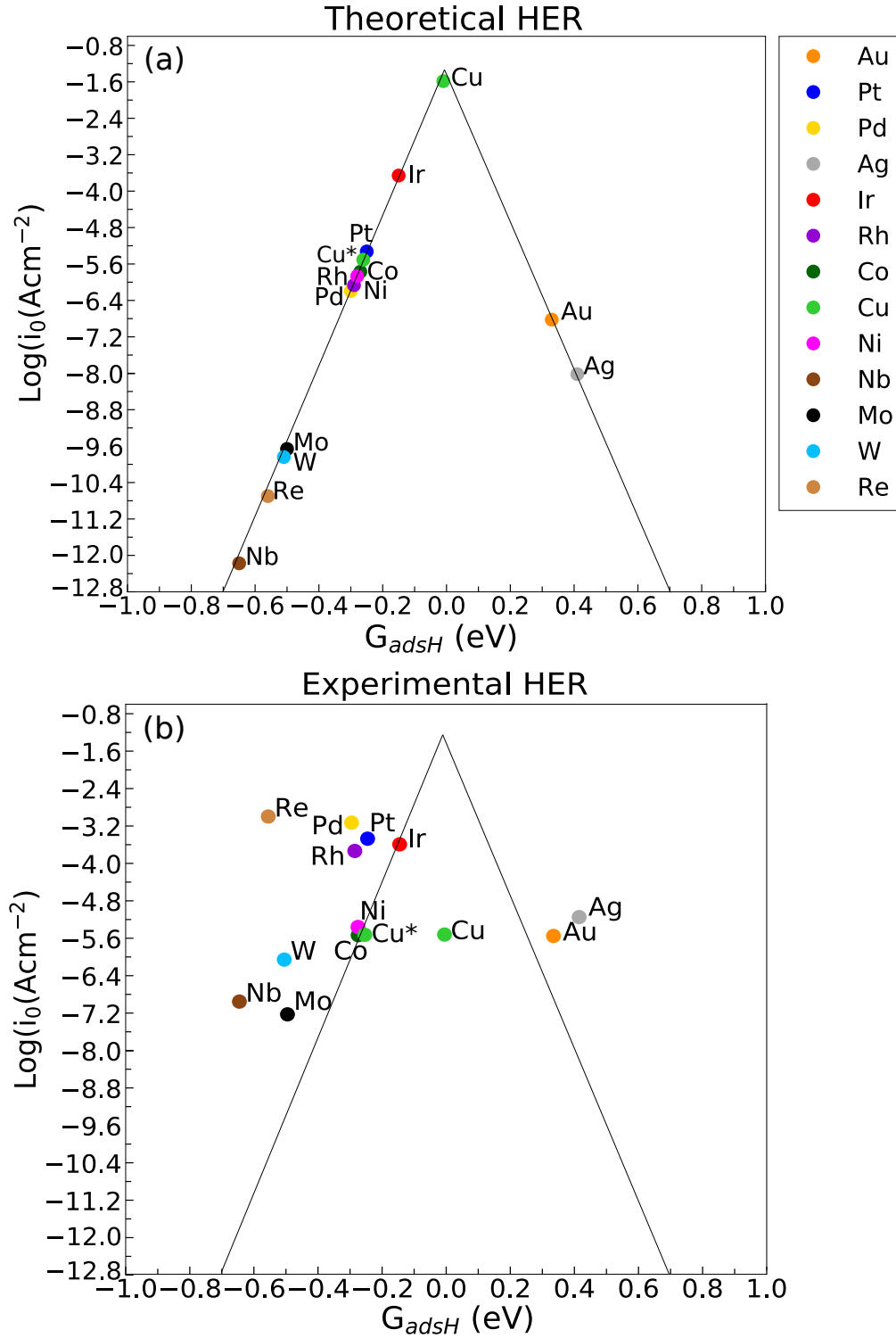


Figure 4.4: (a) Theoretical and (b) experimental volcano plots at mechanical equilibrium for the HER as a function of G_{adsH} . The experimental values of exchange current density are taken from [195]. Cu* corresponds to the free adsorption energy of H obtained from the adsorption energy calculated with the DFT functional SCAN [278].

Metal	$E_{ads_{O^*}}$ (eV)	$E_{ads_{OH}}$ (eV)	$G_0(U_0)$ (eV)	$G_1(U_0)$ (eV)	$G_2(U_0)$ (eV)	Activity
Pt	1.66	1.19	-0.79	0.29	0.49	-0.23
Au	2.43	1.52	0.06	-0.02	-0.04	-0.69
Cu	0.73	0.14	-1.72	0.38	1.34	-0.62
Ag	2.04	0.72	-0.41	-0.35	0.76	-0.36
Pd	1.25	0.85	-1.20	0.57	0.63	-0.29
Ni	0.29	0.03	-2.16	0.71	1.45	-0.68
Ir	0.79	0.76	-1.66	0.94	0.72	-0.44
Rh	0.45	0.27	-2.00	0.78	1.21	-0.56
Cd	1.17	0.31	-1.28	0.11	1.17	-0.54
Zn	0.79	0.37	-1.66	0.54	1.11	-0.52
Co	-0.01	-0.20	-2.46	0.78	1.68	-0.78
Nb	-2.17	-1.80	-4.62	1.34	3.28	-1.53
Mo	-1.67	-1.18	-4.12	1.46	2.66	-1.23
W	-1.65	-1.01	-4.10	1.61	2.49	-1.16
Re	-1.19	-0.64	-3.64	1.52	2.12	-0.98
Ru	-0.41	-0.21	-2.86	1.17	1.69	-0.78
Fe	-0.98	-1.03	-3.43	0.93	2.51	-1.16
Os	-0.31	0.15	-2.76	1.42	1.33	-0.66
Hf	-3.67	-2.54	-6.12	2.10	4.02	-1.87
Ta	-2.39	-1.85	-4.84	1.51	3.33	-1.55
V	-2.99	-1.54	-5.44	2.41	3.02	-1.41
Cr	-2.52	-2.15	-4.97	1.34	3.63	-1.69
Tc	-1.19	-0.78	-3.64	1.38	2.26	-1.05

Table 4.2: Adsorption energy of O ($E_{ads_{O^*}}$) and OH ($E_{ads_{OH}}$) at equilibrium at the most favorable adsorption site for different transition metals. The free energies of the three steps of the dissociative mechanism ($G_0(U_0)$, $G_1(U_0)$, and $G_2(U_0)$) at 300 K and the catalytic activity for the ORR according to eq. (2.45) are also included.

The HER is a one-step process and the reaction path is controlled by the adsorption energy of hydrogen, whereas the ORR includes three steps with their associated free energies, $G_0(U_0)$, $G_1(U_0)$, and $G_2(U_0)$. The corresponding values of the adsorption energies of O and OH were calculated previously on the most favorable site of the transition metals (Chapter 3) and they are given in Table 4.2. They were used to determine the free energies for each of the steps and to calculate the activity according to eq. (2.45), which are also included in Table 4.2. The corresponding volcano plot for the catalytic activity as a function of $E_{ads_{O^*}}$ is plotted in Figure 4.3 b. The highest free energy establishes the rate-limiting step for each metal and determines the catalytic activity. The rate-limiting step in most transition metals is the desorption of HO^* ($HO^* + H^+ + e^- \longrightarrow H_2O + *$) and the highest free energy is $G_2(U_0)$. The exception to this general situation is Au, where the rate-limiting step is the adsorption of O^* ($\frac{1}{2} O_2 + * \longrightarrow O^*$) with the associated free energy $G_0(U_0)$, and Ir and Os, in which the rate-limiting step is the formation of HO^* ($O^* + H^+ + e^- \longrightarrow HO^*$)

and the highest free energy is $G_1(U_0)$. Pt exhibits the maximum catalytic activity in the volcano plot, followed by Pd, Ag, and Ir, in agreement with experimental data [312]. In addition, these results agree with previous simulations by Norskov et al. [198], with the only discrepancy of Ir, in which they report that the rate-limiting step corresponds to the desorption of HO. Additionally, it is interesting to notice that $G_0(U_0)$ is very low for Nb, Mo, W, Re, Fe, Hf, Ta, V, Cr, and Tc. This corresponds to very favorable oxygen adsorption, which could lead to the formation of oxides. Finally, it should be noted that metals on the left side of the periodic table (Hf, Cr, Ta, V, Nb, Mo, and W) with less than half-filled d -bands present the worst catalytic properties for the HER and the ORR. These results also agree with previous studies [87, 195, 226, 315].

It should be noted that the calculation of the catalytic activity explained in Chapter 2 Section 2.1.5 involves the addition of the operating temperature. Although all the volcanos shown in this thesis are calculated at 300K, a representation of the HER volcano plot at 355K and 455K is shown in Figure 4.5. They correspond to the working temperatures of the most common electrolyzers and fuel cells. The differences in the values of catalytic activity for metals close to the cusp of the volcano are negligible, and the tendencies are maintained in all cases.

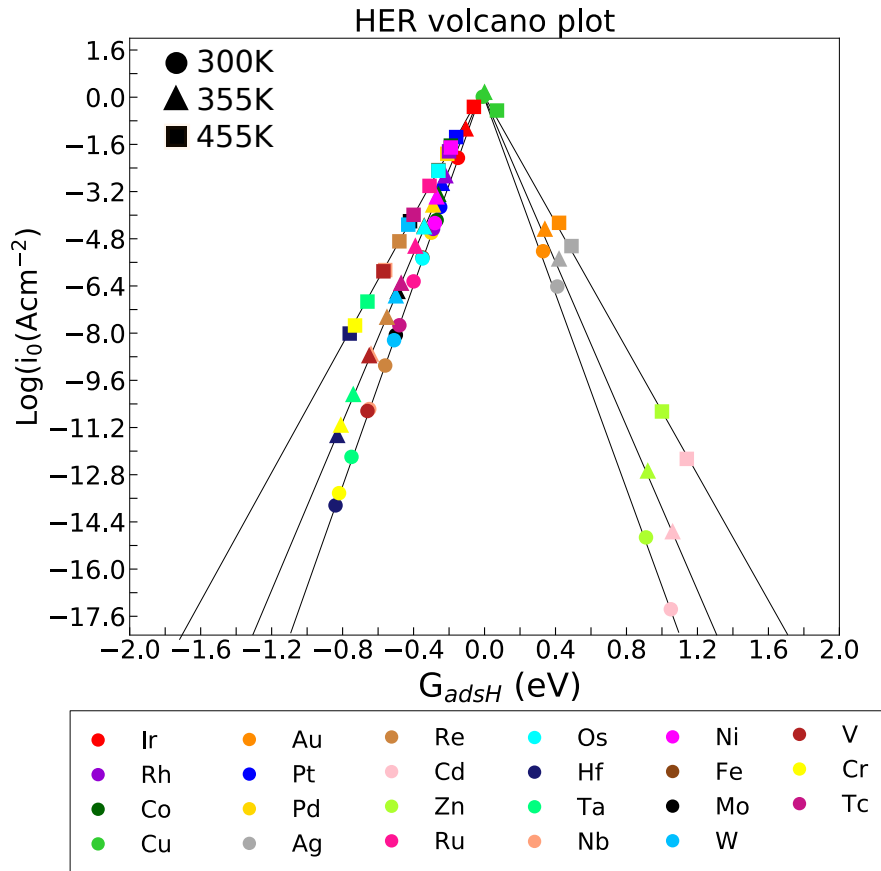


Figure 4.5: Volcano plot at mechanical equilibrium for the HER as a function of G_{adsH} . Values are calculated at 300K (circles), 355K (triangles), and 455K (squares).

4.2.2 Volcano plots under mechanical strain

The effect of elastic strains on the catalytic activity of transition metals for the HER and the ORR is represented by means of volcano plots in Figures 4.6 a and b, respectively. These plots were constructed from the adsorption energies of the biaxially strained slabs of Au, Pt, Pd, Ag, Rh, Co, Ni, Cu, Ir, Ru, and Os from -5% compression to 8% tension, and of Cd and Zn from -2% compression to 8% tension that can be found in Chapter 3. These transition metals were chosen due to their position close to the top of the volcanos in Figure 4.3 and to their widespread use as heterogeneous catalysts. The black dot in each line in Figure 4.6 stands for the catalytic activity when the applied strain is zero. The lines for Cd and Zn are not included for the HER reaction in Figure 4.6 a because they are too far from the top.

The catalytic activity of the transition metals on the left side of the volcanos is limited by the desorption of the products. Compressive strains increase the adsorption energy of the reactants and avoid the poisoning of the catalyst surface, improving the catalytic activity. On the contrary, the catalytic properties of metals on the right side of the volcanos are limited by the adsorption of the reactants and can be improved with the application of tensile strains, which enhance the adsorption of the reactants by reducing the adsorption energy. In all cases, the effect of elastic strains on the catalytic activity is limited by the mechanical stability limits of the surface of the catalyst.

The effect of elastic strains on the catalytic activity (measured by the $\log i_0$) for the HER depends on the metal. The largest variations in the catalytic properties with strain (Figure 4.6 a) are observed for Ir and Au, where the activity (measured by the $\log i_0$) changes 4.5 and 2.7 units, respectively, when the surface slab is subjected to -5% biaxial compression or to 8% biaxial tension, respectively, with respect to the unstrained slab. On the contrary, Co is very insensitive to the mechanical strains because E_{ads_H} does not vary with the elastic strain. There are no well-established trends for the effect of mechanical strains on the adsorption energies but our previous investigation (Chapter 3) showed that the influence of the mechanical strain on the adsorption energy increases with the number of electrons in the valence band for the elements in the 4th period of the periodic table (3d). Nevertheless, the effect of mechanical strains on the adsorption energy is much smaller for the 5th and 6th periods. It should also be noted that the limiting mechanism (either hydrogen adsorption or desorption) does not change with the applied strain (the evolution of the catalytic activity with the applied strain remains to the left or the right of the volcano cusp) except for Cu in which E_{ads_H} is very close to 0 in the unstrained slab. In this case, tensile or compressive stresses activate one of either rate-limiting steps and reduce the catalytic activity.

The elastic strains also lead to important changes in the catalytic activity of transition metals for the ORR, as shown in Figure 4.6 b. The largest ones are found in Pt and Au and both metals can be tuned using either compressive or tensile strains, respectively, to attain the top of the corresponding volcano plot. This result was already detected for Pt, which is known to improve its catalytic activity through the application of elastic strains [52, 104] in agreement with our volcano plot. More interestingly, the application of 2% biaxial tension can improve the catalytic activity of Au (which is known to be a bad catalyst for the

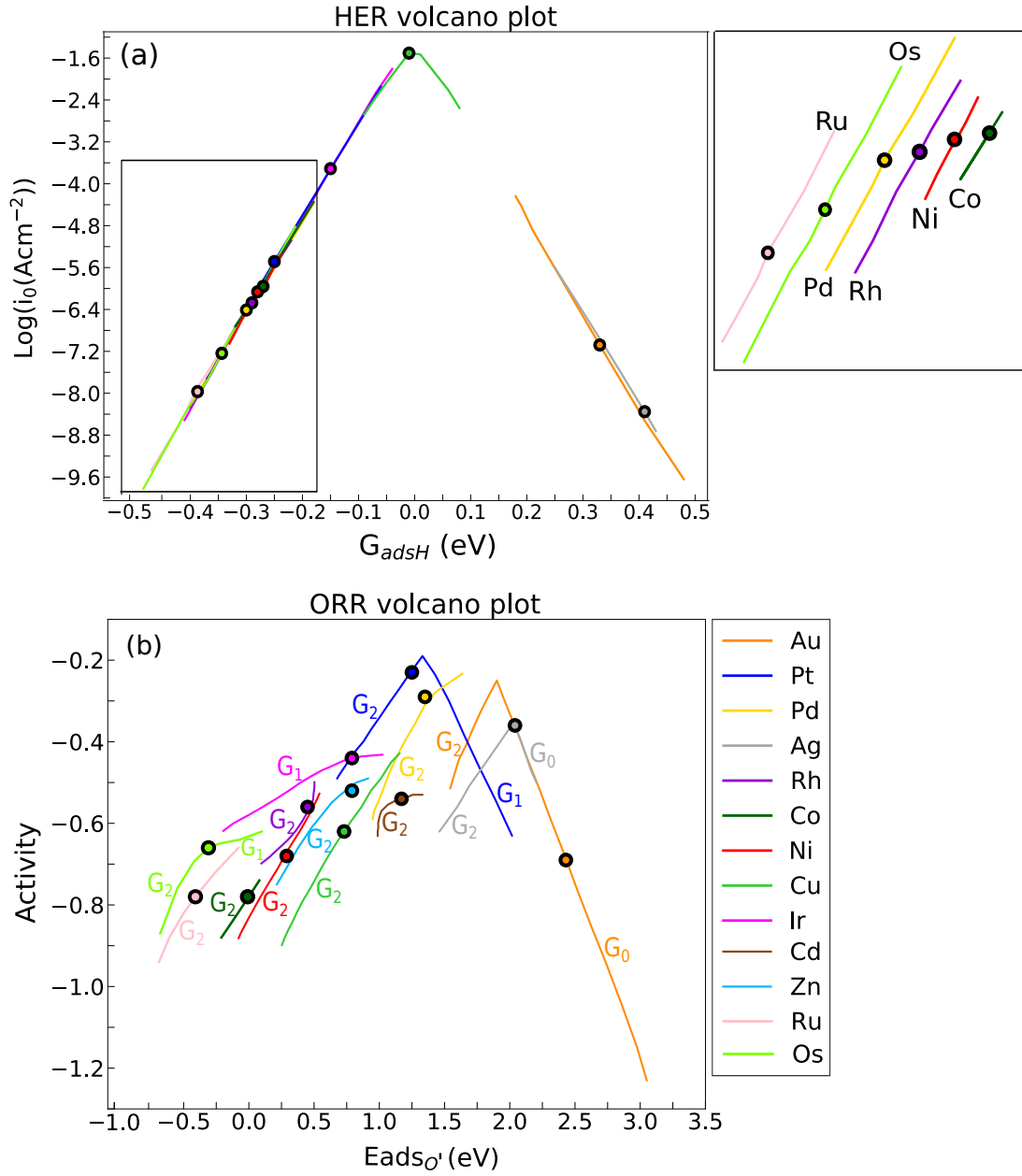


Figure 4.6: (a) Effect of mechanical strains on the volcano plot for the HER as a function of G_{adsH} for transition metals. The range of activities for Pd, Rh, Ni, Co, Ru, and Os within the rectangle have been plotted to the right, shifted by 0.05 eV along the horizontal axis for the sake of clarity. (b) *Idem* for the ORR as a function of EadsO^* . The free energy that limits the reaction rate is indicated at each branch of the volcano plot for each metal. The lines stand for the variation in the catalytic activity of each metal as a function of the applied elastic strain in the range from -5% biaxial compression to 8% biaxial tension in Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir, Co, Ru, and Os, and from -2% biaxial compression to 8% biaxial tension in Cd and Zn. Black circles indicate the activity at the mechanical equilibrium. Cd and Zn are omitted from the HER volcano plot because $\log i_0$ is very low.

ORR) close to that of Pt. In contrast, elastic strains have a minor influence on the catalytic activity of the ORR for Co and Cd. The maximum activity of Ir, Rh, Co, Ni, Cu, Zn, Cd, Pd, Ru, and Os for the ORR is attained when the slab is subjected to the highest compressive strain, while the best catalytic activity of Ag is found in the unstrained condition and the application of tensile or compressive strains always leads to the reduction in activity.

4.2.3 Volcano plots with coverage

In order to study the effect of coverage in the HER and the ORR reactions, the catalytic activity was calculated for the Au fcc(111) surfaces with 0.25 ML, 0.5 ML, and 1 ML analyzed in Section 3.4. As reflected in Figure 3.17 a, the adsorption energy of H into Au becomes more negative as the coverage decreases. This is directly reflected in the HER volcano (Figure 4.7 a), as ΔG_H varies linearly with E_{ads_H} . Au is a noble metal that falls on the right side of the volcano and, therefore, the more negative the adsorption energy the higher the catalytic activity. In the case of the ORR (Figure 4.7 b), the variation of the catalytic activity cannot be directly deduced from the adsorption energy of O and OH, because the three-step mechanism depends in ΔG_O , ΔG_{OH} , and $\Delta G_O - \Delta G_{OH}$. Thus, the optimum coverage associated with the higher catalytic activity is 0.25 ML even though the adsorption energy of OH is more negative in 0.5 ML. This is due to the fact that the rate-limiting step is the adsorption of the O atom into de surface at the three coverages. Therefore, tensile strains presume an increase in the activity, reducing E_{ads_O} .

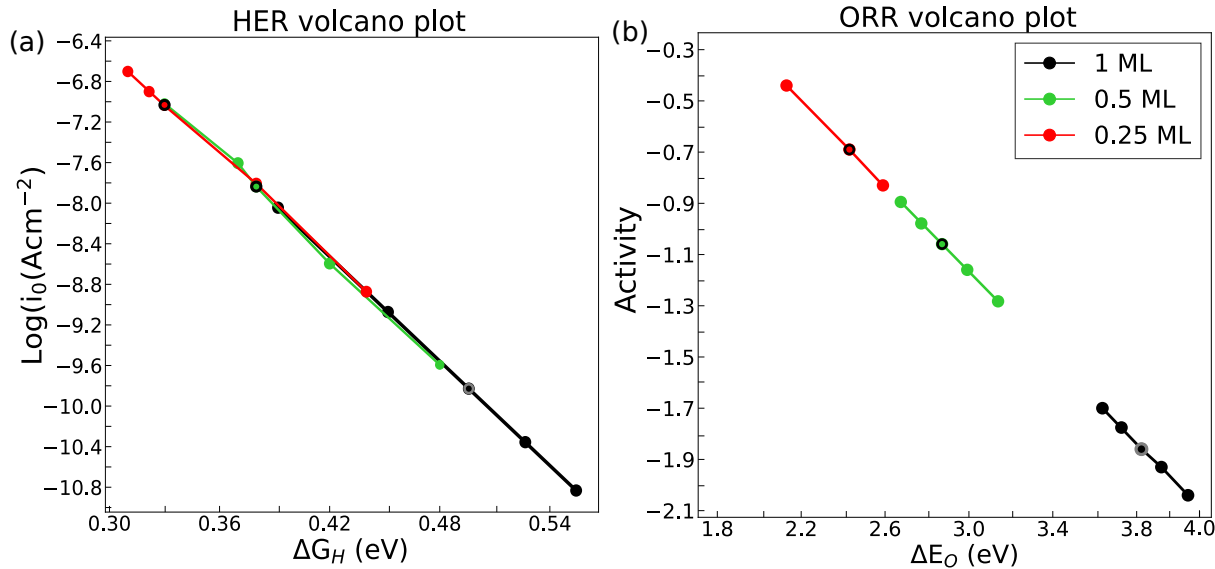


Figure 4.7: Volcano plots for the (a) HER and the (b) ORR in Au fcc(111) as a function of the coverage. Black empty circles indicate the activity at zero strain. A range from -5% biaxial compression to 5% biaxial tension is represented, with the exception of 0.25 ML in the ORR, where the range varies from -2% to 2% (see Figure 3.17).

4.3 Discussion

The results presented above show how the systematic application of elastic strains can be tailored to optimize the catalytic response of transition metals for the HER and the ORR. In the former case, the catalytic activity is determined by E_{ads_H} which determines the free energy of adsorption, G_{ads_H} , at a given temperature. The optimum scenario is achieved when $G_{ads_H} \rightarrow 0$ through the application of compressive or tensile strains and the limitations of this strategy are determined by the sensitivity of E_{ads_H} to the strain and the maximum strains that can be applied before the mechanical instability limit is achieved, leading to fracture. The largest changes in catalytic activity with strain for the HER were found in Pt, Au, and Ir while E_{ads_H} in Co and Ni was very insensitive to elastic strains, which did not modify substantially the catalytic activity.

It should be noted that the catalytic activity of Cu is overestimated in the volcano plot for the HER in Figure 4.3. This discrepancy may be due to the fact that – according to equation (2.28) – the exchange current density depends strongly on G_{ads_H} , which in turn is a linear function of E_{ads_H} . Thus, small errors in the calculation of E_{ads_H} may lead to substantial changes in catalytic activity, particularly near the cusp of the volcano plot. To test this conjecture, E_{ads_H} was calculated again in Pt and Cu using the metaGGA SCAN functional [278] and the methodology presented in Chapter 2. This functional is known to provide more accurate values of the adsorption energy at a much higher computational cost [278]. In the case of Pt, the differences in E_{ads_H} between the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional and the metaGGA SCAN functional were only 0.03 eV but they increased to 0.24 eV in the case of Cu. Moreover, these differences remained constant as a function of strain. Thus, the predictions of the adsorption energy for Cu seem to be particularly sensitive to the selection of the functional and this explains the overestimation of the Cu activity in the volcano plot of Figure 4.3. Cu moves to the appropriate position in the volcano plot for the HER in Figure 4.3 a when the more accurate adsorption energy (denoted by Cu*) is used to calculate the free energy. It should be noted that this sensitivity to the functional is less important in the case of the ORR, because the activity depends on differences in E_{ads} and errors in the calculation of adsorption energies due to selection of the functional tends to cancel each other. This is evidenced by the position of Cu in the volcano plot for the ORR in Figure 4.3, which is in agreement with the experimental data.

The effect of mechanical strains on the catalytic activity of the ORR is a little bit more complex because it depends on the free energy of the rate-limiting reaction, which is the maximum of G_0 , G_1 , and G_2 . G_0 depends on E_{ads_O} , G_1 on $E_{ads_{OH}} - E_{ads_O}$, and G_2 on $-E_{ads_{OH}}$, and the influence of the mechanical strains on the respective adsorption energies is different. Tensile strains reduce E_{ads_O} and $E_{ads_{OH}}$ while compressive strains have the opposite effect. Moreover, E_{ads_O} at zero strain is negative for all the analyzed transition metals while $E_{ads_{OH}}$ is positive under the same conditions for all the analyzed transition metals (except Co, with $E_{ads_{OH}} = -0.2$ eV). As a result, the catalytic activity for the ORR of metals in which the rate is controlled by G_0 (adsorption of O^*) and G_2 (desorption of HO^*) are very sensitive to elastic strains and their catalytic activity increases rapidly with the application of tensile strains in the former (Au) or compressive strains in the latter

(Cu, Ni, Pt, Pd, Rh, Zn, Cd, Co, Ru, and Os). In some hcp metals, such as Cd and Zn, the range of elastic strains before mechanical instabilities develop is reduced and, thus, the tunability of their catalytic activity with mechanical strains is very limited. Finally, the rate-limiting free energy in Ir is G_1 (change from O^* to HO^*) that depends on the difference between $E_{ads_{OH}} - E_{ads_O}$. As both energies evolve in the same direction with strain, their difference is not very sensitive to the applied strain (Figure 4.6) and Ir activity varies slowly (as compared with other metals) with deformation. Thus, the efficiency of elastic strains to modify the catalytic activity not only depends on the catalyst itself but also on the intermediate species that are present in each reaction step. Some reactions are more sensitive to the application of elastic strains than others, which opens the possibility of exploring the mechanism to enhance the activity of many other chemical processes with different intermediate species.

4.3.1 Reaction path

In most metals, mechanical strains change the catalytic activity but not the rate-limiting mechanism. This is not the case, however, for Au, Pt, Ag, and Os. The influence of biaxial strains (in the range -5% to 8%) on the free energies in the ORR reaction path for Au, Pt, and Ag is plotted in Figure 4.8a, b, and c, respectively. At zero strain, the adsorption of O is the limiting step in Au (Figure 4.8 a) and this energy barrier increases with compressive strains while G_1 fluctuates due to the competition between the adsorption energies of O and HO. As a result, compressive strains reduce the catalytic activity for the ORR of Au. However, the application of tensile strains switches the rate-limiting step to the desorption of HO^* because G_2 becomes positive and increases rapidly with the tensile strains while G_0 becomes negative and G_1 fluctuates between negative and positive values. The optimum catalytic activity is obtained at around 2% biaxial tensile strains.

In the case of Pt (Figure 4.8b), the desorption of HO^* is the limiting step at zero strain, while the adsorption of O is strongly exothermic and the reaction from O^* to HO^* is slightly endothermic. The application of compressive strains reduces rapidly the energy barrier for HO^* desorption and the rate-limiting step changes to the reaction from O^* to HO^* , which becomes endothermic. The application of tensile strains increases the energy barrier for HO^* desorption, leading to a constant reduction in the catalytic activity. Thus, the maximum catalytic activity is achieved for small compressive strains (-1.57% biaxial compression). The rate-limiting step also changes from G_2 to G_1 with the application of compressive strains in the case of Os.

Additionally, unstrained Ag is at the cusp of the volcano plot, and the application of either tensile or compressive strains reduces the activity as one limiting reaction becomes dominant. In this case, the rate-limiting step is found to be the desorption of HO^* under tensile strains and the O adsorption under compressive strains (Figure 4.8 c). Finally, the application of strain in Ir does not change the rate-limiting step of the ORR, which is the change from O^* to HO^* in all cases (Figure 4.8 d). G_1 decreases slightly with compressive strains and increases slightly with tensile strains and the optimum catalytic activity is found at the maximum compressive strains allowed by the mechanical stability limits.

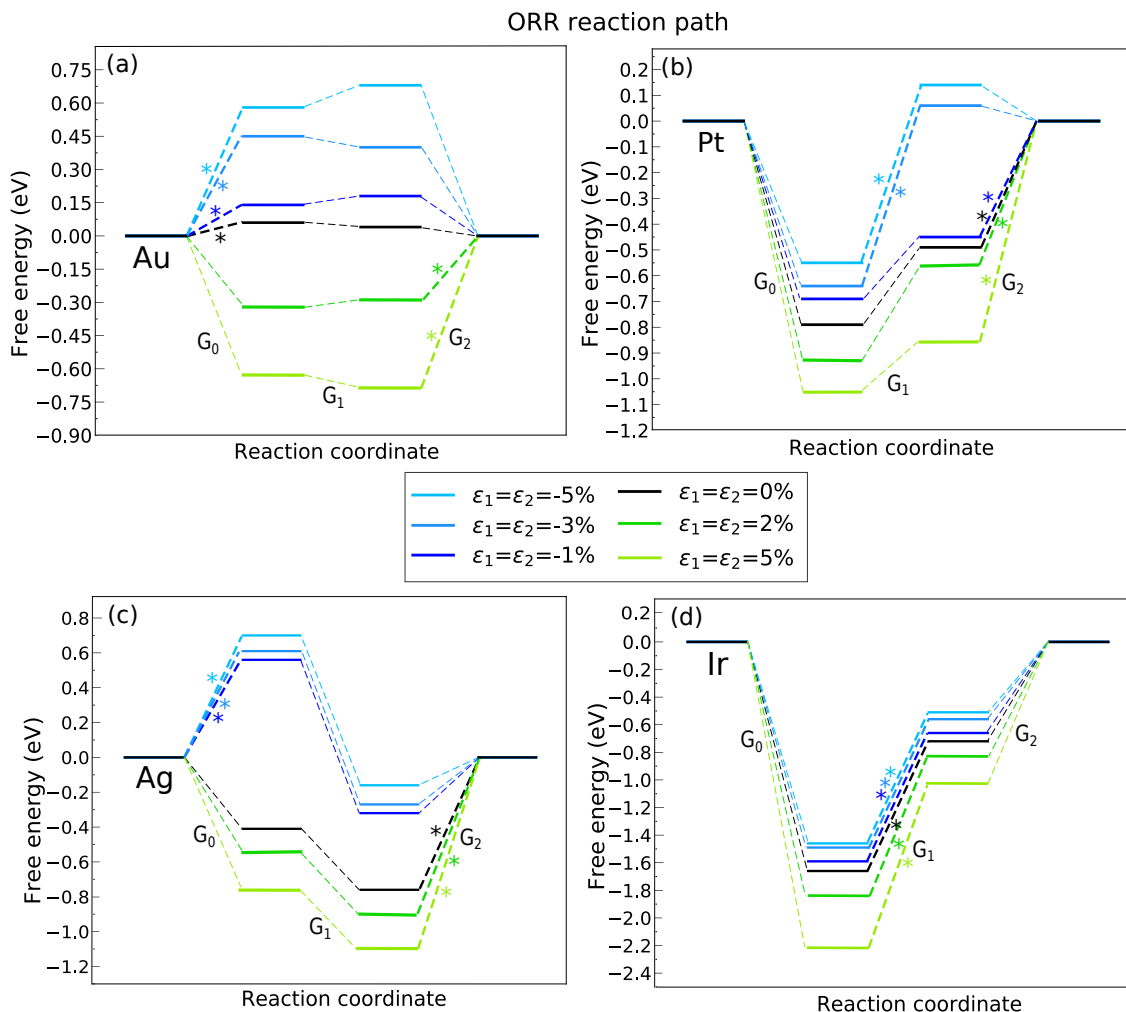


Figure 4.8: Effect of biaxial elastic strains (in the range -5% to 5%) on the free energies along the reaction path for the ORR. (a) Au. (b) Pt. (c) Ag. (d) Ir. The rate-limiting step at each strain is indicated with an asterisk.

Conclusions

The effect of elastic strains on the catalytic activity for the HER and the ORR was analyzed at (111) surfaces of eight fcc transition metals (Ni, Cu, Pd, Ag, Pt, Au, Rh, Ir) and (0001) surfaces of five hcp transition metals (Co, Zn, Cd, Ru, Os). The catalytic activity for both reactions was determined from the adsorption energies for H, O, and OH calculated by density functional theory under strain. Tensile, compressive, and shear stresses were applied to slabs until the mechanical stability limit (given by phonon calculations) was achieved. The volcano plots of the catalytic activity for the HER and the ORR in the absence of strain were in good agreement with the experimental data in the literature, validating the theoretical model. It was found that elastic strains led to significant changes in the catalytic activity of most transition metals, which could be rationalized as a function of changes in the free energy of the rate-limiting step.

In the case of the HER, it was found that compressive strains increased the catalytic ac-

tivity of metals on the ascending branch of the volcanos (Pt, Pd, Rh, Ni, Ir, Ru, and Os) because they decreased the energy barrier for H^* desorption, which is the limiting step. On the contrary, tensile strains improved the activity of metals in the descending branch of the volcano, as they decreased the energy barrier for H adsorption (Au and Ag). The largest improvements in activity were found in Au, Ir, and Ag which combined a large sensitivity of the H adsorption energy to strain while large mechanical strains could be applied without leading to failure.

The catalytic activity of the ORR was controlled by the maximum free energy for the reactions in the dissociative mechanism: adsorption of O, transition from O^* to HO^* , and desorption of HO^* . In particular, the free energies associated with the adsorption of O and the desorption of HO^* were very sensitive to mechanical strains. Thus, the catalytic activity of Au (controlled by the former) could be enhanced by the application of tensile strains while that of Cu, Ni, Pt, Pd, Rh, Zn, Cd, Co, Ru, and Os (controlled by the latter) was improved by the application of compressive strains. The optimum catalytic activity of Ag was found in the unstrained condition and mechanical deformation always reduced the catalytic activity in this metal. Moreover, only small elastic strains could be applied to Cd and Zn before the mechanical instability was reached and elastic strain engineering is not a suitable strategy to modify the catalytic activity of these metals. Finally, it was also found that the application of elastic strains could change the rate-limiting step for the ORR in Au, Pt, Ag, and Os because of the different effects of mechanical deformation of the free energy of the different intermediate reactions.

All in all, the results presented in this Chapter evidence the advantages of using elastic strain engineering technique to modify the catalytic activity of pure transition metals in the HER and the ORR.

Electronic and mechanical contributions

In order to achieve a deeper understanding of the adsorption phenomena of different adsorbates (H, C, N, O, CO, NO, and OH) into a metallic surface, in this chapter we decouple the adsorption energy into two main contributions: electronic and mechanical contributions. Complimentary, we measure the influence of each contribution in the total adsorption process and evaluate the effect of strain on them. Additionally, we compare the results obtained for pure Pt, to that for the platinum oxide PtO₂, to get an idea of the influence of oxygen atoms on the catalyst surface. Finally, we aim to expand the applicability of the *d*-band model to different adsorbates onto the same surface and to oxides.

5.1 Mechanical and electronic decoupling

The adsorption process of seven different adsorbates (H, O, OH, C, CO, N, and NO) on Pt(111) and PtO₂ (110) surfaces under the application of elastic strains are studied by means of DFT simulations and calculated following the methodology exposed in Section 2.1.4. In order to achieve a deeper understanding of the effect of elastic strains in the adsorption process, we separated the adsorption energy into two contributions, electronic and mechanical, following [63] and [131]. The electronic contribution, E_{elec} , accounts for the interactions between the adsorbate atoms and the substrate surface atoms at the adsorption distance, while the mechanical contribution, E_{mech} , includes the elastic energy associated with the deformations induced in the surface due to the presence of the adsorbate. Following Figure 5.1, the sum of both contributions gives the total adsorption energy defined in equation (2.1.4):

$$E_{ads} = E_{elec} + E_{mech} \quad (5.1)$$

where E_{elec} stands for the difference in energy due to the presence of the adsorbate once the surface of the slab has been relaxed, whereas E_{mech} is calculated from the difference between the deformed and undeformed slab without the adsorbed atom. They are given by

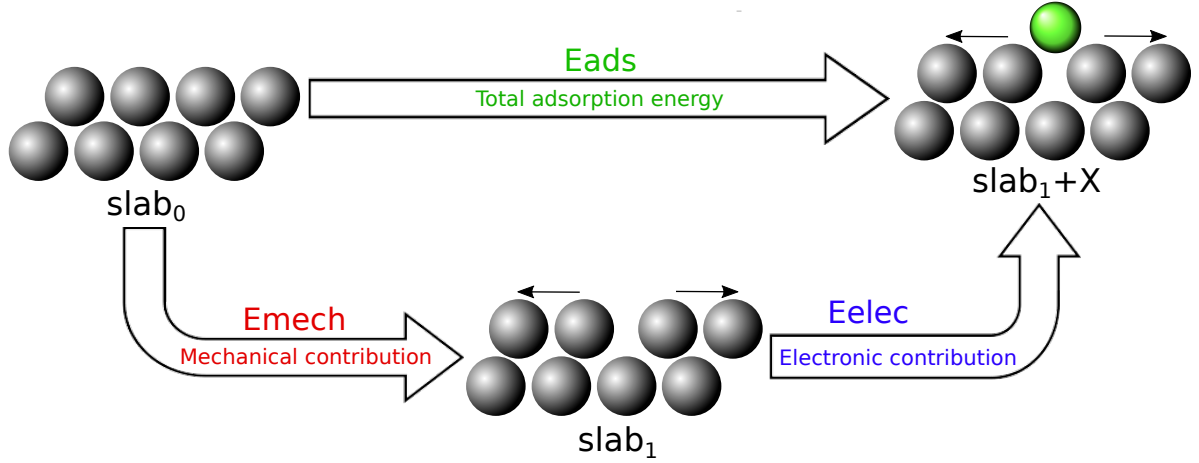


Figure 5.1: Illustration of the separation in electronic and mechanical contributions for the adsorption process. slab_0 is the initial surface undeformed and slab_1 is the final surface deformed by the adsorbate. The black arrows represent the atomic displacements of the substrate atoms of the first layer of the supercell.

$$E_{\text{elec}} = E_{\text{slab}_1+\text{X}} - (E_{\text{slab}_1} + E_{\text{X}_{\text{gas}}}) \quad (5.2)$$

$$E_{\text{mech}} = E_{\text{slab}_1} - E_{\text{slab}_0} \quad (5.3)$$

where E_{slab_0} is the energy of the initial surface undeformed and E_{slab_1} is the energy of the final surface deformed by the adsorbate.

After the application of strains as explained in Section 2.1.8, the equations of the two contributions to the adsorption energy (electronic and mechanical) are given by:

$$E_{\text{elec}}(\epsilon) = E_{\text{slab}_1+\text{X}}(\epsilon) - (E_{\text{slab}_1}(\epsilon) + E_{\text{X}_{\text{gas}}}) \quad (5.4)$$

$$E_{\text{mech}}(\epsilon) = E_{\text{slab}_1}(\epsilon) - E_{\text{slab}_0}(\epsilon = 0) \quad (5.5)$$

DFT calculations of adsorption were carried out in the four possible adsorption sites for Pt (111)(Figure 5.2 a), whereas adsorption can take place in six different positions for PtO_2 (110) surface (Figure 5.2 b).

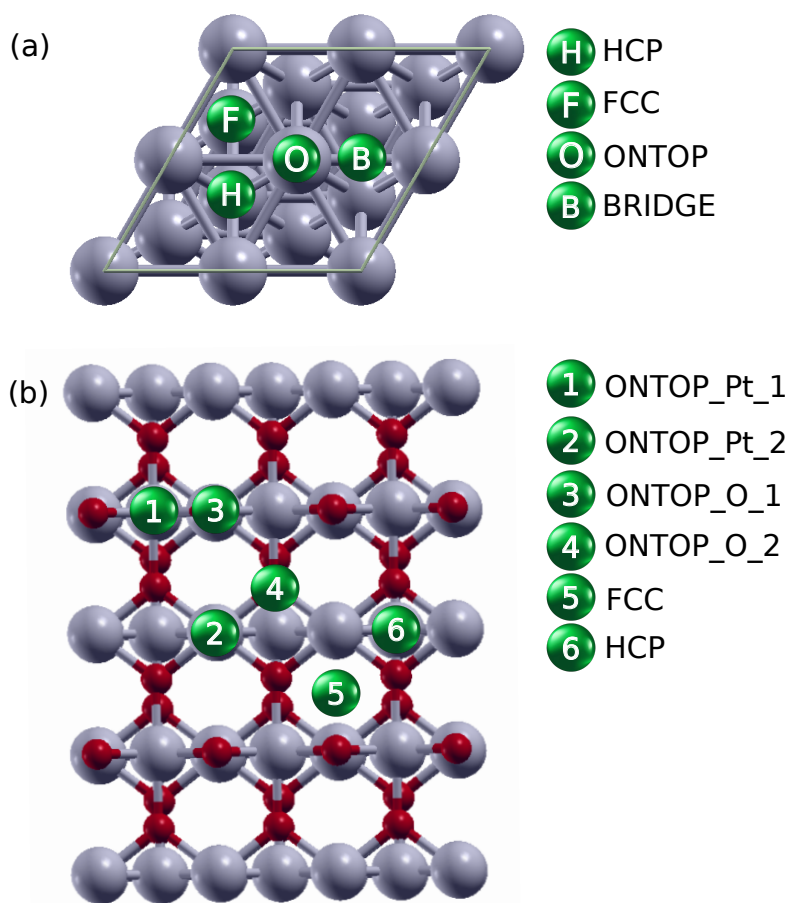


Figure 5.2: Different adsorption positions in (a) Pt (111), and (b) PtO₂ (110).

5.1.1 Pt

Seven molecules (H, O, OH, C, CO, N, and NO) were adsorbed onto Pt fcc(111) to understand the effect of the adsorbates in the electronic-mechanical decoupling under strain. The most favorable adsorption site was the FCC position in all cases (Figure 5.2 a). The diatomic adsorbates OH, CO, and NO, were adsorbed perpendicularly to the metallic slab with O, C, and N atoms closer to the surface, respectively.

The corresponding adsorption energies at the FCC sites, as well as the electronic and mechanical contributions, are detailed in Table 5.1. The adsorption energies of OH, N, and C are positive while those of H, O, NO, and CO are negative. The range of energy values associated with the adsorption process varies from 2.01 eV for carbon to -2.16 eV for oxygen. The mechanical contribution is always positive because it is associated with the elastic accommodation of the atoms in the surface of the slab around the adsorption site (Figure 5.1). Our results show that this contribution is much smaller (in the range of 0.04

System	E_{ads}	E_{elec}	E_{mech}
H/Pt	-0.49	-0.53	0.04
O/Pt	-2.16	-2.31	0.15
OH/Pt	1.19	1.00	0.19
N/Pt	0.27	0.13	0.14
NO/Pt	-2.04	-2.17	0.12
C/Pt	2.01	1.80	0.21
CO/Pt	-1.74	-1.82	0.08

Table 5.1: Total adsorption, electronic, and mechanical energies for the adsorption of H, O, OH, N, NO, C, and CO in FCC sites of Pt fcc(111) at zero strain. All energies are expressed in (eV).

to 0.21 eV) than the electronic one that dominates the total adsorption energy for most adsorbates. The only exception is N, where both E_{elec} and E_{mech} are small, similar, and positive. The mechanical energy (E_{mech}) increases with the atomic radius ($\text{H} < \text{O} \sim \text{N} < \text{C}$) for monoatomic adsorbates. However, the trend is not followed for diatomic adsorbates ($\text{CO} < \text{NO} < \text{OH}$). Here, E_{mech} is inversely proportional to the bond length (O-H: 90 pm, N-O: 115 pm, C-O: 140 pm).

The total adsorption energy, as well as the electronic and mechanical contributions, for the seven adsorbates onto mechanically strained Pt, from -5% compression to 5% tension, are plotted in Figure 5.3. Here, in agreement with our previous results, E_{ads} (represented in green) depends on the applied biaxial elastic strain: decreases with tensile strains and increases with compressive ones. However, it is worth noting that the effect of elastic strains on the adsorption energy is very different among adsorbates. The adsorption energy of CO (Figure 5.3 g) or NO (Figure 5.3 e) only shifts by about 0.2 eV between -5% and 5% biaxial strain, but the variation of the adsorption energy in C (Figure 5.3 f) and N (Figure 5.3 e) is more than three times larger in the same strain range.

The information in Figure 5.3 f also includes the variation of the electronic and mechanical contributions to the adsorption energy under the application of external elastic strains. Remarkably, E_{mech} (red lines) remains practically constant with strain in all cases while the sensitivity of the adsorption energy to the applied elastic strains is dictated by E_{elec} (blue lines). This result indicates that the changes in the adsorption energy with the application of strain is primarily due to the electronic adsorbate-substrate interaction and that the mechanical accommodation of the adsorbate on the surface plays a minor role from the energy viewpoint.

The variation of the electronic and mechanical contributions to the adsorption energy is plotted as a function of the applied biaxial elastic strain in Figure 5.4. The electronic contribution is referenced with respect to the situation where no strain is applied ($E_{\text{elec}}(\epsilon) - E_{\text{elec}}(\epsilon = 0)$) in order to facilitate its visualization. The information in Figure 5.4 a shows that the influence of mechanical strains on the electronic contribution to the adsorption en-

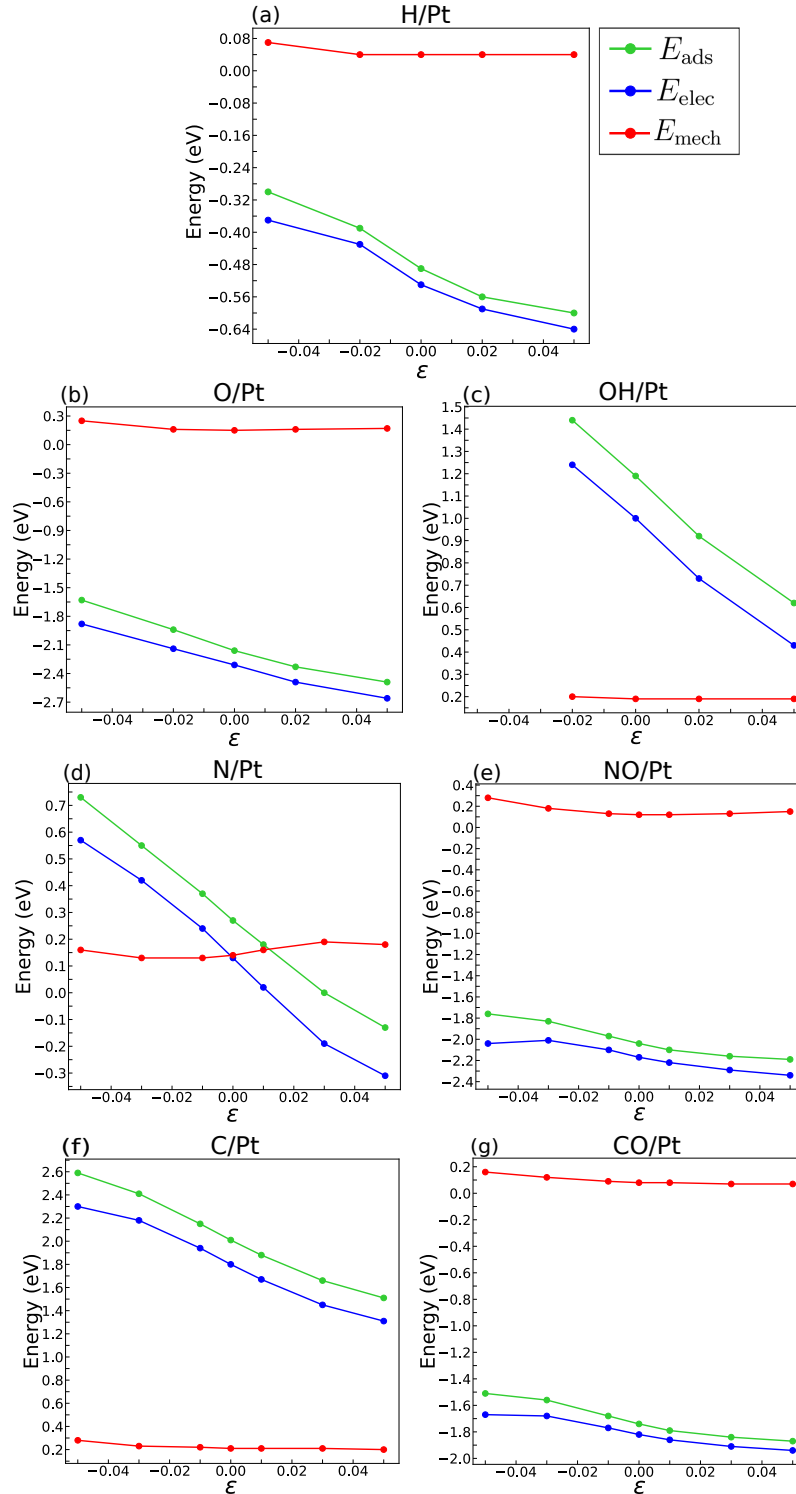


Figure 5.3: Different contributions for the adsorption of (a) H, (b) O, (c) OH, (d) N, (e) NO, (f) C, and (g) CO, into a Pt fcc(111) surface. The green, blue, and red lines represent the total adsorption energy (E_{ads}), as well as the electronic (E_{elec}) and mechanical (E_{mech}) contributions, respectively. Data at -5% compression in (c) was omitted due to the instability of the slab.

ergy (and, thus, on the total adsorption energy) follows the order $C > OH > N > O > NO > CO > H$. In particular, it is maximum for O, C, N, and OH and minimum for H, NO, and CO. This illustrates how the presence of an adsorbate with a higher electronic effect produces bigger displacements in the atoms of the surface, reflected in an increment of E_{mech} .

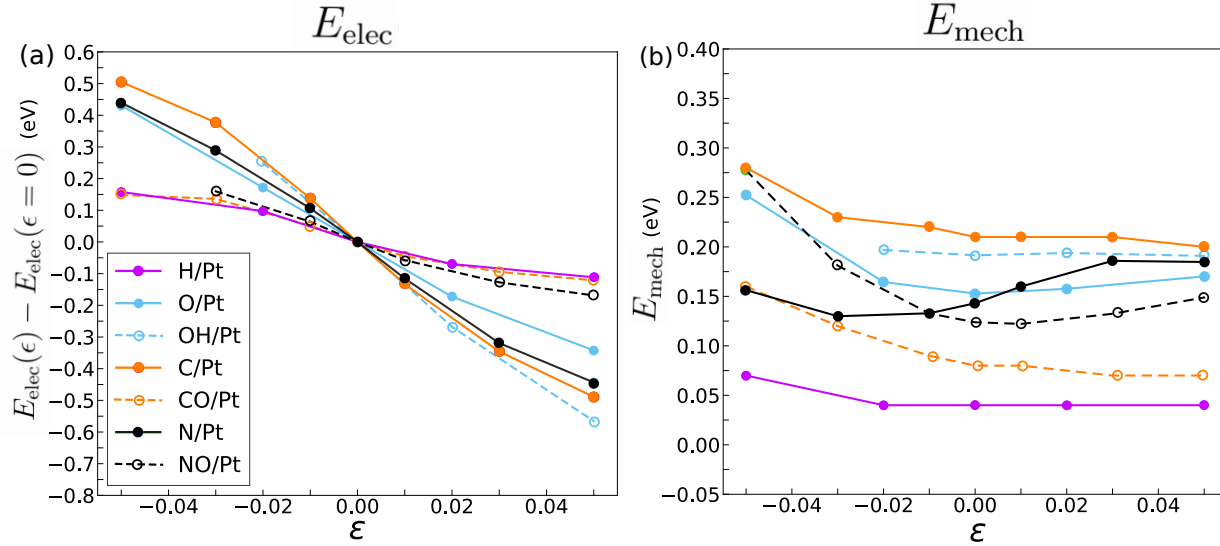


Figure 5.4: (a) Electronic and (b) mechanical contributions to the adsorption energies for different adsorbates onto Pt fcc(111) as a function of the applied strain. The electronic contribution values are referenced with respect to the ones corresponding to zero strain. Solid markers and lines represent monoatomic adsorbates, while dash lines and empty circles illustrate diatomic molecules.

With the aim of comparing the two energy contributions in Pt, with other metallic surfaces, we calculated E_{ads} , E_{mech} , and E_{elec} in the adsorption of H and O onto Au(111), Cd(0001), Ir(111), Nb(110), Ni(111), and Rh(111). Table 5.2 presents the data for the adsorption energy, as well as its electronic and mechanical contributions, for all the studied metals. Firstly, it can be appreciated that for the studied surfaces the dominant component of the energy associated with the adsorption process is the electronic contribution. Indeed, the sign and magnitude of E_{elec} completely determines E_{ads} . In the only two cases where E_{ads} is positive, E_{elec} is also positive. Moreover, there is only one system where E_{mech} is larger in magnitude than E_{elec} , H/Au(111). More generally, and similarly to the results for Pt, we observe that the deformation of the surface caused by H is much smaller than that caused by O, resulting in smaller values of the mechanical contribution for H adsorbate in all metals.

Detailed plots of the variations of each contribution with strain for all the metals studied can be found in the Appendix Chapter B for O (Figure B. 8.11) and H (Figure B. 8.12). In all cases, the electronic contribution becomes more favorable under tensile strain, while compression has the opposite effect. It is evident that the effects of elastic strains on the electronic contribution are more pronounced for oxygen than for hydrogen adsorption, similar to what occurs in platinum. The values of the mechanical contributions are small and positive, in line with the Pt results. In addition, E_{mech} is also higher for oxygen than

System	E_{ads}	E_{elec}	E_{mech}	System	E_{ads}	E_{elec}	E_{mech}
O/Pt(111)	-2.16	-2.31	0.15	H/Pt(111)	-0.49	-0.53	0.04
O/Au(111)	-0.98	-1.25	0.27	H/Au(111)	0.09	0.03	0.06
O/Cd(0001)	-2.24	-2.46	0.22	H/Cd(0001)	0.81	0.72	0.09
O/Ir(111)	-2.62	-2.86	0.24	H/Ir(111)	-0.39	-0.42	0.03
O/Nb(110)	-5.58	-5.72	0.14	H/Nb(110)	-0.89	-0.94	0.04
O/Ni(111)	-3.13	-3.19	0.07	H/Ni(111)	-0.52	-0.53	0.01
O/Rh(111)	-2.96	-3.07	0.11	H/Rh(111)	-0.53	-0.55	0.02

Table 5.2: Total adsorption, electronic, and mechanical energies for oxygen and hydrogen into the 7 metal surfaces at zero strain. All energies are expressed in (eV).

for hydrogen adsorption. The absolute values of E_{mech} for hydrogen do not exceed 0.1 eV in any metal, while for oxygen, E_{mech} can reach up to 0.35 eV. These results indicate that the behavior of the studied metals closely resembles that of Pt. Finally, the ordering of E_{elec} upon strain is as follows: Ir~Pt>Au>Rh>Ni>Cd>Nb, suggesting that gold, iridium, or platinum are significantly more susceptible to changes than niobium or cadmium on its electronic structure due to applied elastic strains.

5.1.2 PtO₂

The role of electronic and mechanical contributions to the adsorption energy was also analyzed in the adsorption process of H, O, OH, C, CO, N, and NO onto a PtO₂ (110) surface. It was found that the most favorable adsorption site for H and N was on top of an oxygen atom (position 3: ONTOP_O_1 in Figure 5.2 b). In contrast, C, CO, NO, O, and OH, get adsorbed on top of a Pt atom (position 2: ONTOP_Pt_2 in Figure 5.2 b). The values for E_{ads} , E_{elec} , and E_{mech} are shown in Table 5.3.

System	E_{ads}	E_{elec}	E_{mech}
H/PtO ₂	-1.01	-1.05	0.04
O/PtO ₂	-0.42	-0.88	0.46
OH/PtO ₂	1.74	1.24	0.50
N/PtO ₂	2.53	2.07	0.46
NO/PtO ₂	-0.70	-1.30	0.60
C/PtO ₂	4.88	4.30	0.58
CO/PtO ₂	-1.42	-1.94	0.53

Table 5.3: Total adsorption, electronic, and mechanical energies for the adsorption of H, O, OH, N, NO, C, and CO in the optimum adsorption site of PtO₂ (110) at zero strain. All energies are expressed in (eV).

The total adsorption energy (green), the electronic contribution (blue), and the mechanical

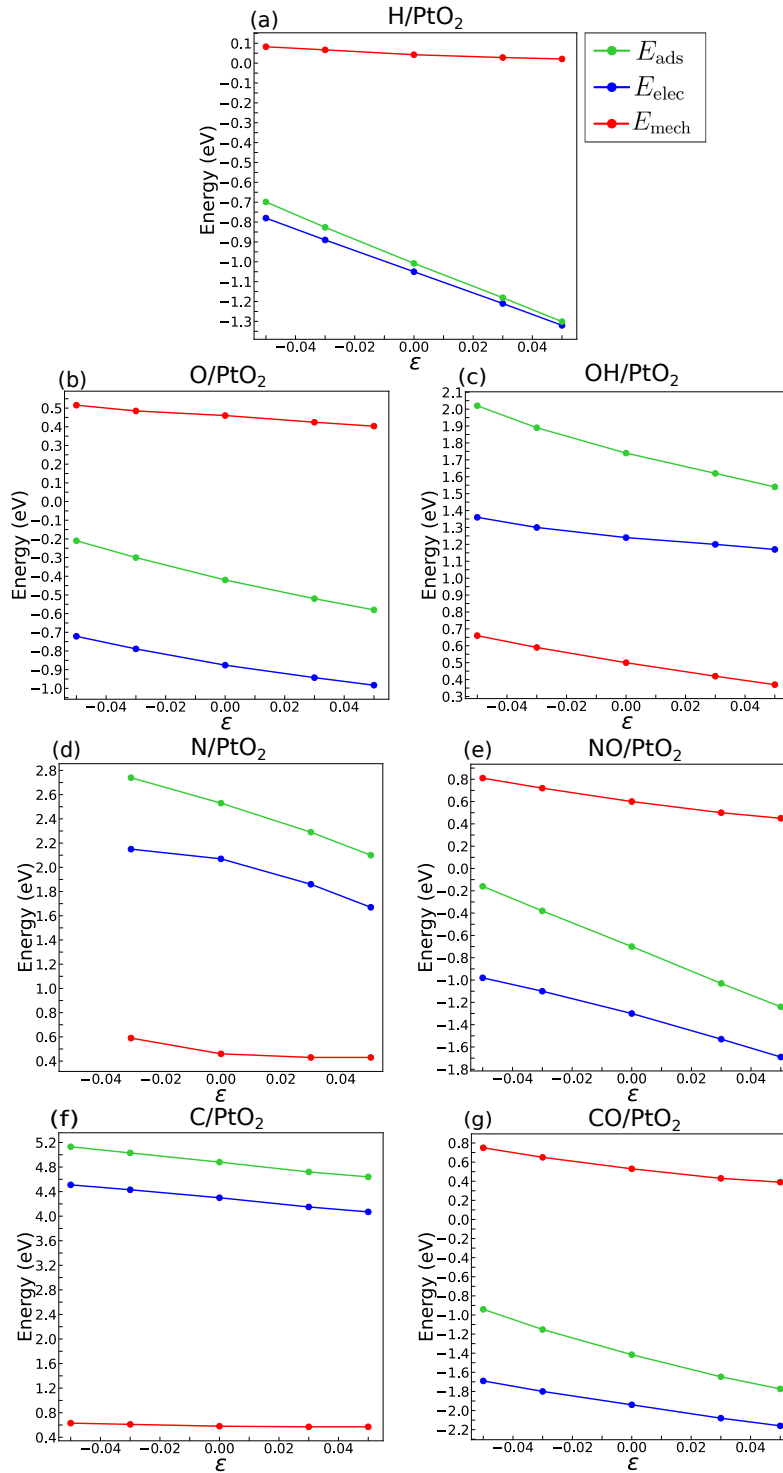


Figure 5.5: Different contributions for the adsorption of (a) H, (b) O, (c) OH, (d) N, (e) NO, (f) C, and (g) CO, into a PtO_2 (110) surface. The green, blue, and red lines represent the total adsorption energy (E_{ads}), as well as the electronic (E_{elec}) and mechanical (E_{mech}) contributions, respectively. Data at -5% compression in (d) was omitted due to the instability of the slab.

contribution (red) of the 7 adsorbates in a PtO_2 (110) surface are plotted in Figure 5.5. As in the case of Pt (111), the total adsorption energy decreased with the application of biaxial tensile strains and increased with compressive ones. It should be noted, however, that the mechanical contribution to the total adsorption energy is in the range of 0.5 eV to 0.7 eV for most adsorbates (the only exception is H) in the case of PtO_2 (110) surfaces. These values are much higher than those found in Pt (111) surfaces.

The differences in the electronic and mechanical contributions to the adsorption energy in PtO_2 (110) with strain are plotted in Figure 5.6 for the 7 different adsorbates. The electronic contribution in Figure 5.6 a is referenced with respect to the situation where no strain is applied ($E_{\text{elec}}(\epsilon) - E_{\text{elec}}(\epsilon = 0)$). The variation of E_{elec} is almost linear with the applied biaxial elastic strain: compressive strains increase the adsorption energy, which decreases with tensile strains. The slope of the quasi-linear relationship between E_{elec} and ϵ follows the order $\text{NO} > \text{N} > \text{H} > \text{CO} > \text{C} > \text{O} > \text{OH}$ (different from the one found onto Pt (111)). The maximum sensitivity to the elastic strains is found in N and NO while the minimum is reported for O and OH. Overall, the comparison of Figures 5.4 a and 5.6 a indicates the electronic contribution to the adsorption energy is more sensitive to the applied elastic strain in the case of Pt (111), as compared with PtO_2 .

Regarding the mechanical contributions to the adsorption energy (Figure 5.6 b), they are constant (or decrease slightly with the tensile strains) in all adsorbates and higher than those found in Pt (111) (Figure 5.4 b) in all cases except for H, in which the mechanical contribution to the adsorption energy is around 0.5 on Pt (111) and PtO_2 (110).

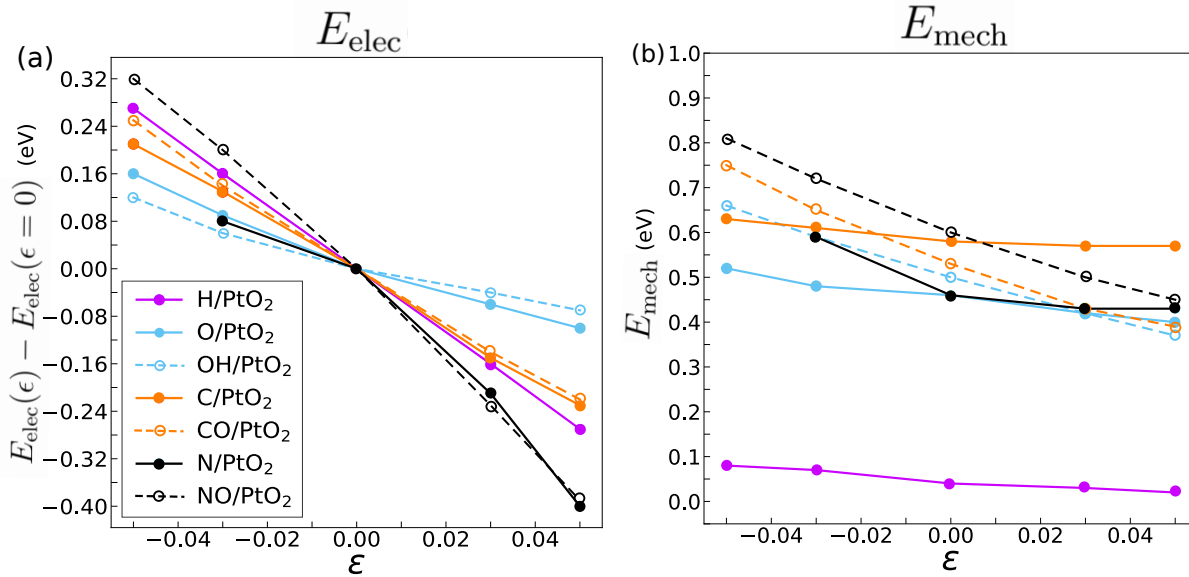


Figure 5.6: (a) Electronic and (b) mechanical contributions to the adsorption energies for different adsorbates onto PtO_2 (110) as a function of the applied strain. The electronic contribution values are referenced with respect to the ones corresponding to zero strain. Solid markers and lines represent monoatomic adsorbates, while dash lines and empty circles illustrate diatomic molecules.

5.2 Discussion

The results presented above show large differences in the variation of E_{elec} (which provides the main contribution to the adsorption energy) with the applied strain for different adsorbates in both Pt and PtO₂. This behavior can be rationalized through the d -band model and the surface charge transfer from/to the adsorbate. As previously mentioned, the d -band center acts as an excellent estimator of the effect of elastic strains on metallic surfaces [178], however, its role in the description of different adsorbates onto the same system has not been quantified. Complimentary, the extension of the d -band theory to the so-called pd -band model in oxides is scarcely explored. The charge transfer from/to the surface to/from the adsorbate is a common approach to elucidate the nature of the interaction as well as the effect of strain [77, 181, 233, 286].

5.2.1 Adsorbate effect in the variation of E_{elec} with strain on Pt

The effect of elastic strains on the adsorption energy of different transition metals has been rationalized through the d -band model [92]. As it is widely known, the changes in the electronic structure can be quantified by the projected density of the states (PDOS) [94]. Hammer and Nørskov proposed the theory of the d -band center to explain the adsorption of hydrogen atoms on the surface of nickel, copper, platinum, and gold [92]. It rationalizes the adsorption energy of the process as a function of the d -band center shift (Section 1.2.2). However, the applicability of this model to explain the influence of different adsorbates on the strain elastic sensitivity has not been analyzed. To this end, the projected density of the states (PDOS) of the d -band onto the Pt surface atoms was analyzed for all adsorbates, and the d -band center shift was calculated.

The shifts in the Fermi energy ($E_{f0} - E_f$) and the d -band center ($E_{d0} - E_d$) are shown in Table 5.4 for all the adsorbates while the full PDOS for the different adsorbates can be found in Appendix Chapter B Figure B. 8.9. In all cases, the Fermi energy shifts toward higher energies whereas the d -band center shifts down. This phenomenon reveals a higher occupancy in the bonding states due to the adsorbate-surface interaction. The d -band center shift allows to rationalize the variations of E_{elec} with the applied elastic strain. The adsorbates that lead to a maximum shift in the d -band center, expressed by $E_{d0} - E_d$, also show the largest variation in E_{elec} with the elastic strain (i.e. C, N, O, and OH). On the contrary, if the change in the d -band center is minimum with the presence of adsorbate (i.e. H, CO, and NO) also shows the lowest influence of the elastic strains in E_{elec} (Figure 5.4 a). Moreover, the Fermi energy (E_f) and the d -band center (E_d) are illustrated in Table 5.5 for the seven X/Pt(111) systems subjected to -3% biaxial compression and 5% biaxial tension. In accordance with the d -band model [92–94], tensile strains narrow the d -band and lead to an upshift of E_d to maintain the d -filling constant, while compressive strains make the bands wider and move the d -band center down. The behavior of all adsorbates follows this behavior.

In addition to the shift of the d -band, the charge transfer between an adsorbate and a surface can shed light on the nature of the interaction. The charge donated from/to the surface to/from the seven different adsorbates in Pt was computed. The Bader program,

System	E_f (eV)	$E_{f0} - E_f$ (eV)	E_d (eV)	$E_{d0} - E_d$ (eV)
Pt(111)	3.57	0.00	-2.09	0.00
H/Pt(111)	3.66	-0.09	-2.22	0.13
O/Pt(111)	3.70	-0.14	-2.52	0.43
C/Pt(111)	3.75	-0.18	-2.59	0.5
N/Pt(111)	3.70	-0.13	-2.55	0.46
OH/Pt(111)	4.30	-0.73	-2.45	0.36
CO/Pt(111)	3.61	-0.04	-2.23	0.14
NO/Pt(111)	3.77	-0.20	-2.38	0.29

Table 5.4: Electronic shifts in Pt(111) due to the adsorption of the 7 adsorbates at zero strain. E_f , $E_{f0} - E_f$, E_d , and $E_{d0} - E_d$ stand for the Fermi energy, the shift in the Fermi energy with the adsorption of the corresponding adsorbate, the d -band center, and the shift in the d -band center after the adsorption, respectively. All values are expressed in eV.

System	Pt1 (e)	Pt2 (e)	Pt3 (e)	Pt4 (e)	Adsorbate (e)	
H/Pt(111)	-0.02	0.04	0.02	0.00	0.11	
N/Pt(111)	-0.26	-0.30	-0.28	0.06	0.80	
O/Pt(111)	-0.25	-0.28	-0.26	0.06	0.80	
C/Pt(111)	-0.17	-0.21	-0.19	0.06	0.50	
OH/Pt(111)	-0.14	-0.16	-0.16	0.08	1.09 (O) -0.62 (H)	0.47
CO/Pt(111)	-0.07	-0.11	-0.08	0.05	-1.69 (C) 1.98 (O)	0.29
NO/Pt(111)	-0.16	-0.20	-0.17	0.07	0.21 (N) 0.29 (O)	0.50

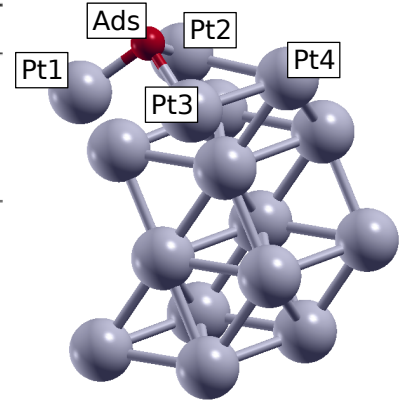


Figure 5.7: Charge transfer for the 7 adsorbates in a Pt fcc(111) surface at FCC position at zero strain. The Pt1, Pt2, Pt3, and Pt4 positions are shown in the scheme at the side of the table. All values are expressed in elemental units where $e = -1$. A positive value expresses a gain of negative charge, whereas a negative value expresses a loss of negative charge.

developed by Yu and Trinkle [347] was used to this end. This code uses the Bader definition of an atom, a 3-D object that is delimited by surfaces having zero flux in the gradient vector field of the electron density [13]. More specifically, the electron density of each of the atoms on the surface and the adsorbate was analyzed, and the differences with respect to the standard charge revealed the electronic transfers.

The charge transfers for the different adsorbates in Pt fcc(111) are depicted in Figure 5.7. A negative charge transfer stands for a loss of electronic density whereas a positive charge transfer represents a gain of electronic density. The four platinum atoms of the model surface are numbered and Pt1, Pt2, and Pt3 are the atoms next to the adsorption site. The charge donated from the surface to the adsorbate is given as a single value for monoatomic

System	Strain (%)	E_f (eV)	E_d (eV)
H/Pt(111)	-3	3.87	-2.31
	0	3.66	-2.22
	5	2.79	-2.00
O/Pt(111)	-3	3.91	-2.56
	0	3.70	-2.52
	5	2.85	-2.31
C/Pt(111)	-3	3.94	-2.65
	0	3.75	-2.59
	5	2.91	-2.49
N/Pt(111)	-3	3.87	-2.65
	0	3.70	-2.55
	5	2.92	-2.49
OH/Pt(111)	-3	4.53	-2.46
	0	4.30	-2.45
	5	3.37	-2.10
CO/Pt(111)	-3	3.80	-2.32
	0	3.61	-2.23
	5	2.76	-2.06
NO/Pt(111)	-3	3.97	-2.39
	0	3.77	-2.38
	5	2.70	-2.16

Table 5.5: Fermi energy (E_f) and d -band center (E_d) for the X/Pt(111) systems under biaxial strain.

adsorbates, while the charge of each atom and the total charge of the adsorbate are shown for the molecular adsorbates.

In all cases, the Pt surface donates electronic density to the adsorbate. The H atom receives the least charge while O and N receive the highest one, in agreement with the different electronegativities of each element. For the molecular adsorbates, the electronic density gained from the surface is distributed among both atoms in the case of OH, CO, and NO, following their corresponding electronegativity, and O atoms receive the majority of the charge.

If the same atoms of the monoatomic and diatomic adsorbates are compared, it is found that variation of E_{elec} with the applied strain increases with the amount of charge donated from the surface to the atom of the adsorbate closest to the surface. That is, the O adsorbate gets 0.8 e from the surface, while the O atom of the OH adsorbate gets 1.09 e from both the surface and the H atom and the variations of E_{elec} with strain for OH are higher than for O. Similar conclusions can be reached for C and CO as well as N and NO as shown in

Figure 5.4 a. This corroborates the conclusions obtained from the PDOS.

The analysis of the effect of elastic strains on the charge transfer led to a familiar result: tensile strains increase the distance of the surface atoms and make the area of the adsorption hole bigger. As a consequence, the distance between the surface and the adsorbate decreases, and the charge transfer increases. Conversely, compressive strains increase the adsorbate-surface distance and minimize the charge transfer. The variations in charge with strain for the seven adsorbates in Pt(111) are shown in Table 5.6. Albeit important, the variation of charge transfer as a function of mechanical strain (from -3% compression to 5% tension) is small and similar for all adsorbates.

begincentering

System	Strain (%)	Pt1 (e)	Pt2 (e)	Pt3 (e)	Pt4 (e)	Ads (e)	Ads-Pt distance (Å)
H/Pt(111)	-3	-0.02	0.05	0.02	-0.01	0.09	0.97
	0	-0.02	0.04	0.02	0.00	0.11	0.86
	5	0.01	0.07	0.03	0.01	0.12	0.68
O/Pt(111)	-3	-0.27	-0.29	-0.25	0.05	0.78	1.29
	0	-0.25	-0.28	-0.26	0.06	0.80	1.18
	5	-0.25	-0.26	-0.22	0.07	0.82	0.96
C/Pt(111)	-3	-0.18	-0.21	-0.19	0.06	0.49	1.14
	0	-0.17	-0.21	-0.19	0.06	0.50	0.96
	5	-0.15	-0.18	0.18	0.07	0.51	0.66
N/Pt(111)	-3	-0.26	-0.29	-0.28	0.06	0.77	1.20
	0	-0.26	-0.30	-0.28	0.06	0.80	1.07
	5	-0.26	-0.29	-0.28	0.08	0.84	0.76
OH/Pt(111)	-3	-0.15	-0.17	-0.16	0.09	0.48	1.62
	0	-0.14	-0.16	-0.16	0.08	0.47	1.46
	5	-0.13	-0.16	-0.14	0.09	0.48	1.31
CO/Pt(111)	-3	-0.07	-0.11	-0.09	0.04	0.31	1.45
	0	-0.07	-0.11	-0.08	0.05	0.29	1.37
	5	-0.06	-0.08	-0.07	0.06	0.33	1.26
NO/Pt(111)	-3	-0.17	-0.19	-0.18	0.07	0.49	1.45
	0	-0.16	-0.20	-0.17	0.07	0.50	1.37
	5	-0.14	-0.17	-0.17	0.09	0.53	1.26

Table 5.6: Effect of strains in the charge transfer of the 7 different adsorbates onto a Pt(111) surface.

5.2.2 Adsorbate effect in the variation of E_{elec} with strain on PtO_2

Following the same methodology as for Pt, the band center shifts when the adsorption occurred on a surface of $\text{PtO}_2(110)$ were analyzed for the 7 adsorbates. In this case, both

the d -bands of the Pt atoms and the p -bands of the O atoms (E_{pd}) on the surface were analyzed.

The Fermi energy (E_f), the band center (E_{pd}), and their shifts with respect to the clean slab for the different adsorbates are depicted in Table 5.7. In addition, the full PDOS for the different adsorbates can be found in Appendix Chapter B Figure B. 8.10. All the Fermi energies shift towards higher energies, while the band centers shift down, in the presence of adsorbates, as was the case for the adsorption on Pt(111). This behavior is in agreement with the phenomenon of adsorption and reflects the higher occupancy in the bonding states due to the presence of the adsorbates ontop of the surface. Again, the shift of the band center explains the variation of E_{elec} with the elastic strain. Large magnitudes of $E_{pd0} - E_{pd}$ lead to a more marked effect of the elastic strains on E_{elec} (Figure 5.6 a). In particular, the variation in E_{elec} with the elastic strains followed the order $NO > N > H > CO > C > O > OH$, while the band shift magnitude was $N > NO > H > CO > C > OH > O$. Thus, the only exceptions to this rule were N/NO and O/OH, whose order was exchanged, but it should be noted that the differences in the calculated adsorption energies were very small and within the error of the DFT simulations.

It should be noted that this information is useful to predict the magnitude of the effect of strains of a specific adsorbate on a specific surface, without the need for any calculation with deformation. When the adsorbate heavily shifts the bands of the surface at zero strain, the effect of elastic strains in that adsorption process is going to be significant. In contrast, if the presence of the adsorbate on the unstrained surface does not notably modify the bands, the application of strains is not going to provoke big changes in the adsorption energy.

System	E_f	$E_{f0} - E_f$	E_{pd}	$E_{pd0} - E_{pd}$
PtO ₂ (110)	2.21	0.00	-1.70	0
H/PtO ₂ (110)	3.06	-0.85	-2.17	0.47
O/PtO ₂ (110)	2.22	-0.01	-1.87	0.17
C/PtO ₂ (110)	2.57	-0.36	-2.06	0.36
N/PtO ₂ (110)	2.96	-0.75	-2.37	0.67
OH/PtO ₂ (110)	2.66	-0.45	-1.94	0.24
CO/PtO ₂ (110)	2.86	-0.65	-2.13	0.43
NO/PtO ₂ (110)	3.19	-0.98	-2.27	0.57

Table 5.7: Electronic shifts in PtO₂ (110) with the 7 adsorbates at zero strain. E_f , $E_{f0} - E_f$, E_{pd} , and $E_{pd0} - E_{pd}$ stand for the Fermi energy, the shift in the Fermi energy with the adsorption of the corresponding adsorbate, the d or p band center, and the shift in the band center after the adsorption, respectively. All values are expressed in eV.

Similarly than for Pt(111), the Bader charge transfer was calculated for PtO₂ in order to understand the variations of E_{elec} , the nature of the interaction and the balance of charges between the adsorbate and the surface. The charge transfers of each of the seven adsorbates into a surface of PtO₂(110) are shown in Figure 5.8. Negative values of charge transfer

report a loss of electronic density, while positive values report a gain. The six atoms that conform the surface were labelled as Pt1, Pt2, O1, O2, O3, and O4. In this case, the adsorbates show two different adsorption sites: ONTOP_Pt_2 and ONTOP_O_1, which have been labeled as Ads and Ads', respectively. In contrast with the case of Pt(111), where the surface donated charge for all the adsorbates, two different tendencies were found. H and N donate charge to the surface O (very electronegative) when the adsorption occurs on top of an oxygen atom (ONTOP_O_1, Ads'). On the contrary, the Pt surface atoms donate charge to the adsorbate if the adsorption occurs on top of a metal atom (ONTOP_Pt_2, Ads). The H atom donates the largest amount of charge to the surface, while the O atom receives the largest from it. This is in accordance with the electronegativity of the adsorbates. For the diatomic adsorbates (OH, CO, and NO), the O retains most of the charge donated from the surface, while H, C, and N, lose charge.

System	Pt1 (e)	Pt2 (e)	O1 (e)	O2 (e)	O3 (e)	O4 (e)	Adsorbate (e)	
H/PtO ₂ (110)	-3.09	-3.09	1.20	2.54	2.23	0.92	-0.72 (Ads')	
N/PtO ₂ (110)	-3.07	-3.07	0.89	2.56	2.50	0.71	-0.49 (Ads')	
O/PtO ₂ (110)	-1.87	-1.98	0.71	0.87	0.87	0.92	0.54 (Ads)	
C/PtO ₂ (110)	-1.67	-1.84	0.79	0.88	0.88	0.93	0.12 (Ads)	
OH/PtO ₂ (110)	2.12	-1.96	0.74	-3.12	-3.12	0.92	1.45 (O) -0.99 (H)	0.45 (Ads)
CO/PtO ₂ (110)	-1.72	-1.85	0.82	0.88	0.88	0.94	-1.72 (C) 1.77 (O)	0.05 (Ads)
NO/PtO ₂ (110)	2.16	-1.85	0.83	-3.12	-3.12	0.94	-0.27 (N) 0.43 (O)	0.16 (Ads)

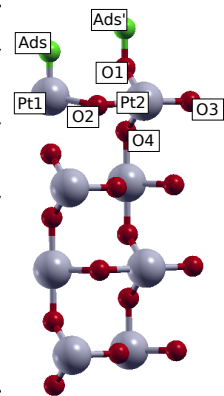


Figure 5.8: Charge transfer for the 7 adsorbates in a PtO₂(110) surface at ONTOP_Pt_2 (Ads) and ONTOP_O_1 (Ads') positions at zero strain. The Pt1, Pt2, O1, O2, and O3 positions are shown in the scheme at the side of the table. All values are expressed in elemental units where $e = -1$. A positive value expresses a gain of negative charge, whereas a negative value expresses a loss of negative charge.

This analysis shows once again the charge transfer between the surface and the adsorbate can be correlated with the variations of E_{elec} with strain and the variation of E_{elec} with the applied strain increases with the charge donated from the surface to the adsorbate. For instance, the charge transfers from N and NO to the surface are -0.49 e and 0.16 e, respectively, and the effect of strain on E_{elec} is much higher in the case of N. In the cases of C/CO, and O/OH, the charge donated from the surface to the adsorbate is similar and the variations of E_{elec} with the applied strain are also comparable (Figure 5.6 a). On average, the amount of charge transferred in PtO₂ is lower than in Pt, as so is the E_{elec} , but the differences are small. Regarding the effect of strain in PtO₂, the outcome is analogous to that for Pt: when subjected to tensile strains, the surface atoms are pushed further apart, thereby expanding the area of the adsorption site. This causes a decrease in the distance between the surface and the adsorbate, resulting in a higher level of charge transfer. Conversely, compressive strains have the opposite effect, increasing the distance between the adsorbate and the surface and reducing the extent of charge transferred. In conclusion, the bigger the amount of charge involved in the adsorption process, the higher the variation

of energy the strain is going to provoke.

5.2.3 E_{mech} in Pt and PtO₂

The mechanical contributions to the adsorption energy, E_{mech} , due to the distortion of the lattice in the presence of the adsorbate, are depicted in Figures 5.4 b 5.6 b for Pt and PtO₂. It should be noted that E_{mech} is much higher in the case of PtO₂ (110) surfaces (up to 0.7 eV) than in Pt (111) surfaces (up to 0.1 eV). In both cases, these contributions are practically independent of the applied elastic strain, indicating that they only depend on the distortion of the lattice induced by the presence of adsorbate. Even in the CO/PtO₂, NO/PtO₂, and OH/PtO₂ cases, with changes in E_{mech} around 0.3 eV, a little bit higher than the commonly accepted 0.1-0.2 eV DFT errors, the variation in E_{elec} with strain is presumably more significant. The correlation between the surface-adsorbate distance and mechanism energy is not that clear in the case of PtO₂ as in the case of pure Pt. Finding a metric in the former case is much more complicated, as when the adsorption happens in the PtO₂ surface, all atoms -not only the ones close to the adsorption site- experience a variation in their position. However, even if not perfect, the proposed correlation can serve as an approximate approach to get a broad sense of how the mechanism energy would be.

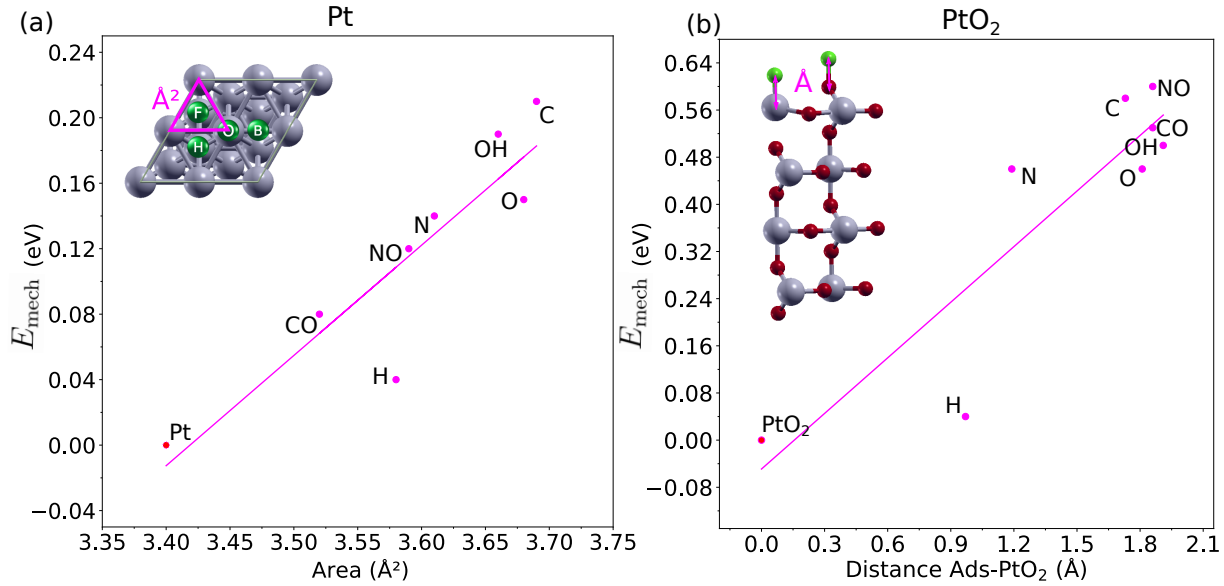


Figure 5.9: Relationship between the values of E_{mech} (eV) and (a) the Area of the adsorption hole (Å²) in Pt (111) and (b) the surface-adsorbate distance (Å) in PtO₂ (110) for the seven adsorbates at zero strain.

The adsorption process in Pt occurs in the hole between three surface atoms. As shown in Figure 5.9 a, the magnitude of E_{mech} increases with the dimensions of the hole, and the larger the distortion, the larger E_{mech} . This metric cannot be applied, however, to PtO₂, as the adsorption occurs on top of Pt and O atoms, and not in a hole. In this case, the presence

of the adsorbate on the surface provokes a vertical displacement of the surface layer towards the adsorbate. E_{mech} is plotted in Figure 5.9 b as a function of the distance between the adsorbate and the surface atom below. In general, longer distances are associated with higher E_{mech} , as the surface atoms have to rearrange more to balance the shift up of the atom below the adsorbate. The lowest adsorption distance appears for H, where E_{mech} is also small. For the rest of the adsorbates, the atomic displacements are similar as so are their values of E_{mech} .

Finally, it should be noted that E_{mech} is higher in PtO_2 , as compared with Pt. This difference can be explained by the nature of the bonding. In the case of Pt, the interactions within the slab are metallic, whereas they are ionic in PtO_2 . The electrons are moving freely around the nucleus in the electronic cloud in Pt while they are localized towards the oxygen atoms in PtO_2 due to the different electronegativity of Pt and O. Thus, the adsorption of an atom causes a higher distortion in the electronic cloud in the latter case, leading to a rearrangement of the atoms to find a most stable position.

Conclusions

In this Chapter, The influence of elastic strain on the adsorption process onto Pt and PtO_2 of seven adsorbates (H, C, N, O, CO, NO, and OH) was calculated by DFT simulations. Moreover, the adsorption energy was split into mechanical and electronic contributions. It was found that the adsorption energies decrease with tensile strains and increase with compressive strains in Pt and PtO_2 for all adsorbates. Moreover, it was found that the mechanical contribution to the adsorption energy was independent of the elastic strain and, thus, the effect of elastic strains on the adsorption energy was due to changes in the electronic structure.

The sensitivity of the electronic contribution to the adsorption energy of a given system (either X/Pt or X/ PtO_2) could be explained by the *d*-band model. The adsorbates that lead to a maximum shift in the *d*-band center also show the largest variation in the electronic contribution to the adsorption energy with the elastic strain. They are C, N, O, and OH in Pt and N and NO in the case of PtO_2 . On the contrary, H adsorption always shows the lowest sensitivity to the application of elastic strains.

Finally, the mechanical contribution to the adsorption energy could be associated with the distortion of the lattice in the presence of the adsorbate. It was very small in the case of Pt (< 0.2 eV) and slightly higher (up to 0.6 eV) in the case of PtO_2 . This difference was attributed to the ionic bonding with the PtO_2 slab, which enhances the distortion.

The results of this Chapter provide a deeper analysis of the adsorption process of different adsorbates into metallic and metal oxides surfaces. Complimentary, the nature of the interaction adsorbate/surface has also been unraveled under the application of elastic strains.

Binary intermetallic compounds

In previous chapters, a complete study of the adsorption energy and the catalytic activity has been conducted in pure metals. However, even under the application of elastic strains, a suitable candidate to replace Pt in the HER and the ORR has not been found. This pushes forward the study to explore binary intermetallic compounds.

6.1 Adsorption energy

As explained in the preceding chapters, the adsorption energy of the intermediates (H, O, and OH) can be used to estimate the catalytic activity of a material. The first step, thus, was to calculate these energies for different binary intermetallic compounds. As a first approach, two different geometries and stoichiometries were selected: A_3B fcc(111) and AB bcc(101). The reason behind this selection was that these configurations are the most common in nature and expose stable surfaces optimal for heterogeneous catalysis. The selected adsorption plane was considered to be the lowest in energy according to the Materials Project Database [118]. As explained in Section 3.1 the optimum adsorption site was determined for all the binary intermetallics (Figures 2.6 f and i) It represents the most favorable position where the substrate is rather to get absorbed. As an example, the adsorption energies for O are presented in Table 6.1 for a series of A_3B binary intermetallic compounds at all the possible adsorption sites. All the calculated H, O, and OH adsorption energies for the different geometries and stoichiometries are uploaded in <https://zenodo.org/doi/10.5281/zenodo.10364546>. A selection of Hydrogen, Oxygen, and Hydroxyl adsorption energies at FCC AAA and FCC AAB sites for A_3B fcc(111) binary intermetallic compounds is shown in the Appendix Chapter C Table C. 8.2.

The most favorable adsorption site is written in bold and in most cases corresponds to the FCC AAB adsorption site. This site is a hole between three atoms: two of element A and one of element B, and it is usually an energetically similar situation to HCP AAB. The only difference is the presence of another atom in the layer below in the HCP case, which in most cases produces a slight increase in the energy.

SYSTEM	FCC AAA	FCC AAB	HCP AAA	HCP AAB	ONTOP A	ONTOP B
O/Ag ₃ In	-1.38	-1.92	-1.24	-1.92	-1.38	-0.58
O/Ag ₃ Mg	-1.32	-2.49	-1.21	-2.44	-1.21	-0.96
O/Al ₃ Li	-4.69	-5.05	-4.58	-4.97	-4.69	-4.97
O/Au ₃ Li	-1.01	-1.66	-0.85	-1.43	-0.85	-1.66
O/Co ₃ Ti	-3.68	-4.51	-4.04	-4.35	-4.04	-
O/Cu ₃ Au	-2.47	-1.90	-2.22	-2.47	-2.47	0.29
O/Cu ₃ Pd	-2.58	-2.25	-2.32	-2.18	-2.58	-0.32
O/In ₃ Y	-1.38	-1.92	-1.24	-1.92	-1.38	-0.58
O/Ir ₃ Ti	-2.58	-3.79	-3.18	-3.84	-3.18	-2.97
O/Ir ₃ Zr	-2.59	-3.83	-3.29	-3.73	-3.29	-2.46
O/Ni ₃ Al	-2.92	-3.52	-3.13	-3.43	-	-3.52
O/Ni ₃ Fe	-2.95	-3.45	-3.07	-3.31	-3.07	-2.27
O/Ni ₃ Mn	-3.31	-3.64	-3.31	-3.57	-3.31	-3.44
O/Ni ₃ Si	-2.49	-3.33	-2.90	-3.19	-2.90	-2.07
O/Pt ₃ In	-1.24	-1.93	-1.55	-1.64	-1.55	0.53
O/Pt ₃ Zn	-1.73	-2.18	-1.82	-1.91	-1.82	0.13
O/Ru ₃ Nb	-3.56	-4.09	-4.15	-4.36	-4.15	-3.27
O/Sn ₃ Ca	-2.12	-3.43	-2.67	-3.32	-2.13	-0.55
O/Zn ₃ Mn	-2.86	-3.48	-2.56	-3.49	-2.86	-2.74
O/Zn ₃ Nb	-2.77	-4.85	-2.29	-4.98	-2.77	-4.80
O/Zn ₃ Ti	-3.01	-4.82	-2.41	-4.99	-3.01	-4.52
O/Zn ₃ V	-2.70	-4.93	-2.19	-4.98	-2.70	-4.91
O/Zr ₃ Al	-6.66	-5.63	-6.34	-5.65	-6.66	-3.10
O/Zr ₃ In	-6.82	-6.46	-6.46	-6.82	-6.82	-1.15

Table 6.1: Oxygen adsorption energies (in eV) for A₃B fcc(111) candidates at the six different adsorption sites. The most favorable adsorption sites (lowest energies) are highlighted in bold font. "-" represents a situation where the adsorbate has migrated to the most favorable adsorption position under relaxation.

This optimum adsorption site energy of A₃B and AB binary intermetallic compounds was compared to the adsorption energy in pure A and pure B, as represented in Figures 6.1, 6.2, and 6.3. The adsorption energies for the binary intermetallic compounds with stoichiometry A₃B and geometry fcc(111) (Figure 6.1) come to the same conclusion in both hydrogen and oxygen adsorption processes: the adsorption energy of the A₃B compound falls in between the adsorption energy of A and the adsorption energy of B in most cases. One of the ways to rationalize this is by analyzing the optimum adsorption site. As observed in Table 6.1, the most favorable adsorption site is -in general- either FCC AAB or HCP AAB. The adsorbate is placed in both cases in a hole between three atoms (A-A-B), so it is not unexpected that the adsorption at this site depends both on the adsorption in pure A and pure B. However, the hydrogen adsorption at Pt₃Zn seems to be an exception to this tendency, as the adsorption energy of the binary intermetallic is even more negative than the energies at pure A and pure B. In this case, the optimum adsorption site is HCP AAA,

so it is reasonable that the E_{ads_H} is closer to the energy of pure A, and the influence of pure B atoms in the adsorption is lower.

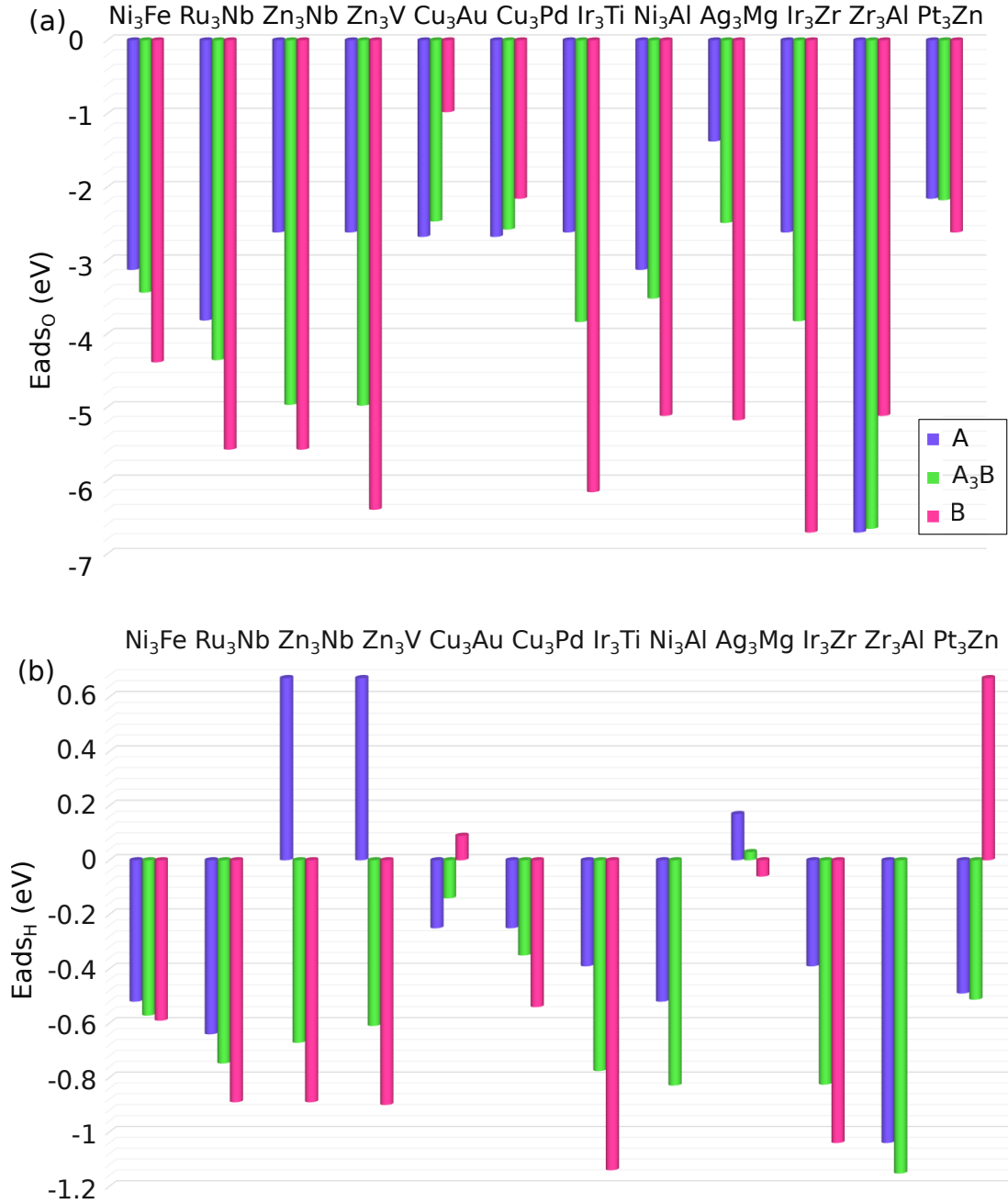


Figure 6.1: (a) Oxygen and (b) Hydrogen adsorption energies for A, B, and A₃B binary intermetallics at the optimum adsorption site.

The conclusion of this analysis is the same for the AB bcc(101) binary intermetallics (Figures 6.2 and 6.3): the majority of the compounds show adsorption energy for H and O in between the adsorption energy of the pure metals which conform the structure. There are also some exceptions such as CuPd, ZnRh, AlFe, AlRu, GaIr, GaRh, ZnRh, AlCo, AlIr,

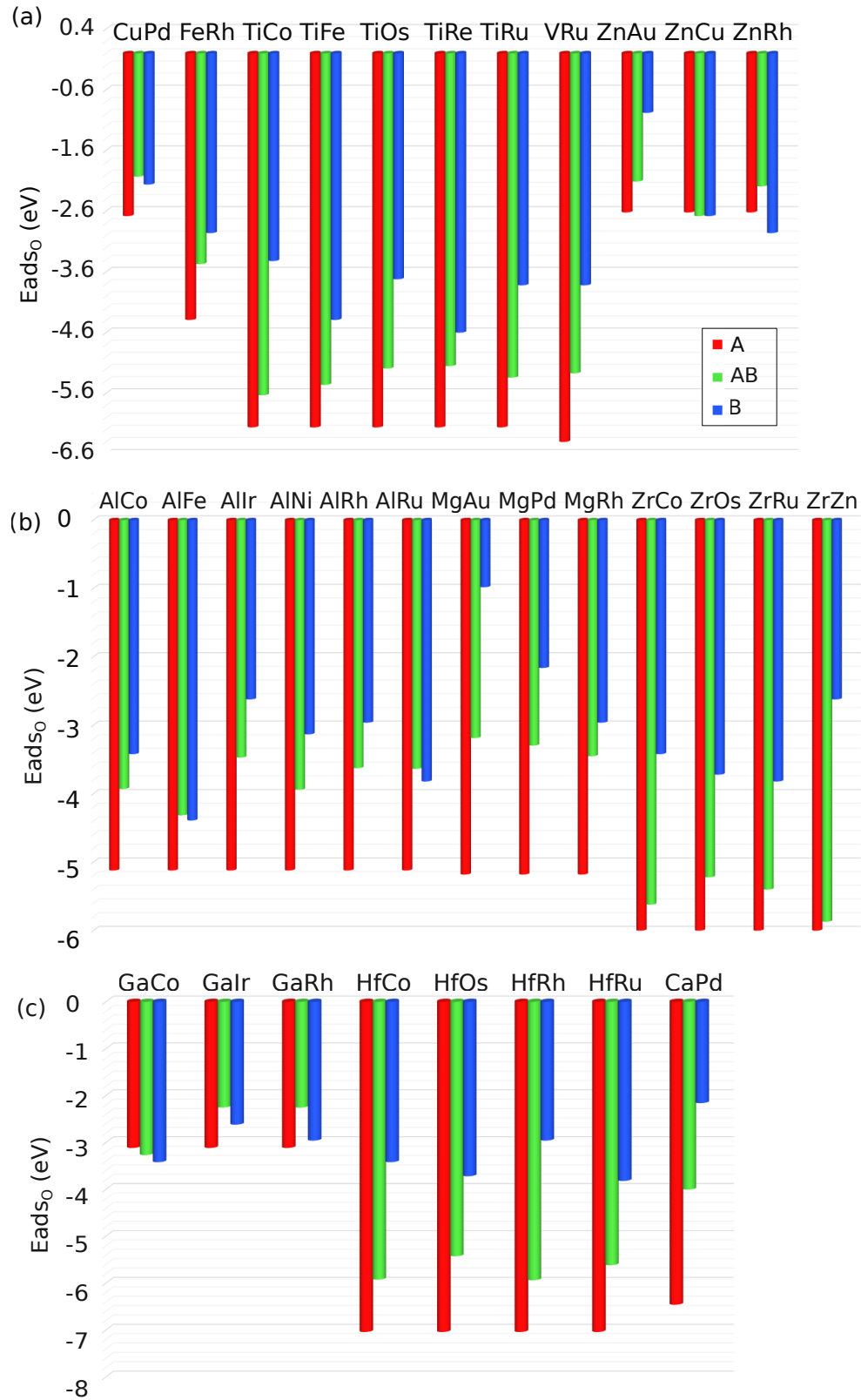


Figure 6.2: Oxygen adsorption energies for A, B, and AB binary intermetallics at the optimum adsorption site.

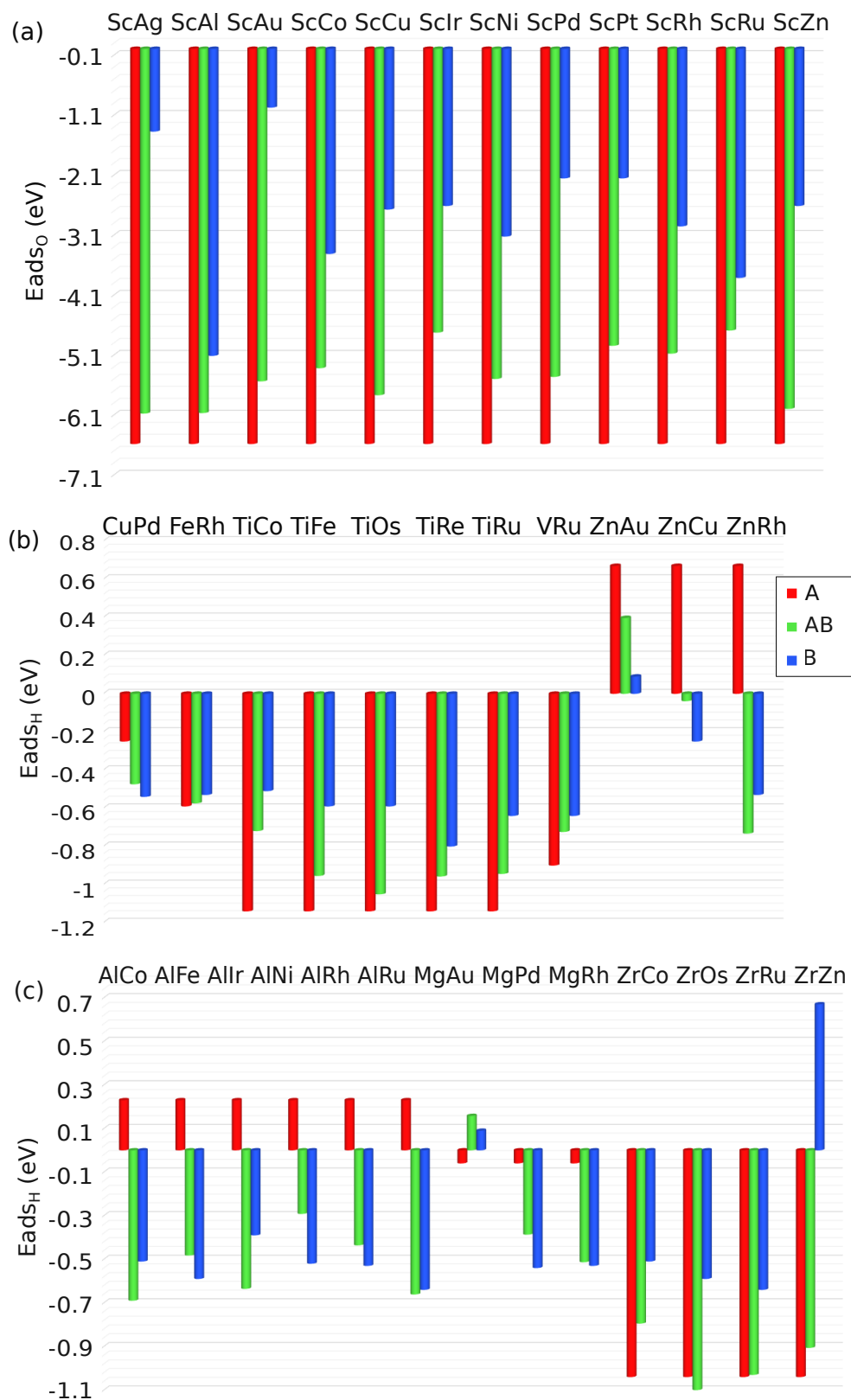


Figure 6.3: (a)(b) Oxygen and (c) Hydrogen adsorption energies for A, B, and AB binary intermetallics at the optimum adsorption site.

MgAu, and ZrOs. In all of these cases, the most favorable adsorption occurs in a THREE-FOLD AAB adsorption site, excluding AlRu, and ZnRh that occur at LONGBRIDGE BB. This leads us to the conclusion that although the adsorption energy of the constituents A and B can give an estimation of the adsorption energy at the A_xB_y compound, there is not a clear rule nor metric to predict the Eads, and DFT calculations are indeed necessary.

6.2 Effect of strain

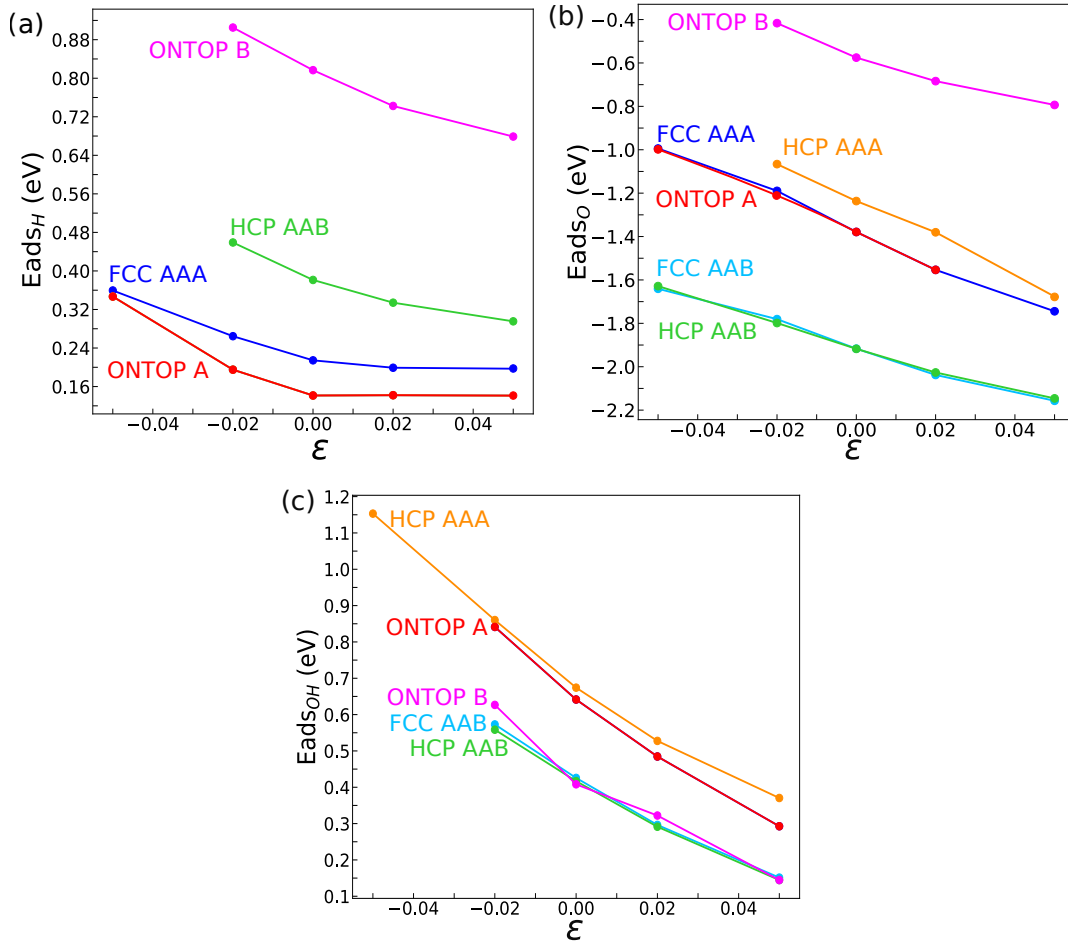


Figure 6.4: (a) Hydrogen (b) Oxygen and (c) Hydroxyl adsorption energies in Ag_3In fcc(111) at all the possible adsorption sites. Points removed at high levels of compression strains represent unstable surface situations. Adsorption position curves where the adsorbate migrates to another position are also omitted.

To discover the effect of elastic strains in the adsorption energy at binary intermetallic surfaces, E_{ads_H} , E_{ads_O} , and $E_{ads_{OH}}$ were computed by DFT under the application of biaxial strains from -5% compression to 5% tension (methodology explained in Chapter 2). In Figure 6.4 the E_{ads_H} , E_{ads_O} , and $E_{ads_{OH}}$ under the application of strains are shown at all positions of Ag_3In fcc(111) as an example. In all cases, tensile strains decrease the adsorption energies, while compressive strains unfavour the adsorption process. The most

favorable adsorption site (ONTOP A, FCC AAB, and HCP AAB) remains constant under strain for the three adsorbates (H, O, and OH). At high levels of compression ($< -2\%$), the surface becomes unstable at some adsorption positions, while the surface stability is higher under tensile strains. The slope of the curves, which corresponds somehow to the effect of strain to tune the process of adsorption, is in the same range as the slopes obtained for pure metals.

A comparison between the curves of pure Au, Ir, Pt, Ni, and Ag, and binary intermetallic compounds is illustrated in Figure 6.5. A_3B fcc(111) binaries shown (Figure 6.5 a) present oxygen adsorption energies that fall in between those values obtained for pure metals. The slopes -indicative of the effect of deformation on the surfaces- are similar for both pure metals and intermetallics. The same conclusion can be reached in the case of AB bcc(111) curves (Figure 6.5 b): the effect of strains in binary intermetallics with this stoichiometry and geometry is equivalent to the effect in pure metals. Thus, it can be concluded that the application of elastic strains to modify the adsorption processes of H, O, and OH is also effective in the case of binary intermetallic compounds, hence the methodology followed in pure metals can be extended to multimetallic materials.

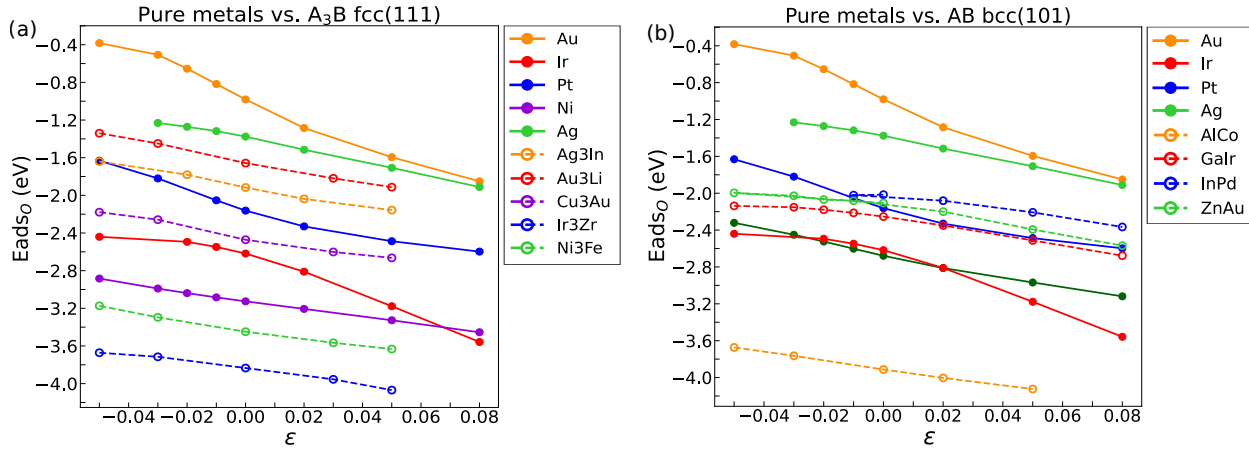


Figure 6.5: Comparison of the oxygen adsorption energies for pure metals and (a) A_3B fcc(111), and (b) AB bcc(111) binary intermetallic compounds under the application of biaxial strains. From -5% compression to 8% tension in pure metals and from -5% compression to 5% tension in binary intermetallics. Dash lines represent the adsorption for intermetallics and regular lines represent the adsorption for pure metals. Adsorption curves are shown at the most favorable adsorption site for each compound.

6.3 Catalytic activity

Similarly than for pure metals, the adsorption energies calculated in the previous section for binary intermetallic compounds can be used to calculate the catalytic activity and to plot the volcano plots for the HER and the ORR.

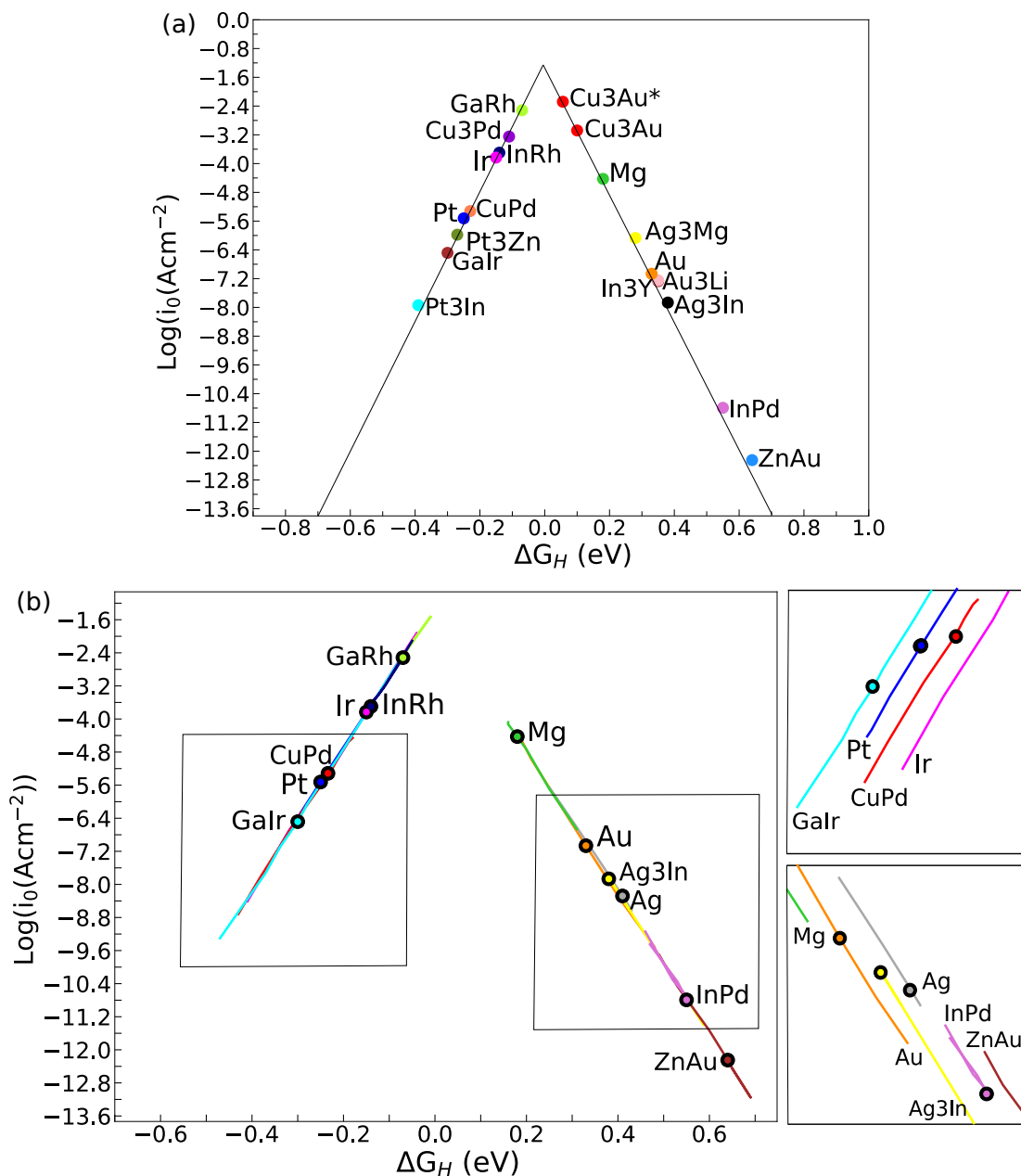


Figure 6.6: (a) Volcano plot at zero strain for the HER as a function of ΔG_H for a selection of A_3B and AB intermetallics, and pure metals. Cu_3Au^* in the HER volcano plot corresponds to the free energy obtained from the adsorption energy calculated with the DFT functional SCAN[278]. (b) Effect of mechanical strains on the volcano plot for the HER as a function of ΔG_H for a selection of A_3B and AB intermetallics, and pure metals. The range of activities for Pt, GaIr, CuPd, Ir, Mg, Au, Ag_3In , Ag, InPd, and ZnAu within the rectangle have been plotted to the right, shifted by 0.05 eV along the horizontal axis for the sake of clarity. Black circles indicate the activity at the mechanical equilibrium.

6.3.1 HER

The catalytic activity in the HER can be calculated from E_{ads_H} and is a one-step process represented by the logarithm of the exchange current density vs. G_H in a volcano plot. In Figure 6.6 a, the volcano plot at zero strain is represented for a selection of A_3B fcc(111) and AB bcc(101) binary intermetallics together with Pt, Ir, Mg, and Au for reference. As observed, there are plenty of bimetallic materials with these geometries that fall close to the top of the volcano for the Hydrogen Evolution Reaction. Cu_3Au was recomputed with the DFT functional SCAN [278] (Cu_3Au^*) to make sure that the differences in energy were not as large as in pure Cu (Figure 4.3 a).

Regarding the volcano plot under the application of elastic strains (Figure 6.6 b), different facts can be pointed out. First of all, the bimetallic materials are placed on both sides of the volcano, which means that the adsorption of O and the desorption of OH can be the rate-limiting steps for these geometries. At the left side of the volcano, where the E_{ads_O} is so low that the surface becomes poisoned, compression strains put both pure metals and binaries up to the volcano plot cusp. This situation is depicted for GaIr, CuPd, InRh, and GaRh. The opposite situation happens for elements on the right hand of the volcano. Tensile deformations favor the adsorption of the O intermediate for ZnAu and InPd, and push the activity up to the volcano. In the case of Ag_3In , the most favorable situation (highest catalytic activity) is found when no strain is applied.

6.3.2 ORR

The Oxygen Reduction Reaction is a three-step process that depends both on the adsorption energy of O and the adsorption energy of OH. Hence, the first move to calculate the catalytic activity in the ORR is to determine which is the rate-limiting step. In Figure 6.7 a, the volcano plot for the ORR is shown at zero strain for a selection of A_3B and AB intermetallics and Pt, Au, Ag, and Ir as a reference of pure metals. Alike the HER, there are also binary intermetallic compounds on both sides of the volcano for the ORR. Pt is clearly on the top, and binaries tend to cluster in the interior of the volcano. This behavior is due to the rate-limiting step, which in these cases is G_2 (Section 2.1.5). The volcano for the ORR under the application of strains is shown for Au, Pt, Ag, It, Ag_3In , CuPd, GaIr, and ZnAu in Figure 6.7 b. In the case of Ag_3In and GaIr, the rate-limiting step is G_2 no matter the level of strain applied. As they are on the left side of the volcano, compression increases the catalytic activity. Conversely, CuPd and ZnAu show a different behavior. In both cases, the equilibrium situation is the most favored, and both tension and compression provoke a decrease in the catalytic activity. Under tensile deformation, the rate-limiting step is the desorption of OH^* (G_2), while the rate-limiting process is the transition from O^* to OH^* (G_1) under compressive strains.

$E_{ads_O}/E_{ads_{OH}}$ linear relationship

The relationship between the adsorption energy of oxygen and hydroxyl has been commonly studied in the surface of pure metals. Those energies have been observed to follow a linear trend, which facilitates the predictions of the catalytic activity of the ORR, where

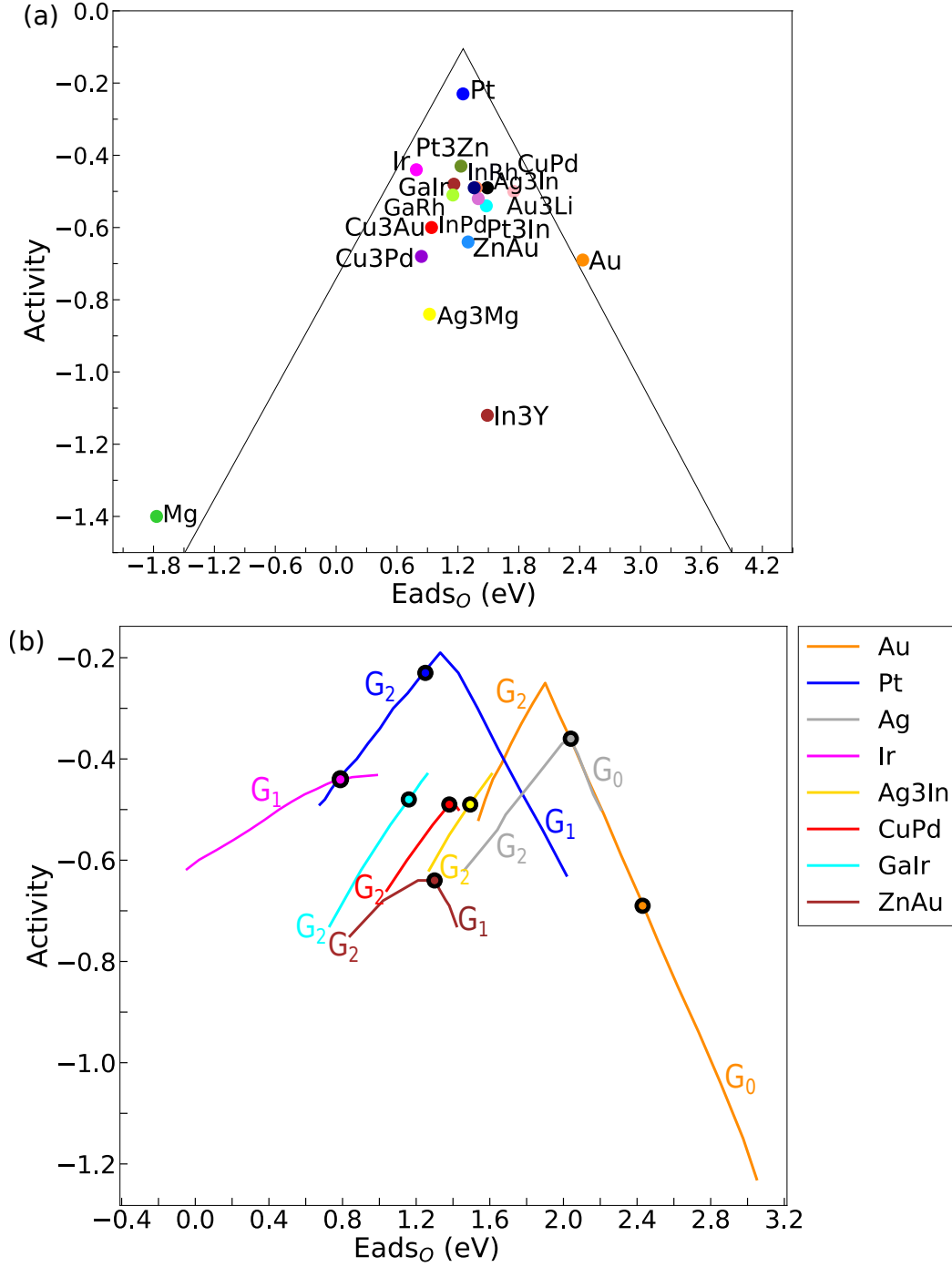


Figure 6.7: (a) Volcano plot at zero strain for the ORR as a function of E_{ads_O} , for a selection of A_3B and AB intermetallics, and pure metals. (b) Effect of mechanical strains on the volcano plot for the ORR as a function of E_{ads_O} . The free energy that limits the reaction rate is indicated at each branch of the volcano plot for each metal. The lines stand for the variation in the catalytic activity of each compound as a function of the applied elastic strain in the range from -5% biaxial compression to 8% biaxial tension in Au, Pt, Ag, and Ir, and from -2% biaxial compression to 5% biaxial tension in binary intermetallics. Black circles indicate the activity at zero strain.

both energies are involved. In Figure 6.8 a, the 3D map of pure metals, where the catalytic activity of the ORR is represented with colors, shows the linearity of both energies and it is in extremely good agreement with the map proposed by Norskov in 2004 [198]. In this 3D plot, Pt is at the peak of the ORR volcano (represented in pink) because it shows the optimum combination between E_{ads_O} and $E_{ads_{OH}}$. The rest of the metals presented a linear trend in the O and OH adsorption energies. Although in this volcano representation the two -ascending and descending- branches can not be observed, metals with more positive adsorption energies -such as Au- would be placed on the right side of the conventional volcano.

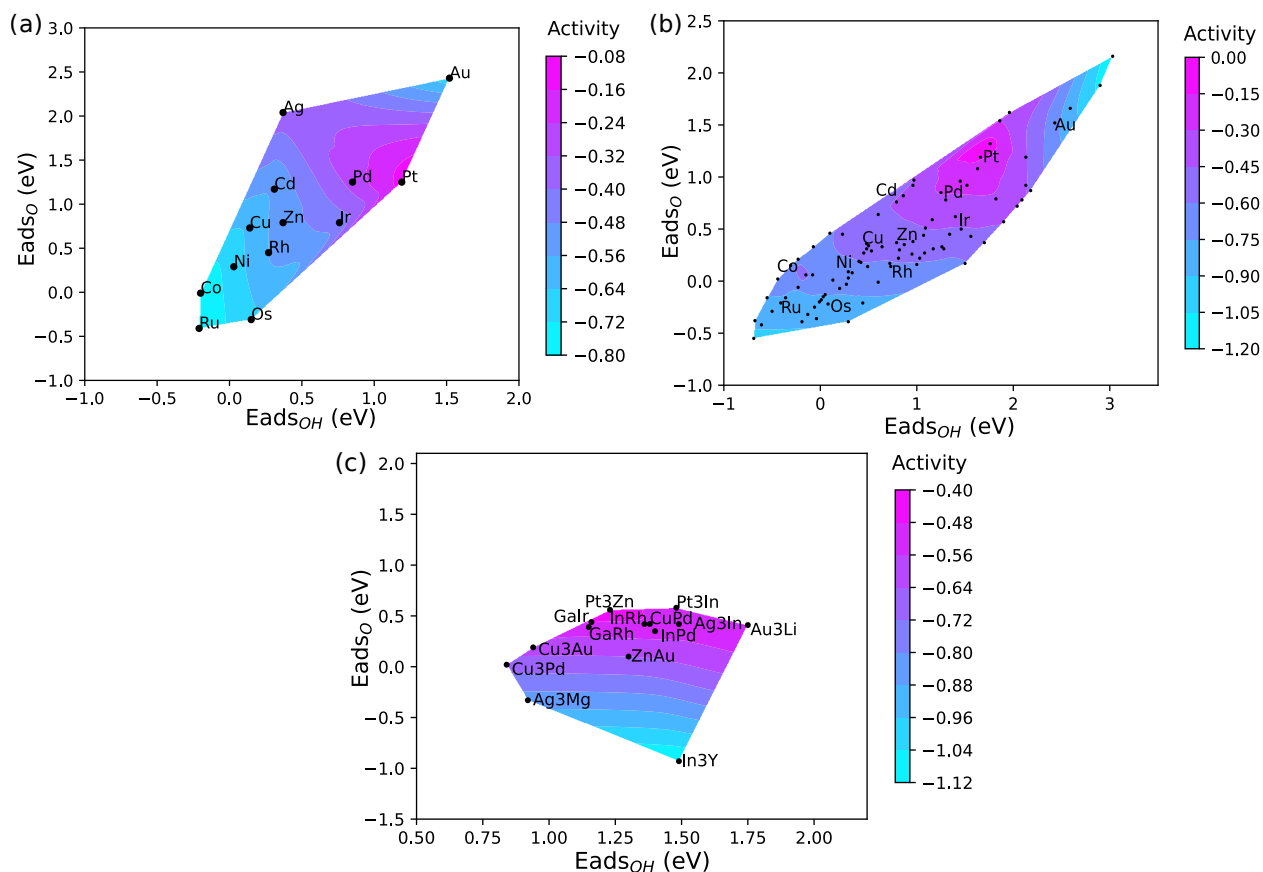


Figure 6.8: Activity maps for the ORR. E_{ads_O} and $E_{ads_{OH}}$ values correspond to the most favorable adsorption site. (a) Pure transition metals calculated by DFT. (b) Transition metals under the application of elastic strains. (c) Binary intermetallic compounds calculated by DFT.

Once this linearity was proved for our DFT calculations, the next step was to test if the linearity was conserved after the application of tensile and compressive strains into the surfaces. In figure 6.8 b, black dots represent the DFT calculations under the application of strains from -5% biaxial compression to 8% biaxial tension. As expected, the calculations under deformation also show a linear relationship between E_{ads_O} and $E_{ads_{OH}}$. Tensile strains downshift E_{ads_O} and $E_{ads_{OH}}$ at a similar proportion and decrease the catalytic activity of the ORR for metals at the left side of the volcano. However, compression strains

increase the value for both O/OH adsorption energies and augment the catalytic activity in them. For metals at the right side of the volcano, such as Au, tensile strains increase the catalytic activity, while compressive strains provoke the opposite effect. The application of strain to pure transition metal surfaces tunes both E_{ads_O} and $E_{ads_{OH}}$ similarly, hence, the linear trend is conserved.

Finally, in order to facilitate the prediction of the ORR in binary intermetallic compounds, the preservation of the linearity was tested in the case of AB bcc(101) and A_3B fcc(111) intermetallics (Figure 6.8 c). In this case, it can be clearly appreciated that the linear trend is not followed. This is in accordance with previous studies [199] which explain this deviation from the scaling relation due to the different coordination to the surface. O and OH present differences in site preference for most intermetallics while they bind in the same adsorption site for pure metals. For example, O binds Ag_3In at an hcpAAB adsorption site, while OH binds at ontopB. O is adsorbed at fccAAA position and OH at fccAAB in Pt_3Zn . Au_3Li binds O and OH at fccAAA and ontopA, respectively. This break of the linear trend for binary intermetallic compounds impedes a simple prediction of the catalytic activity and hinders a straightforward calculation of the $E_{ads_{OH}}$ based on the E_{ads_O} . This phenomenon represents a limiting factor in the straightforward search of new binary intermetallic catalysts for the ORR.

Conclusions

The methodology used in previous chapters to calculate the adsorption energy and the catalytic activity for pure transition metals was extended to binary intermetallic compounds. The adsorption energy of H, O, and OH was calculated for a series of A_3B fcc(111) and AB bcc(101) binary intermetallics at all possible adsorption sites and the most favorable adsorption site was found. FCC AAB and HCP AAB are the optimal adsorption sites in most cases with differences under 0.1 eV. In those cases where the adsorption occurs at a hole between A and B atoms, the adsorption energy of the binary intermetallic falls in between the values of the adsorption energy of pure metal A and pure metal B. If the most favorable adsorption site is FCC XXX, HCP XXX, or ONTOP X, the adsorption energy of the intermetallic is closer to the adsorption energy of pure metal X.

The application of elastic strains from -5% compression to 5% tension produced an equivalent effect in A_3B and AB binaries to that in pure metals. Compression strains increase the values of adsorption energy for the three studied adsorbates (H, O, and OH), while tensile strains make E_{ads} more negative favoring the adsorption process. In most cases, as exemplified with Ag_3In fcc(111), the most favorable adsorption site remains constant at all levels of strain. Compressive strains disrupt the surface stability at lower levels than tensile strains.

The adsorption energies were used to calculate the catalytic activity for the HER and the ORR. As observed in the volcano plots, A_3B fcc(111) and AB bcc(101) binary intermetallic compounds fall in the two branches of the volcano plot: for binaries at the left side of the volcano, compressive strains increase the catalytic activity, while for those at the right side tensile makes the catalytic process more favorable. Similarly than for pure metals,

the rate-limiting step for the ORR can be tuned with the application of strain, for instance, G_2 is the limiting step under tension for ZnAu, while G_1 limits the reaction under tensile strains. By contrast, for intermetallics such as GaIr and Ag_3In , G_2 is the limiting step no matter the amount of strain applied. All in all, it can be said that elastic strain engineering is an effective methodology to tune the catalytic activity not only for metallic surfaces but also for binary intermetallic compounds.

As shown in previous studies [198], a linear relationship can be found for Eads_O and Eads_OH in pure metals, both with and without the application of strain. However, this linear trend is not followed in binary intermetallic compounds. This phenomenon is attributed to the different surface preferences for O and OH, which usually bind the surface at different adsorption sites. This impedes a straightforward analysis of the ORR and makes DFT simulations for the Eads_O and Eads_OH crucial to calculate the catalytic activities.

Machine learning for intermetallics

In previous chapters, DFT simulations have been utilized to calculate the adsorption energy of H, O, and OH for a series of pure metals and intermetallic compounds at equilibrium and under the application of elastic strains. These adsorption energies have been used to calculate the catalytic activity for the HER and the ORR for these metallic surfaces, following the methodology proposed by Norskov [197, 198]. However, this strategy is not suitable to explore the landscape of intermetallic compounds due to their huge number. Thus, machine learning tools were used to overcome this limitation and to extend this study to many intermetallic compounds with different stoichiometries and lattices.

7.1 Machine Learning Model

The objective of this section is to develop an accurate ML model to describe the adsorption processes for the HER and the ORR in pure metals and binary intermetallic compounds. To this end, a large database of the adsorption energies of H, O, and OH was computed by DFT in 24 pure metals and 332 binary intermetallic compounds with different lattice structures, stoichiometries, and surfaces, including the effect of biaxial elastic strains. This information was used to train a random forest model to predict the adsorption energy of ≈ 2700 binary intermetallic compounds including the effect of elastic strains and using descriptors that can be obtained for each compound and surface from physicochemical databases. All the details related to the ML model are exposed in Chapter 2 Section 2.2. A scheme of the strategy followed is shown in Figure 7.1.

7.1.1 Screening and Database

24 pure metals were included in the database in order to build a database of adsorption energies able to cover intermetallic compounds of transition metals. The most stable (minimum energy) surface was selected for each element according to the information available in the Materials Project database [118] and the reference of experimental data [19]. This led us to five different slab geometries: fcc(111) for Ag, Au, Cu, Ir, Ni, Pd, Pt, and Rh,

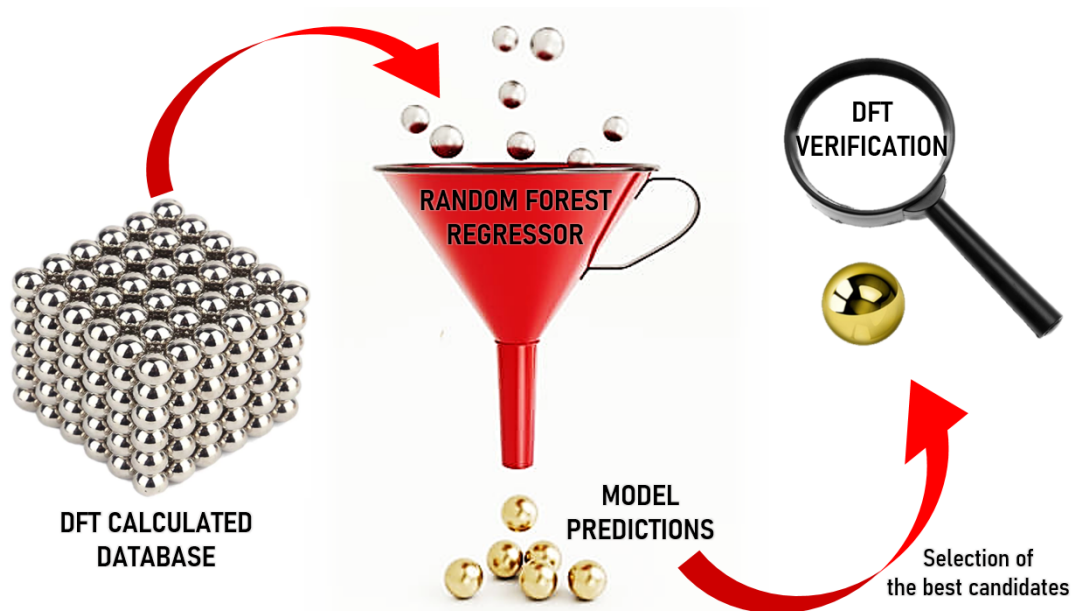


Figure 7.1: Scheme of the high-throughput methodology followed combining DFT and ML tools.

bcc(110) for Cr, Fe, Mo, Nb, Ta, and W, bcc(100) for V, hcp(0001) for Cd, Co, Hf, Os, Re, Ru, Zn, and Zr, and hcp(1010) for Y.

Regarding binary intermetallic compounds, the screening depicted in Fig. 7.2 was carried out to select the best candidates to include in the database. Starting from all the possible binary intermetallic compounds available in the Materials Project database [118], some restraints were included to eliminate elements that are not suitable as catalysts. Thus, environmentally hazardous (Hg, Pb, P, and As), radioactive (Tc, Fr, Ra, Po, At, Rn, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Cn, Nh, Fl, Mc, Lv, Ts, and Og), and toxic (Be, Tl, and Se) elements were excluded from the database. Moreover, unstable binary intermetallic compounds (energy above the convex hull $\neq 0$) [118] were also excluded, leading to 2458 possible binary intermetallic compounds. To keep computational costs as low as possible without compromising the completeness of our database, we computed the adsorption energy for the three adsorbates (H, O, OH) on different adsorption sites only for a diverse and representative subset of the starting list of compounds. Firstly, only compounds with the most common A_nB stoichiometries: AB, A_2B , and A_3B , which comprise 62% of the total number of binary intermetallic compounds, were included. The other 38% was composed of the rest of the A_nB (A_4B 1.9%, A_5B 2.8%, A_6B 0.7%, A_7B 0.2%, A_8B 0.1%, A_9B 0%), and A_nB_m (32.3%) stoichiometries. Even though the compounds with A_nB_m stoichiometry stand for a considerable amount of the available binary intermetallic materials, the possible combinations between n and m are that different, that is unfeasible to find a general trend in the adsorption energy for them. Furthermore, the crystal lattices are very specific on each candidate -orthorhombic, monoclinic, tetragonal, triclinic- and a proper grouping between candidates is not possible to study them. Thus, restricting our study to AB, A_2B , and A_3B materials allows us to cover the majority of the surfaces commonly used in catalysis as

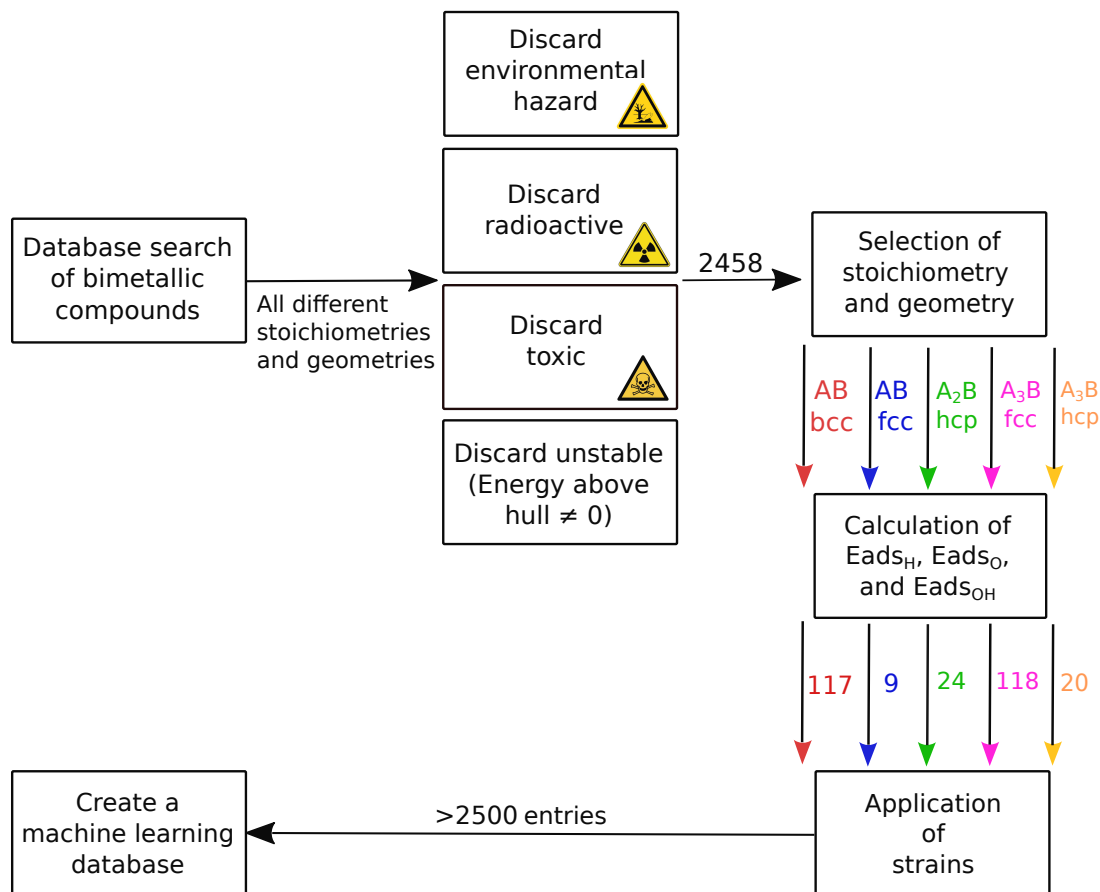


Figure 7.2: Flowchart of the strategy to select the binary intermetallic compounds for the database of adsorption energies.

well as a significant percentage of the existing binary intermetallics. All the binary intermetallics that resulted from the flowchart in Figure 7.2 can be found in Appendix Chapter D.

For each stoichiometry, only the most stable lattice and the lowest energy surface were considered for the calculations, namely 117 AB bcc(101), 9 AB fcc(101), 24 A₂B hcp(0001), 118 A₃B fcc(111), and 20 A₃B hcp(0001) compounds were found, leading to a total of 332 compounds. From those, 106 compounds were randomly selected to compute by DFT the adsorption energy of H, O, and OH with and without the application of biaxial strains.

Adsorption is a very localized process since the adsorption energy depends on the local atomic environment of the adsorption site. Therefore, we explored all possible adsorption sites for both the pure metals and binary intermetallic compounds (See Figure 2.6). The main adsorption sites for pure metals (Figure 2.6 a, b, c, d, and e) are FCC, HCP, ONTOP, and BRIDGE. At FCC and HCP positions, the adsorbate is placed on a hole between three atoms. At FCC, there is no atom in the second layer below, while at HCP, a metal atom is present right under the adsorbate. ONTOP refers to the adsorption above an atom of the first layer, and BRIDGE describes the adsorption at the bond between two atoms. For

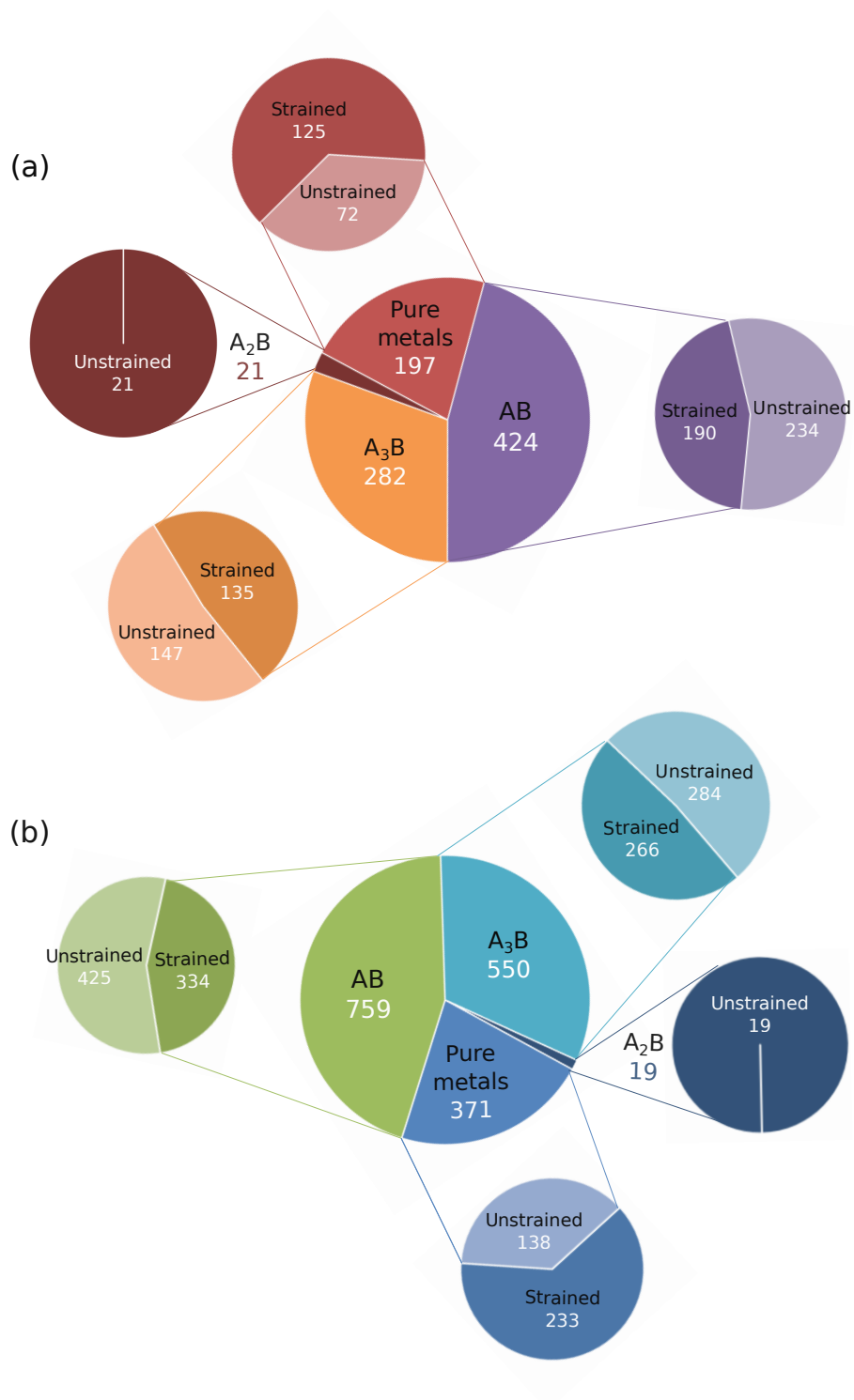


Figure 7.3: Number of entries in the (a) hydrogen and (b) oxygen and hydroxyl databases. The central circles represent the database distribution depending on the stoichiometry: pure metals, AB, A₂B, and A₃B samples, and the small circles represent the amount of strained and unstrained data.

bcc(100) surfaces we must discriminate between SHORTBRIDGE and LONGBRIDGE, as there are two different bond distances on the surface. HOLLOW refers to the adsorption site in the hole between four atoms. For most pure metals, the most favorable adsorption sites (lowest adsorption energies) were FCC and HCP. In contrast, BRIDGE and ONTOP positions were higher in energy and, in some cases, they were unstable (i.e., the adsorbate moved to another position during the geometry optimization). Those cases where the adsorbate moved were not included in the database since they corresponded to repeated entries. For the binary intermetallic compounds (Figure 2.6 f, g, h, i, and j), the number of possible adsorption sites was bigger, as it is necessary to discriminate between A and B atoms on the surface. Here, different FCC and HCP possibilities were studied depending on the three atoms around the hole -AAA, AAB, or ABB-. Similarly, the ONTOP positions could occur above an atom A or an atom B, and BRIDGE sites between two atoms AA, BB, or AB. In AB bcc(101) samples, an extra position appeared: THREEFOLD. It stands for a hole between three atoms where the atom in the second layer below is at an intermediate position between FCC and HCP. The most favorable binding site for binary intermetallics was highly dependent on the affinity of the adsorbate towards A or B.

The adsorption energy varies significantly with the adsorption site. For instance, it was found that the adsorption energy can change in more than 1 eV between a hole between three atoms (FCC, HCP, THREEFOLD) to a bond between two atoms (BRIDGE, LONGBRIDGE, SHORTBRIDGE) or ONTOP a single atom. Additionally, the specific atoms around the adsorption site are also very relevant. For instance, in the adsorption process on a THREEFOLD position in a binary compound A_nB , the three atoms around the adsorbate can be AAA, AAB, or ABB and the adsorption energy can change in more than 0.5 eV by changing one single atom.

Type	H		O		OH		System
	No Strain	Strain	No Strain	Strain	No Strain	Strain	
Pure metals	72	125	70	126	68	107	24
AB bcc(101)	220	190	193	182	218	152	58
AB fcc(101)	14	0	14	0	0	0	8
A_2B hcp(0001)	21	0	19	0	0	0	6
A_3B fcc(111)	111	105	114	110	103	125	26
A_3B hcp(0001)	36	30	36	27	31	4	8

Table 7.1: Number of entries in the databases.

The results of the DFT calculations were included in two different databases: one with E_{ads_H} and the other with E_{ads_O} and $E_{ads_{OH}}$. Given that E_{ads_O} and $E_{ads_{OH}}$ are correlated [151] and that OH binds to the surface by the O atom, it was expected that one single model could be able to predict the adsorption energy of both adsorbates. A total of 130 different pure metals and binary intermetallic compounds were included: 24 pure metals, 58 AB bcc(101), 8 AB fcc(101), 6 A_2B hcp(0001), 26 A_3B fcc(111), and 8 A_3B hcp(0001). The total number of entries in the two databases was 942 and 1699, respectively, considering the different adsorption sites and strain states. The distribution and the number of entries

of the database are shown in Figure 7.3. A tabulated version can be found in Table 7.1 and the datasets in <https://zenodo.org/doi/10.5281/zenodo.10364546>.

7.1.2 Feature selection

Selection of the most appropriate descriptors is a key step to improving the accuracy of an ML model. Previous works on catalysis have focused on descriptors of many different types. Tehrani et al. [177] included the group and period number, the polarizability, the melting point, the boiling point, the specific heat, the crystal system, and the electron density. Wang et al. [313] used the formation enthalpy, the surface energy, and the Bader charge, among others. Hansen et al. [101] and Lamoureux et al. [243] considered the distance between atoms, the bulk formation energies, and the surface termination atoms. Additionally, other authors include descriptors based on the *d*-bands, such as the band gap, the *d*-band center, or the *d*-band width [68, 174]. All of these were considered and finally discarded by either redundancy or because they needed DFT calculations to be determined.

Geometric descriptors	Unit cell volume
	Weighted atomic radius (WAR)
	Generalized coordination number (GCN)
Electronic descriptors	Weighted electronegativity (WEN)
	Weighted first ionization energy (WIE)
	Outer electrons of A (S_A)
	Outer electrons of B (S_B)
	Ψ
Strain descriptor	Biaxial strain

Table 7.2: List of features divided by type.

Following these previous references, 9 descriptors from 3 different types were chosen as features in our ML model. Two of them are characteristic of each adsorption site on the surface of the intermetallic compound and describe the geometry configuration of the adsorption site and the chemical environment around the site. The third descriptor is extrinsic and indicates the biaxial elastic strain applied to the surface. The nine geometrical, electronic, and strain descriptors are depicted in Table 7.2. One important condition for the intrinsic descriptors is that they can be calculated for any compound, surface, and adsorption site from data available in structural and electronic databases. In fact, the values for the atomic radii, the electronegativity, and the first ionization energy were taken from the Mendelev Python Package [185], whereas the unit cell volume was taken from the Materials Project database [118]. Although additional descriptors (such as the *d*-band center and the *d*-band width) can provide a better description of the local chemical environment [157, 172, 262], they require expensive DFT calculations that would hinder an efficient exploration of thousands of intermetallic compounds. Finally, an extra descriptor was needed to describe the prediction of either O or OH in the database for the adsorp-

tion energy of O and OH. It was a categorical and binary descriptor with a value of 0 for O and 1 for OH adsorption. The reason for employing a Boolean descriptor over more elaborate physical or categorical features to encode the information of the adsorbate is simple. The adsorption of OH always happens with the O atom close to the surface and the H atom above it, while O is a single atom interacting with the surface. Thus, there are no other relevant degrees of freedom that characterize adsorbate-slab interactions apart from the position of the adsorbates above the surface (already included in the information of other descriptors that will be described later, such as the generalized coordination number and Ψ). A Boolean descriptor (0/1), which in this scenario is formally equivalent to a categorical feature with values O and OH, serves to encode the only missing information: the identity of the adsorbate. Before feeding the descriptors to train the RF models, all non-categorical descriptors were scaled to a [0,1] range with a MinMax scaler.

Geometric descriptors

The geometric descriptors contain information related to the stoichiometry of the binary intermetallic compound, the size of the supercell, the adsorption plane, and the properties of the binding site. The unit cell volume – expressed in $\text{\AA}^3$ – corresponds to the volume of the unit cell of the bulk that can be retrieved from the Materials Project database [118]. It was considered normalizing the unit cell volume to the number of atoms, but as 98% of the surfaces included have exactly 16 atoms on the supercell, this approximation does not affect the overall performance of our models. It gives information related to the bond distance and the spacing between layers, which plays a significant role in the adsorption process. The weighted atomic radius (WAR) provides information on the individual size of the atoms by weighting the atomic radius of atoms A and B according to the stoichiometry of the system. The size of the atoms is an indirect measurement of the distance between their nucleus and their electrons in the valence shell, which plays a major role in the binding energy. For a binary intermetallic compound A_nB_m , it is calculated as:

$$WAR = \frac{nAR_A + mAR_B}{n + m} \quad (7.1)$$

where n and m are the stoichiometry indexes, and AR_A and AR_B stand for the individual atomic radii of A and B expressed in picometers (pm), respectively [185].

The Generalized Coordination Number (GCN) is the feature employed to describe the adsorption plane as well as the binding site where the adsorption takes place. Each adsorption site at a specific surface plane has a unique GCN, which allows our model to discriminate between geometries and facets. It can be computed as [33]:

$$GCN = \frac{\sum_{i=1}^N CN_i}{CN_{max}} \quad (7.2)$$

where CN_i is the coordination number of the i -th first or second nearest neighbor of the adsorbate. As the adsorption process is a very localized phenomenon, the third or higher

nearest neighbors have negligible influence on this descriptor. M is the total number of atoms composing the sets of first and second nearest neighbors. CN_{max} is the maximum coordination number for a given geometry ($CN_{max} = 8$ for bcc, and $CN_{max} = 12$ for both FCC and HCP).

Other geometrical features, such as the lattice parameters, the cell size, and the area of the adsorption hole, were explored but they provided information equivalent to that of the unit cell volume. The molecular mass was also included but it did not correlate with the adsorption phenomena.

Electronic descriptors

This second set of descriptors aims to describe the electronic properties of the binary inter-metallic compounds and of the binding site where the adsorption occurs. The weighted electronegativity (WEN) is analogous to the WAR and can be defined as:

$$WEN = \frac{nEN_A + mEN_B}{n + m} \quad (7.3)$$

where n and m are the stoichiometry indexes, and EN_A and EN_B stand for the individual Pauling electronegativities of A and B expressed in the Pauling scale.

The weighted first ionization energy (WIE) can similarly be expressed as:

$$WIE = \frac{nIE_A + mIE_B}{n + m} \quad (7.4)$$

where n and m are the stoichiometry indexes, and IE_A and IE_B stand for the individual first ionization energies of A and B expressed in eV, respectively. Both the WEN and the WIE are important magnitudes for the model to learn. The electronegativity describes the power of an atom in a molecule to attract shared-pair electrons toward itself, whereas the ionization energy is the amount of energy required to remove an electron from an isolated atom. They describe two different processes related to the forces between electrons: the same forces that play the major role in the adsorption process.

The outer electrons of A and B range from 1 to 12 and reflect the electronic properties of the valence layer for element A and element B, respectively. These are the electrons that interact with the adsorbate and, therefore, influence the adsorption energy.

The last descriptor of this set is Ψ which was proposed by Gao et al. [73] according to

$$\Psi = \frac{(\prod_{i=1}^N S_i)^{2/N}}{(\prod_{i=1}^N EN_i)^{1/N}} \quad (7.5)$$

where N is the number of atoms at active centers, whereas S_i and EN_i are the outer electrons and the Pauling electronegativity of the i -th atom at active centers. Ψ provides information about the electronegativity and the outer electrons of the specific adsorption site. Whereas S_A , S_B , and WEN describe the outer electrons and the electronegativity of the pure elements A and B, respectively, Ψ describes these properties for the atoms around the binding position. Thus, the electronic properties of A and B are detailed by S_A , S_B , and WEN in an intermetallic A_3B at a fccAAA position, while Ψ would exclusively describe A, which is the only element present in the adsorption site.

The magnetic moment of the intermetallic compounds was also explored as an additional electronic feature but it had very low importance in the description of the adsorption process and the errors of the model experimented no variation when this feature was included. Thus, it was not included among the descriptors.

Strain descriptor

The final descriptor is the biaxial elastic strain applied to the system. It is defined as a percentage with negative values for compressive strains and positive values for tensile strains. This is an extrinsic descriptor, in contrast to the rest of the features, which are intrinsic properties of the materials. The strain descriptor is defined as ϵ (x100) in the deformation gradient $\mathbf{F}$ applied to the supercell (see Chapter 2 Section 2.1.8) and stands as the normal strain applied to the surface of the metallic materials. The stresses perpendicular to the surface plane have been considered equal to zero. The range of strain applied varies from -8% compression to 8% tension as it has been proven to be a stable window.

Descriptor analysis

The maximum and minimum values and the units for each descriptor are shown in Table 7.3. We can expect the predictions of our models not to be reliable for binary intermetallic compounds whose descriptors' values are outside the ranges of the dataset. However, the ranges are very wide, and it is difficult to find binary intermetallics outside those limits. Hence, it is more informative to look at the shape of the distributions for anticipating model performance. In principle, our models should behave correctly for compounds whose features lie within the limits of the distributions. Nevertheless, some distributions have non-uniform shapes. This indicates that training sets must be selected carefully, ensuring the inclusion of compounds from less populated regions. Otherwise, poor model performance could be obtained even for compounds with features within the distributions. The distribution of all the 9 descriptors for $Eads_H$ and $Eads_O$ and $Eads_{OH}$ are shown in Figures 7.4 and 7.5, respectively. The general conclusion is that all the descriptors present a pseudo-normal distribution focused on one or two central values. All intervals within the distributions are populated in most descriptors both for the H and the O/OH databases. In the case of the outer electrons of A and B, the range from 2 to 12 is well described. It is notable that in the case of outer electrons of B, elements with more than half-filled shells are more common. The majority of compounds in our database have a cell volume between 10 and 100 Å³, which is a very large range considering intermetallics with only 5 geometries and stoichiometries. The WEN, WIE, and WAR are also homogeneously dis-

tributed in the complete range, while the GCN and the applied strain have discrete values between 0.25–5.25 and -8–8, respectively. The values of PSI are well distributed among the total range with a slightly higher count in values from 5 to 50.

Descriptor	max value	min value
Unit cell volume	358.93 Å ³	10.49 Å ³
Weighted atomic radius (WAR)	180 pm	127.5 pm
Generalized coordination number (GCN)	5.25	0.5
Weighted electronegativity (WEN)	2.4 (Pauling)	1.23 (Pauling)
Weighted first ionization energy (WIE)	9.39 eV	5.86 eV
Outer electrons of A (S_A)	12	2
Outer electrons of B (S_B)	12	1
Ψ	106.73	3.41
Biaxial strain	-8.00%	8.00%

Table 7.3: Minimum and maximum values of the descriptors.

The Pearson correlation indexes between all the features (in the complete H and O/OH database) in Table 7.2 were calculated to make sure that they provide unique information to the model and avoid features that were strongly correlated. They are presented in Figure D. 8.13 of Appendix Chapter D. The results are similar for both the hydrogen and the oxygen and hydroxyl descriptors: the most correlated features are Ψ and the outer electrons of A (S_A), which is coherent with the description of Ψ . As shown in eq. (6), S_A is included in the numerator, which explains a positive value of the correlation. Additionally, the WIE is relatively correlated with S_A and Ψ due to the definition of ionization energy (energy that an isolated, gaseous atom in the ground electronic state must absorb to discharge an electron). Conversely, WAR and WEN are correlated with a negative index of -0.6, which is in accordance with the basis of chemistry: the larger the atomic radius of an element, the lower the tendency to attract electrons to itself. Finally, the categorical feature "adsorbate" in the model for oxygen and hydroxyl (b) is not related to any other descriptor because it does not represent any chemical property of the binary intermetallic compounds. All in all, we can conclude the final set of 9 descriptors were not correlated with each other.

A Principal Component Analysis (PCA) was also performed for both the H and O/OH adsorption models (Figures D. 8.14 a and b in the Appendix Chapter D, respectively), to study the relationships between features and consider using a reduced number of principal components as descriptors. 6 PCs are needed to describe a 95% of the variance in the model of Hydrogen adsorption, while 8 PCs are needed to describe the same variance for the Oxygen and Hydroxyl model. It can be concluded that replacing 9 descriptors by 6/8 PCs is not worth it and the use of PCs as descriptors was discarded.

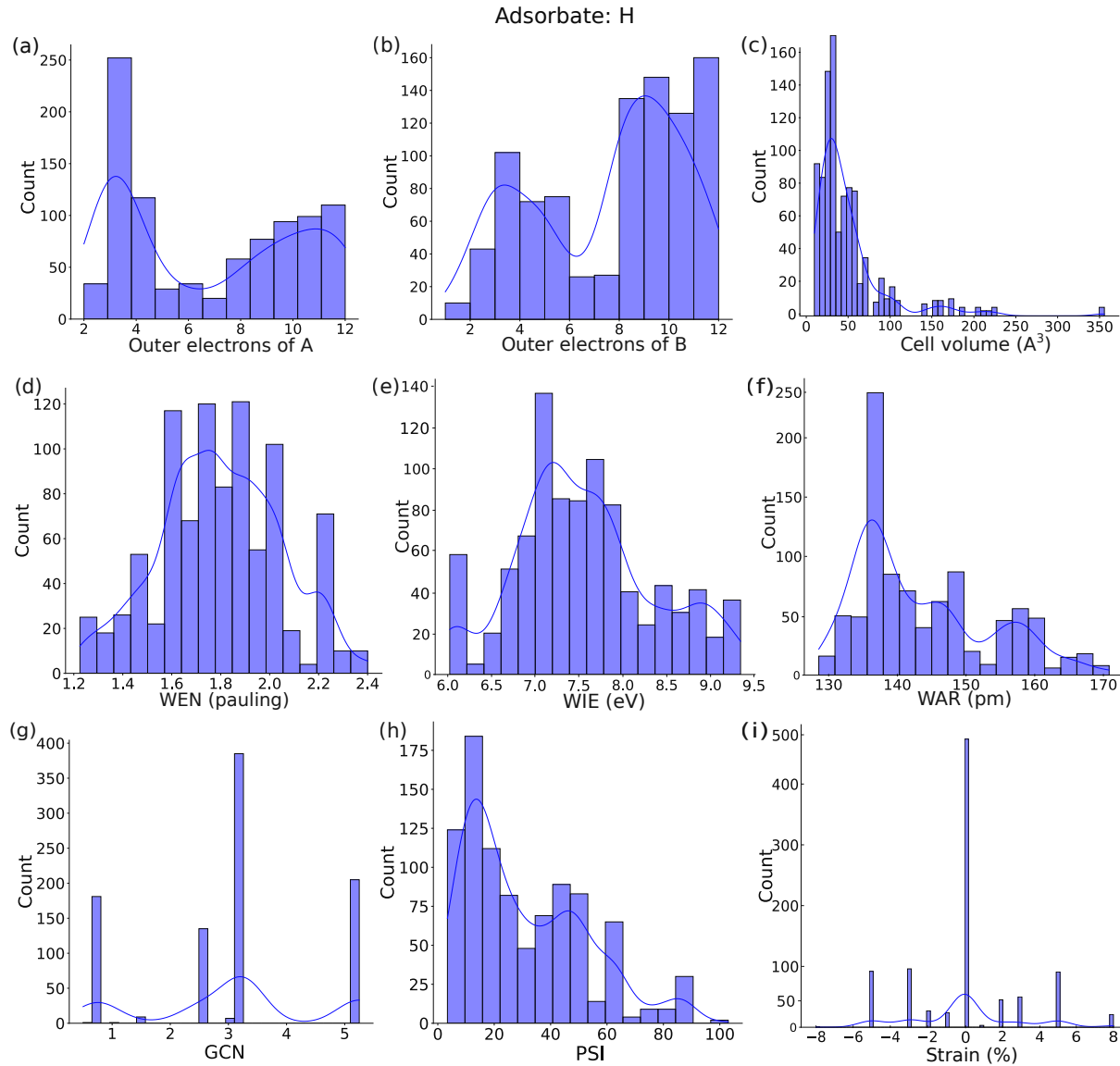


Figure 7.4: Feature distributions for the Hydrogen adsorption database.

7.1.3 Model results

Two RF models were trained with the two datasets of hydrogen and oxygen/hydroxyl adsorption. All pure metal samples were included in the training set, as well as all A_nB_m samples with sites fccXXX, hcpXXX, longbridgeX, and ontopX if X (either A or B) was not available as a pure metal in the datasets. The parity plots that show the correspondence between the adsorption energies calculated by DFT and by the RF model are shown in Figure 7.6 a and c for the hydrogen adsorption and in Figure 7.6 b and d for the oxygen and hydroxyl adsorption. The training data are indicated by blue dots while those not included in the training data (testing data) are shown with red dots. A representation of the learning curves for both ML models is illustrated in Appendix Chapter D Figure D.

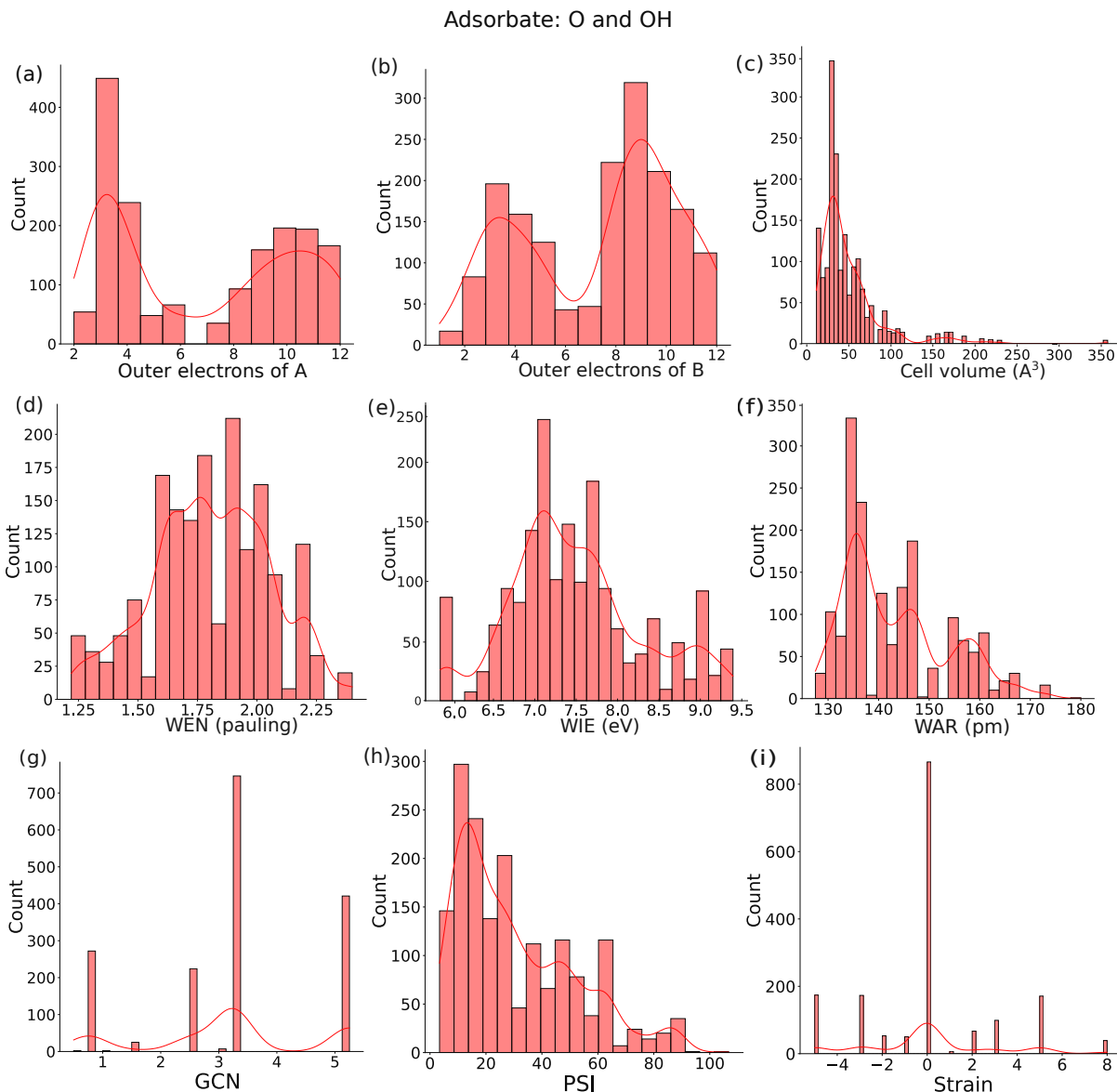


Figure 7.5: Feature distribution for the Oxygen and hydroxyl adsorption database.

8.15.

The adsorption energies in the dataset range from -2 to 2 eV in the case of hydrogen and from -8 to 7 eV in the case of oxygen and hydroxyl (Figure 7.6). Overall, the accuracy of the predictions of the RF is excellent according to various statistical parameters, such as R^2 , MAE, RMSE, and MAD of the testing set, it is indicated in Figure 7.6 a and b. The MAE is 0.07 eV for hydrogen, and MAE = 0.18 eV for oxygen and hydroxyl. Considering that the error of the DFT calculations in the adsorption energy is assumed to be 0.1 eV [26], these models are able to predict the adsorption energy with a similar degree of accuracy. It should be noted that the MAE in the model for O/OH was higher than for the H model due to the wider range of its predictions (-8 to 7 eV vs. -2 to 2 eV). For approximately the

same amount of data in the training, the O/OH model is required to predict a larger scope of energies, thus, the amount of entries at each energy is lower, leading to higher MAE. Hence, more entries in the oxygen and hydroxyl database should be included to achieve a similar performance as that obtained from hydrogen adsorption. A Gaussian Process Regressor model was tested using the same parameters and discarded for presenting higher errors. Violin plots for the H and O/OH model can be found for the RF and the GPR in Appendix Chapter D Figure D. 8.16.

Moreover, the standard deviations from the mean of the testing data are plotted in Figure 7.6 c and d for the sake of clarity. These error bars have been calculated using the Jackknife or “leave one out” procedure. This is an iterative cross-validation technique that gives an estimate of the sampling variance of the random forest. Firstly, each point is estimated from all the data available in the dataset. Then it is recalculated, dropping out one by one other entries in the training. The difference between the whole sample estimate and the partial estimate is calculated and its standard deviation is used to estimate the error and the confidence intervals. In other words, the error bars are a measurement of how much the RF predictions would change if we trained it on a different training set. The results in Figures 7.6 c and d give a reference of two uncertainty quantifications that are crucial in machine learning: calibration, and dispersion. Calibration (or “honesty”) compares the difference among error bars. A “well-calibrated” model has entries whose standard deviations are close to the model’s predicted standard deviations. This means that for those points that are further away from the diagonal in the parity plots, the confidence intervals should be broader. In contrast, the error bars are very small for those entries in which the DFT calculated and the ML predicted adsorption energies are very similar. Thus, it can be concluded from this data that the calibration of our model is correct. Secondly, the models present reasonable error bars along the range of energies (limited dispersion), especially in the middle, because the datasets are well distributed. In the case of the hydrogen model, it can be observed that the error bars are significantly larger at larger energies (between 0.5 and 1 eV) because of the lower number of data in this range. All in all, our model has consistent uncertainty metrics.

As expected, the surfaces and geometries with more entries in the dataset -fcc(111) and bcc(101)- are the ones that are more accurately described by our models. Among the total data for intermetallics, A_3B fcc(111) represents the 32.5% and AB bcc(101) the 56.2%. Yet AB fcc(101), A_2B hcp(0001), and A_3B hcp(0001), only represent the 1.4%, 1.9%, and 8.0%, respectively. The entries in the test set with the highest errors were A_2B hcp(0001), and A_3B hcp(0001).

7.1.4 Feature importance

The role of the descriptors in describing the adsorption energies of binary intermetallic compounds can be assessed from the feature importance, which is plotted in Figure 7.7 a and b for the hydrogen and oxygen/hydroxyl adsorption, respectively. It is measured in % and obtained from the Gini impurity measure, which is one of the methods used in decision-tree ML algorithms to decide the optimal split of the trees [86]. The feature importances are computed as the mean and standard deviation of that impurity decrease

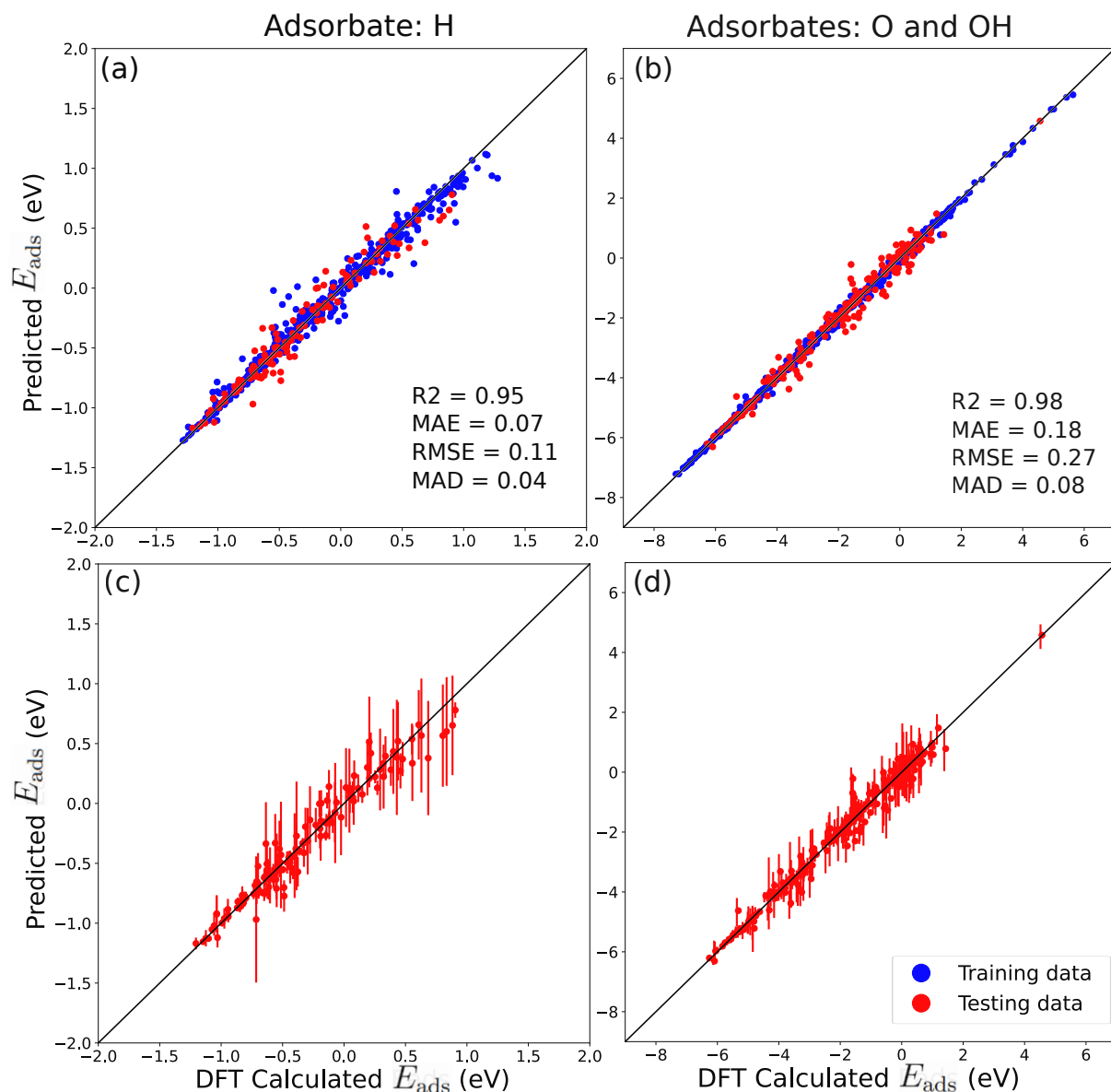


Figure 7.6: Parity plots for the ML models: Adsorption energy of hydrogen (a and c), and of oxygen and hydroxyl (b and d). The blue dots represent the training data (85%) and the red points represent the testing data (15%). The accuracy estimators are shown in (a) and (b), whereas the error bars of the testing data, calculated using the Jackknife or “leave one out” procedure (see text for details) are presented in (c) and (d).

within each tree. Fundamentally they describe which feature is the most useful for the model to distinguish between the samples and give an idea of how it is contributing to the RF output.

The features with the highest weight for hydrogen adsorption are GCN and PSI (Figure 7.7 a). These descriptors contain information about the local geometrical and chemical en-

vironment of the adsorption site and this result demonstrates that the adsorption energy of the small hydrogen atoms onto a surface is highly dependent on the specific adsorption site. Regarding the oxygen and hydroxyl adsorption (Figure 7.7 b), the most relevant descriptor is the type of adsorbate (either O or OH). The second most important feature is the WEN. This was expected because the adsorption of oxygen will be disfavored on a surface with high WEN because oxygen is very electronegative, whereas electropositive surfaces will favor the adsorption. The influence of GCN and Ψ is smaller - compared to the hydrogen adsorption - because, larger adsorbates such as O and OH are not as dependent on the local geometric and chemical features of the binding site as H. Regarding the outer electrons, it can be observed that in both cases S_A has a higher weight than S_B . This reflects that in most cases the proportion of A is larger than B (A_3B , A_2B), and consequently, the feature describing A is somehow more important than the feature for B. Finally, WAR, WIE, and the volume of the cell have a smaller influence on the adsorption energy, except for WIE in the case of hydrogen, which has a significant weight. As the H atom only has one proton and one electron, the quantity of energy that is absorbed to discharge an electron, which corresponds to the definition of IE, is more relevant.

The importance of the strain descriptor is the smallest in both models. It indicates that biaxial strains in the range applied have a limited effect on the adsorption energy as compared with other features, such as GCN, Ψ , or WEN. This is expected since the variation in adsorption energy is larger between different chemical compositions compared to the variation due to strain within one given composition. However, these changes in the adsorption energies (either positive or negative) of 0.1-0.2 eV in the case of hydrogen and of 0.4-0.8 eV in the case of oxygen and hydroxyl [178] can be introduced to any intermetallic surface. Thus, the capability of the RF models to account for elastic strains can be very useful in studying their effect on the catalytic behavior of the particular compounds [179].

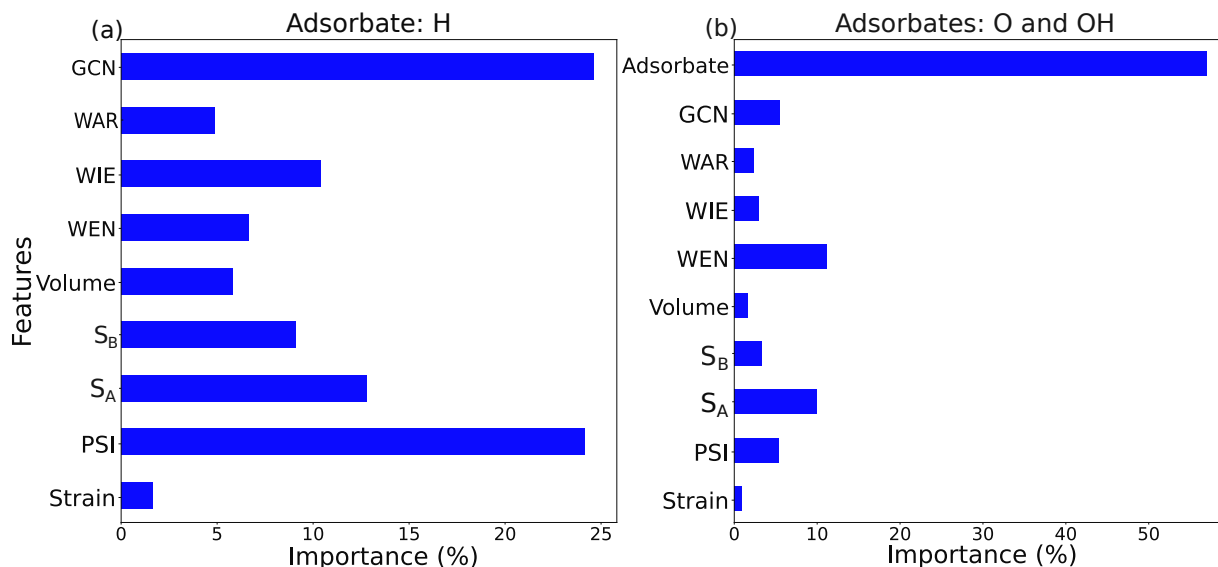


Figure 7.7: Feature importance for the RF models in the prediction of (a) hydrogen and (b) oxygen and hydroxyl adsorption energies.

7.1.5 Model validation

To assess the accuracy of the RF models, the adsorption energies of H, O, and OH of 30 candidates, randomly selected from the 2458 compounds, were calculated by DFT with and without strain. The adsorption energies predicted by the RF models and by DFT are indicated in Table 7.4, together with the difference between them. The upper part of the table summarizes intermetallic compounds and binding sites in which the RF model is expected to provide accurate results as both A and B are present as pure elements in the training set of the database. Moreover, several results with and without strain were included to demonstrate that the RF model can predict accurately the variation in the adsorption energy induced by tensile/compressive elastic strains.

In contrast, the second part of the table shows candidates who were expected to give inaccurate predictions and, thus, highlights the limitations of the RF models. These candidates contain Al, Dy, Sc, Nd, In, Ga, Mn, Pr, Sm, and Sn, which were not included in the database of 24 pure elements for which the adsorption energy of H, O, and OH was computed. The RF models cannot predict accurately the adsorption energies in fccAAA, hcpAAA, longbridgeA, or ontopA locations if the adsorption energy of pure element A is not included in the dataset because the chemical environment in these sites (which is determined by element A) has not been included enough in the training set. The differences between the adsorption energies calculated by RF and DFT were much higher in these sites and reached > 1 eV in some cases, although the differences were below 0.34 eV for Pr₃In, even though pure Pr and In were not included in the database. The parity plot representing the 30 verification candidates is shown in the Appendix Chapter D Figure D.8.17.

In order to test if we could surpass this limitation, we checked the behavior of our model providing enough information in the training of binary intermetallics containing A with an adsorbate in those sites, but without including pure A. To provide clarification some examples are the case of Al, Sc, In, and Dy. These elements are not included as pure metals in the databases, however, there are plenty of binary intermetallic compounds that contain them. As a test of the capability of the model to learn their behavior, we trained the model with 90% of the data containing Al, Sc, In, and Dy, and used 10% of it for the testing set. In Table 7.5 the results of this test are illustrated. In the case of Al, Sc, and In, where there is a total of more than 15 binary intermetallics that contain them, the model is able to learn their behavior without having the pure metal in the training set. The MAE for these cases is no bigger than 0.28 eV in the worst case. Conversely, in the case of Dy, where only 7 and 12 candidates are included in the H and O and OH database, the errors are 0.74 and 0.53, respectively. With this test, we concluded that our models are able to learn new chemical surroundings and geometries without the need to have all pure metals in the training.

7.1.6 Discovery of new catalysts for the HER and ORR

The RF models presented above were used to predict the adsorption energies of hydrogen, oxygen, and hydroxyl of 175 binary intermetallic candidates with and without strain. Those candidates met the criteria indicated in Figure 7.2 and present stoichiometries and

System	Adsorbate	Strain	Binding site	Eads (ML)	Eads (DFT)	Error
Ce3Sn	H	0	fccAAA	-0.47	-0.71	0.24
Ce3Sn	H	0	hcpAAA	-0.50	-0.71	0.21
Ce3Sn	OH	0	fccAAA	-2.09	-2.05	-0.04
Ir3Sc	OH	-1	fccAAA	1.19	1.42	0.23
Nd3In	OH	0	fccAAB	-2.00	-2.13	0.14
Ni3Pt	H	-3	fccAAB	-0.41	-0.44	-0.04
Ni3Pt	O	-5	fccAAB	-1.94	-2.05	-0.11
Pd3Ce	H	1	fccAAA	-0.44	-0.54	-0.10
Pd3Sc	H	-5	fccAAA	-0.47	-0.34	0.13
Pd3Sc	H	-5	hcpAAA	-0.51	-0.70	0.20
Pd3Sc	O	-5	hcpAAA	-1.68	-1.58	-0.10
Pd3Sc	OH	-5	fccAAA	1.00	1.08	-0.08
Pt3Dy	H	0	hcpAAA	-0.68	-0.49	0.19
Pt3Dy	OH	0	hcpAAA	1.01	1.23	-0.22
Pt3Mn	OH	1	ontopA	0.99	0.74	0.25
Pt3Mn	OH	1	hcpAAA	1.17	1.15	0.02
Pt3Sn	O	5	fccAAA	-1.64	-1.39	-0.25
Pt3Y	H	1	hcpAAA	-0.50	-0.70	-0.20
Ir3Sc	O	-3	ontopB	-1.94	-0.79	1.15
Nd3In	H	0	hcpAAA	-0.46	-0.83	0.38
Ni3Ga	O	-3	ontopB	-1.60	0.08	-1.68
Pt3Mn	O	1	hcpAAA	-1.69	-1.43	-0.26
Pt3Mn	OH	1	ontopB	1.09	0.59	0.50
Pr3In	H	3	hcpAAA	-0.46	-0.79	0.34
Pr3In	H	3	fccAAA	-0.46	-0.78	0.32
Pr3In	OH	3	fccAAB	-2.07	-2.07	0.00
Pr3In	OH	3	fccAAA	-1.97	-2.30	0.32
SmRh	H	0	longbridgeA	-0.46	0.02	0.48
Sn3Pr	H	5	fccAAB	-0.45	0.32	-0.77
Sn3Pr	O	5	ontopB	-1.60	-2.41	0.81

Table 7.4: Adsorption energies (in eV) obtained by the RF models and by DFT and the difference between them for 30 different surfaces and binding sites.

geometries equal to the ones included in the databases at the lowest energy surfaces (AB bcc, AB fcc, A2B hcp, A3B fcc, and A3B hcp). It must be kept in mind that including the different adsorption sites and the different strain states, the number of predictions is nearly 2700. The adsorption energies for H, O, and OH obtained with the RF models can be found in <https://zenodo.org/doi/10.5281/zenodo.10364546>.

Element	#entries in training		#entries in testing		MAE	
	H	O,OH	H	O,OH	H	O,OH
Al	16	26	2	3	0.22	0.28
Sc	27	59	3	6	0.1	0.16
In	15	22	2	3	0.24	0.22
Dy	7	12	1	1	0.74	0.53

Table 7.5: Number of entries and mean absolute error of elements containing Al, Sc, In, and Dy.

HER

In the case of the HER, Pt(111) is known to be the optimum catalyst and it was decided to select compounds and surfaces whose adsorption energy for H was that of Pt ± 0.05 eV. We chose this value, instead of 0.07 eV (the MAE of the RF model) to leave all the pure metals that were not Pt or Pd out of range. In this way, the list of possible candidates was set to 25 compounds, which are indicated in Table 7.6. All of them present an A_3B stoichiometry with fcc lattice and fcc(111) geometry. Only 11 do not contain either Pt or Pd, which makes them potentially interesting to replace these metals. It should be noted that adsorption takes place at FCC or HCP adsorption sites in all candidates, which are the optimum ones at fcc(111) geometry. The results are in agreement with the previous DFT screening conducted by Norskov [88], where most of the candidates obtained contain Pt in their structure. Additionally, Ce_3Ga , Ce_3In , Ce_3Sn , Nd_3In , Ni_3Fe , Pr_3In , Rh_3Mo , Sm_3In , Sn_3Nd , Sn_3Sm , and Zn_3Ti were found to have adsorption energies of H similar to those of Pt. Among them, candidates containing Ce, Nd, Pr, or Sm should be discarded because of their extremely negative normal reduction potentials. However, we see Zn_3Ti as a particularly interesting material to further study as the oxidation potential of Zn is closer to that of Pt.

From the experimental viewpoint, Baibars et al.[15] proved that a $NiFeO_xH_y/Ni_3Fe$ interface designed via electro passivation could provide superior catalysis of the HER. Additionally, Cu_3Pt is one of the candidates that has been studied experimentally as a potential candidate to replace Pt, although its application has been hindered by dealloying and passivation phenomena [45, 97, 305, 306].

The application of elastic strains introduces two more candidates with adsorption energies ± 0.05 eV that of Pt(111): Pt_3Sm and Ir_3W . The difference in the adsorption energy of H for both candidates is reduced to 0.01 eV and 0.03 eV in the presence of -3% and -5% compression strains, respectively. Moreover, the candidates whose adsorption energies were close to Pt could get even closer (≈ 0.03 eV) under the application of biaxial strains. This is the case of Ir_3W , Pd_3Ce , Pd_3Fe , Pd_3Nd , Pd_3Pr , Pd_3Sc , Pd_3Sm , Pd_3Y , Pt_3Sc , Pt_3Sm , Pt_3Sn , and Zn_3Ti that become closer to Pt in the presence of compressive strains, while Ce_3Ga , Ce_3In , Ce_3Sn , Nd_3In , Ni_3Pt , Pd_3Dy , Pr_3In , Sm_3In , Sn_3Nd , and Sn_3Sm get closer to Pt under tensile strains. Ni_3Fe , Pt_3Co , Pt_3Dy , Pt_3Y , and Rh_3Mo are the only candidates whose adsorption energies for hydrogen are closer to Pt at zero strain. The optimum applied

Material	Adsorption site	Eads _H (eV)	Material	Adsorption site	Eads _H (eV)
Pt	FCC	-0.49*	Pt	FCC	-0.49
Ce3Ga	hcpAAA	-0.45	Pd3Nd	hcpAAA	-0.53
	fccAAA	-0.45		hcpAAA	-0.52
Ce3In	hcpAAA	-0.46	Pd3Sm	fccAAA	-0.52
	fccAAA	-0.45		fccAAB	-0.51
Ce3Sn	hcpAAA	-0.50	Pd3Y	fccAAA	-0.52
	fccAAB	-0.48	Pr3In	hcpAAA	-0.45
Nd3In	hcpAAA	-0.46		hcpAAA	-0.49
	fccAAB	-0.53	Pt3Co	fccAAB	-0.49
Ni3Fe	hcpAAB	-0.49		fccAAA	-0.49
	fccAAA	-0.48	Pt3Dy	hcpAAA	-0.49
	hcpAAA	-0.48		fccAAA	-0.47
Ni3Pt	fccAAB	-0.47		hcpAAA	-0.53
	hcpAAA	-0.53	Pt3Sc	fccAAA	-0.51
	fccAAA	-0.53		fccAAB	-0.51
Pd3Ce	fccAAB	-0.50	Pt3Sn	fccAAA	-0.53
	hcpAAA	-0.47		fccAAA	-0.51
Pd3Dy	fccAAA	-0.46	Pt3Y	hcpAAA	-0.48
	fccAAA	-0.53		fccAAB	-0.45
Pd3Fe	fccAAA	-0.53	Rh3Mo	fccAAA	-0.46
	fccAAA	-0.53		hcpAAA	-0.46
Pd3Pr	hcpAAA	-0.53	Sm3In	fccAAB	-0.45
	fccAAB	-0.52		fccAAB	-0.49
	fccAAA	-0.52	Sn3Sm	fccAAB	-0.48
Pd3Sc	hcpAAA	-0.51		hcpAAB	-0.44
	fccAAB	-0.48	Zn3Ti		

Table 7.6: Potential candidates with Eads_H similar to Pt at zero strain. The adsorption energies are shown for each possible binding site. The value of Pt Eads matches other studies using VASP instead of QE [294]. It has to be taken into consideration that PBE tends to overbind compared to RPBE/BEEF-vdw.

strain state and adsorption site for each candidate, and a representation of the variation of Eads_H with strain are shown in Table D. 8.3, and Figure D. 8.18 of Appendix Chapter D, respectively. This fact supports the potential of elastic strains to tune the catalytic properties of materials, because changes of a few tenths of eV may lead to important changes in the catalytic activity [52, 179, 196].

ORR

The criteria to select potential catalysts for the ORR were similar to those in the case of the HER. Compounds and surfaces whose adsorption energies for O and OH were within ± 0.2 eV of that for Pt(111) were selected from those reported in the repository <https://zenodo.org/doi/10.5281/zenodo.10364546>. This magnitude is equivalent to the

MAE of the RF model for oxygen and hydroxyl. 13 candidates were identified in this range. All of them were A_3B with an fcc(111) geometry and one (ZnAu) was AB bcc(101). The adsorption energies as well as the adsorption sites of these compounds are indicated in Table 7.7. It is worth noting that the adsorption sites are generally not the same for O and OH even in the same material. Among the 13, only 2 candidates do not contain Pd or Pt on their structure: Ir_3Sc and ZnAu.

Material	Adsorption site	E_{ads_O} (eV)	Adsorption site	$E_{ads_{OH}}$ (eV)
Pt	FCC	-1.79	FCC	1.19
Cu3Pt	fccAAB	-1.82	ontopA	1.3
	hcpAAA	-1.92	ontopB	1.38
Ir3Sc	ontopB	-1.95	fccAAA	1.21
Ni3Pt	hcpAAA	-1.99	ontopB	1.37
	fccAAA	-1.88	fccAAA	1.19
Pd3Dy	fccAAB	-1.83	hcpAAA	1.10
			ontopA	1.37
Pd3Sc	hcpAAA	-1.73	fccAAA	1.00
Pd3Sn	fccAAB	-1.94	fccAAA	1.30
			hcpAAA	1.06
Pt3Co	fccAAA	-1.61	fccAAB	1.37
	fccAAB	-1.64	hcpAAA	1.24
	fccAAA	-1.76	fccAAA	1.14
Pt3Dy	fccAAB	-1.78	hcpAAA	1.01
	hcpAAA	-1.82	ontopA	1.28
			ontopB	1.36
Pt3Mn	fccAAA	-1.67	fccAAA	1.36
	fccAAB	-1.71	fccAAB	1.06
	hcpAAA	-1.69	hcpAAA	1.22
			ontopA	1.05
			ontopB	1.15
Pt3Sc	fccAAB	-1.96	fccAAA	1.21
Pt3Sn	fccAAB	-1.99	fccAAA	1.23
Pt3Y	hcpAAA	-1.63	fccAAA	1.06
ZnAu	threefoldAAB	-1.82	longbridgeB	1.36

Table 7.7: Potential candidates with E_{ads_O} and $E_{ads_{OH}}$ similar to Pt at zero strain. The adsorption energies are shown for each possible binding site.

Another suitable candidate, Ag_3In fcc(111), appears for the ORR if the effect of elastic strains is considered. In this case, the E_{ads_O} is within the ranges of energies close to Pt when 5% of tension strain is applied, while $E_{ads_{OH}}$ needs a -5% compression to be similar to Pt. Among the rest of the candidates, strain drives the adsorption energy closer to Pt up to 0.15 eV. The optimum applied strain level and the specific adsorption sites for each compound are indicated in Table D. 8.4 of Appendix Chapter D. Compressive

strains bring the E_{ads_O} closer to Pt in Cu_3Pt , Ir_3Sc , Ni_3Pt , Pd_3Dy , Pd_3Sn , Pt_3Dy , Pt_3Sc , and Pt_3Sn , while tensile strains have the same result for Ag_3In , Pd_3Sc , Pt_3Co , Pt_3Mn , Pt_3Y , and $ZnAu$. Compressive strains are favorable for $E_{ads_{OH}}$ in Ag_3In , Ir_3Sc , Pd_3Sc , Pt_3Co , and Pt_3Sn , whereas tensile strains bring Cu_3Pt , Ni_3Pt , Pd_3Sn , Pt_3Dy , Pt_3Mn , and Pt_3Sn . Only Pd_3Dy , Pt_3Y , and $ZnAu$ are closer to the $E_{ads_{OH}}$ of Pt at zero strains. A representation of the variation of E_{ads_O} and $E_{ads_{OH}}$ for the candidates with strain, can be found in Appendix Chapter D Figures D. 8.19 and D. 8.20, respectively. These results indicate again the potential of the elastic strains to improve the catalytic performance of good catalysts.

Experimentally, core-shell nanoparticles of Ni_3Pt have demonstrated good catalytic performance for the ORR by Godinez-Salomon et al. [83], but they observed strong segregation of Ni on the topmost layer. Similarly, Pd_3Fe , Pd_3Y , Pt_3Sc , and Pt_3Y have been proven to be an efficient catalyst for ORR [28, 162, 223, 265, 337, 360]. Stamenkovic et al. [269] also measured that Pt_3Co exhibits a similar catalytic activity to Pt, in the ORR. Although there is still little experimental evidence of the effect of elastic strains on the catalytic activity of the ORR, Escudero et al. [52] proved experimentally that the catalytic activity of Pt_5Dy , Pt_5Ce , and Pt_5Sm compounds was enhanced by a factor of 3 to 6 over Pt. These studies match our DFT calculations and ML predictions and therefore represent a starting point for the use of binary intermetallic compounds and elastic strain engineering in the catalysis of the HER and the ORR.

Conclusions

The adsorption energy for H, O, and OH was calculated by means of DFT on the lowest energy surface of 24 pure metals and 106 binary intermetallic compounds with stoichiometries AB , A_2B , and A_3B taking into account the effect of biaxial elastic strains. This information was used to train two RF regression models, one for hydrogen adsorption and another for oxygen and hydroxyl adsorption. These models predicted the adsorption energies based on 9 descriptors that characterized the geometrical and chemical features of the adsorption site as well as the applied strain. All the descriptors for each compound in the models could be obtained from physico-chemical databases. The MAE of the predictions of the RF models was excellent (0.07 and 0.18 eV for the adsorption of hydrogen and oxygen/hydroxyl, respectively) and, in addition, the accuracy of the results was validated against the adsorption energies of 30 randomly selected binary intermetallic compounds.

The ML models were used to predict the adsorption energy for hydrogen, oxygen, and hydroxyl of ≈ 2700 binary intermetallic compounds with stoichiometries AB , A_2B , and A_3B made of metallic elements, excluding those that were environmentally hazardous, radioactive, or toxic. This information was used to search for potential good catalysts for the HER and ORR from the criteria that their adsorption energy for H and O/OH, respectively, should be close to that of Pt, which is the best-known catalyst for both reactions. Including the effect of elastic strains, 27 potential candidates were reported for the HER and 14 for the ORR. The few of them that have been explored experimentally have shown good catalytic performance, validating our methodology.

The results of this thesis provide a large database of adsorption energies of H, O, and OH

in pure metals and binary intermetallic compounds (including the effect of elastic strains) that can be very useful for training other data-driven strategies to search for new catalysts. Moreover, it demonstrates that the ML models -suitably trained- can predict adsorption energies with an accuracy not far away from DFT calculations with minimum computational cost from descriptors that are readily available in physico-chemical databases for any compound.

Conclusions and future work

8.1 Conclusions

The main conclusions of this thesis can be summarized as follows:

1. FCC adsorption sites are more favorable in (111) fcc metallic surfaces, while HCP are preferred in (0001) hcp metallic slabs for H, O, and OH. Tensile strains favor the adsorption process while compressive and shear strains increase the adsorption energy hindering the adsorption of H, O, and OH, in agreement with the *d*-band theory. The adsorption energy in all metals is a function of the change in the area of the adsorption hole, which follows a linear law with the Fermi energy. Coverage is an important parameter in the calculation of the adsorption energy.
2. Elastic strains modify the catalytic activity of most transition metals, which can be explained by changes in the free energy of the rate-limiting step. For the HER, compressive strains enhance the catalytic activity of metals on the ascending branch of the volcanos by reducing the energy barrier for H^{*} desorption. Conversely, tensile strains improve the activity of metals on the descending branch by lowering the energy barrier for H^{*} adsorption. The catalytic activity of the ORR is determined by: O adsorption, the transition from O^{*} to HO^{*}, and HO^{*} desorption. The free energies for O adsorption and HO^{*} desorption are particularly sensitive to mechanical strains. Applying elastic strains can alter the rate-limiting step for the ORR in Au, Pt, Ag, and Os.
3. The mechanical contribution to the adsorption energy remains independent of elastic strain. Therefore, the effect of elastic strains on adsorption energy is attributed to changes in the electronic structure. Adsorbates that cause the largest shift in the *d*-band center also exhibit the greatest variation in the electronic contribution to the adsorption energy under elastic strain. The mechanical contribution is linked to the lattice distortion caused by the adsorbate. This contribution is minimal for Pt (< 0.2 eV) and higher for PtO₂ (up to 0.6 eV).
4. FCC AAB and HCP AAB are the optimal adsorption sites in AB bcc(101) and A₃B

fcc(111) binary intermetallic compounds for H, O, and OH. When adsorption occurs at a site between A and B atoms, the adsorption energy for the binary intermetallic falls between the adsorption energies of pure metals A and B. If the most favorable adsorption site is FCC XXX, HCP XXX, or ONTOP X, the adsorption energy of the intermetallic is closer to that of pure metal X. The effect of elastic strains on adsorption energies in A_3B and AB binaries is similar to that of pure metals. In most cases, the most favorable adsorption site remains constant across all strain levels. Binary intermetallics are placed on both branches of the volcano plots, and, similar to pure metals, the rate-limiting step for the ORR can be adjusted by applying strain. Overall, elastic strain engineering is an effective method to tune the catalytic activity not only for pure metallic surfaces but also for binary intermetallic compounds. The linear correlation between E_{ads_O} and $E_{ads_{OH}}$ demonstrated for pure metals is not observed in binary intermetallic compounds.

5. The DFT calculations for pure metals and intermetallic compounds with and without strain were used to train two ML models able to predict the adsorption energies of H, O, and OH, with 9 descriptors encompassing their geometric and chemical properties with MAE's of 0.07 and 0.18 eV for hydrogen and oxygen/hydroxyl adsorption, respectively. These models can forecast the adsorption energy across binary intermetallic compounds with compositions AB, A_2B , and A_3B , excluding those environmentally hazardous, radioactive, or toxic. These data can be used to identify potential catalysts for the HER and ORR, focusing on candidates whose adsorption energy closely matched that of Pt.

8.2 Future work

The following lines of work are envisioned:

1. The most straightforward strategy would be the calculation of the adsorption energy for *OOH . This extra adsorbate will allow to calculate the catalytic activity of the ORR in alkaline media. An extension of this investigation to alkaline ORR would be extremely useful due to the favorable kinetics and availability of a wide range of catalysts at this pH. Moreover, the adsorption energy of *OOH will allow to determine the catalytic activity of the Oxygen Evolution Reaction (OER). Thus, both anodic and cathodic reactions relevant for the Hydrogen Economy will be analyzed: the production of hydrogen in electrolyzer cells (HER/OER) and the generation of green energy in fuel cells (HOR/ORR).
2. Regarding the Random Forest Machine Learning model, the next step would be the extension to the adsorption energy prediction of H, O, and OH into ternary intermetallic compounds. This will require performing a high-throughput screening to determine which ternary intermetallic compounds are most common and have a determined structure to be potentially active as heterogeneous catalysts. A flowchart of this strategy to select the ternary intermetallic compounds is presented in Figure 8.1. From all the 65529 ternary compounds available in the Materials Project Database [118], the ones with energies above the convex hull equal to zero, previously proved

experimentally, and that present a metallic d -band structure, are 6802. From those, the stoichiometries with the highest number of candidates were ABC (143), A_2BC (74), and A_3BC (20 hcp and 125 fcc). The adsorption energies for H O and Oh of a subset of them can be calculated by DFT calculations to train an RF model, similar to the one developed in this thesis, to predict the adsorption energy, and thus their catalytic activity for the Her and ORR of all relevant ternary intermetallic compounds.

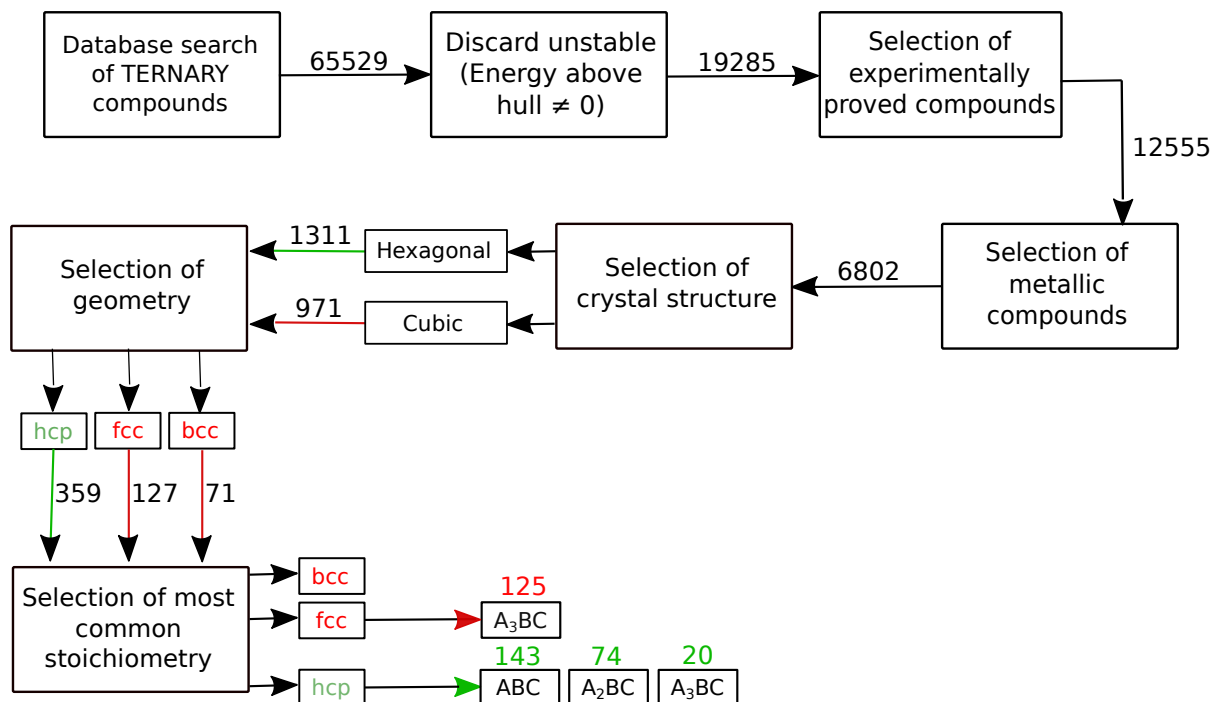


Figure 8.1: Flowchart of the strategy to select the ternary intermetallic compounds for the calculation of adsorption energies.

3. An additional research would be to include Pourbaix diagrams in the selection process of new potential catalysts to replace Pt in the HER and the ORR. Pourbaix diagrams are based on the Nernst equation and they establish a balance of the different phases of an aqueous electrochemical system at different pH as a function of the voltage potential. Including the thermodynamical stability of the metals in a specific environment and the different regions of "immunity," "corrosion" and "passivity," would move us closer to a more practical design of catalysts.
4. Finally, the high-throughput methodology to discover new catalysts presented in this thesis, can be extended to other reactions and catalytic processes. As an example, the calculation/prediction of different adsorbates such as C^* , CO^* , or CO_2^* would allow an estimation of the catalytic activity in carbon capture processes.

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Appendix A

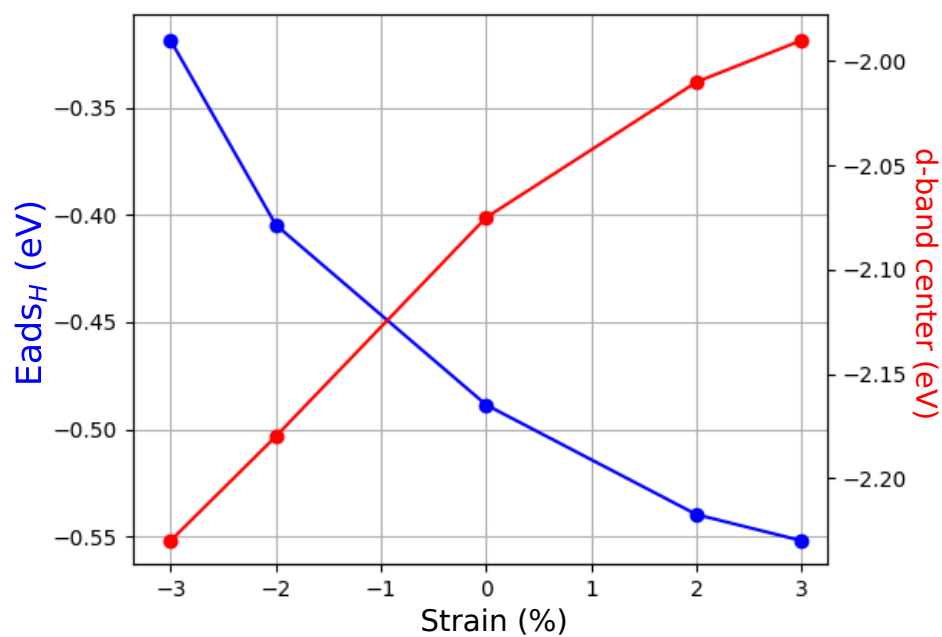


Figure A. 8.2: E_{ads_H} and d -band center variation of a Pt fcc(111) surface at FCC adsorption site under the application of biaxial strains.

System	Strain (%)	Au1 (e)	Au2 (e)	Au3 (e)	Au4 (e)	Ads (e)
OH/Au(0.25ML)	-2	0.16	0.16	0.02	-0.02	-0.42 (Ads1)
	0	0.17	0.17	0.02	-0.02	-0.43 (Ads1)
	2	0.16	0.16	0.03	-0.01	-0.44 (Ads1)
OH/Au(0.5ML)	-2	0.18	0.20	0.20	0.18	-0.42 (Ads1)
						-0.42 (Ads2)
	0	0.18	0.20	0.21	0.18	-0.43 (Ads1)
						-0.43 (Ads2)
	2	0.18	0.21	0.21	0.18	-0.44 (Ads1)
						-0.44 (Ads2)
OH/Au(1ML)	-2	0.35	0.35	0.35	0.35	-0.36 (Ads1)
						-0.37 (Ads2)
						-0.36 (Ads3)
						-0.37 (Ads4)
	0	0.37	0.36	0.36	0.36	-0.38 (Ads1)
						-0.38 (Ads2)
						-0.38 (Ads3)
						-0.38 (Ads4)
	2	0.38	0.38	0.38	0.38	-0.39 (Ads1)
						-0.39 (Ads2)
						-0.39 (Ads3)
						-0.39 (Ads4)

Table A. 8.1: Effect of strains in the charge transfer of the OH adsorbate onto an Au(111) surface at the three different coverages: 0.25ML, 0.5ML, and 1ML.

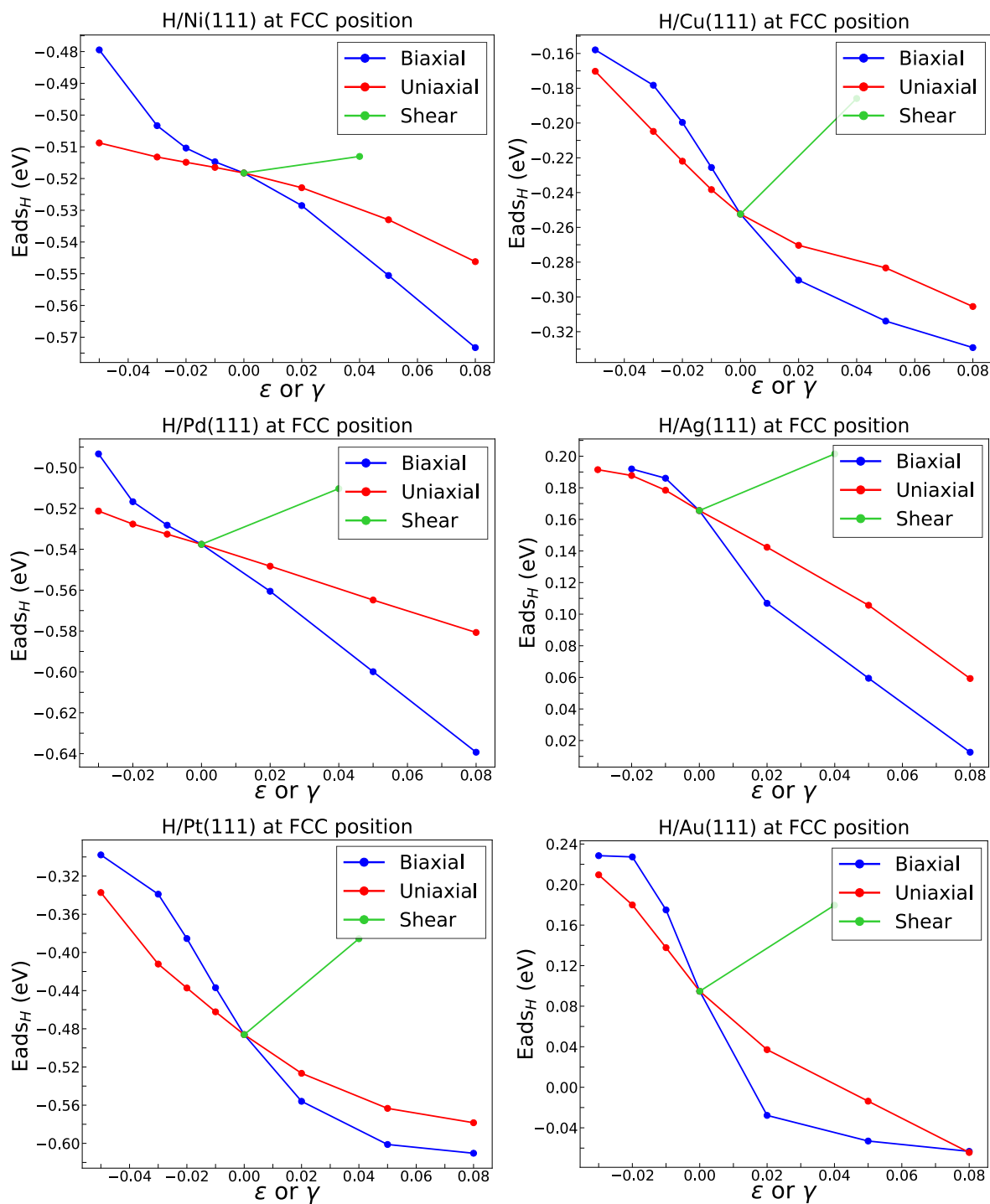


Figure A. 8.3: Adsorption energy of H as a function of strain from 5% compression to 8% tension at FCC position for Ni, Cu, Pd, Ag, Pt, and Au. The legend indicates the type of strain.

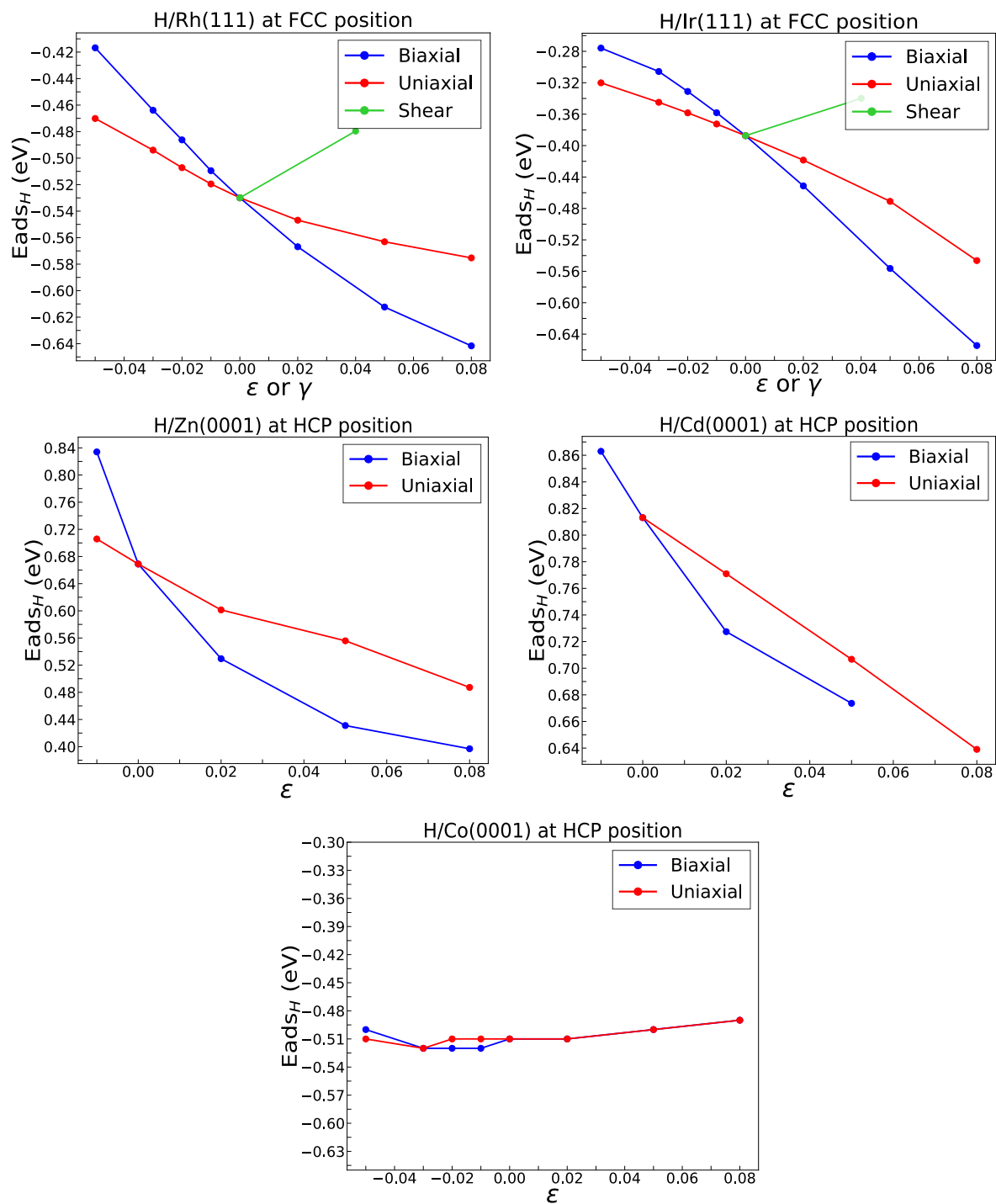


Figure A. 8.4: Adsorption energy of H as a function of strain from 5% compression to 8% tension at FCC position for Rh, and Ir, and HCP position for Zn, Cd, and Co. The legend indicates the type of strain.

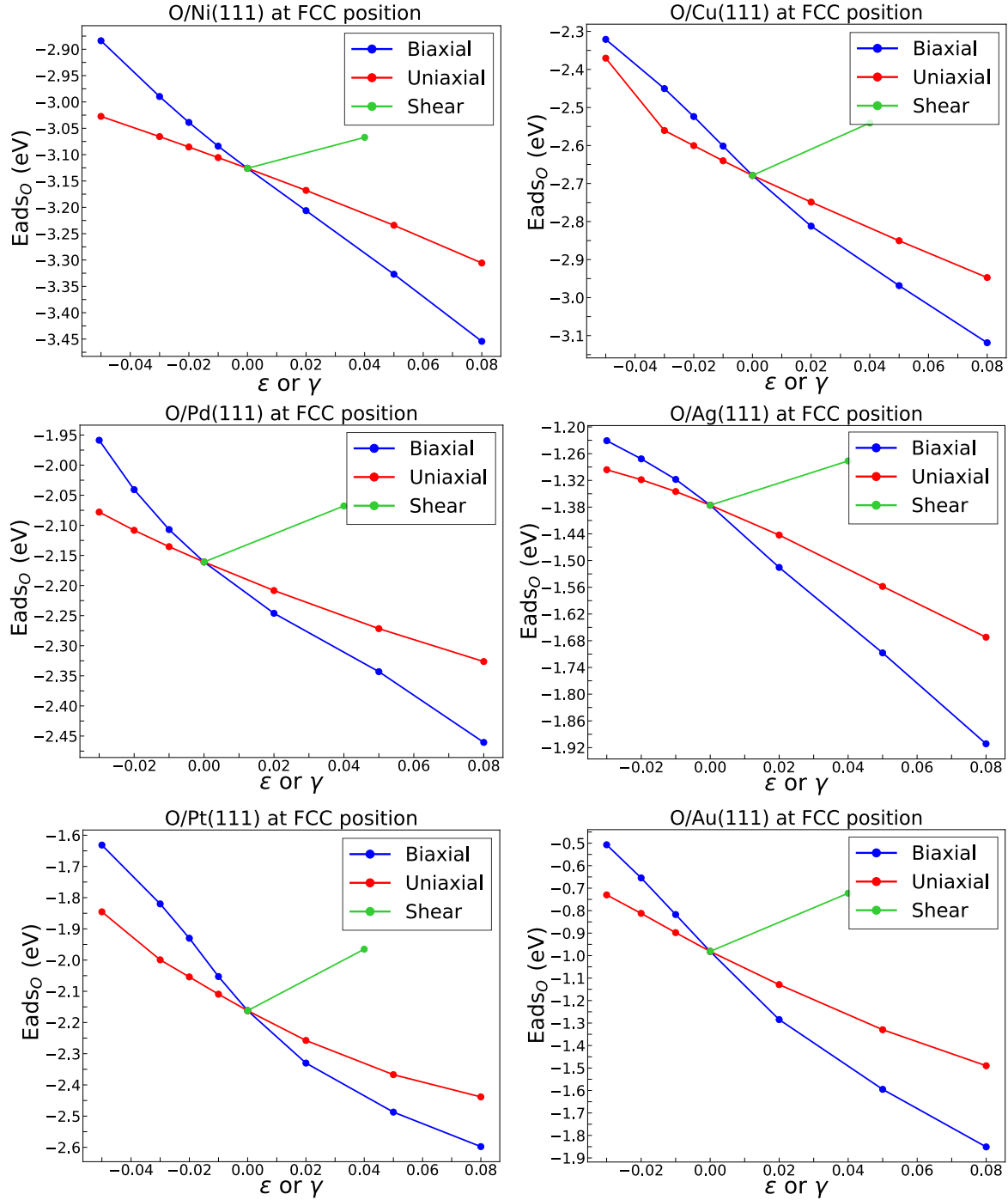


Figure A. 8.5: Adsorption energy of O as a function of strain from 5% compression to 8% tension at FCC position for Ni, Cu, Pd, Ag, Pt, and Au. The legend indicates the type of strain.

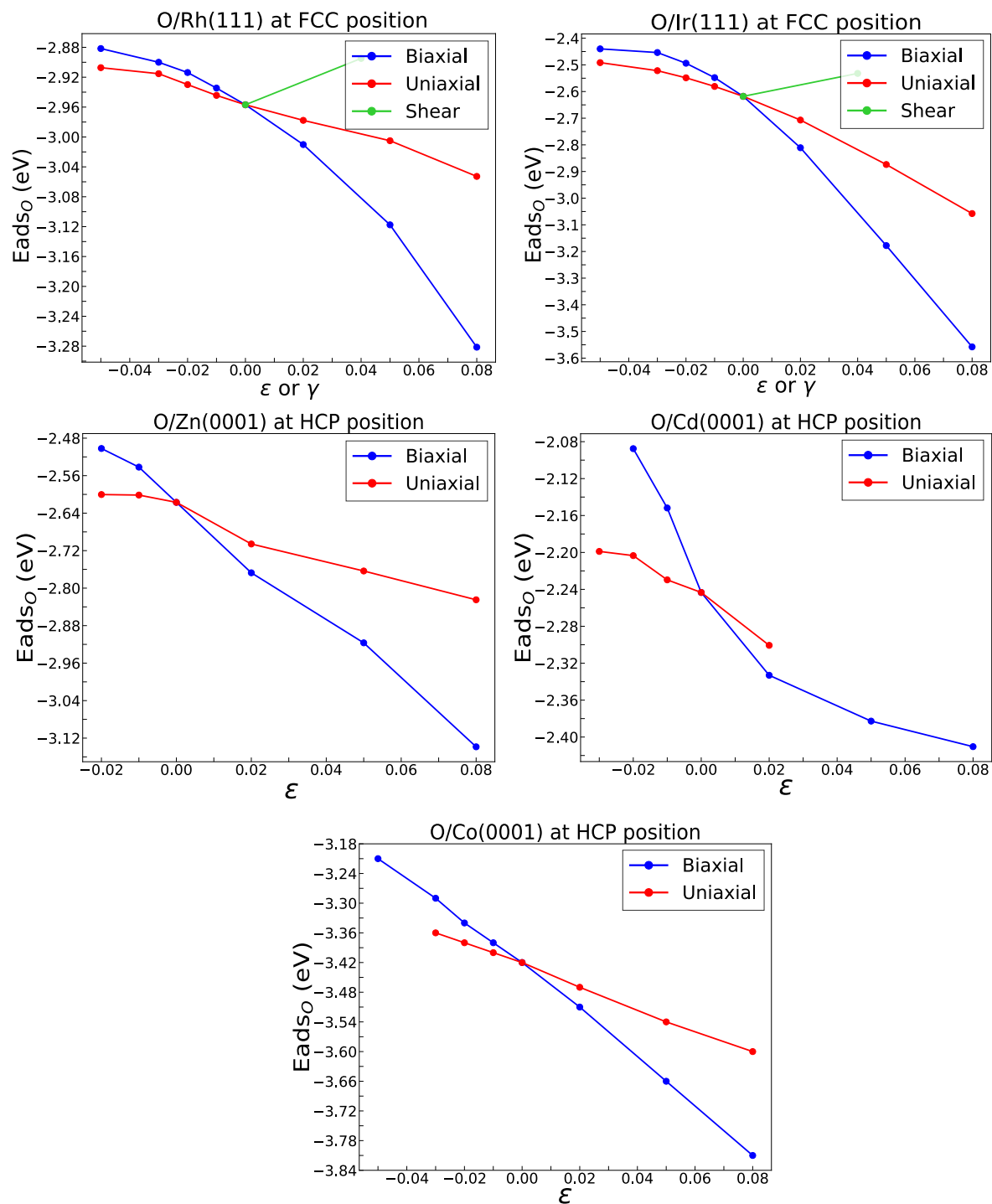


Figure A. 8.6: Adsorption energy of O as a function of strain from 5% compression to 8% tension at FCC position for Rh, and Ir, and HCP position for Zn, Cd, and Co. The legend indicates the type of strain.

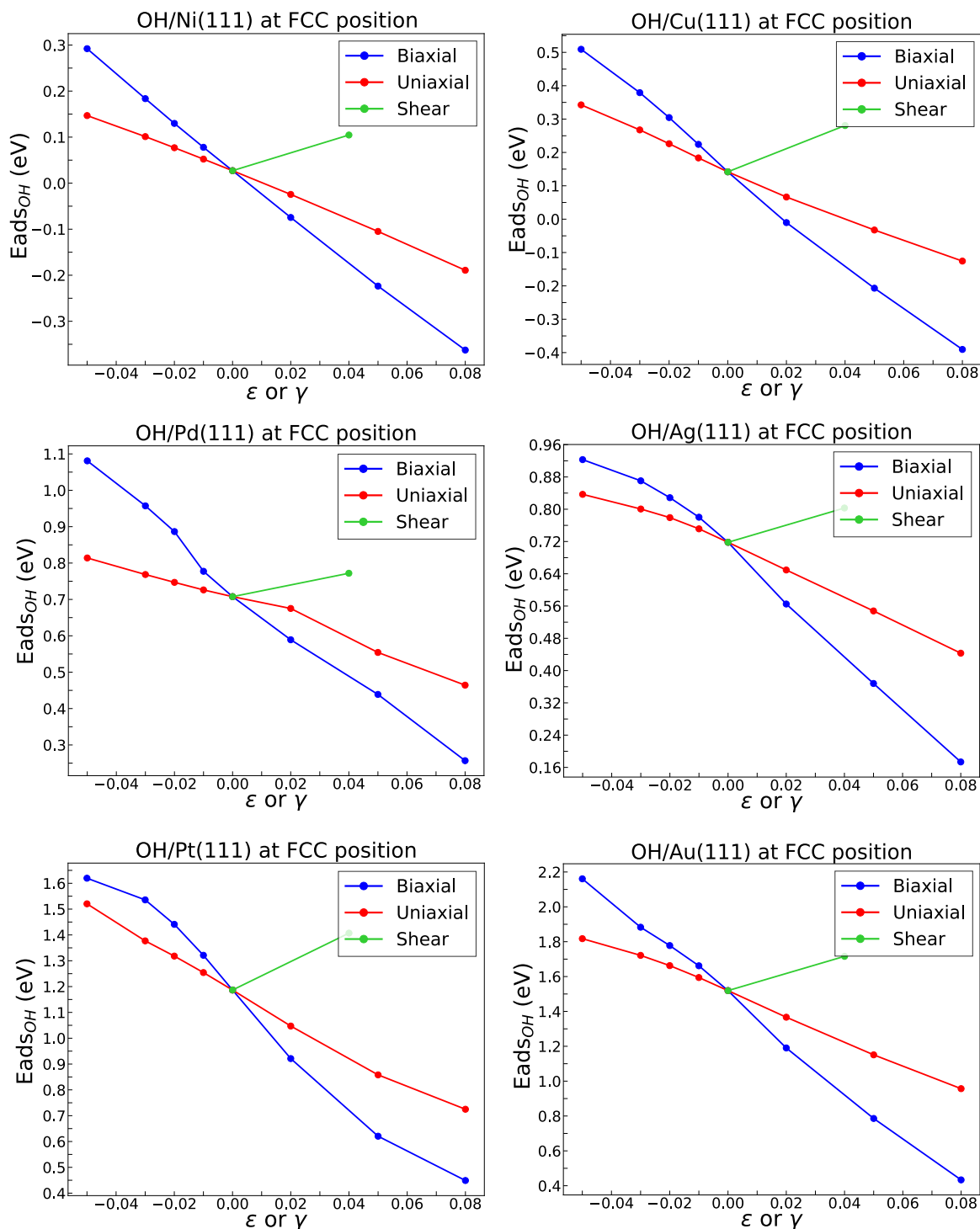


Figure A. 8.7: Adsorption energy of OH as a function of strain from 5% compression to 8% tension at FCC position for Ni, Cu, Pd, Ag, Pt, and Au. The legend indicates the type of strain.

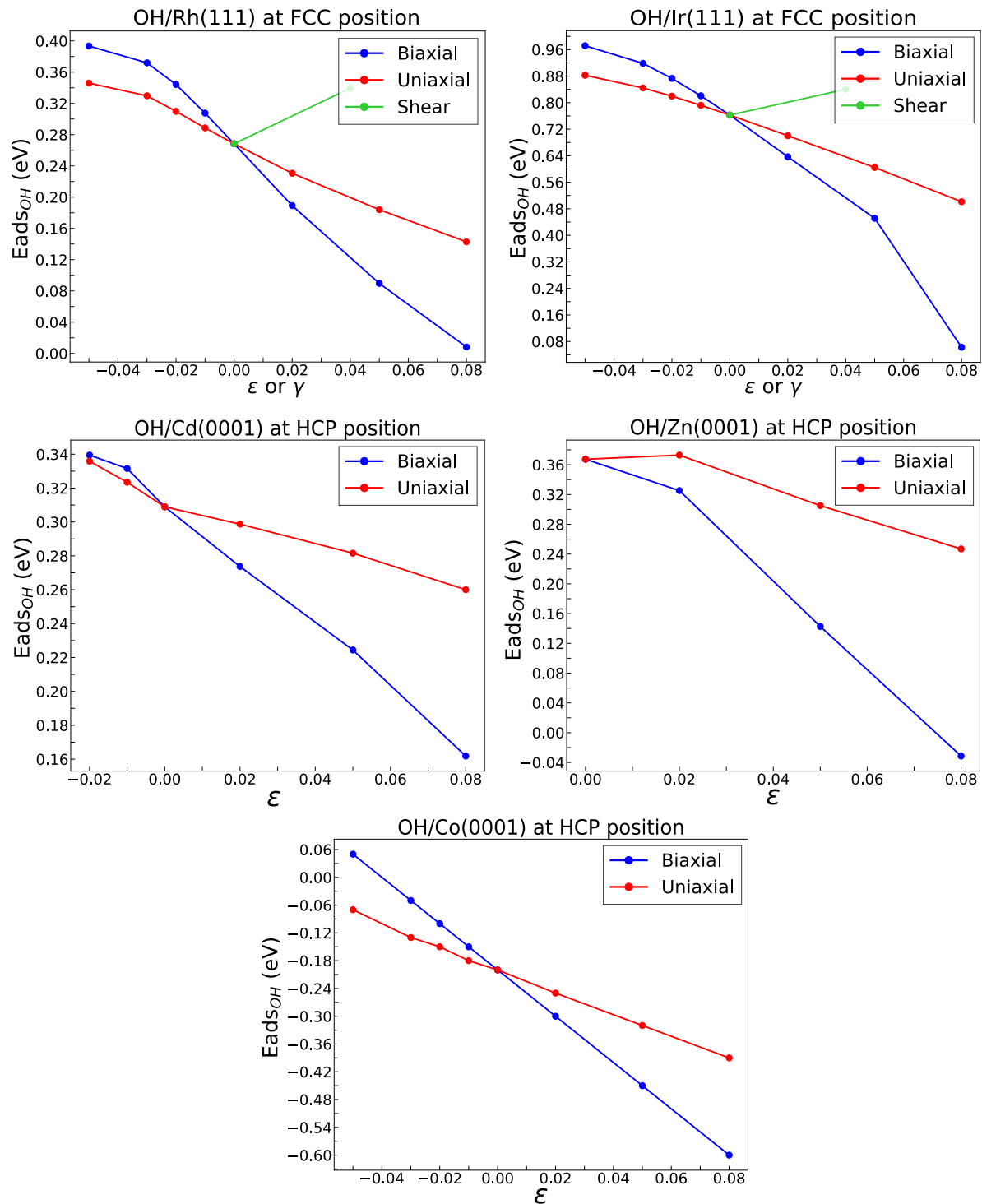


Figure A. 8.8: Adsorption energy of OH as a function of strain from 5% compression to 8% tension at FCC position for Rh, and Ir, and HCP position for Zn, Cd, and Co. The legend indicates the type of strain.

Appendix B

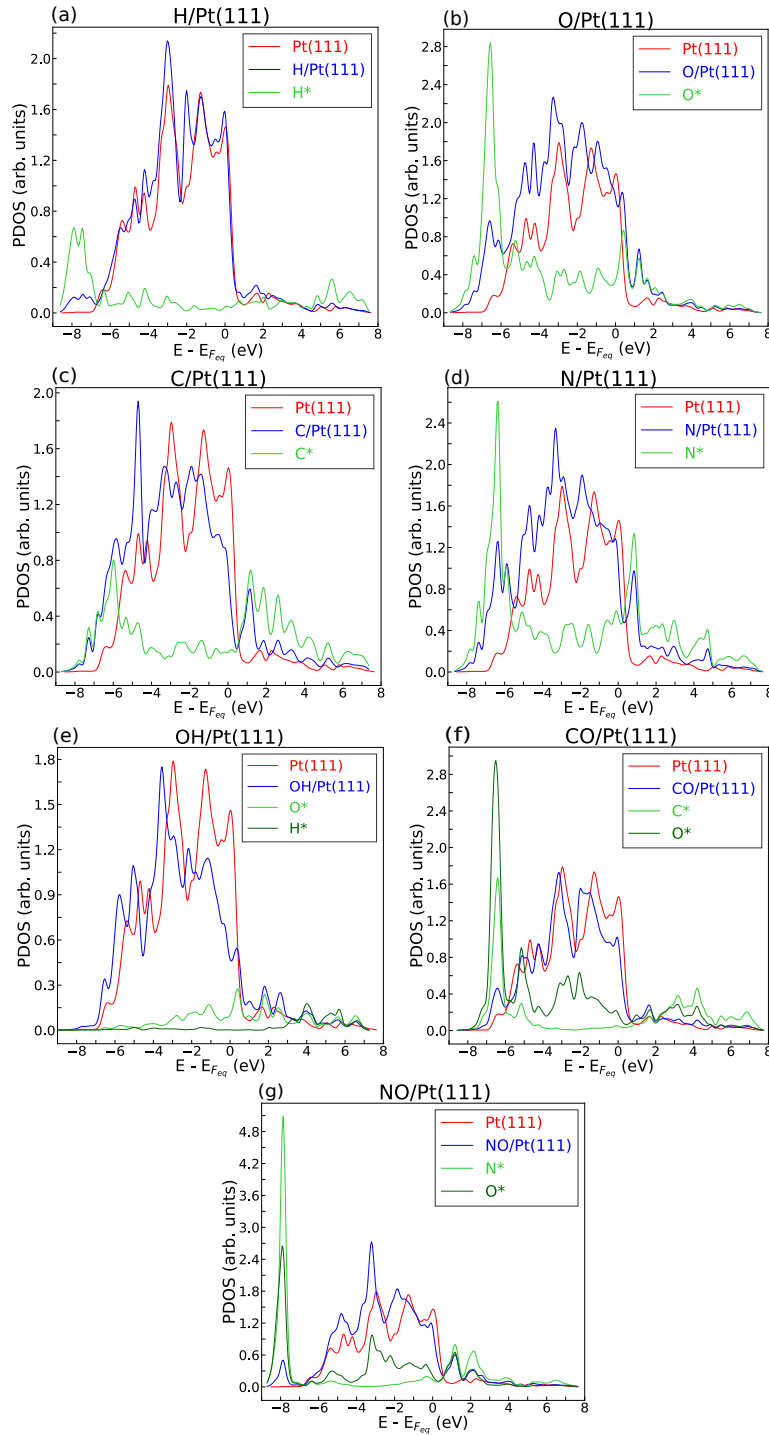


Figure B. 8.9: PDOS of (a) H, (b) O, (c) C, (d) N, (e) OH, (f) CO, and (g) NO adsorption into a Pt(111) surface. Red lines represent the PDOS of the platinum surface atoms of the clean slab, blue lines represent the PDOS of the platinum surface atoms with the adsorbate and green lines represent the PDOS of the adsorbed atoms.

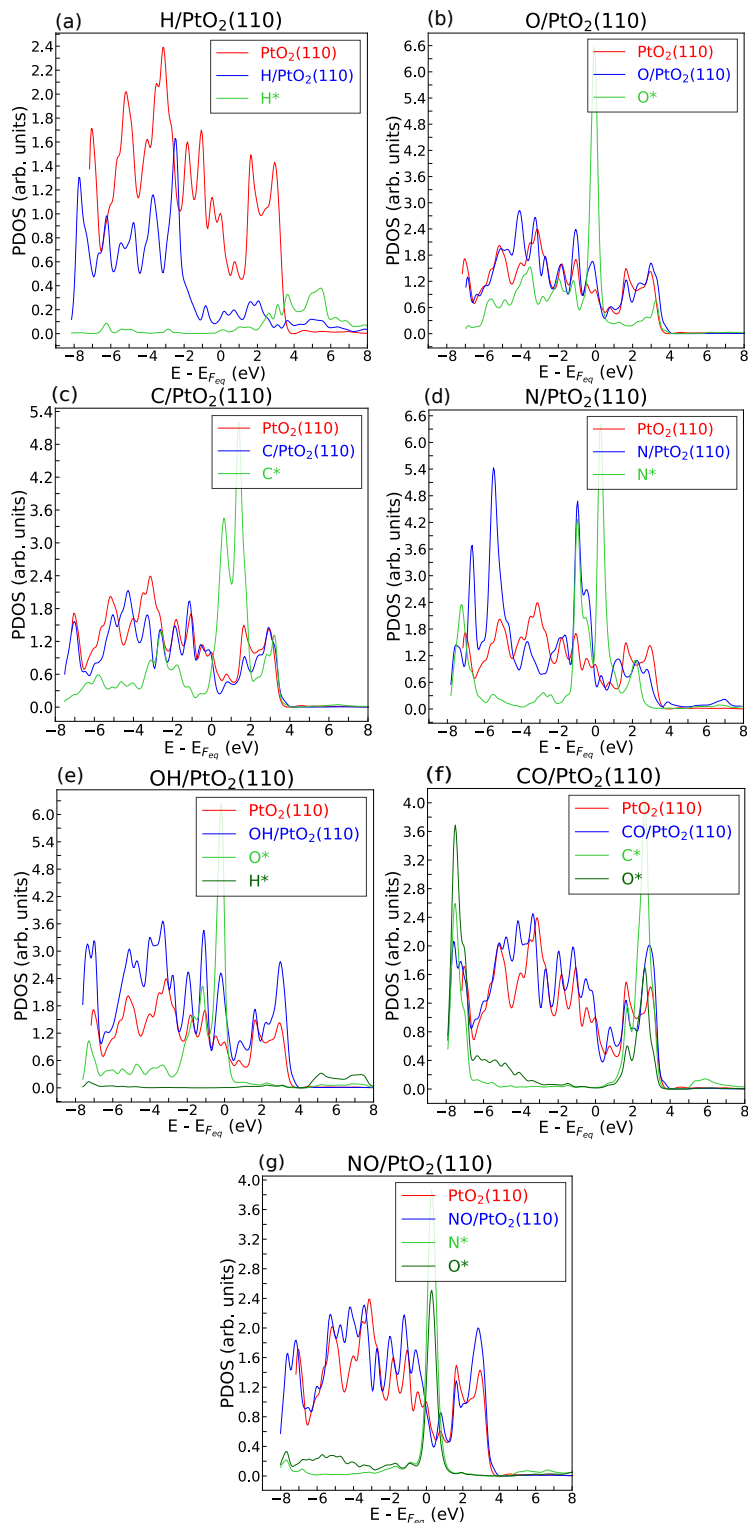


Figure B. 8.10: PDOS of (a) H, (b) O, (c) C, (d) N, (e) OH, (f) CO, and (g) NO adsorption into a $\text{PtO}_2(110)$ surface. Red lines represent the PDOS of the PtO_2 surface atoms of the clean slab, blue lines represent the PDOS of the PtO_2 surface atoms with the adsorbate and green lines represent the PDOS of the adsorbed atoms.

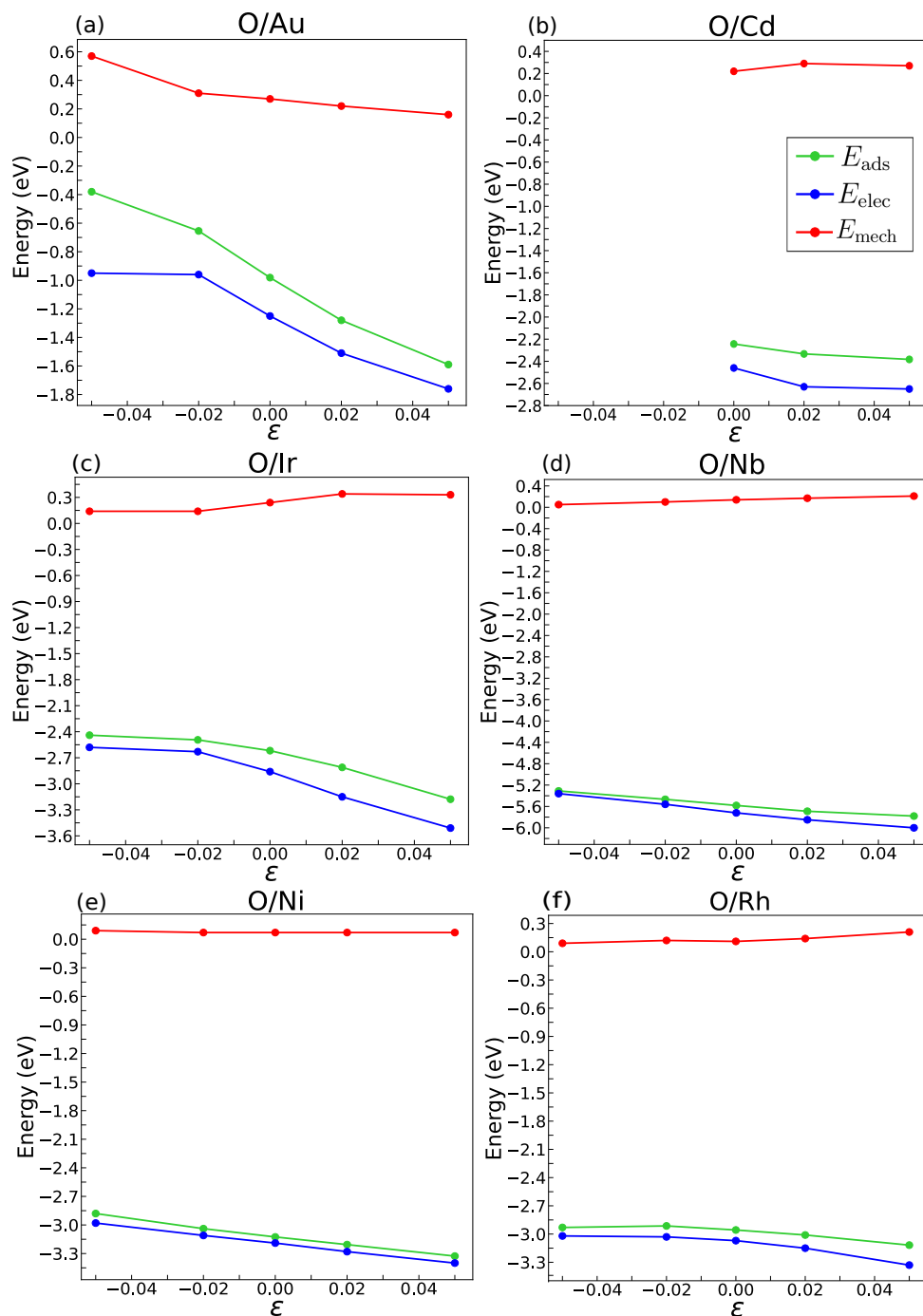


Figure B. 8.11: Different contributions for the oxygen adsorption in (a) Au fcc(111), (b) Cd hcp(0001), (c) Ir fcc(111), (d) Nb bcc(110), (e) Ni fcc(111), (f) Rh fcc(111). The green, blue, and red lines represent the total, electronic, and mechanical energies, respectively. Values with Cd under compression strains have been removed due to surface instabilities.

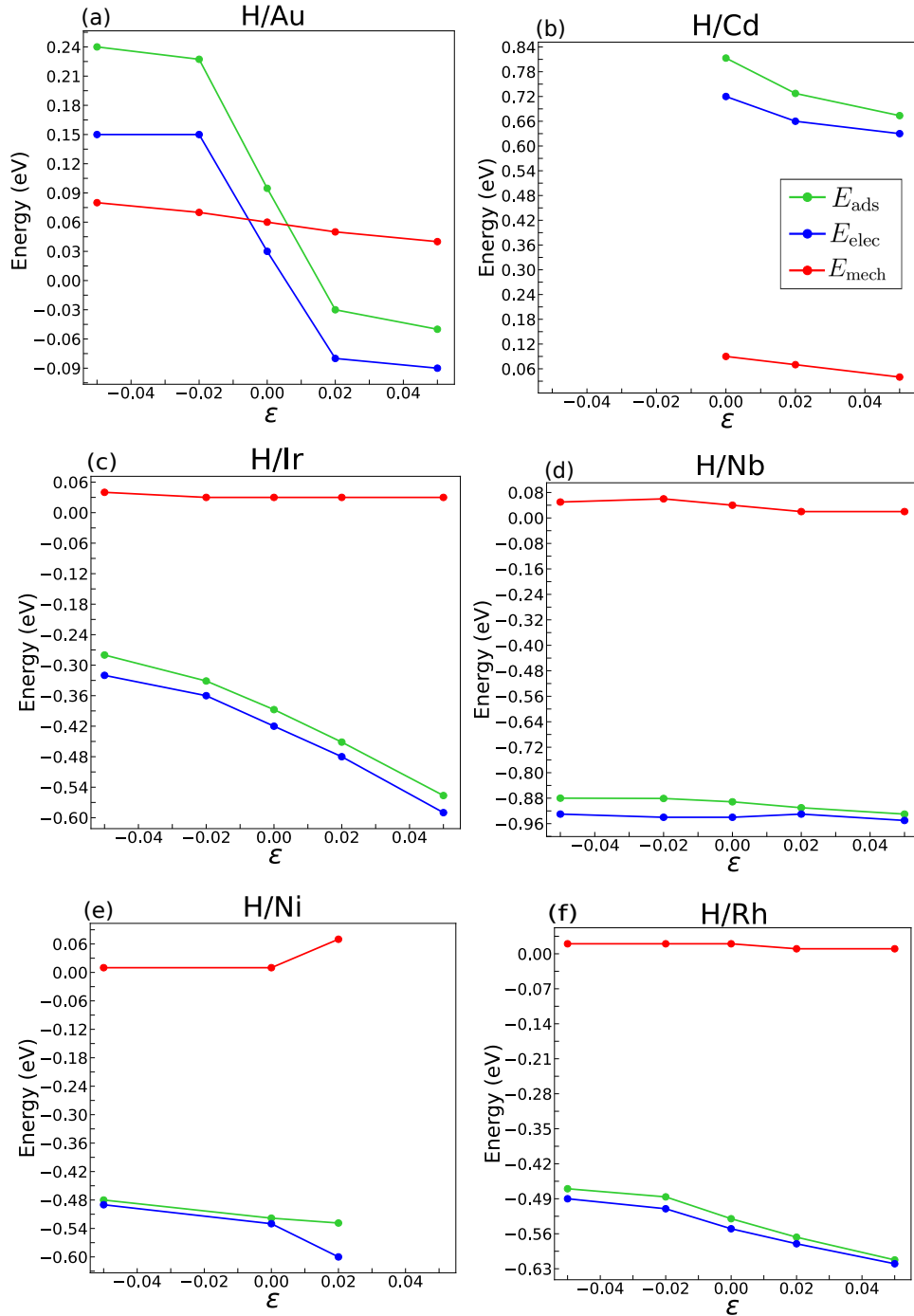


Figure B. 8.12: Different contributions for the hydrogen adsorption in (a) Au fcc(111), (b) Cd hcp(0001), (c) Ir fcc(111), (d) Nb bcc(110), (e) Ni fcc(111), (f) Rh fcc(111). The green, blue, and red lines represent the total, electronic, and mechanical energies, respectively. Values with Cd under compression strains and Ni at 5% tension have been removed due to surface instabilities.

Appendix C

SYSTEM	Eads _H (eV)		Eads _O (eV)		Eads _{OH} (eV)	
	FCC AAA	FCC AAB	FCC AAA	FCC AAB	FCC AAA	FCC AAB
Ag ₃ Mg	-0,01	-0,01	-1,24	-2,42	0,68	-0,31
Ag ₃ In	0,17	0,39	-1,48	-2,01	0,56	0,42
Al ₃ Li	0,56	0,02	-4,63	-5,03	-0,26	-1,15
Al ₃ Y	0,54	-0,37	-4,10	-5,28	0,11	-1,15
Al ₃ Zr	0,75	-0,28	-3,70	-4,90	0,25	-0,83
Co ₃ Ti	-0,71	-0,79	-3,70	-4,52	-0,25	-1,08
In ₃ Y	0,88	0,09	-2,33	-4	0,72	-0,95
Ni ₃ Al	-0,59	-0,82	-2,91	-3,55	0,46	-0,43
Ni ₃ Fe	-0,54	-0,53	-2,85	-3,36	0,26	-0,24
Ni ₃ Mn	-0,63	-0,65	-3,37	-3,69	0,09	-0,38
Ni ₃ Si	-0,49	-0,92	-2,48	-3,33	0,50	0,12
Ru ₃ Nb	-0,71	-0,76	-3,64	-4,16	0,19	-0,77
Sn ₃ Ca	1,08	0,54	-2,08	-3,44	0,91	-0,38
Ti ₃ Sn	-1,17	-1,18	-6,678	-6,38	-2,36	-2,25
Zn ₃ Mn	0,37	-0,20	-2,97	-3,58	0,32	-0,35
Zn ₃ Nb	0,54	-0,65	-2,73	-4,80	0,50	-1,45
Zn ₃ Ti	0,46	-0,48	-3,00	-4,82	0,39	-1,65
Zn ₃ V	0,47	-0,59	-2,67	-4,89	0,57	-1,36
Zr ₃ Al	-1,17	-0,72	-6,68	-5,63	-2,38	-1,57
Zr ₃ In	-1,21	-1,07	-6,84	-6,47	-2,43	-2,23

Table C. 8.2: Hydrogen, Oxygen, and Hydroxyl adsorption energies at FCC AAA and FCC AAB sites for A₃B fcc(111) binary intermetallic compounds. All values are expressed in eV.

Appendix D

A₃B fcc(111)				AB bcc(101)			
	AlNi ₃	HoIn ₃	ScPt ₃		AlCo	HoIr	ScZn
	CaSn ₃	HoPd ₃	ScRh ₃		AlFe	HoMg	SmIn
	Ce ₃ Ga	HoPt ₃	SiNi ₃		AlIr	HoRh	SmMg
	Ce ₃ In	InAg ₃	Sm ₃ In		AlNi	HoZn	SmRh
	Ce ₃ Sn	InPt ₃	SmIn ₃		AlRh	InPd	SmZn
	Ce ₃ Tl	La ₃ In	SmPd ₃		AlRu	InRh	TbCu
	CeIn ₃	La ₃ Sn	SmPt ₃		CaIn	LaIn	TbMg
	CePd ₃	La ₃ Tl	SmSn ₃		CaPd	LaMg	TbRh
	CePt ₃	LaIn ₃	SmTl ₃		CsAu	LaZn	TbZn
	CeRh ₃	LaPd ₃	SnPd ₃		CuPd	LuAu	TiCo
	CeSn ₃	LaSn ₃	SnPt ₃		DyCu	LuIr	TiFe
	CoPt ₃	LiAl ₃	TaIr ₃		DyIn	LuMg	TiOs
	CrIr ₃	LiAu ₃	TaRh ₃		DyMg	LuPd	TiRe
	CrRh ₃	LuAl ₃	TbGa ₃		DyPd	LuRh	TiRu
	Cu ₃ Au	LuGa ₃	TbIn ₃		DyRh	LuRu	TmCu
	Cu ₃ Pd	LuIn ₃	TbPd ₃		DyZn	LuZn	TmIn
	Cu ₃ Pt	LuPd ₃	TbPt ₃		ErCu	MgAu	TmIr
	DyGa ₃	LuPt ₃	TiCo ₃		ErIn	MgPd	TmMg
	DyIn ₃	MgAg ₃	TiIr ₃		ErIr	MgRh	TmPd
	DyPd ₃	MnNi ₃	TiRh ₃		ErMg	MgSc	TmRh
	DyPt ₃	MnPt ₃	TiZn ₃		ErPd	MnRh	TmZn
	ErAl ₃	MnZn ₃	TmAl ₃		ErRh	MnV	VRu
	ErGa ₃	NbRu ₃	TmGa ₃		ErZn	NdAg	YbIn
	ErIn ₃	NbZn ₃	TmIn ₃		EuZn	NdMg	YbPd
	ErPd ₃	Nd ₃ In	TmPd ₃		FeCo	NdZn	YbRh
	ErPt ₃	NdIn ₃	TmPt ₃		FeRh	PrIn	YbZn
	EuSn ₃	NdPd ₃	TmTl ₃		GaCo	PrMg	YIn
	FeNi ₃	NdSn ₃	VZn ₃		GaIr	PrZn	YMg
	FePd ₃	Ni ₃ Ge	YbPd ₃		GaRh	RbAu	YRh
	GaFe ₃	Ni ₃ Pt	YbSn ₃		GdAu	ScAg	YZn
	GaNi ₃	Ni ₃ Sn	YIn ₃		GdCu	ScAl	ZnAu
	GdIn ₃	Pr ₃ In	YPd ₃		GdMg	ScAu	ZnCu
	GdIr ₃	PrIn ₃	YPt ₃		GdRh	ScCo	ZnRh
	GdPd ₃	PrPd ₃	ZnPt ₃		GdZn	ScCu	ZrCo
	GdPt ₃	PrSn ₃	Zr ₃ Al		HfCo	ScIr	ZrOs
	GdSn ₃	ScAl ₃	Zr ₃ In		HfOs	ScNi	ZrRu
	HfIr ₃	ScGa ₃	ZrIr ₃		HfRh	ScPd	ZrZn
	HfRh ₃	ScIn ₃	ZrRh ₃		HfRu	ScPt	
	HoAl ₃	ScIr ₃			HoCu	ScRh	
	HoGa ₃	ScPd ₃			HoIn	ScRu	

A₂B hcp(0001)	Al ₂ Hf	A₃B hcp(0001)	BaSn ₃	AB fcc(101)	AlCu
	Al ₂ Zr		Co ₃ Mo		InRh
	Cr ₂ Ti		Co ₃ W		NbRu
	Fe ₂ Sc		Ir ₃ W		ScAg
	Fe ₂ Ta		LaAl ₃		Vru
	Fe ₂ Zr		MoIr ₃		ZnAu
	Ga ₂ Sr		MoRh ₃		ZnRh
	Ga ₂ Y		NdAl ₃		TiAu
	In ₂ Sr		Ni ₃ Sn		TiCu
	Mn ₂ Sc		PrAl ₃		
	Mn ₂ Ta		Rh ₃ W		
	Mn ₂ Ti		Sc ₃ In		
	Os ₂ Sc		Al ₃ Sm		
	Os ₂ La		TbGa ₃		
	Os ₂ Y		Ti ₃ Al		
	Os ₂ Zr		Ti ₃ Ga		
	Re ₂ Sm		Ti ₃ In		
	Re ₂ Y		YAl ₃		
	Re ₂ Zr		ZrNi ₃		
	Ru ₂ Sm				
	Ti ₂ Ga				
	Ti ₂ Sn				
	Y ₂ In				
	Zn ₂ Nb				

Adsorbate: H

(a)

	Strain	PSI	S_A	S_B	Cell volume	WEN	WIE	WAR	GCN
Strain	1.00	0.03	0.03	0.03	-0.03	0.04	0.03	-0.02	0.02
PSI	0.03	1.00	0.83	0.28	-0.13	0.30	0.65	-0.20	0.15
S_A	0.03	0.83	1.00	-0.04	-0.05	0.42	0.66	-0.24	0.26
S_B	0.03	0.28	-0.04	1.00	-0.38	0.28	0.34	-0.22	-0.08
Cell volume	-0.03	-0.13	-0.05	-0.38	1.00	-0.29	-0.31	0.19	0.04
WEN	0.04	0.30	0.42	0.28	-0.29	1.00	0.49	-0.58	0.20
WIE	0.03	0.65	0.66	0.34	-0.31	0.49	1.00	-0.42	0.17
WAR	-0.02	-0.20	-0.24	-0.22	0.19	-0.58	-0.42	1.00	-0.12
GCN	0.02	0.15	0.26	-0.08	0.04	0.20	0.17	-0.12	1.00

Adsorbates: O and OH

(b)

	Strain	PSI	S_A	S_B	Cell volume	WEN	WIE	WAR	GCN	Adsorbate
Strain	1.00	0.05	0.06	0.02	-0.02	0.05	0.05	-0.01	0.04	-0.00
PSI	0.05	1.00	0.81	0.30	-0.16	0.28	0.67	-0.19	0.14	0.01
S_A	0.06	0.81	1.00	-0.07	-0.05	0.43	0.65	-0.25	0.30	-0.01
S_B	0.02	0.30	-0.07	1.00	-0.43	0.24	0.33	-0.22	-0.06	-0.00
Cell volume	-0.02	-0.16	-0.05	-0.43	1.00	-0.29	-0.32	0.23	0.07	-0.08
WEN	0.05	0.28	0.43	0.24	-0.29	1.00	0.46	-0.59	0.25	0.01
WIE	0.05	0.67	0.65	0.33	-0.32	0.46	1.00	-0.42	0.16	-0.00
WAR	-0.01	-0.19	-0.25	-0.22	0.23	-0.59	-0.42	1.00	-0.15	0.03
GCN	0.04	0.14	0.30	-0.06	0.07	0.25	0.16	-0.15	1.00	-0.07
Adsorbate	-0.00	0.01	-0.01	-0.00	-0.08	0.01	-0.00	0.03	-0.07	1.00

Figure D. 8.13: Pearson correlation matrixes of the features for the (a) hydrogen adsorption and (b) oxygen and hydroxyl adsorption.

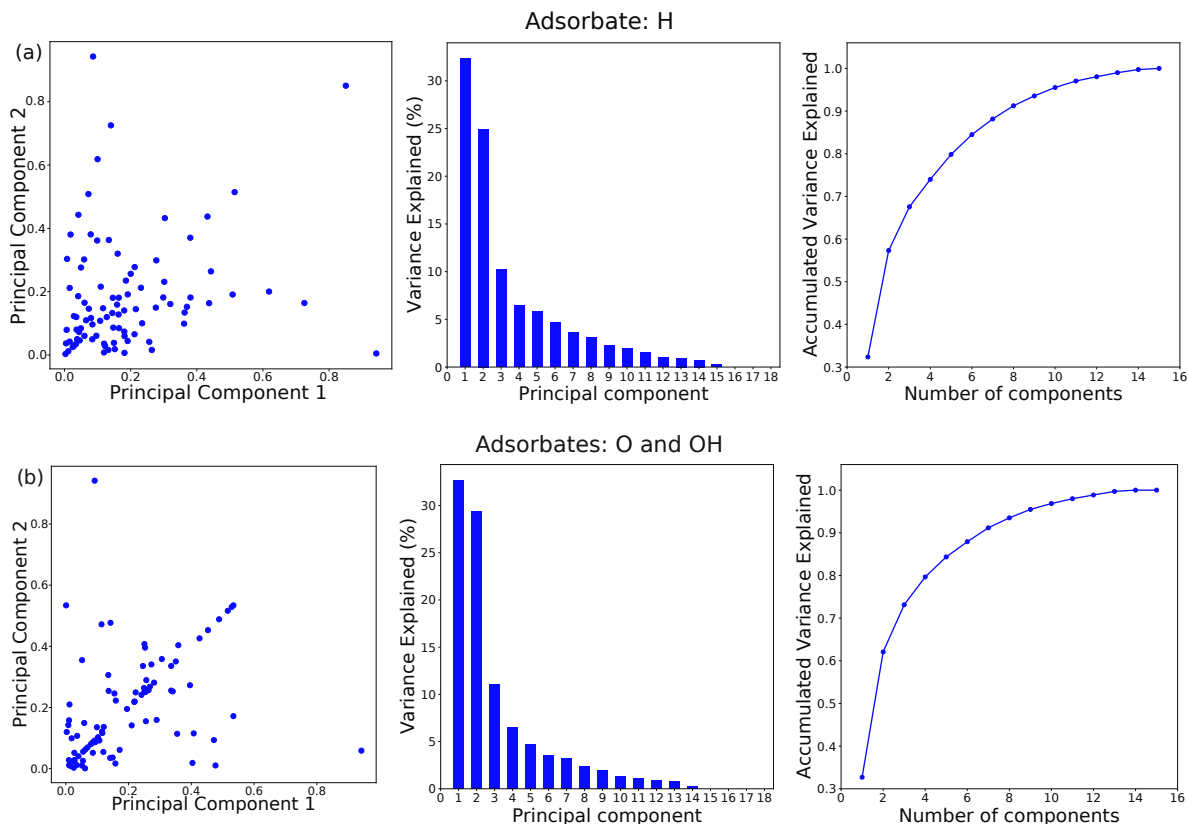


Figure D. 8.14: Principal components analysis for the (a) Hydrogen and (b) Oxygen and Hydroxyl adsorption models.

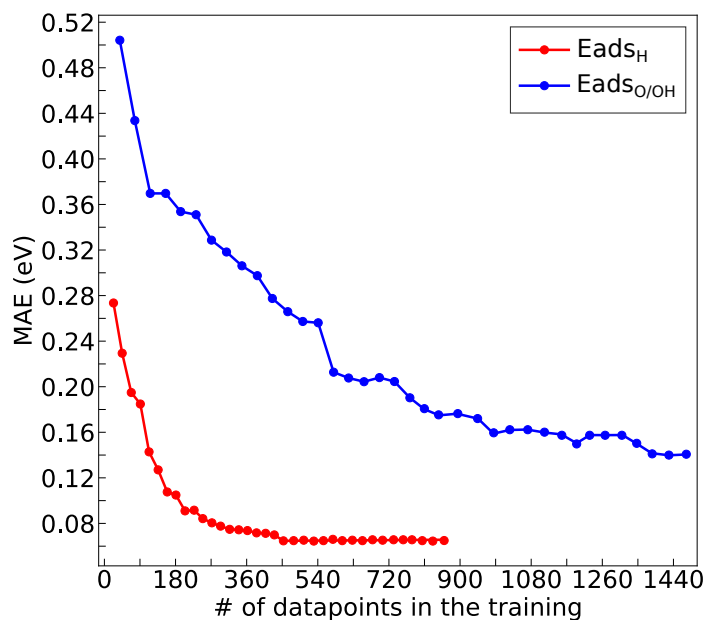


Figure D. 8.15: Learning curves for the hydrogen (red) and the oxygen/hydroxyl (blue) machine learning models.

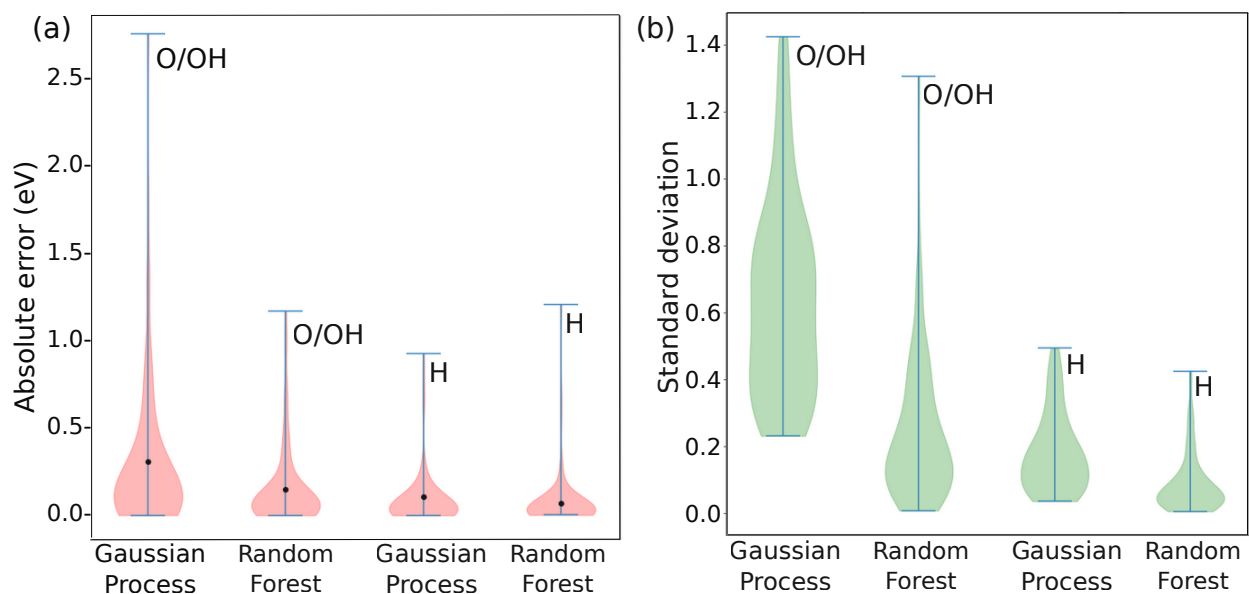


Figure D. 8.16: Violin plots for the absolute error (a) and the standard deviation (b) comparing GPR and the RF models for H and O/OH adsorption. The black dots indicate the MAEs.

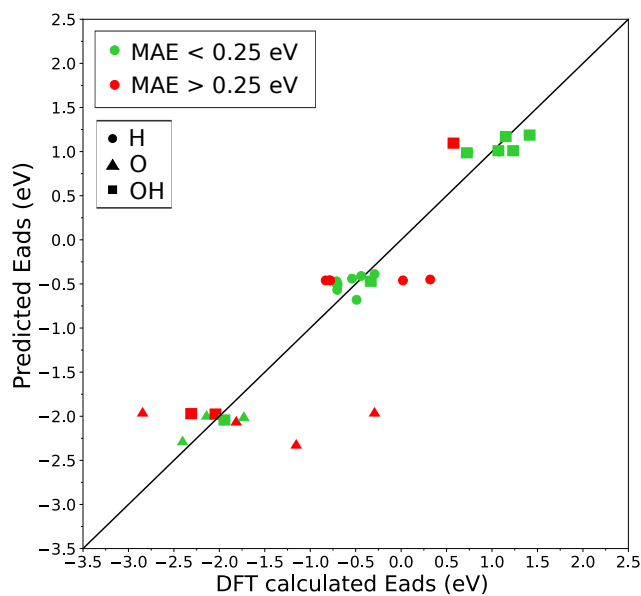


Figure D. 8.17: Parity plot for the 30 verification candidates. Green signs represent the candidates that obtained accurate predictions by the RF model ($\text{MAE} < 0.25 \text{ eV}$). Red signs represent the candidates that obtained high errors ($\text{MAE} > 0.25 \text{ eV}$) by the RF model. Dots, triangles, and squares illustrate the adsorption energies for H, O, and OH, respectively.

Material	Strain	Adsorption site	Eads _H (eV)
Pt	0	FCC	-0.49
Ce ₃ Ga	5	fccAAA	-0.49
Ce ₃ In	5	fccAAA	-0.49
Ce ₃ Sn	1	fccAAB	-0.49
Ir ₃ W	-3	hcpAAA	-0.52
Nd ₃ In	5	hcpAAA	-0.47
Ni ₃ Fe	0	hcpAAB	-0.50
Ni ₃ Pt	1	hcpAAA	-0.49
Pd ₃ Ce	-1	fccAAB	-0.49
Pd ₃ Dy	1	hcpAAA	-0.49
Pd ₃ Fe	-5	fccAAA	-0.49
Pd ₃ Nd	-3	hcpAAA	-0.49
Pd ₃ Pr	-5	hcpAAA	-0.49
Pd ₃ Sc	-3	fccAAA	-0.49
Pd ₃ Sm	-5	hcpAAA	-0.47
Pd ₃ Y	-3	fccAAA	-0.48
Pr ₃ In	5	fccAAB	-0.48
Pt ₃ Co	0	fccAAB	-0.49
Pt ₃ Dy	0	hcpAAA	-0.49
Pt ₃ Sc	-3	fccAAB	-0.49
Pt ₃ Sm	-5	fccAAB	-0.49
Pt ₃ Sn	-5	fccAAA	-0.50
Pt ₃ Y	0	hcpAAA	-0.48
Rh ₃ Mo	0	fccAAA	-0.46
Sm ₃ In	3	hcpAAA	-0.47
Sn ₃ Nd	5	fccAAB	-0.47
Sn ₃ Sm	3	fccAAB	-0.49
Zn ₃ Ti	-5	fccAAB	-0.48

Table D. 8.3: Optimum hydrogen adsorption energies (in comparison with Pt at zero strain). The adsorption sites and the strains are indicated in the table.

Material	Strain	Adsorption site	Eads _O (eV)	Strain	Adsorption site	Eads _{OH} (eV)
Pt	0	FCC	-1.79	0	FCC	1.19
Ag ₃ In	5	fccAAB	-1.79	-5	hcpAAA	1.15
ZnAu	3	threefoldAAB	-1.78	0	longbridgeB	1.36
Cu ₃ Pt	-5	fccAAB	-1.79	3	ontopB	1.19
Ir ₃ Sc	-1	ontopB	-1.94	-1	fccAAA	1.19
Ni ₃ Pt	-5	hcpAAA	-1.89	3	ontopA	1.16
Pd ₃ Dy	-1	fccAAB	-1.81	0	fccAAA	1.19
Pd ₃ Sn	-5	fccAAB	-1.84	3	fccAAA	1.13
Pd ₃ Sc	1	hcpAAA	-1.77	-5	fccAAA	1.00
Pt ₃ Co	5	hcpAAA	-1.76	-1	hcpAAA	1.2
Pt ₃ Dy	-1	hcpAAA	-1.79	1	ontopA	1.18
Pt ₃ Mn	3	hcpAAA	-1.81	1	hcpAAA	1.17
Pt ₃ Sc	-5	fccAAB	-1.84	-5	fccAAA	1.19
Pt ₃ Sn	-5	fccAAB	-1.87	1	fccAAA	1.18
Pt ₃ Y	5	hcpAAA	-1.75	0	fccAAA	1.06

Table D. 8.4: Optimum oxygen and hydroxyl adsorption energies (in comparison with Pt at zero strain). The adsorption sites and the applied strain are indicated in the table.

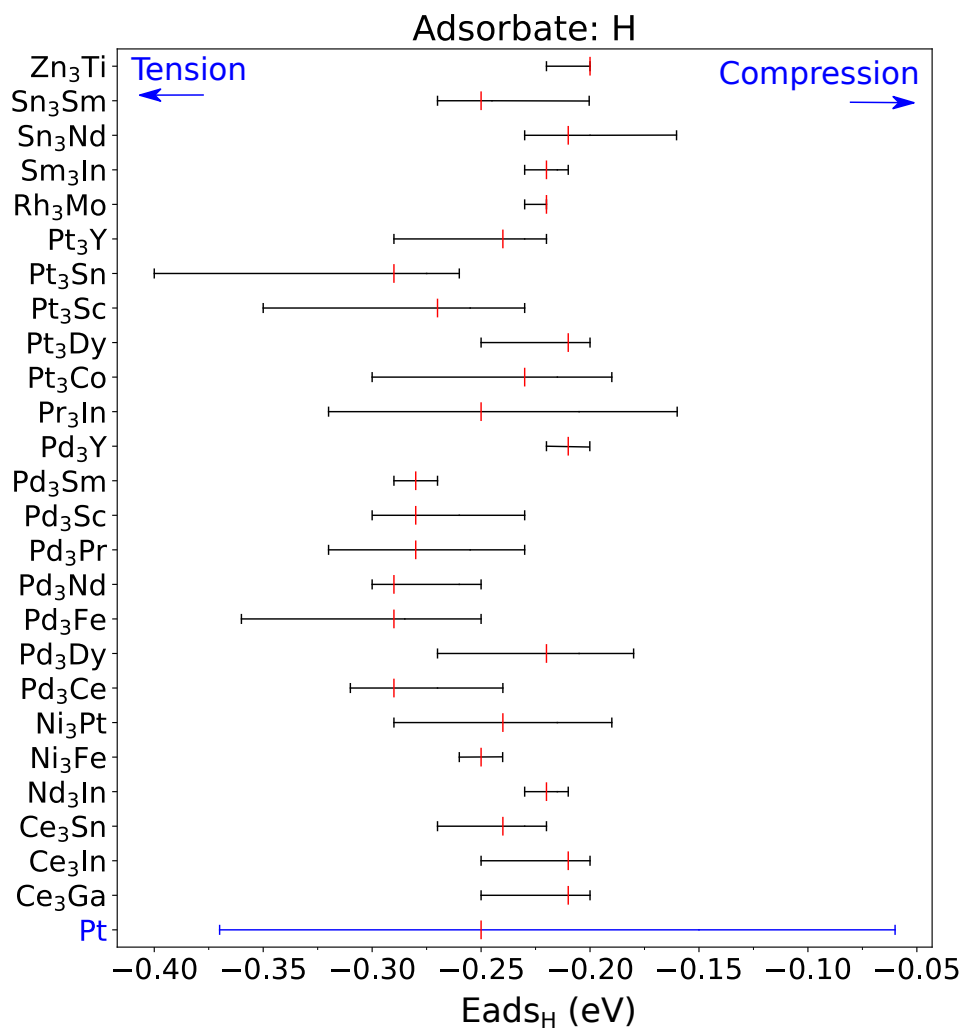


Figure D. 8.18: Variation of E_{ads_H} from -5% compression to 5% tension for the 25 candidates with the most similar energies to pure platinum. The red vertical lines represent the E_{ads_H} at zero strain.

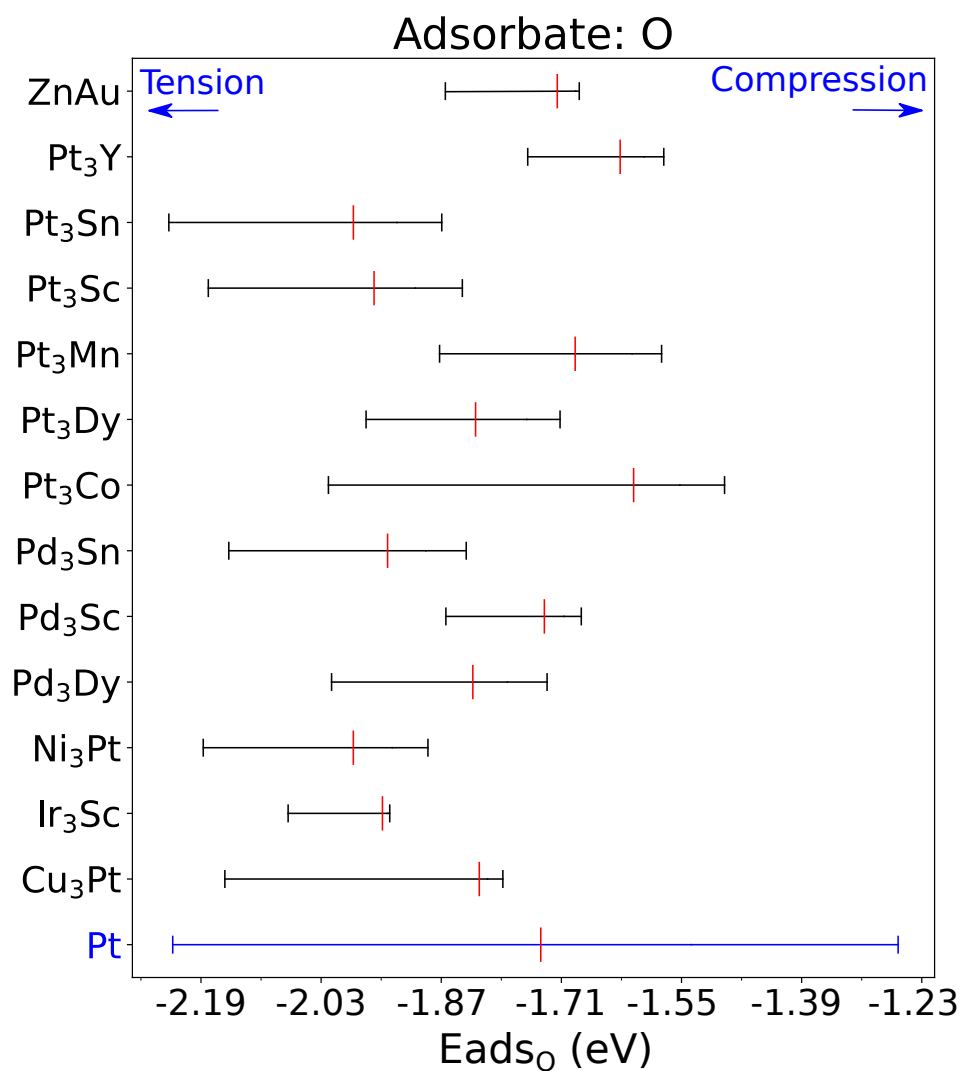


Figure D. 8.19: Variation of E_{ads_O} from -5% compression to 5% tension for the 13 candidates with the most similar energies to pure platinum. The red vertical lines represent the E_{ads_O} at zero strain.

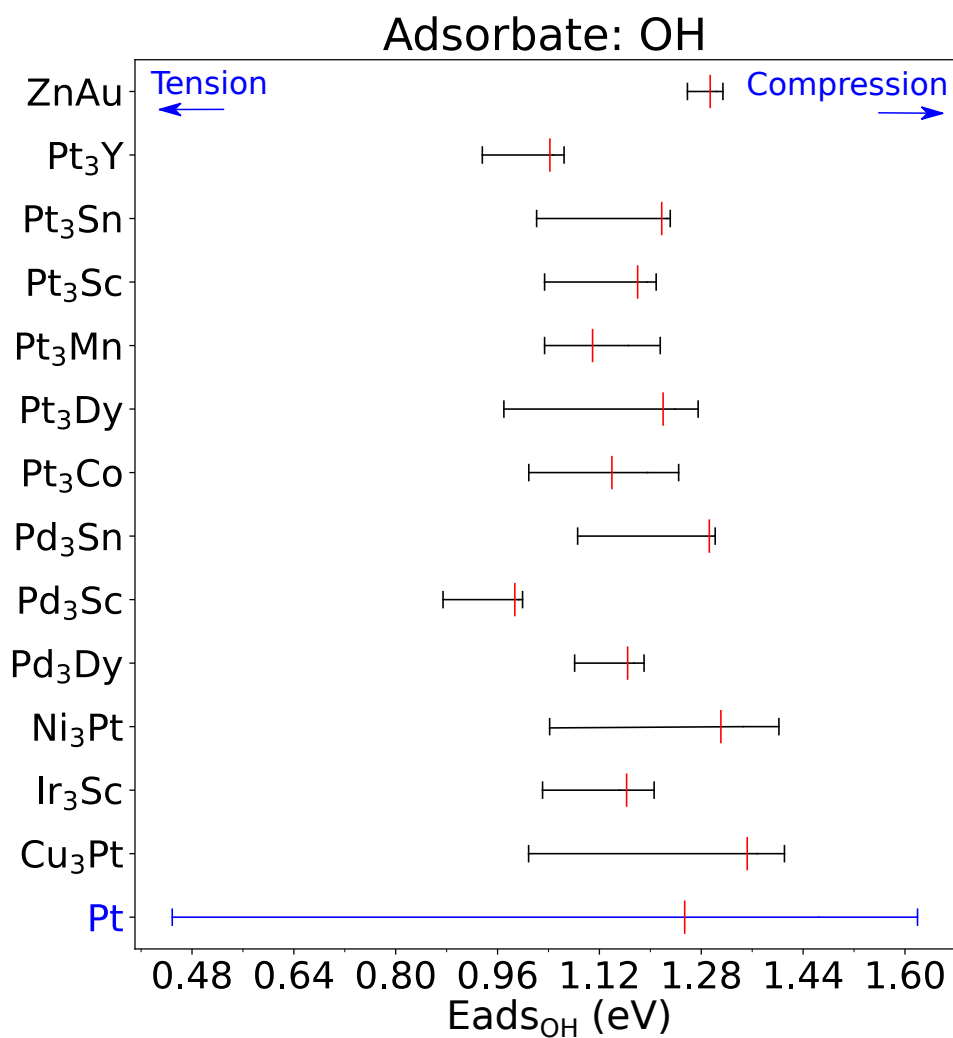


Figure D. 8.20: Variation of $E_{ads_{OH}}$: from -5% compression to 5% tension for the 13 candidates with the most similar energies to pure platinum. The red vertical lines represent the $E_{ads_{OH}}$ at zero strain.