

Density Functional Theory (DFT) application on Single

Atom Catalysts (SACs) for the electrochemical

reduction of carbon dioxide

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A Manuscript-based Thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science

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Abstract

Density functional theory (DFT) is a quantum mechanics method that has been used by physicists, chemists and material scientists since the 1970s. It allows for the compution of important properties of materials and extract valuable information of chemical reactions. Chemical engineers and researchers use this method to enrich and justify their experimental findings, as well as discover new materials for various trending applications such as batteries, catalysis, photovoltaics and nanotechnology. One such important application is the electrochemical conversion of carbon dioxide intro high-valued products, such as methane and methanol. However, an adequate catalyst is needed to make this technology industrially feasable. This catalyst must selectively convert CO_2 into one product, while minimizing the

overall potential required to drive the reaction forward. One emerging solution to this challenge, is the use of Single Atoms Catalysts (SACs). They have unique properties and catalytic activity due to their tunable coordination environment and uniform catalytic active sites. Additionally, MXenes are two dimensional inorganic materials composed of thin layers of nitrides, carbides or carbonitrides of transition metals, which have been recently used as supports for single metal atoms (SMAs) due to their superior electronic, thermal, and mechanical properties. Through this thesis, we screened multiple SMAs MXene catalyst to discover new, performant electrocatalysts for the carbon dioxide reduction reaction (CO_2RR). We show that MXenes supress competing reactions such as the hydrogen evolution reaction (HER) and multi carbon (C_{2+}) formation. Additionally, after performing systemic DFT computations, we show that five catalysts exhibit excellent stability, selectivity, and low limiting potentials for C_1 products, especially methanol: Ni/Pd@Ti₃C₂O₂ and Ru/Fe/Co@Mo₂CO₂. The novel and in-depth understanding attained in this systematic high throughput DFT computations guide the experimentalist to synthesize SACs based on MXene materials, with exceptional activity and selectivity for highly reduced C₁ products. Thus, this thesis presents two manuscripts in the hope of (1) teaching the traditional chemical engineer the principles of DFT, how to use it, how it can benefit them in multiple applications, its strengths and limitations; and (2) applying DFT in the field of electrocatalysis to screen and discover performant catalysts for the CO₂RR.

Résumé

La théorie de la fonctionnelle de la densité (DFT) est une méthode de mécanique quantique utilisée par les physiciens, les chimistes et les scientifiques des matériaux depuis les années 1970. Elle permet le calcul de propriétés importantes des matériaux et l'extraction d'informations précieuses sur les réactions chimiques. Les ingénieurs chimistes et les chercheurs utilisent cette méthode pour enrichir et justifier leurs découvertes expérimentales, ainsi que pour découvrir de nouveaux matériaux pour diverses applications telles que les batteries, la catalyse, la photovoltaïque et la nanotechnologie. Une application importante est la conversion électrochimique du dioxyde de carbone en produits à haute valeur, tels que le méthane et le méthanol. Cependant, un catalyseur adéquat est nécessaire pour rendre cette technologie industriellement réalisable. Ce catalyseur doit convertir sélectivement le CO₂ en un seul produit tout en minimisant le potentiel global requis pour faire avancer la réaction. Une solution émergente à ce défi est l'utilisation de catalyseurs à atomes uniques (SAC). Ils possèdent des propriétés uniques et une excellente activité catalytique grâce à leur environnement de coordination réglable et à leurs sites catalytiques uniformes. De plus, les MXènes sont des matériaux inorganiques bidimensionnels composés de fines couches de nitrures, de carbures ou de carbonitrures de métaux de transition, récemment utilisés comme supports pour les atomes métalliques uniques (SMAs) en raison de leurs excellentes propriétés électroniques, thermiques et mécaniques. Dans cette thèse, nous avons examiné plusieurs catalyseurs MXène à SMAs pour découvrir de nouveaux électro catalyseurs performants pour la réduction du dioxyde de carbone (CO₂RR). Nous montrons que les MXènes suppriment les réactions concurrentes telles que la réaction d'évolution de l'hydrogène (HER) et la formation de plusieurs carbones (C2+). De plus, après avoir effectué des calculs systématiques de DFT, nous montrons que cinq catalyseurs présentent une excellente stabilité, sélectivité et de faibles potentiels pour les produits C₁, en particulier le méthanol : Ni/Pd@Ti3C2O2 et Ru/Fe/Co@Mo2CO2. La compréhension nouvelle et approfondie obtenue grâce à ces calculs systématiques de DFT à haut débit guide l'expérimentateur dans la synthèse de SACs à base de matériaux MXène, avec une activité et une sélectivité exceptionnelle pour les produits C₁ fortement réduits. Ainsi, cette thèse présente deux articles dans l'espoir de (1) enseigner aux ingénieurs chimistes traditionnels les principes de la DFT, comment l'utiliser, comment elle peut leur être bénéfique dans de multiples applications, ses forces et ses limites ; et (2) appliquer la DFT dans le domaine de l'électrocatalyse pour examiner et découvrir des catalyseurs performants pour la CO2RR.

Acknowledgments and Contributions of Authors

Firstly, I want to thank my incredible supervisor Professor Seifitokaldani for teaching me the principles of DFT, and guiding me throughout multiple high-impact publications.

Secondly, I want to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the *Fonds de Recherche du Québec Nature et technologies* (FRQNT) for funding these two projects.

Lastly, I would like to say that in the first manuscript entitled "Experimental methods in chemical engineering: Density functional theory", Xiao Wang contributed equally to the work, making us both first co-authors. I would like to thank the other authors: Jean-Philippe Harvey, Gregory S. Patience. In the second paper, I am the first author, however I would like to thank Rongyu Wang for helping me write a high-throughput code for my DFT computations.

1. Introduction

Chemical engineering is a broad field aiming to extract, transform and purify chemicals[1]. These chemicals can be anything from food to clothes, from biotherapeutics to bulk chemicals, and from drugs to catalysts[1]. Traditionally, a chemical engineering projects starts at the laboratory level, where engineers and chemists will combine their knowledge to produce a recipe for the chemical desired. This recipe must then be scaled up to industrial scale. In the case of catalysis, a suitable catalyst must be synthesized to ensure minimum energy requirements, reactor size, and future separation steps. However, the overall possibilities of structures for catalysts, even for one metal, are large. Synthesizing, characterizing, and evaluating a hundred catalysts in the lab is time consuming and resource intensive.

Density Functional Theory (DFT) is a computational tool that can be used to either screen a grand quantity of catalyst for their performance; or to understand the mechanism of a complex reaction in hope of justifying confusing experimental results. But what is DFT? Simply speaking, DFT is a method that employs a plethora of numerical techniques to solve the famous Schrodinger's equation, which cannot be solved analytically[2]. The mathematics and physics behind the DFT are complex and can sometimes seem, to the traditional engineer, who is not an expert in those fields, overwhelming. Consequently, the learning curve for using DFT is long and many end up quitting after a couple of months. This is because to truly apply DFT in your research or chemical system in general, there needs to be a solid understanding of mathematics, quantum physics, chemistry, material science and programming/computer science. Thus, in the first manuscript of this thesis, entitled *Experimental methods in chemical engineering: Density functional theory*, we break down enough theory behind DFT to make sure any chemical engineer can grasp its concept. Additionally, the paper is written in a tutorial-

like fashion to guide the chemical engineer or experimentalist to apply DFT to calculate material properties (heat capacity, bulk modulus, unit cell size, conductivity) and chemical properties such as energy barriers and kinetics for chemical reactions. We also show the applications of such findings in batteries, photovoltaics, and electrochemical reactions. Finally, we discuss the limitations of DFT and the recent efforts to overcome these challenges, encouraging future DFT users to simulate their system as accurately as possible.

In the second manuscript of this paper, we aim to use the gained knowledge from DFT in the field of electrocatalysis and carbon dioxide conversion to valuable products. Global warming has been classified as the second existential concern to humanity[3]. One emerging strategy to mitigate CO₂ concentration is through CO₂ Capture, Storage and Utilization (CCS) [4-6]. Specifically, the utilization part of this strategy is the newest and has attracted much research attention [7-9] as it aims to close the carbon cycle. In electrocatalysis, much research in recent years have studied the electrochemical conversion of CO₂ into valuable products[10]. Specifically, there are little works that have been able to achieve industrially relevant performances when it comes to methane and methanol production from this process[11]. In this manuscript, we aim to look at a specific, exciting new class of two-dimensional materials: Single Atom Catalysts (SACs) MXenes[12-15]. The goal is to apply the knowledge we have learned from the previous manuscript to screen 100 different configurations of catalysts in hope of finding some that efficiently reduce CO_2 to methane and/or methanol, while maximizing the selectivity, activity of the catalyst, and minimizing the potential required to drive the reaction forwards. Some properties studied include: the stability, the ability to supress competing reactions, and the energy barrier of the rate-determining step (RDS). In parallel, we hope to guide experimentalists and computationalists to use this systemic DFT screening process and

assessment to aid in future material discovery in this field.

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2. Body of Thesis

2.1 Manuscript 1: Experimental methods in chemical engineering: Density functional theory—DFT

Mini-review

Experimental methods in chemical engineering: Density functional theory— DFT

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Link: https://doi.org/10.1002/cjce.24127

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Abstract

Density functional theory (DFT) computations apply to physics, chemistry, material science, and engineering. In chemical engineering, DFT identifies material structure and properties, and mechanisms for phenomena such as chemical reaction and phase transformation that are otherwise impossible to measure experimentally. Even though its practical application dates back only a decade or two, it is already a standard tool for materials modelling. Many textbooks and articles describe the theoretical basis of DFT, but it remains difficult for researchers to autonomously learn the steps to accurately calculate system properties. Here, we first explain the foundations of DFT in a way accessible to chemical engineers with little background in quantum mechanics or solidstate physics. Then, we introduce the basics of the computations and, for most of the rest of the article, we show how to derive physical characteristics of interest to chemical engineers: elastic, thermodynamic, and surface properties, electronic structure, and surface and chemical reaction energy. Finally, we highlight some limitations of DFT; since these calculations are approximations to the Schrödinger equation, their accuracy relies on choosing adequate exchange-correlation functions and basis sets. Since 1991, the number of articles WoS has indexed related to DFT has increased quadratically with respect to time and now numbers 15000. A bibliometric analysis of the top 10000 cited articles in 2018 and 2019 classifies them into four clusters: adsorption, graphene, and nanoparticles; *ab initio* molecular dynamics and crystal structure; electronic structure and optical properties; and total energy calculations and wave basis sets.

KEYWORDS:

DFT, computation, elastic properties, thermodynamic properties, surface energy, chemical reaction, reaction energy barrier

2.1.1 Introduction

Chemical engineers solve scientific problems related to the energetics of systems they operate, such as reactors, distillation columns, electric arc furnaces, mixers, and heat exchangers. Selecting catalysts to lower the activation barrier, optimizing vessel design, and identifying materials to minimize chemical interactions with the reactants/products (corrosion and erosion) are examples of such engineering challenges. Apart from a simple trial-and-error approach, the design and optimization of a technology requires the knowledge of thermodynamic, physical, and chemical properties of the phases constituting the system, such as the following: (1) the density and the heat capacity of solid, liquid, and gas reactants as well as of the desired and parasitic products generated; (2) the surface energy and specific surface area of catalysts that define their efficiency promoting specific reactions; and (3) the yield strength and bulk modulus to design industrial vessels (Table 1).

TABLE 1. Key thermo-physico-chemical properties of materials to consider in chemical engineering technologies that can be evaluated with density functional theory (DFT)-based simulations.

Application	Property	Symbol	Unit	Reference
Catalysis	Surface energy	$E_{ m surface}$	$J m^{-2}$	Swart et al.[1-4]
	Specific surface area	SSA	$m^{-2}kg^{-1}$	Norskov et al.[5-7]
Vessel material	Yield strength	$\sigma_{\scriptscriptstyle Y}$	Ра	Yin et al.[8-10]
	Tensile strength	$\sigma_{ m uts}$	Ра	Jensen et al.[11-14]
	Bulk modulus	В	Ра	Bonny et al.[15-20]
Heat transfer	Thermal conductivity	λ	$W\;m^{\scriptscriptstyle -1}K^{\scriptscriptstyle -1}$	Liu et al.[18, 21, 22]
	Volumetric thermal expansivity	α_{v}	K^{-1}	Shao et al.[13, 16]
	Melting temperature	Т	К	Bonny et al.[15]
	(Liquidus and solidus)			
Liquids	Kinematic viscosity	ν	Pa s	Wan et al.[23-26]
	Density	ρ	kg m⁻³	Wan et al.[23, 25-27]
	Isobaric heat capacity	C_p	J; mol ⁻¹ K ⁻¹	Wu et al.[25, 26, 28]
	Thermal stability	Т	Κ	Wu et al.[25, 26, 28, 29]
	(Evaporation, decomposition)			

To measure all these properties is impractical, especially in a modern context for which fine-tuning new materials for specific applications is required. Moreover, experimental work is expensive and time consuming. Supercomputers provide an alternative. In a nutshell, numerical simulations consist of solving mathematical problems for which no analytical solution exists blue and involves evaluating functions and their derivatives, including computational fluid dynamics, discrete element methods, phase-field and level-set approaches, computational thermochemistry, static and dynamic classical atomistic simulations, and first-principle calculations.

Contrary to all the other heavy computational methods, first-principle calculations are *ab initio* methods; that is, they require neither boundary conditions nor empirical or semi-empirical models. They originate from a rigorous theoretical treatment of quantum chemistry and quantify the energetic interactions involving electrons and nuclei in systems such as isolated molecules and periodic solid lattices. They are used to evaluate optical, electronic, thermodynamic, and physical self-consistent properties for alloys, semi-conductors, and ionic and covalent solids. The chemistry of the simulated phase can also be varied to quantify its impact on the materials' behaviour. This makes first principle calculations an essential tool for the Integrated Computational Materials Engineering (ICME) approach, the central theme of modern material design.

This mini-tutorial review is part of a series on experimental methods in chemical engineering [30]. We first describe the basic theory and the basics of the computations. Although density functional theory (DFT) is not an experimental method in the physical sense of measuring a property using an instrument, it does provide access to thermo-physico-chemical properties as a result of a numerical experiment. Discrete element methods (DEM) [31], CFD-DEM [32], and artificial neural networks (ANNs)[33] are other numerical techniques in the series. Engineers apply DFT to characterize and predict trends of multicomponent systems that often have never been

experimentally explored before. Besides an extensive bibliometric map of keywords, other subjects this article highlights are uncertainties, limitations, and pitfalls, which are seldom discussed in review articles.

2.1.2 Theory

The energetic landscape available for chemical engineers to operate technologies is controlled by the energy transfers occurring between a system (which can be defined as the entire process or as one of its specific units) and its surrounding. Heat interaction (Q) can be used to boil water and produce steam, which can enter a turbine to produce mechanical work (W) (Figure 1). A process contains a given amount of reactants and is typically operated at a constrained temperature and pressure; this is the isobaric isothermal thermodynamic ensemble. The energetic interactions modulate both the internal energy U and the mechanical macroscopic energy E_{mec} of the system through the first law of thermodynamics; solar radiation, for example, directed toward a solid raises its temperature and thus its total internal energy. The four fundamental forces of nature are nuclear, electromagnetic, gravitational, and weak forces (Table 2). Scientists exploit the energy associated with each force; nuclear forces, which induce the strongest energetic interactions, in the order of 1e14, are at the origin of the energy released by nuclear fission reactors. Engineers apply gravity, which induces the weakest force, to produce electrical work from the potential energy of water in dams.



Figure 1: Definition of important concepts in thermochemistry

TABLE 2. Forces of nature and their associated energetic scale

Force	Range	Bond	Energy scale		
			Atomic (eV atom-1)	Macroscopic (J mol-1)	
Nuclear	Short		10°	1014	
Weak	Short		106	1011	
Electromagnetic	Long	Ionic	1 - 10	105	
		Covalent	1-10		
		Metallic	1 - 10		
		Van der Waals	10-2		
		Hydrogen bonds (water)	0.24		
Gravitational	Long	e ⁻ -proton (hydrogen)	10 ⁻³⁸	10-33	

In classical chemistry, electromagnetic forces modulate the strength of the chemical interactions in the electronvolt () range that engineers either utilize or need to overcome. Electromagnetic radiation from the sun belongs to this energy spectrum. Living organisms synthesize organic compounds with this energy. In the macroscopic world, the energetic scale of such interactions is in the order of hundreds of . The energy stored in nuclear interactions is much higher but is typically inaccessible and so ignored in traditional chemistry. At the opposite end of the energetic spectrum are the small gravitational interactions that contribute little to the energetics of chemical systems. Therefore, we define the accessible internal energy of a chemical system by only accounting for the electrostatic (since we solve a time-independent Scrödinger equation) interactions as well as the kinetic energy of each constitutive particle (i.e., electrons and nuclei).

In this context, we consider electron-electron, electron-nucleus, and nucleus-nucleus interactions. The Hamiltonian \mathcal{H} for such an energetic description of the system (not explicitly considering Pauli's exclusion principle) is as follows[34]:

$$\mathcal{H} = -\sum_{I} \frac{\hbar^{2}}{2M_{I}} \cdot \nabla_{I}^{2} - \sum_{i} \frac{\hbar^{2}}{2m_{e}} \cdot \nabla_{i}^{2} + \sum_{i < j} \frac{e^{2}}{|\vec{r}_{i} - \vec{r}_{j}|} - \sum_{I,i} \frac{e^{2} \cdot Z_{I}}{|\vec{R}_{I} - \vec{r}_{i}|} + \sum_{I < j} \frac{e^{2} \cdot Z_{I} Z_{J}}{|\vec{R}_{I} - \vec{R}_{j}|}$$
(1)

A first limitation of Equation (1) is the pure two-body description of the interactions in this system. Our inability to analytically describe many-body interactions cannot be resolved at the moment. In fact, even the Kohn-Sham Hamiltonian (defined using the electronic density function) cannot accurately capture the exact nature of these many-body interactions. As emphasized by Göltl and Sautet[35], all the exchange-correlations functions that are actually available to describe electronic interactions are only approximations. Several papers in the literature highlight this shortcoming and describe various ways to partially overcome it [36-38]. At 0 (no thermal energy), only the electrons have some kinetic energy (second term in Equation (1)). The nuclei are frozen in space and do not contribute to the kinetic energy of the system (first term in Equation (1)). This 0 kinetic contribution is induced by the quantum behaviour of the electrons (fermions) when present in atomic structures. The electron gas theory described by quantum mechanical Fermi-Dirac statistics (which needs to be corrected to account for the Pauli's exclusion principle) provides an approximation of this kinetic energy contribution[39].

Finally, a wave function $\Theta(R, r, t)$ describes the spatio-temporal evolution of this quantummechanical system, which we determine by solving the time-dependent Schrödinger equation:

$$\mathcal{H} \cdot \Theta(R, r, t) = i\hbar \frac{\partial \Theta(R, r, t)}{\partial t}$$
(2)

We assume that the position of each nucleus is fixed and that only the electrons move at the timescale of the problem — the Born-Oppenheimer approximation[40]:

$$\Theta(R,r,t) = \Psi(R,r) \cdot \chi(R,t)$$
(3)

This equation holds that the speed of the electrons is much faster than the speed of the nuclei. In other words, the response of the electrons to the motion of the nuclei is considered to be quasiinstantaneous (i.e., at the speed of light). The integration of Equation (3) into the time-dependent Schrödinger equation gives the following:

$$\left(-\sum_{i}\frac{\hbar^{2}}{2m_{e}}\cdot\nabla_{i}^{2}+\sum_{i< j}\frac{e^{2}}{\left|\vec{r}_{i}-\vec{r}_{j}\right|}-\sum_{I,i}\frac{e^{2}\cdot Z_{I}}{\left|\vec{R}_{I}-\vec{r}_{i}\right|}\right)\cdot\Psi(R,r)$$

$$= E \cdot \Psi(R, r)$$

$$\left(-\sum_{I} \frac{\hbar^{2}}{2M_{I}} \cdot \nabla_{I}^{2} - \sum_{I,i} \frac{e^{2} \cdot Z_{I}}{|\vec{R}_{I} - \vec{r}_{i}|} + \sum_{I < J} \frac{e^{2} \cdot Z_{I} Z_{J}}{|\vec{R}_{I} - \vec{R}_{J}|} \right) \cdot \chi(R, t)$$

$$= i\hbar \frac{\partial \chi(R, t)}{\partial t}$$
(5)

Equation (4), which is an eigenvalue problem, is one central equation of quantum chemistry. It provides the total energy *E* of the system when the position of the nuclei are fixed. We reformulate for an *N*-electron system subject to an external potential $V(\vec{r}_i)$ induced by the nuclei and the repulsive electron-electron contributions embedded in the $U(\vec{r}_i, \vec{r}_j)$ function:

$$\left(-\sum_{i}^{N}\frac{\hbar^{2}}{2m_{e}}\cdot\nabla_{i}^{2}+\sum_{i}^{N}V(\vec{r}_{i})+\sum_{i< j}^{N}U(\vec{r}_{i},\vec{r}_{j})\right)\cdot\Psi(r)=E\cdot\Psi(r)$$
(6)

The Hartree-Fock method is a computationally expensive numerical approach to solve this equation[41-43]. The DFT provides an alternative mathematical treatment of this problem to calculate the energy of the system. Fermi and Thomas originally proposed the concept of an electron density function, n(r), to describe the internal kinetic energy of the system defined by Equation (6)[44]. The strategy is to express the electronic density of a non-interacting Fermi gas of electrons as a function of the Fermi electronic momentum p_f as follows:

$$n(r) = \frac{8}{3h^3} \cdot \left[p_f(r) \right]^3$$
(7)

with

$$p_f(r) = \sqrt{2m_e \cdot E(r)} \tag{8}$$

The electron density function n(r) is related to the time-independent wave function of the system $\Psi(r)$. Limitations of this approach include[45]:

1. The Pauli exclusion principle states that there cannot be two electrons with the exact same quantum numbers. A repulsive exchange energy between two electrons of the same spins need to be accounted for to avoid this situation.

2. Two electrons having antiparallel spins will have correlated motions because of their coulombic interaction. A correlated energy contribution needs to be accounted for.

3. The electron density is not homogeneous and most probably features a gradient in the density.

Kohn's Nobel lecture recounts the historical development of modern DFT theory to overcome these limitations[34]. Two important theorems are at the heart of this theory. The Hohenberg-Kohn Theorem 1 states that the electron density n(r) of an N-electron system, which defines the electron number via the following equation:

$$N = \int n(r)d^3r,\tag{9}$$

describes the energy $E_{ext.}$ of an external potential V(r) and thus the Hamiltonian of ground- and exited-state wavefunctions, as shown below [46]:

$$E_{ext.} = \int V(r)n(r)d^3r \tag{10}$$

Theorem 2 states that this functional provides the ground state energy of the system (i.e., the lowest possible energy) if the input density is the true ground state density. This is the density variational principle. Finally, we add exchange-correlations functions to the Hamiltonian to better describe electronic interactions.

DFT packages and inputs

In this paper we applied CP2K[47] and the Vienna ab-initio simulation Package (VASP)[48]. Other DFT packages include ABINIT[49], CASTEP[50], Wien2K[51], Quantum ESPRESSO[52], ACES II[53], CRYSTAL[54], and Octopus[55]. The CP2K and VASP software require two blocks of parameters: (1) the calculation input file — convergence criteria of the algorithm, the basis sets, the pseudo-potentials, the exchange correlation functional, and the **k**-points mesh sampling and (2) the geometry file that describes the initial atomic structure, which is provided in XYZ, CIF, POSCAR, CUBE, or XSF formats. Parameters that users define include:

1. the cut-off energy that defines the plane waves to be considered,

2. the k-point meshing for the electronic density description,

3. the pseudo-potentials to represent the force field induced by the nucleus and the core electrons,

4. the plane-wave basis sets,

- 5. the exchange-correlation functional, and
- 6. other convergence criteria.

The cut-off energy parameter determines the number of plane-waves required to describe the electron density of a system. A higher cut-off energy is more accurate but requires more computational time. Convergence tests increment parameters until the results reach the defined tolerance. It must be higher than the energy specified in the potential sets.

Under periodic boundary conditions, **k**-point sampling needs to be specified. These **k**-points are used to sample the Brillouin zone that represents the unit cell in the reciprocal space. The first

Brillouin zone contains the wave vectors of all waves that travel within the crystal lattice. Identifying the point group symmetries of a given structure improves the sampling efficiency of the Brillouin zone (i.e., Monkhurst-Pack grid).

The electronic wave function of each element of the system needs to be described by a set of functions (basis sets) in order to convert the Schrödinger equation into a set of algebraic equations that are more suitable for the computational algorithms. These functions, which describe the atomic orbitals of each element, are either plane wave functions (more suitable for solid state physics problems such as crystals) or localized atomic orbital functions (more suitable for molecular chemistry problems). The atomic orbital basis sets are usually Gaussian-type orbitals (GTO), Slater-type orbitals (STO), or numerical atomic orbitals. A large basis set increases accuracy at the expense of the computational time.

Pseudo-potentials describe the coulombic interactions-induced core electrons and nuclei by an effective potential and further reduce computational effort.

Coulombic interactions between the valency electrons induce a correlation in their relative positions, which needs to be accounted for. Similarly, orbital overlaps may lead to similar electronic quantum states, which is excluded by the Pauli principle. For these reasons, exchange-correlation functionals need to be introduced to correct the energetic description of the system. In other words, the exchange-correlation functional (or energy) is a correction to apply to the Kohn-Sham Hamiltonian to better describe the energetic behaviour of the system. Since an analytical exchange-correlation functional is not currently available, it is approximated using different strategies such as PBE[56], BEEF[57], BLYP[58, 59], and B3LYP[60]. For periodic structures such as crystals, PBE, or equivalent local density approximation (LDA) functionals, are mostly used,

where PBE often overestimates the cell size while LDA often underestimates them. BLYP and its hybrid version B3LYP are more accurate for isolated molecular systems.

Convergence criteria constitute the convergence of the self consistent field (SCF) loop and the optimizers. The SCF loop is an iterative process where the Schrödinger equation is numerically solved for a more accurate set of orbitals. This new set is applied to solve the Schrödinger equation again until the convergence criteria is met. The more strict the convergence criteria are, the more accurate the results are. However, if the convergence criteria are too strict, some systems will never converge as they will be unable to satisfy the criteria. We define these criteria with preliminary tests. In geometry and unit cell optimization at each SCF iteration, the position of the atoms are changed until it reaches an energy minima.

DFT corrections

Several DFT corrections are applied to account for inaccuracies inherent in regular DFT computations. Some of the most important and common corrections used in chemical engineering problems are DFT+U correction, dipole correction, and vdW correction (Table3).

In the Kohn-Sham equations, there is an interaction between the electron and itself (on-site Coulomb interaction), which is included in the Hartree potential. Ideally, this interaction will be completely cancelled by some contribution of the exchange potential. However, since the exact, correct exchange correlation potential is unknown, this cancellation does not fully occur. The result is a self-interaction error which can be significant in certain cases. One particular case is transition-metal oxides, as they have strongly localized electrons, leading to high self-interaction error. To counteract this, a correction to the DFT energy is introduced by parameters U (on site Coulomb) and J (on site exchange), or in some methods just their difference (U - J), which is known as

DFT+U correction. These parameters U and J can be extracted from DFT calculations, but are usually obtained semi-empirically.

In non-symmetric systems, a dipole can form. This is problematic in DFT calculations because when we apply periodic boundary conditions, the dipole is replicating in the infinite images created by those conditions. The result is an extra contribution to the total DFT energy resulting from the dipoles of different images interacting. To simply correct this, an equal and opposite dipole is applied to effectively make the net dipole zero. This is known as dipole correction.

DFT calculations of bond energies and length of non-polar molecules exhibiting van der Waals forces, or dispersion forces, deviate from experimental measurements. Adding a correction term to the total DFT energy corrects for the contribution to dispersion forces. This is known as vdW correction. Examples of this correction are the DFTD3 method[61] and the DFT-TS method[62].

2.1.3 General DFT Calculations at 0 K

Here, we describe the fundamentals of the most common DFT computations that estimate energetic and electronic properties at 0 K.

Single point energy calculation

The single point energy calculation, the simplest DFT computation, estimates the internal energy (or enthalpy) while ignoring atom displacements from their initial position. It generates energy-volume cold curves to parameterize equations of state (EOS)[63-65]. From classical thermodynamics, system pressure correlates with volume in the following manner:

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \to \left(\frac{\partial U}{\partial V}\right)_0 = -P_0 \tag{11}$$

Geometry and unit cell optimization

25

DFT packages have minimization algorithms to objectively optimize the geometry and unit cell of a chemical system in an initial configuration state. These numerical strategies used to optimize differentiable functions identify local minima in the energy curve (vs. coordinates graph) that correspond to stable (global minimum) or metastable (local minimum) atomic configurations. Geometric optimization moves atoms from their initial positions to a new set of coordinates that lower the total energy. The minimization algorithm stops when the convergence critieria is met or it reaches the maximum number of iterations. There are two common convergence criteria: the maximum change in consecutive geometries (units of length), and the maximum force applied on all atoms (units of energy/length). The maximum change in consecutive energies is another convergence criterion.

We usually refer to this optimized state as the fully relaxed structure as it represents a local energy minima, which is a state with no external pressure applied (see Equation (11)).

Optimization algorithms include BFGS[66], GPMin[67], FIRE[68], and the conjugate gradient (CG) method[69]. In geometric optimization, the unit cell size is fixed, while the atoms it contains are allowed to be displaced. Unit cell optimization implies that the reduced atomic coordinates are frozen and that only the unit cell vectors change. The Cartesian positions are evaluated based on the change of the unit cell vectors. Global optimization schemes — Basin Hopping and Minima Hopping — identify the most stable crystal structure[70-72].

Density of state and band structure calculations

DFT codes calculate the energy of a given molecular or crystalline system by accounting for all the dominant electromagnetic interactions integrated in the Hamiltonian. The system electronic structure is one fundamental output from which we determine electronic properties such as :

- 1. the charge distribution around each ion in the real space,
- 2. the occupied and unoccupied electron density of states (DOS), and
- 3. the band energy in reciprocal k-space.

The electronic DOS of materials defines the number of distinct states of discrete energy electrons allowed to occupy a valence band (i.e., the number of electron states per unit volume per unit energy)[73, 74].

Built-in packages integrated in the DFT code calculate the DOS, which are computationally more expensive as they require a larger number of **k**-points than regular energy calculations since the details of the DOS are evaluated from integrals in the k-pace. Typically, we apply the Fermi-Dirac smearing method. The Methfessel and Paxton smearing method improves the numerical precision of the integration in k-pace[75].

DOS graphs for semiconductors identify the occupied valence states as well as the unoccupied conduction states (which defines the electronic gap). For metallic systems, the DOS is continuous around the Fermi level. We apply DOS to catalysis and semiconductors as they determine the energy distribution of charge carriers as well as carrier concentrations.

Figure 2 shows DOS plots for Sr2Si and Sr2Sn of the same Pnma space-group (orthorhombic crystal structure) with (5.15, 8.13, and 9.62) as lattice parameters for Sr2Si, and (5.43, 8.40, 10.17) for Sr2Sn. Subplots **a**) and **c**) combine total density of states (TDOS) with atom projected density

of states. In the calculation of atom projected DOS, the volume is considered as spherical around the specific atom. On the other hand, subplots **b**) and **d**) combine TDOS with orbitals projected or partial density of states (PDOS), where PDOS is related to the contribution of certain orbitals to the TDOS. Comparing the DOS plots of Sr2Si (Figure 2A,B) with those of Sr2Sn (Figure (2C,D), it is clear that Sr2Sn has DOS at a lower energy level than Sr2Si does. In other words, compared with the valence electrons in Sr2Si , those in Sr2Sn can exist at a lower energy state in the valence band. In catalysis, especially on transition metals, the *d*-band centre and width play a critical role to determine the activity of a catalyst based on the proximity of its *d*-band centre to the Fermi level, since it dictates whether the anti-bonding orbitals are occupied or not, consequently affecting the binding strength[76, 77].



Figure 2: Total density of state (TDOS) and atom projected DOS plots of (a) Sr2Si and (c) Sr2Sn; TDOS and orbital projected DOS graphs of (b) Sr ₂Si and (d) Sr ₂Sn

Parameter	Meaning	Significance	Example/range
Energy cutoff	Specifies the number of plane wave functions to characterize the wavefunction for plane wave DFT.	Accuracy improves with a larger cutoff at the expense of computation time.	250–250 eV.
K points	Grid sampling the Brillouin Zone that represents the unit cell in reciprocal space.	More <i>k</i> points map the Brillouin zone better but increase computational demand.	$1 \times 1 \times 1$ for Gamma point, $15 \times 15 \times 15$ for DOS(c) with the Monkhorst-Pack mech. method.
Basis sets	Functions that describe atomic orbitals composed of either atomic orbitals (molecular chemistry) or plane waves (solid state physics).	Larger basis sets increase accuracy and computation time. Basis sets that resemble the spin orbital of the material increase accuracy too.	Plane wave basis sets. Localized/centred: Gaussian- type orbitals (GTO), or Slater- type orbitals (STO).
Exchange correlation	Corrects energetic description of systems; describes Coulombic interactions between valence electrons.	Need to choose a suitable XCg potential for the system at hand to avoid inaccuracies.	PBEe or LDAd for periodic structures; B3LYPa for isolated molecules.
2 Convergence criteria	SCF loop: iterative process to solve the Kohn-Sham equations.	A higher SCF convergence criterion increases accuracy.	$10 \times 10^5 \text{ eV}.$
	Optimizers: numerical methods that solve eigenvalue problems.	Higher optimizer convergence criteria improve accuracy.	Force criteria—0.02 eV Å ⁻¹ or distance—0.001 Å.
Corrections to standard DFT	Added potentials to correct for system-related factors.	Improves property accuracy.	DFT+U, D3 vdW, dipole correction.

TABLE 3	DFT	parameters/	inputs
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Abbreviations: B3LYP, Becke-3 Parameter-Lee-Yang-Parr; DFT, density functional theory; DOS, density of states; LDA, localized density approximation; PBE, Perdew, Burke, and Ernzerhof; SCF, self-consistent field; XC, exchange

Another material property that closely relates to the DOS is the band structure. Compared with DOS, which condenses the properties of the electronic states for all possible positions in the reciprocal space into a simplified form, the band structure provides a more nuanced view of a material's electronic structure. It describes the range of energy levels where electrons may locate as well as the range of energy that is inaccessible (i.e., band gaps). We build band structure

diagrams from plane-wave DFT computations. Similar to DOS, a Fermi-Dirac smearing method and Broyden mixing method are common approaches. We have to pay attention to the choice of **k**-points in that the electronic states must be considered as a set of **k**-points spaced closely along certain directions in the reciprocal space corresponding to the band structure diagram. These directions are defined for each crystalline structure[78]. The resulting diagram reflects the energy of the available electronic states along several lines in the reciprocal space that form a closed loop starting and ending at the Γ point[74]. A major application of band structure is that it shows the values and types of band gaps for insulators and semiconductors. Figure 3 illustrates the two band structure plots of Sr2Si and Sr2Sn. E_f at the vertical axes represent the Fermi energy, which is the maximum energy that can be occupied by an electron at 0, while the horizontal axes show the wave vectors. These two plots reveal that both Sr2Si and Sr2Sn contain one direct band gap, while the band gap of Sr2Sn (0.20) is smaller than that of Sr2Si (0.35). Python programs — Python Materials Genomics (pymatgen) and PyProcar — are available tools to produce these plots[79, 80].



Figure 3: Band structure plots of (a) Sr2Si and (b) Sr2Sn in the Pnma space-group structure

Bulk modulus and elastic properties

Equations of state characterize the energetic behaviour of solid materials, like ores which contain minerals and impurities, as a function of both temperature and pressure. DFT calculates elastic constants and the bulk modulus by applying deformations and calculating the corresponding energies. To demonstrate this process, a simple cubic unit cell with lattice constant *a* will be studied. We expressed the unit cell with Bravais lattice vectors in matrix form:

$$\mathbf{R} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{bmatrix}$$
(12)

Firstly, we optimize the cell to identify the fully relaxed structure, which provides the a_0 equilibrium lattice parameter of minimum energy. In the next step, we expand or contract the unit cell to identify the optimal size. For instance, we create a new unit cell $a_1 = (a_0 + \epsilon)$, where ϵ is the deformation (), then perform a single point DFT calculation. We repeat this sequence in both compression and expansion regimes and plot energy (*E*) of the cell as a function of its volume (*V*) (Figure 3). We derive the 0 bulk modulus of the cubic crystal (*B*) from the second derivative of this curve with respect to the cell volume:

$$B = V \frac{\partial^2 E}{\partial V^2} \Big|_{V_0} \tag{13}$$

In the case of non-cubic systems such as a rhombohedral crystals (anisotropic), we apply a strain tensor to calculate the stiffness matrix, which includes stiffness factors in all directions. If a small strain is applied, stiffness factors C_{ij} are the second derivative of the total energy with respect to the applied strain. The total energy $E(V, \epsilon)$ is as follows[81]:

$$E(V,\epsilon) = E(V_0,0)$$

+ $V_0 \left(\sum_i \sigma_i \xi_i \epsilon_i + \frac{1}{2} \sum_{ij} C_{ij} \xi_i \epsilon_i \xi_j \epsilon_j \right)$ (14)

where V_0 and $E(V_0, 0)$ are the volume of the geometry optimized unstrained lattice and its corresponding total energy, respectively. The σ_i term in this equation represents the elements of the stress tensor ($\sigma_i = C_{ij}\epsilon_j$) while the C_{ij} term represents the elastic stiffness constants. Also, since Voigt notation is used in this equation, ϵ 's are symmetric and ξ 's are constants used to compensate this symmetry.^[81]



Figure 4: Total Energy (eV) versus unit cell volume (Å³) for the pure copper face-centred cubic (FCC) crystal. Note that the energy demonstrated in this figure has no physical meaning and is a function of the pseudo-potentials used in DFT computations. However, its second derivative with respect to cell volume is less sensitive to the type of potentials. In this particular example, the

Bulk modulus is calculated as 0.9 eV Å⁻³ (145 GPa) which is in good agreement with

experiments)

Therefore, a small strain is applied on the equilibrium lattice **R** to form a distorted lattice **R'**. Distortion applied to the optimized lattice must be small so that it remains in the elastic limit of the crystal (Figure 3). The vectors of the distorted lattice are denoted in the matrix **R'**, which can be obtained through R' = RD, where **D** is the distortion matrix related to the strain applied on the crystal. For the cubic unit cell example, only three independent elastic stiffness constants (C_{11} , C_{12} , and C_{44}) exist. The matrix representation of those elastic constants is as follows:

$$C = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0\\ 0 & 0 & 0 & C_{44} & 0 & 0\\ 0 & 0 & 0 & 0 & C_{44} & 0\\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$$
(15)

In order to derive these stiffness constants from Equation (14), three distortion matrices $(D_{11}, D_{12}, D_{14}, D_{14})$ and D_{44} , corresponding to C_{11} , C_{12} , and C_{44}) must be determined. D_{11} applies a stress normal to the optimized crystal, while D_{12} and D_{44} are the volume-conserved shear stress distortion. The following three distortion matrices and corresponding total energies are used to calculate the stiffness constants for the above mentioned cubic crystal:

$$\mathbf{D}_{11} = \begin{bmatrix} 1 + \epsilon & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \therefore$$

$$E(V, \epsilon) = E(V_0, 0) + V_0 \left(\sigma_1 \epsilon + \frac{c_{11}}{2} \epsilon^2 \right) \tag{16}$$

$$\mathbf{D}_{12} = \frac{1}{(1 - \epsilon^2)^{\frac{1}{3}}} \begin{bmatrix} 1 + \epsilon & 0 & 0 \\ 0 & 1 - \epsilon & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \therefore$$

$$E(V, \epsilon) = E(V_0, 0) + V_0 \left((\sigma_1 - \sigma_2) \epsilon + (C_{11} - C_{12}) \epsilon^2 \right) \tag{17}$$

$$\mathbf{D}_{44} = \frac{1}{(1 - \epsilon^2)^{\frac{1}{3}}} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 1 \end{bmatrix} \quad \therefore$$

$$E(V, \epsilon) = E(V_0, 0) + V_0 (2\sigma_4 \epsilon + 2C_{44} \epsilon^2) \tag{18}$$

Therefore, the rest is just a matter of multiple single point DFT computations for different values of ϵ , curve fitting for E versus ϵ , then finding its second derivative to attain the corresponding C_{ij} . For the cubic crystal, the elastic compliance constants S_{ij} ($\epsilon_i = S_{ij} \sigma_j$) depend on the stiffness constants according to the following:

$$S_{11} = \frac{(C_{11} + C_{12})}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \tag{19}$$

$$S_{12} = \frac{-c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \tag{20}$$

$$S_{12} = \frac{1}{C_{44}} \tag{21}$$

As for polycrystalline material, by using elastic stiffness constants, Voigt's bulk modulus $(B_V = [C_{11} + 2C_{12}]/3)$ and shear modulus $(G_V = [C_{11} - 2C_{12} + 3C_{44}]/5)$ can be calculated. Alternatively, Reuss' bulk modulus $(B_R = 1/3[S_{11} + 2S_{12}])$ and shear modulus $(G_R = 5/[4S_{11} - 4S_{12} + 3S_{44}])$ can be obtained by using elastic compliance constants. However, it appears that the most practical values are based on Hill's arithmetic averaging[82]. In this case, Hill's bulk modulus (B) is the average of Voigt's and Reuss' bulk moduli. Similarly, Hill's shear modulus (G) is the average of Voigt's and Reuss' shear moduli. Young's modulus, another practical engineering parameter, can also be deduced from Hill's bulk and shear moduli (Y=9BG/[3B+G])[81]. We apply a similar procedure calculating elastic constants of other crystalline structures, albeit with different distortion matrices and formulas for the bulk and shear moduli.



Figure 5: Applying the deformation matrix (**D**) on a cubic

Surface energy

Surface energy is defined as the excess energy induced by the presence of surfaces in a finite size material. The chemical environment of atoms on a surface are distinct from those in the bulk since they have less neighbours (associated to the free surface). Because of this, their electronic structure cannot be relaxed as the atoms in the bulk, resulting in an excess energy in the finite-sized crystal. This phenomenon is the origin of catalytic activity of many metallic surfaces. We determine surface energy by calculating the energy per area that must be introduced in the bulk material to create the surface (Figure 6). To do so, a full relaxation DFT computation is firstly performed on the periodic bulk crystal (or a single point DFT computation on the already optimized bulk material), which provides E_{bulk} (Figures 7B, E). Then, this structure is divided in two equal volumes with the atoms exclusively in the upper part of the cell removed (or alternatively in the lower part). The original unit cell of the system is kept constant, which implies that there is free volume in the crystal (Figures 7D, G). The shape and size of the cell are prohibited from changing
during the full relaxation DFT computation. The energy of this slab is defined as E_{slab} . Due to the free volume above the atoms, the distance between the top layers increases when compared to the interdistances in the bulk material. VESTA, Materials Studio, and Virtual NanoLab are great tools to build these slabs. The surface energy is the difference in the energy of the slab and bulk divided by the cross-section area of the surface, X_A :

$$E_{surface} = \frac{2E_{slab} - E_{bulk}}{2X_A} \tag{22}$$

If the two surfaces obtained by slicing the bulk material are dissimilar, the individual surface energies of both slabs are separately calculated, changing Equation (22) to the following:

$$E_{surface} = \frac{(E_{slab-1} + E_{slab-2}) - E_{bulk}}{2X_{A}}$$
(23)

Even if the bulk material is polar, slicing the material will give two identical surfaces. The crystal surface energy of a given crystal is a function of the exposed surface. For poly-crystalline materials, all possible surfaces must be evaluated, as it is impossible to control which surfaces are exposed to the surrounding. For small finite-size (non-periodic) systems like nano-clusters, the surface energy contribution dominates.



Figure 6: Forming a surface from bulk material. Two DFT computations are required: one for the pristine structure (left), and one for the newly created half cell (right). The created surface is

the area between two new cells



Figure 7: (a) Face-centred cubic (FCC) unit cell, (b) front view of (111) slabs, (c) top view of (111) slabs, (d) half of the (111) slabs in 7B, (e) front view of (100) slabs, (f) top view of (100) slabs, and (g) half of the (100) slabs in 7E

Defect formation and surface reconstruction

In practice, freshly cleaved surfaces reform to reach a new equilibrium state. For DFT computations to capture this transition, we distort the optimized configuration and repeat a full relaxation DFT calculation. This may reproduce the same optimized configuration if the distorted configuration remains in the same local minima region on the free energy surface (FES). Therefore, experimental data about the reconstructed surface configuration are essential in order to correctly identify lower energy states. This process is called surface reconstruction for surfaces that form defects. The defect formation energy is computed as the energy difference between the ideal crystal (or surface) and the defect structure.

Point defects, vacancy defects, charge defects, and impurities (substitution or interstitial defects) all impact the physical properties and performance of materials and technologies such as photovoltaic cells[83, 84]. In fact, the energetics of defects in crystalline materials and surfaces with DFT is explored extensively in the literature[85-87]. Here, we highlight the general procedure to evaluate the formation energy of a specific defect *X* with a point charge state *q* using the following equation[88]:

$$E_f(X^q) = E_{\text{total}}(X^q) - E_{\text{total}}(\text{bulk}) - \sum_i n_i \mu_i + q E_F + E_{\text{corr.}}$$
(24)

where $E_{total}(X^q)$ is the total energy evaluated from a supercell calculation containing the defect X, and E_{total} (bulk) is the total energy for the perfect crystal using an equivalent supercell. In the case of surface defect calculations, the bulk energy is replaced by the perfect (i.e., without defects) surface energy. The number of atoms of type *i* that has been added to (positive integer) or removed from (negative integer) the supercell to form the defect is denoted as n_i . These atoms can be either solvent or solute elements of the considered structure. The chemical potentials μ_i of each *i* species

are also required in this equation, which are derived from the Gibbs free energy at a given temperature and pressure:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_{j \neq i}, P, T} \tag{25}$$

The term E_F is the Fermi energy of electrons which is the analog of the chemical potential for charge. Since, a finite **k**-point sampling is used in DFT computations, it may poorly capture the electronic structure of defects or impurities with low concentration or to accurately capture the elastic and electrostatic interactions between supercells, which compromises the energies. The term $E_{corr.}$ corrects the formation energy of a given defect.

Adsorption

Semi-empirical methods like Langmuir isotherms characterize monolayer adsorption, reversible isotherms, multilayer isotherms, and stepwise multilayer adsorption[89]. DFT, on the other hand, describes all the adsorption phenomena in one unique framework. The property that drives this phenomenon is the adsorption energy ($E_{adsorption}$) of a given molecule onto a specific surface of a given material structure.

To evaluate this property requires three distinct DFT computations. Firstly, a slab of the catalyst is created, and its geometry is optimized. E_{slab} is the energy of the relaxed slab with a fixed size and shape (i.e., the same as for the bulk cell). This slab comprises a few atomic layers with a free volume on top (Figure 8).



Figure 8: Face-centred cubic (FCC)(111) surface with three atomic layers and vacuum on top and bottom of these layers

Adding an adsorbate molecule closes the surface site. The adsorbate molecule should be close to the equilibrium position to ensure it reaches a local minimum energy. In our example, a CO molecule is added to the system (Figure 9). A full relaxation energy calculation is then performed on this structue (again with a fixed cell size and shape); the result is denoted as $E_{slab+adsorbate}$.



Figure 9: Carbon monoxide is adsorbed on top of the surface

Finally, the slab is removed, and the adsorbate molecule energy $E_{adsorbate}$ is evaluated:

$$E_{\text{adsorption}} = E_{\text{slab+substrate}} - (E_{\text{slab}} + E_{\text{adsorbate}})$$
(26)

In order to have consistency in these calculations, all simulation conditions must be kept constant throughout all three energy calculations. For example, parameters like the basis set, pseudopotentials, the exchange correlation functional, and Brillouin zone k-points sampling method, are kept similar. Factors that affect adsorption energies include the adsorbate molecule, catalyst and selected facet, and bonding configuration. Testing these factors with DFT is straightforward and rapid compared to conducting experiments particularly because of the variance and poor control of these parameters. The coupling of DFT simulations with experiments is a powerful approach as it allows to limit the number of experiments to be performed while validating the predicted properties. DFT calculations have been used up to now to calculate adsorption energies in catalysis, but new applications are emerging as well, like separation processes. Nevertheless, when calculating the adsorption energies, DFT users must be aware that DFT alone has problems describing non-local van der Waals dispersion forces related to water adsorption and weak adsorption systems[90]. For that reason, vdW corrections are introduced in DFT calculations[91-94].

2.1.4 Applications

The number of articles, N_{art} , Web of Science (WoS) has indexed since the early 1990s has grown quadratically, with 14508 in 2019 ($N_{art} = 18.4[y - 1991]^2$, $R^2 = 0.999$)[95]. Almost half of the 10000 top cited articles in 2018 and 2019 are in journals that WoS assigns to Physical Chemistry (4561). The other categories with the most articles are Multidisciplinary Materials Science (3482), Multidisciplinary Chemistry (2016), Nanoscience & Nanotechnology (1748), and Applied Physic (1634). Chemical Engineering is ranked 9th with 612 articles. The *Journal of Physical Chemistry C* published 448 of these articles followed by *Physical Chemistry Chemical Physics* (367), *ACS Catalysis* (276), *Physical Review B* (263), and *Journal of the American Chemical Society* (254). The journals that were cited most include *Journal of the American Chemical Society* (4779), *ACS* Catalysis (4056), Advanced Materials (3161), Journal of Physical Chemistry C (3064), and Applied Catalysis B-Environmental (2832).

We generated a bibliometric map of keywords with VOS Viewer of articles indexed in 2018 and 2019 (Figure 10)[95, 96]. The research was grouped into four clusters. The largest cluster (red) is centred on adsorption, graphene, nanoparticles, catalysis, and mechanism. Whereas this cluster focuses on applications, the second largest cluster (green) deals with chemistry and mathematics: *ab initio* molecular dynamics, crystal structure, basis sets, and generalized gradient approximation are among the major keywords. Material properties is the focus of the blue cluster: electronic structure (e- structure), optical properties, stability, transition, and electronic properties. The yellow cluster is centred on total energy calculations and wave basis sets with strong links to *ab initio* molecular dynamics, catalysis, first principles, and graphene.



Figure 10: DFT bibliometric map of keywords from the 10000 top cited articles indexed in 2018 and 2019[95, 96]. VOSViewer software groups keywords together in clusters that are related and gives them the same colour and places them in closer proximity: adsorption (41 keywords), *ab initio* calculations — *ab initio* (29), electronic structure — e- structure (26), and total energy calculations — tot energy cals(5). The size of the circles and fonts are proportional to the number of articles: adsorption (785 articles), *ab initio* (1138), e- structure (636), and tot energy cals (835). The smallest circles for each category are heterogeneous/homogeneous catalysis (113 articles), effective core potentials (114), n-crystals — nano crystals (122), and wave basis sets (120). Lines represent citation links. (DFT appears in 3649 articles and is excluded from the map as the size of the circle is exceedingly large and would cover too many other keywords. VOS Viewer positioned it at the centre in the green cluster)

Energy & Environmental Science, Angewandte Chemie-International Edition, and Advanced Functional Materials published the three most cited papers in 2019 entitled, "Defect-rich and ultrathin N doped carbon nanosheets as advanced trifunctional metal-free electrocatalysts for the ORR, OER and HER", "Heterostructures Composed of N-Doped Carbon Nanotubes Encapsulating Cobalt and beta-Mo2C Nanoparticles as Bifunctional Electrodes for Water Splitting", and "Simultaneously Dual Modification of Ni-Rich Layered Oxide Cathode for High-Energy Lithium-Ion Batteries", respectively [97-99]. All these topics are most closely associated with the red cluster that contains nano-sheets, carbon nanotubes (CNT), nanoparticles (NP), and battery. Besides Energy & Environmental Science, Applied Catalyst B-Environmental published the most cited articles in Chemical Engineering[100, 101]: "All-solid-state artificial Z-scheme porous g-C3N4/Sn2S3-DETA heterostructure photocatalyst with enhanced performance in photocatalytic CO2 reduction" and "In-situ pyrolysis of Enteromorpha as carbocatalyst for catalytic removal of organic contaminants: Considering the intrinsic N/Fe in Enteromorpha and non-radical reaction". has published several articles since 2019 "Sorption of aqueous amino acid species on sulphidic mineral surfaces-DFT study and insights on biosourced-reagent mineral flotation", "Experimental methods in chemical engineering: Specific surface area and pore size distribution measurements-BET, BJH, and DFT", "Recent advances in computational photocatalysis: A review", and "Molecular and electronic structure elucidation of Fe2+/Fe3+ complexed chelators used in iron sulphide scale removal in oil and gas wells".

To demonstrate how DFT how to discover of novel materials from scratch, we examine a few examples here. High throughput DFT material discovery is applied to several fields such as lithium-ion batteries, hydrogen production and storage, supercapacitors, photovoltaics, thermoelectric materials, solid catalysts, and electrocatalysts[102]. In lithium-ion batteries, Ceder[103] predicted that doping Al into a layered LiCoO₂ cathode material would increase the voltage, which was then experimentally verified. For hydrogen production, DFT predicted catalytic activity by calculating binding energies. Bi-Pt alloys were as active as pure Pt but cheaper for water electrolysis[104]. In photovoltaics, DFT band gap calculations demonstrated the feasibiility of carbazoles derivatives as organic photovoltaics (OPV)[102]. Material discovery can also be applied to industrial reactions like methanation, ammonia synthesis, and steam reforming. For example, a NiFe alloy was more active than Ni or Fe alone[105].

2.1.5 Thermodynamic Properties obtained from DFT

2.1.5.1 Molecular dynamics and Monte Carlo DFT simulations

0 K-DFT calculations evaluate the strength of many-body interactions driven by the electronic structure of the atoms that constitute the system when the nuclei are considered frozen in space. It is possible to provide kinetic energy to these nuclei and make them move according to the Newton equations of motion, which leads to *ab initio* molecular dynamics (green cluster)[106]. This deterministic approach works as follows. An initial velocity vector is imposed to each nucleus of the system (random Gaussian distribution), which are at their initial Cartesian position at time t=0. The following set of ordinary differential equations obtained for each *i* nucleus is then solved using a sympletic integration method such as the Verlet algorithm:

$$\frac{\partial v_i}{\partial t} = \frac{F(x_i)}{m_i} \tag{27}$$

$$\frac{\partial x_i}{\partial t} = v_i \tag{28}$$

In Born-Oppenheimer molecular dynamics, the Kohn-Sham energy functional is solved at each time t to compute the forces applied to each atom. In the NVE ensemble, the number of atoms, N, the volume of the system, V, and the energy, E, are fixed. This adiabatic dynamic evolution in the NVE microcanonical ensemble is irrelevant to chemical engineering applications where temperature and pressure are imposed. To work in more industrially meaningful conditions, we need to mimic the imposition of temperature and pressure to the system using a thermostat and barostat[107, 108]. We can then probe the thermodynamic behaviour of the system in NPT ensemble which is the most appropriate for engineering. This ensemble requires the Gibbs free energy.

Molecular dynamics simulations are run until they reach ergodicity (i.e., to ensure that the system enters a dynamic state close to its equilibrium behaviour). Statistical analyses of these simulations provide average properties of the system such as its enthalpy, pressure, volume, and temperature. The analysis of the fluctuation of different thermodynamic properties such as the enthalpy and the volume provide in turn derived thermodynamic properties such as the isobaric heat capacity and isothermal compressibility.

Other transport properties, such as self-diffusion (velocity auto-correlation)[109], viscosity (pressure tensor auto-correlation)[110], and thermal conductivity (heat flux auto-correlation)[111], can also be obtained from these simulations using Green-Kubo relations.

The Monte Carlo method[112] is another approach to evaluate thermodynamic properties of atomistic systems. This stochastic approach is based on the construction of a Markov chain to sample a specific probability distribution (in this case a Boltzmann distribution). It is based on a

simple scheme: nuclei are displaced/permuted from their initial positions which changes the total system energy (which is again evaluated from solving the KS functional). This energy change is associated with an occurrence probability, $\kappa_{1\rightarrow2}$, which is compared to a random number τ obtained from a uniform distribution. The atomic state modification is accepted if $\kappa_{1\rightarrow2} > \tau$ and is rejected otherwise. This process is repeated until ergodicity is reached. Contrary to molecular dynamics simulations, the notion of time is not directly accessible for conventional MC simulations which prevents the evaluation of dynamic properties. Finally, the thermodynamic integration method can be implemented in these approaches to evaluate the Gibbs free energy (or Helmholtz energy) of the system[113, 114].

2.1.5.2 Quasi-harmonic Debye approximation

Temperature-dependent thermodynamic properties of a crystal structure can be indirectly calculated using the elastic constants evaluated from DFT via the quasi-harmonic approach. A simplified QHA approximation is the Debye approach. The Debye temperature (Θ_D) (which represents the highest normal mode of vibration) correlates the elastic properties with the thermodynamic properties, such as specific heat capacity, thermal expansion, thermal conductivity, and lattice enthalpy. The Debye temperature is proportional to the product of Planck's constant, h, and the average phonon wave velocity, v_m , and inversely proportional to the Boltzmann constant, k_B [115]:

$$\Theta_{\rm D} = \left(\frac{h\nu_m}{2k_{\rm B}}\right) \left(\frac{6n}{\nu}\right)^{\frac{1}{3}} \tag{29}$$

where *n* is the number of atoms in one unit cell and *V* is the unit cell volume. v_m in the crystal is determined by the transverse (v_t) and longitudinal (v_l) elastic wave velocities[81, 116]:

$$\nu_t = \sqrt{\frac{G}{\rho}} \tag{30}$$

$$\nu_l = \sqrt{\frac{\left(B + \frac{4G}{3}\right)}{\rho}} \tag{31}$$

$$\nu_m = \left[\frac{1}{3} \left(\frac{2}{\nu_t^3} + \frac{1}{\nu_l^3}\right)\right]^{-\frac{1}{3}}$$
(32)

where ρ is the density, and *B* and *G* are the bulk and shear moduli, respectively. For an isotropic solid, ν_m is derived solely from the bulk modulus[117]:

$$\nu_m \approx \sqrt{\frac{B}{\rho}} \tag{33}$$

and thus,

$$\Theta_{\rm D} = \left(\frac{h}{2k_{\rm B}}\right) (6^2 n N_{\rm av})^{\frac{1}{3}} \sqrt{\frac{B}{M}}$$
(34)

where N_{av} and M are the Avogadro constant and the molecular mass of the solid, respectively. For anisotropic systems, a factor from the elastic constants modifies the Debye temperature $(\Theta_D^m)[118]$. In this simplified QHA, the isochoric vibrational specific heat capacity, (C_V^{vib}) , also called the harmonic contribution to the specific heat, is as follows[119, 120]:

$$C_{\rm V}^{\rm vib} = \frac{9nk_{\rm B}N_{\rm av}}{(\frac{\Theta_{\rm D}}{T})^3} \left[4 \int_0^{\frac{\Theta_{\rm D}}{T}} \frac{x^3}{e^{x}-1} dx - \frac{(\frac{\Theta_{\rm D}}{T})^4}{e^{\frac{\Theta_{\rm D}}{T}}-1} \right]$$
(35)

In many chemical engineering processes, system temperature and pressure are imposed so we must define isobaric specific heat capacity, C_P^{vib}), which includes the energy requirement for the lattice expansion contribution introduced via the lattice thermal expansion (α^{lat}) and the Gruneisen parameter (γ^{lat}):

$$C_{\rm P}^{\rm vib} = C_V^{\rm vib} \left(1 + \alpha^{\rm lat} \gamma^{\rm lat} T \right) \tag{36}$$

The Gruneisen equation provides the thermal expansion $(\alpha^{lat})[121]$:

$$\alpha^{\text{lat}} = \frac{\gamma^{\text{lat}} c_V^{\text{vib}}}{B_{\text{T}} V} \tag{37}$$

where $B_{\rm T}$ is the isothermal bulk modulus and is expressed as follows[121]:

$$B_{\rm T}(T;P) = B_{\rm T}(T;0) + \int_0^T \frac{\gamma^{\rm lat} c_V^{\rm lat}}{V} \left[1 - \left(\frac{\partial B_{\rm T}}{\partial P}\right)_T - q_{Gr} \right] dT$$
(38)

In Equation (38), q_{Gr} is the Gruneisen second parameter which is a constant. $B_{T(0;P)}$ is obtained through the elastic constants; however, all DFT computations must be performed under applied pressure *P*, which is an available option implemented in all DFT codes. One needs to perform DFT computations at different pressures and use numerical methods such as finite difference to calculate $\left(\frac{\partial B_T}{\partial P}\right)_T$. In addition to the harmonic and lattice expansion contributions to the specific heat capacity, thermal electron excitation (C_V^{el}) and thermal defects ($C_P^{(Ther.Def.)}$) can also contribute to the specific heat capacity[81]. These sets of equations should be solved simultaneously to obtain the specific heat capacity at constant pressure[122].

2.1.5.3 Chemical reactions

The ability to produce chemicals with minimal environmental impact is a core tenet of sustainable chemical engineering and catalysis is central to many of these efforts. Catalysis-based chemical synthesis accounts for more than 60 of today's chemical products and is a factor in 90 of current chemical processes. Catalysts offer new chemical pathways for high volume processes, including petroleum refining, energy conversion, fine chemicals, and small molecule pharmaceutical synthesis[123]. From a chemical engineering perspective, understanding the reaction mechanism is paramount for designing an active and selective catalyst. Most catalytic systems are solid-gas or solid-liquid reactions in which the reaction takes place on the surface of the catalyst. Determining elementary reaction rates and identifying molecular species on catalyst surfaces is fast becoming reality[124]. Spectroscopic methods provide valuable molecular-level data, although they can barely provide a full picture of reaction pathways for a complicated reaction. DFT, on the other hand, is capable of capturing each reaction step and generates reaction energy diagrams of reaction pathways (red cluster). In this section we demonstrate how to calculate thermodynamic energy barriers, activation energy barriers, and the reaction full energy diagram (Figure 11). The activation energy constitutes the kinetic energy barrier, while the energy change between reactants and products is the thermodynamic energy barrier. In this energy diagram, the kinetic energy barrier is positive (uphill), but the thermodynamic energy barrier is negative (downhill) and the reaction is exothermic.



Figure 11: Typical energy diagram of a chemical reaction

2.1.5.4 Reaction energy barrier

At constant temperature and pressure, the thermodynamic criterion to judge if a given reaction is energetically favourable or not is defined by the difference of the Gibbs free energy between the products and the reactants. Positive enthalpy variation means that the reaction is endothermic and energy must enter the system for the reaction to proceed. Negative enthalpy variation means that the reaction is exothermic and releases energy to the surrounding. Even the simplest overall reactions require several transition reaction steps with unique reaction energies. The largest elementary energy barrier (i.e,. the largest positive energy) is the reaction energy barrier corresponding to the elementary rate determining step (Figure 12).



Figure 12: An analogue elementary reaction step to R1

In DFT, we break down an overall reaction into elementary steps to predict its formation mechanism. The first step involves the definition of a tentative reaction mechanism. When several alternative mechanisms are possible, we compare their energetics to identify the most favourable. Consider the reaction of A giving B:

$$A \xrightarrow[\Delta G_{tot} = \Delta G_1 + \Delta G_2 + \Delta G_3]{T, P = cte} B$$
(39)

and three elementary reaction steps:

R1:
$$A + * \xrightarrow{T,P = \text{cte}^*} A$$
 (40)

R2: *
$$A \xrightarrow[\Delta G_2]{T,P=cte^*} B$$
 (41)

R3: *B
$$\xrightarrow{T,P=\text{cte}}_{\Delta G_3}$$
 *+B (42)

Here, * represents a vacant site and *A and *B are adsorbed species. A slab which represents the catalyst is first constructed and optimized. Adsorbate on the surface is relaxed through a full relaxation DFT calculation. In this step, the cell size and shape and also a few bottom layers of the

slab are fixed to resemble the catalyst lattice. The top layers and the adsorbate are allowed to relax in response to their energetic interactions. For each elementary step, we calculate the energy of the products and reactants:

$$E_1 = E_{*A} - (E_* + E_A) \tag{43}$$

$$E_2 = E_{*B} - E_{*B}$$
(44)

$$E_3 = (E_B + E_*) - E_{*B}$$
(45)

We calculate these energies at 0 (i.e., in the ground state). To account for temperature and pressure on the energy barrier of reaction, we calculate the Gibbs free energy (G = H - TS) of each subsystem (i.e., the adsorbate and the catalytic slab). For pure gaseous species, the Gibbs free energy of an ideal gas is a good first approximation. Their resulting enthalpy — which is only a function of temperature — is evaluated from the 0 ground state to the relevant temperature using the following equation[125]:

$$H(T) = E_{\text{elec}} + E_{\text{ZPE}} + \int_0^T C_P T$$
(46)

where E_{elec} is the electronic energy (or the energy calculated by DFT, E_{DFT}) and E_{ZPE} is the zeropoint energy which is the vibrational energy at ground state. In Equation (46), the temperature effect is introduced via the integral of the isobaric heat capacity. The heat capacity of a condensed and periodic system can be calculated through its harmonic vibrational frequencies. For pure ideal gas, other degrees of freedom such as translational and rotational, as well as the electronic heat capacity, need to be accounted for to define the isobaric heat capacity[126]:

$$C_{\rm P} = k_{\rm B} + C_{\rm V,vib} + C_{\rm V,rot} + C_{\rm V,trans} + C_{\rm V,elec} \tag{47}$$

where $k_{\rm B}$ is added to account for the extra degree of freedom when passing from a constant-volume to a constant-pressure system. Similarly, the pure ideal gas entropy can be calculated as a function of temperature and pressure:

$$S(T,P) = \int_0^T \frac{C_P^{ideal}(T)}{T} dT - \int_{P_0}^P \frac{\partial v}{\partial T} dP$$
(48)

This ultimately leads to the following general expression[126]:

$$S(T,P) = S_{\text{vib}} + S_{\text{rot}} + S_{\text{trans}} + S_{\text{elec}} - k_{\text{B}} \ln \frac{P}{P^0}$$
(49)

We deduce rotational, translational, and electronic components of ideal gas entropy from the molecular structure rather than DFT[126]. The vibrational contribution to the entropy, however, depends on the vibrational frequencies that we calculate as follows[126]:

$$S_{\text{vib}} = k_{\text{B}} \sum_{i}^{\text{DOF}} \left[\frac{\epsilon_{i}}{k_{\text{BT}} \left(e^{\frac{\epsilon_{i}}{k_{\text{BT}}}} - 1 \right)} - \ln \left(1 - e^{\frac{-\epsilon_{i}}{k_{\text{BT}}}} \right) \right]$$
(50)

or through a similar procedure used to calculate the heat capacity using the Debye temperature (Equation [35]). In Equation [50], DOF is the vibrational degree of freedom, and ϵ_i is the vibrational energy (equivalent to the vibrational frequency). The ideal-gas Gibbs free energy is finally calculated using its definition[125]:

$$G = E_{\text{elec}} + E_{\text{ZPE}} + \int_0^T C_P T - TS$$
(51)

For the (adsorbate+catalytic surface) system, the harmonic or quasi-harmonic approximation is required to define the energetics of the adsorbate.[126] In this model, all 3N degrees of freedom of the adsorbate (with N atoms) are treated harmonically, because the adsorbate often has no real

translational or rotational degrees of freedom. Thus, the internal energy and entropy of the adsorbate are as follows[126]:

$$U(T) = E_{\text{elec}} + E_{\text{ZPE}} + \sum_{i}^{\text{DOF}} \frac{\epsilon_i}{e^{\frac{\epsilon_i}{k_{\text{B}}T}} - 1}$$
(52)

and the entropy is as follows[126]:

$$S = k_{\rm B} \sum_{i}^{\rm DOF} \left[\frac{\epsilon_i}{k_{\rm B} T(e^{\frac{\epsilon_i}{k_{\rm B} T}} - 1)} - \ln(1 - e^{\frac{-\epsilon_i}{k_{\rm B} T}}) \right]$$
(53)

where DOF is the number of harmonic degrees of freedom.

Here is how the zero-point energy of a CO molecule is calculated in this case. Classical mechanics describes the motion of the two bonded atoms and the bond length (b) as a function of time (t) by the following:

$$b(t) = b_0 + a\cos(\omega t)$$
(54)

where b_0 is the optimum bond length with minimum energy (from DFT) and ω (or ν) is the angular frequency (or the vibrational frequency):

$$\nu = \frac{\omega}{2} = \frac{1}{2} \sqrt{\alpha \, \frac{m_C + m_O}{m_C \cdot m_O}} \tag{55}$$

In Equation [55], *m* is atomic mass, and the constant α is as follows:

$$\alpha = \frac{\mathrm{d}^2 E}{\mathrm{d} b^2} \ at \ b_0 \tag{56}$$

Therefore, similar to the procedure to calculate the bulk modulus, we run a series of single point DFT computations to obtain the energy of the system for different bond lengths (i.e., the equation

of state), and then by a simple curve fitting obtain the second derivative at the minima. The energy of the system in classical mechanics, E_{CM} , varies with the square of bond distance, x:

$$E_{\rm CM} = E_0 + \frac{k}{2}x^2 \tag{57}$$

where k is a spring constant, while in quantum mechanics, the energy, $E_{\rm QM}$, varies linearly with v:

$$E_{QM} = E_0 + \frac{h\nu}{2} \tag{58}$$

The zero-point energy is defined as the difference between these two energies at minimum classical energy (i.e., at x = 0):

$$E_{\rm ZPE} = E_{\rm QM} - E_{\rm CM} = \frac{h\nu}{2} \tag{59}$$

For systems with several atoms (many body systems), the quantum mechanics energy is $E_{QM} = E_0 + \sum_i \frac{hv_i}{2}$, and thus the zero-point energy should be replaced by $\sum_i \frac{hv_i}{2}$. In this case, we calculate the Hessian matrix for the second derivatives:

$$H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j} \tag{60}$$

These types of calculations are well formulated in open source codes such as Atomic Simulation Environment (ASE)[126]. Some supported DFT calculators include VASP, Siesta, Quantum Espresso, CP2K, NWChem, CASTEP, FHI-aims, and Abinit. ASE enables calculations of all vibrational frequencies, enthalpy and entropy, as well as the Gibbs and Helmholtz free energy for both ideal gas and adsorbates modelled by the quasi-harmonic approximation.

One important point to be considered in reaction Gibbs free energy calculations is that the vibrational frequencies, and thus the enthalpy and entropy at high temperatures, need to be

calculated only for the adsorbates (not for the catalyst itself). The reason for this simplification is that the vibrational frequencies, and thereby the Gibbs energy, of the solid catalyst with adsorbate $(G_{*A}^{\text{solid cat. contr.}})$ and without adsorbate (G_*) does not significantly change, thus its zero-point energy, enthalpy, and entropy contributions to the Gibbs free energy remain the same before and after the adsorption. Therefore, in reaction **R1**, for instance, the reaction Gibbs free energy can be simplified:

$$\Delta G_1 = G_{*A} - [G_* - G_A]$$

$$\simeq \left[G_{*A}^{\text{solid cat. contr.}} + G_{*A}^{\text{ads. contr.}}\right] - [G_* - G_A]$$

$$\simeq G_{*A}^{\text{ads. contr.}} - G_A$$
(61)

This simplification significantly reduces the computations time, yet does not affect the accuracy of calculations.

2.1.5.5 Transition state and kinetic energy barrier

Estimating a reaction rate — a measured variable — requires the calculation of the kinetic barrier (activation energy barrier) of each elementary reaction. This is an impossible task from an experimental point of view, and very time consuming when using computational methods. To simplify these calculations, we assume that the largest activation energy barrier belongs to the elementary step with the greatest thermodynamic energy barrier. This assumption is used in several models which correlate the activation energy barrier (E_{act}) to the thermodynamic barrier (E_{rxn}), that is, the larger the E_{rxn} , the larger the E_{act} [127]. In the Brønsted–Evans–Polanyi (BEP)

model[128, 129], which is one of the most known approaches, the reaction activation energy is linearly correlated to the enthalpy of the reaction[130]:

$$E_{\rm act} = \alpha E_{\rm rxn} \tag{62}$$

where α is a constant obtained experimentally and characterizes the position of the transition state along the reaction coordinate. This model is accurate for reactions involving small hydrocarbon fragments such as hydrogenation/dehydrogenation of ethylene. The accuracy improves when α is validated with experimental data, which is necessary for systems with closely related reactions and new classes of catalytic materials or reactions.

On the other hand, from a microscopic point of view, calculating the kinetic barrier first involves finding the transition state (TS) of the reaction, from which DFT computations will directly calculate the activation energy barrier. The TS between the reactants and the products in one elementary step has the highest energy. To do this, all the possible positions from the initial state (the reactants) to the final state (the products) must be taken into account and their energy must be calculated. To achieve this task and ensure that the transition state is correctly identified (i.e., the point at which the first derivative of the energy is zero), we apply the nudged elastic band (NEB) method[131]. The NEB creates and optimizes a number of intermediate configurations along the reaction path to find the minimum energy path (MEP). The constructed configurations are some replicas of the system with positions linearly distributed between the start and end positions. The continuity of the path is ensured by adding a spring interaction between the adjacent configuration to imitate an elastic band. The spring constants are typically fixed, but variable spring constants can also be applied to increase the density of configurations near the top of the energy barrier to further improve estimates of the reaction coordinate near the saddle point[131]. Therefore, the reactant and product position are inputs, and the outputs are position and structure with the highest saddle point, which determines the rate of the elementary reaction. The NEB applies to plane-wave based DFT calculations and is implemented as a module in the ASE for VASP, CP2K, or CASTEP DFT codes.

Climbing image NEB (cNEB) methods identify the highest saddle point more accurately (Figure 13)[131]. The cNEB always has one image at the highest saddle point and shows the activation energy precisely with negligible additional computational effort. In the case of multiple saddle points, we must take the highest value.



Figure 13: Comparison of the climbing image nudged elastic band (cNEB) method to the NEB method

Although NEB is a powerful tool to determine the transition state barrier, it relies on static configurations and is unable to capture dynamic changes, which reduces its accuracy.

For example, the hydrogen bonding network dynamically changes for reactions in water, which NEB is incapable of capturing; *ab-initio* molecular dynamics (AIMD) with slow-growth methods

overcome this limitation and account for the varying hydrogen bonding network dynamics[132-135].

Calculating the reaction activation energy barrier helps determine the rate determining step (RDS) and corresponding reaction rate, which in turn suggests a reaction mechanism, activity, and selectivity. We have two scenarios for the mechanism: applying one reaction mechanism to several catalysts or studying the formation of multiple products with one catalyst. In the first case, the catalyst with the lowest overall energy barrier for the RDS is the most active. In the second case, the mechanism with the lowest energy barrier is favoured.

2.1.5.6 Electrochemical reactions

In electrochemical reactions, electrons are directly transferred from one species to another that requires an electric current as well as a counter ions (charged species) flow. Calculation of the reaction energy at a finite temperature and pressure requires Gibbs free energies (or chemical potential) of electrons and ions, which are not directly accessible via DFT. For electrochemical reactions in aqueous environments such as O2 reduction or evolution, H2 evolution, CO2 reduction, N2 fixations, and many other organic molecules oxidation and reductions, electron transfer is coupled with proton (H+) transfer (red cluster). This mechanism is known as the proton coupled electron transfer (PCET)[136]:

$$*X + H^+ + e^- ->^* XH$$
 (63)

*X is an adsorbed compound. The goal here is to calculate the reaction energy barrier:

$$\Delta G = G(^{*}XH) - [G(^{*}X) + G(H^{+}) + G(e^{-})]$$
(64)

Obtaining the Gibbs free energy of a proton and an electron separately requires many DFT calculations. However, considering them together resembles what exists in experimental electrochemistry: standard hydrogen electrode (SHE) as a reference for the potential, where hydrogen gas with activity of 1 (partial pressure is equal to 1 atm) is purged around an electrode made of platinum submerged in an acidic electrolyte of pH equal to 0. Under these conditions, there exists an equilibrium defined by the following:

$$H^{+} + e^{-} < -> \frac{1}{2}H_2$$
(65)

The potential of this electrode is 0. Therefore, the Gibbs free energy of the reaction in standard conditions is 0 at equilibrium, and the following equations are valid:

$$\Delta(G) = \frac{1}{2}G(H_2) - [G(H^+) + G(e^-)] = 0$$
(66)

$$G(H^+) + G(e^-) = \frac{1}{2}G(H_2)$$
(67)

With this equation we replace the expression of the Gibbs free energy of the proton and electron by half the Gibbs free energy of a hydrogen molecule — an easy DFT calculation. It is the computational analogue to the SHE in experiments and is known as the computational hydrogen electrode (CHE)[76]. The CHE is what differentiates electrochemical DFT calculations from regular chemical reactions. When we apply this generic example to electrocatalysis, the Gibbs free energy of **XH* and **X* can be easily computed by DFT and other calculation steps, while we calculate the Gibbs free energy of the proton and electron with Equation (67). Electrochemical reactions always take place under an applied potential. Therefore, we include its contribution to the reaction energy diagram. An applied potential of U changes the energy of each electron by -eU. When n electrons participate in a reaction step, the energy changes by -neU. pH has a similar effect as applied potential, but through changing the energy of protons in the electrolyte. The Nernst equation accounts for the energy (i.e., potential) change due to the change in proton concentration at higher pH:

$$\Delta G_{\rm pH} = \frac{RT}{F} \ln(a_{H+}) = -\frac{RT}{F} \times \rm pH$$
(68)

where a_{H+} , *R*, *T*, and *F* are the activity of protons, gas constant, temperature, and Faraday constant, respectively. At room temperature, -RT/F = -0.059, and thus for each pH increase, the potential will change by -0.059 and subsequently the energy will change by -0.059. When *n* protons react, like for the potential, the pH effect will be multiplied by *n*: $G_{pH} = n \times -0.059$. In the first two setps of the oxygen reduction reaction (ORR), O2 adsorbs and dissociates on the catalyst surface (Figure 14). There is no electron or proton transfer in these steps and the reaction energy is independent of the applied potential or the pH. In the third and forth steps, one electron and one proton react (PCET). We count the cumulative number of electrons the these two steps so that after applying U = 1.23, the reaction energy changes by 1.23 in step 3 and 2.46 in step 4. This change can be seen between the solid line and dash line of each colour. Similarly, comparing the black and blue lines with 5 pH differences, for instance, it is clear that the energy gap between these two lines is equal to $0.059 \times 1 \times 5$ eV (i.e., ≈ 0.3) for the third step and similarly equal to $0.059 \times 2 \times 5$ (i.e., ≈ 0.6) for the fourth step.



Figure 14: Schematic of the effect of an applied potential and electrolyte pH on the reaction energy diagram for the oxygen reduction reaction (ORR) with respect to $O_2 + 4H^+ + e^-$ pathway in acidic media. Dashed line U = 0, solid line U = 1.23 [137]

The CHE model is just one of many models to study electrochemical reactions[138-140]. Although CHE is easy to apply and is widely used for a variety of electrochemical reactions, it oversimplifies several important factors[135]: it assumes the total net charge on the catalyst surface before the reaction is zero, whereas catalysts often have non-zero surface charge, which affects activity[141] and it neglects the chemical interactions between the intermediates formed on the surface and solvent, which are appreciable in aqueous solution where the intermediates contain highly charged atoms to form hydrogen bonds with water[142]. To overcome these limitations, surface charge and models include several layers of water[135].

Another application of DFT calculations in electrochemical systems is the evaluation of the theoretical voltage of different batteries (red cluster). Through the calculations of Gibbs free energy difference between the cathode and anode, we calculate the total energy a battery can release in the form of electrical work; the maximum voltage is the quotient of the Gibbs free energy and the number of electrons. To illustrate the steps, we consider the most widespread Li-ion batteries. Developing active materials for Li-ion batteries with high equilibrium voltage, large capacity, and long term stability is a very active research area[143]. Understanding the maximum attainable equilibrium voltage from a new material for the Li-ion battery is the key driving force to synthesize the material and investigate its capacity, stability, and all other electrochemical properties. Thus, DFT plays an important role to exclude materials with low voltage and draw attention to the most active materials. This role becomes even more important in high throughput discovery of materials for batteries. Lithium iron phosphate (LiFePO4) is one of the most studied cathode materials for the Li-ion battery. Its equilibrium voltage is determined by the difference in lithium chemical potential, μ_{Li} , between cathode and anode:

$$V = -\frac{\mu_{Li}^{\text{Cathode}} - \mu_{Li}^{\text{Anode}}}{nF}$$
(69)

where n is the charge or number of electrons that is transferred, and F is the Faraday constant. The lithium chemical potential is the change of the Gibbs free energy of the electrode material with lithium content. Thus, the average voltage is a function of the Gibbs free energy change of the combined anode/cathode reaction, similar to the Nernst equation for the pH effect above:

$$\overline{V} = -\frac{G_{\text{reaction}}}{nF} \tag{70}$$

Assuming that, at low temperature, the entropic contributions to the reaction Gibbs free energy are negligible, the reaction free energy can be approximated by the internal energy calculated through

DFT at ground state, $G_{\text{reaction}} = E_{\text{reaction}}$. Within this approximation, the equilibrium voltage of the lithium iron phosphate intercalation cathode material (LiFePO4) and a lithium metal anode with the following cell reaction (Equation (71)) can thus be calculated as in Equation (72):

$$Li_x FePO_4 \xrightarrow{charging} Li_y FePO_4 + (x - y)Li$$
 (71)

$$\overline{V}(x,y) \approx -\frac{E(Li_x FePO_4) - E(Li_y FePO_4) - (x-y)E(Li)}{(x-y)F}$$
(72)

where we derive the internal energies of the lithiated and delithiated phases, $E(Li_xFePO4)$ and $E(Li_yFePO4)$, and of the metal (body centred cubic) lithium, E(Li), by DFT. Therefore, with three independent DFT computations, we estimate the voltage. The energy of bcc lithium is independent of the cathode material and hence only needs to be computed once; that is, the average intercalation voltage of LiFePO4 are estimated based on the results of DFT computations of LiFePO4 and the delithiated FePO4. However, the thermodynamically stable phases of Li_xFePO4 and Li_yFePO4 and their respective crystal structures add to the complexity of the problem, and a voltage profile should be used rather than a simple voltage average.

In addition to the calculation of the equilibrium voltage or the voltage profile of a battery material, the stability of reaction intermediates such as partially delithiated lithium iron phosphate compared to the fully lithiated or fully delithiated materials can be calculated. The relevant quantity to compare the stability of different phases is the formation energy with respect to stable reference materials. For this example, an intercalation voltage profile for LiFePO4, the formation energy of any structure with intermediate lithium content, is as follows:

$$E_{\rm f}(Li_x FePO_4) = E(Li_x FePO_4) - xE(LiFePO_4)$$

-(1-x)E(FePO_4) (73)

where *E* is the internal (DFT) energy and the fully lithiated LiFePO₄ and delithiated FePO₄ phases are the relative energy reference. The formation energies of all Li_xFePO₄ phases that are thermodynamically stable compared with the reference phases lie on the lower convex hull of $E_{\rm f}$ versus composition *x*.

Besides the voltage profile and intermediate phase stability, DFT estimates thermodynamic and transport properties such as the temperature effect on the voltage profile, ionic mobility, diffusion and migration dynamics, and thermal and electrochemical stability of the electrolyte[144].

2.1.6 Uncertainties

There are several limitations associated with DFT. An analytical solution to the Schrödinger equation is impossible; DFT provides an approximate solution to the equation by applying an exchange-correlation functional and a basis set. This represents one of DFT's limitations, as the choice of this functional and basis set will dictate the accuracy of the results. Furthermore, DFT can be computationally expensive in time. For reactions, kinetic barrier calculations are computationally very expensive due to the search of unknown transition states. Thus, there is a trade-off between accuracy and computational effort. One way to mitigate this is to calculate the kinetic barrier of the rate determining step only. In addition, ZPE calculations become increasingly

expensive with bigger, more complex molecules. Although DFT calculates thermodynamic data accurately, the same thing cannot be said for kinetics. Considering all these issues, DFT works surprisingly well for these systems; however, it is not yet as accurate as required to be most useful to chemical kinetics.^[145]

In addition, DFT's error associated with its calculations scales with the bond strength. This means that for molecules like CO and N2, the error is especially high because of the triple bonds. Timedependent DFT (TD-DFT) has a deficiency when describing charge separation of two organic molecules. This charge separation occurs when the electron donor donates electrons to an electron acceptor, resulting in a radical-cation and a radical-anion[145]. Also, TD-DFT is less accurate for smaller molecules in general. This is important in the use of DFT for photovoltaics.

Very large systems of more than 1000 atoms are very hard to simulate, as computational costs become prohibitive. This is why DFT cannot be used to describe all biological systems; molecular dynamics can be a better fit for such systems[25].

Moreover, some models often used in DFT are still in need of improvement. The NEB model is unable to capture dynamic changes during a reaction. The CHE model always assumes zero surface charge before the reaction and neglects certain strong chemical interactions. Although some ideas have been proposed to solve these problems and some other issues mentioned in the previous paragraphs, those methods are still not widely applied in the area of DFT computations. DFT in conjunction with experimental results will maximize accuracy.

2.1.7 Conclusion

This article describes the foundations and theoretical background of DFT and identifies practical steps to execute DFT computations. DFT is now accessible to many engineers for their everyday research with the massively parallel supercomputers that perform hundreds of quadrillions of floating point operations per second (10¹⁷ FLOPS). But still, often researchers new to DFT struggle with calculating material properties or chemical reaction systems, although they know how to run a DFT computation. Here we describe procedures to calculate properties of interest to chemcal engineers. We have shown that DFT is a viable tool to calculate structural, electronic, chemical, and thermodynamic properties of materials and provide insights into reaction mechanisms that are otherwise impossible to attain through experiments alone. Nevertheless, it is important to understand the limitations imposed by DFT computations. One of the inherent limitations in DFT is the inaccuracy caused by using approximate exchange — correlation (EC) functionals to describe electronic interactions. Although several EC functionals with high accuracy are available, DFT users must be aware that EC functionals are still approximate and may introduce errors in new systems. Thus, they need to perform several tests and compare results with experimental data to ensure they use the most accurate functionals. Another challenge for DFT users is the projection of ground state DFT to higher temperatures. As we have discussed, there are several models including the quasi-harmonic approximation method, that correlates the ground state properties to those at an elevated temperature. While DFT practitioners apply such models, we discourage overreliance on these approximate models. A more reliable approach would be to use ab-initio MD simulations, however, the progress in this direction needs faster computers which make simulations of thousands of atoms for a reasonable time frame viable. Additionally, developing

faster computational methods is another strategy to reduce computational time. An example of this is ELSI, a unified software interface that solves the Kohn-Sham eigenvalue problem more efficiently[146]. DFT computations generate a large number of data which before were not possible to obtain through experiments. This unique aspect of DFT makes it an interesting target for data analysis efforts based on artificial intelligence (AI) and machine learning (ML) approaches, and we expect to see more work coming out of a combination of these two fields.

Acknowledgments

A.S. would like to acknowledge the NSERC for supporting students involved in this work through the Discovery Grant. A.S. also acknowledges the computational resources provided by Compute Canada, through the rrg-3197 application, to perform DFT computations in this article. H.A-M. and X.W. contributed equally to this work.

Nomenclature

α_{H^+}	
	chemical activity of proton
$\mathbf{\alpha}^{lat}$	
	lattice thermal expansion (K ⁻¹)
b	
D	bound length (m)
В	
C	bulk modulus (J m ⁻³)
\mathbf{C}_P	isobaric specific heat capacity (I K ⁻¹)
C_{v}	isobulic specific field capacity (5 K)
-,	heat capacity (J K ⁻¹)
E	
	total energy (J)
3	

	strain (m m ⁻¹)
e F	elementary charge 1.602 176 634 \times 10 ⁻¹⁹ C
<i>L</i> elec	electronic structure energy obtained through DFT (J)
EZPE	zero-point energy (J)
G	Faraday constant (96 485.3329 A s ⁻¹ mol ⁻¹)
U H	Gibbs free energy (J)
h	enthalpy (J)
ħ	Planck constant (6.626 070 04 × 10 ⁻³⁴ J s)
k	reduced Planck constant (1.054 571 \times 10 ⁻³¹ J s)
k k	string constant (J m ⁻²)
т.	Boltzmann constant (1.380 648 52 × 10 ⁻²³ J K ⁻¹)
m	electron mass (9.109 383 56 × 10 ⁻³¹ kg)
M	atomic mass (kg)
M,	molecular mass (kg)
IVI 1	mass of nucleus I (kg)
Vi	chemical potential (J mol ⁻¹)
V.	longitudinal wave velocity (m s ⁻¹)
V _t	average phonon wave velocity (m s ⁻¹)
<i>(i</i>)	transverse wave velocity (m s ⁻¹)
Р	angular frequency (s ⁻¹)
Por	pressure (Pa)
R	cold pressure (Pa)
0	gas constant (8.3145 J mol ^{-1} K ^{-1})
μ	

density (kg m⁻³)

```
\sigma_i element of stress tensor (J m<sup>-1</sup>)
```

S

entropy (J K⁻¹)

temperature (K)

 θ_D

T

Debye temperature (K)

$\theta^{m_{D}}$

modified Debye temperature (K)

U

internal energy (J)

$U(\overrightarrow{r_{\iota'}}\overrightarrow{r_{J}})$

coulombic potential interaction between electron i and j (J)

$V(\overrightarrow{r_{\iota}})$

external potential on electron i (J)

unit cell volume (m³)

\overline{V}

V

average equilibrium voltage (V)

Vectors

$\vec{r_j}$

Cartesian coordinates of electron j (m)

$\overrightarrow{R_I}$

Cartesian coordinates of nucleus I (m)

Matrices C

stiffness	matrix

\mathbf{H}_{ij}

Hessian matrix

R

Bravais lattice vector **R**'

disordered Bravais lattice vector

S

compliance matrix

Wave functions

$\Theta(\mathbf{R}, \mathbf{r}, t)$
time-dependent wave function $\Psi(\mathbf{R}, \mathbf{r})$ frozen nuclei wave function $\chi(\mathbf{R}, t)$ dynamic nuclei wave function Dimensionless numbers

 γ^{lat} Gruneisen parameter N_{av} Avogadro constant q_{Gr} Gruneisen second parameter Z_I charge number of nucleus IOperators

H

Hamiltonian

 ∇_i^2

Laplacian

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2.2 Manuscript 2: MXene-Supported Single Atom Catalyst Selectively Converts

CO2 into Methanol and Methane

MXene-Supported Single Atom Catalyst Selectively Converts CO₂ into Methanol and Methane

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KEYWORDS: MXene, Single Atom Catalyst, CO₂ Reduction Reaction, Methanol, Methane,

Density Functional Theory

This manuscript was submitted for review in ACS Catalysis

Abstract

Single atom catalysts (SACs) have emerged as new generation catalysts that exhibit unique properties and catalytic activity due to their tunable coordination environment and uniform catalytic active sites. MXenes are two dimensional inorganic materials composed of thin layers of nitrides, carbides or carbonitrides of transition metals, which have been recently used as supports for single metal atoms (SMAs) due to their superior electronic, thermal, and mechanical properties. Catalytic active sites in SACs are too far from each other to enable H-H and C-C coupling through the Tafel process, suggesting that both H₂ production—via the hydrogen evolution reaction—and multi-carbon products (C_{2+}) formation—via the CO₂ reduction reaction—are significantly suppressed on these catalysts. Therefore, these catalysts are expected to be selective towards single carbon (C_1) products in electrochemical CO₂RR. However, there are little computational studies

that investigate MXene-supported SACs towards the CO₂RR, especially for C₁ products such as methane and methanol. In the present study, the density functional theory (DFT) is used to systematically evaluate the stability of the MXene support and SAC; and to screen different MXene structures for selective CO₂RR to C₁ products. Among combination of ten metals and four supports screened, five catalysts exhibit low limiting potentials for C₁ products, especially methanol: Ni/Pd@Ti₃C₂O₂ and Ru/Fe/Co@Mo₂CO₂. Ni exhibits an exceptionally low energy barrier of 0.3 eV towards methane, while all others exhibit low energy barriers toward methanol ranging from 0.37 to 0.60 eV. The novel and in-depth understanding attained in this systematic high throughput DFT study guide the experimentalist to synthesize SACs based on MXene materials, with exceptional activity and selectivity for highly reduced C₁ products.

2.2.1 Introduction

Global warming is an ongoing crisis due to excessive CO₂ emissions into the atmosphere [1-3]. One emerging strategy to mitigate CO₂ concentration is through CO₂ Capture, Storage and Utilization (CCS) [4-6]. Specifically, the utilization part of this strategy is the newest and has attracted much research attention [7-9] as it aims to close the carbon cycle. One pathway to utilize and convert CO₂ into valuable feedstocks and fuels such as alcohols, is through an electrochemical route: the CO₂ reduction reaction (CO₂RR) [10, 11]. However, for commercial viability it requires meeting certain criteria. The energy conversion efficiency of the electrochemical system must be competitive or better than the existing fossil fuel driven chemical synthesis processes, and that requires a low applied potential. In addition, the selectivity of the reaction must be high to reduce the post reaction separation costs [12-15]. Thus, one of the main challenges in the CO₂RR is achieving a high Faradaic efficiency (FE), i.e., the reaction selectivity, and at a low applied potential, which is the driving force of the reaction.



Figure 1. (*a*) Products emerging from the electrochemical reduction of CO_2 . (*b*) Schematic of an MXene support used in this study: $Ti_3C_2O_2$

There are several products that can emerge from the CO_2RR , which can be seen on Figure 1-a, thereby contributing to low FE attained for each product. The main single carbon (C_1) products are carbon monoxide (CO)[16, 17], formate (HCOO⁻)[17-19], formaldehyde[20] (OCH₂), methanol[21-23] (CH₃OH) and methane[24-27] (CH₄). There are numerous multi-carbon (C_{2+})[28, 29] products such as ethylene [28, 30] (C_2H_4), ethane [31] (C_2H_6), ethanol [29, 32] (C_2H_5OH), acetate (CH₃COO-)[33-35], propanol[36, 37] (C₃H₇OH), etc. Additionally, of the main reasons for the existing low FEs is the competing hydrogen evolution reaction (HER). Catalysts that efficiently suppress the HER are needed to improve the FE of the CO_2RR . Some of the products such as CO and HCOO⁻ can be produced with near unity FE [12]. However, FEs for methanol and methane are still too low for commercialization, most being in the range of 30-70% and at a low current density which is not suitable for industrial high-throughput production [12]. Increasing the selectivity of methane and methanol is important for their large market and applications. Methanol, particularly, is a clean fuel, a reagent in emerging direct methanol fuel cells (DMFCs) [21], and is also utilized as an important intermediate for daily used products such as silicone, paint, and plastics [21]. In addition, its liquid form facilitates its use and transportation. Similarly, methane

makes up the majority of natural gas, a high energy density fuel at 55.2 MJ/kg [38]. Methanation is a green method of producing renewable natural gas (RNG), but remains costly, making the electrochemical approach an appealing alternative [39]. However, bringing the CO₂RR technology closer to the large-scale commercialization stage is impossible if we do not learn how to achieve a high selectivity for a single CO₂RR product, how to suppress the HER, how to lower the overpotential of the reaction for optimal cell energy efficiency, and how to promote highly reduced products such as methanol and methane [12].

Single Atom Catalysts (SACs) are recently emerged as promising electrocatalysts to enable achieving these goals of technology commercialization [40]. As suggested by their name, SACs are catalysts that contain isolated metal atoms that are stabilized by a conductive substrate, in the case of electrocatalysis. SACs are distinguished by their unique unsaturated and tunable coordination environment. Since the catalytic metal species is at the atomic level, the electronic structure of SAC is drastically different from nanoparticles and bulk metals, which leads to their exceptional reactivity in addition to their high atomic utilization [40]. Another advantage they hold is the easy tuning of their properties, which can be done by changing the coordination number and environment of the metal species. For the CO₂RR, SACs and their nanoparticle counterparts exhibit different behaviors. For instance, nanoparticles of Fe and Ni are selective towards the HER, while SAC Fe and Ni are selective towards CO_2RR to CO [40]. In fact, the inability to have an adjacent adsorbed hydrogen (*H), or adsorbed carbonaceous intermediate (*C), heavily underpromotes H-H and C-C coupling, thus not only suppresses the HER, but also suppresses the multi-carbon productions. For the HER, the reaction must undergo the Heyrovsky mechanism instead of the preferred Tafel mechanism:

$$^{*}H + H^{+} + e^{-} \xrightarrow{Heyrovsky} H_{2(g)}$$

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$$^{*}H + H^{+} + e^{-} \rightarrow ^{*}H + \ ^{*}H \xrightarrow{Tafel} H_{2(g)}$$

However, from the reaction kinetics perspective, it is known that the Heyrovsky mechanism is less favorable than the Tafel mechanism; yielding an energy barrier of almost twice the value compared to the Tafel on Pt (111) for instance [40].

There exist many types of SACs. They vary based on the substrate or support: metal organic frameworks (MOFs), graphene, molecular (Metal-Phthalocyanine or MPc) or metal-on-metal [41]. Discovered in 2011 [42], MXenes are 2 dimensional materials comprised of 2, 3 or 4 layers of a transition metal M (Ti, Mo, Sc, V, ...) [43, 44]; and with an element X (C or N) between each layer of metal. The MXene can also be surface terminated by an element T (O, H, F, Cl, etc.) [43]. Figure S1-a and b is an example of two and three layered MXenes with M = Ti (a), Mo (b); X = C and T = O. An example of Ti₃C₂O₂ can also be seen in Figure 1-b.

MXene structure is an ideal support for SACs due to their superior electronic structure, conductivity, and stability [43-46]; compared to other SAC supports such as graphene or MOFs. Consequently, MXene supports have been used in a plethora of electrocatalytic applications such as the nitrogen reduction reaction (NRR) [47], the oxygen reduction reaction (ORR) [48], the HER [49], the oxygen evolution reaction (OER) [50] and the CO₂RR [46, 51-53]. The latest literature review shows that a maximum FE of 59% towards methanol, at an applied potential of -1.4 V vs RHE using Cu MXene-based (Cu@Ti₃C₂O₂) SAC structures was achieved [54]. Other groups have used CoPc/CNT [55] to achieve 44% FE at -0.9 V vs RHE, and Cu SAs/ TCNFs (Cu–N4) [56] to achieve the same FE at the same potential. For methane production, Xin *et al.* used an Zn-N₄ [27] to achieve 85% FE at -1.8 V vs SCE; Zheng *et al.* used Cu-CeO₂ [57] to achieve 58% FE at -1.8 V vs RHE. These catalysts, however, suffer from poor stability and/or high overpotentials.

While the attained results so far are impressive, a systematic discovery of new MXene-based SACs is still lacking to find a superior catalyst that exhibits an even lower energy barrier towards C_1 products such as methanol and methane. In addition, the existing studies either do not evaluate the stability of the catalysts, or the reaction mechanism does not cover the full pathways for different possible products [52, 58-61]. Overall, there is a lack of in-depth theoretical studies on SACs MXene catalysts on the CO₂RR which focus on stability, scaling relations and a full reaction pathway that considers numerous products including C-C coupling and the HER.

Here, we aim to investigate Ti- and Mo-based MXenes (the most common transition metals in MXenes) that promote the full reduction of CO_2 to C_1 products; in hopes of finding a novel catalyst that increases the low selectivity. Oxygen-terminated MXenes will be used as they have been found to promote methanol and methane formation [52, 54, 60, 62]. However, these studies are on pure MXene substrates without SACs or are purely experimental with not satisfying performance as explained above. Specifically, the effect of the type of support (Ti or Mo), the number of layers (2 or 3) and the transition metal SAC will be evaluated using theoretical tools in density functional theory (DFT). The goal is to unravel which structure has the lowest energy barrier towards C_1 products, while simultaneously unveiling the unique mechanism that leads to the product.

2.2.2 Computational Details

The MXenes structures were built from MAX phase bulk structures to imitate the synthesis process [63]. For example, Ti_2AIC (MAX) was first optimized to get the lattice vectors, then Ti_2C (MXene) surfaces were created, followed by Ti_2CO_2 (oxygen terminated MXene). The four support structures considered are Ti_2C , Ti_3C_2 , Mo_2C , and Mo_3C_2 . Then, the single metal atom (Ag, Au, Co, Cu, Fe, Ni, Ru, Pd, Pt, Zn) was added on top of the oxygen layer. A vacuum region in the z-direction (i.e., perpendicular to the surface) was set to be 20 Å to avoid interaction between the

layers in periodic imaginary cells. Ti_2CO_2 slab structures were constructed using 18 Ti atoms, 9 C atoms, and 18 O atoms for a final formula of $Ti_{18}C_9O_{18}$. $Ti_3C_2O_2$ structures were constructed using 27 Ti atoms, 18 C atoms, and 18 O atoms for a final formula of $Ti_{27}C_{18}O_{18}$. The same was done for the Mo MXenes, as demonstrated in Figure 2.

All first principles calculations were done using the CP2K package [64]. To obtain the optimal cut-off energy, a standard convergence test was performed [65]. The energy cut-off used was thus 550 Ry. The force convergence was taken to be 3×10^{-4} (Bohr⁻¹× Hartree). A $5 \times 5 \times 1$ Monkhorst-Pack mesh was used for k-points sampling for geometric optimization, while an $8 \times 8 \times 8$ mesh was used for unit cell optimization. Van der Waals corrections enabled by DFT-D3 [66] method are incorporated to calculate the long-range interactions. The dipole moment was considered but did not affect the energy by a significant amount. The PBE functional was used to describe the exchange-correlation functional [67]. Refer to the SI for further computational information.

To evaluate the stability of the MXene products, the formation energy (FE) was used as formulated in Eq 1:

$$FE_{M_{x}C_{y}O_{z}} = E_{M_{x}C_{y}O_{z}} - (xE_{M} + yE_{C} + zE_{O})$$
(Eq1)

 $E_{M_x C_y O_z}$ is the energy of the MXene structure, while E_M , E_C and E_O are the energies per atom of the most stable metal configuration (e.g., for Ti, it is the hexagonal structure with space group P63/mmc), graphene for carbon and oxygen gas, respectively.

To evaluate the binding strength of the SMA to the MXene support, the binding energy (BE) was used.

$$BE_{SMA@M_{x}C_{y}O_{z}} = E_{SMA@M_{x}C_{y}O_{z}} - \left(E_{SMA,vacuum} + E_{M_{x}C_{y}O_{z}}\right)$$
(Eq2)

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 $E_{SMA@M_xC_yO_z}$ is the energy of the SMA adsorbed on the MXene structure and $E_{SMA,vacuum}$ is the energy of the SMA in vacuum. We also define the adsorption energy and desorption energy as following in Eq 3 and 4:

$$\Delta E_{ads} = E_{*reactant} - E_{reactant} - E_{slab} \tag{Eq3}$$

$$\Delta E_{des} = -E_{*product} + E_{product} + E_{slab} \tag{Eq4}$$

2.2.3 Results and Discussion

To evaluate the stability of MXene structure in the closest method possible to experimental conditions, we start with the bulk material: Ti₂AlC for Ti MXene and Mo₂C for Mo MXenes. The formation energy (Eq1) is calculated for this bulk material, then a metal carbide 2D layers are made. The formation energy is calculated again before making the MXene by adding oxygen layers at the top and bottom. This methodology was applied to mimic experimental synthesis of the oxygen terminated MXene. The results are summarized in Table 1 for all four supports.

Table 1 Formation energies (eV/atom) of four MXenes at various stages of synthesis

Synthesis stage/Type	Ti2	Ti3	Mo2	Mo3
Bulk	-0.710	-0.771	-0.410	-0.303
Metal carbide	-0.134	-0.013	0.369	0.003
O-terminated MXene	-2.391	-2.005	-1.496	-1.210

All four O-terminated MXenes have negative formation energies indicating they are stable, and their synthesis is thermodynamically favorable. Starting from the bulk, making the metal carbide layers is slightly endothermic, which is expected as energy input is needed to convert a 3D bulk into a 2D metal carbide layer.

We considered ten total transition metals as SMAs in this study, for they were previously being used as MXene SMC, graphene-based SMC, or as bulk transition metals that have been shown to have considerable CO₂RR performance [54, 55, 68-71]. A DFT study looking at graphene-based SACs [69] suggested that the rate determining step for these catalysts is mostly *CO hydrogenation to *CHO, the usual rate determining step on bulk copper. However, we observe in this work, due to the unique electronic structure of MXenes, *OCHO will be favored to *COOH adsorption and will lead to formic acid instead of CO. This can thus lead to other rate determining steps and the breaking of scaling relations [52, 72-74].

Bulk transition metals such as platinum, nickel and iron do not show any activity towards the CO₂RR, producing hydrogen. However, this differs in the SAC form and the HER is suppressed. Additionally, iron and nickel are particularly interesting to research as they are much cheaper than other transition metals like cobalt or copper. A relatively cheap metal SAC can decrease cost and loading masses which is crucial to commercialization [12].

Metals that favor two electron transfer products in their bulk, such as carbon monoxide and formate, should also be considered as it is hypothesized that SACs will hold on to intermediates better than their bulk counterpart, leading to more electron transfer and easier full reduction of products. This is the case with silver and gold, that mainly produces CO [12]. Copper was included since it is the most researched and effective bulk metal for the CO₂RR [71]. Zinc is included for it has been shown to be a potential catalyst for ethanol production, promoting C-C coupling [75]. It

would be then interesting to see how zinc and copper perform as a SAC, since C-C coupling is inhibited. Altogether, the metals chosen were Fe, Ru, Ni, Co, Pt, Cu, Ag, Au, Pd and Zn.

The binding energy of the selected SACs are calculated (Eq 2) to first find the most stable SAC, and then to see which support each metal prefers. We hypothesize that SACs with a high binding energy to their metals are more stable, and thus will be more performant when it comes to the CO₂RR. Figure 2 below shows the binding energy in eV for each metal and support. Since the absolute value of the BE means little, the plot serves as a comparison point to separate the metals into three distinct categories. Fe, Ru and Ni held "high BEs" compared to Co, Pt, Cu and Pd, which held "moderate BEs." The remaining metals had an average BE of less than 2 eV and were deemed too unstable for their role as a catalyst. This value was chosen based on our generated results on Figure 2, and previous similar works [76, 77], where the rationale is a high binding energy suggests strong affinity and the suppression of diffusion, leading to a more stable structure. It is worth noting that silver and palladium had an average binding energy equal to 2 eV which falls where the cut-off was deducted. Thus, we pick only the best support for each: Ag@Ti3 and Pd@Ti3.



Figure 2: Binding energy of single metals adsorbed on four different structures.

For the supports, there are clear trends when it comes to which support is most viable based on binding strength. Fe, Ru, Ni, Co, and Cu are more stable on Mo2 (light green circles on Figure 2), although some more than others. Specifically, Ru@Mo2 has the highest binding energy, and attaches to the metal atom significantly better than the other three supports. Furthermore, Ti3 (dark blue circles on Figure 2) is systematically more stable than Ti2 (light blue circles in Figure 2), while Mo2 is more stable than Mo3 (dark green on Figure 2). Thus, we predict Mo2 and Ti3 structures to be the most favorable as SACs support, assuming BE plays a role in the catalytic activity in the CO₂RR, which is investigated below. The rest of the catalysts: Ag, Au, Pd and Zn are omitted.

To evaluate the performance of each catalyst for the CO_2RR to C_1 products, different pathways are evaluated, as demonstrated in Figure 3 below. The black pathway leading to CH₃OH in Figure 3 is used for the second stage of screening. This pathway is suggested based on the results for all SACs considered. A high throughput computation was performed, and the results are summarized in Table S1. The following criteria are taken to rationalize how we pick the catalysts that will go through to the next stage of screening:

- We first look at the HER energy barrier compared to the CO₂RR. The first point to look at is the CO₂ and H adsorption on each catalyst. Active catalysts will have a large H adsorption energy (inhibiting the HER) and a negative CO₂ adsorption energy that promotes CO₂ activation and thus the CO₂RR.
- Active catalysts will have a larger H adsorption energy than the energy barrier of the rate determining step (RDS) of the CO₂RR.
- Any catalysts with high energy barrier for the RDS (> 0.8 eV) are omitted for low activity, regardless of the above points.

4) We pick the best performing support for every metal. For example, Ni@Ti2 and Ni@Ti3 both exhibit a low energy barrier for the CO₂RR while suppressing the HER. However, since the rate determining step (RDS) of Ni@Ti3 has an energy barrier of 0.35 eV compared to 0.6 eV for Ni@Ti2, only Ni@Ti3 is considered.



Figure 3 Different pathways for CO₂RR leading to carbon monoxide, formic acid, methane, and methanol. Compounds with an asterisk * are absorbed species, while compounds with no asterisk 93

are either reactants or desorbed products. Red pathways are deemed unfavorable on most catalysts. Species in dashed boxes are final products. Products in blue boxes are intermediate, unfavorable products. Products in green boxes are the targeted products in this study: methanol and methane.

The main products that are investigated are carbon monoxide (CO), formic acid (HCOOH), methanol (CH₃OH), methane (CH₄) and hydrogen (H₂). The HER is the first thing to consider since catalysts that are more selective towards hydrogen production than the CO₂RR are undesirable. After CO₂ adsorption and the first hydrogenation step, the two possible intermediates are *OCHO and *COOH, as seen on Figure S2. The *COOH is considered as the more favorable reaction intermediate in most CO₂RR studies, however, on MXene-based SACs we observed that the *OCHO is the more favorable compound (See Table S2). For example, Cu@Ti3 has an energy barrier of ~ 0 eV towards the formation of *OCHO and 0.52 eV towards *COOH.

Subsequently, *CO can only be produced from *COOH since the carbon in the latter is not hydrogenated. On the other hand, from *OCHO, we expect only *HCOOH to be produced since the carbon in the latter is already hydrogenated. *HCOOH can either desorb as a final product in formate or be further protonated to release water and leave *CHO or *COH. However, *COH is unstable on a SAC as the carbon in an isolated COH form is bonded once to oxygen, meaning it is heavily unsaturated, and one atom catalyst is not enough to provide adequate electrons to the carbon of *COH to share 4 of its valence electrons. On the other hand, the carbon in CHO is bonded three times, meaning *CHO has a better chance to be stabilized by a SAC. Thus, the stability of *CHO/*COH is investigated on Ni@Ti2, and *CHO is found to be 0.95 eV more stable than *COH. On Ni@Ti3, *CHO is 0.77 eV more stable than *COH (see Figure S3). To investigate this difference in stability, Bader charge and charge delocalization calculations were performed. The charge density difference can be seen on Figure S3. As hypothesized, on *COH, there are two blue areas around the carbon, representing electron depletion, forming a dumbbell shape. On the other hand, on *CHO, there is only a small blue area around the carbon and the electron distribution between the metal and carbon (the yellow area) is more uniform than that on *COH, indicating that the carbon in *CHO is more saturated than on *COH. Thus, the *COH pathway is shown in red as unfavorable, in Figure 3. Chemisorption of intermediates after *CHO is shown to be slightly more stable through *O than *C (See Table S4), which is why the pathway involving *CHOH and *CH₂OH is in red. This was observed in 21 out of 24 catalysts. Previous works have shown that *COH is more likely to lead to methane while *CHO leads to methanol formation[78, 79]. Further protonation steps can either be through intermediates adsorbed by the *C atom or the *O atom. From *OCH₃, CH₄ production can occur leaving behind *O which needs to be protonated to form water. The other possibility is *CH₂ formation from *CH₂OH.

Applying the above criteria in the analysis of Table-S1 leads to the conclusion that the six following catalysts are chosen for subsequent steps: Pt@Ti3, Ni@Ti3, Co@Mo2, Fe@Mo2, Ru@Mo2, and Pd@Ti3. Figure 4 shows how the first criterion point is used to screen the catalysts.



Figure 4. (a) The adsorption of CO₂ against the adsorption of H on all 26 catalysts. The figure is split into four regions: the HER-favorable region in the top left, the CO₂RR-favorable region in 95

the bottom right, and mixed regions in the top right and bottom left, (b) Volcano plot showing the energy barrier of the rate-determining step for all catalysts versus the charge of the single metal atom of the catalyst calculated based on the Bader charge analysis [80, 81]. All atoms displayed on the chart correspond to the best performing catalyst for that transition metal.

The color bar on Figure 4-a effectively highlights the selectivity of each catalyst by performing $X - Y = \Delta E_{H_{ads}} - \Delta E_{CO_{2ads}}$. The more positive this value is, the more selective the catalyst is for the CO₂RR. Negative values denote catalysts that prefer the HER to the CO₂RR. There are various key regions, which are delimited by dashed lines. Every catalyst in the top right circle has Mo3 as support, effectively showing that is not an active catalyst for the CO_2RR . This is similar in the bottom left quadrant with Ti2. The bottom right quadrant which is the area for selective catalysts holds a mix of Ti3 and Mo2 catalysts. Applying criterion 4 with this graph, we reduce transition metals that appear twice in the downright quadrant. This leaves two points in the bottom left quadrant which correspond to Pt@Ti3 and Pt@Mo2; and one point in the upper right quadrant corresponding to Cu@Mo3. Since Pt@Mo2 holds a large maximum energy barrier of 1.5 eV (towards CH₃OH production, see Table S1), while Pt@Ti3 has a maximum energy barrier of 0.65 eV (towards *CHO), only the latter is kept. For Cu@Mo3, even though its color suggests high selectivity, the adsorption of CO₂ has a large barrier of 1.35 eV, making it an unviable catalyst based on criterion 3. The preliminary CO₂RR mechanism was still conducted for this catalyst, and on Table-S1 we see the catalyst is selective towards formic acid, as its desorption energy is -0.2 eV compared to the subsequent *CHO formation step evaluated at 1.48 eV (see Table S3). To summarize, there are thus a total of six catalysts that are selected from this stage.

To further justify our findings, Bader charge analysis is conducted on all above catalysts to see the effect of the charge of the SMA on the activity of the catalyst. By taking two lines of best fits, a volcano plot is generated, as can be seen in Figure 4-b. The catalyst with the best activity towards C_1 products is $Ru@Mo_2$ with $\Delta E_{max} = 0.18$ eV, with the Ruthenium atom having a charge of +0.46. When plotting the volcano curve, Ruthenium does sit close at the top, implying that a charge around +0.5 is optimal. Most Mo₃ supported catalysts in dark green have too high of a charge, lowering their activity. Most catalysts are above that optimal charge of +0.5, except Pt and Pd, with their optimal configuration having charges of +0.21 and +0.38, respectively.



Figure 5 Adsorption energies of: (a) H (b) CO_2 on slab and SAC, for the six chosen transition metals. Similarly, desorption energies of: (c) CH_3OH (d) CH_4 . Arrows show the biggest difference between the slab and SAC for each sub-figure.

To highlight the significant difference in properties between SACs and their bulk counterpart, we compared the adsorption of H, CO₂, and the desorption of CH₃OH, CH₄, on both MXene supported SACs and their most stable counterpart slab structure. Figure 5 displays the results. Several trends and conclusions can be derived:

- Five out of six metals exhibit worst H adsorption on SAC than slabs (Figure 5-a), aiding to the HER suppression. Note that the bigger the distance between the red and black dot, for a given metal, the bigger the difference between the slab and MXene SAC.
- 2) The exception to (1) is Pt@Ti3 which has an H adsorption value of -1.15 eV. It shows that the adsorption of H atom is facilitated; however, the HER overall barrier is the absolute value of that i.e., 1.15 eV, a high barrier. Thus, we cannot make a conclusion on Pt based on ΔE values only until we calculate the Gibbs reaction energy (ΔG) values.
- 3) All metals have stronger CO_2 adsorption on SACs than on the slab, as seen on Figure 5-b.
- 4) While the desorption step of products (ΔE_{des}) is small (0-0.3 eV) on slabs, we do not observe the same easy desorption step on SACs. Take methane as an example on Figure 5-d, slab desorption values are all lower than SAC desorption values. The same can be said for methanol in Figure 5-c.
- 5) One exception to (4) is the Ru: Ru@Mo2 has a lower methanol desorption energy than bulk Ru while not replicating the same trend on methane. Ru@Mo2 is thus hypothesized to be an active catalyst for methanol production.

Although the selected catalysts possess a great potential to be selective for C_1 products such as methane and methanol, the reaction mechanism towards C-C coupling needs to be investigated too. The unique active site of SACs makes it difficult to achieve C-C coupling and obtain C_{2+} products. The energy barrier of C-C coupling was investigated via two different pathways which are mostly studied in literature [82-86] for the six catalysts.

$$2*CO \rightarrow *OCCO$$
 (Rx1)

Figure 6-a demonstrates that the distance between two *CO on a SMA increases and the coupling is not favorable, as expected.



Figure 6 (a) *CO + *CO coupling. The first image is before optimization while the bottom image is the optimized structure. (b) *CHO + *CHO coupling and the energy barrier comparatively to methanol and methane production.

C-C coupling by *CHO intermediate can occur as can be seen on Figure 6-b, however at each instance the barrier is higher than it would be for the RDS of methanol or methane production through the CO₂RR. It is worth nothing that iron is the exception, where C-C coupling is at 0.1 eV compared to CH₃OH production at 0.56 eV. *CHO protonation in this catalyst has a ΔE = -0.3 eV which is lower than that for the C-C coupling. Thus, it is inconclusive whether C-C coupling will occur on Fe@Mo2 or the *CHO protonation. On the other five catalysts, the C-C coupling barrier is too high, suppressing the multi-carbon products formation.

Having screened 25 catalysts, six are selected as favorable C₁ producers. The DFT energies were converted to the Gibbs free energies to include the temperature and vibrational effects on the energy (Table S5). One notable difference that arose after performing the Gibbs calculations, is the shift in Pt@Ti3 energy barrier. On Table S6, we see that Pt prefers the *CO₂ conversion into *COOH and subsequently to *CO pathway than the *OCHO pathway. However, the new RDS is through *CO conversion into *CHO which is at a $\Delta G = 1.16$ eV. Furthermore, when looking at CO desorption values on Figure S4, Pt has a remarkably high *CO desorption energy of 3.27 eV. Other catalysts all have similar *CO desorption values ranging from 1.4 to 1.6 eV, except Ru@Mo2 with a value of 0.44 eV. For the four catalysts in the 1.5 eV, a modest value for *CO affinity leads to the best CO₂RR performance. For Ru@Mo2, to produce CO, *COOH must be made instead of *OCHO, however *CO₂ hydrogenation to *COOH has a $\Delta G = 0.78$ eV while its hydrogenation to *OCHO has a $\Delta G = 0.59$ eV and is the RDS. Thus, we conclude that Pt is unfavorable for methanol or methane formation, while the five others are selective for either methanol or methane formation.

Looking back at the mechanism in Figure 3, to produce methane, water must be released through *O hydrogenation to *OH, subsequent hydrogenation to $*H_2O$, and eventually desorption of H_2O . We observed that for products such as water, methane, and methanol, it is imperative to include the desorption step as SACs tend to have significant affinity for products, unlike metal slabs. Therefore, the following reactions in the later steps of the mechanism are considered:

$$CH_{3}OH \xrightarrow{H^{+}+e^{-}} *CH_{4(gas)} + *OH \xrightarrow{des} CH_{4(g)} + *OH$$
(Rx3)

$$^{*}\text{OCH}_{3} \xrightarrow{\text{H}^{+}+\text{e}^{-}} ^{*}O + ^{*}\text{CH}_{4} \xrightarrow{\text{des}} \text{CH}_{4_{(g)}} + ^{*}O \tag{Rx4}$$

$$^{*}OH \xrightarrow{H^{+}+e^{-}} ^{*}H_{2}O \xrightarrow{des} H_{2}O \qquad Rx (5)$$

100

Desorption energy barriers of water and methane compared to methanol determines which product will be formed. If either the desorption of methane or water is higher than methanol, then the latter will be formed. Table S6 shows the desorption energies for these compounds as well as for intermediate products like formate and formaldehyde. Table 2 below summarizes the conclusion drawn from each of these six selected catalysts.

 Table 2. Summary of the performance of the six selected catalysts. Ranking is based on the activity and selectivity of the catalyst.

	Ni@Ti3	Ru@Mo2	Fe@Mo2	Co@Mo2	Pd@Ti3	Pt@Ti3
Product formed	Methane	Methanol	Methanol	Methanol	Methanol	H_2 / CO
RDS	CO2 ads	*CO ₂ →	*CH ₃ OH→	*ОСНО→	CO ₂ ads	*H→ H ₂
	002 445	*OCHO	CH ₃ OH	*HCOOH		
RDS barrier (eV)	0.304	0.594	0.411	0.369	0.426	0.88
Activity (U _{C02}) (eV)	0.305	0.594	0.411	0.369	0.426	0.880
Selectivity (U _{CO2} -U _{H2})	-1.024	-0.537	-0.024	0.098	0.246	-0.008
(eV)	-1.024	-0.337	-0.024	0.078	0.240	-0.008
Activity & Selectivity	0.720	0.057	0.207	0.467	0.672	0.972
(eV)	-0.720	0.057	0.387	0.407	0.072	0.872
Ranking	1	2	3	4	5	6

Based on results in Table S6, all catalysts but Pt SAC which is not active for the CO₂RR, had low methanol desorption values compared to water and methane, making them selective towards methanol. The exception is Ni@Ti3, which has a lower methane and water desorption value, making it a more active catalyst for methane production. Interestingly, we did not observe any similarity among the RDS steps for different catalysts studied here. It is worth noting that Ti3 catalysts have the adsorption of CO₂ as the RDS, while for the other Mo2 catalysts different protonation steps are the RDS. The barriers range from 0.3 to 0.6 eV, as seen on Figure 7, with Ni@Ti3 exhibiting the lowest energy barrier. To create a ranking system, the activity and selectivity of each catalyst was calculated. The activity is defined as the CO₂RR energy barrier while the selectivity is defined as the CO₂RR energy barrier. Note that for both parameters, lower values mean superior performance. Finally, we sum both values as the final number to classify each catalyst. Figure 7 depicts the energy diagram of the best 3 catalysts based on this ranking system; and a full energy diagram is available on Figure S5.



Figure 7 Energy diagram for Ni@Ti3, Ru@Mo2, and Fe@Mo2. The diagram includes the pathways to methane (CH₄) and methanol (CH₃OH). On the bottom, the main intermediates are presented and match the curves above. On top, the final products, side products or intermediates are shown and match the thin curves below them, if applicable. The reaction coordinate number represents the number of PCET steps, except for adsorption and desorption steps.

2.2.4 Conclusion

We have performed systematic high throughput DFT computations to screen and investigate potential single atom MXene catalysts that exhibit high selectivity and low overpotentials towards

the CO₂RR, specifically for highly reduced C₁ products such as methanol and methane. After screening based on formation energy, binding energy, activity, and selectivity, five catalysts were found to exhibit exceptional performance. These catalysts are, in order of performance: Ni@Ti3, Ru@Mo2, Fe@Mo2, Co@Mo2 and Pd@Ti3. Specifically, nickel had the lowest overall energy barrier at 0.3 eV while effectively suppressing the HER. Additionally, iron had an overall energy barrier of 0.4 eV, making these two low-cost transition metals attractive catalysts to synthesize and test in experiment. Finally, we observe that Mo2-based SACs exhibit high performance, opening a chance for further experimental investigation on them, as they have not been very exploited in this domain.

ASSOCIATED CONTENT

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Author Contributions

AS and HA have conceived the project. HA performed all the computations, while AS supervised the project. RY helped with the code for high throughput DFT computations. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was financially supported by the NSERC Discovery Grant (RGPIN-2020-04960), and Canada Research Chair (950-23288). HA was financially supported by the Fonds de Recherche du Québec – Nature et technologies (FRQNT) and the NSERC Master Scholarships. The DFT computations carried out in this study was supported by Calcul Quebec, Compute Canada, and the Digital Research Alliance of Canada.

ACKNOWLEDGMENT

The authors would like to thank Mahdi Salehi for his comments and help with figures

preparation in this study.

ABBREVIATIONS

CO₂RR, CO₂ Reduction reaction; SAC, Single Atom Catalyst; SMA, Single Metal Atom; HER,

Hydrogen Evolution Reaction; RDS, Rate Determining Step.

2.2.5 References

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3 Discussion

The first manuscript shows the mathematics and physics behind the DFT, while highlighting the valuable insight it provides in many chemical engineering fields. The first main challenge associated with DFT is the inaccuracy it holds due to failure of considering the complete experimental environment such as, pH, temperature, electromagnetic field, and electrolyte in electrocatalytic systems, for instance. It is worth noting that there have been many efforts to address these issues. For the electrolyte and pH, implicit models are available such as the selfconsistent continuum solvation (SCCS)[1], which considers the dielectric constant of the electrolyte. For the effect of the electromagnetic field and potential, the Grand Canonical Ensemble^[2] is a method where you can simulate charged surfaces. These efforts also help address the second challenge of DFT: computational power. It is possible, for example, to include ~ 100 molecules of water to simulate explicit solvation[3], however that would increase the computation requirements exponentially. Thus, having an implicit model can allow more accurate simulation of the electrolyte, without adding much computational need. The third challenge is the choice of the exchange-correlation functional. To compare DFT results obtained with others found in literature, it is important to check if the same exchange correlation functional was used, as it has a significant influence on the results. Fortunately, in the electrocatalytic field, the most common functional used for transition metals is the Perdew-Burke-Ernzerhof (PBE) [4]. PBE is a nonempirical functional that is recommended for molecule-metal surface interactions. Thus, this functional was chosen in the second manuscript. It is worth noting that other, new functionals have recently been used in attempt to better predict experimental results. Such functionals include rPBE

and BEEF [5].Finally, as mentioned in the section 2.1.2, there are different DFT packages that allow users to simulate their system. If the same input parameters (basis sets, cutoff, potentials) discussed in 2.1.2 are used, there should not be major discrepancies between different software. To choose input parameters such as grid convergence and kpoints, convergence tests were performed, and adequate convergence criteria was chosen to ensure the energy at the criteria is not changing significantly. In our lab, we use VASP, CP2K and GPAW and we usually observe the same energy differences (adsorption energies, reaction energies) throughout this software; however individual results such as the DFT energy of a system will vary. One main reason for that is software such as VASP[6] use plane wave basis sets whereas CP2K[7] uses mixed Gaussian and plane waves approaches.

Experiments are often conducted at non-zero temperatures and pressure, and this can affect reaction kinetics and thermodynamics. There are several methods to incorporate these two parameters in DFT calculations. The simplest method is to correct the energy obtained from 0K DFT using equations 46, 48 and 51 of the first manuscript. Here, the effect of temperature and pressure are incorporated by calculating the enthalpy and entropy and any temperature and pressures, giving us the Gibbs energy. This was performed in the work of the second manuscript. It is worth noting that for electrocatalytic systems, this method can still adequately simulate experimental conditions, as most experiments are carried under room temperature and pressure. Furthermore, the accuracy of the Gibbs energy calculation relies heavily on the chosen physical model, such as the quasi-harmonic approximation described in section 2.1.5.2. This model was used in the second manuscript, but it is worth noting that other approximations are better fits for other systems [8]. However, for other systems where the temperature has significant impact, many researchers in the field will combine DFT and molecular dynamic (DFT-MD) to get a more

accurate incorporation of temperature[9]. One such MD methods is Ab initio molecular dynamics (AIMD) [10]. This method still neglects the effect of temperature on electron interactions in the DFT simulation. Thus, finally, there is a method entitled finite temperature DFT (FT-DFT), that uses thermal ensembles to simulate thermal systems more accurately[9]. However, this method depends on the validity of these ensembles and is still being developed.

In the field of catalysis, there is an increasing number of papers that combine DFT computations with experimental work. This is because it is difficult and sometimes impossible to understand the mechanism of the reaction that led to the novel findings of the work. Similarly, an investigation can commence with DFT computations to gain insight on what kind of catalyst to synthesize and general direction of the study. Screening many catalysts for their properties and performance is possible using DFT, but is difficult, highly costly and time consuming to perform in the laboratory. This is what the second manuscript demonstrates.

Among the available large DFT studies performed on electrocatalysts, the stability of the former is often ignored or underestimated[11-13]. In the second manuscript, we assess the stability of different structures based on two standardized properties, the formation energy, and the binding energy. This is important as it gives more chance that the catalysts can be synthesized in the laboratory. We also show that there is a strong correlation between the stability and performance of the catalysts. Furthermore, a full reaction network considering all side products and pathways was implemented to ensure the selectivity of the final product.

While the results are promising, there are additional DFT computations that can further fortify the validity of the findings. The most important one is the consideration of kinetics by using NEB to obtain the energy of the transition state, which is discussed thoroughly in the first manuscript.

While favourable thermodynamics usually indicate the same for the kinetics, that is not always the case. Thus, the activation barrier of every step should be calculated, however due to the numerous catalysts and elementary steps of this project, it would be computationally expensive. An alternative is to perform the NEB on the rate-determining step only. Another essential element to add is the effect of the electrolyte and electrode potential, as discussed previously.

One property that was not discussed in the mini review was the Bader charge, and was calculated in the MXene paper by using the electron density computed using DFT. The Bader charge of the active site is important as it is usually correlated to the performance of a catalyst, as seen through the volcano plot in Figure 4-b. The optimal charge was determined to be $\sim +0.45$.

While a total of forty catalysts were considered, there are many more possible MXene SACs. For example, instead of considering only Ti or Mo based MXene, there are works on Sc, Ta, W, V, Cr, Y, Zr, Nb, Hf based MXenes[14] ; although most are not for the CO₂RR. Furthermore, there are works showing that the surface termination of the MXene can play a vital role in the energetics of the elementary steps. While we consider O- terminated MXenes, there are also -OH terminated MXenes[15] that can be investigated in the future.

Finally, to truly verify the findings of this paper, experimental testing must be done on the selected catalysts. We hope to do that next in our laboratory.

4 Conclusion

The first manuscript effectively represents a tutorial for chemical engineers to learn the basics of the DFT, how to use it and how to improve its accuracy. The theory presented was complete enough to give a general understanding of the underlying physics behind DFT, without getting into complex details that will not necessarily be relevant for chemical engineers. Similarly, the application of DFT was explained through the mathematical handling of the DFT's most important output: the energy of the system. From there, we demonstrate how to obtain material properties and the chemical reactivity of systems. In the second manuscript, a systemic and standardized DFT process was implemented to screen one hundred different SACs MXene catalysts for the CO₂RR. DFT findings discussed in the first manuscript were obtained, such as the stability and reactivity of different catalysts. Five catalysts were found to exhibit exceptional performance. These catalysts are, in order of performance: Ni@Ti3, Ru@Mo2, Fe@Mo2, Co@Mo2 and Pd@Ti3. Experimentalists and computationalists are encouraged to use our methodology to aid in material discovery, as well as enrich the validity of the results by considering the kinetics and surrounding chemical environment. Finally, in the future, we wish to synthesize those catalysts in the laboratory and evaluate them for the electrocatalytic performance.

5 References

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