

Screening of Pt/Ni bimetallic electrocatalysts using DFT calculations

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Table of contents

Table of contents	iii
List of tables	vii
List of figures	xi
Declaration	xv
Acknowledgements	xvii
Preface	xix
List of conference poster/oral presentations and publications	xxii
List of publications	xxv
Consent by co-authors	xxvii
Summary.....	xxix

Part 1: Prologue to study

Chapter 1. Introduction

1.1. Background and rational	3
1.2. Problem statement.....	4
1.3. Aim of the study.....	5
1.4. Objectives of the study	5
1.5. Methodology of the study	6
1.6. References	7

Chapter 2. Litratue study

2.1. Introduction.....	13
2.2. Electrochemical devices.....	13
2.2.1. Water splitting reaction (Electrolysers)	14
2.2.1.1. Oxygen evolution reaction (OER)	14
2.2.1.1.1. Gibbs free energy for the OER	15
2.2.1.2. Hydrogen evolution reaction (HER).....	16
2.2.2.1.2. Gibbs free energy for the HER	16
2.2.2. Water formation reaction (Fuel cells)	17
2.2.2.1. Oxygen reduction reaction (ORR).....	17
2.2.2.2. Hydrogen oxidation reaction (HOR)	18
2.2.3. Summary	18
2.3. Electrocatalysts	18
2.3.1. Ideal electrocatalyst	18
2.3.2. Volcano plot as a catalytic activity description of ORR/OER half-reactions	19
2.3.3. Structure of bimetallic surfaces	21

2.3.3. Summary.....	21
2.4. Computational background	22
2.4.1. Surface energy and Work function	23
2.4.2. Adsorption energy	24
2.4.3. Band structure and density of states	24
2.4.2.1 Computational study of the band structure	26
2.4.2.2. Computational study of density of states	28
2.4.3. Adsorption energy, <i>d</i> -band energy and hydrogen binding energies.....	28
2.4.4. Strain, ligand and ensemble effects	29
2.4.4.1. Strain effect	29
2.4.4.2. Ligand effect.....	30
2.4.4.3. Ensemble effect	31
2.4.4.4. Methods to distinguish the ligand effect from the ensemble effect	31
2.4.5. Surface magnetism.....	33
2.5. References	34

Chapter 3. Model development.

3.1. Introduction.....	41
3.2. Computational model	42
3.2.1. Bulk structures calculations	42
3.2.1.1. Validation using lattice parameters	43
3.2.1.2. <i>k</i> -point sampling for Pt and Ni bulk structure.....	43
3.2.2. Surface calculations	43
3.2.2.1. <i>k</i> -point sampling for Pt (111) and Ni (111) surface slabs	43
3.2.2.2. Surface and Electronic properties	43
3.2.3. Hydrogen adsorption onto the (111) surface slabs.....	44
3.3. Results and discussions	45
3.3.1. Bulk structure calculations	45
3.3.1.1. Validation using lattice parameters and interatomic spacing.....	45
3.3.1.2. <i>k</i> -point sampling of Pt and Ni bulk structures	46
3.3.2. Surface calculations	50
3.3.2.1. <i>k</i> -point sampling for Pt (111) and Ni (111) surface slabs	50
3.3.2.2. Electronic properties of pristine surfaces.....	53
3.4. Conclusion	57
3.5. References	58

Part 2: Pt/Ni bimetallic systems

Chapter 4. Construction of $\text{Pt}_{0,x}\text{Ni}_{0,y}$ surface slabs using a random manual technique

4.1. Introduction.....	66
4.2. Computational model	67
4.2.1. Building the bimetallic surfaces	67
4.2.1. Prepping the surfaces for hydrogen adsorption.....	68
4.3. Results and discussions	69
4.3.1. Electronic properties of pristine bimetallic surfaces.....	70
4.3.1.1 Work function (Φ)	70
4.3.1.2. Investigation of the d -band centre (ϵ_d).....	71
4.3.2. Ligand and ensemble effects due to the hydrogen adsorption	73
4.3.2.1. Ligand effects	73
4.3.2.2. Ensemble effects.....	74
4.4. Conclusion	81
4.5. References	81

Chapter 5. Study of surface reactivity of hydrogen adsorbed onto random disordered bimetallic structure

5.1. Introduction.....	87
5.2. Computational method	88
5.3. Results and discussions	89
5.4. Conclusions.....	95
5.5. References	96

Part 3: Epilogue - Application of bimetallic (111) surfaces

Chapter 6. Adsorption of water onto a thermodynamically stable $\text{Pt}_{0.5}\text{Ni}_{0.5}$ slab.

6.1. Introduction.....	103
6.2. Computational method	103
6.2.1. Building the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces	104
6.2.2. Hydrogen adsorption on $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces	106
6.2.3. Water adsorption on $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces	107
6.3. Results and discussions	107
6.3.1. Pristine (111) surface properties.	107
6.3.2. Hydrogen adsorption results	111
6.3.3. Properties of isolated water	114
6.3.4. H_2O adsorption	115
6.3.4.1. Pt (111) and Ni (111) surfaces.....	115
6.3.4.2. $_{1.5}$ (111) and $_{0.5}$ (111) surfaces.....	117

6.4. Conclusion	120
6.5. References	121

Chapter 7. Conclusion and future work

7.1. Conclusion	125
7.1.1. Identification of the most stable ratio of Pt and Ni in a Pt/Ni bimetallic bulk structure using DFT calculations	125
7.1.2. Investigating the stability and reactivity of Pt/Ni bimetallic surfaces constructed from the most stable Pt/Ni bimetallic bulk structure	126
7.1.3. Evaluation of the performance of the most outstanding Pt/Ni bimetallic surface as a viable electrocatalyst for both the OER and ORR	126
7.2. Recommendations	127
7.3. References	127

Appendix

Supplementary 1

S1.1. Introduction.....	152
S1.2. Computational method.....	152
S1.3. Results and discussion	153
S1.3.1. Comparison of optimisation energies for unconstrained surface slabs with different Miller indices	153
S1.3.2. Comparison of optimisation energies for constrained and unconstrained surface slabs.....	155
S1.3.3. Influence of increasing slab thickness on interatomic distances for unconstrained slabs.....	157
S1.4. Summary	159
S1.5. References.....	159

Supplementary 2

S2.1. Introduction.....	163
S2.2. Computational method.....	163
S2.2.1. Creating fourteen layered alloys with various metal arrangements	164
S2.3. Results.....	165
S2.3.1. Comparison of optimisation energies for the various bimetallic slab configurations	165
S2.3.2. Comparison of the interatomic spacing between the most stable bimetallic slabs	167
S2.4. Summary	168
S2.5. References.....	168

List of tables

Chapter 2.

Table 2.1. Catalytic half-cell reactions used in electrolyzers (OER/HER) and fuel cells (HOR/ORR).	13
Table 2.2. The OER mechanism in acidic and alkaline solutions. ^{9, 10, 20}	14
Table 2.3. The OER mechanism in acidic solutions. ^{22, 26}	14
Table 2.4. The OER mechanism in alkaline solutions. ^{11, 26}	15
Table 2.5. Gibbs free energy for each intermediate for the OER. ^{7, 13, 14, 26, 30}	16
Table 2.6. HER mechanism, under acidic conditions, following the Volmer, Heyrovsky and Tafel steps. ³¹⁻³³ ...	16
Table 2.7. The ORR mechanism in acidic and alkaline solutions. ^{22, 28}	17
Table 2.8. Overpotential (η) for the OER (η^{OER}) and the ORR (η^{ORR}). ^{14, 40, 41}	18
Table 2.9. Symmetry k -points of fcc lattice.	27

Chapter 3.

Table 3.1. Comparison of lattice parameters (Lattice_parm) and metal-metal interatomic spacing (d_M - d_M) for the Pt and Ni bulk structures with a Fm3m (225) space group obtained from the current study (*) and from the literature.	46
Table 3.2. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing (d_{Pt} - d_{Pt}), the equilibrium lattice parameter (E_lattice parm), the d -band centre (ϵ_d) and the spin moment (m_s) for various Pt bulk structures k -points grids.	47
Table 3.3. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing (d_{Ni} - d_{Ni}), the equilibrium lattice parameter (E_lattice parm), the d -band centre (ϵ_d) and the spin moment (m_s) for various k -points grids for the Ni bulk structures.	49
Table 3.4. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing (d_{Pt} - d_{Pt}), the equilibrium lattice parameter (E_lattice parm), work function (Φ), the d -band centre (ϵ_d) and the spin moment (m_s) various k -points grids for the Pt (111) surface.	51
Table 3.5. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing (d_{Ni} - d_{Ni}), the equilibrium lattice parameter (E_lattice parm), work function (Φ), the d -band centre (ϵ_d) and the spin moment (m_s) for various k -points grids for the Ni (111) surface.	52
Table 3.6. The surface energy (γ) of unconstrained, pristine Pt (111) and Ni (111) metal surfaces of (3×3)-4L obtained from the current study (*) as compared to computational and experimental values.	53
Table 3.7. The work function (Φ) of unconstrained, pristine Pt (111) and Ni (111) metal surfaces of (3×3)-4L, obtained from the current study (*), as compared to computational and experimental values from the literature.	54

Table 3.8. The comparison of calculated adsorption energy, E_{ads} (in eV), and bond length, $d_{\text{H-M}}$ (in Å), of unconstrained (2×2) Pt (111) and Ni (111) slabs with literature values. The surface coverage was 0.25ML.	54
--	----

Table 3.9. Hydrogen binding energies (HBE) of adsorbed hydrogen onto Pt (111) and Ni (111) surfaces with 0.11 ML surface coverage. Notably, the coverage of the reference is 0.25 ML.	55
---	----

Chapter 4.

Table 4.1 Calculated work function (Φ) and d -band centre (ϵ_d) of the unconstrained pristine, Pt (111), Ni (111), R-Pt _{0.25} Ni _{0.75} (111), R-Pt _{0.5} Ni _{0.5} (111) and R-Pt _{0.75} Ni _{0.25} (111) surfaces.	70
---	----

Table 4.2. Calculated electronic properties for R-Pt _{0.5} Ni _{0.5} bimetallic surface with varying adsorption sites in terms of the adsorbed metal site (H-M _{ads}) work function (Φ), interatomic spacing ($d_{\text{H-M}}$), binding energies (HBE), adsorption energy (E_{ads}) and the d -band centre (ϵ_d).	78
--	----

Chapter 5.

Table 5.1. Atomic charges (q) and atomic spin momenta (m_s) for the pure Pt and Ni metals, as well as for configurations B and C of the bimetallic bulk structures with the Pt _{0.5} Ni _{0.5} composition, as calculated using a Bader analysis. ⁶	95
--	----

Chapter 6.

Table 6.1. Surface energies calculated before optimisation (γ_u), after optimisation (γ_r) and the percentage relaxation (%) for (111) surfaces of the pure Pt, pure Ni and each of the Pt _{0.5} Ni _{0.5} surface terminations. (Structures with identical top layers and varying bottom layers are indicated with matching colours)	108
---	-----

Table 6.2. The average interatomic spacing (d , in Å) after slab optimisation of the relative interatomic spacing for Pt, Ni, Pt _{0.5} Ni _{0.5} bulk and the constrained _{0.0} (111), _{0.5} (111), _{1.0} (111), _{1.5} (111), and _{2.0} (111) surfaces. The spacing was obtained before (Δ_{bulk}) and after relaxation (Δ_{relax}).	109
---	-----

Table 6.3. Charge analysis for the atoms in the pure Pt (111) and Ni (111) surfaces and various Pt _{0.5} Ni _{0.5} surfaces. With respect to the average charge (q/e^-) of either the Pt or Ni atoms in the mixed metal surfaces.	110
--	-----

Table 6.4. Work function (Φ) and d -band centre (ϵ_d) results of pure Pt (111), Ni (111), _{1.5} (111) and _{0.5} (111) surfaces.	111
---	-----

Table 6.5. Calculated geometries and Mulliken charges of the isolated H ₂ O molecule as compared to theoretical ³⁰ and experimental ⁴⁸ values.	114
---	-----

Table 6.6. The work function (Φ), d -band centre (ϵ_d), bond length and bond angles results obtained from H ₂ O adsorption onto the Pt (111) and Ni (111) surfaces.	116
--	-----

Table 6.7. Mulliken charge of water adsorbed onto the Pt (111) and Ni (111) surfaces. The calculated charges are for the, M* and H ₂ O bonds.	116
--	-----

Table 6.8. Work function (Φ), d -band centre (ϵ_d), bond length and bond angles results obtained from H ₂ O adsorption onto the Pt (111), Ni (111), _{0.5} (111) and the _{1.5} (111) surfaces, where the labels (B) and (C)	
--	--

represents an alternative adsorption site of the water molecule on the $_{0.5}(111)$ and $_{1.5}(111)$ metal surface. (The H_2O data is from Table 6.6 for the isolated H_2O molecule).	117
Table 6.9. Mulliken charge of H_2O adsorbed onto the Pt (111), Ni (111), $_{0.5}(111)$ and the $_{1.5}(111)$ surfaces. The calculated charges are for the, M^* and H_2O bonds.	118
Table 6.10. Water monomer adsorption with a flat geometry onto $_{0.5}(111)$ and the $_{1.5}(111)$ surfaces for the [A], [B], [C] and [D] environments.	120

List of figures

Preface.

Figure P.1. Compilation of the thesis and articles. xix

Chapter 2.

Figure 2.1. Illustration of a) an electrolyser and b) a fuel cell. 13

Figure 2.2. Schematic representation for the OER mechanism in an acidic electrolyte. In each step, a proton-electron pair is subtracted from the reactants so that water molecules are subsequently transformed into HO_{ads} , O_{ads} , HOO_{ads} and O_2 15

Figure 2.3. A schematic representation for the HER. In each step, a proton-electron pair is subtracted from the reactants so that water molecules are subsequently transformed into H_2 17

Figure 2.4. An ideal catalyst for the OER reaction at zero potential ($U = 0$) and at the equilibrium potential ($U = 1.23 \text{ eV}$). 19

Figure 2.5. Volcano plots for the OER and ORR where each Gibbs energy is represented by ΔG_1 (blue), ΔG_2 (red), ΔG_3 (green) and ΔG_4 (pink). The solid lines are the volcano plots, while the dashes are an extension of the volcano plot so that the η^{ORR} and η^{OER} values can be calculated. 20

Figure 2.6. Universal volcano plots for the OER reaction regarding η_{OER} as a function of $\Delta G_{\text{Oads}} - \Delta G_{\text{HO}}$ 20

Figure 2.7. A simple representation of different types of solid-solution bimetallic alloys, namely a) a substitutional, b) an interstitial and c) an intermetallic compound. 21

Figure 2.8. Comparison of the flat surface of a) a low-index (111), and b) the high-index (210) surface with atomic steps. 23

Figure 2.9. Forming of energy bands due to overlap of closely spaced orbitals. 25

Figure 2.10. Projected representation of band structure and density of states for a) metal and b) an insulator or semiconductor. 25

Figure 2.11. Simple representation to describe the forming of *s*- and *p*- energy bands. 25

Figure 2.12. Projected representation of the density of states. 26

Figure 2.13. Brillouin zone of an *fcc* lattice with the path as $\Gamma\text{-X-W-K-}\Gamma\text{-L-U-W-L-K|U-X}$.⁹⁷ 27

Figure 2.14. Representation of the electronic structure of Ni metal, where the bands/lines stand for molecular orbitals. 28

Figure 2.15. A simple representation of ligand effects a) before and b) after addition of a secondary metal. 30

Figure 2.16. A schematic relationship of the reactivity, towards O_2 adsorption for the ORR, and the *d*-band centre (ϵ_d) for Pt_3M surfaces, represented as a volcano plot. 30

Figure 2.17. A simple representation of ensemble effects on the adsorption of H_2O molecule a) before and b) after addition of a secondary metal. 31

Figure 2.18. The ensemble effect is obtained graphically by the subtraction of the ligand effect from the total effect.¹¹⁵ The ligand effect is described where the composition of the surface is held constant for similar adsorption sites. 32

Figure 2.19. Ensemble and ligand effects described using tri-fold ensemble (red triangle) where the binding site, functions of n , is shown using a gold atom. ^{55, 115, 121}	32
Figure 2.20. Graphical representation of effects contributed by the ligand and the ensemble effects.	33
Figure 2.21. DOS of a) Ni (111) and b) Pt (111) surface with the minority (β) and the majority (α) spin states.	34

Chapter 3.

Figure 3.1. A simple representation of using the d -band width to determine the d -band centre (ϵ_d), using integration.	44
Figure 3.2. The atop (T), bridge (B), hexagonal close-packed (H) and face-centred cubic (F) adsorption sites that occur on a (111) metal surface.	45
Figure 3.3. The optimisation energy per atom of Pt bulk structures with various k -points.	47
Figure 3.4. The optimisation energy per atom of Ni bulk structures with various k -points.	49
Figure 3.5. The optimisation energy per atom of Pt (111) slab with various k -points.	50
Figure 3.6. The optimisation energy per atom of Ni (111) slab with various k -points.	52
Figure 3.7. Obtaining the binding energy from the optimisation energy (eV) and the bond length where the energy is at a minimum point (●) and where bond breaking occurs (●).	55
Figure 3.8. pDOS of the pristine (3×3)–4L a) Pt (111) and b) hydrogen adsorbed onto Pt (111) surface at a coverage of 0.11 ML on the fcc site.	56
Figure 3.9. pDOS of the pristine (3×3)–4L a) pristine Ni and b) hydrogen adsorbed onto Ni (111) surface at a coverage of 0.11 ML on the fcc site.	57

Chapter 4

Figure 4.1. Top and side view for the a) R-Pt _{0.25} Ni _{0.75} b) R-Pt _{0.5} Ni _{0.5} and c) R-Pt _{0.75} Ni _{0.25} surfaces, where the Pt atoms in green and the Ni atoms in pink/purple.	68
Figure 4.2. Adsorption sites on a) R-Pt _{0.25} Ni _{0.75} b) R-Pt _{0.5} Ni _{0.5} and c) R-Pt _{0.75} Ni _{0.25} surfaces, where F_1 – F_4 = fcc hollow sites and H_1 – H_4 = hcp hollow sites. (Where the atom colours are green and pink/purple for Pt and Ni, respectively.)	69
Figure 4.3. Partial density of states (pDOS) of Pt (111), Ni (111) and the R-Pt _{0.25} Ni _{0.75} (111), R-Pt _{0.5} Ni _{0.5} (111) and R-Pt _{0.75} Ni _{0.25} (111) bimetallic surfaces.	72
Figure 4.4. The comparison of the hydrogen binding energy (HBE) and the d -band energy (ϵ_d) for the F_1 and H_1 adsorption sites for the bimetallic surfaces where the amount of Pt and Ni was varied to obtain R-Pt _{0.25} Ni _{0.75} (111), R-Pt _{0.5} Ni _{0.5} (111) and the R-Pt _{0.75} Ni _{0.25} (111) surfaces.	74
Figure 4.5. The comparison between the binding energies (HBE) for varying environments of the adsorption site for the a) hcp and the b) fcc sites for the for R-Pt _{0.25} Ni _{0.75} (111) surface.	75
Figure 4.6. Comparison between the binding energies (HBE) for varying environments of the adsorption site for the a) hcp and the b) fcc sites for the for the R-Pt _{0.5} Ni _{0.5} (111) surface.	76
Figure 4.7. Comparison between the HBE and the a) hcp and b) fcc binding sites with varying environments, either bonded to Pt ₃ or Pt ₃ Ni ₁ for the R-Pt _{0.75} Ni _{0.25} bimetallic surface.	77
Figure 4.8. Hydrogen binding energy (HBE) vs a) the adsorption energy and b) the d -band centre for Ni (111), Pt (111) and R-Pt _{0.5} Ni _{0.5} (111) surfaces (indicated as F_1 , F_2 , F_4 , H_1 and H_2).	80

Chapter 5

Figure 5.1. A schematic representation of the process to obtain full convergence ($S_{\max}$) for each of the Pt/Ni concentrations with varying degrees of simulation cell sizes.	90
Figure 5.2. The mixing enthalpies (ΔH_{mix}) for the $1 \times 1 \times 1$ simulation cell size, both per atom of $\text{Pt}_{1-x}\text{Ni}_x$ and as a function of the Ni mole fraction (x).	91
Figure 5.3. The partially and fully disordered probability distribution of the energies (E) calculated for the configurations with a $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configuration in the $2 \times 2 \times 1$ simulation cell. The short vertical lines at the top of the graph represent the energy values in the configurational spectrum. The partially disordered probability distribution was calculated using a Boltzmann-modulation at 300 K.	92
Figure 5.4. A schematic representation of configurations A, B and C for the $2 \times 2 \times 1$ simulation cell of the bimetallic bulk structure with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configurations. The [110] plane is represented in red.	92
Figure 5.5. Atomic projections of the partial density of states (pDOS) for the d -electrons of the pure Pt and Ni metals, and configurations B and C of the bimetallic bulk structures with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configuration. The α and β symbolise the majority and minority spin channels, respectively.	93
Figure 5.6. The density of states and band structure for configuration B of the bimetallic bulk structure with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configuration. α and β stand for the majority and minority channel of the spins, respectively.	94

Chapter 6.

Figure 6.1. $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bulk represented by a) supercell ($2 \times 2 \times 1$) and b) supercell ($2 \times 2 \times 2$); Pt in green, Ni in pink/purple.	104
Figure 6.2. A schematic representation of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bulk cleaving process by changing the fractional cleave depth.	105
Figure 6.3. A schematic representation of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bulk cleaved into (111) surface terminations by changing the fractional cleave depth, to 0.0, 0.5, 1.0, 1.5 and 2.0.	105
Figure 6.4. A schematic representation of a hydrogen molecule adsorbed onto the a) atop, b) bridge, c) <i>hcp</i> hollow and d) <i>fcc</i> hollow sites for the five surface terminations.	106
Figure 6.5. A schematic representation of an H_2O molecule adsorbed onto the top sites at a) $_{0.5}\text{Pt}^*$, b) $_{0.5}\text{Ni}^*$, c) $_{1.5}\text{Pt}^*$ and d) $_{1.5}\text{Ni}^*$ surface.	107
Figure 6.6. Hydrogen adsorption energy (E_{ads}) onto the five $(4 \times 4) - 4\text{L}$ surface terminations for <i>fcc</i> adsorption site, where the surface coverage is 0.0625 ML.	111
Figure 6.7. Hydrogen adsorption energy (E_{ads}) onto the five $(4 \times 4) - 4\text{L}$ surface terminations for <i>hcp</i> adsorption site, where the surface coverage is 0.0625 ML.	112
Figure 6.8. Hydrogen adsorption energy calculated on the $_{0.5}(111)$ surface with increasing surface coverage for the <i>fcc</i> adsorption site.	113
Figure 6.9. Comparison of the hydrogen adsorption energy with increasing surface coverage for the Pt (111) Ni (111) and $_{0.5}(111)$ surface termination, for the <i>fcc</i> adsorption site.	113
Figure 6.10. Visual representation of a) isolated H_2O molecule, b) the single water molecule bonded to the metal surface through the metal to hydrogen (MH) and c) metal to metal (MM) bond lengths.	115

Figure 6.11. Iso-density contours of the different electron densities for the water adsorbed metal surfaces. The loss of electrons is indicated in blue, while the red indicates electron enrichment.....	117
Figure 6.12. Iso-density contours of the difference electron densities for the adsorption of one H ₂ O molecule on the mixed metal surfaces.....	119

Declaration

I, Louise Magdalene Botha, declare that the thesis entitled: “Screening of Pt/Ni bimetallic electrocatalysts using DFT calculations”, submitted in fulfilment of the requirements for the degree *Philosophiae Doctor* in Chemistry, is my own original and independent work under the supervision of Prof C.G.C.E. van Sittert and Dr M.J. Ungerer, except where acknowledged in the text, and has not been submitted in whole or in part to any other tertiary institution.

Signed at North-West University (Potchefstroom Campus)

A black rectangular box containing a handwritten signature in black ink. The signature appears to be 'L. Botha'.

Louise Magdalene Botha

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Preface

This thesis describes a combined theoretical and computational study executed within the field of material science and electrocatalyst design. In this thesis, alternative electrode materials for the water-splitting reaction were investigated. The investigation was not limited to existing electrode materials, but also towards the construction of new bimetallic electrode materials, consisting of Pt and Ni. Therefore, this study focussed on elucidating the effectiveness of Pt/Ni bimetallic surfaces as alternative electrocatalysts through several surface and electronic property investigations.

The thesis was submitted in Chapter format, in accordance with the rules stated in the General Academic Rules (2019) for doctoral studies by the North-West University (NWU)¹, and is written in British English. The articles, derived from the results generated in this study, were submitted/published as research articles to/in scientific journals and only one article which was published is included in the supplementary information in this thesis. Overall, this thesis is presented as a unit, as required by the General Academic Rules (2019) and repetition of conclusions/text/tables or figures may occur throughout the thesis including the content of published articles.

The thesis is a compilation of several chapters, graphically outlined in **Figure P.1**.

Part 1: Prologue to study
Chapter 1: Introduction
• Background and rational. • Problem statement. • Aim and objectives of the study. • Methodology of the study.
Chapter 2: Literature study
• Introduction. • Electrochemical devices. • Electrocatalyst and computational background.
Chapter 3: Model development and validation using pure Pt and Ni
• Introduction. • Computational model. • Results and discussions.
Part 2: Pt/Ni bimetallic systems
Chapter 4: Construction of $Pt_{0,x}Ni_{0,y}$ surface slabs using a random manual technique
• Introduction. • Computational model. • Results and discussions. (Draft article 1)
Chapter 5: Developing a thermodynamically stable Pt/Ni bimetal
• Introduction. • Computational model. • Results and discussions. (Published article and draft article 2)
Part 3: Epilogue – Application of bimetallic (111) surfaces.
Chapter 6: Water adsorption onto the most stable $Pt_{0,5}Ni_{0,5}$ surface
• Introduction. • Computational model. • Results and discussions. (Draft article 3)
Chapter 7: Conclusion and future work

Figure P.1. Compilation of the thesis and articles.

As outlined in **Figure P.1**, the thesis is divided into four **Parts**. The first part serves as an introduction to the field of research and consists of three chapters. **Chapter 1** is the introduction Chapter to the thesis and contains the background and rational, the problem statement, the aim, the objectives and the methodology of the study. The next Chapter, **Chapter 2**, covers the electrochemistry theory and related computational models in the form of a comprehensive literature study. This literature chapter is followed by the model development, **Chapter 3**, where existing computational models were adapted to aid in the investigation of Pt/Ni systems. The k -point grids where the energy was the lowest, were obtained for the Pt and Ni bulk structures, as well as the Pt (111) and Ni (111) slabs, by varying the k -points to obtain the lowest energy for these systems. Lattice parameters for the Pt and Ni bulk structures were calculated with the adapted computational model and compared to literature values. Additionally, surface energies and work functions of the Pt (111) and Ni (111) metal surfaces as well as the adsorption energies for hydrogen on these surfaces, were investigated to validate the computational model. After the computational model was validated, the model was applied to all surface calculations throughout the remainder of the thesis.

The next **Part** of this thesis, namely **Part 2**, covers the concept of bimetallic systems. It consists of investigating the two types of construction techniques used to create the Pt/Ni bimetallic surfaces in this study. The first technique investigated was the random manual technique, described in **Chapter 4**. In this technique, a bimetallic surface was constructed from a pre-existing Pt (111) surface by manually and randomly substituting 25 %, 50 % and 75 % of the Pt atoms with Ni atoms. In this Chapter, hydrogen adsorption investigations were carried out to investigate the tune-ability of the bimetallic surfaces in terms of the ensemble and ligand effects. The second technique, an automated systematic technique, is described in **Chapter 5**. In this technique, a Pt/Ni bimetallic unit cell was constructed by using a computer program, namely the site occupancy disorder (SOD) program. This computer program, SOD, automatically creates and calculates all the possible configurations for a specified unit cell size (bulk structures), consisting of predefined ratios of Pt and Ni atoms. The most favourable ratio was obtained using thermodynamic calculations. Thereafter, the total number of calculated Pt/Ni bulk structures configurations (153 configurations) for the most favourable ratio ($\text{Pt}_{0.5}\text{Ni}_{0.5}$) were narrowed down to three configurations using Boltzmann-modulation at 300 K. $\text{Pt}_{0.5}\text{Ni}_{0.5}$ (111) surfaces were constructed from the thermodynamically most stable bulk structure configuration. To conclude this chapter, hydrogen adsorption investigations were conducted on the Pt/Ni bimetallic surfaces. Notably, some of the results obtained from **Chapter 5** have been published as an article in RCS Advances², while three more articles are pending submission for end 2021.

Part 3 of the thesis consists of the preliminary adsorption study of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic (111) surfaces. This part covers the content in **Chapter 6**. In this part, the first steps are taken in applying the thermodynamic stable bimetallic surface, obtained in **Chapter 5**, to investigate Pt/Ni bimetallic surfaces as potential electrocatalysts for either the OER or ORR. This application is done by absorbing a single water molecule (H_2O) onto the thermodynamic stable bimetallic surface. The ability of the bimetal surfaces to adsorb a single water molecule, and the behaviour of the water molecule on the metal surface, were investigated and compared to the performance of Pt (111) and Ni (111) surfaces. A manuscript on the results obtained in this chapter are being finalised for submission to a peer-reviewed journal, namely RCS Advances.

The conclusions reached in **Chapters 4-6** are summarised and an evaluation of the study is presented in **Chapter 7**. Additionally, a section of **Chapter 7** discusses the possibility of conducting future studies where the investigation was beyond the scope of this study.

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2. L. M. Botha, D. Santos-Carballal, U. Terranova, M. G. Quesne, M. J. Ungerer, C. G. C. E. van Sittert and N. H. de Leeuw, *RSC Advances*, 2019, **9**, 16948-16954.

List of conference poster/oral presentations and publications

List of poster presentations

CASTEP model to investigate hydrogen adsorption on Pt (111), Ni (111) and Al (111) surfaces, **L.M. Botha** and C.G.C.E. van Sittert, CATSA2017 (Annual conference of the Catalyst Society of South Africa), Kwa Maritane Bush Lodge, Pilanesberg, North-West, South Africa, November 2017.

Investigating hydrogen adsorption on pure and bimetallic Pt and Ni (111) surfaces – a DFT study, **L.M. Botha** and C.G.C.E. van Sittert, Centre for High-Performance Computing conference, Velmoré Hotel Estate, Pretoria, South Africa, December 2017. (This poster was awarded 2nd prize for the best student poster.)

Mixing thermodynamics and electronic structure of the $Pt_{1-x}Ni_x$ ($0 \leq x \leq 1$) bimetallic alloys, **L.M. Botha**, C.G.C.E. van Sittert, D. Santos-Carballal, U. Terranova, M.G. Quesne, M.J. Ungerer and N.H. de Leeuw, SSCG (Solid-state chemistry group) Christmas Meeting, University College London, London, United Kingdom, December 2018.

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List of oral presentations

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Vermengingstermodinamika, magnetise inskappe en elektroniese struktuur vir Pt_xNi_{1-x} legerings, **L.M. Botha**, C.G.C.E. van Sittert, D. Santos-Carballal, U. Terranova, M.G. Quesne, M.J. Ungerer and N.H. de Leeuw, Studentesimposium in die Natuurwetenskappe, Universiteit van die Vrystaat, Bloemfontein-kampus, Suid-Afrika, November 2019. (Received 4th place for best student presentation.)

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What are electrocatalysts and why are they important, **L.M. Botha**, C.G.C.E. van Sittert and M.J. Ungerer, 5th BRICS Young Scientist Forum, Stand up presentation contest, Chelyabinsk, Russia, September 2020.

List of publications

Mixing thermodynamics and electronic structure of the $\text{Pt}_{1-x}\text{Ni}_x$ ($0 \leq x \leq 1$) bimetallic alloy, **L.M. Botha**, D. Santos-Carballal, U. Terranova, M.G. Quesne, M.J. Ungerer, C.G.C.E. van Sittert and N.H. de Leeuw, RSC Advances, 2019, **9**, 16948-16954.

Vermengingstermodinamika, magnetiese eienskappe en elektroniese struktuur vir $\text{Pt}_x\text{Ni}_{1-x}$ legerings, **L.M. Botha**, M.J. Ungerer and C.G.C.E. van Sittert, Vol 39 No 1 (2020), Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie / South African Journal of Science and Technology.

Catalytic dissociation of a water molecule on the (111) surfaces of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetal: Density Functional Theory (DFT) study. **L.M. Botha**, M.J. Ungerer and C.G.C.E. van Sittert, to be submitted, RSC Advances, early 2021.

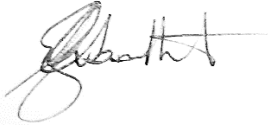
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Comparison of the reactivity of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ (111) surfaces created with different construction methods, **L.M. Botha**, C.G.C.E. van Sittert and M.J. Ungerer, unpublished. (Plan to submit the manuscript to RSC Advances, 2021)

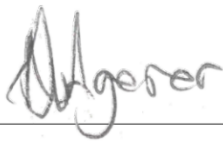
Catalytic dissociation of molecular hydrogen on $\text{Pt}_{0.5}\text{Ni}_{0.5}$ (111) surfaces, **L.M. Botha**, M.J. Ungerer and C.G.C.E. van Sittert, unpublished. (Plan to submit the manuscript to RSC Advances, 2021)

Consent by co-authors

The co-authors of the article(s)/manuscript(s) were informed that the PhD thesis would be submitted in chapter format for examination, and they gave their consent.



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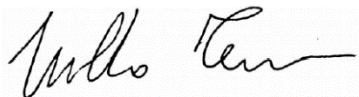
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Summary

Clean, renewable energy could be produced from the electrocatalytic splitting and recombination of water in electrolyzers and fuel cells, called electrochemical devices. However, the development of these electrochemical devices is limited by the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). These reactions require an overpotential of 1.23 V, leading to slow reaction kinetics. The overpotential could be lowered and the reaction kinetics improved by using electrocatalysts and using acidic electrolytes. In the case of electrocatalysts, the electrode materials that could be used are limited. It is limited even further if an acidic media is used because acidic media destabilises electrode materials by dissolution/corrosion.

In previous studies, precious metal electrodes, amongst others, have shown catalytic activity towards the OER and ORR. Of these precious metal electrodes, platinum (Pt) is the most used commercial electrocatalyst. However, Pt is only catalytically active for the ORR but not for the OER. Additionally, Pt is a rare, expensive resource that is not stable in acidic media. For these reasons, various studies have been conducted to identify an alternative cost-effective and stable electrocatalyst for the OER and ORR.

One possibility that has shown potential is the development of bimetallic surfaces since the activity, selectivity and stability (also called lifetime) of a metal, such as Pt, could be fine-tuned through the addition of a secondary metal. In this study, nickel (Ni) was chosen as the secondary metal because Ni-based electrodes showed excellent performance towards the OER.

However, before the Pt/Ni bimetallic surfaces could be investigated as potential electrocatalysts for the OER and ORR, a computational model had to be developed. Pure Pt and Ni unit cells were used to develop the computational model by adapting existing density functional theory (DFT) models for Pt and Ni. The adapted computational model was validated by comparing the structural and electronic properties of the pure Pt and Ni unit cells with literature values. Slab systems with (111) surfaces were created for Pt and Ni. Further validation of the adapted computational model was done by comparing the structural and electronic properties of Pt (111) and Ni (111) slabs to literature values.

The next step in this study was to construct Pt/Ni bimetallic systems. Two techniques for the construction of Pt/Ni bimetallic systems, namely a random manual and an automated systematic technique, were employed.

The random manual technique is a simplistic technique that involves the manual substitution of Pt atoms with Ni atoms in a pre-existing Pt (111) surface constructed from optimised pure Pt bulk structures. Using the manual substitution technique, the ensemble and the ligand effect were investigated separately. Moreover, hydrogen adsorption investigations were performed on these bimetallic surfaces. The results obtained for these investigations showed that the adsorption ability of a bimetallic surface could be fine-tuned by using either the ligand or the ensemble effects. However, this random manual is not sufficient to investigate all inequivalent configurations and is not scientific reproducible.

In contrast, the automated systematic technique is a more scientific reproducible technique that uses a computer program, SOD, to create all possible inequivalent configurations for a selected size of the Pt/Ni bulk structures. In addition, SOD allowed the user to obtain thermodynamic data, which was used to calculate thermodynamic properties such as the full-disorder entropy, mixing enthalpy and a probability distribution. These thermodynamic properties were used to narrow down the possible inequivalent configurations, and to obtain the optimal Pt/Ni ratio and Pt/Ni atomic arrangement for a bimetallic bulk structure. A Pt/Ni bimetallic surface was constructed from the optimal Pt/Ni ratio and Pt/Ni atomic arrangement bulk structures obtained from the automated systematic technique.

Finally, the reactivity of the Pt/Ni bimetallic surfaces, constructed with the random manual technique and the automated systematic technique, were investigated. The surface and electronic properties, namely the surface energy, work function, *d*-band centre, binding energy and the adsorption energy which was obtained by the adsorption of an elementary hydrogen on the Pt/Ni bimetallic slab surfaces. From the comparison of the results obtained for the Pt/Ni bimetallic bulk structures and surface systems, constructed by the two techniques, it was obvious that the automated systematic technique gave more consisted results. The reason being that the surface slabs created using the random manual technique resulted in an uncertainty of the configuration stability, which was observed from the varying surface reactivity results for each of the adsorption sites. However, the results obtained using the automated systematic technique concluded that a bimetallic bulk structures consisting of a Pt_{0.5}Ni_{0.5} mixture was stable and exhibited favourable magnetic properties, which is a contributing factor towards the reactivity of the surface. In addition, the *d*-band centre of the Pt/Ni bimetallic surface, constructed from the Pt_{0.5}Ni_{0.5} bulk structures, shifted towards the Fermi level. This shift indicated an increase in the hydrogen binding energy (HBE). The HBE exhibited by the Pt/Ni (111) bimetallic surface was higher than the HBE obtained for the Pt (111) surface, but weaker than the HBE for the Ni (111) surface. This HBE indicated that the surface reactivity of the Pt surface was successfully modified by the addition of Ni.

Lastly, the adsorption of a single H₂O molecule on the bimetallic surfaces constructed from the Pt_{0.5}Ni_{0.5} bulk structures was investigated. From the H₂O adsorption results it could be concluded that these bimetallic surface slabs could be potential electrocatalysts for either the OER or ORR, since cleavage of the water molecule occurs on the surface.

Although experimental data is needed to support the results in this thesis, the conclusion is that Pt/Ni bimetallic surfaces are the future for the water splitting reactions.

Keywords: Oxygen evolution reaction, Oxygen reduction reaction, Electrocatalysts, Bimetallic catalysts, Hydrogen adsorption

PART 1

Prologue to study

1

Introduction

This chapter provides a general overview of the importance of electrochemical devices, such as electrolyzers and fuel cells. Electrochemical devices are used to convert chemical energy, obtained from bond breaking (electrolyzers) or bond formation (fuel cell) reactions, into electrical energy. In the case of water electrolysis, these electrochemical devices could be viewed as a battery which can provide sustainable energy by repeatedly splitting water into hydrogen and oxygen followed by the formation of water from hydrogen and oxygen. However, the development of these electrochemical devices is hindered by the overpotential required for some of the half-reactions taking place during the splitting and formation of water. The overpotential is indirectly influenced by the type of material used for the electrocatalyst in these devices. Hence, in this chapter, the overpotential hindrances of these electrochemical devices are outlined by the problem statement. The desired outcome of this study is stated in the aim and objectives, along with the methodology which was applied to achieve the outcome.

1.1. Background and rational	3
1.2. Problem statement	4
1.3. Aim of the study.....	5
1.4. Objectives of the study	5
1.5. Methodology of the study	6
1.6. References	7

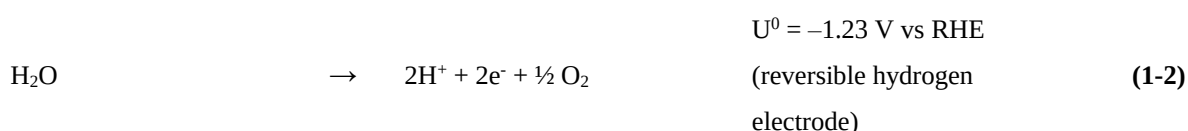
1.1. Background and rational

One of the biggest concerns today is climate change. Climate change is a result of increased fossil fuel usage due to population growth and the increasing demand for electrical energy for transport, industry and electricity. It is of utmost importance to decrease the usage of fossil fuel and as a result decrease the amount of greenhouse gasses produced. These greenhouse gasses are released into the atmosphere, preventing solar heat from escaping through the earth's atmosphere. The increased solar heat leads to global warming, which leads to climate change.

To address the ever-increasing demand for electrical energy but decrease the usage of fossil fuels, the development of affordable, clean and renewable energy sources and technology (mechanical or electrochemical devices) have become crucial in recent years.¹⁻⁸ Examples of renewable energy sources are the sun, wind, water and hydrogen. All these renewable energy sources need some sort of technology to convert the energy to electrical energy. Solar panels are used to convert the energy from the sun, whereas turbines are used to convert the energy generated from wind and water resources. In the case of hydrogen as a resource, electrochemical devices, such as electrolyzers and fuel cells are used.⁹⁻¹² Of the above mentioned renewable energy sources, hydrogen is the energy source that excels in the storage and discharge rate of energy.^{13, 14} However, hydrogen does not occur naturally and has to be obtained from the catalytic splitting of water into hydrogen and oxygen, as shown in equation (1-1).¹⁵



The electrochemical splitting of water takes place in electrolyzers. In the electrolyzers, the water-splitting involves two half-reactions, namely the oxygen evolution reaction (OER)^{16, 17} and the hydrogen evolution reaction (HER)¹⁴. The OER, shown in equation (1-2), is the oxidation which occurs at the anode and the HER, shown in equation (1-3), is the reduction process which occurs at the cathode.



On the other hand, the reformation of water (reverse reaction of equation (1-1)) takes place in fuel cells, where the fuel is hydrogen and the oxidising agent is oxygen. In these fuel cells, the water reformation involves the reverse half-cell reactions used in electrolyzers, namely the hydrogen oxidation reaction (HOR) at the anode (1-4) and the oxygen reduction reaction (ORR) at the cathode (1-5).^{18, 19}



As could be seen above, an overpotential (U^0) of 1.23 V vs RHE is required for the OER and ORR to occur.²⁰⁻²² This overpotential leads to slow reaction kinetics, which hinders the development of electrolyzers and ultimately

fuel cells.²⁰⁻²² The overpotential can be lowered with an appropriate electrocatalyst.^{8, 23-25} However, the choice of electrocatalyst is influenced by the pH of the electrolyte (medium) in which the OER and ORR take place.^{24, 26}

1.2. Problem statement

In acidic media, the OER and ORR occur faster than in alkaline media.²⁷ In an attempt to lower the overpotentials required by the OER and the ORR in acidic media, mainly precious metals have been used as electrocatalysts.²⁸ Hence, the overpotential trend for the OER in acidic media with precious metal electrocatalysts is ruthenium (Ru) < iridium (Ir) < palladium (Pd) < rhodium (Rh) < platinum (Pt), while the reverse trend is observed for the ORR.^{15, 28, 29} Based on this trend, Pt-based electrocatalysts are used in ORR due to the excellent performance of these electrocatalysts towards the ORR.^{15, 28, 30-34} An alternative to precious metal electrocatalysts are precious metal oxides.^{23, 35} For example, the benchmark electrocatalysts for the OER consists of precious metal oxides, IrO₂ and RuO₂, which are highly reactive due to their high current density.^{10, 20, 36} However, although lower overpotentials are exhibited by these benchmark electrocatalysts, they cannot be used on a large scale due to their high cost, low natural abundance and their instability in acidic and alkaline solutions.^{10, 20, 36} At present, the OER and the ORR cannot be used on a commercial or industrial scale due to the high cost and instability in acidic and alkaline solutions of the available electrocatalysts.

As a result, numerous investigations have been conducted on various electrocatalysts^{15, 37, 38} to obtain an alternative cost-effective and stable electrocatalyst for the OER and ORR. Some of the alternative electrocatalysts that have been investigated are non-precious (transition) metal oxides^{15, 37, 38} and bimetallic surfaces containing less Pt and a secondary metal.^{8, 25, 39-41}

Although transition metal oxides have long term corrosion resistance in alkaline solutions,²⁴ since most metal oxides and hydroxides are chemically stable at high pH, the number of transition metal oxides resistant to the oxidative potentials in acidic conditions are scarce.⁴² In the case of bimetallic surfaces, the activity, selectivity and lifetimes of a metal, such as Pt, could be fine-tuned through the addition of a secondary metal.^{1-7, 43} One example of a bimetallic electrocatalyst is nanoparticles consisting of a combination of Pt and Ni.^{8, 19, 44} A record low overpotential of 0.69 V was obtained for the ORR with these Pt/Ni nanoparticles.^{8, 19, 44} Additionally, Ni-based electrocatalysts have shown excellent performance towards the OER.^{8, 38, 45} Therefore, electrodes consisting of a combination of Pt and Ni, could be a possible bifunctional electrocatalyst for the OER and ORR.

In order to investigate combinations of Pt and Ni as electrocatalysts, the following research questions have been formulated:

- Could a computational model be developed to deliver calculated structural and electronic properties that are comparable with literature values?
- Can a Pt/Ni bimetallic slab be created by the random substitution of Pt atoms with Ni atoms (the random manual technique)?
- Is this Pt/Ni bimetallic slab, created by the random manual technique, viable for adsorption investigations?
- What is the influence of the ligand and ensemble effects on the reactivity of the Pt/Ni bimetallic slab? And can these effects be used to fine-tune the Pt/Ni bimetallic slabs?

- How do the surfaces of the abovementioned Pt/Ni bimetallic slabs compare to pure Pt (111) and Ni (111) surfaces?
- Is there a more scientifically repeatable method of constructing Pt/Ni bimetallic slabs?
- What are the optimal ratio and atomic arrangement of Pt and Ni in a stable bimetallic bulk structure?
- Are the Pt/Ni bimetallic surfaces, constructed from the optimal ratio and the atomic arrangement bimetallic bulk structures, stable?
- Are the abovementioned Pt/Ni bimetallic surfaces viable for adsorption investigations?
- How do the abovementioned bimetallic slabs compare to pure Pt (111) and Ni (111) surfaces?
- How will the Pt/Ni bimetallic surface fair as an alternative electrocatalyst, for the water splitting reaction, by using water as an adsorbate?
- What further steps need to be investigated to determine the suitability of these Pt/Ni bimetallic slabs for the OER and ORR reactions?

1.3. Aim of the study

The aim of the study is three-fold, namely:

- to use density functional theory (DFT) calculations to identify the most stable ratio of Pt and Ni in a Pt/Ni bimetallic bulk structure;
- to investigate the stability and reactivity of Pt/Ni bimetallic surfaces constructed from the most stable Pt/Ni bimetallic bulk structures; and
- to evaluate the performance of the most outstanding Pt/Ni bimetallic surface as a viable electrocatalyst for both the OER and ORR reaction.

1.4. Objectives of the study

To reach the stated aim of this study, the following objectives have been formulated:

- Review the literature in the areas of electrochemistry and computational modelling in surface science, to gain an understanding of these fields.
- Develop and validate a computational model for surface and electronic investigations of metal surfaces, and surface reaction investigations on these metal surfaces.
- Construct Pt/Ni bimetal bulk structures using two constructions techniques, namely a random manual technique and an automated systematic technique.
- Apply the computational model, developed and validated in objective 2, to investigate surface and electronic properties of Pt/Ni bimetallic surfaces constructed with the random manual technique.
- Use Pt/Ni bimetallic bulk structure constructed with the automated systematic technique to determine the optimal Pt/Ni ratio and atomic arrangement in the bimetal bulk structures.
- Construct Pt/Ni bimetallic surfaces from the abovementioned (optimal) Pt/Ni bimetal bulk structures obtained from the automated systematic technique.
- Apply the computational model, developed and validated in objective 2, to investigate surface and electronic properties of Pt/Ni bimetallic surfaces constructed with the automated systematic technique.

- Compare the Pt/Ni bimetallic surfaces, constructed with the random manual technique and the automated systematic techniques, to identify the best construction technique.
- Investigate surface reactivity, as an alternative electrocatalyst for both the OER and ORR, through an examination of the performance of the surfaces toward hydrogen and water adsorptions.

1.5. Methodology of the study

In pursue of the investigation of Pt/Ni bimetallic surfaces as alternative electrocatalysts for both the OER and ORR, density functional theory (DFT) calculations were employed. DFT calculations are essential in the description of the chemical bond formation between a surface and a molecule. This bond formation is related to the magnetic states and *d*-band centres of transition metals, which in turn is an indication of the reactivity of the transition metals.

In this study the investigation consists of two distinct parts, namely the development and validation of a DFT model to be used in Pt/Ni systems: and the application of the validated DFT model to Pt/Ni bimetallic systems.

In the first part, pure Pt and Ni were used to develop a computational model by adapting existing DFT models.^{46, 47} The adapted computational model was validated by comparing structural and electronic properties, of the Pt and Ni metal unit cells, with literature values. Furthermore, surface slabs along the (111) Miller index were constructed from the Pt and Ni bulk structures, which were validated through the comparison of structural and electronic properties to literature values for Pt (111) and Ni (111) slabs. Moreover, the (111) surface was used in this study since it is known to be the most stable and dominant surface in nanoparticles of *fcc* metals.

The principal research technique employed in the adapted computational model were the Cambridge serial total energy package (CASTEP)⁴⁸ module, which is part of the BIOVIA Materials Studio software package.⁴⁹ The generalised gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (PBE)^{50, 51} and the Koelling-Hammon relativistic treatment were used.⁵² A computational cost effective geometric optimisation algorithm, two-point steepest descent (TPSD),⁵³ was used. The interaction between the core and valence electrons was described using Ultrasoft pseudopotentials (USP),^{54, 55} while an energy cut-off of 400 eV and a smearing value of 0.2 eV were used. A Monkhorst-Pack grid⁵⁶ of 11×11×11 *k*-points was used to carry out the integrations in the reciprocal space of the metal bulk structures, while a Monkhorst-Pack grid⁵⁶ of 5×5×1 *k*-points was used for the surface slabs. Notably, the zero-point energy is already incorporated in the results obtained with CASTEP and will not be mentioned throughout this study.

In the second part of this study, two construction techniques were used to create Pt/Ni bimetallic bulk structures, namely the random manual technique and the automated systematic technique.

The bimetallic surfaces constructed, using the random manual technique, consists of random Ni atom substitutions into an optimised Pt (111) slab. In other words, the construction of the (1:1) bimetallic Pt/Ni slab consists of substituting 25 %, 50 % and 75 % of the Pt atoms with Ni atoms in a (3×3)-4L Pt (111) surface slab. Notably, in this technique a Pt/Ni bulk structures was not constructed, nor was the bimetallic surface cut from a Pt/Ni bulk structures. The reason for not constructing a Pt/Ni bulk structures was to regulate the placement of Ni atoms in

the top layer of the bimetallic slab to separately investigate the ensemble and ligand effects. In order to investigate the ensemble effect, the environment surrounding the adsorption site must be varied. Therefore, the atoms surrounding the adsorption site was varied for only the first layer while the rest of the substitutions in the sublayers (layers 2-4) were held constant for all the surfaces investigated. As a result, the tune-ability of bimetallic surfaces will be studied to determine if it is possible. These bimetallic surfaces were optimised using the validated computational model based on CASTEP, developed in the first part.

On the other hand, the automated systematic technique used a more scientific and repeatable approach to create the Pt/Ni bimetallic bulk structures bulk arrangements. It also enabled the identification of the optimal Pt/Ni ratio in the bimetallic bulk structures. The automated systematic technique consisted of using a computer program, SOD, to calculate all the possible configurations for a Pt/Ni bimetallic unit cell (bulk structures) for a wide range of Pt/Ni ratios with 0% Ni, 25% Ni, 50% Ni, 75% Ni and 100% Ni. Thereafter, thermodynamic calculations, such as the full-disorder entropy, mixing enthalpy and a probability distribution, were calculated with the Vienna Ab initio Software Package (VASP)⁵⁷⁻⁶⁰ or the general utility lattice program (GULP)^{61, 62}, depending on the size of the bulk structures. These thermodynamic properties were used to determine the most stable ratio and configuration for a Pt/Ni bimetallic bulk structure. The most thermodynamically stable configuration for a Pt/Ni bimetallic bulk structures was used to construct (111) bimetallic surfaces. The Pt/Ni bimetallic bulk structures and surfaces were optimised using the validated DFT model.

The random manual and automated systematic techniques were compared by investigating the surface reactivity of the Pt/Ni bimetallic slabs, constructed by these techniques. The surface reactivity was investigated through the adsorption of elementary hydrogen. The surface reactivity could be determined by investigating the surface and electronic properties of the surface involved in the adsorption of elementary hydrogen. The surface and electronic properties calculated for the Pt/Ni bimetallic slabs were the surface energy, work function, *d*-band centre, binding energy and the adsorption energy. The systematic technique was identified, from these adsorption investigations, as the best construction technique.

The first step towards determining the suitability of these Pt/Ni bimetallic slabs, as electrocatalysts for the OER and ORR reactions, was taken by investigating the adsorption of a single H₂O molecule onto a Pt/Ni bimetallic surface.

All the CASTEP calculations were carried out using the facilities at the Centre for High-Performance Computing (CHPC) of South Africa.^{57-60, 63} While, the GULP, and a small amount of VASP calculations, were carried out using the facilities of the High-performance computing Wales (HPC Wales).⁶⁴

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2

Literature study

The objective of this Chapter is to review the literature in the areas of electrochemistry and computational modelling in surface science to gain an understanding in these fields.

2.1. Introduction	13
2.2. Electrochemical devices.....	13
2.2.1. Water splitting reaction (Electrolysers)	14
2.2.1.1. Oxygen evolution reaction (OER).....	14
2.2.1.1.1. Gibbs free energy for the OER.....	15
2.2.1.2. Hydrogen evolution reaction (HER).....	16
2.2.2.1.2. Gibbs free energy for the HER.....	16
2.2.2. Water formation reaction (Fuel cells).....	17
2.2.2.1. Oxygen reduction reaction (ORR).....	17
2.2.2.2. Hydrogen oxidation reaction (HOR)	18
2.2.3. Summary.....	18
2.3. Electrocatalysts	18
2.3.1. Ideal electrocatalyst	18
2.3.2. Volcano plot as a catalytic activity description of ORR/OER half-reactions	19
2.3.3. Structure of bimetallic surfaces	21
2.3.3. Summary.....	21
2.4. Computational background	22
2.4.1. Surface energy and Work function	23
2.4.2. Adsorption energy	24
2.4.3. Band structure and density of states	24
2.4.2.1 Computational study of the band structure	26
2.4.2.2. Computational study of density of states	28
2.4.3. Adsorption energy, <i>d</i> -band energy and hydrogen binding energies.....	28
2.4.4. Strain, ligand and ensemble effects	29
2.4.4.1. Strain effect	29
2.4.4.2. Ligand effect.....	30
2.4.4.3. Ensemble effect	31
2.4.4.4. Methods to distinguish the ligand effect from the ensemble effect	31
2.4.5. Surface magnetism.....	33
2.5. References	34
	95

2.1. Introduction

Global warming and climate change, due to pollution by fossil fuels, are the result of the ever-increasing demand for electrical energy. In order to keep up with the increasing demand for electrical energy, clean and renewable energy sources are needed.¹ To this end, technologies such as fuel cells, water-splitting technology including proton exchange membranes (PEM)² and photoelectrochemical (PEC) devices³, as well as metal-air batteries and CO₂ to fuel conversion,⁴ are the forerunners in achieving renewable energy. However, due to the high energy density and storage capacity of hydrogen, interest regarding the production of hydrogen as a renewable energy source has increased.^{3, 5, 6} To produce and use hydrogen as a renewable energy source, electrochemical devices such as electrolyzers and fuel cells are needed.^{6, 7} In the electrolyzers water is split into hydrogen and oxygen, and in fuel cells hydrogen and oxygen are combined to form water.

2.2. Electrochemical devices

As mentioned previously, electrochemical devices are electrolyzers and fuel cells, as shown in **Figure 2.1**.

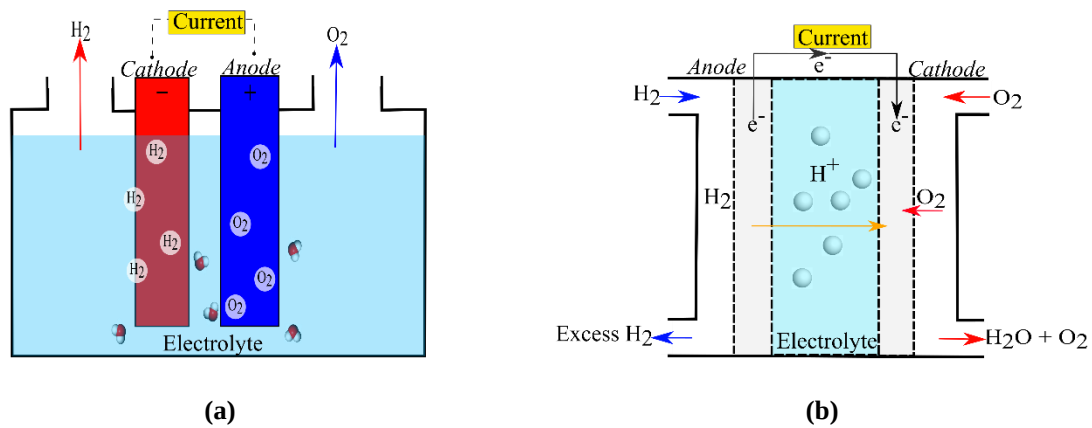


Figure 2.1. Illustration of **a)** an electrolyser and **b)** a fuel cell.

The core of the working of electrolyzers and fuel cells are a series of electrochemical processes, shown in **Table 2.1**. The electrochemical splitting of water in an electrolyser, **Figure 2.1 (a)**, involves two half-cell redox reactions, namely, the oxidation process at the anode **(2-1)** known as the oxidation evolution reaction (OER), and the reduction process at the cathode **(2-2)** known as the hydrogen evolution reaction (HER).^{8-10 9-11} The formation of water in the hydrogen-oxygen fuel cell, **Figure 2.1 (b)**, involves the hydrogen oxidation reaction (HOR) at the anode **(2-3)** and the electrocatalytic oxygen reduction reaction (ORR) at the cathode **(2-4)**.¹²

Table 2.1. Catalytic half-cell reactions used in electrolyzers (OER/HER) and fuel cells (HOR/ORR).

Anode				Cathode			
OER	$2\text{H}_2\text{O}$	$\rightleftharpoons$	$4\text{H}^+ + \text{O}_2 + 4\text{e}^-$	(2-1)	HER	$2\text{H}^+ + 2\text{e}^-$	$\rightleftharpoons$ H_2 (2-2)
HOR	H_2	$\rightleftharpoons$	$2\text{H}^+ + 2\text{e}^-$	(2-3)	ORR	$4\text{H}^+ + \text{O}_2 + 4\text{e}^-$	$\rightleftharpoons$ $2\text{H}_2\text{O}$ (2-4)

2.2.1. Water splitting reaction (Electrolysers)

As mentioned above, the electrocatalytic splitting of water is divided into two half-cell redox reactions: the oxidation process (OER) at the anode, and the reduction process at the cathode (HER).

2.2.1.1. Oxygen evolution reaction (OER)

The OER electrolysis is an important half-reaction involved in water splitting, and have been intensively investigated, both theoretically^{13, 14} and experimentally.¹⁵⁻¹⁸ Due to sluggish reaction kinetics, a catalyst is required to accelerate the reaction, which primarily depends on the nature of the electrode material and the electrolyte.¹⁹⁻²³ Moreover, the type of electrocatalysts and the efficiency of this electrocatalyst^{7, 14, 24} are limited by the large overpotential of 1.23 eV required for the reaction to occur.^{23, 25}

The mechanism for the OER is shown in **Table 2.2** for acidic and alkaline solutions. Molecular oxygen is produced at the anode during the electrolysis of water for acidic (2-5)²⁰ or alkaline (2-6) solutions.^{9, 10, 20}

Table 2.2. The OER mechanism in acidic and alkaline solutions.^{9, 10, 20}

$2\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{O}_2 + 4\text{H}_2^+ + 4\text{e}^-$	[acidic/ pH 0]	(2-5)
4OH^-	$\rightleftharpoons$	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	[alkaline/ pH 14]	(2-6)

In acidic solutions, hydrogen and oxygen molecules are produced from the oxidation of water molecules. This production of hydrogen and oxygen molecules is accompanied by the loss of electrons, as shown in **Table 2.3**.^{22, 26} In the equations adsorption on the surface of a catalyst is indicated as _{ads}. In the OER mechanism, the water dissociates on the surface and binds with the metal surface to form metal oxides, which then forms surface bonded hydroxyl species (2-7). These surface-bound species are then further oxidised to form adsorbed oxygen (2-8). Thereafter, a superoxide intermediate (2-9) is formed, which is a precursor to oxygen evolution (2-10).

Table 2.3. The OER mechanism in acidic solutions.^{22, 26}

$2\text{H}_2\text{O}$	$\rightarrow$	$\text{H}_2\text{O} + \text{OH}_{\text{ads}} + \text{H}^+ + \text{e}^-$	(2-7)
$\text{H}_2\text{O} + \text{OH}_{\text{ads}} + \text{H}^+ + \text{e}^-$	$\rightarrow$	$\text{H}_2\text{O} + \text{O}_{\text{ads}} + 2\text{H}^+ + 2\text{e}^-$	(2-8)
$\text{H}_2\text{O} + \text{O}_{\text{ads}} + 2\text{H}^+ + 2\text{e}^-$	$\rightarrow$	$\text{OOH}_{\text{ads}} + 3\text{H}^+ + 3\text{e}^-$	(2-9)
$\text{OOH}_{\text{ads}} + 3\text{H}^+ + 3\text{e}^-$	$\rightarrow$	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	(2-10)

However, the OER in acidic solutions is limited by the type of material that could be used as the catalyst, since the number of non-precious metal oxides which are resistant to the oxidative potentials in acidic solutions is scarce.²⁷ However, these metal oxides have a long term corrosion resistance in alkaline solutions,²⁰ since most metal oxides and hydroxides are chemically stable in alkaline solutions.

In alkaline solutions, oxygen and water are produced from the oxidation of the hydroxyl groups. This production of water and oxygen is accompanied by the loss of four electrons, as shown in **Table 2.4**.^{11, 26} The OH groups

adsorb onto the surface (2-11), which are then oxidised to form adsorbed oxygen (2-12). Thereafter, a superoxide intermediate (2-13) is formed from which oxygen is produced (2-14).

Table 2.4. The OER mechanism in alkaline solutions.^{11, 26}

4OH^-	$\rightarrow$	$\text{OH}_{\text{ads}} + 3\text{OH}^- + \text{e}^-$	(2-11)
$\text{OH}_{\text{ads}} + 3\text{OH}^- + \text{e}^-$	$\rightarrow$	$\text{O}_{\text{ads}} + \text{H}_2\text{O} + 2\text{OH}^- + 2\text{e}^-$	(2-12)
$\text{O}_{\text{ads}} + \text{H}_2\text{O} + 2\text{OH}^- + 2\text{e}^-$	$\rightarrow$	$\text{HOO}_{\text{ads}} + \text{H}_2\text{O} + \text{OH}^- + 3\text{e}^-$	(2-13)
$\text{HOO}_{\text{ads}} + \text{H}_2\text{O} + \text{OH}^- + 3\text{e}^-$	$\rightarrow$	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	(2-14)

Although the OER reaction will occur faster in the acidic solution than in the alkaline solutions,²⁸ the OER is still sluggish. To explain this, a schematic representation of the OER mechanism in an acidic electrolyte is described in terms of the Gibbs free energy, in the next section.

2.2.1.1.1. Gibbs free energy for the OER

The Gibbs free energy plot of the reactive species and the intermediates of the OER mechanism is shown in **Figure 2.2**, where the adsorbed intermediates are represented by O_{ads} , OH_{ads} and OOH_{ads} .

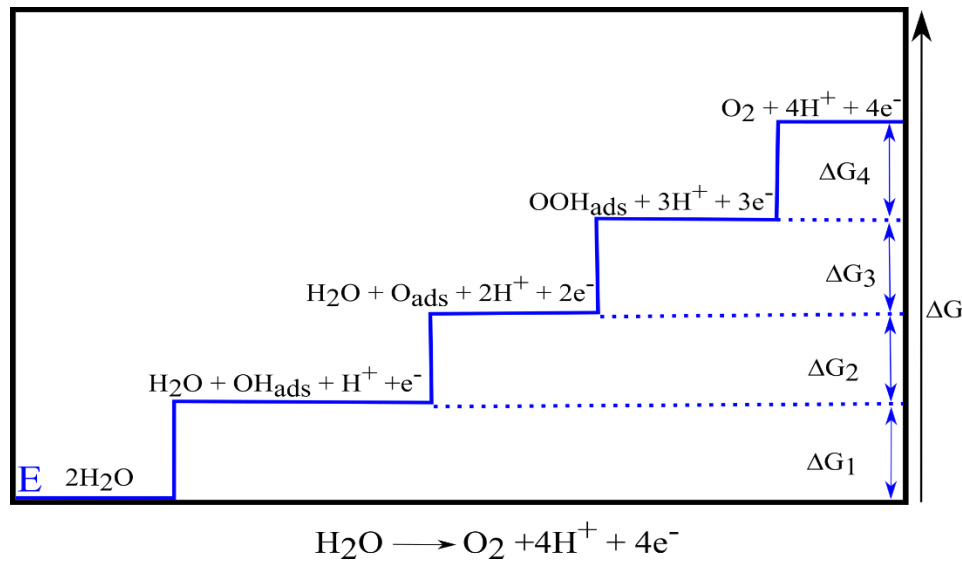


Figure 2.2. Schematic representation for the OER mechanism in an acidic electrolyte. In each step, a proton-electron pair is subtracted from the reactants so that water molecules are subsequently transformed into HO_{ads} , O_{ads} , HOO_{ads} and O_2 .

A function of the applied electrode potential for the reaction is represented by the blue line. The reaction energy of these steps shown in **Figure 2.2**, can be expressed in terms of the Gibbs free energies (ΔG , eV) of the intermediates (O_{ads} , HO_{ads} and HOO_{ads}), as shown in **Table 2.5**.²⁹ The Gibbs free energy is the energy obtained by subtracting the energies of the products from the reagents. In **Table 2.5**, the Gibbs free energies of the steps are expressed in terms of the activity of the proton (a_{H^+} ($a_{\text{H}^+} = 1$)) shift in the electron energy (V), the applied overpotential (eU), the Boltzmann constant (K_b , eV/K) and the temperature (T, 298.15 K).^{13, 14}

Table 2.5. Gibbs free energy for each intermediate for the OER.^{7, 13, 14, 26, 30}

ΔG_1	=	$\Delta G_{\text{HO ads}} - \Delta G_{\text{H}_2\text{O}} - eU + K_b T \ln a_{\text{H}^+}$ 1.23 eV	(2-15)
ΔG_2	=	$\Delta G_{\text{O ads}} - \Delta G_{\text{HO ads}} - eU + K_b T \ln a_{\text{H}^+}$ 2.46 eV	(2-16)
ΔG_3	=	$\Delta G_{\text{HOO ads}} - \Delta G_{\text{O ads}} - \Delta G_{\text{H}_2\text{O}} - eU + K_b T \ln a_{\text{H}^+}$ 3.69 eV	(2-17)
ΔG_4	=	$\Delta G_{\text{O}_2} - \Delta G_{\text{HOO ads}} - eU + K_b T \ln a_{\text{H}^+}$	(2-18)
ΔG^{OER}	=	Max [$\Delta G_1, \Delta G_3$] Max [$\Delta G_1, (3.2 \text{ V} - \Delta G_3)$]	(2-19)
ΔG^{ORR}	=	Max [$\Delta G_1, \Delta G_4$]	(2-20)

The value of $\Delta G_{\text{H}_2\text{O}}$ is zero since all the energies refer to water.^{7, 14} The thermodynamically least favourable reaction step is known as the potential-determining step **(2-19)**. This potential-determining step can either be where HO_{ads} is formed from O_{ads} (ΔG_2) or the transformation of O_{ads} to HOO_{ads} (ΔG_3) for the OER, which will be discussed in detail in section §2.3.1, using a volcano plot.⁷

2.2.1.2. Hydrogen evolution reaction (HER)

The HER reaction is kinetically favourable, as shown by the $E_{\text{H}_2/\text{H}^+}^0 = 0 \text{ V}$ (equilibrium potential) vs RHE.²⁸ The HER is a two-electron transfer reaction with one catalytic intermediate, namely H_{ads} , which is an adsorbed hydrogen on the surface of the catalyst.²⁸ The two-electron transfer reactions, such as HER, tend to have low overpotentials which can be easily reduced, and are discussed in detail later in the overpotential section (§2.3.2).^{7, 22} The HER mechanism, under acidic conditions, consists of a combination of the Volmer **(2-21)**, Heyrovsky **(2-22)** and Tafel **(2-23)** steps, as shown in **Table 2.6**.

Table 2.6. HER mechanism, under acidic conditions, following the Volmer, Heyrovsky and Tafel steps.³¹⁻³³

$2\text{H}^+ + 2\text{e}^-$	$\rightleftharpoons$	$\text{H}_{\text{ads}} + \text{H}^+ + \text{e}^-$	(2-21)
$\text{H}_{\text{ads}} + \text{H}^+ + \text{e}^-$	$\rightleftharpoons$	H_2	(2-22)
2H_{ads}	$\rightleftharpoons$	H_2	(2-23)

The reaction pathway either follows the 2-electron Volmer-Heyrovsky sequence **(2-21**³¹ and **2-22**³³) or the Volmer-Tafel sequence **(2-21**³¹ and **2-23**³²) depending on the electrode material.

2.2.2.1.2. Gibbs free energy for the HER

Since the HER is not the main focus of this study, it is only briefly discussed in terms of the free energy, as shown in **Figure 2.3**.

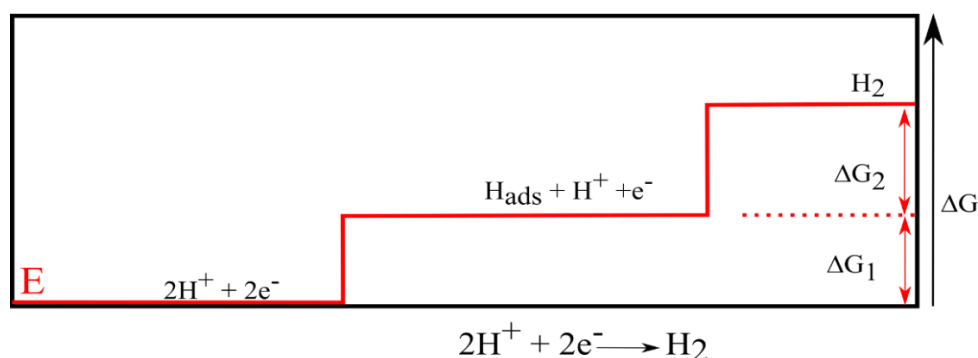


Figure 2.3. A schematic representation for the HER. In each step, a proton-electron pair is subtracted from the reactants so that water molecules are subsequently transformed into H₂.

The free energy is constructed as a function of the applied electrode potentials (E) and represented as a red line. In **Figure 2.3**, ΔG_1 and ΔG_2 express the elementary Gibbs reaction energies for the equations while the adsorbed intermediate is represented by H_{ads}. Since the HER is a simple reaction, only the adsorption free energy (ΔG_H) is needed to investigate the activity of this reaction.^{11, 23}

2.2.2. Water formation reaction (Fuel cells)

As mentioned previously, the water-forming reaction is divided into two half-cell redox reactions, namely, the oxidation process, i.e. HOR, at the anode and the reduction process at the cathode, i.e. ORR.

2.2.2.1. Oxygen reduction reaction (ORR)

Unlike with the HOR, the ORR is kinetically slow and requires an electrocatalyst. The electrocatalyst material that can be used is hindered by an overpotential of 1.23 eV vs RHE, which is required for the reaction to occur.^{22, 28} Moreover, the ORR reaction is also influenced by the electrolyte used, for instance, it was found that this reaction occurs faster under acidic conditions than under alkaline conditions.^{22, 28} The ORR and the OER mechanisms are similar, but in the reversed directions. The OER mechanism was discussed in detail in §2.2.1.1.

The ORR is a multi-step mechanism (as shown in **Table 2.7**) where the transfer of a proton-electron occurs to form a surface-adsorbed superoxide intermediate (2-24). Thereafter, a precursor (OOH_{ads}) occurs from an O–O bond break, as shown in (2-25). Finally, water is produced from (2-26) the reduction of a surface bonded HO_{ads}.

Table 2.7. The ORR mechanism in acidic and alkaline solutions.^{22, 28}

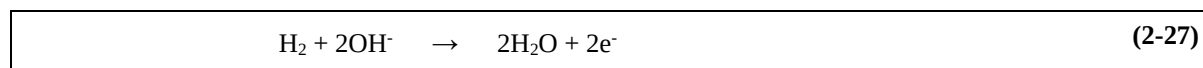
$O_2 + H^+ + e^-$	$\rightleftharpoons$	HOO_{ads}	(2-24)
$HOO_{ads} + H^+ + e^-$	$\rightleftharpoons$	$2OH_{ads}$	(2-25)
$HO_{ads} + H^+ + e^-$	$\rightleftharpoons$	H_2O	(2-26)

Since the Gibbs energies are similar for the ORR and the OER, the Gibbs energies, described in **Table 2.5**, can also be used for the ORR. Since the adsorption energies of O_{ads}, HO_{ads} and HOO_{ads} are scalable with one another, a linear combination of these equations is used to determine the potential-determining steps.⁷ Therefore, the ORR

has one potential-determining step for the ΔG^{ORR} (2-20), expressed as either $-\Delta G_1$ or $-\Delta G_4$ which is discussed in detail in the next section, §2.3.1, namely volcano plots.⁷

2.2.2.2. Hydrogen oxidation reaction (HOR)

The HOR half-reaction occurs with direct association and is a kinetically favoured reaction with an equilibrium potential (U^0) of 0 V vs RHE (reversible hydrogen electrode).²⁸ The overall HOR in an alkaline media is described in equation (2-27).³⁴ However, the detailed mechanism of the HOR is not discussed here, since it also follows the reversed pathway as the HER, which was discussed under the water-splitting reaction.



2.2.3. Summary

Future development of electrochemical devices is hindered by the large overpotential, 1.23 eV, required for the OER/ORR to occur. To overcome this hurdle, various studies were conducted in the field of electrocatalysts for the water-splitting reactions.^{8-10 9-11} Overall, the catalytic performance of the ORR and OER can be calculated from the magnitude of the potential determining step, G^{ORR} (2-20) and G^{OER} (2-19), respectively.

2.3. Electrocatalysts

Numerous studies have been conducted on transition metal oxides,^{14, 27, 35} perovskites,¹⁸ tri-metal alloys³⁶, bimetal alloys²¹ and doped⁷ materials to search for alternative OER/ORR electrocatalysts. The ideal electrocatalyst for the OER/ORR should be highly durable, have a low-cost, be high-earth abundant and be catalytically active. The catalytic activity of electrocatalysts could be characterised through overpotential.³⁷⁻³⁹

The overpotential (η) is the added potential needed to drive an electrochemical reaction at a certain rate. The calculation of the overpotential is shown in (2-28), where E is the electrode potential at equilibrium (no net flow or current) and E' is the electrode potential when a current is drawn from the cell.³⁹ Hence the overpotential for an electrode is the difference between the electrode potential and the equilibrium potential.^{40, 41} The theoretical overpotential at standard conditions for the OER and the ORR is shown in (2-29) and (2-30).¹⁴

Table 2.8. Overpotential (η) for the OER (η^{OER}) and the ORR (η^{ORR}).^{14, 40, 41}

η	=	$E' - E$	(2-28)
η^{OER}	=	$(G^{\text{OER}}) - 1.23 \text{ eV}$	(2-29)
η^{ORR}	=	$1.23 \text{ eV} - (G^{\text{ORR}})$	(2-30)

2.3.1. Ideal electrocatalyst

An ideal electrocatalyst, according to the Sabatier principle,⁴² should have medium bond strengths and bind the reaction intermediates not too weakly or too strongly. Hence, if a catalyst can be fine-tuned, then the strength of the adsorption of the reaction intermediates can be changed so that the reaction kinetics can be increased and a

minimum overall free energy can be obtained.⁴³ Overall, an ideal electrocatalyst for the OER and ORR should be able to facilitate the water oxidation just above the equilibrium potential (1.23 eV).¹⁴ This means for an ideal electrocatalyst, the free energy of the reaction intermediates, the reactant and the product, must have the same energy level. An example of an ideal catalyst is represented in **Figure 2.4**.

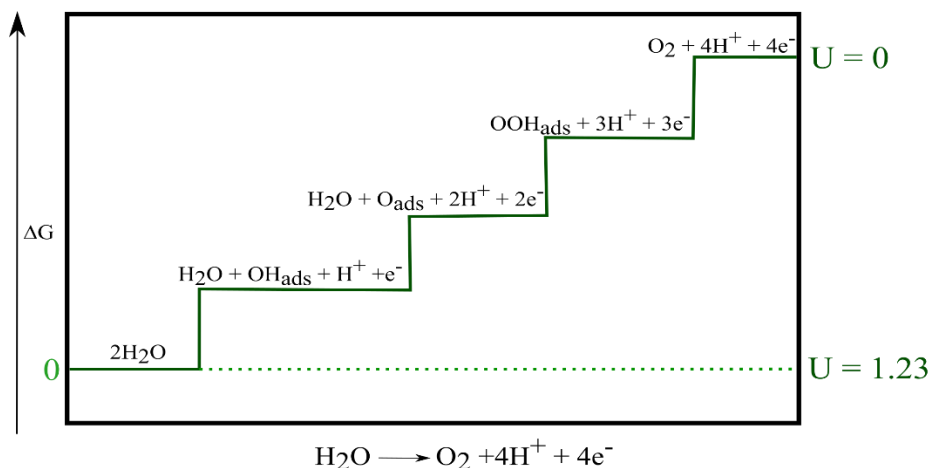


Figure 2.4. An ideal catalyst for the OER reaction at zero potential ($U = 0$) and at the equilibrium potential ($U = 1.23$ eV).

An ideal catalyst is when the difference in energy between the free energy steps is 2.46 eV.⁴⁴ This difference in energy (2.46 eV) is due to the transfer of the two protons and electrons that results in the energy values of $\Delta G_{\text{HOads}} = 1.23$ eV, $\Delta G_{\text{HOOads}} = 3.69$ eV and $\Delta G_{\text{Oads}} = 2.46$ eV.^{7, 14}

The catalytic activity of an electrocatalyst for the ORR/OER, on various surfaces, can be determined with the use of scaling relations, such as volcano plots.^{7, 14}

2.3.2. Volcano plot as a catalytic activity description of ORR/OER half-reactions

In the volcano plot (**Figure 2.5**), the reduction reaction is shown as a “^” shaped plot where the ORR volcano top is labelled, while the oxidation reaction is a “v” shaped plot where the OER volcano top is labelled. From **Figure 2.5**, the theoretical overpotentials (η_{OER} or η_{ORR}) are calculated by extending the ORR ($\Delta G_1 - \Delta G_4$) and OER ($\Delta G_2 - \Delta G_3$) volcano lines and finding the point where the (solid and dashed) lines meet with the equilibrium potential (1.23 eV). In the case of η_{OER} , this point is where the extended dashed line of ΔG_2 (---) meets the equilibrium potential and the solid line of ΔG_3 (—).

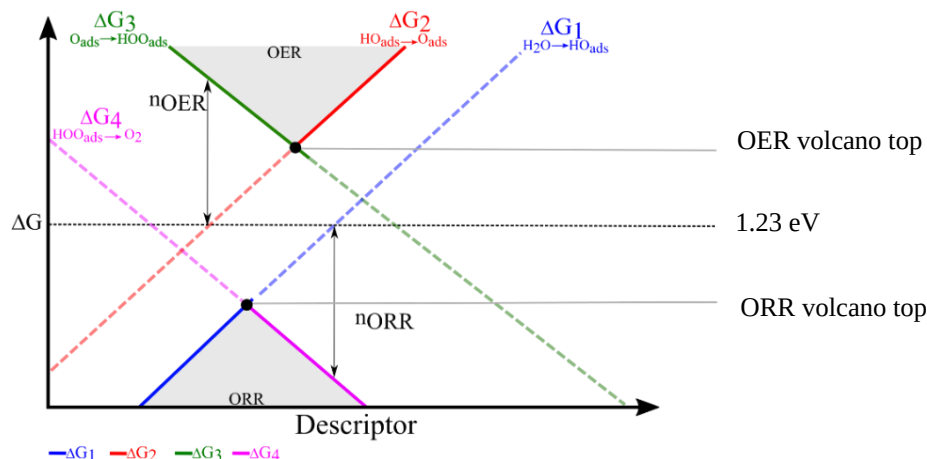


Figure 2.5. Volcano plots for the OER and ORR where each Gibbs energy is represented by ΔG_1 (blue), ΔG_2 (red), ΔG_3 (green) and ΔG_4 (pink). The solid lines are the volcano plots, while the dashes are an extension of the volcano plot so that the η^{ORR} and η^{OER} values can be calculated.

In volcano plots, the universal descriptor of the OER activities of a large set of data is $\Delta G_{\text{Oads}} - \Delta G_{\text{HOads}}$. This descriptor is used since the difference in energy levels between the potential-determining steps for the ORR [$-(\Delta G_1 + \Delta G_4)$] and the OER [$(\Delta G_2 + \Delta G_3)$] reaction is equivalent to $\Delta G_{\text{Oads}} - \Delta G_{\text{HOads}}$.¹⁴ A universal volcano plot can be obtained by plotting η^{OER} as a function of $\Delta G_{\text{Oads}} - \Delta G_{\text{HOads}}$ (**Figure 2.6**). Moreover, metal oxides are used in **Figure 2.6** since metal oxides (NiFeO_x ,⁴⁵ PtO_2 ,⁴⁶ IrO_2 (110)¹⁴) are more reactive towards the OER.

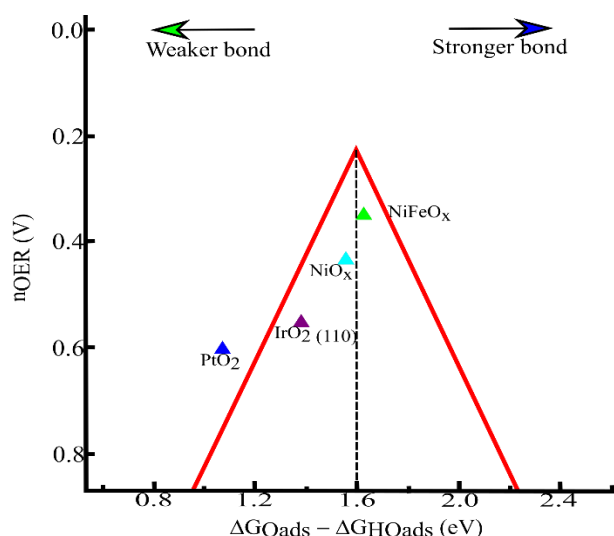


Figure 2.6. Universal volcano plots for the OER reaction regarding η^{OER} as a function of $\Delta G_{\text{Oads}} - \Delta G_{\text{HO}}$.

The bond strength of the catalyst is dependent on the position on the volcano plot. For instance, an ideal catalyst for the OER is where the catalyst is at the top of the volcano plot.

However, the number of transition metal oxides resistant to the oxidative potentials in acidic conditions are scarce.²⁷ For this reason, bimetallic surfaces where the activity, selectivity and lifetimes of a metal, such as Pt, could be fine-tuned through the addition of a secondary metal have been identified as possible catalysts for the OER.⁴⁷⁻⁵⁴

2.3.3. Structure of bimetallic surfaces

The development of bimetallic surfaces is used to fine-tune the activity and selectivity of the surfaces. This fine-tuning allows for the adjustment of the bimetallic surface, using metals with similar structural and electronic properties, to create a bimetallic surface with bifunctional properties for both the OER and ORR.

The mixing of two metals, to create a solid solution bimetallic alloy, is shown in **Figure 2.7**. The solid solution bimetallic alloy is dependent on the crystal structure, atomic radii and the electronic properties of the two parent metals. The properties of the two parent metals determine if the solid-solution bimetallic alloy is a substitutional (**Figure 2.7 (a)**), an interstitial (**Figure 2.7 (b)**), or an intermetallic (**Figure 2.7 (c)**) alloy. In a substitutional alloy, the two metals share the same crystal structure and electronic properties, while in an interstitial alloy the secondary metal has a smaller atomic radius which leads to the placement of the secondary metal atoms into the voids of the primary metal surface. However, if the two metals have distinct crystal structures and electronic properties an intermetallic compound is formed.⁵⁵

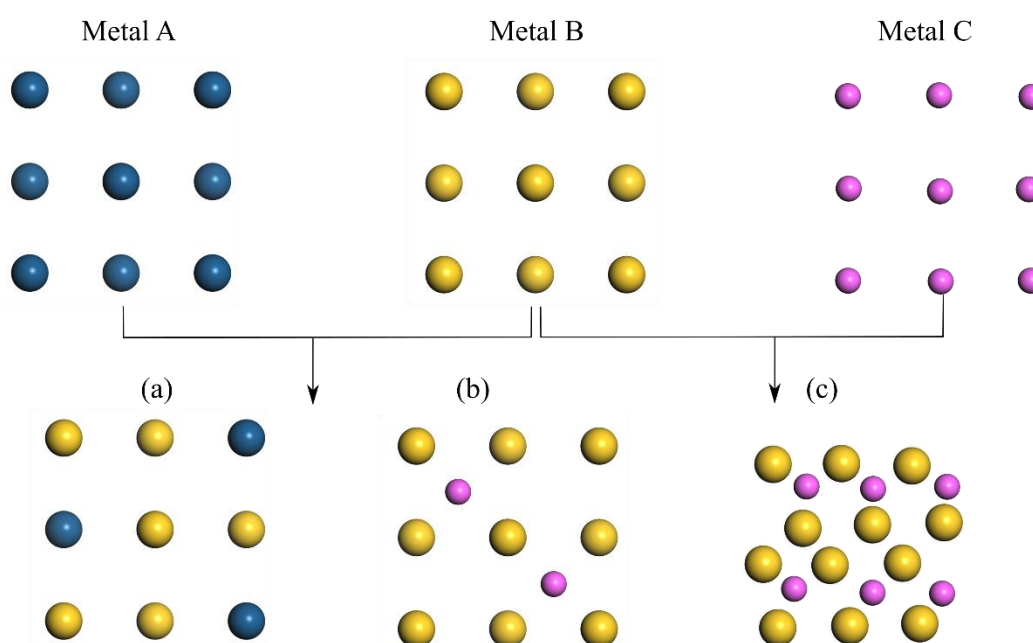


Figure 2.7. A simple representation of different types of solid-solution bimetallic alloys, namely **a)** a substitutional, **b)** an interstitial and **c)** an intermetallic compound.

2.3.3. Summary

In summary, numerous experimental¹⁵⁻¹⁸ and theoretical studies^{13, 14} have been conducted on various metal surfaces, which provide an understanding of the above-mentioned reactions (OER/ORR).¹⁹⁻²¹ This understanding enables the improvement of existing platinum group (PGM) electrocatalysts,^{4, 56} or the development of alternative catalysts, such as Pt⁵⁷ or Ni⁵⁸ skins, metal oxides,^{9, 13, 18} and bimetallic surfaces.^{7, 22, 59-64}

Although excellent performance in acidic solutions was obtained when IrO₂ and RuO₂ catalysts were used,^{9, 13, 18} these catalysts are expensive.⁶⁵ In the case of a bimetallic nanoparticle consisting of PtNi, a record low overpotential of 0.69 eV for the ORR was obtained. This indicated that PtNi nanoparticles are highly active

electrocatalyst for the ORR reaction.⁶⁶ On the other hand, excellent performance for the OER was obtained with a Ni-based electrode consisting of Ni-oxides ((oxy) hydroxide).^{66, 67}

These results imply that an electrode containing a combination of Pt and Ni, could have great potential as a bifunctional electrocatalyst for both the ORR and the OER.^{7, 18, 52, 68-73} Furthermore, bimetals have shown promise as an alternative electrocatalyst material since the catalytic reactivity, lifetime and selectivity of a bimetallic surface can be tailored to meet the requirements of the above-mentioned ideal electrocatalyst, i.e. lowering the free energy difference with respect to HOO_{ads} and HO_{ads} closer to 2.42 eV.^{51, 74-78}

However, despite the large amount of literature on the enhanced electrocatalytic activity of Pt/Ni alloys,^{58, 71, 72, 79-81} the relationship between the equilibrium composition of the mixture, the distribution of the metal atoms and the electronic structure are not yet fully understood.^{72, 52}

2.4. Computational background

Over the past three decades, various electronic and surface properties for metal surfaces have been investigated using computational means.^{68, 71, 82-87} It has been shown that the data obtained from these computational investigations, such as the binding energy and the adsorption energy, correlates well with experimental data.^{68, 71, 82-87} It has also been proven that the computational investigations are successful in explaining trends that are observed with regard to the reactivity of transition metals, bimetal surfaces and metal oxide surfaces.⁷ For this reason, computational investigations could be used in the design and fine-tuning of metal surfaces as catalysts.

The metal surface properties, such as the catalytic behaviour, reactivity, adsorption and surface segregation, are of interest for these surfaces to be used as catalysts. These surface properties are closely related to the electronic properties of the metal surfaces.^{41, 69, 71, 88, 89} Measurements of surface electronic properties are obtained from the surface energy (γ), work function (Φ), d -band centre (ϵ_d), adsorption energies (E_{ads}) and hydrogen binding energies (HBE).⁸³

There are various surface structures that can be created from cleaving the metal bulk structures using various Miller indices. As shown in **Figure 2.8**,⁴ different surface arrangements and surface densities are obtained from (a) low and (b) high-index surfaces. Moreover, the catalytic activity of the metal surface is influenced by the type of Miller indices used.⁸³

In **Figure 2.8 (a)**, the surface areas on the low-index surfaces, such as (111) and (100), are large. However, these types of surfaces show low catalytic activity. On the other hand, the high-index surfaces, **Figure 2.8 (b)**, are atomically dense, open structures with atomic steps and defects, which allows these surfaces to exhibit high catalytic activity.⁴ However, the high-index surfaces are impractical to use due to their small surface. Overall, it is more practical to carry out studies on the low-indexed (111) surfaces due to the large surface area and the numerous amounts of comparable computational and experimental data available for the (111) surfaces.

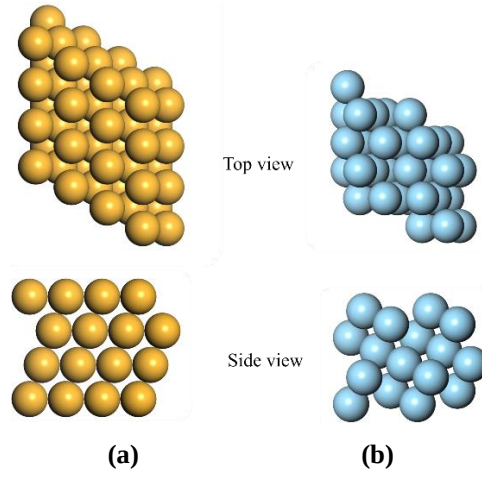


Figure 2.8. Comparison of the flat surface of **a)** a low-index (111), and **b)** the high-index (210) surface with atomic steps.

2.4.1. Surface energy and Work function

The surface energy (γ) is the amount of energy required to create a new surface when an infinite crystal is cleaved.⁸³ The surface energy of the unrelaxed system (γ_u) is calculated from equation (2-31), where E_{slab} is the total energy of the slab, $E_{\text{bulk structures}}$ is the total energy of the bulk structures in eV/atom, N is the number of atoms in the slab and A is the area of the slab. In a periodic slab system the area is multiplied by two (2A) since the surface consists of a top and a bottom surface;⁹⁰ whereas the relaxed system (γ_r) is calculated by subtracting the energies of the relaxed system ($E_{\text{slab relaxed}} - NE_{\text{bulk structures}}/A$) from the unrelaxed surface energies (shown in (2-32)).⁹⁰ In the relaxed system, the top two layers of atoms are allowed to relax.

$$\gamma_u = \frac{(E_{\text{slab unrelaxed}} - NE_{\text{bulk structures}})}{2A} \quad (2-31)$$

$$\gamma_r = \frac{(E_{\text{slab relaxed}} - NE_{\text{bulk structures}})}{A} - \gamma_u \quad (2-32)$$

The surface energy is dependent on the metal that is being studied. For example, in the case of Ni (which is a 3d metal) and of Pt (which is a 5d metal) the number of valence electrons in both metals is 10. However, their calculated surface energies are 2.60 J/m² and 2.45 J/m² for Ni (111) and 2.35 J/m² and 2.50 J/m² for Pt (111), respectively.^{86, 91, 92} The stability of a surface can be determined from the surface energy. For instance, a more stable surface exhibits lower surface energy, e.g., the surface energies show that Ni (111) surfaces are stable and that the removal of an electron from this surface will be more difficult than for Pt (111) surface.

The surface energy is also closely related to the work function (Φ). The work function is defined by equation (2-33), where e is the electron charge, ϕ is the electrostatic potential in the vacuum close to the surface and the Fermi level (E_F) inside the surface. The energy of an electron at rest in the vacuum near the surface is obtained by multiplying the electron charge with the electrostatic potential, $e\phi$.⁹⁰ The energy required to remove an electron from the surface is obtained by subtracting the Fermi level from the energy of an electron at rest in the vacuum near the surface.⁸³ The work function of each of the transition metal groups, for example, 3d and 5d, is similar to one another in regard to computational⁹¹ and experimental studies.⁸⁶ The work function for Ni have been

calculated to be between 5.4 eV to 5.8 eV, while for the work function for Pt metal have been calculated as being between 5.6 eV and 6.6 eV, depending on the computational settings used.⁹¹

$$\Phi = - (e.\varphi) - E_F \quad (2-33)$$

The surface energy and the work function are inversely proportional to one another for face-centred cubic (*fcc*) metals, such as Pt and Ni.^{83, 85} For instance, large surface energies indicate a stable slab surface where removing an electron from the metal surface will be difficult, and are indicated by a smaller work function value.⁸³ It has been shown that a notable difference in the computational and experimental values have been obtained, which is due to the dependency that slab approximations have on the thickness of the slab.⁸⁵

It is clear from the above-mentioned surface energies and work function values that the Ni surface is highly stable, resulting in the difficult removal of an electron from this surface as indicated by the low work function value. This low work function value means that strong bonding of adsorbents will occur on the Ni surface, while weak bonding occurs on the Pt surface. To conclude, the bond strength of the adsorbents to the metal surface is crucial when determining the type of electrocatalyst material that will be used during the electrochemical reaction investigated. For the OER and ORR, a preferred electrocatalyst material is a surface which binds the intermediates strongly enough to result in the production of all the reaction intermediates (O_{ads} , HO_{ads} and HOO_{ads}).

2.4.2. Adsorption energy

Hydrogen readily adsorbs/desorbs onto transition metal surfaces^{68, 71, 87} and reacts differently for each transition metal surface. This behaviour of hydrogen has been widely studied both experimentally and computationally.^{68, 71, 82-87} The reason is that adsorption and desorption of hydrogen, on transition metal surfaces, are promoted by energetically available *d*-orbitals.^{82, 87, 93, 94} The electronic structure of the surface changes due to adsorption of an adsorbate which is measured by the shift in the *d*-band centre.^{71, 88} Also, the shift in the *d*-band centre can be used to determine the reactivity of a metal surface since these two terms can be directly correlated with one another. Numerous studies investigating the shift of the *d*-band centre have been conducted to investigate the reactivity of transition metals, such as Pt^{82, 84, 93} and Ni.^{82, 94-96}

One method to characterise the nature of a metal and to describe the bonding of the material is to observe the electronic structure by calculating the Fermi level, band gap, type of the band gap, width of valence and conduction bands, effective mass of electron and hole, charge densities, band structures and the total and partial density of states (pDOS).⁹⁷

2.4.3. Band structure and density of states

As shown in **Figure 2.9** for solid systems, the orbitals overlap which give rise to energy level bands, which are separated by energy gaps, referred to as band gaps. Two states arise from the interaction of the electrons of the surface with the adsorbent state, known as the bonding (valence band) and the anti-bonding (conduction band) states which depends on the position of the bands relative to the Fermi level.⁹⁸ The Fermi level (E_F) is defined as the highest occupied state, at $T = 0$ K, in a solid.⁹⁹

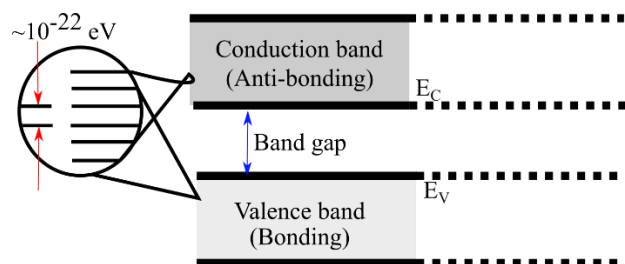


Figure 2.9. Forming of energy bands due to overlap of closely spaced orbitals.

In order to determine the bond strength of a surface with respect to an adsorbent, the filling of the conducting band, relative to the Fermi level ($E_F = 0$ eV), is determined.⁶⁹ In **Figure 2.10**, a notable observation for metallic surfaces is the lack of band gaps, which are values of the energy for which there is no molecular orbital. This lack of band gaps agrees with the conducting properties of metals.⁹⁸

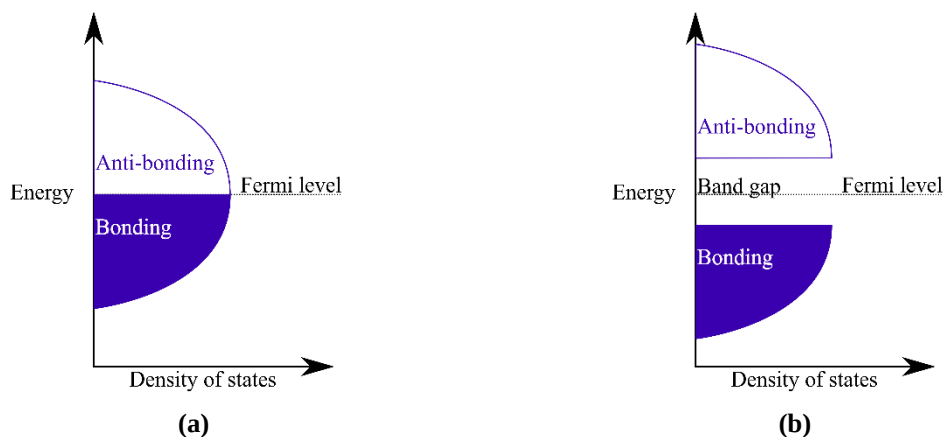


Figure 2.10. Projected representation of band structure and density of states for **a)** metal and **b)** an insulator or semiconductor.

The overlap of the s -, p - and d -orbitals give rise to energy level bands (s -, p - and d -bands) separated by band gaps. Therefore, the DOS is defined as the number of energy levels in an energy range where the energies across the bands are not uniform since some of the energy levels are more densely packed at the edges than at the centre which can be seen from **Figure 2.11**.⁹⁸

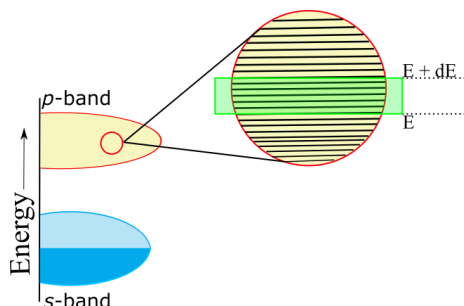


Figure 2.11. Simple representation to describe the forming of s - and p - energy bands.

The d -orbitals are mostly responsible for the bonding ability in transition metals while small influences are observed from the s - and p -orbitals.⁹⁸ A simple representation of the DOS in transition metals is shown in **Figure 2.12**, which is an approximate description of the bond formation on a transition metal surface.^{69, 66} In

transition metals, the *s*- and *p*-band are broad whereas the *d*-band is narrow. The *d*-band width and the orbital overlap are dependent on the type of material since the nuclear charge depends on the position in the periodic table.⁹⁸ Moreover, most of the electrons responsible for bonding are in the *d*-orbitals even though the *s*-, *p*-band penetrates the *d*-band (as shown in **Figure 2.12**).⁹⁸

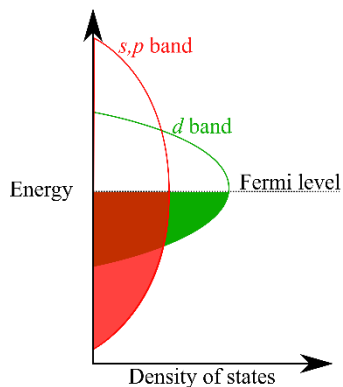


Figure 2.12. Projected representation of the density of states.

Two general trends apply regarding the bonding properties of transition metals.⁷¹ Firstly, the bond strength is stronger as one moves to the left in the periodic table. Secondly, interactions become weaker as one moves down the periodic table. These rules explain why the 5*d* metals are more noble than the 4*d* and the 3*d* metals.⁷¹ Therefore, the higher in energy the *d*-states are relative to the Fermi level the higher in energy the conducting band will be, and thus the stronger the bond.⁶⁹ In short, the strength of the bonds formed with the *d*-orbitals depend on the width of the *d*-band.⁹⁸

The structural properties of transitional metals are similar but the electronic properties of the transition metals differ from one another.⁷¹ Therefore, the position of a transition metal *d*-band is calculated from the *d*-band centre relative to the Fermi level, and is a good indicator of the bond strength between the metal surface and an adsorbate.^{69, 99} The position of the *d*-band centre on strained surfaces and metal overlayers correlates well with binding energies and reactivity of small adsorbates.^{100, 101} For instance, the anti-bonding states of the Pt and Ni metals are empty, and therefore adsorption will readily occur on these metal surfaces. Overall, the periodic trends of the chemisorption energy and the bonding strength of metal-adsorbate systems can be based on the coupling of the *d*-electrons in the metals due to the interaction between the *s*-, *p*- and *d*-bands of the adsorbate and the *d*-band the surface.^{71, 93}

Overall, the DOS is used to obtain information on the electronic structure of a material since this knowledge is a fundamental basis for understanding surface chemical reactivity and catalysis, and is used to describe the chemical bond between a surface and a molecule.⁶⁹ The *d*-band theory has successfully been used as an activity descriptor for metal surfaces,⁷¹ such as transition metal oxides,¹⁸ noble metals⁶⁸ and bimetals.¹⁰²

2.4.2.1 Computational study of the band structure

The electronic properties of a solid material are related to the underlying crystal symmetry of the material. The crystal symmetry of the material, i.e., face-centred cubic (*fcc*) and body-centred-cubic (*bcc*) packing arrangement, determines *k*-paths that divide the Brillouin zone.⁹⁷ The Brillouin zone for an *fcc* lattice is shown in **Figure 2.13**,

where the k -path of the Brillouin zone for the band structure analysis is along Γ -X-W-K- Γ -L-U-W-L-K|U-X, listed in **Table 2.9** for the primitive reciprocal lattice vectors b_1 , b_2 and b_3 . It is crucial that the correct k -path is used during the calculation of the reciprocal lattice; otherwise, an incorrect band structure will be calculated.

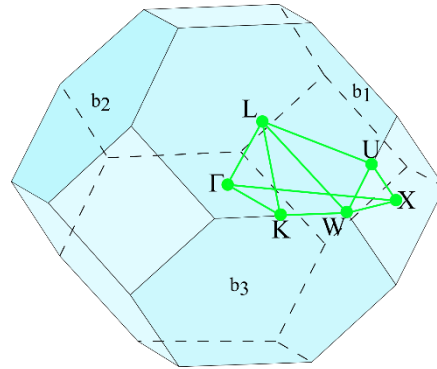


Figure 2.13. Brillouin zone of an *fcc* lattice with the path as Γ -X-W-K- Γ -L-U-W-L-K|U-X.⁹⁷

Table 2.9. Symmetry k -points of *fcc* lattice.

k -path	b_1	b_2	b_3	k -path	b_1	b_2	b_3
Γ	0	0	0	U	5/8	1/4	5/8
K	3/8	3/8	3/4	W	1/2	1/4	3/4
L	1/2	1/2	1/2	X	1/2	0	1/2

A reciprocal lattice is defined as a set of imaginary points, which was constructed in such a way that the direction of a vector from one point to another coincides with the direction of a real space plane. In the reciprocal space, there are points close to the origin which are spanned over the Brillouin zone. These points are known as k -points, which are integrated using the Bloch wave vector.¹⁰³ The k -points used in the *fcc* lattice are shown in **Table 2.9** where b_1, b_2 and b_3 are the primitive reciprocal lattice vectors and the values of these vectors are the coordinates of the symmetry k -points given in fractions.

During the calculations of the reciprocal lattice, the k -points can be integrated over either the entire Brillouin zone or over a specified portion of the Brillouin zone.¹⁰⁴ If the integration is over a specified portion of the Brillouin zone, then the number of k -points in the Brillouin zones is changed. This change in the number of k -points is done with a selected k -point mesh, such as the Monkhorst pack and Gamma point k -point mesh.¹⁰⁴ This selection of k -points is called k -point sampling.

For an accurate approximation of the electronic potential and the total energy for a metal a dense k -point mesh is needed to determine the Fermi level.¹⁰⁵ However, the denser the k -point mesh used in a system, the more computational time is used.

A full list of Brillouin zones, calculated with DFT (VASP), can be found in the article by Setyawan et al.⁹⁷ The band structure is easily obtained from Materials Studio for the investigated surfaces by editing the k -path in the

CASTEP band structure options.¹⁰⁵ The band structure for the Ni surface is shown in **Figure 2.14**, along the Γ -X-W-K- Γ -L-U-W-L-K|U-X Brillouin path.^{97, 98}

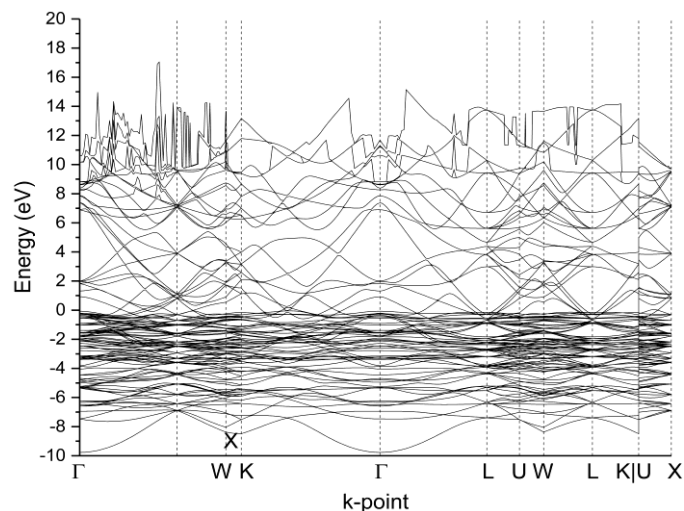


Figure 2.14. Representation of the electronic structure of Ni metal, where the bands/lines stand for molecular orbitals.

2.4.2.2. Computational study of density of states

The d -band centre is unique for each transition metal and is an effective method for observing changes in the electronic structure of transition metal surfaces.^{71, 88} The bond strength of an adsorbate can be described by comparing the position of the d -band centre of the pristine metal with the d -band centre of the adsorbed metal. During adsorption, the d -band centre experiences an upwards or downwards shift (filling states of metal surfaces) through the Fermi level, which can be observed.⁷¹ DFT calculations have shown that both the binding energies and the reactivity of small adsorbates, correlate well with the position of the d -band centre for metal surfaces,^{100, 101} enabling the development of new catalysts.^{106, 107}

2.4.3. Adsorption energy, d -band energy and hydrogen binding energies

Adsorption of hydrogen onto transition metal surfaces is one of the most important intermediates for a large number of catalytic and electrocatalytic processes.^{82, 93} Therefore, numerous experimental and theoretical studies have been conducted on hydrogen adsorption onto various transition metal surfaces for the past few decades. The adsorption energy of hydrogen is used to compare the surface reactivity of various metals to one another, to determine the most reactive metal surface for processes that contain hydrogen adsorption. For example, in order to understand the activity, reactivity and catalytic behaviour of the Pt, Ni and Pt/Ni bimetallic surfaces, adsorbates were adsorbed onto these surfaces.^{68, 71, 82-87} Hydrogen atoms form a moderately strong chemical bond with transition metal surfaces, hence being very reactive intermediates, but are also very sensitive to catalytic poisons.¹⁰⁸

Another electronic property which can be used to investigate the reactivity of a surface is the adsorption energy, E_{ads} , of an adsorbate. The adsorption energy is calculated using equation (2-34), where N is the number of hydrogen atoms adsorbed onto the slab, E_{slab} is the energy of the pristine slab, $(E_{\text{slab}} + N_{\text{Hads}})$ is the energy of the metal slab with the adsorbed hydrogen on the surface, and $E_{\text{H}_2, \text{isol}}$ is the total energy of the isolated H_2 molecule.

$$E_{\text{ads}} = \frac{1}{N} ((E_{\text{slab}} + N_{\text{Hads}}) - (E_{\text{slab}} + \frac{N}{2} E_{\text{H}_2, \text{isol}})) \quad (2-34)$$

A positive adsorption energy indicates that hydrogen adsorption is not favourable and will result in dissociative chemisorption.^{82, 93} However, a negative E_{ads} indicates a stable surface, which in turn favours hydrogen adsorption.

The hydrogen binding energy (HBE) and the adsorption energy (E_{ads}) could be used to successfully explain the reactivity of metal surfaces.⁷ The hydrogen binding energy and the adsorption energy have a linear correlation since the energy gained by the metal surface from the adsorbate can be correlated with the strength with which this adsorbate is bound to the surface. Moreover, the energy gain of the surfaces with respect to the adsorbate is described using the adsorption energy.⁸⁷⁻⁷ The binding energy is calculated by extending, and constraining, the bond length between the adsorbate and the metal surface and optimising the slab.

As previously mentioned, the d -band centre of metal surfaces is a critical factor in determining the adsorption properties of simple adsorbates since the d -band centre describes and measures the reactivity of various types of metal surfaces, and is not limited to describing pure metal surfaces.⁷¹ This description of the reactivity is because the d -band centre value is unique for every transition metal as a result of the metals' electronic structures.^{71, 88} In addition, this d -band centre value can also be correlated with the binding energy, obtained from adsorption calculations, which results in a linear trend for the Pt (111) and Ni (111) surfaces.⁵⁸ A linear correlation is obtained since metal surfaces with large binding energy results in smaller d -band centre values, which are closer to the Fermi level. The binding energy is also dependent on the electronic structure of the metal surface.²³ The relationship between these two measurements can also be observed from a plot between the adsorption energy and the binding energy since stronger bonding of an adsorbate to a metal surface results in larger adsorption energy values. Therefore, there is also a linear correlation between these electronic properties.

The catalytic properties of metals are influenced by the coverage of the surface with the adsorbate, which causes an increased adsorption energy.⁸⁴ Therefore, the coverage of an adsorbate on a metal surface plays an important role in determining the adsorption configurations of the reactants as well as the final mechanism for reactions on the surface.⁸⁴

2.4.4. Strain, ligand and ensemble effects

In the construction of bimetallic surfaces, the electronic properties of the primary metal are influenced by the nature of the secondary metal. There are three effects that control and influence the reactivity of these bimetallic surfaces, namely, the strain effect, the ligand effect (electronic effect), and the ensemble effect (geometric effect).⁵⁵

2.4.4.1. Strain effect

The first effect, namely the strain effect, occurs due to compression or stretching of the lattice because of the addition of a secondary metal to the primary metal. The influence of this effect is dependent on the size of the secondary metal. As a result, the binding energies^{81, 109-111} of bimetallic surface^{54, 112-114} are affected by the strain effect, since the chemical properties of the surfaces are altered. The contribution of the strain effect for surfaces

is determined by plotting the hydrogen binding energy against the adsorption sites where the lattice parameters are varied.

2.4.4.2. Ligand effect

The ligand effect occurs when the electronic structure of the bimetallic surface changes due to the distribution of a secondary metal in the bimetallic surface and/or bulk structures, as shown in **Figure 2.15**.⁵⁵ In simpler terms, the electronic states are modified due to the addition of a secondary metal, which influences the catalytic or adsorption properties of the bimetallic surface.^{55, 115, 116} As shown in **Figure 2.15**, the degree of modification of the electronic structure, the energy of the *d*-band, strongly depends on the nature and composition of the secondary metal which either shifted upward or downward relative to the Fermi level.^{55, 116}

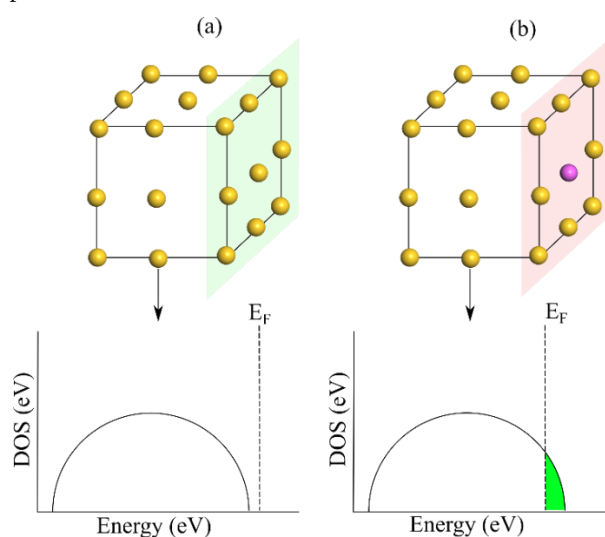


Figure 2.15. A simple representation of ligand effects **a)** before and **b)** after addition of a secondary metal.

A clearer relationship between the reactivity and the *d*-band centre, as a result of the ligand effect, is shown in **Figure 2.16**.¹¹⁷ This relationship is shown as a volcano plot, which clearly shows how the adsorption is affected by the secondary metal used in the surface.

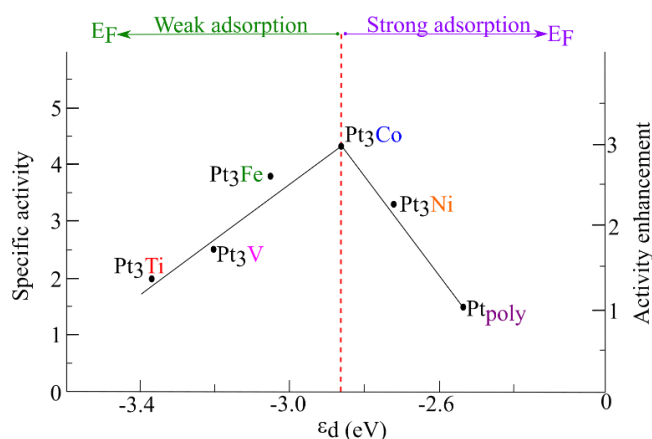


Figure 2.16. A schematic relationship of the reactivity, towards O₂ adsorption for the ORR, and the *d*-band centre (ϵ_d) for Pt₃M surfaces, represented as a volcano plot.

According to **Figure 2.16**, strong O₂ adsorption occurs on the metal surfaces if the *d*-band centre shifted up towards the Fermi level. On the other hand, weak O₂ adsorption is obtained when the *d*-band centre shifts downwards in the Fermi level.

2.4.4.3. Ensemble effect

The ensemble effect occurs due to changes in the environment surrounding the adsorption site (**Figure 2.17**) influencing the adsorption of the adsorbate.^{55, 118} In simpler terms, if the electronic properties of the secondary metal significantly differ from that of the primary metal, drastic changes occur in the electronic structure which will influence the adsorption strength.⁵⁵

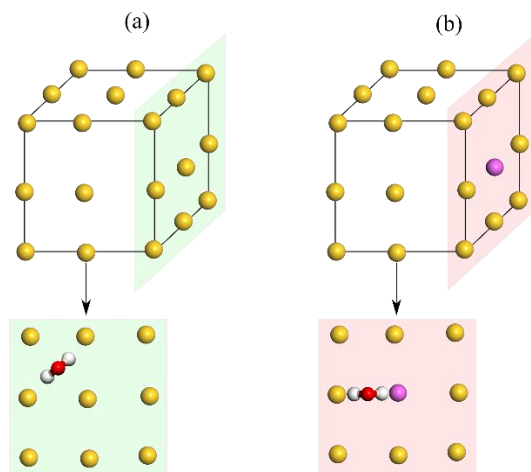


Figure 2.17. A simple representation of ensemble effects on the adsorption of H₂O molecule **a)** before and **b)** after addition of a secondary metal.

Previously, the ligand and ensemble effects have been used to fine-tune the adsorption properties of bimetallic surfaces.^{115, 119} However, distinguishing the ligand effect from the ensemble effect are challenging since these effects are closely related to one another.^{115, 120}

2.4.4.4. Methods to distinguish the ligand effect from the ensemble effect

Investigations that focus on distinguishing between the ligand and ensemble effects for bimetallic surfaces are limited.^{55, 115, 121} Although limited, these investigations provide useful insight for distinguishing these effects from one another and will be discussed using the similar Pd/Au surfaces.^{115, 121}

The first method uses a graphical plot to determine the ensemble effects by the subtraction of ligand effects from the total effects, as shown in **Figure 2.18**.^{115, 121}

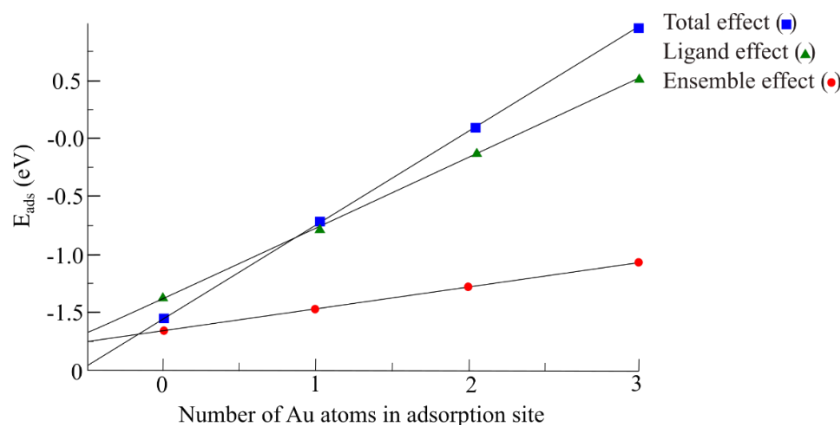


Figure 2.18. The ensemble effect is obtained graphically by the subtraction of the ligand effect from the total effect.¹¹⁵ The ligand effect is described where the composition of the surface is held constant for similar adsorption sites.

In **Figure 2.18**, a change in the adsorption energy (E_{ads}) occurs due to a contribution of both the ensemble and the ligand effects, described by the total effect ($E_{n+1} - E_n$).¹¹⁵ The ligand effect, $E'_n - E_n$, is calculated from the difference in adsorption energy where the composition of the surface metal ($\text{Pd}_x\text{Au}_{1-x}$) is varied while the binding site (neighbouring atoms) is held constant (**Figure 2.19**).

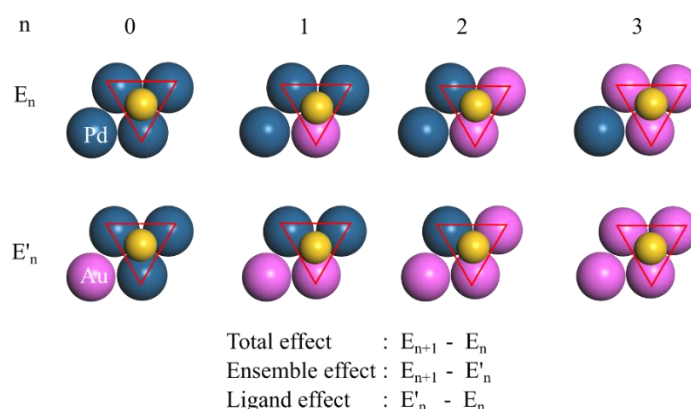


Figure 2.19. Ensemble and ligand effects described using tri-fold ensemble (red triangle) where the binding site, functions of n , is shown using a gold atom.^{55, 115, 121}

Moreover, in **Figure 2.19**, a variety of adsorption sites are described using Pd and Au atoms. This variance in the binding site is also known as a tri-fold ensemble. In **Figure 2.19**, the number of Pd and Au in the binding site is changed, which changes the chemical properties of the environment surrounding the binding site.^{115, 121}

The second method that can be used to determine the amount of ligand and ensemble effects can be obtained by direct comparison, as shown in **Figure 2.20**, by plotting the average HBE against the binding sites. In this instance, these effects are discussed using the Pd/Au (111) and Pt/Au (111) bimetallic surface where the binding sites are varied.¹²¹ The contribution from ligand effects can be observed for the metal surfaces where the composition is varied while the bindings sites are held constant.¹²¹ On the other hand, the contribution from the ensemble effect can be observed for the metal surfaces where the surface composition is held constant with varying binding sites.¹²¹

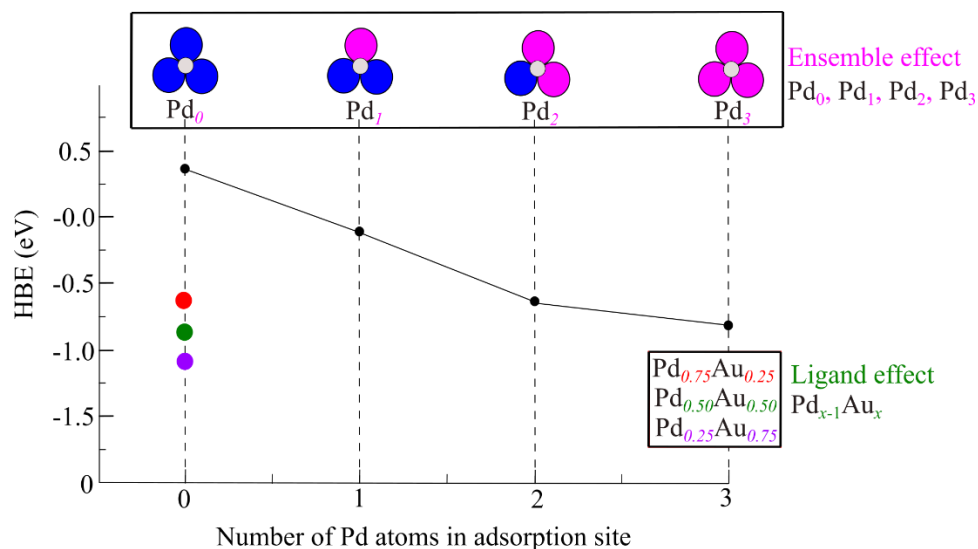


Figure 2.20. Graphical representation of effects contributed by the ligand and the ensemble effects.

It is important to mention that the nature of the secondary metal is not only affected by the size, but also by the magnetic properties of the metal. As a result, the magnetic properties of the secondary metal can cause significant changes in the electronic properties of the bimetallic surface and will be discussed in the next section.¹²²

2.4.5. Surface magnetism

The difference in the valence electron configuration of the metal determines a metal's magnetic property. In the case of Pt, there is an equal population of electrons which are divided into up (α) and down (β) spins, within the full $5d^{10}$ level¹²², which is why this metal is deemed non-magnetic.¹²³ On the other hand, the incomplete $3d^9$ level of the Ni metal means that the electrons' spins are unpaired and become parallel, exhibiting ferromagnetic properties.^{124, 125} Another significant difference between these two metals is the observed electron affinities. The electron affinity of Pt is 247 kJ/mol, the largest among the transition metals,¹²⁶ while the electron affinity for Ni is 156 kJ/mol. As a result, Pt metal is a better electron acceptor than Ni when present in a bimetallic surface. A representation of the PDOS, in terms of the d -band, for the Ni (111)¹²⁷ and Pt (111)¹²⁸ surfaces are shown in **Figure 2.21 (a)**. In this figure, the α and β spin states for the Ni metal are unsymmetrical due to an unpaired electron which causes the metal to exhibit paramagnetic properties. Hence, the minority spin is attractive for metal-adsorbate bonding due to the unpaired electrons in the metal surface.¹²² In contrast, there are no unpaired electrons which makes the Pt metal diamagnetic.

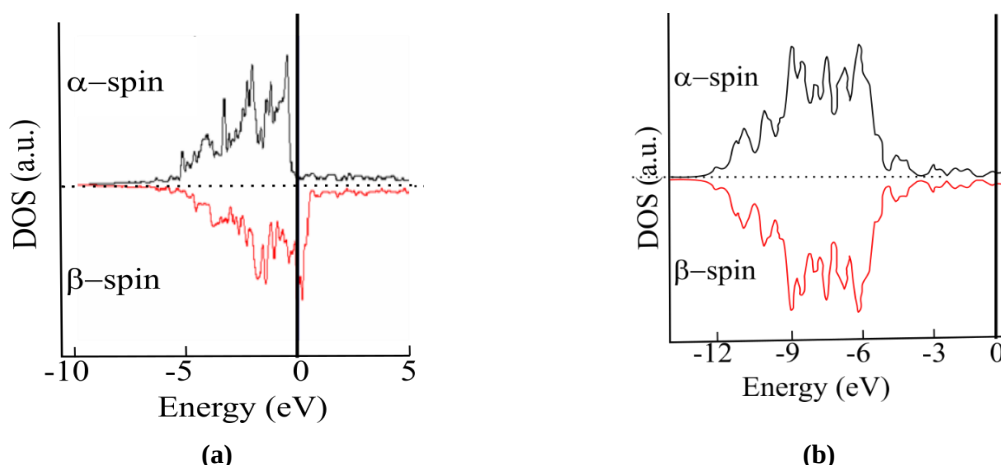


Figure 2.21. DOS of **a)** Ni (111) and **b)** Pt (111) surface with the minority (β) and the majority (α) spin states.

Most investigations focus on describing the surface properties using adsorption energy, while overlooking the importance of magnetic moments.¹²⁹ In a recent study, the scaling relationships of magnetic bimetallic transition metal surfaces were investigated by adding the magnetic moment in the scaling calculations.¹²⁹ The results showed that the scaling relation for bimetallic magnetic systems can be recalibrated to include magnetic moments.¹²⁹

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3

Model development and validation using pure Pt and Ni

In the last three decades, several computational and experimental studies on Platinum (Pt) and Nickel (Ni) have been conducted. In these computational studies, the parameters for the computational models were altered to improve the accuracy, in comparison with experimental values, of various properties calculated for pure Pt and Ni. Using these parameters as a starting point, the adapted computational model used in this study was developed. However, from the earlier studies, it was evident that a universal k -point grid, which is crucial in determining the accuracy of the electronic properties of the metals, was not well defined for the Pt and Ni bulk structures. Therefore, in this study, an energetic minimum and stable k -point grid was determined for the pure Pt and Ni bulk structures, as well as energetically stable and active Pt (111) and Ni (111) surfaces. To validate the adapted computational model, the lattice parameters obtained in this study were compared to literature values. Furthermore, the surface energies, work functions and the d -band centre of the Pt (111) and the Ni (111) surfaces were calculated, using the adapted computational model, and compared to literature values to strengthen the validation of the adapted computational model. Finally, the surface reactivity of the Pt (111) and Ni (111) surfaces were evaluated by adsorbing an elemental hydrogen atom onto these surfaces. The values obtained from the hydrogen adsorption are the hydrogen adsorption energies (E_{ads}) and the hydrogen bonding energies (HBE) for the Pt (111) and the Ni (111) surfaces. These energies were compared to energies obtained from published computational studies. The adapted computational model developed in this chapter was validated by comparing the results from this model with literature values. Moreover, the data obtained from the computational model developed in this chapter, after validation, were used as a baseline for all the calculations throughout the rest of this study.

3.1. Introduction	41
3.2. Computational model	42
3.2.1. Bulk structures calculations	42
3.2.1.1. Validation using lattice parameters	43
3.2.1.2. k -point sampling for Pt and Ni bulk structure.....	43
3.2.2. Surface calculations	43
3.2.2.1. k -point sampling for Pt (111) and Ni (111) surface slabs	43
3.2.2.2. Surface and Electronic properties	43
3.2.3. Hydrogen adsorption onto the (111) surface slabs.....	44
3.3. Results and discussions	45
3.3.1. Bulk structure calculations	45
3.3.1.1. Validation using lattice parameters and interatomic spacing.....	45
3.3.1.2. k -point sampling of Pt and Ni bulk structures	46
3.3.2. Surface calculations	50
3.3.2.1. k -point sampling for Pt (111) and Ni (111) surface slabs	50
3.3.2.2. Electronic properties of pristine surfaces.....	53

3.3.2.2.1. Adsorption energy	54
3.3.2.2.2. Binding energy	55
3.3.2.2.3. Electronic structure	56
3.4. Conclusion	57
3.5. References	58

3.1. Introduction

To develop a computational model that calculates the electronic properties discussed in **Chapter 2**, comparable parameters are needed. Therefore, computational studies were identified, with similar computational parameters and calculated electronic properties, to be used as a baseline for the adapted computational model. The four chosen studies were by Watson *et al.*,¹ Shi *et al.*,² Singh-Miller *et al.*³ and Wang *et al.*⁴ In all these studies, the (111), (110) or (100) low indices were investigated. Of these indices, the (111) Miller index is an excellent surface for adsorption studies due to its high surface area and have been used in numerous computational studies.⁵

The DFT calculations in these studies were conducted using the Vienna Ab initio Software Package (VASP)⁶⁻⁹ or Quantum ESPRESSO.²³ The generalised gradient approximation (GGA) along with the Perdew-Burke-Ernzerhof (PBE) functional were used by three of the above-mentioned authors,²⁻⁴ whereas the parameterisation of Perdew *et al.*¹⁰ was used by Watson *et al.*^{1, 10} Notably, the revised-Perdew-Burke-Ernzerhof (RPBE) functional is more suited to investigate metal surfaces, but since neither of the above-mentioned authors used this functional, it was disregarded for consistency of the computational model.¹¹

Ultrasoft pseudopotentials (USP) along with a smearing value of $0.1 \text{ eV}/\text{\AA}$ were used by Watson *et al.*¹ and Wang *et al.*⁴ On the other hand, smearing values of 0.2 eV and 0.27 eV were used by Shi *et al.*² and Singh-Miller *et al.*³, who did not mention which pseudopotentials were used. Therefore, a smearing value of 0.2 eV was used in this study for comparability with values obtained by Shi *et al.*² The reason for this decision was that the study by Shi *et al.*² aligned with the objectives of this study.

The cut-off energies, which is related to the number of planewaves, used varied amongst these authors with energies of 300 eV (Watson *et al.*,¹), 400 eV (Shi *et al.*²), 400 eV (Wang *et al.*⁴) and 435.38 eV (Singh-Miller *et al.*³); whereas the cut-off energies used for Ni in other publications were 270 eV and 350 eV .^{1, 12, 13} Using an energy cut-off value of 400 eV is reasonable, although it may make the calculations expensive.

It is important to note that the slab size and the slab thickness were different between the above-mentioned studies. In two of these studies, smaller and thinner slabs of $(2 \times 2)\text{--}3\text{L}$, $(2 \times 2)\text{--}5\text{L}$ ¹ and $(3 \times 3)\text{--}4\text{L}$ ² were used. Comparing the average adsorption energy between the $(2 \times 2)\text{--}3\text{L}$ and $(2 \times 2)\text{--}5\text{L}$ slabs, a difference of 0.011 eV was obtained for the *fcc* sites. Thicker slabs of $(1 \times 1)\text{--}13\text{L}$ and 3 to 16 layers with an unspecified dimension were used by Wang *et al.*⁴ and Singh-Miller *et al.*³ Looking at the slab sizes, it was deemed that the surface of the (2×2) surface slab is not large enough for adequate adsorption calculations and cannot be used to investigate various adsorption sites. Therefore, a slab size and slab thickness of $(3 \times 3)\text{--}4\text{L}$ surface slab was identified to be large enough to be used for these calculations.

The vacuum gap used by these authors varied between $12 \text{ \AA}$, $15 \text{ \AA}$ ⁴ and $16 \text{ \AA}$ ³. Since the adsorption calculation in this study was conducted for a small adsorbent, such as hydrogen with an atomic radius of $0.53 \text{ \AA}$ ^{14, 15}, a vacuum gap of $12 \text{ \AA}$ is large enough to prevent interference between hydrogen and the repetitive slabs.

A universal k -point grid could not be identified from the studies mentioned above. However, a k -point grid of $11 \times 11 \times 11$ was used by Shi *et al.*² to verify the lattice parameters and determine the interatomic spacing between the metal atoms in the bulk structures. It is also known that the choice of k -points for the pure Pt and Ni usually require higher mesh parameters to reach a proper ground state. Therefore, a k -point grid of $11 \times 11 \times 11$ was used as a starting point in this study. It may be insufficient to give good convergence.

3.2. Computational model

DFT calculations, as implemented in the Cambridge serial total energy package (CASTEP)¹⁶ which is part of the Materials Studio 2016 package,¹⁶ were carried out to optimise the structures, and to calculate the energies and properties of the Pt and Ni metal bulk structures and surfaces. In the results obtained with CASTEP, the zero-point energy is already incorporated.

The generalised gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (PBE)^{17, 18} was used. The geometry was optimised using the two-point steepest descent (TPSD) algorithm, which achieves good performance and is computationally cost-effective.¹⁹ The interaction between the core and valence electrons, defined as those in level 5d6s for Pt and 3d4s for Ni, were described with the Ultrasoft pseudopotentials (USPP).^{20, 21} This model allows calculations to operate with the lowest possible cut-off energy for the plane-wave basis set, based on the Koelling-Hammon²² relativistic treatment. The Monkhorst-Pack grid²³ was used to carry out the integrations in the reciprocal space of the metal bulk structures and metal slabs. The broadening of the electronic width was set to a smearing value of 0.2 eV. The self-consistent field (SCF) convergence tolerance per atom, the convergence threshold for the maximum energy change, and the convergence threshold for the maximum force were left as the default values of 2.0×10^{-6} eV, 2.0×10^{-5} eV/atom and 0.05 eV/Å, respectively.

Due to the ferromagnetic properties of the Ni, spin polarisation was added to the metal surfaces. Although Pt is paramagnetic, and do not need spin polarisation to be added to the metal surface, it was decided to add spin polarisation to the Pt surface to keep a level of consistency in the computational model. The addition of spin polarisation was important since Pt/Ni bimetallic systems were also investigated with this model.

The computational model was applied to the metal bulk structures, as well as to the (111) surface slabs of Pt and Ni. As a result, the computational model section is divided into two parts, namely, §3.2.1 for the bulk structures calculations and §3.2.2 for the surface calculations.

3.2.1. Bulk structures calculations

The unit cells for Pt and Ni were imported from the Biovia Materials Studio²⁴ crystallographic database, which is a part of the Biovia Materials Studio package. The lattice parameters for the imported Pt unit cell were $a = 3.924$ Å, $b = 3.924$ Å and $c = 3.924$ Å. The lattice parameters for the imported Ni unit cell were $a = 3.524$ Å, $b = 3.524$ Å and $c = 3.524$ Å.²⁴

3.2.1.1. Validation using lattice parameters

During the geometric optimisations, the internal coordinates, lattice parameters, atomic spin moments and cell shape were allowed to change. A comparison between the calculated lattice parameters and experimental lattice parameters^{2,3,47-49}, obtained from the Inorganic Crystal Structure Database (ICSD)²⁵, was made.

3.2.1.2. *k*-point sampling for Pt and Ni bulk structure

In order to obtain more accurate results for the Pt and Ni bulk structure, with the dimension of (3×3×3) consisting of 32 atoms, various *k*-point grids were used to optimise the bulk structures, while the rest of the computational settings mentioned above were used. Even though the metal bulk structures are larger than literature values, the interatomic spacing and energies of the bulk structures should be comparable. A widespread of *k*-point grids, from 1×1×1 to 11×11×11, was selected for the *k*-point sampling. The results obtained for the *k*-point sampling of the metal bulk structures, with varying *k*-point grids, were discussed and compared with one another by plotting the optimisation energy per atom against the number of *k*-points per grid. Since the 1×1×1 *k*-point grid is the smallest grid, it was selected as the starting point; whereas the 11×11×11 *k*-point grid was chosen as the maximum grid because it is dense enough to correctly describe the electronic properties without increasing the computational time exponentially.

3.2.2. Surface calculations

Surface slabs of Pt and Ni were created by cutting the optimised bulk structure along the (111) Miller plane. The slabs consisted of four unconstrained layers, totalling 36 atoms per slab. A 12 Å vacuum gap, which was large enough to avoid interactions between the repetitive layers and accommodate the adsorption of a hydrogen atom, was added to the surfaces.

3.2.2.1. *k*-point sampling for Pt (111) and Ni (111) surface slabs

It is important to make sure that the correct *k*-point grid is used to ensure that accurate electronic properties are obtained. Shi *et al.*² and Watson *et al.*¹ used a 5×5×1 *k*-point grid during hydrogen adsorption.

The *k*-point sampling in this study was conducted by geometrically optimising the Pt (111) and Ni (111) surface slabs with the above-mentioned computational settings. The only exception was that a wide array of *k*-point grids were used for the *k*-point sampling. As with the metal bulk structures, a *k*-point sampling was investigated for the Pt (111) and Ni (111) slabs, by varying the *k*-point grid, from 1×1×1 to 7×7×1. The results obtained from the *k*-point sampling, for each of the surface slabs with the varying *k*-point grids, are discussed and compared with one another by plotting the optimisation energy per atom against the number of *k*-points per grid. Also, the interatomic spacing between the atoms for each of the *k*-point grids was calculated and compared against literature values.

3.2.2.2. Surface and Electronic properties

The surface and electronic properties, including the surface energies (γ), work functions (Φ) and the *d*-band centres (ϵ_d), for the pristine Pt (111) and Ni (111) surface slabs were calculated using the settings as listed in §3.2.

The surface energy was calculated by using equation (2-31) and (2-32) mentioned in **Chapter 2**. In order to calculate the surface energy, the optimised energies and the area of the metal surfaces were calculated. The work function was automatically calculated in CASTEP during optimisation calculations and was obtained from the potential's files.

As mentioned earlier, the *d*-orbitals are mostly responsible for the bonding ability of transition metals and can be observed from a density of states (DOS) graph.²⁶ Using the DOS graph, the centre of the *d*-band (ϵ_d) was calculated from the *d*-band width, as shown in **Figure 3.1**.

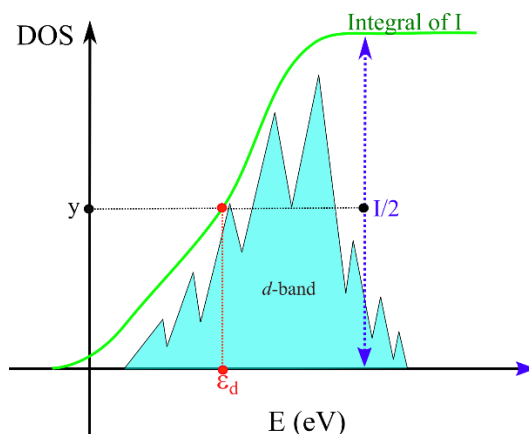


Figure 3.1. A simple representation of using the *d*-band width to determine the *d*-band centre (ϵ_d), using integration.

This calculation was done by importing the *d*-band (DOS) data and integrating the region in the *xy*-plane bounded by the graph. To calculate the *d*-band width (*I*), (the area under the curved line) as shown in **Figure 3.1**, the middle of the *d*-band (*y*-axis) was obtained by dividing the *d*-band width by two. Thereafter, the point where the *y*-axis intersects with the integration curve was identified, and the value on the *x*-axis was determined. This value is the *d*-band centre (ϵ_d) in eV (electron volt). A two dimensional (2D) plotting tool for numerical data, such as the freely available QtGrace,²⁷ was used to calculate the *d*-band centre value.

The electronic property values obtained were compared to literature values to validate the computational model. The validated computational model was further utilised to investigate the adsorption of an elementary hydrogen atom, using an unconstrained metal slab with a vacuum gap of 12 Å.

3.2.3. Hydrogen adsorption onto the (111) surface slabs

In this section, adsorption investigations were performed by adding a single hydrogen atom onto the metal surface followed by geometrical optimisation of the surface. For these adsorption calculations, the same computational settings were used as those for the pristine surfaces.

However, before the adsorption investigations could be done, an isolated H₂ molecule was geometrically optimised in a periodic system with the same lattice parameters, $a = 8.507$ Å, $b = 8.507$ Å and $c = 18.946$ Å, as the Pt (111) and Ni (111) surfaces. The reasoning for optimising the isolated H₂ molecule in the same lattice parameter was to keep the system of the H₂ molecule consistent to that of the metal surfaces for adsorption purposes.

A single hydrogen atom was added onto specific sites, known as adsorption sites, on both Pt (111) and Ni (111) surfaces as shown in **Figure 3.2**.^{1, 2} The four adsorption sites that were investigated are the atop (T), the bridge (B), the hexagonal close-packed (*hcp*) and the face-centred cubic (*fcc*) sites. The coordination number of the adsorbed hydrogen, with the surface metal atoms, corresponds to one for the atop, two for the bridge and three for the hollow sites (*hcp* and *fcc*).

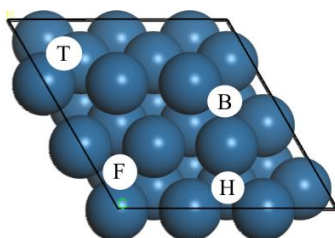


Figure 3.2. The atop (T), bridge (B), hexagonal close-packed (H) and face-centred cubic (F) adsorption sites that occur on a (111) metal surface.

For this study, the (3×3) surface, with a (111) Miller index, has a total of nine possible adsorption sites. If all nine sites were occupied by an adsorbed hydrogen atom, the monolayer (ML) will equal one. In this case, a single elementary hydrogen atom is adsorbed onto the (3×3)-4L surface slab, resulting in a surface coverage of 0.11 ML. For instance, for a (2×2) surface there are a total of four adsorptions sites, which will result in a surface coverage of 0.25 ML when a single hydrogen atom is adsorbed.

The adsorption energies (E_{ads}) and the *d*-band centre (ϵ_d) values were calculated for the hydrogen adsorbed metal surfaces. The adsorption energy values were calculated by using equation (2-34), as discussed in **Chapter 2**. To determine the amount of interaction between the metal's *d*-band with the hydrogen's *s*-band, the *d*-band centre was calculated. The amount of interaction, also known as a *d*-band centre shift, is observed by comparing the *d*-band centre values before and after adsorption.

3.3. Results and discussions

The results obtained were divided into two parts that cover the bulk structures (§3.3.1) and the surface slab calculations (§3.3.2).

3.3.1. Bulk structure calculations

To validate the computational model, the lattice parameters, the *k*-point sampling and the interatomic spacing between the atoms in both the bulk structures for each *k*-point grid were calculated and compared to the literature.

3.3.1.1. Validation using lattice parameters and interatomic spacing

The lattice parameters and interatomic spacing calculated for the Pt and Ni bulk structures, after geometric optimisation, are compared to literature values in **Table 3.1**. The lattice parameters and the interatomic spacing (shown in **Table 3.1**) are relatable to that of the literature values.

Looking at the results for Pt bulk structures, it is clear that the calculated lattice parameters obtained in this study are close to the values in literature references, with a difference of ~0.06 Å.²⁸⁻³⁰ Similarly, the lattice parameters

for the Ni bulk structures shows a difference of $\sim 0.05 \text{ \AA}$ ^{1, 31} and $\sim 0.1 \text{ \AA}$ ²⁹ in comparison with the lattice parameters in literature. Looking at the calculated and literature interatomic spacing values, a difference of $\sim 0.3 \text{ \AA}$ and $\sim 0.5 \text{ \AA}$ were obtained.^{1, 31}

Table 3.1. Comparison of lattice parameters (Lattice_parm) and metal-metal interatomic spacing ($d_M - d_M$) for the Pt and Ni bulk structures with a $Fm\bar{3}m$ (225) space group obtained from the current study (*) and from the literature.

Name	Space group	Lattice_parm (Å)			Lattice_parm [Ref]	$d_M - d_M$ (Å)
		a	b	c		
Pt	$Fm\bar{3}m$ (225)	3.924	3.924	3.924	*	2.839
		3.923	3.923	3.923	28	2.776
		3.923	3.923	3.923	29	2.774
		3.924	3.924	3.924	30	2.775
Ni	$Fm\bar{3}m$ (225)	3.473	3.473	3.473	*	2.531
		3.528	3.528	3.528	31	2.494
		3.526	3.526	3.526	1, 32	2.024
		3.580	3.580	3.580		2.532

Overall, the calculated lattice parameters and the d_{M-M} interatomic spacing (using an $11 \times 11 \times 11$ k -point grid) for the Pt and Ni bulk structures (**Table 3.1**) are in good agreement with literature values.

3.3.1.2. k -point sampling of Pt and Ni bulk structures

In this section, a suitable k -point grid was investigated for the Pt and Ni metal bulk structures. This k -point grid should not only be energetically stable, but also accurate for the investigation of electronic properties. In the case of this study, the criteria for a suitable k -point grid is where the optimisation energy difference between consecutive k -point grids should be 0 eV.

In **Figure 3.3**, the optimisation energy per atom for the Pt bulk structures was plotted against the number of k -points (density) for a widespread of k -point grids, from $1 \times 1 \times 1$ to $11 \times 11 \times 11$. The k -point densities ranged from 1 k -point ($1 \times 1 \times 1$) to 666 k -points ($11 \times 11 \times 11$). As mentioned previously, the more k -points a grid has, the more accurate the electronic property calculations will be, but at a higher computational cost. For this study, unsuitable k -point grid criteria include those which are computationally costly and those which result in inaccurate electronic property calculations.

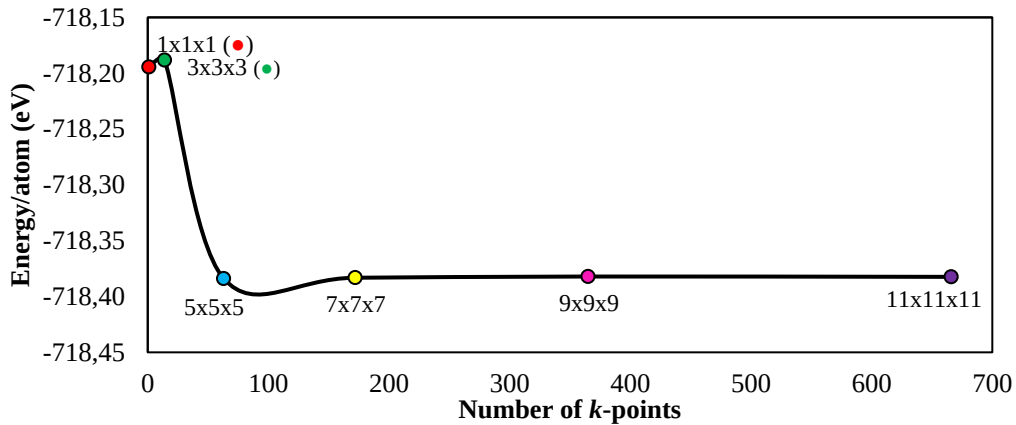


Figure 3.3. The optimisation energy per atom of Pt bulk structures with various k -points.

In **Figure 3.3**, it is difficult to distinguish between the $1 \times 1 \times 1$ k -point grid (red) and the $3 \times 3 \times 3$ k -point grid (green) due to the close proximity of the optimisation energies. However, these two k -point grids were undesirable in this study due to the large optimisation energies and the low number of k -points in these grids (as shown in **Table 3.2**). The optimisation energy of the $5 \times 5 \times 5$ k -point grid had the lowest optimisation energy with 63 k -points in the grid. However, measured against the criteria, this grid was unsuitable since the optimisation energies between the $5 \times 5 \times 5$ and consecutive $7 \times 7 \times 7 \neq 0$ eV. Nevertheless, the optimisation energies from $7 \times 7 \times 7$ to the $11 \times 11 \times 11$ k -points were constant, with the optimisation energy difference between the $7 \times 7 \times 7$ to the $11 \times 11 \times 11$ k -point grids at 0.001 eV, deeming them suitable for this study.

Table 3.2. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing ($d_{Pt}-d_{Pt}$), the equilibrium lattice parameter (E_lattice parm), the d -band centre (ϵ_d) and the spin moment (m_s) for various Pt bulk structures k -points grids.

k -point	No k -points	E/atom (eV)	ΔE (eV)	E_lattice parm (Å)	$d_{Pt}-d_{Pt}$ (Å)	ϵ_d (eV)	m_s (μ_B /atom)
$1 \times 1 \times 1$	1	-718.194	0.006	4.002	2.830	-2.786	0.670
$3 \times 3 \times 3$	14	-718.188	0.006	4.010	2.835	-2.745	0.590
$5 \times 5 \times 5$	63	-718.384	0.001	4.010	2.836	-2.739	0.610
$7 \times 7 \times 7$	172	-718.383	0.001	4.010	2.835	-2.753	0.580
$9 \times 9 \times 9$	365	-718.382	0.001	4.010	2.835	-2.750	0.590
$11 \times 11 \times 11$	666	-718.382	0.000	4.010	2.835	-2.750	0.590

To determine the accuracy of the equilibrium lattice parameter (E_lattice parm), interatomic spacing ($d_{Pt}-d_{Pt}$), the d -band centre (ϵ_d) and the spin moment (m_s) obtained for each of the k -point grids, the calculated values were compared to literature values, as shown in **Table 3.2**.

The calculated equilibrium lattice parameter, as shown in **Table 3.2**, is comparable to the literature lattice parameters for the Pt bulk structures (3.920 Å and 3.990 Å) within 97 %.^{33, 3} From these results, it can be seen that the lattice parameters increased as the k -point grid increased. This increase in the lattice parameters was small, with an increase of 0.008 Å between the first two k -point grids. Hence, it will be advisable to use the larger k -point grids in terms of the lattice parameters.

The lattice parameter was followed by the comparison of the interatomic spacing ($d_{Pt}-d_{Pt}$) to literature values to aid in the k -point grid determination. There was little variance in the interatomic spacing ($d_{Pt}-d_{Pt}$) values across the different k -point grids. Furthermore, the calculated interatomic spacing in the Pt bulk structures (**Table 3.2**) is comparable within 70 % to that of literature values, 2.827 Å and 2.774 Å.^{34, 29}

Next, the d -band centre was investigated for each of the k -point grids (**Table 3.2**). The results obtained shows that the d -band centre value varied between the k -point grids, further implying that the k -point grid affects the accuracy of the electronic properties. The calculated d -band centre values are within 90 % comparable to those obtained in literature for the Pt bulk structures, namely, -2.520 eV for the $9\times 9\times 9$ and the $11\times 11\times 11$ k -point grids³⁵. The high correlation at larger k -point grids indicates that the larger k -point grids deliver more accurate electronic properties.

Lastly, the accuracy of the k -point sampling was determined by investigating the spin momenta calculated for the Pt bulk structures for the widespread of k -point grids. The experimental spin moment for a Pt bulk structure is $0.300\ \mu B$ ³⁶, which is comparable (within 50 %) to the spin momenta obtained in this study. Looking at the calculated spin moment for the k -point grids, these values became closer to that of experimental values as the k -point density increased. The results obtained for the Pt bulk structures is comparable to the values obtained by Shi *et al.*²

Overall, it was concluded that the $11\times 11\times 11$ k -point grid was the most suitable to accurately determine the electronic properties of a Pt bulk structure and for this reason was used for the rest of this study.

The same procedure was followed for the Ni bulk structures to determine the most suitable k -point grid to calculate the electronic properties. The Ni bulk structures consisted of 32 atoms, the same as the Pt bulk structures. From **Figure 3.4**, the optimisation energy per atom was plotted against the k -point density for widespread of k -point grids from $1\times 1\times 1$ to $11\times 11\times 11$. From **Figure 3.4** it can be seen that the optimisation energies followed a similar trend to Pt. Again, the $1\times 1\times 1$ k -point grid was not suitable for this study due to its high optimisation energy. Although the optimisation energy for the $3\times 3\times 3$ k -point grid was at an energetically minimum point, it was not stable when the energy difference relative to the next k -point grid ($5\times 5\times 5$) was taken into consideration. The optimisation energy difference between the $5\times 5\times 5$ and $7\times 7\times 7$ k -point grid was 0.001 eV, as shown in **Table 3.3**. Overall, the denser k -point grid resulted in constant and stable optimisation energies between the $7\times 7\times 7$ and the $11\times 11\times 11$ k -point grids.

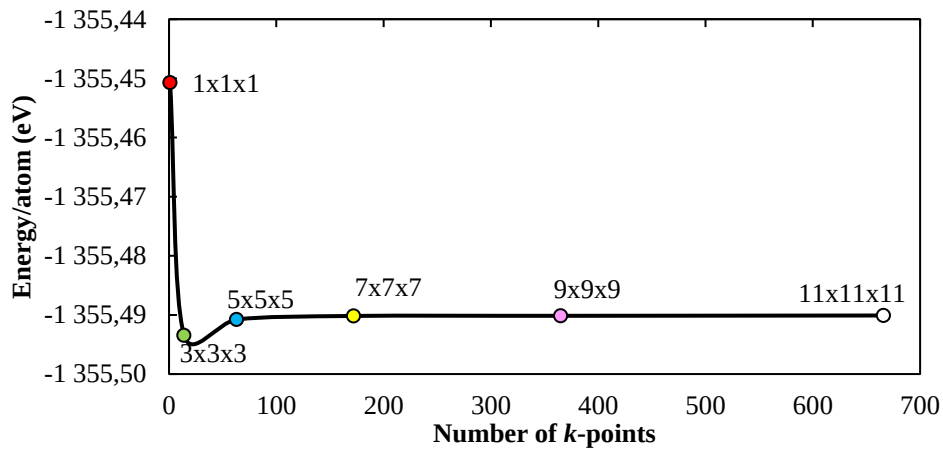


Figure 3.4. The optimisation energy per atom of Ni bulk structures with various k -points.

Table 3.3. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing ($d_{\text{Ni-dNi}}$), the equilibrium lattice parameter ($E_{\text{lattice parm}}$), the d -band centre (ϵ_d) and the spin moment (m_s) for various k -points grids for the Ni bulk structures.

k -point	No k -points	E/atom (eV)	ΔE (eV)	$E_{\text{lattice parm}}$ (Å)	$d_{\text{Ni-dNi}}$ (Å)	ϵ_d (eV)	m_s ($\mu\text{B}/\text{atom}$)
1×1×1	1	-1355.451	0.043	3.574	2.527	-1.632	0.650
3×3×3	14	-1355.493	0.043	3.595	2.542	-1.536	0.710
5×5×5	63	-1355.491	0.003	3.593	2.540	-1.531	0.660
7×7×7	172	-1355.490	0.001	3.593	2.541	-1.530	0.660
9×9×9	365	-1355.490	0.000	3.593	2.540	-1.533	0.660
11×11×11	666	-1355.490	0.000	3.593	2.540	-1.532	0.660

The calculated equilibrium lattice parameter for Ni (as shown in **Table 3.3**) is within 98 % to 99 % comparable to the literature lattice parameters for the Ni, namely, 3.528 Å and 3.526 Å.^{1,3} The difference between the literature values and that of the calculated equilibrium lattice parameter increased from the first k -point grid (0.0021 Å) to the final k -point grid (0.067 Å).

The interatomic spacing for Ni for all of the k -point grids (**Table 3.3**) is comparable to literature values, namely, 2.492 Å and 2.532 Å,^{37,32} with a comparability of 98%. It is also clear from the results (shown in **Table 3.3**) that the d -band centre varies between the different k -point grids, similar to that observed for the Pt bulk structures. The calculated d -band centre values are comparable to that of the literature Ni bulk structures values of – 1.566 eV for all the k -point grids investigated.³⁵

The spin moment for a Ni bulk structure obtained from literature is 0.620 μB (PBE)³⁸, 0.610 μB (PW)³⁸, 0.590 μB (LDA and GGA)³⁹ and 0.610 μB (experimental)³³, which is comparable within a 87 % to 93 % to the spin moment obtained in this study. The spin moment changed as the k -point grid was varied for the Ni bulk structures but became stable as the k -point grid became denser. Overall, the 11×11×11 k -point grid was accurate in determining the electronic properties for the Ni bulk structures.

In conclusion, the results obtained for the k -point sampling concluded that the selected k -point grid spread of $9 \times 9 \times 9$ and $11 \times 11 \times 11$ were sufficient to study the Pt and Ni bulk structures. Therefore, the consistency of the optimisation energy obtained showed that the $11 \times 11 \times 11$ k -point grid was suitable and that larger k -point grids were not required to describe the electronic properties.

The next section of this chapter will focus on applying this established model to the Pt (111) and Ni (111) surfaces. As with the bulk structures, k -point sampling was performed first, followed by the hydrogen adsorption onto the metal surfaces to determine the reactivity and catalytic ability of the metal surfaces.

3.3.2. Surface calculations

Similar to the procedure followed for the bulk structures, the k -point sampling was performed for the Pt (111) and Ni (111) surface slabs. Thereafter, the electronic properties of the Pt (111) and Ni (111) surfaces were compared with literature values, for validation of the computational model.

3.3.2.1. k -point sampling for Pt (111) and Ni (111) surface slabs

The Pt (111) slab had a thickness of four layers which consisted of 32 atoms. **Figure 3.5** shows the optimisation energy per atom, plotted against the number of k -points for a widespread of k -point grids from $1 \times 1 \times 1$ to $7 \times 7 \times 1$. Similar to the results from the Pt bulk structure, **Figure 3.5** shows that the $1 \times 1 \times 1$ k -point grid was not suitable for this study due to the small number of k -points and the high optimisation energy (as shown in **Table 3.4**). This was similar for the $3 \times 3 \times 1$ k -point grid, which had a low k -point density and would have resulted in less accurate calculations. The optimisation energy for the $3 \times 3 \times 1$ k -point grids was close to that of the next k -point grid, namely $5 \times 5 \times 1$. A constant optimisation energy was observed between the $5 \times 5 \times 1$ and the $7 \times 7 \times 1$ k -point grids.

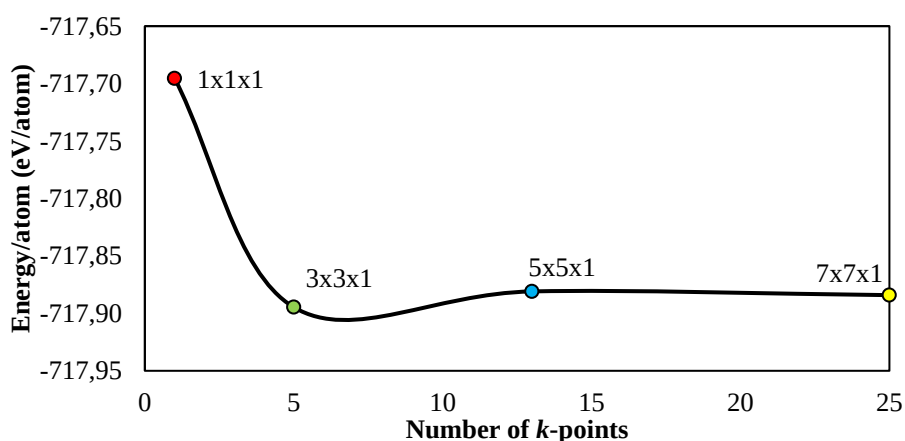


Figure 3.5. The optimisation energy per atom of Pt (111) slab with various k -points.

Table 3.4. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing (d_{Pt-Pt}), the equilibrium lattice parameter (E_lattice parm), work function (Φ), the d -band centre (ϵ_d) and the spin moment (m_s) various k -points grids for the Pt (111) surface.

k -point	No k -points	E/atom (eV)	ΔE (eV)	E_lattice parm (Å)	d_{Pt-Pt} (Å)	Φ (eV)	ϵ_d (eV)	m_s (μ_B /atom)
1×1×1	1	-717.695	0.000	4.253	2.755	4.916	-2.264	0.990
3×3×1	5	-717.895	-0.199	4.253	2.826	5.001	-2.413	0.360
5×5×1	13	-717.881	0.014	4.253	2.823	4.995	-2.430	0.520
7×7×1	25	-717.884	-0.003	4.253	2.820	5.075	-2.094	0.550

As with the bulk structure, the lattice parameters of the Pt (111) surface were determined for each of the k -point grids and compared to literature values (as shown in **Table 3.4**). The lattice parameters for the Pt bulk structure were 3,920 Å and 3,990 Å,^{33, 3} which were ~0.26 Å and ~0.33 Å smaller than the calculated lattice parameters for the Pt (111) surface. As a result, the calculated values correlated well with the literature values.

Moreover, the Pt – Pt interatomic spacing distance (d_{Pt-Pt}) was calculated for each of the k -point grids and is shown in **Table 3.4**. The Pt – Pt interatomic spacing was calculated as 2.823 Å for the 5×5×1 k -point grid, while an interatomic spacing of 2.820 Å was obtained with the 7×7×1 k -point grid. Both of these interatomic spacing distance results corresponded well with the literature values of 2.776 Å, 2.774 Å, 2.775 Å and 2.830 Å for the Pt bulk structure.^{28, 29, 30, 13}

The changes in the electronic properties, in terms of the work function and the d -band centre, were calculated for the various k -point grids, as shown in **Table 3.4**. The experimental work function for a Pt (111) surface is 5.70 eV,⁴⁰ which is smaller than the work function value obtained for all the k -point grids. The work function values calculated for all the k -point grids were closely related but still showed that the work function values are dependent on the surfaces k -point grid.

The theoretical d -band centre value for a Pt (111) surface is – 2.52 eV,³⁵ which is the closest to the calculated d -band centre value for the 5×5×1 k -point grid. Lastly, the spin moment for the Pt (111) surface slab was not constant throughout the slab and varied between the layers. The spin momenta for the denser k -point grids varied less per layer than for the less dense k -point grids (as shown in **Table 3.4**). The spin moment for a Pt surface of a Pt bulk structure is 0.300 μ_B ,³⁶ which is comparable to the spin moment obtained for the 5×5×1 and the 7×7×1 k -point grids. Moreover, the value of the spin moment became stable, with an increase in k -point density. As a result, it was decided that the 5×5×1 k -point grid was suitable to be used for the Pt (111) surface.

The k -point sampling for the Ni (111) surface used the same method as that of the Pt (111) surface. As with the Pt (111) surfaces, the Ni (111) surface consisted of 32 atoms over a slab thickness of four layers. The optimisation energy per atom was plotted against the number of k -points over the 1×1×1 to 11×11×11 k -point grids, as shown in **Figure 3.6**. From the results, it is clear that the 1×1×1 k -point grid was not only higher in optimisation energy, but also had a low amount of k -points. Therefore, the 1×1×1 k -point grid is not suitable for this study. The

optimisation energy for the $3 \times 3 \times 1$, $5 \times 5 \times 1$ and the $7 \times 7 \times 1$ k -point grids is similar. However, the energy difference between the $5 \times 5 \times 1$ and the $7 \times 7 \times 1$ k -point grids was 0.002 eV (as shown in **Table 3.5**).

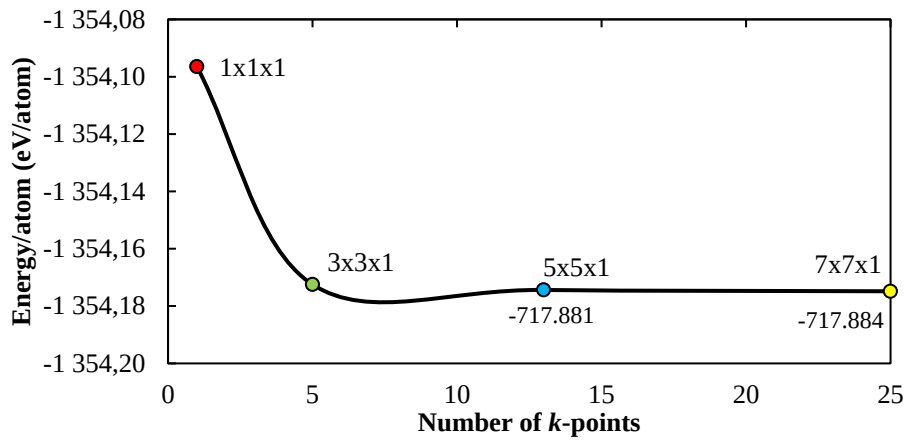


Figure 3.6. The optimisation energy per atom of Ni (111) slab with various k -points.

Table 3.5. The total number of k -points (No k -points), optimisation energy per atom, the energy difference between the k -points, the interatomic spacing ($d_{\text{Ni-dNi}}$), the equilibrium lattice parameter ($E_{\text{lattice parm}}$), work function (Φ), the d -band centre (ϵ_d) and the spin moment (m_s) for various k -points grids for the Ni (111) surface.

k -point	No k -points (a.u.)	E/atom (eV)	ΔE (eV)	$E_{\text{lattice parm}}$ (Å)	$d_{\text{Ni-dNi}}$ (Å)	Φ (eV)	ϵ_d (eV)	m_s (μ_B /atom)
$1 \times 1 \times 1$	1	-1354.10	0.000	3.764	2.450	3.017	-1.413	0.960
$3 \times 3 \times 1$	5	-1354.17	-0.076	3.764	2.478	3.060	-1.453	0.570
$5 \times 5 \times 1$	13	-1354.17	-0.002	3.764	2.478	3.068	-1.481	0.710
$7 \times 7 \times 1$	25	-1354.17	0.000	3.764	2.480	3.073	-1.477	0.680

The lattice parameters for a Ni bulk structure were found to be 3.528 Å,³¹ 3.580 Å,³² and 3.526 Å.¹ These literature values are comparable to the values calculated for the Ni (111) surfaces, within ~ 94 %. The lattice parameters values calculated for each of the k -point grids are the same. From **Table 3.5**, it is clear that the calculated Ni - Ni interatomic spacing distance ($d_{\text{Ni-dNi}}$) for the k -point grids is comparable to the literature values of 2.490 Å,¹³ 2.532 Å,³² and 2.949 Å, within ~ 98 %³¹

The change in the electronic properties, in terms of the work function and d -band centre, was calculated for each of the k -point grids and shown in **Table 3.5**. The experimental work function value for a Ni (111) surface is 5.35 eV,⁴¹ which is not comparable to the values obtained within this study. However, this larger value, as observed, is normal and not necessarily incorrect according to Wojciechowski *et al.*⁴² and is dependent on the method used during the calculations. Accordingly, the calculated value was influenced by the large number of electrons in the Ni sphere, which lowered the calculated value. As a result, the Ni values calculated in this study is not inaccurate but is larger due to the calculation method, which should be refined in future studies. The work function values obtained for this study are smaller than that of the experimental values, and as the k -point grids increased the values became larger. The theoretical d -band centre value is -1.56 eV for Ni,³⁵ which is 0.079 eV

larger than calculated in this study. Overall, the work function values calculated is still comparable to that of literature studies.

The calculated spin moment for the Ni (111) surface slab is comparable (86 % to 91 %) to the literature values of 0.620 μB (PBE),³⁸ 0.610 μB (PW),³⁸ 0.590 μB (LDA and GGA)³⁹ and 0.610 μB (experimental)³³ for the Ni bulk structure. Looking at the spin moment of the k -point grids, it is clear that the $7 \times 7 \times 1$ k -point grid is the closest to that of the experimental spin moment for a Ni bulk structure.

In conclusion, the results obtained for the k -point sampling for both Pt and Ni (111) surfaces further concluded that the selected k -point grid spread of $5 \times 5 \times 1$ and the $7 \times 7 \times 1$ was sufficient to study the optimisation energy for the metal surfaces. Therefore, the consistency of the optimisation energy obtained showed that the $7 \times 7 \times 1$ k -point grid was suitable and that larger k -point grids were not required to describe the electronic properties. Overall, the $5 \times 5 \times 1$ k -point grid was determined to be energetically the most favourable for both the Pt (111) and the Ni (111) surfaces and was used as the preferred k -point grid for the remainder of this study.

3.3.2.2. Electronic properties of pristine surfaces

The calculated surface energy (**Table 3.6**) and work function (**Table 3.7**) values were compared to values obtained from literature.^{3, 4, 43, 44} The surface energy (γ) values obtained for the Pt (111) surface, 1.20 J^2/m^{-2} , predicts that an adsorbent will most likely form weak bonds on the metal surface due to the stability of the surface. In the case of the Ni (111) surface, a value of 1.63 J^2/m^{-2} was obtained, which indicates that strong bonding of the adsorbent will occur on the surface. Although Pt and Ni are both transition metals with similar surface structures, the differences in the electronic structure causes a variation in the trends between these metals.^{4, 17} From **Table 3.6** and **Table 3.7**, it can be seen that a large surface energy value results in smaller work functions indicating that the surface energy is indirectly proportional to the work function. As a result, removal of electrons from the surface will be difficult since the surface is highly stable as indicated by larger surface energies and lower work functions.

Table 3.6. The surface energy (γ) of unconstrained, pristine Pt (111) and Ni (111) metal surfaces of (3×3) -4L obtained from the current study (*) as compared to computational and experimental values.

Metal	Name	Computational		Experimental	
		(J^2/m^{-2})	[Ref]	(J^2/m^{-2})	[Ref]
Pt	Pt (3x3)	1.200	*	2.490	-
		1.490	43		45
		2.000	4		-
Ni	Ni (3x3)	1.630	*	2.380	45
		1.920	44, 46	2.450	47, 48

Table 3.7. The work function (Φ) of unconstrained, pristine Pt (111) and Ni (111) metal surfaces of (3×3)-4L, obtained from the current study (*), as compared to computational and experimental values from the literature.

Metal	Name	Computational		Experimental	
		(eV)	[Ref]	(eV)	[Ref]
Pt	Pt (3x3)	5.070	*	6,080±0,150	49
		5.690	3		
		5.700	4		
Ni	Ni (3x3)	3.090	*	5.35	50

3.3.2.2.1. Adsorption energy

The results obtained for the adsorption of hydrogen on pure metal slabs are shown in **Table 3.8**, where the adsorption energy results are compared to literature values.^{1, 51} The adsorption energy obtained in this study closely relates ($\pm 90\%$) to the unconstrained metal slabs of Watson *et al.*¹ In this study, the most stable site was the atop site for Pt with an adsorption energy of -0.465 eV, while the *hcp* site was the most stable site for Ni with an adsorption energy of -0.589 eV. However, the reference adsorption energies show that the *fcc* site for Pt with an adsorption energy of -0.477 eV and the *fcc* site for Ni metal with an adsorption energy of -0.651 eV are the most stable sites.¹ Although the adsorption sites in this study vary from the reference, there is a reason for the difference between the calculated adsorption energies and the reference energies. It has been shown that slab thickness plays a role in the stability of metal surfaces.³ Thus, the difference may be due to the slab thickness since the reference values were obtained from a thicker slab (5 layers). On the other hand, the inconsistency of the adsorption energies may be due to poor convergence.

The calculated bond lengths, between the hydrogen and the metal, and those obtained from literature^{1, 51} correlated well for the Pt and Ni. The most stable site for the Ni was the *hcp*, which had the longest Ni-H bond length when compared to the other sites. In the case of Pt, the most stable site was that of the atop site, which was 0.009 eV smaller than the stable *hcp* hollow site. The difference in the adsorption energies between the different sites is negligible which means that all these sites should be equivalent. Therefore, hydrogen can be adsorbed on any of the sites on the Pt or Ni surface.

Table 3.8. The comparison of calculated adsorption energy, E_{ads} (in eV), and bond length, $d_{\text{H-M}}$ (in Å), of unconstrained (2×2) Pt (111) and Ni (111) slabs with literature values. The surface coverage was 0.25ML.

Sites	Current study	Ref [1]	Current study	Ref [1]
	Pt E_{ads} (eV)		Ni E_{ads} (eV)	
<i>Atop</i>	- 0.465	- 0.450	- 0.588	- 0.081
$d_{\text{H-M}}$	1.520	1.560	1.730	1.550
<i>Bridge</i>	- 0.462	- 0.440	- 0.536	- 0.511
$d_{\text{H-M}}$	1.870	1.560	1.730	1.720
<i>hcp</i>	- 0.456	- 0.450	- 0.589	- 0.642
$d_{\text{H-M}}$	1.880	1.880	1.730	1.810
<i>fcc</i>	- 0.409	- 0.477	- 0.571	- 0.651
$d_{\text{H-M}}$	1.870	1.870	1.720	1.810
Layer	4	5	4	5

3.3.2.2.2. Binding energy

The binding energies and adsorption energies for each of the adsorption sites were calculated. For this study, the hydrogen binding energy was calculated by extending, and constraining, the bond length between the hydrogen atom and the metal surface and optimising the slab (**Figure 3.7**). Thereafter, the bond length with the lowest energy (●) was subtracted from the bond length where the energy was constant (●), indicating bond breakage. Although this method is more time consuming than the existing hydrogen binding energy equation, the results obtained in this method yielded more accurate values, and the method is consistent.

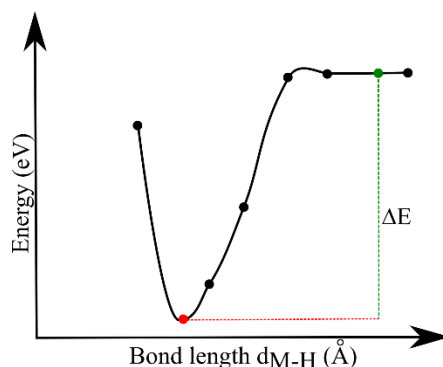


Figure 3.7. Obtaining the binding energy from the optimisation energy (eV) and the bond length where the energy is at a minimum point (●) and where bond breaking occurs (●).

The hydrogen binding energies (HBE) and the d_{M-H} bond distances of a single hydrogen adsorbed onto the surface of a (3×3)–4L Pt (111) and a (3×3)–4L Ni (111) metal, is shown in **Table 3.9**. The calculated binding energies are comparable (~ 94 % to 97 %) with those obtained from literature, as shown in **Table 3.9**.^{1, 35, 52-54} These calculated binding energy values are an indication of the bond strength between the hydrogen atom and the metal surface. Moreover, the binding energy values obtained, indicated that the binding energies were small between the four sites for the Pt (111) and Ni (111) surfaces. From the results, it was clear that stronger binding energies resulted in stronger adsorption energies which correlate with literature results that binding energy and the adsorption energy have a linear correlation.¹³

Table 3.9. Hydrogen binding energies (HBE) of adsorbed hydrogen onto Pt (111) and Ni (111) surfaces with 0.11 ML surface coverage. Notably, the coverage of the reference is 0.25 ML.

	Pt (111) (eV)	[Ref]	Ni (111) (eV)	[Ref]
Atop	-2.500 -2.660	* 35	-2.880 -	*
Bridge	-2.770	*	-2.900	*
hcp	-2.820 -2.680	* 35	-2.900 -2.880	* 35
fcc	-2.690 -2.720 -2.720	* 54 35	-2.880 -2.940 -2.890	* 54 35

3.3.2.2.3. Electronic structure

The atomic projections of the density of states (pDOS) for the Pt (111) and adsorbed Pt.H (111) metal for the (3×3)–4L with a 0.11 ML, is shown in **Figure 3.8**. In **Figure 3.8 (a)**, the *d*-band filling is between 1.65 eV and – 7.22 eV, after adsorption of a single hydrogen atom the *d*-band centre shifted to between 1.08 eV and – 7.44 eV. The interaction between the hydrogen's *s*-orbital and the *d*-orbital of the Pt metal caused a shift in the *d*-band centre, from 2.39 eV to 1.99 eV. This shift in the *d*-band centre values indicates that the energy moved towards the Fermi level, which indicates that strong bonding occurred between the hydrogen atom and the Pt surface. This strong hydrogen bonding to the surface was also observed from the binding energy for the *fcc* site, – 2.69 eV, on the Pt metal.¹

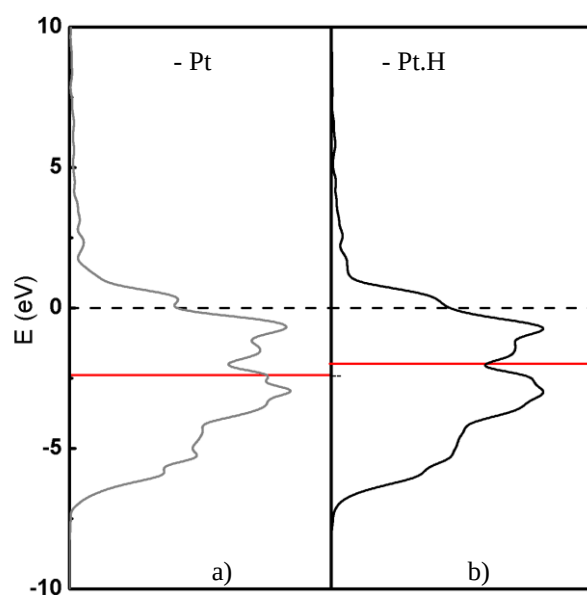


Figure 3.8. pDOS of the pristine (3×3)–4L a) Pt (111) and b) hydrogen adsorbed onto Pt (111) surface at a coverage of 0.11 ML on the *fcc* site.

The *d*-band of the Ni metal is narrow, which indicates that the *d*-band is contracted, as shown in **Figure 3.9**. This observed contraction in the Ni metal *d*-orbitals is due to ferromagnetism. In ferromagnetic metals, the electron spins unpair and the spin becomes parallel. The narrow *d*-band of the Ni metal gives rise to a strong interaction (strong chemisorption) that can be observed from the binding energies.^{55, 56} In the Ni, the *d*-band filling was between 0.77 eV and – 5.00 eV, while after the adsorption of single hydrogen the *d*-band filling changed to 1.35 eV and – 5.26 eV. The *d*-band centre shifted from 1.51 eV to 1.47 eV, respectively. The binding energy of a metal consists of the coupling of the hydrogen's *s*-state and the metal *d*-states.⁵⁷ The binding energy of hydrogen to Ni metal on the *fcc* site was – 2.88 eV, which concluded that hydrogen binds even stronger to Ni metal than Pt metal.

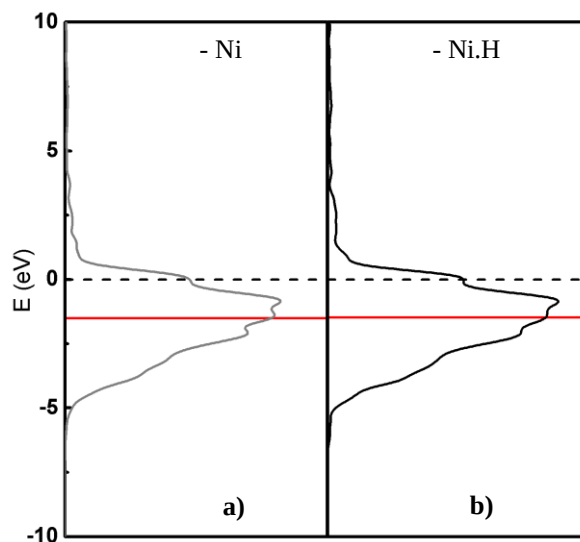


Figure 3.9. pDOS of the pristine (3×3)–4L **a)** pristine Ni and **b)** hydrogen adsorbed onto Ni (111) surface at a coverage of 0.11 ML on the *fcc* site.

3.4. Conclusion

It was clear that the calculated interatomic spacing, lattice parameters, the *d*-band centre (ϵ_d) and the spin moment (m_s) obtained in this study are close to the values in literature references for the Pt and Ni bulk structures. Furthermore, the results from the *k*-point sampling have shown that the 11×11×11 and 5×5×1 *k*-point grids were sufficient to carry out the integrations in the reciprocal space of the metal bulk structures and the surface slabs.

The calculated electronic and surface properties, such as the surface energies, work functions, hydrogen binding energies and the adsorption energies, are comparable to literature studies.^{1, 2} Although the slab thickness varied from literature studies¹, the calculated surface and electronic properties are comparable. Moreover, the difference in the adsorption energies between the sites for the metal surfaces were small enough that the hydrogen can adsorb to any site on the metal surfaces. However, strong chemisorption of the hydrogen occurred on the surface of the Ni metal, while in the case of the Pt metal, the chemisorption was less.

In conclusion, the adapted computational model, which was developed in this chapter, is comparable to literature data and therefore was suitable to be used in the remainder of this thesis. In summary, the Cambridge serial total energy package (CASTEP)⁵⁸ module, which is part of the BIOVIA Materials Studio software package, was used.²⁴ The generalised gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (PBE)^{17, 18} and the Koelling-Hammon relativistic treatment were used.²² A computational cost-effective geometric optimisation algorithm, two-point steepest descent (TPSD),¹⁹ was used. The interaction between the core and valence electrons was described using Ultrasoft pseudopotentials (USP),^{20, 21} while an energy cut-off of 400 eV and a smearing value of 0.2 eV were used. A Monkhorst-Pack grid²³ of 11×11×11 *k*-points was used to carry out the integrations in the reciprocal space of the metal bulk structures, while a Monkhorst-Pack grid²³ of 5×5×1 *k*-points was used for the surface slabs.

Results not included in this chapter, on a study where the slab thickness was increased from 4 to 14 layers to obtain the most stable slab thickness, are given in the Supplementary (S1) section. The reason for not including this part of the study in the main text of the chapter is that it did not affect the outcome of this study.

3.5. References

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PART 2

Pt/Ni bimetallic systems

It has been found that platinum (Pt) metal is active towards the oxygen reduction reaction (ORR), but it is not active towards the oxygen evolution reaction (OER).^{1,2} Therefore, various experimental and computational studies have been conducted for the past three decades to identify alternative electrocatalysts which are more cost-effective, active, selective and stable than Pt. However, the type of electrocatalytic material that can be used is limited due to the large overpotential, 1.23 V, required for these reactions to occur.

One possible solution is by creating cost-effective bimetallic electrocatalyst from the earth-abundant metals, such as the first-row transition metals.³⁻⁵ In bimetallic surfaces, the electronic structure and reactivity of the primary metal, such as Pt metal, are changed, brought on by the addition of a secondary metal.^{6,7} The bimetallic surfaces are attractive alternative electrocatalysts since the activity, selectivity and stability of these metals can be fine-tuned.⁸⁻¹³ Moreover, the cost of the bimetal can be lowered by lowering the amount of the Pt in the surface with a more earth-abundant and less expensive secondary metal.^{3,4,6,11,14-28} As a result, various bimetallic surfaces have been extensively studied experimentally^{11,27,29-33} and computationally.^{28,34-43}

A bimetallic surface which is capable of catalysing two different types of reactions (OER and ORR) is known as a bifunctional electrocatalyst.^{15,44,45} Pt-based electrocatalysts exhibit excellent performance towards the ORR reaction, while excellent performance towards the OER is obtained using nickel (Ni)-based electrocatalysts.^{23,46,47} Moreover, Pt/Ni nanoparticles have been shown to be an excellent bimetallic electrocatalyst with a record low overpotential of 0.69 V for the ORR.⁴⁷ Further suggesting that electrodes consisting of a combination of Pt and Ni could be a possible bifunctional electrocatalyst for the OER and ORR.

Despite the large amount of literature on the enhanced electrocatalytic activity of Pt/Ni bimetallics,^{40,41,48-51} the relationship between the equilibrium composition of the mixture, the distribution of the metal atoms in the mixture and the electronic structure are not yet fully understood. For example, there are numerous publications which were not limited to determining the surface properties of transition metals,⁵²⁻⁵⁶ but also transition metal oxides,^{4,57-59} bimetallic surfaces^{11,13,26,41} or nanoparticles⁶⁰⁻⁶⁸ for various electrochemical processes, such as the water-splitting reaction.

In conclusion, insight into the relationship between the catalytic intermediates and the catalyst, and the energy of their interaction, is a crucial step in theoretically understanding a multi-step catalytic reaction such as the OER and ORR. By using computational studies, the reactivity of a surface can be determined from a wide range of surface and electronic properties, such as the catalytic behaviour, reactivity, the surface energy (γ), work function (Φ), d -band centre (ϵ_d), adsorption energies (E_{ads}) and hydrogen bonding energies (HBE).^{51,69-73}

Therefore, **Part 2** of this study focused on constructing different Pt/Ni bimetallics using the random manual (**Chapter 4**) and an automated systematic technique (**Chapter 5**). In this study, the bimetallic surfaces constructed were substitutional solid solutions due to the similar crystal structure and electronic properties between the Pt and Ni metals.

The main focus of **Chapter 4** is using a simplistic technique that involves the manual substitution of Pt atoms with Ni atoms in a pre-existing Pt (111) surface. In this Chapter, the ligand and ensemble effects were distinguished using different Pt/Ni ratios and different adsorption sites. Additionally, the electronic properties and

hydrogen adsorption on these bimetallic surfaces were investigated to determine the reactivity of these surfaces as a potential bifunctional electrocatalyst for the OER and ORR reactions.

In contrast, a more scientifically reproducible approach was followed in **Chapter 5**. In this approach, a site occupancy disorder program (SOD)⁷⁴ was used to construct all of the inequivalent configurations for a selected size of the Pt/Ni bulk structure. Thereafter, the possible inequivalent configurations were narrowed down by using thermodynamic properties, such as the full-disorder entropy, mixing enthalpy and probability distribution, to obtain the optimal Pt/Ni ratio and Pt/Ni atomic arrangement for bimetallic bulk structures.

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4

Construction of $Pt_{0.x}Ni_{0.y}$ surface slabs using a random manual technique

In this Chapter, $Pt_{0.25}Ni_{0.75}$ (111), $Pt_{0.5}Ni_{0.5}$ (111) and $Pt_{0.75}Ni_{0.25}$ (111) surface slabs (labelled R- $Pt_{0.x}Ni_{0.y}$) were constructed using a random manual technique to investigate the stability and electronic properties of a Pt/Ni bimetallic surface. This technique consists of using a pre-existing (3×3) -4L Pt (111) surface slab and substituting nine (25%), eighteen (50%) or twenty-seven (75%) of the Pt atoms with Ni atoms to create the $Pt_{0.25}Ni_{0.75}$ (111), $Pt_{0.5}Ni_{0.5}$ (111) and $Pt_{0.75}Ni_{0.25}$ (111) slabs. A manual substitution was done to control the atom arrangement in the top layer of the surface slab. The reason for controlling the atom arrangement in the top layer of the surface slab was to ensure diverse fcc and hcp adsorption sites for hydrogen, to study the ligand and the ensemble effect on the bimetallic surfaces. The ligand effect and the ensemble effect both influence the reactivity of bimetallic surfaces. The ligand effect was investigated for the $Pt_{0.25}Ni_{0.75}$ (111), $Pt_{0.5}Ni_{0.5}$ (111) and $Pt_{0.75}Ni_{0.25}$ (111) surfaces, since the Pt/Ni composition of these surfaces varied. In addition, the ensemble effects were investigated for the bimetallic surfaces where the environment surrounding the adsorption sites, were varied. The results showed that the ligand and the ensemble effects could be used to fine-tune the reactivity of the investigated bimetallic surfaces. However, the calculated electronic properties obtained for the R- $Pt_{0.5}Ni_{0.5}$ bimetallic slab were not stable and varied between the adsorption sites and the bimetallic surface. In conclusion, erratic electronic properties proved that a randomly substituted surface slab is not effective, and a more systematic technique is needed for the construction of bimetallic surfaces.

4.1. Introduction.....	66
4.2. Computational model	67
4.2.1. Building the bimetallic surfaces	67
4.2.1. Prepping the surfaces for hydrogen adsorption.....	68
4.3. Results and discussions	69
4.3.1. Electronic properties of pristine bimetallic surfaces.....	70
4.3.1.1 Work function (Φ)	70
4.3.1.2. Investigation of the d -band centre (ϵ_d).....	71
4.3.2. Ligand and ensemble effects due to the hydrogen adsorption	73
4.3.2.1. Ligand effects	73
4.3.2.2. Ensemble effects.....	74
4.4. Conclusion	81
4.5. References	81

4.1. Introduction

As mentioned previously, according to the Sabatier principle,¹⁻⁸ an ideal catalyst should have medium bond strengths. It has been proven through numerous hydrogen investigations that the bonding on Pt (111)⁶ surfaces is feeble, while the bonding on Ni (111)⁹ is extreme.¹⁻⁸ Furthermore, these results were confirmed in **Chapter 3**, in terms of the adsorption energy (E_{ads}) in §3.3.2.2.1 and the hydrogen binding energies (HBE) in §3.3.2.2.2.

It has been shown that the strength of the hydrogen bonding can be fine-tuned by using a weak hydrogen bonding metal such, as Pt, and creating a bimetallic surface through the addition of a secondary metal.⁹⁻¹² This addition of a strong binding secondary metal could be used to fine-tune the electronic properties and the reactivity of the primary metal.⁹⁻¹² Moreover, the nature of the secondary metal affects the electronic property of the bimetallic surface and ultimately, the reactivity of the bimetallic surfaces. These influences are known as the strain effect, the ligand effect (electronic effect), and the ensemble effect (geometric effect).¹⁰

If the atomic size of the two metals is very different, then the addition of the secondary metal will lead to a compression or stretching effect of the lattice of the primary metal. This change in the lattice will alter the chemical properties of the surface, which in turn will affect the binding energies¹³⁻¹⁶ of bimetallic surfaces.¹⁷⁻²⁰ This effect is known as the strain effect.

However, when a change occurs in the catalytic or adsorption properties of the primary metal by the addition of a secondary metal, it is known as the ligand effect. The ligand effect is a result of adjusting the position of the d -band centre by changing the electronic states of the primary metal when the d -bands of the primary metal overlap with the electronic states (s -, p - and d -bands) of the secondary metal.^{11, 21} Moreover, the degree of the electronic structure modification is strongly dependent on the nature and the composition of the d -band of the secondary metal.^{10, 22}

In the case that the environment surrounding the adsorption site (active site or ensemble) is changed, the adsorption of the adsorbate is influenced, and this is known as the ensemble effect.^{10, 21, 23} There is a clear-cut relationship between the reactivity and the electronic state of the surface, and the ensemble effects are known to modify the electronic state of the surface.¹⁰ As a result, the ensemble effect is used for fine-tuning the adsorption sites (active sites) in terms of the adsorption strength with the intermediates, during catalytic reactions.^{21, 24}

However, distinguishing the ligand effects from the ensemble effect are challenging, since these effects are closely related to one another.^{11, 25} Moreover, studies which focused on distinguishing the strain, ligand and ensemble effects are scarce, and the available studies only focus on Pt/Au, Rh/Au or Pd/Au surfaces.^{11, 21, 26-28} Therefore, the results obtained in this chapter are not comparable to literature studies.

An excellent method of investigating the relationship between reactivity and the d -band centre (ϵ_d) for bimetallic surfaces is a volcano plot.²⁹ From these volcano graphs, a clear trend can be observed which shows that when a d -band centre value is close to the Fermi level ($E_F = 0$ eV), strong adsorption occurs and vice versa.²⁹

In this study, the ligand and ensemble effects for Pt/Ni bimetallic surfaces were investigated. The strain effects were not considered in this study, since it should be negligible as the crystal structure for Pt and Ni are identical

with similar atomic sizes, i.e. Pt (1.75 Å)³⁰ and Ni (1.63 Å).³⁰ Furthermore, the lattice parameter of the surface slabs was held constant for the bimetallic surfaces, further reducing strain effects.³⁰

The ligand effect was investigated by varying the amount of Pt and Ni in the surfaces, which in turn controls the adsorbate binding.^{21, 28} Since the catalytic active sites are controlled by the ensemble effects, this effect was investigated by varying the environment surrounding the adsorption site, while keeping the Pt/Ni composition constant.^{11, 12, 26}

Overall, the number of ligand and ensemble effects for the Pt/Ni bimetallic surfaces was observable from plotting the binding energies against the adsorption energies for all the adsorption sites (discussed in detail in **Chapter 2**, in section §2.3.2.)^{11, 21, 25}.

4.2. Computational model

The number of steric effects in the bimetallic surfaces were minimised by using constant lattice parameters. As a result, the ligand and ensemble effects could be thoroughly investigated. These two effects were investigated separately by changing either the composition of the bimetallic surfaces or the adsorption sites used. Therefore, the ligand effects were investigated by varying the composition of the bimetallic surface (Pt_{0.25}Ni_{0.75} to Pt_{0.75}Ni_{0.25}), while the environment surrounding the adsorption sites were held constant. On the other hand, the ensemble effects were investigated only for the Pt_{0.5}Ni_{0.5} bimetallic surface, while the environment surrounding the adsorption site (also known as the ensemble) was changed. The random manual technique requires a large number of configurations which would have been time taxing. As a result, the configurations were limited to eight adsorption sites.

4.2.1. Building the bimetallic surfaces

The Pt_{0.25}Ni_{0.75} (111), Pt_{0.5}Ni_{0.5} (111) and Pt_{0.75}Ni_{0.25} (111) surfaces were constructed from the (3×3)-4L Pt (111) surface slab, created and optimised in **Chapter 3**. This (3×3)-4L Pt (111) surface slab consisted of 36 Pt atoms, with a vacuum gap of 12 Å.

The Pt_{0.25}Ni_{0.75} (111), Pt_{0.5}Ni_{0.5} (111) and Pt_{0.75}Ni_{0.25} (111) bimetallic surface slabs were constructed by randomly substituting nine (25%), eighteen (50%) or twenty-seven (75%) Pt atoms with Ni atoms, as shown in **Figure 4.1**. These constructed bimetallic surface slabs were labelled as R-Pt_{0,x}Ni_{0,x} throughout this Chapter. (**Note:** This labelling was done to eliminate any confusion with the Pt_{0.5}Ni_{0.5} (111) surfaces, which are used in **Chapter 5** and **Chapter 6**).

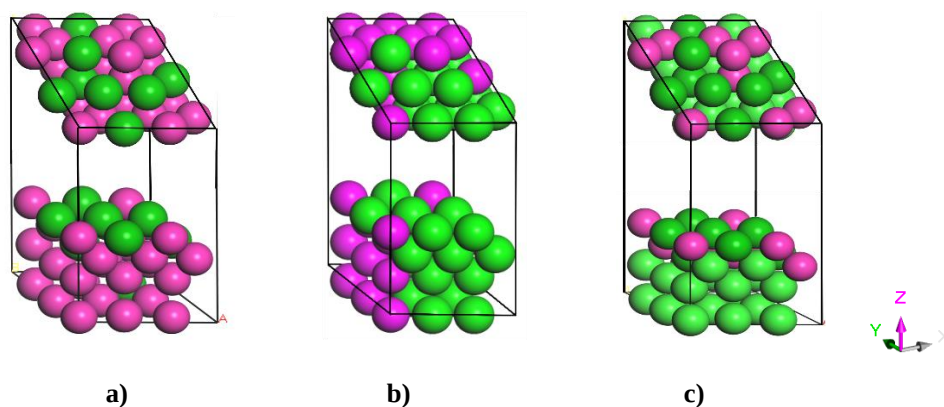


Figure 4.1. Top and side view for the a) R-Pt_{0.25}Ni_{0.75} b) R-Pt_{0.5}Ni_{0.5} and c) R-Pt_{0.75}Ni_{0.25} surfaces, where the Pt atoms in green and the Ni atoms in pink/purple.

During the construction of the Pt/Ni surfaces, the atomic arrangement of the top layer was the main focus where the Pt atoms of the top layer were replaced with Ni. The environment surrounding the adsorption site was investigated in terms of the ensemble effect, as shown in §4.2.1. Furthermore, the investigation of the ensemble effect was only conducted for the R-Pt_{0.5}Ni_{0.5} bimetallic surface, since this Pt/Ni ratio has been shown to be the most stable.³¹ The ligand effect was investigated for the R-Pt_{0.25}Ni_{0.75}, R-Pt_{0.5}Ni_{0.5} and R-Pt_{0.75}Ni_{0.25} bimetallic slab while keeping the adsorption sites constant, as shown in the next section (§4.2.1.).

These bimetallic surface slabs, namely R-Pt_{0.25}Ni_{0.75}, R-Pt_{0.5}Ni_{0.5} and R-Pt_{0.75}Ni_{0.25}, were optimised using DFT calculations as described in the computational model developed and validated in Chapter 3. The optimisation was followed by energy calculations, using the same settings as the optimisation to calculate the electronic properties for the bimetallic surface slabs.

The electronic properties, such as the *d*-band centre (ϵ_d), hydrogen binding energy (HBE), adsorption energy (E_{ads}) and the work function (Φ), were calculated to aid in the description of the surface reactivity. The *d*-band centre is obtained from the density of states (DOS), where the overlap of the *s*-, *p*- and *d*-orbitals are shown as energy level bands (*s*-, *p*- and *d*-bands), separated by energy gaps.³²

The adsorption of an elementary hydrogen atom on the bimetallic surfaces to investigate the electronic and catalytic properties of these surfaces was investigated. The isolated H₂ molecule was optimised before the adsorption was performed on to the R-Pt_{0.5}Ni_{0.5} (111) surface. For consistency, the isolated H₂ molecule was optimised in a lattice (periodic system) with the same lattice parameters, 8.507 Å, 8.507 Å and 18.946 Å, as the Pt (111) metal system.

4.2.1. Prepping the surfaces for hydrogen adsorption

The elementary hydrogen adsorption was investigated on (3×3)–4L surface slabs, with nine adsorption sites simulating a coverage of 0.11 ML. The 3-fold energetically most stable hollow adsorption sites for transition metals, namely, the hexagonal close packed (*hcp*) and the face centred cubic (*fcc*) sites,³³⁻³⁵ shown in Figure 4.2, were investigated. The adsorption sites were labelled as (F_1 – F_4) in the *fcc* sites and (H_1 – H_4) for the *hcp* sites.

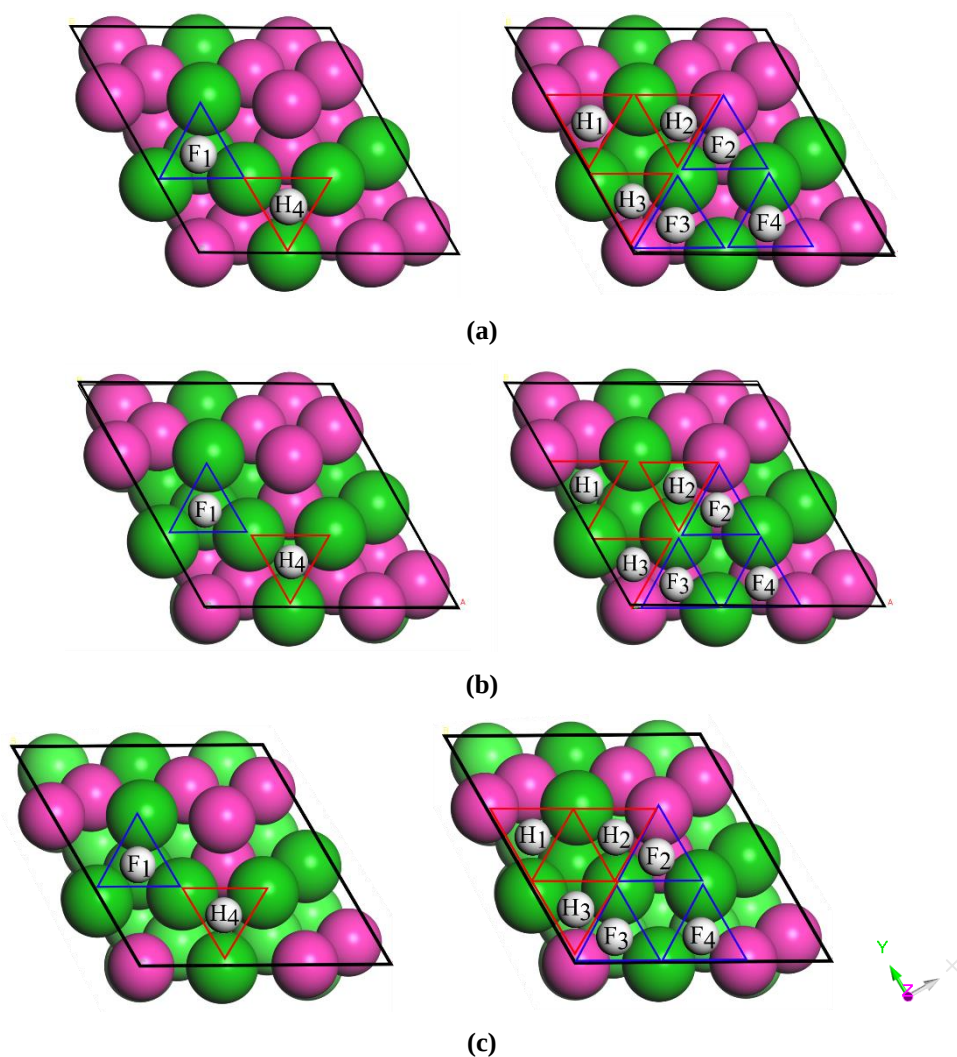


Figure 4.2. Adsorption sites on a) R-Pt_{0.25}Ni_{0.75} b) R-Pt_{0.5}Ni_{0.5} and c) R-Pt_{0.75}Ni_{0.25} surfaces, where F₁-F₄ = *fcc* hollow sites and H₁-H₄ = *hcp* hollow sites. (Where the atom colours are green and pink/purple for Pt and Ni, respectively.)

In **Figure 4.2**, it is apparent that the environment surrounding the adsorption sites is diverse. As shown in **Figure 4.2**, a Pt₃ triatomic adsorption site (indicated with a triangle) was obtained for the F₁ and H₄ adsorption sites, while the rest of the adsorption sites had a Pt₃Ni₂ relationship. Furthermore, the second layer below the adsorption site was a Pt (pink/purple) atom for the H₁, H₂, H₄ and F₄ adsorption sites. Whereas, a Ni (green) atom was in the second layer below the adsorption site for the H₃, F₂ and F₄.

Hydrogen was adsorbed onto all the possible *hcp* and *fcc* adsorption sites of this surface, to study the surface reactivity influenced by the ensemble effect due to the nearest neighbours. No dipole-correction schemes were employed during the adsorption of hydrogen due to the simplicity of the isolated hydrogen.

4.3. Results and discussions

The results and discussion are divided into two parts where the first part, as shown in §4.3.1, investigates the electronic properties of the pristine R-Pt_{0.25}Ni_{0.75} (111), R-Pt_{0.5}Ni_{0.5} (111) and R-Pt_{0.75}Ni_{0.25} (111) surfaces and

compares the results to the pristine Pt (111) and Ni (111) surfaces. In the second part, a single hydrogen atom was adsorbed onto the bimetallic surfaces to investigate the influence of the ligand (§4.3.2.1) and the ensemble (§4.3.2.2) effects on these surfaces.

4.3.1. Electronic properties of pristine bimetallic surfaces

Electronic properties of the R-Pt_{0.25}Ni_{0.75} (111), R-Pt_{0.5}Ni_{0.5} (111) and R-Pt_{0.75}Ni_{0.25} (111) bimetallic surface slabs, including the work function and the *d*-band centre (as shown in **Table 4.1**), were calculated and compared to pristine Pt (111) and Ni (111) surfaces values obtained in **Chapter 3**.

Table 4.1 Calculated work function (Φ) and *d*-band centre (ϵ_d) of the unconstrained pristine, Pt (111), Ni (111), R-Pt_{0.25}Ni_{0.75} (111), R-Pt_{0.5}Ni_{0.5} (111) and R-Pt_{0.75}Ni_{0.25} (111) surfaces.

Surface	Φ (eV)	Reference	ϵ_d (eV)	Reference
Ni (111)	3.090	*	− 1.484*	*
	5.680	36	− 1.560	6
Pt (111)	5.070	*		
	5.690	4	− 2.612*	*
	5.702	2	− 2.520	6
	6.740	36		
R-Pt _{0.25} Ni _{0.75}	4.367	*	− 1.332*	*
R-Pt _{0.5} Ni _{0.5}	4.781	*	− 1.886*	*
R-Pt _{0.75} Ni _{0.25}	4.519	*	− 1.096*	*

Present study (*) and literature values.^{2, 6, 36, 37}

4.3.1.1 Work function (Φ)

As mentioned previously, the minimum amount of energy required to remove an electron from the surface is indicated with the work function, which determines the bond strength between the surface and the adsorbent.² As per the definition of the work function, the more stable the surface, the more difficult it is for the electrons to escape from the surface. The removal of an electron from the pure Pt (111) metal surface should be easy due to its large work function.² Moreover, the *d*-orbitals of Pt are filled, which results in an easier donation of electrons to an adsorbate on the metal surfaces. On the other hand, the small work function value obtained for the pure Ni (111) surface, indicates that the removal of an electron from this surface should be difficult.⁶ Moreover, the *d*-orbitals of Ni are not filled, which influences the binding ability of the metal. As a result, removal of electrons from the Ni is difficult, since the metal clings to the electrons which will result in strong bonding of adsorbates. Overall, due to the difficulty of removing electrons from the Ni (111) surface, the binding energy for the Ni (111) surface should be large and vice versa for the Pt (111) surface.⁶

The work function for the pristine pure metals, as shown in **Chapter 3 (§3.3.2.2)** and from previous studies in literature, showed that pure Ni is not an ideal electrocatalyst since strong bonding occurs between hydrogen and the Ni surface. This strong bonding is a result of the unwillingness of the metal surface to lose the electron obtained from the hydrogen.⁶ On the other hand, hydrogen bonds weakly to Pt (111) surfaces, which interferes with the

formation of the intermediates during the OER or the ORR. However, in the bimetallic surfaces, the electronic properties of the Pt metal surface changes due to the addition of a secondary metal, Ni, to the metal surface.

The calculated work function obtained for the pure metal surfaces were 5.070 eV for Pt (111) and 3.090 eV for Ni (111). However, work function values of 5.690 eV and 4.600 eV for Pt (111) and Ni (111), respectively, have been reported in literature.^{2, 4, 36, 38, 39} In section §3.3.2.1, it was mentioned that observing a larger value is not necessarily incorrect, as it is dependent on the method used during the calculations of the metals shown by Wojciechowski *et al.*⁴⁰

From **Table 4.1**, it is clear that the calculated *d*-band centre is comparable to literature values within a range of 50 % to 89 %. Furthermore, the calculated work function values for the Pt/Ni bimetal slabs surfaces, 4.367 eV, 4.781 eV and 4.519 eV, are between the work functions values of the pure Pt (111) and Ni (111) surfaces of 5.070 eV and 3.090 eV (**Table 4.1**). Therefore, according to the calculated values, adsorbates should bind less strongly to the bimetallic surface than on Ni (111) surface and more strongly than on the pure Pt (111) surface. This indicates a trend in the bonding strength where $\text{Ni} > \text{R-Pt}_{0.25}\text{Ni}_{0.75} > \text{R-Pt}_{0.75}\text{Ni}_{0.25} > \text{R-Pt}_{0.50}\text{Ni}_{0.50} > \text{Pt}$. This trend of the calculated work function values of the bimetallic surface indicates that electrons moved from the Pt atoms towards the Ni atoms, lowering the work function of the Pt metal during Ni atom substitution. This movement of the electrons from the Ni atoms to the Pt atoms in the bimetallic slab surfaces will induce a shift in the *d*-band centre.

4.3.1.2. Investigation of the *d*-band centre (ϵ_d)

An effective method for the observation of electronic structure changes can be observed from the *d*-band centre values (**Table 4.1**). The shift in the *d*-band centre is measured to ascertain the amount of influence that an adsorbate has on the bonding orbitals (*d*-orbitals) of the metal surfaces. This *d*-band centre of the pristine surfaces was compared to the *d*-band centre of the adsorbed surfaces to determine the shift in the *d*-band centre, which is shown in **Chapter 2**.

In the primary metal, the completeness of the *d*-orbital in the core metal⁴¹ is maintained by shifting the *d*-band centre towards the Fermi level when a secondary metal is added. This downshift in the *d*-band centre towards the Fermi level, results in an increase in the bonding strength between the metal and an adsorbate because the anti-bonding states becomes empty. The opposite is true when the anti-bonding states are filled, decreasing the bond strength, due to an upshift in the *d*-band centre away from the Fermi level. The *d*-band is observed from the partial density of states (pDOS), which is the overlap of the *d*-orbitals as shown as energy levels. This pDOS is used to give an approximate description of the bond formation of a transition metal surface.⁴²

The atomic projections of the pDOS, with regard to the *d*-band of the Pt (111), Ni (111), $\text{R-Pt}_{0.25}\text{Ni}_{0.75}$ (111), $\text{R-Pt}_{0.5}\text{Ni}_{0.5}$ (111) and $\text{R-Pt}_{0.75}\text{Ni}_{0.25}$ (111) surfaces, are shown in **Figure 4.3**.

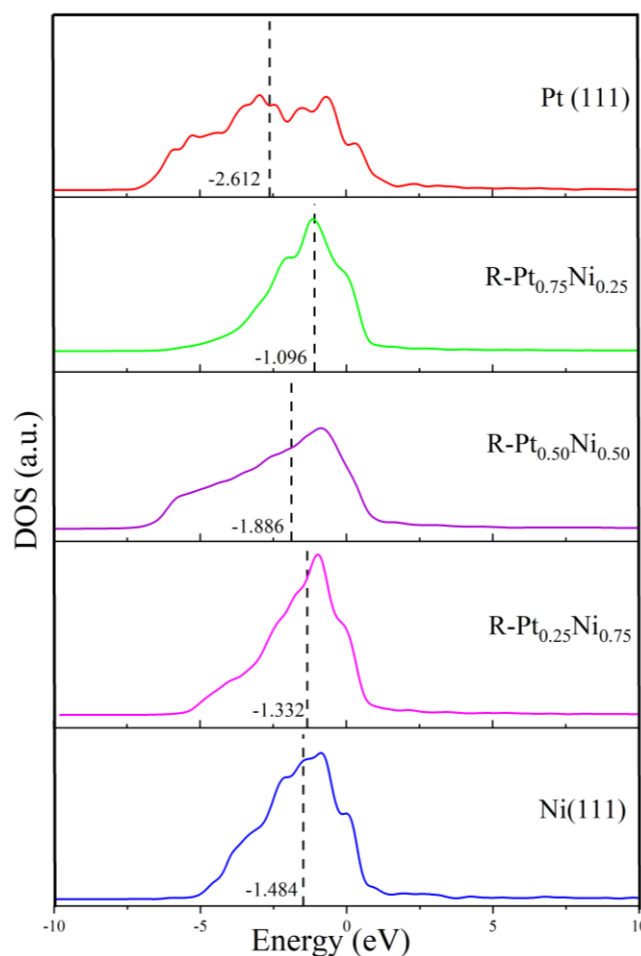


Figure 4.3. Partial density of states (pDOS) of Pt (111), Ni (111) and the R-Pt_{0.25}Ni_{0.75} (111), R-Pt_{0.5}Ni_{0.5} (111) and R-Pt_{0.75}Ni_{0.25} (111) bimetallic surfaces.

The observed difference in the *d*-band centre values between the Pt (111) and R-Pt_{0.5}Ni_{0.5} (111) surface, is known as a downshift, which is usually observed in bimetals. This downshift is a means of conserving the number of *d*-states in the metal when a secondary metal is added.⁴³ As shown in **Figure 4.3**, the *d*-band width of the R-Pt_{0.25}Ni_{0.75} (111) surface is similar to that of the Ni (111) surface with a narrow peak. This narrow peak means that strong bonding will occur on this surface, like with the Ni (111) surface. Whereas the *d*-band width of the R-Pt_{0.5}Ni_{0.5} (111) surface is broader than that of the Ni (111) metal, due to the molecular orbital overlap between the Pt and Ni atoms in the metal surface. Therefore, this broadening of the *d*-band indicates that the bond strength on the R-Pt_{0.5}Ni_{0.5} (111) surface should be weaker than that of the Ni (111) surface. In the case of the R-Pt_{0.75}Ni_{0.25} (111) surface, the *d*-band width is narrower than that of Pt (111), while also exhibiting a narrow peak similar to the peak observed for Ni (111). As a result, the bond strength should be close in value to that of the Pt (111) surface, but stronger than the Pt (111) due to the narrow peak of the *d*-band.

The electronic structure, with regard to the *d*-band centre of the Pt (111) metal, shifted downwards in the Fermi level when 50 % (– 1.886 eV) of the Pt metal was substituted with Ni. On the other hand, the *d*-band centre shifted upwards in the Fermi level as the percentage of the Ni was changed to 25% (– 1.096 eV) and 75% (– 1.332 eV).

The upwards shift in the *d*-band centre, in the Fermi level for the R-Pt_{0.25}Ni_{0.75} (111) and the R-Pt_{0.75}Ni_{0.25} (111), will result in strong binding onto these surfaces, which is not ideal for adsorption. On the other hand, the value of the *d*-band centre for the R-Pt_{0.5}Ni_{0.5} (111) bimetallic surface (– 1.886 eV) lies between the calculated values of the Pt (111) and Ni (111) surfaces with respect to the Fermi level of – 2.612 eV and – 1.484 eV, respectively. This shift in the *d*-band centre indicates that bonding will be more favourable on the Pt_{0.5}Ni_{0.5} (111) bimetallic surface, compared to the other bimetallic surfaces or even the Pt (111) and Ni (111) surfaces.

In conclusion, strong hydrogen adsorption occurs on Ni (111) due to the high energy level of the anti-bonding state formed by the hydrogen 1s-orbital and the metal *d*-orbital, leading to a low filling of this state and thus strong adsorption.⁴⁴ Moreover, by examining the binding energy and the *d*-band centre of a metal surface, the strength with which the hydrogen adsorbs to the metal surface can be determined.⁴⁵ The electronic structure of the catalysts, the reaction trends of transition metals, their bimetals and their alloys, have been successfully described using the linear correlation between the binding energy and the *d*-band centre.⁴⁶⁻⁴⁹

The difference in the *d*-band centre values between the bimetallic surfaces indicates that the electronic structure is influenced by either the ligand or the ensemble effect. As a result, the ligand (§4.3.2.1) and the ensemble (§4.3.2.2) effect were investigated in the next section.

4.3.2. Ligand and ensemble effects due to the hydrogen adsorption

The changes in the electronic properties, such as the *d*-band centre, adsorption energy and the binding energy, were investigated to determine the amount of ligand and ensemble effects that occur on the bimetallic surface using hydrogen adsorption as a case study.

4.3.2.1. Ligand effects

The influence that the ligand effect has on the electronic structure for the R-Pt_{0.25}Ni_{0.75}, R-Pt_{0.5}Ni_{0.5} and the R-Pt_{0.75}Ni_{0.25} bimetallic surfaces was investigated.

4.3.2.1.1. Difference in the binding energies due to the ligand effect

The binding energy was plotted against the *d*-band centre to investigate if there are changes in the reactivity of the surface, as a result of the ligand effect, shown in **Figure 4.4**. The values used in **Figure 4.4**, are available in the Appendix (**Table A4.1**).

To determine the number of ligand effects, the adsorption sites were held constant for all the surfaces to minimise the contribution of ensemble effects, while the ratio of Pt and Ni was changed. In **Figure 4.4**, it is apparent that the number of Pt and Ni atoms in the bimetallic surface influenced the *d*-band centres, which is an indication of the presence of ligand effects. Looking at the F₁ adsorption site, the *d*-band centre values obtained were – 1.999 eV, – 1.679 eV and – 1.456 eV for the Pt_{0.25}Ni_{0.75}, Pt_{0.5}Ni_{0.5} and Pt_{0.75}Ni_{0.25} surfaces. Moreover, the binding energies for the F₁ adsorption site varied as the amount of Pt and Ni in the bimetallic surface varied. Looking at the H₁ adsorption site, the *d*-band centre values obtained were – 1.878 eV, – 1.679 eV and – 1.456 eV for the Pt_{0.25}Ni_{0.75}, Pt_{0.5}Ni_{0.5} and Pt_{0.75}Ni_{0.25} surfaces.

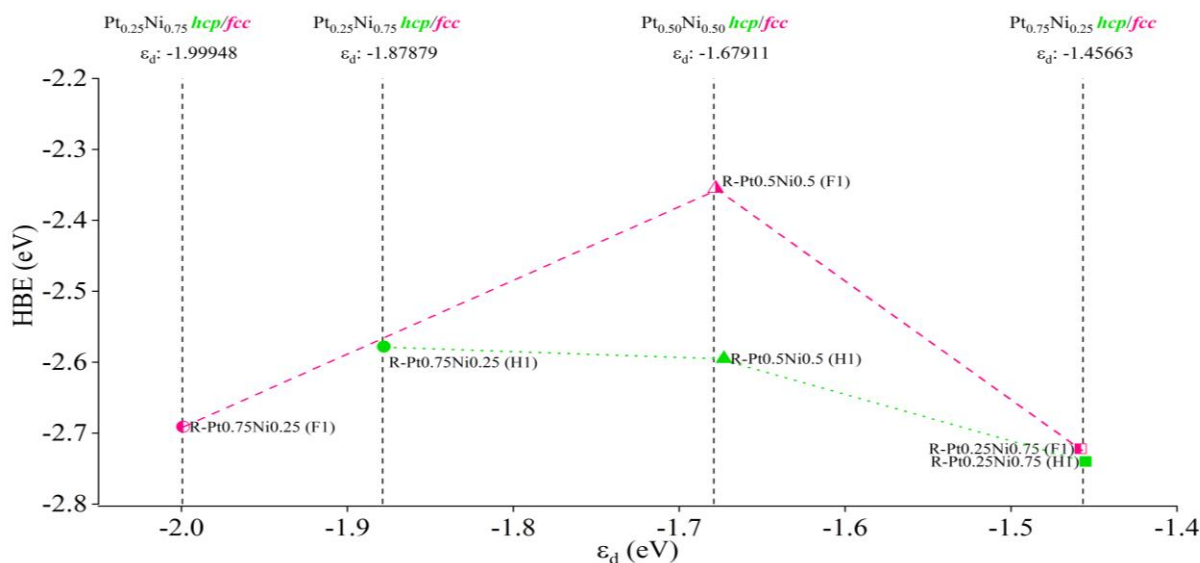


Figure 4.4. The comparison of the hydrogen binding energy (HBE) and the d -band energy (ϵ_d) for the F_1 and H_1 adsorption sites for the bimetallic surfaces where the amount of Pt and Ni was varied to obtain R-Pt_{0.25}Ni_{0.75} (111), R-Pt_{0.5}Ni_{0.5} (111) and the R-Pt_{0.75}Ni_{0.25} (111) surfaces.

It is interesting to note that the hydrogen bonds are the strongest for the F_1 and H_1 adsorption sites on the R-Pt_{0.5}Ni_{0.5} bimetallic surface, as compared to the other bimetallic surfaces. On the other hand, the weakest hydrogen bonding was obtained for the R-Pt_{0.25}Ni_{0.75} bimetallic surface.

In conclusion, the ligand effect can be used to fine-tune the bimetallic surfaces, in terms of the binding energy by changing the ratio of Pt and Ni in the metal surface. This phenomenon can be used to fine-tune these bimetallic surfaces for specific catalytic purposes. However, it is not conclusive that these values are only contributed by the ligand effect and that a contribution from the ensemble effects does not occur. As a result, the influence of the surrounding environment on the adsorption site was also investigated and discussed in the next section (§4.3.2.2).

4.3.2.2. Ensemble effects

4.3.2.2.1. Difference in the binding energies due to the ensemble effect

The influence that the ensemble effect has on the adsorption properties for the R-Pt_{0.25}Ni_{0.75}, R-Pt_{0.5}Ni_{0.5} and R-Pt_{0.75}Ni_{0.25} bimetallic (111) surfaces was investigated in terms of the *hcp* and the *fcc* adsorption sites. The results are shown for the R-Pt_{0.25}Ni_{0.75}, R-Pt_{0.5}Ni_{0.5} and for the R-Pt_{0.75}Ni_{0.25} bimetallic surfaces in **Figure 4.5**, **Figure 4.6** and **Figure 4.7**, respectively. The environment of the hydrogen adsorption sites, in terms of the amount of Pt and Ni in the adsorption site, are indicated with a red triangle (▼) for the *hcp* and a blue triangle (▲) for the *fcc* adsorption sites.

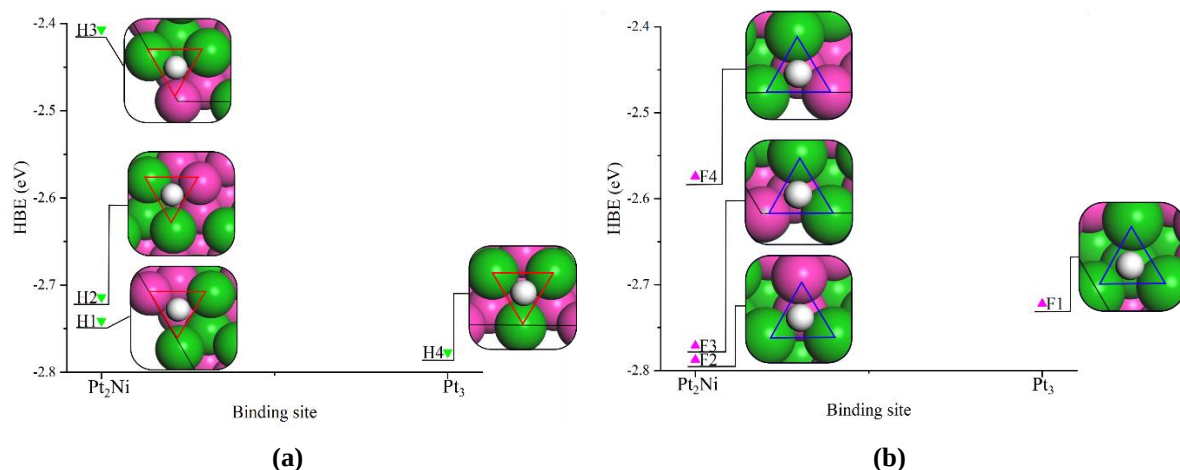


Figure 4.5. The comparison between the binding energies (HBE) for varying environments of the adsorption site for the **a)** *hcp* and the **b)** *fcc* sites for the for R-Pt_{0.25}Ni_{0.75} (111) surface.

In **Figure 4.5**, the change in the binding energy for the R-Pt_{0.25}Ni_{0.75} bimetallic surfaces was due to the ensemble effect and not the ligand effect since only one surface was investigated (R-Pt_{0.25}Ni_{0.75}), while varying the environment surrounding the adsorption sites (H₁ – H₄ and F₁ – F₄). The calculated binding energies for the *hcp* adsorption sites were – 2.741 eV, – 2.714 eV, – 2.407 eV and – 2.777 eV for H₁, H₂, H₃ and H₄, respectively. Excessive bonding was obtained for the H₁ and the H₄ sites, with a difference of 0.036 eV between these sites. On the other hand, weaker bond strengths were obtained for the H₂ and the H₃ (weakest) site, which had a large energy difference of 0.307 eV between these sites. In the case of the *fcc* adsorption sites, the binding energies were found to be – 2.722 eV, – 2.787 eV, – 2.771 eV and – 2.574 eV for F₁, F₂, F₃ and F₄, respectively. The values of the bond strength between the F₁, F₂ and F₃ adsorption sites were close with a difference between 0.016 eV and 0.065 eV. Moreover, linear tune-ability was observed as a result of the amount of Pt atoms in the binding site. However, the F₃ and F₂ (Pt₂Ni₁) bonding sites were an exception and resulted in weaker bonding than the F₁ site, because it is a Pt₃ site.

Comparing the *hcp* and the *fcc* adsorption sites, it is clear that the strongest bonding occurred for the F₂ and the H₄ adsorption sites, closely followed by the F₃ adsorption site. The weakest bonding was obtained for the H₄ adsorption site. The ideal bond strength between the Pt (111) and Ni (111) surfaces, should be 2.690 eV and 2.880 eV, respectively. Therefore, the F₄ binding site is more suited for catalysts using an R-Pt_{0.25}Ni_{0.75} (111) surface.

Similar results were obtained for the R-Pt_{0.50}Ni_{0.50} bimetallic surface and are shown in **Figure 4.6**. The binding energies for the *hcp* adsorption sites were calculated as – 2.595 eV, – 2.655 eV, – 2.417 eV and – 2.259 eV for H₁, H₂, H₃ and H₄, respectively. The strongest adsorption sites were the H₁ and the H₂ site. The difference in bond strength between the H₁ and the second strongest adsorption site, H₂, was 0.06 eV. The difference in bond strength between the H₁ and H₃ was large, namely 0.238 eV. The weakest binding on the R-Pt_{0.50}Ni_{0.50} surface was obtained for the H₄ site. From the results it is clear that the strongest bonding was obtained for the H₂ adsorption site, which was a (Pt₂Ni) adsorption site where a Pt atom is available in the second layer. The H₂ site was the second strongest site, while the hydrogen was bonded weakly to the H₄ absorption site. In the case of the *fcc* adsorption sites, the binding energies were calculated as – 2.355 eV, – 2.417 eV, – 2.696 eV and – 2.261 eV for F₁, F₂, F₃ and F₄,

respectively. The trend in bond strength towards hydrogen for the adsorption sites was $F_3 > F_2 > F_1 > F_4$, with the largest energy difference between F_3 and F_2 , namely 0.279 eV. The binding energy of the F_2 adsorption site is more suitable for adsorption than that of the other *fcc* adsorption sites investigated.

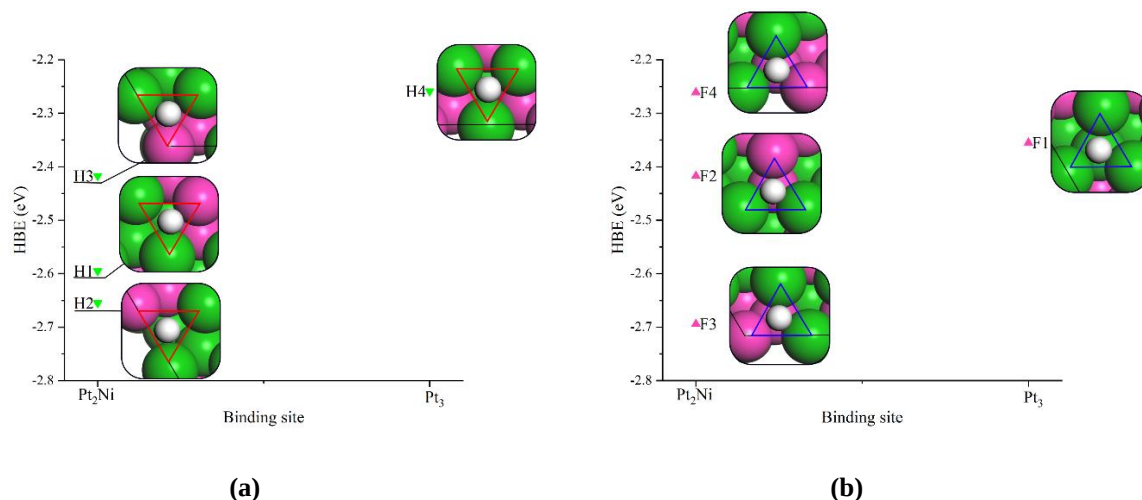


Figure 4.6. Comparison between the binding energies (HBE) for varying environments of the adsorption site for the a) *hcp* and the b) *fcc* sites for the R-Pt_{0.5}Ni_{0.5} (111) surface.

Comparing the *hcp* and *fcc* adsorption sites, it was seen that the bond strength was the strongest on the F_3 site, followed by the second strongest on the *hcp* adsorption site (labelled as H_2). On the other hand, the weakest hydrogen bonding was obtained for the H_4 and F_4 sites. Once again, it was observed that an increase of Pt atoms in the adsorption site caused a weakening of the binding energy for both the *hcp* and *fcc* adsorption sites. In conclusion, the hydrogen bond strength for the R-Pt_{0.5}Ni_{0.5} (111) surface, for both the *hcp* and the *fcc* sites, was stronger than the bond strengths observed for the Pt (111) surface (2.690 eV).

The binding energies obtained for the R-Pt_{0.75}Ni_{0.25} surfaces, with both the *hcp* and *fcc* adsorption sites, are compared in **Figure 4.7**. The binding energies for the *hcp* adsorption sites were calculated at -2.578 eV, -2.665 eV, -2.805 eV and -2.693 eV, for H_1 , H_2 , H_3 and H_4 , respectively, while the bonding energies calculated for the *fcc* adsorption sites were -2.691 eV, -2.878 eV and -2.665 eV for F_1 , F_3 and F_4 , respectively. It is important that there was no F_2 adsorption site for the R-Pt_{0.75}Ni_{0.25} surface since adsorption did not occur on this site since the site was not suited for hydrogen bonding. This unsuitable site means that the hydrogen, which was added to the hydrogen site, moved to a more suitable adsorption site which was a bridge site and was not investigated further. Once again, it is clear that an influence was seen for each of the adsorption sites due to the ensemble effects. The direction of the linear tune-ability was the same as with the R-Pt_{0.25}Ni_{0.75} bimetallic surface. This linear tune-ability further concludes that the downward shift of the *d*-band centre in the Fermi level, observed for the R-Pt_{0.72}Ni_{0.75} surface and R-Pt_{0.75}Ni_{0.25} surface bimetallic surfaces, affects the adsorption on these bimetallic surfaces. Now that the ensemble effects have been investigated between these bimetallic surfaces, the ligand effect was investigated by comparing the *hcp* and the *fcc* sites for all three the compositions, hence changing the compositions while keeping the adsorption sites constant.

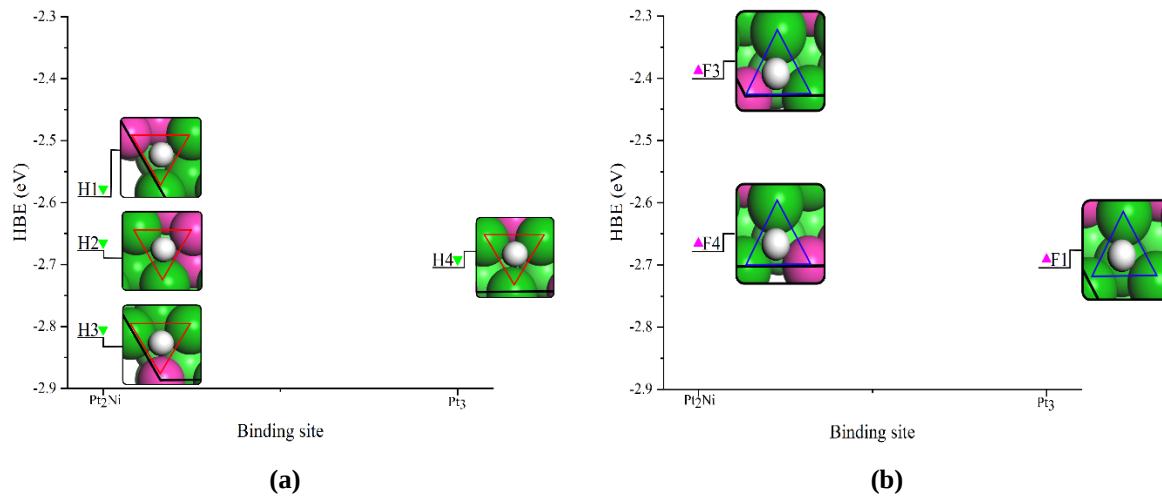


Figure 4.7. Comparison between the HBE and the a) *hcp* and b) *fcc* binding sites with varying environments, either bonded to Pt_3 or Pt_3Ni_1 for the $\text{R-Pt}_{0.75}\text{Ni}_{0.25}$ bimetallic surface.

By comparing the binding energies for the H_1 adsorption site for the $\text{R-Pt}_{0.25}\text{Ni}_{0.75}$, $\text{R-Pt}_{0.5}\text{Ni}_{0.5}$ and the $\text{R-Pt}_{0.25}\text{Ni}_{0.75}$ bimetallic (111) surfaces, binding energy differences of -2.741 eV ($\text{R-Pt}_{0.25}\text{Ni}_{0.75}$), -2.595 eV ($\text{R-Pt}_{0.25}\text{Ni}_{0.75}$) and -2.578 eV ($\text{R-Pt}_{0.25}\text{Ni}_{0.75}$) were observed.

It is clear that the environment surrounding the adsorption sites affected the binding energy. Comparing the *fcc* and *hcp* adsorption sites with one another, it is clear that the binding energies were similar in respect to the same surfaces.

The hydrogen bond strength obtained for the $\text{R-Pt}_{0.25}\text{Ni}_{0.75}$ surface showed that an ideal bond strength was obtained for the H_3 (-2.407 eV) and F_4 (-2.720 eV) adsorption sites, while a less ideal strength was observed for the H_4 and F_2 sites. In the case of the $\text{R-Pt}_{0.5}\text{Ni}_{0.5}$ surface, the hydrogen bonded too strongly onto the H_2 and F_3 adsorption sites, which is not the ideal. However, more ideal hydrogen bond strengths, between Pt (111) and Ni (111) surfaces, were obtained for the H_4 (-2.259 eV) and F_4 (-2.261 eV) adsorption sites. The hydrogen bond strength obtained for the $\text{R-Pt}_{0.75}\text{Ni}_{0.25}$ surface was less ideal for the H_3 and the F_1 adsorption sites, with more ideal bond strengths obtained for the H_1 (2.578 eV) and F_3 (2.387 eV) sites.

In conclusion, the most ideal bond strengths were obtained between -2.5 eV and -2.6 eV for all bimetallic surfaces investigated. Moreover, the differences in binding energies between the *hcp* sites and the *fcc* sites were stable, where the differences in the energies for the $\text{R-Pt}_{0.5}\text{Ni}_{0.5}$ surface was close in value. The least stable *hcp* and the *fcc* sites were that of the $\text{R-Pt}_{0.70}\text{Ni}_{0.25}$ surface with energy differences between 0.23 eV and 0.31 eV, for the *hcp* and *fcc* sites, respectively.

4.3.2.2.2. Difference in the adsorption energies due to the ensemble effect

As described in §4.3.1.2, the *d*-band centre values calculated for the pristine $\text{R-Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surface indicated that the surface had a medium bond strength when compared to the pure metals and the other two bimetallic surfaces. Therefore, the ensemble effects were studied in terms of the $\text{R-Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surface.

Moreover, as already mentioned, Pt_{0.5}Ni_{0.5} compositions are the most stable ratio for a Pt/Ni bimetal,^{31, 50} which was why ensemble effect was studied in detail for this surface.⁵⁰

The calculated work function, the interatomic spacing (d_{H-M}) between the metal and the adsorbed hydrogen, the binding energy, the adsorption energy, and the d -band centre were calculated, as shown in **Table 4.2**. In addition, $H-M_{ads}$ represents which surface the hydrogen was adsorbed to. In **Table 4.2**, the spacing between the hydrogen and the bonded metal/s (d_{H-M}) was 1.726 Å and 1.800 Å for Pt (111) and Ni (111), respectively. Furthermore, the interatomic spacing for the R-Pt_{0.5}Ni_{0.5} surface was larger than that of the pure metals, depending on the adsorption site and the ensemble effects. This interatomic spacing varied between ~2.008 Å and ~2.062 Å for the *hcp* site, and ~1.942 Å and ~2.048 Å for the *fcc* site. Overall, the difference in the atomic spacing between the metal surfaces was minor, with no large spacing differences observed due to the minimisation of the strain effect.

Table 4.2. Calculated electronic properties for R-Pt_{0.5}Ni_{0.5} bimetallic surface with varying adsorption sites in terms of the adsorbed metal site ($H-M_{ads}$), work function (Φ), interatomic spacing (d_{H-M}), binding energies (HBE), adsorption energy (E_{ads}) and the d -band centre (ϵ_d).

	Surface	$H-M_{ads}$	Φ (eV)	d_{H-M} (Å)	HBE (eV)	E_{ads} (eV)	ϵ_d (eV)
<i>hcp</i>	Ni (111) H	Ni	3.089	1.729	– 2.900	– 0.561	– 1.474
	Pt (111) H	Pt	5.002	1.800	– 2.785	– 0.516	– 2.451
	R-Pt _{0.5} Ni _{0.5} (H ₁)	Pt ₂ N	4.152	2.038	– 2.595	– 0.350	– 1.673
	R-Pt _{0.5} Ni _{0.5} (H ₂)	Pt ₂ N	4.376	2.008	– 2.655	– 0.533	– 1.682
	R-Pt _{0.5} Ni _{0.5} (H ₃)	Pt ₂ N	4.774	2.062	– 2.417	– 0.067	– 1.684
	R-Pt _{0.5} Ni _{0.5} (H ₄)	Pt ₃	4.359	2.018	– 2.259	– 0.479	– 1.681
<i>fcc</i>	Ni (111) F	Ni	3.097	1.725	– 2.880	– 0.539	– 1.474
	Pt (111) F	Pt	5.025	1.800	– 2.737	– 0.461	– 2.461
	R-Pt _{0.5} Ni _{0.5} (F ₁)	Pt ₃	4.875	2.048	– 2.355	– 0.067	– 1.678
	R-Pt _{0.5} Ni _{0.5} (F ₂)	Pt ₂ Ni	4.901	2.021	– 2.417	– 0.133	– 1.675
	R-Pt _{0.5} Ni _{0.5} (F ₃)	Pt ₂ Ni	4.661	1.942	– 2.694	– 0.381	– 1.681
	R-Pt _{0.5} Ni _{0.5} (F ₄)	Pt ₂ Ni	4.367	2.002	– 2.261	– 0.308	– 1.678

In **Chapter 3** in section §3.3.2.1, it was shown that the calculated work function for the pristine Pt (111) and Ni (111) surfaces was 5.070 eV and 3.090 eV, respectively. Comparing this to the R-Pt_{0.5}Ni_{0.5} bimetallic surface, the work function value was different for hydrogen adsorbed at the different adsorption sites. The shift in the work function, between the pristine surfaces and the adsorbed surfaces, was relatively small with a difference of less than ~ 0.15 eV. The reason for the small shift in the work function is due to the small effect that an elementary hydrogen atom has on the metal surfaces. Elemental hydrogen has only 1 electron (s^1), which bonds to the d -band of the metal surface during adsorption.

The adsorption energies obtained for the Pt (111) surface, **Table 4.2**, were – 0.516 eV and – 0.461 eV for the *fcc* and *hcp* adsorption sites, respectively. These adsorption results correlate with literature values, where the

adsorption energies were, -0.455 eV and -0.448 eV, for the *fcc* and *hcp* adsorption sites, respectively.¹ In addition, the adsorption energies obtained for the Ni (111) surface, **Table 4.2**, were -0.561 eV and -0.539 eV, for the *fcc* and *hcp* adsorption sites. These adsorption energies values correspond well with literature values of -0.659 eV and -0.661 eV, for the *fcc* and *hcp* adsorption sites.¹

The adsorption sites investigated for the bimetallic surfaces were the H₃, H₄ (R-Pt_{0.75}Ni_{0.25}) and F₂ (R-Pt_{0.5}Ni_{0.5}) adsorption sites (-2.787 eV). The bond strength in these adsorption sites are strong and are close to the bond strength obtained for Ni (111) surfaces, which is not ideal for multi-step reactions where more than one intermediate is formed. On the other hand, the bond strength obtained is between -2.25 eV and -2.66 eV (H₁-H₄) and between -2.35 eV to -2.70 eV (F₁-F₄). Therefore, the R-Pt_{0.5}Ni_{0.5} surface showed weaker adsorption and therefore, the more ideal catalytic surfaces for the water splitting reaction. In the next section the influence of the ensemble effect was investigated for the stable R-Pt_{0.5}Ni_{0.5} surface by comparison of the electronic properties.

4.3.2.2.3. Linear correlation between electronic properties.

A linear correlation exists between the binding energy and the adsorption energy since the binding energy of the hydrogen to the metal surface is dependent on the electronic surface.⁴⁴ In **Figure 4.8 (a)**, the binding energy is plotted against the adsorption energy for the R-Pt_{0.5}Ni_{0.5} (111) surface. As expected, the results show a linear correlation between the binding energy and the adsorption energy, especially for the H₃ and F₃ adsorption sites, although not all the adsorption sites correlate well. The adsorption energies of the R-Pt_{0.5}Ni_{0.5} (111) surface varied for each of the adsorption sites (**Figure 4.8 (b)**). The *d*-band centre value for the pristine metal indicated that the adsorption energies should be between the pure Pt (111) and Ni (111) metals, as observed in the results. Strong adsorption occurred on the H₂ (-0.533 eV) and H₄ (-0.479 eV) adsorption sites, which was still weaker than on the Ni (111) surface. On the other hand, the binding energy for all the other sites calculated was weaker than Pt (111).

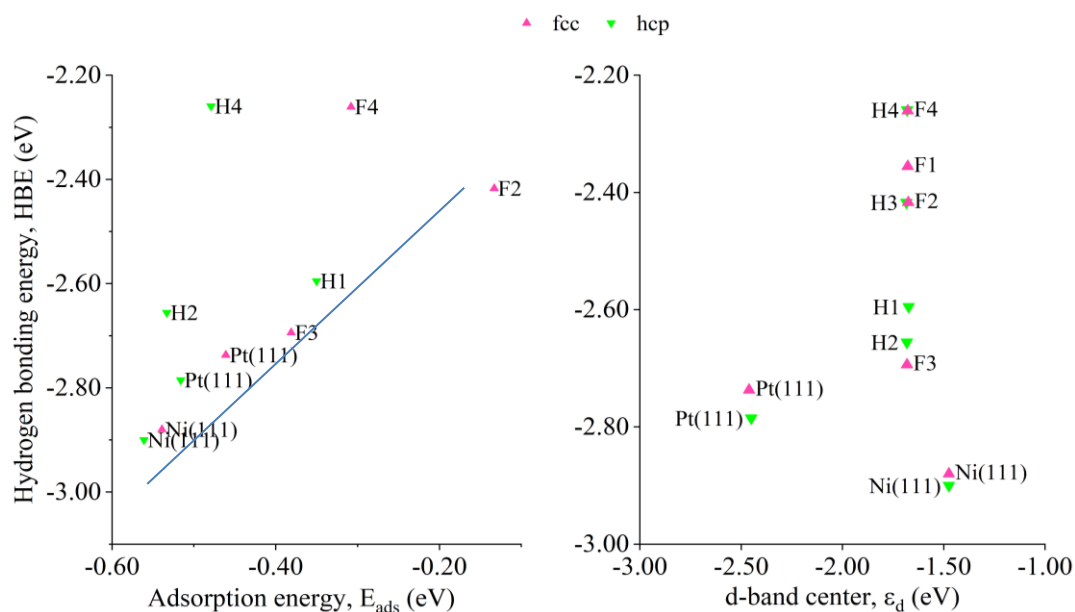


Figure 4.8. Hydrogen binding energy (HBE) vs **a)** the adsorption energy and **b)** the d -band centre for Ni (111), Pt (111) and R-Pt_{0.5}Ni_{0.5} (111) surfaces (indicated as F₁, F₂, F₄, H₁ and H₂).

When hydrogen is adsorbed onto transition metal surfaces, all the s - and p - orbitals are filled and therefore, the same for all the transition states.⁴⁹ However, the contribution of the d -band states varies between the transition metal surfaces and the adsorbed hydrogen. The structures of these d -band states are narrow, which are easily affected by small perturbations in the environment.^{8, 14, 15} Therefore, the binding energy was plotted against the d -band energy for the pure metals and the R-Pt_{0.5}Ni_{0.5} (111) surfaces, as shown in **Figure 4.8 (b)**.

According to literature studies, the binding energy varies approximately linearly with the d -band centre for the Pt (111) and Ni (111) surfaces,^{6, 34, 49} as observed in **Figure 4.8 (b)**. The trend in the binding energy for the parent metals was Pt < Ni, which is consistent with literature studies.⁶ Furthermore, the hydrogen bonding increased as the d -band centre shifted down towards the Fermi level, where $E_F = 0$. Consequently, the interaction of the hydrogen with Ni (111) was strong due to the d -states being close to the Fermi level, but higher in energy than that of the Pt (111) surface.

Moving to the results of the R-Pt_{0.5}Ni_{0.5} (111) surface, the observed d -band centre for all the adsorption sites did not vary. However, the binding energy varied for each of the adsorption sites. This varying binding energy is a possible indication of the nearest neighbour and environmental influences on the adsorption sites. In addition, there are many possible arrangements of the Pt and Ni metals in the R-Pt_{0.5}Ni_{0.5} (111), which were not determined. Hence, the R-Pt_{0.5}Ni_{0.5} (111) surface used in this chapter was most likely not the most stable surface arrangements for a Pt/Ni bimetal with a 1:1 ratio. This instability of the R-Pt_{0.5}Ni_{0.5} (111) surface could also be a contributing factor to the varying adsorption results on this surface.

The binding energies on the bimetallic surfaces are less than that of either the parent metals for thermodynamically stable bimetallic surfaces.⁴⁹ Experimentally, it has been observed that hydrogen atoms bind more weakly on Pt – Ni – Pt surfaces than on either Pt or Ni surfaces.^{34, 49} This was observed in **Figure 4.8 (b)**, which shows that the R-Pt_{0.5}Ni_{0.5} (111) bimetal surfaces exhibited binding energies which are lower than that of the corresponding

Pt (111) metal and higher than the Ni (111) metal surface. In conclusion, hydrogen bonding on the bimetallic surfaces was still weaker than that observed for the Ni (111) surface, which depending on the electrocatalytic reaction used, is more reactive than the parent metals.

Even though the binding energies for the H₄ and F₄ adsorption sites were identical, the adsorption energy indicated that adsorption was preferred for the H₄ site, rather than on the F₄ site. This difference in the adsorption energies could be a contribution of the ensemble effect and not the ligand effect. The reason for this is that the binding energies were constant for both adsorption sites. Furthermore, ligand effects occur due to the difference in the electronic properties between the parent metals. From the results, it is obvious that the electronic property of the R-Pt_{0.5}Ni_{0.5} (111) surface was constant between the binding sites. Therefore, the changing binding energies and adsorption energies must be due to the ensemble effects.

In conclusion, although the surface of the metal consists of various parent metals, the strength of the hydrogen bond is dependent on the adsorption site and the type of adsorption metal. The electronic properties of various metal surfaces, i.e. *d*-band structure, can be studied by examining the changes in the adsorption energies. As previously mentioned, the shift in the *d*-band centre affects the degree of interaction, either towards a weaker or stronger chemical bond, between the transition metal surface and the hydrogen adsorbate. Furthermore, downward shifts in the *d*-band centre have been shown to cause a significant effect on the surface reactivity, due to the weakened interaction between the reactants and substrates.⁵¹

Overall, a linear correlation was observed between the parent metals, which correlates with literature findings.^{14, 34} However, the adsorption sites calculated on the R-Pt_{0.5}Ni_{0.5} surface were inconsistent, which showed the presence of ensemble effects. The ensemble effects that occur on the bimetallic surface influenced the bonding energies and adsorption energies of each of the adsorption sites investigated, resulting in varying energy values.

4.4. Conclusion

In conclusion, the reactivity of a metal surface can be determined by the adsorption energy, *d*-band centre and the binding energy. The results obtained for the R-Pt_{0.5}Ni_{0.5} bimetallic surface showed varying results for each of the adsorption sites brought on by a change in the adsorption environment, and as a result, the contribution of ensemble effects. Ultimately, a conclusive trend could not be observed for this bimetallic surface. The method used in this chapter did not determine the most stable R-Pt_{0.5}Ni_{0.5} bimetallic surface mixture. However, the results indicated that by varying the adsorption sites, a more stable atomic arrangement of the surface could be possible. Therefore, the results concluded that the manual random technique was not an ideal technique to create bimetallic surfaces or to assess all the arrangements possible for a Pt/Ni bimetallic mixture with a 1:1 ration. Therefore, **Chapter 5** will focus on a systematic method, using the site occupancy disorder (SOD) program⁵², to create bimetallic slabs with more stable atomic arrangements.

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5

Developing a thermodynamically stable Pt/Ni bimetal using a systematic method

In this chapter a series of face-centred cubic (fcc) Pt/Ni bimetallic unit cells (Pt_xNi_{1-x} , where $x = 0, 0.25, 0.50, 0.75$ or 1) were created using the site occupancy disorder (SOD) program. These Pt/Ni bimetallic unit cells were created by performing substituting of Pt by Ni for various simulation cell sizes of the unit cell. The electronic and thermodynamic properties for these Pt/Ni bimetallic unit cells were studied. The results showed that a Pt/Ni bimetallic unit cell with a 1:1 Pt/Ni ratio was thermodynamically the most stable mixture. It is important to note that the previously mentioned adapted model (CASTEP), as discussed in Chapter 3, was not used in this chapter, but instead, the Vienna ab initio simulation program (VASP) was used. The reason being that this research was done during a brief exchange visit to Cardiff University in Wales, UK, and VASP is the software of choice used within the host research group. The results obtained in this part of the study was published in Issue 30 of RSC Advances.¹

5.1. Introduction.....	87
5.2. Computational method.....	88
5.3. Results and discussions	89
5.4. Conclusions.....	95
5.5. References.....	96

5.1. Introduction

In **Chapter 2 (§2.4.5)**, the electronic and magnetic properties of metallic surfaces were discussed in detail. From the discussion, it was clear that the magnetic property of a metal is determined by the valence electron configuration. Pt is non-magnetic due to the equal population of electrons, divided into the up (α) and down (β) spins, within the full $5d^{10}$ level.^{1, 2} On the other hand, Ni exhibits ferromagnetic properties due to the incomplete $3d^9$ level of the Ni metal which leads to unpaired electrons spins.^{3, 4}

A large number of investigations use adsorption energy to describe the surface properties of surfaces, which overlooks the importance of the magnetic properties of the surface, such as the magnetic moments.⁵ Moreover, scaling relations of magnetic bimetallic transition metal surfaces have been recently investigated through the addition of magnetic moment in the scaling calculations.⁵ As a result, it was shown that magnetic moments could be successfully added to the scaling relation for bimetallic magnetic systems.⁵ A Bader partitioning (also known as Bader charge analysis) have been developed to calculate the charge density and the magnetism of materials when using DFT investigations.⁶⁻¹² As a result, a Bader analysis was performed on the Pt/Ni bimetallic bulk surfaces to determine the magnetic properties of these surfaces.

Despite the large amount of literature published on enhanced electrocatalytic activity of Pt/Ni bimetals,¹³⁻¹⁸ the relationship between the electronic structure, the distribution of the metal atoms in the mixture, and the equilibrium composition of the mixture are not yet fully understood. This relationship could be investigated by investigating various thermodynamic properties, such as the entropy (S) and the enthalpy (H) of the equilibrium compositions of the Pt/Ni bimetals. These thermodynamic properties are influenced by the size of the cell being investigated. For example, the convergence of the free energies and entropies are slower with an increase in the cell size, while the convergence of the calculated enthalpies of the disordered systems tends to occur rapidly with an increase in the cell size.¹⁹

The entropy of convergence ($S_{\max}$) of varying simulation cell sizes could be determined using equation (5-1). This entropy of convergence was used to determine the rate of convergence with varying simulation cell sizes and to determine if the simulation cell size would converge. In equation (5-1), the number of atoms in the simulation cell is N, the Boltzmann constant is k_B ²⁰ and the Ni mole fraction in the bimetal is indicated by x .¹⁹

$$S_{\max}(x, N) = \frac{1}{N} k_B \ln \frac{N!}{[xN]![(1-x)N]!} \quad (5-1)$$

Entropy described by a Boltzmann-like probability is called the full-disordered entropy. The ideal full-disorder entropy (S_{ideal}), for when the simulation cell size approaches an infinite size, could be calculated using equation (5-2),²¹ where the variables are the same as in equation (5-1).

$$S_{\text{ideal}}(x) = \lim_{N \rightarrow \infty} S_{\max}(x, N) = -k_B [x \ln x + (1-x) \ln (1-x)] \quad (5-2)$$

In order to identify the most stable Pt/Ni ratio in the bimetal, the enthalpy of mixing (ΔH_{mix}) was calculated using equation (5-3).²¹ In equation (5-3) the total energy of the various bimetallic bulk structures are represented by $E(\text{Pt}_{1-x}\text{Ni}_x)$, while the energies of the Pt and Ni atoms are represented by $E(\text{Pt})$ and $E(\text{Ni})$.

$$\Delta H_{\text{mix}} = E(\text{Pt}_{1-x}\text{Ni}_x) - (1-x)E(\text{Pt}) - xE(\text{Ni}) \quad (5-3)$$

The total energy of the various bimetallic bulk structures was calculated using equation (5-4). The probability of the occurrence of an inequivalent configuration (m) is represented by P_m , while the full spectrum configuration in the various bimetallic bulk structures contains M inequivalent configurations.²¹⁻²³ The energy of the inequivalent configuration (m) is given by E_m .

$$E(\text{Pt}_{1-x}\text{Ni}_x) = \sum_{m=1}^M P_m E_m \quad (5-4)$$

The probability of occurrence of an inequivalent configuration (m) follows the Boltzmann distribution, shown in equation (5-5), where the degeneracy of the inequivalent configuration is shown as Ω_m and the other variables are the same as in the previous equation.²¹⁻²³

$$P_m = \frac{\Omega_m}{Z} e^{(-E_m/k_B T)} \quad (5-5)$$

The configurational partition function (Z), which describes the statistical properties of a system in the thermodynamic equilibrium, is shown in equation (5-6). The variables in this function are the same as those in previous equations.²¹⁻²³

$$Z = \sum_{m=1}^M \Omega_m e^{(-E_m/k_B T)} \quad (5-6)$$

5.2. Computational method

Both Pt and Ni metals adopts the face-centred cubic (*fcc*) crystal structure along the [111] direction, which belongs to the $Fm\bar{3}m$ space group (No. 225).^{24, 25} The Pt and Ni unit cells contains four atoms.²⁶ Ni is a ferromagnetic material with a Curie temperature of $T_C = 624$ K, while Pt is a closed shell paramagnetic metal.²⁷ The lattice coordinates for the Pt and Ni unit cells (four atoms) were obtained from the Inorganic Crystal Structure Database (ICSD).²⁸

Unique (inequivalent) bimetallic bulk structures were obtained from the SOD (site-occupancy disorder) program,²⁹ which generated all the possible configurations for $\text{Pt}_x\text{Ni}_{1-x}$ bimetallic bulk structures, where $x = 0, 0.25, 0.50, 0.75$ or 1 . The SOD program also eliminated similar configurations.³⁰ In the setup of SOD, the simulation cell sizes used were $1 \times 1 \times 1$ and $2 \times 2 \times 1$. The $1 \times 1 \times 1$ simulation cell is small and may not be as accurate

as larger simulation cells. However, a $2\times 2\times 2$ simulation cell size is computationally expensive and increases computational time due to the number of inequivalent configurations generated by SOD and, therefore, could not be considered. The cubic symmetry of the unit cell was doubled in the a and b directions to form a $2\times 2\times 1$ simulation cell size, which was used to increase the accuracy of the data sampling while still limiting the calculation cost. Notably, the cubic symmetry of the unit cell was broken by using a $2\times 2\times 1$ simulation cell size, but this symmetry breaks only occurred in the c -direction which did not hinder the results.

The inequivalent configurations were optimised with the General Utility Lattice Program (GULP).^{31, 32} The Sutton and Chen³³ interatomic potential (IP) was used to calculate the structures and energies for the inequivalent configurations generated for the $1\times 1\times 1$ and $2\times 2\times 1$ simulation cells for the bimetallic bulk structures, as well as the pure Pt and Ni. Additionally, the $1\times 1\times 1$ simulation cells for the bimetallic bulk structures, as well as the pure Pt and Ni, bulk structures were optimised by using Density functional theory (DFT) calculations, as implemented in the Vienna *ab initio* simulation program (VASP).³⁴⁻³⁷ The lattice parameters, internal coordinates, cell shape and atomic spin momentum were allowed to change during the geometry optimisations.

For the DFT calculations, the generalised-gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (PBE)^{38, 39} corrected with the semiempirical D3 approach of Grimme with the Becke-Johnson (BJ) damping⁴⁰⁻⁴² was used. The projected augmented-wave (PAW)⁴³ method, as implemented by Kresse and Joubert,⁴⁴ was used to describe the interaction between the core and valence electrons, which is defined in the 5d6s levels for Pt and 3d4s levels for Ni. A fixed kinetic energy cut-off at 400 eV,⁴⁵ which was large enough to avoid Pulay stress. Spin-polarisation was added to the pure metal and bimetallic bulk structures, where the initial spin momenta were set to parallel for the Ni atoms. A Γ -centred Monkhorst-Pack grid⁴⁶ of $11\times 11\times 11$ k -points was used to carry out the integrations in the reciprocal space of the metal bulk structures. convergence of the Brillouin-zone integrations was improved by determining the electronic partial occupancies using the Methfessel-Paxton⁴⁷ order. A smearing width of 0.2 eV were set for all of the calculations. Accurate total energies was obtained in static simulations by using the tetrahedron method with Blöchl corrections.⁴⁸ As previously mentioned, the magnetic moments and the atomic charges were analysed using the Bader charge analysis.⁶⁻¹²

5.3. Results and discussions

The calculated lattice parameter for the bulk structures of Pt and of Ni was $a = 3.924$ Å and 3.473 Å, respectively. These lattice parameters are firmly aligned with the experimental value of Pt (3.923 Å)²⁴ and Ni (3.528 Å).²⁵ Hence, the performance of the DFT model used in this chapter of the study for determining the lattice parameters of the pure metal bulk structures, are acceptable. This performance of the DFT model enabled confidence in the predictions and the results obtained throughout the rest of this chapter.

In the case of the bimetallic bulk structures obtained from the SOD, it is important to note that the $2\times 2\times 1$ configuration generated 805 inequivalent configurations, while only five inequivalent configurations were obtained with a $1\times 1\times 1$ simulation cell size.

The $2\times 2\times 1$ simulation cell size, containing 16 atoms, resulted in a full-disorder configurational entropy, which was an improvement with respect to the smaller $1\times 1\times 1$ simulation cell. Therefore, these results suggest a slow

rate of convergence with respect to the size of the simulation cell which are in an agreement with previous reports.¹⁹ Even though the maximum entropies were not fully converged, they are useful in evaluating the measure of disorder in bimetallic bulk structures at equilibrium conditions.

The maximum entropy values for different simulation cell sizes relative to the Ni contents are shown in **Figure 5.1**.

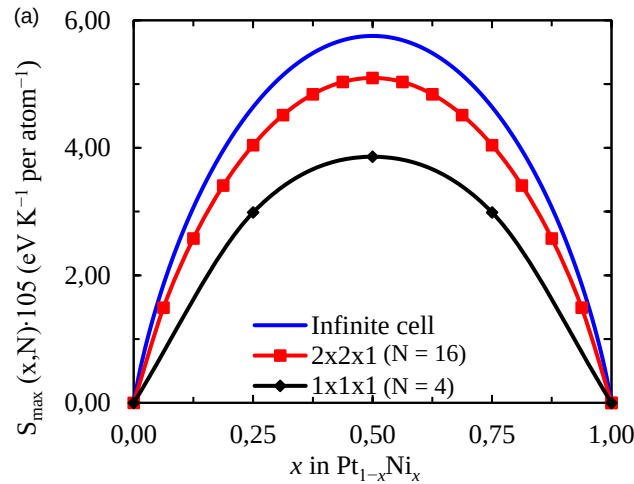


Figure 5.1. A schematic representation of the process to obtain full convergence ($S_{\max}$) for each of the Pt/Ni concentrations with varying degrees of simulation cell sizes.

According to the entropy convergence shown in **Figure 5.1**, the largest full-disorder entropies were reached where the concentrations of Pt and Ni atoms were equal, starting at $S_{\max} = 0$ for the pure metals. The calculated high-temperature entropies for the smaller $1 \times 1 \times 1$ simulation cell, containing four atoms, were below the full-disorder values by $\sim 33\%$ and $\sim 36\%$ at $x = 0.25$ and 0.50 , respectively.

The next step was to determine how the enthalpy was influenced by the Pt and Ni fractions in the simulation cell. The enthalpy of mixing (ΔH_{mix}), calculated with DFT and IP, for the $1 \times 1 \times 1$ simulation cell, as a function of the Ni mole fraction x is shown in **Figure 5.2**. The accuracy of the IP and DFT calculations were compared using the enthalpy of mixing (ΔH_{mix}) to determine which bimetallic mixture is thermodynamically most stable at 300 K.

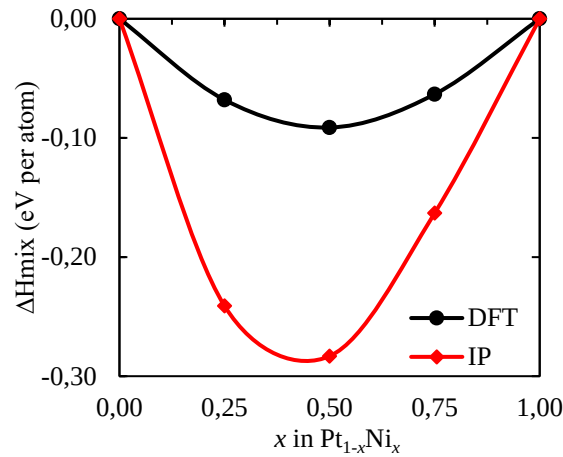


Figure 5.2. The mixing enthalpies (ΔH_{mix}) per atom of $\text{Pt}_{1-x}\text{Ni}_x$ and as a function of the Ni mole fraction (x) for the $1 \times 1 \times 1$ simulation cell size.

The $\text{Pt}_{1-x}\text{Ni}_x$ bimetallic bulk structure formation is an exothermic process as indicated by the negative enthalpy of mixing values for the partially disordered bimetal for any Ni fraction. The IP results suggest a slight asymmetry shape, while the DFT suggests a symmetric shape for the enthalpy of mixing as Ni is incorporated into the Pt lattice. The incorporation of Pt into Ni lattice is exothermic, indicated by the ΔH_{mix} values which was 0.005 eV per atom and 0.078 eV per atom obtained with DFT and IP, respectively. Although larger enthalpies of mixing was predicted by the IP method than the DFT approach, especially for $x = 0.5$, similar behaviour for the thermochemistry was described for the Pt–Ni bimetallic bulk structure. Specifically, both predicted that the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ would be the equilibrium composition. Similar results has been observed for ordered and disordered special quasi-random structured $\text{Pt}_{1-x}\text{Ni}_x$ bimetallic bulk structures.⁴⁹

After the most probable and thermodynamically stable configuration of the bimetallic bulk structure was identified, the electronic and the magnetic properties of this configuration were calculated and compared to that of the pure Pt and Ni bulk structures.

In **Figure 5.3**, the difference in energy and the probability distributions of the 153 inequivalent configurations (m) for $\text{Pt}_{0.5}\text{Ni}_{0.5}$, obtained with a simulation cell size of $2 \times 2 \times 1$, are plotted against one another. It is important to note that the 153 configurations at different energies are represented by vertical lines, but these lines have been grouped together to create the histogram plot shown in **Figure 5.3**. Ambient conditions are represented by 300 K for the probability distribution for the partially disordered $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configurations.

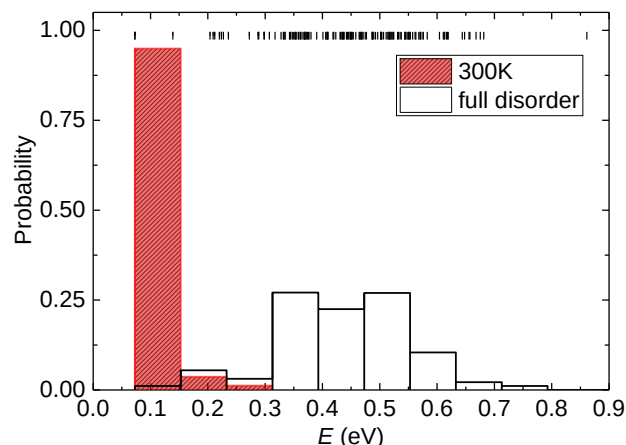


Figure 5.3. The fully and partial disordered probability distribution of the energies (E) calculated for the configurations with a $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configuration in the $2 \times 2 \times 1$ simulation cell at 300 K. (The short vertical lines at the top of the graph represent the energy values in the configurational spectrum.)

The results for the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configurations in **Figure 5.3** clearly indicate a difference of 0.7 eV per atom between the low- and high-end energy configurations. The bimetallic bulk structure (bimetal) is fully disordered at high temperatures which leads to a normal probability distribution. However, at 300 K, there were configurations that had a high probability of occurrence but with decreasing energy.

Overall, **Figure 5.3** indicates that 153 equivalent configurations were obtained at 300 K. However, only three configurations, which accounts for 3.7 %, 47.6 % and 47.3 % as obtained from SOD result file, of the probability of occurrence are probable to occur out of the total probability spectrum. These three configurations will be referred to as A, B and C. The results strongly suggest that $\text{Pt}_{1-x}\text{Ni}_x$ bimetal prefer to form ordered rather than a random distribution of atoms at 300 K, however, this preference is reduced at higher temperatures. The favourability of the highly ordered bimetal at 300 K strongly suggests that at lower temperatures, the bond energy associated with the Pt–Pt and Ni–Ni bonds outweighs the entropy costs. The opposite is true at high temperatures where a relatively normal probability distribution, centred on the maximum entropy structure, indicates that entropy contributions dominate.¹ A schematic representation of the configurations A, B and C are shown in **Figure 5.4**.

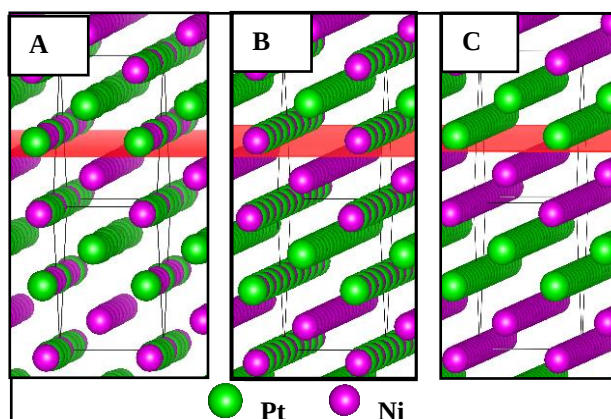


Figure 5.4. A schematic representation of the A, B and C configurations of the bimetallic bulk structure with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configurations. The red plane represents the [110] plane.

This schematic representation provides evidence of a preferential ordering pattern, while no segregation of the Pt and Ni atoms into two separate phases was observed. Configuration A consisted of alternating Pt and Ni atoms, which were perpendicular to the [110] direction. The layers observed comprised of a layer of Pt, followed by a mixed layer of Pt/Ni and then followed by a layer of Ni. The mixed atoms in the mixed layer consisted of 4Pt|2Ni|4Pt, whereas, in the following mixed layer the sequence became 4Ni|2Pt|4Ni. For configuration B, three different alternating atomic planes perpendicular to the [110] direction, which are represented as a layer of Pt, followed by a mixed layer of Pt/Ni and terminated by a single layer of Ni, were observed. Configuration C also exhibits the ordering pattern in the [110] direction, where every other mixed layer was replaced by a plane containing only one type of atom, leading to alternating double layers of Pt and Ni metals. The atomic orderings observed for configurations A, B and C along the [110] direction are equivalent to the surface segregation patterns predicted computationally⁵⁰ and later confirmed experimentally,^{51, 52,52-55} which showed a strong effect on the catalytic properties of the bimetal. As a result of the probabilities of the A, B and C configurations, it was decided to continue the investigation with the B and C configurations, since these configurations had an almost 50 % probability of occurring.

Subsequently, the electronic structures and magnetic properties of the highest probability configurations, B and C, of the Pt_{0.5}Ni_{0.5} bimetallic bulk structure were modelled and compared to the parent metals. In **Figure 5.5**, the partial density of states (pDOS) for the *d*-electrons of the pure Pt and Ni metals and configurations B and C are shown.

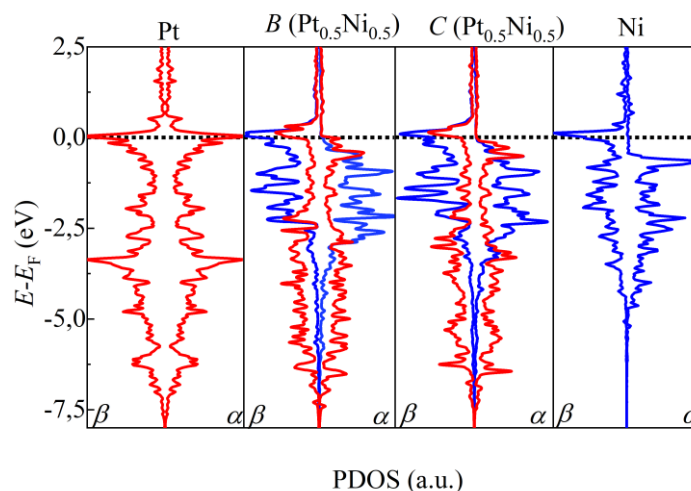


Figure 5.5. The partial density of states (pDOS) in terms of the *d*-electrons for the Pt, Ni and the Pt_{0.5}Ni_{0.5} metals. The B and C configuration was used for the bimetallic bulk structures. The α and β symbolise the majority and minority spin channels, respectively.

It was observed in **Figure 5.5** that Ni has an asymmetric pDOS, especially around the Fermi level, due to its incomplete 3*d*⁹ level. The valence band in the majority channel of the spins in Ni spans from – 5.0 eV to – 0.5 eV, while occupied levels in the β channel are shifted approximately 1 eV towards the Fermi level. In contrast, Pt metal is non-magnetic and exhibits a symmetrical pDOS in both spin channels due to the equal population of electrons with α - and β - spins within the full 5*d*¹⁰ level. The occupied *d*-levels of Pt appear between – 7.5 eV and the Fermi level (*E*_F), with prominent bands at – 3.0 eV and 0.0 eV.

The DFT results suggest that the electronic structures of the B and C configurations are similar. Looking at the pDOS it is clear that the bimetallic configuration exhibits electron magnetism inherited from the Pt and Ni atoms. This asymmetric shape of the pDOS can be understood as an electronic delocalisation due to the strong interaction between the d -electrons of the two metals.

The electronic properties of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic bulk structure were further analysed by comparing the band structure and the pDOS of configuration B, as shown in **Figure 5.6**. The Brillouin zone path suggested by Setyawan *et al* was followed.⁵⁶ A lack of a band gap for any of the spin channels and their asymmetry was observed for the band structure which is in agreement with the pDOS. The minority spin channel is larger than in the majority spin channel which suggests that the contribution of the β electrons to the metallic properties of the bimetal is larger. The α spin contribution to the band structure for the Pt states are mostly below and above the Ni bands down to -7.40 eV and up to the Fermi level, while the Ni states is between -0.50 eV and -2.90 eV for Ni. Similar features is showed in the β spin channel but is displaced towards the Fermi level by approximately 1.00 eV. Interestingly, the band structure of configuration B clearly indicates the origin of the hybridisation between the d -states of both atoms as the Pt d -levels have a larger contribution than the Ni ones at the lines connecting the high-symmetry points W-K, U-W and U-X of the first Brillouin zone in both spin channels.

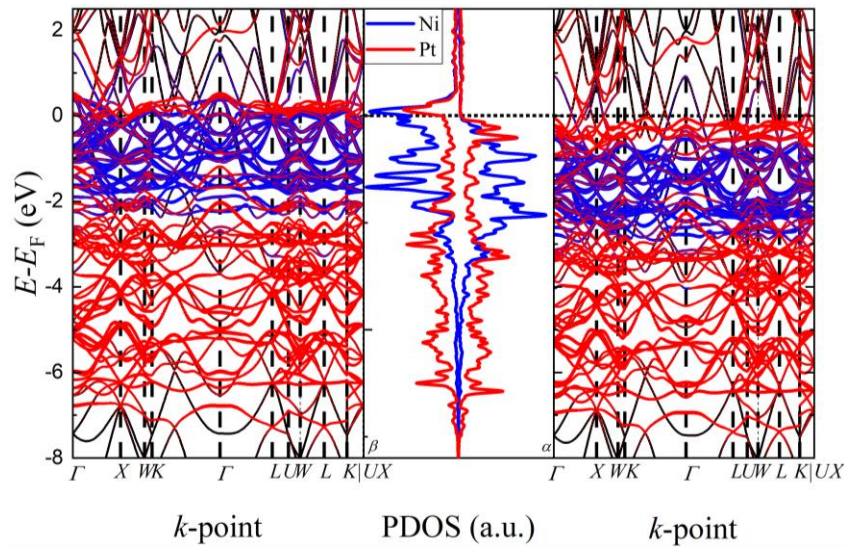


Figure 5.6. The density of states and band structure for configuration B of the bimetallic bulk structure with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ configuration. α and β stand for the majority and minority channel of the spins, respectively.

From **Figure 5.5** and **Figure 5.6**, it is apparent that the occupation of the d -electrons in configurations B and C were influenced by the addition of Pt and Ni. However, the influence of the occupation of the d -electrons in the bimetallic bulk structures is unknown. Therefore, the magnetic properties of the bimetallic bulk structure were investigated by determining the atomic charges (q) and atomic spin moments (m_s) of the pure Pt and Ni, as well as of the B and C configurations. The q and m_s for the Pt, Ni and bimetallic bulk structures are given in **Table 5.1**

Table 5.1. Atomic charges (q) and atomic spin momenta (m_s) for the pure Pt and Ni metals, as well as for configurations B and C of the bimetallic bulk structures with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition, as calculated using a Bader analysis.⁶

Bulk structures	Configuration	Atom	q (e per atom ⁻¹)	m_s (μ_B per atom ⁻¹)
Pt	–	Pt	0.000	– 0.002
Ni	–	Ni	0.000	0.630
$\text{Pt}_{0.5}\text{Ni}_{0.5}$	<i>B</i>	Pt	– 0.230	0.330
		Ni	0.230	0.740
	<i>C</i>	Pt	– 0.230	0.350
		Ni	0.230	0.760

The results confirmed that the atoms are neutrally charged for the two pure metals. The Pt atom is not magnetic, and the Ni had a spin momentum of $0.630 \mu_B$ per atom⁻¹, which compares well with the experimental value of $0.62 \mu_B$ per atom⁻¹.⁴ The results indicated that Pt became magnetic upon insertion of the Ni atoms in the bimetallic bulk structure as it gained electrons in its 6s level.⁵⁷ The atomic quantities are very similar for $\text{Pt}_{0.5}\text{Ni}_{0.5}$, albeit that the Pt magnetic moment was marginally lower in configuration B than in C. The total spin magnetisation of saturation (M_s) was $1.070 \mu_B$ per atom and $1.110 \mu_B$ per atom for configurations B and C, while the Ni atoms lost $\sim 30\%$ of their atomic spin moments to Pt.

5.4. Conclusions

The objectives for this chapter were to find a more scientifically repeatable method to simulate bimetallic mixtures and to obtain the optimal ratio of Pt and Ni in these bimetallic mixtures.

The site occupancy disorder (SOD) program³⁰ was used to obtain symmetrically inequivalent configurations for $1 \times 1 \times 1$ and $2 \times 2 \times 1$ simulation cell sizes. SOD is a scientifically repeatable method to simulate bimetallic mixtures.

Moreover, from the mixing thermodynamic calculations, the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic configuration was identified to be the optimal ratio of Pt and Ni. The calculated results also showed that the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ mixture was highly ordered up to at least 300 K and did not experience segregation of the atomic species. At 300 K, there were two configurations, B and C, which had the highest probability to occur. The B and C configurations both showed metallic properties.

Additionally, the magnetic and electronic properties of the two configurations were investigated. It was shown that electrons were transferred to the Pt from the Ni, and Pt became magnetic with the addition of Ni. In §2.3.6 in **Chapter 2**, it was discussed that the reactivity of an electrocatalyst is influenced by the magnetic properties of the metal surface since the catalytic activity is strongly affected by a magnetic field.² For this reason, the conclusion could be made that the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic configuration would be a better catalyst than Pt alone. The catalytic activity of various $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surfaces was investigated in **Chapter 6**.

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PART 3

Epilogue – Application of bimetallic (111) surfaces

Adsorption onto transition metal surfaces is promoted by the energetically available *d*-orbitals, and this is the reason why hydrogen readily adsorbs onto these surfaces.¹⁻⁶ However, the reaction of hydrogen with transition metal surfaces, which have been widely studied both experimentally and computationally, is different for each transition metal surface.^{1, 4-10} The reactivity of a transition metal surface can be determined from the change (shift) in the *d*-band centre (ϵ_d), before and after adsorption.^{6, 11} Numerous studies have shown that the electronic structures of Pt^{1, 2, 8} and Ni^{1, 3, 12, 13} surfaces could be studied by adsorption of an adsorbate, such as hydrogen or an H₂O molecule.

In **Chapter 5**, the Pt_{0.5}Ni_{0.5} bimetal mixture was identified to be the bimetallic bulk structure with the optimal Pt/Ni ratio. Additionally, the atomic arrangements with the highest probability to exist, namely the B and C configuration (see **Chapter 5**) were identified. Furthermore, magnetic and electronic properties of these configurations were investigated. These magnetic properties may indicate that the obtained Pt_{0.5}Ni_{0.5} bimetal has great potential as an alternative electrocatalyst for both the OER and the ORR.^{14, 15} However, the reactivity of the Pt_{0.5}Ni_{0.5} bimetal as a potential alternative electrode material for OER and ORR is unknown.

In **Chapter 6**, the Pt_{0.5}Ni_{0.5} bimetal bulk structure was cleaved into five different surface terminations (0.0, 0.5, 1.0, 1.5, and 2.0) for which the reactivity was investigated. The reactivity was investigated by the adsorption of a single hydrogen atom or an H₂O molecule on the five Pt_{0.5}Ni_{0.5} (111) bimetallic surfaces. The hollow point adsorption sites (*fcc* and *hcp*) were used to investigate the hydrogen adsorption, while the atop site was used to investigate the H₂O molecule adsorption.

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6

Hydrogen and water adsorption onto $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surface

In this chapter, spin-polarised density functional theory calculations were employed to investigate the surface properties of five surface terminations cleaved from the thermodynamically stable $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic unit cell. Furthermore, the five $\text{Pt}_{0.5}\text{Ni}_{0.5}$ (111) surface terminations, 0.0, 0.5, 1.0, 1.5 and 2.0, were characterised and the surface stability was compared to the pure Pt (111) and Ni (111) surfaces. The results showed that the $_{1.5}$ (111) and $_{0.5}$ (111) surface terminations were energetically the most favourable surfaces. On the other hand, the $_{2.0}$ (111) surface termination was energetically the least favourable surface but was energetically more favourable than pure Ni. In the second part of the chapter, a single hydrogen atom was added to the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surfaces, and the adsorption energy was calculated. The adsorption results confirmed that at a low hydrogen surface coverage, these surfaces were more stable than the pure metal surfaces. This part concluded that a $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surface may be a viable electrocatalyst for the oxygen evolution reaction and the oxygen reduction reaction. In the third part of this chapter, the adsorption of a single water (H_2O) molecule was investigated on the five $\text{Pt}_{0.5}\text{Ni}_{0.5}$ (111) surface terminations. The H_2O molecule was adsorbed onto the atop site in the most stable orientation, namely, parallel to the surface (a flat geometry). The d-band centre revealed that the bonding of the H_2O molecule on the $_{0.5}$ (111) surface termination was stronger than on the pure Pt surface, but weaker than on the pure Ni surface. The bond elongation of the OH bonds and an increase in the HOH bond angle were observed in the H_2O molecule adsorbed on the $_{0.5}$ (111) surface. This bond elongation is an indication of bond breakage occurring on the metal surface. Ultimately, the results showed that the $_{0.5}$ (111) surface termination could potentially be used as an electrocatalyst for the water-splitting reaction, but experimental data is needed to confirm these results.

6.1. Introduction.....	103
6.2. Computational method.....	103
6.2.1. Building the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces.....	104
6.2.2. Hydrogen adsorption on $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces.....	106
6.2.3. Water adsorption on $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces.....	107
6.3. Results and discussions.....	107
6.3.1. Pristine (111) surface properties.....	107
6.3.2. Hydrogen adsorption results.....	111
6.3.3. Properties of isolated water.....	114
6.3.4. H_2O adsorption.....	115
6.3.4.1. Pt (111) and Ni (111) surfaces.....	115
6.3.4.2. $_{1.5}$ (111) and $_{0.5}$ (111) surfaces.....	117
6.4. Conclusion.....	120
6.5. References.....	121

6.1. Introduction

The surface energy, work function and *d*-band centre of a surface slab provide information on surface phenomena, such as the stability of the surface, hydrogen binding energy (HBE) and adsorption energy to the surface.¹⁻⁴ These surface phenomena could be used to successfully explain the reactivity of metal surfaces.⁵

Hydrogen binding and adsorption energy have a linear correlation since the energy gained by the metal surface from the adsorbate can be correlated with the strength with which the adsorbate is bound to the surface. During the bonding of the adsorbate to the surface, electrons move between the adsorbate and the surface. This movement of electrons leads to a change in energy. To study the movement of the electrons between the adsorbate and the surface, Mulliken charges could be investigated. Hence, the charge-transfer between the surface and the adsorbate is influenced by the orbital occupation of the metal surface.^{6, 7} The metal surface's orbital occupation determines the spin-structure of the metal surface,^{6, 7} which describes the magnetic properties of a metal.^{6, 7} The magnetic properties of the metal determine the reactivity of a metal surface.^{7, 8}

In **Chapter 5**, the magnetic property of the Pt_{0.5}Ni_{0.5} bulk structure was calculated. This calculation showed that the magnetic property of Pt changes due to the increasing insertion of Ni atoms in the bimetal.⁹ This conclusion was reached after observing the atomic charges, the atomic spin momenta, the projected density of states (pDOS) and the band structure of Pt_{0.5}Ni_{0.5}.⁹ Therefore, due to the observed magnetic properties of the Pt_{0.5}Ni_{0.5} metal surface, it could have potential as an alternative electrocatalyst for both the OER and the ORR.^{10, 11 34}

In this chapter, the electronic properties of various (111) Pt_{0.5}Ni_{0.5}⁹ surfaces and the adsorption of hydrogen or a single H₂O molecule on the Pt_{0.5}Ni_{0.5} surfaces were investigated.

6.2. Computational method

DFT calculations were implemented in the CASTEP¹² code, which is a module from Materials Studio software.¹³ The generalised-gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (PBE)¹⁴ was used. Since elemental hydrogen is a simple atom with a single electron, a complex description of the intermolecular reactions was not required and therefore, dispersion correction was not added. The geometry was optimised using the two-point steepest descent (TPSD)¹⁵ algorithm, which provides better performance and cheaper computational cost.¹⁵ The interaction between the core and valence electrons, defined as those in level 5d6s for Pt, 3d4s for Ni and 1s for H and 4s4p for H₂O, was described with the Ultrasoft pseudopotentials (USP)¹⁶ method. This method allows calculations to be performed with the lowest possible cut-off energy for the plane-wave basis set, based on the Koelling–Hamon¹⁷ relativistic treatment. A Monkhorst-Pack grid¹⁸ of 11×11×11 *k*-points was used to carry out the integrations in the reciprocal space of the primitive unit cells and 5×5×1 for the (111) surfaces. To improve the convergence of the Brillouin-zone integrations, the electronic partial occupancies were determined using the Gaussian smearing with the width for all calculations set at 0.2 eV. The kinetic energy cut-off was fixed at 400 eV for the plane-wave basis set expansion of the Kohn-Sham (KS) valence states, which was large enough to avoid the Pulay stress.¹⁹ The internal coordinates, lattice parameters and cell shape of the Pt_{0.5}Ni_{0.5} bulk were set to relax (change) in all directions during geometry optimisation. The energy of the

unrelaxed bulk was calculated with a single point calculation using the same settings as that used with the geometry optimisation.

For the adsorption study, a single hydrogen atom or a single water (H₂O) molecule was added to the Pt (111), Ni (111) and Pt_{0.5}Ni_{0.5} (111) bimetallic (4×4) – 4L surfaces. As described before, the (4×4) – 4L surface has 16 adsorption sites, which resulted in a 0.0625 monolayer (ML) coverage when one hydrogen atom or H₂O molecule was adsorbed onto the surface. In the case of water adsorption, a self-consistent electronic dispersion correction (Hirshfeld partitioning)²⁰ was added, which was excluded for the hydrogen adsorption.

The atomic charges of the isolated H₂O molecule and the H₂O molecule adsorbed onto the surfaces were calculated using the Mulliken atomic charges.²¹⁻²⁴ In contrast, the atomic charges were not calculated for the hydrogen atom since it is a simple atom. The optimisation settings for the Pt (111), the Ni (111) and all the Pt_{0.5}Ni_{0.5} slabs were the same as the bulk, except for the Monkhorst-Pack grid,¹⁸ namely the 5×5×1 *k*-point grid.¹⁸ The energy of the unrelaxed slabs was calculated with a single point calculation at the same settings than the geometry optimisation.

In **Chapter 5**, a thermodynamically stable Pt_{0.5}Ni_{0.5} unit cell was identified for a (2×2×1) supercell (**Figure 6.1 (a)**), which is composed of eight Pt atoms and eight Ni atoms distributed in the Wyckoff 4*a* positions.⁹

²⁵ In **Figure 6.1 (a)**, the lattice parameters of the cell is $a = 7.546 \text{ \AA}$, $b = 7.546 \text{ \AA}$ and $c = 3.776 \text{ \AA}$ which belong to the *Pmmn* space group (No. 59) and is base centred orthorhombic, along the [110] direction.⁹

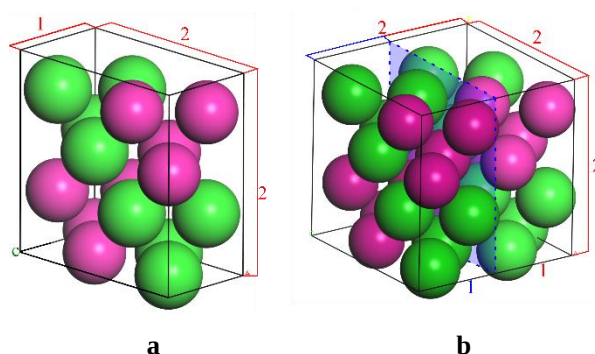


Figure 6.1. Pt_{0.5}Ni_{0.5} bulk represented by a) supercell (2×2×1) and b) supercell (2×2×2); Pt in green, Ni in pink/purple.

To restore the cubic symmetry, the (2×2×1) Pt_{0.5}Ni_{0.5} bulk structure was duplicated in the *c*-direction and is shown in **Figure 6.1 (b)**. As a result, the cubic symmetric bulk (2×2×2) consists of 32 atoms of which 16 of the atoms were Ni atoms and the other 16 were Pt atoms. Now that the cubic symmetry was restored to the Pt_{0.5}Ni_{0.5} bulk, five surface terminations using the low-index (111) were cleaved.

6.2.1. Building the Pt_{0.5}Ni_{0.5} surfaces

Five surface terminations were cleaved along the (111) Miller plane from the (2×2×2) Pt_{0.5}Ni_{0.5} bulk structure by varying the cleave position of the fractional top positions at 0.0, 0.5, 1.0, 1.5 and 2.0, as shown in **Figure 6.2**. (Note: To ease the reading of this chapter, the surface terminations will be referred to as _{0.0}(111), _{0.5}(111), _{1.0}(111), _{1.5}(111) and _{2.0}(111).)

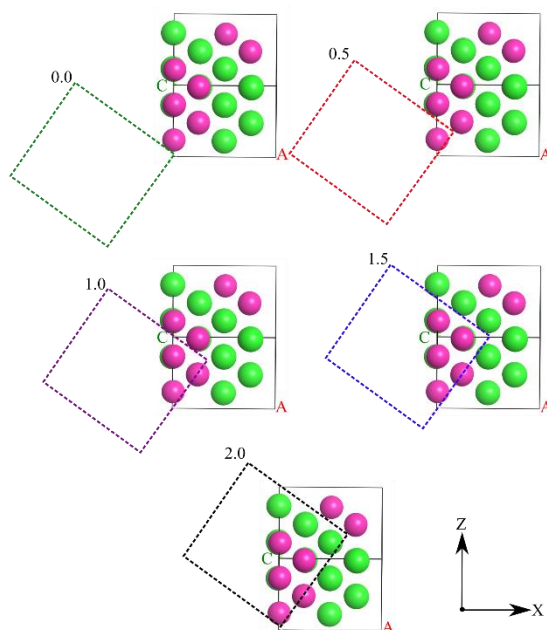


Figure 6.2. A schematic representation of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bulk cleaving process by changing the fractional cleave depth.

This cleaving method allowed the creation of (111) surfaces, where each surface layer consisted of different atomic arrangements, as shown in **Figure 6.3**. The surface area was increased to a (4×4) supercell, which led to a slab containing 64 atoms, distributed over four layers where the bottom two layers of each slab were constrained in their fractional positions. A vacuum gap of 12 Å was added between vertically repeating slabs, which is similar to the Pt (111) and Ni (111) slabs created in **Chapter 3**.

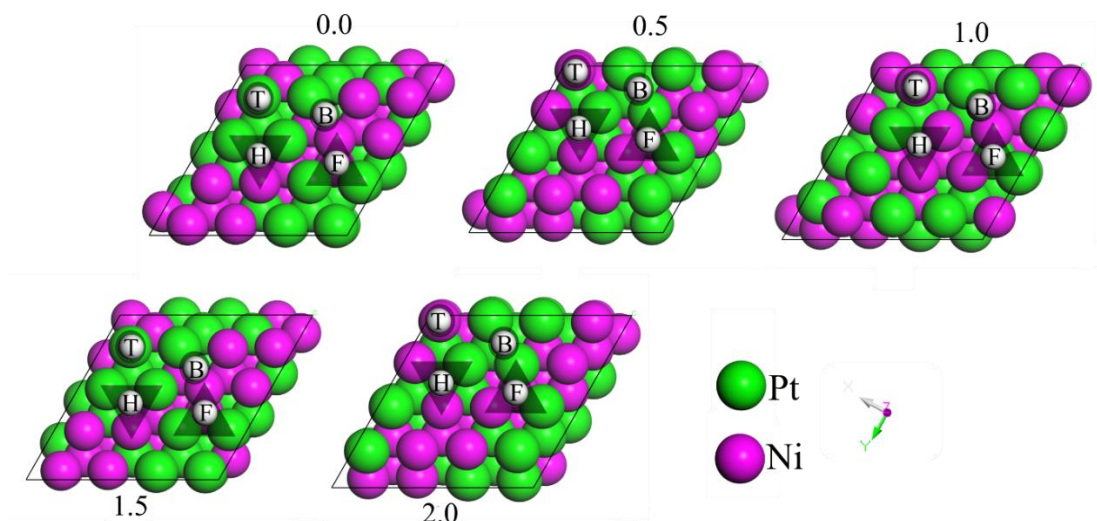


Figure 6.3. A schematic representation of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bulk cleaved into (111) surface terminations by changing the fractional cleave depth, to 0.0, 0.5, 1.0, 1.5 and 2.0. The adsorption sites which will be investigated is indicated by the semi-transparent shapes, where T, B, H and F indicates the atop, bridge, *hcp* and *fcc* adsorption sites.

The cleaving of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bulk structure (**Figure 6.2**) resulted in some similarity between the surfaces which is a result of the duplication of the c -direction used to obtain the cubic system. Since the surface terminations share similar physical appearances, the difference in the electronic properties was measured in terms of the surface energy, the work function, adsorption energy and the d -band energy.

The unrelaxed surface (γ_u) energy was calculated by performing an energy (single point) calculation. Thereafter, the bottom two layers of the slab were constrained (frozen) and a full geometric optimisation was performed so that the relaxed surface could be obtained for the calculation of the relaxed surface (γ_r) energy.

In this chapter, an isolated H_2O molecule and an isolated H_2 molecule were geometrically optimised, using the same settings as those discussed in **Chapter 3** and §6.2. The geometric optimisation was carried out in a cell which had the following lattice parameters, $a = 8.507 \text{ \AA}$, $b = 8.507 \text{ \AA}$ and $c = 18.946 \text{ \AA}$. The lattice parameter of the cell was spacious enough so that intermolecular interactions could be avoided.

6.2.2. Hydrogen adsorption on $\text{Pt}_{0.5}\text{Ni}_{0.5}$ surfaces

There are four possible adsorption sites for the hydrogen atom, namely, the top, bridge, face centred cubic (fcc) and hexagonal close packed (hcp) sites, as shown in **Figure 6.4**.

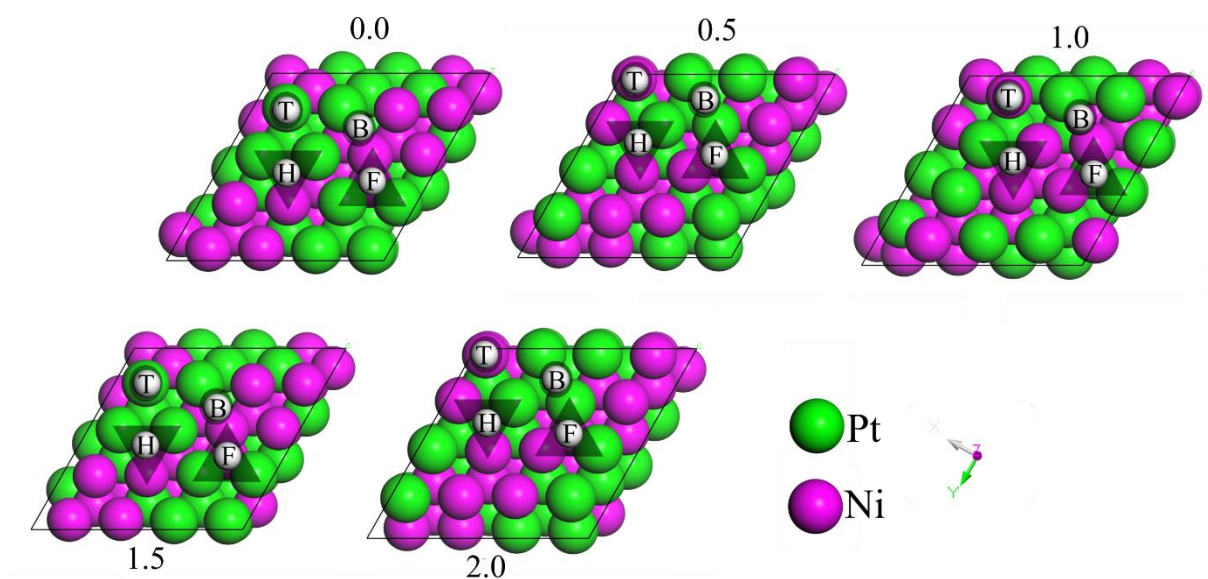


Figure 6.4. A schematic representation of a hydrogen molecule adsorbed onto the atop (T), bridge (B), hcp (H) hollow and fcc (F) hollow sites for the five surface terminations.

According to DFT studies, the hollow sites, fcc and hcp , were found to be the most reactive sites for the parent metals, Pt and Ni.²⁶⁻²⁹ Therefore, in this study, a single hydrogen atom which corresponds to 0.625 ML, was adsorbed onto the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ (111) surfaces at the reactive fcc and hcp adsorption sites. It is important to note that the bridge site and the top site were not studied. Also, that the sizes of the surfaces investigated in **Chapter 3** were smaller, i.e. $(3 \times 3) - 4\text{L}$, and therefore the surface coverage in **Chapter 3** corresponded to 0.11 ML. It is important to mention that the adsorption energy (E_{ads}) is dependent on the surface coverage.²⁸

6.2.3. Water adsorption on Pt_{0.5}Ni_{0.5} surfaces

A single H₂O molecule prefers adsorption onto the top site with a flat geometry.^{30, 31} Therefore, an H₂O molecule was added with a flat geometry (parallel to the surface) on the atop adsorption site for the various Pt_{0.5}Ni_{0.5} surfaces, shown in **Figure 6.5**. The atop adsorption site is energetically the most favourable site for the pure Pt (111)³⁰ and Ni (111) surfaces.³²⁻³⁴

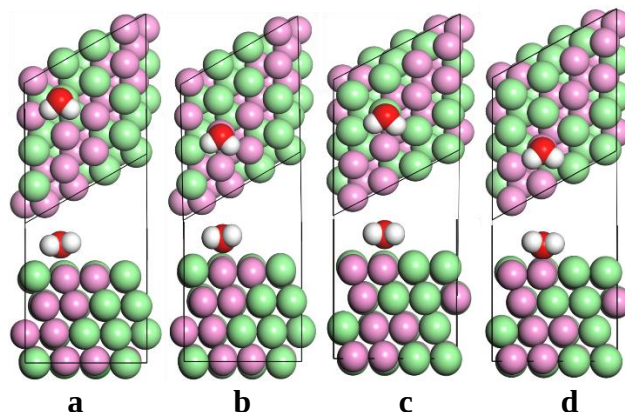


Figure 6.5. A schematic representation of an H₂O molecule adsorbed onto the top sites at a) 0.5Pt*, b) 0.5Ni*, c) 1.5Pt* and d) 1.5Ni* surface.

The stability of water adsorbed on surfaces is determined by two fundamental forces, namely the interaction that occurs between the H₂O molecule and the contacting metal layer (M–H₂O).³⁰ Since the adsorption of only one H₂O molecule was investigated in this chapter, the only interaction which was studied in this chapter is between the metal surface and the H₂O molecule. The adsorption energy (E_{ads}) of the H₂O molecule on the metal surface was calculated by using **(6-1)**.

$$E_{\text{ads}} = [E_{\text{slab}}^{\text{relax}} + \text{H}_2\text{O}_{(\text{ads})}] - [E_{\text{slab}}^{\text{relax}} + \text{EH}_2\text{O}_{\text{isol}}] \quad (6-1)$$

The energy of the optimised slab is represented by $E_{\text{slab}}^{\text{relax}}$, while the energy of the optimised slab with the adsorbed H₂O molecule on the surface is represented by $(E_{\text{slab}}^{\text{relax}} + \text{H}_2\text{O}_{(\text{ads})})$, and the total energy of the isolated H₂O molecule is represented by $\text{EH}_2\text{O}_{\text{isol}}$. The atomic charges of the isolated H₂O molecule, the pure metal surfaces and the H₂O molecule on the surfaces, were calculated using the Mulliken atomic charges.²¹⁻²⁴

6.3. Results and discussions

The characterisation of the relaxed and constrained Pt_{0.5}Ni_{0.5} bimetallic surfaces with various arrangements is discussed in §6.3.1. Thereafter in §6.3.2, the adsorption of a single hydrogen and a H₂O molecule onto these surfaces was investigated.

6.3.1. Pristine (111) surface properties.

The lattice parameters were $a = 11.342 \text{ \AA}$, $b = 11.342 \text{ \AA}$ and $c = 18.945 \text{ \AA}$ for the pure Pt (111) slab, and $a = 10.037 \text{ \AA}$, $b = 10.037 \text{ \AA}$ and $c = 18.146 \text{ \AA}$ for the pure Ni (111) slab. The difference in the lattice parameters indicated that the Pt (111) slab was slightly larger in size, 1.305 Å (a,b) and 0.591 Å (c), than that of the Ni (111)

slab, which is due to the size difference between Pt and Ni atoms. In the case of the Pt_{0.5}Ni_{0.5} bulk structure, the lattice parameters were $a = 7.690 \text{ \AA}$, $b = 7.690 \text{ \AA}$ and $c = 7.513 \text{ \AA}$, after optimisation. Furthermore, the Pt_{0.5}Ni_{0.5} bulk structure belongs to the P4₂/mmc space group (No.131). The lattice parameters for the Pt_{0.5}Ni_{0.5} (111) surface slabs were $a = 10.751 \text{ \AA}$, $b = 10.751 \text{ \AA}$ and $c = 18.725 \text{ \AA}$, after optimisation. The lattice parameters of the Pt_{0.5}Ni_{0.5} (111) bimetallic surface slabs, for each of the terminations, were comparable ($\pm 93\%$) to that of the pure metal slabs. Moreover, the surface area at one side of the Pt_{0.5}Ni_{0.5} (111) slab, of $115.583 \text{ \AA}^2$ for all the surface terminations was used.

The nearest neighbours of atoms in these structures will have an immediate influence on the properties of the surface.³⁵⁻³⁸ Hence, it is plausible to investigate all of the surface terminations even if they are similar in order to see if deeper layers may have an influence on surface properties.

The surface energies were calculated for the pure Pt, pure Ni and each of the Pt_{0.5}Ni_{0.5} (111) surfaces before optimisation (γ_u), and after optimisation (γ_r) which are shown in **Table 6.1**. Also, the relaxation percentage (%) is the amount of change between the surface energies (γ_u and γ_r) for the surfaces.

Table 6.1. Surface energies calculated before optimisation (γ_u), after optimisation (γ_r) and the percentage relaxation (%) for (111) surfaces of the pure Pt, pure Ni and each of the Pt_{0.5}Ni_{0.5} surface terminations. (Structures with identical top layers and varying bottom layers are indicated with matching colours)

Surface	γ_u (J ² /m ²)	γ_r (J ² /m ²)	Relaxation (%)
Pt	1.3429	1.3428	0.008
Ni	1.6336	1.6327	0.064
0.0	1.3682	1.3684	− 0.017
0.5	1.3681	1.3679	0.016
1.0	1.3684	1.3687	− 0.021
1.5	1.3685	1.3684	0.008
2.0	1.3682	1.3688	− 0.043

The surface energies obtained for the pure Pt (111) and pure Ni (111) surfaces corresponded well to the literature values for a (3×3) surface slab. The theoretical values for Pt (111) were $1.49 \text{ J}^2/\text{m}^2$ ³⁹ and $2.004 \text{ J}^2/\text{m}^2$ ¹, while the experimental value was $2.48 \text{ J}^2/\text{m}^2$.² These values for Ni (111) were $2.380 \text{ J}^2/\text{m}^2$ ² and $2.450 \text{ J}^2/\text{m}^2$,^{40, 41} experimentally. The value obtained using the theoretical method was $1.920 \text{ J}^2/\text{m}^2$.^{42, 43} The difference between the calculated values in this chapter and the literature values may be due to the different slab thickness and surface sizes that were used.

According to the literature, the slab thickness influences the surface energy, which is mostly stable for (111) slabs from seven or more layers. This influence of the surface thickness on the stability of the surface had been confirmed in the added Supplementary Information (S2) for a Pt/Ni bimetallic surfaces at the end of this thesis.³ The results in the Supplementary Information (S2) are not discussed here, since the results did not directly influence the outcome of this chapter.

The average interatomic spacing between the Ni – Ni, Pt – Pt, and the Pt – Ni, is shown in **Table 6.2** for the pure Pt (111), pure Ni (111) and each of the Pt_{0.5}Ni_{0.5} (111) bimetallic surfaces.

Table 6.2. The average interatomic spacing (d , in Å) after slab optimisation of the relative interatomic spacing for Pt, Ni, Pt_{0.5}Ni_{0.5} bulk and the constrained _{0.0}(111), _{0.5}(111), _{1.0}(111), _{1.5}(111), and _{2.0}(111) surfaces. The spacing was obtained before (Δ_{bulk}) and after relaxation (Δ_{relax}).

	Ni-Ni				Pt - Pt				Pt-Ni			
	d	Δ_{bulk}	Δ_{relax}	%	d	Δ_{bulk}	Δ_{relax}	%	d	Δ_{bulk}	Δ_{relax}	%
	(Å)	(Å)	(Å)		(Å)	(Å)	(Å)		(Å)	(Å)	(Å)	
Pt (111)	N/A	N/A	N/A	N/A	2.836	2.836	2.836	0.00	N/A	N/A	N/A	N/A
Ni (111)	2.509	2.509	2.509	0.00	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Pt _{0.5} Ni _{0.5}	2.702	2.681	2.615	6.60	2.705	2.675	2.742	6.70	2.731	2.699	2.668	3.10
_{0.0} (111)	2.625	– 0.056	– 0.077	2.10	2.738	0.015	0.033	1.80	2.697	0.029	– 0.034	6.30
_{0.5}(111)	2.625	– 0.056	– 0.076	2.00	2.743	0.020	0.039	1.90	2.691	– 0.023	– 0.039	1.60
_{1.0} (111)	2.625	– 0.056	– 0.077	2.10	2.744	0.021	0.039	1.80	2.691	– 0.023	– 0.039	1.60
_{1.5}(111)	2.625	– 0.056	– 0.077	2.10	2.744	0.021	0.039	1.80	2.691	– 0.023	– 0.039	1.60
_{2.0} (111)	2.625	– 0.056	– 0.077	2.10	2.743	0.020	0.039	1.90	2.691	– 0.023	– 0.039	1.60

From **Table 6.3**, it is clear that the difference between the Δ_{bulk} and the Δ_{relax} is small for all of the surfaces ~1.60 % to 6.60 %, for all the atoms. In terms of the interatomic spacing, the most stable surface is obtained where differences between the Δ_{bulk} and the Δ_{relax} values are the smallest.

The results obtained from **Table 6.2** indicates that the change in the bond lengths occurred to accommodate a more stable structure. Therefore, the pure metal surfaces were stable with minor movement in the metal surface before and after geometric optimisation. The interatomic spacing between the Ni – Ni, Pt – Pt and Pt – Ni atoms in the bimetallic bulk was 2.702 Å, 2.705 Å and 2.731 Å. The interatomic spacing value (d) for the Ni – Ni, Pt – Pt and Pt – Ni hardly changed (~0 Å or 0.001 Å) for all the surface terminations. The only exception was the _{0.0} surface termination which had a 0.076 Å (Ni – Ni), 0.033 Å (Pt – Pt) and 0.037 Å (Pt – Ni) difference with regards to the bulk structure.

The magnitude that the interatomic spacing (**Table 6.2**) had on the surface stability was compared to the surface energies (**Table 6.1**). For the pure Pt (111) and Ni (111) surfaces, it is clear that the small interatomic changes between the Pt – Pt and the Ni – Ni resulted in a stable surface, as indicated by the surface energies. The surface energies of the _{0.0}(111) termination indicated that the surface was semi-stable, as observed with an energy difference of 0.017 % between the relaxed and unrelaxed states. This means that the atoms in the surface rearranged to obtain a more stable surface energy. The change in the interatomic distance between the Δ_{bulk} and Δ_{relax} was 6.30 %. Since the _{1.5}(111) termination had a similar surface to the _{0.0}(111), we discussed this surface. The changes that occurred in the interatomic spacing before and after relaxation were less than 2.00 %. However, the relaxation percentage indicates that, due to atomic arrangements in the surface, a 0.008 % change in the surface energy occurred before and after relaxation. Hence, the _{1.5}(111) surface was stable with only minimal changes occurring in the surface to improve the stability. Comparing these two surface terminations, it is clear that although these surfaces were similar, the stability between these surfaces was not similar, with more atomic arrangement

was required for the $_{0.0}$ (111) termination. The most probable reason for the stability difference is the influence of the nearest neighbours of the bottom two layers, which varied.

Looking at the interatomic spacing for the $_{0.5}$ (111) surface, small changes occurred. The relaxation percentage (%) was 0.016 %, indicating the surface energy lowered during optimisation, stabilising the surface. Moving on to the $_{2.0}$ (111) surface, a relaxation percentage of 0.043 % was obtained. The interatomic spacing difference in this surface was 0.1 % more in the Ni – Ni spacing and 0.1 % less in the Pt–Pt spacing, as observed for the $_{0.5}$ (111) surface. However, the relaxation percentage was 0.027 % more than that obtained in the $_{0.5}$ (111) surface. This relaxation percentage means that the $_{2.0}$ (111) surface is less stable than that of the $_{0.5}$ (111) surface. Furthermore, the $_{1.0}$ (111) surface was less stable than the $_{0.0}$ (111), $_{0.5}$ (111) and $_{1.5}$ (111) surfaces, which needed to be stabilised more than these surface terminations but less than the $_{2.5}$ (111) surface termination.

Overall, the $_{1.5}$ (111) surface termination was the most stable surface termination, which required less movement of the atoms in the surface to accommodate more stable surfaces. In conclusion, according to the surface energies (**Table 6.2**) and the interatomic spacing (**Table 6.3**), all the surface terminations were stable with small amounts of changes, as compared to the bulk. Consequently, the stable $_{0.5}$ (111) and $_{1.5}$ (111) surface termination were used to investigate the H₂O adsorption.

The Mulliken²⁴ charge analysis was carried out to identify any changes in the various Pt_{0.5}Ni_{0.5} (111) bimetal surface charge as compared to the surface charge of parent metal surfaces, as shown in **Table 6.4**.

Table 6.3. Charge analysis for the atoms in the pure Pt (111) and Ni (111) surfaces and various Pt_{0.5}Ni_{0.5} surfaces.

With respect to the average charge (q/e^-) of either the Pt or Ni atoms in the mixed metal surfaces.

Surfaces	Ni (q/e^-)	Pt (q/e^-)
Pure surfaces	0.000	0.000
0.0	0.083	– 0.083
0.5	0.084	– 0.083
1.0	0.084	– 0.083
1.5	0.083	– 0.083
2.0	0.084	– 0.083

The total surface charge for the pure Pt (111) and pure Ni (111) surfaces was zero, as well as the charge average with respect to the atoms in the surface for both metals. In the case of the mixed metal surfaces, the total surface charge was zero. However, the charge average for the mixed metal surfaces, with respect to either the Pt or Ni atoms, was not zero. The Pt atoms became more negative and the Ni atoms became more positive. The changes observed were due to a shifting of the electrons towards the Pt. Pt became magnetic upon insertion of Ni atoms, which was also observed for the Pt_{0.5}Ni_{0.5} unit cell, shown in **Chapter 5**.⁹ Moreover, due to the magnetic properties of the Pt_{0.5}Ni_{0.5} surface (in **Table 6.4**) bonding was observed.⁸ The work function and the *d*-band centre of the pure Pt (111), pure Ni (111), $_{0.5}$ (111) and $_{1.5}$ (111) surfaces was determined (**Table 6.4**) and compared to literature data.

Table 6.4. Work function (Φ) and d -band centre (ϵ_d) results of pure Pt (111), Ni (111), $_{1.5}$ (111) and $_{0.5}$ (111) surfaces.

Name	Φ (eV)	ϵ_d (eV)
Pt(111)	5.168	– 2.453
	5.690 ³	– 2.520 ⁴⁴
	5.702 ¹	– 2.440 ⁴⁵
Ni(111)	3.055	– 1.477
	5.110 ⁴⁶	– 1.560 ⁴⁴
$_{0.5}$ (111)	4.684	– 1.772
$_{1.5}$ (111)	4.773	– 1.765

The calculated work function and d -band centre values, obtained for the pure Pt (111) and pure Ni (111) surfaces, correlated well with the literature data. Notably, the addition of a secondary metal changes the electronic properties of metal surfaces, indicated with a shift in the d -band centre value, altering the surface reactivity.⁴⁷ This can be seen from the d -band centre results of the pure $_{0.5}$ (111) and $_{1.5}$ (111) surface terminations, namely, – 1.772 eV and – 1.765 eV.

6.3.2. Hydrogen adsorption results

It has been shown that the preferred site for hydrogen adsorption onto Pt (111) or Ni (111) surfaces is the hollow point sites, *fcc* or *hcp*.^{26, 28} The adsorption energy for hydrogen on the pure metals was calculated as – 0.460 eV (– 0.517 eV), – 0.511 eV (– 0.535 eV) and – 0.391 eV (– 0.531 eV) for Pt (Ni) metal, on the *fcc*, *hcp* and atop adsorption sites, respectively. The adsorption of hydrogen on the five (111) bimetallic surfaces was performed onto the *fcc* adsorption site with a surface coverage of 0.0625 ML, as shown in **Figure 6.6**.

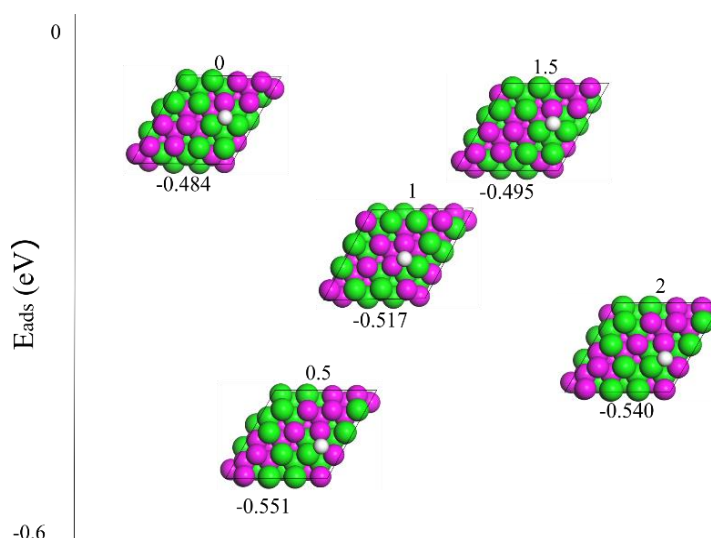


Figure 6.6. Hydrogen adsorption energy (E_{ads}) onto the five $(4 \times 4) - 4L$ surface terminations for *fcc* adsorption site, where the surface coverage is 0.0625 ML.

The most stable surface termination was that of the $_{0.5}(111)$ surface which had an adsorption energy of -0.551 eV, making it more stable than either of the pure metals for the *fcc* site. In addition, the adsorption of hydrogen onto the *fcc* site was favourable for the bimetallics for all the surface terminations. The ensemble site or adsorption site was the same for the $_{0.5}(111)$, $_{1.0}(111)$ and $_{2.0}(111)$ surfaces, which resulted in different adsorption energy values which suggest the tuneability of the adsorption sites. Furthermore, the best adsorption was obtained for the adsorption sites where the number of Pt atoms in the ensemble was Pt_1Ni_2 . Whereas weaker adsorption was obtained with a higher Pt content, indicating a linear tuneability due to the Pt content in the ensemble.

In the case of the *hcp* site, the adsorption was performed onto all the surface terminations with a surface coverage of 0.0625 ML, as shown in **Figure 6.7**.

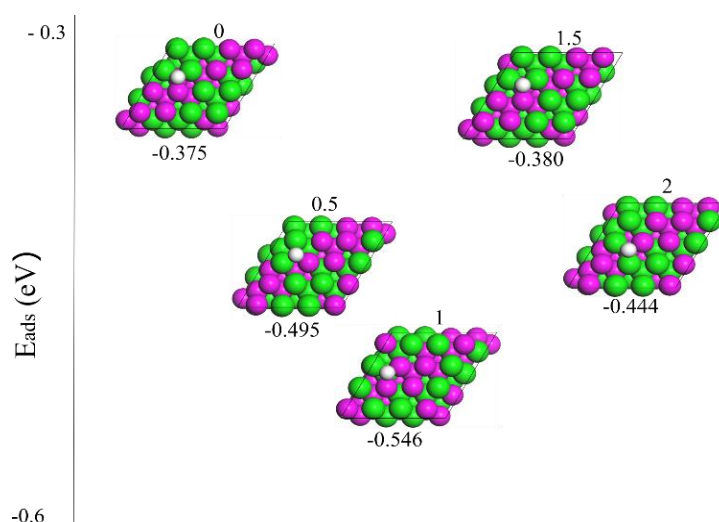


Figure 6.7. Hydrogen adsorption energy (E_{ads}) onto the five $(4 \times 4) - 4\text{L}$ surface terminations for *hcp* adsorption site, where the surface coverage is 0.0625 ML.

For this threefold hollow site, the surface termination which yielded the most stable adsorption was that of the $_{1.0}(111)$ surface termination with an adsorption energy of -0.546 eV. Hence, the $_{1.0}(111)$ surface termination was more stable than that of the $_{0.5}(111)$ surface termination for the *hcp* site but less stable than that of the $_{0.5}(111)$ surface termination for the *fcc* adsorption site. Overall, the $_{0.5}(111)$ surface termination was the most stable surface, observed in terms of the surface energies and also for the hydrogen adsorption. The results suggest that the surface is tuneable for hydrogen adsorption where a stronger adsorption is obtained for adsorption sites with an ensemble of Pt_1Ni_2 .

In conclusion, the most stable surface termination obtained was that of the $_{0.5}(111)$ surface with the *fcc* threefold hollow point adsorption site which also showed that the adsorption site is tuneable by adjusting the number of Ni atoms in the adsorption site. A full hydrogen surface coverage, 1.00 ML, for the *fcc* adsorption site was investigated, as shown in **Figure 6.8**. According to the adsorption energies in **Figure 6.8**, the adsorption energy decreases with an increase in the surface coverage, which is generally observed²⁸ and shown for the $_{0.5}(111)$ surface termination.

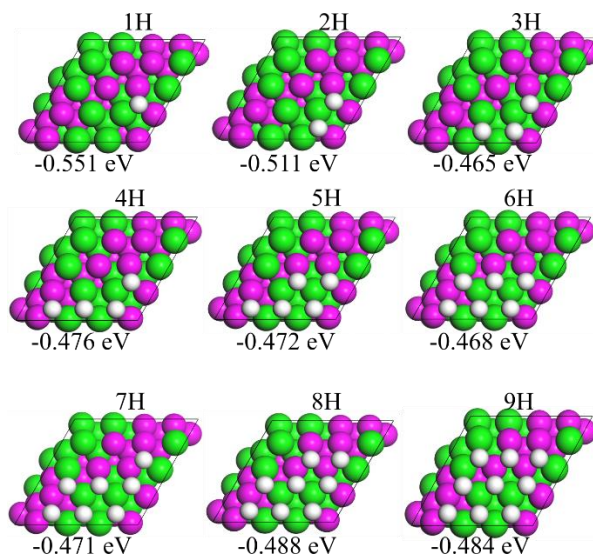


Figure 6.8. Hydrogen adsorption energy calculated on the $_{0.5}(111)$ surface with increasing surface coverage for the *fcc* adsorption site.

The adsorption energy was plotted against the surface coverage for the $_{0.5}(111)$ surface termination, Pt (111)^{27, 28} surface and a Ni (111) surface, and is shown in **Figure 6.9**.

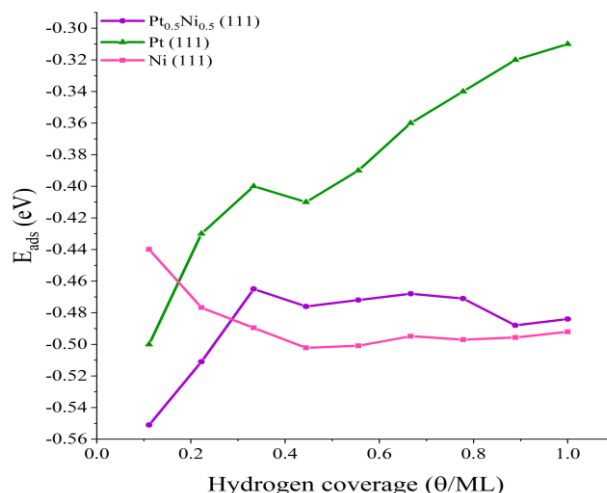


Figure 6.9. Comparison of the hydrogen adsorption energy with increasing surface coverage for the Pt (111) Ni (111) and $_{0.5}(111)$ surface termination, for the *fcc* adsorption site.

From the results obtained an increase in the adsorption energy of the Pt (111) and the $_{0.5}(111)$ surface termination resulted in an increase in the surface coverage, while, the opposite is true with regards to the Ni (111) surface. A more negative adsorption energy value shows that adsorption was more favoured on the Pt_{0.5}Ni_{0.5} surface than on the Pt (111) surface. Also, the favourability was not affected by the surface coverage since Pt_{0.5}Ni_{0.5} was still more favourable than Pt (111), no matter the surface coverage. Notably, Ni (111) was more favourable than the Pt_{0.5}Ni_{0.5} (111) surface, which was expected, since hydrogen is known to bond strongly to Ni (111). Nevertheless, the adsorption energy between the Pt_{0.5}Ni_{0.5} (111) surface and the Ni (111) surface was relatively close at a full surface coverage. In the case of the $_{0.5}(111)$ surface, the increase in the surface coverage, after a 0.40 ML coverage,

caused the adsorption energy to become stable with a difference of only 0.008 eV between the 0.44 ML and 1.00 ML surface coverage.

The results obtained from the hydrogen adsorption onto five different surface terminations (0.0, 0.5, 1.0, 1.5 and 2.0) concluded that the adsorption site is tuneable by adjusting the site to have a Pt_1Ni_2 ensemble. The adsorption strength was weaker when the number of Pt atoms increased in the adsorption site, which also confirms that the ensemble effect can be used to increase the adsorption strength of bimetallic surfaces. The stable configurations of the clean surface terminations and the hydrogen adsorbed terminations were identified. The most stable surface termination was that of the $_{0.5}(111)$ surface termination, which was also the most stable surface termination after hydrogen adsorption on the *fcc* adsorption site.

Overall, the adsorption energy on the $_{0.5}(111)$ surface termination was more stable than those of the pure metal surfaces at a low surface coverage. An increase in the surface coverage also yielded adsorption energies which were smaller than those observed for the Pt (111) surfaces.

In conclusion, the surface of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surface was more stable than those of the parent metals for a simple adsorption such as hydrogen. This bimetal may be an improved electrocatalyst for either the OER or the ORR.

6.3.3. Properties of isolated water

To determine the adsorption influence of the single H_2O molecule on the metal surface, the properties of the surfaces and isolated adsorbate were determined. The properties of a single isolated water molecule, used in this study, was examined and compared to literature data (**Table 6.5**).

Table 6.5. Calculated geometries and Mulliken charges of the isolated H_2O molecule as compared to theoretical³⁰ and experimental⁴⁸ values.

	This study [*]	Theoretical [Ref] ³⁰	Experimental [Ref] ⁴⁸
OH bond length (Å)	0.978 (a) 0.977 (b)	0.973	0.957
HOH bond angle (°)	104.20	104.85	104.52
H(a) (e ⁻)	0.520	-	-
H(b) (e ⁻)	0.520	-	-
O (e ⁻)	- 1.050	-	-

From **Table 6.5**, it can be seen that the OH bond lengths and the HOH bond angle used in this study, is in excellent agreement with theoretical⁵⁰ and experimental data.⁴⁸ In addition, the Mulliken charges were calculated for the two hydrogens and the oxygen. The calculation of the Mulliken charges was done so that charge changes can be observed during the adsorption section of this chapter. The OH bond lengths and bond angle are depicted in **Figure 6.10 (a)**. In the water molecule, the OH bond lengths are referred to as OH (a) and OH (b).

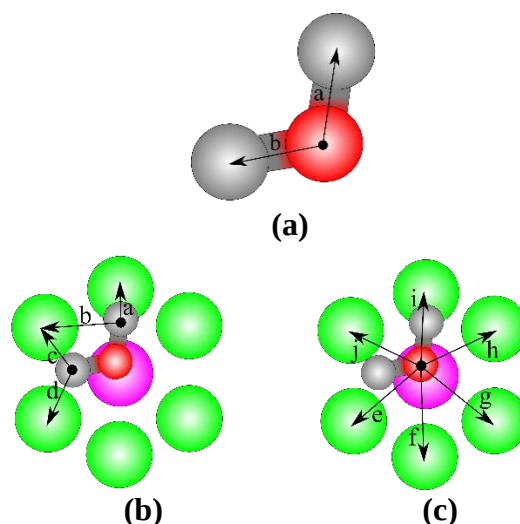


Figure 6.10. Visual representation of a) isolated H₂O molecule, b) the single water molecule bonded to the metal surface through the metal to hydrogen (MH) and c) metal to metal (MM) bond lengths.

In §6.3.4, a single H₂O molecule was added to the stable *fcc* and *hcp* hollow sites for the (4×4) – 4L metal surface which resulted in a surface coverage of 0.0625 ML.

6.3.4. H₂O adsorption

Two important fundamental forces determine the stability of water adsorbed on surfaces, namely the water–surface interaction (M–H₂O) which occurs in the water-metal interface layer and the hydrogen bonding between the water molecules.³⁰ However, in this study, the only interaction was between the metal surface and the H₂O molecule since only a single H₂O molecule was investigated. Physisorption or chemisorption could occur between the adsorbed H₂O molecule and the metal surface. In the case of physisorption, no new chemical bonds are formed, and the bonds within the molecule stay the same as in the isolated molecule. However, in chemisorption, the adsorbate forms covalent or ionic bonds with the surface. As a result, the bond lengths and angles within the molecule will also change.

6.3.4.1. Pt (111) and Ni (111) surfaces

From literature it was observed that a single H₂O molecule prefer adsorption in a flat geometry onto the top sites of the metal surface.^{30, 31} As a result, a single H₂O molecule was added to the top site of the pure Pt (111) and Ni (111) surfaces. The bond lengths and bond angle of the adsorbed single H₂O molecule (**Table 6.6**) were compared to that of the single isolated water molecule (**Table 6.5**). As a result of the water adsorption, elongation of the OH (a), OH (b) bond lengths and an increase in the HOH bond angle, were observed. Thus, indicating a weakening of the OH bond and a possible bond breaking between the hydrogens and oxygen.

Furthermore, the calculated work function and the *d*-band energy values for the pure Pt (111) and Ni (111) surfaces, correlate well with literature values (**Table 6.6**).^{1, 3, 44, 46} The adsorption of an H₂O molecule resulted in a reduction of the work function value from 5.168 eV to 4.803 eV for the pure Pt (111) surface and 3.055 eV to 2.699 eV for the pure Ni (111) surface. This reduction in the work function is an indication that electron transfer occurred from the H₂O molecule to the surface.³⁰

Table 6.6. The work function (Φ), d -band centre (ϵ_d), bond length and bond angles results obtained from H₂O adsorption onto the Pt (111) and Ni (111) surfaces.

	Angle (°)	M*-O (Å)	O-H (a) (Å)	O-H (b) (Å)	Φ (eV)	ϵ_d (eV)	E_{ads} (eV)
Pt (111)	105.328	2.400	0.982	0.983	4.803	− 2.464	− 0.330
Ni (111)	105.624	2.497	0.984	0.985	2.699	− 1.477	− 0.475

Moreover, the surface reactivity of transition metals is determined by the position of the d -band centre, which indicates changes in the electronic structure.^{6, 49} The d -band energy, represents the average energy in the d -band, with reference to the Fermi level where $E_F = 0$.⁵⁰ The d -band energy is a good indicator of strong or weak bonding of an adsorbate.⁶ In this case, strong binding was observed from Ni (111), shown by the d -band energy of − 1.477 eV which was closer to the Fermi level than either the Pt (111) or the Pt_{0.5}Ni_{0.5} (111) surfaces.

The adsorption energy (E_{ads}) gives an indication of the strength with which the H₂O molecule binds to the metal surface (**Table 6.6**). According to the calculated adsorption energy, the H₂O molecule adsorbed the strongest onto the Ni (111) surface ($E_{ads} = -0.475$ eV), whereas weaker binding occurred on the Pt (111) surface as indicated with an adsorption energy of − 0.330 eV. In addition, bond cleavage of the adsorbate on the metal surface can be indicated with the adsorption energy. As a result, a higher chance of bond cleavage occurs on the Ni (111) metal surface as shown by the hydrogen bonding energies (HBE) of the metal.^{44, 51}

To further determine the electron transfer between the pure metal surfaces and the adsorbent, the Mulliken charges were calculated for the pure Pt (111), pure Ni (111) and for the H₂O molecule, as shown in **Table 6.7** and visualised in **Figure 6.11**.

Table 6.7. Mulliken charge of water adsorbed onto the Pt (111) and Ni (111) surfaces. The calculated charges are for the, M* and H₂O bonds.

Surface	M*(e ⁻)	H (a) (e ⁻)	O (e ⁻)	H (b) (e ⁻)	Electron donation (e ⁻)
H ₂ O molecule	-	0.520	− 1.050	0.520	
Pt (111)	− 0.040	0.440	− 0.790	0.440	− 0.710
Ni (111)	0.000	0.440	− 0.840	0.450	0.140

The Mulliken charges per atom obtained for the Pt (111) surface, were − 0.100 (e⁻) for the top and bottom layers and + 0.100 for the two middle layers. In the case of the Ni (111) metal surface, the charges for the top and bottom layer were − 0.050 (e⁻) per atom, while the charges obtained for the two middle two layers were + 0.050 (e⁻) per atom. Overall, the calculated Mulliken charges (**Table 6.7** and **Figure 6.11**) confirmed that electron transfer occurred between the surface and the water molecule.

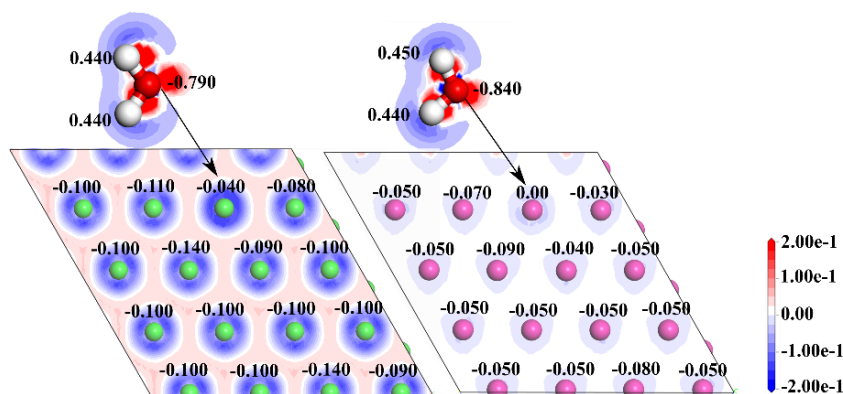


Figure 6.11. Iso-density contours of the different electron densities for the water adsorbed metal surfaces. The loss of electrons is indicated in blue, while the red indicates electron enrichment.

From **Table 6.7**, the shift in the charges of the isolated water molecule occurred after binding to the metal surfaces, which caused a reduction in the work function. Focusing on the Pt (111) metal, it is clear that the H₂O molecule donated – 0.71 electrons to the Pt* site (**Table 6.7**). The increasing electron charge from the Pt* site donated 0.140 electrons to its nearest neighbours as seen in **Figure 6.11**. The same trend is seen for the Ni (111) metal.

The next step was to adsorb the H₂O molecule onto the _{0.5} and the _{1.5} surfaces on either a Pt* or a Ni* site, as shown in the computational methods in section §6.2.

6.3.4.2. _{1.5} (111) and _{0.5}(111) surfaces.

The OH (a), OH (b), HOH and MO* bond lengths and bond angles are shown in **Table 6.8**.

Table 6.8. Work function (Φ), d -band centre (ϵ_d), bond length and bond angles results obtained from H₂O adsorption onto the Pt (111), Ni (111), _{0.5} (111) and the _{1.5} (111) surfaces, where the labels (B) and (C) represents an alternative adsorption site of the water molecule on the _{0.5} (111) and _{1.5} (111) metal surface. (The H₂O data is from **Table 6.6** for the isolated H₂O molecule).

	Angle (°)	M*-O (Å)	O-H (a) (Å)	O-H (b) (Å)	Φ (eV)	ϵ_d (eV)	Eads (eV)
H ₂ O molecule	104.20	N/A	0.978	0.977	N/A	N/A	N/A
_{0.5} Pt*	105.086	2.416	0.985	0.983	4.323	– 1.781	– 0.212
_{0.5} Ni*	105.885	2.401	0.991	0.984	4.339	– 1.754	– 0.318
_{1.5} Pt*	105.716	2.491	0.984	0.985	4.300	– 1.769	– 0.185
_{1.5} Ni*	106.804	2.045	0.983	0.988	4.705	– 1.773	– 0.369
_{0.5} Ni*(B)	105.885	2.401	0.991	0.984	4.227	– 1.769	– 0.139
_{1.5} Pt*(B)	105.716	2.362	0.984	0.985	4.340	– 1.788	– 0.224
_{1.5} Ni*(C)	106.804	2.204	0.983	0.988	4.417	– 1.770	– 0.279
_{0.5} Pt*(C)	105.086	2.448	0.985	0.983	4.275	– 1.782	– 0.118

From the results, the bond elongated, and the bond angle increased in the water molecules upon adsorption. The largest OH (b) bond elongation observed for the mixed surfaces was that of the _{1.5}Ni* surface. In addition, an adsorption energy of – 0.369 eV, indicates that the H₂O molecule adsorbed strongly onto the _{1.5}Ni* surface. For

the Pt* metal surfaces, elongation of the OH bond and HOH bond angle were observed but smaller than that on the Ni* surfaces. Overall, the OH bond lengths, as well as the HOH angle, increased after adsorption onto this metal surface which indicates that the water molecule dissociated from the $_{1.5}\text{Ni}^*$ metal surface. However, the 0.01 eV bond elongation is insignificant to conclude that cleavage of the bond has occurred. As a result, the Mulliken charges will be investigated to determine changes in the electron densities.

For the $_{0.5}(111)$ metal surface, a reduction of the work function occurred from 4.384 eV to 4.323 eV, 4.339 eV, 4.227 eV and 4.275 eV, depending on the adsorption metal and the environment surrounding the adsorption site. The largest work function reduction was observed for the $_{0.5}\text{Ni}^*(\text{B})$ with 0.457 eV. In the case of the $_{1.5}(111)$ metal surfaces, a reduction of 4.773 eV to 4.300 eV, 4.705 eV, 4.340 eV and 4.417 eV, were observed for the various adsorption sites. The largest reduction of the work function was observed for the $_{1.5}\text{Pt}^*$ site with a reduction of 0.473 eV. Therefore, the electron transfer between the H_2O molecule and the bimetallic surfaces was the largest for the $_{0.5}\text{Ni}^*(\text{B})$ and the $_{1.5}\text{Pt}^*$ sites.

The Mulliken charges obtained per atom for $_{0.5}(111)$ metal surface and $_{1.5}(111)$ metal surfaces, given in **Table 6.9**, varied throughout the slab.

Table 6.9. Mulliken charge of H_2O adsorbed onto the Pt (111), Ni (111), $_{0.5}(111)$ and the $_{1.5}(111)$ surfaces. The calculated charges are for the, M^* and H_2O bonds.

Surface	M^* (e^-)	H (a) (e^-)	O (e^-)	H (b) (e^-)
H_2O molecule	-	0.520	- 1.050	0.520
Pt(111)	- 0.040	0.440	- 0.790	0.440
Ni(111)	0.000	0.440	- 0.840	0.450
$_{0.5}\text{Pt}^*$	- 0.090	0.430	- 0.790	0.440
$_{0.5}\text{Ni}^*$	0.090	0.420	- 0.810	0.450
$_{1.5}\text{Pt}^*$	- 0.060	0.420	- 0.770	0.420
$_{1.5}\text{Ni}^*$	0.150	0.440	- 0.770	0.410
$_{0.5}\text{Ni}^*(\text{B})$	0.100	0.430	- 0.810	0.430
$_{1.5}\text{Pt}^*(\text{B})$	- 0.060	0.430	- 0.790	0.430
$_{1.5}\text{Ni}^*(\text{C})$	0.090	0.430	- 0.780	0.420
$_{0.5}\text{Pt}^*(\text{C})$	- 0.090	0.410	- 0.780	0.430

This difference in the charges was not as constant throughout the bimetallic surface as those observed for the pure Pt (111) and Ni (111) surfaces. The Mulliken charges and the electron density differences of the bimetallic surfaces are shown in **Figure 6.12**. It was already discussed from the perspective of the work function that electron transfer occurs between the metal surfaces and the H_2O molecule. From the Mulliken charges, the size of the electron charge between the surface and the H_2O molecule can be studied in detail. The Mulliken charges of the hydrogen (a, b) in the H_2O molecule decreased because of the adsorption from an initial charge of 0.520 (e^-). Also, the charge of the oxygen decreased from the initial - 1.050 (e^-) to - 0.780 (e^-), depending on the metal surface.

These Mulliken charges in **Table 6.9**, show that electron transfer occurs between the hydrogens, oxygen and metal atoms.

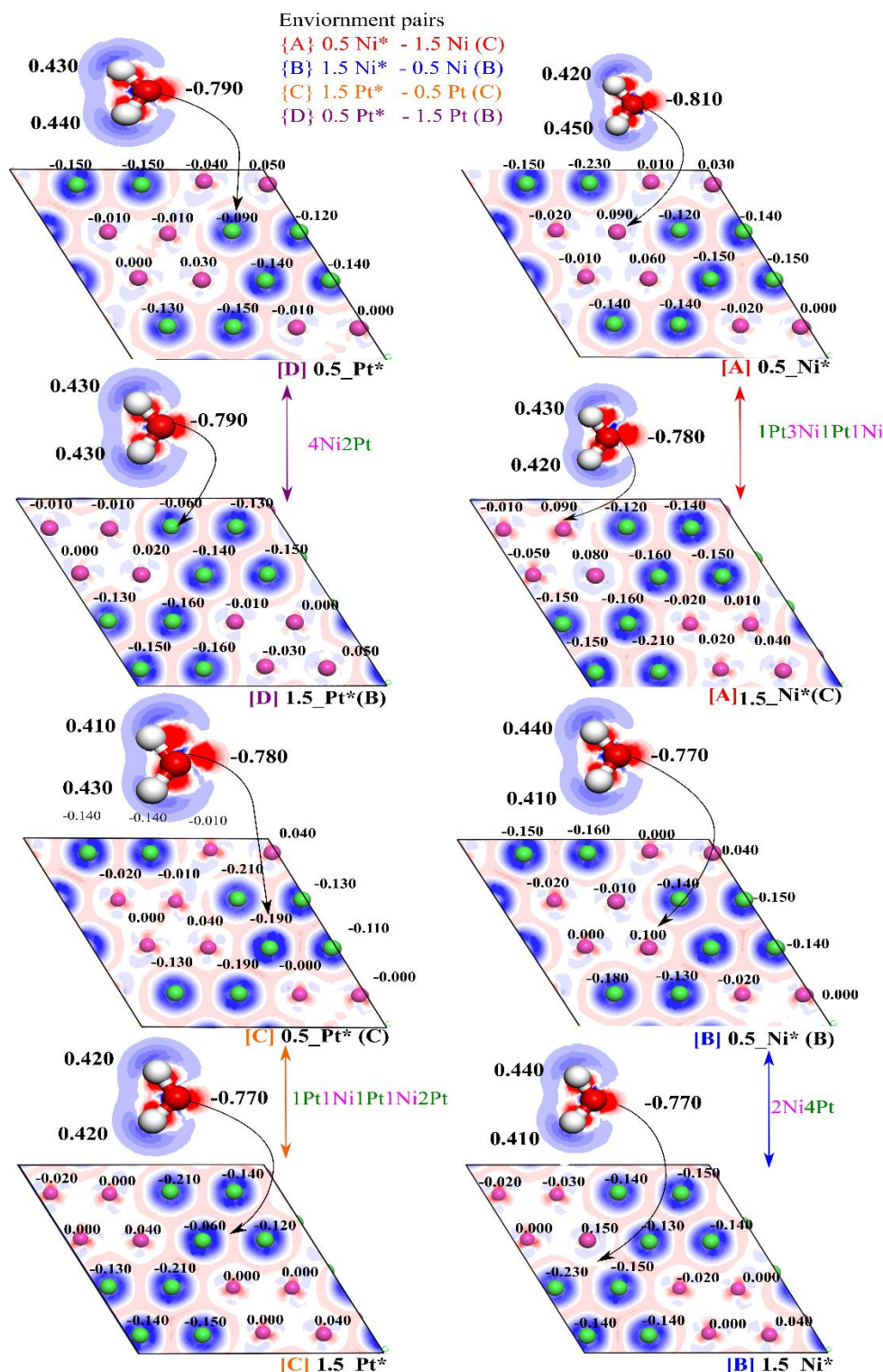


Figure 6.12 Iso-density contours of the difference electron densities for the adsorption of one H_2O molecule on the mixed metal surfaces.

Furthermore, from **Figure 6.12**, it is clear that electron transfer also occurred between the adsorption site and the nearest neighbours. It is known that the reactivity of bimetals varies from that of pure metals due to the influence

of the nearest and second nearest neighbours.⁵² Since there are eight surfaces (four of each surface termination), the metal surfaces were then grouped into four categories, [A-D]. These categories are dependent on the environment surrounding the adsorption site. Category [A] is where the nearest neighbours to the adsorbed metal are 1Pt|3Ni|Pt|Ni. The nearest neighbours to category [B] are 2Ni|4Pt, for category [C] the nearest neighbours are 1Pt|1Ni|1Pt|1Ni|2Pt and for category [D] are 4Ni|2Pt.

Furthermore, in **Table 6.10**, the bond lengths between the H₂O molecule and the nearest neighbours were calculated.

Table 6.10. Water monomer adsorption with a flat geometry onto _{0.5}(111) and the _{1.5}(111) surfaces for the [A], [B], [C] and [D] environments.

[A]	[B]		[C]		[D]		[D]	[D]
	_{0.5} (111)	_{1.5} (111)	_{0.5} (111)	_{1.5} (111)	_{0.5} (111)	_{1.5} (111)		
	Ni*	Ni*(C)	Ni*(B)	Ni*	Pt*(C)	Pt*	Pt*	Pt*(B)
Pt(a)	2.888	2.838	Ni 2.883	2.984	Pt 2.935	2.974	Ni 2.989	3.008
Ni(b)	3.337	3.168	Ni 3.301	3.206	Ni 3.374	3.300	Ni 3.500	3.356
Ni(c)	3.336	3.144	Ni 3.275	3.206	Ni 3.511	3.209	Ni 3.489	3.137
Ni(d)	3.145	2.787	Pt 3.019	2.724	Pt 3.143	2.916	Ni 3.141	3.137
Ni(e)	3.517	3.311	Pt 3.447	3.327	Pt 3.649	3.468	Ni 3.927	3.687
Ni(f)	3.739	3.403	Pt 3.687	3.456	Ni 3.822	3.814	Pt 3.944	3.867
Pt(g)	3.719	3.500	Pt 3.797	3.525	Pt 3.690	3.854	Pt 3.813	3.924
Ni(h)	3.489	3.701	Pt 3.671	3.469	Pt 3.679	3.820	Ni 3.652	3.779
Pt(i)	3.910	3.282	Ni 3.449	3.410	Pt 3.637	3.593	Ni 3.604	3.540
Ni(j)	3.490	3.273	Ni 3.439	3.339	Ni 3.711	3.497	Ni 3.757	3.477

The calculated metal-hydrogen bond lengths (MH), between the hydrogen and the nearest neighbour, are represented in **Figure 6.12 (b)** and indicated as either (a-d). Also, the bond length between the nearest neighbour (e-j) and the bonded oxygen (MO) was calculated and shown in **Figure 6.12 (c)**. It was already shown that bond elongation occurred between the OH and the HOH angle upon adsorption. The results from **Table 6.10** show whether the cleaved water molecule (oxygen or hydrogen) moves towards one of the nearest neighbours.

6.4. Conclusion

In the first part of this chapter, various (111) surface terminations (0.0, 0.5, 1.0, 1.5 and 2.0) were built from the most stable configuration in **Chapter 5**. According to the surface energies of these surface terminations, the _{0.5}(111) surface termination was identified to be the most stable surface, followed by the _{0.5}(111) surface termination. However, there was not a large difference in surface energies between the surface terminations.

In the second part of this chapter, a single hydrogen atom was added to the five surface terminations where the H₂O molecule laid flat on the metal surfaces. The most stable surface, in terms of the adsorption energy for the *fcc* adsorption site, was that of the _{0.5}(111) surface termination. Moreover, the _{1.0}(111) surface termination

(− 0.546 eV) was more stable than that of the $_{0.5}(111)$ surface termination (− 0.495 eV) but only in regard to the *hcp* adsorption site. Overall, the stability and reactivity of the $\text{Pt}_{0.5}\text{Ni}_{0.5}(111)$ surface bimetal is comparable to both the Pt (111) and the Ni (111) surfaces and could be a possible alternative bimetal for the OER or the ORR.

Electron transfer was also observed between the H_2O molecule and the nearest neighbours in the metal surfaces. The adsorption resulted in a reduction of the work function from 5.168 eV to 4.803 eV for the Pt (111) and from 3.055 eV to 2.699 eV for the Ni (111) surface. Furthermore, electron transfer was also observed for the $_{0.5}(111)$ and $_{1.5}(111)$ surfaces. Overall, the most stable adsorption was on the $_{1.5}\text{Ni}^*$ surface with an adsorption energy of − 0.369 eV.

Cleavage of the H_2O molecule occurred on the metal surfaces, which was a result of the increase in the HOH bond angle whereas the increase in the OH bond length is insignificant to indicate bond cleavage. . This HOH elongation is an indication of the weakening of the H-O-H bonds and the reduced bonding electrons in the water, which is consistent with other studies.³⁰ The largest HOH angle increase, 104.200 ° to 106.804 °, was observed for the $_{1.5}\text{Ni}^*$ and the $_{1.5}\text{Ni}^*(\text{C})$ surfaces. The largest bond elongation for the OH (a) bond was observed for the $_{0.5}\text{Ni}^*$ and $_{0.5}\text{Ni}^*(\text{B})$ with an elongation of 0.013 Å. Meanwhile the largest bond elongation of 0.011 Å along the OH (b) bond was observed for the $_{1.5}\text{Ni}^*$ and the $_{1.5}\text{Ni}^*(\text{C})$ surfaces. Overall, cleavage and adsorption of the water molecule were the most apparent on the most stable $_{1.5}\text{Ni}^*$ surface. Notably, the results can vary with the adsorption of multiple water molecules due to interactions between the molecules, but this was beyond the scope of the study.

In conclusion, the $_{1.5}\text{Ni}^*$ surface termination could be a potential electrocatalyst material for either the OER or the ORR since cleavage of the water molecule occurs on the surface. Furthermore, future work will involve the investigation of the other intermediates involved in the OER (HOO^* and HO^*) of the $\text{Pt}_{0.5}\text{Ni}_{0.5}(111)$ bimetallic surface, which is discussed in the next chapter.

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7

Conclusion and recommendations

This chapter is the 4th and final part of this thesis and consists of the conclusion and the recommendations for future studies.

7.1. Conclusion	125
7.1.1. Identification of the most stable ratio of Pt and Ni in a Pt/Ni bimetallic bulk structure using DFT calculations	125
7.1.2. Investigating the stability and reactivity of Pt/Ni bimetallic surfaces constructed from the most stable Pt/Ni bimetallic bulk structure	126
7.1.3. Evaluation of the performance of the most outstanding Pt/Ni bimetallic surface as a viable electrocatalyst for both the OER and ORR	126
7.2. Recommendations	127
7.3. References	127

7.1. Conclusion

As stated in **Chapter 1**, the aim of this study was three-fold, namely:

- to use density functional theory (DFT) calculations to identify the most stable ratio of Pt and Ni in a Pt/Ni bimetallic bulk structure;
- to investigate the stability and reactivity of Pt/Ni bimetallic surfaces constructed from the most stable Pt/Ni bimetallic bulk structure; and
- to evaluate the performance of the most outstanding Pt/Ni bimetallic surface as a viable electrocatalyst for both the oxygen evolution reaction (OER)^{1, 2} and the oxygen reduction reaction (ORR).^{3, 4}

However, before the aim of this study could be addressed an understanding of the field of research, namely electrochemistry, as well as related computational models was needed.⁵⁻¹⁴ Obtaining an understanding of necessary background was accomplished by conducting a comprehensive literature study, which was summarised in **Chapter 2**. Using the knowledge gained in the comprehensive literature study, a computational model, based on the Cambridge serial total energy package (CASTEP)¹⁵ module, for surface and electronic investigations of metal surfaces, and surface reaction investigations on these metal surfaces, was developed and validated in **Chapter 3**.

The development and validation of the computational model were done by calculating the structure and electronic properties of the bulk structures and pure Pt and pure Ni metal (111) surface slabs, and comparing the results to literature values.^{14, 16-19} These properties that were used in the validation included, lattice parameters,^{7, 20, 21} surface energy (γ),²² work function (Φ),²² d -band centre (ϵ_d),^{14, 17} density of states (DOS), adsorption energies (E_{ads})¹²⁻¹⁴ and the binding energy (HBE).⁸ The validated computational model was applied to calculations performed throughout the rest of this thesis. This computational model was supplemented by a DFT model using the Vienna Ab initio Software Package (VASP)²³⁻²⁶ or the general utility lattice program (GULP),^{27, 28} depending on the size of the bulk structures.

7.1.1. Identification of the most stable ratio of Pt and Ni in a Pt/Ni bimetallic bulk structure using DFT calculations

In this study, the application of two techniques to construct Pt/Ni bimetal structures was investigated, namely, a random manual technique and an automated systematic technique.

In **Chapter 4**, the random manual technique was applied to construct Pt/Ni bimetallic surface slabs, namely, Pt_{0.25}Ni_{0.75} (111), Pt_{0.5}Ni_{0.5} (111) and Pt_{0.75}Ni_{0.25} (111) by random substitution of Pt atoms with Ni atoms in a pre-optimised Pt (111) slab. Although this technique did not enable the determination of the most stable bimetallic surface mixture, the results did indicate that by varying the adsorption sites, a more stable atomic arrangement of the surface was possible. It gave some insight into the ligand and ensemble effects in bimetallic surface mixtures. Moreover, the adsorption ability of the surface could be fine-tuned by varying the environment surrounding the adsorption site by using the ligand and the ensemble effects.

Furthermore, the results obtained from the random manual technique indicated that a more systematic technique was needed to construct Pt/Ni bimetallic structures. The requirements for this systematic technique was that it

should be repeatable and all possible unique configurations of a specific ratio of Pt to Ni in the Pt/Ni bimetallic mixtures must be included. An automated program, namely the site-occupancy disorder (SOD)²⁹ program, was identified to systematically construct the Pt/Ni bimetallic bulk structure mixtures that complied with the requirements given above.

In **Chapter 5**, the Pt/Ni bimetallic bulk structures were constructed with the SOD.²⁹ From mixing thermodynamic calculations, the Pt_{0.5}Ni_{0.5} bimetallic ratio was identified to be the most stable ratio of Pt and Ni in a Pt/Ni bimetallic bulk structure.³⁰ The calculated results also showed that the Pt_{0.5}Ni_{0.5} bimetallic bulk structure was highly ordered up to at least 300 K and did not experience segregation of the atomic species. At 300 K, two configurations of the Pt_{0.5}Ni_{0.5} bimetallic bulk structure with the highest probability to exist were identified. The band structures of both configurations showed that these bimetallic bulk structures have metallic properties.^{30, 31} Additionally, the magnetic and electronic properties of the two configurations were investigated.^{30, 31} It was shown that electrons were transferred to the Pt from the Ni and Pt became magnetic with the addition of Ni.

7.1.2. Investigating the stability and reactivity of Pt/Ni bimetallic surfaces constructed from the most stable Pt/Ni bimetallic bulk structure

In **Chapter 6**, various (111) surface slabs with terminations at a depth of 0.0, 0.5, 1.0, 1.5 and 2.0 into the bulk structure were built from the most stable configuration in **Chapter 5**. The surface energies of these (111) surface slabs with different terminations were calculated, and the surface slab with the 1.5 (111) surface termination was identified to be the surface slab with the most stable surface.³² A single hydrogen atom was added to the slab surfaces with different surface terminations and the adsorption energies were calculated.³² It should be noted that there was a small difference in the surface energies between all of the surface terminations and the surface slabs. From the adsorption energy results for the *fcc* adsorption site, the 0.5 (111) surface termination delivered the most stable surface in terms of hydrogen adsorption.

Overall, the results obtained for the hydrogen adsorption on the slab surfaces indicated that the stability and reactivity of these surfaces are comparable to that of either the parent metals or other bimetallic surface studies.³³⁻

44

7.1.3. Evaluation of the performance of the most outstanding Pt/Ni bimetallic surface as a viable electrocatalyst for both the OER and ORR

The surface reactivity was investigated to determine if the most stable slab surface, identified in the previous section, is a viable alternative electrocatalyst for both the OER and ORR. This evaluation was done through an examination of the performance of the surfaces towards water adsorptions.

In **Chapter 6** a single H₂O molecule was adsorbed onto the Pt_{0.5}Ni_{0.5} bimetallic surface slab. It was observed that the OH bond in the HOH elongated after the H₂O molecule was adsorbed on the metal surfaces. The elongation is an indication of the weakening of the H-O-H bonds and the reduced bonding electrons in the water, which is consistent with other studies.⁴⁵ The largest bond elongation for the OH (a) bond was observed for the 0.5Ni* and 0.5Ni*(B) (as shown in **Table 6.8**) with an elongation of 0.013 Å, while the largest bond elongation of 0.011 Å along the OH (b) bond was observed for the 1.5Ni* and the 1.5Ni*(C) surfaces (as shown in **Table 6.8**). The largest

HOH angle increase, 104.200 ° to 106.804 °, was observed for the $_{1.5}\text{Ni}^*$ and the $_{1.5}\text{Ni}^*(\text{C})$ surfaces. Additionally, electron transfer was also observed between the H_2O molecule and the nearest neighbours in the metal surfaces, as shown in **Figure 6.12** in **Chapter 6**. Overall, the most stable adsorption was on the $_{1.5}\text{Ni}^*$ surface with an adsorption energy of -0.369 eV.

Due to the fact that the spontaneous cleavage of the H_2O molecule was observed on the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ bimetallic surfaces, which is desirable for the water-splitting reaction,⁷⁻¹⁴ the conclusion is that the Pt/Ni bimetallic surfaces are a viable alternative electrocatalysts for the water-splitting reaction. However, experimental data is needed to confirm this conclusion.

7.2. Recommendations

It is recommended that the adsorption of other reaction intermediates, such as the OH_{ads} and HOO_{ads} which occur in the OER and ORR, be investigated to determine the suitability of these Pt/Ni bimetallic slabs for the OER and ORR. In addition, investigations into the performance of other Miller plane surfaces and nanoparticles consisting of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ will be beneficial in the development of Pt/Ni bimetallic materials as electrocatalysts for use in electrolyzers and fuel cells.

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APPENDIX

Table A3-1. Interatomic spacing, lattice parameter and energy per atom for various k -point meshes for Pt (111) slab.

k -point	Amount k -points (a.u.)	E/atom (eV)	ΔE (eV)	Lattice parameters (Å)	Interatomic spacing (Å)
$1 \times 1 \times 1$	1	– 717.695	0.000	8.507	2.755
$3 \times 3 \times 1$	5	– 717.895	– 0.199	8.507	2.826
$5 \times 5 \times 1$	13	– 717.881	0.014	8.507	2.823
$7 \times 7 \times 1$	25	– 717.884	– 0.003	8.507	2.820

Table A3-2. Interatomic spacing, lattice parameter and energy per atom for various k -point meshes for Ni (111) slab.

k -point	Amount k -points (a.u.)	E/atom (eV)	ΔE (eV)	Lattice parameters (Å)	Interatomic spacing (Å)
$1 \times 1 \times 1$	1	– 1354.10	0.000	7.528	2.450
$3 \times 3 \times 1$	5	– 1354.17	– 0.076	7.528	2.478
$5 \times 5 \times 1$	13	– 1354.17	– 0.002	7.528	2.478
$7 \times 7 \times 1$	25	– 1354.17	0.000	7.528	2.480

Table A4-1. Calculated electronic properties for R-Pt_{0,x}Ni_{0,y} bimetallic surface with varying adsorption sites.

Surface	H-M _{ads}	Φ (eV)	d _{H-M} (Å)	HBE (eV)	E _{ads} (eV)	ϵ_d (eV)
R-Pt _{0.25} Ni _{0.75} (H ₁)	Pt ₂ Ni	4.181	1.795	− 2.740	− 0.505	− 1.455
R-Pt _{0.25} Ni _{0.75} (H ₂)	Pt ₂ Ni	3.931	1.917	− 2.741	− 0.376	− 1.450
R-Pt _{0.25} Ni _{0.75} (H ₃)	Pt ₂ Ni	4.583	1.782	− 2.407	− 0.529	− 1.452
R-Pt _{0.25} Ni _{0.75} (H ₄)	Pt ₃	4.188	1.728	− 2.777	− 0.441	− 1.452
R-Pt _{0.5} Ni _{0.5} (H ₁)	Pt ₂ N	4.152	2.038	− 2.595	− 0.350	− 1.673
R-Pt _{0.5} Ni _{0.5} (H ₂)	Pt ₂ N	4.376	2.008	− 2.655	− 0.533	− 1.682
R-Pt _{0.5} Ni _{0.5} (H ₃)	Pt ₂ N	4.774	2.062	− 2.417	− 0.067	− 1.684
R-Pt _{0.5} Ni _{0.5} (H ₄)	Pt ₃	4.359	2.018	− 2.259	− 0.479	− 1.681
R-Pt _{0.75} Ni _{0.25} (H ₁)	Pt ₂ Ni	4.969	1.938	− 2.578	− 1.425	− 1.878
R-Pt _{0.75} Ni _{0.25} (H ₂)	Pt ₂ Ni	4.615	1.906	− 2.665	− 0.403	− 1.903
R-Pt _{0.75} Ni _{0.25} (H ₃)	Pt ₂ Ni	4.501	1.765	− 2.805	− 1.643	−
R-Pt _{0.75} Ni _{0.25} (H ₄)	Pt ₃	5.175	1.700	− 2.793	− 0.414	−1.923
R-Pt _{0.25} Ni _{0.75} (F ₁)	Pt ₃	4.085	1.834	− 2.722	− 0.395	−1.458
R-Pt _{0.25} Ni _{0.75} (F ₂)	Pt ₂ Ni	4.372	1.877	− 2.788	− 0.480	−1.449
R-Pt _{0.25} Ni _{0.75} (F ₃)	Pt ₂ Ni	4.344	1.801	− 2.771	− 0.434	−1.450
R-Pt _{0.25} Ni _{0.75} (F ₄)	Pt ₂ Ni	4.286	1.708	− 2.574	− 0.306	−1.451
R-Pt _{0.5} Ni _{0.5} (F ₁)	Pt ₃	4.875	2.048	− 2.355	− 0.067	− 1.678
R-Pt _{0.5} Ni _{0.5} (F ₂)	Pt ₂ Ni	4.901	2.021	− 2.417	− 0.133	− 1.675
R-Pt _{0.5} Ni _{0.5} (F ₃)	Pt ₂ Ni	4.661	1.942	− 2.694	− 0.381	− 1.681
R-Pt _{0.5} Ni _{0.5} (F ₄)	Pt ₂ Ni	4.367	2.002	− 2.261	− 0.308	− 1.678
R-Pt _{0.75} Ni _{0.25} (F ₁)	Pt ₃	4.484	1.905	− 2.691	− 1.528	− 1.999
R-Pt _{0.75} Ni _{0.25} (F ₂)	Pt ₂ Ni	*	*	*	*	*
R-Pt _{0.75} Ni _{0.25} (F ₃)	Pt ₂ Ni	4.471	1.883	− 2.380	− 1.240	− 2.005
R-Pt _{0.75} Ni _{0.25} (F ₄)	Pt ₂ Ni	1.826	1.700	− 2.665	− 0.404	− 1.908

Table A4-2. Calculated electronic properties for R-Pt_{0.5}Ni_{0.5} bimetallic surface with varying adsorption sites.

	Surface	H-M _{ads}	Φ (eV)	d_{H-M} (Å)	HBE (eV)	E _{ads} (eV)	ϵ_d (eV)
<i>hcp</i>	Ni (111) H	Ni	3.089	1.729	− 2.900	− 0.561	− 1.474
	Pt (111) H	Pt	5.002	1.800	− 2.785	− 0.516	− 2.451
	R-Pt _{0.5} Ni _{0.5} (H ₁)	Pt ₂ N	4.152	2.038	− 2.595	− 0.350	− 1.673
	R-Pt _{0.5} Ni _{0.5} (H ₂)	Pt ₂ N	4.376	2.008	− 2.655	− 0.533	− 1.682
	R-Pt _{0.5} Ni _{0.5} (H ₃)	Pt ₂ N	4.774	2.062	− 2.417	− 0.067	− 1.684
	R-Pt _{0.5} Ni _{0.5} (H ₄)	Pt ₃	4.359	2.018	− 2.259	− 0.479	− 1.681
<i>fcc</i>	Ni (111) F	Ni	3.097	1.725	− 2.880	− 0.539	− 1.474
	Pt (111) F	Pt	5.025	1.800	− 2.737	− 0.461	− 2.461
	R-Pt _{0.5} Ni _{0.5} (F ₁)	Pt ₃	4.875	2.048	− 2.355	− 0.067	− 1.678
	R-Pt _{0.5} Ni _{0.5} (F ₂)	Pt ₂ Ni	4.901	2.021	− 2.417	− 0.133	− 1.675
	R-Pt _{0.5} Ni _{0.5} (F ₃)	Pt ₂ Ni	4.661	1.942	− 2.694	− 0.381	− 1.681
	R-Pt _{0.5} Ni _{0.5} (F ₄)	Pt ₂ Ni	4.367	2.002	− 2.261	− 0.308	− 1.678

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Mixing thermodynamics and electronic structure of the $\text{Pt}_{1-x}\text{Ni}_x$ ($0 \leq x \leq 1$) bimetallic alloy

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The development of affordable bifunctional platinum alloys as electrode materials for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) remains one of the biggest challenges for the transition towards renewable energy sources. Yet, there is very little information on the optimal ratio between platinum and the transition metal used in the alloy and its impact on the electronic properties. Here, we have employed spin-polarised density functional simulations with long-range dispersion corrections [DFT–D3–(BJ)], to investigate the thermodynamics of mixing, as well as the electronic and magnetic properties of the $\text{Pt}_{1-x}\text{Ni}_x$ solid solution. The Ni incorporation is an exothermic process and the alloy composition $\text{Pt}_{0.5}\text{Ni}_{0.5}$ is the most thermodynamically stable. The $\text{Pt}_{0.5}\text{Ni}_{0.5}$ solid solution is highly ordered as it is composed mainly of two symmetrically inequivalent configurations of homogeneously distributed atoms. We have obtained the atomic projections of the electronic density of states and band structure, showing that the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ alloy has metallic character. The suitable electronic properties of the thermodynamically stable $\text{Pt}_{0.5}\text{Ni}_{0.5}$ solid solution shows promise as a sustainable catalyst for future regenerative fuel cells.

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1 Introduction

Clean and renewable energy resources are needed to decrease pollution and climate change, whilst also keeping up with increasing energy demand. To this end, electrocatalysts are crucial components of regenerative fuel cells.^{1–3} In these devices, both the forward oxygen evolution reaction (OER), producing the clean hydrogen energy vector through water electrolysis, and the reverse oxygen reduction reaction (ORR), generating energy *via* the recombination of oxygen and hydrogen into water, take place following different mechanisms. However, the future development of regenerative fuel cells is hindered by the large over-potential exceeding the 1.23 eV required by the oxygen producing anode and slow reaction kinetics, which reduces the efficiency of the process.^{4–6} Pt-based electrocatalysts exhibit excellent activity for the ORR reaction,^{7–14} but poor performance for the OER reaction, while

state of the art IrO_2 and RuO_2 OER electrocatalysts are only moderately active towards the ORR reaction.² Electrocatalysts which combine two of these precious metals, Pt, Ir and Ru, show reasonable activity towards both the ORR and the OER reactions, but their use is limited due to low abundance and high cost.^{15,16} Therefore, the development of efficient bifunctional electrocatalysts which can be used for both the ORR and the OER reactions remains a challenge.

Previous work has reported the enhanced bifunctional electrocatalytic activity of a Pt/Ni alloy.³ However, the relationship between the equilibrium composition of the mixture, the distribution of the metal atoms and the electronic structure of the alloy are not yet fully understood. Insights into all these properties are, however, essential if we are to utilise these types of bimetallic materials as fuel cell catalysts for the ORR and OER reactions. In this paper, we have used density functional theory (DFT) calculations to study the mixing thermodynamics of the solid solution with Pt and Ni as end members, as well as the electronic and thermodynamic properties for the equilibrium composition.

2 Computational details

We have used DFT calculations as implemented in the Vienna ab initio simulation program (VASP)^{17–20} to calculate the structures and energies of the Pt–Ni solid solution. The generalised-gradient approximation (GGA) functional developed by Perdew,

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Burke, and Ernzerhof (PBE),^{21,22} corrected with the semi-empirical D3 approach of Grimme with the Becke–Johnson (BJ) damping,^{23–25} was used for the simulations. The interaction between the core and valence electrons, defined as those in the 3d4s levels for Ni and 5d6s for Pt, was described with the projected augmented-wave (PAW)²⁶ method in the implementation of Kresse and Joubert.²⁷ A *F*-centred Monkhorst–Pack grid²⁸ of $11 \times 11 \times 11$ *k*-points was used to carry out the integrations in the reciprocal space of the primitive unit cells. The *k*-point grids for larger supercells were chosen in such a way that a similar spacing of points in the reciprocal space was maintained. To improve the convergence of the Brillouin-zone integrations, the electronic partial occupancies were determined using the Methfessel–Paxton order 1 smearing, with a width for all calculations set at 0.2 eV. However, the tetrahedron method with Blöchl corrections was used in static simulations to obtain very accurate total energies as well as all the electronic and magnetic properties. The kinetic energy cut-off was fixed at 400 eV for the plane-wave basis set expansion of the Kohn–Sham (KS) valence states, which was large enough to avoid Pulay stress. The atomic charges and magnetic moments were analysed using the Bader partitioning.^{29–34}

The crystal structure of both Pt and Ni metals is face-centred cubic (fcc), which belongs to the *Fm* $\bar{3}$ *m* space group (No. 225).^{35,36} The primitive cubic unit cell of the pure metals contains 4 atoms distributed in the Wyckoff 4a positions. Pt is a closed shell paramagnetic metal, while Ni is a ferromagnetic material with a Curie temperature of $T_C = 624$ K.³⁷ For the pure metals and solid solutions, all the calculations were spin-polarised and the initial spin moments were set parallel for the Ni atoms.

The internal coordinates, lattice parameters, atomic spin moments and cell shape were all allowed to change during geometry optimisations. Using this methodology, we have calculated a lattice parameter *a* for the bulk unit cell of the pure Pt and Ni end member phases of 3.924 and 3.473 Å, in excellent agreement with the experimental values of 3.923³⁵ and 3.528 Å,³⁶ respectively. Taking into account the performance of our DFT setup for predicting the lattice parameters of the pure metal phases, we are confident of our predictions for the solid solution containing various Pt/Ni compositions.

In addition to the DFT calculations, atomistic simulations based on interatomic potentials (IP) were also carried out using the General Utility Lattice Program (GULP).^{38,39} The Sutton and Chen interatomic potentials were used to calculate the energies and structures of the pure Pt and Ni metals.⁴⁰ The interatomic potentials for the alloy were obtained using the standard geometric and arithmetic average rules.⁴¹ The complementary use of a less compute-intensive method allowed us to sample larger simulation cells in our mixing studies.

We have used the site occupancy disorder (SOD) code⁴² to study a series of substitutions of Pt by Ni in the $1 \times 1 \times 1$ and $2 \times 2 \times 1$ supercells of the fcc unit cell, containing 4 and 16 sites, respectively. This program constructs the full configurational spectrum for each composition of the supercell and then uses the symmetry operators of the parent structure to separate the symmetrically inequivalent configurations. Note

that the $2 \times 2 \times 1$ supercell breaks the cubic symmetry of the unit cell, which affects the atomic interactions with the neighbouring cells in the *c* direction with respect to the *a* and *b* directions. However, the fully symmetric $2 \times 2 \times 2$ supercell, has a prohibitively large computational cost when considering all inequivalent substitutional configurations, even when employing atomistic simulations.

3 Results and discussion

3.1 Configurational entropy of mixing

Firstly, we discuss the full-disorder or maximum configurational entropy ($S_{\max}$), which we have defined as the number of ways the Pt and Ni atoms pack together in the solid solution for a given composition in the high temperature limit. The maximum configurational entropy for a finite simulation cell is obtained from⁴³

$$S_{\max}(x, N) = \frac{1}{N} k_B \ln \frac{N!}{[xN]![(1-x)N]!}, \quad (1)$$

where *N* is the number of formula units in the supercell, k_B is the Boltzmann constant and *x* is the Ni mole fraction in the alloy. The ideal full-disorder entropy (S_{ideal})⁴³ as the cell size approaches infinity is calculated as

$$S_{\text{ideal}}(x) = \lim_{N \rightarrow \infty} S_{\max}(x, N) = -k_B [x \ln x + (1-x) \ln(1-x)]. \quad (2)$$

Fig. 1(a) displays the maximum entropy values for different simulation cell sizes and Ni contents. As expected from eqn (2), the largest full-disorder entropies are reached when both Pt and Ni atoms have equal concentrations, starting at $S_{\max} = 0$ for the pure metal phases. For the smallest $1 \times 1 \times 1$ supercell, used for our DFT calculations, the maximum entropy varies significantly from the ideal value for any Ni mole fraction. For example, the calculated high temperature entropies for the simulation cell containing 4 f.u. are below the full-disorder values by ~36 and ~33% at $x = 0.25$ and 0.50 , respectively. Given the cubic symmetry of the primitive unit cell, we chose to double any two axes to form the $2 \times 2 \times 1$ supercell used in the atomistic simulations. The resulting full-disorder configurational entropies improve significantly with respect to the cell containing 4 f.u. Configurational entropies have a slow rate of convergence with respect to the size of the simulation cell, in agreement with previous reports.⁴⁴ Although not fully converged, the maximum entropies are still useful to evaluate the level of disorder in solid solutions at equilibrium conditions.

3.2 Enthalpy of mixing

To gain insight into the thermochemistry of Ni incorporation in Pt, we have calculated the enthalpy of mixing (ΔH_{mix}) as⁴⁵

$$\Delta H_{\text{mix}} = E(\text{Pt}_{1-x}\text{Ni}_x) - (1-x)E(\text{Pt}) - xE(\text{Ni}), \quad (3)$$

where $E(\text{Pt}_{1-x}\text{Ni}_x)$, $E(\text{Pt})$ and $E(\text{Ni})$ are the total energies of the $\text{Pt}_{1-x}\text{Ni}_x$ mixed system and the pure Pt and Ni metals, respectively. In particular, $E(\text{Pt}_{1-x}\text{Ni}_x)$ corresponds to the average^{43,45,46}

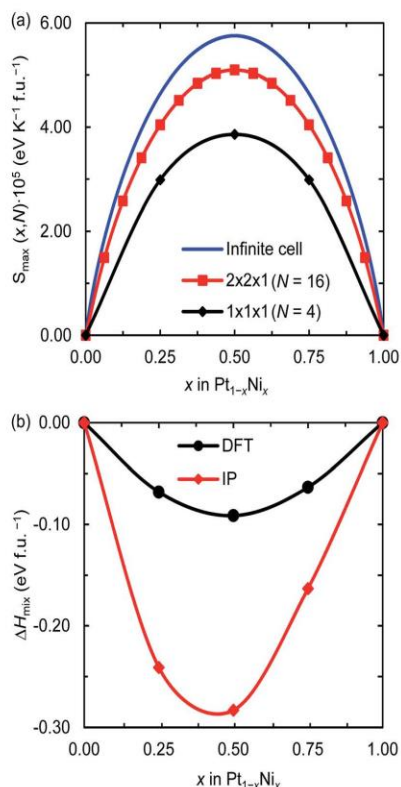


Fig. 1 (a) Maximum configurational entropy ($S_{\max}$) for different number of f.u. (N) and (b) mixing enthalpies (ΔH_{mix}) for the $1 \times 1 \times 1$ supercell both per formula unit of $\text{Pt}_{1-x}\text{Ni}_x$ and as a function of the Ni mole fraction (x). ΔH_{mix} was calculated using DFT and IP-based simulations.

$$E = \sum_{m=1}^M P_m E_m, \quad (4)$$

where P_m and E_m are the occurrence probability and the energy of configuration m , respectively, in the full spectrum containing

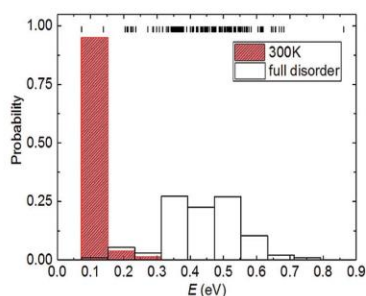


Fig. 2 Partially and fully disordered probability distribution of the energies (E) calculated for the configurations with Ni composition $x = 0.50$ in the $2 \times 2 \times 1$ supercell. The short vertical lines represent the energy values in the configurational spectrum. The partially disordered probability distribution was calculated using a Boltzmann-modulation at 300 K.

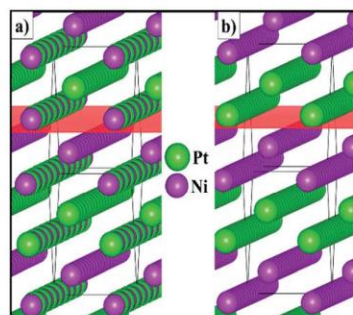


Fig. 3 Schematic representation of configurations (a) B and (b) C for the $2 \times 2 \times 1$ supercell of the solid solution with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition. The (110) plane is represented in red.

M inequivalent configurations. We recall that the configurational probabilities follow the Boltzmann distribution

$$P_m = \frac{\Omega_m}{Z} e^{(-E_m/k_B T)}, \quad (5)$$

where Ω_m is the degeneracy of the inequivalent configuration m and Z is the configurational partition function

$$Z = \sum_{m=1}^M \Omega_m e^{(-E_m/k_B T)}. \quad (6)$$

At this point it is worth mentioning that the configurational space of the $1 \times 1 \times 1$ supercell contains only one symmetrically inequivalent configuration for each of the 5 possible Ni mole fractions. Thus, the corresponding energetics of the mixing does not depend on temperature, as described in eqn (4).

Fig. 1(b) shows the DFT and IP enthalpy of mixing as a function of the Ni mole fraction x for the $1 \times 1 \times 1$ supercell. The calculated ΔH_{mix} values for the partially disordered alloy are negative for any Ni concentration, indicating that the formation of the $\text{Pt}_{1-x}\text{Ni}_x$ solid solution is an exothermic process. Our DFT (IP) simulations suggest that there is a small asymmetry in the enthalpy of mixing of the disordered system as Ni incorporation in Pt is 0.005 (0.078) eV per formula unit (f.u.) more exothermic than Pt incorporation in Ni. Although the IP method predicts larger enthalpies of mixing than the DFT approach, especially for $x = 0.5$, they describe the same behaviour for the thermochemistry of the Pt–Ni solid solution. In particular, they both predict $\text{Pt}_{0.5}\text{Ni}_{0.5}$ to be the equilibrium composition, which has also been observed in a computational study into the ordered and disordered special quasi-random structured $\text{Pt}_{1-x}\text{Ni}_x$ solid solution.⁴⁷

3.3 Probability distribution

We now consider the relationship between the configurational energy and the probability of the partially and fully disordered system with $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition. In Fig. 2, we have plotted the probability distributions of the 153 inequivalent configurations for the $2 \times 2 \times 1$ supercell at Ni mole fraction $x = 0.50$. Our

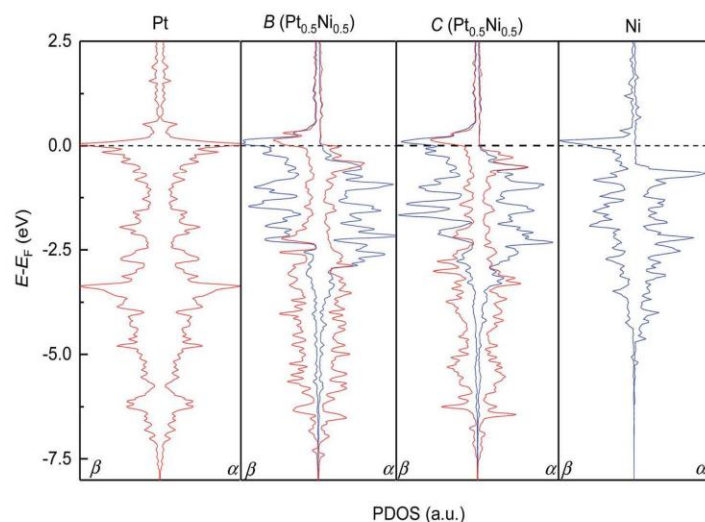


Fig. 4 Atomic projections of the spin-decomposed density of states (PDOS) for the d-electrons of the pure Pt and Ni metals (left and right panels) and configurations B and C of the solid solution with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition (middle panels). α and β stand for the majority and minority channel of the spins, respectively.

atomistic simulations clearly indicate that there is a 0.7 eV f.u.^{-1} difference between the low- and high-end energy configurations for the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition. At high temperatures, where the solid solution is fully disordered, we have found that the degeneracy weighting leads to a normal probability distribution where those configurations with intermediate energies of $\sim 0.45 \text{ eV f.u.}^{-1}$ are favoured. However, upon equilibration at

lower temperatures the lowest-energy configurations have a high weighting while the probabilities decrease with the energy of the configurations. For example, we have predicted the probability distribution for the partially disordered solid solution with $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition at 300 K to represent the ambient conditions. Fig. 2 shows that when considering temperature effects, the probability of occurrence vanishes for

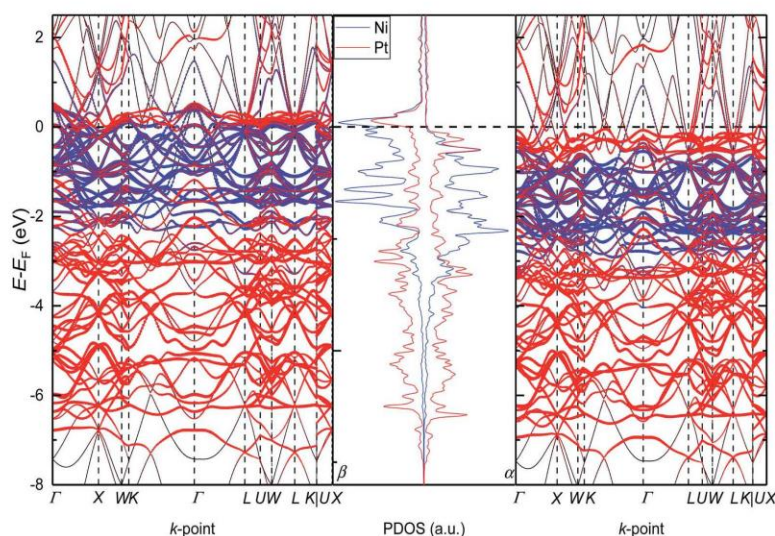


Fig. 5 Electronic density of states and band structure for configuration B of the solid solution with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition. α and β stand for the majority and minority channel of the spins, respectively.



Table 1 Atomic charges (q) and atomic spin moments (m_s) for the pure Pt and Ni metals as well as for configurations *B* and *C* of the solid solution with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition. Atomic properties were calculated by means of a Bader analysis

Phase	Configuration	Atom	q (e per atom)	m_s (μ_B per atom)
Pt	—	—	0.00	0.00
Ni	—	—	0.00	0.63
$\text{Pt}_{0.5}\text{Ni}_{0.5}$	<i>B</i>	Pt	−0.23	0.33
		Ni	0.23	0.74
	<i>C</i>	Pt	−0.23	0.35
		Ni	0.23	0.76

150 configurations. The remaining three configurations, to which we will refer as “A”, “B” and “C” account for 3.7, 47.6 and 47.3%, respectively, of the total probability at 300 K. The ground state configurations *B* and *C* strongly suggest that $\text{Pt}_{1-x}\text{Ni}_x$ bimetallic alloys prefer to form an ordered rather than a random distribution of atoms at 300 K, a preference that is reduced at higher temperatures. This effect is not surprising, as previous simulations of the $\text{Ca}_{1-x}\text{Mn}_x\text{CO}_3$ system have also shown that full disorder is unlikely at equilibrium conditions, suggesting a significant deviation from a random distribution of cations.⁴⁸ We do not consider configuration *A* for further analysis because of its low probability, which makes it very unlikely to occur in real samples.

3.4 Ground state configurations

Fig. 3 shows the schematic representation of the lowest energy configurations *B* and *C* identified for the $2 \times 2 \times 1$ supercell. Although the Pt and Ni atoms do not segregate in two separate phases, our atomistic simulations provide evidence of a preferential ordering pattern. For configuration *B*, we have found three different alternating atomic planes perpendicular to the [110] direction which are represented as a layer of Pt, followed by a mixed layer of Pt/Ni and terminated by a single layer of Ni. Configuration *C* also exhibits the ordering pattern in the [110] direction, where every other mixed layer is replaced by a plane containing only one type of atom, leading to alternating double layers of Pt and Ni metals. The atomic orderings that we have found for configurations *B* and *C* along the [110] direction are equivalent to the surface segregation patterns predicted computationally⁴⁸ and later confirmed experimentally,^{49–53} which were shown to have a strong effect on the catalytic properties of the alloy.

3.5 Density of states

We subsequently modelled the electronic structures and magnetic properties of the highest probability configurations *B* and *C* of the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ solid solution and compared them to those of the parent metals. Fig. 4 depicts the projected density of states (PDOS) for the d-electrons of the pure metals Pt and Ni and configurations *B* and *C*. As expected, we have found that Pt metal is non-magnetic and has a very symmetric PDOS in both channels of the spins due to the equal population of electrons

with α - and β -spins within the full $5d^{10}$ level. The occupied d levels of Pt appear between -7.5 eV and the Fermi level (set to 0.0 eV), with prominent bands at -3.0 and 0.0 eV. In contrast, Ni has an asymmetric PDOS, especially around the Fermi level, due to its incomplete $3d^9$ level. The valence band in the majority channel of the spins in Ni spans from -5.0 to -0.5 eV, while states in the β channel are shifted approximately 1 eV towards the Fermi level. The Ni levels with the largest PDOS are located at the valence band maximum for the α channel and at the conduction band maximum for the β channel. Despite the slightly different Pt and Ni metal arrangement, our DFT simulations suggest that the electronic structures of configurations *B* and *C* are very similar. The itinerant electron magnetism between the Pt and Ni atoms induces an asymmetry in the PDOS, which can be understood as an electronic delocalisation due to the strong interaction between the d electrons of the two metals. Furthermore, the Pt and Ni bands are strongly hybridised, particularly around the Fermi level and at -2.0 eV for the two channels of the spins of configurations *B* and *C*. The top and bottom edges of the d valence bands for the Pt and Ni atoms run within similar energy values in the solid solution and in the pure phases. We have found that the PDOS of the conduction bands are negligible for the pure metals Pt and Ni as well as configurations *B* and *C* of $\text{Pt}_{0.5}\text{Ni}_{0.5}$, apart from the bands crossing the Fermi level.

3.6 Electronic band structure

To further analyse the electronic properties of the solid solution with the $\text{Pt}_{0.5}\text{Ni}_{0.5}$ composition, we have also plotted in Fig. 5 the band structure of configuration *B* alongside its PDOS. We have chosen the path suggested by Setyawan *et al.*⁵⁴ to connect the high symmetry points of the first Brillouin zone. We have confirmed the lack of band gap for any of the spin channels and their asymmetry, in agreement with the PDOS. The number of bands crossing the Fermi level (E_F) in the minority spin channel is larger than in the majority spin channel, suggesting a larger contribution of the β electrons to the metallic properties of the alloy. The α spin contribution to the band structure is spread between -0.5 and -2.9 eV for Ni, while the Pt states are mostly below and above the Ni bands down to -7.40 eV and up to the Fermi level, respectively. The β spin channel shows similar features to the opposite channel but are all displaced towards the Fermi level by approximately 1.0 eV. Interestingly, the band structure of configuration *B* clearly indicates the origin of the hybridisation between the d states of both atoms as the Pt d levels have a larger contribution than the Ni ones at the lines connecting the high-symmetry points $W-K$, $U-W$ and $U-X$ of the first Brillouin zone in both spin channels.

3.7 Atomic charges and spin moments

Table 1 summarises the atomic charges (q) and atomic spin moments (m_s) for the pure metallic phases as well as the two major configurations of the solid solution with the equilibrium composition. For the two metals, we have confirmed that the atoms are charge-neutral. The Pt atom is not magnetic and the Ni has $0.630 \mu_B$ per atom, comparing well with the experimental



value.⁵⁵ We have found that Pt becomes magnetic upon insertion of the Ni atoms in the solid solution as it gains electrons in its 6s level.⁵⁶ The atomic quantities are very similar for Pt_{0.5}Ni_{0.5}, albeit that the Pt magnetic moment is marginally lower in configuration *B* than in *C*. The total spin magnetisation of saturation (M_s) is 1.07 and 1.11 μ_B f.u.⁻¹ for configurations *B* and *C*, while the Ni atoms lose ~30% of their atomic spin moments to Pt.

4 Conclusions

In this study, we have reported the mixing thermodynamics along with the geometrical, electronic and magnetic structures for the Pt_{1-x}Ni_x solid solution. We have modelled all symmetrically inequivalent configurations for five Ni concentrations by using the $1 \times 1 \times 1$ supercell, and for the equilibrium composition in the $2 \times 2 \times 1$ supercell. The equilibrium Ni mole fraction *x* determined for the Pt_{1-x}Ni_x system shows that Pt and Ni have a 1 : 1 ratio in the solid solution, in agreement with the available experimental data. The solid solution with the Pt_{0.5}Ni_{0.5} composition is highly ordered and up to at least 300 K does not experience segregation of the atomic species, as the only two major symmetrically inequivalent configurations each have approximately a 50% probability of occurring. The Pt and Ni atoms in the two major configurations *B* and *C* tend to form similar ordered patterns in the [110] direction. The projected density of states for the Ni metal is asymmetric due to its magnetic nature, while the non-magnetic Pt is symmetric. We have found that both configurations have metallic properties. The d levels of the two atoms cross the Fermi level, but the Pt contribution is only larger in those lines connecting the high-symmetry points *W-K*, *U-W* and *U-X* of the first Brillouin zone. The Pt atoms gain negative charge following the formation of the solid solution, thereby allowing them to become magnetic. The calculated lattice parameters, atomic charges and spin moments are in excellent agreement with experiments for the pure phases. Future work will involve the simulation of the electrocatalytic activity on the major Pt_{0.5}Ni_{0.5} surfaces for the two most stable configurations.

Conflicts of interest

There are no conflicts to declare.

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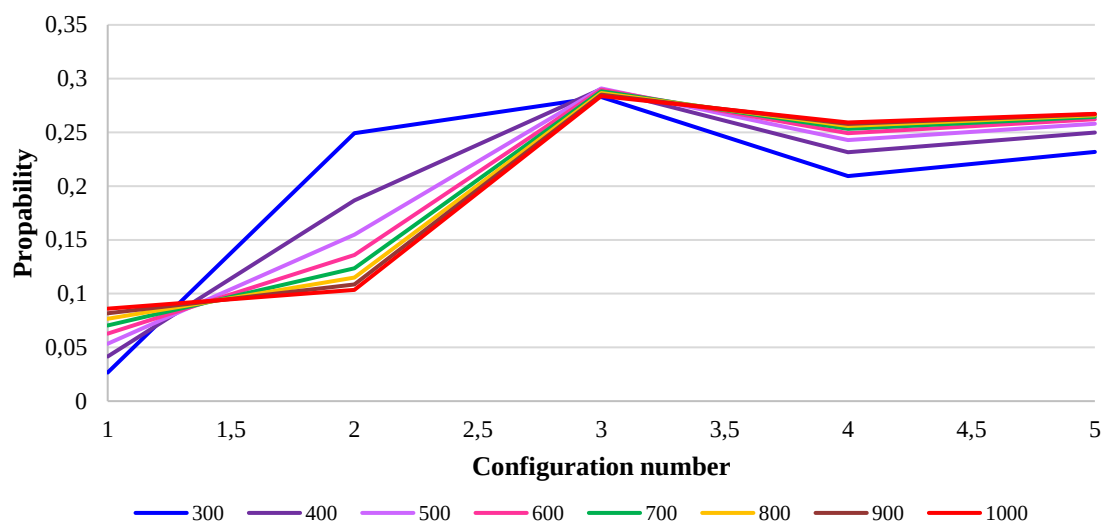


Figure A5-1. The probability for configurations to occur in the $\text{Ni}_2\text{Pt}_{14}$ 2x2x1 supercell various temperatures (K).

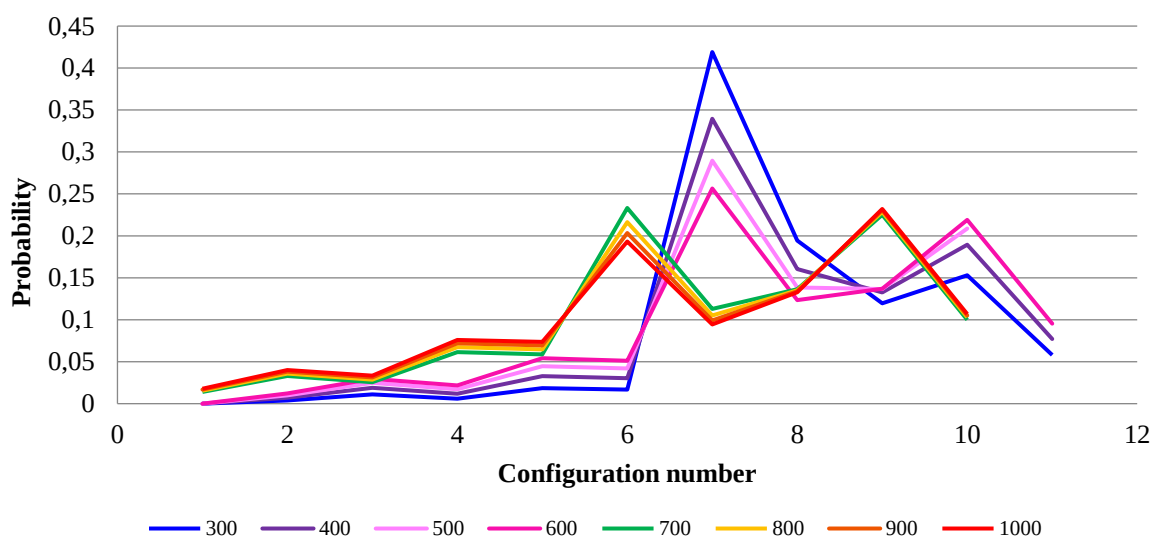


Figure A5-2. The probability for configurations to occur in the $\text{Ni}_3\text{Pt}_{13}$ 2x2x1 supercell various temperatures (K).

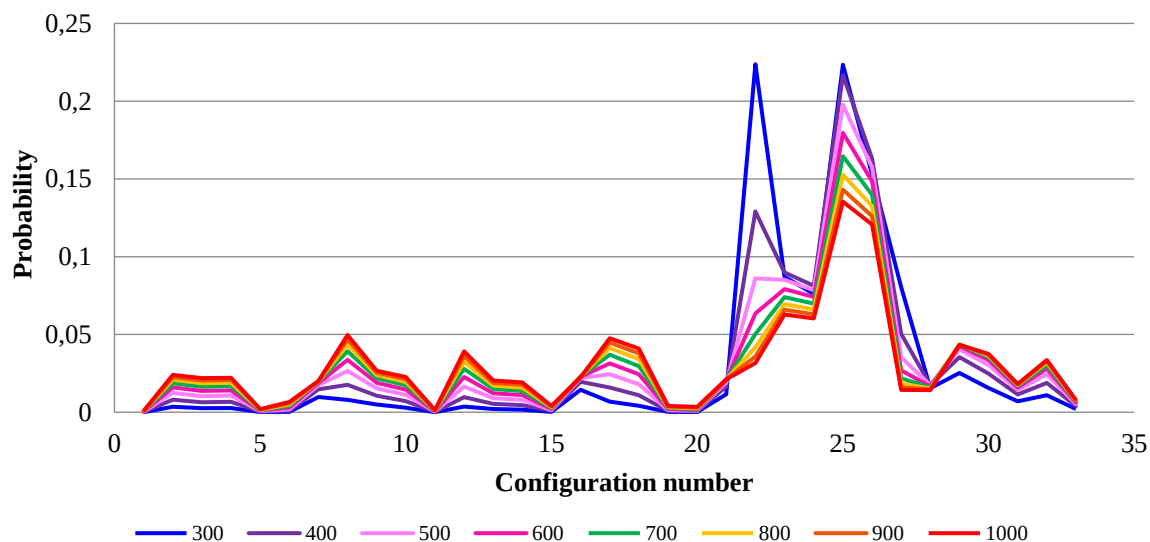


Figure A5-3. Probable configurations for the Ni₄Pt₁₆ (25:75) 2x2x1 unit cell to occur at various temperatures (K).

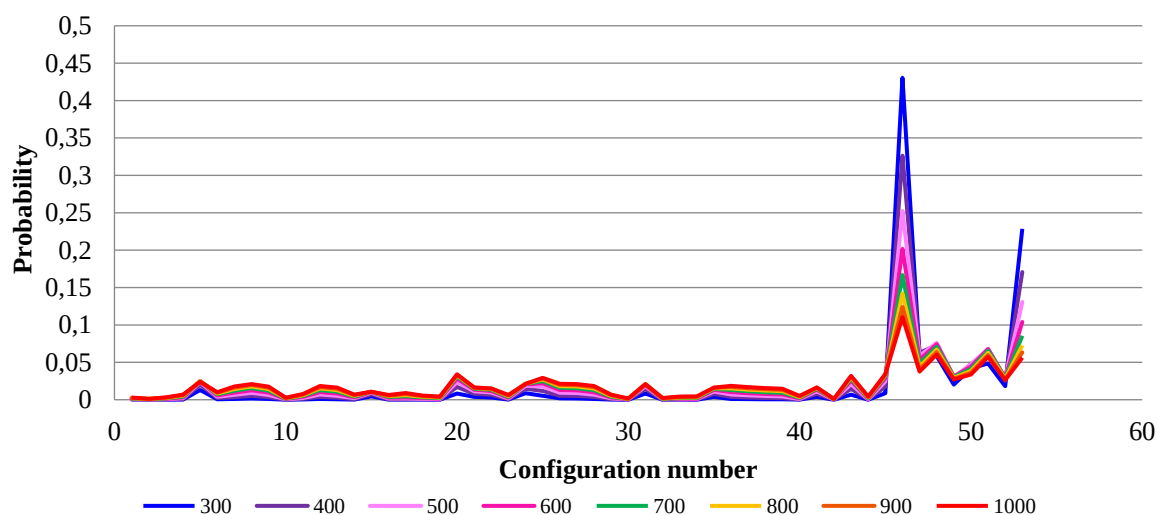


Figure A5-4. Probable configurations for the Ni₅Pt₁₁ (31:69) 2x2x1 unit cell to occur at various temperatures (K).

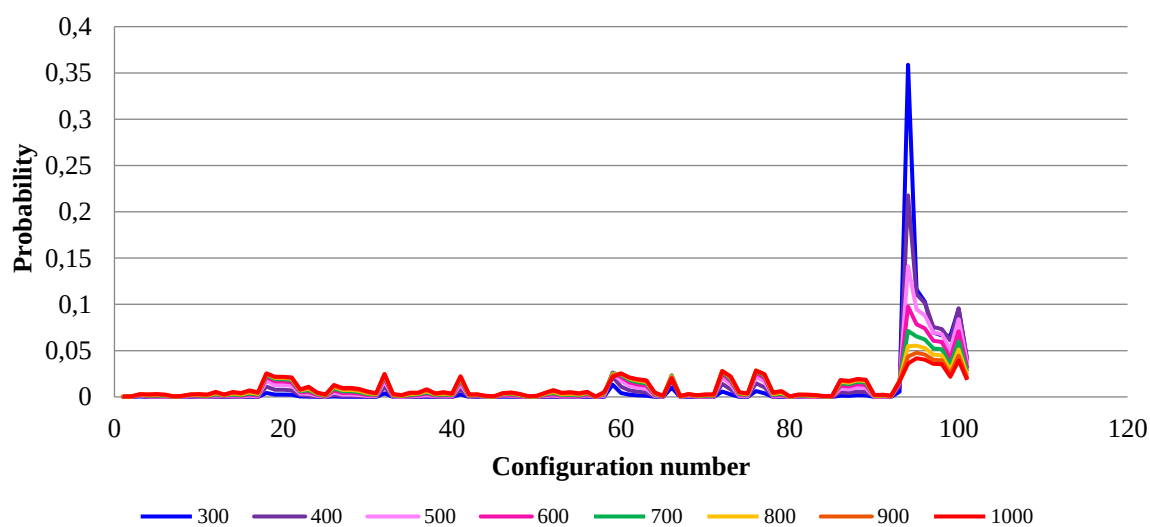


Figure A5-5. Probable configurations for the Ni₆Pt₁₀ (37:63) 2x2x1 unit cell to occur at various temperatures (K).

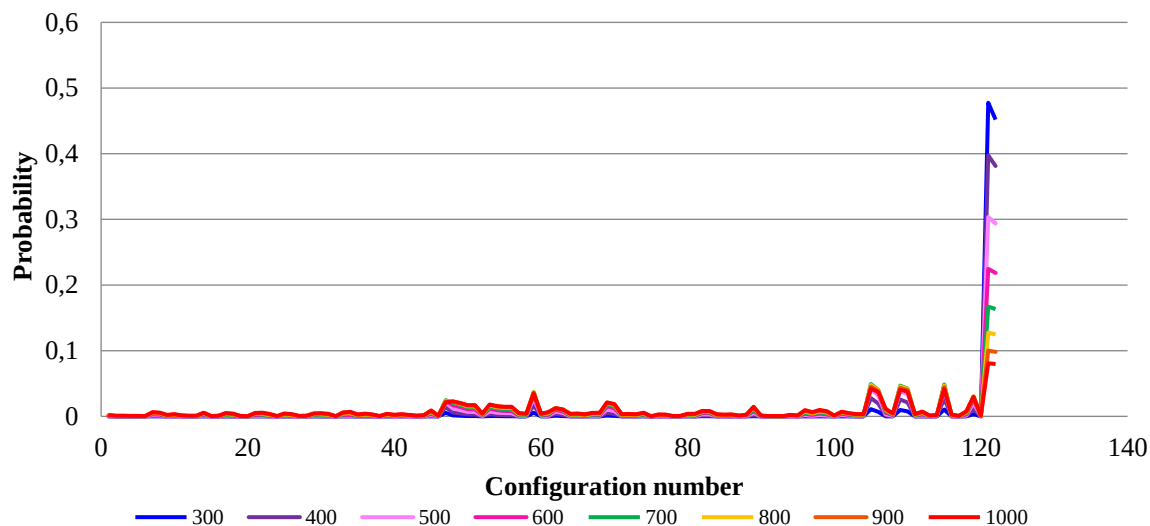


Figure A5-6. The probability for configurations to occur in the Ni₇Pt₉ 2x2x1 supercell various temperatures (K).

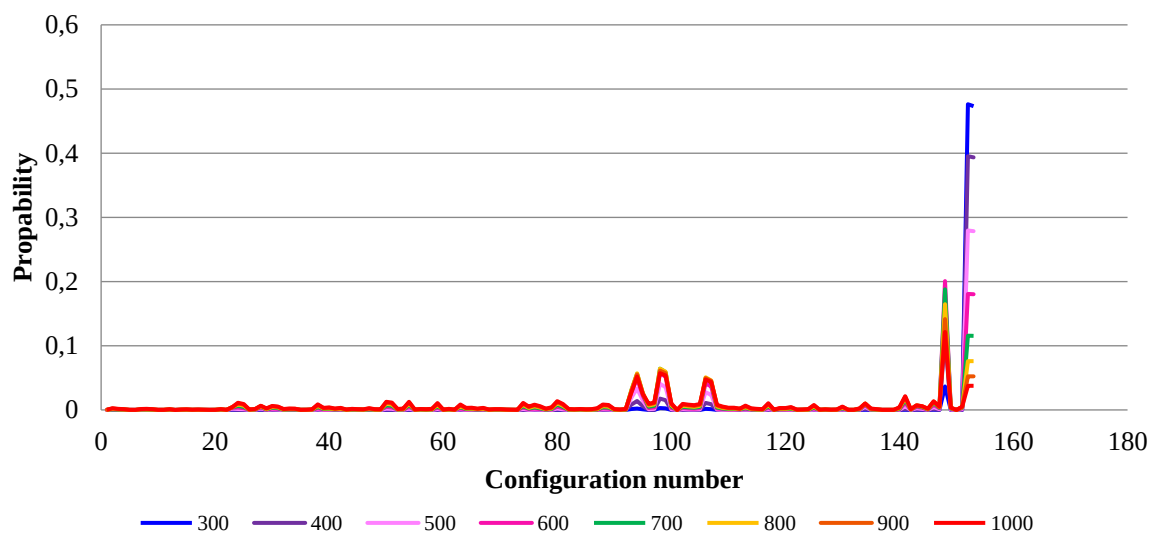


Figure A5-7. The probability for configurations to occur in the Ni₈Pt₈ 2x2x1 supercell various temperatures (K).

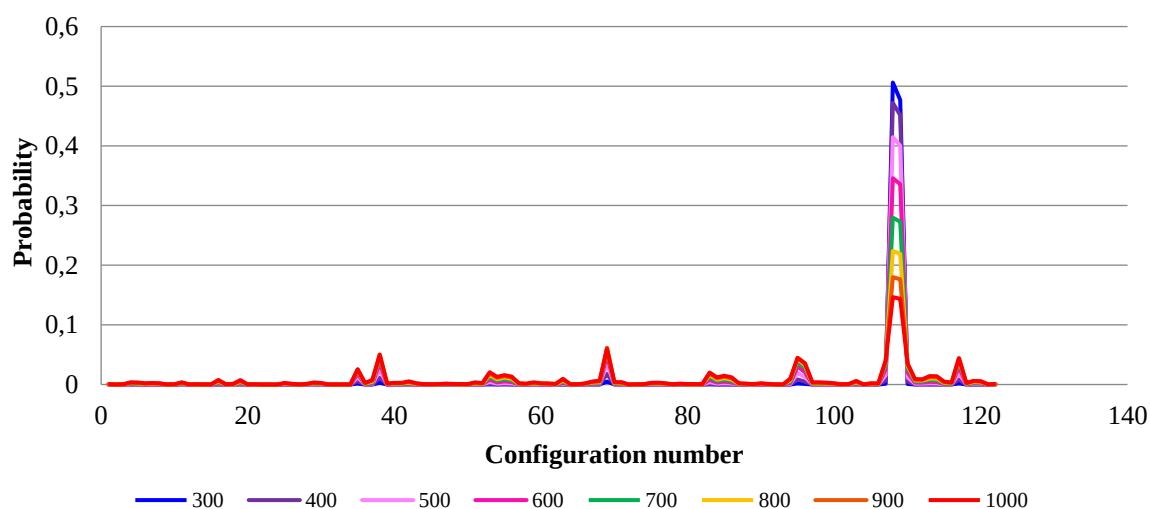


Figure A5-8. The probability for configurations to occur in the Ni₉Pt₇ 2x2x1 supercell various temperatures (K).

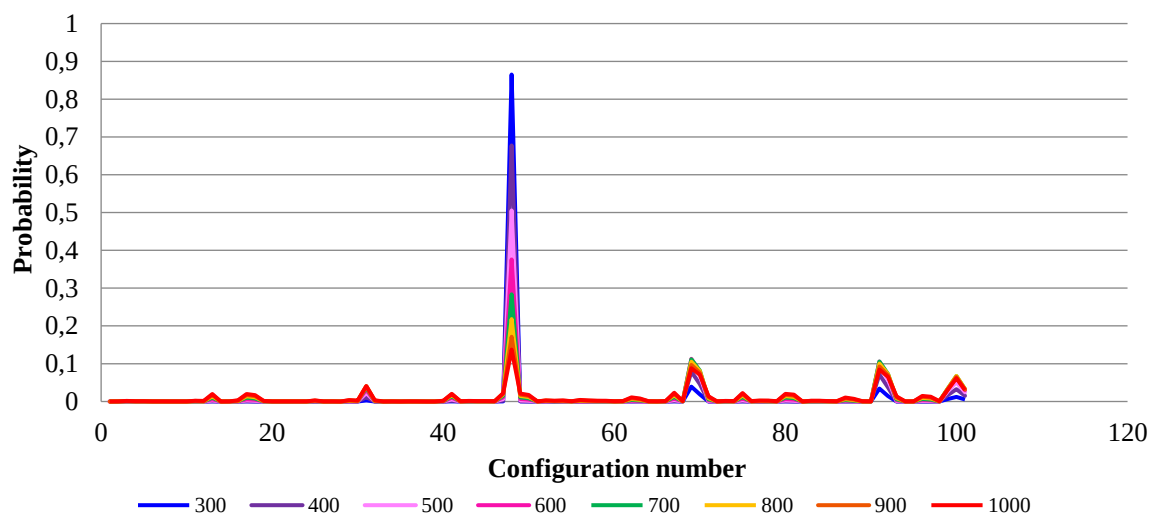


Figure A5-9. The probability for configurations to occur in the Ni₁₀Pt₆ 2x2x1 supercell various temperatures (K).

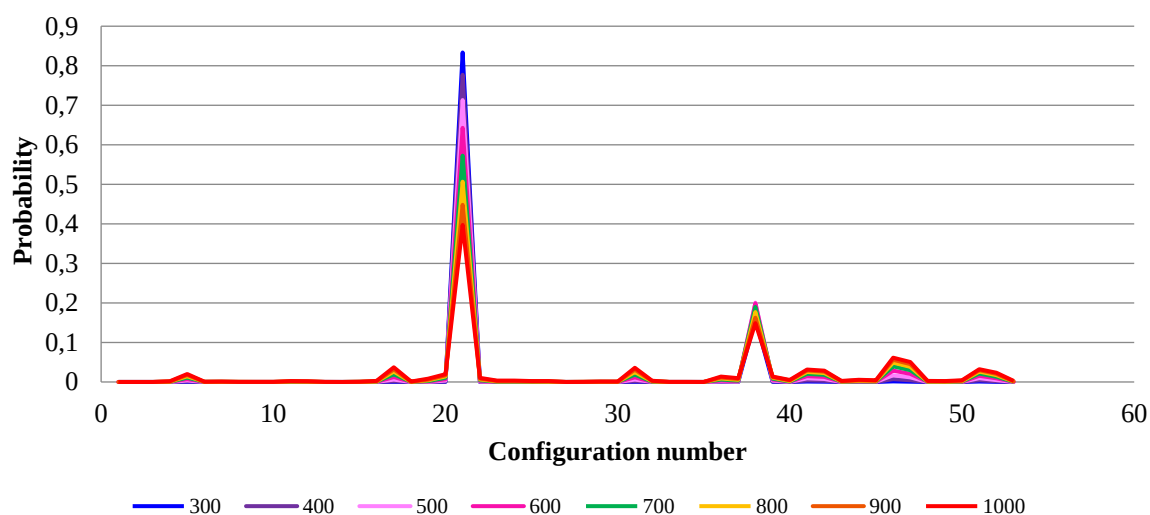


Figure A5.10. The probability for configurations to occur in the Ni₁₁Pt₅ 2x2x1 supercell various temperatures (K).

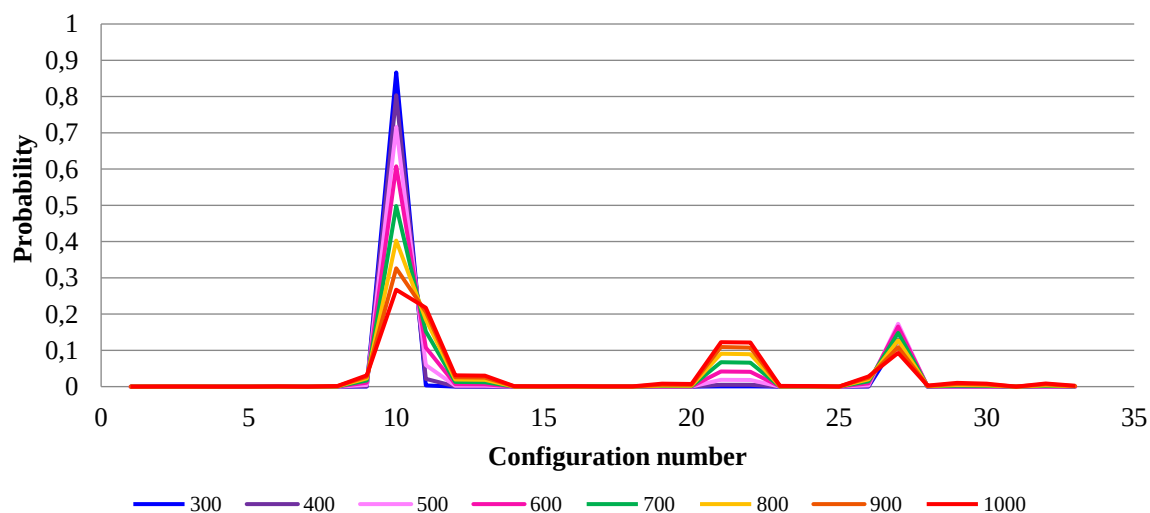


Figure A5-10. The probability for configurations to occur in the Ni₁₂Pt₄ 2x2x1 supercell various temperatures (K).

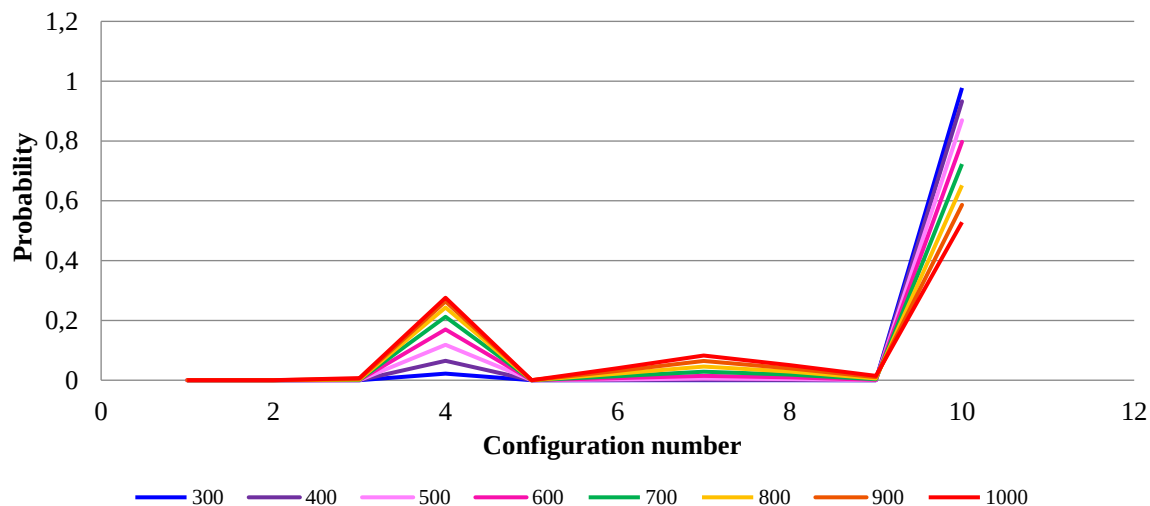


Figure A5-11. The probability for configurations to occur in the $\text{Ni}_{13}\text{Pt}_3$ 2x2x1 supercell various temperatures (K).

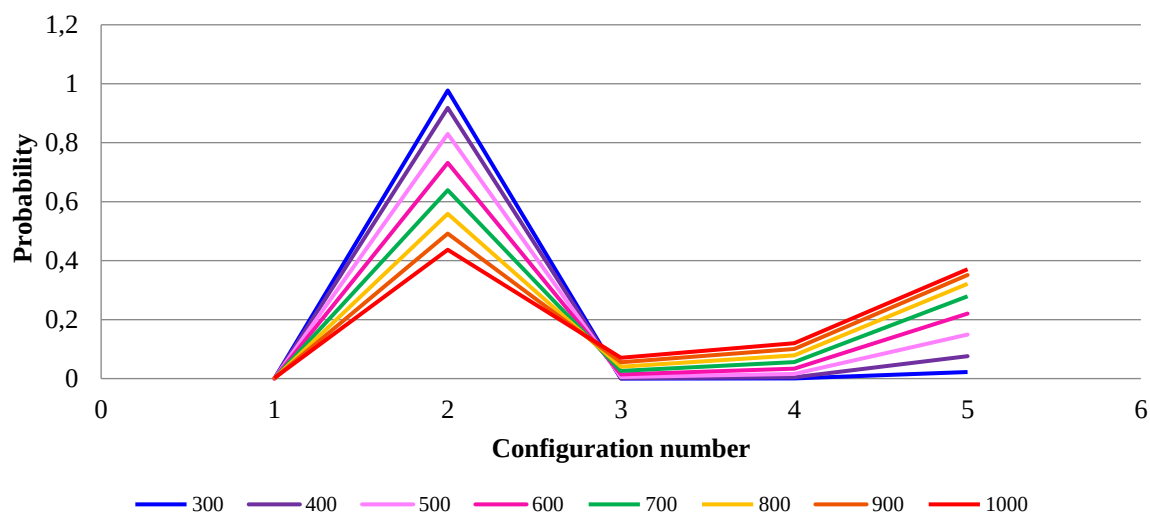


Figure A5-12. The probability for configurations to occur in the $\text{Ni}_{14}\text{Pt}_2$ 2x2x1 supercell various temperatures (K).

Table A5-1. Adsorption energy (in eV) of the constrained and relaxed surfaces with 0.125 ML.

ML	Surface	Site	E_{ads} (eV)
Relaxed surfaces			
0.125	0.0		− 0.398
0.125	0.5		− 0.509
0.125	1.0		− 0.453
0.125	1.5	Pt top	− 0.392
0.125	2.0	Ni/Pt top	− 0.502
Constrained surfaces			
0.125	0.0		− 0.394
0.125	0.5		− 0.509
0.125	1.0		− 0.452
0.125	1.5	Pt top	− 0.400
0.125	2.0	*Ni/Pt top	− 0.500

Table A5-2. Adsorption energy (in eV) of the constrained and unconstrained surfaces with 0.0625 ML.

ML	Surface	$E_{\text{ads}}(\text{fcc})$ (eV)	$E_{\text{ads}}(\text{hcp})$ (eV)	$E_{\text{ads}}(\text{atop})$ (eV)
Relaxed surfaces				
0.0625	Pt	– 0.460	– 0.513	– 0.394
0.0625	Ni	– 0.512	– 0.529	– 0.531
0.0625	0.0	– 0.487	– 0.375	– 0.353
0.0625	0.5	– 0.550	– 0.483	– 0.472
0.0625	1.0	– 0.513	– 0.537	– 0.591
0.0625	1.5	– 0.489	– 0.376	– 0.343
0.0625	2.0	– 0.545	– 0.480	– 0.463
Constrained surfaces				
0.0625	Pt	– 0.460	– 0.511	– 0.391
0.0625	Ni	– 0.517	– 0.535	– 0.531
0.0625	0.0	– 0.484	– 0.375	– 0.348
0.0625	0.5	– 0.551	– 0.483	– 0.551
0.0625	1.0	– 0.517	– 0.546	– 0.586
0.0625	1.5	– 0.495	– 0.380	– 0.349
0.0625	2.0	– 0.540	– 0.444	– 0.461

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S1

Supplementary 1: Influence of Miller index, constraints and slab thickness on optimisation energy of Pt and Ni surface slabs

This chapter is a supplementary chapter which provides additional results which were obtained but not needed to complete this thesis. The Pt (111) and Ni (111) surface slabs were investigated where the slab thickness, constrained layers and the Miller indices were varied. In the first section of this supplementary the slab thickness was increased by one layer from the starting slab thickness of four to an ending slab thickness of fourteen. The optimisation energy and the interatomic distances between the metal atoms were calculated and investigated for the (111) and the (210) surfaces. In order to determine if the optimisation time could be shortened by using constrained layers, the layers were constrained and compared with the unconstrained layers. The constrained layers consisted of fixing the fractional positions of the atoms during optimisation. These constrained layers were steadily increased until half of the layers in the surface slabs were constrained. On the other hand, the unconstrained surface slabs were where the entire slab was allowed to relax.

As a result, it was determined that the activity of a slab surface is influenced by the Miller indexes and therefore, the most common low-Miller index (111) was calculated and compared to a high-Miller index plane (210) with varying degrees of slab thickness. Overall, it was possible to gain insight into the influence that layers of a slab have on the stability of the slab, in terms of the interatomic spacing between the atoms in the slab.

S1.1. Introduction.....	152
S1.2. Computational method.....	152
S1.3. Results and discussion	153
S1.3.1. Comparison of optimisation energies for unconstrained surface slabs with different Miller indices	153
S1.3.2. Comparison of optimisation energies for constrained and unconstrained surface slabs.....	155
S1.3.3. Influence of increasing slab thickness on interatomic distances for unconstrained slabs.....	157
S1.4. Summary	159
S1.5. References.....	159

S1.1. Introduction

In order to create better and more affordable catalysts an understanding of the physical properties of the metal surface of an electrode is needed.¹ Through understanding the surface properties of metals prediction of the reactivity of the surface including the effect of alloying, the effect of structure and the effect of co-adsorbed species or doping is possible.

Techniques such as the density functional theory (DFT) or other quantum-chemical calculations enable researchers to obtain an insight into numerous atomic-scale processes. Through the usage of DFT, it is possible to study the physical properties of surfaces to describe the energetics of adsorption and dissociation reactions, study the role of electronics and geometric effects, surface relaxation and un-relaxation separately.² Moreover, DFT is used in surface science to investigate the catalytic properties of metals³⁻⁸ which are influenced by the chemical composition and the surface atomic arrangement. The atomic arrangement is dependent on the crystallographic axes (hkl), direction and planes of a crystal which is known as the Miller plane or Miller index.¹¹ The Miller indexes are categorised into either low index and high index Miller indices, where the high index Miller indices have open structures which show high stability and catalytic activity^{9, 10} that is not observed in the flat and close packed low index Miller plane surfaces.¹¹ However, the surface area of high index surfaces is small and costly, making them difficult to be used as a catalyst, even though they show promise for the PGM catalyst field.

S1.2. Computational method

The DFT calculations that were used was implemented in CASTEP¹² which is part of the Material studio 2016¹³ program, to calculate the structures and energies of the pure Pt and Ni metals. The generalised gradient approximation (GGA) function developed and revised by Perdrew, Burke, and Ernzerhof (RPBE)¹⁴ with no dipole corrections and no spin polarisation was implemented. The geometry was optimised using the two-point steepest descent (TPSD)¹⁵ algorithm, which is recommended when working with lattice parameters of solid-solid interfaces. The interaction between the core and valence electrons, defined as those in level 5d6s for Pt and 3d4s for Ni, was described with the Ultrasoft pseudopotentials (USP)¹⁶ method which allows calculations to be performed with the lowest possible cut-off energy for the plane-wave basis set, based on the Koelling-Hamon¹⁷ relativistic treatment. The plane-wave energy cut-off for the wave function basis was set to 350 eV for both metals. The broadening of the electronic width was set to a smearing value of 0.1 eV. The SCF convergence tolerance per atom, the convergence threshold for the maximum energy change and convergence threshold for the maximum force was left as the default values of 2.0×10^{-6} eV, 2.0×10^{-5} eV/atom and 0.05 eV/Å. *k*-point sampling was performed to obtain the optimum Monkhorst-Pack grid¹⁸ for the integrations in the reciprocal space of the unit cells, ensuring similar spacing of points in the reciprocal space, which can be maintained throughout the study. Calculations were carried out using Monkhorst-pack grids of $1 \times 1 \times 1$ *k*-points for the bulk structures and $4 \times 4 \times 1$ ¹⁹ for the Pt and Ni surface slabs.

The Pt and Ni metals adopts a face centred cubic (*fcc*) crystal structure, along the [111] direction which belongs to the $Fm\bar{3}m$ space group (No. 225).^{20, 21} The primitive cubic unit cell of these two metals contains four atoms

distributed in the Wyckoff *4a* positions. The internal coordinates, lattice parameters, atomic spin momentum and cell shape were all allowed to change during geometry optimisations. Using this methodology, a lattice parameter (a) for the bulk unit cell of the pure Pt and Ni were calculated. The calculated lattice parameter was 4.014 Å for Pt and 3.579 Å for Ni, which is in excellent agreement with the experimental values of 3.923 Å²⁰ and 3.528 Å,²¹ respectively.

Surface scientist have shown that high Miller index Pt (210) surfaces possesses high catalytic activity for the electro-reduction of CO₂.²² These high Miller indexed surfaces, such as the Pt (210) surface, usually exhibit enhanced stability and activity due to their open structures and high density of atomic steps.^{23, 24} It is important to note that the (210) surface index was only used for comparison since high Miller index for Pt metal is not easily obtained through chemical synthesis.²

The surface slabs for the (111) and (210) Miller indices were cleaved from the optimised bulk structure as shown in **Figure S1.1**.

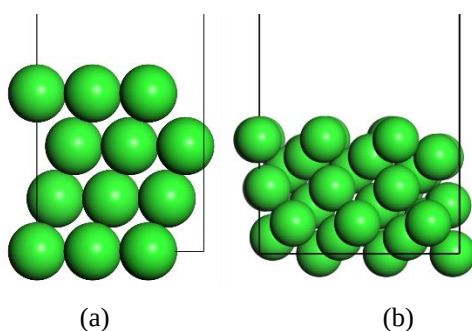


Figure S1.1. Comparison of **a)** low Miller-index (111) and **b)** high Miller-index (210) surfaces

From **Figure S1.1** it could be observed that the surface obtained with the (111) Miller index is flat, while the surface with the (210) Miller index is a stepped surface. High Miller indexed surfaces have been shown to have high reactivity, which is due to the stepped surface.¹¹ Each of the Pt (111), Ni (111), Pt (210) and Ni (210) surface slabs was distributed over 4-, 5-, 6-, 7-, 8-, 10-, 12 and 14 layers, with a vacuum gap of 20Å.¹⁹

S1.3. Results and discussion

The results were divided into three parts, namely, the comparison of high (210) and low (111) Miller indices, the comparison between the optimisation energy and optimisation time and the influence of the number of layers in surface slabs on the stability of the slabs.

S1.3.1. Comparison of optimisation energies for unconstrained surface slabs with different Miller indices

In **Figure S1.2** and **Figure S1.3**, the optimisation energy of the unconstrained (210) surface slabs is compared to the optimisation energy of the unconstrained (111) surface slabs.

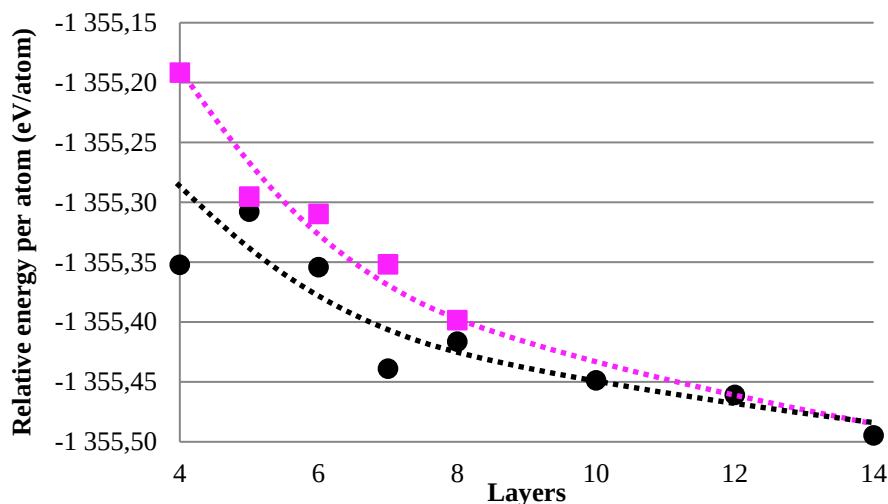


Figure S1.2. The comparison between the unconstrained Ni (111) (●) and Ni (210) (■) surface slabs.

The comparison between the optimisation energy and the layer thickness for the Ni (111) and Ni (210) surface slabs indicated that the Ni (111) is more favourable, **Figure S1.2**. The trend observed for both of these Miller indexed surface slabs indicated that the optimisation energy decreases with increase in layer thickness. A noteworthy observation while optimising the Ni (210) surface slabs was that the optimisation was more difficult than for the Ni (111) surface slabs.

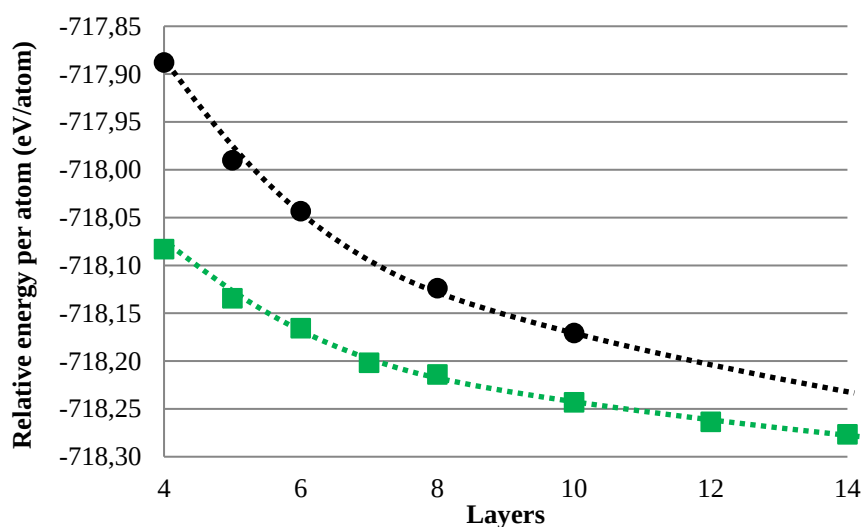


Figure S1.3. The comparison between the unconstrained Pt (111) (●) and Pt (210) (■) surface slabs.

The comparison of the optimisation energy and the layer thickness between the Pt (210) and Pt (111) surface slabs (**Figure S1.3**) indicates that the optimisation energy of the Pt (111) surface slabs is more favourable.. There is a meagre difference, 0.19 eV, in the optimisation energy between the high Miller index and the low Miller index surfaces. According to these calculations, although the high index (210) surface slabs may be more active, the (111) surface slabs yields the lowest optimisation energy.

S1.3.2. Comparison of optimisation energies for constrained and unconstrained surface slabs

In the constrained slabs, the bottom two layers are fixed at their fractional positions while the rest of the layers in the slab is left unconstrained as shown in **Figure S1.4**.

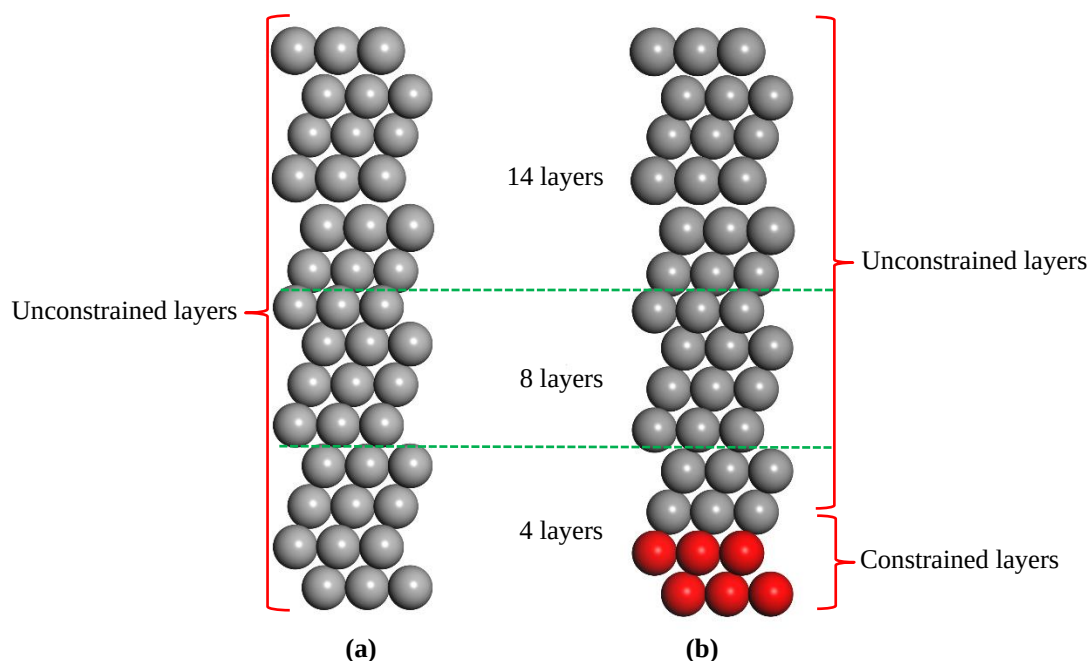


Figure S1.4. A comparison between the **a)** unconstrained slab (14N) and the **b)** constrained slab (14C).

In **Figure S1.5** and **Figure S1.6**, the energy of the constrained (C) slabs is compared to the optimisation energy of unconstrained (N) slabs for the (111) surface slabs.

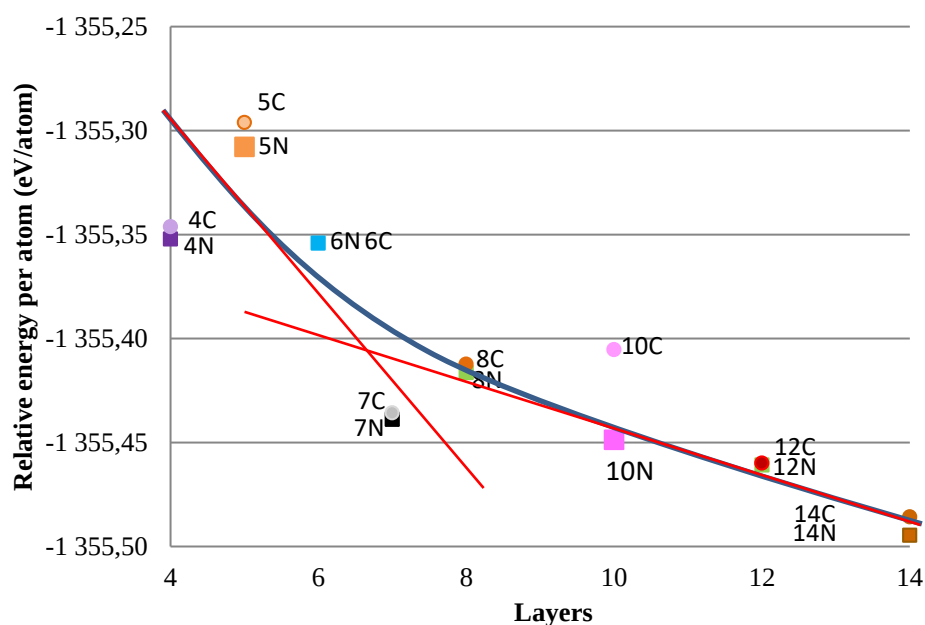


Figure S1.5. The energy of constrained (C) and unconstrained (N) Ni (111) surface slabs plotted against layer thickness.

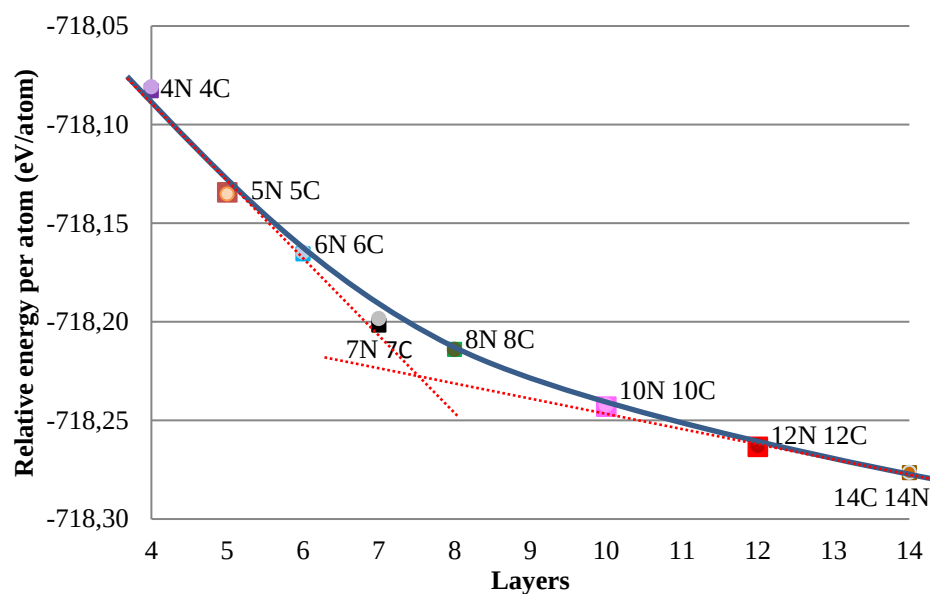


Figure S1.6. The energy of constrained (C) and unconstrained (N) Pt (111) surface slabs plotted against the optimisation energy.

In **Figure S1.5**, the optimisation energy for the constrained and unconstrained Ni (111) surface slabs were plotted against the number of layers in the slab. An increase in the number of layers results in a decrease in the relative optimisation energy per atom for the Ni (111) surfaces. There are a few exceptions observed, such as that of the five layered Ni (111) surface slab is higher in energy than the four layered Ni (111) surface slab, the seven layered Ni (111) surface slab is lower in energy than the eight layered Ni (111) surface slab and the ten layered constrained Ni (111) surface slab is higher in energy than the unconstrained ten layered Ni (111) surface slab. The suggestion here is that the trend may be caused by the magnetic properties of the Ni metal, since Ni is ferromagnetic with a Curie temperature of $T_C = 624$ K.²⁵ Overall, the difference in optimisation energy between the constrained and unconstrained surface slabs is small.

In **Figure S1.6**, the optimisation energy for the constrained and unconstrained Pt (111) surface slabs were plotted against the number of layers for the surface slab which resulted in an exponential trend. The optimisation energy decreased with an increase in the thickness of the surface slab. Furthermore, there is no noteworthy difference between the optimisation energy of the constrained and unconstrained Pt (111) surface slabs. In both the Ni (111) and Pt (111) slabs, the computation time for both the constrained and the unconstrained slabs was less than an hour. This led to the conclusion that the constraining layers does not have an adverse effect on the computing time. It should however be mentioned that only two out of fourteen layers was constrained and an increase in the number of layers constrained should be investigated to draw a final conclusion about the influence of constrained layers on optimisation energy and calculation time.

To conclude, the stability of the slabs and how the slab thickness affects the stability cannot be described by looking at the optimisation energy. Therefore, the next part determines the stability of the slabs by comparing the interatomic spacing between the layers with increasing slab thickness. Only the interatomic spacing for the unconstrained slabs will be discussed in this part.

S1.3.3. Influence of increasing slab thickness on interatomic distances for unconstrained slabs

The interatomic spacing between the Ni and Pt primitive unit cells were calculated using Materials Studio and compared with the interatomic spacing values obtained from the MedeA software package.²⁶ The interatomic spacing between the atoms in the Ni primitive unit cell, was calculated as 2.509 Å, shown in **Figure S1.7**, which corresponds to the literature value of 2.492 Å.²⁷

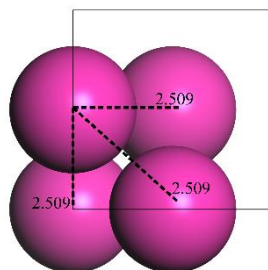


Figure S1.7. Ni bulk structure with a Ni–Ni bond length value of 2.509 Å.

The bond distance (Ni–Ni) between the layers for each of the Ni (111) surface slabs, with incrementing slab thickness, is shown in **Figure S1.8**. In the above-mentioned **Figure S1.5**, the lowest optimisation energy was observed for the fourteen layered Ni (111) surface slab.



Figure S1.8. Interatomic spacing between the layers of unconstrained Ni (111) surface slabs with varying slab thickness.

In the fourteen layered Ni (111) surface slab, the middle layers of the slab were similar to the interatomic spacing of the bulk structure which indicates a stable slab. Hence, the top and bottom layers of the fourteen layered Ni (111) surface slab is not stable while the middle layers (two to twelve) were stable. Using this approach, all of

the Ni (111) surface slabs are stable since the interatomic spacing between the layers were close in value to that of the bulk structure.

The interatomic spacing between the atoms in the Pt primitive unit cell was calculated as 2.839 Å and is shown in **Figure S1.9** which corresponds with the literature value of 2.827 Å.²⁸

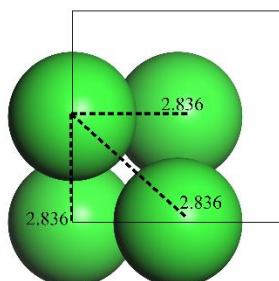


Figure S1.9. Pt bulk structure with a Pt–Pt bond length value of 2.836 Å.

The interatomic spacing between the Pt (111) surface slabs with incremented slab thickness is shown in **Figure S1.10**.

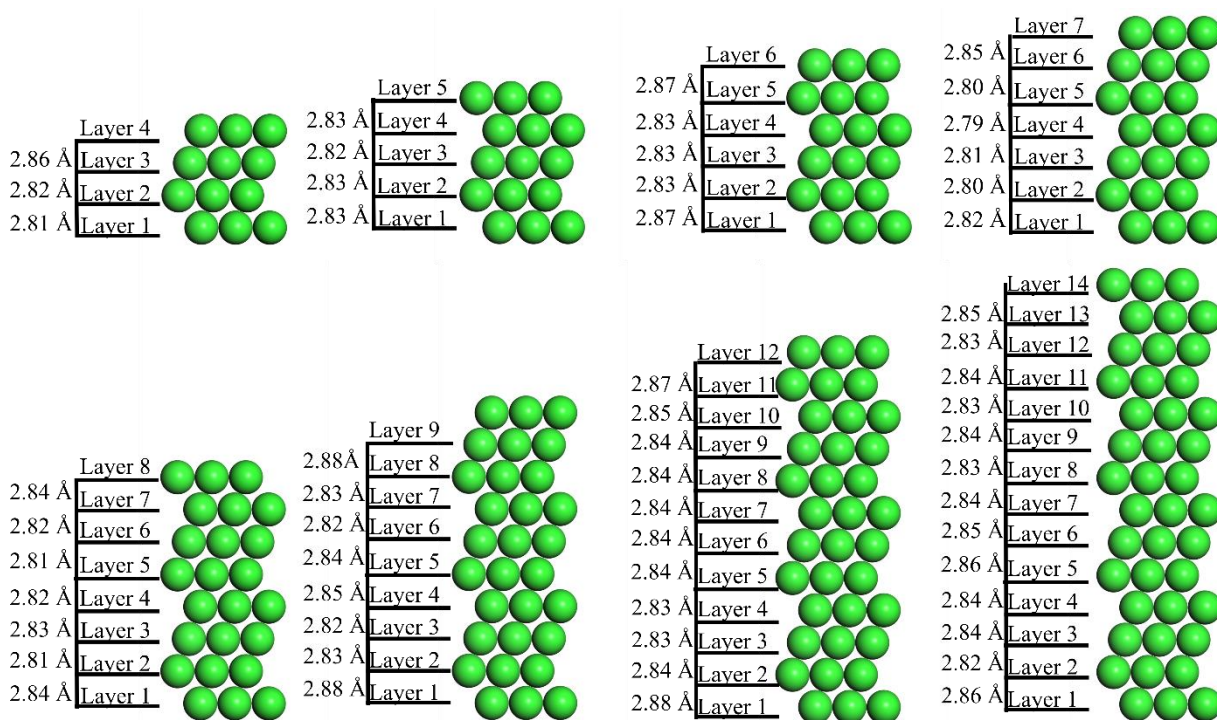


Figure S1.1. The interatomic spacing between the layers of various unconstrained Pt (111) surface slabs with varying slab thickness.

The interatomic spacing for the slabs was comparable with that of the bulk metal with a percentage of 97 % to 99 %. The top and bottom layers of the slabs were less stable since the interatomic spacing between the layers were larger than the bulk material, while the middle layers was stable and close in value to the bulk material (2.826 Å) for all of the slabs. Hence, with increasing thickness, the interatomic spacing were close to that of the bulk systems especially in the middle layers of the thick slabs. Therefore, the thicker Pt (111) metal slabs resulted in more stable surfaces than the thinner surfaces.

S1.4. Summary

Results obtained for the optimisation energies indicate that the optimisation energy decreased with the increase in the slab thickness. The increase in the slab thickness also resulted in an increase in the optimisation time. In addition, the difference in the optimisation energy and optimisation time between the constrained and the unconstrained slabs were minimal. On the other hand, a difference was observed between the interatomic spacing of the various slab thicknesses which indicates that the midsections of these slabs are relatively close to that of the bulk systems. Overall, the most stable slab thickness was that of the fourteen layered slab which also resulted in an optimal optimisation time and energy. Furthermore, it is not necessary to use the constrained slab for further calculations since both the constrained and the unconstrained slabs are similar in optimisation energy. However, it would be best to use the constrained slab and constrain the bottom 7 layers.

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S2

Supplementary 2: Surface properties of bimetallic fourteen layered (111) surface slabs

This chapter consisted of creating various concentrations of the Pt/Ni (111) bimetallic surfaces. In these surfaces seven random layers in the parent metal were replaced with a secondary metal while constraining the bottom seven layers of the parent metal was constrained. In this chapter the optimisation energy, optimisation time and the interatomic spacing between the atomic layers was investigated.

The results obtained showed that the Pt/Ni concentration of the bimetallic surfaces influenced the optimisation energy, optimisation time and the interatomic distance. However, the computation method used in Chapter 5 was superior to the computation method used in this supplementary and as a result the results obtained in this supplementary was deemed obsolete.

S2.1. Introduction.....	163
S2.2. Computational method.....	163
S2.2.1. Creating fourteen layered alloys with various metal arrangements	164
S2.3. Results.....	165
S2.3.1. Comparison of optimisation energies for the various bimetallic slab configurations.....	165
S2.3.2. Comparison of the interatomic spacing between the most stable bimetallic slabs	167
S2.4. Summary	168
S2.5. References.....	168

S2.1. Introduction

The three types of surface alloys that exist are showed in **Figure S2.1**. Each of these types of surface alloys contains effects which is caused by the physical and chemical properties of the metals.¹

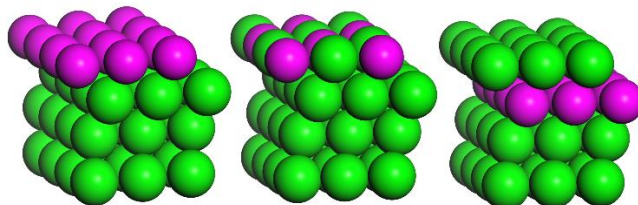


Figure S2.1. Alloyed surface arrangements are divided into **a)** overlayer (strain and ligand effects), **b)** surface alloy (strain, ligand effects and bifunctionalities) and **c)** Near surface alloy (ligand effects).

The first observable effect is the strain effect. This strain effect is observed in the overlayer and the surface alloy arrangements. The strain effect occurs when the metals are different with regard to the lattice constraints of the surface slab. The strain that occurs in these surface arrangements modifies the chemisorption properties of the alloys which make them different from the chemisorption properties of the pure metals.²⁻⁵ The reactivity of the pure metal surface can be manipulated through the addition of a secondary metal which induce the strain effect and changes the ability of the surface to form bonds with an adsorbate.⁶ The second effect is the ligand effect which is observed for all three these arrangements (**Figure S2.1**) and occurs due to the difference in the electronic structure of the components. Lastly, bifunctionalities are only observed in surface alloys and occurs when one metal appropriately binds to one key intermediate while the second metal does the same with the other, optimising the catalytic activity.¹

In this investigation, the atomic arrangements of the pure metals will be changed by substituting a primary metal layer with a secondary metal layer and measuring the effects that this has on the metal properties. The secondary metal is substituted as a layer and therefore the surface alloy arrangement will not be studied. The overlayer and the near surface alloy arrangements will be used in this investigation for surface arrangements consisting of Pt and Ni which have been studied extensively on smaller slabs.⁷⁻¹²

S2.2. Computational method

Density functional theory (DFT) calculations, as implemented in CASTEP¹³ which is part of the Material studio 2016¹⁴ program, was used to calculate the structures and energies of the pure Pt and Ni metals. The generalised-gradient approximation (GGA) function developed and revised by Perdrew, Burke, and Ernzerhof (RPBE)¹⁵ with no dipole corrections and no spin polarisation was used. The geometry was optimised using the two-point steepest descent (TPSD)¹⁶ algorithm which is recommended when working with lattice parameters of solid-solid interfaces. The interaction between the core and valence electrons, defined as those in level 5d6s for Pt and 3d4s for Ni, was described with the Ultrasoft pseudopotentials (USP)¹⁷ method which allows calculations to be performed with the lowest possible cut-off energy for the plane-wave basis set, based on the Koelling-Hamon¹⁸ relativistic treatment. The plane-wave energy cut-off for the wave function basis was set to 350 eV for both of

these metals. The broadening of the electronic width was set to a smearing value of 0.1 eV. The SCF convergence tolerance per atom, the convergence threshold for the maximum energy change and convergence threshold for the maximum force was left as the default values of 2.0×10^{-6} eV, 2.0×10^{-5} eV/atom and 0.05 eV/Å. *k*-point sampling was performed to obtain the optimum Monkhorst-Pack grid¹⁹ for the integrations in the reciprocal space of the unit cells, ensuring similar spacing of points in the reciprocal space, which can be maintained throughout the study. Calculations were carried out using Monkhorst-pack grids of $1 \times 1 \times 1$ *k*-points for the bulk structure and $4 \times 4 \times 1$ ²⁰ for the Pt and Ni surface slabs.

The Pt and Ni metals adopts a face centred cubic (*fcc*) crystal structure, along the [111] direction which belongs to the $Fm\bar{3}m$ space group (No. 225).^{21, 22} The primitive unit cell of these two metals contains four atoms distributed in the Wyckoff 4*a* positions. The internal coordinates, lattice parameters, atomic spin moments and cell shape were all allowed to change during geometry optimisations. Using this methodology, we have calculated a lattice parameter (*a*) for the bulk unit cell of the pure Pt and Ni end member phases of 4.014 Å and 3.579 Å, in excellent agreement with the experimental values of 3.923 Å²¹ and 3.528 Å,²² respectively. Each of the Pt and Ni (111) parent metal surfaces was distributed over 14 layers, with a vacuum gap of 20 Å.²⁰

S2.2.1. Creating fourteen layered alloys with various metal arrangements

In this study, the fractional positions of the bottom seven layers of the parent metal were constrained (C) while the top seven layers of the parent metal was left unconstrained (N) as shown in **Figure S2.2**. The unconstrained layers of the parent metal were substituted with a secondary metal to obtain various fourteen layered slabs with different arrangements, shown in **Figure S2.3** and **Figure S2.4**.

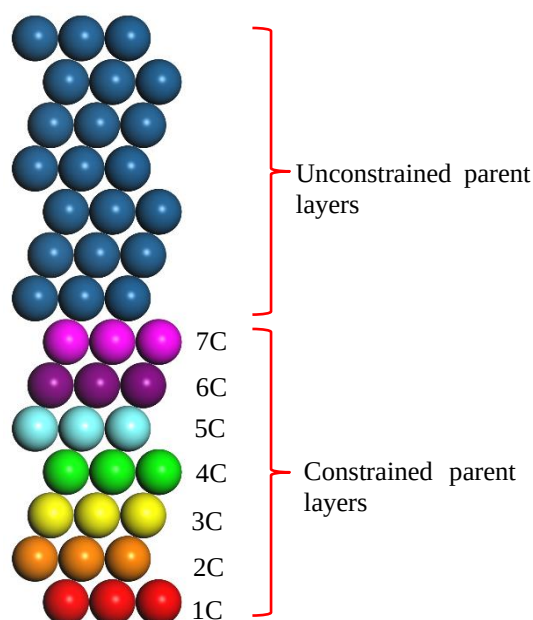


Figure S2.2. Fourteen layered surface slab where C is the number of layers constrained in the (111) surface slab.

The constrained layers of the parent metal were not substituted and remains as the same as the parent metal. The parent metal is either a Ni or a Pt slab where the substitute's secondary metal is either Pt or Ni, depending on the parent metal.

M(111)A	M(111)B	M(111)C	M(111)D	M(111)E
A	B	A	A	A
B	A	A	A	B
A	A	B	B	B
B	B	B	B	B
A	B	A	B	B
B	A	A	A	B
A	A	A	A	A

Figure S2.3. The grid used to categorise the (111) bimetallic surface slabs where A and B represents either Pt or Ni metal.

In **Figure S2.3**, there are five different alloy arrangements of a slab consisting of 168 atoms where the ratio of the two metals A and B are as follows; Slab A, B and D consist of $A_{132}B_{36}$ atoms, Slab C consists of $A_{144}B_{24}$ and Slab E consists of $A_{108}B_{60}$ atoms. Hence, the ratios of the primary and secondary metals are the same for the A, B and D slabs which have different arrangements of these metals which enables the study of the effects induced by the secondary metal, steric or ligand effects, and the stability of the alloyed metal.

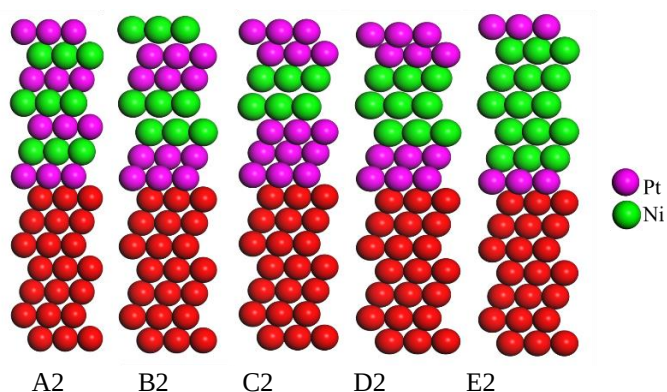


Figure S2.4. The various combinations (A2-E2) used in the bimetallic Ni/Pt, where the bottom 7 layers (red) are constrained. Constrained layers consist of the parent metal.

The various alloy arrangements discussed in **Figure S2.3** are shown in **Figure S2.4**, where Ni is the parent metal while Pt is the secondary metal which was substituted into the slab. The arrangements where Pt is the parent metal is denoted as either Pt/Ni or A-E, while if Ni was the parent metal the arrangements are denoted as Ni/Pt or A2 – E2.

S2.3. Results

To obtain the best combination of the Pt/Ni and Ni/Pt alloys, the optimisation energies of the alloys, the surface energies and the adsorption energies were examined.

S2.3.1. Comparison of optimisation energies for the various bimetallic slab configurations

The relative optimisation energy and the optimisation time for the various arrangements of the alloys is shown in **Figure S2.5**.

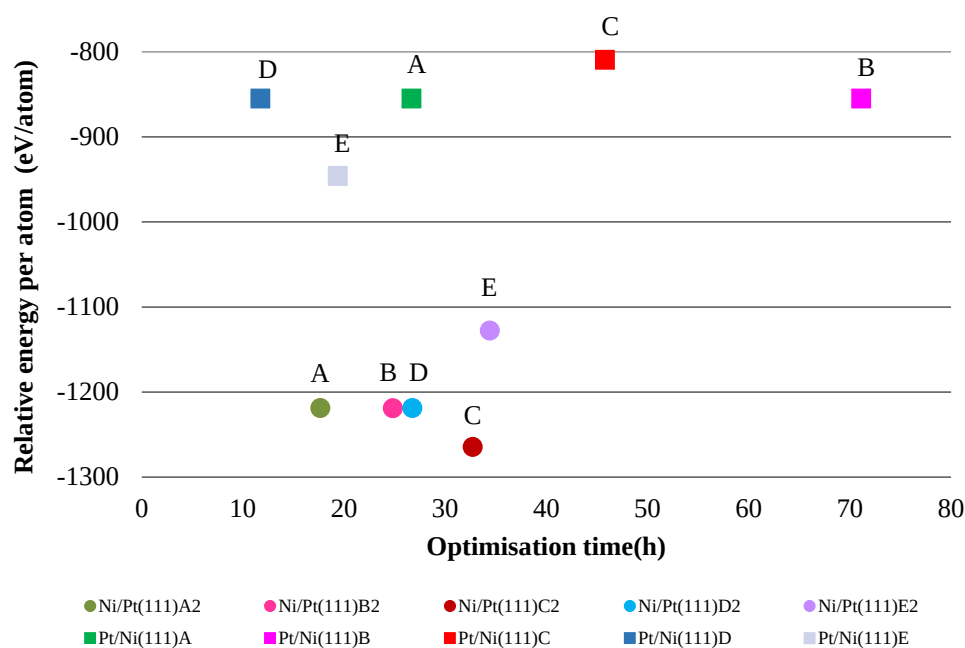


Figure S2.5. Ni/Pt (111) and Pt/Ni (111) alloyed slabs plotted against the optimisation energy and optimisation time.

For the Ni/Pt (111) alloy, where Ni is the parent metal, the most stable arrangement is the C2 arrangement which took 33 hours to optimise. In the C arrangement, the top two layers consists of Ni metal followed by two layers of Pt and then the last three unconstrained layers consists of Ni metal. On the other hand, in the Pt/Ni (111) alloy arrangements, the most stable arrangement is that of the E arrangement. In the E arrangement of the Pt/Ni alloy, the top and bottom layer consists of the parent metal (Pt) while the middle five layers are the substituted Ni metal. In conclusion, the alloys where the parent metal consists of Ni is the most stable in comparison where the parent metal is Pt. Although, the metal arrangements are opposites from one another, the results in the stability are largely different which is possible due to the type of parent.

In the next section, the interatomic spacing between the metals was studied for the different metal arrangements to obtain any insight into the high stability for some of these metals. The parent metal and the substituted metal ratios are the same for the A, B and D slab arrangements but with differences in the atomic arrangements. The difference in the optimisation energy between these arrangements are minimum, with $-1218,752$ eV for slab A, $-1218,806$ eV for slab B and $-1218,733$ eV for slab D. In addition, the metal thickness of the Pt layers is different for each of these slab arrangements but the top and the bottom layers of these slabs consists of Ni. The A configuration metal is eight layers of Ni and nine layers of Ni for the B and D configurations. Also, the A configuration follows an alternating sequence of 1 layer for the metallic layers while in the B configuration this alternating thickness is two layers per metal with the top layer being a single layer of Pt. In the D configuration, the middle layer is three layers of Pt with two layers of Ni on the top and bottom. Therefore, the configurations that have the most stable optimisation energy for the Ni/Pt bimetal are configuration B, A then D.

Overall, even though the thickness of the layers varies, the difference between the optimisation energies are minimum between slabs with the same ratio of metallic atoms. This is also observed for the other bimetals used in this study.

The next section compares the interatomic spacing of each alloy arrangements against one another. This is a means to test whether the Ni/Pt alloys are more stable in terms of physical properties.

S2.3.2. Comparison of the interatomic spacing between the most stable bimetallic slabs

In **Figure S2.6**, the alloy arrangements of the A slab is shown, which has a ratio of $A_{132}B_{36}$ where A is the parent metal and B, the substituted metal.

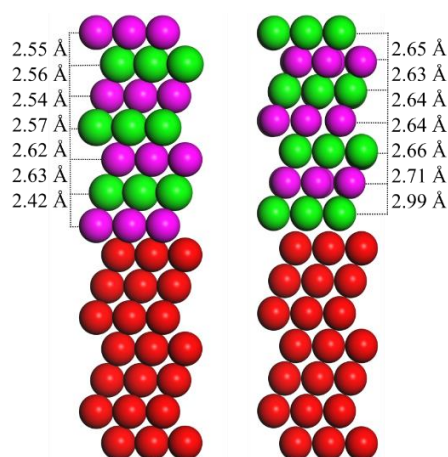


Figure S2.6. Interatomic spacing comparison between the **a)** A2 and **b)** A slabs

It was already shown in the previous figure that the alloys where the parent metal is Ni (A2) is more stable. The interatomic spacing of the A2 surface slab is close to the calculated (literature) interatomic spacing values for the pure Ni bulk structure, which is 2.509 (2.492 Å)²³. Whereas the interatomic spacing observed in a Pt bulk structure is 2.836 (2.827 Å).²⁴ Therefore, the interatomic spacing of the A2 alloy is closer to that of the interatomic spacing observed in the Ni bulk structure and the reason why the Ni parent (A2) surface slab is more stable than that of the Pt parent (A) surface slab. Overall, the interatomic spacing between the layers of the A slab is stable with small margin of difference between the unconstrained layers in the slab (0,024 Å for Ni/Pt and 0,018 Å for Pt/Ni). Even though both Pt and Ni are transition metals with the same structure, the difference in the optimisation energy between the Ni/Pt and Pt/Ni alloys is – 363.918 eV, which is due to the influence of the amount of Ni metal to the magnetic nature of the alloy. To test this theory, the surface energy and magnetic moment is needed, which was discussed in **Chapter 5**.²⁵ Overall, the stability of the slab was dependant on the interatomic spacing where stable surfaces was determined where the interatomic spacing was close in value to the bulk structure. In **Figure S2.7**, the alloy arrangements of the A slab are shown which has a ratio of $A_{108}B_{60}$ where A is the parent metal and B, the substituted metal.

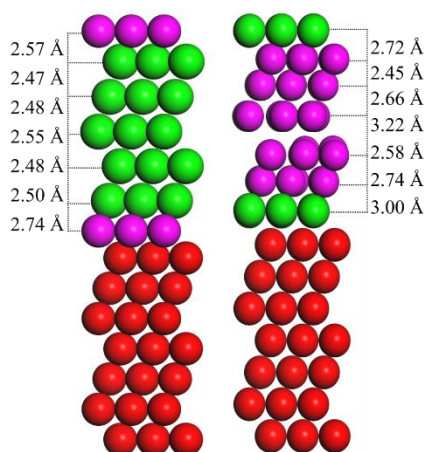


Figure S2.7. Interatomic spacing comparison between the a) E2 and b) E slab

S2.4. Summary

The stability of the bimetallic slabs was dependent on the interatomic distance between the layers. If the interatomic distances in the slabs are close to the bond distances obtained from the pure bulk metal structures, then the surface slab is stable. However, if the interatomic distance between the layers varied largely to that of the bulk structure metals, then the surface slab was less stable. Overall, the most stable surface slabs were found to be the Ni/Pt slabs with Ni/Pt (111)C (– 1264,343 eV) < Ni/Pt (111)B (– 1218,806 eV) < Ni/Pt (111)A (– 1218,752 eV). In addition, the metallic atom ratios play a role in the stability of the bimetallic slabs. The A and B slabs consisted of the metallic ratios of Ni₁₃₂Pt₃₆, while the C slab consists of the metallic ratio of Ni₁₄₄Pt₂₄. Therefore, the slab with a larger ratio of Ni to Pt was the best to use.

In conclusion, the results obtained in this supplementary chapter was deemed insignificant since the computational method used in **Chapter 5** was deemed superior.

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