**Introduction/Summary**

**Questions & Answers**

*Structure and computational details*

1. What is a supercell?

A supercell of a unit cell can be used to describe the same crystal structure but has much larger volume. In other words, a supercell is made up of repeating unit cell of the crystal which involves some primitive cells.

1. Why do we need a supercell in our system?

Because a supercell could make sure that there is no self-interaction of the displaced atom with itself and allow the use of periodic boundary conditions for computational models of crystal defects.

1. What periodic boundary conditions are and why do we use them?
2. Why we have a vacuum region in our system?

We need a vacuum region to avoid interactions between two layers.

1. Can you tell:
   1. what is the basis set used?

TZVP-MOLOPT-SR-GTH basis set is used for Ag.

TZVP-MOLOPT-SR-GTH basis set is used for Au.

TZV2P-MOLOPT-SR-GTH basis set is used for Mo.

TZV-GTH-LDA-q18 basis set is used for Pt.

TZVP-GTH basis set is used for H.

* 1. what kind of calculation did you perform?

Use Density Function Theory to simplify Born Oppenheimer approximation and solve the Kohn and Sham equations to do geometry optimisation calculations.

* 1. what is the target accuracy for force calculation?

1e-3

* 1. what is the target accuracy for the SCF convergence?

1e-7

* 1. can you extract from the input the lattice parameters for your supercell?

|  |  |  |  |
| --- | --- | --- | --- |
| A | 11.2005996704 | 0.0000000000 | 0.0000000000 |
| B | -5.6002998352 | 9.7000038522 | 0.0000000000 |
| C | 0.0000000000 | 0.000000000 | 26.8589000702 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Ag | A | 11.7687997818 | 0.0000000000 | 0.0000000000 |
|  | B | -5.8843998909 | 10.1920795831 | 0.0000000000 |
|  | C | 0.0000000000 | 0.0000000000 | 27.2068996429 |
| Au | A |  |  |  |
|  | B |  |  |  |
|  | C |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |

* 1. how many atoms do you have in your cell and describe the shape of your shell?

There are 65 atoms in my cell including 1 hydrogen atom.

Lattice point A is parallel to the x-axis, lattice point B is in the xy-plane and lattice point C is parallel to the z-axis. In addition to that |a| = |b|. Hence, the shape of the cell is orthorhombic, and it is hexagonal.

* 1. what is the hydrogen coverage in your system?

There is one hydrogen atom on the surface of the Ag.

There is one hydrogen atom on the surface of the Au.

There is one hydrogen atom on the surface of the Mo.

There is one hydrogen atom on the surface of the Pt.

1. analysing the output files for your calculations, can you tell
   1. How many self-consistent cycles takes to converge for every geometry optimization steps on average?

SCF run converged in 166 steps.

SCF run converged in 49 steps.

* 1. what is the number of electrons and the number of occupied orbitals in your system?

Number of electrons: 1153

Number of occupied orbitals: 599

* 1. did your calculation converge?

Yes, my calculation converged.

1. Why do we need to optimise the geometric structure of our system?

Because an optimised geometry structure allows us to find the minimum potential (ground state) energy which associate to the equilibrium position of the atoms in the structure.

1. Describe the optimisation process in general and what you observed in the output of your calculations.

The geometry optimisation starts with an initial configuration, then we use the density field theory (DFT) to evaluate the ground state electron density. This step involves guessing an electron density which could be a random number, then use the guessed electron density to solve the Kohn and Sham equations and calculate a new electron density. If the difference between the new electron density and the initial guessed electron density is not smaller than the target accuracy of the SCF convergency, then set a new guess electron density to the previous calculated electron density and iterate the calculation again until the difference is smaller than the target accuracy of the SCF convergency.

Once the ground state electron density is calculated, we need to calculate the force by differentiating the potential energy surface equation, then update the atomic positions. If the force is smaller than the target accuracy, then the geometry optimisation is done. Otherwise, return to the step that solving the DFT problem until the force is smaller than the target accuracy.

1. Compare the geometry of the initial and final structures of your Pt system (trajectory provided). Please include a picture which depicts the cell.

Use VMD and Murcury to show the geometry.

Chose one of the Pt positions from each optimisation calculation to show that there is tiny changes.

1. Do you think you would obtain the same energy if you started from another initial guess?

No, I don’t think I would obtain the same energy if I started from another initial guess.

1. Find the value for the equilibrium lattice parameter and bulk modulus for all the simulated metals. How these values compare with experiments?

*Error estimation and selection of simulation parameters*

1. Can you qualitatively describe what k points are and why we need to use them?
2. Can you qualitatively describe what a basis set is and why we need to use it?
3. How does the total energy of a Pt surface change as a function of kpoints? (trajectory provided).
4. How do the errors in the evaluation of hydrogen chemisorption energy vary versus the size of the kpoint grid and with the size of the basis sets used? (data provided for a 3 layer thick Pt metal slab)? Show this for both systems with 1ML and ¼ ML H coverage
5. How the error in the evaluation Hydrogen chemisorption energy versus k points and basis sets compares with the error in the evaluation of the total energy?
6. Assuming that the observation done in question above is general, which K points grid size and basis set is appropriate for calculations of chemisorption energy accurate to ?
7. How large should be a supercell to reproduce the chemisorption energy with the same accuracy in at G?
8. Do you expect in principle any effect in H chemisorption energy if H chemisorbed on a different metal facet or a different H coverage?

*The Hydrogen evolution reaction and electrocatalysis*

1. What is the computational hydrogen electrode?
2. Can you describe the Hydrogen evolution reaction at metal electrodes and its energetics?
3. Illustrate qualitatively the Sabatier principle and how it is at the foundation of the observation of a volcano plot.
4. How do we evaluate the H adsorption energy and the free energy of the adsorbed state?
5. Based on your volcano plot can you tell which metal is the best catalyst for Hydrogen evolution? Can you explain why?
6. Is there any complicating issue which might make your prediction less reliable?
7. Free energy diagram for hydrogen evolution at equilibrium (U = 0). for ‘‘standard’’ conditions corresponding to 1 bar of H2 and pH = 0 at 300 K?

**Conclusions**

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*Tips to write a report:*

*The golden rule: Aim for clarity*

* *Structured statements that flow in a logical manner.*
* *Good use of diagrams and appropriate level of theory.*
* *Careful choice of content.*
* *Keep your language clear and simple.*
* *Label all tables and figures. Labels should be self-contained, which means that tables and figures should be interpretable by themself.*
* *Appropriate referencing of figures and tables.*
* *Cite previous works (with an accepted citation style) whenever is appropriate.*

*Introduction/Summary:*

*The purpose of the Introduction/Summary is to put the reader in the context of the experiment and to explain how the experiment was carried in the lab. It may contain a brief review of previous research, why the research was undertaken, an explanation of the techniques and why they are used and why it is important in a broader context.*

*Questions & Answers:*

* *There are a number of questions in the lab script that need to be answered in this section of the report.*
* *Depending on the nature of the question, it might be appropriate to use figures or tables to give a proper answer.*
* *It is highly encouraged to rationalise the answers.*

*Conclusions:*

*\*The Conclusions gives a general description of the results and findings and it should be related back to the Introduction. If appropriate, suggest improvements or additional experiment*

VMD: drag the file to the VMD main

Graphics -> representations -> Drawing Method : CPK