

Project Results

Nikolas Vitaliti s223455,

Andreas Nielsen s174665,

Mathias Grønborg s194080

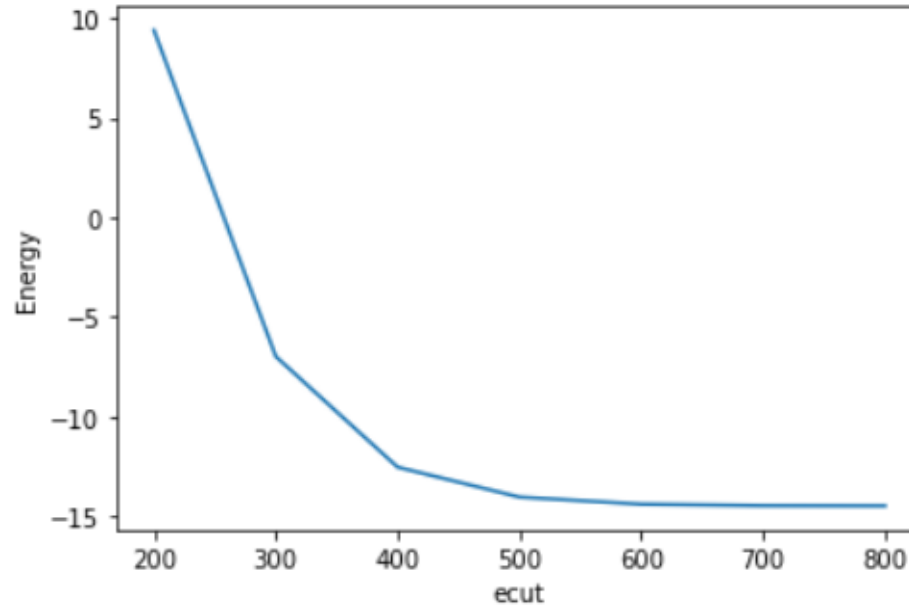
Exercise 1

- 1) Energy cut-off convergence calculations for H_2O
- 2) Energy calculations for LCAO and PW
- 3) Results expectations
- 4) Water splitting reaction energy evaluation
- 5) Discussion Exercise 1

All results are given in eV

(1) Reaction energy of water splitting

- What we have found out along the way:
 - E-cut should only be calculated for water and not also on the single molecules.
 - ***The value to which the E-cut converged was 600***
 - dzp is not needed in PW calculations, however it gives a greater approximation of the wave function



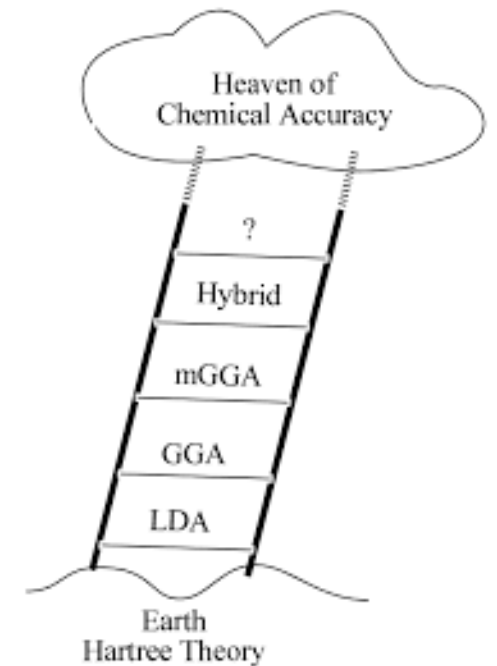
(2) Results expectations

LCAO

- **LDA:** $E_{xc} = E_{xc} [n(r)]$
 - Underestimate x
 - Overestimate c
- **GGA:** $E_{xc} = E_{xc} [n(r), \nabla n(r)]$
 - *PBE*: pbex, pbec
 - *RPBE*: rpbex, pbec
 - *PBESol*: pbesolx, pbesolc
- Polarization functions very important for small basis sets to account for asymmetric densities.

PW

- PW are usually used for periodic solid systems.
- The mode works fine for ab initio molecular dynamics too
- No Gaussian functions
- Dzp gives a good starting point.



(3) Energy results

- 2 Water molecules have been taken into account for the calculations as it's a more realistic scenario
- Functionals are ordered in increasing accuracy top-to-bottom following Jacob's ladder

Considering sz basis set	LCAO	PW
LDA	-3.260	-5.758
PBE	-2.828	-5.032
PBE-Sol	-2.940	-5.280
RPBE	-2.601	-4.723

Considering dzp basis set	LCAO	PW *
LDA	-5.094	-5.708
PBE	-4.387	-5.011
PBE-Sol	-4.644	-5.264
RPBE	-4.088	-4.724

**Note: dzp for PW has been taken into account just to see what would have happened with a better initial guess of the wave function, although we understand it is not needed if ecut convergence is performed.*

(4) Result Analysis - Accuracy

- Reference value from literature and thermodynamically calculated of $\Delta G = -4.92 \text{ eV}$

			<u>Difference from literature</u>	
LCAO	sz	dzp	$ \Delta sz $	$ \Delta dzp $
LDA	-3.260	-5.094	1.660	0.174
PBE	-2.828	-4.387	2.092	0.533
PBE-Sol	-2.940	-4.644	1.980	0.276
RPBE	-2.601	-4.088	2.319	0.832

PW	sz	dzp	$ \Delta sz $	$ \Delta dzp $
LDA	-5.758	-5.708	0.838	0.788
PBE	-5.032	-5.011	0.112	0.091
PBE-Sol	-5.280	-5.264	0.360	0.344
RPBE	-4.723	-4.724	0.197	0.196

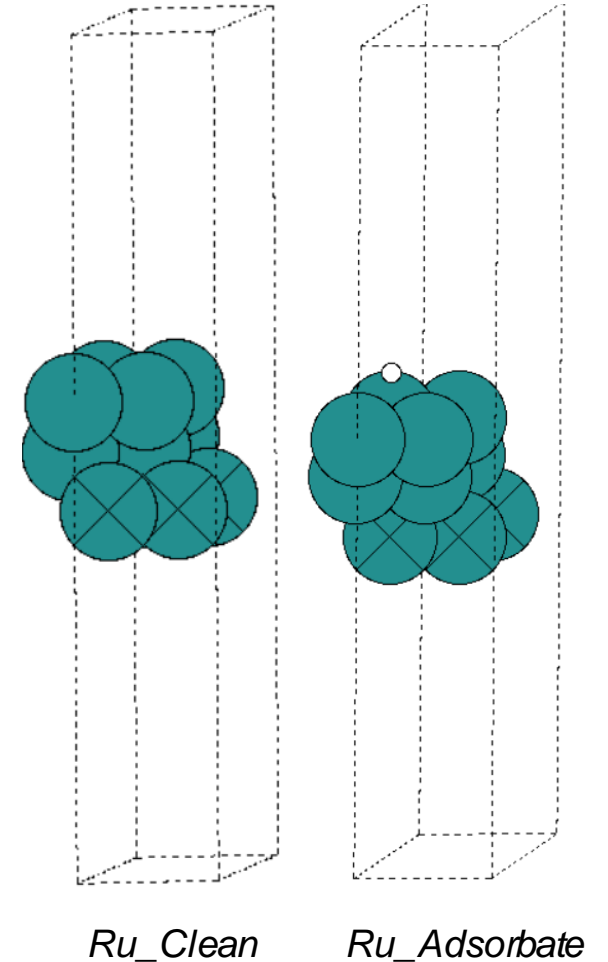
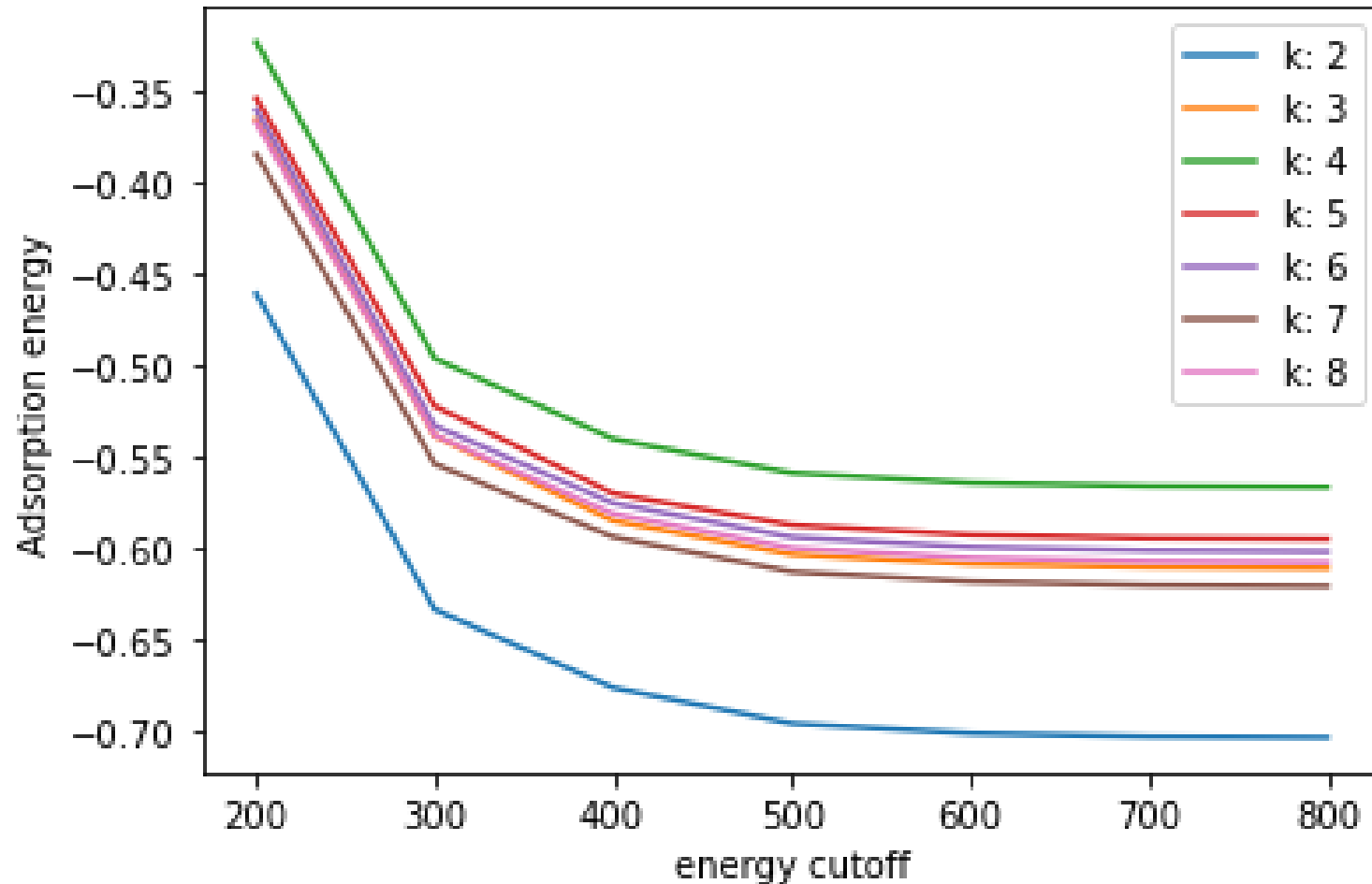
Exercise 2

- 1) Catalytic properties of FCC(111) Ru (Task 1)
- 2) Supercell accuracy (Task 2)
- 3) Most accurate estimation (Task 3)
- 4) H adsorption on all possible sites (Task 4)
- 5) Ru with Cu top layer replacement (Task 5)
- 6) Discussion - Why Adsorption?

All results are given in eV

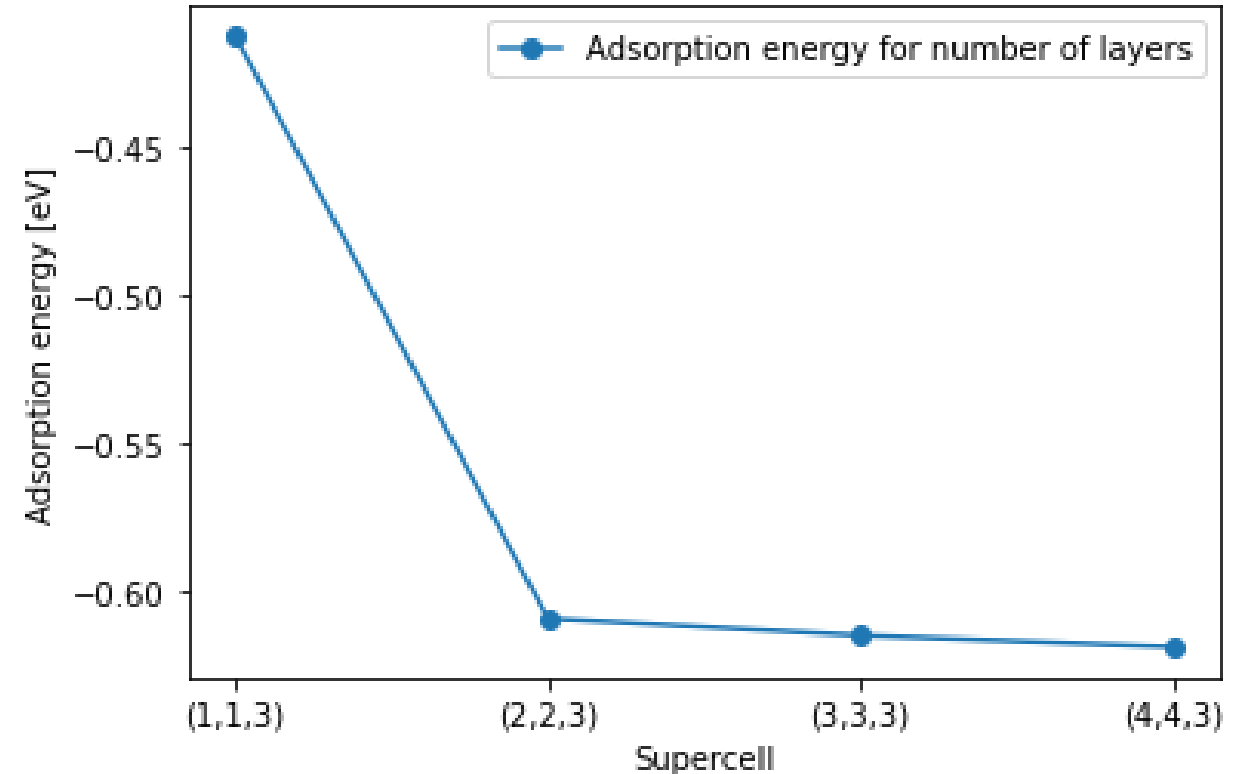
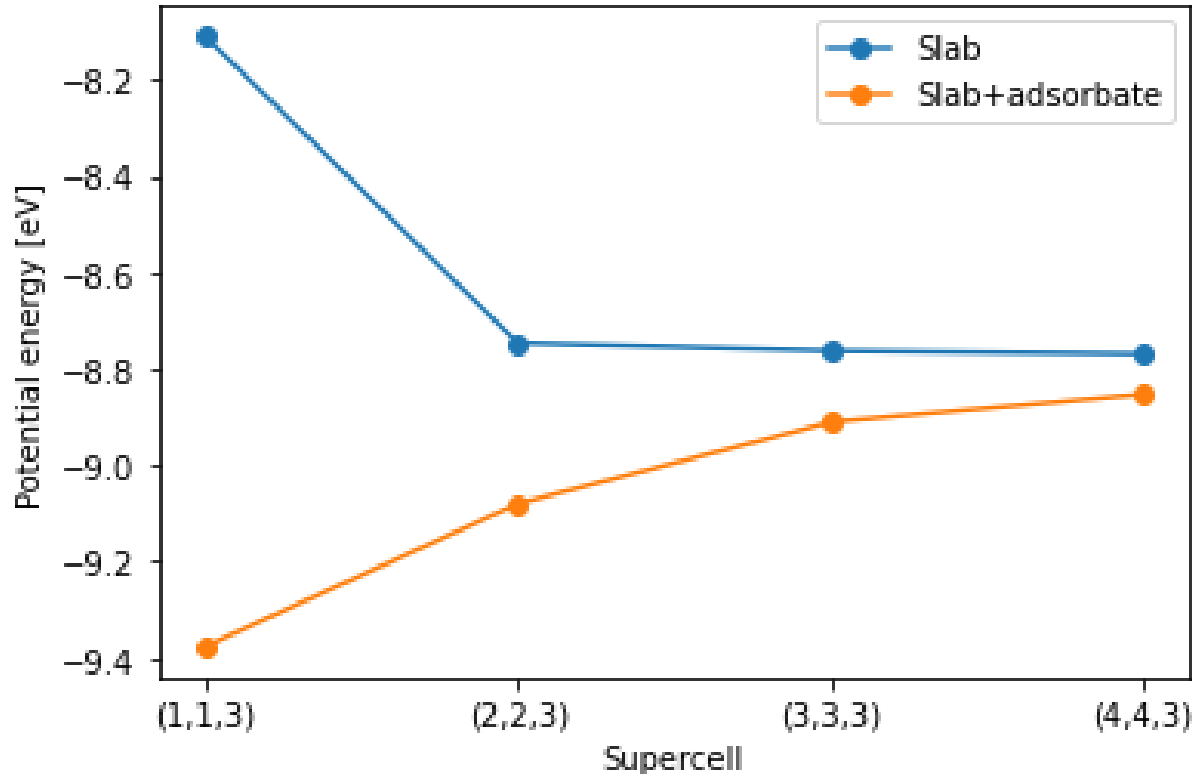
Catalytic properties of FCC(111) Ru (Task 1)

- Presence of **oscillations**, so a value of K in the middle has been chosen
- **Convergence** for: $\mathbf{k} = (8, 8, 1)$, $\mathbf{ecut} = 600$



Supercell accuracy (Task 2)

- The supercell has been further investigated in an **(n, n, 3)** fashion by cycling through **(x,y)** different sizes
- The **z direction has been kept fixed** since after 3 the change is negligible
- A size equal to (4,4,3) has been found to be the best choice, however since we know scaling typically involves a steep increase in computational time, we decided instead to use a size of (2, 2, 3).



Most accurate estimation (Task 3)

- From theoretical studies the adsorption energy has been found to be **-0.573** using PBE.
This suggests us that we can be confident with the calculations performed.
- The adsorption energy has been calculated with respect to the H_2 molecule

	E_{slab}	E_{H-slab}	E_{ads}
LDA	-121.173	-125.527	-1.002
PBE	-104.876	-108.874	-0.613
PBE-Sol	-114.678	-118.851	-0.805
RPBE	-97.664	-101.497	-0.463

Where $\longrightarrow E_{ads} = E_{H-slab} - E_{slab} - E_H$

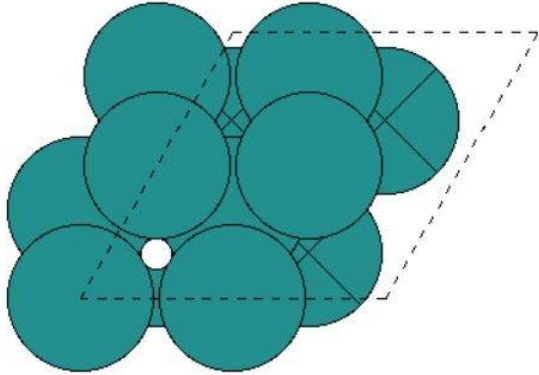
Note: Negative adsorption energy indicates hydrogen is likely to be adsorbed on the surface.

*PBE result has been found for Ru(001)

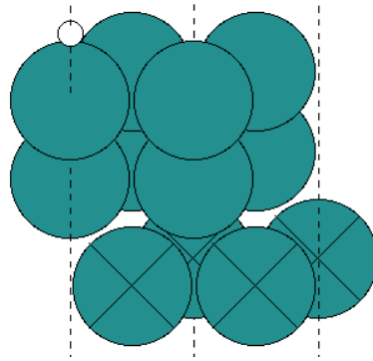
H adsorption on all possible sites (Task 4)

Ru (111)

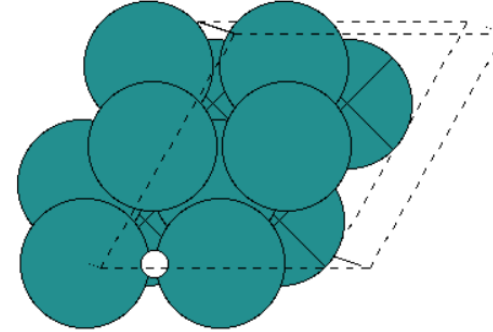
fcc



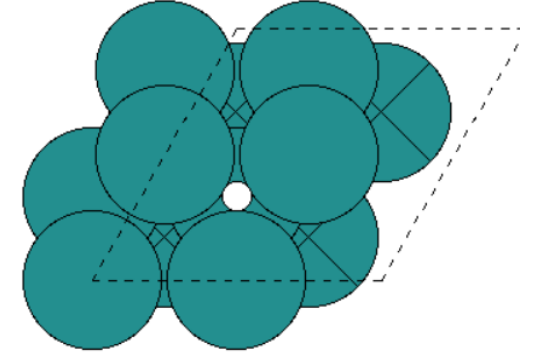
ontop



bridge

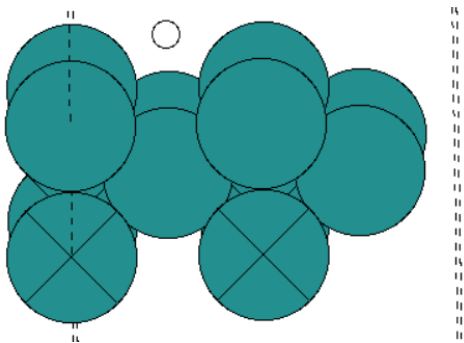


hcp

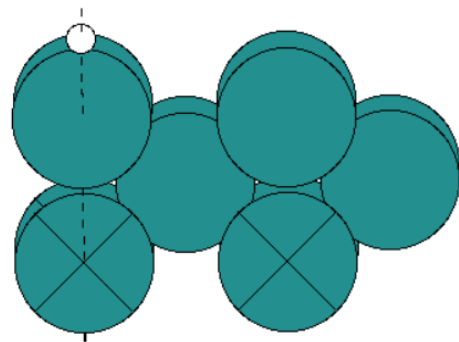


Ru (110)

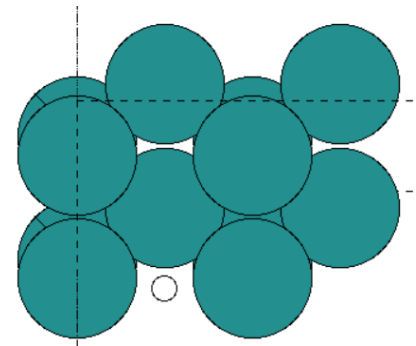
hollow



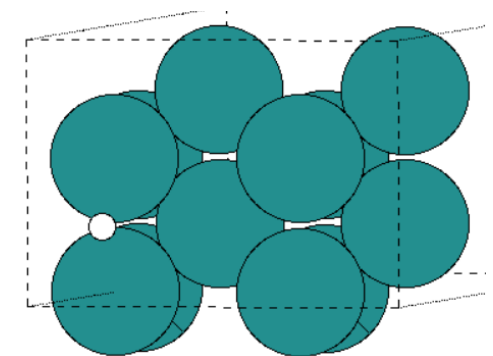
ontop



longbridge



shortbridge



All sites adsorption – Ru(111), Ru(110) (Task 4)

Ru(111)

k=8, ecut=600, size=(2, 2, 3)

	<i>Ru (111)</i>
ontop	-0.001
bridge	-0.617
fcc	-0.618
hcp	-0.581

Ru(110)

k=8, ecut=600, size=(2, 2, 3)

	<i>Ru (110)</i>
ontop	0.071
long bridge	-0.243
short bridge	-0.545
hollow	-0.372

- In some cases it has been studied that the adsorbed atom/molecule actually tends to fall into different and more favourable sites during relaxation. Such error has to be avoided and could be fixed by constraining the adsorbate to only move in the z direction.

*This is what we **believe** we see in Ru(111), where bridge \approx fcc.*

All sites adsorption – Cu(111), Cu(110) (Task 4)

Cu(111)

k=8, ecut=600, size=(2, 2, 3)

	<i>Cu(111)</i>
ontop	0.390
bridge	-0.055
fcc	-0.199
hcp	-0.186

Cu(110)

k=8, ecut=600, size=(2, 2, 3)

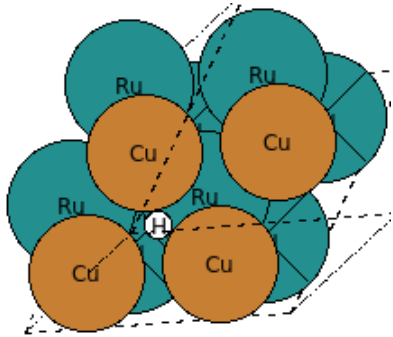
	<i>Cu(110)</i>
ontop	0.524
long bridge	0.002
short bridge	-0.110
hollow	0.169

System	FCC	HCP	ONTOP
H/Ni	-0.52	-0.50	0.06
H/Cu	-0.25	-0.23	0.39

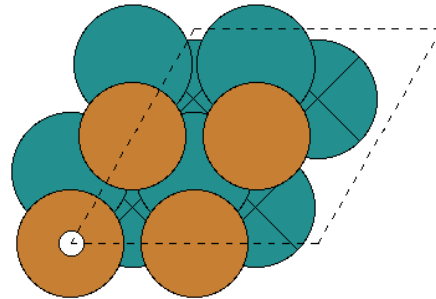
Ru with Cu top layer replacement (Task 5)

Cu+Ru (111)

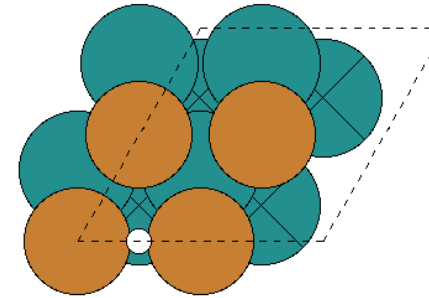
fcc



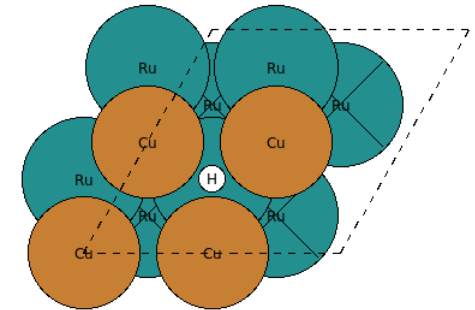
ontop



bridge

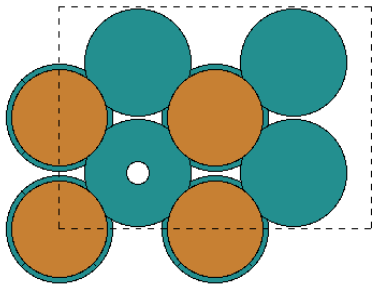


hcp

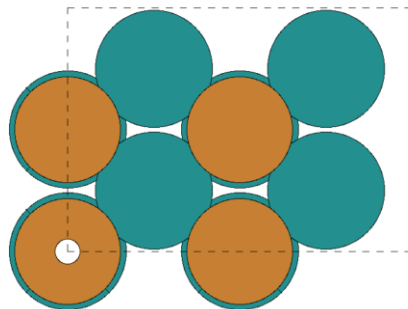


Cu+Ru (110)

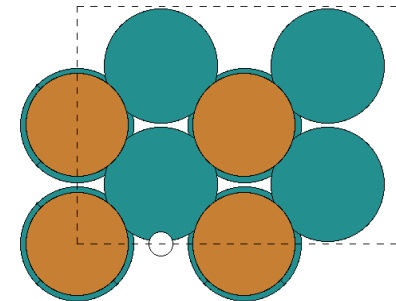
hollow



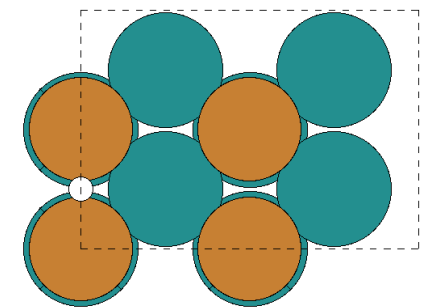
ontop



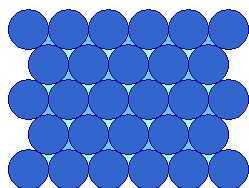
longbridge



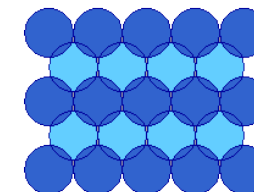
shortbridge



Ru with Cu top layer replacement (Task 5)

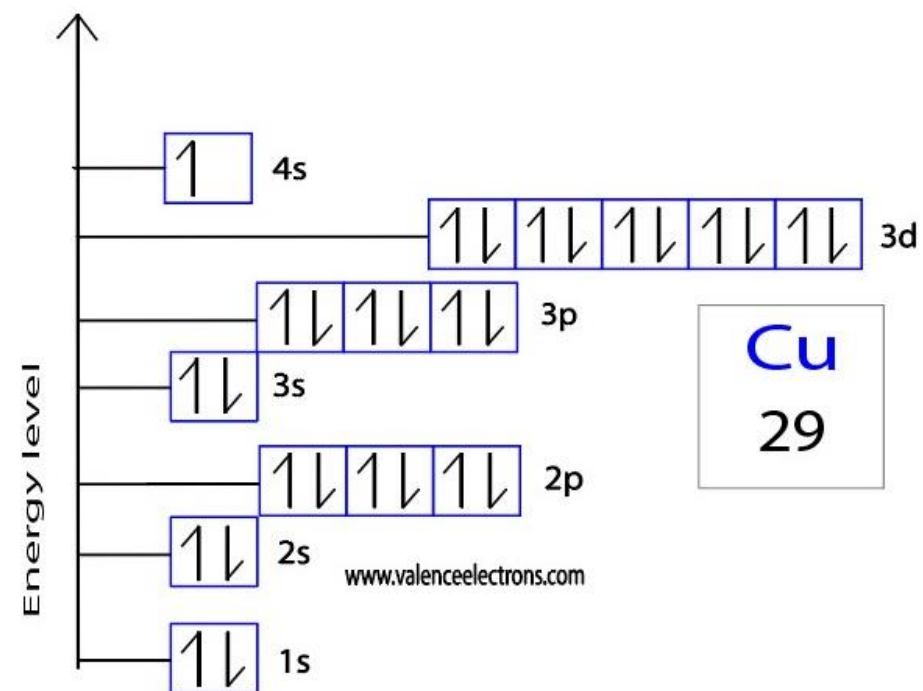
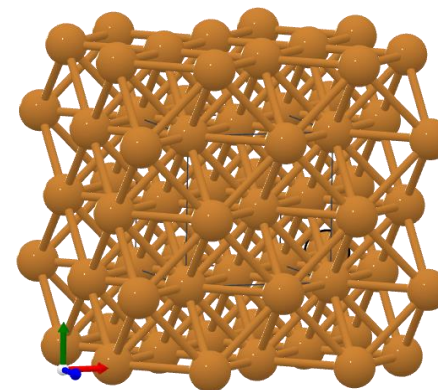
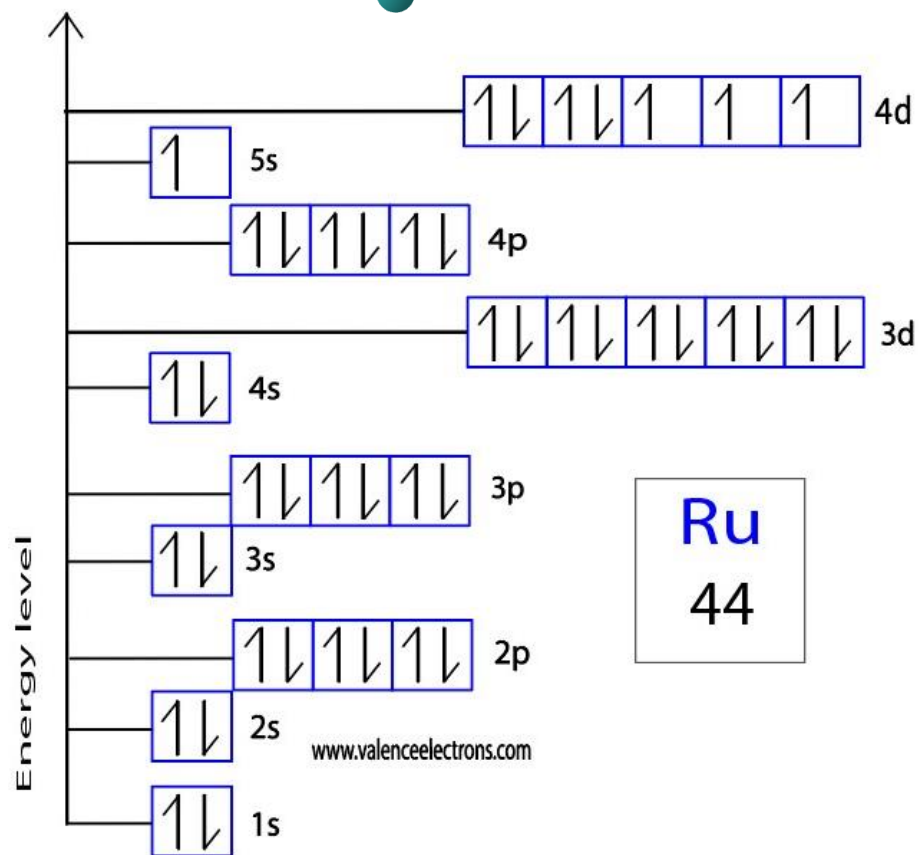
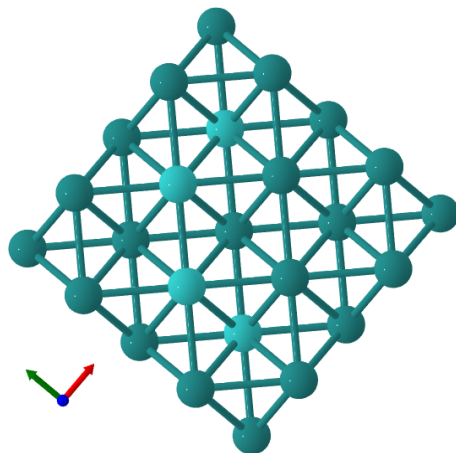


	<i>Cu + Ru(111)</i>
ontop	0.804
bridge	-0.270
fcc	-0.271
hcp	-0.172



	<i>Cu + Ru(110)</i>
ontop	0.104
long bridge	-0.337
short bridge	-0.314
hollow	-0.299

- Ontop position has a much higher repulsive energy due to the added Cu layer
- For (111) we appreciate the same bridge shift into fcc
- For (110) Ruthenium is more exposed to the adsorbate as the atoms are less tightly packed, which reflects on the better possibility of Hydrogen to be adsorbed on to the slab



Why Adsorption?

- Essential descriptor of Catalysis
- Adsorbed atom/molecule form an intermediate surface that is more likely to react
- Adsorbate represents an active site
- Given the adsorbate weaker bond, reactions are more likely to occur
- Reduces activation energy, therefore increasing the rate of the reaction

*“The adsorption theory states that **adhesion results from molecular contact between two materials and the surface forces that develop**. A bond develops from the adsorption of adhesive molecules on the substrate and the resulting attractive forces, usually designated as secondary or van der Waals forces.”*

Conclusion

- Generally in our calculations PBE was better than RPBE. It was also easier to find literature on PBE, so we stuck with that.
- RPBE should be the best due to Ru being a late transition metal.
- Fix the adsorbant to only move in z-direction to avoid similar energies for bridge and fcc.
- Ontop position is a tricky one due to coulomb repulsions.
- Fcc best for (111) structures and short-bridge for (110) because it is most similar to fcc (111)
- (110) adsorbs more due to the exposed second layer of Ru. But is it also the most durable? And do we want it to adsorb this much?

References

- <https://aip.scitation.org/doi/pdf/10.1063/1.3382342>
- <https://reader.elsevier.com/reader/sd/pii/S0301010405001126?token=69CA7F775259DD369C586C80E0DAA70744BE4F954899F623E4F6173DA60024AB4EDBF0529D22FE67618E570148320279&originRegion=eu-west-1&originCreation=20221209103305>
- <https://reader.elsevier.com/reader/sd/pii/S0039602816301509?token=2811BB5A17751BBAD98083591ACADEDEFB54CD22DBD2059ABDC1A91AAE98F869D47E2B8D5215372BA0DF60351964353F&originRegion=eu-west-1&originCreation=20221209094404>
- <https://pubs.rsc.org/en/content/articlepdf/2021/cp/d1cp03312c>
- [What is the difference between PBE and PBEsol functional? | ResearchGate](#)
- [Theoretical Study of Hydrogen Adsorption on Ruthenium Clusters | SpringerLink](#)

Thank you!

DTU



Discussion (Exercise 1)

- In both cases the worst result is given by the Single- ζ (**sz**) basis set.
 - This makes sense as the former is the least accurate way to approximate the wave function, although being at the same time the fastest route to the results possible
 - The same and opposite concept can be applied to the Double- ζ Polarized (**dzp**).
- **LCAO results** present several sources of discussion:
 - GGAs were expected to give the best results, in particular **RPBE was expected to be the best one**, as RPBE is just PBE revised for molecules.
 - In turn, LDA was expected to give worse results as the density gradient is not taken into account and it usually has poor performance for bond energies.
- **PW results** show better accuracy, but however not expected values still:
 - GGAs results are the best ones, however once again RPBE was expected to be the best one
 - LDA results are the least accurate, which was expected.

- Chemisorption energies of atoms and molecules on late transition surfaces LDA functional exchange-correlation yields too large energies. Including a nonlocal xc effects with PW91 or PBE functionals approximately halves this error. Using RPBE further reduces this overbinding by a factor of two. RPBE differ from PBE in the choice of mathematical form for the exchange energy enhancement factor [1].
- PBEsol after the error cancelation between exchange and correlation can apparently account for medium-range interaction better than PBE
- Meta-GGA includes the second derivative of the electron density (the Laplacian).
- GGA includes the electron density and the first derivative of the exchange-correlation potential.
- At the GGA level one can at most satisfy two out of the three constraints:
 - Second-order gradient expansion for exchange
 - Second-order gradient expansion for correlation
 - The local spin density (LSD)-like linear density response of a uniform electron gas.
- PBE satisfies 2 and 3. PBEsol satisfies 1 and compromises between 2 and 3

[1] PhysRevB.59.7413, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, Hammer, B. and Hansen, L. B. and Nørskov, J. K.

[2] The Burke Research Group, <https://dft.uci.edu/pubs/PBEsol.html>