

Adsorption on Surfaces

Objectives:

In this activity, you will

- 1) construct the supercell models for the adsorption of O atom on fcc(111) surface
- 2) calculate the adsorption energies of O atom on different sites of the (111) surface
- 3) write a written report of the results

Theory:

Studying the adsorption of atoms or molecules on surfaces is at the cornerstone of surface physics and catalysis. Weak or strong adsorption of particles on the surface can dictate the catalytic activities of catalysts, selective functionality of surfaces, among others. Modeling the adsorption of particles on surfaces is similar to the modeling of clean surfaces; i.e., slab models separated by large vacuum space are used. Atoms or molecules are adsorbed on one side of the slab, and an electric dipole correction is included in the calculation to avoid the spurious interaction between repeated slabs.

The adsorption energies of molecules at different configurations and positions on the surfaces describe the strength of its interaction with the surface. Typically, the summed energies of the slab and isolated molecules are used as reference energies for adsorption energies. In this convention, a more negative value for adsorption energy denotes a stronger adsorption of the atom or molecule on the surface. Its value also depends on the surface coverage. Depending on the lateral interaction of the molecules (attractive or repulsive), the adsorption energies can increase or decrease.

There are two types of adsorption which can highly depend on the distance of the adsorbate from the surface. In the *chemisorption* type of adsorption, the energy gain from orbital hybridization between the adsorption and surface electronic states provides the adsorption energy. Because of the electron transfer between the adsorbate and the surface, polarization may occur due to the difference in electronegativities of atoms in the

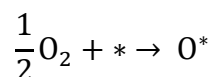
adsorbate and the surface. When the electron transfer is large, the adsorbate is ionized, and the characteristic of coupling by electrostatic attraction also appears. In the chemisorption process, bonds in the adsorbate can break as it forms new bonds with the surface, resulting in its dissociation (dissociative adsorption). The reverse process is the associative desorption. On the other hand, the adsorption is of *physisorption* type if the adsorbate is relatively far from the surface and no orbital hybridization is involved in the adsorption process; that is, the energy gain is by virtue of the long-range intermolecular forces. In a broader sense, intermolecular forces include the van der Waals force, as well as the interionic Coulomb attraction and hydrogen bonding force. However, in a physisorption state, the interaction is usually by van der Waals force.

Computational Model:

DFT calculations will be implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons will be described using the projector augmented wave (PAW) method. Plane wave basis sets will be employed with an energy cut-off of 400 eV. The surface Brillouin zone integrations will be performed on a grid of 4×4×1 Monkhorst-Pack k-points using Methfessel-Paxton smearing of $\sigma=0.2$ eV. Electric dipole correction should be included along the direction of the vacuum space.

Method:

- 1) You will be assigned a particular metal with an fcc structure. Set up the position of the atoms as you have learned in the previous computational activities.
- 2) Cleave the bulk fcc metal at the (111) facet and form a 4-atomic layer slab.
- 3) To simulate the adsorption of O atom on the surface, consider the following reaction:



Here, O_2 is in gas phase, $*$ is a site on the slab, and O^* is an O atom adsorbed on site $*$.

- 4) Place an O atom at a distance of about 2.0 Å from the surface. Use an adsorbate coverage of $\frac{1}{4}$ ML. Optimize the ionic positions of atoms, allowing the first two layers of the slab and the O atom to relax while the bottom two layers fixed at their bulk positions. Note that the size of the supercell will be held fixed. Do this for the following initial positions O atom:

- a. fcc hollow site
 - b. hcp hollow site
 - c. bridge site
 - d. top site
- 5) Calculate the adsorption energy of O* for each position using the following equation:

$$E_{\text{ads}} = E_{\text{O}^*} - (E_* + \frac{1}{2}E_{\text{O}_2})$$

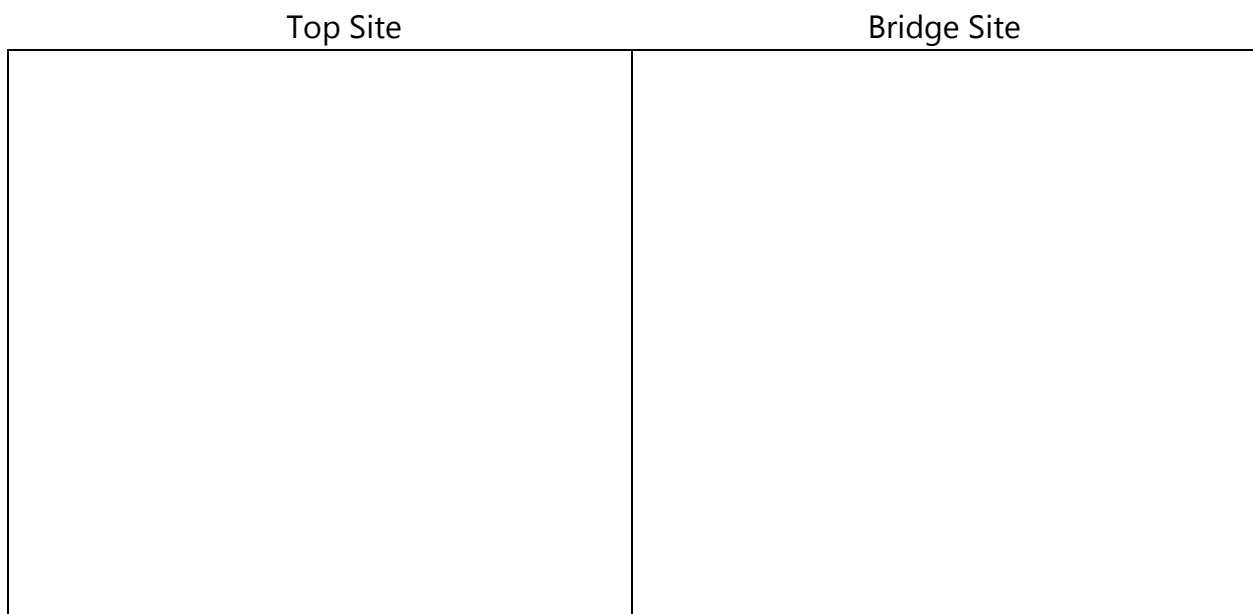
where E_{O^*} is the energy of the system of slab with adsorbed H atom, E_* is the energy of the slab, and E_{H_2} is the energy of an isolated O₂ gas molecule.

- 6) In a separate calculation, calculate E_{O_2} using a similar model used in Activity 1. Using an initial distance of separation of 1.20 Å, optimize the system to find the stable O-O bond length. Using this result, run an SCF calculation to calculate the total of the system. This corresponds to E_{O_2} .

Results and Guide Questions:

FCC Metal Assigned to you: _____

Figure 1: Optimized adsorption configuration of an O adatom on an fcc surface



HCP Hollow Site	FCC Hollow Site

Table 1: Computation of the Adsorption Energy

E_{O_2} (eV): _____
 E_* (eV): _____

Surface Site	E_{O^*} (eV)	E_{ads} (eV)
Top		
Bridge		
HCP Hollow		
FCC Hollow		

1) Based on the calculated adsorption energies, compare the relative stabilities of O^* on the different surface sites. Compare your calculated results with the reported values in the literature.

2) Explain the relative stability of O^* adsorption on different surface sites based on the coordination of O^* on each site. Comment on the possible bonding mechanism of O on the surface.

Conclusion:
