Lab9

April 4, 2024

1 Geometry Optimization of Si Bulk

Use keyword 'relax' for geometry optimization process.

1. Prepare the Quantum Espresso input files for Si bulk.
2. Set the 'relax' keyword to initiate geometry optimization.
3. Run the calculation to optimize the geometry of Si bulk.

[ ]:
```
&CONTROL
    prefix='silicon',
    pseudo_dir = './',
    outdir     ='./',
    calculation = 'relax'
    ! relax: only the atomic positions
    ! vc-relax: both atomic positions and lattice constants
 /

 &SYSTEM
    ibrav = 2,
    celldm(1) = 10.2,
    nat =  2,
    ntyp = 1,
    ecutwfc = 35.0,
    ecutrho = 140.0,
 /

 &ELECTRONS
    conv_thr=1d-06
 /

 &IONS
/


ATOMIC_SPECIES
   Si  28.086  Si.pz-vbc.UPF

ATOMIC_POSITIONS alat
```

```
   Si 0.00 0.00 0.00
   Si 0.25 0.25 0.25
   ! this is a comment

K_POINTS automatic
   10 10 10   1 1 1
```

2 Calculate Surface Energy

To determine which surface is more stable, calculate the surface energy using the following steps:

1. Verify the Python scripts. Execute them to obtain input coordinates and cell parameters for Si bulk and Si surfaces 100 and 111.
2. Generate Quantum Espresso input files for Si surfaces 100 and 111.
3. Perform self-consistent field (SCF) calculations. Note: Geometry optimization is time-consuming; hence, perform SCF calculations for now.
4. Compute the unrelaxed surface energy using the formula: Surface energy = (1/2) * (E_slab - N * E_bulk)

   Where:

   - E_bulk: Energy per atom, obtained by running SCF energy calculation on bulk material and then calculating energy per atom.
   - E_slab: Energy of the slab.

5. Repeat the above procedure for a new system. Work in the new directory.

[ ]:
```python
from ase import Atoms
from ase.build import bulk, make_supercell
from ase.io import write

# Define lattice constant for Si diamond structure
a = 5.431  # Lattice constant of Si in angstroms

# Create Si diamond bulk structure
si_bulk = bulk('Si', 'diamond', a=a, cubic=True)

# Create 6x6x6 supercell
si_supercell = make_supercell(si_bulk, [[2,0,0],[0,2,0],[0,0,2]])

# Save Si diamond bulk structure as PDB file
write('si_bulk_supercell.pdb', si_supercell)
```

[ ]:
```python
from ase import Atoms
from ase.build import diamond100, diamond111
from ase.io import write
```

```
a = 5.4  # Lattice constant in angstroms

# Generate diamond(100) surface
diamond_100 = diamond100('Si', size=(4, 4, 4), a=a, vacuum=10.0,␣
 ↪orthogonal=True)

# Generate diamond(111) surface
diamond_111 = diamond111('Si', size=(4, 4, 4), a=a, vacuum=10.0)

# save as xyz file - second line consists of cell parameters
write("si_100.pdb", diamond_100)
write("si_111.pdb", diamond_111)
```

3 Calculate Adsorption Energy

To calculate the adsorption energy, use the following formula:

E_abs = E_total - (E_surface + E_adsorbant)

1. Check the Python script.
2. Utilize the Python script to generate the system (adsorbant: H2O).
3. Set up Quantum Espresso input files and execute geometry optimization for three systems.
4. Employ the aforementioned formula to compute the adsorption energy.
5. Repeat the aforementioned procedure for a new molecule (you decide the adsorbant).

[ ]:
```
from ase import Atoms
from ase.build import diamond111, molecule
from ase.io import write
import numpy as np

# Define lattice constant for Si diamond structure
a = 5.4

# Generate diamond(111) surface
diamond_111 = diamond111('Si', size=(4, 4, 4), a=a, vacuum=10.0)

# Calculate the center of the surface
center = np.mean(diamond_111.positions[:, :2], axis=0)  # Calculate mean of x␣
 ↪and y coordinates

# Create a molecule
adsorbant = molecule('H2O', vacuum=0.0)

# Place adsorbant molecule at the center of the surface only along x and y␣
 ↪directions
```

```
adsorbant.translate(np.hstack((center - adsorbant.positions[0][:2], 0)))

# Calculate distance from top layer
distance = 2.5  # Distance in angstroms
z_top = max(diamond_111.positions[:, 2])  # Maximum z-coordinate of Si atoms
z = z_top + distance
adsorbant.translate([0, 0, z])

# Add adsorbant molecule to surface
surface_with_adsorbant = diamond_111 + adsorbant

# Save Si(111) surface with CO molecule as PDB file
write("si_111_with_adsorbant.pdb", surface_with_adsorbant)
```

[ ]: