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Geometry optimization: CO/Pd(100)

Version: 2015.1

Downloads & Links

- PDF version
- Pd_bulk.py
- Pd100.py
- Pd100_CO_rigid.py
- Pd100_CO.py
- CO.py
- adsorption_energy.py
- Pd_CO_cp.py

Basic QuantumATK Tutorial
ATK Reference Manual
Building molecule–surface systems: Benzene on Au(111)
Molecular builder

In this tutorial you will learn how to do a geometry optimization using *Fixed* and *Rigid* constrains on the atoms. As an example, you will study adsorption of the CO molecule on a Pd(100) surface. You will use the ATK-DFT calculator engine and a standard GGA functional.

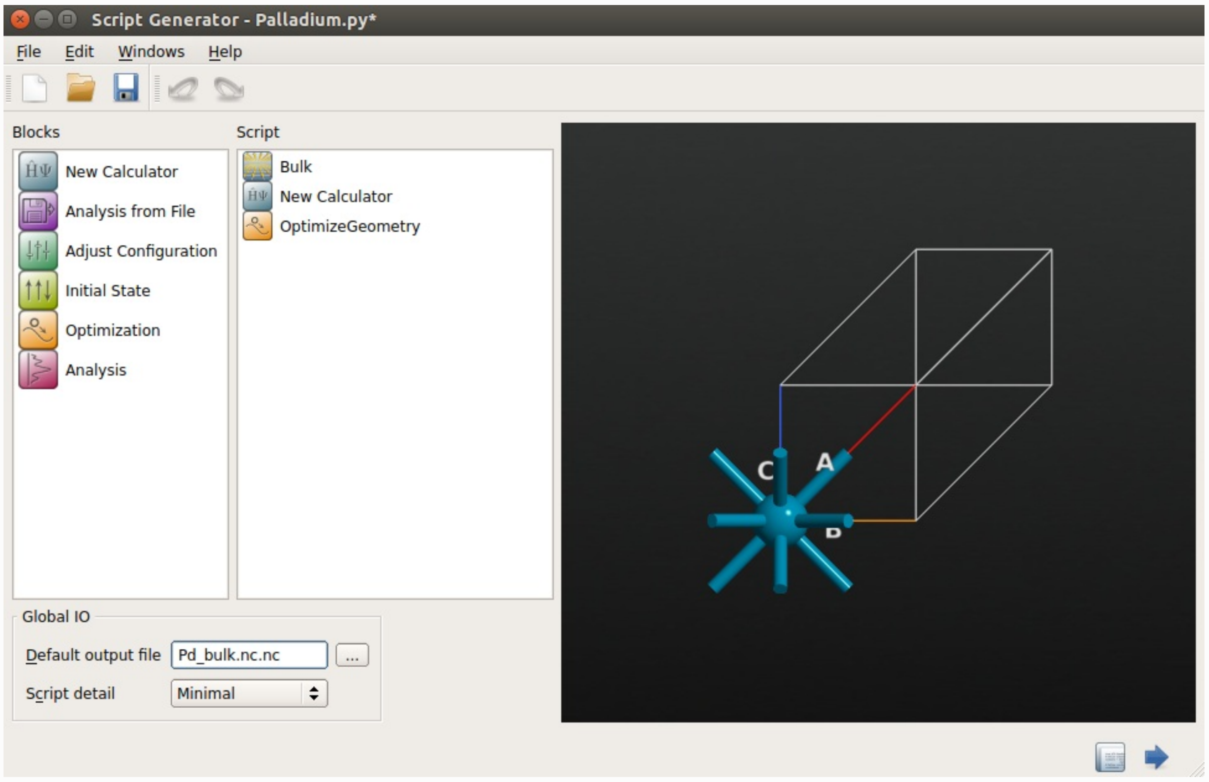
Specifically, you will:

1. optimize the bulk palladium crystal;
2. cleave the bulk to create the Pd(100) surface and relax it;
3. adsorb the CO molecule in the surface, and relax the system in two steps;
    1. first apply *Rigid* constraints on atoms during an initial relaxation;
    2. then apply *Fixed* constraints on the bottom Pd atoms in a final optimization.
4. lastly, relax the CO molecule and calculate the adsorption energy.

Bulk palladium

Create a new project called “Pd100_CO” and open the **Builder**.

- Use Add ‣ From Database to import the Pd bulk to the Stash and send the configuration to the **Script Generator** using the send to button.
- In the Script Generator, add the **New Calculator** and **OptimizeGeometry** blocks to the script by double-clicking them, and change the default output file name to `Pd_bulk.hdf5`.



Script Generator - Palladium.py*

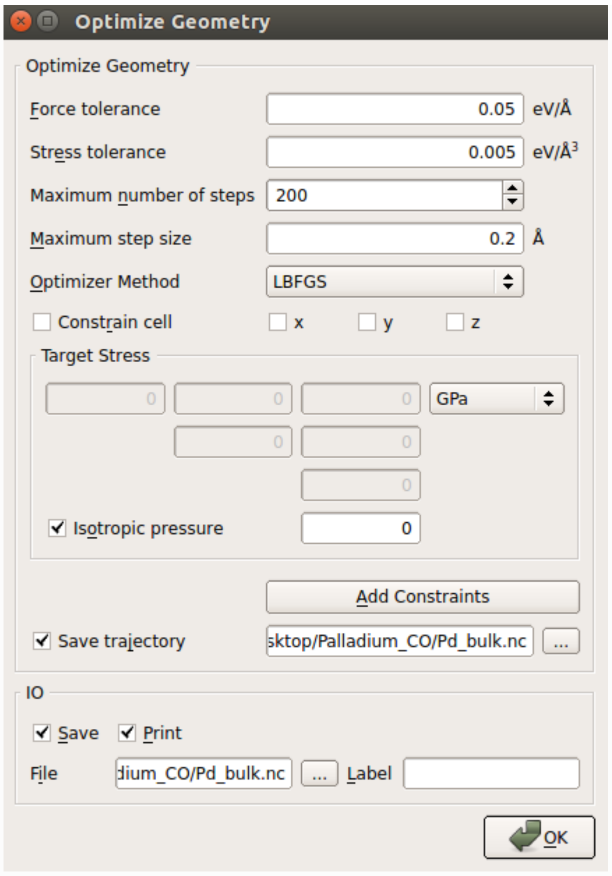
Script: Bulk, New Calculator, OptimizeGeometry

Global IO

Default output file: Pd_bulk.nc.nc

Script detail: Minimal

- Double-click the **New Calculator** block and set the following parameters in the window that opens up:
  - *k-point sampling*: 9x9x9;
  - *exchange-correlation*: GGA-PBE functional.
- Open the **OptimizeGeometry** block, and set the parameters as shown in the image below. In particular:
  - enable stress relaxation by unticking *Constrain cell*;
  - decrease the stress tolerance to 0.005 eV/Å^3;
  - save the relaxation trajectory by ticking *Save trajectory* and enter `Pd_bulk.hdf5` for the trajectory file name.



Optimize Geometry

Optimize Geometry

Force tolerance	0.05	eV/Å
Stress tolerance	0.005	eV/Å^3
Maximum number of steps	200	
Maximum step size	0.2	Å
Optimizer Method	LBFGS	

☐ Constrain cell ☐ x ☐ y ☐ z

Target Stress

0	0	0	GPa
	0	0	
		0	

✓ Isotropic pressure 0

Add Constraints

✓ Save trajectory sktop/Palladium_CO/Pd_bulk.nc ...

IO

✓ Save ✓ Print

File dium_CO/Pd_bulk.nc ... Label

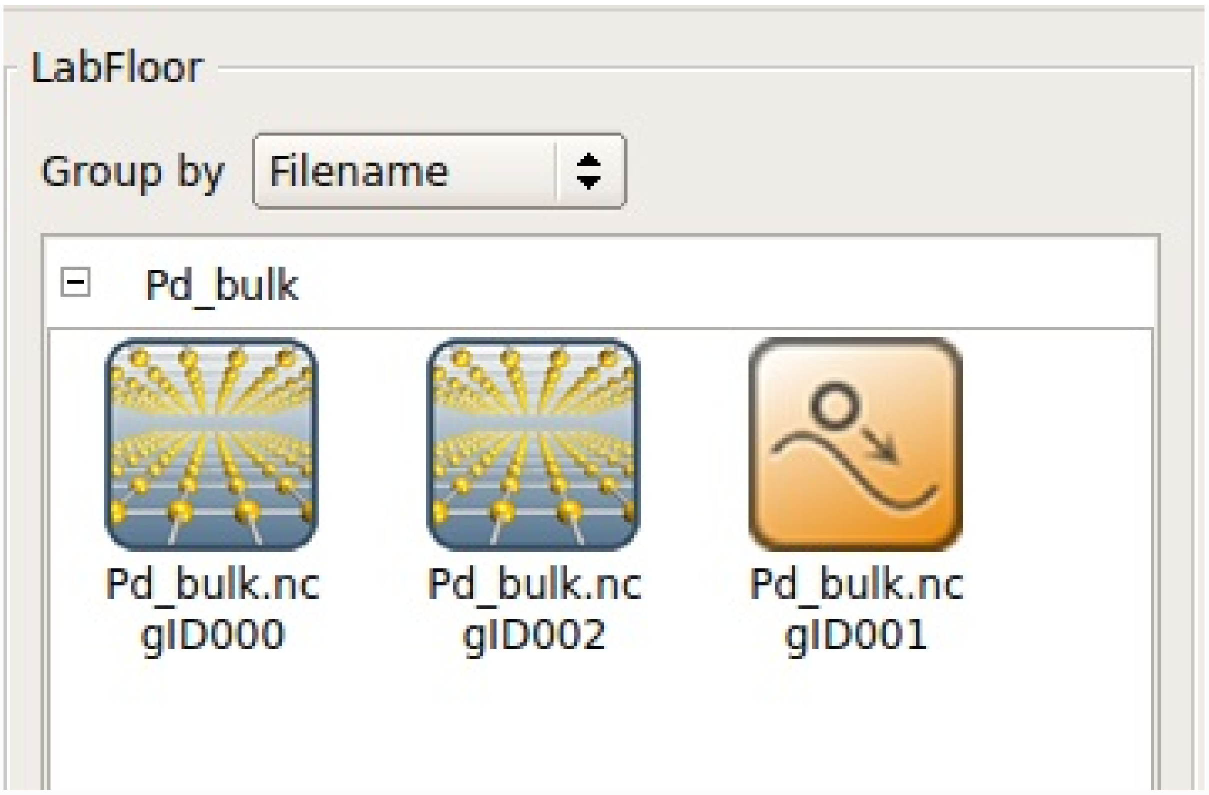
OK

Tip

It is usually a good idea to save the trajectory file. In case your geometry optimization is interrupted you can simply restart it from one of the latest images in the trajectory. If you would like to know more about how to restart a stopped calculation, check out the tutorial Restarting a stopped calculation.

- Click *OK* and the OptimizeGeometry window will close.
- The script is now finished. Send it to the **Job Manager** using the button. Save the script in the window that appears and run the calculation. It will take a few seconds. If needed, you can download the script here: Pd_bulk.py.

Once the bulk relaxation is finished, the calculation output will appear on the LabFloor. The bulk configurations with IDs *gID000* and *gID002* are the initial and final structures, respectively, while the relaxation trajectory has ID *gID001*.

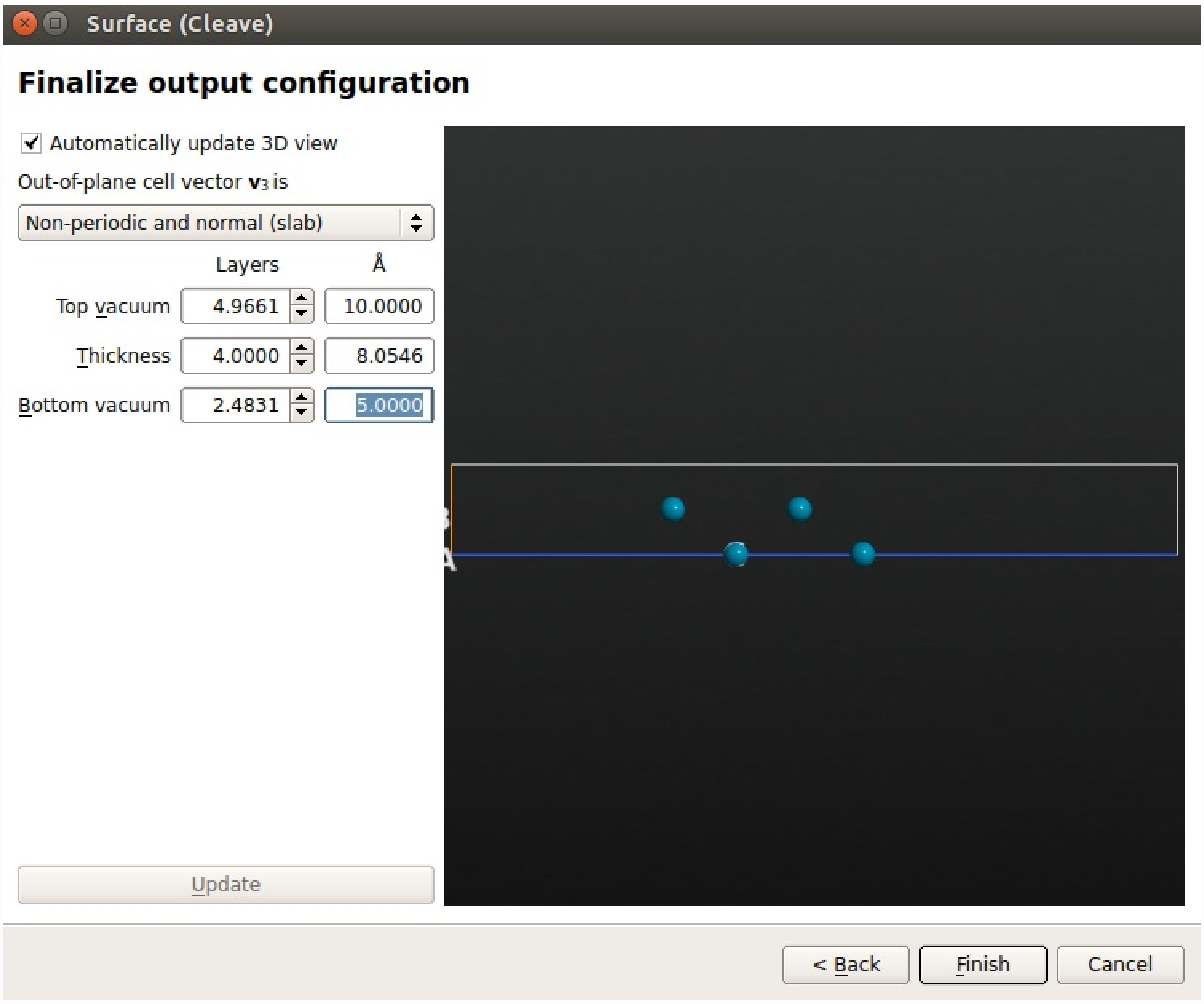


You can drag and drop these objects to the **Viewer** to visualize them. In the Viewer, you can check the lattice constant by hovering the mouse on the cell boundaries. You could also check the lattice constant in the newly formed log file.

In the following, you should of course use the relaxed bulk structure, *gID002*.

Build the Pd(100) surface and relax it

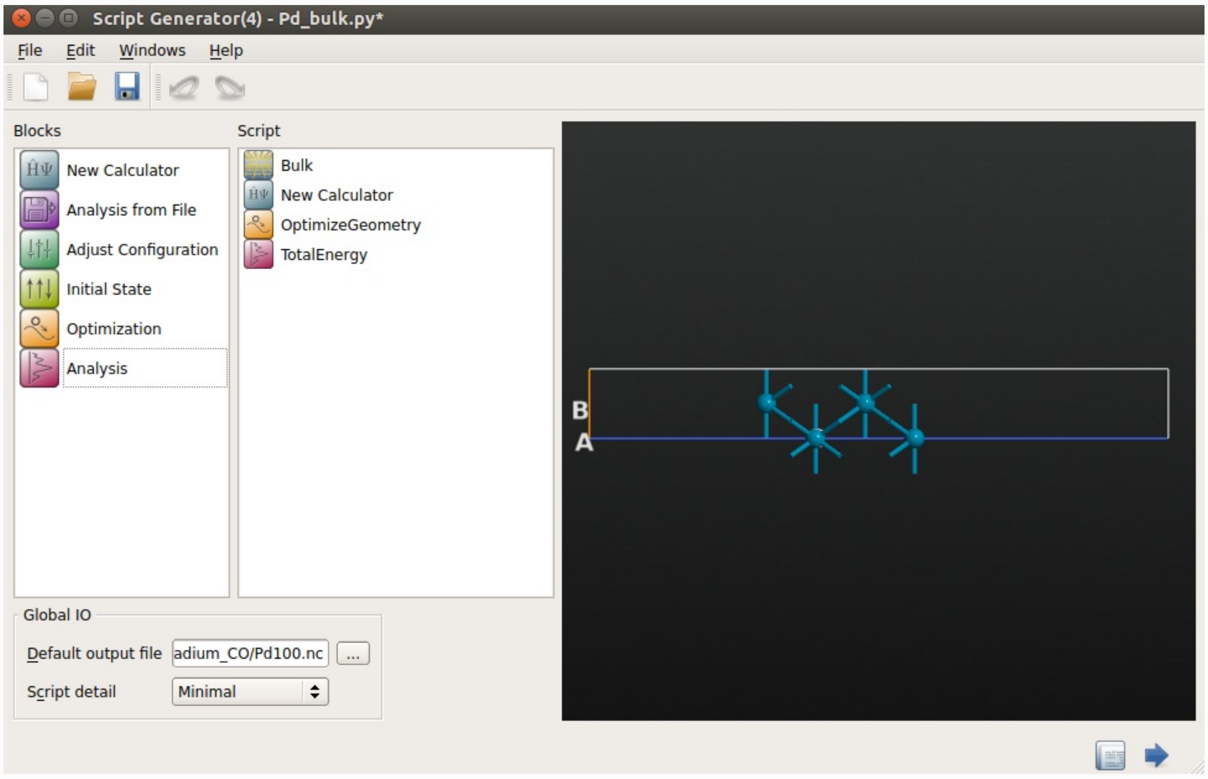
- Drag and drop the relaxed bulk configuration to the **Builder** .
- Open the Builders -‣ Surface (Cleave) plug-in.
- Keep the default Miller indices and click *Next*.
- Keep the default 1x1 surface lattice and click *Next*.
- Choose a *Non-periodic* and *normal (slab) out-of-plane cell vector*, 4 slab metal layers, and 10 Å and 5 Å for the top and bottom vacuums, respectively. Click *Finish* to build the surface.



☑ Automatically update 3D view
Out-of-plane cell vector $\mathbf{v}_3$ is: Non-periodic and normal (slab)

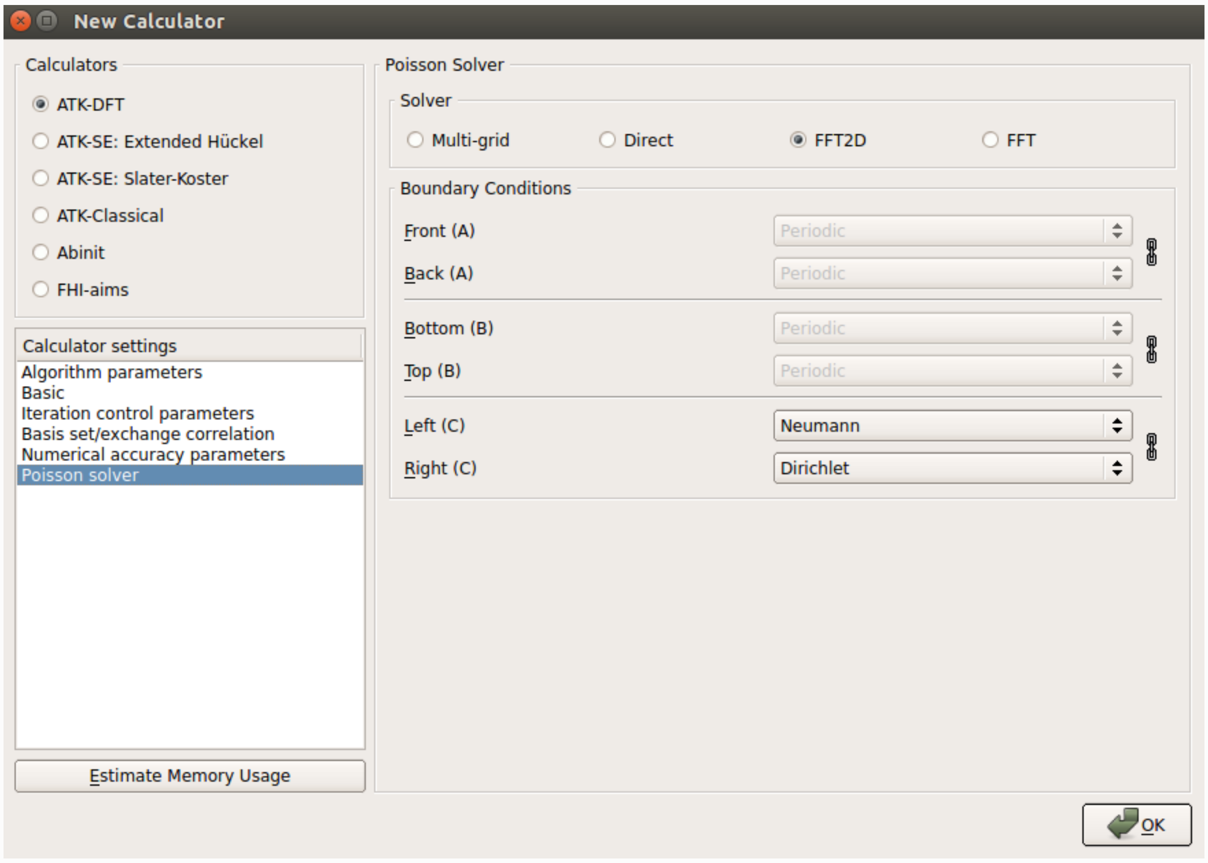
	Layers	Å
Top vacuum	4.9661	10.0000
Thickness	4.0000	8.0546
Bottom vacuum	2.4831	5.0000

- Send the slab structure to the **Script Generator** and add the **New Calculator**, **OptimizeGeometry** and **TotalEnergy** blocks to the script, and set the default output file name to `Pd100.hdf5`.



Global IO
Default output file: adium_CO/Pd100.nc
Script detail: Minimal

- Choose the following set of calculator parameters:
    - *k-point sampling*: 9x9x1 k-points;
    - *exchange-correlation*: GGA-PBE;
    - *FFT2D Poisson solver* with *Neumann* boundary conditions under the slab and *Dirichlet* boundary conditions above the slab:



Poisson Solver

Solver: Multi-grid, Direct, [✓ FFT2D], FFT

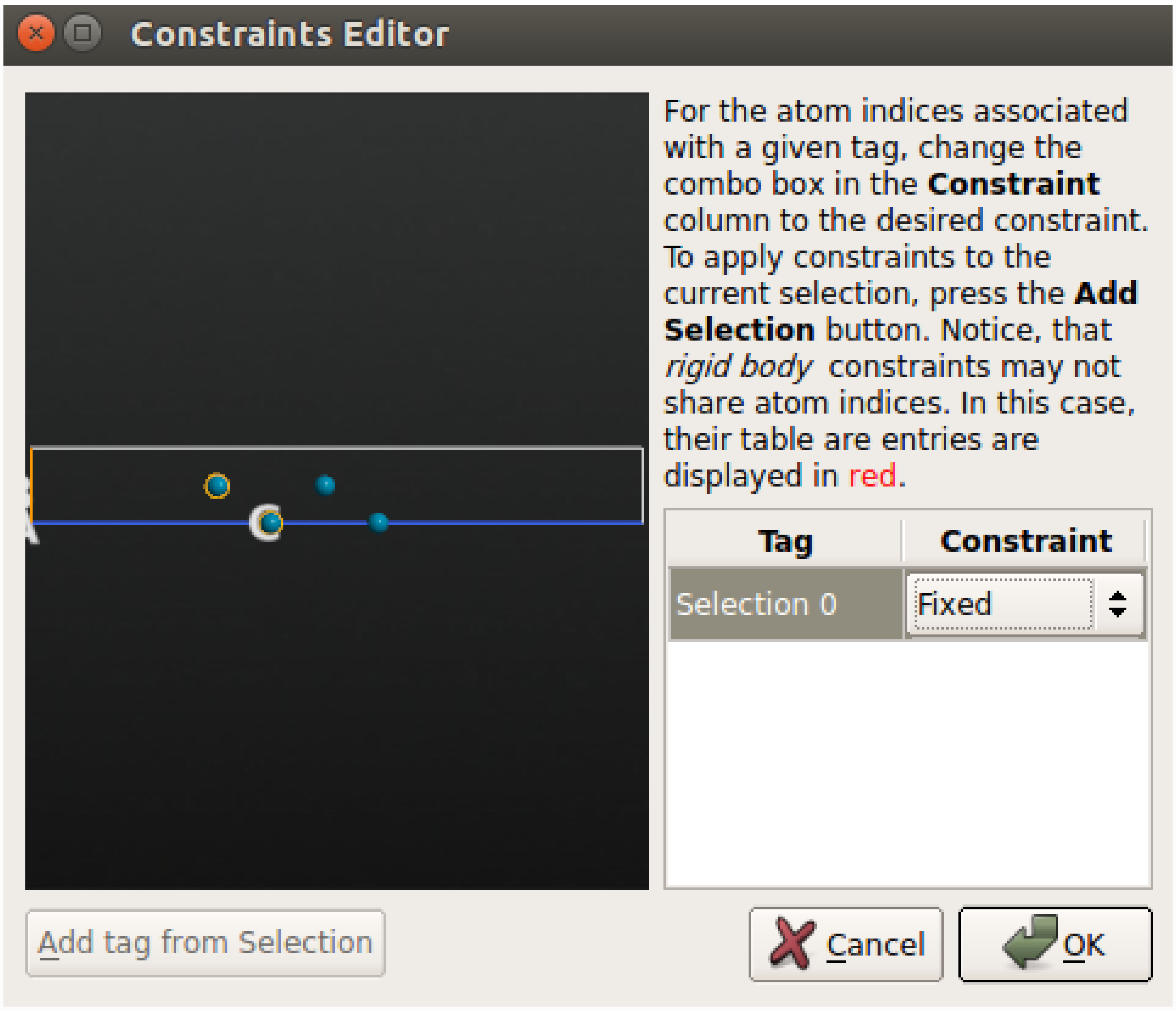
Boundary Conditions

Front (A)	Periodic
Back (A)	Periodic
Bottom (B)	Periodic
Top (B)	Periodic
Left (C)	Neumann
Right (C)	Dirichlet

Note

This particular set of boundary conditions along the C direction of the simulation cell is appropriate for slab calculations, where the vacuum above the slab could in principle extend to infinity.

- Open the **OptimizeGeometry** block and set it up for force relaxation:
    - save the trajectory to `Pd100_traj.hdf5`;
    - click **Add Constraints** to open the Constraints Editor;
    - use the mouse to select the bottom two layers of the Pd(100) surface and click *Add tag from selection*. Those two atoms are now tagged “Selection 0”. Then choose the *Fixed* constraint for the “Selection 0” group.


Constraints Editor

For the atom indices associated with a given tag, change the combo box in the **Constraint** column to the desired constraint. To apply constraints to the current selection, press the **Add Selection** button. Notice, that *rigid body* constraints may not share atom indices. In this case, their table are entries are displayed in red.

Tag	Constraint
Selection 0	Fixed

- There is nothing to edit in the **TotalEnergy** block, so the script is now finished. Save it as `Pd100.py` and execute it using the **Job Manager**. The calculation will take roughly one minute. If needed, you can download the script here: Pd100.py.

Once the Pd(100) surface has been geometry optimized, the results will appear on the **LabFloor**. You can again visualize the relaxation trajectory using the **Viewer**.

Tip

You can check the total energy of the relaxed Pd(100) surface by selecting the TotalEnergy object and clicking on the **Text Representation** plugin. The energy is also printed in the log file.

Relax the CO/Pd(100) system

The next step is to add the CO molecule to the surface and relax the system. You should use the CO/Pd(100) structure available here: CO_Pd100.py. If needed, you can learn how to add a molecule to a surface from the tutorial Building molecule–surface systems: Benzene on Au(111).

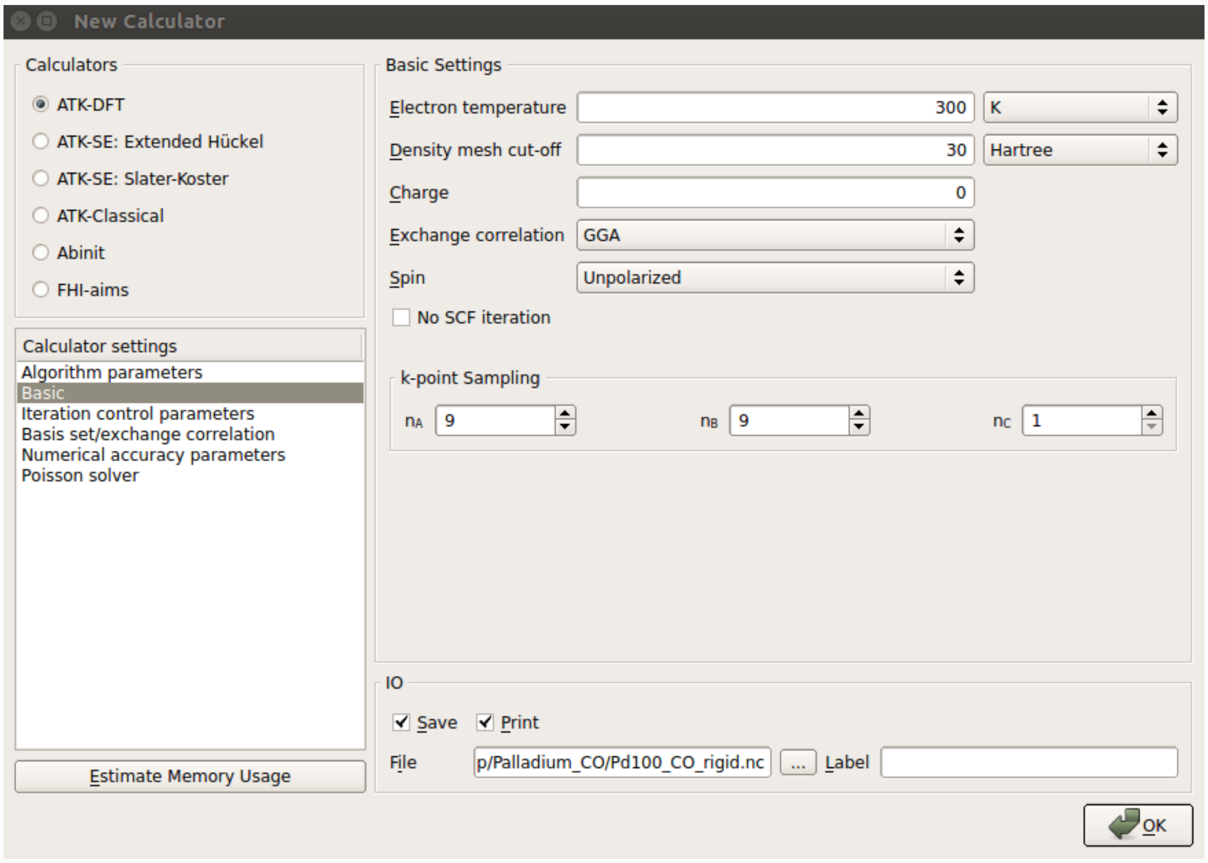
As mentioned in the introduction, you will relax the CO/Pd(100) configuration in two steps:

1. use a *Rigid* constraint for CO and *Fixed* constrain for the surface, together with a relatively low electron density mesh cut-off, in order to get a quick idea of where the CO will be adsorbed;
2. the final relaxation step does not constrain the CO molecule and just fixes the bottom of the Pd(100) slab.

Rigid relaxation

Transfer the provided CO/Pd(100) configuration (CO_Pd100.py) to the **Script Generator** and add the **New Calculator** and **OptimizeGeometry** blocks. Enter `Pd100_CO_rigid.hdf5` for the default output file name, and then edit the script:

- In the **New Calculator** block, use the same settings as for the Pd(100) relaxation in the previous section, but decrease the density mesh-cut off to 30 Hartree.



Basic Settings

Electron temperature	300	K
Density mesh cut-off	30	Hartree
Charge	0	
Exchange correlation	GGA	
Spin	Unpolarized	

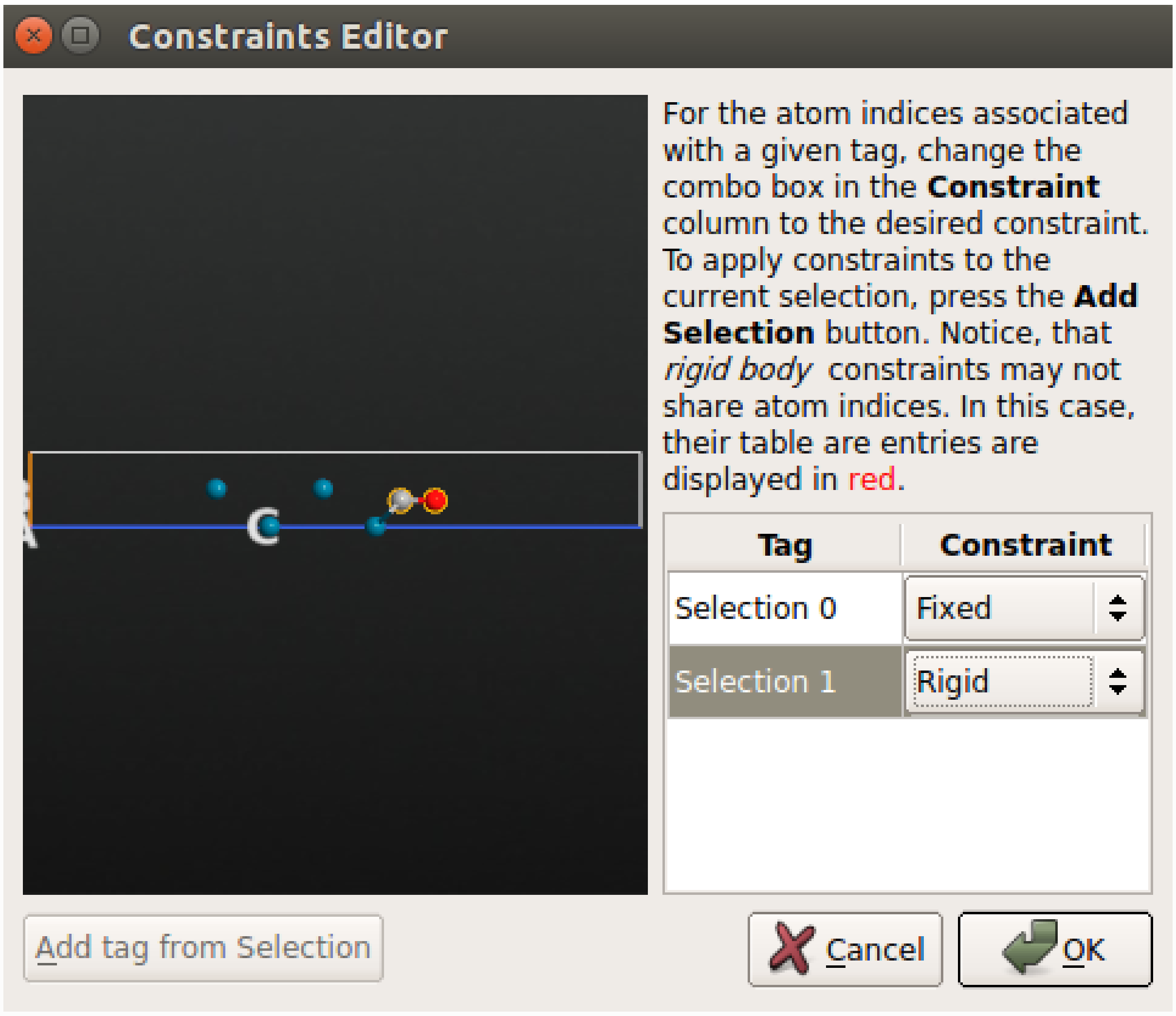
☐ No SCF iteration

k-point Sampling: nA 9, nB 9, nC 1

IO: ✓ Save ✓ Print

File: p/Palladium_CO/Pd100_CO_rigid.nc ... Label

- Set up the **OptimizeGeometry** block similarly to the one used for Pd(100), but choose a slightly different set of constraints:
  - select the *Fixed* constraint for all atoms in the metal slab;
  - select the *Rigid* constraint for the CO molecule (add the C and O atoms to the group “Selection 1”).



Constraints Editor

For the atom indices associated with a given tag, change the combo box in the **Constraint** column to the desired constraint. To apply constraints to the current selection, press the **Add Selection** button. Notice, that *rigid body* constraints may not share atom indices. In this case, their table are entries are displayed in red.

Tag	Constraint
Selection 0	Fixed
Selection 1	Rigid

Note

The Rigid constraint on a group of atoms causes those atoms to move like a rigid body during force optimization.

- Save the script as `Pd100_CO_rigid.py` and run it using the **Job Manager**. The simulation should take roughly 5 minutes if executed in serial. You can download the script here: Pd100_CO_rigid.py.

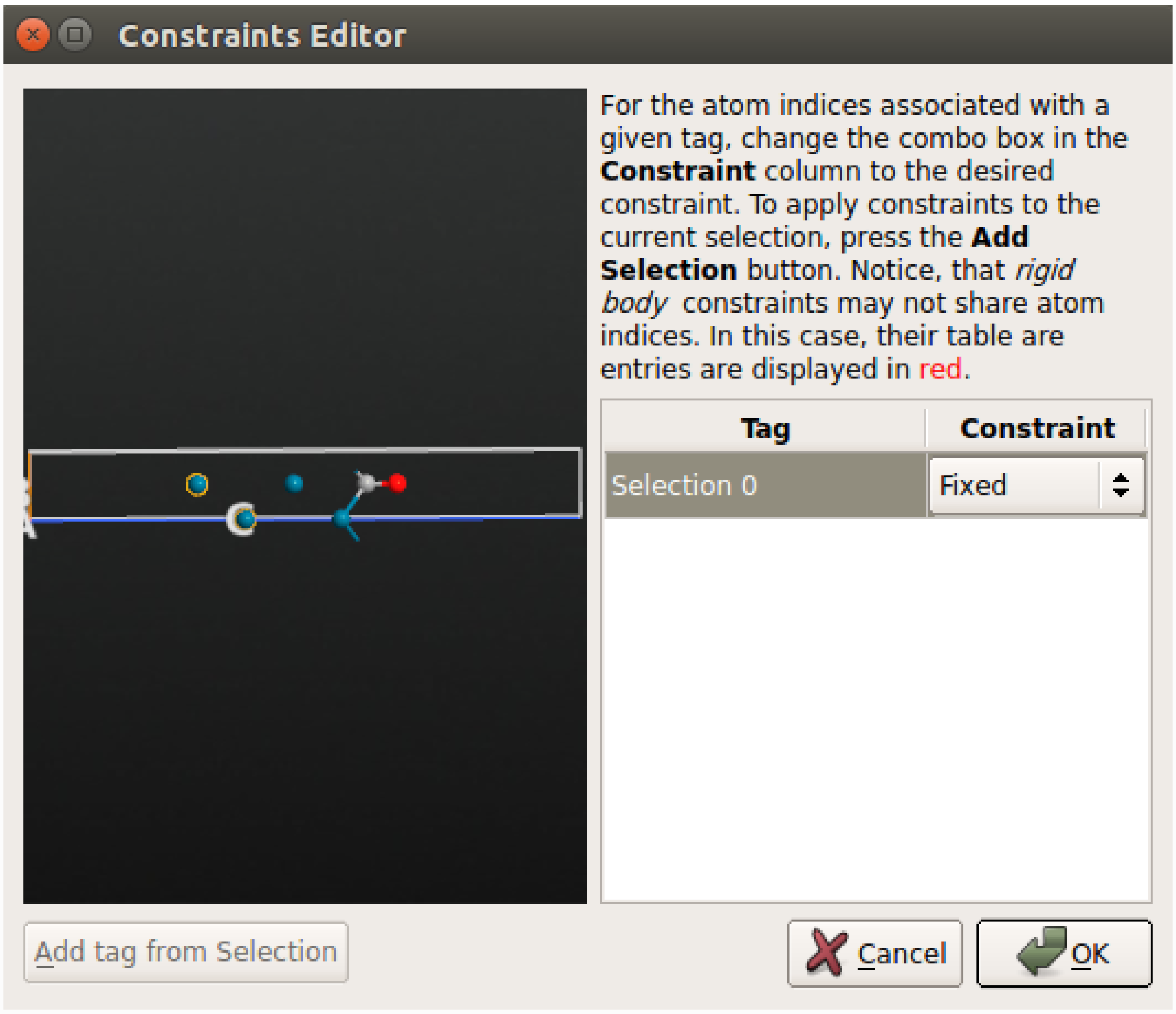
Important

If you take a look at the trajectory, you will see that the CO molecule has moved slightly away from its initial position, but the C–O bond length has not changed, and the molecule has not rotated. This is how the rigid constraint works.

Final relaxation

You will now perform the final geometry optimization of the CO/Pd(100) structure, starting from the result of the previous step.

- Send the configuration with ID *gID002* in `Pd_CO_rigid.hdf5` to the **Scripter**, and enter `Pd_CO.hdf5` for the default output file name.
- Once again, add the **New Calculation**, **OptimizeGeometry** and **TotalEnergy** blocks, and edit them similarly to what you did in the previous section. This time, however, use a 75 Hartree mesh-cutoff for the ATK-DFT calculator, and use only a *Fixed* constraint for the bottom two Pd atoms:



For the atom indices associated with a given tag, change the combo box in the **Constraint** column to the desired constraint. To apply constraints to the current selection, press the **Add Selection** button. Notice, that *rigid body* constraints may not share atom indices. In this case, their table are entries are displayed in red.

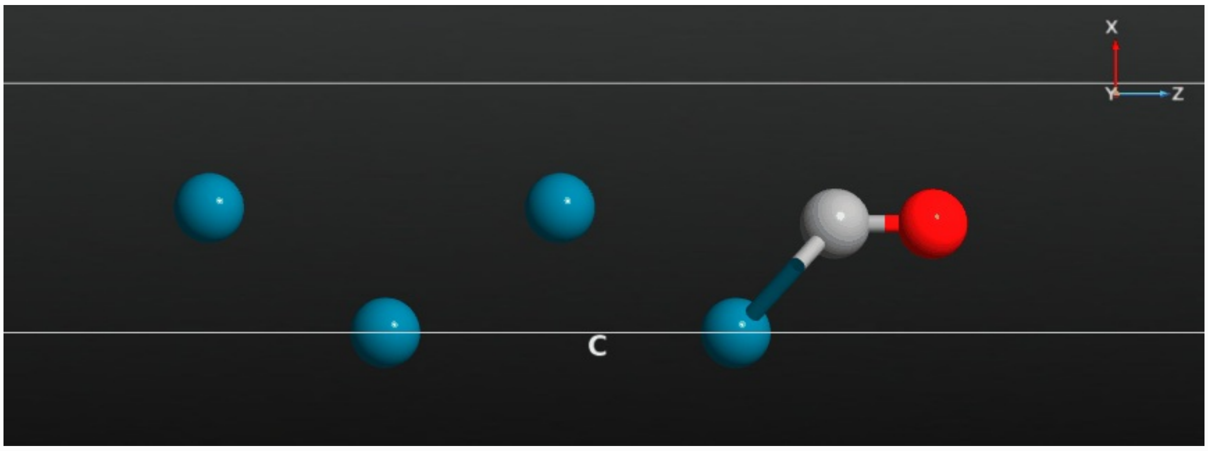
Tag	Constraint
Selection 0	Fixed

- Save the script as `Pd_CO.py` and execute it using the Job Manager or in a Terminal. The calculations should take about 20 min in total, but can of course be quicker if run in parallel on more CPUs. The script is also available here: Pd100_CO.py.

Tip

You can actually use the **Viewer** tool to monitor the progress of the geometry optimization while the calculation is running. The trajectory object is continuously updated as new relaxations steps are taken.

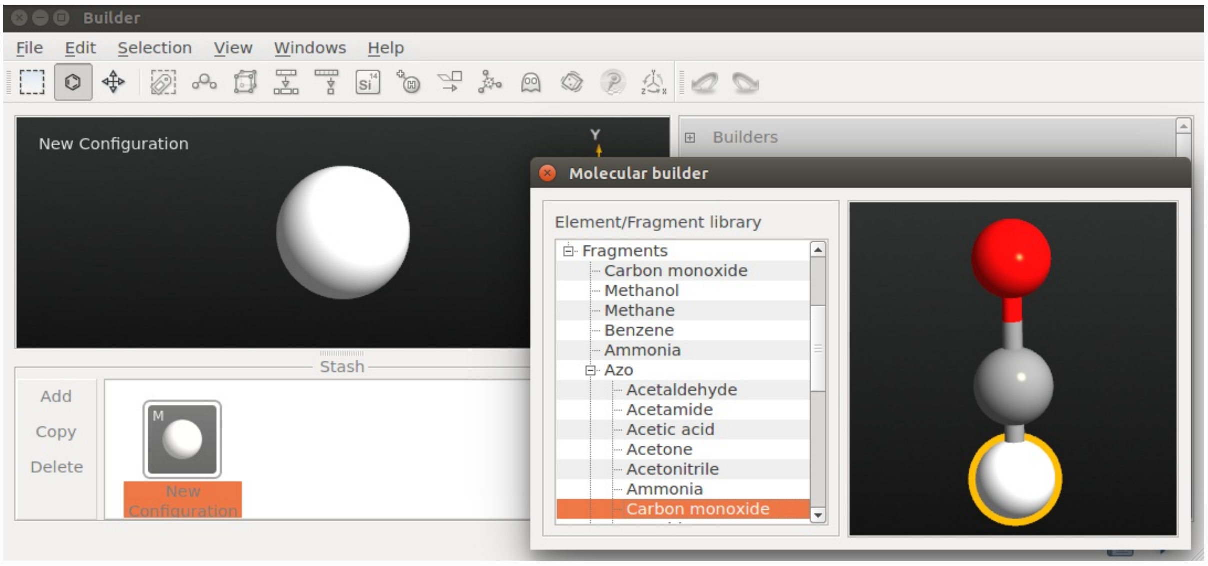
When the calculation has finished you should have a look at the full relaxation trajectory, and see how the CO molecule has moved from a position around the hollow adsorption site on the Pd(100) surface to a bridge site between two Pd surface atoms:



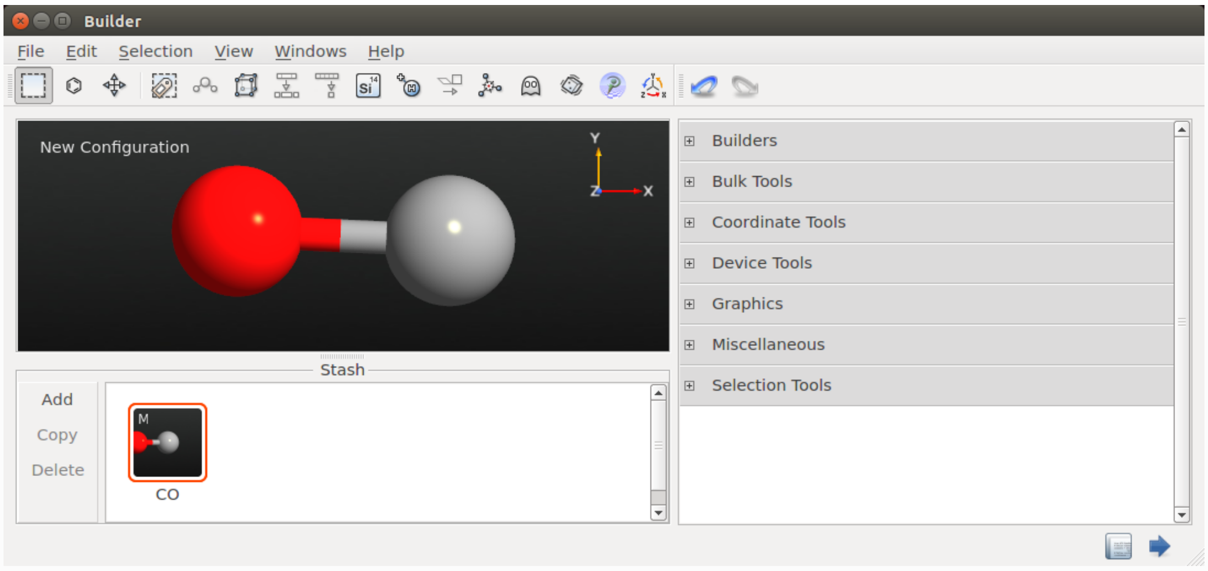
Relax the CO molecule

In order to calculate the CO adsorption energy on Pd(100) you also need to relax the isolated CO molecule. We can obtain it following the next steps:

- go to the **Builder** and add a new configuration using Add ‣ New Configuration;
- click the **Molecular Builder** tool and click Fragments ‣ Carbon monoxide in the panel that opens up;



- next, click the hydrogen atom in the `New Configuration` Stash item to substitute it for the CO fragment, close the Molecular Builder window, and rename the Stash item to `CO`.



Tip

For more details about how to use the **Molecular Builder**, you can check out this tutorial: Molecular builder.

Now you just need to relax the CO atomic coordinates and compute the total energy. Send the structure to the **Script Generator** and add the **New Calculator**, **OptimizeGeometry** and **TotalEnergy** blocks. Enter `CO.hdf5` for the default output file name, and then edit the blocks a bit:

- **New Calculator**: Choose the GGA-PBE functional;
- **OptimizeGeometry**: You may want to save the trajectory or decrease the force tolerance, but it's not mandatory;

Save the script as `CO.py` and run the calculation – it should be very fast. The script is also available for download: CO.py.

You will find that the C–O bond length relaxes to 1.143 Å, which matches experiments very well.

Adsorption energy

You are now ready to calculate the CO/Pd(100) adsorption energy at a full monolayer coverage, ΔE, which is of course given by total energy differences:

$$\Delta E = E_{\mathrm{products}} - E_{\mathrm{reactants}} = E_{\mathrm{Pd(100)/CO}} - E_{\mathrm{Pd(100)}} - E_{\mathrm{CO}}$$

You can use the **Text Representation** plugin to see all three total energies and then calculate ΔE, or you can use a script to do it: adsorption_energy.py.

The adsorption energy, calculated using PBE and the FHI pseudopotentials with a DZP basis set, is ΔE = –1.97 eV. However, this number is affected by the so-called basis set superposition error, so you should proceed to the next section to correct for this.

Counterpoise correction

The basis set superposition error (BSSE) is due to the incompleteness of the LCAO basis set, and can have a significant impact on energy differences between different sub-systems. As explained in a tutorial (DFT-D and basis-set superposition error), the superposition of Pd and CO basis sets in the CO/Pd(100) system can give rise to an artificial lowering of the total energy because the Pd(100) and CO sub-systems can “borrow” basis functions from each other. The result is a too large adsorption energy.

The standard approach to neutralize the BSSE is to apply a so-called counterpoise correction. In

QuantumATK, this is done using the `counterpoiseCorrected` .

You should therefore calculate the counterpoise (CP) corrected total energy for the CO/Pd(100) system in order to compute the CP corrected adsorption energy:

$$\Delta E^{\mathrm{CP}} = E^{\mathrm{CP}}_{\mathrm{Pd(100)/CO}} - E_{\mathrm{Pd(100)}} - E_{\mathrm{CO}}$$

Use the script shown below (can be downloadad here: Pd_CO_cp.py). The script reads in the previously relaxed CO/Pd(100) configuration and the calculator that was used, and creates a new calculator that applies the CP correction. The configuration is then relaxed and the total energy is calculated.

Run the script using the Job Manager or in a Terminal. It should perform 4 very small relaxation steps, and finish within 10 minutes. The CP correction will increase the total energy of the CO/Pd(100) system, resulting in an adsorption energy of
ΔE^{CP} = −1.68 eV.

```
# -------------------------------------------------------------
# Bulk Configuration
# -------------------------------------------------------------

bulk_configuration = nlread('Pd100_CO.nc', BulkConfiguration)[-1]

# Add tags
bulk_configuration.addTags('CO',          [4, 5])
bulk_configuration.addTags('Pd',          [0, 1, 2, 3])
bulk_configuration.addTags('Selection 0', [0, 1])

# -------------------------------------------------------------
# Calculator
# -------------------------------------------------------------

# Get the calculator settings from non-BSSE calculation.
calculator = bulk_configuration.calculator()
basis_set = calculator.basisSet()
exchange_correlation = calculator.exchangeCorrelation()
numerical_accuracy_parameters = calculator.numericalAccuracyParameters()
poisson_solver = calculator.poissonSolver()

# Create BSSE calculator.
bsse_calculator = counterpoiseCorrected(LCAOCalculator, ["CO", "Pd"])
calculator = bsse_calculator(
    basis_set=basis_set,
    exchange_correlation=exchange_correlation,
    numerical_accuracy_parameters=numerical_accuracy_parameters,
    poisson_solver=poisson_solver,
    )

bulk_configuration.setCalculator(calculator)
nlprint(bulk_configuration)
bulk_configuration.update()
nlsave('Pd100_CO_cp.nc', bulk_configuration)

# -------------------------------------------------------------
# Optimize Geometry
# -------------------------------------------------------------
constraints = [0, 1]

bulk_configuration = OptimizeGeometry(
        bulk_configuration,
        max_forces=0.05*eV/Ang,
        max_steps=200,
        max_step_length=0.2*Ang,
        constraints=constraints,
        trajectory_filename='Pd100_CO_cp.nc',
        disable_stress=True,
        optimizer_method=LBFGS(),
        )
nlsave('Pd100_CO_cp.nc', bulk_configuration)
nlprint(bulk_configuration)

# -------------------------------------------------------------
# Total Energy
# -------------------------------------------------------------
total_energy = TotalEnergy(bulk_configuration)
nlsave('Pd100_CO_cp.nc', total_energy)
nlprint(total_energy)
```

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