



Laboratoire
de Physique & Chimie
des Nano-Objets



tools4VASP

Quick tutorial

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Example 1: Vibrational and Thermochemical properties of Ru₃CO₁₂

folder Vibrational-and-ThermochemicalProperties/Ru3CO12/Ru3CO12-RefCalculations

1. Geometry optimization in Ru3CO12/

2. Vibrational calculation

```
cpVASP Ru3CO12 Ru3CO12-VIB_2CO 1
cd Ru3CO12-VIB_2CO
```

setup the frequency calculation in the INCAR file

```
(IBRION=5; NFREE = 2; NSW = 1; POTIM=0.0005; ediff=1.e-7)
```

edit and save a SELECTCAR file to calculate only two CO vibrational modes (1 axial CO and 1 in-plane CO; the only purpose of this example is to exemplify a selective dynamics calculation) by running the command (SELECTCAR is the default):

```
selvib4VASP -POS POSCAR
```

then:



```
diff POSCAR POSCARv #just to see the differences between the two POSCARs
cp POSCARv POSCAR
sbatch VASP.runjob
```

when the calculation is finished:

```
vibVASP
```

check the content of the freq.dat file

(in the example folder, the assignments in the right column were written afterwards)

visualize the modes.xyz file with a molecular viewer (jmol is strongly recommended; keyword = *vibration on*. Then use the arrows   to navigate between modes)

3. Doing thermochemistry with VASP

(it is now necessary to calculate the vibrations of interest, i.e. all normal modes in this small cluster)

```
cpVASP Ru3CO12 Ru3CO12-VIB4Thermo 1
cd Ru3CO12-VIB4Thermo
```

setup the frequency calculation in the INCAR file

```
(IBRION=5; NFREE = 2; NSW = 1; POTIM=0.0005; ediff=1.e-7)
```

edit and save a SELECTCAR file to calculate all vibrational modes by running the command:

```
selvib4VASP -POS POSCAR
```

then:

```
cp POSCARv POSCAR
sbatch VASP.runjob
```

when the calculation is finished:

```
vibVASP
```

check the content of the freq.dat file

visualize the modes.xyz file with a molecular viewer, just to check that everything seems OK

and then:

```
pos2xyz.pl CONTCAR; ThermoWithVASP
```

4. Hands-on tutorial

Start at step 2 in the folder

Vibrational-and-ThermochemicalProperties/Ru3CO12/Ru3CO12-DoItYourself

Example 2: Manipulation of unitcells

folder ManipCell/

Run the ManipCell-Pt.sh (Pt-111 slab), ManipCell-C.sh (graphene sheet) and ManipCell-cluster.sh (Ru₁₃ cluster with surface ligands) shell commands.

They all call the ManipCell tool, with different options.

► **Graphene sheet:** ManipCell-C.sh makes a 3x3 unitcell, shifts the graphene sheet along *c* and finally changes the *c* parameter to 20 Å:

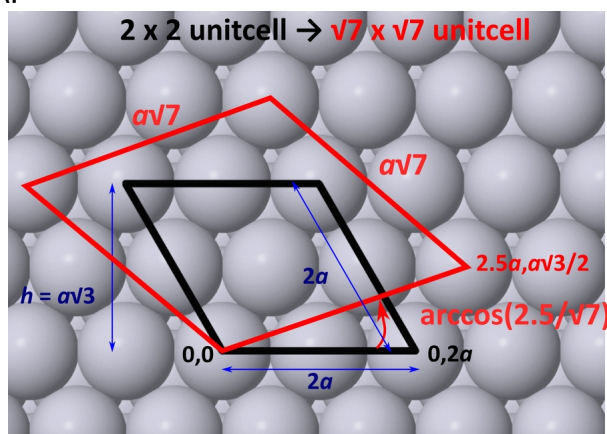
-fa & -fb: makes a 3x3 supercell

-shc: shifts the graphene sheet to 3 ang (original *c* x 0.11778)

-c adjust *c* to 20 ang

ManipCell -POS CONTCAR-murnfit-PBE-D3 -fa 3.0 -fb 3.0 -shc 0.11778 -c 20.0

► **Pt-111 Slab:** ManipCell-Pt.sh rotates a 2x2 Pt-111 unitcell to make a $\sqrt{7} \times \sqrt{7}$ unitcell, and also sets the *c* parameter to 30 Å:

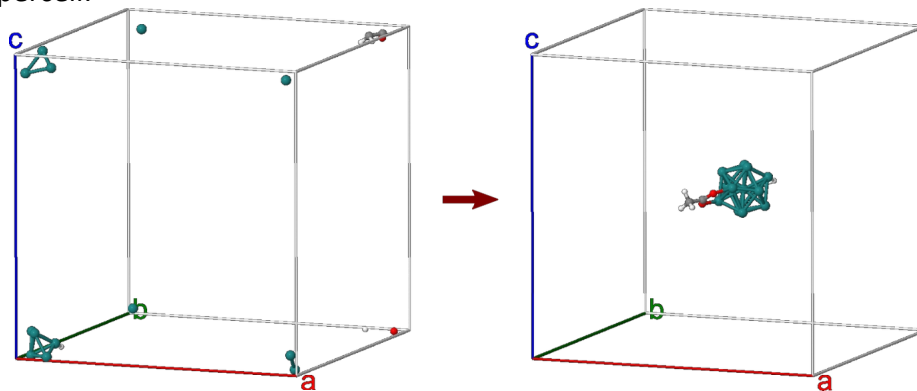


angle = arccos(2.5/sqrt(7))

fa = fb = sqrt(7)/2 (initial slab = 2x2)

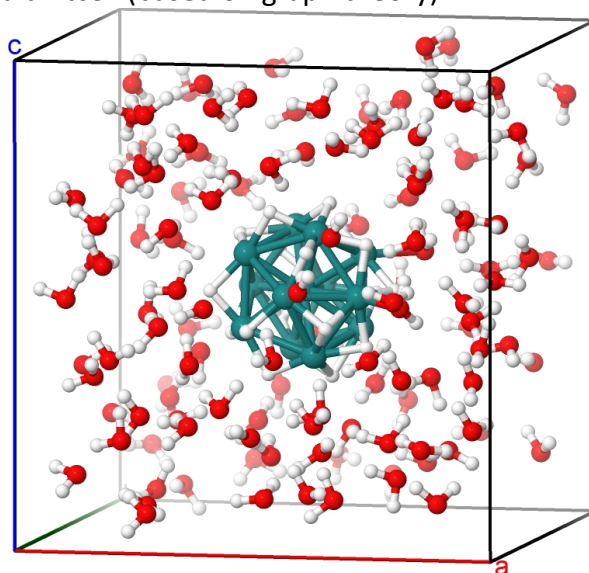
ManipCell -POS CONTCAR_Pt_111_PBE_D3-ShiftedC -a 19.10660535086911 -fa 1.322875655532295 -fb 1.322875655532295 -c 30.0

► **Ru13C012 cluster.** ManipCell-cluster.sh shifts a molecule centered at 0 toward the center of the *axbxc* supercell:



ManipCell -POS CONTCAR-Ru13cluster -sha 0.5 -shb 0.5 -shc 0.5

► **Ru13H17-solv-GA-option folder.** ManipCell-cluster.sh counts the total number non-covalently bound species in a unitcell (based on graph theory).



ManipCell -GA

returns 125 and two files (fgraph.dat and fgraphJ.dat) that could be useful for further analysis.

Example 3: Thermochemical properties, comparison with Gaussian

folder `Vibrational-and-ThermochemicalProperties/CompareWithGaussian/`

See README and then run `ThermoWithVASP` in `test-Benzene` and `test-TransitionState`. Check that you find the same as the original `ThermoWithVASP.log.org` outputs. Compare also with Gaussian logs.

Example 4: Analysis of the electronic structure. Selection of the LOBSTER outputs with **selectLOBSTER**

folder `selectLOBSTER/Ru13IC-Ethanoate-H/`

▶ **General pDOS and pCOHP analysis.**

Command: `selectLOBSTER`

▶ **Search for the upper-part of the d-band.**

Command: `selectLOBSTER -F selectLOBSTER-Emax-dband.in`

▶ **Calculation of atomic d-band centers.**

Command: `selectLOBSTER -F selectLOBSTER-dbc.in`

Bibliography

- VASP: [1, 2]
- LOBSTER: [3-7]
- COOP, DOS, slabs and quantum chemistry within periodic boundary conditions: [8,9]
- Articles of the MPC group with applications of the tools4VASP tools: [10-17]

References

- 1 G. Kresse, J. Fürthmüller, Efficiency of ab initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set, *Comput. Mater. Sci.* **1996**, 6, 15-50, ([https://dx.doi.org/10.1016/0927-0256\(96\)00008-0](https://dx.doi.org/10.1016/0927-0256(96)00008-0)).
- 2 G. Kresse, J. Fürthmüller, Efficient Iterative Schemes for ab initio Total-Energy Calculations Using a Plane-Wave Basis Set, *Phys. Rev. B* **1996**, 54, 11169-11186, (<https://dx.doi.org/10.1103/PhysRevB.54.11169>).
- 3 V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, Crystal Orbital Hamilton Population (COHP) Analysis As Projected from Plane-Wave Basis Sets, *J. Phys. Chem. A* **2011**, 115, 5461-5466, (<https://dx.doi.org/10.1021/jp202489s>).
- 4 S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, Analytic projection from plane-wave and PAW wavefunctions and application to chemical-bonding analysis in solids, *J. Comp. Chem.* **2013**, 34, 2557-2567, (<https://dx.doi.org/10.1002/jcc.23424>).
- 5 M. Esser, V. L. Deringer, M. Wuttig, R. Dronskowski, Orbital mixing in solids as a descriptor for materials mapping, *Solid State Commun.* **2015**, 203, 31-34, (<https://dx.doi.org/10.1016/j.ssc.2014.11.008>).
- 6 S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, LOBSTER: A tool to extract chemical bonding from plane-wave based DFT, *J. Comp. Chem.* **2016**, 37, 1030-1035, (<https://dx.doi.org/10.1002/jcc.24300>).
- 7 S. Maintz, M. Esser, R. Dronskowski, Efficient Rotation of Local Basis Functions Using Real Spherical Harmonics, *Acta Phys. Pol. B* **2016**, 47, 1165, (<https://dx.doi.org/10.5506/aphyspolb.47.1165>).
- 8 R. Hoffmann, How Chemistry and Physics Meet in the Solid State, *Angew. Chem., Int. ed. Eng.* 1987, 26, 846-878, (<https://dx.doi.org/10.1002/anie.198708461>).
- 9 Hoffmann, R., **1988**. *Solids And Surfaces. A Chemist's View of Bonding in Extended Structures*. Wiley-VCH, Weinheim.

- 10 L. Cusinato, L. M. Martinez-Prieto, B. Chaudret, I. del Rosal, R. Poteau, Theoretical characterization of the surface composition of ruthenium nanoparticles in equilibrium with syngas, *Nanoscale* **2016**, *8*, 10974-10992, (<https://dx.doi.org/10.1039/C6NR01191H>).
- 11 L. Cusinato, I. del Rosal, R. Poteau, Shape, electronic structure and steric effects of organometallic nanocatalysts: relevant tools to improve the synergy between theory and experiments, *Dalton Trans.* **2017**, *46*, 378-395, (<https://dx.doi.org/10.1039/C6DT04207D>).
- 12 J. Creus, S. Drouet, S. Suriñach, P. Lecante, V. Collière, R. Poteau, K. Philippot, J. García-Antón, X. Sala, Ligand-capped Ru Nanoparticles as Efficient Electrocatalyst for the Hydrogen Evolution Reaction, *ACS Catal.* **2018**, *8*, 11094-11102, (<https://dx.doi.org/10.1021/acscatal.8b03053>).
- 13 I. C. Gerber, R. Poteau, Critical assessment of charge transfer estimates in non-covalent graphene doping, *Theo. Chem. Acc.* **2018**, *137*, 156, (<https://dx.doi.org/10.1007/s00214-018-2365-2>).
- 14 R. González Gómez, I. del Rosal, K. Philippot, R. Poteau, DFT calculations in periodic boundary conditions of gas-phase acidities and of transition-metal anionic clusters: case study with carboxylate-stabilized ruthenium clusters, *Theor. Chem. Acc.* **2019**, *138*, 95, (<https://dx.doi.org/10.1007/s00214-019-2484-4>).
- 15 R. González-Gómez, L. Cusinato, C. Bijani, Y. Coppel, P. Lecante, C. Amiens, I. del Rosal, K. Philippot, R. Poteau, Carboxylic acid-capped ruthenium nanoparticles: experimental and theoretical case study with ethanoic acid, *Nanoscale* **2019**, *11*, 9392-9409, (<https://dx.doi.org/10.1039/c9nr00391f>).
- 16 E. Martin Morales, Y. Coppel, P. Lecante, I. del Rosal, R. Poteau, J. Esvan, P. Sutra, K. Philippot, A. Igau, When organophosphorus ruthenium complexes covalently bind to ruthenium nanoparticles to form nanoscale hybrid materials, *Chem. Commun.* **2020**, *56*, 4059-4062, (<https://dx.doi.org/10.1039/D0CC00442A>).
- 17 del Rosal, I. & Poteau, R. (2021). *Sabatier principle and surface properties of small Ruthenium nanoparticles and clusters. Case studies*. In: Philippot, K. & Roucoux, A. (Ed.), *Nanoparticles in Catalysis: Advances in Synthesis and Applications*, Wiley-VCH.