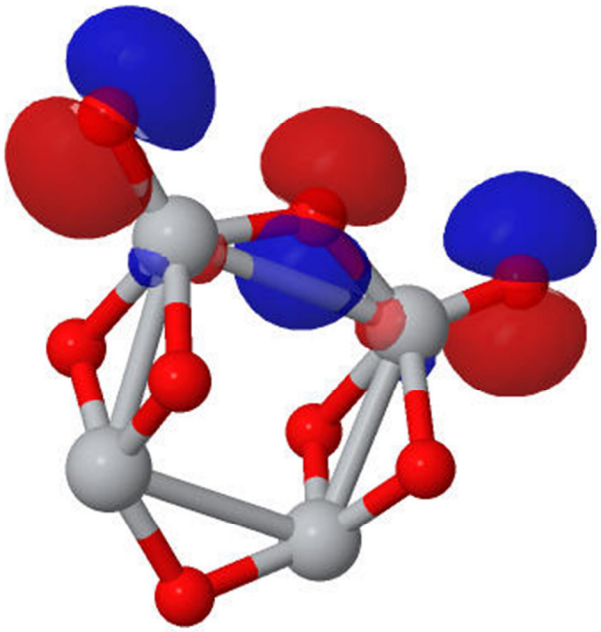
Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules

Los Angeles, July 21 - August 1, 2014



Tutorial 7: Integrating Concepts- Cluster Structure Prediction and Spectroscopy

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Introduction

The aim of this tutorial is to integrate some of the concepts learned in previous tutorials to solve the problem of assigning structures to spectroscopic data for TiO_2 clusters. To this end we will combine configuration space exploration by basin hopping with theoretical spectroscopy using GW and compare the results to experiment.

Atomic clusters, comprising up to a few tens of atoms, are appealing for applications in catalysis. Even noble metals, such as gold and platinum are highly reactive as atomic clusters. The electronic properties and reactivity of clusters depend strongly on their size and structure and may potentially be tailored for specific reactions.

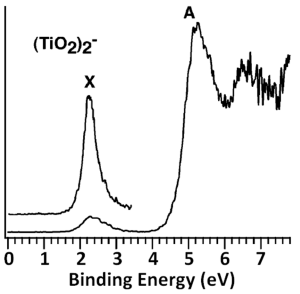

Figure 1: PES of $(TiO_2)_2^-$, adapted from Ref. 1.

Unlike molecules and crystalline solids, atomic clusters do not have a fixed structure. A cluster with a given stoichiometry may have many different isomers. The structure of clusters cannot be measured directly by x-ray diffraction due to their lack of crystallinity. Mass selected clusters are often characterized indirectly by spectroscopic techniques, such as photoemission spectroscopy (PES), IR/ Raman spectroscopy, and x-ray photoemission spectroscopy (XPS). Structures are assigned by comparing the measured spectra to simulated spectra of different structures.

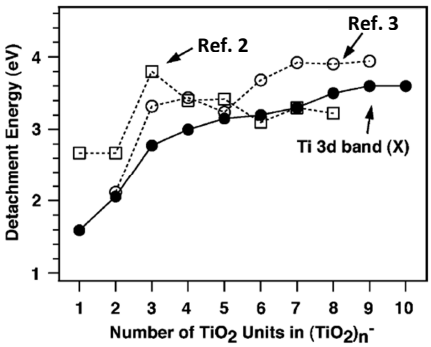

Figure 2: Measured electron detachment energies of $(TiO_2)_n^-$ compared with two DFT calculations, adapted from Ref. 1.

In Ref. 1, the vertical electron affinities (VEAs) and vertical detachment energies (VDEs) of $(TiO_2)_n$ clusters with n=1-10 were measured by PES for singly charged anions. For example, Figure 1 shows the PES of $(TiO_2)_2^-$. The structures of these clusters were not assigned, as the results of two earlier calculations[2-3] were not in agreement with experiment, as shown in Figure 2.

Simulations of clusters typically start with configuration space exploration to search for stable isomers.[4-5] Several global optimization methods are in use, combined with force fields or DFT simulations. These include, for example: random sampling,[6] simulated annealing,[7-8] parallel tempering (replica exchange),[9] basin hopping,[10-11] genetic algorithms,[12-13] and swarm algorithms.[14-15]

It is important to perform an unbiased search, rather than guess structures, because intuition may be misleading. For example, in 2007 Szwacki *et al*. proposed the existence of a B_{80} fullerene.[16] The proposed structure was based on intuition. Later, others performed global optimization by simulated annealing[8] and basin hopping[11] and demonstrated that the Szwacki fullerene was in fact quite far from the global minimum structure and thus unlikely to exist. The more stable structures of B_{80}, shown in Figure 3, have a centered icosahedron motif.

In Ref. 2 a force-field based genetic algorithm was used for global optimization and the DFT eigenvalue of the lowest unoccupied molecular orbital (LUMO) was calculated with the B97-2 hybrid functional.[17] In Ref. 3 structures were proposed based on intuition and electron

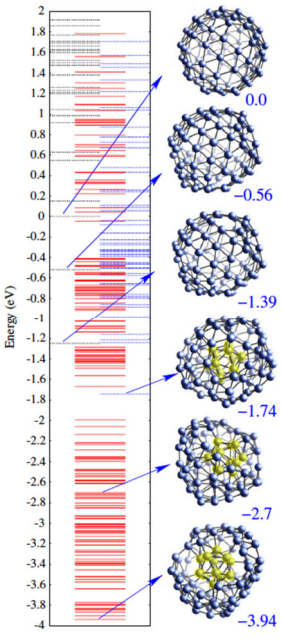

Figure 3: Relative energies of B_{80} isomers. The Szwacki fullerene is set to zero. Reproduced from Ref. 11.

detachment energies were calculated from the total energy difference between an anion and a neutral (ΔSCF) calculated with the B3LYP[18] hybrid functional. In both cases, either the structures are wrong, or the VDEs are wrong, or both. Here, we will take $(TiO_2)_2$ as a case study and follow the procedure of Ref. 19. We will use basin hopping (BH) based on the PBE[20-21] functional to search for low-lying isomers and then calculate electron affinities and vertical detachment energies using G_0W_0 based on a PBE0[22] hybrid starting point.

Part I: Configuration Space Exploration with Basin Hopping (1:30 hr)

In this part of the tutorial the "Effernir" basin hopping utility will be used to find low-lying isomers of a $(TiO_2)_2$ cluster. Effernir is described and benchmarked in Ref. 10. Typically, it is effective for global optimization of clusters with up to 25 atoms.

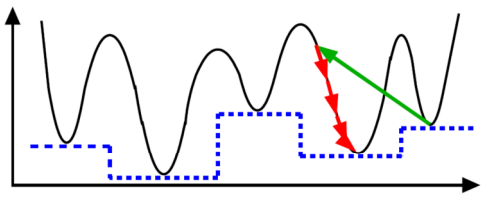

Figure 4: Illustration of the real (solid black line) and transformed (dashed blue line) potential energy surface and of a basin hopping step, reproduced from Ref. 10.

The potential energy surface (PES) is explored by performing consecutive jumps from one local minimum to another. In each BH step the positions of the atoms in the cluster are randomly perturbed. Then, a local geometry optimization is performed to bring the system into a local minimum, as illustrated in Figure 4. This transforms the PES into a series of plateaus, representing basins of attraction corresponding to the set of configurations that relax to a given minimum.

The number of local minima increases rapidly with cluster size, requiring an increasing number of BH steps for sufficient sampling of the PES. Because the jumps between basins are based on a random change of the coordinates, each BH trajectory (i.e., a series of BH steps) will be different than the other. Starting several trajectories from different structures increases the likelihood of sampling different regions of the PES.

Effernir is distributed with the FHI-aims package. The source files may be found in:

utilities/Cluster_structure_prediction

Best practices for conducting a comprehensive search with Effernir:

- Run 3-6 trajectories, depending on the cluster size.
- Start the trajectories from different structures.
- Run each trajectory for 100-1000 steps, depending on the cluster size.
- If many of the structures are found repeatedly in more than one trajectory, this is an indication that a reasonably good coverage of the potential energy surface has been achieved.
- For efficiency, run Effernir with light/t1 settings and then post-relax and re-rank a smaller number of low-lying structures with tight/t2 settings.

For the purpose of this exercise, we will run only one trajectory with 50 steps.

Input files required by Effernir:

The following files are found in:

$HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/BH/

1. **control.in**
   This is the usual control.in file with settings for running FHI-aims. It is set up to run calculations with the PBE functional and light/t1 settings.

2. **geometry.in.basic**
   This is the initial structure for the basin hopping trajectory.

3. **control.in.opt**
   This file contains the settings for Effernir. A detailed explanation of all the options is provided in:

   Cluster_structure_prediction/some_documentation/control.in.opt.explained_by_ralf

   A copy of this file is provided in Appendix I. Parameters to pay attention to:

   ```
   bh_max_loop 50
   ```

   The number of BH steps is set to 50

   ```
   atomic_energy O -0.204240941241283E+04 8
   atomic_energy Ti -0.232269265656541E+05 22
   ```

   The energies of free O and Ti atoms were pre-calculated with the same functional and numerical settings (light/t1) as in the control.in for the BH run. These are the reference energies for calculating the cohesive energies of the isomers found in BH.

4. **bh_optimization.pl**
   This is a wrapper Perl script that runs the BH optimization. It has two parts that need to be modified for your local machine:
   (i) The paths to the FHI-aims and Effernir executables. In this case, they are set to:

   ```
   $EXE_AIMS = '/usr/local/gss2014/bin/aims.060914.scalapack.mpi.x' ;
   $EXE_BH = '/usr/local/gss2014/bin/effernir.250209.x' ;

   $exe_aims_local = '/usr/local/gss2014/bin/aims.060914.scalapack.mpi.x';
   $exe_bh_local = '/usr/local/gss2014/bin/effernir.250209.x';
   ```

   (ii) The command for running FHI-aims (line 101). In this case, it's set to:

   ```
   system "mpirun -np 4 $exe_aims_local > $out_file 2>&1" ;
   ```

<u>Step 1:</u> BH optimization

1. Copy the input files into your work directory:

   cp –r $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/BH ./ ↵

2. Start the BH optimization with the command:

   perl bh_optimization.pl & ↵

   The BH run should take about an hour. While it's running the script may produce the error message "cp: cannot stat `restart.dat': No such file or directory". This is completely harmless.

3. When the BH run is done, compare your bh_analysis.dat file (see explanation of output files below) to your neighbor's. You'll see that they are different because of the random BH moves.

Output files of Effernir:

Effernir outputs many logs and files, most of which you can delete. The important ones are:

1. **geometry.in.#### and structure####.xyz** (#### stands for a 4-digit number)
   These are all the isomers found in the search, numbered in order of increasing energy in both geometry.in and xyz formats.

2. **bh_analysis**
   This is a summary of the isomers found in the search, ranked by increasing energy:

```
energy of minimum [eV] (total energy, diff to E_0, dissociation energy), hist_in, hist_out, checksum, deviation, min, max\
, compact, found in loop
#    1   -9132.411806   0.000000 -28.496676     18      0     18   0.000202   -9132.411860   -9132.411658   3.2032    2
#    2   -9132.364198   0.047609 -28.449068     19      1     37   0.000219   -9132.364350   -9132.364132   2.7425    1
#    3   -9132.311789   0.100018 -28.396658      2      0     39   0.000003   -9132.311792   -9132.311789   2.4643   30
#    4   -9132.311187   0.100620 -28.396056      1      0     40   0.000000   -9132.311187   -9132.311187   2.4663   39
#    5   -9131.642412   0.769395 -27.727281      1      0     41   0.000000   -9131.642412   -9131.642412   2.1706    3
#    6   -9131.434524   0.977282 -27.519394      1      0     42   0.000000   -9131.434524   -9131.434524   3.1633   28
 number of all occured minima:     42
 average compact ratio:   2.9165
```

   The first column (after the isomer number) is the total energy; the second is the relative energy; the third is the cohesive energy; the fourth is how many times each isomer was found in the search; the fifth has 1 for the initial structure and 0 for all other structures; the second column from the right is the compactness index, which helps determine whether two structures are identical (in this case, structures 3 and 4 may be identical because their energies and compactness ratios are very similar).

3. **bh_log.out**
   If the basin hopping run didn't proceed to completion (e.g., because the calculation timed out or crashed) the bh_analysis information of the last step can be extracted from bh_log.out

Step 2: Re-optimization and final ranking with tight/t2 settings

1. In your work directory, create directories for the three structures with the lowest energy found in your search. Name the directories, e.g., "structure1".

   ```
   mkdir structure1 ↵
   ```

2. Copy the corresponding geometry.in.000# files into: structure#/geometry.in

   ```
   cp BH/geometry.in.0001 structure1/. ↵
   ```

3. Copy the control.in file for relaxation with tight/t2 settings for O and Ti:

   ```
   cp $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/control.in.rlx
   structure#/control.in ↵
   ```

4. In each directory, run the re-optimization:

   ```
   mpirun -np 4 aims.x > structure#_PBE_t2.out & ↵
   ```

5. When all three calculations are done (they should take 2-3 minute each) extract the final total energies from the output files by:

   ```
   tail -200 structure#/structure#_PBE_t2.out | grep "Total energy uncorrected" ↵
   ```

6. Calculate the final relative energies of the three structures. Set the most stable structure to zero. Structures 2 and 3 should be 0.27 and 0.57 eV above structure 1, respectively.

Step 3: Visualization with Jmol

1. Start Jmol with the command:

   ```
   jmol & ↵
   ```

2. From the File menu, open the script console
3. Jmol can visualize both geometry.in and xyz files. To visualize a structure, type in the console (see Figure 5):

   ```
   load /home/<user_name>/TiO2_2/structure#/geometry.in ↵
   ```

4. Select: File -> Export -> Export Image… and save the image in your favorite format
5. Tip: to change the background color, type in the console the command:

   ```
   background white ↵
   ```

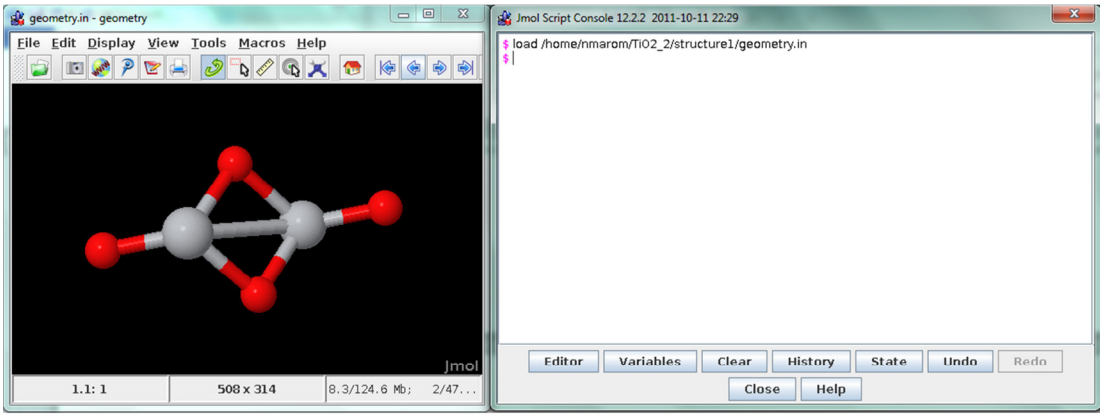

Figure 5: Visualizing structures with Jmol

Part II: Theoretical Spectroscopy with G_0W_0@PBE0 (1:45 hr)

Now that we have obtained the geometries and relative energies of the three structures we will use G_0W_0@PBE0 to calculate accurate electron affinities and vertical detachment energies.

GW, where G is the one-particle Green's function and W is the screened Coulomb interaction,[23-24] is the method of choice for describing charged excitations, i.e. the addition or removal of an electron from the system. Properties associated with charged excitations include: ionization potentials (IP), electron affinities, fundamental gaps (IP-EA), defect/dopant charge transition levels, and energy level alignment at interfaces. Unlike DFT, GW accounts for the electronic response, i.e., the relaxation of the energy levels following the addition or removal of an electron. This is a dynamic correlation effect, which is absent from DFT.

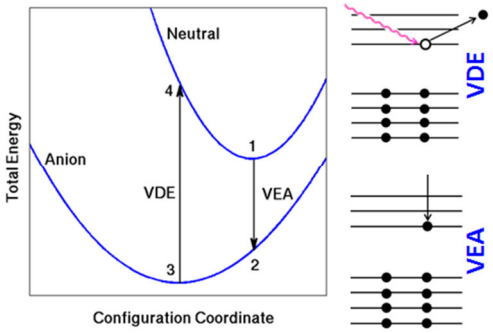

Figure 6: Illustrations of the electronic processes corresponding to the vertical electron affinity (VEA) and vertical detachment energy (VDE)

To reduce the computational cost GW calculations are typically performed within the G_0W_0 approximation.[25] The quasiparticle excitation energies, ε_i^{QP}, are obtained non-self-consistently as first order perturbative corrections to the Kohn-Sham eigenvalues from a DFT calculation, ε_i^{KS} by solving the linearized quasiparticle equation:

$$\varepsilon_i^{QP} = \varepsilon_i^{KS} + \langle \varphi_i | \Sigma(\varepsilon_i^{QP}) - v_{xc}^{KS} | \varphi_i \rangle \quad (1)$$

The difference between the self-energy, $\Sigma = iGW$, and the exchange correlation potential, v_{xc}^{KS}, is treated as a small perturbation. The Kohn-Sham orbitals, φ_i, are used to calculate G_0 and W_0. It is assumed that the Kohn-Sham orbitals are a good approximation to the Dyson orbitals. This assumption is often, but not always, valid.

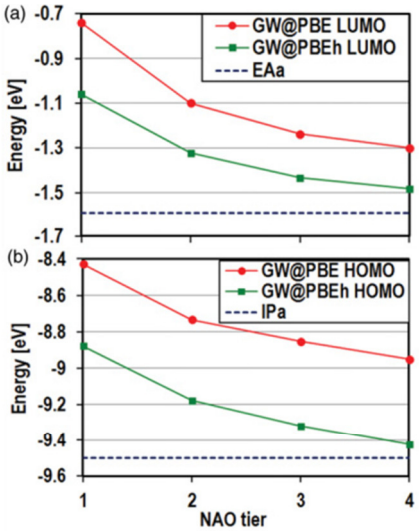

Figure 7: Convergence of G_0W_0 calculations for a) the EA and b) the IP of a TiO_2 molecule, reproduced from Ref. 26.

In the standard implementation of G_0W_0 the expressions for

the Green's function and the self-energy contain infinite sums over states. Therefore, a large number of unoccupied states are required to achieve convergence. Figure 7 shows an example for the convergence of G_0W_0 calculations with the FHI-aims NAO basis sets for a TiO_2 molecule.[26] Convergence to ~0.05 eV is typically achieved at the tier 4 level.

Because the G_0W_0 scheme is non-self-consistent the results depend strongly on the underlying mean-field calculation. Hybrid functionals, such as PBE0 (AKA, PBEh), often provide a better starting point for G_0W_0 than PBE. Figure 8 shows a comparison of DFT and G_0W_0 spectra of TiO_2^- to the PES from Ref. 1. The DFT spectra are shifted to align the HOMO peak with the VDE, calculated from the total energy difference between the anion and neutral species. G_0W_0 spectra are not shifted because their results correspond directly to absolute ionization energies. G_0W_0@PBE0 is in better agreement with experiment than G_0W_0@PBE. Therefore, we will now use it to calculate accurate VEAs and VDEs for the structures found in BH.

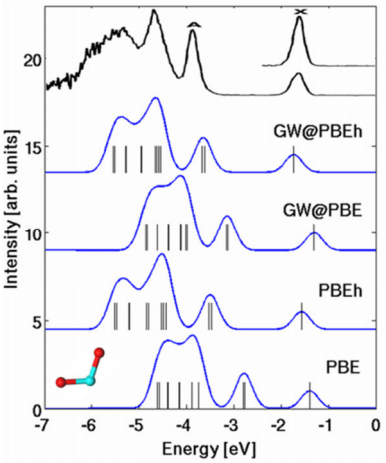

Figure 8: Comparison of DFT and G_0W_0 spectra of TiO_2^- to PES, reproduced from Ref. 26.

<u>Step 1:</u> G_0W_0@PBE0 calculations

For each structure:

1. Update the geometry to the relaxed tight/t2 geometry:

   cp geometry.in.next_step geometry.in ↵

2. The control.in.gw file in:
   $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/
   is set up for running G_0W_0 calculations starting from the PBE0 hybrid functional. Note the flags:
   xc pbe0
   qpe_calc gw
   Note also that a large number of basis functions is required to converge G_0W_0 calculations. This is why we use the largest available *tier 4* NAO basis sets.
   Copy this file into your work directory:

   cp $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/control.in.gw structure#/control.in ↵

3. Run the G_0W_0@PBE0 calculation for each structure:

   mpirun -np 4 aims.x > structure#_GW_PBE0_t4.out & ↵

   These calculations should take about 35 minutes each. Please run them one by one.
4. To follow the progress of a calculation, use:
   tail –f structure#_GW_PBE0_t4.out ↵

<u>Step 2:</u> Comparison to experiment and structure assignment

When the G_0W_0@PBE0 calculations are done, extract the vertical electron affinities (VEA) from the output files:

GW quasi-particle energy levels

e_qp = e_gs + e_x^ex - e_xc^gs + e_c^nloc

state	occ_num	e_gs	e_x^ex	e_xc^gs	e_c^nloc	e_qp
1	2.0000	-4904.6282	-301.1403	-187.0160	5.5332	-5013.2193
2	2.0000	-4904.6279	-301.1407	-187.0165	5.5331	-5013.2190
3	2.0000	-550.8390	-102.3091	-63.3702	12.1985	-577.5794
4	2.0000	-550.8389	-102.3038	-63.3660	12.1979	-577.5788
5	2.0000	-522.9115	-99.6625	-63.1704	8.7176	-550.6860
6	2.0000	-522.9114	-99.6625	-63.1707	8.7188	-550.6845
7	2.0000	-522.2954	-99.6804	-63.1725	8.6673	-550.1360
34	2.0000	-9.0568	-18.2211	-14.9100	1.5013	-10.8666
35	2.0000	-8.8108	-18.0038	-14.5463	1.6376	-10.6308
36	2.0000	-8.6202	-18.3152	-14.9490	1.6120	-10.3744
37	2.0000	-8.4449	-19.0357	-15.3865	1.8681	-10.2259
38	2.0000	-8.2450	-18.2538	-14.6856	1.8059	-10.0072
39	0.0000	-2.6998	-5.0600	-9.6997	-3.2764	-1.3364
40	0.0000	-2.5102	-4.5546	-9.0052	-3.1379	-1.1976
41	0.0000	-1.9481	-8.3893	-14.1456	-4.2346	-0.4264
42	0.0000	-1.8450	-7.3731	-12.7819	-3.9166	-0.3528

The VEA is equal in magnitude and opposite in sign to the GW quasiparticle energy of the lowest unoccupied molecular orbital (LUMO), highlighted in pink. This is process 1→2 in Fig. 6. In this case, the VEA is 1.34 eV.

The EA of $(TiO_2)_2$, measured by photoemission spectroscopy in Ref. 1 is 2.06 eV.

- What are the VEAs of the three structures you found in basin hopping?
- Which one is in closest agreement with experiment?
- Is it the global minimum structure?

It has been shown that experiments on mass-selected anions may select for isomers with a high electron affinity, rather than the global minimum structures.[19, 27]

Part III. Visualizing molecular orbitals

Now let's have a look at the frontier orbitals of the different structures and try to associate them with the electronic properties.

<u>Step 1:</u> Output orbital densities

The molecular orbitals are the eigenfunctions corresponding to the Kohn-Sham eigenvalues of a DFT calculation. FHI-aims can output the total electron density and orbital densities as "cube" files. This is a standard format for density information, where space is divided into small cubes called voxels (these are like 3D pixels) and the probability to find an electron is given for each voxel.

1. The control.in.cube file in:

   $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/

   is set up for outputting cube files of the total density, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These are calculated with tight/t2 settings and the PBE0 functional, such that they are consistent with the quasiparticle energies of the G_0W_0@PBE0 calculation. Note the following flags:

   ```
   output cube total_density
   cube origin 0.0 0.0 0.0
   cube edge 51 0.2 0.0 0.0
   cube edge 51 0.0 0.2 0.0
   cube edge 51 0.0 0.0 0.2
   output cube eigenstate 38
   output cube eigenstate 39
   ```

   These control which densities to output and the parameters of the cube file:

   - Here, we're asking for the total density, the HOMO (eigenstate 38), and the LUMO (eigenstate 39).
   - The cube origin is the center of the cube. It should be close to the center of the coordinates specified in geometry.in.
   - The size of the cube is determined by the size of each voxel, in this case, 0.2 Å in each direction, times the number of voxels, in this case, 51 voxels in each direction. So, the cube volume is 10.2^3 $Å^3$.
   - Always make sure that the cube is large enough to contain your system with some extra room around the edges (because the electron density may extend around the atoms).
   - The resolution of the cube file is determined by the voxel size. A very dense cube file may be very large and require several MB of storage space.

   Copy the control.in.cube file into your work directory:

   ```
   cp $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/control.in.gw
   structure#/control.in ↵
   ```

2. Run the calculation:

   ```
   mpirun -np 4 aims.x > structure#_PBE0_t2_cube.out & ↵
   ```

Each calculation should take about 5 minutes. When it's done you will see the files: cube_001_total_density.cube, cube_002_eigenstate_00038_spin_1.cube, and cube_003_eigenstate_00039_spin_1.cube

Step 2: Visualization with Jmol

1. Start Jmol with the command:

   jmol & ↵

2. From the File menu, open the script console
3. To load the structural information from a cube file, type in the console:

   load /home/<user_name>/TiO2_2/structure#/<file_name>.cube ↵

4. To visualize the density, type in the console:

   isosurface sign cutoff 0.1
   "/home/<user_name>/TiO2_2/structure#/<file_name>.cube" translucent ↵

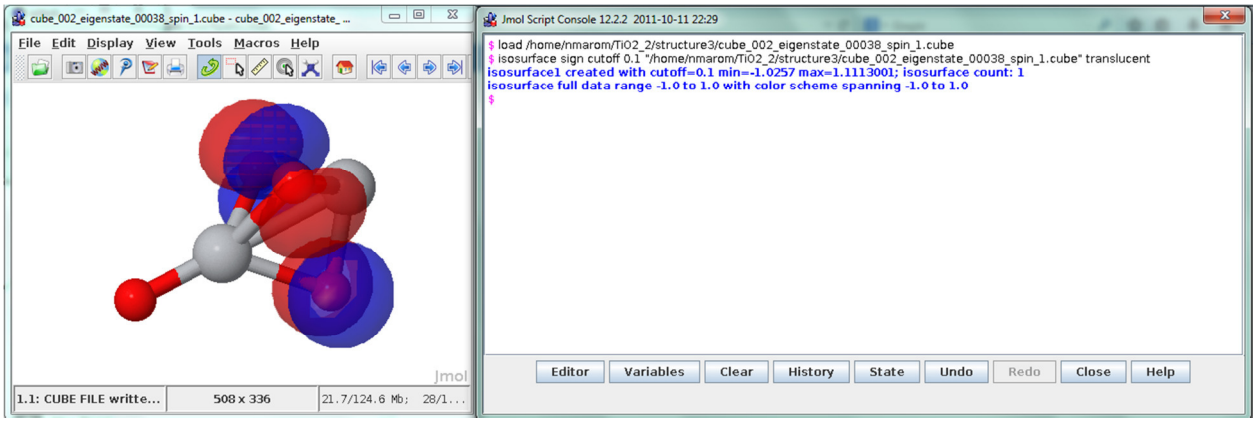

Figure 9: Visualizing molecular orbitals with Jmol

5. Select: File -> Export -> Export Image… and save the image in your favorite format
6. Repeat this for the other structures

Visualization can provide information on the chemical character of the frontier orbitals. We can see that the HOMO orbital of the clusters is derived from O 2p states (two lobes centered on O atoms), while the LUMO orbital is derived from Ti $3d_{z^2}$ states (two lobes and a ring, centered on the Ti atom). A high VEA of this cluster may be associated with the localization of the LUMO on a tri-coordinated Ti site, while a low VEA may be associated with delocalization of the LUMO on opposite ends of the cluster.[19]

Part IV. Optional: calculating the vertical detachment energy (1 hr)

Ref. 1 also reports vertical detachment energies (VDE) measured for $(TiO_2)_n$ anions. The VDE is equal in magnitude and opposite in sign to the GW quasiparticle energy of the highest occupied molecular orbital (HOMO). It corresponds to process 3→4 in Fig. 6. For the structure whose VEA is in closest agreement with experiment, we will also compare the VDE to experiment.

Step 1: Structural relaxation of the anion

The geometry of a charged species is not the same as that of a neutral species. Process 2→3 in Fig. 6 represents the structural relaxation following the addition of an electron.

1. The control.in.anion file in:
   $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/
   is set up for running geometry relaxation for an anion with the PBE functional and tight/t2 settings. Note the flags:
   ```
   spin            collinear
   default_initial_moment hund
   fixed_spin_moment  1.0
   charge          -1.0
   ```
   Copy this file into your work directory:

   ```
   cp $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/control.in.anion
   structure#/control.in ↵
   ```

2. Run the anion relaxation:

   ```
   mpirun -np 4 aims.x > structure#_anion_PBE_t2.out & ↵
   ```

   This calculation should take 2-5 minutes

Step 2: G_0W_0@PBE0 calculation

1. Update the geometry to the relaxed geometry of the anion:

   ```
   cp geometry.in.next_step geometry.in ↵
   ```

2. The control.in.gw.anion file in:
   $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/
   is set up for running G_0W_0 calculations for an anion, starting from the PBE0 hybrid functional with tier 4 NAO basis sets. Copy this file into your work directory:

   ```
   cp $HANDSON/hands-on-2014-tutorials/tutorial_7/TiO2_2/control.in.gw.anion
   structure#/control.in ↵
   ```

3. Run the G_0W_0@PBE0 calculation:

```
mpirun -np 4 aims.x > structure#_anion_GW_PBE0_t4.out & ↵
```

This calculation should take about 50 minutes.

<u>Step 3:</u> Comparison to experiment

When the G_0W_0@PBE0 calculation is done, extract the VDE from the output file. Note that because this is a spin-polarized calculation, the quasiparticle energies are given for the two spin channels separately:

GW quasi-particle energy levels

e_qp = e_gs + e_x^ex - e_xc^gs + e_c^nloc

state	occ_num	e_gs	e_x^ex	e_xc^gs	e_c^nloc	e_qp
			Spin Up			
1	1.0000	-4899.7460	-301.1571	-187.0239	5.7797	-5008.0996
2	1.0000	-4899.3527	-301.1402	-187.0149	5.5621	-5007.9159
3	1.0000	-546.1496	-102.3068	-63.3657	12.2472	-572.8435
4	1.0000	-545.5809	-102.4094	-63.4238	12.2804	-572.2861
35	1.0000	-3.6889	-19.5667	-15.8924	2.1727	-5.1905
36	1.0000	-3.6120	-17.8458	-14.3459	1.9411	-5.1708
37	1.0000	-3.6105	-17.8497	-14.3486	1.9425	-5.1691
38	1.0000	-2.7519	-18.7904	-15.0967	2.1780	-4.2676
39	1.0000	-0.7788	-13.5783	-11.5632	0.5354	-2.2586
40	0.0000	2.2134	-5.9467	-9.1848	-2.0649	3.3866
			Spin Down			
1	1.0000	-4899.7445	-301.1552	-187.0230	5.7793	-5008.0974
2	1.0000	-4899.3449	-301.1291	-187.0109	5.5610	-5007.9022
3	1.0000	-546.1457	-102.3023	-63.3636	12.2507	-572.8337
4	1.0000	-545.4063	-102.2255	-63.3238	12.3282	-571.9799
35	1.0000	-3.6079	-19.4345	-15.8734	2.0436	-5.1254
36	1.0000	-3.5912	-17.8649	-14.3810	1.9280	-5.1471
37	1.0000	-3.5896	-17.8665	-14.3817	1.9290	-5.1454
38	1.0000	-2.7876	-18.8682	-15.1201	2.2366	-4.2991
39	0.0000	2.7674	-3.6021	-7.5728	-3.0081	3.7300
40	0.0000	2.8515	-5.5948	-9.7581	-3.0058	4.0090

In this case, the HOMO, highlighted in pink, is in the spin up channel. Is it in agreement with the measured VDE of 2.27 eV for $(TiO_2)_2$?

In Ref. 19 the same combination of basin hopping and G_0W_0@PBE0 was used to show that $(TiO_2)_{2\text{-}10}$ isomers with high VEA are in better agreement with the results of Ref. 1 than the global minimum structures.

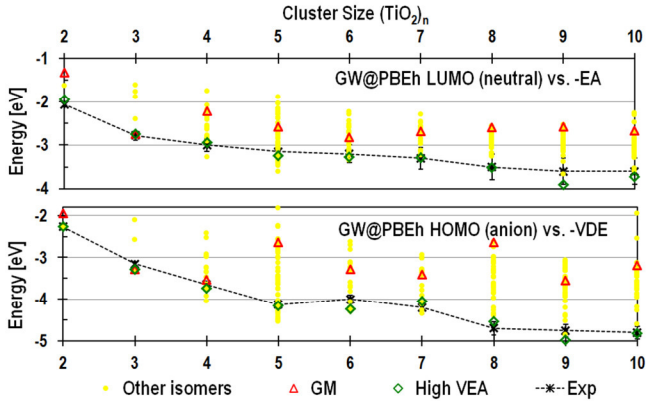

Figure 10: The VEAs and VDEs of $(TiO_2)_{2-10}$ clusters found by basin hopping in an energy window of 1.25 eV from the global minimum, compared to the measured values from Ref. 1. Isomers with high VEA are in better agreement with experiment than the global minimum structures, reproduced from Ref. 19.

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Appendix I: control.in.opt.explained_by_ralf

```
bh_max_loop     1000
# number of basin-hopping moves
bh_cavity_radius 100
# cavity radius that comprises the whole cluster.
# Moves that bring atoms outside the cavity are discarded
# In principle, this parameter is obsolete since dissociation is checked otherwise (by bh_max_distance, vide infra)
# and center of gravity is always set to the origin of the coordinate axes. A slow drift of the cluster is therewith
# prevented. So just set it to a significantly large value. I think I will set it to a large default value or
# throw it out completely in the next version.
hard_sphere_radius 1.5
# The minimal distant two atoms are allowed to come close to each other after a trial move.
bh_kind_of_move collective-vista
# Kind of move for basin-hopping sampling.
# -> single-particle  : only one atom is moved at once
# -> collective       : all atoms at once but with a primitive scheme to fulfil hard_sphere constraint
#                     : so it's obsolete (and does not work for large clusters)
# -> collective-vista : new collective move with a hard-sphere prerelaxing so that the hard-sphere constraint
#                       can be fulfilled for larger clusters
# angular_move 0.2
# Performs an angular move if the following condition for the atomic energies are fulfilled:
# If the ratio of the largest atomic energy to the lowest atomic energy is smaller than 0.2
# (so if the largest atomic energy, which is negative, is large enough) than an angular move
# is done on this atom. It's position is then replaced by
# vec(r) = r*e_r (theta, phi), where theta and phi are determined randomly and r is the largest
# distance that occurs in the cluster w.r.t. to the center of gravity.
# So the atom will be put somewhere on the surface of the cluster.
# Not yet tested !
# rotation_move 3
# Every 3rd trial move, a rotation move is performed.
bh_move_distribution poisson
# Distribution of the step width with which atoms are displaced.
# -> poisson    : A poisson-distribution (effectively a gaussian, but called poisson due to historical reasons) that
#               : focuses on the move distance bh_max_move
# -> uniform    : A uniform distribution centered on bh_max_move, so it ranges from 0...2 x bh_max_move.
bh_max_move 1.15
# Maximum step width with which atoms are displaced.
bh_max_distance 4.5
# Maximum distance an atom is allowed to be w.r.t. all other atoms. Otherwise the cluster will be considered
# as dissociated and the corresponding move is discarded.
potential NN
# What kind of potential is used.
# ->    NN              : neural-network potential
# ->    LJ              : Lennard-Jones
# ->    external        : FHI-aims
species Cu
# species
# In case of LJ, the species name is followed by epsilon and sigma.
bh_energy_threshold_theta 0.2
# In case of LJ, the species name is followed by epsilon and sigma.
bh_energy_threshold_theta 0.2
# Acceptance criterium of basin-hopping sampling. If a new structure with E_new is energetically higher
# then it is accepted if (E_new - E_old)/atom < bh_energy_threshold_theta.
bh_energy_threshold_boltzmann 0.0001
```

```
# Puts an additional boltzmann tail on the energy window defined by bh_energy_threshold_theta.
# By a small value it is effectivly switched off.
atomic_energy Cu -44634.56837 29
# Atomic reference energy to calculated cohesive energies and atomic energy contribution w.r.t.
# to the free atomic limit.
#
# structure distinction parameter
#
diff_tolerance 1e-4
# Two structures are considered to be equivalent if the difference in the distance norm is less than diff_tolerance.
# The distance norm compares all sorted distances of both clusters (see my paper)
energy_tolerance 0.0008
# An additional energy threshold. Two structures are only identical if both the distance norm and
# the energies are similar enough.
# With that, the problem to distinguish larger clusters calculated with the NN might easily be solved.
verbose .false.
# Verbosity flag. For your HD's sake, switch it off (default)
r_cut_off 3.0
# Cutoff parameter for o4 order-parameter (not debugged yet).
```