

Day 1: Hands-on Tutorial session using AIMS code

Energy optimization and band structure calculation for periodic systems.

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1 Overview

We will investigate the performance of several state of the art density functional for structure and property predictions^{1,2} taking Methylammonium Lead Iodide (MAPI), a classic Hybrid Organic-Inorganic Perovskite (HOIP), as our material. We will use first-principles calculations to understand the optimization procedure that finds a minimum-energy geometry (so-called geometry relaxation). This is an important step to eliminate any potential uncertainties that arise from experimental structures – which may, for example, not be able to resolve all atomic positions with the same precision (e.g., H atoms are hard to pin down in X-ray diffraction). In

the present tutorial, the electronic properties will be computed for the computationally "relaxed structure".

This tutorial aims to give the participants an experience to calculate quantum mechanical properties using FHI-aims code [Blum et al., 2009]. In the first task we will optimize the geometry to attain the most stable structure. Following this, we will use the converged structure from Task 1 to calculate the electronic structure in Task 2. The details of the calculations are demonstrated below.

2 Summary of Tasks

Task 1: Perform the geometry optimization of 48-atom MAPI orthorhombic unit cell.

- Perform calculations with the PBE functional plus vdW correction [Perdew et al., 1997, Tkatchenko and Scheffler, 2009].

Analyze the the total energy change as the structure advances to its most stable form. (Use any 2D plotting tool to plot the energy change for e.g gnuplot, xmgrace, origin ...etc).

Task 2: Perform a band structure, DOS and species-projected DOS calculation for the converged structure obtained from previous step.

- Perform state of the art calculations with HSE06 functional [Heyd et al., 2003, 2006].

Comment on the resulting band structures and densities of states. What is the effect of the explicit treatment of spin-orbit coupling?

3 Task 1: Perform the Geometry Optimization of 48-atom MAPI Orthorhombic Unit Cell

3.1 Accessing the Day 1 directory

In order to perform the desired to tasks, it is important to systematically assign them to folders. We have spared the trouble and already made one. You need to copy the Day1 folder from the folder mentioned below.

```
cp -r /location/Day1 ./
('cp -r' is the command for recursive copying a folder.

 './' means copying to your current folder.)
```

Now, a folder called 'Day1' can be found if you type

```
ls
```

in your command line.

Then, you may enter the newly built folder to check the input files we prepared for you.

```
cd Day1
cd relax
ls
```

3.2 Input files

The FHI-aims executable file to calculate all the calculations is located at :

```
/nas/longleaf/home/sryatunc/2021Hybrid3/Intel_compile/aims.201231.scalapack.mpi.x
```

In order to run FHI-aims, the user must include two input files in the folder (where they desire to run the calculations); `geometry.in` and `control.in`. The ‘`geometry.in`’ contains the structural information of the system and the ‘`control.in`’ mentions the constrains needed to run a specific calculation.(Please make sure to check that the `geometry.in` and `control.in` files are present in the working directory/folder before running calculations).

3.2.1 The MAPI Structure: ‘`geometry.in`’

MAPI is one of the most interesting materials in the field due to its exquisite opto-electronic properties. Our tasks aim to introduce first principles calculations for condensed matter systems using a 48-atom MAPI unit cell.

lattice_vector	9.001593	0.000007	-0.000006	
lattice_vector	0.000003	12.724229	0.000000	
lattice_vector	-0.000006	0.000001	8.477449	
atom	4.500285	0.000055	0.000023	Pb
atom	0.000499	6.362323	4.238442	Pb
atom	0.000410	-0.000290	4.238498	Pb
atom	4.500255	6.361998	0.000139	Pb
atom	0.132889	3.180500	3.706240	I
atom	4.367945	9.543290	7.944974	I
atom	8.868659	9.543774	4.771087	I
atom	4.633726	3.180799	0.532394	I
atom	2.826223	0.241211	5.746847	I
atom	1.674511	6.603300	1.508326	I
atom	1.674183	12.483106	1.508569	I
atom	6.175208	6.603323	2.730625	I
atom	6.175340	12.483049	2.730753	I
atom	7.327261	6.120829	6.969437	I
atom	7.327523	0.241217	6.969043	I
atom	2.826463	6.120877	5.747034	I
atom	8.486172	3.181084	0.148774	N
atom	5.016200	9.543173	4.387520	N
atom	0.515391	9.543163	8.328636	N

atom	3.985386	3.181089	4.089904	N
atom	0.806058	3.181079	7.940440	C
atom	3.694716	9.543174	3.701733	C
atom	8.195512	9.543173	0.536974	C
atom	5.306858	3.181083	4.775707	C
atom	1.352022	2.282461	8.237562	H
atom	3.148757	8.644554	3.998851	H
atom	3.148759	10.441797	3.998847	H
atom	7.649548	8.644557	0.239857	H
atom	7.649555	10.441795	0.239858	H
atom	5.852822	4.079704	4.478598	H
atom	5.852819	2.282464	4.478588	H
atom	1.352012	4.079706	8.237553	H
atom	0.639602	3.181073	6.859033	H
atom	3.861170	9.543170	2.620326	H
atom	8.361972	9.543172	1.618381	H
atom	5.140390	3.181074	5.857113	H
atom	7.939941	4.023366	-0.128777	H
atom	5.562426	10.385460	4.109962	H
atom	5.562428	8.700890	4.109960	H
atom	1.061618	10.385454	8.606194	H
atom	1.061620	8.700873	8.606200	H
atom	3.439158	2.338797	4.367455	H
atom	3.439155	4.023378	4.367462	H
atom	7.939941	2.338797	-0.128766	H
atom	8.591549	3.181093	1.185677	H
atom	4.910828	9.543169	5.424423	H
atom	0.410015	9.543157	7.291729	H
atom	4.090774	3.181093	3.052998	H

The content above is the same as the geometry.in file in the folder you copied. You may use the embedded 'vim' to directly view the data in that file. Usage of vim can be found on the official website

<https://www.vim.org/>

To have a 3D view of the geometry.in, people may use several different softwares. In this hands-on session, we recommend a free open-source package, Jmol. People can easily obtain the package on its official website:

<http://jmol.sourceforge.net/download/>

The 'Jmol.jar' and 'jmol.sh' in that package are two executable files written in java and bash. Here we just list two simple command line for using these two. Other details for Jmol usage can be found on their website.

Jmol.jar usage:

```
java -jar <your jmol directory>/Jmol.jar geometry.in
```

jmol.sh usage:

```
bash <your jmol directory>/jmol.sh geometry.in
```

Note that the computing cluster Doogwood itself also has the Jmol package installed. It is located at:

```
/nas/longleaf/apps-dogwood/jmol/14.29.17/jmol-14.29.17/
```

The only disadvantage of using Jmol remotely on Dogwood is that you may experience some time delay before anything happens.

3.2.2 'control.in file'

For geometry optimization of MAPI, the PBE functional can provide us a good balance between accuracy and computational cost. However, PBE itself cannot treat the long-range vdW interactions well enough, specifically, the interactions between the inorganic framework and the methylammonium cations in our case. Therefore, we add the Tkatchenko-Scheffler (TS) vdW correction on top of PBE.

In order to perform geometry optimization using FHI-AIMS, we also need to have the right constraints for the calculation. In this case we are using a k-space grid of $5 \times 3 \times 5$ and a convergence energy value for the geometry relaxation of 5×10^{-3} eV/Å (the magnitude of any forces on atoms and lattice vectors in the system should be smaller than this value to be considered converged). In the control.in file, this looks like:

```
xc pbe
vdw_correction_hirshfeld
relativistic atomic_zora scalar

relax_geometry bfgs 5.e-3
relax_unit_cell full

k_grid 5 3 5
```

After the specifications of tasks shown above, we need to include the desired numerical settings in the control.in file – these settings (called “species defaults”) include basis sets, integration grid, electrostatic potentials and possibly other numerical choices. For example, in the above task we are using pre-defined ‘intermediate’ settings.

3.3 Job running

In order to run the calculation, you need to have the submission script `submit.sh` along with the above two input files. The command to submit a job is:

```
sbatch submit.sh
```

(Details of submission script and submitting jobs to queue are given in Section 6.)

The output file, here called ‘aims.out’ (chosen name in the job submission script) is the output file containing all important information. You may use ‘vi’ to check it from time to time. If the ‘Have a nice day’ line appears, congratulations, you have successfully finished a FHI-aims run.

3.4 Plotting and Post-Processing

After the calculation is complete, you can obtain the relaxation energy change and number of steps it took to reach the ‘converged geometry’, by running the following script .

```
perl get_relaxation_info.pl aims.out > '<desired name>'
```

Using the new `< desiredname >` output file you can visualise the energy change using any plotting software.

4 Task 2: State-of-the-Art Band Structure Calculations

4.1 Basic knowledge

Hybrid Functionals

Semilocal density functionals such as PBE are known to not give reliable energy band structures; in particular, the band gap and relative alignments of energy levels can be wrong. A much better approach would be to use many-body theory derived formalisms such as the *GW* approximation, but these approaches can be computationally prohibitive for large, complex structures.

One approximate, DFT based approach to obtain at least qualitatively better energy band structures is to use so-called hybrid-density functionals, long established in quantum chemistry. Early hybrid functionals (e.g., the PBE0 functional) mix a Hartree-Fock like non-local exchange operator with the exchange energy term of semilocal DFT. For solids, including the full long-range Coulomb interaction between electrons in the Hartree-Fock part is not, however, the best choice. In fact, part of the correlation in solids can be mimicked better by including the long-range “screening” (reduction) of the Coulomb interaction between two well-separated electrons due to the fact that the motion of all *other* electrons inbetween will act to cancel out part of the long-range Coulomb interaction of a given electron.

One such functional, suggested by Heyd, Scuseria, and Ernzerhof (HSE), is a variant of PBE0 by employing an error-function $\text{erf}(\omega|\mathbf{r} - \mathbf{r}'|)$ to remove the long range part of the Coulomb interaction in the Hartree-Fock expression:

$$E_{xc}^{\text{hybrid}}(\omega) = \alpha E_x^{\text{HF,SR}}(\omega) + (1 - \alpha) E_x^{\text{PBE,SR}}(\omega) + E_x^{\text{PBE,LR}}(\omega) + E_c^{\text{PBE}}. \quad (1)$$

The screening parameter ω determines the range of the screening. The mixing is only done for the short-range (SR) part of the xc-potential while the long-range (LR) part is solely described on the PBE level. This approach improves the quality of band gap calculations over pure LDA/PBE calculations and can also address certain issues related to self-interaction errors.

We emphasize that this part of the field is still in flux. Hybrid functionals are a step forward, but often, the parameters α and ω turn out to be system-dependent; unbiased prescriptions to choose α and ω for a *given* system are an active and ongoing part of the field.

Spin-Orbit Coupling

Relativistic effects create another important set of modifications to a material's band structure. The effect is relatively small for light-element materials but decidedly noticeable already, e.g., for GaAs ($Z=31$ and 33 , respectively).

A general framework for a sufficient treatment of relativistic effects in all practically available materials was briefly discussed in class in the context of *Dirac's Equation* and its reduction to a specific Schrödinger-like form (in our case, leading to the atomic zero-order regular approximation, "atomic ZORA").

However, a key observation is that the wave function of Dirac's equation is a four-component vector of functions, not a single function as in Schrödinger's equation. In the non-relativistic limit, two of these components can be identified with the "spin-up" and "spin-down" channels of electrons – coupled by the vector of Pauli matrices, σ .

Since the Pauli matrices appeared in the kinetic energy term, they correspond to a coupling of the two different spin channels and the electron motion, known as "spin-orbit coupling". For heavy elements, spin-orbit coupling is a large effect, most visible in effective single-electron eigenvalues, i.e., the "band structure" of Kohn-Sham theory.

In FHI-aims, spin-orbit coupling can be treated in a so-called "non-self-consistent" approximation, that is, by computing the self-consistent scalar-relativistic solution (no spin-orbit coupling) first [Huhn and Blum \[2017\]](#). After the scalar-relativistic s.c.f. cycle is complete, the orbitals and eigenvalues are used to compute the matrix elements of the spin-orbit coupling terms for the scalar-relativistic Kohn-Sham orbitals and solving for the effect of spin-orbit coupling on the orbitals and eigenvalues in this approximation.

4.2 'geometry.in': for Task 2

We prepared the input files (control.in submit.sh) in the 'Band' folder. We will use the relaxed geometry.in from Task 1 by simply copying the optimised structure. To do that we simply copy the **converged structure** from the Task 1 and use it as input geometry for the Task 2 calculation.

```
cp ../geometry.in.next_step ./
mv geometry.in.next_step geometry.in
```

Note that at the final part of the converged geometry file, there are two lines about the trust radius information of the geometry relaxation step. You need to delete them using the following commands:

```
vi geometry.in
```

(you will be in vim and viewing the content of this file now)

```
G
```

(you will be be at the bottom line of this file)

```
dd  
dd
```

(you have deleted the last 2 lines)

```
:x
```

(you have saved the file and exited vim)

4.3 'control.in': for Task 2

For the band structure calculations, we need to specify reciprocal paths in the Brillouin zone for which the energy bands will be plotted. Below, we follow the path suggested by Setyawan & Curtarolo: The high symmetry path is $\Gamma - X - S - Y - \Gamma - Z - U - R - T - Z | Y - T | U - X | S - R$. In this hands on session, we recommend to include only three featured segments $X - \Gamma - Z | \Gamma - Y$ instead of doing the full band plot to save time. Contents of the control.in file used in this section are listed below:

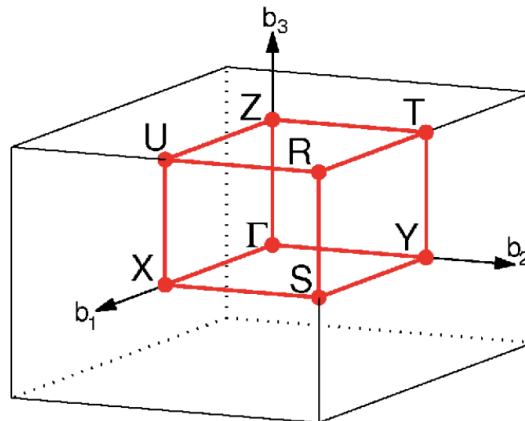


Figure 1: Brillouin zone for Orthorhombic [Curtarolo and Setyawan, 2010]

```
xc hse06 0.11  
hse_unit bohr-1  
#xc pbe
```



```

#vdw_correction_hirshfeld
relativistic atomic_zora scalar

include_spin_orbit

#relax_geometry bfgs 1.e-2
#relax_unit_cell full

k_grid 5 3 5

#use_local_index .true.
#load_balancing .true.
#energy_tolerance 0.1
#aggregated_energy_tolerance 1

output dos_tetrahedron -20 30 1000 0.1
output species_proj_dos_tetrahedron -20 30 1000 0.1

exx_band_structure_version 1
output band 0.50 0.00 0.00 0.00 0.00 0.00 21 X Gamma
output band 0.00 0.00 0.00 0.00 0.00 0.50 21 Gamma Z
output band 0.00 0.00 0.00 0.00 0.50 0.00 21 Gamma Y
# High-symmetry k-points for simple-cubic band structure output
#output band 0.00 0.00 0.00 0.50 0.00 0.00 21 Gamma X
#output band 0.50 0.00 0.00 0.50 0.50 0.00 21 X S
#output band 0.50 0.50 0.00 0.00 0.50 0.00 21 S Y
#output band 0.00 0.50 0.00 0.00 0.00 0.00 21 Y Gamma
#output band 0.00 0.00 0.00 0.00 0.00 0.50 21 Gamma Z
#output band 0.00 0.00 0.50 0.50 0.00 0.50 21 Z U
#output band 0.50 0.00 0.50 0.50 0.50 0.50 21 U R
#output band 0.50 0.50 0.50 0.00 0.50 0.50 21 R T
#output band 0.00 0.50 0.50 0.00 0.00 0.50 21 T Z
#output band 0.00 0.50 0.00 0.00 0.50 0.50 21 Y T
#output band 0.50 0.00 0.50 0.50 0.00 0.00 21 U X
#output band 0.50 0.50 0.00 0.50 0.50 0.50 21 S R

```

Each line plots a particular band segment, starting from a given point $(k_{ini,1}, k_{ini,2}, k_{ini,3})$ and ending at a different point $(k_{fin,1}, k_{fin,2}, k_{fin,3})$. These values define multiples of the unit vectors of the reciprocal lattice. 21 actual k -points will be sampled in each segment. As mentioned in Task 1 we need to add the desired numerical defaults in the `control.in` file in order to run the calculation. And then you can just edit the submission script if needed and run the calculation as mentioned in Sec. 6.

4.4 Band structure plotting

In order to plot the band structure, first make sure that the calculation is finished. You can view your file and check:

```
vim aims.out
```

Do you see the keyword ‘Have a nice day.’ at the end of calculation? If yes , Voila! your calculation is complete. In order to plot the band structure you can use two scripts, mentioned in the folder , **aimsplot_non_soc.py** to plot bands without spin orbit coupling and **aimsplot_soc.py** to plot spin orbit coupled bands. You can also print some interesting information about the band structure using the script **determine_band_info.py**. Details of the run are as follows. First load the `python/2.7.12` module. You can do this by typing the following,

```
module load python/2.7.12
```

Once you have loaded the module, you can see if it is loaded by typing:

```
module list
```

Do you see it?

If you succeeded with the above steps, you can run the following command to get important information about the band structure by simply typing.

```
python determine_band_info.py aims.out
```

Do you see some information on the screen?

Once you have successfully ahead of the above steps, then simply run,

```
python aimsplot_non_soc.py -5 5
```

To plot the non SOC bands within an energy range of -5eV to 5eV (you can format this to any energy range, just by following the above syntax). Once the bands are plotted, they should automatically appear on the screen, and you can visualise them. The script also save them in the directory, so if you type `ls`, you will be able to see a file like **aimsplot_non_soc.png** in the list of files. Likewise, perform the band structure for the SOC corrected bands,

```
python aimsplot_soc.py -5 5
```

And follow exactly same steps as in the non-SOC case to visualise. Do you see any difference between the band structure? What are your observations?

5 More on Finding Minimum Energy Geometries

5.1 Basic knowledge

Structure prediction is still a central problem in computational materials science and theoretical chemistry due to the large number of degrees of freedom included even in a system that one already understands in principle (e.g. bond lengths, bond angles, inorganic octahedron tilting directions and organic cation orientations in the MAPI system). If there is more than one local minimum-energy structure, the results generated by geometry relaxations can depend significantly on the initial input structure.

In practice, the steps to find initial structures often include:

- Experimental structures (e.g. XRD structures) can provide good initial guidance for most degrees of freedom. However, especially in MAPI, experimental XRD structures may not be fully reliable regarding molecular orientation (C and N are very similar scatterers) hydrogen positions, and/or other degrees of freedom involving disordered atomic positions in crystallographic information files (cif). These aspects can require significant care and thought when setting up a simulation.
- Geometry relaxation algorithm (e.g. the BFGS algorithm used here) will reliably find computationally consistent local minimum-energy structures if the initial structure is reasonably close to such a minimum.

5.2 Overnight Geometry Relaxation Starting from Experimental Structure

The input geometry we provided above is different from the full experimental geometry. You may use the same settings to run another geometry relaxation, starting from the $T=130\text{K}$ orthorhombic MAPI structure obtained from the Hybrid³ database. The inputs files are located in the 'overnight_relax' folder. This calculation can take up to 3 hours. You may submit the job before leaving and then compare the new relaxed geometry with the one you used today on the beginning of the Day2 hands-on session tomorrow.

6 Job Script Submission on Dogwood Cluster

Following is the job submission script. You can create it yourself by simply doing

```
vim submit.sh
```

```
#!/bin/bash
#SBATCH -p debug_queue # name of the queue
#SBATCH --job-name=aims # name of the job
#SBATCH --ntasks-per-node=44
#SBATCH -reservation=1
#SBATCH -c 1
```

```

#SBATCH --time=0-04:00:00 # format days-hh:mm:ss

module use ~markreed/modules_dogwood
module load intel/19.4
module load mvapich2-2.3.4/intel_19.4

export MV2_USE_THREAD_WARNING=0

ulimit -s unlimited

AIMS=/nas/longleaf/home/sryatunc/2021Hybrid3/Intel_compile/aims.201231.scalapack.mpi.x

home='pwd'

mpirun -n 44 $AIMS > aims.out

```

Go ahead and submit the job. On the terminal just type the following command to queue in the job for running.

```

sbatch submit.ah

```

Do you see it running? If not you can use the following to see the status of the job.

```

squeue -u <username>

```

What is the name of the output file? You can monitor the progress of the job simply by using

```

tail -f <name>.out #name of the output file

```

References

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