Computational Chemistry Laboratory II (CBE 60553)

Prateek Mehta, William F. Schneider

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1 A review of what we know

So far we have learned how to:

- navigate the linux terminal
- create create and edit files using Emacs
- numerical analysis and plotting with Python
- different concepts in molecular simulations, e.g. potential energy surfaces, geometry optimizations, etc.

It might make sense to go back and read the lecture notes and notes from Lab 1 and Lab 2 if you feel the need to re-familiarize yourself with these things. In this lab, we will combine some of the things we learned and to perform DFT calculations with a powerful software package, `VASP`.

2 Loading the required software

Before we can actually proceed, we will need to tell our computer how it can find all the tools we need. We will store this information so that the software is already loaded for us every time we login in the future. Depending on your unix shell, the things we need to do will be a little different. You can see which shell you are using with the command `echo $0`.

The software we need is dependent on the bash shell and thus we (all users) need to add a few commands to our `.bashrc` file. Go to your home directory and open the `.bashrc` file, i.e., run the following two commands.

```
cd
emacs .bashrc
```

Once there, add the following line at the bottom of the file and save it (Make sure there are no typos!).

```
source /afs/crc.nd.edu/user/w/wschnei1/CBE547/software/course_bashrc.sh
```

If there is a line that says `module load ase` in your file, remove it.

For tsch users, there is an additional step. Go to the terminal and run,

```
cd
emacs .cshrc
```

Once there, add the following line at the bottom of the file and save it (Make sure there are no typos!).

`source /afs/crc.nd.edu/user/w/wschnei1/CBE547/software/course_cshrc.sh`

If there is a line that says `module load ase` in your file, remove it.

Now logout and log back in. Once this is done, go to computational-chemistry/Lab3/ and open it Lab3.org in emacs.

3 Introduction to Software

`VASP` or the Vienna ab-inito Simulation Package is a density functional theory (DFT) package that utilizes periodic boundary conditions and planewave basis sets. It was developed at the Theoretical Physics Department at the Institute for Materials Physics in Vienna, Austria. More information about `VASP` can be obtained at http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html. We will use a combination of the `ASE` (https://wiki.fysik.dtu.dk/ase/index.html) and `jasp` (https://github.com/jkitchin/jasp) packages to help prepare input files, manage job submission to the queue system, and analysis of results.

Note: The original `jasp` code has been slightly modified to work with the Notre Dame queue system.

Prof. J. R. Kitchin wrote a book to accompany `jasp` (http://kitchingroup.cheme.cmu.edu/dft-book/). It contains 100s of examples of using `jasp` for almost every kind of calculation that can be performed using `VASP`. Most of the examples in this document were from that book!

Note: This is not the most recent version of the book, so some of the functionality might be different to reflect the most recent version of `ase`. For the most recent version go to, https://github.com/jkitchin/dft-book.

4 Creating Molecules

Molecules are defined in `ase` using something called Atoms objects, which are a combination of Atom objects (obviously!). There are various ways to create Atoms objects - by hand, reading them from files, databases, etc.

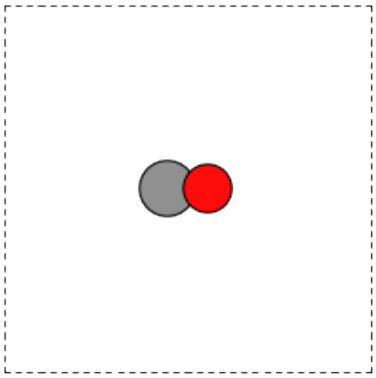
4.1 From Scratch

We can build atoms by hand by specifying the type and position of each atom, and the unit cell the atoms are in.

```
from ase import Atoms, Atom
from ase.io import write
from ase.visualize import view
```

```
4
5  # define an Atoms object
6  atoms = Atoms([Atom('C', [0., 0., 0.]),
7                 Atom('O', [1.1, 0., 0.])],
8                cell=(10, 10, 10))
9
10 atoms.center() # For a better visualization
11
12 print('V = {0:1.0f} Angstrom^3'.format(atoms.get_volume()))
13 write('images/simple-cubic-cell.png', atoms, show_unit_cell=2)
14 # view(atoms)
```

```
V = 1000 Angstrom^3
```



4.2 Using in-built databases

We can load predefined molecules from `ase.structure.molecule`. For example, the database contains the molecules in the G2 set (http://www.cse.anl.gov/OldCHMwebsiteContent/compmat/comptherm.htm) among others. These are generally the result of MP2/6-31g(d) calculations from a code like `GAUSSIAN` or `GAMESS`. Consequently, they will not have unit cell information, and will have a default unit cell of ((1. 0. 0.), (0. 1. 0.), (0. 0. 1.)). We need to manually specify the unit cell for a `VASP` calculation.

```
1  from ase.structure import molecule
2  from ase.visualize import view
3
4  atoms = molecule('CO')
5
6  # view(atoms)
7  print atoms
8  print 'Old Cell:'
9  print atoms.get_cell()
10
11 atoms.set_cell((10,10,10), scale_atoms=False)
12 print 'New Cell:'
13 print atoms.get_cell()
14 view(atoms)
```

```
Atoms(symbols='OC', positions=..., cell=[1.0, 1.0, 1.0], pbc=[False, False, False])
Old Cell:
[[ 1.  0.  0.]
 [ 0.  1.  0.]
 [ 0.  0.  1.]]
```

```
New Cell:
[[ 10.   0.   0.]
 [  0.  10.   0.]
 [  0.   0.  10.]]
```

The g2 set as implemented in ase is given below.

isobutene	CH3CH2OH	CH3COOH
COF2	CH3NO2	CF3CN
CH3OH	CCH	CH3CH2NH2
PH3	Si2H6	O3
O2	BCl3	CH2_s1A1d
Be	H2CCl2	C3H9C
C3H9N	CH3CH2OCH3	BF3
CH3	CH4	S2
C2H6CHOH	SiH2_s1A1d	H3CNH2
CH3O	H	BeH
P	C3H4_C3v	C2F4
OH	methylenecyclopropane	F2O
SiCl4	HCF3	HCCl3
C3H7	CH3CH2O	AlF3
CH2NHCH2	SiH2_s3B1d	H2CF2
SiF4	H2CCO	PH2
OCS	HF	NO2
SH2	C3H4_C2v	H2O2
CH3CH2Cl	isobutane	CH3COF
HCOOH	CH3ONO	C5H8
2-butyne	SH	NF3
HOCl	CS2	P2
C	CH3S	O
C4H4S	S	C3H7Cl
H2CCHCl	C2H6	CH3CHO
C2H4	HCN	C2H2
C2Cl4	bicyclobutane	H2
C6H6	N2H4	C4H4NH
H2CCHCN	H2CCHF	cyclobutane
HCl	CH3OCH3	Li2
Na	CH3SiH3	NaCl
CH3CH2SH	OCHCHO	SiH4
C2H5	SiH3	NH
ClO	AlCl3	CCl4
NO	C2H3	ClF
HCO	CH3CONH2	CH2SCH2
CH3COCH3	C3H4_D2d	CH
CO	CN	F
CH3COCl	N	CH3Cl
Si	C3H8	CS
N2	Cl2	NCCN
F2	CO2	Cl

CH2OCH2	H2O	CH3CO
SO	HCOOCH3	butadiene
ClF3	Li	PF3
B	CH3SH	CF4
C3H6_Cs	C2H6NH	N2O
LiF	H2COH	cyclobutene
LiH	SiO	Si2
C2H6SO	C5H5N	trans-butane
Na2	C4H4O	SO2
NH3	NH2	CH2_s3B1d
ClNO	C3H6_D3h	Al
CH3SCH3	H2CO	CH3CN

4.3 Reading structures from files

ASE can read a variety of data formats using `ase.io.read`. For example, here is a cif file I downloaded from http://materialsproject.org.

mp-22862_NaCl.cif

```
from ase.io import read
from ase.visualize import view

atoms = read('mp-22862_NaCl.cif')

view(atoms)
print atoms
```

```
Atoms(symbols='Na4Cl4', positions=..., cell=[[5.69169356, 0.0, 0.0], [3.485157149990802e-16, 5
```

5 Simple SCF calculations

We will now perform a simple calculation on our CO molecule. This is done by creating a `jasp` calculator, which is an extension of the default Vasp calculator in ase (`ase.calculators.vasp`). The two properties that we will calculate in this example are the energy and the forces on the atoms.

The first time we run this code, a calculation will be submitted to the Notre Dame queue system. So when you try to print the potential energy of you will get an exception saying VaspSubmitted. You can check the status of the job by going back to the terminal and typing `qstat -u netid`. Once the job has finished running you can rerun the code, and if all went well, it should give you the energies and the forces.

```
from ase import Atoms, Atom
from ase.io import write
from ase.visualize import view
from jasp import jasp

# define an Atoms object
co = Atoms([Atom('C', [0., 0., 0.]),
                Atom('O', [1.1, 0., 0.])],
```

```
              cell=(10, 10, 10))

with jasp('molecules/simple-co',  # output dir relative to current dir
          xc='PBE',  # the exchange-correlation functional
          nbands=8,    # number of bands
          encut=350,    # planewave cutoff
          ismear=1,    # Methfessel-Paxton smearing
          sigma=0.01,  # very small smearing factor for a molecule
          atoms=co) as calc:
    print('energy = {0} eV'.format(co.get_potential_energy()))
    print 'Forces (eV/Ang.):'
    print(co.get_forces())
    print 'SCF iterations = {0}'.format(calc.get_number_of_iterations())
    print calc # Prints a summary of the calculation
    #Note: some properties are attributes of the atoms object and some of the calc.
```

We can also look at the files created by `VASP` to see if everything went ok.

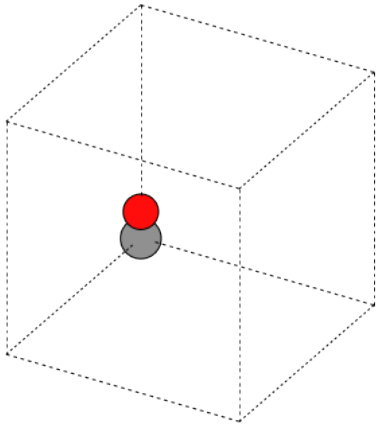
6 Geometry Optimizations

Now let us try to do a geometry optimization. For this `VASP` needs two additional keywords (at least) - `IBRION` and `NSW`. `IBRION` controls the relaxation algorithm and `NSW` specifies the total number of steps.

```
from ase import Atoms, Atom
from ase.io import write
from ase.visualize import view
from jasp import jasp

# define an Atoms object
co = Atoms([Atom('C', [0., 0., 0.]),
               Atom('O', [1.1, 0., 0.])],
              cell=(10, 10, 10))

with jasp('molecules/geometry-co',  # output dir relative to current dir
          xc='PBE',  # the exchange-correlation functional
          nbands=8,    # number of bands
          encut=350,    # planewave cutoff
          ismear=1,    # Methfessel-Paxton smearing
          sigma=0.01,  # very small smearing factor for a molecule
          nsw=20, # Number of ionic steps
          ibrion=2, # Conjugate gradient alogrithm
          atoms=co) as calc:
    print('energy = {0} eV'.format(co.get_potential_energy()))
    print 'Forces (eV/Ang.):'
    print(co.get_forces())
    print 'Equilibrium Positions (Angs.):'
    for atom in co:
        print atom.symbol, atom.position

# Save an image. Note that this is done outside the with statement
write('images/CO-relaxed.png', co, show_unit_cell=2, rotation='60x,-30y,90z')
```

```
energy = -14.81175954 eV
Forces (eV/Ang.):
[[ 0.003  0.     0.   ]
 [-0.003  0.     0.   ]]
Equilibrium Positions (Angs.):
C [-0.022  0.     0.   ]
```

```
O [ 1.122  0.     0.   ]
```

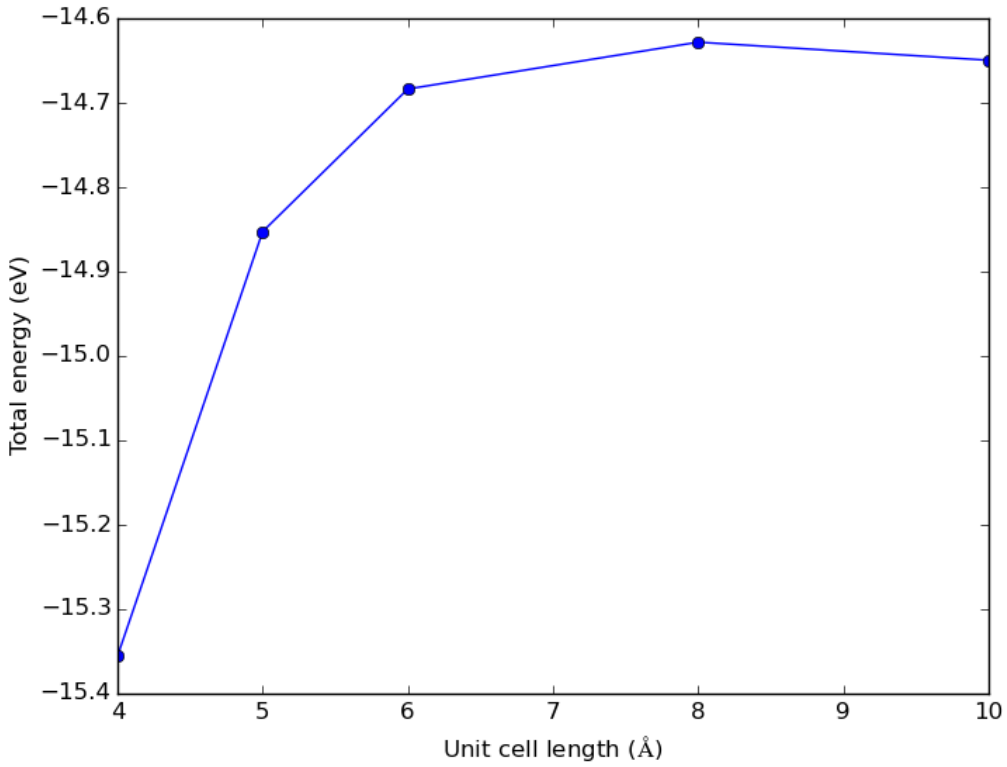


We might also want to visualize the relaxation trajectory. Using the terminal, change into the directory where you performed the calculation, and type in `jaspsum -t`.

7 Effect of Unit Cell Size

Let us consider a more complicated example. Here we will vary the size of the unit cell, to see how interactions between periodic images affect the energy.

```
from jasp import *
from ase import Atoms,Atom
import numpy as np

atoms = Atoms([Atom('C',[0,   0, 0]),
               Atom('O',[1.2, 0, 0])])

L = [4, 5, 6, 8, 10]

energies = []

ready = True

for a in L:
    atoms.set_cell([a,a,a], scale_atoms=False)
    atoms.center()
    with jasp('molecules/co-L-{0}'.format(a),
              encut=350,
              xc='PBE',
              atoms=atoms) as calc:
        try:
            energies.append(atoms.get_potential_energy())
        except (VaspSubmitted, VaspQueued):
            ready = False

if not ready:
    import sys; sys.exit()

import matplotlib.pyplot as plt
plt.plot(L, energies, 'bo-')
plt.xlabel('Unit cell length ($\AA$)')
plt.ylabel('Total energy (eV)')
plt.savefig('images/co-e-v.png')
plt.show()
```



We can see that at small box sizes, there are attractive interactions between CO molecules that lower the total energy. At larger box sizes the energy starts to converge to a fixed value as the interactions are minimized. Now let's check the effect on the computational cost.

```
from jasp import *

L = [4, 5, 6, 8, 10]

for a in L:
    with jasp('molecules/co-L-{0}'.format(a)) as calc:
        print '{0} {1} seconds'.format(a, calc.get_elapsed_time())
```

```
4 2.616 seconds
5 3.907 seconds
6 5.891 seconds
8 16.588 seconds
10 30.543 seconds
```

We can see the computational cost went up by a factor of 15! Perhaps you can now appreciate the computational cost involved in simulating 100s of atoms in large boxes!

8 Miscellaneous

8.1 Building pdfs from org files

Using the software you loaded at the beginning of lab, you should be able to build a pdf from your .org files. Let us try that, click on the Org menu and click Export/Publish. Then press 'l' and 'o'. This let's you build a pdf and open it.

Alternately, you can type, `C-c C-e l o`

8.2 Viewing latex equations in org documents

Click on `org-toggle-latex-overlays`. You should be able to see the Schrodinger equation below.

- $H\psi = E\psi$