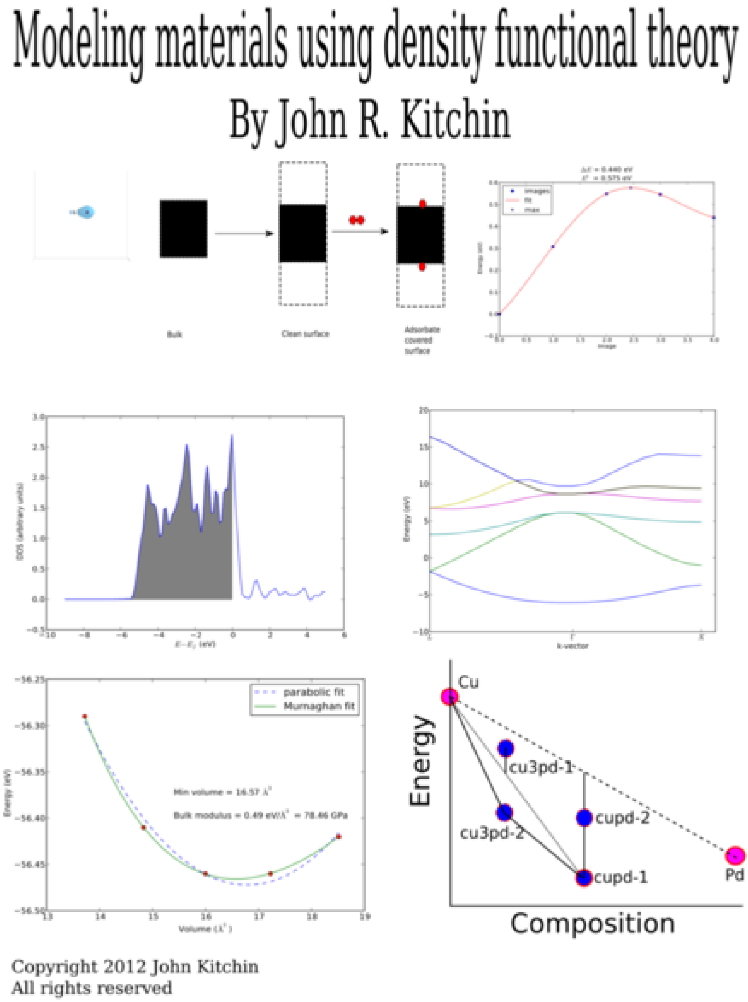


Modeling materials using density functional theory
By John R. Kitchin
Bulk
Clean surface
Adsorbate covered surface
parabolic fit
Murnaghan fit
Energy
Composition
Cu
cu3pd-1
cupd-2
cu3pd-2
cupd-1
Pd
Copyright 2012 John Kitchin
All rights reserved

Modeling materials using density functional theory

John Kitchin

2012-07-11 Wed

Contents

1 Introduction to this book

This book serves two purposes: 1) to provide worked examples of using DFT to model materials properties, and 2) to provide references to more advanced treatments of these topics in the literature. It is not a definitive reference on density functional theory. Along the way to learning how to perform the calculations, you will learn how to analyze the data, make plots, and how to interpret the results. This book is very much "recipe" oriented, with the intention of giving you enough information and knowledge to start your research. In that sense, many of the computations are not publication quality with respect to convergence of calculation parameters.

You will read a lot of python code in this book. I believe that computational work should always be scripted. Scripting provides a written record of everything you have done, making it more probable you (or others) could reproduce your results or report the method of its execution exactly at a later time.

This book makes heavy use of many computational tools including:

- Python
  - Module index
- Atomic Simulation Environment (ase)
- numpy
- scipy
- matplotlib
- emacs
  - org-mode This book is written in org-mode, and is best read in emacs in org-mode. This format provides clickable links, easy navigation, syntax highlighting, as well as the ability to interact with the tables and code. The book is also available in PDF.
- git This book is available at `https://github.com/jkitchin/dft-book`
- vasp This is the Python module used extensively here. It is available at `https://github.com/jkitchin/vasp`

The DFT code used primarily in this book is VASP.

- VASP wiki
- VASP Manual

Similar code would be used for other calculators, e.g. GPAW, Jacapo, etc... you would just have to import the python modules for those codes, and replace the code that defines the calculator.

> **Exercise 1.1**
> Review all the hyperlinks in this chapter.

2 Introduction to DFT

A comprehensive overview of DFT is beyond the scope of this book, as excellent reviews on these subjects are readily found in the literature, and are suggested reading in the following paragraph. Instead, this chapter is intended to provide a useful starting point for a non-expert to begin learning about and using DFT in the manner used in this book. Much of the information presented here is standard knowledge among experts, but a consequence of this is that it is rarely discussed in current papers in the literature. A secondary goal of this chapter is to provide new users with a path through the extensive literature available and to point out potential difficulties and pitfalls in these calculations.

A modern and practical introduction to density functional theory can be found in Sholl and Steckel.[1] A fairly standard textbook on DFT is the one written by Parr and Yang.[2] The Chemist's Guide to DFT[3] is more readable and contains more practical information for running calculations, but both of these books focus on molecular systems. The standard texts in solid state physics are by Kittel[4] and

Ashcroft and Mermin.[5] Both have their fine points, the former being more mathematically rigorous and the latter more readable. However, neither of these books is particularly easy to relate to chemistry. For this, one should consult the exceptionally clear writings of Roald Hoffman,[6,7] and follow these with the work of Nørskov and coworkers.[8,9]

In this chapter, only the elements of DFT that are relevant to this work will be discussed. An excellent review on other implementations of DFT can be found in Reference[10], and details on the various algorithms used in DFT codes can be found in Refs.[11,12].

One of the most useful sources of information has been the dissertations of other students, perhaps because the difficulties they faced in learning the material are still fresh in their minds. Thomas Bligaard, a coauthor of Dacapo, wrote a particularly relevant thesis on exchange/correlation functionals[13] and a dissertation illustrating the use of DFT to design new alloys with desirable thermal and mechanical properties.[14] The Ph.D. thesis of Ari Seitsonen contains several useful appendices on k-point setups, and convergence tests of calculations, in addition to a thorough description of DFT and analysis of calculation output.[15] Finally, another excellent overview of DFT and its applications to bimetallic alloy phase diagrams and surface reactivity is presented in the PhD thesis of Robin Hirschl.[16]

2.1 Background

In 1926, Erwin Schrödinger published the first accounts of his now famous wave equation.[17] He later shared the Nobel prize with Paul A. M. Dirac in 1933 for this discovery. Schrödinger's wave function seemed extremely promising, as it contains all of the information available about a system. Unfortunately, most practical systems of interest consist of many interacting electrons, and the effort required to find solutions to Schrödinger's equation increases exponentially with the number of electrons, limiting this approach to systems with a small number of relevant electrons, $N \lesssim O(10)$.[18] Even if this rough estimate is off by an order of magnitude, a system with 100 electrons is still very small, for example, two Ru atoms if all the electrons are counted, or perhaps ten Pt atoms if only the valence electrons are counted. Thus, the wave function method, which has been extremely successful in studying the properties of small molecules, is unsuitable for studies of large, extended solids. Interestingly, this difficulty was recognized by Dirac as early as 1929, when he wrote "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the application of these laws leads to equations much too complicated to be soluble.".[19]

In 1964, Hohenberg and Kohn showed that the ground state total energy of a system of interacting electrons is a unique functional of the electron density.[20] By definition, a function returns a number when given a number. For example, in $f(x) = x^2$, $f(x)$ is the function, and it equals four when $x = 2$. A functional returns a number when given a function. Thus, in $g(f(x)) = \int_0^\pi f(x)dx$, $g(f(x))$ is the functional, and it is equal to two when $f(x) = \sin(x)$. Hohenberg and Kohn further identified a variational principle that appeared to reduce the problem of finding the ground state energy of an electron gas in an external potential (i.e., in the presence of ion cores) to that of the minimization of a functional of the three-dimensional density function. Unfortunately, the definition of the functional involved a set of 3N-dimensional trial wave functions.

In 1965, Kohn and Sham made a significant breakthrough when they showed that the problem of many interacting electrons in an external potential can be mapped exactly to a set of noninteracting electrons in an effective external potential.[21] This led to a set of self-consistent, single particle equations known as the Kohn-Sham (KS) equations:

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) - \epsilon_j\right)\varphi_j(\mathbf{r}) = 0, \tag{1}$$

with

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}(\mathbf{r}), \tag{2}$$

where $v(\mathbf{r})$ is the external potential and $v_{xc}(\mathbf{r})$ is the exchange-correlation potential, which depends on the entire density function. Thus, the density needs to be known in order to define the effective potential so that Eq. (1) can be solved. $\varphi_j(\mathbf{r})$ corresponds to the j^{th} KS orbital of energy ϵ_j.

The ground state density is given by:

$$n(\mathbf{r}) = \sum_{j=1}^{N} |\varphi_j(\mathbf{r})|^2 \tag{3}$$

To solve Eq. (1) then, an initial guess is used for $\varphi_j(r)$ which is used to generate Eq. (3), which is subsequently used in Eq. (2). This equation is then solved for $\varphi_j(\mathbf{r})$ iteratively until the $\varphi_j(\mathbf{r})$ that result from the solution are the same as the $\varphi_j(\mathbf{r})$ that are used to define the equations, that is, the solutions are self-consistent. Finally, the ground state energy is given by:

$$E = \sum_j \epsilon_j + E_{xc}[n(\mathbf{r})] - \int v_{xc}(\mathbf{r})n(\mathbf{r})d\mathbf{r} - \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\mathbf{r}, \tag{4}$$

where $E_{xc}[n(\mathbf{r})]$ is the exchange-correlation energy functional. Walter Kohn shared the Nobel prize in Chemistry in 1998 for this work.[18] The other half of the prize went to John Pople for his efforts in wave function based quantum mechanical methods.[22] Provided the exchange-correlation energy functional is known, Eq. (4) is exact. However, the exact form of the exchange-correlation energy functional is not known, thus approximations for this functional must be used.

2.2 Exchange correlation functionals

The two main types of exchange/correlation functionals used in DFT are the local density approximation (LDA) and the generalized gradient approximation (GGA). In the LDA, the exchange-correlation functional is defined for an electron in a uniform electron gas of density n.[21] It is exact for a uniform electron gas, and is anticipated to be a reasonable approximation for slowly varying densities. In molecules and solids, however, the density tends to vary substantially in space. Despite this, the LDA has been very successfully used in many systems. It tends to predict overbonding in both molecular and solid systems,[23] and it tends to make semiconductor systems too metallic (the band gap problem).[24]

The generalized gradient approximation includes corrections for gradients in the electron density, and is often implemented as a corrective function of the LDA. The form of this corrective function, or "exchange enhancement" function determines which functional it is, e.g. PBE, RPBE, revPBE, etc.[25] In this book the PBE GGA functional is used the most. Nørskov and coworkers have found that the RPBE functional gives superior chemisorption energies for atomic and molecular bonding to surfaces, but that it gives worse bulk properties, such as lattice constants compared to experimental data.[25]

Finally, there are increasingly new types of functionals in the literature. The so-called hybrid functionals, such as B3LYP, are more popular with gaussian basis sets (e.g. in Gaussian), but they are presently inefficient with planewave basis sets. None of these other types of functionals were used in this work. For more details see Chapter 6 in Ref.[3] and Thomas Bligaard's thesis on exchange and correlation functionals.[13]

2.3 Basis sets

Briefly, VASP utilizes planewaves as the basis set to expand the Kohn-Sham orbitals. In a periodic solid, one can use Bloch's theorem to show that the wave function for an electron can be expressed as the product of a planewave and a function with the periodicity of the lattice:[5]

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) \tag{5}$$

where $\mathbf{r}$ is a position vector, and $\mathbf{k}$ is a so-called wave vector that will only have certain allowed values defined by the size of the unit cell. Bloch's theorem sets the stage for using planewaves as a basis set, because it suggests a planewave character of the wave function. If the periodic function $u_{n\mathbf{k}}(\mathbf{r})$ is also expanded in terms of planewaves determined by wave vectors of the reciprocal lattice vectors, **G**, then the wave function can be expressed completely in terms of a sum of planewaves:[11]

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp(i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}). \quad (6)$$

where $c_{i,\mathbf{k}+\mathbf{G}}$ are now coefficients that can be varied to determine the lowest energy solution. This also converts Eq. (1) from an integral equation to a set of algebraic equations that can readily be solved using matrix algebra.

In aperiodic systems, such as systems with even one defect, or randomly ordered alloys, there is no periodic unit cell. Instead one must represent the portion of the system of interest in a supercell, which is then subjected to the periodic boundary conditions so that a planewave basis set can be used. It then becomes necessary to ensure the supercell is large enough to avoid interactions between the defects in neighboring supercells. The case of the randomly ordered alloy is virtually hopeless as the energy of different configurations will fluctuate statistically about an average value. These systems were not considered in this work, and for more detailed discussions the reader is referred to Ref.[26]. Once a supercell is chosen, however, Bloch's theorem can be applied to the new artificially periodic system.

To get a perfect expansion, one needs an infinite number of planewaves. Luckily, the coefficients of the planewaves must go to zero for high energy planewaves, otherwise the energy of the wave function would go to infinity. This provides justification for truncating the planewave basis set above a cutoff energy. Careful testing of the effect of the cutoff energy on the total energy can be done to determine a suitable cutoff energy. The cutoff energy required to obtain a particular convergence precision is also element dependent, shown in Table 1. It can also vary with the "softness" of the pseudopotential. Thus, careful testing should be done to ensure the desired level of convergence of properties in different systems. Table 1 refers to convergence of total energies. These energies are rarely considered directly, it is usually differences in energy that are important. These tend to converge with the planewave cutoff energy much more quickly than total energies, due to cancellations of convergence errors. In this work, 350 eV was found to be suitable for the H adsorption calculations, but a cutoff energy of 450 eV was required for O adsorption calculations.

Table 1: Planewave cutoff energies (in eV) required for different convergence precisions for two different elements with different pseudopotential setups.

Precision	Low	High
Mo	168	293
O	300	520
O_sv	1066	1847

Bloch's theorem eliminates the need to calculate an infinite number of wave functions, because there are only a finite number of electrons in the unit (super) cell. However, there are still an infinite number of discrete k points that must be considered, and the energy of the unit cell is calculated as an integral over these points. It turns out that wave functions at k points that are close together are similar, thus an interpolation scheme can be used with a finite number of k points. This also converts the integral used to determine the energy into a sum over the k points, which are suitably weighted to account for the finite number of them. There will be errors in the total energy associated with the finite number of k, but these can be reduced and tested for convergence by using higher k-point densities. An excellent discussion of this for aperiodic systems can be found in Ref.[26].

The most common schemes for generating k points are the Chadi-Cohen scheme,[27] and the Monkhorst-Pack scheme.[28] The use of these k point setups amounts to an expansion of the periodic function in reciprocal space, which allows a straight-forward interpolation of the function between the points that is more accurate than with other k point generation schemes.[28]

2.4 Pseudopotentials

The core electrons of an atom are computationally expensive with planewave basis sets because they are highly localized. This means that a very large number of planewaves are required to expand their wave functions. Furthermore, the contributions of the core electrons to bonding compared to those of the valence electrons is usually negligible. In fact, the primary role of the core electron wave functions is to ensure proper orthogonality between the valence electrons and core states. Consequently, it is desirable to replace the atomic potential due to the core electrons with a pseudopotential that has the same effect on the valence electrons.[29] There are essentially two kinds of pseudopotentials, norm-conserving soft pseudopotentials[29] and Vanderbilt ultrasoft pseudopotentials.[30] In either case, the pseudopotential function is generated from an all-electron calculation of an atom in some reference state. In norm-conserving pseudopotentials, the charge enclosed in the pseudopotential region is the same as that enclosed by the same space in an all-electron calculation. In ultrasoft pseudopotentials, this requirement is relaxed and charge augmentation functions are used to make up the difference. As its name implies, this allows a "softer" pseudopotential to be generated, which means fewer planewaves are required to expand it.

The pseudopotentials are not unique, and calculated properties depend on them. However, there are standard methods for ensuring the quality and transferability (to different chemical environments) of the pseudopotentials.[31]

TODO PAW description

VASP provides a database of PAW potentials.[32,33]

2.5 Fermi Temperature and band occupation numbers

At absolute zero, the occupancies of the bands of a system are well-defined step functions; all bands up to the Fermi level are occupied, and all bands above the Fermi level are unoccupied. There is a particular difficulty in the calculation of the electronic structures of metals compared to semiconductors and molecules. In molecules and semiconductors, there is a clear energy gap between the occupied states and unoccupied states. Thus, the occupancies are insensitive to changes in the energy that occur during the self-consistency cycles. In metals, however, the density of states is continuous at the Fermi level, and there are typically a substantial number of states that are close in energy to the Fermi level. Consequently, small changes in the energy can dramatically change the occupation numbers, resulting in instabilities that make it difficult to converge to the occupation step function. A related problem is that the Brillouin zone integral (which in practice is performed as a sum over a finite number of k points) that defines the band energy converges very slowly with the number of k points due to the discontinuity in occupancies in a continuous distribution of states for metals.[12,34] The difficulty arises because the temperature in most DFT calculations is at absolute zero. At higher temperatures, the DOS is smeared across the Fermi level, resulting in a continuous occupation function over the distribution of states. A finite-temperature version of DFT was developed,[35] which is the foundation on which one solution to this problem is based. In this solution, the step function is replaced by a smoothly varying function such as the Fermi-Dirac function at a small, but non-zero temperature.[12] The total energy is then extrapolated back to absolute zero.

2.6 Spin polarization and magnetism

There are two final points that need to be discussed about these calculations, spin polarization and dipole corrections. Spin polarization is important for systems that contain net spin. For example, iron, cobalt and nickel are magnetic because they have more electrons with spin "up" than spin "down" (or vice versa). Spin polarization must also be considered in atoms and molecules with unpaired electrons, such as hydrogen and oxygen atoms, oxygen molecules and radicals. For example, there are two spin configurations for an oxygen molecule, the singlet state with no unpaired electrons, and the triplet state with two unpaired electrons. The oxygen triplet state is lower in energy than the oxygen singlet state, and thus it corresponds to the ground state for an oxygen atom. A classically known problem involving spin polarization is the dissociation of a hydrogen molecule. In this case, the molecule starts with no net spin, but it dissociates into two atoms, each of which has an unpaired electron. See section 5.3.5 in Reference[3] for more details on this.

In VASP, spin polarization is not considered by default; it must be turned on, and an initial guess for the magnetic moment of each atom in the unit cell must be provided (typically about one Bohr-magneton per unpaired electron). For Fe, Co, and Ni, the experimental values are 2.22, 1.72, and 0.61 Bohr-magnetons, respectively[4] and are usually good initial guesses. See Reference[31] for a very thorough discussion of the determination of the magnetic properties of these metals with DFT. For a hydrogen atom, an initial guess of 1.0 Bohr-magnetons (corresponding to one unpaired electron) is usually good. An oxygen atom has two unpaired electrons, thus an initial guess of 2.0 Bohr-magnetons should be used. The spin-polarized solution is sensitive to the initial guess, and typically converges to the closest solution. Thus, a magnetic initial guess usually must be provided to get a magnetic solution. Finally, unless an adsorbate is on a magnetic metal surface, spin polarization typically does not need to be considered, although the gas-phase reference state calculation may need to be done with spin-polarization.

The downside of including spin polarization is that it essentially doubles the calculation time.

2.7 Recommended reading

The original papers on DFT are.[20,21]

Kohn's Nobel Lecture[18] and Pople's Nobel Lecture[22] are good reads.

This paper by Hoffman[7] is a nice review of solid state physics from a chemist's point of view.

All calculations in this book were performed using VASP[12,36–38] with the projector augmented wave (PAW) potentials provided in VASP.

3 Molecules

In this chapter we consider how to construct models of molecules, how to manipulate them, and how to calculate many properties of molecules. For a nice comparison of VASP and Gaussian see[39].

3.1 Defining and visualizing molecules

We start by learning how to define a molecule and visualize it. We will begin with defining molecules from scratch, then reading molecules from data files, and finally using some built-in databases in `ase`.

3.1.1 From scratch

When there is no data file for the molecule you want, or no database to get it from, you have to define your atoms geometry by hand. Here is how that is done for a CO molecule (Figure 1). We must define the type and position of each atom, and the unit cell the atoms are in.

```python
from ase import Atoms, Atom
from ase.io import write

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

print('V = {0:1.0f} Angstrom^3'.format(atoms.get_volume()))

write('images/simple-cubic-cell.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-1.py).

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

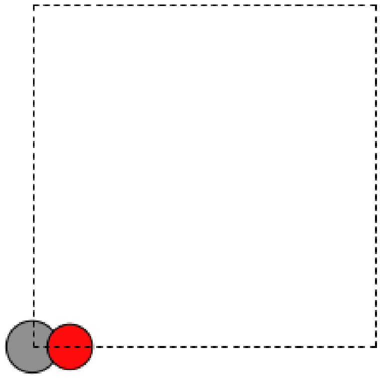


Figure 1: Image of a CO molecule with the C at the origin.

There are two inconvenient features of the simple cubic cell:

1. Since the CO molecule is at the corner, its electron density is spread over the 8 corners of the box, which is not convenient for visualization later (see Visualizing electron density).
2. Due to the geometry of the cube, you need fairly large cubes to make sure the electron density of the molecule does not overlap with that of its images. Electron-electron interactions are repulsive, and the overlap makes the energy increase significantly. Here, the CO molecule has 6 images due to periodic boundary conditions that are 10 Å away. The volume of the unit cell is 1000 Å^3.

The first problem is easily solved by centering the atoms in the unit cell. The second problem can be solved by using a face-centered cubic lattice, which is the lattice with the closest packing. We show the results of the centering in Figure 2, where we have guessed values for b until the CO molecules are on average 10 Å apart. Note the final volume is only about 715 Å^3, which is smaller than the cube. This will result in less computational time to compute properties.

```python
from ase import Atoms, Atom
from ase.io import write

b = 7.1
atoms = Atoms([Atom('C', [0., 0., 0.]),
               Atom('O', [1.1, 0., 0.])],
              cell=[[b, b, 0.],
                    [b, 0., b],
                    [0., b, b]])

print('V = {0:1.0f} Ang^3'.format(atoms.get_volume()))

atoms.center()  # translate atoms to center of unit cell
write('images/fcc-cell.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-2.py).

```
V = 716 Ang^3
```

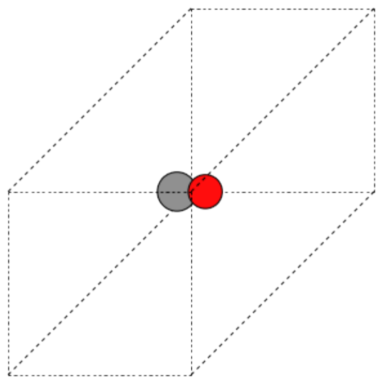


Figure 2: CO in a face-centered cubic unit cell.

At this point you might ask, "How do you know the distance to the neighboring image?" The `ag` viewer lets you compute this graphically, but we can use code to determine this too. All we have to do is figure out the length of each lattice vector, because these are what separate the atoms in the images. We use the `numpy` module to compute the distance of a vector as the square root of the sum of squared elements.

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

b = 7.1
atoms = Atoms([Atom('C', [0., 0., 0.]),
               Atom('O', [1.1, 0., 0.])],
              cell=[[b, b, 0.],
                    [b, 0., b],
                    [0., b, b]])

# get unit cell vectors and their lengths
(a1, a2, a3) = atoms.get_cell()
print('|a1| = {0:1.2f} Ang'.format(np.sum(a1**2)**0.5))
print('|a2| = {0:1.2f} Ang'.format(np.linalg.norm(a2)))
print('|a3| = {0:1.2f} Ang'.format(np.sum(a3**2)**0.5))
```

Open the python script (dft-scripts/script-3.py).

```
|a1| = 10.04 Ang
|a2| = 10.04 Ang
|a3| = 10.04 Ang
```

3.1.2 Reading other data formats into a calculation

`ase.io.read` supports many different file formats:

```
Known formats:

=========================  ===========
format                     short name
=========================  ===========
GPAW restart-file          gpw
Dacapo netCDF output file  dacapo
Old ASE netCDF trajectory  nc
Virtual Nano Lab file      vnl
ASE pickle trajectory      traj
ASE bundle trajectory      bundle
```

```
GPAW text output            gpaw-text
CUBE file                   cube
XCrySDen Structure File     xsf
Dacapo text output          dacapo-text
XYZ-file                    xyz
VASP POSCAR/CONTCAR file    vasp
VASP OUTCAR file            vasp_out
SIESTA STRUCT file          struct_out
ABINIT input file           abinit
V_Sim ascii file            v_sim
Protein Data Bank           pdb
CIF-file                    cif
FHI-aims geometry file      aims
FHI-aims output file        aims_out
VTK XML Image Data          vti
VTK XML Structured Grid     vts
VTK XML Unstructured Grid   vtu
TURBOMOLE coord file        tmol
TURBOMOLE gradient file     tmol-gradient
exciting input              exi
AtomEye configuration       cfg
WIEN2k structure file       struct
DftbPlus input file         dftb
CASTEP geom file            cell
CASTEP output file          castep
CASTEP trajectory file      geom
ETSF format                 etsf.nc
DFTBPlus GEN format         gen
CMR db/cmr-file             db
CMR db/cmr-file             cmr
LAMMPS dump file            lammps
Gromacs coordinates         gro
=========================   ===========
```

You can read XYZ file format to create `ase.Atoms` objects. Here is what an XYZ file format might look like:

```
#+include: molecules/isobutane.xyz
```

The first line is the number of atoms in the file. The second line is often a comment. What follows is one line per atom with the symbol and Cartesian coordinates in Å. Note that the XYZ format does not have unit cell information in it, so you will have to figure out a way to provide it. In this example, we center the atoms in a box with vacuum on all sides (Figure 3).

```python
from ase.io import read, write

atoms = read('molecules/isobutane.xyz')
atoms.center(vacuum=5)
write('images/isobutane-xyz.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-4.py).

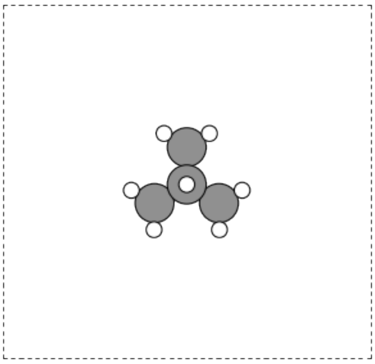


Figure 3: An isobutane molecule read in from an XYZ formatted data file.

3.1.3 Predefined molecules

`ase` defines a number of molecular geometries in the `ase.data.molecules` database. For example, the database includes the molecules in the G2/97 database.[40] This database contains a broad set of atoms and molecules for which good experimental data exists, making them useful for benchmarking studies. See this site for the original files.

The coordinates for the atoms in the database are MP2(full)/6-31G(d) optimized geometries. Here is a list of all the species available in `ase.data.g2`. You may be interested in reading about some of the other databases in `ase.data` too.

```
from ase.data import g2
keys = g2.data.keys()
# print in 3 columns
for i in range(len(keys) / 3):
    print('{0:25s}{1:25s}{2:25s}'.format(*tuple(keys[i * 3: i * 3 + 3])))
```

Open the python script (dft-scripts/script-5.py).

```
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
C4H4S
H2CCHCl
C2H4
C2Cl4
C6H6
H2CCHCN
HCl
Na
CH3CH2SH
C2H5
ClO
NO
HCO
CH3COCH3
CO
CH3COCl
Si
N2
F2
CH2OCH2
SO
ClF3
B
C3H6_Cs
LiF
LiH
C2H6SO
Na2
NH3
ClNO
CH3SCH3
CH3S
S
C2H6
HCN
bicyclobutane
N2H4
H2CCHF
CH3OCH3
CH3SiH3
OCHCHO
SiH3
AlCl3
C2H3
CH3CONH2
C3H4_D2d
CN
N
C3H8
Cl2
CO2
H2O
HCOOCH3
Li
CH3SH
C2H6NH
H2COH
SiO
C5H5N
C4H4O
NH2
C3H6_D3h
H2CO
O
C3H7Cl
CH3CHO
C2H2
H2
C4H4NH
cyclobutane
Li2
NaCl
SiH4
NH
CCl4
ClF
CH2SCH2
CH
F
CH3Cl
CS
NCCN
Cl
CH3CO
butadiene
PF3
CF4
N2O
cyclobutene
Si2
trans-butane
SO2
CH2_s3B1d
Al
CH3CN
```

Some other databases include the `ase.data.s22` for weakly interacting dimers and complexes, and `ase.data.extra_molecules` which has a few extras like biphenyl and C60.

Here is an example of getting the geometry of an acetonitrile molecule and writing an image to a file. Note that the default unit cell is a 1 Å $\times$ Å $\times$ Å cubic cell. That is too small to use if your calculator uses periodic boundary conditions. We center the atoms in the unit cell and add vacuum on each side. We will add 6 Å of vacuum on each side. In the write command we use the option `show_unit_cell` =2 to draw the unit cell boundaries. See Figure 4.

```python
from ase.structure import molecule
from ase.io import write

atoms = molecule('CH3CN')

atoms.center(vacuum=6)
print('unit cell')
print('---------')
print(atoms.get_cell())

write('images/ch3cn.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-6.py).

```
unit cell
```

```
---------
[[ 13.775328   0.          0.        ]
 [  0.        13.537479   0.        ]
 [  0.         0.        15.014576]]
```

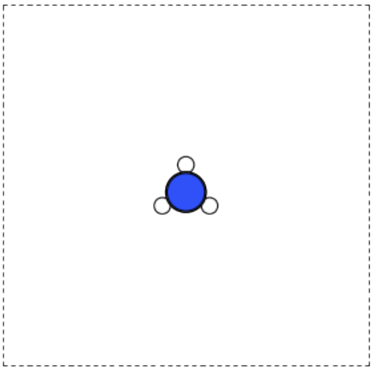


Figure 4: A CH_3CN molecule in a box.

It is possible to rotate the atoms with `ase.io.write` if you wanted to see pictures from another angle. In the next example we rotate 45 degrees about the x-axis, then 45 degrees about the y-axis. Note that this only affects the image, not the actual coordinates. See Figure 5.

```python
from ase.structure import molecule
from ase.io import write

atoms = molecule('CH3CN')

atoms.center(vacuum=6)
print('unit cell')
print('---------')
print(atoms.get_cell())

write('images/ch3cn-rotated.png', atoms,
      show_unit_cell=2, rotation='45x,45y,0z')
```

Open the python script (dft-scripts/script-7.py).

```
unit cell
---------
[[ 13.775328   0.          0.        ]
 [  0.        13.537479   0.        ]
 [  0.         0.        15.014576]]
```

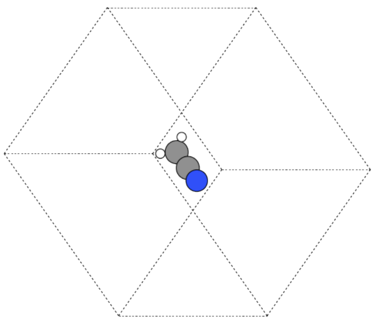


Figure 5: The rotated version of CH_3CN.

If you actually want to rotate the coordinates, there is a nice way to do that too, with the `ase.Atoms.rotate` method. Actually there are some subtleties in rotation. One rotates the molecule an angle (in radians) around a vector, but you have to choose whether the center of mass should be fixed or not. You also must decide whether or not the unit cell should be rotated. In the next example you can see the coordinates have changed due to the rotations. Note that the write function uses the rotation angle in degrees, while the rotate function uses radians.

```python
from ase.structure import molecule
from ase.io import write
from numpy import pi

atoms = molecule('CH3CN')
atoms.center(vacuum=6)
p1 = atoms.get_positions()

atoms.rotate('x', pi/4, center='COM', rotate_cell=False)
atoms.rotate('y', pi/4, center='COM', rotate_cell=False)

write('images/ch3cn-rotated-2.png', atoms, show_unit_cell=2)
print('difference in positions after rotating')
print('atom    difference vector')
print('--------------------------------------')
p2 = atoms.get_positions()

diff = p2 - p1
for i, d in enumerate(diff):
    print('{0} {1}'.format(i, d))
```

Open the python script (dft-scripts/script-8.py).

```
difference in positions after rotating
atom    difference vector
--------------------------------------
0 [-0.65009456  0.91937255  0.65009456]
1 [ 0.08030744 -0.11357187 -0.08030744]
2 [ 0.66947344 -0.94677841 -0.66947344]
3 [-0.32532156  0.88463727  1.35030756]
4 [-1.35405183  1.33495444 -0.04610517]
5 [-0.8340703   1.33495444  1.2092413 ]
```

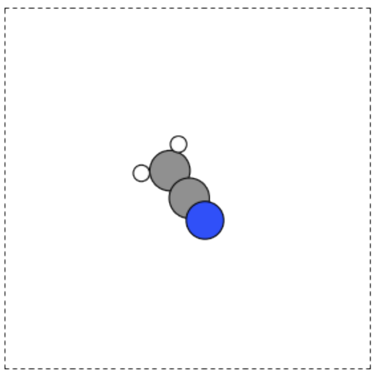


Figure 6: Rotated CH_3CN molecule

Note in this last case the unit cell is oriented differently than the previous example, since we chose not to rotate the unit cell.

3.1.4 Combining Atoms objects

It is frequently useful to combine two `Atoms` objects, e.g. for computing reaction barriers, or other types of interactions. In `ase`, we simply add two `Atoms` objects together. Here is an example of getting an ammonia and oxygen molecule in the same unit cell. See Figure 7. We set the `Atoms` about three Å apart using the `ase.Atoms.translate` function.

```python
from ase.structure import molecule
from ase.io import write

atoms1 = molecule('NH3')

atoms2 = molecule('O2')
atoms2.translate([3, 0, 0])

bothatoms = atoms1 + atoms2
bothatoms.center(5)

write('images/bothatoms.png', bothatoms, show_unit_cell=2, rotation='90x')
```

Open the python script (dft-scripts/script-9.py).

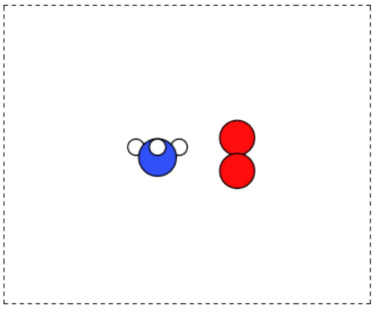


Figure 7: Image featuring ammonia and oxygen molecule in one unit cell.

3.2 Simple properties

Simple properties do not require a DFT calculation. They are typically only functions of the atom types and geometries.

3.2.1 Getting cartesian positions

If you want the (x, y, z) coordinates of the atoms, use the `ase.Atoms.get_positions`. If you are interested in the fractional coordinates, use `ase.Atoms.get_scaled_positions`.

```python
from ase.structure import molecule

atoms = molecule('C6H6')  # benzene

# access properties on each atom
print(' #  sym   p_x      p_y      p_z')
print('------------------------------')
for i, atom in enumerate(atoms):
   print('{0:3d}{1:^4s}{2:-8.2f}{3:-8.2f}{4:-8.2f}'.format(i,
                                                        atom.symbol,
                                                        atom.x,
                                                        atom.y,
                                                        atom.z))

# get all properties in arrays
sym = atoms.get_chemical_symbols()
pos = atoms.get_positions()
```

```python
num = atoms.get_atomic_numbers()

atom_indices = range(len(atoms))

print()
print('  # sym    at#    p_x     p_y     p_z')
print('-------------------------------------')
for i, s, n, p in zip(atom_indices, sym, num, pos):
    px, py, pz = p
    print('{0:3d}{1:>3s}{2:8d}{3:-8.2f}{4:-8.2f}{5:-8.2f}'.format(i, s, n,
                                                              px, py, pz))
```

Open the python script (dft-scripts/script-10.py).

```
 #  sym   p_x      p_y      p_z
------------------------------
  0 C      0.00     1.40     0.00
  1 C      1.21     0.70     0.00
  2 C      1.21    -0.70     0.00
  3 C      0.00    -1.40     0.00
  4 C     -1.21    -0.70     0.00
  5 C     -1.21     0.70     0.00
  6 H      0.00     2.48     0.00
  7 H      2.15     1.24     0.00
  8 H      2.15    -1.24     0.00
  9 H      0.00    -2.48     0.00
 10 H     -2.15    -1.24     0.00
 11 H     -2.15     1.24     0.00
()
  # sym    at#    p_x     p_y     p_z
-------------------------------------
  0  C       6    0.00    1.40    0.00
  1  C       6    1.21    0.70    0.00
  2  C       6    1.21   -0.70    0.00
  3  C       6    0.00   -1.40    0.00
  4  C       6   -1.21   -0.70    0.00
  5  C       6   -1.21    0.70    0.00
  6  H       1    0.00    2.48    0.00
  7  H       1    2.15    1.24    0.00
  8  H       1    2.15   -1.24    0.00
  9  H       1    0.00   -2.48    0.00
 10  H       1   -2.15   -1.24    0.00
 11  H       1   -2.15    1.24    0.00
```

3.2.2 Molecular weight and molecular formula

We can quickly compute the molecular weight of a molecule with this recipe. We use `ase.Atoms.get_masses` to get an array of the atomic masses of each atom in the `Atoms` object, and then just sum them up.

```python
from ase.structure import molecule

atoms = molecule('C6H6')
masses = atoms.get_masses()

molecular_weight = masses.sum()
molecular_formula = atoms.get_chemical_formula(mode='reduce')

# note use of two lines to keep length of line reasonable
```

```python
s = 'The molecular weight of {0} is {1:1.2f} gm/mol'
print(s.format(molecular_formula, molecular_weight))
```

Open the python script (dft-scripts/script-11.py).

```
The molecular weight of C6H6 is 78.11 gm/mol
```

Note that the argument `reduce=True` for `ase.Atoms.get_chemical_formula` collects all the symbols to provide a molecular formula.

3.2.3 Center of mass

The center of mass (COM) is defined as:

$$\mathrm{COM} = \frac{\sum m_i \cdot r_i}{\sum m_i}$$

The center of mass is essentially the average position of the atoms, weighted by the mass of each atom. Here is an example of getting the center of mass from an `Atoms` object using `ase.Atoms.get_center_of_mass`.

```python
from ase.structure import molecule
import numpy as np

# ammonia
atoms = molecule('NH3')

  # cartesian coordinates
print('COM1 = {0}'.format(atoms.get_center_of_mass()))

# compute the center of mass by hand
pos = atoms.positions
masses = atoms.get_masses()

COM = np.array([0., 0., 0.])
for m, p in zip(masses, pos):
    COM += m*p
COM /= masses.sum()

print('COM2 = {0}'.format(COM))

# one-line linear algebra definition of COM
print('COM3 = {0}'.format(np.dot(masses, pos) / np.sum(masses)))
```

Open the python script (dft-scripts/script-12.py).

```
COM1 = [  0.00000000e+00   5.91843349e-08   4.75457009e-02]
COM2 = [  0.00000000e+00   5.91843349e-08   4.75457009e-02]
COM3 = [  0.00000000e+00   5.91843349e-08   4.75457009e-02]
```

You can see see that these centers of mass, which are calculated by different methods, are the same.

3.2.4 Moments of inertia

The moment of inertia is a measure of resistance to changes in rotation. It is defined by $I = \sum_{i=1}^{N} m_i r_i^2$ where r_i is the distance to an axis of rotation. There are typically three moments of inertia, although some may be zero depending on symmetry, and others may be degenerate. There is a convenient function to get the moments of inertia: `ase.Atoms.get_moments_of_inertia`. Here are several examples of molecules with different types of symmetry.:

```python
from ase.structure import molecule

print('linear rotors: I = [0 Ia Ia]')
atoms = molecule('CO2')
```

```
print('  CO2 moments of inertia: {}'.format(atoms.get_moments_of_inertia()))
print('')

print('symmetric rotors (Ia = Ib) < Ic')
atoms = molecule('NH3')
print('  NH3 moments of inertia: {}'.format(atoms.get_moments_of_inertia()))

atoms = molecule('C6H6')
print('  C6H6 moments of inertia: {}'.format(atoms.get_moments_of_inertia()))
print('')

print('symmetric rotors Ia < (Ib = Ic)')
atoms = molecule('CH3Cl')
print('CH3Cl moments of inertia: {}'.format(atoms.get_moments_of_inertia()))
print('')

print('spherical rotors Ia = Ib = Ic')
atoms = molecule('CH4')
print('  CH4 moments of inertia: {}'.format(atoms.get_moments_of_inertia()))
print('')

print('unsymmetric rotors Ia != Ib != Ic')
atoms = molecule('C3H7Cl')
print('  C3H7Cl moments of inertia: {}'.format(atoms.get_moments_of_inertia()))
```

Open the python script (dft-scripts/script-13.py).

```
linear rotors: I = [0 Ia Ia]
  CO2 moments of inertia: [  0.          44.45384271  44.45384271]

symmetric rotors (Ia = Ib) < Ic
  NH3 moments of inertia: [ 1.71012426  1.71012548  2.67031768]
  C6H6 moments of inertia: [  88.77914641   88.77916799  177.5583144 ]

symmetric rotors Ia < (Ib = Ic)
CH3Cl moments of inertia: [  3.20372189  37.97009644  37.97009837]

spherical rotors Ia = Ib = Ic
  CH4 moments of inertia: [ 3.19145621  3.19145621  3.19145621]

unsymmetric rotors Ia != Ib != Ic
  C3H7Cl moments of inertia: [  19.41351508  213.18961963  223.16255537]
```

If you want to know the principle axes of rotation, we simply pass `vectors=True` to the function, and it returns the moments of inertia and the principle axes.

```
from ase.structure import molecule

atoms = molecule('CH3Cl')
moments, axes = atoms.get_moments_of_inertia(vectors=True)
print('Moments = {0}'.format(moments))
print('axes = {0}'.format(axes))
```

Open the python script (dft-scripts/script-14.py).

```
Moments = [  3.20372189  37.97009644  37.97009837]
axes = [[ 0.  0.  1.]
 [ 0.  1.  0.]
 [ 1.  0.  0.]]
```

This shows the first moment is about the z-axis, the second moment is about the y-axis, and the third moment is about the x-axis.

3.2.5 Computing bond lengths and angles

A typical question we might ask is, "What is the structure of a molecule?" In other words, what are the bond lengths, angles between bonds, and similar properties. The Atoms object contains an ase.Atoms.get_distance method to make this easy. To calculate the distance between two atoms, you have to specify their indices, remembering that the index starts at 0.

```
from ase.structure import molecule

# ammonia
atoms = molecule('NH3')

print('atom symbol')
print('===========')
for i, atom in enumerate(atoms):
    print('{0:2d} {1:3s}' .format(i, atom.symbol))

# N-H bond length
s = 'The N-H distance is {0:1.3f} angstroms'
print(s.format(atoms.get_distance(0, 1)))
```

Open the python script (dft-scripts/script-15.py).

```
atom symbol
===========
 0 N
 1 H
 2 H
 3 H
The N-H distance is 1.017 angstroms
```

Bond angles are a little trickier. If we had vectors describing the directions between two atoms, we could use some simple trigonometry to compute the angle between the vectors: $\vec{a} \cdot \vec{b} = |\vec{a}||\vec{b}| \cos(\theta)$. So we can calculate the angle as $\theta = \arccos\left(\frac{\vec{a} \cdot \vec{b}}{|\vec{a}||\vec{b}|}\right)$, we just have to define our two vectors $\vec{a}$ and $\vec{b}$. We compute these vectors as the difference in positions of two atoms. For example, here we compute the angle H-N-H in an ammonia molecule. This is the angle between N-H_1 and N-H_2. In the next example, we utilize functions in numpy to perform the calculations, specifically the numpy.arccos function, the numpy.dot function, and numpy.linalg.norm functions.

```
from ase.structure import molecule

# ammonia
atoms = molecule('NH3')

print('atom symbol')
print('===========')
for i, atom in enumerate(atoms):
    print('{0:2d} {1:3s}'.format(i, atom.symbol))

a = atoms.positions[0] - atoms.positions[1]
b = atoms.positions[0] - atoms.positions[2]

from numpy import arccos, dot, pi
from numpy.linalg import norm

theta_rad = arccos(dot(a, b) / (norm(a) * norm(b)))  # in radians

print('theta = {0:1.1f} degrees'.format(theta_rad * 180./pi))
```

Open the python script (dft-scripts/script-16.py).

```
atom symbol
===========
```

```
 0 N
 1 H
 2 H
 3 H
theta = 106.3 degrees
```

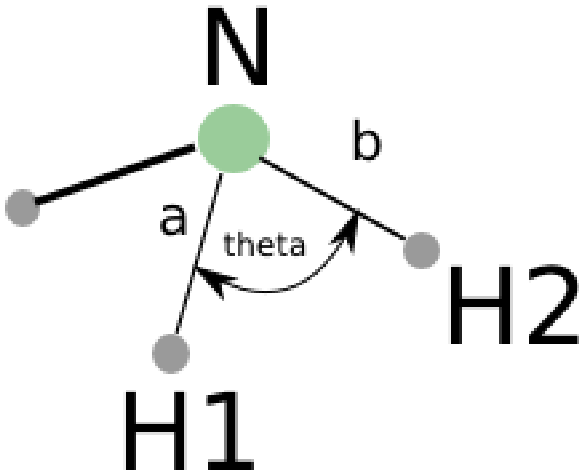


Figure 8: Schematic of the vectors defining the H-N-H angle.

Alternatively you could use `ase.Atoms.get_angle`. Note we want the angle between atoms with indices [1, 0, 2] to get the H-N-H angle.

```python
from ase.structure import molecule
from numpy import pi
# ammonia
atoms = molecule('NH3')

print('theta = {0} degrees'.format(atoms.get_angle([1, 0, 2]) * 180. / pi))
```

Open the python script (dft-scripts/script-17.py).

```
theta = 106.334624232 degrees
```

Dihedral angles There is support in ase for computing dihedral angles. Let us illustrate that for ethane. We will compute the dihedral angle between atoms 5, 1, 0, and 4. That is a H-C-C-H dihedral angle, and one can visually see (although not here) that these atoms have a dihedral angle of 60ř (Figure 9).

```python
# calculate an ethane dihedral angle
from ase.structure import molecule
import numpy as np
```

```python

atoms = molecule('C2H6')

print('atom symbol')
print('===========')
for i, atom in enumerate(atoms):
  print('{0:2d} {1:3s}'.format(i, atom.symbol))

da = atoms.get_dihedral([5, 1, 0, 4]) * 180. / np.pi
print('dihedral angle = {0:1.2f} degrees'.format(da))
```

Open the python script (dft-scripts/script-18.py).

```
atom symbol
===========
 0 C
 1 C
 2 H
 3 H
 4 H
 5 H
 6 H
 7 H
dihedral angle = 60.00 degrees
```

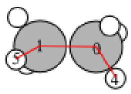


Figure 9: Schematic of the calculated ethane dihedral angle.

In this section we covered properties that require simple calculations, but not DFT calculations, to compute.

3.3 Simple properties that require single computations

There are many properties that only require a single DFT calculation to obtain the energy, forces, density of states, electron density and electrostatic potential. This section describes some of these calculations and their analysis.

3.3.1 Energy and forces

Two of the most important quantities we are interested in are the total energy and the forces on the atoms. To get these quantities, we have to define a calculator and attach it to an `ase.Atoms` object so that `ase` knows how to get the data. After defining the calculator a DFT calculation must be run.

Here is an example of getting the energy and forces from a CO molecule. The forces in this case are very high, indicating that this geometry is not close to the ground state geometry. Note that the forces are only along the x-axis, which is along the molecular axis. We will see how to minimize this force in Manual determination and Automatic geometry optimization with VASP.

Note:
This is your first DFT calculation in the book! See ISMEAR, SIGMA, NBANDS, and ENCUT to learn more about these VASP keywords.

```python
from ase import Atoms, Atom
from vasp import Vasp

co = Atoms([Atom('C', [0, 0, 0]),
            Atom('O', [1.2, 0, 0])],
           cell=(6., 6., 6.))

calc = Vasp('molecules/simple-co',  # output dir
            xc='pbe',  # the exchange-correlation functional
            nbands=6,    # number of bands
            encut=350,    # planewave cutoff
            ismear=1,    # Methfessel-Paxton smearing
            sigma=0.01,  # very small smearing factor for a molecule
            atoms=co)

print('energy = {0} eV'.format(co.get_potential_energy()))
print(co.get_forces())
```

Open the python script (dft-scripts/script-19.py).

```
energy = -14.69111507 eV
[[ 5.09138064  0.          0.        ]
 [-5.09138064  0.          0.        ]]
```

We can see what files were created and used in this calculation by printing the vasp attribute of the calculator.

```python
from vasp import Vasp
print(Vasp('molecules/simple-co').vasp)
```

Open the python script (dft-scripts/script-20.py).

```
INCAR
-----
INCAR created by Atomic Simulation Environment
 ENCUT = 350
 LCHARG = .FALSE.
 NBANDS = 6
 ISMEAR = 1
 LWAVE = .FALSE.
 SIGMA = 0.01


POSCAR
------
 C  O
 1.0000000000000000
     6.0000000000000000    0.0000000000000000    0.0000000000000000
     0.0000000000000000    6.0000000000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000    6.0000000000000000
   1   1
Cartesian
  0.0000000000000000  0.0000000000000000  0.0000000000000000
  1.2000000000000000  0.0000000000000000  0.0000000000000000
```

```
KPOINTS
-------
KPOINTS created by Atomic Simulation Environment
0
Monkhorst-Pack
1 1 1
0.0 0.0 0.0
```

```
POTCAR
------
cat $VASP_PP_PATH/potpaw_PBE/C/POTCAR $VASP_PP_PATH/potpaw_PBE/O/POTCAR > POTCAR
```

Running a job in parallel

```python
from ase import Atoms, Atom
from vasp import Vasp
from vasp.vasprc import VASPRC

VASPRC['queue.ppn'] = 4

co = Atoms([Atom('C', [0, 0, 0]),
            Atom('O', [1.2, 0, 0])],
           cell=(6., 6., 6.))

calc = Vasp('molecules/simple-co-n4',  # output dir
            xc='PBE',  # the exchange-correlation functional
            nbands=6,    # number of bands
            encut=350,    # planewave cutoff
            ismear=1,    # Methfessel-Paxton smearing
            sigma=0.01,  # very small smearing factor for a molecule
            atoms=co)

print('energy = {0} eV'.format(co.get_potential_energy()))
print(co.get_forces())
```

Open the python script (dft-scripts/script-21.py).

```
energy = -14.69072754 eV
[[ 5.09089107  0.          0.        ]
 [-5.09089107  0.          0.        ]]
```

Convergence with unit cell size There are a number of parameters that affect the energy and forces including the calculation parameters and the unit cell. We will first consider the effect of the unit cell on the total energy and forces. The reason that the unit cell affects the total energy is that it can change the distribution of electrons in the molecule.

```python
from vasp import Vasp
from ase import Atoms, Atom
import numpy as np
np.set_printoptions(precision=3, suppress=True)

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()
    calc = Vasp('molecules/co-L-{0}'.format(a),
```

```
                 encut=350,
                 xc='PBE',
                 atoms=atoms)

    energies.append(atoms.get_potential_energy())

print(energies)
calc.stop_if(None in energies)

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')
```

Open the python script (dft-scripts/script-22.py).

```
[-15.35943747, -14.85641864, -14.68750595, -14.63202061, -14.65342838]
```

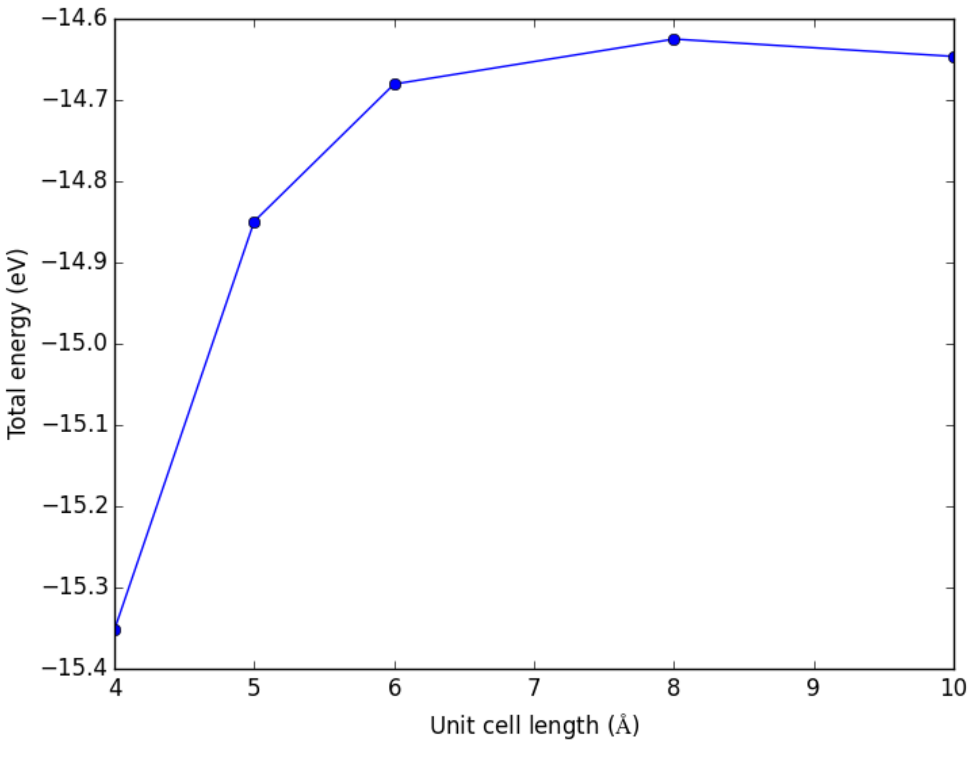


Figure 10: Total energy of a CO molecule as a function of the unit cell length.

Here there are evidently attractive interactions between the CO molecules which lower the total energy for small box sizes. We have to decide what an appropriate volume for our calculation is, and the choice depends on the goal. We may wish to know the total energy of a molecule that is not interacting with any other molecules, e.g. in the ideal gas limit. In that case we need a large unit cell so the electron density from the molecule does not go outside the unit cell where it would overlap with neighboring images.

It pays to check for convergence. The cost of running the calculation goes up steeply with increasing cell size. Doubling a lattice vector here leads to a 20-fold increase in computational time! Note that doubling a lattice vector length increases the volume by a factor of 8 for a cube. The cost goes up because the number of planewaves that fit in the cube grows as the cube gets larger.

```python
from vasp import Vasp

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

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

Open the python script (dft-scripts/script-23.py).

```
4 10.748 seconds
5 11.855 seconds
6 15.613 seconds
8 28.346 seconds
10 45.259 seconds
```

Let us consider what the pressure in the unit cell is. In the ideal gas limit we have $PV = nRT$, which gives a pressure of zero at absolute zero. At non-zero temperatures, we have $P = n/VRT$. Let us consider some examples. In atomic units we use k_B instead of R.

```python
from ase.units import kB, Pascal
import numpy as np
import matplotlib.pyplot as plt

atm = 101325 * Pascal

L = np.linspace(4, 10)
V = L**3

n = 1  # one atom/molecule per unit cell

for T in [298, 600, 1000]:
    P = n / V * kB * T / atm  # convert to atmospheres

    plt.plot(V, P, label='{0}K'.format(T))

plt.xlabel('Unit cell volume ($\AA^3$)')
plt.ylabel('Pressure (atm)')
plt.legend(loc='best')
plt.savefig('images/ideal-gas-pressure.png')
```

Open the python script (dft-scripts/script-24.py).

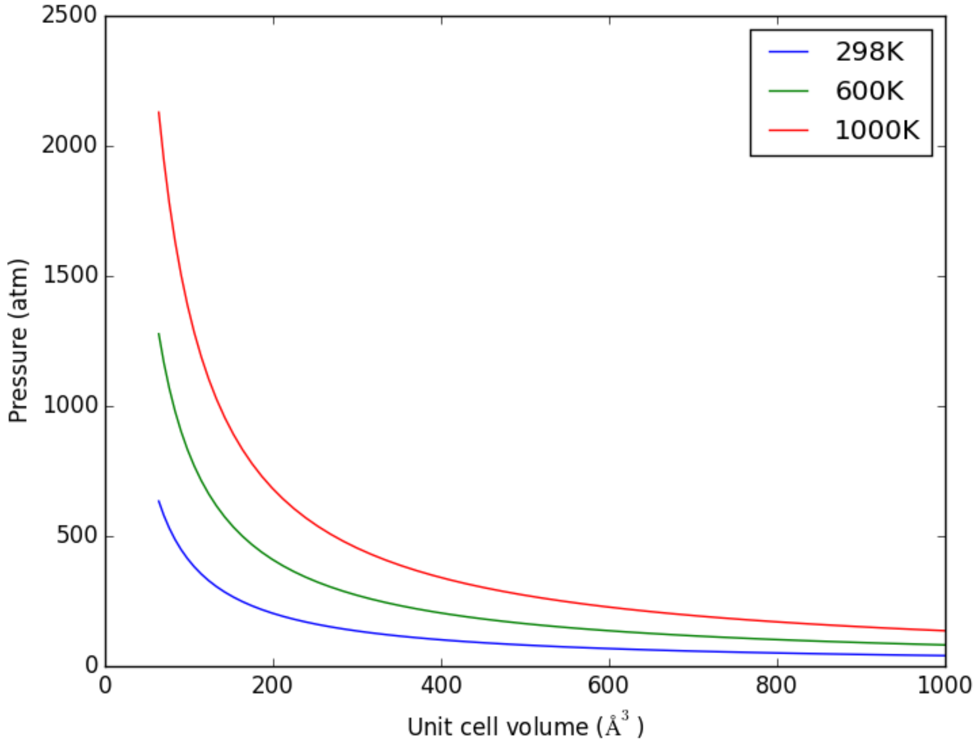


Figure 11: Ideal gas pressure dependence on temperature and unit cell volume.

Convergence of ENCUT The total energy and forces also depend on the computational parameters, notably ENCUT.

```
from ase import Atoms, Atom
from vasp import Vasp
import numpy as np
np.set_printoptions(precision=3, suppress=True)

atoms = Atoms([Atom('C', [0, 0, 0]),
               Atom('O', [1.2, 0, 0])],
              cell=(6, 6, 6))
atoms.center()

ENCUTS = [250, 300, 350, 400, 450, 500]

calcs = [Vasp('molecules/co-en-{0}'.format(en),
              encut=en,
              xc='PBE',
              atoms=atoms)
         for en in ENCUTS]

energies = [calc.potential_energy for calc in calcs]
print(energies)
calcs[0].stop_if(None in energies)

import matplotlib.pyplot as plt
plt.plot(ENCUTS, energies, 'bo-')
plt.xlabel('ENCUT (eV)')
plt.ylabel('Total energy (eV)')
plt.savefig('images/co-encut-v.png')
```

Open the python script (dft-scripts/script-25.py).

```
[-14.95250419, -14.71808896, -14.68750595, -14.66725733, -14.65604528, -14.65012078]
```

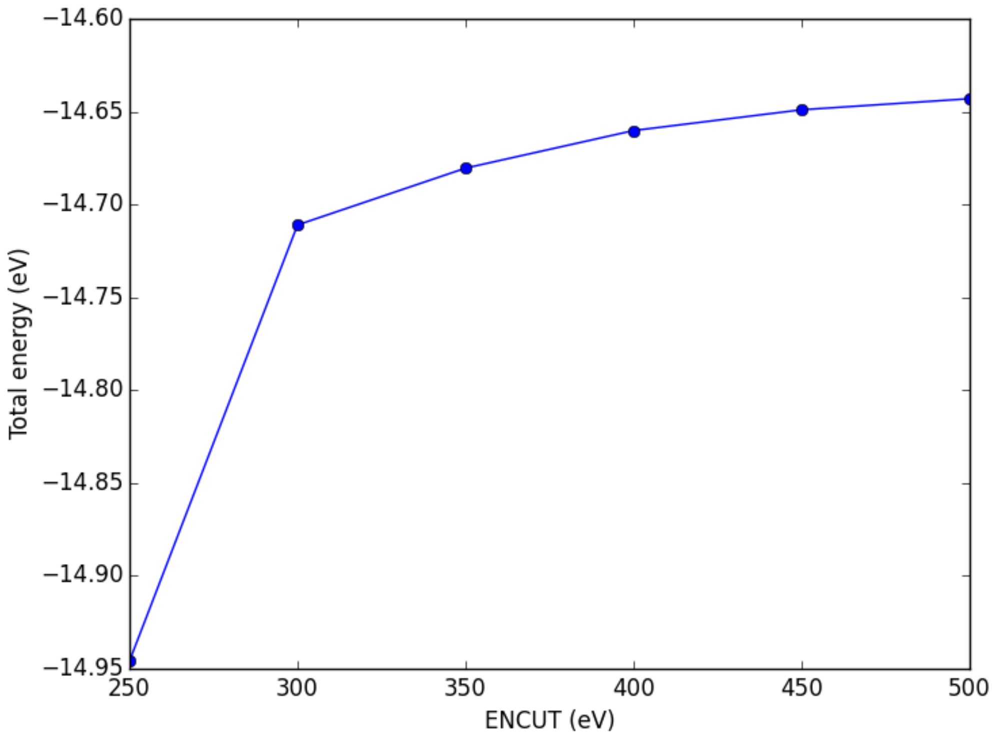


Figure 12: Dependence of the total energy of CO molecule on ENCUT.

You can see in this figure that it takes a cutoff energy of about 400 eV to achieve a convergence level around 10 meV, and that even at 500 meV the energy is still changing slightly. Keep in mind that we are generally interested in differences in total energy, and the differences tend to converge faster than a single total energy. Also it is important to note that it is usually a single element that determines the rate of convergence. The reason we do not just use very high ENCUT all the time is it is expensive.

```
grep "Elapsed time (sec):" molecules/co-en-*/OUTCAR
```

Open the python script (dft-scripts/script-26.py).

```
molecules/co-en-250/OUTCAR:                     Elapsed time (sec):       11.634
molecules/co-en-300/OUTCAR:                     Elapsed time (sec):       14.740
molecules/co-en-350/OUTCAR:                     Elapsed time (sec):       13.577
molecules/co-en-400/OUTCAR:                     Elapsed time (sec):       16.310
molecules/co-en-450/OUTCAR:                     Elapsed time (sec):       17.704
molecules/co-en-500/OUTCAR:                     Elapsed time (sec):       11.658
```

Cloning You may want to clone a calculation, so you can change some parameter without losing the previous result. The clone function does this, and changes the calculator over to the new directory.

```
from ase import Atoms, Atom
from vasp import Vasp
```

```

calc = Vasp('molecules/simple-co')
print('energy = {0} eV'.format(calc.get_atoms().get_potential_energy()))

# This creates the directory and makes it current working directory
calc.clone('molecules/clone-1')
calc.set(encut=325)  # this will trigger a new calculation

print('energy = {0} eV'.format(calc.get_atoms().get_potential_energy()))
```

Open the python script (dft-scripts/script-27.py).

```
energy = -14.69111507 eV
energy = -14.77117554 eV
```

3.3.2 Visualizing electron density

The electron density is a $3d$ quantity: for every (x, y, z) point, there is a charge density. That means we need 4 numbers for each point: (x, y, z) and $\rho(x, y, z)$. Below we show an example (Figure 13) of plotting the charge density, and we consider some issues we have to consider when visualizing volumetric data in unit cells with periodic boundary conditions. We will use the results from a previous calculation.

```
from vasp import Vasp
from enthought.mayavi import mlab
from ase.data import vdw_radii
from ase.data.colors import cpk_colors

calc = Vasp('molecules/simple-co')
calc.clone('molecules/co-chg')
calc.set(lcharg=True)
calc.stop_if(calc.potential_energy is None)

atoms = calc.get_atoms()
x, y, z, cd = calc.get_charge_density()


# make a white figure
mlab.figure(1, bgcolor=(1, 1, 1))

# plot the atoms as spheres
for atom in atoms:
    mlab.points3d(atom.x,
                  atom.y,
                  atom.z,
                  #this determines the size of the atom
                  scale_factor=vdw_radii[atom.number] / 5.,
                  resolution=20,
                  # a tuple is required for the color
                  color=tuple(cpk_colors[atom.number]),
                  scale_mode='none')

# draw the unit cell - there are 8 corners, and 12 connections
a1, a2, a3 = atoms.get_cell()
origin = [0, 0, 0]
cell_matrix = [[origin,  a1],
               [origin,  a2],
               [origin,  a3],
               [a1,      a1 + a2],
               [a1,      a1 + a3],
               [a2,      a2 + a1],
               [a2,      a2 + a3],
               [a3,      a1 + a3],
               [a3,      a2 + a3],
               [a1 + a2, a1 + a2 + a3],
               [a2 + a3, a1 + a2 + a3],
               [a1 + a3, a1 + a3 + a2]]

for p1, p2 in cell_matrix:
    mlab.plot3d([p1[0], p2[0]], # x-positions
                [p1[1], p2[1]], # y-positions
                [p1[2], p2[2]], # z-positions
                tube_radius=0.02)
```

```

# Now plot the charge density

mlab.contour3d(x, y, z, cd)
mlab.view(azimuth=-90, elevation=90, distance='auto')

mlab.savefig('images/co-cd.png')
```

Open the python script (dft-scripts/script-28.py).

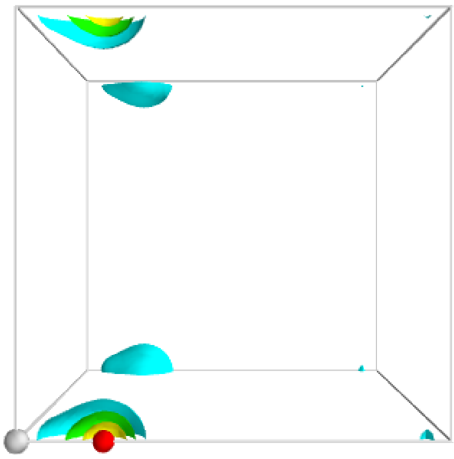


Figure 13: Charge density of a CO molecule that is located at the origin. The electron density that is outside the cell is wrapped around to the other corners.

If we take care to center the CO molecule in the unit cell, we get a nicer looking result.

```
from vasp import Vasp
from enthought.mayavi import mlab
from ase.data import vdw_radii
from ase.data.colors import cpk_colors
from ase import Atom, Atoms

atoms = Atoms([Atom('C', [2.422, 0.0, 0.0]),
               Atom('O', [3.578, 0.0, 0.0])],
               cell=(10,10,10))

atoms.center()

calc = Vasp('molecules/co-centered',
            encut=350,
            xc='PBE',
            atoms=atoms)
calc.set(lcharg=True,)
calc.stop_if(calc.potential_energy is None)

atoms = calc.get_atoms()
x, y, z, cd = calc.get_charge_density()

mlab.figure(bgcolor=(1, 1, 1))

# plot the atoms as spheres
for atom in atoms:
    mlab.points3d(atom.x,
                  atom.y,
                  atom.z,
                  scale_factor=vdw_radii[atom.number]/5,
                  resolution=20,
                  # a tuple is required for the color
                  color=tuple(cpk_colors[atom.number]),
                  scale_mode='none')

```

```
# draw the unit cell - there are 8 corners, and 12 connections
a1, a2, a3 = atoms.get_cell()
origin = [0, 0, 0]
cell_matrix = [[origin,  a1],
               [origin,  a2],
               [origin,  a3],
               [a1,      a1 + a2],
               [a1,      a1 + a3],
               [a2,      a2 + a1],
               [a2,      a2 + a3],
               [a3,      a1 + a3],
               [a3,      a2 + a3],
               [a1 + a2, a1 + a2 + a3],
               [a2 + a3, a1 + a2 + a3],
               [a1 + a3, a1 + a3 + a2]]

for p1, p2 in cell_matrix:
    mlab.plot3d([p1[0], p2[0]], # x-positions
                [p1[1], p2[1]], # y-positions
                [p1[2], p2[2]], # z-positions
                tube_radius=0.02)


# Now plot the charge density
mlab.contour3d(x, y, z, cd, transparent=True)

# this view was empirically found by iteration
mlab.view(azimuth=-90, elevation=90, distance='auto')

mlab.savefig('images/co-centered-cd.png')
mlab.show()
```

Open the python script (dft-scripts/script-29.py).

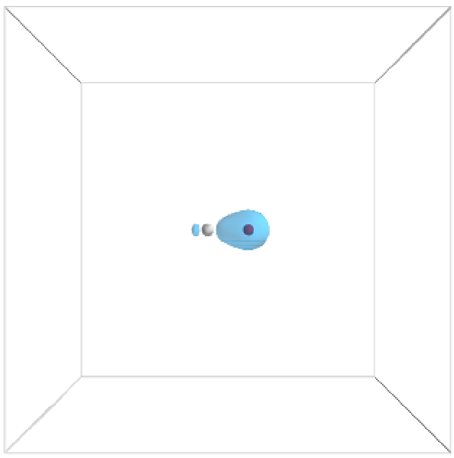


Figure 14: Charge density of a CO molecule centered in the unit cell. Now the electron density is centered in the unit cell.

TODO: how to make this figure http://www.zid.tuwien.ac.at/fileadmin/files_zid/zidline/images/zl22/vasp--fig1.jpg

3.3.3 Visualizing electron density differences

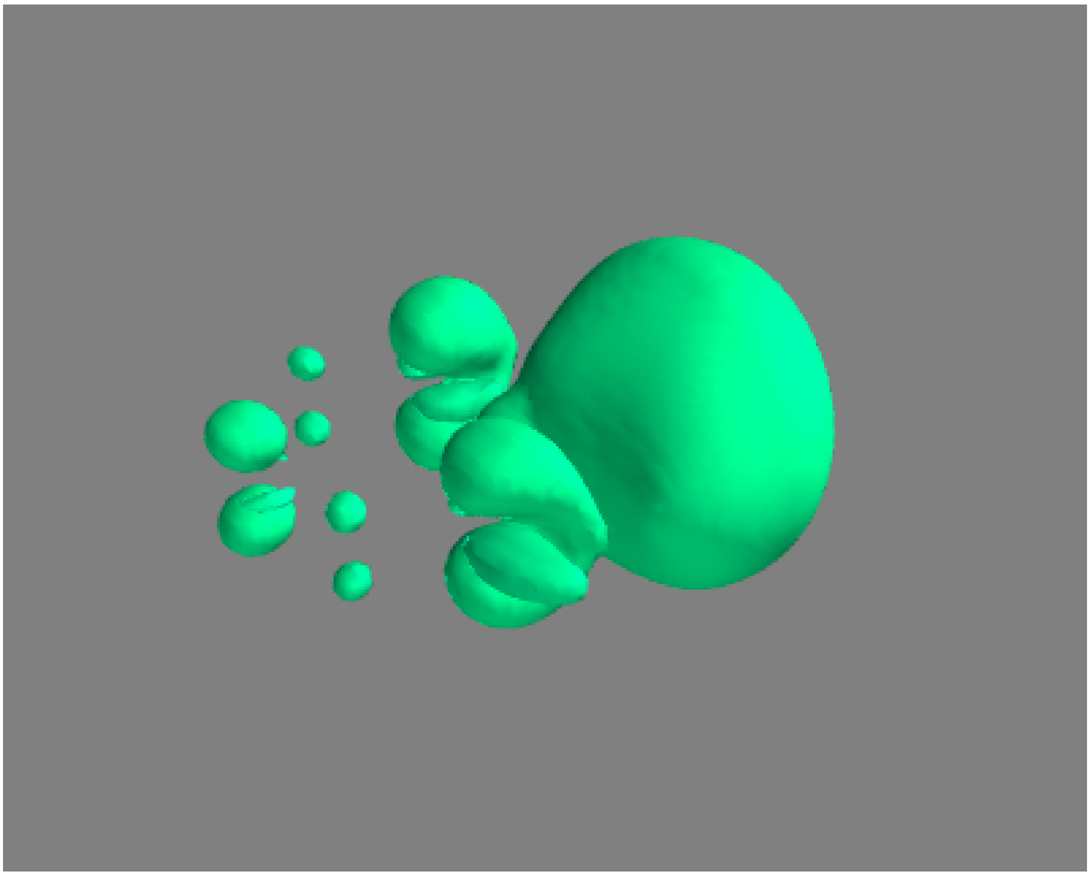
Here, we visualize how charge moves in a benzene ring when you substitute an H atom with an electronegative Cl atom.

```
#!/usr/bin/env python
from ase import *
from ase.structure import molecule
```

```python
from vasp import Vasp

### Setup calculators
benzene = molecule('C6H6')
benzene.set_cell([10, 10, 10])
benzene.center()

calc1 = Vasp('molecules/benzene',
            xc='PBE',
            nbands=18,
            encut=350,
            atoms=benzene)
calc1.set(lcharg=True)

chlorobenzene =  molecule('C6H6')
chlorobenzene.set_cell([10, 10, 10])
chlorobenzene.center()
chlorobenzene[11].symbol ='Cl'

calc2 = Vasp('molecules/chlorobenzene',
            xc='PBE',
            nbands=22,
            encut=350,
            atoms=chlorobenzene)
calc2.set(lcharg=True)
calc2.stop_if(None in (calc1.potential_energy, calc2.potential_energy))

x1, y1, z1, cd1 = calc1.get_charge_density()
x2, y2, z2, cd2 = calc2.get_charge_density()

cdiff = cd2 - cd1

print(cdiff.min(), cdiff.max())
##########################################


##### set up visualization of charge difference
from enthought.mayavi import mlab
mlab.contour3d(x1, y1, z1, cdiff,
               contours=[-0.02, 0.02])

mlab.savefig('images/cdiff.png')
```

Open the python script (dft-scripts/script-30.py).

```
(-2.0821159999999987, 2.9688999999999979)
```

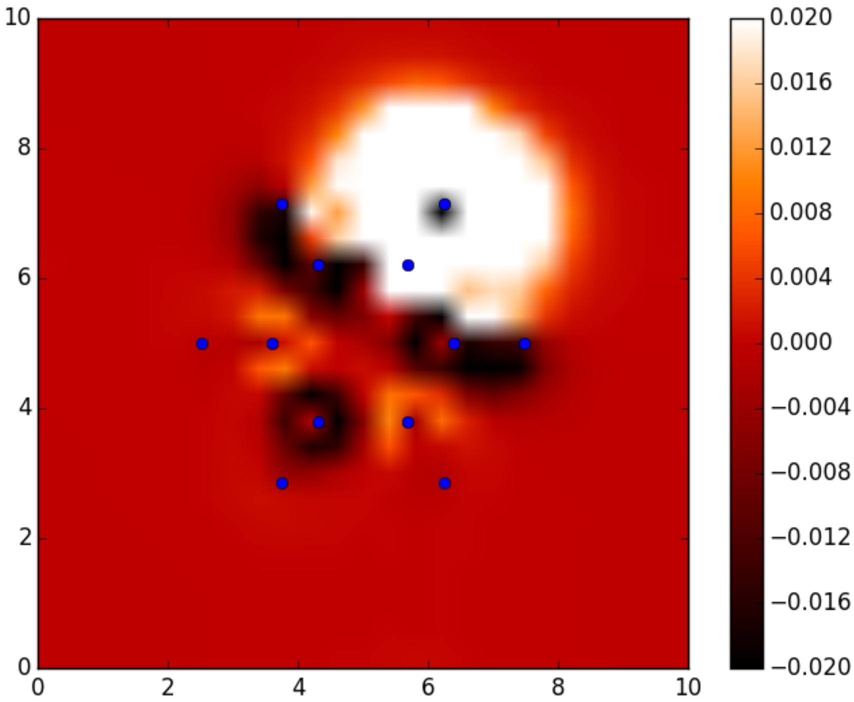


```python
#!/usr/bin/env python
from ase import *
from ase.structure import molecule
from vasp import Vasp
import bisect
import numpy as np

def vinterp3d(x, y, z, u, xi, yi, zi):
    "Interpolate the point (xi, yi, zi) from the values at u(x, y, z)"
    p = np.array([xi, yi, zi])

    #1D arrays of coordinates
    xv = x[:, 0, 0]
    yv = y[0, :, 0]
    zv = z[0, 0, :]

    # we subtract 1 because bisect tells us where to insert the
    # element to maintain an ordered list, so we want the index to the
    # left of that point
    i = bisect.bisect_right(xv, xi) - 1
    j = bisect.bisect_right(yv, yi) - 1
    k = bisect.bisect_right(zv, zi) - 1

    if i == len(x) - 1:
        i = len(x) - 2
    elif i < 0:
        i = 0

    if j == len(y) - 1:
        j = len(y) - 2
    elif j < 0:
        j = 0

    if k == len(z) - 1:
        k = len(z) - 2
    elif k < 0:
```

```
        k = 0

    # points at edge of cell. We only need P1, P2, P3, and P5
    P1 = np.array([x[i, j, k],
                   y[i, j, k],
                   z[i, j, k]])
    P2 = np.array([x[i + 1, j, k],
                   y[i + 1, j, k],
                   z[i + 1, j, k]])
    P3 = np.array([x[i, j + 1, k],
                   y[i, j + 1, k],
                   z[i, j + 1, k]])
    P5 = np.array([x[i, j, k + 1],
                   y[i, j, k + 1],
                   z[i, j, k + 1]])

    # values of u at edge of cell
    u1 = u[i, j, k]
    u2 = u[i+1, j, k]
    u3 = u[i, j+1, k]
    u4 = u[i+1, j+1, k]
    u5 = u[i, j, k+1]
    u6 = u[i+1, j, k+1]
    u7 = u[i, j+1, k+1]
    u8 = u[i+1, j+1, k+1]

    # cell basis vectors, not the unit cell, but the voxel cell containing the point
    cbasis = np.array([P2 - P1,
                       P3 - P1,
                       P5 - P1])

    # now get interpolated point in terms of the cell basis
    s = np.dot(np.linalg.inv(cbasis.T), np.array([xi, yi, zi]) - P1)

    # now s = (sa, sb, sc) which are fractional coordinates in the vector space
    # next we do the interpolations
    ui1 = u1 + s[0] * (u2 - u1)
    ui2 = u3 + s[0] * (u4 - u3)

    ui3 = u5 + s[0] * (u6 - u5)
    ui4 = u7 + s[0] * (u8 - u7)

    ui5 = ui1 + s[1] * (ui2 - ui1)
    ui6 = ui3 + s[1] * (ui4 - ui3)

    ui7 = ui5 + s[2] * (ui6 - ui5)

    return ui7

### Setup calculators
calc = Vasp('molecules/benzene')
benzene = calc.get_atoms()
x1, y1, z1, cd1 = calc.get_charge_density()

calc = Vasp('molecules/chlorobenzene')
x2, y2, z2, cd2 = calc.get_charge_density()

cdiff = cd2 - cd1

#we need the x-y plane at z=5
import matplotlib.pyplot as plt
from scipy import mgrid

X, Y = mgrid[0: 10: 25j, 0: 10: 25j]

cdiff_plane = np.zeros(X.shape)
ni, nj = X.shape

for i in range(ni):
    for j in range(nj):
        cdiff_plane[i, j] = vinterp3d(x1, y1, z1, cdiff,
                                      X[i, j], Y[i, j], 5.0)

plt.imshow(cdiff_plane.T,
           vmin=-0.02,  # min charge diff to plot
           vmax=0.02,  # max charge diff to plot
           cmap=plt.cm.gist_heat,  # colormap
           extent=(0., 10., 0., 10.))  # axes limits
```

```
# plot atom positions. It is a little tricky to see why we reverse the x and y coordinates. That is because imshow does that.
x = [a.x for a in benzene]
y = [a.y for a in benzene]
plt.plot(x, y, 'bo')

plt.colorbar() #add colorbar
plt.savefig('images/cdiff-imshow.png')
plt.show()
```

Open the python script (dft-scripts/script-31.py).



3.3.4 Dipole moments

The dipole moment is a vector describing the separation of electrical (negative) and nuclear (positive) charge. The magnitude of this vector is the dipole moment, which has units of Coulomb-meter, or more commonly Debye. The symmetry of a molecule determines if a molecule has a dipole moment or not. Below we compute the dipole moment of CO. We must integrate the electron density to find the center of electrical charge, and compute a sum over the nuclei to find the center of positive charge.

```
from vasp import Vasp
from vasp.VaspChargeDensity import VaspChargeDensity
import numpy as np
from ase.units import Debye
import os

calc = Vasp('molecules/co-centered')
atoms = calc.get_atoms()
calc.stop_if(atoms.get_potential_energy() is None)

vcd = VaspChargeDensity('molecules/co-centered/CHG')

cd = np.array(vcd.chg[0])

```

```python
n0, n1, n2 = cd.shape

s0 = 1.0 / n0
s1 = 1.0 / n1
s2 = 1.0 / n2

X, Y, Z = np.mgrid[0.0:1.0:s0,
                   0.0:1.0:s1,
                   0.0:1.0:s2]

C = np.column_stack([X.ravel(),
                     Y.ravel(),
                     Z.ravel()])

atoms = calc.get_atoms()
uc = atoms.get_cell()
real = np.dot(C, uc)

# now convert arrays back to unitcell shape
x = np.reshape(real[:, 0], (n0, n1, n2))
y = np.reshape(real[:, 1], (n0, n1, n2))
z = np.reshape(real[:, 2], (n0, n1, n2))


nelements = n0 * n1 * n2
voxel_volume = atoms.get_volume() / nelements
total_electron_charge = -cd.sum() * voxel_volume

electron_density_center = np.array([(cd * x).sum(),
                                    (cd * y).sum(),
                                    (cd * z).sum()])
electron_density_center *= voxel_volume
electron_density_center /= total_electron_charge

electron_dipole_moment = -electron_density_center * total_electron_charge

# now the ion charge center. We only need the Zval listed in the potcar
from vasp.POTCAR import get_ZVAL

LOP = calc.get_pseudopotentials()
ppp = os.environ['VASP_PP_PATH']

zval = {}
for sym, ppath, hash in LOP:
    fullpath = os.path.join(ppp, ppath)
    z = get_ZVAL(fullpath)
    zval[sym] = z
    ion_charge_center = np.array([0.0, 0.0, 0.0])
    total_ion_charge = 0.0

for atom in atoms:
    Z = zval[atom.symbol]
    total_ion_charge += Z
    pos = atom.position
    ion_charge_center += Z * pos

ion_charge_center /= total_ion_charge
ion_dipole_moment = ion_charge_center * total_ion_charge

dipole_vector = (ion_dipole_moment + electron_dipole_moment)

dipole_moment = ((dipole_vector**2).sum())**0.5 / Debye
print('The dipole vector is {0}'.format(dipole_vector))
print('The dipole moment is {0:1.2f} Debye'.format(dipole_moment))
```

Open the python script (dft-scripts/script-32.py).

```
The dipole vector is [ 0.02048406  0.00026357  0.00026357]
The dipole moment is 0.10 Debye
```

Note that a function using the code above exists in `vasp` which makes it trivial to compute the dipole moment. Here is an example of its usage.

```python
from vasp import Vasp
from ase.units import Debye
```

```python

calc = Vasp('molecules/co-centered')

dipole_moment = calc.get_dipole_moment()
print('The dipole moment is {0:1.2f} Debye'.format(dipole_moment))
```

Open the python script (dft-scripts/script-33.py).

```
The dipole moment is 0.10 Debye
```

3.3.5 The density of states (DOS)

The density of states (DOS) gives you the number of electronic states (i.e., the orbitals) that have a particular energy. We can get this information from the last calculation we just ran without having to run another DFT calculation.

```python
from vasp import Vasp
from ase.dft.dos import DOS
import matplotlib.pyplot as plt

calc = Vasp('molecules/simple-co')   # we already ran this!
dos = DOS(calc)
plt.plot(dos.get_energies(), dos.get_dos())
plt.xlabel('Energy - $E_f$ (eV)')
plt.ylabel('DOS')

# make sure you save the figure outside the with statement, or provide
# the correct relative or absolute path to where you want it.
plt.savefig('images/co-dos.png')
```

Open the python script (dft-scripts/script-34.py).

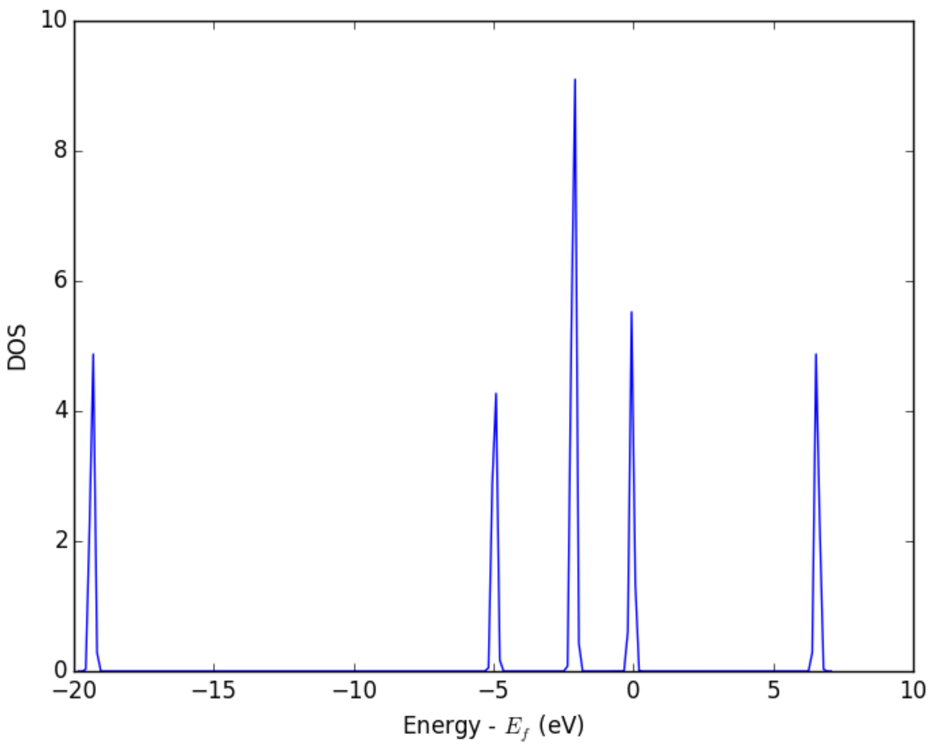


Figure 15: Density of states for a CO molecule.

3.3.6 Atom-projected density of states on molecules

Let us consider which states in the density of states belong to which atoms in a molecule. This can only be a qualitative consideration because the orbitals on the atoms often hybridize to form molecular orbitals, e.g. in methane the s and p orbitals can form what we call sp^3 orbitals. We can compute atom-projected density of states in VASP, which is done by projecting the wave function onto localized atomic orbitals. Here is an example. We will consider the CO molecule. To get atom-projected density of states, we must set RWIGS for each atom. This parameter defines the radius of the sphere around the atom which cuts off the projection. The total density of states and projected density of states information comes from the DOSCAR file.

Note that unlike the DOS, here we must run another calculation because we did not specify the atom-projected keywords above. Our strategy is to get the atoms from the previous calculation, and use them in a new calculation. You could redo the calculation in the same directory, but you risk losing the results of the first step. That can make it difficult to reproduce a result. We advocate our approach of using multiple directories for the subsequent calculations, because it leaves a clear trail of how the work was done.

Note:
The RWIGS is not uniquely determined for an element. There are various natural choices, e.g. the ionic radius of an atom, or a value that minimizes overlap of neighboring spheres, but these values can change slightly in different environments.
You can also get spin-polarized atom-projected DOS, and magnetization projected DOS. See `http://cms.mpi.univie.ac.at/vasp/vasp/DOSCAR_file.html#doscar` for more details.

```
from vasp import Vasp
from ase.dft.dos import DOS
import matplotlib.pyplot as plt

# get the geometry from another calculation
calc = Vasp('molecules/simple-co')
atoms = calc.get_atoms()

calc = Vasp('molecules/co-ados',
            encut=300,
            xc='PBE',
            rwigs={'C': 1.0, 'O': 1.0},     # these are the cutoff radii for projected states
            atoms=atoms)

calc.stop_if(calc.potential_energy is None)

# now get results
dos = DOS(calc)
plt.plot(dos.get_energies(), dos.get_dos() + 10)

energies, c_s = calc.get_ados(0, 's')
_, c_p = calc.get_ados(0, 'p')
_, o_s = calc.get_ados(1, 's')
_, o_p = calc.get_ados(1, 'p')

_, c_d = calc.get_ados(0, 'd')
_, o_d = calc.get_ados(1, 'd')

plt.plot(energies, c_s + 6, energies, o_s + 5)
plt.plot(energies, c_p + 4, energies, o_p + 3)
plt.plot(energies, c_d, energies, o_d + 2)
plt.xlabel('Energy - $E_f$ (eV)')
plt.ylabel('DOS')
plt.legend(['DOS',
            'C$_s$', 'O$_s$',
            'C$_p$', 'O$_p$',
            'C$_d$', 'O$_d$'],
           ncol=2, loc='best')
plt.savefig('images/co-ados.png')
```

Open the python script (dft-scripts/script-35.py).

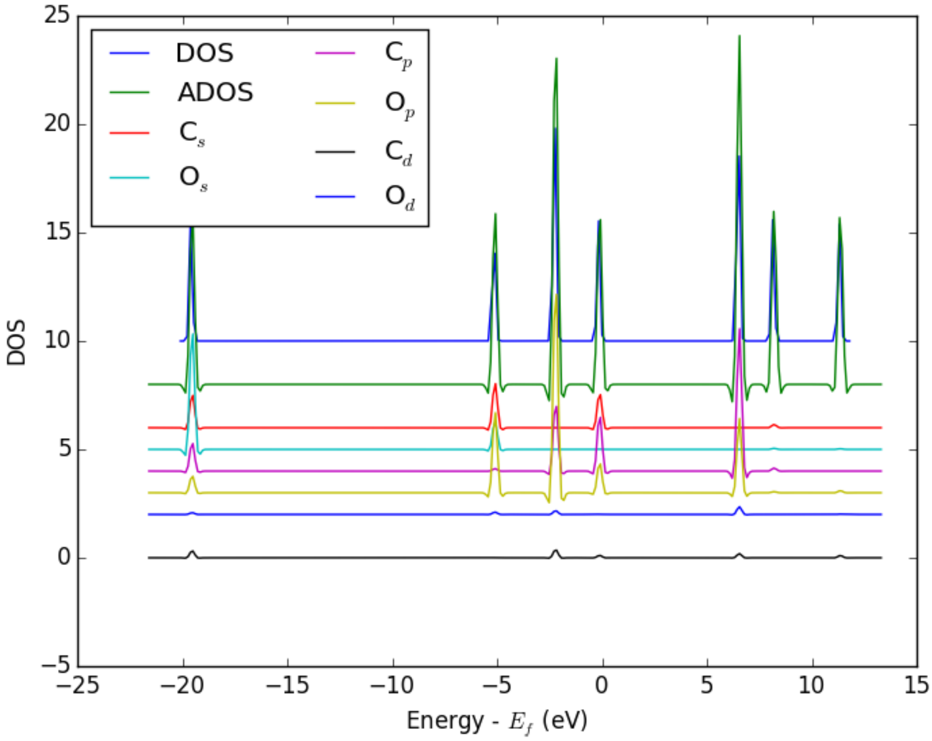


Figure 16: Atom-projected DOS for a CO molecule. The total density of states and the s, p and d states on the C and O are shown.

3.3.7 Electrostatic potential

This is an example of the so-called σ hole in a halogen bond. The coordinates for the CF_3Br molecule were found at http://cccbdb.nist.gov/exp2.asp?casno=75638.

```
from vasp import Vasp
from ase import Atom, Atoms
from ase.io import write

from enthought.mayavi import mlab
from ase.data import vdw_radii
from ase.data.colors import cpk_colors

atoms = Atoms([Atom('C',  [ 0.0000,       0.0000,                -0.8088]),
               Atom('Br', [ 0.0000,       0.0000,                 1.1146]),
               Atom('F',  [ 0.0000,       1.2455,                -1.2651]),
               Atom('F',  [ 1.0787,   -0.6228,                -1.2651]),
               Atom('F',  [-1.0787,   -0.6228,                -1.2651])],
               cell=(10, 10, 10))
atoms.center()

calc = Vasp('molecules/CF3Br',
            encut=350,
            xc='PBE',
            ibrion=1,
            nsw=50,
            lcharg=True,
            lvtot=True,
            lvhar=True,
            atoms=atoms)
calc.set_nbands(f=2)
calc.stop_if(calc.potential_energy is None)
```

```python

x, y, z, lp = calc.get_local_potential()
x, y, z, cd = calc.get_charge_density()

mlab.figure(1, bgcolor=(1, 1, 1)) # make a white figure

# plot the atoms as spheres
for atom in atoms:
    mlab.points3d(atom.x,
                  atom.y,
                  atom.z,
                  scale_factor=vdw_radii[atom.number]/5.,
                  resolution=20,
                  # a tuple is required for the color
                  color=tuple(cpk_colors[atom.number]),
                  scale_mode='none')
# plot the bonds. We want a line from C-Br, C-F, etc...
# We create a bond matrix showing which atoms are connected.
bond_matrix = [[0, 1],
               [0, 2],
               [0, 3],
               [0, 4]]

for a1, a2 in bond_matrix:
    mlab.plot3d(atoms.positions[[a1,a2], 0], # x-positions
                atoms.positions[[a1,a2], 1], # y-positions
                atoms.positions[[a1,a2], 2], # z-positions
                [2, 2],
                tube_radius=0.02,
                colormap='Reds')

mlab.contour3d(x, y, z, lp)
mlab.savefig('images/halogen-ep.png')
mlab.show()
```

Open the python script (dft-scripts/script-36.py).

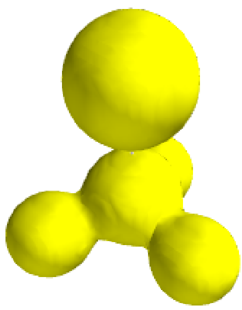


Figure 17: Plot of the electrostatic potential of CF_3Br. TODO: figure out how to do an isosurface of charge, colormapped by the local potential.

See http://www.uni-due.de/~hp0058/?file=manual03.html&dir=vmdplugins for examples of using VMD for visualization.

3.3.8 Bader analysis

Note: Thanks to @prtkm for helping improve this section (https://github.com/jkitchin/dft-book/issues/2). Bader analysis is a charge partitioning scheme where charge is divided by surfaces of zero flux that define atomic basins of charge. The most modern way of calculating the Bader charges is using the `bader` program from Graeme Henkelmen's group.[41,42] Let us consider a water molecule, centered in a box. The strategy is first to run the calculation, then run the bader program on the results.

We have to specify laechg to be true so that the all-electron core charges will be written out to files. Here we setup and run the calculation to get the densities first.

```
from vasp import Vasp

from ase.structure import molecule
atoms = molecule('H2O')
atoms.center(vacuum=6)

calc = Vasp('molecules/h2o-bader',
            xc='PBE',
            encut=350,
            lcharg=True,
            laechg=True,
            atoms=atoms)
print calc.potential_energy
```

Open the python script (dft-scripts/script-37.py).

```
-14.22250648
```

Now that the calculation is done, get the bader code and scripts from http://theory.cm.utexas.edu/henkelman/code/bader/.

We use this code to see the changes in charges on the atoms.

```
from vasp import Vasp

calc = Vasp('molecules/h2o-bader')
calc.bader(ref=True, overwrite=True)
atoms = calc.get_atoms()
for atom in atoms:
    print('|{0} | {1} |'.format(atom.symbol, atom.charge))
```

Open the python script (dft-scripts/script-38.py).

```
|O | -1.2326 |
|H | 0.6161 |
|H | 0.6165 |
```

The results above are comparable to those from gpaw at https://wiki.fysik.dtu.dk/gpaw/tutorials/bader/bader.html.

You can see some charge has been "transferred" from H to O.

3.4 Geometry optimization

3.4.1 Manual determination of a bond length

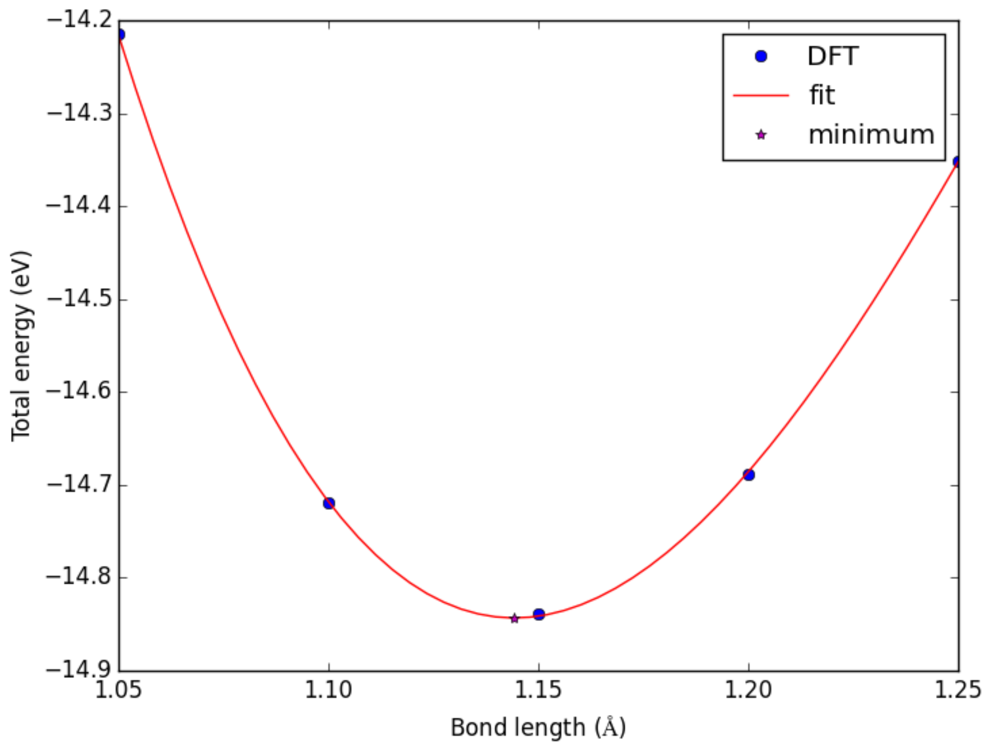
The equilibrium bond length of a CO molecule is approximately the bond length that minimizes the total energy. We can find that by computing the total energy as a function of bond length, and noting where the minimum is. Here is an example in VASP. There are a few features to point out here. We want to compute 5 bond lengths, and each calculation is independent of all the others. vasp is set up to automatically handle jobs for you by submitting them to the queue. It raises a variety of exceptions to let you know what has happened, and you must handle these to control the workflow. We will illustrate this by the following examples.

```
from vasp import Vasp
from ase import Atom, Atoms

bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
```

```python
energies = []

for d in bond_lengths:  # possible bond lengths

    co = Atoms([Atom('C', [0, 0, 0]),
                Atom('O', [d, 0, 0])],
               cell=(6, 6, 6))

    calc = Vasp('molecules/co-{0}'.format(d),  # output dir
                xc='PBE',
                nbands=6,
                encut=350,
                ismear=1,
                sigma=0.01,
                atoms=co)

    energies.append(co.get_potential_energy())
    print('d = {0:1.2f} ang'.format(d))
    print('energy = {0:1.3f} eV'.format(energies[-1] or 0))
    print('forces = (eV/ang)\n {0}'.format(co.get_forces()))
    print('')  # blank line

if None in energies:
    calc.abort()
else:
    import matplotlib.pyplot as plt
    plt.plot(bond_lengths, energies, 'bo-')
    plt.xlabel(r'Bond length ($\AA$)')
    plt.ylabel('Total energy (eV)')
    plt.savefig('images/co-bondlengths.png')
```

Open the python script (dft-scripts/script-39.py).

```
d = 1.05 ang
energy = -14.216 eV
forces = (eV/ang)
 [[-14.93017486   0.           0.        ]
 [ 14.93017486   0.           0.        ]]

d = 1.10 ang
energy = -14.722 eV
forces = (eV/ang)
 [[-5.81988086  0.          0.        ]
 [ 5.81988086  0.          0.        ]]

d = 1.15 ang
energy = -14.841 eV
forces = (eV/ang)
 [[ 0.63231023  0.          0.        ]
 [-0.63231023  0.          0.        ]]

d = 1.20 ang
energy = -14.691 eV
forces = (eV/ang)
 [[ 5.09138064  0.          0.        ]
 [-5.09138064  0.          0.        ]]

d = 1.25 ang
energy = -14.355 eV
forces = (eV/ang)
 [[ 8.14027842  0.          0.        ]
 [-8.14027842  0.          0.        ]]
```



Before continuing, it is worth looking at some other approaches to setup and run these calculations. Here we consider a functional approach that uses list comprehensions pretty extensively.

```
from vasp import Vasp
from ase import Atom, Atoms

bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]

ATOMS = [Atoms([Atom('C', [0, 0, 0]),
                Atom('O', [d, 0, 0])],
               cell=(6, 6, 6))
         for d in bond_lengths]

calcs = [Vasp('molecules/co-{0}'.format(d),  # output dir
                xc='PBE',
                nbands=6,
                encut=350,
                ismear=1,
                sigma=0.01,
                atoms=atoms)
         for d, atoms in zip(bond_lengths, ATOMS)]

energies = [atoms.get_potential_energy() for atoms in ATOMS]

print(energies)
```

Open the python script (dft-scripts/script-40.py).

```
[-14.21584765, -14.72174343, -14.84115208, -14.69111507, -14.35508371]
```

We can retrieve data similarly.

```
from vasp import Vasp

bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
```

```python
calcs = [Vasp('molecules/co-{0}'.format(d)) for d in bond_lengths]

energies = [calc.get_atoms().get_potential_energy() for calc in calcs]

print(energies)
```

Open the python script (dft-scripts/script-41.py).

```
[-14.21584765, -14.72174343, -14.84115208, -14.69111507, -14.35508371]
```

```python
from vasp import Vasp
from ase.db import connect

bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
calcs = [Vasp('molecules/co-{0}'.format(d)) for d in bond_lengths]

con = connect('co-database.db', append=False)
for atoms in [calc.get_atoms() for calc in calcs]:
    con.write(atoms)
```

Open the python script (dft-scripts/script-42.py).

Here we just show that there are entries in our database. If you run the code above many times, each time will add new entries.

```
ase-db co-database.db
```

Open the python script (dft-scripts/script-43.py).

```
id|age|user    |formula|calculator| energy|  fmax|pbc| volume|charge|  mass| smax|magmom
 1|12s|jkitchin|CO     |vasp      |-14.216|14.930|TTT|216.000| 0.000|28.010|0.060| 0.000
 2|10s|jkitchin|CO     |vasp      |-14.722| 5.820|TTT|216.000| 0.000|28.010|0.017| 0.000
 3| 9s|jkitchin|CO     |vasp      |-14.841| 0.632|TTT|216.000| 0.000|28.010|0.017| 0.000
 4| 9s|jkitchin|CO     |vasp      |-14.691| 5.091|TTT|216.000| 0.000|28.010|0.041| 0.000
 5| 7s|jkitchin|CO     |vasp      |-14.355| 8.140|TTT|216.000| 0.000|28.010|0.060| 0.000
Rows: 5
```

This database is now readable in Python too. Here we read in all the results. Later we will learn how to select specific entries.

```python
from ase.io import read

ATOMS = read('co-database.db', ':')
print([a[0].x - a[1].x for a in ATOMS])
print([atoms.get_potential_energy() for atoms in ATOMS])
```

Open the python script (dft-scripts/script-44.py).

```
[-1.0499999999999998, -1.09999998, -1.15000002, -1.2000000000000002, -1.2499999800000001]
[-14.21584765, -14.72174343, -14.84115208, -14.69111507, -14.35508371]
```

Now, back to the goal of finding the minimum. To find the minimum we could run more calculations, but a simpler and faster way is to fit a polynomial to the data, and find the analytical minimum. The results are shown in Figure 18.

```python
from vasp import Vasp
import numpy as np
import matplotlib.pyplot as plt

bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
energies = []
```

```python

for d in bond_lengths:  # possible bond lengths

    calc = Vasp('molecules/co-{0}'.format(d))
    atoms = calc.get_atoms()
    energies.append(atoms.get_potential_energy())

# Now we fit an equation - cubic polynomial
pp = np.polyfit(bond_lengths, energies, 3)
dp = np.polyder(pp)  # first derivative - quadratic

# we expect two roots from the quadratic eqn. These are where the
# first derivative is equal to zero.
roots = np.roots(dp)

# The minimum is where the second derivative is positive.
dpp = np.polyder(dp)  # second derivative - line
secd = np.polyval(dpp, roots)

minV = roots[secd > 0]
minE = np.polyval(pp, minV)

print('The minimum energy is {0[0]} eV at V = {1[0]} Ang^3'.format(minE, minV))

# plot the fit
x = np.linspace(1.05, 1.25)
fit = np.polyval(pp, x)

plt.plot(bond_lengths, energies, 'bo ')
plt.plot(x, fit, 'r-')
plt.plot(minV, minE, 'm* ')
plt.legend(['DFT', 'fit', 'minimum'], numpoints=1)
plt.xlabel(r'Bond length ($\AA$)')
plt.ylabel('Total energy (eV)')
plt.savefig('images/co-bondlengths.png')
```

Open the python script (dft-scripts/script-45.py).

```
The minimum energy is -14.8458440947 eV at V = 1.14437582331 Ang^3
```

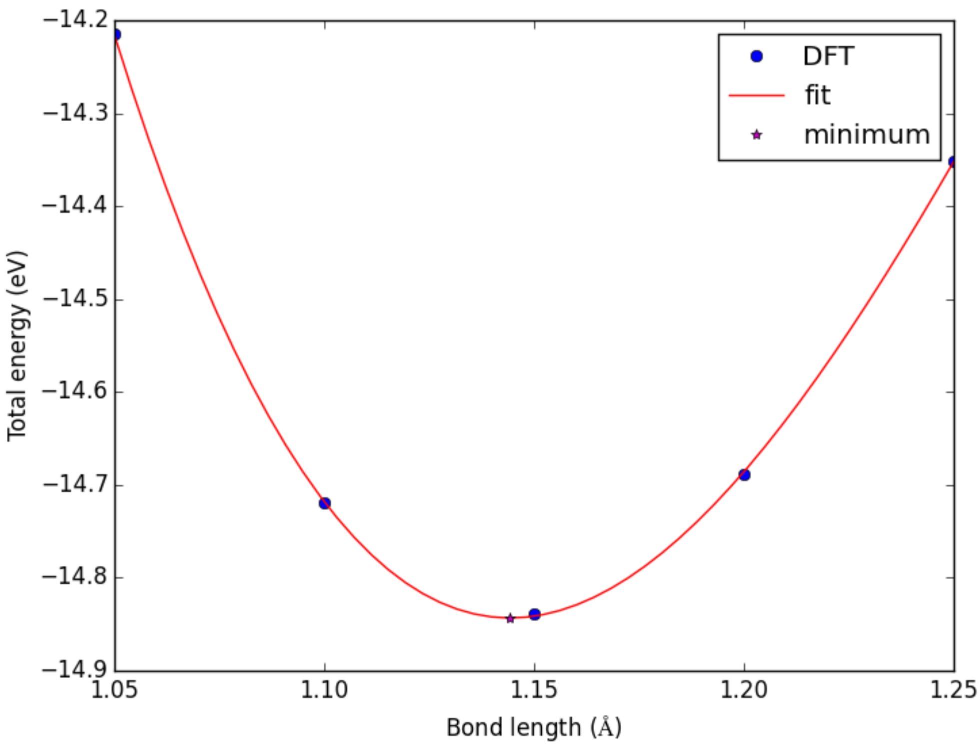


Figure 18: Energy vs CO bond length.

3.4.2 Automatic geometry optimization with VASP

It is generally the case that the equilibrium geometry of a system is the one that minimizes the total energy and forces. Since each atom has three degrees of freedom, you can quickly get a high dimensional optimization problem. Luckily, VASP has built-in geometry optimization using the IBRION and NSW tags. Here we compute the bond length for a CO molecule, letting VASP do the geometry optimization for us.

Here are the most common choices for IBRION.

IBRION value	algorithm
1	quasi-Newton (use if initial guess is good)
2	conjugate gradient

Note:
VASP applies a criteria for stopping a geometry optimization. When the change in energy between two steps is less than 0.001 eV (or 10*EDIFF), the relaxation is stopped. This criteria is controlled by the EDIFFG tag. If you prefer to stop based on forces, set EDIFFG=-0.05, i.e. to a negative number. The units of force is eV/Å. For most work, a force tolerance of 0.05 eV/Å is usually sufficient.

```
from ase import Atom, Atoms
from vasp import Vasp

co = Atoms([Atom('C',[0, 0, 0]),
            Atom('O',[1.2, 0, 0])],
            cell=(6, 6, 6))
```

```python

calc = Vasp('molecules/co-cg',
          xc='PBE',
          nbands=6,
          encut=350,
          ismear=1,
          sigma=0.01, # this is small for a molecule
          ibrion=2,   # conjugate gradient optimizer
          nsw=5,      # do at least 5 steps to relax
          atoms=co)

print('Forces')
print('=======')
print(co.get_forces())

pos = co.get_positions()
d = ((pos[0] - pos[1])**2).sum()**0.5
print('Bondlength = {0:1.2f} angstroms'.format(d))
```

Open the python script (dft-scripts/script-46.py).

```
Forces
=======
[[-0.8290116  0.          0.        ]
 [ 0.8290116  0.          0.        ]]
Bondlength = 1.14 angstroms
```

3.4.3 Relaxation of a water molecule

It is not more complicated to relax more atoms, it just may take longer because there are more electrons and degrees of freedom. Here we relax a water molecule which has three atoms.

```python
from ase import Atoms, Atom
from vasp import Vasp

atoms = Atoms([Atom('H', [0.5960812, -0.7677068, 0.0000000]),
               Atom('O', [0.0000000,  0.0000000, 0.0000000]),
               Atom('H', [0.5960812,  0.7677068, 0.0000000])],
              cell=(8, 8, 8))

atoms.center()

calc = Vasp('molecules/h2o-relax-centered',
            xc='PBE',
            encut=400,
            ismear=0,  # Gaussian smearing
            ibrion=2,
            ediff=1e-8,
            nsw=10,
            atoms=atoms)

print("forces")
print('=======')
print(atoms.get_forces())
```

Open the python script (dft-scripts/script-47.py).

```
[[ 4.2981572   3.23149312  4.        ]
 [ 3.70172616  4.          4.        ]
 [ 4.2981572   4.76850688  4.        ]]
forces
=======
[[ -3.49600000e-05   5.06300000e-05   0.00000000e+00]
 [  6.99200000e-05   0.00000000e+00   0.00000000e+00]
 [ -3.49600000e-05  -5.06300000e-05   0.00000000e+00]]
```

```python
from vasp import Vasp
calc = Vasp('molecules/h2o-relax-centered')

from ase.visualize import view
view(calc.traj)
```

Open the python script (dft-scripts/script-48.py).

3.5 Vibrational frequencies

3.5.1 Manual calculation of vibrational frequency

The principle idea in calculating vibrational frequencies is that we consider a molecular system as masses connected by springs. If the springs are Hookean, e.g. the force is proportional to the displacement, then we can readily solve the equations of motion and find that the vibrational frequencies are related to the force constants and the masses of the atoms. For example, in a simple molecule like CO where there is only one spring, the frequency is:

$\nu = \frac{1}{2\pi}\sqrt{k/\mu}$ where $\frac{1}{\mu} = \frac{1}{m_C} + \frac{1}{m_O}$ and k is the spring constant. We will compute the value of k from DFT calculations as follows:

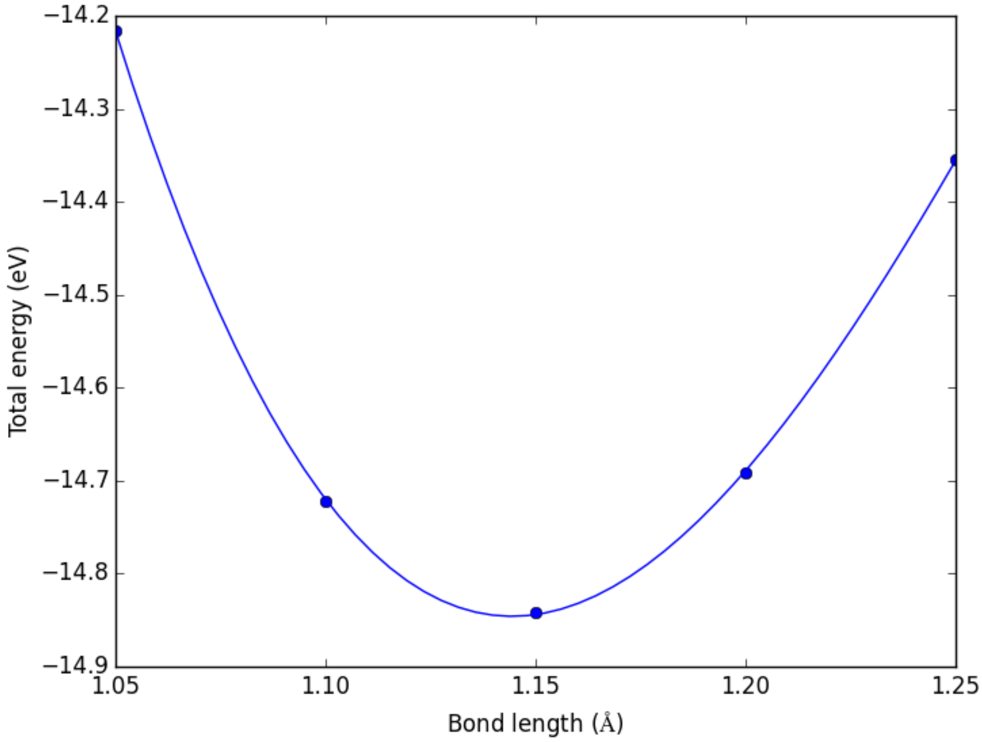
$k = \frac{\partial^2 E}{\partial x^2}$ at the equilibrium bond length. We actually already have the data to do this from Manual determination. We only need to fit an equation to the energy vs. bond-length data, find the minimum energy bond-length, and then evaluate the second derivative of the fitted function at the minimum. We will use a cubic polynomial for demonstration here. Polynomials are numerically convenient because they are easy to fit, and it is trivial to get the roots and derivatives of the polynomials, as well as to evaluate them at other points using `numpy.polyfit`, `numpy.polyder`, and `numpy.polyval`.

```python
from vasp import Vasp
import numpy as np
from ase.units import *

bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
energies = []

for d in bond_lengths:
    calc = Vasp('molecules/co-{0}'.format(d))
    atoms = calc.get_atoms()
    energies.append(atoms.get_potential_energy())

# fit the data
pars = np.polyfit(bond_lengths, energies, 3)
xfit = np.linspace(1.05, 1.25)
efit = np.polyval(pars, xfit)

# first derivative
dpars = np.polyder(pars)
# find where the minimum is. chose the second one because it is the
# minimum we need.
droots = np.roots(dpars)

# second derivative
ddpars = np.polyder(dpars)

d_min = droots[np.polyval(ddpars, droots) > 0]

# curvature at minimum = force constant in SI units
k = np.polyval(ddpars, d_min) / (J / m**2)

# mu, reduced mass
from ase.data import atomic_masses
C_mass = atomic_masses[6] / kg
O_mass = atomic_masses[8] / kg

mu = 1.0 / (1.0 / C_mass + 1.0 / O_mass)

frequency = 1. / (2. * np.pi) * np.sqrt(k / mu)
print('The CO vibrational frequency is {0} Hz'.format(*frequency))
print('The CO vibrational frequency is {0[0]} cm^{{-1}}'.format(frequency / 3e10))
```

```python

import matplotlib.pyplot as plt
plt.plot(bond_lengths, energies, 'bo ')
plt.plot(xfit, efit, 'b-')
plt.xlabel('Bond length ($\AA$)')
plt.ylabel('Total energy (eV)')
plt.savefig('images/co-freq.png')
```

Open the python script (dft-scripts/script-49.py).

```
The CO vibrational frequency is 6.43186126691e+13 Hz
The CO vibrational frequency is 2143.95375564 cm^{-1}
```



This result is in good agreement with experiment. The procedure described above is basically how many vibrational calculations are performed. With more atoms, you have to determine a force constant matrix and diagonalize it. For more details, see.[43] In practice, we usually allow a packaged code to automate this, which we cover in Automated vibrational calculations.

We now consider how much energy is in this vibration. This is commonly called zero-point energy (ZPE) and it is defined as $E_{ZPE} = \frac{1}{2}h\nu$ for a single mode, and h is Planck's constant (4.135667516e-15 eV/s).

```python
c = 3e10  # speed of light cm/s
h = 4.135667516e-15  # eV*s

nu = 2143.6076625*c  # 1/s

E_zpe = 0.5*h*nu

print('E_ZPE = {0:1.3f} eV'.format(E_zpe))
```

Open the python script (dft-scripts/script-50.py).

```
E_ZPE = 0.133 eV
```

This is a reasonable amount of energy! Zero-point energy increases with increasing vibrational frequency, and tends to be very important for small atoms.

A final note is that this analysis is in the "harmonic approximation". The frequency equation is the solution to a harmonic oscillator. If the spring is non-linear, then there are anharmonic effects that may become important, especially at higher temperatures.

3.5.2 TODO Automated vibrational calculations

VASP has built-in capability for performing vibrational calculations. We access the capability by using a new value for IBRION. The values of 5 and 6 calculated the Hessian matrix using finite differences. For IBRION=5, all atoms that are not constrained are displaced. For IBRION=6, only symmetry inequivalent displacements are considered, which makes the calculations slightly cheaper. You can specify the number of displacements with NFREE. The default number of displacements is 2. You can also specify the size of the displacement with POTIM (the default is 0.015 Å).

```python
# <<water-vib>>
# adapted from http://cms.mpi.univie.ac.at/wiki/index.php/H2O_vibration
from ase import Atoms, Atom
from vasp import Vasp
import ase.units

atoms = Atoms([Atom('H', [0.5960812,  -0.7677068,   0.0000000]),
               Atom('O', [0.0000000,   0.0000000,   0.0000000]),
               Atom('H', [0.5960812,   0.7677068,   0.0000000])],
               cell=(8, 8, 8))
atoms.center()

calc = Vasp('molecules/h2o_vib',
            xc='PBE',
            encut=400,
            ismear=0,     # Gaussian smearing
            ibrion=6,     # finite differences with symmetry
            nfree=2,      # central differences (default)
            potim=0.015,  # default as well
            ediff=1e-8,   # for vibrations you need precise energies
            nsw=1,        # Set to 1 for vibrational calculation
            atoms=atoms)

print('Forces')
print('======')
print(atoms.get_forces())
print('')
calc.stop_if(calc.potential_energy is None)

# vibrational energies are in eV
energies, modes = calc.get_vibrational_modes()
print('energies\n========')
for i, e in enumerate(energies):
    print('{0:02d}: {1} eV'.format(i, e))
```

Open the python script (dft-scripts/script-51.py).

```
Forces
======
[[ 0.01810349 -0.03253721 -0.00127275]
 [-0.03620698  0.          0.0025455 ]
 [ 0.01810349  0.03253721 -0.00127275]]

energies
========
00: 0.475855773 eV
01: 0.46176517 eV
```

```
02: 0.196182182 eV
03: 0.007041992 eV
04: 0.002445078 eV
05: (0.000292003+0j) eV
06: (0.012756432+0j) eV
07: (0.01305212+0j) eV
08: (0.015976377+0j) eV
```

Note we get 9 frequencies here. Water has 3 atoms, with three degrees of freedom each, leading to 9 possible combinations of collective motions. Three of those collective motions are translations, i.e. where all atoms move in the same direction (either x, y or z) and there is no change in the total energy of the molecule. Another three of those motions are rotations, which also do not change the total energy of the molecule. That leaves 3N-6 = 3 degrees of vibrational freedom where some or all of the bonds are stretched, resulting in a change in the total energy. The modes of water vibration are (with our calculated values in parentheses):

1. a symmetric stretch at 3657 cm^{-1} (3723)
2. an asymmetric stretch at 3756 cm^{-1} (3836)
3. and a bending mode at 1595 cm^{-1} (1583)

http://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185&Mask=800#Electronic-Spec

The results are not too far off, and more accurate frequencies may be possible using tighter tolerance on POTIM, or by using IBRION=7 or 8.

Let us briefly discuss how to determine which vectors are vibrations and which are rotations or translations. One way is to visualize the modes. The vibrations are easy to spot. The rotations/translations are not always cleanly separable. This is an issue of accuracy and convergence. We usually do not worry about this because these modes are usually not important.

1. mode 0 is an asymmetric stretch
2. mode 1 is a symmetric stretch
3. mode 2 is a bending mode
4. mode 3 is a mixed translation/rotation
5. mode 4 is a rotation
6. mode 5 is a translation
7. mode 6 is a rotation
8. mode 7 is a partial translation
9. mode 8 is a rotation

```python
# <<h2o-vib-vis>>
from vasp import Vasp
import numpy as np
calc = Vasp('molecules/h2o_vib')
energies, modes = calc.get_vibrational_modes(mode=0, massweighted=True,
                                             show=True)
```

Open the python script (dft-scripts/script-52.py).

See http://www.gaussian.com/g_whitepap/vib.htm for a more quantitative discussion of these modes, identifying them, and a method to project the rotations and translations out of the Hessian matrix.

Zero-point energy for multiple modes For a molecule with lots of vibrational modes the zero-point energy is defined as the sum over all the vibrational modes:

$E_{ZPE} = \sum_i \frac{1}{2}h\nu_i$

Here is an example for water. Note we do not sum over the imaginary modes. We should also ignore the rotational and translational modes (some of those are imaginary, but some are just small).

```
from vasp import Vasp
import numpy as np
c = 3e10  # speed of light cm/s
h = 4.135667516e-15  # eV/s

# first, get the frequencies.
calc = Vasp('molecules/h2o_vib')
freq = calc.get_vibrational_frequencies()

ZPE = 0.0
for f in freq:
    if not isinstance(f, float):
        continue  # skip complex numbers
    nu = f * c  # convert to frequency
    ZPE += 0.5 * h * nu

print(np.sum([0.5 * h * f * c for f in freq if isinstance(f, float)]))

print('The ZPE of water is {0:1.3f} eV'.format(ZPE))

# one liner
ZPE = np.sum([0.5 * h * f * c for f in freq if isinstance(f, float)])
print('The ZPE of water is {0:1.3f} eV'.format(ZPE))
```

Open the python script (dft-scripts/script-53.py).

Note the zero-point energy of water is also fairly high (more than 0.5 eV). That is because of the high frequency O-H stretches.

3.6 Simulated infrared spectra

At http://homepage.univie.ac.at/david.karhanek/downloads.html#Entry02 there is a recipe for computing the Infrared vibrational spectroscopy intensities in VASP. We are going to do that for water here. First, we will relax a water molecule.

```
from ase import Atoms, Atom
from vasp import Vasp

atoms = Atoms([Atom('H', [0.5960812,  -0.7677068,   0.0000000]),
               Atom('O', [0.0000000,   0.0000000,   0.0000000]),
               Atom('H', [0.5960812,   0.7677068,   0.0000000])],
              cell=(8, 8, 8))

calc = Vasp('molecules/h2o_relax',
            xc='PBE',
              encut=400,
              ismear=0,  # Gaussian smearing
              ibrion=2,
              ediff=1e-8,
              nsw=10,
              atoms=atoms)
print('Forces')
print('===========================')
print(atoms.get_forces())
```

Open the python script (dft-scripts/script-54.py).

```
Forces
===========================
[[ -3.80700000e-05   5.32200000e-05   0.00000000e+00]
 [  7.61400000e-05   0.00000000e+00   0.00000000e+00]
 [ -3.80700000e-05  -5.32200000e-05   0.00000000e+00]]
```

Next, we instruct VASP to compute the vibrational modes using density functional perturbation theory with IBRION=7. Note, this is different than in 3.5 where finite differences were used.

```
from vasp import Vasp

# read in relaxed geometry
calc = Vasp(’molecules/h2o_relax’)
atoms = calc.get_atoms()

# now define a new calculator
calc = Vasp(’molecules/h2o_vib_dfpt’,
            xc=’PBE’,
            encut=400,
            ismear=0,  # Gaussian smearing
            ibrion=7,  # switches on the DFPT vibrational analysis (with
            # no symmetry constraints)
            nfree=2,
            potim=0.015,
            lepsilon=True,  # enables to calculate and to print the BEC
            # tensors
            lreal=False,
            nsw=1,
            nwrite=3,  # affects OUTCAR verbosity: explicitly forces
            # SQRT(mass)-divided eigenvectors to be printed
            atoms=atoms)

print(calc.potential_energy)
```

Open the python script (dft-scripts/script-55.py).

```
-14.22662275
```

To analyze the results, this shell script was provided to extract the results.

```
#!/bin/bash
# A utility for calculating the vibrational intensities from VASP output (OUTCAR)
# (C) David Karhanek, 2011-03-25, ICIQ Tarragona, Spain (www.iciq.es)

# extract Born effective charges tensors
printf "..reading OUTCAR"
BORN_NROWS=‘grep NIONS OUTCAR | awk ’{print $12*4+1}’‘
if [ ‘grep ’BORN’ OUTCAR | wc -l‘ = 0 ] ; then \
   printf " .. FAILED! Born effective charges missing! Bye! \n\n" ; exit 1 ; fi
grep "in e, cummulative" -A $BORN_NROWS OUTCAR > born.txt

# extract Eigenvectors and eigenvalues
if [ ‘grep ’SQRT(mass)’ OUTCAR | wc -l‘ != 1 ] ; then \
   printf " .. FAILED! Restart VASP with NWRITE=3! Bye! \n\n" ; exit 1 ; fi
EIG_NVIBS=‘grep -A 2000 ’SQRT(mass)’ OUTCAR | grep ’cm-1’ | wc -l‘
EIG_NIONS=‘grep NIONS OUTCAR | awk ’{print $12}’‘
EIG_NROWS=‘echo "($EIG_NIONS+3)*$EIG_NVIBS+3" | bc‘
grep -A $(($EIG_NROWS+2)) ’SQRT(mass)’ OUTCAR | tail -n $(($EIG_NROWS+1)) | sed ’s/f\/i/fi /g’ > eigenvectors.txt
printf " ..done\n"

# set up a new directory, split files - prepare for parsing
printf "..splitting files"
mkdir intensities ; mv born.txt eigenvectors.txt intensities/
cd intensities/
let NBORN_NROWS=BORN_NROWS-1
let NEIG_NROWS=EIG_NROWS-3
let NBORN_STEP=4
let NEIG_STEP=EIG_NIONS+3
tail -n $NBORN_NROWS born.txt > temp.born.txt
tail -n $NEIG_NROWS eigenvectors.txt > temp.eige.txt
mkdir inputs ; mv born.txt eigenvectors.txt inputs/
split -a 3 -d -l $NEIG_STEP temp.eige.txt temp.ei.
split -a 3 -d -l $NBORN_STEP temp.born.txt temp.bo.
mkdir temps01 ; mv temp.born.txt temp.eige.txt temps01/
for nu in ‘seq 1 $EIG_NVIBS‘ ; do
 let nud=nu-1 ; ei=‘printf "%03u" $nu‘ ; eid=‘printf "%03u" $nud‘ ; mv temp.ei.$eid eigens.vib.$ei
done
for s in ‘seq 1 $EIG_NIONS‘ ; do
 let sd=s-1 ; bo=‘printf "%03u" $s‘ ; bod=‘printf "%03u" $sd‘ ; mv temp.bo.$bod borncs.$bo
```

```
done
printf " ..done\n"

# parse deviation vectors (eig)
printf "..parsing eigenvectors"
let sad=$EIG_NIONS+1
for nu in `seq 1 $EIG_NVIBS` ; do
 nuu=`printf "%03u" $nu`
 tail -n $sad eigens.vib.$nuu | head -n $EIG_NIONS | awk '{print $4,$5,$6}' > e.vib.$nuu.allions
 split -a 3 -d -l 1 e.vib.$nuu.allions temp.e.vib.$nuu.ion.
 for s in `seq 1 $EIG_NIONS` ; do
  let sd=s-1; bo=`printf "%03u" $s`; bod=`printf "%03u" $sd`; mv temp.e.vib.$nuu.ion.$bod e.vib.$nuu.ion.$bo
 done
done
printf " ..done\n"

# parse born effective charge matrices (born)
printf "..parsing eff.charges"
for s in `seq 1 $EIG_NIONS` ; do
 ss=`printf "%03u" $s`
 awk '{print $2,$3,$4}' borncs.$ss | tail -3 > bornch.$ss
done
mkdir temps02 ; mv eigens.* borncs.* temps02/
printf " ..done\n"

# parse matrices, multiply them and collect squares (giving intensities)
printf "..multiplying matrices, summing "
for nu in `seq 1 $EIG_NVIBS` ; do
 nuu=`printf "%03u" $nu`
 int=0.0
 for alpha in 1 2 3 ;  do            # summing over alpha coordinates
  sumpol=0.0
  for s in `seq 1 $EIG_NIONS` ; do   # summing over atoms
   ss=`printf "%03u" $s`
   awk -v a="$alpha" '(NR==a){print}' bornch.$ss > z.ion.$ss.alpha.$alpha
   # summing over beta coordinates and multiplying Z(s,alpha)*e(s) done by the following awk script
   paste z.ion.$ss.alpha.$alpha  e.vib.$nuu.ion.$ss | \
   awk '{pol=$1*$4+$2*$5+$3*$6; print $0,"  ",pol}' > matr-vib-${nuu}-alpha-${alpha}-ion-${ss}
  done
  sumpol=`cat matr-vib-${nuu}-alpha-${alpha}-ion-* | awk '{sum+=$7} END {print sum}'`
  int=`echo "$int+($sumpol)^2" | sed 's/[eE]/*10^/g' |  bc -l`
 done
 freq=`awk '(NR==1){print $8}' temps02/eigens.vib.$nuu`
 echo "$nuu $freq $int">> exact.res.txt
 printf "."
done
printf " ..done\n"

# format results, normalize intensities
printf "..normalizing intensities"
max=`awk '(NR==1){max=$3} $3>=max {max=$3} END {print max}' exact.res.txt`
awk -v max="$max" '{printf "%03u %6.1f %5.3f\n",$1,$2,$3/max}' exact.res.txt > results.txt
printf " ..done\n"

# clean up, display results
printf "..finalizing:\n"
mkdir temps03; mv bornch.* e.vib.*.allions temps03/
mkdir temps04; mv z.ion* e.vib.*.ion.* temps04/
mkdir temps05; mv matr-* temps05/
mkdir results; mv *res*txt results/
let NMATRIX=$EIG_NVIBS**2
printf "%5u atoms found\n%5u vibrations found\n%5u matrices evaluated" \
       $EIG_NIONS $EIG_NVIBS $NMATRIX > results/statistics.txt
  # fast switch to clean up all temporary files
  rm -r temps*
cat results/results.txt
```

Open the python script (dft-scripts/script-56.py).

Note that the results above include the rotational and translational modes (modes 4-9). The following shell script removes those, and recalculates the intensities. Note that it appears to just remove the last 6 modes and req compute the intensities. It is not obvious that will always be the right way to do it as the order of the eigenvectors is not guaranteed.

```
#!/bin/bash
# reformat intensities, just normal modes: 3N -> (3N-6)
```

```
printf "..reformatting and normalizing intensities"
cd intensities/results/
nlns=`wc -l exact.res.txt | awk '{print $1}' `; let bodylns=nlns-6
head -n $bodylns exact.res.txt > temp.reform.res.txt
max=`awk '(NR==1){max=$3} $3>=max {max=$3} END {print max}' temp.reform.res.txt`
awk -v max="$max" '{print $1,$2,$3/max}' temp.reform.res.txt > exact.reform.res.txt
awk -v max="$max" '{printf "%03u %6.1f %5.3f\n",$1,$2,$3/max}' temp.reform.res.txt > reform.res.txt
printf " ..done\n..normal modes:\n"
rm temp.reform.res.txt
cat reform.res.txt
cd ../..
```

Open the python script (dft-scripts/script-57.py).

```
..reformatting and normalizing intensities ..done
..normal modes:
```

The interpretation of these results is that the mode at 3713 cm^{-1} would be nearly invisible in the IR spectrum. Earlier we interpreted that as the symmetric stretch. In this mode, there is only a small change in the molecule dipole moment, so there is a small IR intensity.

See also.[44] For HREELS simulations see.[45]

The shell script above has been translated to a convenient python function in vasp.

```python
from vasp import Vasp
calc = Vasp('molecules/h2o_vib_dfpt')
print('mode  Relative intensity')
for i, intensity in enumerate(calc.get_infrared_intensities()):
    print('{0:02d}     {1:1.3f}'.format(i, intensity))
```

Open the python script (dft-scripts/script-58.py).

```
mode  Relative intensity
00     0.227
01     0.006
02     0.312
03     1.000
04     0.002
05     0.000
06     0.006
07     0.000
08     0.350
```

3.7 Thermochemical properties of molecules

ase.thermochemistry can be used to estimate thermodynamic properties of gases in the ideal gas limit. The module needs as input the geometry, the total energy, the vibrational energies, and some information about the molecular symmetry. We first consider an N_2 molecule.

The symmetry numbers are determined by the molecular point group.[46] Here is a table of the most common ones.

```python
from ase.structure import molecule
from ase.thermochemistry import IdealGasThermo
from vasp import Vasp

atoms = molecule('N2')
atoms.set_cell((10,10,10), scale_atoms=False)

# first we relax a molecule
calc = Vasp('molecules/n2-relax',
            xc='PBE',
            encut=300,
```

Table 2: Symmetry numbers for common point groups

point group	σ	examples
C_1	1	
C_s	1	
C_2	2	
C_{2v}	2	H_2O
C_{3v}	3	NH_3
$C_{\infty v}$	1	CO
D_{2h}	4	
D_{3h}	6	
D_{5h}	10	
$D_{\infty h}$	2	CO_2, H_2
D_{3d}	6	
T_d	12	CH_4
O_h	24	

```
            ibrion=2,
            nsw=5,
            atoms=atoms)
electronicenergy = atoms.get_potential_energy()

# next, we get vibrational modes
calc2 = Vasp('molecules/n2-vib',
             xc='PBE',
             encut=300,
             ibrion=6,
             nfree=2,
             potim=0.15,
             nsw=1,
             atoms=atoms)

calc2.wait()

vib_freq = calc2.get_vibrational_frequencies() # in cm^1

#convert wavenumbers to energy
h = 4.1356675e-15 # eV*s
c = 3.0e10 #cm/s
vib_energies = [h*c*nu for nu in vib_freq]
print('vibrational energies\n====================')
for i,e in enumerate(vib_energies):
    print('{0:02d}: {1} eV'.format(i,e))


# # now we can get some properties. Note we only need one vibrational
# energy since there is only one mode. This example does not work if
# you give all the energies because one energy is zero.
thermo = IdealGasThermo(vib_energies=vib_energies[0:0],
                        potentialenergy=electronicenergy, atoms=atoms,
                        geometry='linear', symmetrynumber=2, spin=0)

# temperature in K, pressure in Pa, G in eV
G = thermo.get_gibbs_energy(temperature=298.15, pressure=101325.)
```

Open the python script (dft-scripts/script-59.py).

```
vibrational energies
====================
00: 0.281619180732 eV
01: 0.0302718194691 eV
02: 0.0302718194691 eV
03: 6.20350125e-10 eV
04: 4.962801e-10 eV
```

```
05: 0.0 eV
Enthalpy components at T = 298.15 K:
===============================
E_pot                  -16.484 eV
E_ZPE                    0.000 eV
Cv_trans (0->T)          0.039 eV
Cv_rot (0->T)            0.026 eV
Cv_vib (0->T)            0.000 eV
(C_v -> C_p)             0.026 eV
-------------------------------
H                      -16.394 eV
===============================

Entropy components at T = 298.15 K and P = 101325.0 Pa:
=================================================
                           S               T*S
S_trans (1 atm)    0.0015579 eV/K        0.464 eV
S_rot              0.0007868 eV/K        0.235 eV
S_elec             0.0000000 eV/K        0.000 eV
S_vib              0.0000000 eV/K        0.000 eV
S (1 atm -> P)    -0.0000000 eV/K       -0.000 eV
-------------------------------------------------
S                  0.0023447 eV/K        0.699 eV
=================================================

Free energy components at T = 298.15 K and P = 101325.0 Pa:
=======================
    H        -16.394 eV
 -T*S         -0.699 eV
-----------------------
    G        -17.093 eV
=======================
```

Let us compare this to what is in the Nist webbook via the Shomate equations.

```python
import numpy as np
A = 28.98641
B = 1.853978
C = -9.647459
D = 16.63537
E = 0.000117
F = -8.671914
G = 226.4168
H = 0.0

T = 298.15
t = T/1000.

S = A*np.log(t) + B*t + C*t**2/2 + D*t**3/3 - E/(2*t**2) + G
print('-T*S = {0:1.3f} eV'.format(-T*S/1000/96.4853))
```

Open the python script (dft-scripts/script-60.py).

```
-T*S = -0.592 eV
```

This is reasonable agreement for the entropy. You will get different results if you use different exchange correlation functionals.

3.8 Molecular reaction energies

3.8.1 O_2 dissociation

The first reaction we consider is a simple dissociation of oxygen molecule into two oxygen atoms: $O_2 \rightarrow$ 2O. The dissociation energy is pretty straightforward to define: it is the energy of the products minus the energy of the reactant. $D = 2 * E_O - E_{O_2}$. It would appear that we simply calculate the energy of an oxygen atom, and the energy of an oxygen molecule and evaluate the formula. Let us do that.

Simple estimate of O_2 dissociation energy

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('O', [5, 5, 5])],
              cell=(10, 10, 10))

calc = Vasp('molecules/O',
            xc='PBE',
            encut=400,
            ismear=0,
            atoms=atoms)

E_O = atoms.get_potential_energy()

# now relaxed O2 dimer
atoms = Atoms([Atom('O', [5, 5, 5]),
               Atom('O', [6.22, 5, 5])],
              cell=(10, 10, 10))

calc = Vasp('molecules/O2',
            xc='PBE',
            encut=400,
            ismear=0,
            ibrion=2,
            nsw=10,
            atoms=atoms)

E_O2 = atoms.get_potential_energy()

if None not in (E_O, E_O2):
    print('O2 -> 2O  D = {0:1.3f} eV'.format(2 * E_O - E_O2))
```

Open the python script (dft-scripts/script-61.py).

```
O2 -> 2O  D = 8.619 eV
```

The answer we have obtained is way too high! Experimentally the dissociation energy is about 5.2 eV (need reference), which is **very** different than what we calculated! Let us consider some factors that contribute to this error.

We implicitly neglected spin-polarization in the example above. That could be a problem, since the O_2 molecule can be in one of two spin states, a singlet or a triplet, and these should have different energies. Furthermore, the oxygen atom can be a singlet or a triplet, and these would have different energies. To account for spin polarization, we have to tell VASP to use spin-polarization, and give initial guesses for the magnetic moments of the atoms. Let us try again with spin polarization.

Estimating O_2 dissociation energy with spin polarization in triplet ground states To tell VASP to use spin-polarization we use ISPIN=2, and we set initial guesses for magnetic moments on the atoms with the magmom keyword. In a triplet state there are two electrons with spins of the same sign.

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('O', [5, 5, 5], magmom=2)],
```

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

calc = Vasp('molecules/O-sp-triplet',
            xc='PBE',
            encut=400,
            ismear=0,
            ispin=2,  # turn spin-polarization on
            atoms=atoms)

E_O = atoms.get_potential_energy()


print('Magnetic moment on O = {0} Bohr'
      ' magnetons'.format(atoms.get_magnetic_moment()))

# now relaxed O2 dimer
atoms = Atoms([Atom('O', [5,    5, 5], magmom=1),
               Atom('O', [6.22, 5, 5], magmom=1)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O2-sp-triplet',
            xc='PBE',
            encut=400,
            ismear=0,
            ispin=2,   # turn spin-polarization on
            ibrion=2,  # make sure we relax the geometry
            nsw=10,
            atoms=atoms)

E_O2 = atoms.get_potential_energy()

# verify magnetic moment
print('Magnetic moment on O2 = {0} Bohr'
      ' magnetons'.format(atoms.get_magnetic_moment()))

if None not in (E_O, E_O2):
    print('O2 -> 2O  D = {0:1.3f} eV'.format(2 * E_O - E_O2))
```

Open the python script (dft-scripts/script-62.py).

```
Magnetic moment on O = 2.0000072 Bohr magnetons
Magnetic moment on O2 = 2.0000084 Bohr magnetons
O2 -> 2O  D = 6.746 eV
```

This is much closer to accepted literature values for the DFT-GGA O_2 dissociation energy. It is still more than 1 eV above an experimental value, but most of that error is due to the GGA exchange correlation functional. Some additional parameters that might need to be checked for convergence are the SIGMA value (it is probably too high for a molecule), as well as the cutoff energy. Oxygen is a "hard" atom that requires a high cutoff energy to achieve high levels of convergence.

Looking at the two spin densities In a spin-polarized calculation there are actually two electron densities: one for spin-up and one for spin-down. We will look at the differences in these two through the density of states.

```
from vasp import Vasp
from ase.dft.dos import *

calc = Vasp('molecules/O2-sp-triplet')

dos = DOS(calc, width=0.2)
d_up = dos.get_dos(spin=0)
d_down = dos.get_dos(spin=1)
e = dos.get_energies()

ind = e <= 0.0
# integrate up to 0eV
print('number of up states = {0}'.format(np.trapz(d_up[ind], e[ind])))
print('number of down states = {0}'.format(np.trapz(d_down[ind], e[ind])))

import pylab as plt
```

```
plt.plot(e, d_up,
         e, -d_down)
plt.xlabel('energy [eV]')
plt.ylabel('DOS')
plt.legend(['up', 'down'])
plt.savefig('images/O2-sp-dos.png')
```

Open the python script (dft-scripts/script-63.py).

```
number of up states = 6.11729553486
number of down states = 5.00000794208
```

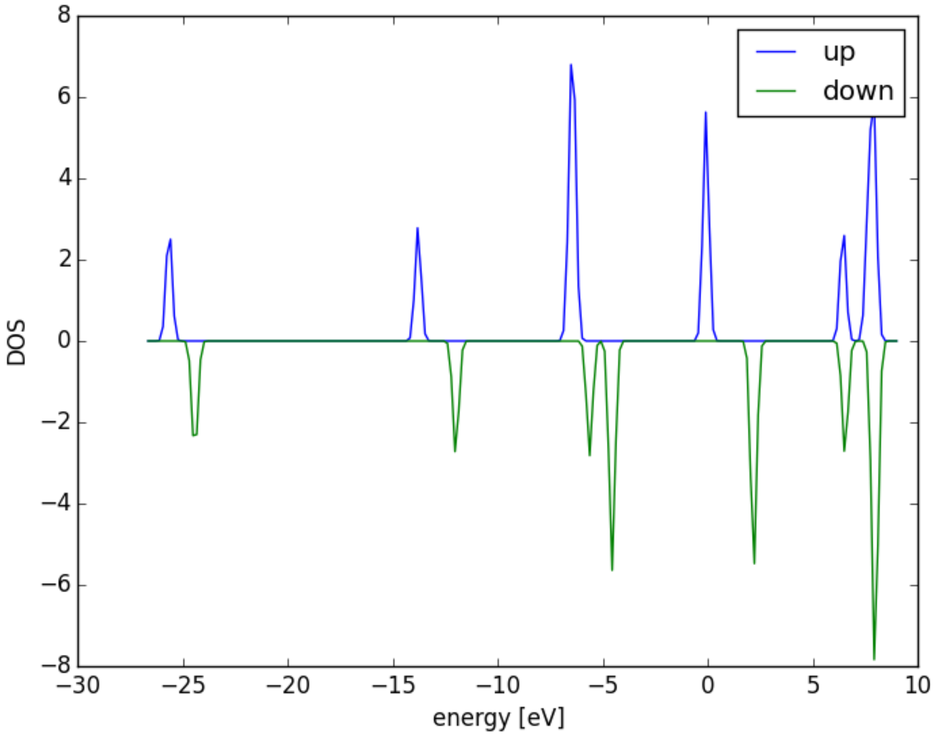


Figure 19: Spin-polarized DOS for the O_2 molecule.

You can see in Figure 19 that there are two different densities of states for the two spins. One has 7 electrons in it (the blue lines), and the other has 5 electrons in it (the green line). The difference of two electrons leads to the magnetic moment of 2 which we calculated earlier. Remember that only peaks in the DOS below the Fermi level are occupied. It is customary to set the Fermi level to 0 eV in DOS plots. The peaks roughly correspond to electrons. For example, the blue peak between -25 and -30 eV corresponds to one electron, in a 1s orbital, where as the blue peak between -5 and -10 eV corresponds to three electrons.

Convergence study of the O_2 dissociation energy

```
from vasp import Vasp
from ase import Atom, Atoms
encuts = [250, 300, 350, 400, 450, 500, 550]

```

```python
D = []
for encut in encuts:
    atoms = Atoms([Atom('O', [5, 5, 5], magmom=2)],
                  cell=(10, 10, 10))

    calc = Vasp('molecules/O-sp-triplet-{0}'.format(encut),
                xc='PBE',
                encut=encut,
                ismear=0,
                ispin=2,
                atoms=atoms)

    E_O = atoms.get_potential_energy()

    # now relaxed O2 dimer
    atoms = Atoms([Atom('O', [5,    5, 5], magmom=1),
                   Atom('O', [6.22, 5, 5], magmom=1)],
                  cell=(10, 10, 10))

    calc = Vasp('molecules/O2-sp-triplet-{0}'.format(encut),
                xc='PBE',
                encut=encut,
                ismear=0,
                ispin=2,   # turn spin-polarization on
                ibrion=2,  # this turns relaxation on
                nsw=10,
                atoms=atoms)

    E_O2 = atoms.get_potential_energy()

    if None not in (E_O, E_O2):
        d = 2*E_O - E_O2
        D.append(d)
        print('O2 -> 2O encut = {0}  D = {1:1.3f} eV'.format(encut, d))

if not D or None in D: calc.abort()

import matplotlib.pyplot as plt
plt.plot(encuts, D)
plt.xlabel('ENCUT (eV)')
plt.ylabel('O$_2$ dissociation energy (eV)')
plt.savefig('images/O2-dissociation-convergence.png')
```

Open the python script (dft-scripts/script-64.py).

```
O2 -> 2O encut = 250  D = 6.774 eV
O2 -> 2O encut = 300  D = 6.804 eV
O2 -> 2O encut = 350  D = 6.785 eV
O2 -> 2O encut = 400  D = 6.746 eV
O2 -> 2O encut = 450  D = 6.727 eV
O2 -> 2O encut = 500  D = 6.725 eV
O2 -> 2O encut = 550  D = 6.727 eV
```

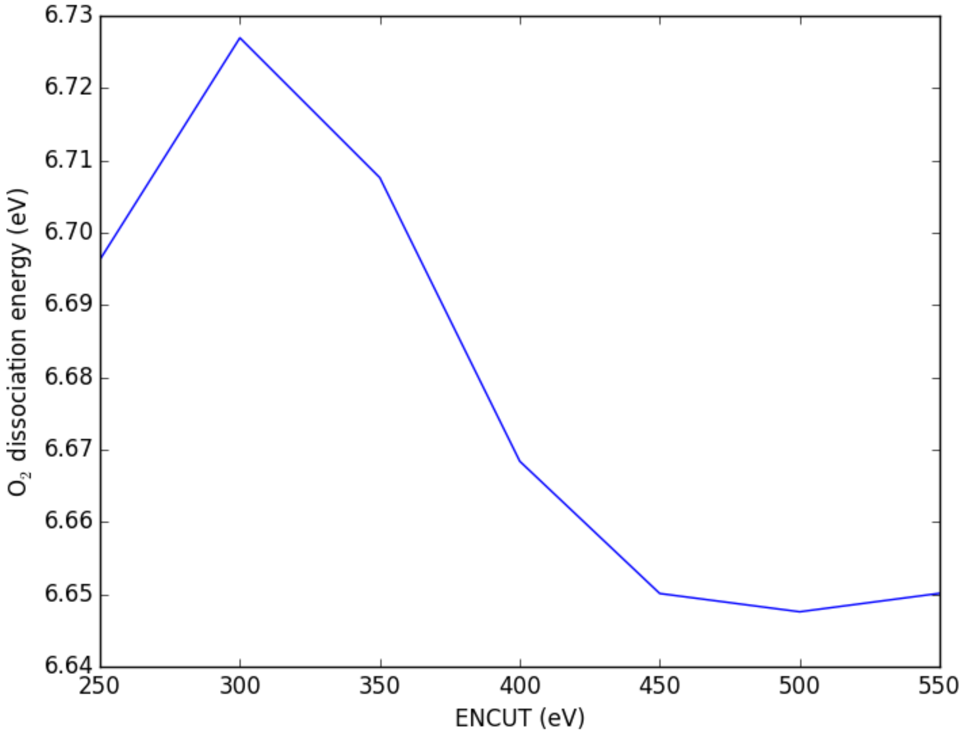


Figure 20: Convergence study of the O_2 dissociation energy as a function of ENCUT.

Based on these results (Figure 20), you could argue the dissociation energy is converged to about 2 meV at a planewave cutoff of 450 eV, and within 50 meV at 350 eV cutoff. You have to decide what an appropriate level of convergence is. Note that increasing the planewave cutoff significantly increases the computational time, so you are balancing level of convergence with computational speed. It would appear that planewave cutoff is not the cause for the discrepancy between our calculations and literature values.

```
encuts = [250, 300, 350, 400, 450, 500, 550]
print('encut (eV)            Total CPU time')
print('--------------------------------------------------------')

for encut in encuts:
    OUTCAR = 'molecules/O2-sp-triplet-{0}/OUTCAR'.format(encut)
    f = open(OUTCAR, 'r')
    for line in f:
        if 'Total CPU time used (sec)' in line:
            print('{0} eV: {1}'.format(encut, line))
    f.close()
```

Open the python script (dft-scripts/script-65.py).

```
encut (eV)            Total CPU time
--------------------------------------------------------
250 eV:                     Total CPU time used (sec):     1551.338

300 eV:                     Total CPU time used (sec):     2085.191

350 eV:                     Total CPU time used (sec):     2795.841
```

```
400 eV:                  Total CPU time used (sec):    2985.064

450 eV:                  Total CPU time used (sec):    5155.562

500 eV:                  Total CPU time used (sec):    4990.818

550 eV:                  Total CPU time used (sec):    5262.052
```

Illustration of the effect of SIGMA The methodology for extrapolation of the total energy to absolute zero is only valid for a continuous density of states at the Fermi level.[12] Consequently, it should not be used for semiconductors, molecules or atoms. In VASP, this means a very small Fermi temperature (SIGMA) should be used. The O_2 dissociation energy as a function of SIGMA is shown in Figure 21. A variation of nearly 0.2 eV is seen from the default Fermi temperature of $k_bT = 0.2$ eV and the value of $k_bT = 0.0001$ eV. However, virtually no change was observed for a hydrogen atom or molecule or for an oxygen molecule as a function of the Fermi temperature. It is recommended that the total energy be calculated at several values of the Fermi temperature to make sure the total energy is converged with respect to the Fermi temperature.

We were not careful in selecting a good value for SIGMA in the calculations above. The default value of SIGMA is 0.2, which may be fine for metals, but it is not correct for molecules. SIGMA is the broadening factor used to smear the electronic density of states at the Fermi level. For a metal with a continuous density of states this is appropriate, but for molecules with discrete energy states it does not make sense. We are somewhat forced to use the machinery designed for metals on molecules. The solution is to use a very small SIGMA. Ideally you would use SIGMA=0, but that is not practical for convergence reasons, so we try to find what is small enough. Let us examine the effect of SIGMA on the dissociation energy here.

```python
from vasp import Vasp
from ase import Atom, Atoms

sigmas = [0.2, 0.1, 0.05, 0.02, 0.01, 0.001]

D = []
for sigma in sigmas:
    atoms = Atoms([Atom('O',[5, 5, 5], magmom=2)],
                  cell=(10, 10, 10))

    calc = Vasp('molecules/O-sp-triplet-sigma-{0}'.format(sigma),
                xc='PBE',
                encut=400,
                ismear=0,
                sigma=sigma,
                ispin=2,
                atoms=atoms)

    E_O = atoms.get_potential_energy()

    # now relaxed O2 dimer
    atoms = Atoms([Atom('O',[5,    5, 5],magmom=1),
                   Atom('O',[6.22, 5, 5],magmom=1)],
                  cell=(10, 10, 10))

    calc = Vasp('molecules/O2-sp-triplet-sigma-{0}'.format(sigma),
                xc='PBE',
                encut=400,
                ismear=0,
                sigma=sigma,
                ispin=2,   # turn spin-polarization on
                ibrion=2,  # make sure we relax the geometry
                nsw=10,
                atoms=atoms)

    E_O2 = atoms.get_potential_energy()

    if None not in (E_O, E_O2):
```

```
        d = 2 * E_O - E_O2
        D.append(d)
        print('O2 -> 2O sigma = {0}  D = {1:1.3f} eV'.format(sigma, d))

import matplotlib.pyplot as plt
plt.plot(sigmas, D, 'bo-')
plt.xlabel('SIGMA (eV)')
plt.ylabel('O$_2$ dissociation energy (eV)')
plt.savefig('images/O2-dissociation-sigma-convergence.png')
```

Open the python script (dft-scripts/script-66.py).

```
O2 -> 2O sigma = 0.2  D = 6.669 eV
O2 -> 2O sigma = 0.1  D = 6.746 eV
O2 -> 2O sigma = 0.05  D = 6.784 eV
O2 -> 2O sigma = 0.02  D = 6.807 eV
O2 -> 2O sigma = 0.01  D = 6.815 eV
O2 -> 2O sigma = 0.001  D = 6.822 eV
```

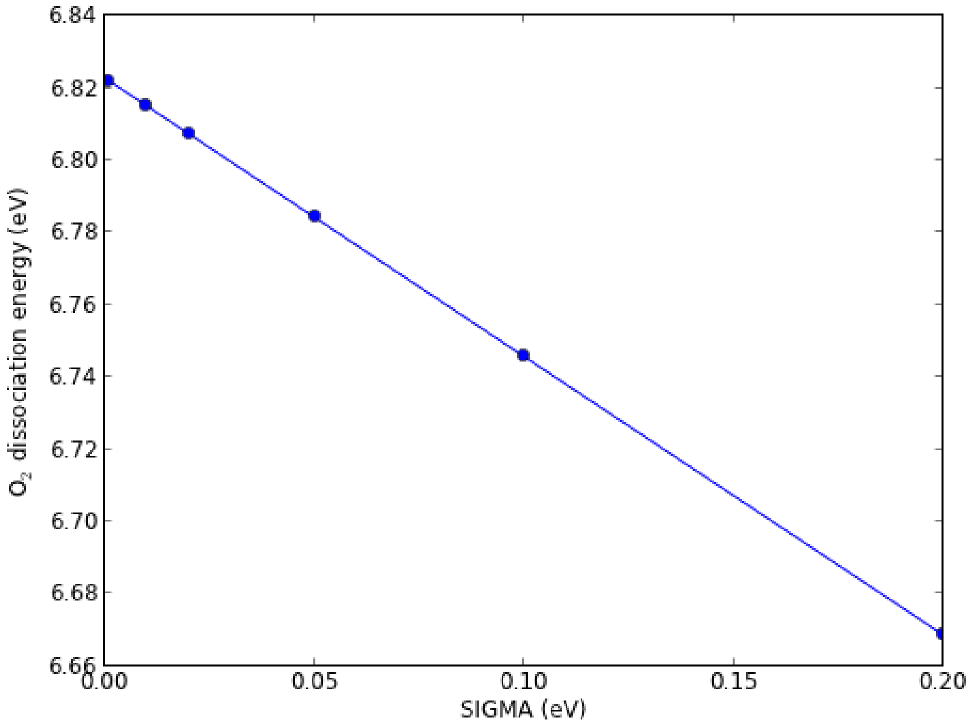


Figure 21: Effect of SIGMA on the oxygen dissociation energy.

Clearly SIGMA has an effect, but it does not move the dissociation energy closer to the literature values!

Estimating singlet oxygen dissociation energy Finally, let us consider the case where each species is in the singlet state.

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('O', [5, 5, 5], magmom=0)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O-sp-singlet',
            xc='PBE',
            encut=400,
            ismear=0,
            ispin=2,
            atoms=atoms)

E_O = atoms.get_potential_energy()

print('Magnetic moment on O = {0} Bohr'
      ' magnetons'.format(atoms.get_magnetic_moment()))

# now relaxed O2 dimer
atoms = Atoms([Atom('O', [5, 5, 5], magmom=1),
               Atom('O', [6.22, 5, 5], magmom=-1)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O2-sp-singlet',
            xc='PBE',
            encut=400,
            ismear=0,
            ispin=2,  # turn spin-polarization on
            ibrion=2, # make sure we relax the geometry
            nsw=10,
            atoms=atoms)

E_O2 = atoms.get_potential_energy()

# verify magnetic moment
print('O2 molecule magnetic moment = ', atoms.get_magnetic_moment())

if None not in (E_O, E_O2):
    print('O2 -> 2O  D = {0:1.3f} eV'.format(2 * E_O - E_O2))
```

Open the python script (dft-scripts/script-67.py).

```
Magnetic moment on O = 0.0001638 Bohr magnetons
('O2 molecule magnetic moment = ', 0.0)
O2 -> 2O  D = 8.619 eV
```

Let us directly compare their total energies:

```python
from vasp import Vasp

calc = Vasp('molecules/O2-sp-singlet')
print('singlet: {0} eV'.format(calc.potential_energy))

calc = Vasp('molecules/O2-sp-triplet')
print('triplet: {0} eV'.format(calc.potential_energy))
```

Open the python script (dft-scripts/script-68.py).

```
singlet: -8.77378302 eV
triplet: -9.84832389 eV
```

You can see here the triplet state has an energy that is 1 eV more stable than the singlet state.

Estimating triplet oxygen dissociation energy with low symmetry It has been suggested that breaking spherical symmetry of the atom can result in lower energy of the atom. The symmetry is broken by putting the atom off-center in a box. We will examine the total energy of an oxygen atom in a few geometries. First, let us consider variations of a square box.

```
from vasp import Vasp
from ase import Atom, Atoms

# square box origin
atoms = Atoms([Atom('O', [0, 0, 0], magmom=2)],
              cell=(10, 10, 10))

pars = dict(xc='PBE',
            encut=400,
            ismear=0,
            sigma=0.01,
            ispin=2)

calc = Vasp('molecules/O-square-box-origin',
            atoms=atoms, **pars)

print('Square box (origin): E = {0} eV'.format(atoms.get_potential_energy()))

# square box center
atoms = Atoms([Atom('O', [5, 5, 5], magmom=2)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O-square-box-center',
            atoms=atoms, **pars)
print('Square box (center): E = {0} eV'.format(atoms.get_potential_energy()))

# square box random
atoms = Atoms([Atom('O', [2.13, 7.32, 1.11], magmom=2)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O-square-box-random',
            atoms=atoms, **pars)

print('Square box (random): E = {0} eV'.format(atoms.get_potential_energy()))
```

Open the python script (dft-scripts/script-69.py).

```
Square box (origin): E = -1.51654778 eV
Square box (center): E = -1.51654804 eV
Square box (random): E = -1.5152871 eV
```

There is no significant difference in these energies. The origin and center calculations are identical in energy. The meV variation in the random calculation is negligible. Now, let us consider some non-square boxes.

```
# calculate O atom energy in orthorhombic boxes
from vasp import Vasp
from ase import Atom, Atoms

# orthorhombic box origin
atoms = Atoms([Atom('O', [0, 0, 0], magmom=2)],
              cell=(8, 9, 10))

calc = Vasp('molecules/O-orthorhombic-box-origin',
            xc='PBE',
            encut=400,
            ismear=0,
            sigma=0.01,
            ispin=2,
            atoms=atoms)

print('Orthorhombic box (origin): E = {0} eV'.format(atoms.get_potential_energy()))

# orthorhombic box center
atoms = Atoms([Atom('O', [4, 4.5, 5], magmom=2)],
              cell=(8, 9, 10))
calc = Vasp('molecules/O-orthorhombic-box-center',
            xc='PBE',
            encut=400,
            ismear=0,
            sigma=0.01,
            ispin=2,
```

```python
            atoms=atoms)

print('Orthorhombic box (center): E = {0} eV'.format(atoms.get_potential_energy()))

# orthorhombic box random
atoms = Atoms([Atom('O', [2.13, 7.32, 1.11], magmom=2)],
              cell=(8, 9, 10))

calc = Vasp('molecules/O-orthorhombic-box-random',
            xc='PBE',
            encut=400,
            ismear=0,
            sigma=0.01,
            ispin=2,
            atoms=atoms)

print('Orthorhombic box (random): E = {0} eV'.format(atoms.get_potential_energy()))
```

Open the python script (dft-scripts/script-70.py).

```
Orthorhombic box (origin): E = -1.89375092 eV
Orthorhombic box (center): E = -1.89375153 eV
Orthorhombic box (random): E = -1.87999536 eV
```

This is a surprisingly large difference in energy! Nearly 0.4 eV. This is precisely the amount of energy we were in disagreement with the literature values. Surprisingly, the "random" position is higher in energy, similar to the cubic boxes. Finally, we put this all together. We use a non-symmetric box for the O-atom.

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('O', [5.1, 4.2, 6.1], magmom=2)],
              cell=(8, 9, 10))

calc = Vasp('molecules/O-sp-triplet-lowsym',
            xc='PBE',
            encut=400,
            ismear=0,
            sigma=0.01,
            ispin=2,
            atoms=atoms)

E_O = atoms.get_potential_energy()
print('Magnetic moment on O = {0} Bohr  magnetons'.format(atoms.get_magnetic_moment()))

# now relaxed O2 dimer
atoms = Atoms([Atom('O', [5,    5, 5], magmom=1),
               Atom('O', [6.22, 5, 5], magmom=1)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O2-sp-triplet',
            xc='PBE',
            encut=400,
            ismear=0,
            sigma=0.01,
            ispin=2,   # turn spin-polarization on
            ibrion=2,  # make sure we relax the geometry
            nsw=10,
            atoms=atoms)

E_O2 = atoms.get_potential_energy()
# verify magnetic moment
print('Magnetic moment on O2 = {0} Bohr magnetons'.format(atoms.get_magnetic_moment()))


if None not in (E_O, E_O2):
    print('E_O: ', E_O)
    print('O2 -> 2O  D = {0:1.3f} eV'.format(2 * E_O - E_O2))
```

Open the python script (dft-scripts/script-71.py).

```
Magnetic moment on O = 2.0000073 Bohr  magnetons
Magnetic moment on O2 = 2.0000084 Bohr magnetons
('E_O: ', -1.89307116)
O2 -> 2O  D = 6.062 eV
```

This actually agrees within 30-50 meV of reported literature values, although still nearly an eV greater than the experimental dissociation energy. Note that with a different "random" position, we get the lower energy for the O atom. All the disagreement we had been seeing was apparently in the O atom energy. So, if you do not need the dissociation energy in your analysis, you will not see the error. Also note that this error is specific to there being a spherical atom in a symmetric cell. This is not a problem for most molecules, which are generally non-spherical.

Verifying the magnetic moments on each atom It is one thing to see the total magnetic moment of a singlet state, and another to ask what are the magnetic moments on each atom. In VASP you must use LORBIT = 11 to get the magnetic moments of the atoms written out.

```python
from vasp import Vasp

calc = Vasp('molecules/O2-sp-singlet')
calc.clone('molecules/O2-sp-singlet-magmoms')


calc.set(lorbit=11)
atoms = calc.get_atoms()
magmoms = atoms.get_magnetic_moments()

print('singlet ground state')
for i, atom in enumerate(atoms):
    print('atom {0}: magmom = {1}'.format(i, magmoms[i]))
print(atoms.get_magnetic_moment())

calc = Vasp('molecules/O2-sp-triplet')
calc.clone('molecules/O2-sp-triplet-magmoms')

calc.set(lorbit=11)
atoms = calc.get_atoms()
magmoms = atoms.get_magnetic_moments()
print()
print('triplet ground state')
for i, atom in enumerate(atoms):
    print('atom {0}: magmom = {1}'.format(i, magmoms[i]))
print(atoms.get_magnetic_moment())
```

Open the python script (dft-scripts/script-72.py).

```
singlet ground state
atom 0: magmom = 0.0
atom 1: magmom = 0.0
0.0
()
triplet ground state
atom 0: magmom = 0.815
atom 1: magmom = 0.815
2.0000083
```

Note the atomic magnetic moments do not add up to the total magnetic moment. The atomic magnetic moments are not really true observable properties. The moments are determined by a projection method that probably involves a spherical orbital, so the moments may be over or underestimated.

Using a different potential It is possible we need a higher quality potential to get the 6.02 eV value quoted by many in the literature. Here we try the O_sv potential, which treats the 1s electrons as valence electrons. Note however, the ENMIN in the POTCAR is very high!

```
grep ENMIN $VASP_PP_PATH/potpaw_PBE/O_sv/POTCAR
```

Open the python script (dft-scripts/script-73.py).

```
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('O', [4, 4.5, 5], magmom=2)],
              cell=(8, 9, 10))

calc = Vasp('molecules/O-sp-triplet-lowsym-s',
          xc='PBE',
            ismear=0,
            ispin=2,
            sigma=0.01,
            setups=[['O', '_s']],
            atoms=atoms)

E_O = atoms.get_potential_energy()
print(E_O)
```

Open the python script (dft-scripts/script-74.py).

```
-1.57217591
```

In the following calculation, we let VASP select an appropriate ENCUT value.

```
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('O', [4, 4.5, 5], magmom=2)],
              cell=(8, 9, 10))

calc = Vasp('molecules/O-sp-triplet-lowsym-s',
          xc='PBE',
            ismear=0,
            ispin=2,
            sigma=0.01,
            setups=[['O', '_s']],
            atoms=atoms)

E_O = atoms.get_potential_energy()

print('Magnetic moment on O = {0} Bohr'
      ' magnetons'.format(atoms.get_magnetic_moment()))

# now relaxed O2 dimer
atoms = Atoms([Atom('O', [5,    5, 5], magmom=1),
               Atom('O', [6.22, 5, 5], magmom=1)],
              cell=(10, 10, 10))

calc = Vasp('molecules/O2-sp-triplet-s',
            xc='PBE',
            ismear=0,
            sigma=0.01,
            ispin=2,   # turn spin-polarization on
            ibrion=2,  # make sure we relax the geometry
            nsw=10,
            setups=[['O', '_s']],
            atoms=atoms)

E_O2 = atoms.get_potential_energy()

# verify magnetic moment
print('Magnetic moment on O2 = {0} Bohr'
      ' magnetons'.format(atoms.get_magnetic_moment()))

if None not in (E_O, E_O2):
    print('O2 -> 2O  D = {0:1.3f} eV'.format(2*E_O - E_O2))
```

Open the python script (dft-scripts/script-75.py).

```
Magnetic moment on O = 1.9999982 Bohr magnetons
Magnetic moment on O2 = 2.0000102 Bohr magnetons
O2 -> 2O  D = 6.120 eV
```

This result is close to other reported values. It is possibly not converged, since we let VASP choose the ENCUT value, and that value is the ENMIN value in the POTCAR. Nevertheless, the point is that a harder potential does not fix the problem of overbinding in the O_2 molecule. That is a fundamental flaw in the GGA exchange-correlation functional.

3.8.2 Water gas shift example

We consider calculating the reaction energy of the water-gas shift reaction in this example.

$CO + H_2O \leftrightharpoons CO_2 + H_2$

We define the reaction energy as the difference in energy between the products and reactants.

$\Delta E = E_{CO_2} + E_{H_2} - E_{CO} - E_{H_2O}$

For now, we compute this energy simply as the difference in DFT energies. In the next section we will add zero-point energies and compute the energy difference as a function of temperature. For now, we simply need to compute the total energy of each molecule in its equilibrium geometry.

```python
from ase.structure import molecule
from vasp import Vasp

# first we define our molecules. These will automatically be at the coordinates from the G2 database.

CO = molecule('CO')
CO.set_cell([8, 8, 8], scale_atoms=False)

H2O = molecule('H2O')
H2O.set_cell([8, 8, 8], scale_atoms=False)

CO2 = molecule('CO2')
CO2.set_cell([8, 8, 8], scale_atoms=False)

H2 = molecule('H2')
H2.set_cell([8, 8, 8], scale_atoms=False)

# now the calculators to get the energies
c1 = Vasp('molecules/wgs/CO',
          xc='PBE',
          encut=350,
          ismear=0,
          ibrion=2,
          nsw=10,
          atoms=CO)

eCO = CO.get_potential_energy()

c2 = Vasp('molecules/wgs/CO2',
          xc='PBE',
          encut=350,
          ismear=0,
          ibrion=2,
          nsw=10,
          atoms=CO2)

eCO2 = CO2.get_potential_energy()

c3 = Vasp('molecules/wgs/H2',
          xc='PBE',
          encut=350,
          ismear=0,
          ibrion=2,
          nsw=10,
          atoms=H2)

eH2 = H2.get_potential_energy()

c4 = Vasp('molecules/wgs/H2O',
          xc='PBE',
          encut=350,
```

```python
            ismear=0,
            ibrion=2,
            nsw=10,
            atoms=H2O)

eH2O = H2O.get_potential_energy()

if None in (eCO2, eH2, eCO, eH2O):
    pass
else:
    dE = eCO2 + eH2 - eCO - eH2O
    print('Delta E = {0:1.3f} eV'.format(dE))
    print('Delta E = {0:1.3f} kcal/mol'.format(dE * 23.06035))
    print('Delta E = {0:1.3f} kJ/mol'.format(dE * 96.485))
```

Open the python script (dft-scripts/script-76.py).

```
Delta E = -0.723 eV
Delta E = -16.672 kcal/mol
Delta E = -69.758 kJ/mol
```

We estimated the enthalpy of this reaction at standard conditions to be -41 kJ/mol using data from the NIST webbook, which is a fair bit lower than we calculated here. In the next section we will examine whether additional corrections are needed, such as zero-point and temperature corrections.

It is a good idea to verify your calculations and structures are what you expected. Let us print them here. Inspection of these results shows the geometries were all relaxed, i.e., the forces on each atom are less than 0.05 eV/Å.

```python
from vasp import Vasp

print('**** Calculation summaries')
print('***** CO')
calc = Vasp('molecules/wgs/H2O')
print('#+begin_example')
print(calc)
print('#+end_example')
```

Open the python script (dft-scripts/script-77.py).

Calculation summaries

CO

```
Vasp calculation in /home-research/jkitchin/dft-book-new-vasp/molecules/wgs/H2O

INCAR created by Atomic Simulation Environment
 ENCUT = 350
 LCHARG = .FALSE.
 IBRION = 2
 ISMEAR = 0
 LWAVE = .TRUE.
 SIGMA = 0.1
 NSW = 10

 O  H
 1.0000000000000000
     8.0000000000000000    0.0000000000000000    0.0000000000000000
     0.0000000000000000    8.0000000000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000    8.0000000000000000
```

```
    1   2
Cartesian
  0.0000000000000000  0.0000000000000000  0.1192620000000000
  0.0000000000000000  0.7632390000000000 -0.4770470000000000
  0.0000000000000000 -0.7632390000000000 -0.4770470000000000
```

3.8.3 Temperature dependent water gas shift equilibrium constant

To correct the reaction energy for temperature effects, we must compute the vibrational frequencies of each species, and estimate the temperature dependent contributions to vibrational energy and entropy. We will break these calculations into several pieces. First we do each vibrational calculation. After those are done, we can get the data and construct the thermochemistry objects we need to estimate the reaction energy as a function of temperature (at constant pressure).

CO vibrations

```python
from vasp import Vasp

# get relaxed geometry
calc = Vasp('molecules/wgs/CO')
CO = calc.get_atoms()

# now do the vibrations
calc = Vasp('molecules/wgs/CO-vib',
          xc='PBE',
            encut=350,
            ismear=0,
            ibrion=6,
            nfree=2,
            potim=0.02,
            nsw=1,
            atoms=CO)
calc.wait()
vib_freq = calc.get_vibrational_frequencies()
for i, f in enumerate(vib_freq):
    print('{0:02d}: {1} cm^(-1)'.format(i, f))
```

Open the python script (dft-scripts/script-78.py).

```
00: 2064.699153 cm^(-1)
01: 170.409559 cm^(-1)
02: 170.409559 cm^(-1)
03: (1.171397+0j) cm^(-1)
04: (6.354831+0j) cm^(-1)
05: (6.354831+0j) cm^(-1)
```

CO has only one vibrational mode (3N-5 = 6 - 5 = 1). The other 5 modes are 3 translations and 2 rotations.

CO_2 vibrations

```python
from vasp import Vasp

# get relaxed geometry
calc = Vasp('molecules/wgs/CO2')
CO2 = calc.get_atoms()

# now do the vibrations
calc = Vasp('molecules/wgs/CO2-vib',
            xc='PBE',
            encut=350,
            ismear=0,
            ibrion=6,
```

```
            nfree=2,
            potim=0.02,
            nsw=1,
            atoms=CO2)
calc.wait()
vib_freq = calc.get_vibrational_frequencies()
for i, f in enumerate(vib_freq):
    print('{0:02d}: {1} cm^(-1)'.format(i, f))
```

Open the python script (dft-scripts/script-79.py).

```
00: 2339.140984 cm^(-1)
01: 1309.517832 cm^(-1)
02: 639.625419 cm^(-1)
03: 639.625419 cm^(-1)
04: (0.442216+0j) cm^(-1)
05: (1.801034+0j) cm^(-1)
06: (1.801034+0j) cm^(-1)
07: (35.286745+0j) cm^(-1)
08: (35.286745+0j) cm^(-1)
```

CO_2 is a linear molecule with 3N-5 = 4 vibrational modes. They are the first four frequencies in the output above.

H_2 vibrations

```
from vasp import Vasp

# get relaxed geometry
H2 = Vasp('molecules/wgs/H2').get_atoms()

# now do the vibrations
calc = Vasp('molecules/wgs/H2-vib',
            xc='PBE',
            encut=350,
            ismear=0,
            ibrion=6,
            nfree=2,
            potim=0.02,
            nsw=1,
            atoms=H2)
calc.wait()
vib_freq = calc.get_vibrational_frequencies()
for i, f in enumerate(vib_freq):
    print('{0:02d}: {1} cm^(-1)'.format(i, f))
```

Open the python script (dft-scripts/script-80.py).

```
00: 4484.933386 cm^(-1)
01: 0.0 cm^(-1)
02: 0.0 cm^(-1)
03: (1.5e-05+0j) cm^(-1)
04: (586.624928+0j) cm^(-1)
05: (586.624928+0j) cm^(-1)
```

There is only one frequency of importance (the one at 4281 cm^{-1}) for the linear H_2 molecule.

H_2O vibrations

```
from vasp import Vasp

# get relaxed geometry
H2O = Vasp('molecules/wgs/H2O').get_atoms()
```

```python

# now do the vibrations
calc = Vasp('molecules/wgs/H2O-vib',
          xc='PBE',
            encut=350,
            ismear=0,
            ibrion=6,
            nfree=2,
            potim=0.02,
            nsw=1,
            atoms=H2O)
calc.wait()
vib_freq = calc.get_vibrational_frequencies()
for i, f in enumerate(vib_freq):
    print('{0:02d}: {1} cm^(-1)'.format(i, f))
```

Open the python script (dft-scripts/script-81.py).

```
00: 3846.373652 cm^(-1)
01: 3734.935388 cm^(-1)
02: 1573.422217 cm^(-1)
03: 16.562103 cm^(-1)
04: 8.00982 cm^(-1)
05: (0.375952+0j) cm^(-1)
06: (225.466583+0j) cm^(-1)
07: (271.664033+0j) cm^(-1)
08: (286.859818+0j) cm^(-1)
```

Water has 3N-6 = 3 vibrational modes.

Thermochemistry Now we are ready. We have the electronic energies and vibrational frequencies of each species in the reaction. ase.thermochemistry.IdealGasThermo

```python
from ase.thermochemistry import IdealGasThermo
from vasp import Vasp
import numpy as np
import matplotlib.pyplot as plt

# first we get the electronic energies
c1 = Vasp('molecules/wgs/CO')
E_CO = c1.potential_energy
CO = c1.get_atoms()

c2 = Vasp('molecules/wgs/CO2')
E_CO2 = c2.potential_energy
CO2 = c2.get_atoms()

c3 = Vasp('molecules/wgs/H2')
E_H2 = c3.potential_energy
H2 = c3.get_atoms()

c4 = Vasp('molecules/wgs/H2O')
E_H2O = c4.potential_energy
H2O = c4.get_atoms()

# now we get the vibrational energies
h = 4.1356675e-15  # eV * s
c = 3.0e10  # cm / s

calc = Vasp('molecules/wgs/CO-vib')
vib_freq = calc.get_vibrational_frequencies()
CO_vib_energies = [h * c * nu for nu in vib_freq]

calc = Vasp('molecules/wgs/CO2-vib')
vib_freq = calc.get_vibrational_frequencies()
CO2_vib_energies = [h * c * nu for nu in vib_freq]

calc = Vasp('molecules/wgs/H2-vib')
vib_freq = calc.get_vibrational_frequencies()
H2_vib_energies = [h * c * nu for nu in vib_freq]
```

```python

calc = Vasp('molecules/wgs/H2O-vib')
vib_freq = calc.get_vibrational_frequencies()
H2O_vib_energies = [h * c * nu for nu in vib_freq]

# now we make a thermo object for each molecule
CO_t = IdealGasThermo(vib_energies=CO_vib_energies[0:0],
                      potentialenergy=E_CO, atoms=CO,
                      geometry='linear', symmetrynumber=1,
                      spin=0)

CO2_t = IdealGasThermo(vib_energies=CO2_vib_energies[0:4],
                      potentialenergy=E_CO2, atoms=CO2,
                      geometry='linear', symmetrynumber=2,
                      spin=0)

H2_t = IdealGasThermo(vib_energies=H2_vib_energies[0:0],
                      potentialenergy=E_H2, atoms=H2,
                      geometry='linear', symmetrynumber=2,
                      spin=0)

H2O_t = IdealGasThermo(vib_energies=H2O_vib_energies[0:3],
                      potentialenergy=E_H2O, atoms=H2O,
                      geometry='nonlinear', symmetrynumber=2,
                      spin=0)

# now we can compute G_rxn for a range of temperatures from 298 to 1000 K
Trange = np.linspace(298, 1000, 20)  # K
P = 101325. # Pa
Grxn = np.array([(CO2_t.get_gibbs_energy(temperature=T, pressure=P)
                  + H2_t.get_gibbs_energy(temperature=T, pressure=P)
                  - H2O_t.get_gibbs_energy(temperature=T, pressure=P)
                  - CO_t.get_gibbs_energy(temperature=T, pressure=P)) * 96.485
                 for T in Trange])

Hrxn = np.array([(CO2_t.get_enthalpy(temperature=T)
                  + H2_t.get_enthalpy(temperature=T)
                  - H2O_t.get_enthalpy(temperature=T)
                  - CO_t.get_enthalpy(temperature=T)) * 96.485
                 for T in Trange])

plt.plot(Trange, Grxn, 'bo-', label='$\Delta G_{rxn}$')
plt.plot(Trange, Hrxn, 'ro:', label='$\Delta H_{rxn}$')
plt.xlabel('Temperature (K)')
plt.ylabel(r'$\Delta G_{rxn}$ (kJ/mol)')
plt.legend(loc='best')
plt.savefig('images/wgs-dG-T.png')

plt.figure()
R = 8.314e-3  # gas constant in kJ/mol/K

Keq = np.exp(-Grxn/R/Trange)
plt.plot(Trange, Keq)
plt.ylim([0, 100])
plt.xlabel('Temperature (K)')
plt.ylabel('$K_{eq}$')
plt.savefig('images/wgs-Keq.png')
```

Open the python script (dft-scripts/script-82.py).

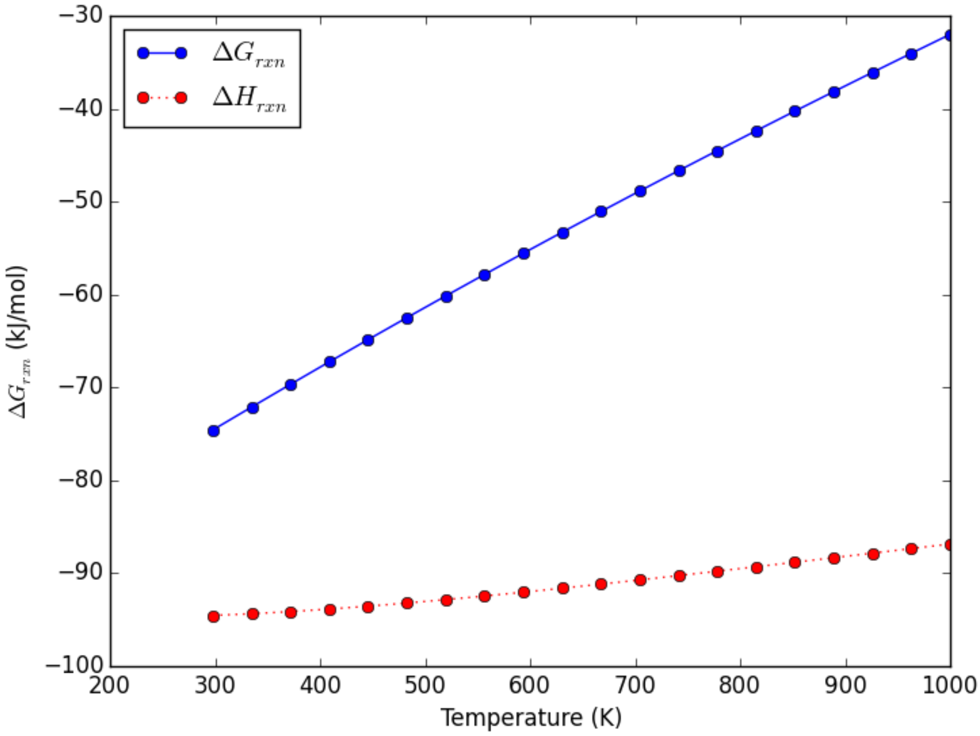


Figure 22: Thermodynamic energies of the water gas shift reaction as a function of temperature.

You can see a few things here. One is that at near 298K, the Gibbs free energy is about -75 kJ/mol. This is too negative compared to the experimental standard free energy, which we estimated to be about -29 kJ/mol from the NIST webbook. There could be several reasons for this disagreement, but the most likely one is errors in the exchange-correlation functional. The error in energy has a significant effect on the calculated equilibrium constant, significantly overestimating it.

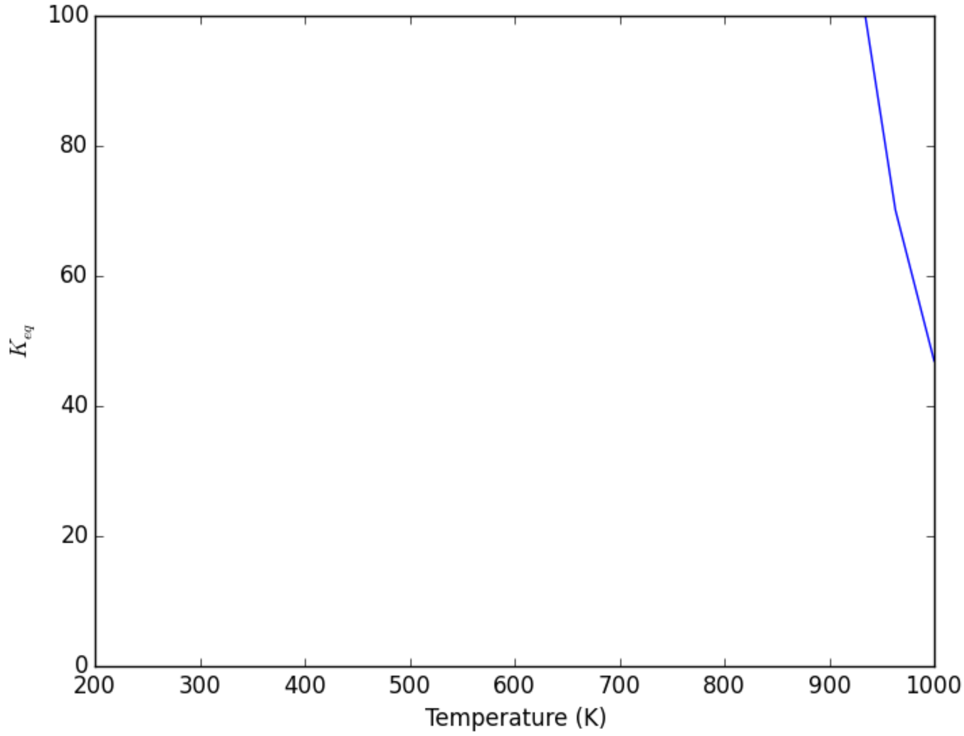


Figure 23: Temperature dependence of the equilibrium constant.

3.9 Molecular reaction barriers

We will consider a simple example of the barrier for NH_3 inversion. We have to create an NH_3 molecule in the initial and inverted state (these have exactly the same energy), and then interpolate a band of images. Then, we use the NEB method[47] to compute the barrier to inversion. The NEB class of methods are pretty standard, but other algorithms for finding barriers (saddle-points) exist that may be relevant.[48]

3.9.1 Get initial and final states

```
# compute initial and final states
from ase import Atoms
from ase.structure import molecule
import numpy as np
from vasp import Vasp
from ase.constraints import FixAtoms

atoms = molecule('NH3')
constraint = FixAtoms(mask=[atom.symbol == 'N' for atom in atoms])
atoms.set_constraint(constraint)

Npos = atoms.positions[0]

# move N to origin
atoms.translate(-Npos)
atoms.set_cell((10, 10, 10), scale_atoms=False)

atoms2 = atoms.copy()
pos2 = atoms2.positions

for i,atom in enumerate(atoms2):
    if atom.symbol == 'H':
```

```
        # reflect through z
        pos2[i] *= np.array([1, 1, -1])
atoms2.positions = pos2

#now move N to center of box
atoms.translate([5, 5, 5])
atoms2.translate([5, 5, 5])

calcs = [Vasp('molecules/nh3-initial',
              xc='PBE',
              encut=350,
              ibrion=1,
              nsw=10,
              atoms=atoms),
         Vasp('molecules/nh3-final',
             xc='PBE',
             encut=350,
             ibrion=1,
             nsw=10,
             atoms=atoms2)]

print [c.potential_energy for c in calcs]
```

Open the python script (dft-scripts/script-83.py).

3.9.2 Run band calculation

Now we do the band calculation.

```
# Run NH3 NEB calculations
from vasp import Vasp
from ase.neb import NEB
from ase.io import read

atoms = Vasp('molecules/nh3-initial').get_atoms()
atoms2 = Vasp('molecules/nh3-final').get_atoms()

# 5 images including endpoints
images = [atoms]   # initial state
images += [atoms.copy() for i in range(3)]
images += [atoms2]  # final state

neb = NEB(images)
neb.interpolate()

calc = Vasp('molecules/nh3-neb',
            xc='PBE',
            ibrion=1, encut=350,
            nsw=90,
            spring=-5.0,
            atoms=images)

#calc.write_db(atoms, 'molecules/nh3-neb/00/DB.db')
#calc.write_db(atoms2, 'molecules/nh3-neb/04/DB.db')
images, energies = calc.get_neb()
calc.stop_if(None in energies)

print images
print energies
p = calc.plot_neb(show=False)
import matplotlib.pyplot as plt
plt.savefig('images/nh3-neb.png')
```

Open the python script (dft-scripts/script-84.py).

```
[Atoms(symbols='NH3', positions=..., magmoms=..., cell=[10.0, 10.0, 10.0], pbc=[True, True, True], c
[  0.00000000e+00   1.26688520e-01   2.25038820e-01   1.26688620e-01
   9.99999727e-09]
Optimization terminated successfully.
         Current function value: -0.225039
         Iterations: 15
```

```
Function evaluations: 30
```

The calculator view function shows you the band.

```
from vasp import Vasp

calc = Vasp('molecules/nh3-neb')
calc.view()
```

Open the python script (dft-scripts/script-85.py).

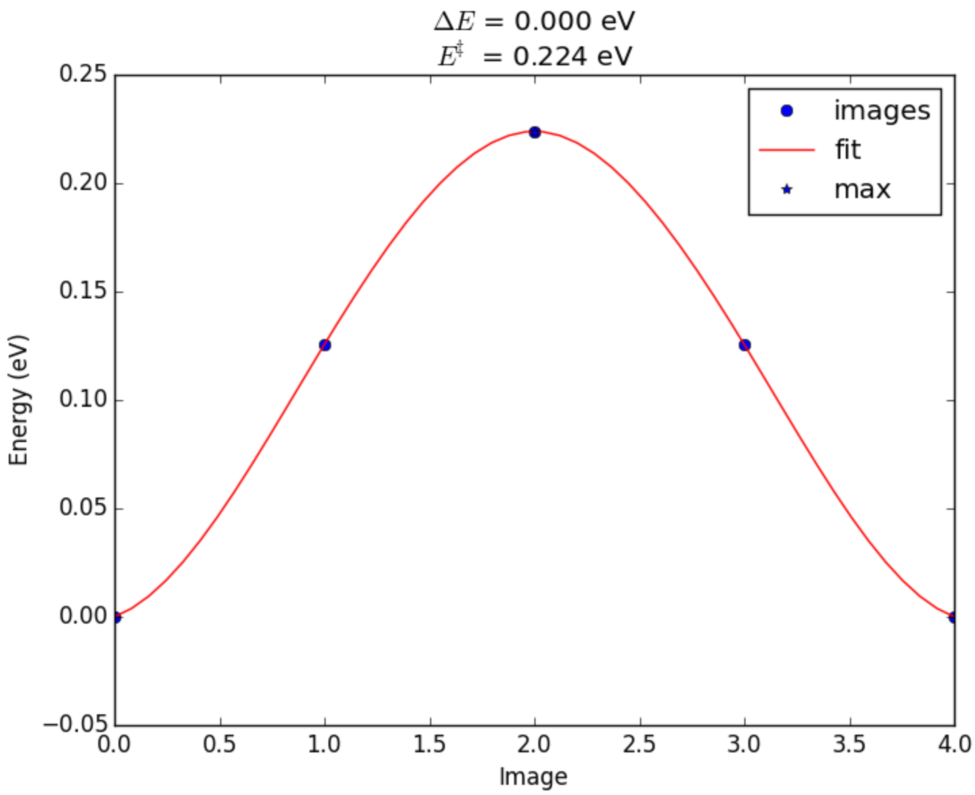


Figure 24: Nudged elastic band results for ammonia flipping.

3.9.3 Make a movie of the animation

It is helpful sometimes to animate the Nudged elastic band path. Here is a script to do that. I have not figured out how to embed the movie in this document

```
# make neb movie
from ase.io import write
from ase.visualize import view
from vasp import Vasp

calc = Fasp('molecules/nh3-neb') as calc:
images, energies = calc.get_neb()

# this rotates the atoms 90 degrees about the y-axis
[atoms.rotate('y', np.pi/2.) for atoms in images]

for i,atoms in enumerate(images):
    write('images/00{0}-nh3.png'.format(i), atoms, show_unit_cell=2)

```

```
# animated gif
os.system('convert -delay 50 -loop 0 images/00*-nh3.png images/nh3-neb.gif')

# Shockwave flash
os.system('png2swf -o images/nh3-neb.swf images/00*-nh3.png ')
```

Open the python script (dft-scripts/script-86.py).
./images/nh3-neb.gif
./images/nh3-neb.swf

4 Bulk systems

See http://arxiv.org/pdf/1204.2733.pdf for a very informative comparison of DFT codes for computing different bulk properties.

4.1 Defining and visualizing bulk systems

4.1.1 Built-in functions in ase

As with molecules, ase provides several helper functions to create bulk structures. We highlight a few of them here. Particularly common ones are:

- ase.lattice.cubic.FaceCenteredCubic
- ase.lattice.cubic.BodyCenteredCubic
- ase.lattice.hexagonal.Graphite
- ase.lattice.compounds.NaCl

For others, see https://wiki.fysik.dtu.dk/ase/ase/lattice.html

We start with a simple example, fcc Ag. By default, ase knows Ag is an fcc metal, and knows the experimental lattice constant. We have to specify the directions (vectors along each axis) to get something other than the default output. Here, the default fcc cell contains four atoms.

```
from ase.io import write
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic('Ag')

write('images/Ag-fcc.png', atoms, show_unit_cell=2)

print(atoms)
```

Open the python script (dft-scripts/script-87.py).

```
Lattice(symbols='Ag4', positions=..., cell=[4.09, 4.09, 4.09], pbc=[True, True, True])
```

Note:
A ase.lattice.bravais.Lattice object is returned! This is practically the same as as an ase.atoms.Atoms object.

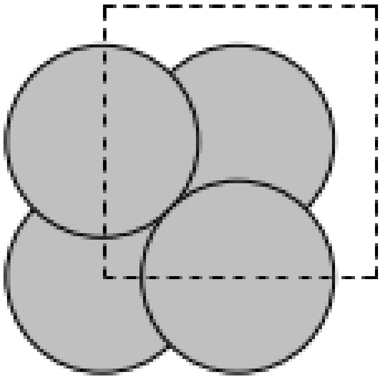


Figure 25: A simple fcc Ag bulk structure in the primitive unit cell.

Here we specify the primitive unit cell, which only has one atom in it.

```
from ase.io import write
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic('Ag', directions=[[0, 1, 1],
                                            [1, 0, 1],
                                            [1, 1, 0]])

write('images/Ag-fcc-primitive.png', atoms, show_unit_cell=2)

print atoms
```

Open the python script (dft-scripts/script-88.py).

```
Lattice(symbols='Ag', positions=..., cell=[[2.892066735052979, 0.0, 0.0], [1.4460333675264898, 2.504
```

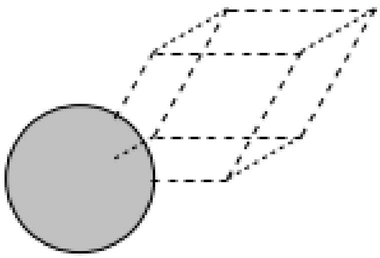


Figure 26: A simple fcc Ag bulk structure in the primitive unit cell.

```
Lattice(symbols='Ag', positions=..., cell=[[2.892066735052979, 0.0, 0.0], [1.4460333675264898, 2.504
```

We can use these modules to build alloy unit cells. The basic strategy is to create the base unit cell in one element and then selectively change some atoms to different chemical symbols. Here we examine an Ag_3Pd alloy structure.

```
from ase.io import write
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic(directions=[[1, 0, 0],
                                      [0, 1, 0],
                                      [0, 0, 1]],
                          size=(1, 1, 1),
                          symbol='Ag',
```

```
                          latticeconstant=4.0)

write('images/Ag-bulk.png', atoms, show_unit_cell=2)

# to make an alloy, we can replace one atom with another kind
atoms[0].symbol = 'Pd'
write('images/AgPd-bulk.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-89.py).

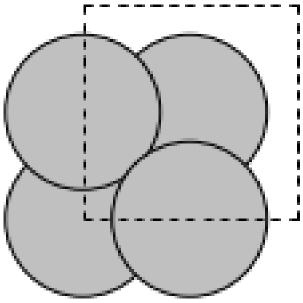


Figure 27: A simple fcc Ag bulk structure in the traditional unit cell.

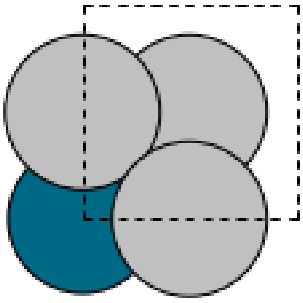


Figure 28: A simple Ag_3Pd bulk structure.

To create a graphite structure we use the following code. Note that we have to specify the lattice constants (taken from http://www.phy.ohiou.edu/~asmith/NewATOMS/HOPG.pdf) because ase has C in the diamond structure by default. We show two views, because the top view does not show the spacing between the layers.

```
from ase.lattice.hexagonal import Graphite
from ase.io import write

atoms = Graphite('C', latticeconstant={'a': 2.4612,
                                       'c': 6.7079})
write('images/graphite.png',
      atoms.repeat((2, 2, 1)),
      rotation='115x', show_unit_cell=2)

write('images/graphite-top.png',
      atoms.repeat((2, 2, 1)),
      show_unit_cell=2)
```

Open the python script (dft-scripts/script-90.py).

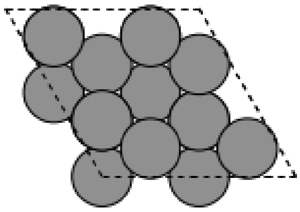


Figure 29: A top view of graphite.

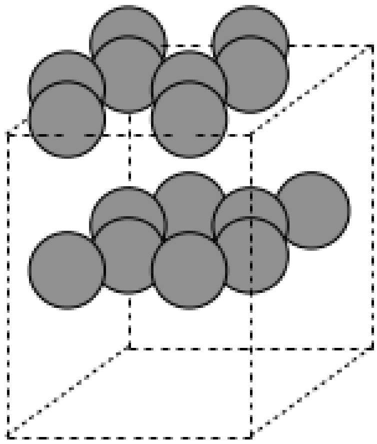


Figure 30: A side view of graphite.

To get a compound, we use the following code. We have to specify the basis atoms to the function generating the compound, and the lattice constant. For NaCl we use the lattice constant at (http://en.wikipedia.org/wiki/Sodium_chloride).

```
from ase.lattice.compounds import NaCl
from ase.io import write

atoms = NaCl(['Na', 'Cl'], latticeconstant=5.65)
write('images/NaCl.png', atoms, show_unit_cell=2, rotation='45x,45y,45z')
```

Open the python script (dft-scripts/script-91.py).

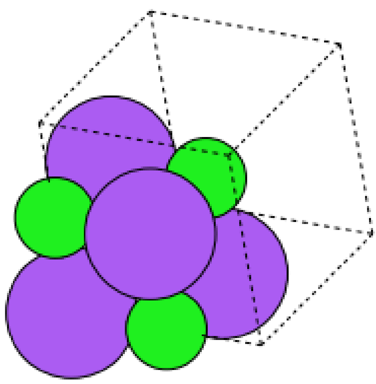


Figure 31: A view of a NaCl crystal structure.

ase.spacegroup A final alternative to setting up bulk structures is ase.spacegroup. This is a concise way to setup structures if you know the following properties of the crystal structure:

1. Chemical symbols
2. Coordinates of the non-equivalent sites in the unit cell
3. the spacegroup
4. the cell parameters (a, b, c, alpha, beta, gamma)

```python
from ase.lattice.spacegroup import crystal
# FCC aluminum
a = 4.05
al = crystal('Al', [(0, 0, 0)],
             spacegroup=225,
             cellpar=[a, a, a, 90, 90, 90])
print(al)
```

Open the python script (dft-scripts/script-92.py).

```
Atoms(symbols='Al4', positions=..., cell=[[4.05, 0.0, 0.0], [2.4799097682733903e-16, 4.05, 0.0], [2.
```

Here is rutile TiO_2.

```python
from ase.lattice.spacegroup import crystal

a = 4.6
c = 2.95
rutile = crystal(['Ti', 'O'], basis=[(0, 0, 0), (0.3, 0.3, 0.0)],
                 spacegroup=136, cellpar=[a, a, c, 90, 90, 90])
print rutile
```

Open the python script (dft-scripts/script-93.py).

Atoms(symbols'Ti2O4', positions=. . . , cell=[[4.6, 0.0, 0.0], [2.816687638038912e-16, 4.6, 0.0], [1.806354028742346e-16, 1.806354028742346e-16, 2.95]], pbc=[True, True, True]) =Atoms(symbols'Ti2O4', positions=. . . , cell=[[4.6, 0.0, 0.0], [2.816687638038912e-16, 4.6, 0.0], [1.806354028742346e-16, 1.806354028742346e-16, 2.95]], pbc=[True, True, True]) =sho

4.1.2 Using http://materialsproject.org

The Materials Project offers web access to a pretty large number of materials (over 21,000 at the time of this writing), including structure and other computed properties. You must sign up for an account at the website, and then you can access the information. You can search for materials with lots of different criteria including formula, unit cell formula, by elements, by structure, etc. . . The website allows you to download the VASP files used to create the calculations. They also develop the pymatgen project (which requires python 2.7+).

For example, I downloaded this cif file for a RuO_2 structure (Material ID 825).

```
#\#CIF1.1
##########################################################################
#               Crystallographic Information Format file
#               Produced by PyCifRW module
#
#  This is a CIF file.  CIF has been adopted by the International
#  Union of Crystallography as the standard for data archiving and
#  transmission.
#
#  For information on this file format, follow the CIF links at
#  http://www.iucr.org
##########################################################################

data_RuO2
```

```
_symmetry_space_group_name_H-M          'P 1'
_cell_length_a                          3.13970109
_cell_length_b                          4.5436378
_cell_length_c                          4.5436378
_cell_angle_alpha                       90.0
_cell_angle_beta                        90.0
_cell_angle_gamma                       90.0
_chemical_name_systematic               'Generated by pymatgen'
_symmetry_Int_Tables_number             1
_chemical_formula_structural            RuO2
_chemical_formula_sum                   'Ru2 O4'
_cell_volume                            64.8180127062
_cell_formula_units_Z                   2
loop_
  _symmetry_equiv_pos_site_id
  _symmetry_equiv_pos_as_xyz
   1  'x, y, z'

loop_
  _atom_site_type_symbol
  _atom_site_label
  _atom_site_symmetry_multiplicity
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_attached_hydrogens
  _atom_site_B_iso_or_equiv
  _atom_site_occupancy
   O  O1  1  0.000000  0.694330  0.694330  0  .  1
   O  O2  1  0.500000  0.805670  0.194330  0  .  1
   O  O3  1  0.000000  0.305670  0.305670  0  .  1
   O  O4  1  0.500000  0.194330  0.805670  0  .  1
   Ru  Ru5  1  0.500000  0.500000  0.500000  0  .  1
   Ru  Ru6  1  0.000000  0.000000  0.000000  0  .  1
```

Open the python script (dft-scripts/script-94.py).

We can read this file in with `ase.io.read`. That function automatically recognizes the file type by the extension.

```python
from ase.io import read, write

atoms = read('bulk/Ru2O4_1.cif')

write('images/Ru2O4.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-95.py).

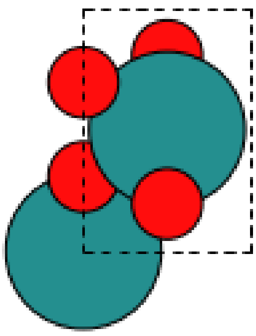


Figure 32: An RuO_2 unit cell prepared from a cif file.

4.2 Computational parameters that are important for bulk structures

4.2.1 k-point convergence

In the section on molecules, we learned that the total energy is a function of the planewave cutoff energy (ENCUT) used. In bulk systems that is true also. There is also another calculation parameter you must consider, the k-point grid. The k-point grid is a computational tool used to approximate integrals of some property, e.g. the electron density, over the entire unit cell. The integration is performed in reciprocal space (i.e. in the Brillouin zone) for convenience and efficiency, and the k-point grid is where the property is sampled for the integration. The higher the number of sampled points, the more accurately the integrals are approximated.

We will typically use a Monkhorst-Pack[28] \$k\$-point grid, which is essentially a uniformly spaced grid in the Brillouin zone. Another less commonly used scheme is the Chadi-Cohen k-point grid.[27] The Monkhorst-Pack grids are specified as $n1 \times n2 \times n3$ grids, and the total number of k-points is $n1 \cdot n2 \cdot n3$. The computational cost is linear in the total number of k-points, so a calculation on a $4 \times 4 \times 4$ grid will be roughly 8 times more expensive than on a $2 \times 2 \times 2$ grid. Hence, one seeks again to balance convergence with computational tractability. Below we consider the k-point convergence of fcc Ag.

```
from ase.lattice.cubic import FaceCenteredCubic
from vasp import Vasp
import numpy as np

atoms = FaceCenteredCubic('Ag')

KPTS = [2, 3, 4, 5, 6, 8, 10]

TE = []

for k in KPTS:
    calc = Vasp('bulk/Ag-kpts-{0}'.format(k),
                xc='PBE',
                kpts=[k, k, k],  # specifies the Monkhorst-Pack grid
                encut=300,
                atoms=atoms)
    TE.append(atoms.get_potential_energy())

if None in TE:
    calc.abort()

import matplotlib.pyplot as plt

# consider the change in energy from lowest energy state
TE = np.array(TE)
TE -= TE.min()

plt.plot(KPTS, TE)
plt.xlabel('number of k-points in each dimension')
plt.ylabel('Total Energy (eV)')
plt.savefig('images/Ag-kpt-convergence.png')
```

Open the python script (dft-scripts/script-96.py).

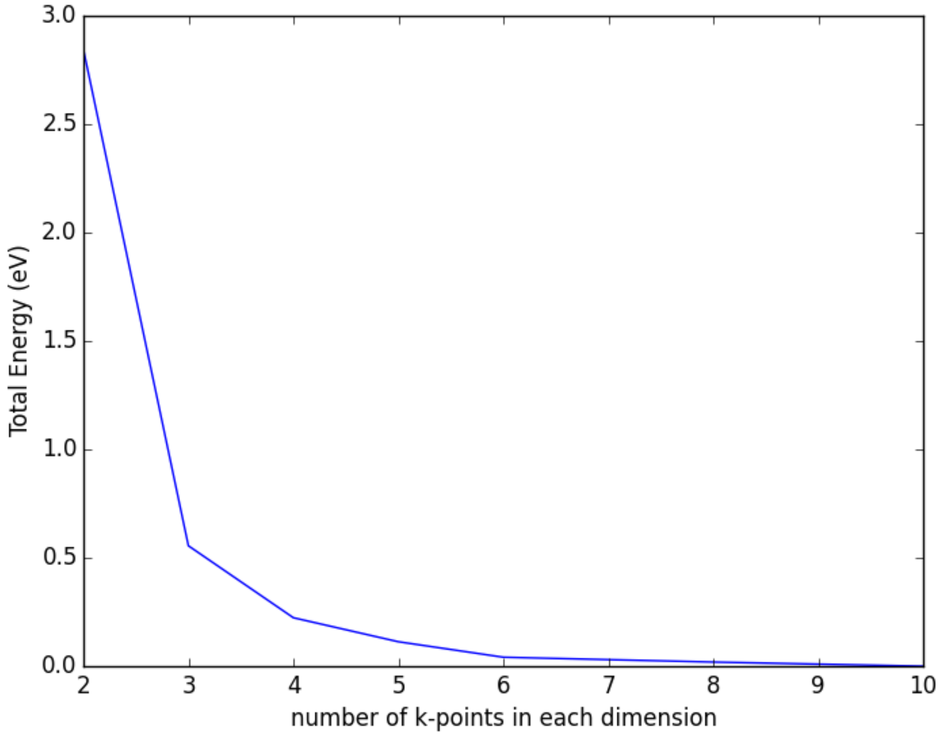


Figure 33: k-point convergence of the total energy of fcc Ag.

Based on this figure, we need at least a $6 \times 6 \times 6$ k-point grid to achieve a convergence level of at least 50 meV. Note: the k-point convergence is not always monotonic like it is in this example, and sometimes very dense grids (e.g. up to $20 \times 20 \times 20$) are needed for highly converged properties such as the density of states in smaller unit cells. Oscillations in the total energy are typical, and it can be difficult to get high levels of convergence. The best practices are to use the same k-point sampling grid in energy differences where possible, and dense (high numbers of k-points) otherwise. It is important to check for convergence in these cases.

As unit cells get larger, the number of k-points required becomes smaller. For example, if a $1 \times 1 \times 1$ fcc unit cell shows converged energies in a $12 \times 12 \times 12$ k-point grid, then a $2 \times 2 \times 2$ fcc unit cell would show the same level of convergence with a $6 \times 6 \times 6$ k-point grid. In other words, doubling the unit cell vectors results in a halving of the number of k-points.

Sometimes you may see k-points described as k-points per reciprocal atom. For example, a $12 \times 12 \times 12$ k-point grid for a primitive fcc unit cell would be 1728 k-points per reciprocal atom. A $2 \times 2 \times 2$ fcc unit cell has eight atoms in it, or 0.125 reciprocal atoms, so a $6 \times 6 \times 6$ k-point grid has 216 k-points in it, or $216/0.125 = 1728$ k-points per reciprocal atom, the same as we discussed before.

In the k-point convergence example above, we used a $6 \times 6 \times 6$ k-point grid on a unit cell with four atoms in it, leading to 864 k-points per reciprocal atom. If we had instead used the primitive unit cell, we would need either a $9 \times 9 \times 9$ or $10 \times 10 \times 10$ k-point grid to get a similar level of accuracy. In this case, there is no exact matching of k-point grids due to the difference in shape of the cells.

4.2.2 TODO Effect of SIGMA

In the self-consistent cycle of a DFT calculation, the total energy is minimized with respect to occupation of the Kohn-Sham orbitals. At absolute zero, a band is either occupied or empty. This discrete occupation results in discontinuous changes in energy with changes in occupation, which makes it difficult to converge. One solution is to artificially broaden the band occupancies, as if they were occupied at a higher temperature where partial occupation is possible. This results in a continuous dependence of energy on the partial occupancy, and dramatically increases the rate of convergence. SIGMA and ISMEAR affect how the partial occupancies of the bands are determined.

Some rules to keep in mind:

1. The smearing methods were designed for metals. For molecules, semiconductors and insulators you should use a very small SIGMA (e.g. 0.01).
2. Standard values for metallic systems is SIGMA=0.1, but the best SIGMA may be material specific.

The consequence of this finite temperature is that additional bands must be included in the calculation to allow for the partially occupied states above the Fermi level; the number of extra bands depends on the temperature used. An example of the maximum occupancies of the bands for an Cu bulk as a function of SIGMA is shown in Figure 34. Obviously, as SIGMA approaches 0, the occupancy approaches a step function. It is preferable that the occupancy of several of the highest bands be zero (or at least of order 1×10^{-8}) to ensure enough variational freedom was available in the calculation. Consequently, it is suggested that fifteen to twenty extra bands be used for a SIGMA of 0.20. In any case, it should be determined that enough bands were used by examination of the occupancies. It is undesirable to have too many extra bands, as this will add computational time.

Below we show the effect of SIGMA on the band occupancies.

```python
from vasp import Vasp
from ase import Atom, Atoms
import matplotlib.pyplot as plt
import numpy as np

a = 3.61
atoms = Atoms([Atom('Cu', (0, 0, 0))],
              cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
                                       [0.0, 1.0, 1.0],
                                       [1.0, 0.0, 1.0]])).repeat((2, 2, 2))

SIGMA = [0.001, 0.05, 0.1, 0.2, 0.5]

for sigma in SIGMA:

    calc = Vasp('bulk/Cu-sigma-{0}'.format(sigma),
                xc='PBE',
                encut=350,
                kpts=[4, 4, 4],
                ismear=-1,
                sigma=sigma,
                nbands=9 * 8,
                atoms=atoms)

    if calc.potential_energy is not None:
        nbands = calc.parameters.nbands
        nkpts = len(calc.get_ibz_k_points())

        occ = np.zeros((nkpts, nbands))
        for i in range(nkpts):
            occ[i, :] = calc.get_occupation_numbers(kpt=i)

        max_occ = np.max(occ, axis=0) #axis 0 is columns

        plt.plot(range(nbands), max_occ, label='$\sigma = {0}$'.format(sigma))

plt.xlabel('band number')
plt.ylabel('maximum occupancy (electrons)')
plt.ylim([-0.1, 2.1])
plt.legend(loc='best')
plt.savefig('images/occ-sigma.png')
```

Open the python script (dft-scripts/script-97.py).

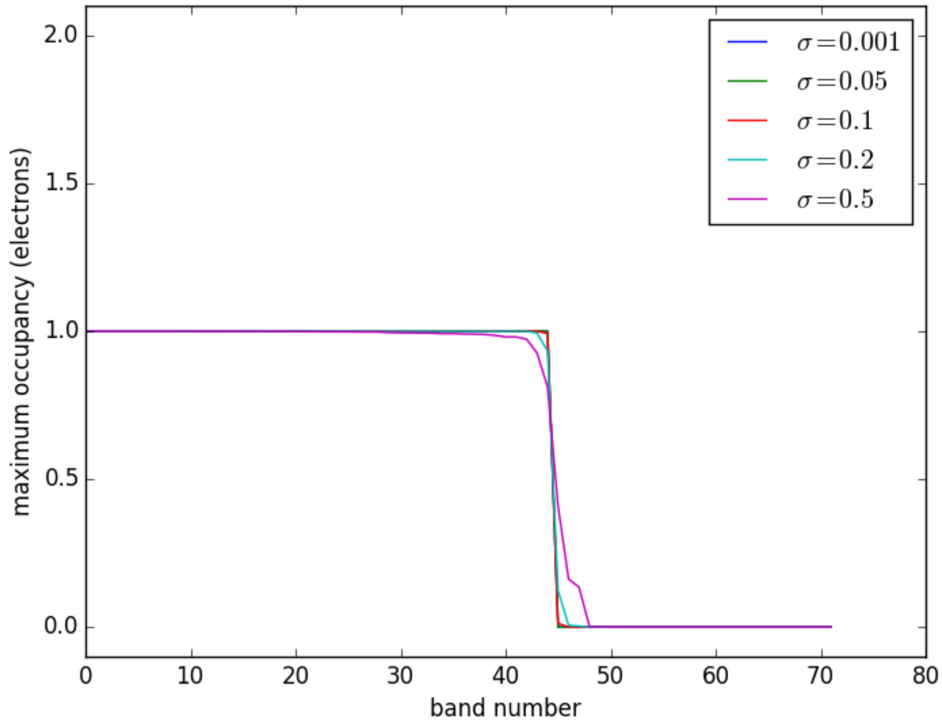


Figure 34: Effects of SIGMA on the occupancies of the Cu system.

4.2.3 The number of bands

In the last figure, it is evident that due to the smearing of the electronic states you need to have extra bands to accommodate the electrons above the Fermi level, and the higher the SIGMA value is, the more bands you need. You need enough bands so that the highest energy bands are unoccupied, and VASP will give you a warning that looks like this:

```
 -----------------------------------------------------------------------------
|                                                                             |
|  ADVICE TO THIS USER RUNNING 'VASP/VAMP'   (HEAR YOUR MASTER'S VOICE ...):  |
|                                                                             |
|      Your highest band is occupied at some k-points! Unless you are         |
|      performing a calculation for an insulator or semiconductor, without    |
|      unoccupied bands, you have included TOO FEW BANDS!! Please increase    |
|      the parameter NBANDS in file 'INCAR' to ensure that the highest band   |
|      is unoccupied at all k-points. It is always recommended to             |
|      include a few unoccupied bands to accelerate the convergence of        |
|      molecular dynamics runs (even for insulators or semiconductors).       |
|      Because the presence of unoccupied bands improves wavefunction         |
|      prediction, and helps to suppress 'band-crossings.'                    |
|      Following all k-points will be listed (with the Fermi weights of       |
|      the highest band given in paranthesis) ... :                           |
|                                                                             |
|                      6       (-0.01472)                                     |
|                      8       (-0.01413)                                     |
```

```
|                        13       (-0.01733)                                    |
|                        14       (-0.01838)                                    |
|                                                                              |
|      The total occupancy of band no.    49 is  -0.00932 electrons ...        |
|                                                                              |
 -----------------------------------------------------------------------------
```

We tell VASP the number of bands to use with the NBANDS keyword. VASP will set the NBANDS automatically if you do not provide a value, but this is in general bad practice (even though it is often done in this book!). There are a few general guidelines for setting NBANDS. First we recognize that a band can only have two electrons in it (one spin up, and one spin down) in an calculation without spin-polarization, or one electron per band for a spin-polarized calculation (note that spin-polarization doubles the number of bands). There absolutely must be enough bands to accommodate all the electrons, so the minimum number of bands is int(ceil(nelectrons/2)).

Here is an example of what this equation does.

```python
import numpy as np

print int(np.ceil(50 / 2.))
print int(np.ceil(51 / 2.))
```

Open the python script (dft-scripts/script-98.py).

```
25
26
```

However, due to the smearing, the minimum number of bands is almost never enough, and we always add more bands. The default behavior in VASP is:

non-spin polarized	NELECT/2 + NIONS/2
spin-polarized	0.6*NELECT + NMAGIONS

These do not always work, especially for small molecular systems where NIONS/2 may be only 1, or transition metals where it may be necessary to add up to 2*NIONS extra bands.

To figure out how many bands you need, it is necessary to know how many electrons are in your calculation. The `Vasp.get_valence_electrons` provides this for you. Alternatively, you can look in the Appendix for a table listing the number of valence electrons for each POTCAR file. Armed with this information you can set NBANDS the way you want.

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Cu',  [0.000, 0.000, 0.000])],
              cell= [[1.818, 0.000, 1.818],
                     [1.818, 1.818, 0.000],
                     [0.000, 1.818, 1.818]])

calc = Vasp('bulk/alloy/cu',
            xc='PBE',
            encut=350,
            kpts=[13, 13, 13],
            nbands=9,
            ibrion=2,
            isif=4,
            nsw=10,
            atoms=atoms)

print(calc.get_valence_electrons())
print(calc.potential_energy)
```

Open the python script (dft-scripts/script-99.py).

```
11.0
-3.73436945
```

For this calculation we need at least 6 bands (11/2=5.5 which is rounded up to 6) and we need to include some extra bands. The default rule would only add half a band, which is not enough. We add three additional bands. This system is so small it does not substantially increase the computational cost.

If you are too trifling to do that much work, you can use the `Vasp.set_nbands` to automatically set the number of bands. This function takes an argument `N` to set the number of bands to N, **or** an argument `f` to set the NBANDS according to the formula $nbands = int(nelectrons/2 + len(atoms) * f)$. The default value of `f` is 1.5. If you want the default VASP behavior, set f=0.5. For transition metals, it may be required that f=2. This function does not consider whether the calculation is spin-polarized or not. Here is an example of using `Vasp.set_nbands`.

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000])],
              cell=[[1.818, 0.000, 1.818],
                    [1.818, 1.818, 0.000],
                    [0.000, 1.818, 1.818]])

calc = Vasp('bulk/alloy/cu',
            xc='PBE',
            encut=350,
            kpts=[13, 13, 13],
            ibrion=2,
            isif=4,
            nsw=10,
            atoms=atoms)
calc.set_nbands(f=7)
calc.write_input()  # you have to write out the input for it to take effect
print calc
```

Open the python script (dft-scripts/script-100.py).

```
*************** VASP CALCULATION SUMMARY ***************
Vasp calculation directory:
---------------------------
  [[/home-research/jkitchin/dft-book/bulk/alloy/cu]]

Unit cell:
----------
       x       y       z             |v|
  v0   1.818   0.000   1.818       2.571 Ang
  v1   1.818   1.818   0.000       2.571 Ang
  v2   0.000   1.818   1.818       2.571 Ang
  alpha, beta, gamma (deg):   60.0  60.0  60.0
  Total volume:                   12.017 Ang^3
  Stress:     xx      yy      zz      yz      xz      xy
             nan     nan     nan     nan     nan     nan GPa

  ID  tag     sym    x         y         z        rmsF (eV/A)
  0   0       Cu     0.000     0.000     0.000        nan
  Potential energy: nan eV

INPUT Parameters:
-----------------
  pp        : PBE
  isif      : 4
```

```
  xc         : pbe
  kpts       : [13, 13, 13]
  encut      : 350
  lcharg     : False
  ibrion     : 2
  nbands     : 13
  ismear     : 1
  lwave      : True
  sigma      : 0.1
  nsw        : 10

Pseudopotentials used:
----------------------
  Cu: potpaw_PBE/Cu/POTCAR (git-hash: 13fa889d46be8b12a676c1063c5e4faede17e89b)
```

Note the defaults that were set.

```python
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000])],
              cell=[[1.818, 0.000, 1.818],
                    [1.818, 1.818, 0.000],
                    [0.000, 1.818, 1.818]])

calc = Vasp('bulk/alloy/cu-setnbands',
            xc='PBE',
            encut=350,
            kpts=[13, 13, 13],
            ibrion=2,
            isif=4,
            nsw=10,
            atoms=atoms)
calc.set_nbands(f=3)
calc.write_input()
print calc
```

Open the python script (dft-scripts/script-101.py).

```
*************** VASP CALCULATION SUMMARY ***************
Vasp calculation directory:
---------------------------
  [[/home-research/jkitchin/dft-book/bulk/alloy/cu-setnbands]]

Unit cell:
----------
       x       y       z             |v|
  v0   1.818   0.000   1.818       2.571 Ang
  v1   1.818   1.818   0.000       2.571 Ang
  v2   0.000   1.818   1.818       2.571 Ang
  alpha, beta, gamma (deg):   60.0  60.0  60.0
  Total volume:                   12.017 Ang^3
  Stress:     xx      yy      zz      yz      xz      xy
            nan     nan     nan     nan     nan     nan GPa

  ID  tag     sym    x         y         z        rmsF (eV/A)
  0   0       Cu     0.000     0.000     0.000        nan
  Potential energy: nan eV
```

```
INPUT Parameters:
-----------------
  pp         : PBE
  isif       : 4
  xc         : pbe
  kpts       : [13, 13, 13]
  encut      : 350
  lcharg     : False
  ibrion     : 2
  nbands     : 9
  ismear     : 1
  lwave      : True
  sigma      : 0.1
  nsw        : 10

Pseudopotentials used:
----------------------
  Cu: potpaw_PBE/Cu/POTCAR (git-hash: 13fa889d46be8b12a676c1063c5e4faede17e89b)
```

You are, of course, free to use any formula you want to set the number of bands. Some formulas I have used in the past include:

1. NBANDS = 0.65*NELECT + 10
2. NBANDS = 0.5*NELECT + 15
3. etc...

4.3 Determining bulk structures

What we typically mean by determining bulk structures includes the following:

- What is the most stable crystal structure for a material?
- What is the lattice constant of fcc Cu?
- What are the lattice parameters and internal atom parameters for TiO_2?

All of these questions can often be addressed by finding the volume, shape and atomic positions that minimize the total energy of a bulk system. This is true at 0K. At higher temperatures, one must consider minimizing the free energy, rather than the internal energy.

4.3.1 fcc/bcc crystal structures

The fcc and bcc structures are simple. They only have one degree of freedom: the lattice constant. In this section we show how to calculate the equilibrium volume of each structure, and determine which one is more stable. We start with the fcc crystal structure of Cu. We will manually define the crystal structure based on the definitions in Kittel[4] (Chapter 1).

```python
from vasp import Vasp
from ase import Atom, Atoms
import numpy as np

# fcc
LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
fcc_energies = []
ready = True
for a in LC:
```

```
    atoms = Atoms([Atom('Cu', (0, 0, 0))],
                  cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
                                           [0.0, 1.0, 1.0],
                                           [1.0, 0.0, 1.0]]))

    calc = Vasp('bulk/Cu-{0}'.format(a),
                xc='PBE',
                encut=350,
                kpts=[8, 8, 8],
                atoms=atoms)

    e = atoms.get_potential_energy()
    fcc_energies.append(e)

calc.stop_if(None in fcc_energies)

import matplotlib.pyplot as plt
plt.plot(LC, fcc_energies)
plt.xlabel('Lattice constant ($\AA$)')
plt.ylabel('Total energy (eV)')
plt.savefig('images/Cu-fcc.png')

print '#+tblname: cu-fcc-energies'
print r'| lattice constant ($\AA$) | Total Energy (eV) |'
for lc, e in zip(LC, fcc_energies):
    print '| {0} | {1} |'.format(lc, e)
```

Open the python script (dft-scripts/script-102.py).

lattice constant (Å)	Total Energy (eV)
3.5	-3.66182568
3.55	-3.70817569
3.6	-3.73109713
3.65	-3.73432446
3.7	-3.72094163
3.75	-3.69342783

Exercise 4.2
Use the data in the table above to plot the total energy as a function of the lattice constant. Fit a cubic polynomial to the data, and find the volume that minimizes the total energy.

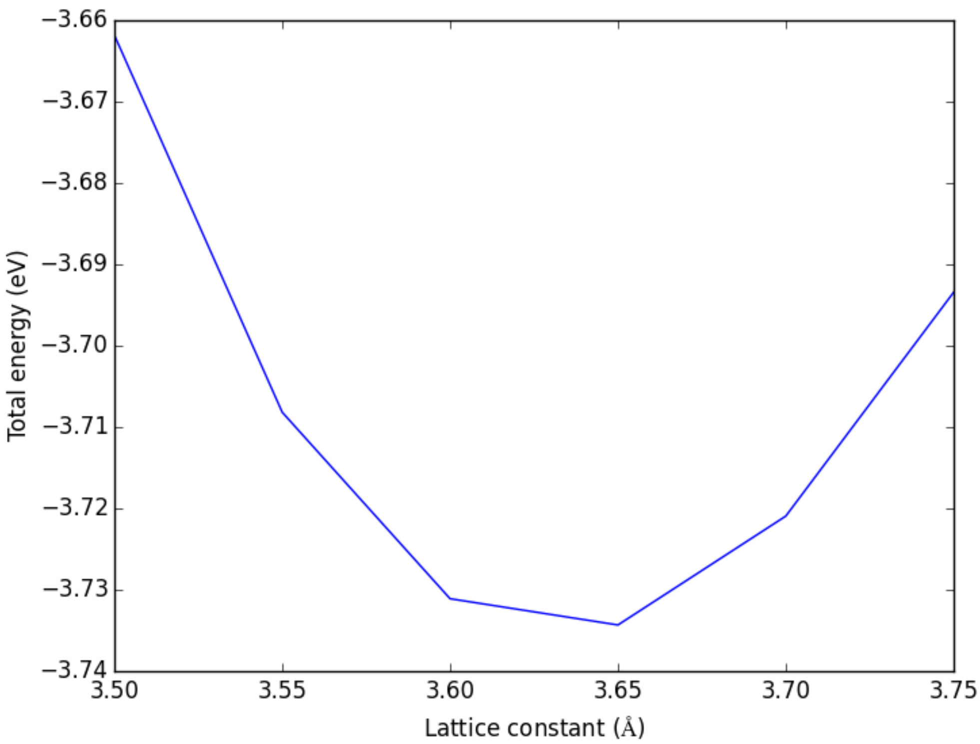


Figure 35: Total energy vs. fcc lattice contant for Cu. It appears the minimum is near 3.65 Å.

If you want to know the lattice constant that gives the lowest energy, you would fit an equation of state to the data. Here is an example using `ase.utils.eos`. See also the appendix equations of state.

```
from vasp import Vasp
from ase.utils.eos import EquationOfState
LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
energies = []
volumes = []
for a in LC:
    calc = Vasp('bulk/Cu-{0}'.format(a))
    atoms = calc.get_atoms()
    volumes.append(atoms.get_volume())
    energies.append(atoms.get_potential_energy())

calc.stop_if(None in energies)

eos = EquationOfState(volumes, energies)
v0, e0, B = eos.fit()

print '''
v0 = {0} A^3
E0 = {1} eV
B  = {2} eV/A^3'''.format(v0, e0, B)

eos.plot('images/Cu-fcc-eos.png')
```

Open the python script (dft-scripts/script-103.py).

```
v0 = 11.9941760954 A^3
E0 = -3.73528237713 eV
B  = 0.862553823078 eV/A^3
```

```
3.63585568663 3.63585568663 3.63585568663
```

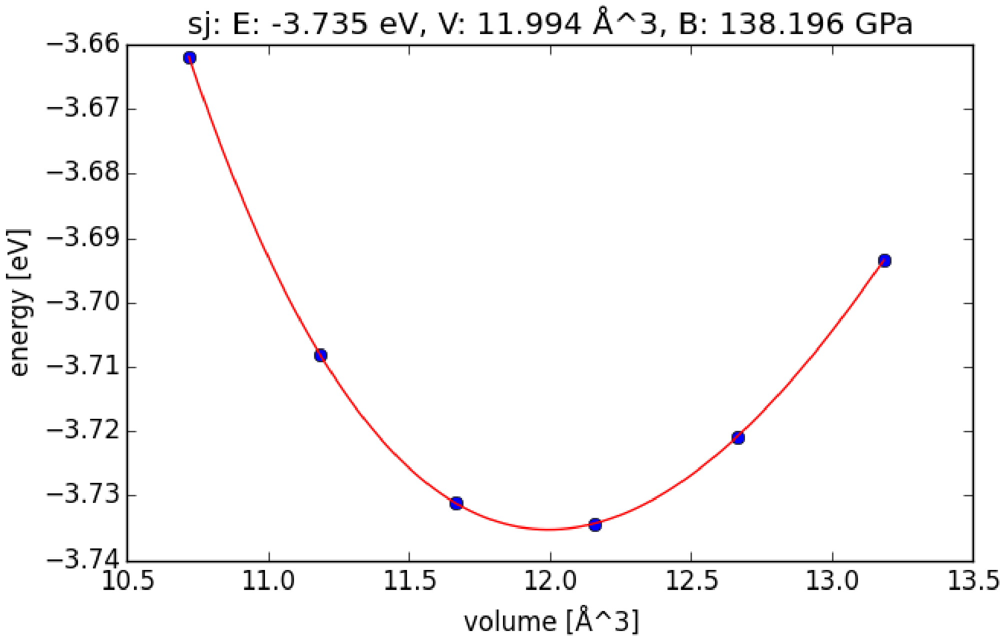


Figure 36: Total energy vs. volume for fcc Cu with fitted cubic polynomial equation of state.

Before we jump into the bcc calculations, let us consider what range of lattice constants we should choose. The fcc lattice is close-packed, and the volume of the primitive cell is $V = 1/4a^3$ or about 11.8 Å^3/atom. The volume of the equilibrium bcc primitive cell will probably be similar to that. The question is: what bcc lattice constant gives that volume? The simplest way to answer this is to compute the answer. We will make a bcc crystal at the fcc lattice constant, and then compute the scaling factor needed to make it the right volume.

```python
from ase import Atom, Atoms
import numpy as np
a = 3.61 # lattice constant

atoms = Atoms([Atom('Cu', [0,0,0])],
              cell=0.5 * a*np.array([[ 1.0,  1.0, -1.0],
                                     [-1.0,  1.0,  1.0],
                                     [ 1.0, -1.0,  1.0]]))

print 'BCC lattice constant = {0:1.3f} Ang'.format(a * (11.8 / atoms.get_volume())**(1./3.))
```

Open the python script (dft-scripts/script-104.py).

```
BCC lattice constant = 2.868 Ang
```

Now we run the equation of state calculations.

```python
from vasp import Vasp
from ase import Atom, Atoms
import numpy as np

LC = [2.75, 2.8, 2.85, 2.9, 2.95, 3.0]

for a in LC:
```

```
    atoms = Atoms([Atom('Cu', [0, 0, 0])],
                  cell=0.5 * a * np.array([[ 1.0,  1.0, -1.0],
                                           [-1.0,  1.0,  1.0],
                                           [ 1.0, -1.0,  1.0]]))

    calc = Vasp('bulk/Cu-bcc-{0}'.format(a),
                xc='PBE',
                encut=350,
                kpts=[8, 8, 8],
                atoms=atoms)
    print(calc.potential_energy)
```

Open the python script (dft-scripts/script-105.py).

```
-3.59937543
-3.67930795
-3.71927399
-3.72637899
-3.70697046
-3.66645678
```

Finally, we will compare the two crystal structures.

```
from vasp import Vasp

# bcc energies and volumes
bcc_LC = [2.75, 2.8, 2.85, 2.9, 2.95, 3.0]
bcc_volumes = []
bcc_energies = []
for a in bcc_LC:
    calc = Vasp('bulk/Cu-bcc-{0}'.format(a))
    atoms = calc.get_atoms()
    bcc_volumes.append(atoms.get_volume())
    bcc_energies.append(atoms.get_potential_energy())

# fcc energies and volumes
fcc_LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
fcc_volumes = []
fcc_energies =[]
for a in fcc_LC:
    calc = Vasp('bulk/Cu-{0}'.format(a))
    atoms = calc.get_atoms()
    fcc_volumes.append(atoms.get_volume())
    fcc_energies.append(atoms.get_potential_energy())

import matplotlib.pyplot as plt
plt.plot(fcc_volumes, fcc_energies, label='fcc')
plt.plot(bcc_volumes, bcc_energies, label='bcc')

plt.xlabel('Atomic volume ($\AA^3$/atom)')
plt.ylabel('Total energy (eV)')
plt.legend()
plt.savefig('images/Cu-bcc-fcc.png')

# print table of data
print '#+tblname: bcc-data'
print '#+caption: Total energy vs. lattice constant for BCC Cu.'
print '| Lattice constant (\AA$^3$) | Total energy (eV) |'
print '|-'
for lc, e in zip(bcc_LC, bcc_energies):
    print '| {0} | {1} |'.format(lc, e)
```

Open the python script (dft-scripts/script-106.py).

Exercise 4.3
Use the data for FCC and BCC Cu to plot the total energy as a function of the lattice constant.

Table 3: Total energy vs. lattice constant for BCC Cu.

Lattice constant (Å^3)	Total energy (eV)
2.75	-3.59937543
2.8	-3.67930795
2.85	-3.71927399
2.9	-3.72637899
2.95	-3.70697046
3.0	-3.66645678

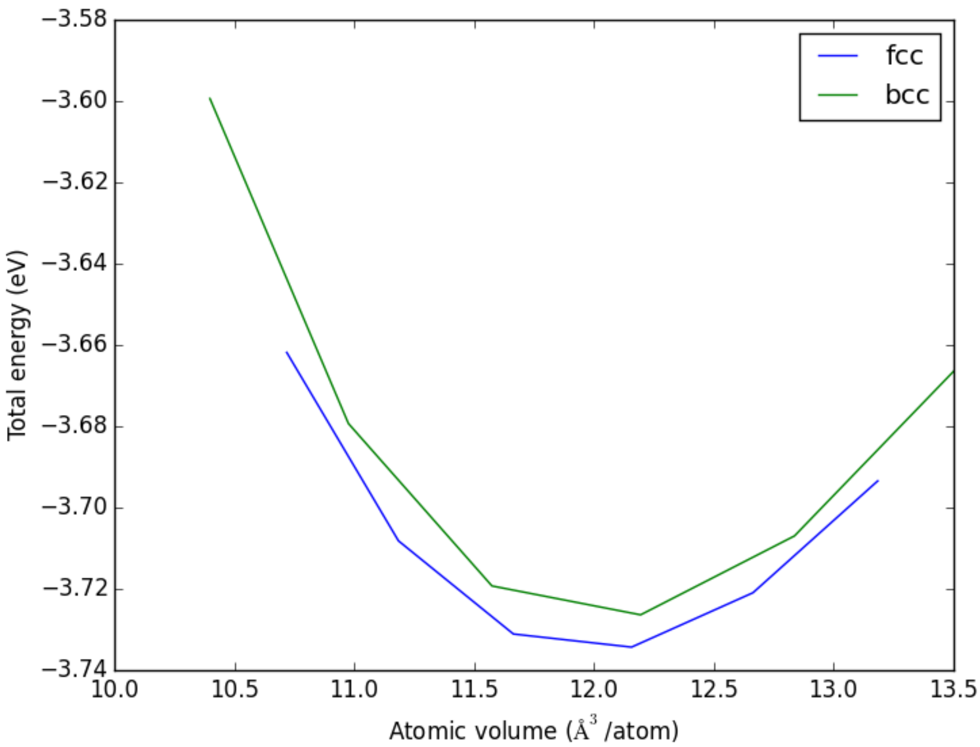


Figure 37: Comparison of energies between fcc and bcc Cu. The fcc structure is lower in energy.

Note we plot the energy vs. atomic volume. That is because the lattice constants of the two crystal structures are very different. It also shows that the atomic volumes in the two structures are similar.

What can we say here? The fcc structure has a lower energy than the bcc structure, so we can conclude the fcc structure is more favorable. In fact, the fcc structure is the experimentally found structure for Cu. Some caution is in order; if you run these calculations at a $4 \times 4 \times 4$ \$k\$-point grid, the bcc structure is more stable because the results are not converged!

Exercise 4.4
Compute the energy vs. volume for fcc and bcc Cu for different \$k\$-point grids. Determine when each result has converged, and which structure is more stable.

What can we say about the relative stability of fcc to hcp? Nothing, until we calculate the hcp equation of state.

4.3.2 Optimizing the hcp lattice constant

The hcp lattice is more complicated than the fcc/bcc lattices because there are two lattice parameters: a and c or equivalently: a and c/a. We will start by making a grid of values and find the set of parameters that minimizes the energy. See Figure 38.

```
from ase.lattice.hexagonal import HexagonalClosedPacked
from vasp import Vasp
import matplotlib.pyplot as plt

atoms = HexagonalClosedPacked(symbol='Ru',
                              latticeconstant={'a': 2.7,
                                               'c/a': 1.584})

a_list = [2.5, 2.6, 2.7, 2.8, 2.9]
covera_list = [1.4, 1.5, 1.6, 1.7, 1.8]

for a in a_list:
    energies = []
    for covera in covera_list:

        atoms = HexagonalClosedPacked(symbol='Ru',
                              latticeconstant={'a': a,
                                               'c/a': covera})

        wd = 'bulk/Ru/{0:1.2f}-{1:1.2f}'.format(a, covera)

        calc = Vasp(wd,
                    xc='PBE',
                    # the c-axis is longer than the a-axis, so we use
                    # fewer kpoints.
                    kpts=[6, 6, 4],
                    encut=350,
                    atoms=atoms)

        energies.append(atoms.get_potential_energy())
    if not None in energies:
        plt.plot(covera_list, energies, label=r'a={0} $\AA$'.format(a))

plt.xlabel('$c/a$')
plt.ylabel('Energy (eV)')
plt.legend()
plt.savefig('images/Ru-covera-scan.png')
```

Open the python script (dft-scripts/script-107.py).

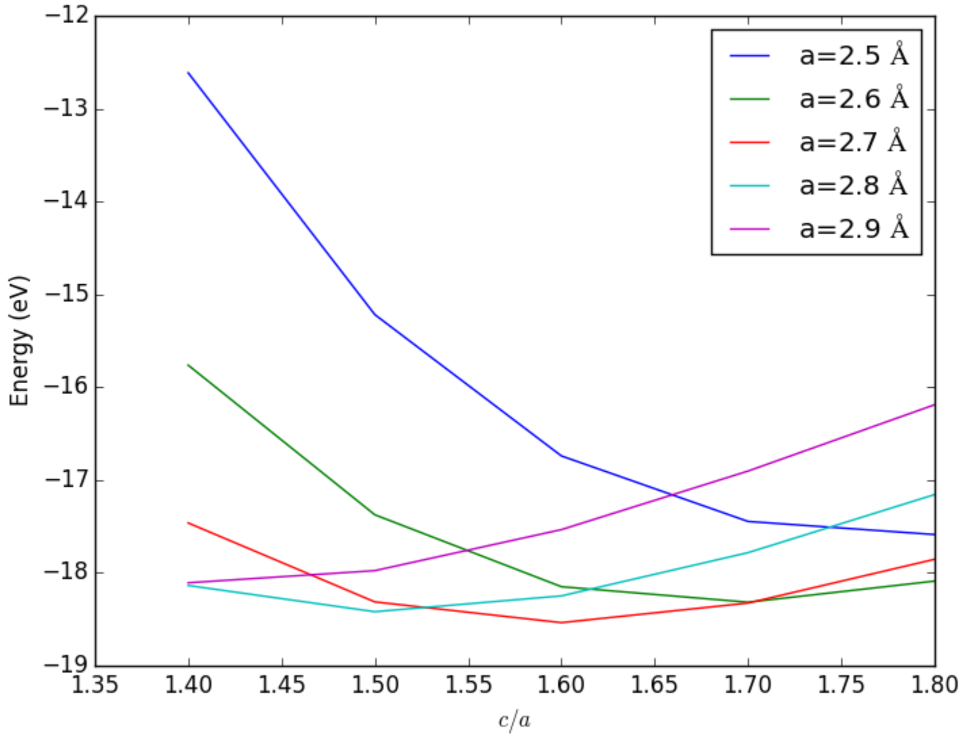


Figure 38: Total energy vs. c/a for different values of a.

It looks like there is a minimum in the a=2.7 Å curve, at a c/a ratio of about 1.6. We can look at the same data in a contour plot which shows more clearly there is minimum in all directions near that point (Figure 39).

```
from vasp import Vasp
import matplotlib.pyplot as plt
import numpy as np

x = [2.5, 2.6, 2.7, 2.8, 2.9]
y = [1.4, 1.5, 1.6, 1.7, 1.8]

X,Y = np.meshgrid(x, y)
Z = np.zeros(X.shape)

for i,a in enumerate(x):
    for j,covera in enumerate(y):
        wd = 'bulk/Ru/{0:1.2f}-{1:1.2f}'.format(a, covera)
        calc = Vasp(wd)
        Z[i][j] = calc.potential_energy

calc.stop_if(None in Z)

cf = plt.contourf(X, Y, Z, 20,
                  cmap=plt.cm.jet)

cbar = plt.colorbar(cf)
cbar.ax.set_ylabel('Energy (eV)')

plt.xlabel('$a$ ($\AA$)')
plt.ylabel('$c/a$')

plt.legend()
plt.savefig('images/ru-contourf.png')
plt.show()
```

Open the python script (dft-scripts/script-108.py).

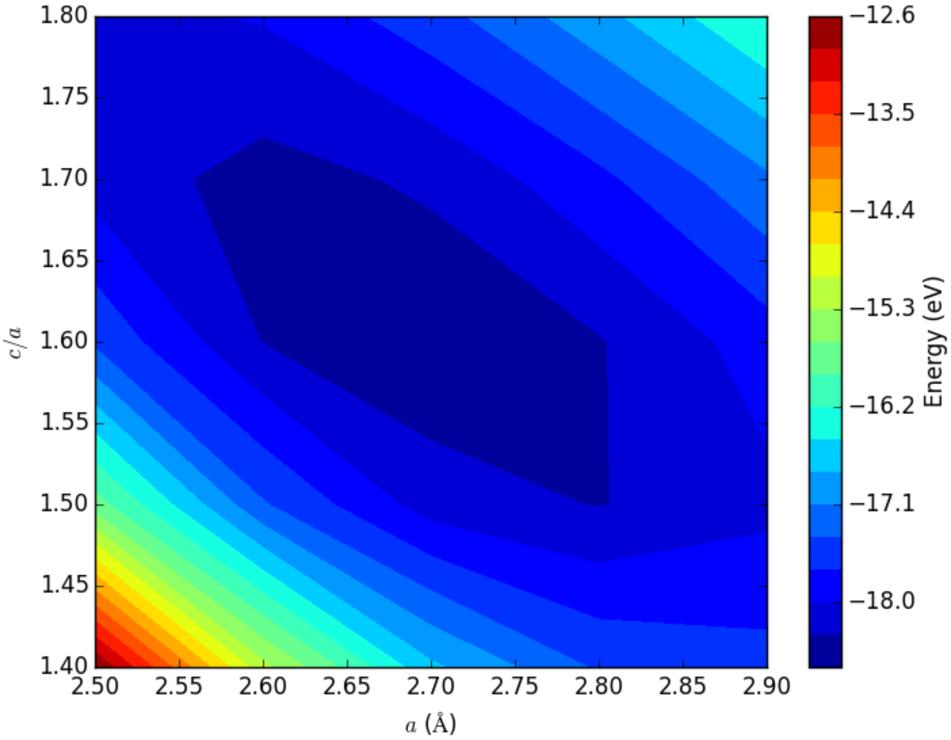


Figure 39: Contour plot of the total energy of hcp Ru for different values of a and c/a.

4.3.3 Complex structures with internal degrees of freedom

A unit cell has six degrees of freedom: the lengths of each unit cell vector, and the angle between each vector. There may additionally be internal degrees of freedom for the atoms. It is impractical to try the approach used for the hcp Ru on anything complicated. Instead, we rely again on algorithms to optimize the unit cell shape, volume and internal degrees of freedom. It is usually not efficient to make a wild guess of the geometry and then turn VASP loose on to optimize it. Instead, the following algorithm works pretty well.

1. Find the volume (at constant shape, with relaxed ions) that minimizes the total energy (ISIF=2). The goal here is to just get an idea of where the right volume is.
2. Using the results from step 1 as a starting point, perform a set of calculations at constant volume around the minimum from step 1, but the shape and internal atom positions are allowed to change (ISIF=4).
3. Finally, do a final calculation near the minimum energy allowing the volume to also change. (ISIF=3).

This multistep process is pretty reasonable to get a converged structure pretty quickly. It is not foolproof, however, and if you have materials such as graphite it may not work well. The problem with graphite is that it is a layered compound that is held together by weak van der waal type forces which are not modeled well by typical GGA functionals. Thus the change in energy due to a volume change is larger in the plane of the graphite sheet than in the direction normal to the sheet. With a typical GGA, the sheets may just move apart until they do not interact any more.

We will illustrate the process on a well-behaved system (rutile TiO_2) which has two lattice parameters and one internal degree of freedom. There are a few subtle points to mention in doing these calculations. The VASP manual recommends that you set PREC to 'high', and that ENCUT be set to 1.3*max(ENMAX) of the pseudopotentials. This is necessary to avoid problems caused by small basis sets when the volume changes, and Pulay stress. It is important to ensure that the energies are reasonably converged with respect to k-point grids. Hence, it can be a significant amount of work to do this right! Let us start with determining the ENCUT value that is appropriate for TiO_2.

```
grep ENMAX $VASP_PP_PATH/potpaw_PBE/Ti/POTCAR
grep ENMAX $VASP_PP_PATH/potpaw_PBE/O/POTCAR
```

Open the python script (dft-scripts/script-109.py).

```
ENMAX  =  178.330; ENMIN  =  133.747 eV
ENMAX  =  400.000; ENMIN  =  300.000 eV
```

According to the manual, we should use ENCUT = 1.3*400 = 520 eV for good results.

Now we consider the k-point convergence. The lattice vectors of the rutile TiO_2 structure are not all the same length, which means it is not essential that we use the same number of k-points in each direction. For simplicity, however, we do that here.

```
# step 1 frozen atoms and shape at different volumes
from ase import Atom, Atoms
import numpy as np
from vasp import Vasp
import matplotlib.pyplot as plt

'''
create a TiO2 structure from the lattice vectors at
http://cst-www.nrl.navy.mil/lattice/struk/c4.html
This site does not exist anymore.
'''
a = 4.59  # experimental degrees of freedom.
c = 2.96
u = 0.3  # internal degree of freedom!

#primitive vectors
a1 = a * np.array([1.0, 0.0, 0.0])
a2 = a * np.array([0.0, 1.0, 0.0])
a3 = c * np.array([0.0, 0.0, 1.0])

atoms = Atoms([Atom('Ti', [0., 0., 0.]),
               Atom('Ti', 0.5 * a1 + 0.5 * a2 + 0.5 * a3),
               Atom('O', u * a1 + u * a2),
               Atom('O', -u * a1 - u * a2),
               Atom('O', (0.5 + u) * a1 + (0.5 - u) * a2 + 0.5 * a3),
               Atom('O', (0.5 - u) * a1 + (0.5 + u) * a2 + 0.5 * a3)],
              cell=[a1, a2, a3])

KPOINTS = [2, 3, 4, 5, 6, 7, 8]
energies = []

ready = True
for k in KPOINTS:
    calc = Vasp('bulk/tio2/kpts-{0}'.format(k),
                encut=520,
                kpts=[k, k, k],
                xc='PBE',
                sigma=0.05,
                atoms=atoms)

    energies.append(atoms.get_potential_energy())

calc.stop_if(None in energies)
```

```
plt.plot(KPOINTS, energies)
plt.xlabel('number of k-points in each vector')
plt.ylabel('Total energy (eV)')
plt.savefig('images/tio2-kpt-convergence.png')
```

Open the python script (dft-scripts/script-110.py).

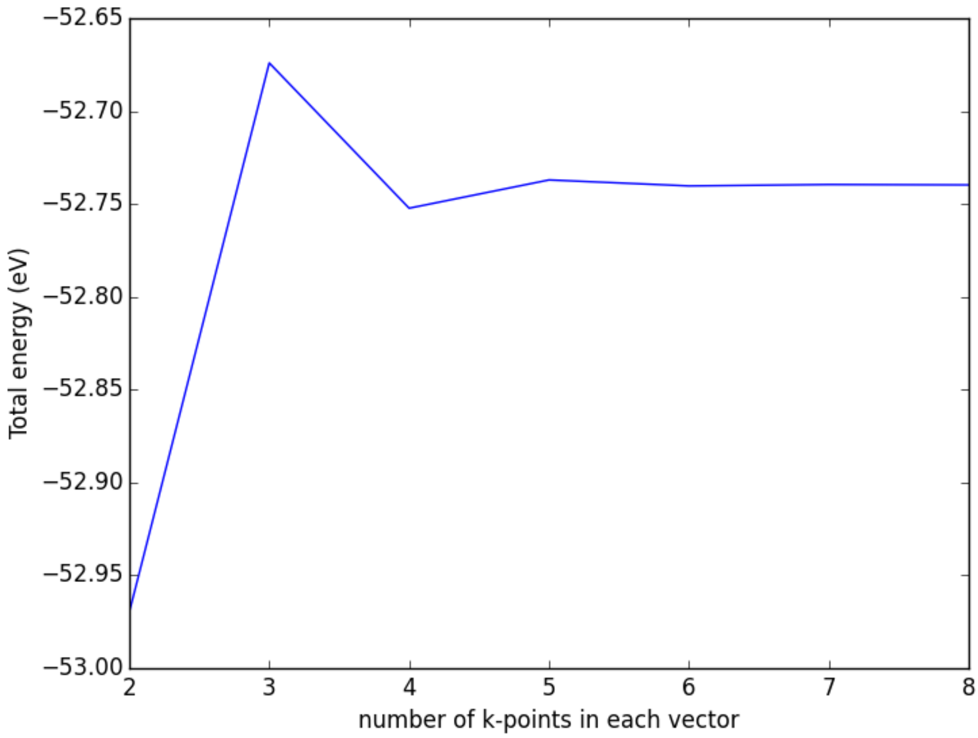


Figure 40: k-point convergence of rutile TiO_2.

A k-point grid of 5 × 5 × 5 appears suitable for reasonably converged results. Now we proceed with step 1: Compute the total energy of the unit cell allowing internal degrees of freedom to relax, but keeping a constant cell shape.

```
# step 1 frozen atoms and shape at different volumes
from ase import Atom, Atoms
import numpy as np
from vasp import Vasp
import matplotlib.pyplot as plt

'''
create a TiO2 structure from the lattice vectors at
http://cst-www.nrl.navy.mil/lattice/struk/c4.html
'''
a = 4.59  # experimental degrees of freedom.
c = 2.96
u = 0.3  # internal degree of freedom!

#primitive vectors
a1 = a * np.array([1.0, 0.0, 0.0])
a2 = a * np.array([0.0, 1.0, 0.0])
a3 = c * np.array([0.0, 0.0, 1.0])

```

```
atoms = Atoms([Atom('Ti', [0., 0., 0.]),
               Atom('Ti', 0.5 * a1 + 0.5 * a2 + 0.5 * a3),
               Atom('O', u * a1 + u * a2),
               Atom('O', -u * a1 - u * a2),
               Atom('O', (0.5 + u) * a1 + (0.5 - u) * a2 + 0.5 * a3),
               Atom('O', (0.5 - u) * a1 + (0.5 + u) * a2 + 0.5 * a3)],
              cell=[a1, a2, a3])

v0 = atoms.get_volume()
cell0 = atoms.get_cell()

factors = [0.9, 0.95, 1.0, 1.05, 1.1] #to change volume by

energies, volumes = [], []

ready = True
for f in factors:
    v1 = f * v0
    cell_factor = (v1 / v0)**(1. / 3.)

    atoms.set_cell(cell0 * cell_factor, scale_atoms=True)

    calc = Vasp('bulk/tio2/step1-{0:1.2f}'.format(f),
                encut=520,
                kpts=[5, 5, 5],
                isif=2, # relax internal degrees of freedom
                ibrion=1,
                nsw=50,
                xc='PBE',
                sigma=0.05,
                atoms=atoms)

    energies.append(atoms.get_potential_energy())
    volumes.append(atoms.get_volume())

calc.stop_if(None in energies)

plt.plot(volumes, energies)
plt.xlabel('Vol. ($\AA^3)$')
plt.ylabel('Total energy (eV)')
plt.savefig('images/tio2-step1.png')

print '#+tblname: tio2-vol-ene'
print '#+caption: Total energy of TiO_{2} vs. volume.'
print '| Volume ($\AA^3$) | Energy (eV) |'
print '|-'
for v, e in zip(volumes, energies):
    print '| {0} | {1} |'.format(v, e)
```

Open the python script (dft-scripts/script-111.py).

Table 4: Total energy of TiO_2 vs. volume.

Volume (Å^3)	Energy (eV)
56.1254185488	-51.81932158
59.2434971663	-52.46118036
62.361576	-52.76017908
65.4796549456	-52.80043775
68.5977335623	-52.64628895

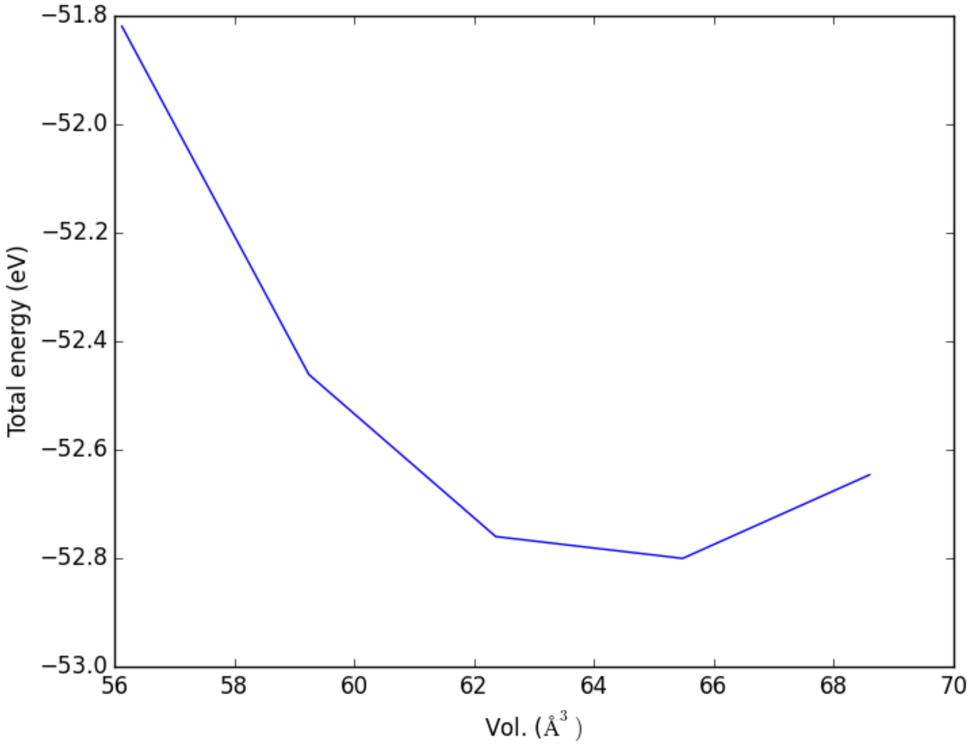


Figure 41: Total energy vs. volume for rutile TiO_2 in step 1 of the optimization.

Now, we know the minimum energy volume is near 64 Å^3. You could at this point fit an equation of state to find that minimum. However, we now want to use these initial starting points for a second round of optimization where we allow the unit cell shape to change, at constant volume: ISIF=4.

```
from vasp import Vasp

calc = Vasp('bulk/tio2/step1-0.90')
calc.clone('bulk/tio2/step2-0.90')
#calc.set(isif=4)
print calc.set(isif=4)
print calc.calculation_required()
```

Open the python script (dft-scripts/script-112.py).

```
clone:  Atoms(symbols='Ti2O4', positions=..., magmoms=..., cell=[4.41041021, 4.41041021, 2.88537073]
{}
False
```

```
from vasp import Vasp

factors = [0.9, 0.95, 1.0, 1.05, 1.1]  # to change volume by

energies1, volumes1 = [], []  # from step 1
energies, volumes = [], []  # for step 2
ready = True
for f in factors:
    calc = Vasp('bulk/tio2/step1-{0:1.2f}'.format(f))
    atoms = calc.get_atoms()
    energies1.append(atoms.get_potential_energy())
    volumes1.append(atoms.get_volume())
```

```

    calc.clone('bulk/tio2/step2-{0:1.2f}'.format(f))
    calc.set(isif=4)
    # You have to get the atoms again.
    atoms = calc.get_atoms()

    energies.append(atoms.get_potential_energy())
    volumes.append(atoms.get_volume())

print(energies, volumes)
calc.stop_if(None in energies)

import matplotlib.pyplot as plt
plt.plot(volumes1, energies1, volumes, energies)
plt.xlabel('Vol. ($\AA^3)$')
plt.ylabel('Total energy (eV)')
plt.legend(['step 1', 'step 2'], loc='best')
plt.savefig('images/tio2-step2.png')
```

Open the python script (dft-scripts/script-113.py).

```
([-51.82715553, -52.46235848, -52.76127768, -52.80903199, -52.67597935], [56.125418401558292, 59.243
```

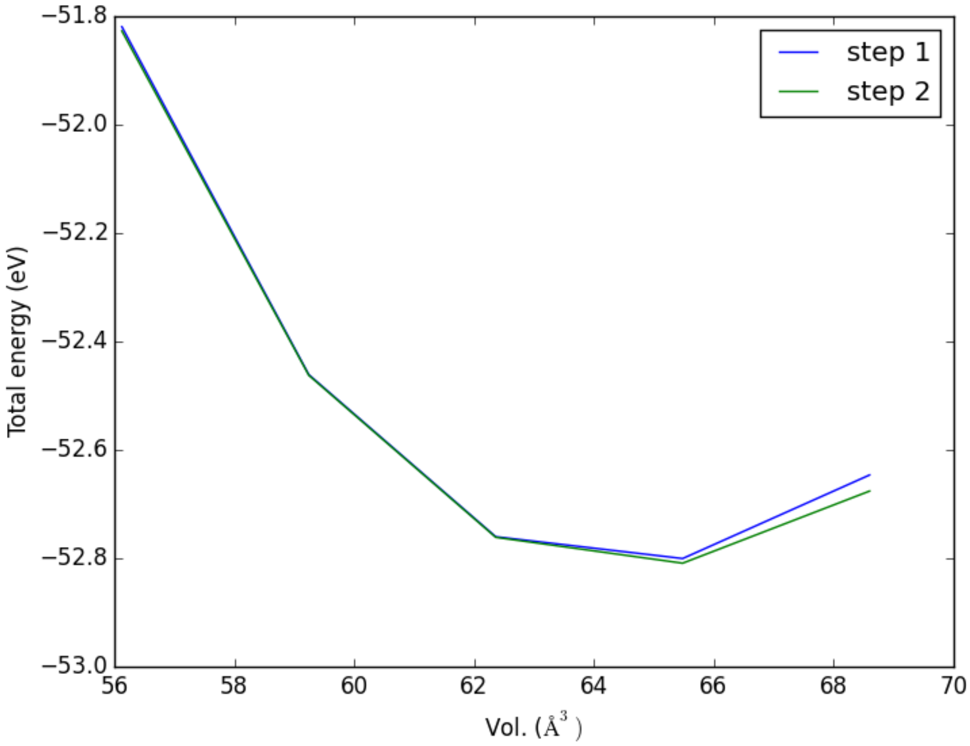


Figure 42: Total energy vs. volume for step 2 of the unit cell optimization.

The take away message here is that the total energy slightly decreases when we allow the unit cell shape to change, especially for the larger unit cell deformation. This has little effect on the minimum volume, but would have an effect on the bulk modulus, which is related to the curvature of the equation of state. At this point, you could fit an equation of state to the step 2 data, and estimate the volume at the minimum volume, and recalculate the total energy at that volume.

An alternative is a final calculation with ISIF=3, which optimizes the unit cell volume, shape and internal coordinates. It looks like the calculation at bulk/tio2/step2-1.05 is close to the minimum, so we will use that as a starting point for the final calculation.

```
from vasp import Vasp

calc = Vasp('bulk/tio2/step2-1.05')
calc.clone('bulk/tio2/step3')

calc = Vasp('bulk/tio2/step3',
            isif=3)
calc.wait()
print calc

from pyspglib import spglib
print '\nThe spacegroup is {0}'.format(spglib.get_spacegroup(calc.atoms))
```

Open the python script (dft-scripts/script-114.py).

```
*************** VASP CALCULATION SUMMARY ***************
Vasp calculation directory:
---------------------------
  [[/home-research/jkitchin/dft-book/bulk/tio2/step3]]

Unit cell:
----------
       x        y        z              |v|
  v0   4.661    0.000    0.000          4.661 Ang
  v1   0.000    4.661    0.000          4.661 Ang
  v2   0.000    0.000    2.970          2.970 Ang
  alpha, beta, gamma (deg):   90.0   90.0   90.0
  Total volume:                      64.535 Ang^3
  Stress:     xx      yy      zz      yz      xz      xy
        -0.002 -0.002 -0.000 -0.000 -0.000 -0.000 GPa

  ID  tag     sym    x          y          z         rmsF (eV/A)
  0   0       Ti     0.000      0.000      0.000        0.00
  1   0       Ti     2.331      2.331      1.485        0.00
  2   0       O      1.420      1.420      0.000        0.00
  3   0       O      3.241      3.241      0.000        0.00
  4   0       O      3.751      0.910      1.485        0.00
  5   0       O      0.910      3.751      1.485        0.00
  Potential energy: -52.8176 eV

INPUT Parameters:
-----------------
  pp        : PBE
  isif      : 3
  xc        : pbe
  kpts      : [5, 5, 5]
  encut     : 520
  lcharg    : False
  ibrion    : 1
  ismear    : 1
  lwave     : False
  sigma     : 0.05
```

```
  nsw       : 50

Pseudopotentials used:
----------------------
  Ti: potpaw_PBE/Ti/POTCAR (git-hash: 39cac2d7c620efc80c69344da61b5c43bc16e9b8)
  O: potpaw_PBE/O/POTCAR (git-hash: 592f34096943a6f30db8749d13efca516d75ec55)

The spacegroup is P4_2/mnm (136)
```

This is the final result. You can see that the forces on all the atoms are less than 0.01 eV/Å, and the stress is also very small. The final volume is close to where we expect it to be based on steps 1 and 2. The space group is still correct. The lattice vectors are close in length to the experimentally known values, and the angles between the vectors has not changed much. Looks good!

As a final note, the VASP manual recommends you do not use the final energy directly from the calculation, but rather run a final calculation with ISMEAR set to -5. Here we examine the effect.

```
from vasp import Vasp

calc = Vasp('bulk/tio2/step3')
atoms = calc.get_atoms()
print 'default ismear: ', atoms.get_potential_energy()

calc.clone('bulk/tio2/step4')
calc.set(ismear=-5,
         nsw=0)
atoms = calc.get_atoms()
print 'ismear=-5:      ', atoms.get_potential_energy()
```

Open the python script (dft-scripts/script-115.py).

```
default ismear:  -52.81760338
ismear=-5:       -52.8004532
```

The difference here is on the order of a meV. That does not seem significant here. I suspect the recommended practice stems from early days when much smaller ENCUT values were used and changes in the number of basis functions were more significant.

4.3.4 Effect of XC on bulk properties

The exchange correlation functional can significantly affect computed bulk properties. Here, we examine the effect on the bulk lattice constant of Pd (exp. 3.881). An excellent review of this can be found in.[49] We examine several functionals. The `xc` keyword in `Vasp` is used to select the POTCARs. Let us consider the LDA functional first.

```
from vasp import Vasp
from ase import Atom, Atoms
from ase.utils.eos import EquationOfState
import numpy as np

LC = [3.75, 3.80, 3.85, 3.90, 3.95, 4.0, 4.05, 4.1]

volumes, energies = [], []
for a in LC:
    atoms = Atoms([Atom('Pd', (0, 0, 0))],
                  cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
                                           [0.0, 1.0, 1.0],
                                           [1.0, 0.0, 1.0]]))
    calc = Vasp('bulk/Pd-LDA-{0}'.format(a),
                encut=350,
                kpts=[12, 12, 12],
                xc='LDA',
                atoms=atoms)

```

```
    e = atoms.get_potential_energy()
    energies.append(e)
    volumes.append(atoms.get_volume())

calc.stop_if(None in energies)

eos = EquationOfState(volumes, energies)
v0, e0, B = eos.fit()
print('LDA lattice constant is {0:1.3f} Ang^3'.format((4*v0)**(1./3.)))
```

Open the python script (dft-scripts/script-116.py).

```
LDA lattice constant is 3.841 Ang^3
```

For a GGA calculation, it is possible to specify which functional you want via the GGA tag. This tag was designed to use the LDA POTCAR files, but with a GGA functional. We will consider four different functionals here.

```
from vasp import Vasp
from ase import Atom, Atoms
from ase.utils.eos import EquationOfState
import numpy as np

LC = [3.75, 3.80, 3.85, 3.90, 3.95, 4.0, 4.05, 4.1]

GGA = {'AM': 'AM05',
       'PE': 'PBE',
       'PS': 'PBEsol',
       'RP': 'RPBE'}

for key in GGA:
    volumes, energies = [], []
    for a in LC:
        atoms = Atoms([Atom('Pd', (0, 0, 0))],
                      cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
                                               [0.0, 1.0, 1.0],
                                               [1.0, 0.0, 1.0]]))
        calc = Vasp('bulk/Pd-GGA-{1}-{0}'.format(a, key),
                    encut=350,
                    kpts=[12, 12, 12],
                    xc='LDA',
                    gga=key,
                    atoms=atoms)

        e = atoms.get_potential_energy()
        energies.append(e)
        volumes.append(atoms.get_volume())

    if None not in energies:
        eos = EquationOfState(volumes, energies)
        v0, e0, B = eos.fit()
        print '{1:6s} lattice constant is {0:1.3f} Ang^3'.format((4*v0)**(1./3.),
                                                                  GGA[key])
    else:
        print energies, LC
        print '{0} is not ready'.format(GGA[key])
```

Open the python script (dft-scripts/script-117.py).

```
PBEsol lattice constant is 3.841 Ang^3
AM05   lattice constant is 3.841 Ang^3
RPBE   lattice constant is 3.841 Ang^3
PBE    lattice constant is 3.939 Ang^3
```

These results compare very favorably to those in.[49] It is typical that LDA functionals underestimate the lattice constants, and that GGAs tend to overestimate the lattice constants. PBEsol and AM05 were designed specifically for solids, and for Pd, these functionals do an exceptional job of reproducing the lattice constants. RPBE is particularly bad at the lattice constant, but it has been reported to be a superior functional for reactivity.[25]

4.4 TODO Using built-in ase optimization with vasp

ASE has some nice optimization tools built into it. We can use them in vasp too. This example is adapted from this test: https://trac.fysik.dtu.dk/projects/ase/browser/trunk/ase/test/vasp/vasp_Al_volrelax.py

First the VASP way.

```python
from vasp import Vasp
from ase.lattice import bulk

Al = bulk('Al', 'fcc', a=4.5, cubic=True)
calc = Vasp('bulk/Al-lda-vasp',
            xc='LDA', isif=7, nsw=5,
            ibrion=1, ediffg=-1e-3,
            lwave=False, lcharg=False,
            atoms=Al)
print(calc.potential_energy)
print(calc)
```

Open the python script (dft-scripts/script-118.py).

```
-10.07430725

Vasp calculation in /home-research/jkitchin/dft-book/bulk/Al-lda-vasp

INCAR created by Atomic Simulation Environment
 ISIF = 7
 LCHARG = .FALSE.
 IBRION = 1
 EDIFFG = -0.001
 ISMEAR = 1
 LWAVE = .TRUE.
 SIGMA = 0.1
 NSW = 5

Al
 1.0000000000000000
     4.5000000000000000     0.0000000000000000     0.0000000000000000
     0.0000000000000000     4.5000000000000000     0.0000000000000000
     0.0000000000000000     0.0000000000000000     4.5000000000000000
   4
Cartesian
  0.0000000000000000  0.0000000000000000  0.0000000000000000
  0.0000000000000000  2.2500000000000000  2.2500000000000000
  2.2500000000000000  0.0000000000000000  2.2500000000000000
  2.2500000000000000  2.2500000000000000  0.0000000000000000
```

```python
#+BEGIN_SRC python
from vasp import Vasp
calc = Vasp('bulk/Al-lda-vasp')
calc.view()
print [atoms.get_volume() for atoms in calc.traj]
print [atoms.get_potential_energy() for atoms in calc.traj]
```

Open the python script (dft-scripts/script-119.py).

```
[91.124999999999986, 78.034123525818302, 72.328582812881763, 73.422437849114189, 73.368474506164134]
[-9.58448747, -10.02992063, -10.07180132, -10.07429962, -10.07430725]
```

Now, the ASE way. TODO

```
from vasp import Vasp
from ase.lattice import bulk
from ase.optimize import BFGS as QuasiNewton

Al = bulk('Al', 'fcc', a=4.5, cubic=True)

calc = Vasp('bulk/Al-lda-ase',
            xc='LDA',
            atoms=Al)

from ase.constraints import StrainFilter
sf = StrainFilter(Al)
qn = QuasiNewton(sf, logfile='relaxation.log')
qn.run(fmax=0.1, steps=5)
print('Stress:\n', calc.stress)
print('Al post ASE volume relaxation\n', calc.get_atoms().get_cell())
print(calc)
```

Open the python script (dft-scripts/script-120.py).

Now for a detailed comparison:

```
from vasp import Vasp

atoms = Vasp('bulk/Al-lda-vasp').get_atoms()

atoms2 = Vasp('bulk/Al-lda-ase').get_atoms()

import numpy as np

cellA = atoms.get_cell()
cellB = atoms2.get_cell()

print((np.abs(cellA - cellB) < 0.01).all())
```

Open the python script (dft-scripts/script-121.py).

```
False
```

This could be handy if you want to use any of the optimizers in `ase.optimize` in conjunction with `ase.constraints`, which are more advanced than what is in VASP.

4.5 Cohesive energy

The cohesive energy is defined as the energy to separate neutral atoms in their ground electronic state from the solid at 0K at 1 atm. We will compute this for rhodium. Rh is normally an fcc metal, so we will use that structure and let VASP find the equilibrium volume for us.

```
from vasp import Vasp
from ase.lattice.cubic import FaceCenteredCubic
from ase import Atoms, Atom

# bulk system
atoms = FaceCenteredCubic(directions=[[0, 1, 1],
                                      [1, 0, 1],
                                      [1, 1, 0]],
                                      size=(1, 1, 1),
                                      symbol='Rh')

calc = Vasp('bulk/bulk-rh',
            xc='PBE',
            encut=350,
            kpts=[4, 4, 4],
            isif=3,
            ibrion=2,
            nsw=10,
            atoms=atoms)
```

```
bulk_energy = atoms.get_potential_energy()

# atomic system
atoms = Atoms([Atom('Rh',[5, 5, 5])],
              cell=(7, 8, 9))

calc = Vasp('bulk/atomic-rh',
            xc='PBE',
            encut=350,
            kpts=[1, 1, 1],
            atoms=atoms)
atomic_energy = atoms.get_potential_energy()

calc.stop_if(None in (bulk_energy, atomic_energy))

cohesive_energy = atomic_energy - bulk_energy
print 'The cohesive energy is {0:1.3f} eV'.format(cohesive_energy)
```

Open the python script (dft-scripts/script-122.py).

```
The cohesive energy is 6.184 eV
```

According to Kittel,[4] the cohesive energy of Rh is 5.75 eV. There are a few reasons we may have discrepancy here:

1. The k-point grid used in the bulk state is not very dense. However, you can see below that the total energy is pretty converged by a $6 \times 6 \times 6$ \$k\$-point grid.
2. We did not check for convergence with the planewave cutoff.
3. We neglected spin on the atomic state. Rh in the atomic state has this electronic structure: [Kr] 4d8 5s1 and is a doublet.

First we consider the k-point convergence.

```
from vasp import Vasp

calc = Vasp('bulk/atomic-rh')
atomic_energy = calc.potential_energy

calc = Vasp('bulk/bulk-rh')
atoms = calc.get_atoms()

kpts = [3, 4, 6, 9, 12, 15, 18]

calcs = [Vasp('bulk/bulk-rh-kpts-{0}'.format(k),
                xc='PBE',
                encut=350,
                kpts=[k, k, k],
                atoms=atoms)
         for k in kpts]

energies = [calc.potential_energy for calc in calcs]

calcs[0].stop_if(None in energies)

for k, e in zip(kpts, energies):
    print('({0:2d}, {0:2d}, {0:2d}):'
          ' cohesive energy = {1} eV'.format(k,
                                             e - atomic_energy))
```

Open the python script (dft-scripts/script-123.py).

```
( 3,  3,  3): cohesive energy = -4.76129426 eV
( 4,  4,  4): cohesive energy = -6.17915613 eV
( 6,  6,  6): cohesive energy = -6.20654198 eV
( 9,  9,  9): cohesive energy = -6.20118094 eV
(12, 12, 12): cohesive energy = -6.20897225 eV
(15, 15, 15): cohesive energy = -6.2091123 eV
(18, 18, 18): cohesive energy = -6.21007962 eV
```

Using only 1 k-point for the bulk energy is a terrible approximation! It takes at least a 6 × 6 × 6 grid to get the total energy converged to less than 10 meV. Note we do not need to check the k-point convergence of the atomic state because it is surrounded by vacuum on all sides, and so there should not be any dispersion in the bands.

We will examine the magnetic state next.

```
from vasp import Vasp
from ase.lattice.cubic import FaceCenteredCubic
from ase import Atoms, Atom
# bulk system
atoms = FaceCenteredCubic(directions=[[0, 1, 1],
                                      [1, 0, 1],
                                      [1, 1, 0]],
                                     size=(1, 1, 1),
                                     symbol='Rh')

calc = Vasp('bulk/bulk-rh',
            xc='PBE',
            encut=350,
            kpts=[4, 4, 4],
            isif=3,
            ibrion=2,
            nsw=10,
            atoms=atoms)
bulk_energy = atoms.get_potential_energy()

# atomic system
atoms = Atoms([Atom('Rh',[5, 5, 5], magmom=1)],
              cell=(7, 8, 9))

calc = Vasp('bulk/atomic-rh-sp',
            xc='PBE',
            encut=350,
            kpts=[1, 1, 1],
            ispin=2,
            atoms=atoms)
atomic_energy = atoms.get_potential_energy()

calc.stop_if(None in [atomic_energy, bulk_energy])

cohesive_energy = atomic_energy - bulk_energy
print 'The cohesive energy is {0:1.3f} eV'.format(cohesive_energy)
```

Open the python script (dft-scripts/script-124.py).

```
The cohesive energy is 6.127 eV
```

Again, the value in Kittel[4] is 5.75 eV which is very close to this value. Finally, it is also possible there is a lower energy non-spherical atom energy; we did not check that at all (see Estimating triplet oxygen dissociation energy with low symmetry).

4.6 Elastic properties

See this reference.[50]

We seek the elastic constant tensor that relates stress (σ) and strain (ϵ) via $\sigma = c\epsilon$. The stress and strain are six component vectors, so c will be a 6 × 6 symmetric matrix.

4.6.1 Fe elastic properties

As with molecular vibrations, we need a groundstate geometry. Let us get one for BCC Fe.

```
from vasp import Vasp
from ase.lattice.cubic import BodyCenteredCubic

atoms = BodyCenteredCubic(symbol='Fe')
for atom in atoms:
```

```python
    atom.magmom = 3.0

from vasp.vasprc import VASPRC
VASPRC['mode'] = None

import logging
log = logging.getLogger('Vasp')
#log.setLevel(logging.DEBUG)

calc = Vasp('bulk/Fe-bulk',
            xc='PBE',
            kpts=[6, 6, 6],
            encut=350,
            ispin=2,
            isif=3,
            nsw=30,
            ibrion=1,
            atoms=atoms)
print(atoms.get_potential_energy())
print(atoms.get_stress())
```

Open the python script (dft-scripts/script-125.py).

```
-15.53472773
[ 0.00031141  0.00031141  0.00031141 -0.          -0.          -0.        ]
```

Ok, now with a relaxed geometry at hand, we proceed with the elastic constants. This is accomplished with IBRION=6 and ISIF > 3 in VASP. See this reference (from the VASP page) Y. Le Page and P. Saxe, Phys. Rev. B 65, 104104 (2002)

```python
from vasp import Vasp

calc = Vasp('bulk/Fe-bulk')
calc.clone('bulk/Fe-elastic')

calc.set(ibrion=6,    #
         isif=3,      # gets elastic constants
         potim=0.05,  # displacements
         nsw=1,
         nfree=2)

print(calc.potential_energy)
```

Open the python script (dft-scripts/script-126.py).

```
-15.52764065
```

Now, the results are written out to the OUTCAR file. Actually, three sets of moduli are written out 1) the elastic tensor for rigid ions, 2) the contribution from allowing the atoms to relax, and 3) the total elastic modulus, all in kBar.

```
 SYMMETRIZED ELASTIC MODULI (kBar)
Direction    XX          YY          ZZ          XY          YZ          ZX
--------------------------------------------------------------------------------
XX        2803.5081   1622.6085   1622.6085      0.0000      0.0000      0.0000
YY        1622.6085   2803.5081   1622.6085      0.0000      0.0000      0.0000
ZZ        1622.6085   1622.6085   2803.5081      0.0000      0.0000      0.0000
XY           0.0000      0.0000      0.0000    866.8792      0.0000      0.0000
YZ           0.0000      0.0000      0.0000      0.0000    866.8792      0.0000
ZX           0.0000      0.0000      0.0000      0.0000      0.0000    866.8792
--------------------------------------------------------------------------------
```

and

```
 ELASTIC MODULI CONTR FROM IONIC RELAXATION (kBar)
 Direction    XX          YY          ZZ          XY          YZ          ZX
 --------------------------------------------------------------------------------
 XX            0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
 YY            0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
 ZZ            0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
 XY            0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
 YZ            0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
 ZX            0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
 --------------------------------------------------------------------------------


 TOTAL ELASTIC MODULI (kBar)
 Direction    XX          YY          ZZ          XY          YZ          ZX
 --------------------------------------------------------------------------------
 XX         2803.5081   1622.6085   1622.6085      0.0000      0.0000      0.0000
 YY         1622.6085   2803.5081   1622.6085      0.0000      0.0000      0.0000
 ZZ         1622.6085   1622.6085   2803.5081      0.0000      0.0000      0.0000
 XY            0.0000      0.0000      0.0000    866.8792      0.0000      0.0000
 YZ            0.0000      0.0000      0.0000      0.0000    866.8792      0.0000
 ZX            0.0000      0.0000      0.0000      0.0000      0.0000    866.8792
 --------------------------------------------------------------------------------
```

Let us write a small code here to extract the Total elastic moduli from the OUTCAR file. First we get the line where the total elastic moduli start, then take the six lines that start three lines after that. Finally we parse out the matrix elements and cast them as floats.

```python
import numpy as np
EM = []

with open('bulk/Fe-elastic/OUTCAR') as f:
    lines = f.readlines()
    for i, line in enumerate(lines):
        if line.startswith(' TOTAL ELASTIC MODULI (kBar)'):
            j = i + 3
            data = lines[j:j+6]
            break

for line in data:
    EM += [[float(x) for x in line.split()[1:]]]

print np.array(EM)
```

Open the python script (dft-scripts/script-127.py).

```
[[ 1125.1405  3546.8135  3546.8135     0.         0.         0.     ]
 [ 3546.8135  1125.1405  3546.8135     0.         0.         0.     ]
 [ 3546.8135  3546.8135  1125.1405     0.         0.         0.     ]
 [    0.         0.         0.      1740.2372     0.         0.     ]
 [    0.         0.         0.         0.      1740.2372     0.     ]
 [    0.         0.         0.         0.         0.      1740.2372]]
```

Fe is in a BCC crystal structure, which is high in symmetry. Consequently, many of the elements in the matrix are equal to zero.

See http://www.nist.gov/data/PDFfiles/jpcrd34.pdf for a lot of detail about Fe-Ni alloys and general theory about elastic constants. In the next section, we show how the code above is integrated into Vasp.

4.6.2 Al elastic properties

First, the relaxed geometry.

```
from vasp import Vasp
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic(symbol='Al')

calc = Vasp('bulk/Al-bulk',
            xc='PBE',
            kpts=[12, 12, 12],
            encut=350,
            prec='High',
            isif=3,
            nsw=30,
            ibrion=1,
            atoms=atoms)
print(calc.potential_energy)
```

Open the python script (dft-scripts/script-128.py).

```
-14.97511793
```

Ok, now with a relaxed geometry at hand, we proceed with the elastic constants. This is accomplished with IBRION=6 and ISIF $\geq$ 3 in VASP.

```
from vasp import Vasp

calc = Vasp('bulk/Al-bulk')
calc.clone('bulk/Al-elastic')

calc.set(ibrion=6,    #
         isif=3,      # gets elastic constants
         potim=0.015,  # displacements
         nsw=1,
         nfree=2)

calc.wait(abort=True)

EM = calc.get_elastic_moduli()

print(EM)

c11 = EM[0, 0]
c12 = EM[0, 1]
B = (c11 + 2 * c12) / 3.0
print(B)
```

Open the python script (dft-scripts/script-129.py).

```
[[ 110.17099   59.54652   59.54652    0.          0.          0.      ]
 [  59.54652  110.17099   59.54652    0.          0.          0.      ]
 [  59.54652   59.54652  110.17099    0.          0.          0.      ]
 [   0.          0.          0.        11.52331    0.          0.      ]
 [   0.          0.          0.          0.        11.52331    0.      ]
 [   0.          0.          0.          0.          0.        11.52331]]
76.4213433333
```

This example shows the basic mechanics of getting the elastic constants. The C_{44} constant above is too low, and probably we need to check these constants for convergence with respect to kpoints, planewave cutoff, and maybe the value of POTIM.

4.6.3 Manual calculation of elastic constants

It is possible to manually calculate single elastic constants; you just need to know what strain corresponds to the elastic constant.

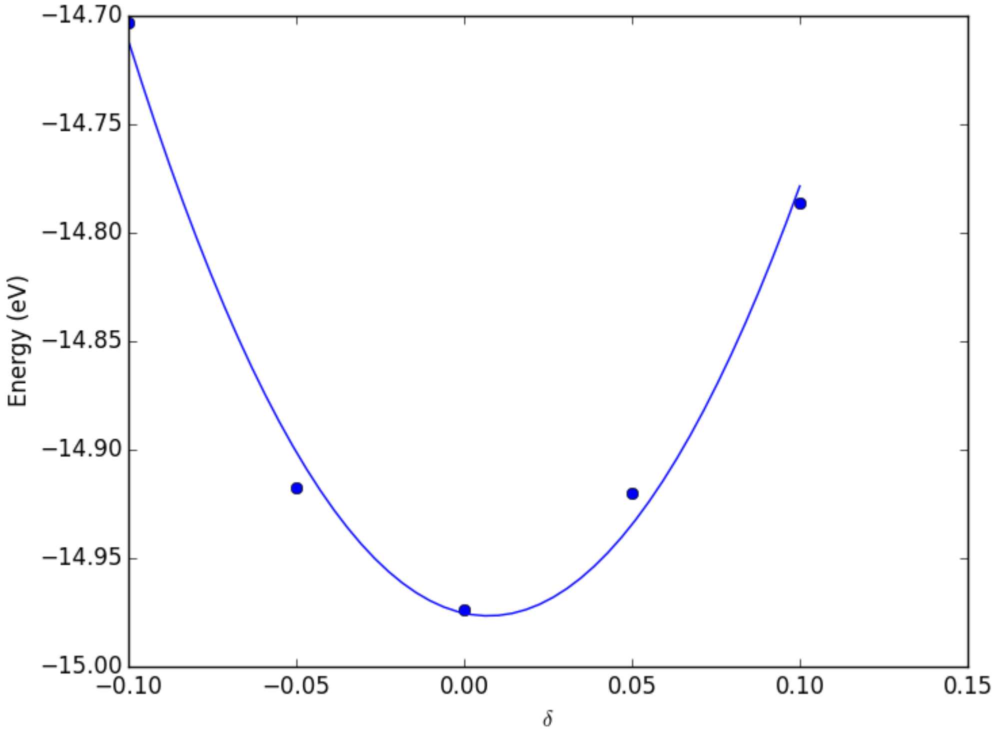
For the C11 elastic constant in a cubic system, we simply strain the cell along the x-axis, and then evaluate the second derivative at the minimum to calculate C11 like this.

$C_{11} = \frac{1}{V_C}\frac{\partial^2 E^{tot}}{\partial \gamma^2}$

```python
from vasp import Vasp
from ase.lattice.cubic import FaceCenteredCubic
import numpy as np
import matplotlib.pyplot as plt

DELTAS = np.linspace(-0.05, 0.05, 5)
calcs = []
volumes = []

for delta in DELTAS:
    atoms = FaceCenteredCubic(symbol='Al')

    cell = atoms.cell

    T = np.array([[1 + delta, 0, 0],
                  [0,1, 0],
                  [0, 0, 1]])
    newcell = np.dot(cell, T)
    atoms.set_cell(newcell, scale_atoms=True)
    volumes += [atoms.get_volume()]

    calcs += [Vasp('bulk/Al-c11-{}'.format(delta),
                   xc='pbe',
                   kpts=[12, 12, 12],
                   encut=350,
                   atoms=atoms)]

Vasp.run()
energies =  [calc.potential_energy for calc in calcs]

# fit a parabola
eos = np.polyfit(DELTAS, energies, 2)

# first derivative
d_eos = np.polyder(eos)

print(np.roots(d_eos))

xfit = np.linspace(min(DELTAS), max(DELTAS))
yfit = np.polyval(eos, xfit)

plt.plot(DELTAS, energies, 'bo', xfit, yfit, 'b-')
plt.xlabel('$\delta$')
plt.ylabel('Energy (eV)')
plt.savefig('images/Al-c11.png')
```

Open the python script (dft-scripts/script-130.py).

```
[ 0.00727102]
```



4.7 Bulk thermodynamics

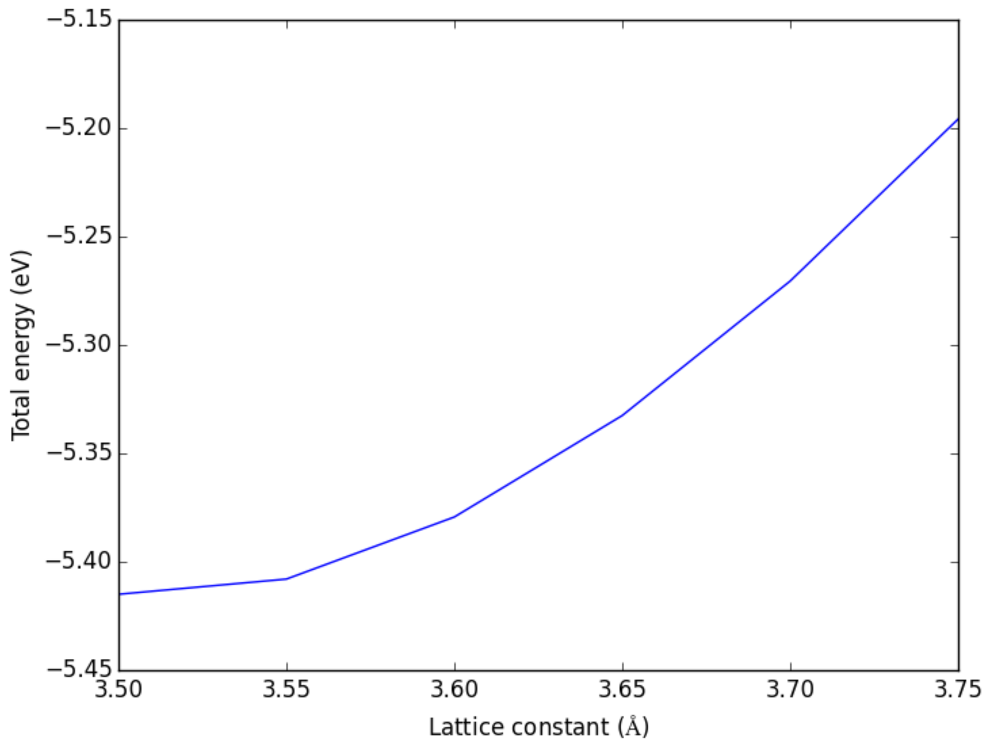
We can predict temperature dependent thermodynamic properties of bulk materials without too much effort. As with the thermochemical properties of ideal gases, we must use some simple models that we parameterize by DFT. Here we follow the example in Reference[51] for computing the thermal coefficient of expansion, heat capacity, enthalpy and entropy for Ni as a function of temperature.

We start by computing the equation of state for fcc Ni.

```
from vasp import Vasp
from ase import Atom, Atoms
import numpy as np
# fcc
LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
volumes, energies = [], []
for a in LC:
    atoms = Atoms([Atom('Ni', (0, 0, 0), magmom=2.5)],
                  cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
                                           [0.0, 1.0, 1.0],
                                           [1.0, 0.0, 1.0]]))

    calc = Vasp('bulk/Ni-{0}'.format(a),
                xc='PBE',
                encut=350,
                kpts=[12, 12, 12],
                ispin=2,
                atoms=atoms)
    energies.append(calc.potential_energy)
    volumes.append(atoms.get_volume())

calc.stop_if(None in energies)

import matplotlib.pyplot as plt
plt.plot(LC, energies)
plt.xlabel('Lattice constant ($\AA$)')
```

```
plt.ylabel('Total energy (eV)')
plt.savefig('images/Ni-fcc.png')
```

Open the python script (dft-scripts/script-131.py).



4.8 Effect of pressure on phase stability

So far we have only considered relative stability at a pressure of 0 Pa. We now consider the relative stability of two phases under pressure. We will consider TiO_2 in the rutile and anatase phases.

The pressure is defined by: $P = -\left(\frac{\partial E}{\partial V}\right)_T$. So if we have an equation of state $E(V)$ we can calculate the pressure at any volume, or alternatively, given a pressure, compute the volume. Pressure can affect the energy of two phases differently, so that one may become stable under pressure. The condition where a phase transition occurs is when the pressure in the two phases is the same, which occurs at a common tangent.

To show this, we need $E_{rutile}(V)$ and $E_{anatase}(V)$.

```
# run the rutile calculations
from vasp import Vasp
from ase import Atom, Atoms
import numpy as np

B = 'Ti'; X = 'O'; a = 4.59; c = 2.958; u = 0.305;
'''
create a rutile structure from the lattice vectors at
http://cst-www.nrl.navy.mil/lattice/struk/c4.html

spacegroup: 136 P4_2/mmm
'''
a1 = a * np.array([1.0, 0.0, 0.0])
a2 = a * np.array([0.0, 1.0, 0.0])
a3 = c * np.array([0.0, 0.0, 1.0])

```

```python
atoms = Atoms([Atom(B, [0., 0., 0.]),
               Atom(B, 0.5*a1 + 0.5*a2 + 0.5*a3),
               Atom(X,  u*a1 + u*a2),
               Atom(X, -u*a1 - u*a2),
               Atom(X, (0.5+u)*a1 + (0.5-u)*a2 + 0.5*a3),
               Atom(X, (0.5-u)*a1 + (0.5+u)*a2 + 0.5*a3)],
              cell=[a1, a2, a3])

nTiO2 = len(atoms) / 3.
v0 = atoms.get_volume()
cell0 = atoms.get_cell()

volumes = [28., 30., 32., 34., 36.]  #vol of one TiO2

for v in volumes:
    atoms.set_cell(cell0 * ((nTiO2 * v / v0)**(1. / 3.)),
                   scale_atoms=True)

    calc = Vasp('bulk/TiO2/rutile/rutile-{0}'.format(v),
                encut=350,
                kpts=[6, 6, 6],
                xc='PBE',
                ismear=0,
                sigma=0.001,
                isif=2,
                ibrion=2,
                nsw=20,
                atoms=atoms)
    calc.update()
```

Open the python script (dft-scripts/script-132.py).

```python
# run the anatase calculations
import numpy as np
from vasp import Vasp
from ase import Atom, Atoms
# http://cst-www.nrl.navy.mil/lattice/struk/c5.html

B = 'Ti'; X = 'O'; a = 3.7842; c = 2*4.7573; z = 0.0831;

a1 = a * np.array([1.0, 0.0, 0.0])
a2 = a * np.array([0.0, 1.0, 0.0])
a3 = np.array([0.5 * a, 0.5 * a, 0.5 * c])

atoms = Atoms([Atom(B, -0.125 * a1 + 0.625 * a2 + 0.25 * a3),
               Atom(B,  0.125 * a1 + 0.375 * a2 + 0.75 * a3),
               Atom(X, -z*a1 + (0.25-z)*a2 + 2.*z*a3),
               Atom(X, -(0.25+z)*a1 + (0.5-z)*a2 + (0.5+2*z)*a3),
               Atom(X, z*a1 - (0.25 - z)*a2 + (1-2*z)*a3),
               Atom(X, (0.25 + z)*a1 + (0.5 + z)*a2 + (0.5-2*z)*a3)],
               cell=[a1,a2,a3])

nTiO2 = len(atoms) / 3.
v0 = atoms.get_volume()
cell0 = atoms.get_cell()

volumes = [30., 33., 35., 37., 39.]  #vol of one TiO2

for v in volumes:
    atoms.set_cell(cell0 * ((nTiO2*v/v0)**(1./3.)),
                   scale_atoms=True)

    calc = Vasp('bulk/TiO2/anatase/anatase-{0}'.format(v),
                encut=350,
                kpts=[6, 6, 6],
                xc='PBE',
                ismear=0,
                sigma=0.001,
                isif=2,
                ibrion=2,
                nsw=20,
                atoms=atoms)
    calc.update()
```

Open the python script (dft-scripts/script-133.py).

Now we will fit cubic polynomials to the data.

```
# fit cubic polynomials to E(V) for rutile and anatase
from vasp import Vasp
import matplotlib.pyplot as plt
import numpy as np
np.set_printoptions(precision=2)

# anatase equation of state
volumes = [30., 33., 35., 37., 39.]  # vol of one TiO2 formula unit
a_volumes, a_energies = [], []
for v in volumes:
    calc = Vasp('bulk/TiO2/anatase/anatase-{0}'.format(v))
    atoms = calc.get_atoms()
    nTiO2 = len(atoms) / 3.0
    a_volumes.append(atoms.get_volume() / nTiO2)
    a_energies.append(atoms.get_potential_energy() / nTiO2)

# rutile equation of state
volumes = [28., 30., 32., 34., 36.]  # vol of one TiO2
r_volumes, r_energies = [], []
for v in volumes:
    calc = Vasp('bulk/TiO2/rutile/rutile-{0}'.format(v))
    atoms = calc.get_atoms()
    nTiO2 = len(atoms) / 3.0
    r_volumes.append(atoms.get_volume() / nTiO2)
    r_energies.append(atoms.get_potential_energy() / nTiO2)

# cubic polynomial fit to equation of state E(V) = pars*[V^3 V^2 V^1 V^0]
apars = np.polyfit(a_volumes, a_energies, 3)
rpars = np.polyfit(r_volumes, r_energies, 3)

print 'E_anatase(V) = {0:1.2f}*V^3 + {1:1.2f}*V^2 + {2:1.2f}*V + {3:1.2f}'.format(*apars)
print 'E_rutile(V) =  {0:1.2f}*V^3 + {1:1.2f}*V^2 + {2:1.2f}*V + {3:1.2f}'.format(*rpars)
print 'anatase epars: {0!r}'.format(apars)
print 'rutile epars: {0!r}'.format(rpars)
# get pressure parameters P(V) = -dE/dV
dapars = -np.polyder(apars)
drpars = -np.polyder(rpars)

print 'anatase ppars: {0!r}'.format(dapars)
print 'rutile ppars: {0!r}'.format(drpars)

print
print 'P_anatase(V) = {0:1.2f}*V^2 + {1:1.2f}*V + {2:1.2f}'.format(*dapars)
print 'P_rutile(V) =  {0:1.2f}*V^2 + {1:1.2f}*V + {2:1.2f}'.format(*drpars)

vfit = np.linspace(28, 40)

# plot the equations of state
plt.plot(a_volumes, a_energies,'bo ', label='Anatase')
plt.plot(vfit, np.polyval(apars, vfit), 'b-')

plt.plot(r_volumes, r_energies,'gs ', label='Rutile')
plt.plot(vfit, np.polyval(rpars, vfit), 'g-')

plt.xlabel('Volume ($\AA^3$/f.u.)')
plt.ylabel('Total energy (eV/f.u.)')
plt.legend()
plt.xlim([25, 40])
plt.ylim([-27, -26])
plt.savefig('imag
```

Open the python script (dft-scripts/script-134.py).

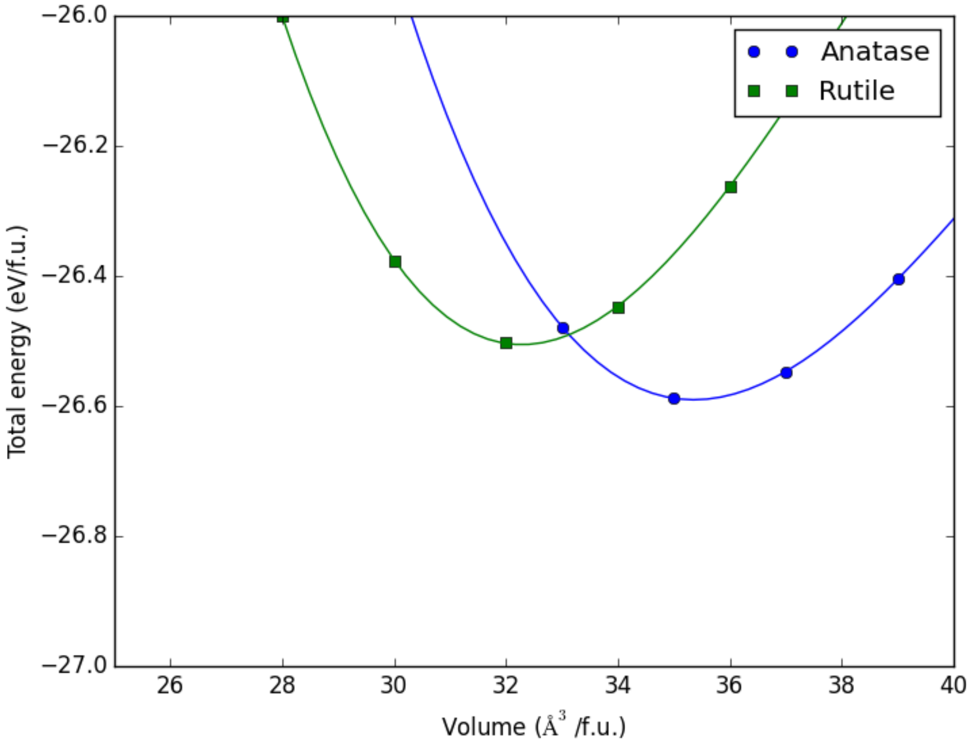


Figure 43: Equations of state (E(V)) for anatase and rutile TiO_2.

To find the conditions where a phase transition occurs, we have to find the common tangent line between the rutile and anatase phases. In other words we have to solve these two equations:

$(E_{anatase}(V1) - E_{rutile}(V2))/(V1 - V2) = P_{anatase}(V1)$

$(E_{anatase}(V1) - E_{rutile}(V2))/(V1 - V2) = P_{rutile}(V2)$

This is a nonlinear algebra problem. We use the `scipy.optimize.fsolve` to solve this problem.

```
from ase.units import GPa
from numpy import array, linspace, polyval

# copied from polynomial fit above
anatase_epars = array([-1.06049246e-03,   1.30279404e-01,  -5.23520055e+00,
         4.25202869e+01])
rutile_epars = array([-1.24680208e-03,   1.42966536e-01,  -5.33239733e+00,
         3.85903670e+01])

# polynomial fits for pressures
anatase_ppars = array([3.18147737e-03,  -2.60558808e-01,   5.23520055e+00])
rutile_ppars = array([3.74040625e-03,  -2.85933071e-01,   5.33239733e+00])


def func(V):
    V1 = V[0] # rutile volume
    V2 = V[1] # anatase volume

    E_rutile = polyval(rutile_epars, V1)
    E_anatase = polyval(anatase_epars, V2)

    P_rutile =  polyval(rutile_ppars, V1)
    P_anatase = polyval(anatase_ppars, V2)

    return [(E_anatase - E_rutile) / (V1 - V2) - P_anatase,
            (E_anatase - E_rutile) / (V1 - V2) - P_rutile]

```

```
from scipy.optimize import fsolve
x0 = fsolve(func, [28, 34])
print 'The solutions are at V = {0}'.format(x0)
print 'Anatase pressure: {0} GPa'.format(polyval(anatase_ppars, x0[1]) / GPa)
print 'Rutile  pressure: {0} GPa'.format(polyval(rutile_ppars, x0[0]) / GPa)

# illustrate the common tangent
import matplotlib.pyplot as plt

vfit = linspace(28, 40)
plt.plot(vfit, polyval(anatase_epars,vfit), label='anatase')
plt.plot(vfit, polyval(rutile_epars,vfit), label='rutile')
plt.plot(x0, [polyval(rutile_epars,x0[0]),
              polyval(anatase_epars,x0[1])], 'ko-', label='common tangent')
plt.legend()
plt.xlabel('Volume ($\AA^3$/f.u.)')
plt.ylabel('Total energy (eV/f.u.)')
plt.savefig('images/eos-common-tangent.png')
```

Open the python script (dft-scripts/script-135.py).

```
The solutions are at V = [ 31.67490656  34.60893508]
Anatase pressure: 4.5249494236 GPa
Rutile  pressure: 4.52494942374 GPa
```

At a pressure of 4.5 GPa, we expect that anatase will start converting into rutile. Along this common tangent, a mixture of the two phases will be more stable than either pure phase.

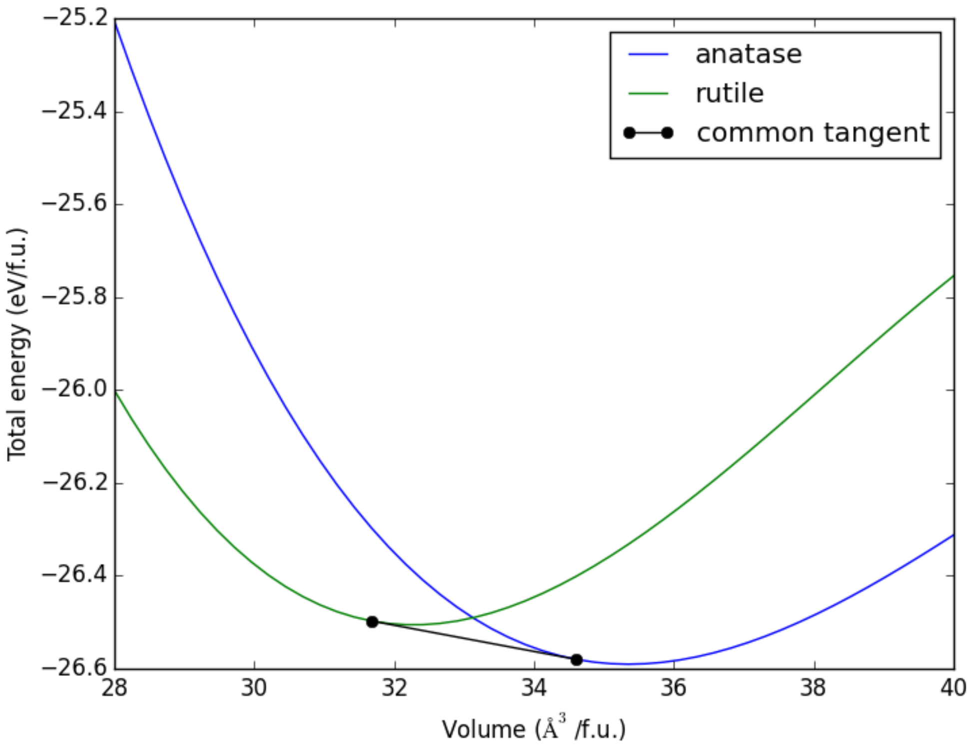


Figure 44: Illustration of the common tangent that shows the pressure where anatase and rutile coexist before anatase converts to rutile.

TODO add literature discussion

there is some controversy about the most stable phase. add discussion here.

4.9 Bulk reaction energies

4.9.1 Alloy formation energies

In this section we will consider how to calculate the formation energy of an fcc Cu-Pd alloy and how to use that information to discuss relative stabilities. The kinds of questions we can easily answer are:

1. Is the formation of an alloy at a particular composition and structure energetically favorable?
2. Given two alloy structures at the same composition, which one is more stable?
3. Given a set of alloy structures at different compositions, which ones are stable with respect to phase separation?

Each of these questions is answered by calculating the formation energy of the alloy from the parent metals. Thus, we will need the total energies of fcc Cu and fcc Pd. To get started. We get those first. Rather than compute a full equation of state for these, we will rely on the built in unit cell optimization algorithm in VASP (ISIF=3).

Basic alloy formation energy

```
# get bulk Cu and Pd energies. <<pure-metal-components>>
from vasp import Vasp
from ase import Atom, Atoms


atoms = Atoms([Atom('Cu',  [0.000,      0.000,      0.000])],
              cell=  [[ 1.818,  0.000,  1.818],
                      [ 1.818,  1.818,  0.000],
                      [ 0.000,  1.818,  1.818]])

cuc = Vasp('bulk/alloy/cu',
          xc='PBE',
          encut=350,
          kpts=[13, 13, 13],
          nbands=9,
          ibrion=2,
          isif=3,
          nsw=10,
          atoms=atoms)

cu = cuc.potential_energy

atoms = Atoms([Atom('Pd',  [0.000,      0.000,      0.000])],
              cell=[[ 1.978,  0.000,  1.978],
                    [ 1.978,  1.978,  0.000],
                    [0.000,  1.978,  1.978]])

pd = Vasp('bulk/alloy/pd',
          xc='PBE',
          encut=350,
          kpts=[13, 13, 13],
          nbands=9,
          ibrion=2,
          isif=3,
          nsw=10,
          atoms=atoms).potential_energy

print 'Cu energy = {0} eV'.format(cu)
print 'Pd energy = {0} eV'.format(pd)
```

Open the python script (dft-scripts/script-136.py).

```
Cu energy = -3.73437194 eV
Pd energy = -5.22003433 eV
```

Note that the Pd energy is more negative than the Cu energy. This does not mean anything significant. We cannot say Pd is more stable than Cu; it is not like Cu could transmutate into Pd!

Next, we will consider a question like which of two structures with composition of CuPd is more stable. These coordinates for these structures came from research of the author. The approach is pretty general, you must identify the coordinates and unit cell of the candidate structure, and then run a calculation to find the optimized geometry and unit cell. This may take some work, as previously described in the multistep process for optimizing a bulk system. Here the geometry is pretty close to optimized, so we can use the VASP optimization routines. We consider two structures with composition CuPd.

```
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Cu',  [0.000,      0.000,      0.000]),
               Atom('Pd',  [-1.652,     0.000,      2.039])],
              cell=  [[0.000, -2.039,  2.039],
                      [0.000,  2.039,  2.039],
                      [-3.303,  0.000,  0.000]])

calc = Vasp('bulk/alloy/cupd-1',
            xc='PBE',
            encut=350,
            kpts=[12, 12, 8],
            nbands=17,
            ibrion=2,
            isif=3,
            nsw=10,
            atoms=atoms)
cupd1 = atoms.get_potential_energy()

atoms = Atoms([Atom('Cu',  [-0.049,     0.049,      0.049]),
               Atom('Cu',  [-11.170,   11.170,     11.170]),
               Atom('Pd',  [-7.415,     7.415,      7.415]),
               Atom('Pd',  [-3.804 ,    3.804,      3.804])],
              cell=[[-5.629,  3.701,  5.629 ],
                    [-3.701,  5.629,  5.629 ],
                    [-5.629,  5.629,  3.701 ]])

calc = Vasp('bulk/alloy/cupd-2',
            xc='PBE',
            encut=350,
            kpts=[8, 8, 8],
            nbands=34,
            ibrion=2,
            isif=3,
            nsw=10,
            atoms=atoms)
cupd2 = atoms.get_potential_energy()

print 'cupd-1 = {0} eV'.format(cupd1)
print 'cupd-2 = {0} eV'.format(cupd2)
```

Open the python script (dft-scripts/script-137.py).

```
cupd-1 = -9.17593835 eV
cupd-2 = -18.07779325 eV
```

Looking at these energies, you could be tempted to say cupd-2 is more stable than cupd-1 because its energy is much lower. This is wrong, however, because cupd-2 has twice as many atoms as cupd-1. We should compare the normalized total energies, that is the energy normalized per CuPd formula unit, or as an alternative the number of atoms in the unit cell. It does not matter which, as long as we normalize consistently. It is conventional in alloy calculation to normalize by the number of atoms in the unit cell.

```
from vasp import Vasp

```

```
calc = Vasp('bulk/alloy/cupd-1')
atoms = calc.get_atoms()
e1 = atoms.get_potential_energy()/len(atoms)

calc = Vasp('bulk/alloy/cupd-2')
atoms = calc.get_atoms()
e2 = atoms.get_potential_energy()/len(atoms)

print 'cupd-1: {0} eV/atom'.format(e1)
print 'cupd-2: {0} eV/atom'.format(e2)
```

Open the python script (dft-scripts/script-138.py).

```
cupd-1: -4.587969175 eV/atom
cupd-2: -4.5194483125 eV/atom
```

After normalizing by number of atoms, we can see that cupd-1 is a more stable structure. However, we are looking at total energies, and we might ask: is cupd-1 more stable than an unreacted mixture of the parent compounds, fcc Cu and Pd? In other words, is the following reaction exothermic:

Cu + Pd → CuPd for the two configurations we examined? Below, we show some pretty general code that computes these formation energies, and normalizes them by the number of atoms in the unit cell.

```
from vasp import Vasp

# bulk energy 1
calc = Vasp('bulk/alloy/cu')
atoms = calc.get_atoms()
cu = atoms.get_potential_energy()/len(atoms)

# bulk energy 2
calc = Vasp('bulk/alloy/pd')
atoms = calc.get_atoms()
pd = atoms.get_potential_energy()/len(atoms)

calc = Vasp('bulk/alloy/cupd-1')
atoms = calc.get_atoms()
e1 = atoms.get_potential_energy()
# subtract bulk energies off of each atom in cell
for atom in atoms:
    if atom.symbol == 'Cu':
        e1 -= cu
    else:
        e1 -= pd

e1 /= len(atoms)  # normalize by number of atoms in cell

calc = Vasp('bulk/alloy/cupd-2')
atoms = calc.get_atoms()
e2 = atoms.get_potential_energy()
for atom in atoms:
    if atom.symbol == 'Cu':
        e2 -= cu
    else:
        e2 -= pd
e2 /= len(atoms)

print 'Delta Hf cupd-1 = {0:1.2f} eV/atom'.format(e1)
print 'Delta Hf cupd-2 = {0:1.2f} eV/atom'.format(e2)
```

Open the python script (dft-scripts/script-139.py).

```
Delta Hf cupd-1 = -0.11 eV/atom
Delta Hf cupd-2 = -0.04 eV/atom
```

The answer is yes. Both structures are energetically more favorable than an equal composition mixture of the parent metals. The heat of formation for both structures is exothermic, but the cupd-1 structure is more stable than the cupd-2 structure. This is shown conceptually in Figure 45.

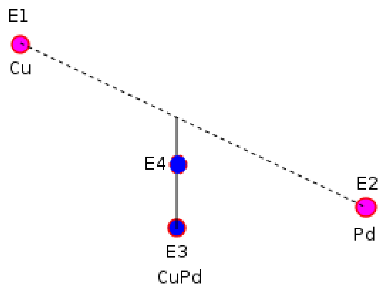


Figure 45: Conceptual picture of two alloys with exothermic formation energies. The dashed line represents a composition weighted average energy of the parent metals. E4 and E3 are energies associated with two different alloy structures at the same composition. Both structures are more stable than a mixture of pure metals with the same composition, but E3 is more stable than E4.

We will now examine another structure at another composition and its stability.

```
from vasp import Vasp
from ase import Atom, Atoms

# parent metals

atoms = Vasp('bulk/alloy/cu').get_atoms()
cu = atoms.get_potential_energy() / len(atoms)

atoms = Vasp('bulk/alloy/pd').get_atoms()
pd = atoms.get_potential_energy() / len(atoms)

atoms = Atoms([Atom('Cu',  [-3.672,     3.672,      3.672]),
               Atom('Cu',  [0.000,      0.000,      0.000]),
               Atom('Cu',  [-10.821,    10.821,     10.821]),
               Atom('Pd',  [-7.246,     7.246,      7.246])],
               cell=[[-5.464,  3.565,  5.464],
                     [-3.565,  5.464,  5.464],
                     [-5.464,  5.464,  3.565]])

calc = Vasp('bulk/alloy/cu3pd-1',
            xc='PBE',
            encut=350,
            kpts=[8, 8, 8],
            nbands=34,
            ibrion=2,
            isif=3,
            nsw=10,
            atoms=atoms)

e3 = atoms.get_potential_energy()

Vasp.wait(abort=True)

for atom in atoms:
    if atom.symbol == 'Cu':
        e3 -= cu
    else:
        e3 -= pd
e3 /= len(atoms)

print 'Delta Hf cu3pd-1 = {0:1.2f} eV/atom'.format(e3)
```

Open the python script (dft-scripts/script-140.py).

```
Delta Hf cu3pd-1 = -0.02 eV/atom
```

The formation energy is slightly exothermic, which means the structure is more stable than a mixture of the parent metals. However, let us consider whether the structure is stable with respect to phase separation into pure Cu and the cupd-1 structure. We define the following quantities:

$H_{f,Cu} = 0.0$ eV/atom, $x_0 = 0$, $H_{f,cupd-1} =$ -0.12 eV/atom, $x_3 = 0.5$.

The composition weighted average at $x_{Pd} = 0.25$ is:

$H_f = H_{f,Cu} + \frac{x0-x}{x0-x3}(H_{f,cupd-1} - H_{f,Cu})$

```
x0 = 0.0; x3 = 0.5; x = 0.25;
Hf1 = 0.0; Hf3 = -0.12;

print 'Composition weighted average  = {0} eV'.format(Hf1 +
                                                     (x0 - x)
                                                     / (x0 - x3)
                                                     * (Hf3 - Hf1))
```

Open the python script (dft-scripts/script-141.py).

```
Composition weighted average  = -0.06 eV
```

We find the weighted composition formation energy of pure Cu and cupd-1 is more favorable than the formation energy of cu3pd-1. Therefore, we could expect that structure to phase separate into a mixture of pure Cu and cupd-1. Schematically what we are seeing is shown in Figure **??**fig:alloy-phase-separation.

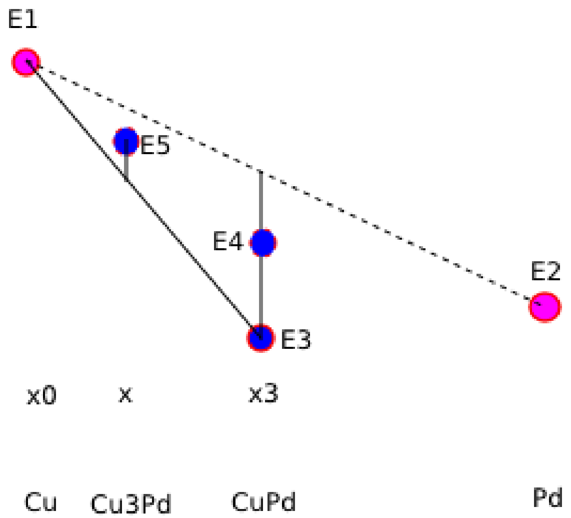


Figure 46: Illustration of of an alloy structure with an exothermic formation energy that is not stable with respect to phase separation. The solid line shows the composition weighted average energy of a mixture of Cu and cupd-2. Since the energy of cu3pd-1 is above the solid line, it is less favorable than a mixture of Cu and cupd-2 with the same composition.

Finally, let us consider one more structure with the Cu_3Pd stoichiometry.

```
from vasp import Vasp
from ase import Atom, Atoms

# parent metals
cu = Vasp('bulk/alloy/cu')
cu_e = cu.potential_energy / len(cu.get_atoms())

pd = Vasp('bulk/alloy/pd')
```

```
pd_e = pd.potential_energy / len(pd.get_atoms())

atoms = Atoms([Atom('Cu',  [-1.867,     1.867,      0.000]),
               Atom('Cu',  [0.000,      0.000,      0.000]),
               Atom('Cu',  [0.000,      1.867,      1.867]),
               Atom('Pd',  [-1.867,     0.000,      1.86])],
               cell=[[-3.735,  0.000,  0.000],
                     [0.000,  0.000,  3.735],
                     [0.000,  3.735,  0.000]])

calc = Vasp('bulk/alloy/cu3pd-2',
            xc='PBE',
            encut=350,
            kpts=[8, 8, 8],
            nbands=34,
            ibrion=2,
            isif=3,
            nsw=10,
            atoms=atoms)
e4 = atoms.get_potential_energy()

Vasp.wait(abort=True)

for atom in atoms:
    if atom.symbol == 'Cu':
        e4 -= cu_e
    else:
        e4 -= pd_e
e4 /= len(atoms)
print('Delta Hf cu3pd-2 = {0:1.2f} eV/atom'.format(e4))
```

Open the python script (dft-scripts/script-142.py).

```
Delta Hf cu3pd-2 = -0.10 eV/atom
```

This looks promising: the formation energy is much more favorable than cu3pd-1, and it is below the composition weighted formation energy of -0.06 eV/atom. Consequently, we conclude that this structure will not phase separate into a mixture of Cu and CuPd. We cannot say, however, if there is a more stable phase not yet considered, or if it might phase separate into two other phases. We also note here that we have ignored a few other contributions to alloy stability. We have only considered the electronic energy contributions to the formation energy. At temperatures above absolute zero there are additional contributions including configurational and vibrational entropy, which may stabilize some structures more than others. Finally, our analysis is limited to comparisons of the structures computed on the fcc lattice. In fact, it is known that the CuPd alloy forms a bcc structure. We did not calculate that structure, so we can not say if it is more or less stable than the obvious fcc structure we found.

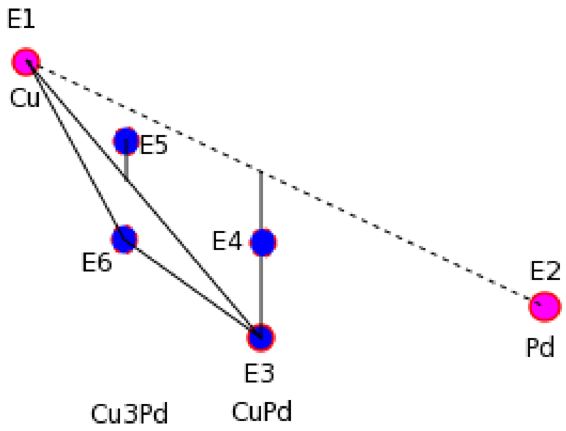


Figure 47: Illustration that cu3pd-2 is more stable than cu3pd-1 and that is it is more stable than a composition weighted mixture of Cu and cupd-1. The dotted line shows the energy of a composition weighted average energy of a mixture of Cu and cupd-1. Since cu3pd-2 is below the dotted line, it is more stable than the phase-separated mixture.

The construction of alloy phase diagrams is difficult. You are always faced with the possibility that there is a phase that you have not calculated that is more stable than the ones you did calculate. One approach is to use a tool that automates the discovery of relevant structures such as the Alloy Theoretic Automated Toolkit (ATAT)[52,53] which uses a cluster expansion methodology.

4.9.2 Metal oxide oxidation energies

We will consider here the reaction 2 Cu_2O + O_2 ⇌ 4 CuO. The reaction energy is:
$\Delta E = 4E_{CuO} - 2E_{Cu_2O} - E_{O_2}$. We need to compute the energy of each species.

Cu_2O calculation

```
# run Cu2O calculation
from vasp import Vasp
from ase import Atom, Atoms

# http://phycomp.technion.ac.il/~ira/types.html#Cu2O
a = 4.27

atoms = Atoms([Atom('Cu', [0, 0, 0]),
               Atom('Cu', [0.5, 0.5, 0.0]),
               Atom('Cu', [0.5, 0.0, 0.5]),
               Atom('Cu', [0.0, 0.5, 0.5]),
               Atom('O', [0.25, 0.25, 0.25]),
               Atom('O', [0.75, 0.75, 0.75])])

atoms.set_cell((a, a, a), scale_atoms=True)

calc = Vasp('bulk/Cu2O',
            encut=400,
            kpts=[8, 8, 8],
            ibrion=2,
            isif=3,
            nsw=30,
            xc='PBE',
            atoms=atoms)

```

```
print atoms.get_potential_energy()
print atoms.get_stress()
```

Open the python script (dft-scripts/script-143.py).

```
-27.27469148
[-0.01018402 -0.01018402 -0.01018402 -0.          -0.          -0.         ]
```

CuO calculation

```
# run CuO calculation
from vasp import Vasp
from ase import Atom, Atoms
import numpy as np

# CuO
# http://cst-www.nrl.navy.mil/lattice/struk/b26.html
# http://www.springermaterials.com/docs/info/10681727_51.html
a = 4.6837
b = 3.4226
c = 5.1288
beta = 99.54/180*np.pi
y = 0.5819

a1 = np.array([0.5*a, -0.5*b, 0.0])
a2 = np.array([0.5*a, 0.5*b, 0.0])
a3 = np.array([c*np.cos(beta), 0.0, c*np.sin(beta)])

atoms = Atoms([Atom('Cu', 0.5*a2),
               Atom('Cu', 0.5*a1 + 0.5*a3),
               Atom('O', -y*a1 + y*a2 + 0.25*a3),
               Atom('O',  y*a1 - y*a2 - 0.25*a3)],
               cell=(a1, a2, a3))

calc = Vasp('bulk/CuO',
            encut=400,
            kpts=[8, 8, 8],
            ibrion=2,
            isif=3,
            nsw=30,
            xc='PBE',
            atoms=atoms)
print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-144.py).

```
-19.61568557
```

TODO Reaction energy calculation

```
from vasp import Vasp

# don't forget to normalize your total energy to a formula unit. Cu2O
# has 3 atoms, so the number of formula units in an atoms is
# len(atoms)/3.
calc = Vasp('bulk/Cu2O')
atoms1 = calc.get_atoms()
cu2o_energy = atoms1.get_potential_energy()

calc = Vasp('bulk/CuO')
atoms2 = calc.get_atoms()
cuo_energy = atoms2.get_potential_energy()

# make sure to use the same cutoff energy for the O2 molecule!
calc = Vasp('molecules/O2-sp-triplet-400')
atoms3 = calc.get_atoms()
o2_energy = atoms3.get_potential_energy()

calc.stop_if(None in [cu2o_energy, cuo_energy, o2_energy])

```

```
cu2o_energy /= (len(atoms1) / 3)  # note integer math
cuo_energy /= (len(atoms2) / 2)
rxn_energy = 4.0 * cuo_energy - o2_energy - 2.0 * cu2o_energy
print 'Reaction energy = {0} eV'.format(rxn_energy)
```

Open the python script (dft-scripts/script-145.py).

```
Reaction energy = -2.11600154 eV
```

This is the reaction energy for 2 $Cu_2O \rightarrow 4$ CuO. In,[54] the experimental reaction is estimated to be about -3.14 eV.

There are a few reasons why our number does not agree with the experimental reaction energy. One reason is related to errors in the O_2 dissociation energy, and another reason is related to localization of electrons in the Cu 3*d* orbitals.[54] The first error of incorrect O_2 dissociation error is a systematic error that can be corrected empirically.[54] Fixing the second error requires the application of DFT+U (see DFT+U).

The heat of reaction is reported to be 1000 J/g product at http://onlinelibrary.wiley.com/doi/10.1002/er.4440130107/pdf for the reaction 2CuO $\rightleftharpoons$ Cu_2O + 1/2 O_2.

```
from ase import Atoms
atoms = Atoms('Cu2O')
MW = atoms.get_masses().sum()

H = 1.  # kJ/g
print 'rxn energy = {0:1.1f} eV'.format(-2 * H * MW / 96.4)  # convert to eV
```

Open the python script (dft-scripts/script-146.py).

```
rxn energy = -3.0 eV
```

This is pretty close to the value in[54] and might need a temperature correction to get agreement at 298K.

4.10 Bulk density of states

The density of states refers to the number of electronic states in a particular energy range.

The solution to Eq. (1) yields a set of Kohn-Sham (K-S) orbitals and an associated set of eigenvalues that correspond to the energies of these orbitals, neither of which have any known directly observable meaning.[18] The sum of the squared K-S orbitals, however, is equal to the electron density (Eq. (3)), and the sum of the eigenvalues is a significant part of the total energy (Eq. (4)). Thus, it seems reasonable to suppose these quantities have other significant relationships to physical observables. Perdew et al. showed that the highest occupied eigenvalue is equal to the ionization energy of a system within an exact density functional theory,[24] but their interpretation has been vigorously debated in the literature,[55–57] and is only true for the exact exchange/correlation functional, not the approximate ones used in practice.[3] Stowasser and Hoffmann discussed an approach to using the K-S orbitals in more traditional molecular orbital interpretations, but the results were primarily qualitative.[58] More recently, a DFT analog of Koopmans' theorem has been developed that formally identifies the eigenvalues with vertical ionization potentials, which can be measured with photoelectron spectroscopy.[59]

Despite the arguments against ascribing physical meaning to the K-S orbitals and eigenvalues, it has become fairly standard, especially for solids, to use them to calculate the density of states (DOS)[60] [Sec. VI. B]. This has been found to yield reasonable results for the valence bands in metals, but poor results for tightly bound orbitals and band gaps.[24] A highly technical discussion of this issue can be found in Ref.[61]. The density of states can be calculated by a sum over the k-points:[15]

$$\rho(\epsilon) = \sum_{\mathrm{k}} \omega_{\mathrm{k}} \sum_i \beta(\epsilon - \epsilon_{i\mathrm{k}}) \tag{7}$$

where ω_k is the weight associated with the k-point, and β is a broadening function, typically a gaussian function, to account for the finite number of k-points used in the calculations. The amount of broadening is arbitrary, and should tend to zero as the number of k-points approaches infinity.

```
from vasp import Vasp

npoints = 200
width = 0.5

def gaussian(energies, eik):
    x = ((energies - eik) / width)
    return np.exp(-x**2) / np.sqrt(np.pi) / width

calc = Vasp('bulk/pd-dos')

# kpt weights
wk = calc.get_k_point_weights()

# for each k-point there are a series of eigenvalues
# here we get all the eigenvalues for each k-point
e_kn = []
for i, k in enumerate(wk):
    e_kn.append(calc.get_eigenvalues(kpt=i))

e_kn = np.array(e_kn) - calc.get_fermi_level()

# these are the energies we want to evaluate the dos at
energies = np.linspace(e_kn.min(), e_kn.max(), npoints)

# this is where we build up the dos
dos = np.zeros(npoints)

for j in range(npoints):
    for k in range(len(wk)): # loop over all kpoints
        for i in range(len(e_kn[k])): # loop over eigenvalues in each k
            dos[j] += wk[k] * gaussian(energies[j], e_kn[k][i])

import matplotlib.pyplot as plt
plt.plot(energies, dos)
plt.savefig('images/manual-dos.png')
plt.show()
```

Open the python script (dft-scripts/script-147.py).

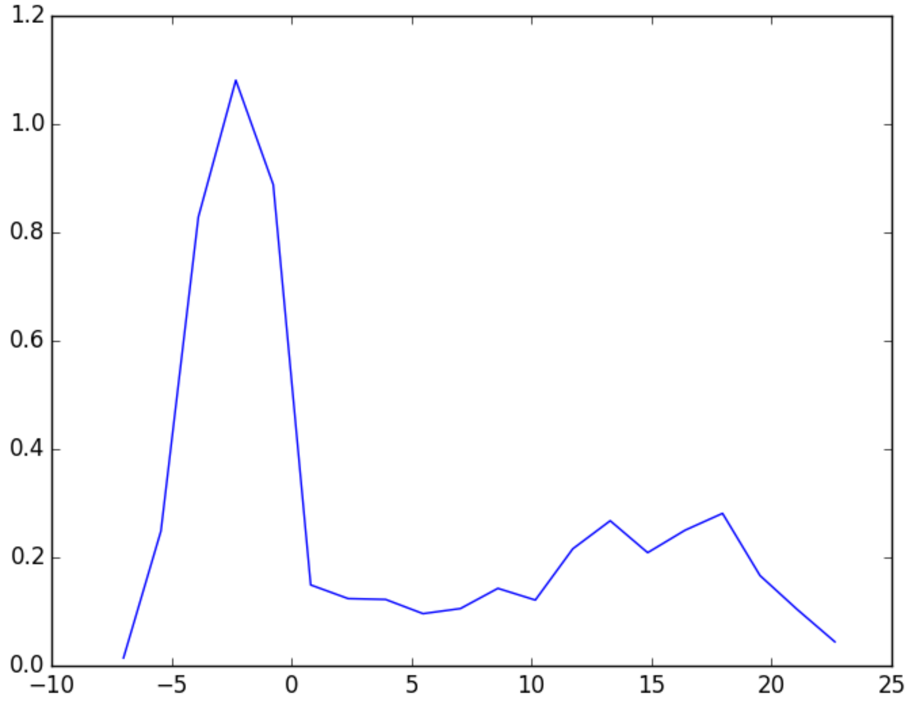


Figure 48: Density of states.

Here is a more convenient way to compute the DOS using `ase.dft`.

```
from vasp import Vasp
import matplotlib.pyplot as plt
from ase.dft import DOS

calc = Vasp('bulk/pd-dos')
dos = DOS(calc, width=0.2)
d = dos.get_dos()
e = dos.get_energies()

import pylab as plt
plt.plot(e, d)
plt.xlabel('energy (eV)')
plt.ylabel('DOS')
plt.savefig('images/pd-dos.png')
```

Open the python script (dft-scripts/script-148.py).

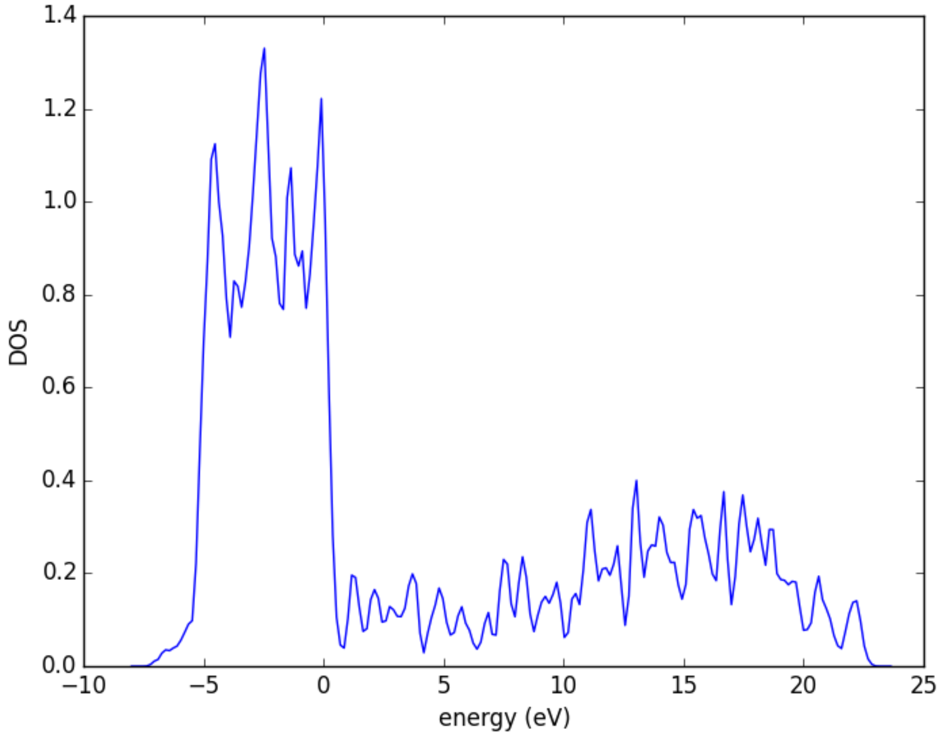


Figure 49: Total DOS for bulk Pd.

This DOS looks roughly like you would expect. The peak between -5 to 0 eV is the Pd d-band.

The VASP manual recommends a final run be made with ISMEAR=-5, which uses the tetrahedron method with Bl\"ochl corrections.

```
from vasp import Vasp
from ase.dft import DOS
calc = Vasp('bulk/pd-dos')
calc.clone('bulk/pd-dos-ismear-5')


bulk = calc.get_atoms()
calc.set(ismear=-5)

bulk.get_potential_energy()
dos = DOS(calc, width=0.2)
d = dos.get_dos()
e = dos.get_energies()

import pylab as plt
plt.plot(e, d)
plt.xlabel('energy [eV]')
plt.ylabel('DOS')
plt.savefig('images/pd-dos-ismear-5.png')
```

Open the python script (dft-scripts/script-149.py).

This not notably different to me.

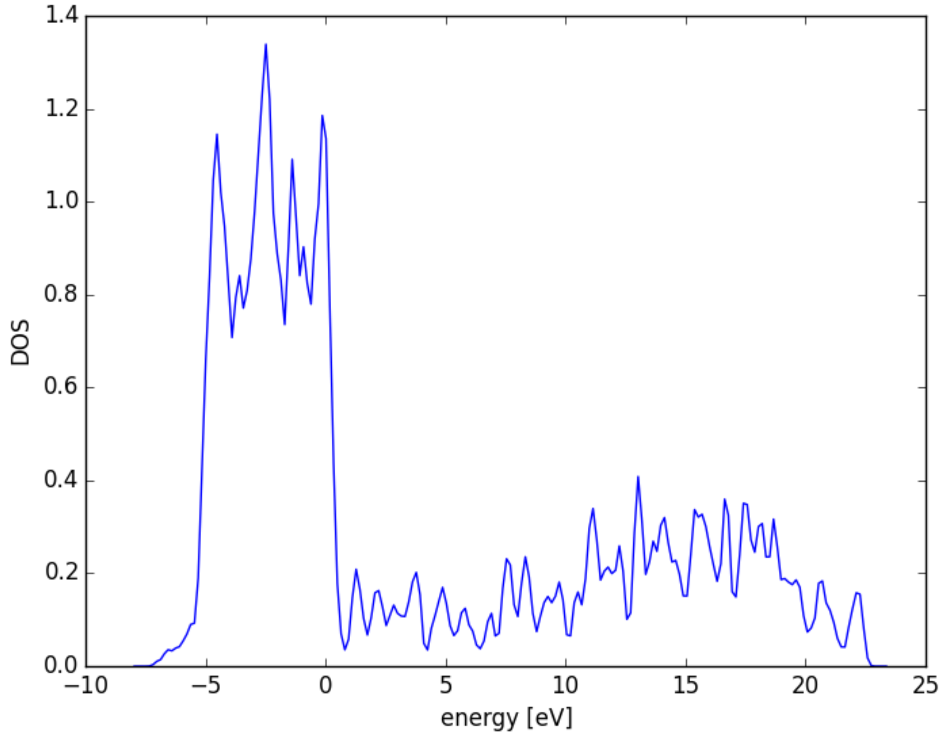


Figure 50: Total DOS for Pd computed with ISMEAR=-5

We can test for convergence of the DOS. The k-points are most important.

```
from ase import Atoms, Atom
from vasp import Vasp
Vasp.vasprc(mode=None)
#Vasp.log.setLevel(10)

import matplotlib.pyplot as plt
import numpy as np
from ase.dft import DOS
import pylab as plt

a = 3.9  # approximate lattice constant
b = a / 2.
bulk = Atoms([Atom('Pd', (0.0, 0.0, 0.0))],
             cell=[(0, b, b),
                   (b, 0, b),
                   (b, b, 0)])

kpts = [8, 10, 12, 14, 16, 18, 20]

calcs = [Vasp('bulk/pd-dos-k{0}-ismear-5'.format(k),
              encut=300,
              xc='PBE',
              kpts=[k, k, k],
              atoms=bulk) for k in kpts]

Vasp.wait(abort=True)

for calc in calcs:
    # this runs the calculation
    if calc.potential_energy is not None:
        dos = DOS(calc, width=0.2)
        d = dos.get_dos() + k / 4.0
        e = dos.get_energies()
```

```python

        plt.plot(e, d, label='k={0}'.format(k))
    else:
        pass
plt.xlabel('energy (eV)')
plt.ylabel('DOS')
plt.legend()
plt.savefig('images/pd-dos-k-convergence-ismear-5.png')
plt.show()
```

Open the python script (dft-scripts/script-150.py).

```
got here
<ase.dft.dos.DOS instance at 0xec2d710>
```

```python
from vasp import Vasp
from ase.dft import DOS
# This seems very slow...
calc = Vasp('bulk/pd-dos-k20-ismear-5')
print DOS(calc, width=0.2)
```

Open the python script (dft-scripts/script-151.py).

```
<ase.dft.dos.DOS instance at 0x168a1ea8>
```

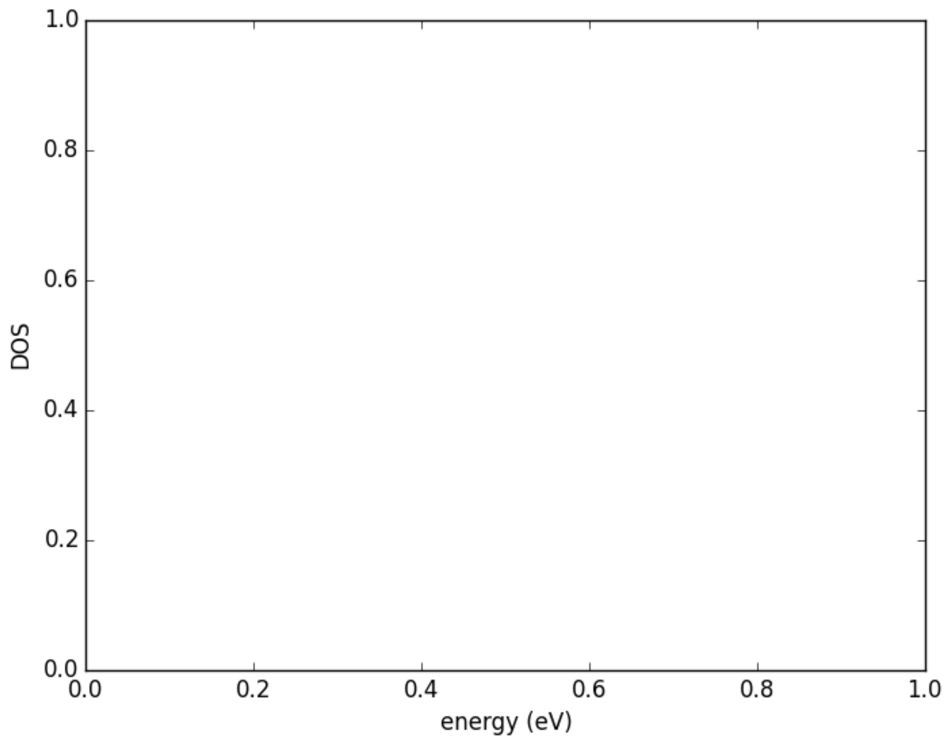


Figure 51: Convergence of the total DOS with k-points

4.11 Atom projected density of states

One major disadvantage of a planewave basis set is that it is difficult to relate the completely delocalized planewaves to localized phenomena such as bonding. Much insight into bonding has been gained by atomic/molecular orbital theory, which has carried over to the solid-state arena.[7] Consequently, several schemes have been developed to project the one-electron Kohn-Sham wave functions onto atomic wave functions.[62–64] In VASP, the one electron wave functions can be projected onto spherical harmonic orbitals. The radial component of the atomic orbitals extends to infinity. In a solid, this means that the projection on one atom may overlap with the projection on a neighboring atom, resulting in double counting of electrons. Consequently, a cutoff radius was introduced, beyond which no contributions are included. It is not obvious what the best cutoff radius is. If the radius is too small, it might not capture all of the electrons associated with the atom. However, if it is too large, it may include electrons from neighboring atoms. One might want to use different cutoff radii for different atoms, which have different sizes. Furthermore, the ideal cutoff radius for an atom may change in different environments, thus it would require an iterative procedure to determine it. This difficulty arises because the orbital-band occupations are not observable, thus how the electrons are divided up between atoms is arbitrary and, as will be seen later, is sensitive to the cutoff radius (and in other DFT implementations, the basis set). However, Mulliken orbital populations have been used successfully for many years to examine the qualitative differences between similar systems, and that is precisely what these quantities are used for here. Thus, a discussion of the analysis and results is warranted.

The s and p states in a metal are typically delocalized in space and more like free-electrons, whereas the d-orbitals are fairly localized in space and have been treated successfully with tight-binding theories such as extended H\"u ckel theory,[7] and linear muffin tin orbital theory.[65] Consequently, the remaining discussion will be focused on the properties of the projected d-states.

In this example, we consider how to get the atom-projected density of states (ADOS). We are interested in properties of the \$d\$-band on Pd, such as the \$d\$-band center and \$d\$-band width. You must set the RWIGS tag to get ADOS, and these are the Wigner-Seitz radii for each atom. By integrating the projected d-band up to the Fermi level, the d-band filling can be determined. It is not obvious what the electron count in the d-band should be for an atom in a metal. For a gas-phase, neutral metal atom in the ground state, however, the d-orbital electron count is well defined, so it will be used as an initial reference point for comparison.[4]

A powerful method for characterizing distributions is to examine various moments of the distribution (see Chapter 4 in Ref.[66] and Chapter 6 in Refs.[67] and[68]). The n^{th} order moment, μ_n, of a distribution of states $\rho(\epsilon)$ with respect to a reference ϵ_o is defined by

$$\mu_n = \frac{\int_{-\infty}^{\infty} \epsilon^n \rho(\epsilon - \epsilon_o) d\epsilon}{\int_{-\infty}^{\infty} \rho(\epsilon - \epsilon_o) d\epsilon} \tag{8}$$

In this work, the reference energy is always the Fermi level. The zeroth moment is just the total number of states, in this case it will be normalized to unity. The first moment is the average energy of distribution, analogous to the center of mass for a mass density distribution. The second moment is the mean squared width of the distribution. The third moment is a measure of skewness and the fourth moment is related to kurtosis, but these moments are rarely used, and only the first and second moments are considered in this work.

It is important to note that these projected density of states are not physical observables. They are the wavefunctions projected onto atomic orbitals. For some situations this makes sense, e.g. the *d* orbitals are fairly localized and reasonably approximated by atomic orbitals. The *s* valence orbitals in a metal, in contrast, are almost totally delocalized. Depending on the cutoff radius (RWIGS) you choose, you can see very different ADOS.

```
from ase import Atoms, Atom
from vasp import Vasp

import matplotlib.pyplot as plt
import numpy as np
```

```python

a = 3.9  # approximate lattice constant
b = a / 2.
bulk = Atoms([Atom('Pd', (0.0, 0.0, 0.0))],
             cell=[(0, b, b),
                   (b, 0, b),
                   (b, b, 0)])

calc = Vasp('bulk/pd-ados',
            encut=300,
            xc='PBE',
            lreal=False,
            rwigs={'Pd': 1.5},  # wigner-seitz radii for ados
            kpts=[8, 8, 8],
            atoms=bulk)

# this runs the calculation
calc.wait(abort=True)

# now get results
energies, ados = calc.get_ados(0, 'd')

# we will select energies in the range of -10, 5
ind = (energies < 5) & (energies > -10)

energies = energies[ind]
dos = ados[ind]

Nstates = np.trapz(dos, energies)
occupied = energies <= 0.0
N_occupied_states = np.trapz(dos[occupied], energies[occupied])
# first moment
ed = np.trapz(energies * dos, energies) / Nstates

# second moment
wd2 = np.trapz(energies**2 * dos, energies) / Nstates

print 'Total # states = {0:1.2f}'.format(Nstates)
print 'number of occupied states = {0:1.2f}'.format(N_occupied_states)
print 'd-band center = {0:1.2f} eV'.format(ed)
print 'd-band width  = {0:1.2f} eV'.format(np.sqrt(wd2))

# plot the d-band
plt.plot(energies, dos, label='$d$-orbitals')

# plot the occupied states in shaded gray
plt.fill_between(x=energies[occupied],
                 y1=dos[occupied],
                 y2=np.zeros(dos[occupied].shape),
                 color='gray', alpha=0.25)

plt.xlabel('$E - E_f$ (eV)')
plt.ylabel('DOS (arbitrary units)')

plt.savefig('images/pd-ados.png')
```

Open the python script (dft-scripts/script-152.py).

```
Total # states = 9.29
number of occupied states = 7.95
d-band center = -1.98 eV
d-band width  = 2.71 eV
```

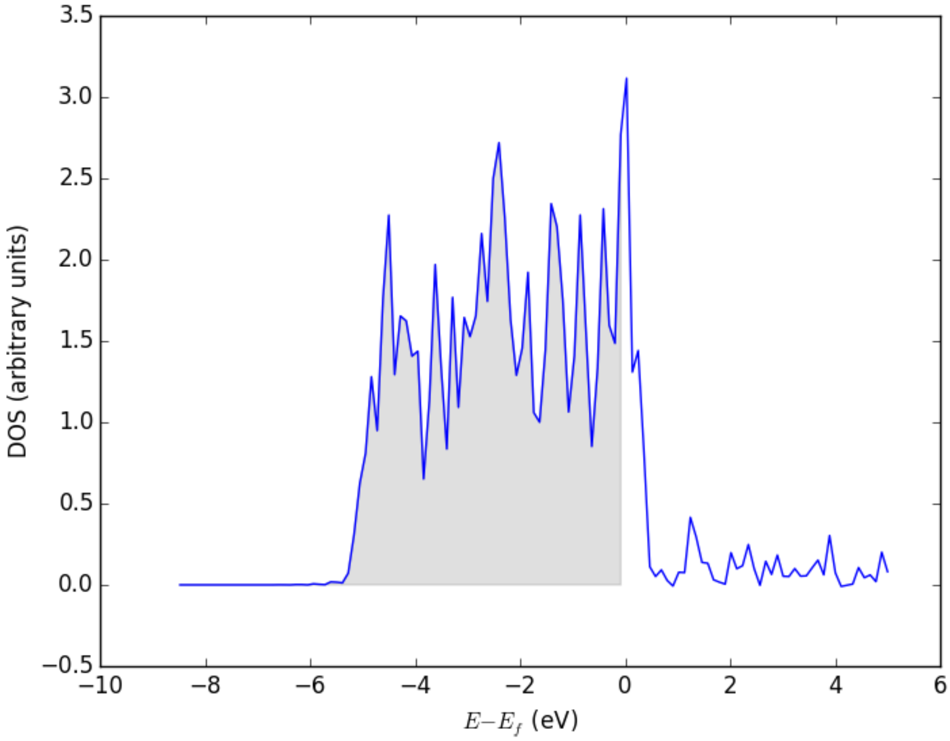


Figure 52: Atom projected \$d\$-band for bulk Pd. The shaded area corresponds to the occupied states below the Fermi level.

4.11.1 Effect of RWIGS on ADOS

Here we examine the effect of changing RWIGS on the number of counted electrons, and properties of the d-band moments.

```
from ase import Atoms, Atom
from vasp import Vasp

import matplotlib.pyplot as plt
import numpy as np

a = 3.9  # approximate lattice constant
b = a / 2.
bulk = Atoms([Atom('Pd', (0.0, 0.0, 0.0))],
             cell=[(0, b, b),
                   (b, 0, b),
                   (b, b, 0)])

RWIGS = [1.0, 1.1, 1.25, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 ]

ED, WD, N = [], [], []

for rwigs in RWIGS:
    calc = Vasp('bulk/pd-ados')
    calc.clone('bulk/pd-ados-rwigs-{0}'.format(rwigs))
    calc.set(rwigs={'Pd': rwigs})
    if calc.potential_energy is None:
        continue

        # now get results
        ados = VaspDos(efermi=calc.get_fermi_level())

```

```python
        energies = ados.energy
        dos = ados.site_dos(0, 'd')

        #we will select energies in the range of -10, 5
        ind = (energies < 5) & (energies > -10)

        energies = energies[ind]
        dos = dos[ind]

        Nstates = np.trapz(dos, energies)
        occupied = energies <= 0.0
        N_occupied_states = np.trapz(dos[occupied], energies[occupied])
        ed = np.trapz(energies * dos, energies) / np.trapz(dos, energies)
        wd2 = np.trapz(energies**2 * dos, energies) / np.trapz(dos, energies)

        N.append(N_occupied_states)
        ED.append(ed)
        WD.append(wd2**0.5)

plt.plot(RWIGS, N, 'bo', label='N. occupied states')
plt.legend(loc='best')
plt.xlabel('RWIGS ($\AA$)')
plt.ylabel('# occupied states')
plt.savefig('images/ados-rwigs-occupation.png')


fig, ax1 = plt.subplots()
ax1.plot(RWIGS, ED, 'bo', label='d-band center (eV)')
ax1.set_xlabel('RWIGS ($\AA$)')
ax1.set_ylabel('d-band center (eV)', color='b')
for tl in ax1.get_yticklabels():
    tl.set_color('b')

ax2 = ax1.twinx()
ax2.plot(RWIGS, WD, 'gs', label='d-band width (eV)')
ax2.set_ylabel('d-band width (eV)', color='g')
for tl in ax2.get_yticklabels():
    tl.set_color('g')

plt.savefig('images/ados-rwigs-moments.png')
plt.show()
```

Open the python script (dft-scripts/script-153.py).

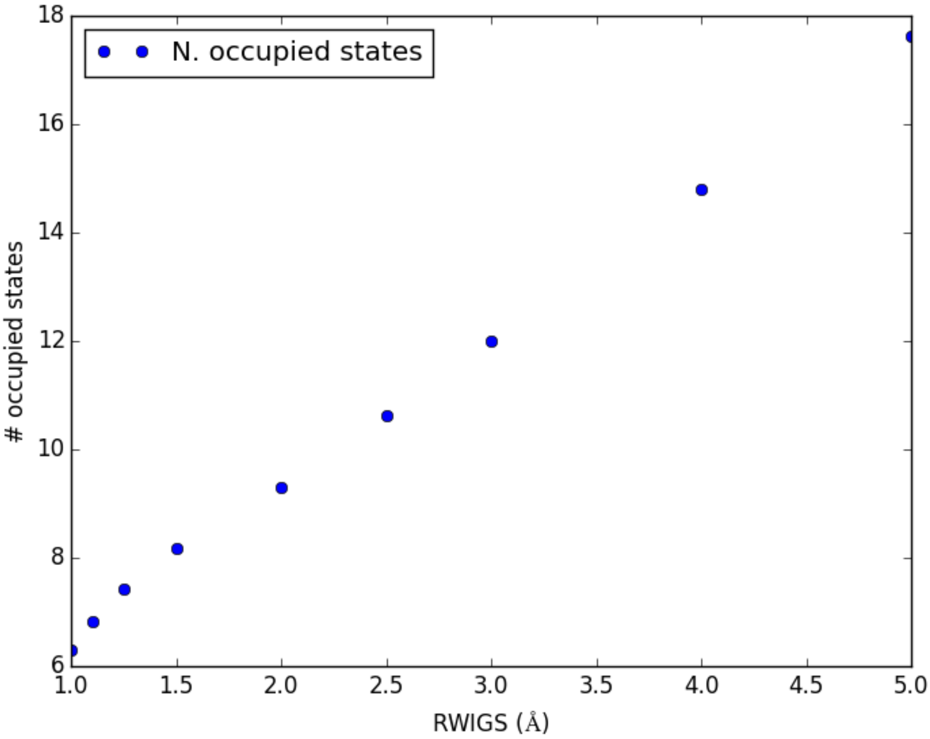


Figure 53: Effect of the RWIGS on the number of occupied *d*-states.

You can see the number of occupied states increases approximately linearly here with RWIGS. This is due to overcounting of neighboring electrons.

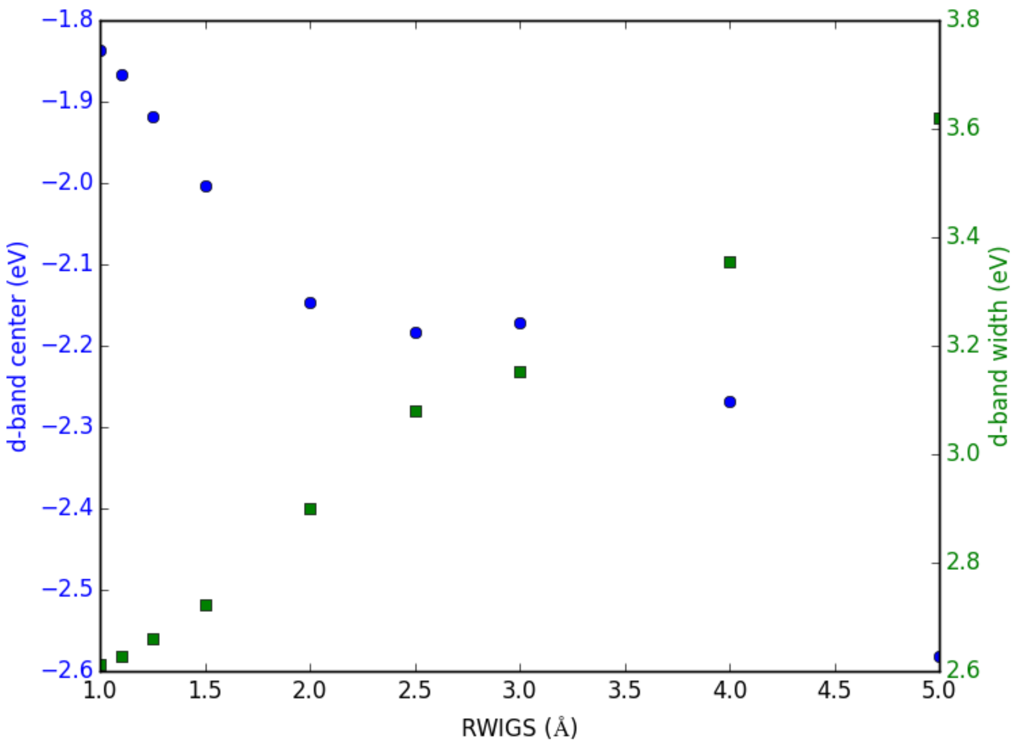


Figure 54: Effect of the RWIGS on the *d*-band center and width.

q
The d-band center and width also change.

4.12 Band structures

To compute a band structure we do two things. First, we compute the self-consistent band structure. Then we compute the band structure at the desired k-points. We will use Si as an example (adapted from http://bbs.sciencenet.cn/bbs/upload/20083418325986.pdf).

First, we get the self-consistent electron density in a calculation.

```
from vasp import Vasp
from ase import Atom, Atoms
from ase.visualize import view

a = 5.38936
atoms = Atoms([Atom('Si', [0, 0, 0]),
               Atom('Si', [0.25, 0.25, 0.25])])

atoms.set_cell([[a / 2., a / 2., 0.0],
                [0.0,  a / 2., a / 2.],
                [a / 2., 0.0, a / 2.]], scale_atoms=True)

calc = Vasp('bulk/Si-selfconsistent',
            xc='PBE',
            prec='Medium',
            lcharg=True,
            lwave=True,
            kpts=[4, 4, 4],
            atoms=atoms)
calc.run()
```

Open the python script (dft-scripts/script-154.py).

Now, we run a new calculation along the k-point path desired. The standard VASP way of doing this is to modify the INCAR and KPOINTS file and rerun VASP. We will not do that. Doing that results in some lost information if you overwrite the old files. We will copy the old directory to a new directory, using code to ensure this only happens one time.

```
from vasp import Vasp

wd = 'bulk/Si-bandstructure'

calc = Vasp('bulk/Si-selfconsistent')
calc.clone(wd)

kpts = [[0.5, 0.5, 0.0],   # L
        [0, 0, 0],         # Gamma
        [0, 0, 0],
        [0.5, 0.5, 0.5]]  # X

calc.set(kpts=kpts,
         reciprocal=True,
         kpts_nintersections=10,
         icharg=11)

print calc.run()
```

Open the python script (dft-scripts/script-155.py).

```
-3.62224484
```

We will learn how to manually parse the EIGENVAL file here to generate the band structure. The structure of the EIGENVAL file looks like this:

```
head -n 20 bulk/Si-bandstructure/EIGENVAL
```

Open the python script (dft-scripts/script-156.py).

```
    2     2     1     1
  0.1956688E+02  0.3810853E-09  0.3810853E-09  0.3810853E-09  0.5000000E-15
  1.000000000000000E-004
  CAR
 unknown system
      8      20       8

  0.5000000E+00  0.5000000E+00  0.0000000E+00  0.5000000E-01
    1       -1.826747
    2       -1.826743
    3        3.153321
    4        3.153347
    5        6.743989
    6        6.744017
    7       16.392596
    8       16.393943

  0.4444444E+00  0.4444444E+00  0.0000000E+00  0.5000000E-01
    1       -2.669487
    2       -0.918463
```

We can ignore the first five lines.

```python
f = open('bulk/Si-bandstructure/EIGENVAL', 'r')

line1 = f.readline()
line2 = f.readline()
line3 = f.readline()
line4 = f.readline()
comment = f.readline()
unknown, nkpoints, nbands = [int(x) for x in f.readline().split()]

blankline = f.readline()

band_energies = [[] for i in range(nbands)]

for i in range(nkpoints):
    x, y, z, weight = [float(x) for x in f.readline().split()]

    for j in range(nbands):
        fields = f.readline().split()
        id, energy = int(fields[0]), float(fields[1])
        band_energies[id - 1].append(energy)
    blankline = f.readline()
f.close()

import matplotlib.pyplot as plt

for i in range(nbands):
    plt.plot(range(nkpoints), band_energies[i])

ax = plt.gca()
ax.set_xticks([]) # no tick marks
plt.xlabel('k-vector')
plt.ylabel('Energy (eV)')
ax.set_xticks([0, 10, 19])
ax.set_xticklabels(['$L$', '$\Gamma$', '$X$'])
plt.savefig('images/Si-bandstructure.png')
```

Open the python script (dft-scripts/script-157.py).

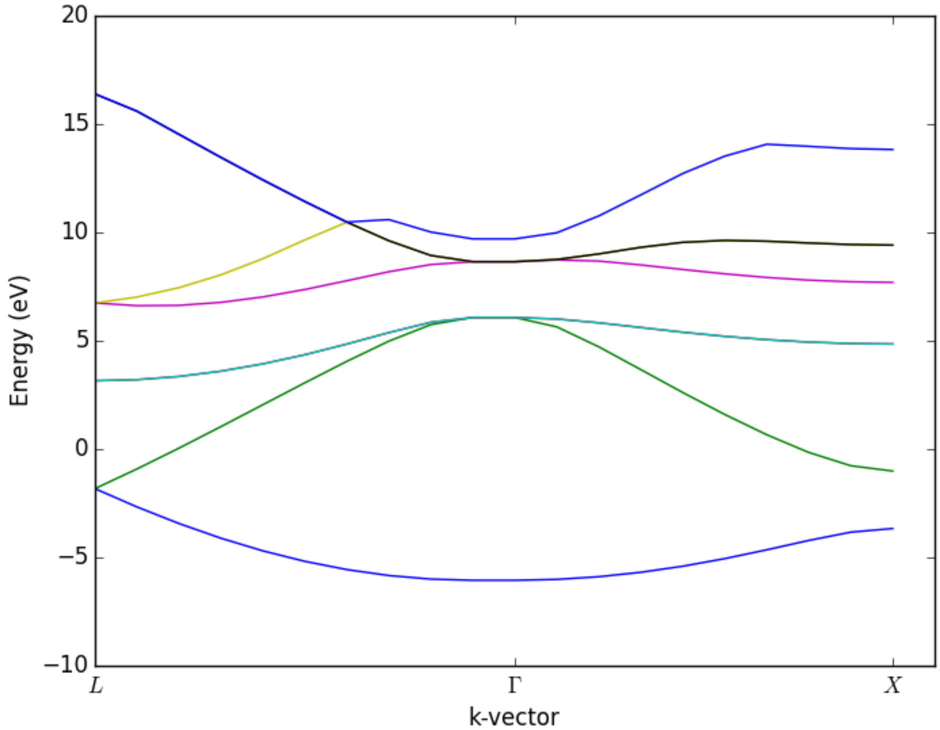


Figure 55: Calculated band-structure for Si.

Next we will examine the connection between band structures and density of states. In this example, we will compute the band structure of TiO_2 using a function built into vasp to do the analysis described above.

```
from vasp import Vasp

calc = Vasp('bulk/tio2/step3')
print calc.get_fermi_level()
calc.abort()
n, bands, p = calc.get_bandstructure(kpts_path=[('$\Gamma$', [0.0, 0.0, 0.0]),
                                                ('X', [0.5, 0.5, 0.0]),
                                                ('X', [0.5, 0.5, 0.0]),
                                                ('M', [0.0, 0.5, 0.5]),
                                                ('M', [0.0, 0.5, 0.5]),
                                                ('$\Gamma$', [0.0, 0.0, 0.0])])

p.savefig('images/tio2-bandstructure-dos.png')
```

Open the python script (dft-scripts/script-158.py).

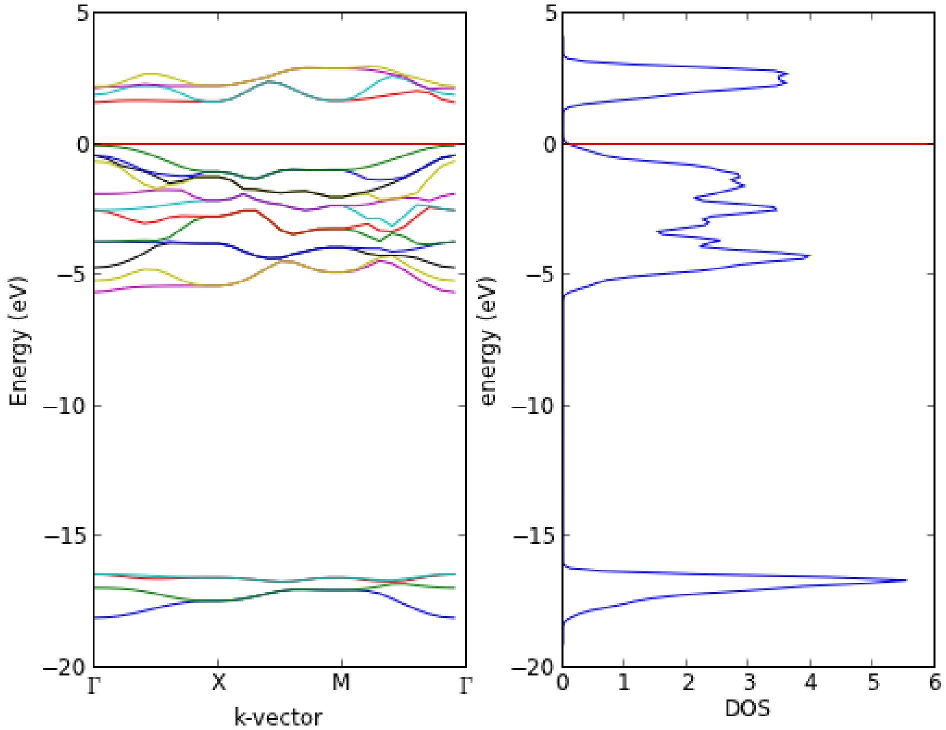


Figure 56: Band structure and total density of states for TiO_2.

4.12.1 create example showing band dispersion with change in lattice constant

In this section, we examine the effect of the lattice constant on the band structure. Since the lattice constant affects the overlap of neighboring atoms, we expect that smaller lattice constants will show more dispersion, i.e. broader bands. Larger lattice constants, in contrast, should show narrower bands. We examine this in silicon.

```
from vasp import Vasp
from ase import Atom, Atoms

calcs = []
for i, a in enumerate([4.7, 5.38936, 6.0]):

    atoms = Atoms([Atom('Si', [0, 0, 0]),
                   Atom('Si', [0.25, 0.25, 0.25])])

    atoms.set_cell([[a/2., a/2., 0.0],
                    [0.0,  a/2., a/2.],
                    [a/2., 0.0, a/2.]], scale_atoms=True)

    calc = Vasp('bulk/Si-bs-{0}'.format(i),
                xc='PBE',
                lcharg=True,
                lwave=True,
                kpts=[4, 4, 4],
                atoms=atoms)

    print(calc.run())
    calcs += [calc]


Vasp.wait(abort=True)
```

```python

for i, calc in enumerate(calcs):
    n, bands, p  = calc.get_bandstructure(kpts_path=[('L', [0.5,0.5,0.0]),
                                                      ('$\Gamma$', [0, 0, 0]),
                                                      ('$\Gamma$', [0, 0, 0]),
                                                      ('X', [0.5, 0.5, 0.5])],
                                          kpts_nintersections=10)

    if p is not None:
        png = 'images/Si-bs-{0}.png'.format(i)
        p.savefig(png)
```

Open the python script (dft-scripts/script-159.py).

```
-7.55662509
-10.80024435
-10.13735105
```

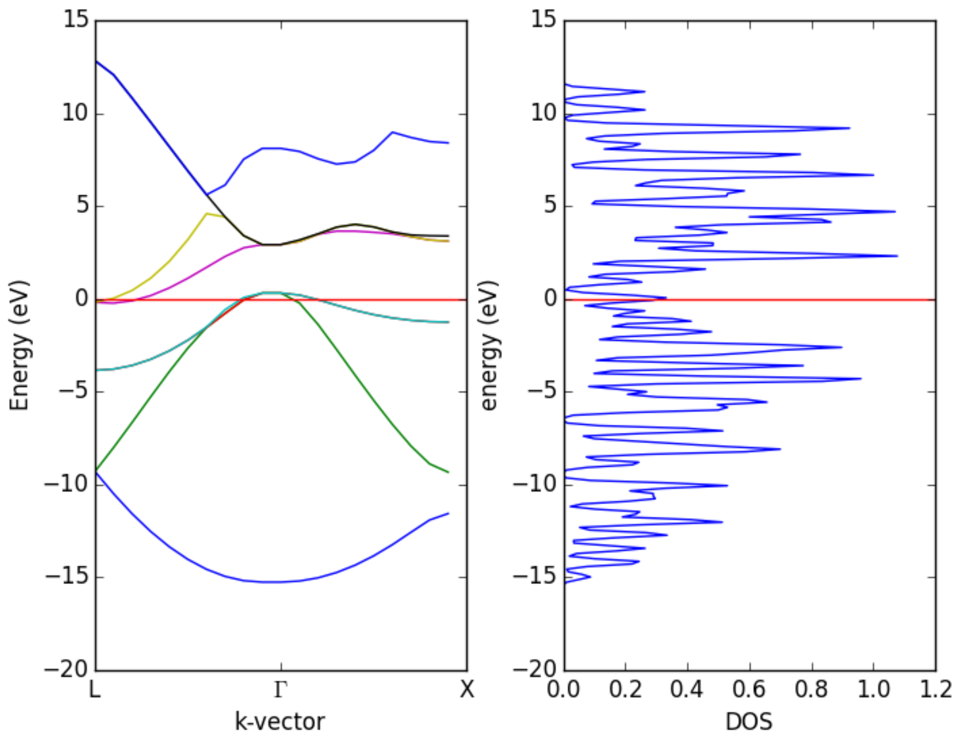


Figure 57: Si band structure for a=4.7

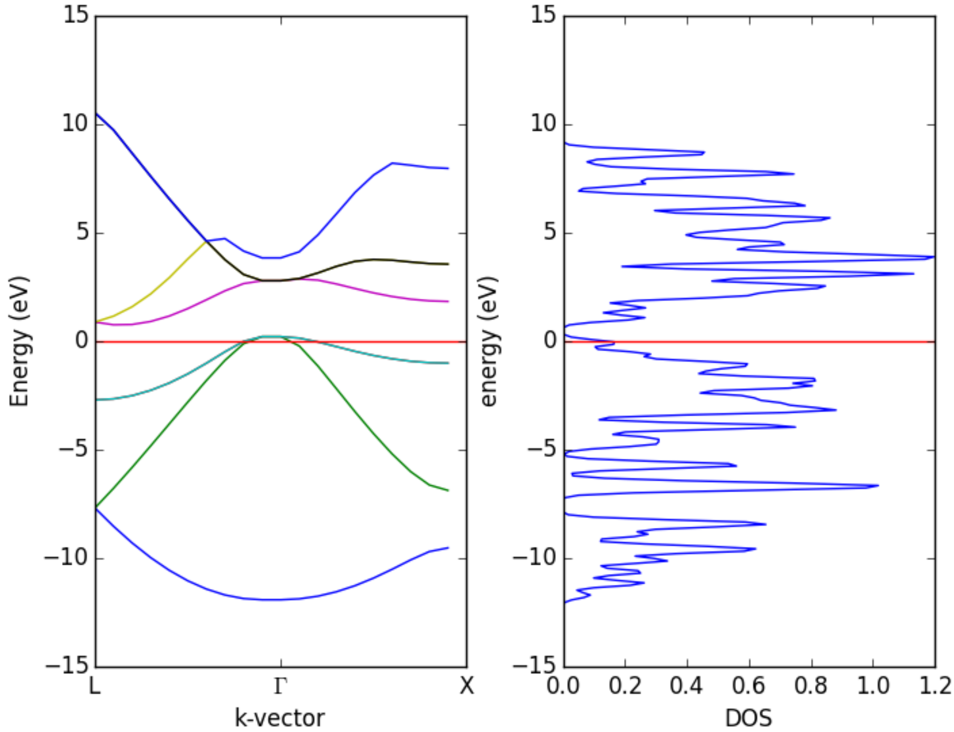


Figure 58: Si band structure for a=5.38936

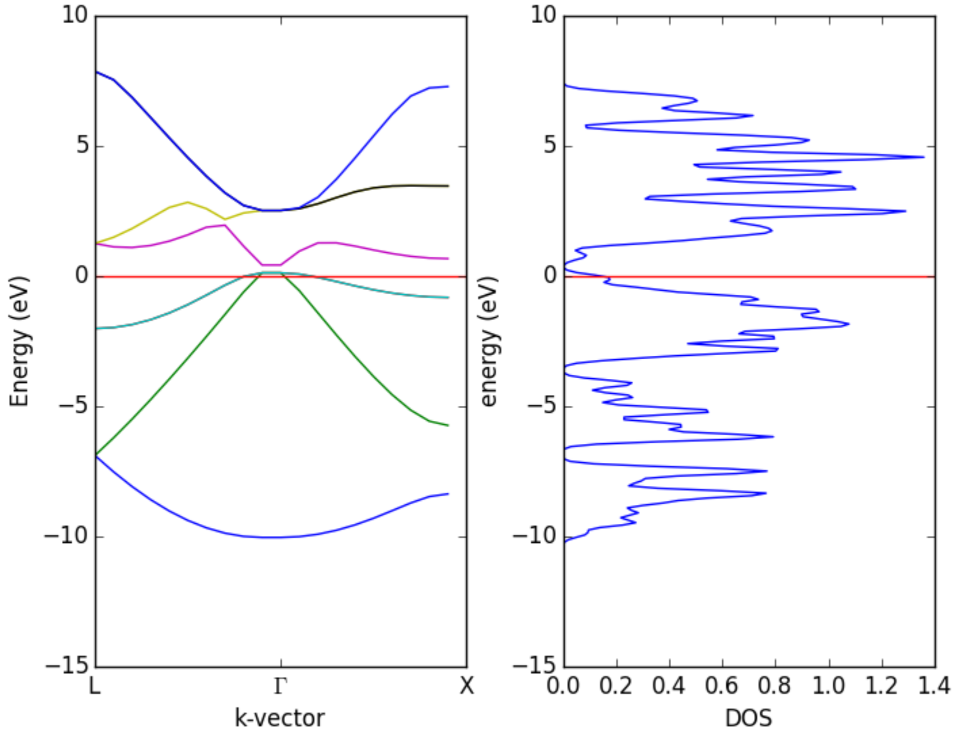


Figure 59: Si band structure for a=6.0

You can see the band structure for a=6.0 is notably sharper than the band structure for a=4.0.

4.13 Magnetism

4.13.1 Determining if a magnetic solution is energetically favorable

We can force a total magnetic moment onto a unit cell and compute the total energy as function of the total magnetic moment. If there is a minimum in the energy, then we know there is a lower energy magnetic solution than a non-magnetic solution. We use NUPDOWN to enforce the magnetic moment in the cell. Note that NUPDOWN can only be an integer. You cannot set it to be an arbitrary float.

```
from vasp import Vasp
from ase.lattice.cubic import BodyCenteredCubic

atoms = BodyCenteredCubic(directions=[[1, 0, 0],
                                      [0, 1, 0],
                                      [0, 0, 1]],
                                      size=(1, 1, 1),
                                      symbol='Fe')


calc = Vasp('bulk/Fe-bcc-fixedmagmom-{0:1.2f}'.format(0.0),
            xc='PBE',
            encut=300,
            kpts=[4, 4, 4],
            ispin=2,
            nupdown=0,
            atoms=atoms)

print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-160.py).

```
-15.34226703
```

```python
from vasp import Vasp
from ase.lattice.cubic import BodyCenteredCubic

atoms = BodyCenteredCubic(directions=[[1, 0, 0],
                                      [0, 1, 0],
                                      [0, 0, 1]],
                                      size=(1, 1, 1),
                                      symbol='Fe')

NUPDOWNS = [0.0, 2.0, 4.0, 5.0, 6.0, 8.0]
energies = []
for B in NUPDOWNS:
    calc = Vasp('bulk/Fe-bcc-fixedmagmom-{0:1.2f}'.format(B),
                xc='PBE',
                encut=300,
                kpts=[4, 4, 4],
                ispin=2,
                nupdown=B,
                atoms=atoms)
    energies.append(atoms.get_potential_energy())

if None in energies:
    calc.abort()

import matplotlib.pyplot as plt
plt.plot(NUPDOWNS, energies)
plt.xlabel('Total Magnetic Moment')
plt.ylabel('Energy (eV)')
plt.savefig('images/Fe-fixedmagmom.png')
```

Open the python script (dft-scripts/script-161.py).

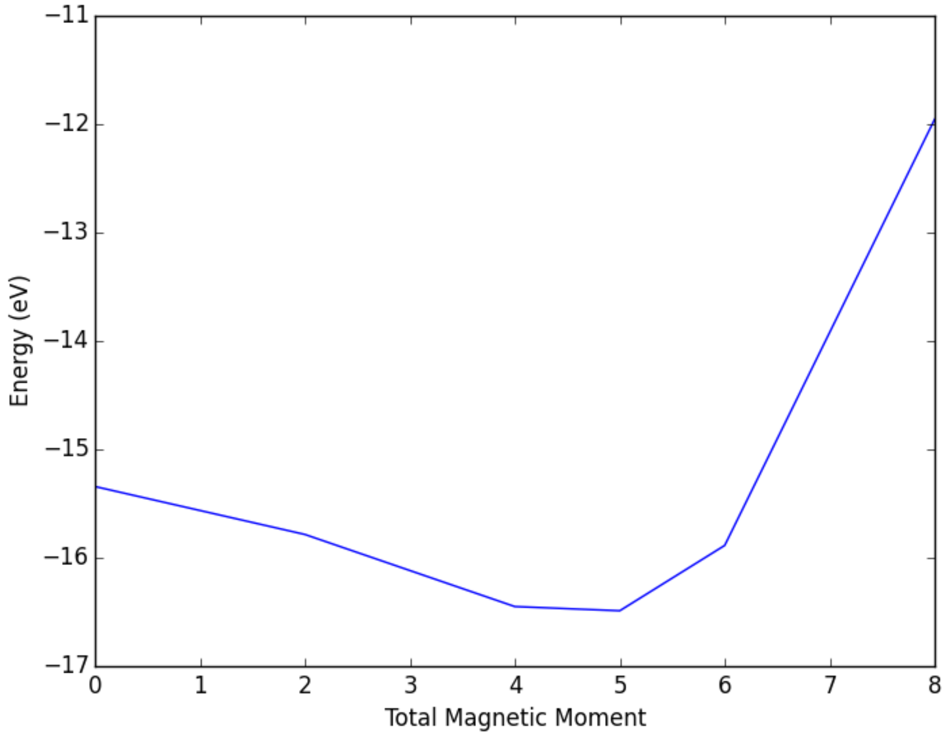


Figure 60: Total energy vs. total magnetic moment for bcc Fe.

You can see here there is a minimum in energy at a total magnetic moment somewhere between 4 and 5. There are two Fe atoms in the unit cell, which means the magnetic moment on each atom must be about 2.5 Bohr-magnetons. This is a good guess for a real calculation. Note that VASP recommends you overestimate the magnetic moment guesses if you are looking for ferromagnetic solutions.

To run a spin-polarized calculation with initial guesses on each atom, we must set the magnetic moment on the atoms. Here we set it through the `magmom` attribute on the atom. In the example after this, we set it in the `Atoms` object.

```
from vasp import Vasp
from ase.lattice.cubic import BodyCenteredCubic

atoms = BodyCenteredCubic(directions=[[1, 0, 0],
                                      [0, 1, 0],
                                      [0, 0, 1]],
                                      size=(1, 1, 1),
                                      symbol='Fe')

# set magnetic moments on each atom
for atom in atoms:
    atom.magmom = 2.5

calc = Vasp('bulk/Fe-bcc-sp-1',
            xc='PBE',
            encut=300,
            kpts=[4, 4, 4],
            ispin=2,
            lorbit=11, # you need this for individual magnetic moments
            atoms=atoms)

e = atoms.get_potential_energy()
B = atoms.get_magnetic_moment()
magmoms = atoms.get_magnetic_moments()
```

```

print 'Total magnetic moment is {0:1.2f} Bohr-magnetons'.format(B)
print 'Individual moments are {0} Bohr-magnetons'.format(magmoms)
```

Open the python script (dft-scripts/script-162.py).

```
Total magnetic moment is -0.01 Bohr-magnetons
Individual moments are [-0.013 -0.013] Bohr-magnetons
```

4.13.2 Antiferromagnetic spin states

In an antiferromagnetic material, there are equal numbers of spin up and down electrons that align in a regular pattern, but pointing in opposite directions so that there is no net magnetism. It is possible to model this by setting the magnetic moments on each `ase.Atom` object. lreal

```
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Fe', [0.00,  0.00,  0.00], magmom=5),
               Atom('Fe', [4.3,   4.3,   4.3],  magmom=-5),
               Atom('O', [2.15,  2.15,  2.15], magmom=0),
               Atom('O', [6.45,  6.45,  6.45], magmom=0)],
               cell=[[4.3,    2.15,    2.15],
                     [2.15,    4.3,     2.15],
                     [2.15,    2.15,     4.3]])

ca = Vasp('bulk/afm-feo',
          encut=350,
          prec='Normal',
          ispin=2,
          nupdown=0, # this forces a non-magnetic solution
          lorbit=11, # to get individual moments
          lreal=False,
          atoms=atoms)
print 'Magnetic moments = ', atoms.get_magnetic_moments()
print 'Total magnetic moment = ', atoms.get_magnetic_moment()
```

Open the python script (dft-scripts/script-163.py).

```
Magnetic moments =  [-0.061 -0.061  0.063  0.063]
Total magnetic moment =  -5e-06
```

You can see that even though the total magnetic moment is 0, there is a spin on both Fe atoms, and they are pointing in opposite directions. Hence, the sum of spins is zero, and this arrangement is called anti-ferromagnetic.

4.13.3 TODO NiO-FeO formation energies with magnetism

4.14 TODO phonons

[69]

phonopy

4.15 TODO solid state NEB

[70] Carter paper [71] recent Henkelman paper
http://scitation.aip.org/content/aip/journal/jcp/137/10/10.1063/1.4752249

5 Surfaces

5.1 Surface structures

As with molecules and bulk systems `ase` provides several convenience functions for making surfaces.

5.1.1 Simple surfaces

ase provides many utility functions to setup surfaces. Here is a simple example of an fcc111 Al surface. There are built in functions for fcc111, bcc110, bcc111, hcp001 and diamond111.

```
from ase.lattice.surface import fcc111
from ase.io import write
from ase.visualize import view

slab = fcc111('Al', size=(2, 2, 3), vacuum=10.0)
from ase.constraints import FixAtoms
constraint = FixAtoms(mask=[atom.tag >= 2 for atom in slab])
slab.set_constraint(constraint)

view(slab)
write('images/Al-slab.png', slab, rotation='90x', show_unit_cell=2)
```

Open the python script (dft-scripts/script-164.py).

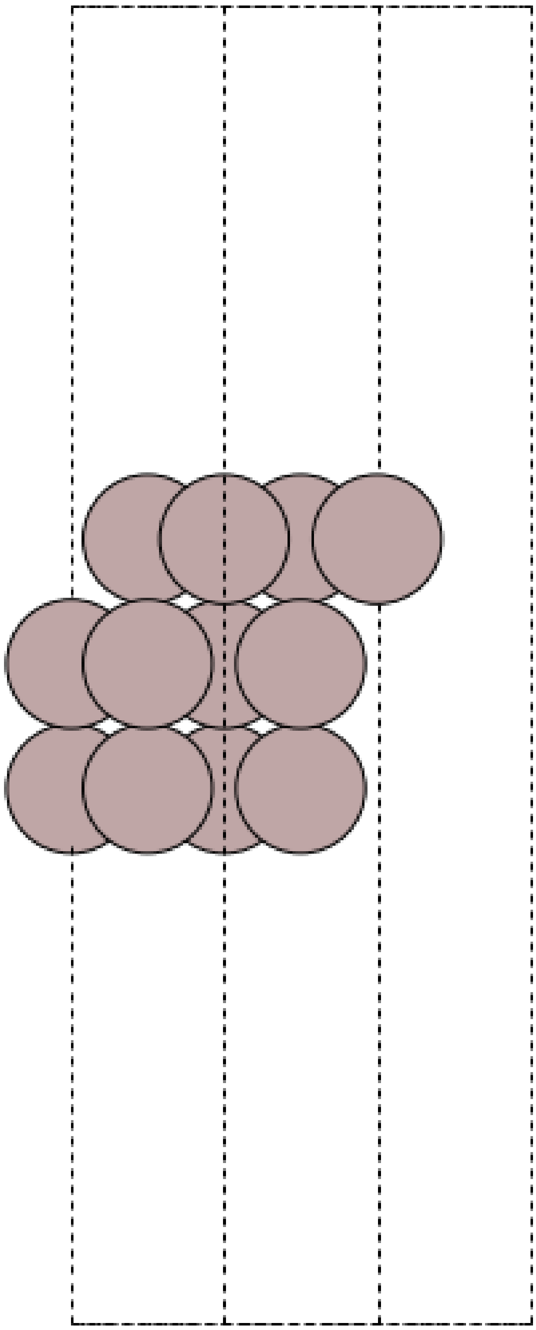


Figure 61: An Al(111) slab with three layers and 20 Å of vacuum.

5.1.2 Vicinal surfaces

The vast majority of surface calculations are performed on flat surfaces. This is partially because these surfaces tend to have the lowest surface energies, and thus are likely to be experimentally observed. The flat surfaces, also known as low Miller index surfaces, also have small unit cells, which tends to make them computationally affordable. There are, however, many reasons to model the properties of surfaces that are not flat. You may be interested in the reactivity of a step edge, for example, or you may use the lower cooridnation of steps as a proxy for nanoparticle reactivity. Many stepped surfaces are not that difficult to make now. The main idea in generating them is described here. `ase` provides a general function for making vicinal surfaces. Here is an example of a (211) surface.

```
from ase.lattice.surface import surface
from ase.io import write

# Au(211) with 9 layers
s1 = surface('Au', (2, 1, 1), 9)
s1.center(vacuum=10, axis=2)

write('images/Au-211.png',
      s1.repeat((3, 3, 1)),
      rotation='-30z,90x',  # change the orientation for viewing
      show_unit_cell=2)
```

Open the python script (dft-scripts/script-165.py).

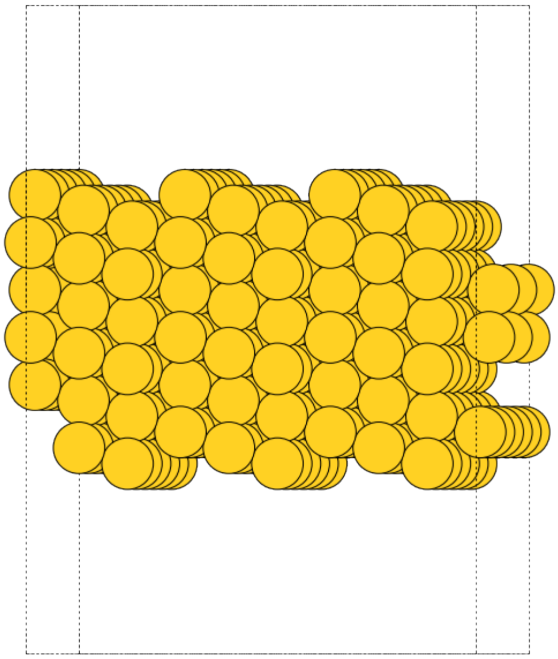


Figure 62: An Au(211) surface constructed with `ase`.

5.2 TODO Surface calculation parameters

There is one important parameter that is different for surfaces than for bulk calculations, the k-point grid. Assuming you have followed the convention that the z-axis is normal to the surface, the k-point grids for slab calculations always have the form of $M \times N \times 1$. To illustrate why, consider this example:

```
from ase.lattice.surface import fcc111
from vasp import Vasp

slab = fcc111('Al', size=(1, 1, 4), vacuum=10.0)

calc = Vasp('surfaces/Al-bandstructure',
            xc='PBE',
            encut=300,
            kpts=[6, 6, 6],
```

```
            lcharg=True,  # you need the charge density
            lwave=True,   # and wavecar for the restart
            atoms=slab)

n, bands, p = calc.get_bandstructure(kpts_path=[(r'$\Gamma$', [0, 0, 0]),
                                                ('$K1$', [0.5, 0.0, 0.0]),
                                                ('$K1$', [0.5, 0.0, 0.0]),
                                                ('$K2$', [0.5, 0.5, 0.0]),
                                                ('$K2$', [0.5, 0.5, 0.0]),
                                                (r'$\Gamma$', [0, 0, 0]),
                                                (r'$\Gamma$', [0, 0, 0]),
                                                ('$K3$', [0.0, 0.0, 1.0])],
                                     kpts_nintersections=10)

if p is None: calc.abort()

p.savefig('images/Al-slab-bandstructure.png')
```

Open the python script (dft-scripts/script-166.py).

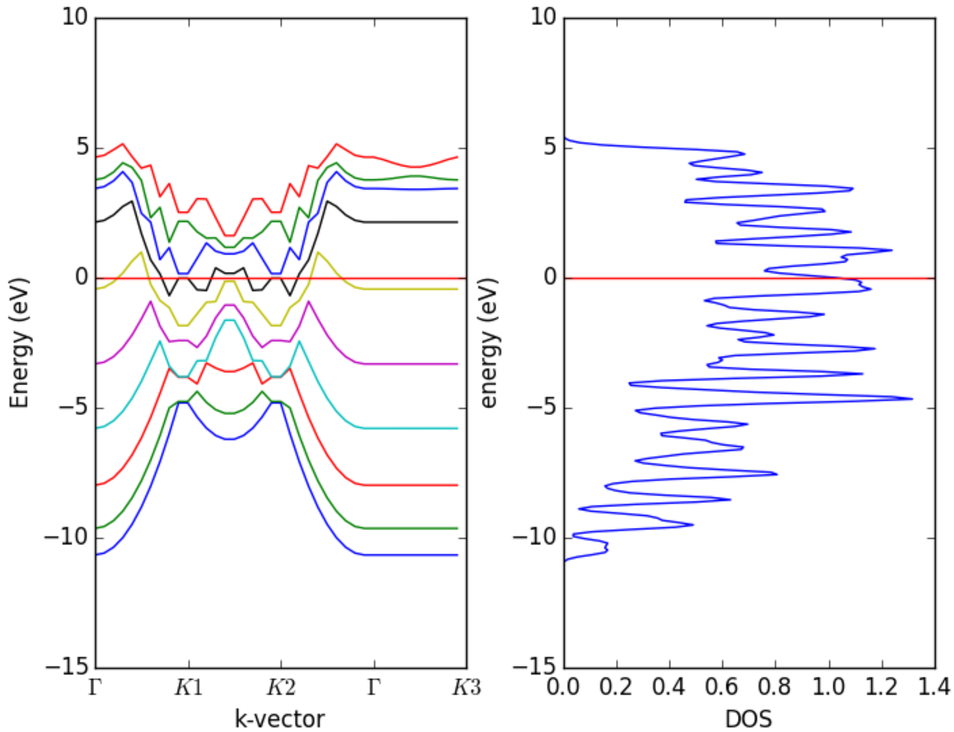


Figure 63: Band structure of an Al slab in the plane (path from Gamma to K1 to K2 to Gamma) and normal to the surface (Gamma to K3). Note the bands are flat in the direction normal to the surface, hence only one k-point is needed in this direction.

5.3 Surface relaxation

When a surface is created, the bulk symmetry is broken and consequently there will be forces on the surface atoms. We will examine some consequences of this with a simple Al slab. First, we show there are forces on the slab atoms.

```
from vasp import Vasp
from ase.lattice.surface import fcc111
```

```

atoms = fcc111('Al', size=(1, 1, 4), vacuum=10.0)

calc = Vasp('surfaces/Al-slab-unrelaxed',
            xc='PBE',
            kpts=[6, 6, 1],
            encut=350,
            atoms=atoms)

print(atoms.get_forces())
```

Open the python script (dft-scripts/script-167.py).

```
[[ 0.          0.         -0.01505445]
 [ 0.          0.          0.18818605]
 [ 0.          0.         -0.18818605]
 [ 0.          0.          0.01505445]]
```

Some points to note. The forces on the atoms have symmetry to them. That is because the slab is centered. Had the slab had an odd number of atoms, it is likely the center atom would have no forces on it. Next we consider the spacing between each layer in the slab. We do this for comparison later.

```
from vasp import Vasp

calc = Vasp('surfaces/Al-slab-unrelaxed')
atoms = calc.get_atoms()
print 'Total energy: {0:1.3f} eV'.format(atoms.get_potential_energy())

for i in range(1, len(atoms)):
    print '{0}  deltaz = {1:1.3f} angstroms'.format(i, atoms[i].z - atoms[i-1].z)
```

Open the python script (dft-scripts/script-168.py).

```
Total energy: -14.179 eV
1  deltaz = 2.338 angstroms
2  deltaz = 2.338 angstroms
3  deltaz = 2.338 angstroms
```

To reduce the forces, we can let VASP relax the geometry. We have to make some decisions about how to relax the slab. One choice would be to relax all the atoms in the slab. If we do that, then there will be no atoms with bulk like spacing unless we increase the slab thickness pretty dramatically. It is pretty common to freeze some atoms at the bulk coordinates, and let the others relax. We will freeze the bottom two layers (defined by tags 3 and 4) and let the first two layers relax. To do that we add constraints to the slab.

Note: the ase constraints are only partially used by `Vasp`. The `ase.constraints.FixAtoms` constraint gets written to the POSCAR file, and is then used internally in VASP. The only other constraint that VASP can use internally is `ase.constraints.FixScaled`. The other constraints are not written to the POSCAR and are not used by VASP.

```
from ase.lattice.surface import fcc111
atoms = fcc111('Al', size=(2, 2, 4), vacuum=10.0)
print([atom.z for atom in atoms])
print [atom.z <= 13 for atom in atoms]
```

Open the python script (dft-scripts/script-169.py).

```
[9.9999999999999982, 9.9999999999999982, 9.9999999999999982, 9.9999999999999982, 12.338268590217982,
[True, True, True, True, True, True, True, True, False, False, False, False, False, False, False, Fa
```

```python
from vasp import Vasp
from ase.lattice.surface import fcc111
from ase.constraints import FixAtoms

atoms = fcc111('Al', size=(1, 1, 4), vacuum=10.0)

constraint = FixAtoms(mask=[atom.tag >= 3 for atom in atoms])
atoms.set_constraint(constraint)

calc = Vasp('surfaces/Al-slab-relaxed',
            xc='PBE',
            kpts=[6, 6, 1],
            encut=350,
            ibrion=2,
            isif=2,
            nsw=10,
            atoms=atoms)

print(calc.potential_energy)
print(calc)
```

Open the python script (dft-scripts/script-170.py).

```
-14.17963819


Vasp calculation directory:
---------------------------
  [[/home-research/jkitchin/dft-book/surfaces/Al-slab-relaxed]]

Unit cell:
----------
       x       y       z             |v|
  v0   2.864   0.000   0.000       2.864 Ang
  v1   1.432   2.480   0.000       2.864 Ang
  v2   0.000   0.000  27.015      27.015 Ang
  alpha, beta, gamma (deg):   90.0  90.0  60.0
  Total volume:                  191.872 Ang^3
  Stress:    xx     yy     zz     yz     xz     xy
          0.006  0.006  0.002 -0.000 -0.000 -0.000 GPa

  ID  tag     sym    x         y         z        rmsF (eV/A)
  0   4       Al     0.000*    0.000*   10.000*      0.00
  1   3       Al     1.432*    0.827*   12.338*      0.00
  2   2       Al     2.864     1.653    14.677       0.19
  3   1       Al     0.000     0.000    17.015       0.01
  Potential energy: -14.1796 eV

INPUT Parameters:
-----------------
  pp         : PBE
  isif       : 2
  xc         : pbe
  kpts       : [6, 6, 1]
  encut      : 350
  lcharg     : False
  ibrion     : 2
  ismear     : 1
  lwave      : True
```

```
  sigma      : 0.1
  nsw        : 10

Pseudopotentials used:
----------------------
  Al: potpaw_PBE/Al/POTCAR (git-hash: ad7c649117f1490637e05717e30ab9a0dd8774f6)
```

You can see that atoms 2 and 3 (the ones we relaxed, because the have tags of 1 and 2, which are less than 3) now have very low forces on them and it appears that atoms 0 and 1 have no forces on them. That is because the FixAtoms constraint works by setting the forces on those atoms to zero. We can see in the next example that the z-positions of the relaxed atoms have indeed relaxed and changed, while the position of the frozen atoms did not change.

Note there are two versions of the forces. The true forces, and the forces when constraints are applied. ase.atoms.Atoms.get_forces

```python
from vasp import Vasp

calc = Vasp('surfaces/Al-slab-relaxed')
atoms = calc.get_atoms()

print('Constraints = True: ', atoms.get_forces(apply_constraint=True))

print('Constraints = False: ', atoms.get_forces(apply_constraint=False))
```

Open the python script (dft-scripts/script-171.py).

```
('Constraints = True: ', array([[ 0.        ,  0.        ,  0.        ],
       [ 0.        ,  0.        ,  0.        ],
       [ 0.        ,  0.        , -0.00435222],
       [ 0.        ,  0.        , -0.07264519]]))
('Constraints = False: ', array([[ 0.        ,  0.        ,  0.        ],
       [ 0.        ,  0.        ,  0.        ],
       [ 0.        ,  0.        , -0.00435222],
       [ 0.        ,  0.        , -0.07264519]]))

Constraints = True:  [[ 0.     0.     0.   ]
 [ 0.     0.     0.   ]
 [ 0.     0.    -0.049]
 [ 0.     0.    -0.019]]
Constraints = False:  [[ 0.     0.    -0.002]
 [ 0.     0.     0.069]
 [ 0.     0.    -0.049]
 [ 0.     0.    -0.019]]
```

```python
from vasp import Vasp
from ase.lattice.surface import fcc111

calc = Vasp('surfaces/Al-slab-relaxed')
atoms = calc.get_atoms()
print 'Total energy: {0:1.3f}'.format(atoms.get_potential_energy())

for i in range(1, len(atoms)):
    print 'd_({0},{1}) = {2:1.3f} angstroms'.format(i, i-1,
                                                    atoms[i].z - atoms[i-1].z)
```

Open the python script (dft-scripts/script-172.py).

```
Total energy: -14.182
d_(1,0) = 2.338 angstroms
d_(2,1) = 2.309 angstroms
d_(3,2) = 2.370 angstroms
```

Depending on the layer there is either slight contraction or expansion. These quantities are small, and careful convergence studies should be performed. Note the total energy change from unrelaxed to relaxed is not that large in this case (e.g., it is about 5 meV). This is usually the case for metals, where the relaxation effects are relatively small. In oxides and semiconductors, the effects can be large, and when there are adsorbates, the effects can be large also.

5.4 Surface reconstruction

We previously considered how relaxation can lower the surface energy. For some surfaces, a more extreme effect can reduce the surface energy: reconstruction. In a simple surface relaxation, the basic structure of a surface is preserved. However, sometimes there is a different surface structure that may have a lower surface energy. Some famous reconstructions include: Si-$\sqrt{7} \times \sqrt{7}$, Pt(100) hex reconstruction,[72,73] and the Au(111) herringbone reconstruction.

We will consider the (110) missing row reconstruction.[74] For some metals, especially Pt and Au, it is energetically favorable to form the so-called missing row reconstruction where every other row in the surface is "missing". It is favorable because it lowers the surface energy. Let us consider how we might calculate and predict that. It is straightforward to compute the energy of a (110) slab, and of a (110) slab with one row missing. However, these slabs contain different numbers of atoms, so we cannot directly compare the total energies to determine which energy is lower.

We have to consider where the missing row atoms have gone, so we can account for their energy. We will consider that they have gone into the bulk, and so we to consider the energy associated with the following transformation:

$\mathrm{slab}_{110} \rightarrow \mathrm{slab}_{\mathrm{missing\ row}} + \mathrm{bulk}$

Thus, if this change in energy: $E_{bulk} + E_{slab_{missingrow}} - E_{slab_{110}}$ is negative, then the formation of the missing row is expected to be favorable.

5.4.1 Au(110) missing row reconstruction

We first consider the Au(110) case, where the reconstruction is known to be favorable.

Clean Au(110) slab

```python
from ase.lattice.surface import fcc110
from ase.io import write
from ase.constraints import FixAtoms
from ase.visualize import view

atoms = fcc110('Au', size=(2, 1, 6), vacuum=10.0)
constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)
view(atoms)
```

Open the python script (dft-scripts/script-173.py).

```python
from vasp import Vasp
from ase.lattice.surface import fcc110
from ase.io import write
from ase.constraints import FixAtoms

atoms = fcc110('Au', size=(2, 1, 6), vacuum=10.0)
constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)

write('images/Au-110.png', atoms.repeat((2, 2, 1)), rotation='-90x', show_unit_cell=2)

print Vasp('surfaces/Au-110',
           xc='PBE',
           kpts=[6, 6, 1],
           encut=350,
           ibrion=2,
           isif=2,
```

```
            nsw=10,
            atoms=atoms).potential_energy
```

Open the python script (dft-scripts/script-174.py).

```
-35.92440066
```

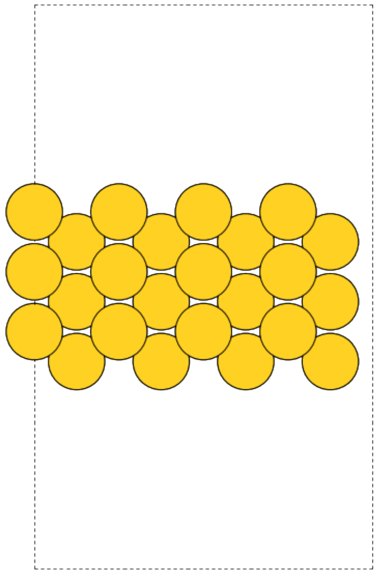


Figure 64: The unreconstructed Au(110) surface viewed from the side.

Missing row in Au(110)

```
from vasp import Vasp
from ase.lattice.surface import fcc110
from ase.io import write
from ase.constraints import FixAtoms

atoms = fcc110('Au', size=(2, 1, 6), vacuum=10.0)
del atoms[11]  # delete surface row

constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)

write('images/Au-110-missing-row.png',
      atoms.repeat((2, 2, 1)),
      rotation='-90x',
      show_unit_cell=2)

calc = Vasp('surfaces/Au-110-missing-row',
            xc='PBE',
            kpts=[6, 6, 1],
            encut=350,
            ibrion=2,
            isif=2,
            nsw=10,
            atoms=atoms)

calc.update()
```

Open the python script (dft-scripts/script-175.py).

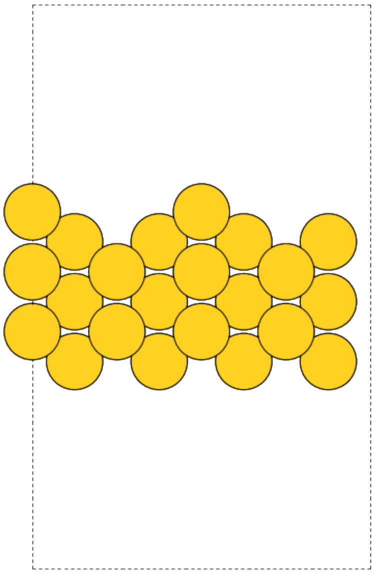


Figure 65: Au(110) with the missing row reconstruction.

Bulk Au

```
from vasp import Vasp
from ase.visualize import view
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic(directions=[[0, 1, 1],
                                      [1, 0, 1],
                                      [1, 1, 0]],
                                     size=(1, 1, 1),
                                     symbol='Au')

print Vasp('bulk/Au-fcc',
           xc='PBE',
           encut=350,
           kpts=[12, 12, 12],
           atoms=atoms).potential_energy
```

Open the python script (dft-scripts/script-176.py).

```
-3.19446244
```

Analysis of energies

```
from vasp import Vasp

print 'dE = {0:1.3f} eV'.format(Vasp('surfaces/Au-110-missing-row').potential_energy
                                + Vasp('bulk/Au-fcc').potential_energy
                                - Vasp('surfaces/Au-110').potential_energy)
```

Open the python script (dft-scripts/script-177.py).

```
natoms slab        = 12
natoms missing row = 11
natoms bulk        = 1
dE = -0.070 eV
```

The missing row formation energy is slightly negative. The magnitude of the formation energy is pretty small, but just slightly bigger than the typical convergence errors observed, so we should cautiously conclude that the reconstruction if favorable for Au(110). We made a lot of shortcuts in computing this quantity, including using the experimental lattice constant of Au, not checking for convergence in k-points or planewave cutoff, and not checking for convergence with respect to slab thickness or number of relaxed layers.

5.4.2 Ag(110) missing row reconstruction

Clean Ag(110) slab

```
from vasp import Vasp
from ase.lattice.surface import fcc110
from ase.io import write
from ase.constraints import FixAtoms

atoms = fcc110('Ag', size=(2, 1, 6), vacuum=10.0)
constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)

calc = Vasp('surfaces/Ag-110',
            xc='PBE',
            kpts=[6, 6, 1],
            encut=350,
            ibrion=2,
            isif=2,
            nsw=10,
            atoms=atoms)
calc.update()
```

Open the python script (dft-scripts/script-178.py).

Missing row in Ag(110)

```
from vasp import Vasp
from ase.lattice.surface import fcc110
from ase.io import write
from ase.constraints import FixAtoms

atoms = fcc110('Ag', size=(2, 1, 6), vacuum=10.0)
del atoms[11]  # delete surface row

constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)

Vasp('surfaces/Ag-110-missing-row',
     xc='PBE',
     kpts=[6, 6, 1],
     encut=350,
     ibrion=2,
     isif=2,
     nsw=10,
     atoms=atoms).update()
```

Open the python script (dft-scripts/script-179.py).

Bulk Ag

```
from vasp import Vasp
from ase.visualize import view
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic(directions=[[0, 1, 1],
                                      [1, 0, 1],
                                      [1, 1, 0]],
                                      size=(1, 1, 1),
                                      symbol='Ag')
```

```

Vasp('bulk/Ag-fcc',
     xc='PBE',
     encut=350,
     kpts=[12, 12, 12],
     atoms=atoms).update()
```

Open the python script (dft-scripts/script-180.py).

Analysis of energies

```
from vasp import Vasp

eslab = Vasp('surfaces/Ag-110').potential_energy

emissingrow = Vasp('surfaces/Ag-110-missing-row').potential_energy

ebulk = Vasp('bulk/Ag-fcc').potential_energy

print 'dE = {0:1.3f} eV'.format(emissingrow + ebulk - eslab)
```

Open the python script (dft-scripts/script-181.py).

```
dE = -0.010 eV
```

For Ag(110), the missing row formation energy is practically thermoneutral, i.e. not that favorable. This energy is so close to 0eV, that we cannot confidently say whether the reconstruction is favorable or not. Experimentally, the reconstruction is not seen on very clean Ag(110) although it is reported that some adsorbates may induce the reconstruction.[75]

5.4.3 Cu(110) missing row reconstruction

Clean Cu(110) slab

```
from vasp import Vasp
from ase.lattice.surface import fcc110
from ase.constraints import FixAtoms

atoms = fcc110('Cu', size=(2, 1, 6), vacuum=10.0)
constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)

Vasp('surfaces/Cu-110',
     xc='PBE',
     kpts=[6, 6, 1],
     encut=350,
     ibrion=2,
     isif=2,
     nsw=10,
     atoms=atoms).update()
```

Open the python script (dft-scripts/script-182.py).

Missing row in Cu(110)

```
from vasp import Vasp
from ase.lattice.surface import fcc110
from ase.constraints import FixAtoms

atoms = fcc110('Cu', size=(2, 1, 6), vacuum=10.0)
del atoms[11]  # delete surface row

constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
atoms.set_constraint(constraint)

Vasp('surfaces/Cu-110-missing-row',
```

```
      xc='PBE',
      kpts=[6, 6, 1],
      encut=350,
      ibrion=2,
      isif=2,
      nsw=10,
      atoms=atoms).update()
```

Open the python script (dft-scripts/script-183.py).

Bulk Cu

```
from vasp import Vasp
from ase.visualize import view
from ase.lattice.cubic import FaceCenteredCubic

atoms = FaceCenteredCubic(directions=[[0, 1, 1],
                                      [1, 0, 1],
                                      [1, 1, 0]],
                                     size=(1, 1, 1),
                                     symbol='Cu')

Vasp('bulk/Cu-fcc',
      xc='PBE',
      encut=350,
      kpts=[12, 12, 12],
      atoms=atoms).update()
```

Open the python script (dft-scripts/script-184.py).

Analysis

```
from vasp import Vasp

eslab = Vasp('surfaces/Cu-110').potential_energy

emissingrow = Vasp('surfaces/Cu-110-missing-row').potential_energy

ebulk = Vasp('bulk/Cu-fcc').potential_energy

print 'natoms slab        = {0}'.format(len(slab))
print 'natoms missing row = {0}'.format(len(missingrow))
print 'natoms bulk        = {0}'.format(len(bulk))

print 'dE = {0:1.3f} eV'.format(emissingrow + ebulk - eslab)
```

Open the python script (dft-scripts/script-185.py).

It is questionable whether we should consider this evidence of a missing row reconstruction because the number is small. That does not mean the reconstruction will not happen, but it could mean it is very easy to lift.

5.5 Surface energy

The easiest way to calculate surface energies is from this equation:

$\sigma = \frac{1}{2}(E_{slab} - \frac{N_{slab}}{N_{bulk}} E_{bulk})$

where E_{slab} is the total energy of a symmetric slab (i.e. one with inversion symmetry, and where both sides of the slab have been relaxed), E_{bulk} is the total energy of a bulk unit cell, N_{slab} is the number of atoms in the slab, and N_{bulk} is the number of atoms in the bulk unit cell. One should be sure that the bulk energy is fully converged with respect to k-points, and that the slab energy is also converged with respect to k-points. The energies should be compared at the same cutoff energies. The idea is then to increase the thickness of the slab until the surface energy σ converges.

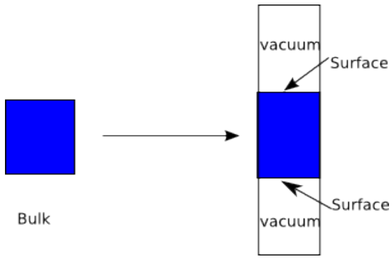


Figure 66: Schematic figure illustrating the calculation of a surface energy.

Unfortunately, this approach does not always work. The bulk system is treated subtly different than the slab system, particularly in the z-direction where the vacuum is (where typically only one k-point is used in slabs). Consequently, the k-point sampling is not equivalent in the two systems, and one can in general expect some errors due to this, with the best case being cancellation of the errors due to total k-point convergence. In the worst case, one can get a linear divergence in the surface energy with slab thickness.[76]

A variation of this method that usually results in better k-point error cancellation is to calculate the bulk unit cell energy using the slab unit cell with no vacuum space, with the same k-point mesh in the x and y directions, but with increased k-points in the z-direction. Thus, the bulk system and slab system have the same Brillouin zone in at least two dimensions. This maximizes the cancellation of k-point errors, but still does not guarantee convergence of the surface energy, as discussed in.[76,77]

For quick estimates of the surface energy, one of the methods described above is likely sufficient. The advantage of these methods is the small number of calculations required to obtain the estimate, one needs only a bulk calculation (which must be done anyhow to get the bulk lattice constant to create the slab), and a slab calculation that is sufficiently thick to get the estimate. Additional calculations are only required to test the convergence of the surface energy.

An alternative method for calculating surface energies that does not involve an explicit bulk calculation follows Ref.[77] The method follows from equation (ref{eq:se}) where for a N-atom slab, in the limit of N $\rightarrow \infty$,

$E_{slab} \approx 2\sigma + \frac{N_{slab}}{N_{bulk}} E_{bulk}$

Then, we can estimate E_{bulk} by plotting the total energy of the slab as a function of the slab thickness.

$\sigma = \lim_{N \rightarrow \infty} \frac{1}{2}(E_{slab}^N - N\Delta E_N)$

where $\Delta E_N = E_{slab}^N - E_{slab}^{N-1}$.

We will examine this approach here. We will use unrelaxed slabs for computational efficiency.

```python
from vasp import Vasp
from ase.lattice.surface import fcc111
import matplotlib.pyplot as plt

Nlayers = [3, 4, 5, 6, 7, 8, 9, 10, 11]
energies = []
sigmas = []

for n in Nlayers:

    slab = fcc111('Cu', size=(1, 1, n), vacuum=10.0)
    slab.center()

    calc = Vasp('bulk/Cu-layers/{0}'.format(n),
                xc='PBE',
                encut=350,
                kpts=[8, 8, 1],
                atoms=slab)
    calc.set_nbands(f=2)  # the default nbands in VASP is too low for Cu
    energies.append(slab.get_potential_energy())

calc.stop_if(None in energies)

for i in range(len(Nlayers) - 1):
```

```
    N = Nlayers[i]
    DeltaE_N = energies[i + 1] - energies[i]
    sigma = 0.5 * (-N * energies[i + 1] + (N + 1) * energies[i])
    sigmas.append(sigma)
    print 'nlayers = {1:2d} sigma = {0:1.3f} eV/atom'.format(sigma, N)

plt.plot(Nlayers[0:-1], sigmas, 'bo-')
plt.xlabel('Number of layers')
plt.ylabel('Surface energy (eV/atom)')
plt.savefig('images/Cu-unrelaxed-surface-energy.png')
```

Open the python script (dft-scripts/script-186.py).

```
nlayers =  3 sigma = 0.561 eV/atom
nlayers =  4 sigma = 0.398 eV/atom
nlayers =  5 sigma = 0.594 eV/atom
nlayers =  6 sigma = 0.308 eV/atom
nlayers =  7 sigma = 0.590 eV/atom
nlayers =  8 sigma = 0.332 eV/atom
nlayers =  9 sigma = 0.591 eV/atom
nlayers = 10 sigma = 0.392 eV/atom
```

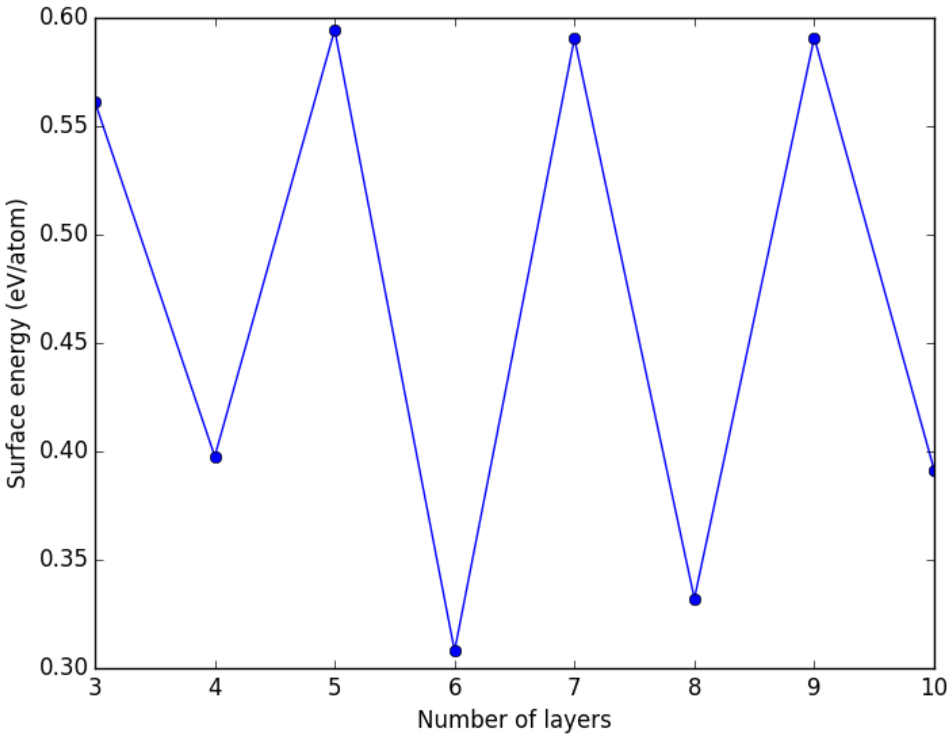


Figure 67: Surface energy of a Cu(111) slab as a function of thickness.

One reason for the oscillations may be quantum size effects.[78] In[79] the surface energy of Cu(111) is reported as 0.48 eV/atom, or 1.36 J/m^2. Here is an example showing a conversion between these two units. We use ase to compute the area of the unit cell from the norm of the cross-product of the vectors defining the surface unit cell.

```python
from ase.lattice.surface import fcc111
from ase.units import J, m
import numpy as np

slab = fcc111('Cu', size=(1, 1, 3), vacuum=10.0)
cell = slab.get_cell()

area = np.linalg.norm(np.cross(cell[0], cell[1]))  # area per atom

sigma = 0.48  # eV/atom

print 'sigma = {0} J/m^2'.format(sigma / area / (J / m**2))
```

Open the python script (dft-scripts/script-187.py).

```
sigma = 1.36281400415 J/m^2
```

5.5.1 Advanced topics in surface energy

The surface energies can be used to estimate the shapes of nanoparticles using a Wulff construction. See[80] for an example of computing Mo_2C surface energies and particle shapes, and[81] for an example of the influence of adsorbates on surface energies and particle shapes of Cu.

For a classic paper on trends in surface energies see.[82]

5.6 Work function

To get the work function, we need to have the local potential. This is not written by default in VASP, and we have to tell it to do that with the LVTOT and LVHAR keywords.

```python
from vasp import Vasp
import matplotlib.pyplot as plt
import numpy as np

calc = Vasp('surfaces/Al-slab-relaxed')
atoms = calc.get_atoms()

calc = Vasp('surfaces/Al-slab-locpot',
            xc='PBE',
            kpts=[6, 6, 1],
            encut=350,
            lvtot=True,  # write out local potential
            lvhar=True,  # write out only electrostatic potential, not xc pot
            atoms=atoms)
calc.wait()
ef = calc.get_fermi_level()
x, y, z, lp = calc.get_local_potential()

nx, ny, nz = lp.shape

axy = np.array([np.average(lp[:, :, z]) for z in range(nz)])
# setup the x-axis in realspace
uc = atoms.get_cell()
xaxis = np.linspace(0, uc[2][2], nz)

plt.plot(xaxis, axy)
plt.plot([min(xaxis), max(xaxis)], [ef, ef], 'k:')
plt.xlabel('Position along z-axis')
plt.ylabel('x-y averaged electrostatic potential')
plt.savefig('images/Al-wf.png')

ind = (xaxis > 0) & (xaxis < 5)
wf = np.average(axy[ind]) - ef
print ' The workfunction is {0:1.2f} eV'.format(wf)
```

Open the python script (dft-scripts/script-188.py).

```
The workfunction is 4.17 eV
```

The workfunction of Al is listed as 4.08 at http://hyperphysics.phy-astr.gsu.edu/hbase/tables/photoelec.html.

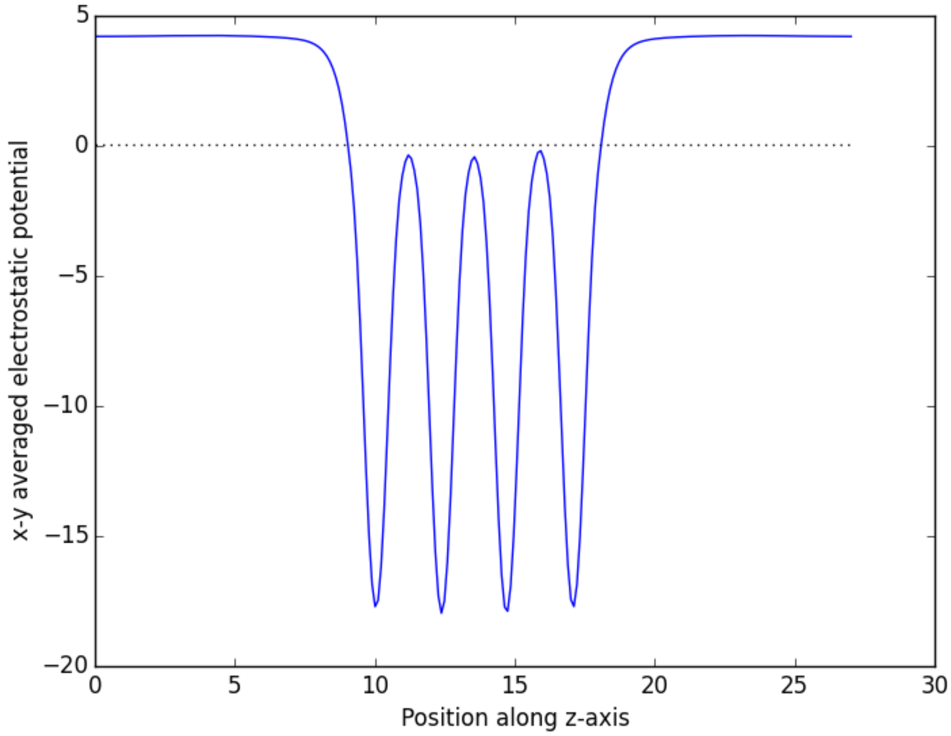


Figure 68: xy averaged local electrostatic potential of an Al(111) slab.

5.7 Dipole correction

A subtle problem can arise when an adsorbate is placed on one side of a slab with periodic boundary conditions, which is currently the common practice. The problem is that this gives the slab a dipole moment. The array of dipole moments created by the periodic boundary conditions generates an electric field that can distort the electron density of the slab and change the energy. The existence of this field in the vacuum also makes the zero-potential in the vacuum ill-defined, thus the work function is not well-defined. One solution to this problem is to use slabs with adsorbates on both sides, but then very thick (eight to ten layers) slabs must be used to ensure the adsorbates do not interact through the slab. An alternative solution, the dipole correction scheme, was developed by Neugebauer and Scheffler [83] and later corrected by Bengtsson. [84] In this technique, an external field is imposed in the vacuum region that exactly cancels the artificial field caused by the slab dipole moment. The advantage of this approach is that thinner slabs with adsorbates on only one side can be used.

There are also literature reports that the correction is small. [85] Nevertheless, in the literature the use of this correction is fairly standard, and it is typical to at least consider the correction.

Here we will just illustrate the effect.

5.7.1 Slab with no dipole correction

We simply run the calculation here, and compare the results later.

```python
# compute local potential of slab with no dipole
from ase.lattice.surface import fcc111, add_adsorbate
from vasp import Vasp
import matplotlib.pyplot as plt
from ase.io import write

slab = fcc111('Al', size=(2, 2, 2), vacuum=10.0)
add_adsorbate(slab, 'Na', height=1.2, position='fcc')

slab.center()
write('images/Na-Al-slab.png', slab, rotation='-90x', show_unit_cell=2)

print(Vasp('surfaces/Al-Na-nodip',
           xc='PBE',
           encut=340,
           kpts=[2, 2, 1],
           lcharg=True,
           lvtot=True,  # write out local potential
           lvhar=True,  # write out only electrostatic potential, not xc pot
           atoms=slab).potential_energy)
```

Open the python script (dft-scripts/script-189.py).

```
-22.55264459
```

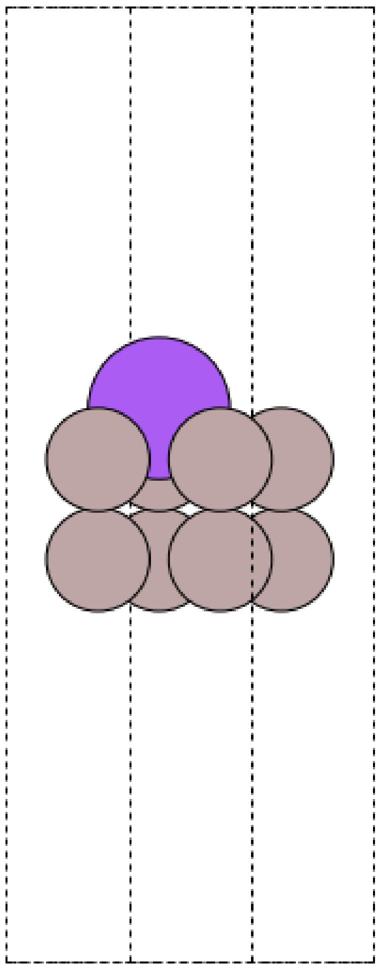


Figure 69: Example slab with a Na atom on it for illustrating the effects of dipole corrections.

5.7.2 TODO Slab with a dipole correction

Note this takes a considerably longer time to run than without a dipole correction! In VASP there are several levels of dipole correction to apply. You can use the IDIPOL tag to turn it on, and specify which direction to apply it in (1=x, 2=y, 3=z, 4=(x, y, z)). This simply corrects the total energy and forces. It does not change the contents of LOCPOT. For that, you have to also set the LDIPOL and DIPOL tags. It is not efficient to set all three at the same time for some reason. The VASP manual recommends you first set IDIPOL to get a converged electronic structure, and then set LDIPOL to True, and set the center of electron density in DIPOL. That makes these calculations a multistep process, because we must run a calculation, analyze the charge density to get the center of charge, and then run a second calculation.

```
# compute local potential with dipole calculation on
from ase.lattice.surface import fcc111, add_adsorbate
from vasp import Vasp
import numpy as np

slab = fcc111('Al', size=(2, 2, 2), vacuum=10.0)
add_adsorbate(slab, 'Na', height=1.2, position='fcc')

slab.center()

calc = Vasp('surfaces/Al-Na-dip',
            xc='PBE',
            encut=340,
            kpts=[2, 2, 1],
            lcharg=True,
            idipol=3,   # only along z-axis
            lvtot=True,  # write out local potential
            lvhar=True,  # write out only electrostatic potential, not xc pot
            atoms=slab)

calc.stop_if(calc.potential_energy is None)

x, y, z, cd = calc.get_charge_density()
n0, n1, n2 = cd.shape
nelements = n0 * n1 * n2
voxel_volume = slab.get_volume() / nelements
total_electron_charge = cd.sum() * voxel_volume

electron_density_center = np.array([(cd * x).sum(),
                                    (cd * y).sum(),
                                    (cd * z).sum()])
electron_density_center *= voxel_volume
electron_density_center /= total_electron_charge

print 'electron-density center = {0}'.format(electron_density_center)
uc = slab.get_cell()

# get scaled electron charge density center
sedc = np.dot(np.linalg.inv(uc.T), electron_density_center.T).T

# we only write 4 decimal places out to the INCAR file, so we round here.
sedc = np.round(sedc, 4)

calc.clone('surfaces/Al-Na-dip-step2')

# now run step 2 with dipole set at scaled electron charge density center
calc.set(ldipol=True, dipol=sedc)
print(calc.potential_energy)
```

Open the python script (dft-scripts/script-190.py).

5.7.3 Comparing no dipole correction with a dipole correction

To see the difference in what the dipole correction does, we now plot the potentials from each calculation.

```
from vasp import Vasp
import matplotlib.pyplot as plt
```

```python

calc = Vasp('surfaces/Al-Na-nodip')
atoms = calc.get_atoms()

x, y, z, lp = calc.get_local_potential()
nx, ny, nz = lp.shape

axy_1 = [np.average(lp[:, :, z]) for z in range(nz)]
# setup the x-axis in realspace
uc = atoms.get_cell()
xaxis_1 = np.linspace(0, uc[2][2], nz)

e1 = atoms.get_potential_energy()

calc = Vasp('surfaces/Al-Na-dip-step2')
atoms = calc.get_atoms()

x, y, z, lp = calc.get_local_potential()
nx, ny, nz = lp.shape

axy_2 = [np.average(lp[:, :, z]) for z in range(nz)]
# setup the x-axis in realspace
uc = atoms.get_cell()
xaxis_2 = np.linspace(0, uc[2][2], nz)

ef2 = calc.get_fermi_level()
e2 = atoms.get_potential_energy()

print 'The difference in energy is {0} eV.'.format(e2-e1)

plt.plot(xaxis_1, axy_1, label='no dipole correction')
plt.plot(xaxis_2, axy_2, label='dipole correction')
plt.plot([min(xaxis_2), max(xaxis_2)], [ef2, ef2], 'k:', label='Fermi level')
plt.xlabel('z ($\AA$)')
plt.ylabel('xy-averaged electrostatic potential')
plt.legend(loc='best')
plt.savefig('images/dip-vs-nodip-esp.png')
```

Open the python script (dft-scripts/script-191.py).

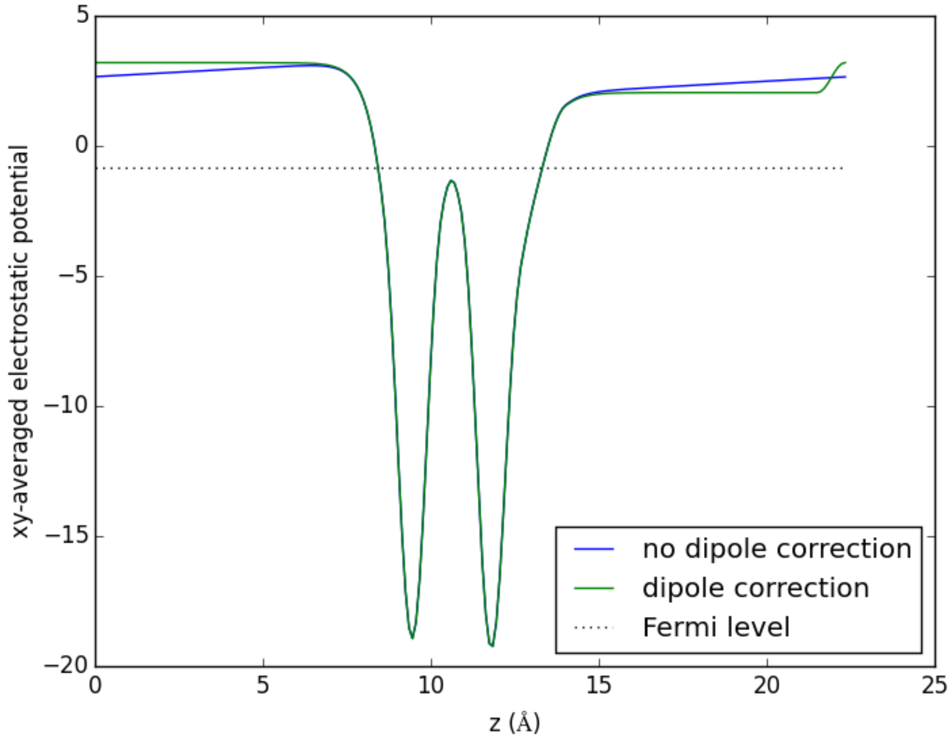


Figure 70: Comparison of the electrostatic potentials with a dipole correction and without it.

The key points to notice in this figure are:

1. The two deep dips are where the atoms are.
2. Without a dipole correction, the electrostatic potential never flattens out. there is near constant slope in the vacuum region, which means there is an electric field there.
3. With a dipole correction the potential is flat in the vacuum region, except for the step jump near 23 Å.
4. The difference between the Fermi level and the flat vacuum potential is the work function.
5. The difference in energy with and without the dipole correction here is small.

5.8 Adsorption energies

5.8.1 Simple estimate of the adsorption energy

Calculating an adsorption energy amounts to computing the energy of the following kind of reaction:
slab + gas-phase molecule → slab_adsorbate + products

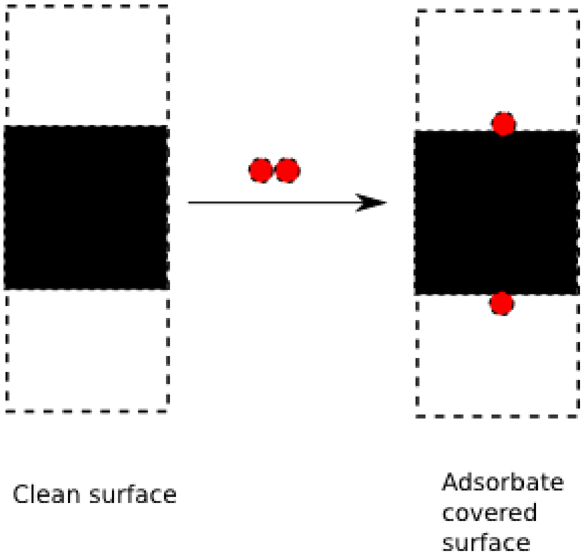


Figure 71: Schematic of an adsorption process.

There are many variations of this idea. The slab may already have some adsorbates on it, the slab may reconstruct on adsorption, the gas-phase molecule may or may not dissociate, and the products may or may not stick to the surface. We have to decide where to put the adsorbates, i.e. what site to put them on, and some sites will be more stable than others. We will consider the dissociative adsorption of O_2 on three sites of a Pt(111) slab. We will assume the oxygen molecule has split in half, and that the atoms have moved far apart. We will model the oxygen coverage at 0.25 ML, which means we need to use a 2×2 surface unit cell. For computational speed, we will freeze the slab, but allow the adsorbate to relax.

$\Delta H_{ads}(eV/O) = E_{slab+O} - E_{slab} - 0.5 * E_{O_2}$

Calculations

clean slab calculation

```
from vasp import Vasp
from ase.lattice.surface import fcc111
from ase.constraints import FixAtoms

atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)
constraint = FixAtoms(mask=[True for atom in atoms])
atoms.set_constraint(constraint)

from ase.io import write
write('images/Pt-fcc-ori.png', atoms, show_unit_cell=2)

print(Vasp('surfaces/Pt-slab',
           xc='PBE',
           kpts=[4, 4, 1],
           encut=350,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-192.py).

```
-68.23616204
```

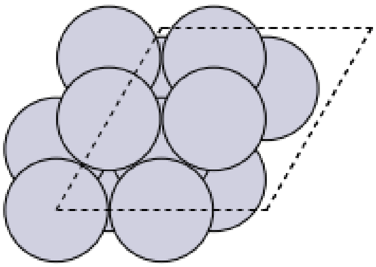


Figure 72: Pt(111) fcc surface

fcc site

```
from vasp import Vasp

from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms

atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)

# note this function only works when atoms are created by the surface module.
add_adsorbate(atoms, 'O', height=1.2, position='fcc')

constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
atoms.set_constraint(constraint)

from ase.io import write
write('images/Pt-fcc-site.png', atoms, show_unit_cell=2)

print(Vasp('surfaces/Pt-slab-O-fcc',
           xc='PBE',
           kpts=[4, 4, 1],
           encut=350,
           ibrion=2,
           nsw=25,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-193.py).

```
-74.23018764
```

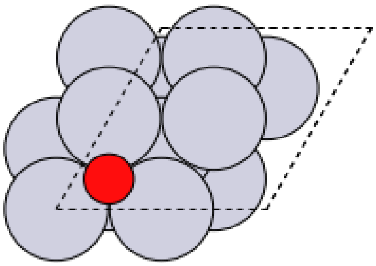


Figure 73: FCC site.

O atom on the bridge site

```
from vasp import Vasp
from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms

atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)

```

```
# note this function only works when atoms are created by the surface module.
add_adsorbate(atoms, 'O', height=1.2, position='bridge')

constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
atoms.set_constraint(constraint)

print(Vasp('surfaces/Pt-slab-O-bridge',
           xc='PBE',
           kpts=[4, 4, 1],
           encut=350,
           ibrion=2,
           nsw=25,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-194.py).

```
-74.23023073
```

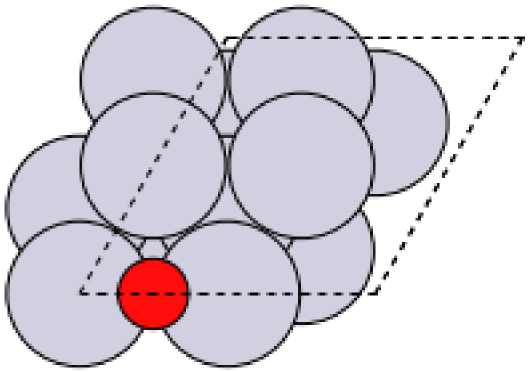


Figure 74: Initial geometry of the bridge site. It is definitely on the bridge.

hcp site

```
from vasp import Vasp
from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms

atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)

# note this function only works when atoms are created by the surface module.
add_adsorbate(atoms, 'O', height=1.2, position='hcp')

constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
atoms.set_constraint(constraint)

from ase.io import write
write('images/Pt-hcp-o-site.png', atoms, show_unit_cell=2)

print(Vasp('surfaces/Pt-slab-O-hcp',
           xc='PBE',
           kpts=[4, 4, 1],
           encut=350,
           ibrion=2,
           nsw=25,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-195.py).

```
-73.76942127
```

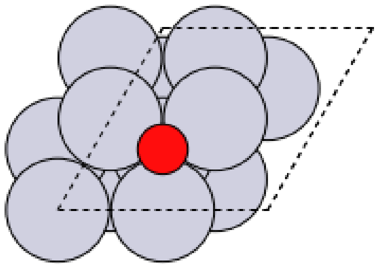


Figure 75: HCP site.

Analysis of adsorption energies

```
from vasp import Vasp
from ase.io import write

calc = Vasp('surfaces/Pt-slab')
atoms = calc.get_atoms()
e_slab = atoms.get_potential_energy()
write('images/pt-slab.png', atoms,show_unit_cell=2)

calc = Vasp('surfaces/Pt-slab-O-fcc')
atoms = calc.get_atoms()
e_slab_o_fcc = atoms.get_potential_energy()
write('images/pt-slab-fcc-o.png', atoms,show_unit_cell=2)

calc = Vasp('surfaces/Pt-slab-O-hcp')
atoms = calc.get_atoms()
e_slab_o_hcp = atoms.get_potential_energy()
write('images/pt-slab-hcp-o.png', atoms,show_unit_cell=2)

calc = Vasp('surfaces/Pt-slab-O-bridge')
atoms = calc.get_atoms()
e_slab_o_bridge = atoms.get_potential_energy()
write('images/pt-slab-bridge-o.png', atoms,show_unit_cell=2)

calc = Vasp('molecules/O2-sp-triplet-350')
atoms = calc.get_atoms()
e_O2 = atoms.get_potential_energy()

Hads_fcc = e_slab_o_fcc - e_slab - 0.5 * e_O2
Hads_hcp = e_slab_o_hcp - e_slab - 0.5 * e_O2
Hads_bridge = e_slab_o_bridge - e_slab - 0.5 * e_O2

print 'Hads (fcc)    = {0} eV/O'.format(Hads_fcc)
print 'Hads (hcp)    = {0} eV/O'.format(Hads_hcp)
print 'Hads (bridge) = {0} eV/O'.format(Hads_bridge)
```

Open the python script (dft-scripts/script-196.py).

You can see the hcp site is not as energetically favorable as the fcc site. Interestingly, the bridge site seems to be as favorable as the fcc site. This is not correct, and to see why, we have to look at the final geometries of each calculation. First the fcc (Figure 76 and hcp (Figure 77 sites, which look like we expect.

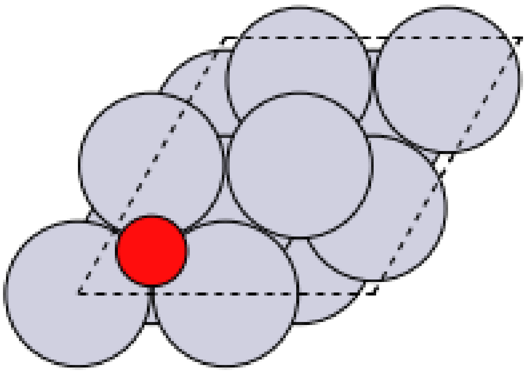


Figure 76: Final geometry of the fcc site.

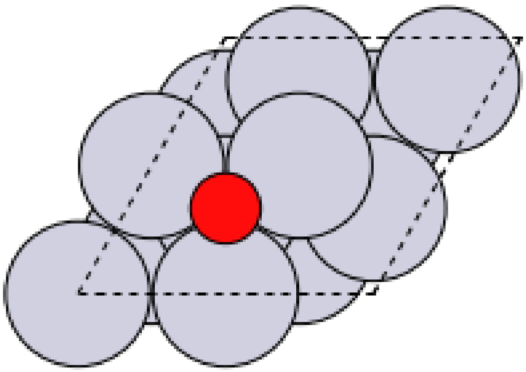


Figure 77: Final geometry of the hcp site.

The bridge site (Figure 78, however, is clearly not at a bridge site!

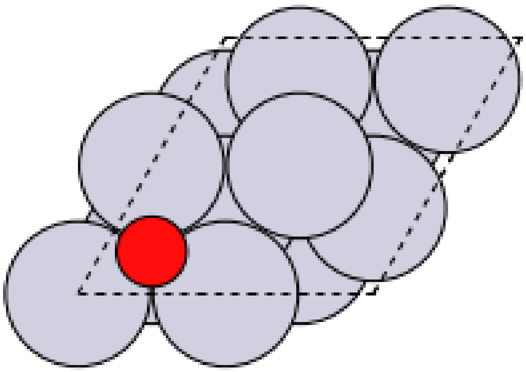


Figure 78: Final geometry of the bridge site. You can see that the oxygen atom ended up in the fcc site.

Let us see what the original geometry and final geometry for the bridge site were. The POSCAR contains the initial geometry (as long as you haven't copied CONTCAR to POSCAR), and the CONTCAR contains the final geometry.

```python
from ase.io import read, write

atoms = read('surfaces/Pt-slab-O-bridge/POSCAR')
write('images/Pt-o-brige-ori.png', atoms, show_unit_cell=2)

atoms = read('surfaces/Pt-slab-O-bridge/CONTCAR')
write('images/Pt-o-brige-final.png', atoms, show_unit_cell=2)
```

Open the python script (dft-scripts/script-197.py).

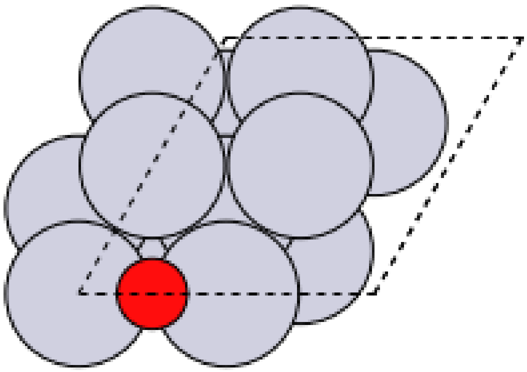


Figure 79: Initial geometry of the bridge site. It is definitely on the bridge.

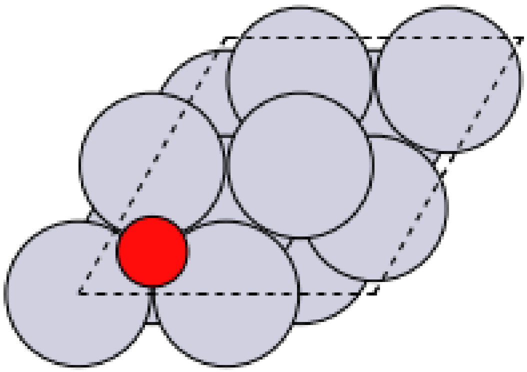


Figure 80: Final geometry of the bridge site. It has fallen into the fcc site.

You can see the problem. We should not call the adsorption energy from this calculation a bridge site adsorption energy because the O atom is actually in an fcc site! This kind of result can happen with relaxation, and you should always check that the result you get makes sense. Next, we consider how to get a bridge site adsorption energy by using constraints.

Some final notes:

1. We did not let the slabs relax in these examples, and allowing them to relax is likely to have a big effect on the adsorption energies. You have to decide how many layers to relax, and check for convergence with respect to the number of layers.
2. The slabs were pretty thin. It is typical these days to see slabs that are 4-5 or more layers thick.
3. We did not consider how well converged the calculations were with respect to k-points or ENCUT.
4. We did not consider the effect of the error in O_2 dissociation energy on the adsorption energies.
5. We did not consider coverage effects (see Coverage dependence).

Adsorption on bridge site with constraints To prevent the oxygen atom from sliding down into the fcc site, we have to constrain it so that it only moves in the z-direction. This is an artificial constraint; the bridge site is only metastable. But there are lots of reasons you might want to do this anyway. One is the bridge site is a transition state for diffusion between the fcc and hcp sites. Another is to understand the role of coordination in the adsorption energies. We use a `ase.constraints.FixScaled` constraint in ase to constrain the O atom so it can only move in the z-direction (actually so it can only move in the direction of the third unit cell vector, which only has a z-component).

```
from vasp import Vasp

from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms, FixScaled
from ase.io import write

atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)

# note this function only works when atoms are created by the surface module.
add_adsorbate(atoms, 'O', height=1.2, position='bridge')
constraint1 = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
# fix in xy-direction, free in z. actually, freeze movement in surface
# unit cell, and free along 3rd lattice vector
constraint2 = FixScaled(atoms.get_cell(), 12, [True, True, False])

atoms.set_constraint([constraint1, constraint2])
write('images/Pt-O-bridge-constrained-initial.png', atoms, show_unit_cell=2)
print 'Initial O position: {0}'.format(atoms.positions[-1])

calc = Vasp('surfaces/Pt-slab-O-bridge-xy-constrained',
            xc='PBE',
            kpts=[4, 4, 1],
            encut=350,
            ibrion=2,
            nsw=25,
            atoms=atoms)
e_bridge = atoms.get_potential_energy()

write('images/Pt-O-bridge-constrained-final.png', atoms, show_unit_cell=2)
print 'Final O position   : {0}'.format(atoms.positions[-1])

# now compute Hads
calc = Vasp('surfaces/Pt-slab')
atoms = calc.get_atoms()
e_slab = atoms.get_potential_energy()


calc = Vasp('molecules/O2-sp-triplet-350')
atoms = calc.get_atoms()
e_O2 = atoms.get_potential_energy()

calc.stop_if(None in [e_bridge, e_slab, e_O2])

Hads_bridge = e_bridge - e_slab - 0.5*e_O2

print 'Hads (bridge) = {0:1.3f} eV/O'.format(Hads_bridge)
```

Open the python script (dft-scripts/script-198.py).

```
Initial O position: [  1.38592929   0.          15.72642611]
Final O position   : [  1.38592929   0.          15.9685262 ]
Hads (bridge) = -0.512 eV/O
```

You can see that only the z-position of the O atom changed. Also, the adsorption energy of O on the bridge site is **much** less favorable than on the fcc or hcp sites.

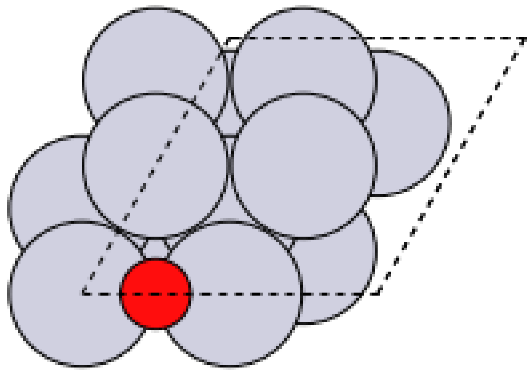


Figure 81: Initial state of the O atom on the bridge site.

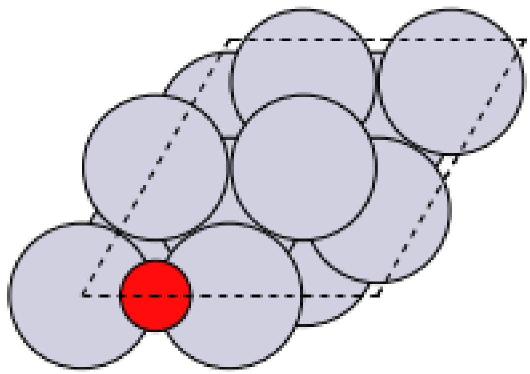


Figure 82: Final state of the constrained O atom, still on the bridge site.

5.8.2 Coverage dependence

The adsorbates on the surface can interact with each other which results in coverage dependent adsorption energies.[86] Coverage dependence is not difficult to model; we simply compute adsorption energies in different size unit cells, and/or with different adsorbate configurations. Here we consider dissociative oxygen adsorption at 1ML on Pt(111) in an fcc site, which is one oxygen atom in a 1×1 unit cell.

For additional reading, see these references from our work:

- Correlations of coverage dependence of oxygen adsorption on different metals[87,88]
- Coverage effects of atomic adsorbates on Pd(111)[89]
- Simple model for estimating coverage dependence[86]
- Coverage effects on alloys[90]

clean slab calculation

```
from vasp import Vasp
from ase.io import write
from ase.lattice.surface import fcc111
from ase.constraints import FixAtoms

atoms = fcc111('Pt', size=(1, 1, 3), vacuum=10.0)
constraint = FixAtoms(mask=[True for atom in atoms])
atoms.set_constraint(constraint)
```

```

write('images/Pt-fcc-1ML.png', atoms, show_unit_cell=2)

print(Vasp('surfaces/Pt-slab-1x1',
           xc='PBE',
           kpts=[8, 8, 1],
           encut=350,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-199.py).

```
-17.05903301
```

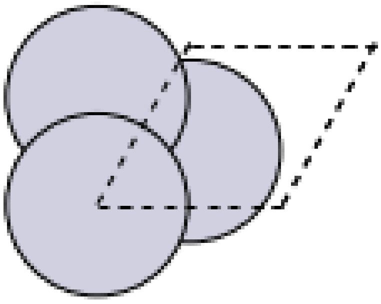


Figure 83: 1 × 1 unit cell.

fcc site at 1 ML coverage

```
from vasp import Vasp

from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms
from ase.io import write

atoms = fcc111('Pt', size=(1, 1, 3), vacuum=10.0)

# note this function only works when atoms are created by the surface module.
add_adsorbate(atoms, 'O', height=1.2, position='fcc')

constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
atoms.set_constraint(constraint)

write('images/Pt-o-fcc-1ML.png', atoms, show_unit_cell=2)

print(Vasp('surfaces/Pt-slab-1x1-O-fcc',
           xc='PBE',
           kpts=[8, 8, 1],
           encut=350,
           ibrion=2,
           nsw=25,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-200.py).

```
-22.13585728
```

Adsorption energy at 1ML

```
from vasp import Vasp

e_slab_o = Vasp('surfaces/Pt-slab-1x1-O-fcc').potential_energy

# clean slab
```

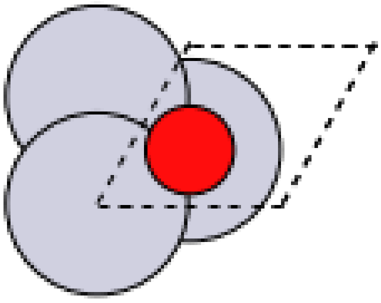


Figure 84: 1 ML oxygen in the fcc site.

```
e_slab = Vasp('surfaces/Pt-slab-1x1').potential_energy

e_O2 = Vasp('molecules/O2-sp-triplet-350').potential_energy

hads = e_slab_o - e_slab - 0.5 * e_O2
print 'Hads (1ML) = {0:1.3f} eV'.format(hads)
```

Open the python script (dft-scripts/script-201.py).

```
Hads (1ML) = -0.099 eV
```

The adsorption energy is **much** less favorable at 1ML coverage than at 0.25 ML coverage! We will return what this means in Atomistic thermodynamics effect on adsorption.

5.8.3 Effect of adsorption on the surface energy

There is a small point to make here about what adsorption does to surface energies. Let us define a general surface formation energy scheme like this:

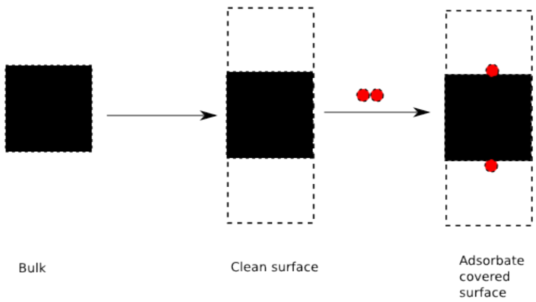


Figure 85: Schematic of forming a surface with adsorbates. First we form two clean surfaces by cleaving the bulk, then allow adsorption to occur on the surfaces.

Let us presume the surfaces are symmetric, and that each surface contributes half of the energy change. The overall change in energy:

$\Delta E = E_{slab,ads} - E_{ads} - E_{bulk}$

where the the energies are appropriately normalized for the stoichiometry. Let us rearrange the terms, and add and subtract a constant term E_{slab}.

$\Delta E = E_{slab,ads} - E_{slab} - E_{ads} - E_{bulk} + E_{slab}$

We defined $\gamma_{clean} = \frac{1}{2A}(E_{slab} - E_{bulk})$, and we defined $H_{ads} = E_{slab,ads} - E_{slab} - E_{ads}$ for adsorption on a single side of a slab. In this case, there are adsorbates on both sides of the slab, so $E_{slab,ads} - E_{slab} - E_{ads} = 2\Delta H_{ads}$. If we normalize by $2A$, the area for both sides of the slab, we get $\frac{\Delta E}{2A} = \gamma = \gamma_{clean} + \frac{H_{ads}}{A}$

You can see here that the adsorption energy serves to stabilize, or reduce the surface energy, provided that the adsorption energy is negative.

Some final notes about the equations above:

- We were not careful about stoichiometry. As written, it is assumed there are the same number of atoms (not including the adsorbates) in the slabs and bulk, and the same number of adsorbate atoms in the slab and E_{ads}. Appropriate normalization factors must be included if that is not true.
- It is not necessary to perform a symmetric slab calculation to determine the effect of adsorption on the surface energy! You can examine $\gamma - \gamma_{clean}$ with knowledge of only the adsorption energies!

5.9 Adsorbate vibrations

Adsorbates also have vibrational modes. Unlike a free molecule, the translational and rotational modes of an adsorbate may actually have real frequencies. Sometimes they are called frustrated translations or rotations. For metal surfaces with adsorbates, it is common to only compute vibrational modes of the adsorbate on a frozen metal slab. The rationale is that the metal atoms are so much heavier than the adsorbate that there will be little coupling between the surface and adsorbates. You can limit the number of modes calculated with constraints (`ase.constraints.FixAtoms` or `ase.constraints.FixScaled`) if you use IBRION=5. The other IBRION settings (6, 7, 8) do not respect the selective dynamics constraints. Below we consider the vibrational modes of an oxygen atom in an fcc site on Pt(111).

```
from vasp import Vasp

calc = Vasp('surfaces/Pt-slab-O-fcc')
calc.clone('surfaces/Pt-slab-O-fcc-vib')

calc.set(ibrion=5,      # finite differences with selective dynamics
         nfree=2,       # central differences (default)
         potim=0.015,   # default as well
         ediff=1e-8,
         nsw=1)
atoms = calc.get_atoms()
f, v = calc.get_vibrational_modes(0)
print 'Elapsed time = {0} seconds'.format(calc.get_elapsed_time())
allfreq = calc.get_vibrational_modes()[0]

from ase.units import meV
c = 3e10  # cm/s
h = 4.135667516e-15  # eV*s

print 'vibrational energy = {0} eV'.format(f)
print 'vibrational energy = {0} meV'.format(f/meV)
print 'vibrational freq   = {0} 1/s'.format(f/h)
print 'vibrational freq   = {0} cm^{{-1}}'.format(f/(h*c))
print
print 'All energies = ', allfreq
```

Open the python script (dft-scripts/script-202.py).

There are three modes for the free oxygen atom. One of them is a mode normal to the surface (the one with highest frequency. The other two are called frustrated translations. Note that we did not include the surface Pt atoms in the calculation, and this will have an effect on the result because the O atom could be coupled to the surface modes. It is typical to neglect this coupling because of the large difference in mass between O and Pt. Next we look at the difference in results when we calculate all the modes.

```
from vasp import Vasp

```

```python
calc = Vasp('surfaces/Pt-slab-O-fcc')
calc.clone('Pt-slab-O-fcc-vib-ibrion=6')
calc.set(ibrion=6,  # finite differences with symmetry
         nfree=2,  # central differences (default)
         potim=0.015,  # default as well
         ediff=1e-8,
         nsw=1)
calc.update()
print 'Elapsed time = {0} seconds'.format(calc.get_elapsed_time())

f, m = calc.get_vibrational_modes(0)
allfreq = calc.get_vibrational_modes()[0]

from ase.units import meV
c = 3e10  # cm/s
h = 4.135667516e-15  # eV*s

print 'For mode 0:'
print 'vibrational energy = {0} eV'.format(f)
print 'vibrational energy = {0} meV'.format(f / meV)
print 'vibrational freq   = {0} 1/s'.format(f / h)
print 'vibrational freq   = {0} cm^{{-1}}'.format(f / (h * c))
print
print 'All energies = ', allfreq
```

Open the python script (dft-scripts/script-203.py).

```
Elapsed time = 77121.015 seconds
For mode 0:
vibrational energy = 0.063537929 eV
vibrational energy = 63.537929 meV
vibrational freq   = 1.53634035507e+13 1/s
vibrational freq   = 512.113451691 cm^{-1}

All energies =  [0.06353792899999999, 0.045628623, 0.045628623, 0.023701702, 0.023701702, 0.02322374
```

Note that now there are 39 modes, which is 3*N where N=13 atoms in the unit cell. Many of the modes are low in frequency, which correspond to slab modes that are essentially phonons. The O frequencies are not that different from the previous calculation (497 vs 512 cm^{-1}. This is why it is common to keep the slab atoms frozen.

Calculating these results took 39*2 finite differences. It took about a day to get these results on a single CPU. It pays to use constraints to minimize the number of these calculations.

5.9.1 Vibrations of the bridge site

Here we consider the vibrations of an O atom in a bridge site, which we saw earlier is a metastable saddle point.

```python
from vasp import Vasp
from ase.constraints import FixAtoms

# clone calculation so we do not overwrite previous results
calc = Vasp('surfaces/Pt-slab-O-bridge-xy-constrained')
calc.clone('surfaces/Pt-slab-O-bridge-vib')

calc.set(ibrion=5,  # finite differences with selective dynamics
         nfree=2,   # central differences (default)
         potim=0.015,  # default as well
         ediff=1e-8,
         nsw=1)

atoms = calc.get_atoms()
del atoms.constraints
constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
atoms.set_constraint([constraint])

f, v = calc.get_vibrational_modes(2)
```

```
print(calc.get_vibrational_modes()[0])

from ase.units import meV
c = 3e10  # cm/s
h = 4.135667516e-15  # eV*s

print('vibrational energy = {0} eV'.format(f))
print('vibrational energy = {0} meV'.format(f/meV))
print('vibrational freq   = {0} 1/s'.format(f/h))
print('vibrational freq   = {0} cm^(-1)'.format(f/(h*c)))
```

Open the python script (dft-scripts/script-204.py).

```
[0.06691932, 0.047345270999999994, (0.020649715000000003+0j)]
vibrational energy = (0.020649715+0j) eV
vibrational energy = (20.649715+0j) meV
vibrational freq   = (4.99307909065e+12+0j) 1/s
vibrational freq   = (166.435969688+0j) cm^(-1)
```

Note that we have one imaginary mode. This corresponds to the motion of the O atom falling into one of the neighboring 3-fold sites. It also indicates this position is not a stable minimum, but rather a saddle point. This position is a transition state for hopping between the fcc and hcp sites.

5.10 Surface Diffusion barrier

See this review[91] of diffusion on transition metal surfaces.

5.10.1 Standard nudged elastic band method

Here we illustrate a standard NEB method. You need an initial and final state to start with. We will use the results from previous calculations of oxygen atoms in an fcc and hcp site. then we will construct a band of images connecting these two sites. Finally, we let VASP optimize the band and analyze the results to get the barrier.

```
from vasp import Vasp
from ase.neb import NEB
import matplotlib.pyplot as plt

calc = Vasp('surfaces/Pt-slab-O-fcc')
initial_atoms = calc.get_atoms()

final_atoms = Vasp('surfaces/Pt-slab-O-hcp').get_atoms()

# here is our estimated transition state. we use vector geometry to
# define the bridge position, and add 1.451 Ang to z based on our
# previous bridge calculation. The bridge position is half way between
# atoms 9 and 10.
ts = initial_atoms.copy()
ts.positions[-1] = 0.5 * (ts.positions[9] + ts.positions[10]) + [0, 0, 1.451]

# construct the band
images = [initial_atoms]
images += [initial_atoms.copy()]
images += [ts.copy()]  # this is the TS

neb = NEB(images)
# Interpolate linearly the positions of these images:
neb.interpolate()

# now add the second half
images2 = [ts.copy()]
images2 += [ts.copy()]
images2 += [final_atoms]

neb2 = NEB(images2)
neb2.interpolate()

```

```python
# collect final band. Note we do not repeat the TS in the second half
final_images = images + images2[1:]


calc = Vasp('surfaces/Pt-O-fcc-hcp-neb',
            ibrion=1,
            nsw=90,
            spring=-5,
            atoms=final_images)

images, energies = calc.get_neb()
p = calc.plot_neb(show=False)
plt.savefig('images/pt-o-fcc-hcp-neb.png')
```

Open the python script (dft-scripts/script-205.py).

```
Optimization terminated successfully.
         Current function value: -26.953429
         Iterations: 12
         Function evaluations: 24
```

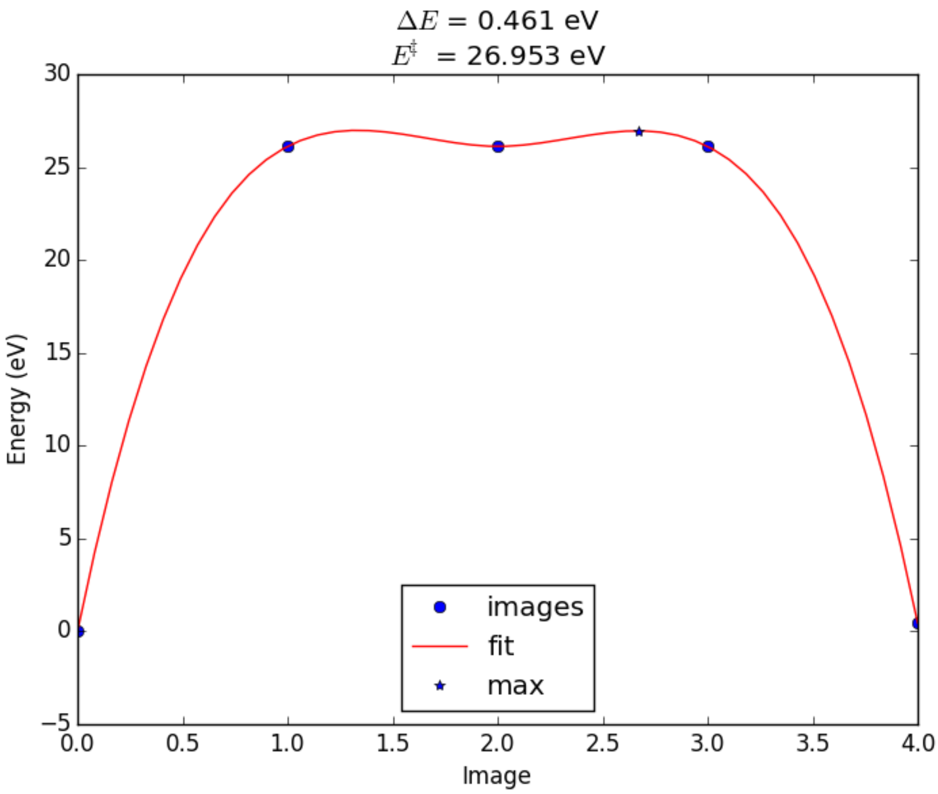


Figure 86: Energy pathway for O diffusion from an fcc to hcp site with a spline fit to determine the barrier.

We should compare this barrier to what we could estimate from the simple adsorption energies in the fcc and bridge sites. The adsorption energy in the fcc site was -1.04 eV, and in the bridge site was -0.49 eV. The difference between these two is 0.55 eV, which is very close to the calculated barrier from the NEB calculation. In cases where you can determine what the transition state is, e.g. by symmetry, or other means, it is much faster to directly compute the energy of the initial and transition states for barrier determinations. This is not usually possible though.

5.10.2 Climbing image NEB

One issue with the standard NEB method is there is no image that is exactly at the transition state. That means there is some uncertainty of the true energy of the transition state, and there is no way to verify the transition state by vibrational analysis. The climbing image NEB method[92] solves that problem by making one image climb to the top. You set LCLIMB==True= in `Vasp` to turn on the climbing image method. Here we use the previous calculation as a starting point and turn on the climbing image method.

```
# perform a climbing image NEB calculation
from vasp import Vasp

calc = Vasp('surfaces/Pt-O-fcc-hcp-neb')
calc.clone('surfaces/Pt-O-fcc-hcp-cineb')
calc.set(ichain=0, lclimb=True)

images, energies = calc.get_neb()
calc.plot_neb(show=False)
import matplotlib.pyplot as plt
plt.savefig('images/pt-o-cineb.png')
plt.show()
```

Open the python script (dft-scripts/script-206.py).

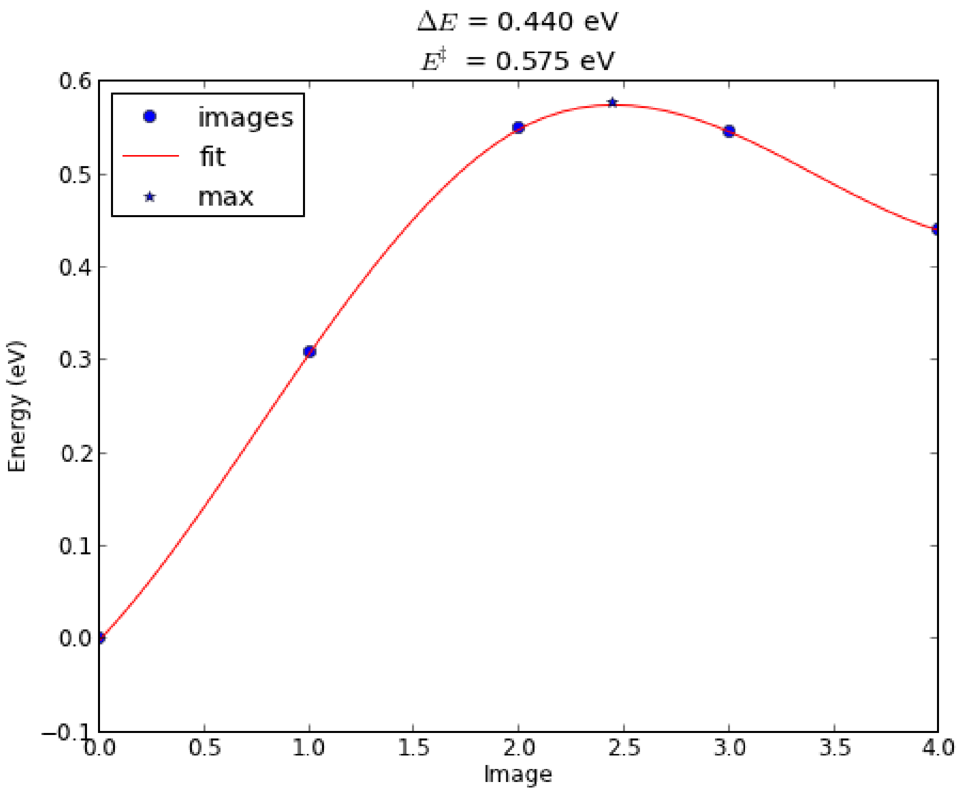


Figure 87: Climbing image NEB

5.10.3 Using vibrations to confirm a transition state

A transition state should have exactly one imaginary degree of freedom which corresponds to the mode that takes reactants to products. See Vibrations of the bridge site for an example.

6 Atomistic thermodynamics

Let us consider how much the Gibbs free energy of an O_2 molecule changes as a function of temperature, at 1 atm. We use the Shomate polynomials to approximate the temperature dependent entropy and enthalpy, and use the parameters from the NIST Webbook for O_2.

```
from ase.units import *
K = 1.0

print J, mol, K

print 0.100 * kJ / mol / K

print 1 * eV / (kJ / mol)
```

Open the python script (dft-scripts/script-207.py).

```
6.24150912588e+18 6.022140857e+23 1.0
0.00103642695747
96.4853328825
```

```
import numpy as np
import matplotlib.pyplot as plt
from ase.units import *
K = 1.  # Kelvin not defined in ase.units!

# Shomate parameters
A = 31.32234; B = -20.23531; C = 57.86644
D = -36.50624; E = -0.007374; F = -8.903471
G = 246.7945; H = 0.0


def entropy(T):
    '''entropy returned as eV/K
    T in K
    '''
    t = T / 1000.
    s = (A * np.log(t) + B * t + C * (t**2) / 2.
         + D * (t**3) / 3. - E / (2. * t**2) + G)
    return s * J / mol / K


def enthalpy(T):
    ''' H - H(298.15) returned as eV/molecule'''
    t = T / 1000.
    h = (A * t + B * (t**2) / 2. + C * (t**3) / 3.
         + D * (t**4) / 4. - E / t + F - H)
    return h * kJ / mol

T = np.linspace(10, 700)

G = enthalpy(T) - T * entropy(T)

plt.plot(T, G)
plt.xlabel('Temperature (K)')
plt.ylabel(r'$\Delta G^\circ$ (eV)')
plt.savefig('images/O2-mu.png')
```

Open the python script (dft-scripts/script-208.py).

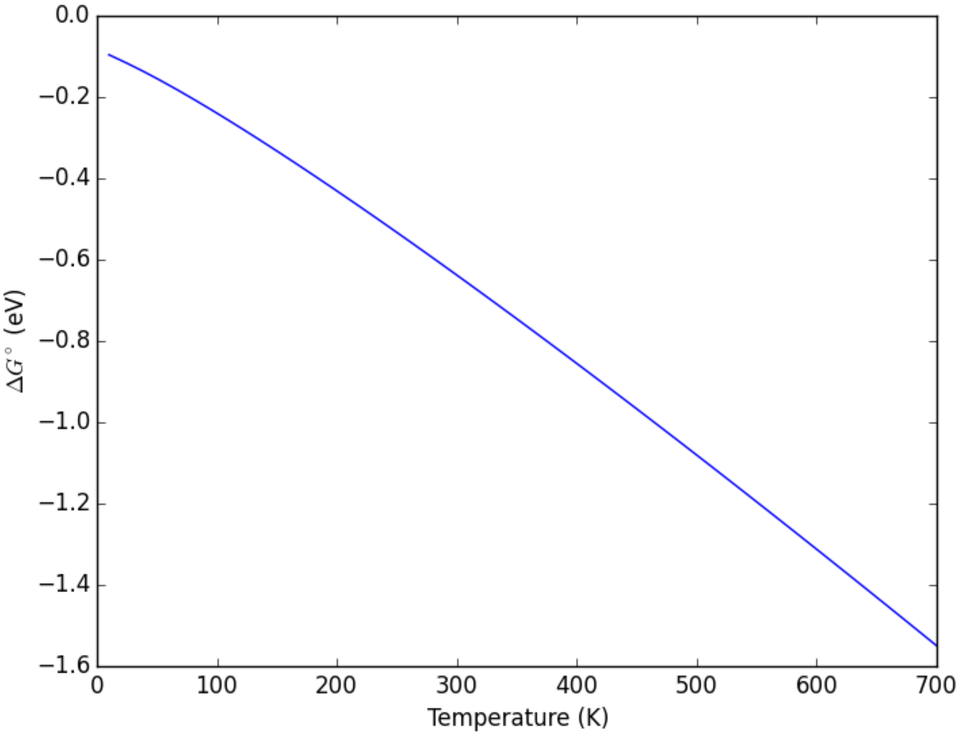


Figure 88: Effect of temperature on the Gibbs free energy of an O_2 molecule at standard state (1 atm).

This is clearly a big effect! Between 500-600K, the energy has dropped by nearly 1 eV.

Pressure also affects the free energy. In the ideal gas limit, the pressure changes the free energy by $kT \ln P/P_0$ where P_0 is the standard state pressure (1 atm or 1 bar depending on the convention chosen). Let us see how this affects the free energy at different temperatures.

```
import matplotlib.pyplot as plt
import numpy as np
from ase.units import *

atm = 101325 * Pascal #atm is not defined in units
K = 1 # Kelvin

# examine range over 10^-10 to 10^10 atm
P = np.logspace(-10, 10) * atm

plt.semilogx(P / atm, kB * (300 * K) * np.log(P / (1 * atm)), label='300K')
plt.semilogx(P / atm, kB * (600 * K) * np.log(P / (1 * atm)), label='600K')
plt.xlabel('Pressure (atm)')
plt.ylabel(r'$\Delta G$ (eV)')
plt.legend(loc='best')
plt.savefig('images/O2-g-p.png')
```

Open the python script (dft-scripts/script-209.py).

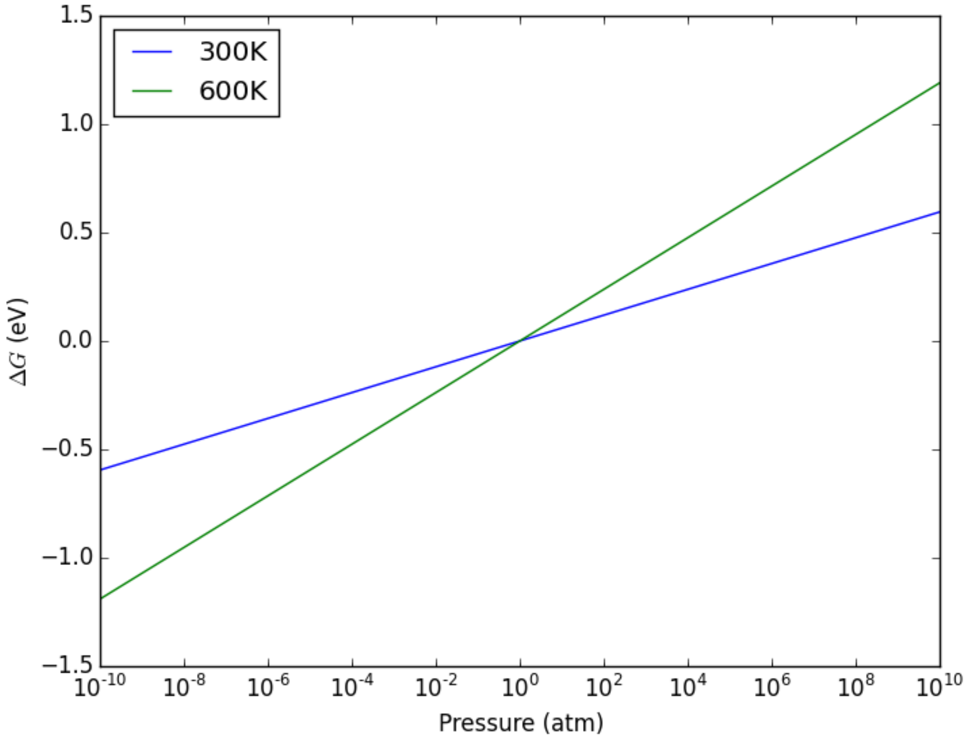


Figure 89: Effects of pressure on the ideal gas Gibbs free energy of O_2.

Similarly, you can see that simply changing the pressure has a large effect on the Gibbs free energy of an ideal gas through the term: $kT\ln(P/P_0)$, and that this effect is also temperature dependent. This leads us to the final formula we will use for the chemical potential of oxgyen:

$\mu_{O_2} = E_{O_2}^{DFT} + E_{O_2}^{ZPE} + \Delta\mu(T) + kT\ln(P/P_0)$

We can use μ_{O_2} in place of E_{O_2} everywhere to include the effects of pressure and temperature on *the gas phase* energy. If T=0K, and P=1 bar, we are at standard state, and this equation reduces to the DFT energy (+ the ZPE).

6.1 Bulk phase stability of oxides

We will consider the effects of oxygen pressure and temperature on the formation energy of Ag_2O and Cu_2O. For now, we neglect the effect of pressure and temperature on the solid phases. Neglecting pressure is pretty reasonable, as the solids are not that compressible, and we do not expect the energy to change for small pressures. For neglecting the temperature, we assume that the temperature dependence of the oxide is similar to the temperature dependence of the metal, and that these dependencies practically cancel each other in the calculations. That is an assumption, and it may not be correct.

$2Cu + 1/2O_2 \rightarrow Cu_2O$

In atomistic thermodynamics, we define the free energy of formation as:

$G_f = G_{Cu_2O} - 2G_{Cu} - 0.5G_{O_2}$

We will at this point assume that the solids are incompressible so that $p\Delta V \approx 0$, and that $S_{Cu_2O} - 2S_{Cu} \approx 0$, which leads to $G_{Cu_2O} - 2G_{Cu} \approx E_{Cu_2O} - 2E_{Cu}$, which we directly compute from DFT. We express $G_{O_2} = \mu_{O_2} = E_{O_2}^{DFT} + E_{O_2}^{ZPE} + \Delta\mu(T) + kT\ln(P/P_0)$. In this example we neglect the zero-point energy of the oxygen molecule, and finally arrive at:

$G_f \approx E_{Cu_2O} - 2E_{Cu} - 0.5(E_{O_2}^{DFT} + \Delta\mu(T) + kT\ln(P/P_0))$

Which, after grouping terms is:
$G_f \approx E_{Cu_2O} - 2E_{Cu} - 0.5(E_{O_2}^{DFT}) - 0.5 * \Delta\mu_{O_2}(P,T)$
with $\Delta\mu_{O_2}(P,T) = \Delta\mu(T) + kT\ln(P/P_0)$. We get $\Delta\mu(T)$ from the Janaf Tables, or the NIST Webbook.

- we are explicitly neglecting all entropies of the solid: configurational, vibrational and electronic
- we also neglect enthalpic contributions from temperature dependent electronic and vibrational states

You will recognize in this equation the standard formation energy we calculated in Metal oxide oxidation energies plus a correction for the non standard state pressure and temperature ($\Delta\mu_{O_2}(P,T) = 0$ at standard state).
$G_f \approx H_f - 0.5 * \Delta\mu_{O_2}(P,T)$
The formation energy of Cu_2O is -1.9521 eV/formula unit. The formation energy for Ag_2O is -0.99 eV/formula unit. Let us consider what temperature the oxides decompose at a fixed oxygen pressure of 1×10^{-10} atm. We need to find the temperature where:
$H_f = 0.5 * \Delta\mu_{O_2}(P,T)$
which will make the formation energy be 0.

```
import numpy as np
import matplotlib.pyplot as plt
from ase.units import *
from scipy.optimize import fsolve

K = 1. #not defined in ase.units!
atm = 101325 * Pascal

# Shomate parameters valid from 100-700K
A = 31.32234; B = -20.23531; C = 57.86644
D = -36.50624; E = -0.007374; F = -8.903471
G = 246.7945; H = 0.0


def entropy(T):
    '''entropy returned as eV/K
    T in K
    '''
    t = T/1000.
    s = (A * np.log(t) + B * t + C * (t**2) / 2.
         + D * (t**3) / 3. - E / (2. * t**2) + G)
    return s * J / mol / K


def enthalpy(T):
    ''' H - H(298.15) returned as eV/molecule'''
    t = T / 1000.
    h = (A * t + B * (t**2) / 2. + C * (t**3) / 3.
         + D * (t**4) / 4. - E / t + F - H)
    return h * kJ / mol


def DeltaMu(T, P):
    '''
    returns delta chemical potential of oxygen at T and P
    T in K
    P in atm
    '''
    return enthalpy(T) - T * entropy(T) + kB * T * np.log(P / atm)

P = 1e-10*atm


def func(T):
    'Cu2O'
    return -1.95 - 0.5*DeltaMu(T, P)

print 'Cu2O decomposition temperature is {0:1.0f} K'.format(fsolve(func,
                                                                    900)[0])

```

```
def func(T):
    'Ag2O'
    return -0.99 - 0.5 * DeltaMu(T, P)

print 'Ag2O decomposition temperature is {0:1.0f} K'.format(fsolve(func,
                                                                   470)[0])


T = np.linspace(100, 1000)
# Here we plot delta mu as a function of temperature at different pressures
# you have use \\times to escape the first \ in pyplot
plt.plot(T, DeltaMu(T, 1e10*atm), label=r'1$\times 10^{10}$ atm')
plt.plot(T, DeltaMu(T, 1e5*atm), label=r'1$\times 10^5$ atm')
plt.plot(T, DeltaMu(T, 1*atm), label='1 atm')
plt.plot(T, DeltaMu(T, 1e-5*atm), label=r'1$\times 10^{-5}$ atm')
plt.plot(T, DeltaMu(T, 1e-10*atm), label=r'1$\times 10^{-10}$ atm')

plt.xlabel('Temperature (K)')
plt.ylabel(r'$\Delta \mu_{O_2}(T,p)$ (eV)')
plt.legend(loc='best')
plt.savefig('images/O2-mu-diff-p.png')
```

Open the python script (dft-scripts/script-210.py).

```
Cu2O decomposition temperature is 917 K
Ag2O decomposition temperature is 478 K
```

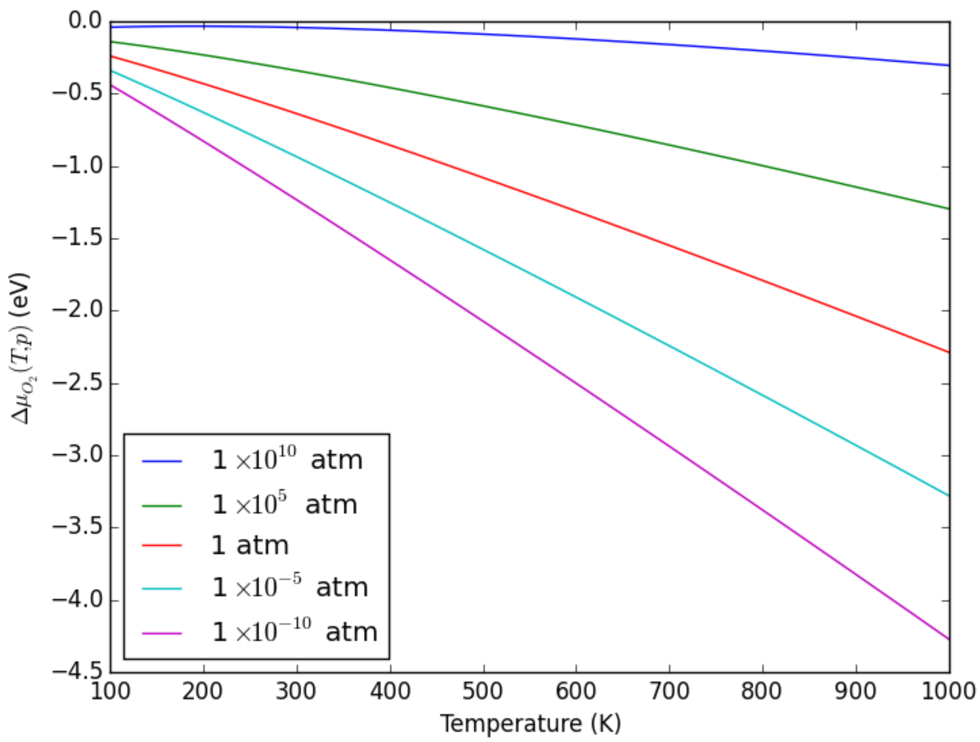


Figure 90: $\Delta\ \mu_{O_2}$(T,p) at different pressures and temperatures.

Now, let us make a phase diagram that shows the boundary between silver oxide, and silver metal in P and T space.

```python
import numpy as np
import matplotlib.pyplot as plt
from ase.units import *
from scipy.optimize import fsolve

K = 1. #not defined in ase.units!
atm = 101325*Pascal

# Shomate parameters valid from 100-700K
A = 31.32234; B = -20.23531; C = 57.86644
D = -36.50624; E = -0.007374; F = -8.903471
G = 246.7945; H = 0.0


def entropy(T):
    '''entropy returned as eV/K
    T in K
    '''
    t = T/1000.
    s = (A*np.log(t) + B*t + C*(t**2)/2.
         + D*(t**3)/3. - E/(2.*t**2) + G)
    return s*J/mol/K


def enthalpy(T):
    ''' H - H(298.15) returned as eV/molecule'''
    t = T/1000.
    h = (A*t + B*(t**2)/2. + C*(t**3)/3.
         + D*(t**4)/4. - E/t + F - H)
    return h*kJ/mol


def DeltaMu(T, P):
    '''
    T in K
    P in atm
    '''
    return enthalpy(T) - T * entropy(T) + kB * T * np.log(P / atm)

P = np.logspace(-11, 1, 10) * atm
T = []
for p in P:

    def func(T):
        return -0.99 - 0.5 * DeltaMu(T, p)
    T.append(fsolve(func, 450)[0])

plt.semilogy(T, P / atm)
plt.xlabel('Temperature (K)')
plt.ylabel('Pressure (atm)')
plt.text(800, 1e-7, 'Ag')
plt.text(600, 1e-3, 'Ag$_2$O')
plt.savefig('images/Ag2O-decomposition.png')
```

Open the python script (dft-scripts/script-211.py).

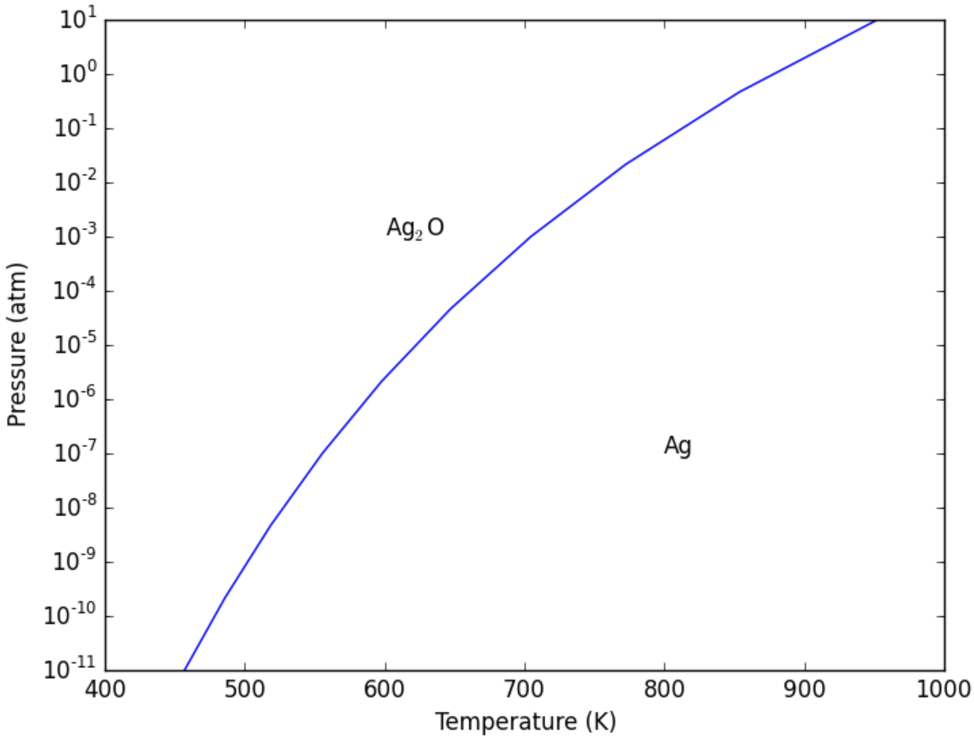


Figure 91: Temperature dependent decomposition pressure for Ag_2O.

This shows that at high temperature and low p_{O_2} metallic silver is stable, but if the p_{O_2} gets high enough, the oxide becomes thermodynamically favorable. Here is another way to look at it.

```
import numpy as np
import matplotlib.pyplot as plt
from ase.units import *

K = 1.  # not defined in ase.units!
atm = 101325*Pascal
Hf = -0.99

P = 1 * atm

Dmu = np.linspace(-4, 0)

Hf = -0.99 - 0.5*Dmu

plt.plot(Dmu, Hf, label='Ag$_2$O')
plt.plot(Dmu, np.zeros(Hf.shape), label='Ag')
plt.xlabel(r'$\Delta \mu_{O_2}$ (eV)')
plt.ylabel('$H_f$ (eV)')
plt.savefig('images/atomistic-thermo-hf-mu.png')
```

Open the python script (dft-scripts/script-212.py).

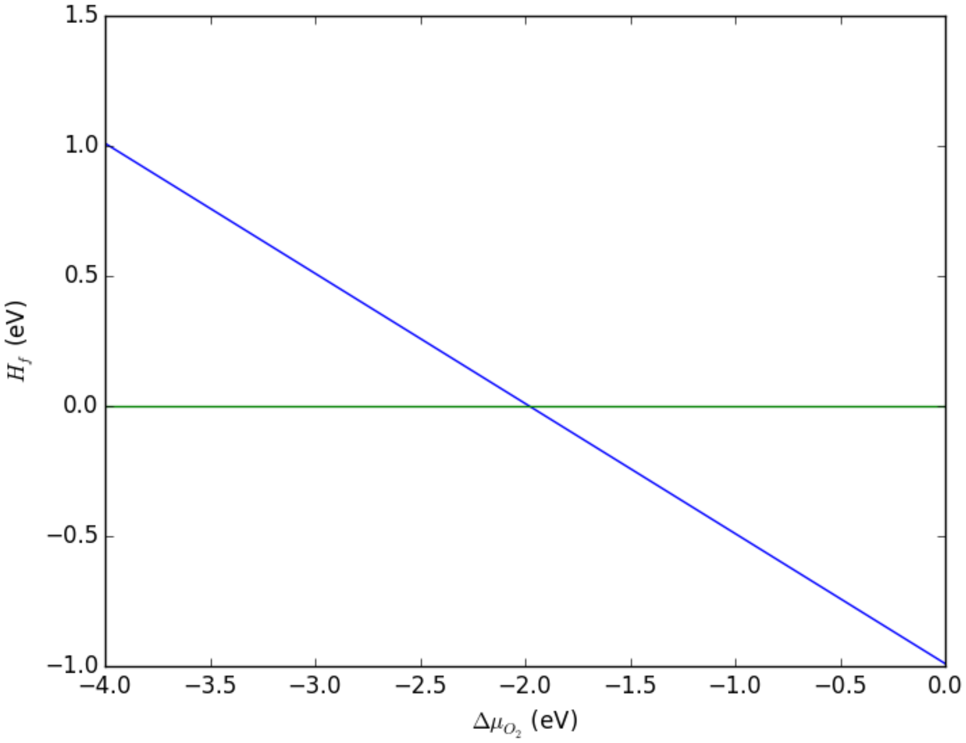


Figure 92: Dependence of the formation energy on the oxygen chemical potential.

This graph shows graphically the $\Delta\mu_{O_2}$ required to make the metal more stable than the oxide. Anything less than about -2 eV will have the metal more stable. That can be achieved by any one of the following combinations (graphically estimated from Figure 90): About 500K at $1{\times}10^{-10}$ atm, 600K at $1{\times}10^{-5}$ atm, 900K at 1atm, etc...

6.2 Effect on adsorption

We now consider the question: Given a pressure and temperature, what coverage would you expect on a surface? We saw earlier that adsorption energies depend on the site and coverage. We lso know the coverage depends on the pressure and temperature. Above some temperature, desorption occurs, and below some pressure adsorption will not be favorable. We seek to develop a quantitative method to determine those conditions.

We redefine the adsorption energy as:

$\Delta G_{ads} \approx E_{slab,ads} - E_{slab} - \mu_{ads}$

where again we neglect all contributions to the free energy of the slabs from vibrational energy and entropy, as well as configurational entropy if that is relevant. That leaves only the pressure and temperature dependence of the adsorbate, which we treat in the ideal gas limit.

We expand μ_{ads} as $E_{ads} + \Delta\mu(T,p)$, and thus:

$\Delta G_{ads} \approx E_{slab,ads} - E_{slab} - E_{ads} - \Delta\mu(T,p)$

or

$\Delta G_{ads} \approx \Delta H_{ads} - \Delta\mu(T,p)$

where ΔH_{ads} is the adsorption energy we defined earlier. Now we can examine the effect of $\Delta\mu(T,p)$ on the adsorption energies. We will use the adsorption energies for the oxygen on Pt(111) system we computed earlier:

Table 5: Adsorption site dependence of adsorption energies of oxygen on Pt(111).

system	$\Delta H(eV/O)$
fcc (0.25 ML)	-1.04
hcp (0.25 ML)	-0.60
bridge (0.25 ML)	-0.49
fcc(1ML)	-0.10

```
import numpy as np
import matplotlib.pyplot as plt

fcc25 = -1.04
hcp25 = -0.60
bridge25 = -0.49
fcc1 = -0.10

Dmu = np.linspace(-4, 2)

plt.plot(Dmu, np.zeros(Dmu.shape), label='Pt(111)')
plt.plot(Dmu, 0.25 * (fcc25 - 0.5*Dmu), label='fcc - 0.25 ML')
plt.plot(Dmu, 0.25 * (hcp25 - 0.5*Dmu), label='hcp - 0.25 ML')
plt.plot(Dmu, 0.25 * (bridge25 - 0.5*Dmu), label='bridge - 0.25 ML')
plt.plot(Dmu, 1.0 * (fcc1 - 0.5*Dmu), label='fcc - 1.0 ML')

plt.xlabel(r'$\Delta \mu O_2$ (eV)')
plt.ylabel(r'$\Delta G_{ads}$ (eV/O)')
plt.legend(loc='best')
plt.savefig('images/atomistic-thermo-adsorption.png')
```

Open the python script (dft-scripts/script-213.py).

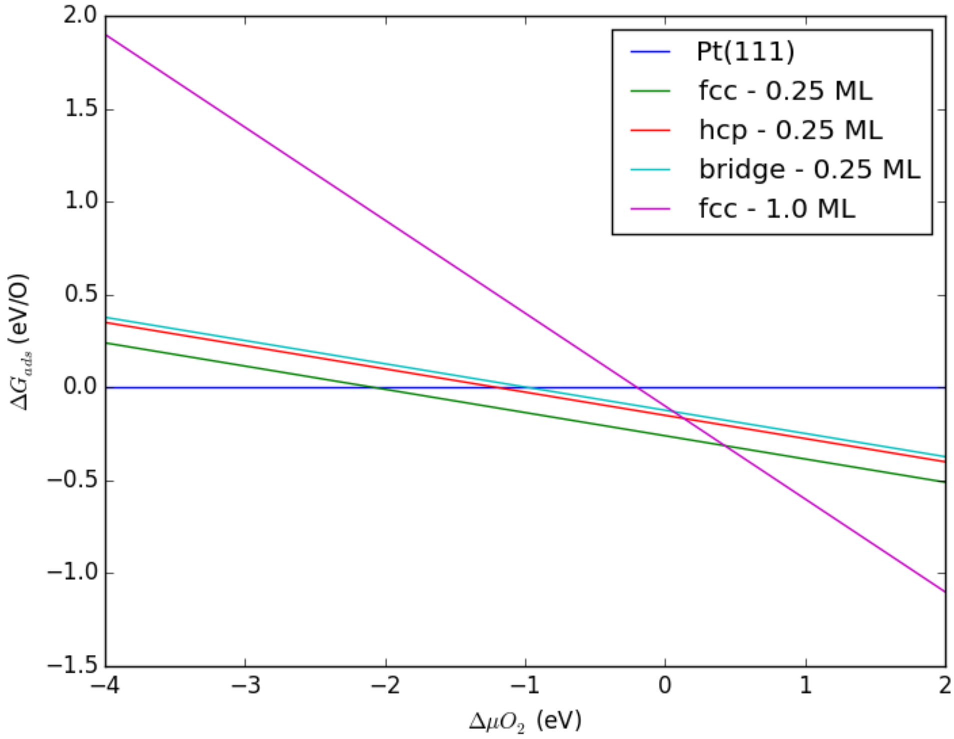


Figure 93: Effect of oxygen chemical potential on the adsorption energy.

6.3 Atomistic therodynamics and multiple reactions

In[81] we considered multiple reactions in an atomistic thermodynamic framework. Let us consider these three reactions of dissociative adsorption of hydrogen and hydrogen disulfide, and consider how to compute the reaction energy for the third reaction.

1. $H_2 + 2* \leftrightharpoons 2H*$
2. $H_2S + 2* \leftrightharpoons H * + SH*$
3. $SH * + * \leftrightharpoons S * + H*$

The reaction energy of interest is $E_{rxn} = \mu_{S*} + \mu H * - \mu SH*$ The question is, what are these chemical potentials? We would like them in terms of pressures and temperature, preferrably of molecules that can be approximated as ideal gases. By equilibrium arguments we can say that $\mu_{H*} = \frac{1}{2}\mu_{H_2}$. It follows that at equilibrium:

$\mu_{H*} + \mu_{SH*} = \mu_{H_2S}$ and $\mu_{H*} + \mu_{S*} = \mu_{SH*}$.

From the first equation we have:

$\mu_{SH*} = \mu_{H_2S} - \frac{1}{2}\mu_{H_2}$

and from the second equation we have:

$\mu_{S*} = \mu_{SH*} - \mu_{H*} = \mu_{H_2S} - \mu_{H_2}$.

Thus, the chemical potentials of all these three adsorbed species depend on the chemical potentials of two gas-phase species. The chemical potentials of each of these gases can be defined as:

$\mu_{gas}(T, p) = E_{gas}(0K) + \delta\mu + kT \ln\left(p/p^0\right)$, as we have defined before, so that only simple DFT calculations are needed to estimate them.

7 Advanced electronic structure methods

7.1 DFT+U

VASP manual on DFT+U

It can be difficult to find the lowest energy solutions with DFT+U. Some strategies for improving this are discussed in.[93]

7.1.1 Metal oxide oxidation energies with DFT+U

We will reconsider here the reaction (see Metal oxide oxidation energies) 2 Cu_2O + O_2 ⇌ 4 CuO. We need to compute the energy of each species, now with DFT+U. In[54] they use a U parameter of 4 eV for Cu which gave the best agreement with the experimental value. We will also try that.

Cu_2O calculation with U=4.0

```
from vasp import Vasp
from ase import Atom, Atoms
import logging

calc = Vasp('bulk/Cu2O')
calc.clone('bulk/Cu2O-U=4.0')

calc.set(ldau=True,   # turn DFT+U on
         ldautype=2,  # select simplified rotationally invariant option
         ldau_luj={'Cu':{'L':2,  'U':4.0, 'J':0.0},
                    'O':{'L':-1, 'U':0.0, 'J':0.0}},
         ldauprint=1,
         ibrion=-1,  #do not rerelax
         nsw=0)
atoms = calc.get_atoms()

print(atoms.get_potential_energy())
#print calc
```

Open the python script (dft-scripts/script-214.py).

```
-22.32504781
```

```
grep -A 3 "LDA+U is selected, type is set to LDAUTYPE" bulk/Cu2O-U=4.0/OUTCAR
```

Open the python script (dft-scripts/script-215.py).

```
LDA+U is selected, type is set to LDAUTYPE =  2
  angular momentum for each species LDAUL =     2   -1
  U (eV)           for each species LDAUU =   4.0  0.0
  J (eV)           for each species LDAUJ =   0.0  0.0
```

CuO calculation with U=4.0

```
from vasp import Vasp
from ase import Atom, Atoms

calc = Vasp('bulk/CuO')
calc.clone('bulk/CuO-U=4.0')

calc.set(ldau=True,   # turn DFT+U on
         ldautype=2,  # select simplified rotationally invariant option
         ldau_luj={'Cu':{'L':2,  'U':4.0, 'J':0.0},
                    'O':{'L':-1, 'U':0.0, 'J':0.0}},
         ldauprint=1,
         ibrion=-1,  #do not rerelax
         nsw=0)
```

```

atoms = calc.get_atoms()
print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-216.py).

```
-16.91708676
```

TODO Reaction energy calculation with DFT+U

```
from vasp import Vasp

calc = Vasp('bulk/Cu2O-U=4.0')
atoms = calc.get_atoms()
cu2o_energy = atoms.get_potential_energy() / (len(atoms) / 3)

calc = Vasp('bulk/CuO-U=4.0')
atoms = calc.get_atoms()
cuo_energy = atoms.get_potential_energy() / (len(atoms) / 2)

# make sure to use the same cutoff energy for the O2 molecule!
calc = Vasp('molecules/O2-sp-triplet-400')
o2_energy = calc.results['energy']

calc.stop_if(None in [cu2o_energy, cuo_energy, o2_energy])

# don't forget to normalize your total energy to a formula unit. Cu2O
# has 3 atoms, so the number of formula units in an atoms is
# len(atoms)/3.

rxn_energy = 4.0 * cuo_energy - o2_energy - 2.0 * cu2o_energy

print('Reaction energy  = {0} eV'.format(rxn_energy))
print('Corrected energy = {0} eV'.format(rxn_energy - 1.36))
```

Open the python script (dft-scripts/script-217.py).

```
Reaction energy  = 7.36775847 eV
Corrected energy = 6.00775847 eV
```

This is still not in quantitative agreement with the result in,[54] which at U=4 eV is about -3.14 eV (estimated from a graph). We have not applied the O_2 correction here yet. In that paper, they apply a constant shift of -1.36 eV per O_2. After we apply that correction, we agree within 0.12 eV, which is pretty good considering we have not checked for convergence.

How much does U affect the reaction energy? It is reasonable to consider how sensitive our results are to the U parameter. We do that here.

```
from vasp import Vasp
for U in [2.0, 4.0, 6.0]:
    ## Cu2O ########################################
    calc = Vasp('bulk/Cu2O')
    calc.clone('bulk/Cu2O-U={0}'.format(U))


    calc.set(ldau=True,   # turn DFT+U on
             ldautype=2,  # select simplified rotationally invariant option
             ldau_luj={'Cu':{'L':2,  'U':U, 'J':0.0},
                       'O':{'L':-1, 'U':0.0, 'J':0.0}},
             ldauprint=1,
             ibrion=-1,  # do not rerelax
             nsw=0)
    atoms1 = calc.get_atoms()
    cu2o_energy = atoms1.get_potential_energy() / (len(atoms1) / 3)

    ## CuO ########################################
    calc = Vasp('bulk/CuO')
```

```
    calc.clone('bulk/CuO-U={0}'.format(U))


    calc.set(ldau=True,   # turn DFT+U on
             ldautype=2,  # select simplified rotationally invariant option
             ldau_luj={'Cu':{'L':2,  'U':U, 'J':0.0},
                       'O':{'L':-1, 'U':0.0, 'J':0.0}},
             ldauprint=1,
             ibrion=-1,  # do not rerelax
             nsw=0)
    atoms2 = calc.get_atoms()
    cuo_energy = atoms2.get_potential_energy() / (len(atoms2) / 2)

    ## O2 ########################################
    # make sure to use the same cutoff energy for the O2 molecule!
    calc = Vasp('molecules/O2-sp-triplet-400')
    atoms = calc.get_atoms()
    o2_energy = atoms.get_potential_energy()

    if not None in [cu2o_energy, cuo_energy, o2_energy]:

        rxn_energy = (4.0 * cuo_energy
                      - o2_energy
                      - 2.0 * cu2o_energy)

        print 'U = {0}  reaction energy = {1}'.format(U, rxn_energy - 1.99)
```

Open the python script (dft-scripts/script-218.py).

```
U = 2.0  reaction energy = 3.32752349
U = 4.0  reaction energy = 5.37775847
U = 6.0  reaction energy = 5.71849513
```

```
U = 2.0  reaction energy = -3.876906
U = 4.0  reaction energy = -3.653819
U = 6.0  reaction energy = -3.397605
```

In,[54] the difference in reaction energy from U=2 eV to U=4 eV was about 0.5 eV (estimated from graph). Here we see a range of 0.48 eV from U=2 eV to U=4 eV. Note that for U=0 eV, we had a (corrected reaction energy of -3.96 eV). Overall, the effect of adding U decreases this reaction energy.

This example highlights the challenge of using an approach like DFT+U. On one hand, U has a clear effect of changing the reaction energy. On the other hand, so does the correction factor for the O_2 binding energy. In[54] the authors tried to get the O_2 binding energy correction from oxide calculations where U is not important, so that it is decoupled from the non-cancelling errors that U fixes. See[94] for additional discussion of how to mix GGA and GGA+U results.

In any case, you should be careful to use well converged results to avoid compensating for convergence errors with U.

7.2 Hybrid functionals

7.2.1 FCC Ni DOS

This example is adapted from http://cms.mpi.univie.ac.at/wiki/index.php/FccNi_DOS

```
from vasp import Vasp
from ase.lattice.cubic import FaceCenteredCubic
from ase.dft import DOS

atoms = FaceCenteredCubic(directions=[[0, 1, 1],
                                      [1, 0, 1],
                                      [1, 1, 0]],
                                      size=(1, 1, 1),
                                      symbol='Ni')
atoms[0].magmom = 1

calc = Vasp('bulk/Ni-PBE',
```

```
            ismear=-5,
            kpts=[5, 5, 5],
            xc='PBE',
            ispin=2,
            lorbit=11,
            lwave=True, lcharg=True,  # store for reuse
            atoms=atoms)

e = atoms.get_potential_energy()
print('PBE energy:   ',e)
calc.stop_if(e is None)

dos = DOS(calc, width=0.2)
e_pbe = dos.get_energies()
d_pbe = dos.get_dos()


calc.clone('bulk/Ni-PBE0')
calc.set(xc='pbe0')
atoms = calc.get_atoms()
pbe0_e = atoms.get_potential_energy()

if atoms.get_potential_energy() is not None:
    dos = DOS(calc, width=0.2)
    e_pbe0 = dos.get_energies()
    d_pbe0 = dos.get_dos()

## HSE06
calc = Vasp('bulk/Ni-PBE')
calc.clone('bulk/Ni-HSE06')

calc.set(xc='hse06')
atoms = calc.get_atoms()
hse06_e = atoms.get_potential_energy()
if hse06_e is not None:
    dos = DOS(calc, width=0.2)
    e_hse06 = dos.get_energies()
    d_hse06 = dos.get_dos()

calc.stop_if(None in [e, pbe0_e, hse06_e])

import pylab as plt
plt.plot(e_pbe, d_pbe, label='PBE')
plt.plot(e_pbe0, d_pbe0, label='PBE0')
plt.plot(e_hse06, d_hse06, label='HSE06')
plt.xlabel('energy [eV]')
plt.ylabel('DOS')
plt.legend()
plt.savefig('images/ni-dos-pbe-pbe0-hse06.png')
```

Open the python script (dft-scripts/script-219.py).

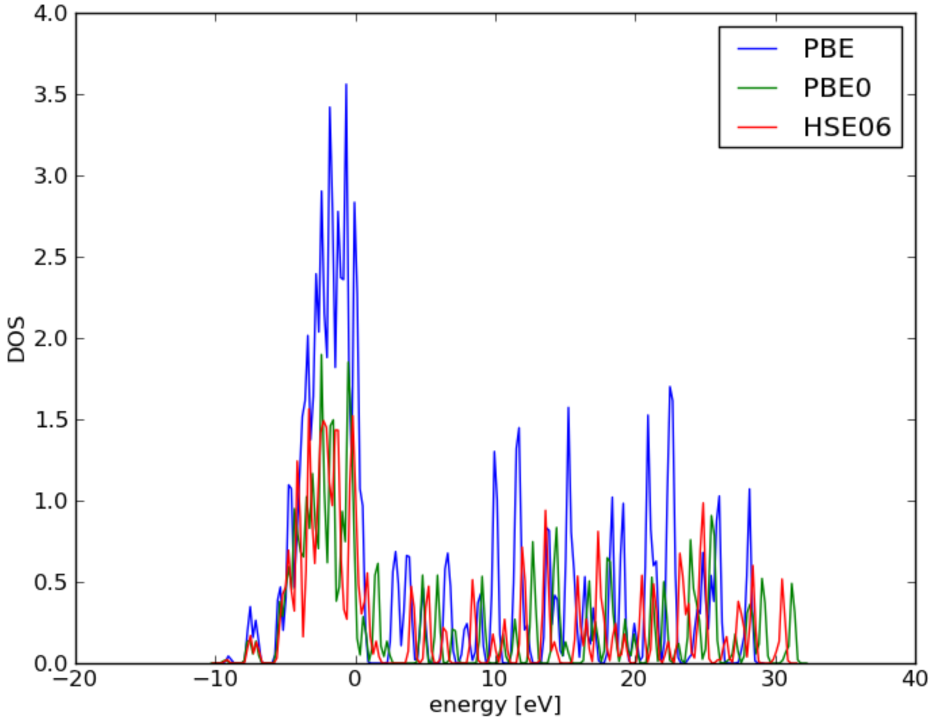


Figure 94: Comparison of DOS from GGA, and two hybrid GGAs (PBE0 and HSE06).

7.3 van der Waals forces

Older versions (5.2.11+) implement DFT+D2[95] with the LVDW tag.

The vdW-DF[96] is accessed with LUSE_VDW. See `http://cms.mpi.univie.ac.at/vasp/vasp/vdW_DF_functional_Langreth_Lundqvist_et_al.html` for notes on its usage.

In Vasp 5.3+, the IVDW tag turns van der Waal calculations on.

You should review the links below before using these

IVDW	method
0	no correction
1 or 10	DFT-D2 method of Grimme (available as of VASP.5.2.11)
11	zero damping DFT-D3 method of Grimme (available as of VASP.5.3.4)
12	DFT-D3 method with Becke-Jonson damping (available as of VASP.5.3.4)
2 or 20	Tkatchenko-Scheffler method[97] (available as of VASP.5.3.3)

Van der Waal forces can play a considerable role in binding of aromatic molecules to metal surfaces (ref). Here we consider the effects of these forces on the adsorption energy of benzene on an Au(111) surface.First, we consider the regular PBE functional.

7.3.1 PBE

gas-phase benzene

```
from vasp import Vasp
from ase.structure import molecule
```

```
benzene = molecule('C6H6')
benzene.center(vacuum=5)

print(Vasp('molecules/benzene-pbe',
           xc='PBE',
           encut=350,
           kpts=[1, 1, 1],
           ibrion=1,
           nsw=100,
           atoms=benzene).potential_energy)
```

Open the python script (dft-scripts/script-220.py).

```
-76.03718564
```

clean slab

```
# the clean gold slab
from vasp import Vasp
from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms

atoms = fcc111('Au', size=(3,3,3), vacuum=10)

# now we constrain the slab
c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
atoms.set_constraint(c)

#from ase.visualize import view; view(atoms)

print(Vasp('surfaces/Au-pbe',
           xc='PBE',
           encut=350,
           kpts=[4, 4, 1],
           ibrion=1,
           nsw=100,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-221.py).

```
-81.22521492
```

benzene on Au(111)

```
# Benzene on the slab
from vasp import Vasp
from ase.lattice.surface import fcc111, add_adsorbate
from ase.structure import molecule
from ase.constraints import FixAtoms

atoms = fcc111('Au', size=(3,3,3), vacuum=10)
benzene = molecule('C6H6')
benzene.translate(-benzene.get_center_of_mass())

# I want the benzene centered on the position in the middle of atoms
# 20, 22, 23 and 25
p = (atoms.positions[20] +
     atoms.positions[22] +
     atoms.positions[23] +
     atoms.positions[25])/4.0 + [0.0, 0.0, 3.05]

benzene.translate(p)
atoms += benzene

# now we constrain the slab
c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
atoms.set_constraint(c)

#from ase.visualize import view; view(atoms)

```

```
print(Vasp('surfaces/Au-benzene-pbe',
           xc='PBE',
           encut=350,
           kpts=[4, 4, 1],
           ibrion=1,
           nsw=100,
           atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-222.py).

```
/home-research/jkitchin/dft-book/surfaces/Au-benzene-pbe submitted: 1413525.gilgamesh.cheme.cmu.edu
None
```

resubmitted

```
/home-research/jkitchin/dft-book/surfaces/Au-benzene-pbe submitted: 1399668.gilgamesh.cheme.cmu.edu
None
```

```
from vasp import Vasp

e1, e2, e3 = [Vasp(wd).potential_energy
              for wd in ['surfaces/Au-benzene-pbe',
                         'surfaces/Au-pbe',
                         'molecules/benzene-pbe']]


print('PBE adsorption energy = {} eV'.format(e1 - e2 - e3))
```

Open the python script (dft-scripts/script-223.py).

This is a very weak energy. It is similar to the result in the reference (0.15 eV), and considerably weaker than the experiment. Next we consider one form of a VDW correction.

7.3.2 DFT-D2

To turn on the van der Waals corrections[95] we set LVDW to `True`.

gas-phase benzene

```
from vasp import Vasp
from ase.structure import molecule

benzene = molecule('C6H6')
benzene.center(vacuum=5)

print(Vasp('molecules/benzene-pbe-d2',
          xc='PBE',
          encut=350,
          kpts=[1, 1, 1],
          ibrion=1,
          nsw=100,
          lvdw=True,
          atoms=benzene).potential_energy)
```

Open the python script (dft-scripts/script-224.py).

```
-76.17670701
```

clean slab

```
# the clean gold slab
from vasp import Vasp
from ase.lattice.surface import fcc111, add_adsorbate
from ase.constraints import FixAtoms

```

```
atoms = fcc111('Au', size=(3, 3, 3), vacuum=10)

# now we constrain the slab
c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
atoms.set_constraint(c)

print(Vasp('surfaces/Au-pbe-d2',
          xc='PBE',
          encut=350,
          kpts=[4, 4, 1],
          ibrion=1,
          nsw=100,
          lvdw=True,
          atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-225.py).

```
-106.34723065
```

benzene on Au(111)

```
# Benzene on the slab
from vasp import Vasp
from ase.lattice.surface import fcc111, add_adsorbate
from ase.structure import molecule
from ase.constraints import FixAtoms

atoms = fcc111('Au', size=(3,3,3), vacuum=10)
benzene = molecule('C6H6')
benzene.translate(-benzene.get_center_of_mass())

# I want the benzene centered on the position in the middle of atoms
# 20, 22, 23 and 25
p = (atoms.positions[20] +
     atoms.positions[22] +
     atoms.positions[23] +
     atoms.positions[25])/4.0 + [0.0, 0.0, 3.05]

benzene.translate(p)
atoms += benzene

# now we constrain the slab
c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
atoms.set_constraint(c)

#from ase.visualize import view; view(atoms)

print(Vasp('surfaces/Au-benzene-pbe-d2',
          xc='PBE',
          encut=350,
          kpts=[4, 4, 1],
          ibrion=1,
          nsw=100,
          lvdw=True,
          atoms=atoms).potential_energy)
```

Open the python script (dft-scripts/script-226.py).

```
-184.07495285
```

```
from vasp import Vasp

e1, e2, e3 = [Vasp(wd).potential_energy
              for wd in ['surfaces/Au-benzene-pbe-d2',
                         'surfaces/Au-pbe-d2',
                         'molecules/benzene-pbe-d2']]

print('Adsorption energy = {0:1.2f} eV'.format(e1 - e2 - e3))
```

Open the python script (dft-scripts/script-227.py).

```
Adsorption energy = -1.54 eV
```

That is significantly more favorable. This is much higher than this reference though (0.56 eV), so there could be some issues with convergence or other computational parameters that should be considered.

7.4 Electron localization function

The electron localization function (ELF) can be used to characterize chemical bonds, e.g. their ionicity/covalency.[98] Here we reproduce an example from Ref. 98. We compute and plot the ELF for tetrafluoromethane. The LELF tag turns this on.

```
# compute ELF for CF4
from vasp import Vasp
from ase.structure import molecule
from enthought.mayavi import mlab

atoms = molecule('CF4')
atoms.center(vacuum=5)

calc = Vasp('molecules/cf4-elf',
            encut=350,
            prec='high',
            ismear=0,
            sigma=0.01,
            xc='PBE',
            lelf=True,
            atoms=atoms)

x, y, z, elf = calc.get_elf()
mlab.contour3d(x, y, z, elf, contours=[0.3])
mlab.savefig('../../images/cf4-elf-3.png')

mlab.figure()
mlab.contour3d(x, y, z, elf, contours=[0.75])
mlab.savefig('../../images/cf4-elf-75.png')
```

Open the python script (dft-scripts/script-228.py).

```
None
```

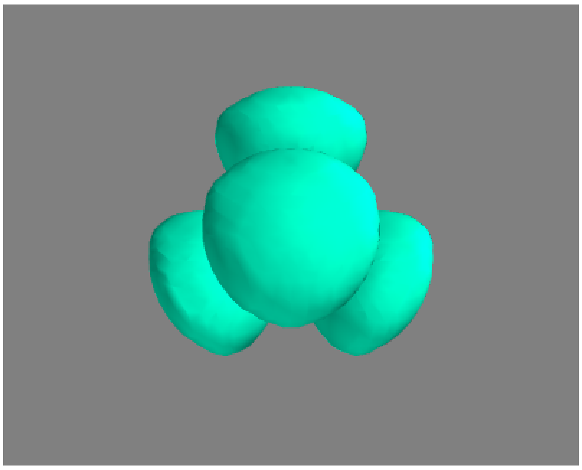


Figure 95: ELF for an isosurface of 0.3 for CF_4.

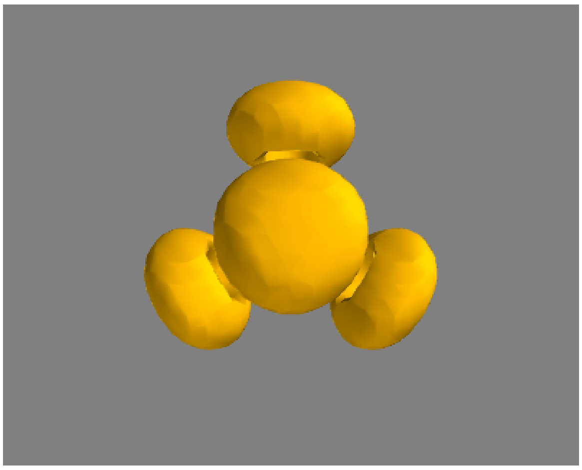


Figure 96: ELF for an isosurface of 0.75 for CF_4.

These images (Figure 95 and 96) are basically consistent with those in Reference.[98]

7.5 TODO Charge partitioning schemes

7.6 TODO Modeling Core level shifts

We need to setup four calculations. First, we setup the bulk Cu and bulk alloy calculations and let them relax. We use similar unit cells for each one to maximize cancellation of errors.

```
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Cu',  [0.000,     0.000,     0.000]),
               Atom('Cu',  [-1.652,    0.000,     2.039])],
              cell=  [[0.000, -2.039,  2.039],
                      [0.000,  2.039,  2.039],
                      [-3.303,  0.000,  0.000]])

atoms = atoms.repeat((2, 2, 2))
print atoms[0]

calc = Vasp('bulk/Cu-cls-0',
            xc='PBE',
            encut=350,
            kpts=[4, 4, 4],
            ibrion=2,
            isif=3,
            nsw=40,
            atoms=atoms)
print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-229.py).

```
Atom('Cu', [0.0, 0.0, 0.0], index=0)
-59.98232341
```

Here, we setup the alloy calculation.

```
from vasp import Vasp
from ase import Atom, Atoms

atoms = Atoms([Atom('Cu',  [0.000,     0.000,     0.000]),
               Atom('Pd',  [-1.652,    0.000,     2.039])],
              cell=  [[0.000, -2.039,  2.039],
```

```
                      [0.000,  2.039,  2.039],
                      [-3.303,  0.000,  0.000]])

atoms = atoms.repeat((2, 2, 2))

calc = Vasp('bulk/CuPd-cls-0',
            xc='PBE',
            encut=350,
            kpts=[4, 4, 4],
            ibrion=2,
            isif=3,
            nsw=40,
            atoms=atoms)

print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-230.py).

```
-73.55012322
```

Next, we have to do the excitation in each structure. For these, we do not relax the structure. We clone the previous results and modify them.

```
from vasp import VAsp

calc = Vasp('bulk/Cu-cls-0')
calc.clone('bulk/Cu-cls-1')

calc.set(ibrion=None,
         isif=None,
         nsw=None,
         setups=[[0, 'Cu']],  # Create separate entry in POTCAR for atom index 0
         icorelevel=2,        # Perform core level shift calculation
         clnt=0,              # Excite atom index 0
         cln=2,               # 2p3/2 electron for Cu core level shift
         cll=1,
         clz=1)

calc.update()
```

Open the python script (dft-scripts/script-231.py).

```
-345.05440951
```

```
from vasp import Vasp

calc = Vasp('bulk/CuPd-cls-0')
calc.clone('bulk/CuPd-cls-1')

calc.set(ibrion=None,
         isif=None,
         nsw=None,
         setups=[[0, 'Cu']],  # Create separate entry in POTCAR for atom index 0
         icorelevel=2,        # Perform core level shift calculation
         clnt=0,              # Excite atom index 0
         cln=2,               # 2p3/2 electron for Cu core level shift
         cll=1,
         clz=1)
calc.update()
```

Open the python script (dft-scripts/script-232.py).

```
-359.87250408
```

Finally we calculate the CLS:

```python
from vasp import Vasp

alloy_0 = Vasp('bulk/CuPd-cls-0').potential_energy

alloy_1 = Vasp('bulk/CuPd-cls-1').potential_energy

ref_0 = Vasp('bulk/Cu-cls-0').potential_energy

ref_1 = Vasp('bulk/Cu-cls-1').potential_energy

CLS = (alloy_1 - alloy_0) - (ref_1 - ref_0)

print('CLS = {} eV'.format(CLS))
```

Open the python script (dft-scripts/script-233.py).

```
CLS = -1.2378242 eV
```

This is a little negative compared to the literature but that could be due to the highly ordered structure we used.

7.7 The BEEF functional in Vasp

In Vasp 5.3.5 it is possible to use the BEEF functional.[99]

some addtional variables to setup van der Waals and to get the BEEF ensemble energies. Let us consider the dissociation energy of H_2.

```python
from vasp import Vasp
from ase.structure import molecule
import matplotlib.pyplot as plt

H2 = molecule('H2')
H2.set_cell([8, 8, 8], scale_atoms=False)
H2.center()

calc = Vasp('molecules/H2-beef',
          xc='beef-vdw',
            encut=350,
            ismear=0,
            ibrion=2,
            nsw=10,
            atoms=H2)

eH2 = H2.get_potential_energy()
print(eH2)
```

Open the python script (dft-scripts/script-234.py).

```
-7.13332059
```

Next, we get an H atom.

```python
from vasp import Vasp
from ase.structure import molecule

H = molecule('H')
H.set_cell([8, 8, 8], scale_atoms=False)
H.center()

calc = Vasp('molecules/H-beef',
            xc='beef-vdw',
            encut=350,
            ismear=0,
            atoms=H)

print(calc.potential_energy)
```

Open the python script (dft-scripts/script-235.py).

```
-0.22476997
```

Now, the dissociation energy.

```
from vasp import Vasp

print('D = {} eV'.format(2 * Vasp('molecules/H-beef').potential_energy -
                         Vasp('molecules/H2-beef').potential_energy))
```

Open the python script (dft-scripts/script-236.py).

```
D = 6.68378065 eV
```

```
-1.15994056 -7.13332059
D = 4.81343947 eV
```

It doesn't look like we have done much so far. How certain are we of the dissociation energy? Let us consider the ensemble of energies. In the calculation, an ensemble of functionals is used, and each one produces a different energy. We can look at the distribution of these energies to estimate the uncertainty in energy differences. We use the `Vasp.get_beefens` to get the ensemble. We calculate the uncertainty in our reaction energy by calculating the standard deviation of the appropriately weighted difference of ensembles.

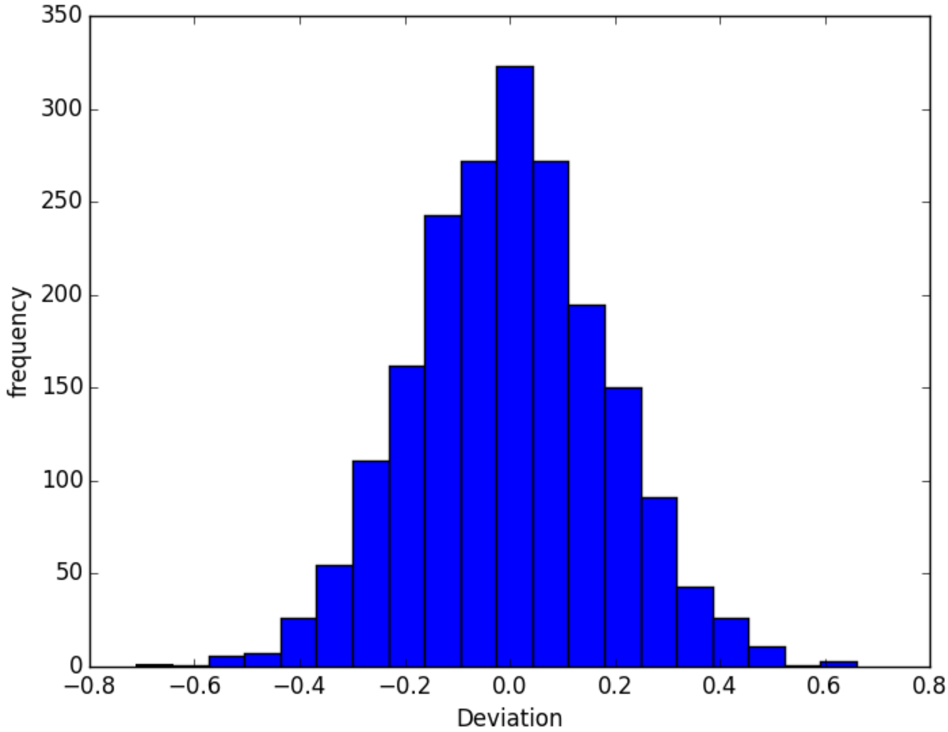
Note that this ensemble represents the contribution just from the functionals, and not all the other contributions. So, the differences in the ensembles only represents that part of the uncertainty

```
from vasp import Vasp

calc = Vasp('molecules/H-beef')
ensH = calc.get_beefens()

calc = Vasp('molecules/H2-beef')
ensH2 = calc.get_beefens()

ensD = 2 * ensH - ensH2

print('mean = {} eV'.format(ensD.mean()))
print('std = {} eV'.format(ensD.std()))

import matplotlib.pyplot as plt
plt.hist(ensD, 20)
plt.xlabel('Deviation')
plt.ylabel('frequency')
plt.savefig('images/beef-ens.png')
```

Open the python script (dft-scripts/script-237.py).

```
mean = 0.00661973433552 eV
std = 0.278495927893 eV
```

You can see the mean is nearly zero, suggesting the deviations are symmetrically distributed. The std error is 0.184 eV, which represents about a 68% confidence interval.



7.8 TODO Solvation

See http://vaspsol.mse.ufl.edu/download/,[100,101]

You need a specially patched version of Vasp.

First, we run our calculation in vacuum. We need this to get the WAVECAR. The following calculation mimics one of the example calculations in the Vaspsol package. The combination of nsw=0 and ibrion=2 does not make sense, but that is the example. I do not use the npar=4 parameter here.

```
from vasp import Vasp
from ase.structure import molecule

atoms = molecule('CO')
atoms.center(vacuum=5)

calc = Vasp('molecules/CO-vacuum',
            encut=600,
            prec='Accurate',
            ismear=0,
            sigma=0.05,
            ibrion=2,
            nsw=0,
            ediff=1e-6,
            atoms=atoms)
print(atoms.get_potential_energy())
print(atoms.get_forces())
print('Calculation time: {} seconds'.format(calc.get_elapsed_time()))
```

Open the python script (dft-scripts/script-238.py).

```
-14.81547852
[[ 0.      0.     -0.949]
 [ 0.      0.      0.949]]
Calculation time: 257.546 seconds
```

The forces are high because nsw was set to 0, so only one iteration was run.

Next, we do the solvation calculation. We use the default solvent dielectric constant of water, which is 80.

```
from vasp import Vasp

calc = Vasp('molecules/CO-vacuum')
calc.clone('molecules/CO-solvated')

calc.set(istart=1,  #
         lsol=True)
print(calc.get_atoms().get_potential_energy())
print(calc.get_atoms().get_forces())
print('Calculation time: {} seconds'.format(calc.get_elapsed_time()))
```

Open the python script (dft-scripts/script-239.py).

```
-14.82289079
[[ 0.      0.     -1.007]
 [ 0.      0.      1.007]]
Calculation time: 2937.72 seconds
```

Note these take quite a bit longer to calculate (e.g. 10 times longer)! The energies here are a little different than the vacuum result. To use this energy in an energy difference, you need to make sure the other energies were run with lsol=True also, and the same parameters.

Here is the evidence that we actually ran a calculation with solvation:

```
grep -A 5 Solvation molecules/CO-solvated/OUTCAR
```

Open the python script (dft-scripts/script-240.py).

```
   LSOL =       T    Solvation

 Electronic Relaxation 1
   ENCUT  =  600.0 eV  44.10 Ry    6.64 a.u.  19.97 19.97 22.27*2*pi/ulx,y,z
   ENINI  =  600.0     initial cutoff
   ENAUG  =  644.9 eV  augmentation charge cutoff
--
 Solvation parameters
   EB_K     = 80.000000     relative permittivity of the bulk solvent
   SIGMA_K =  0.600000     width of the dielectric cavity
   NC_K     =  0.002500     cutoff charge density
   TAU      =  0.000525     cavity surface tension

--
  Solvation contrib.  Ediel  =        -2.06361062
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82417510 eV

  energy without entropy =      -14.82417510  energy(sigma->0) =      -14.82417510

--
  Solvation contrib.  Ediel  =        -2.08692034
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82331872 eV
```

```
  energy without entropy =      -14.82331872  energy(sigma->0) =      -14.82331872

--
  Solvation contrib.  Ediel  =       -2.11316669
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82319429 eV

  energy without entropy =      -14.82319429  energy(sigma->0) =      -14.82319429

--
  Solvation contrib.  Ediel  =       -2.16318931
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82278947 eV

  energy without entropy =      -14.82278947  energy(sigma->0) =      -14.82278947

--
  Solvation contrib.  Ediel  =       -2.17570687
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82272160 eV

  energy without entropy =      -14.82272160  energy(sigma->0) =      -14.82272160

--
  Solvation contrib.  Ediel  =       -2.19188585
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82267271 eV

  energy without entropy =      -14.82267271  energy(sigma->0) =      -14.82267271

--
  Solvation contrib.  Ediel  =       -2.19395757
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82272442 eV

  energy without entropy =      -14.82272442  energy(sigma->0) =      -14.82272442

--
  Solvation contrib.  Ediel  =       -2.19698448
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82288242 eV

  energy without entropy =      -14.82288242  energy(sigma->0) =      -14.82288242

--
  Solvation contrib.  Ediel  =       -2.19737905
  ---------------------------------------------------
  free energy    TOTEN  =      -14.82288470 eV

  energy without entropy =      -14.82288470  energy(sigma->0) =      -14.82288470

--
```

```
  Solvation contrib.  Ediel  =        -2.19908571
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82287091 eV

  energy without entropy =      -14.82287091  energy(sigma->0) =      -14.82287091

--
  Solvation contrib.  Ediel  =        -2.19782575
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82288497 eV

  energy without entropy =      -14.82288497  energy(sigma->0) =      -14.82288497

--
  Solvation contrib.  Ediel  =        -2.19878993
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82288031 eV

  energy without entropy =      -14.82288031  energy(sigma->0) =      -14.82288031

--
  Solvation contrib.  Ediel  =        -2.19875585
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82288727 eV

  energy without entropy =      -14.82288727  energy(sigma->0) =      -14.82288727

--
  Solvation contrib.  Ediel  =        -2.19894718
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82288935 eV

  energy without entropy =      -14.82288935  energy(sigma->0) =      -14.82288935

--
  Solvation contrib.  Ediel  =        -2.19902584
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82289064 eV

  energy without entropy =      -14.82289064  energy(sigma->0) =      -14.82289064

--
  Solvation contrib.  Ediel  =        -2.19905589
  ---------------------------------------------------
  free energy    TOTEN  =       -14.82289079 eV

  energy without entropy =      -14.82289079  energy(sigma->0) =      -14.82289079
```

8 Databases in molecular simulations

The continued increase in computing power has enabled us to create massive amounts of computational data. Some of this data is accessible in papers, or at websites, e.g. https://cmr.fysik.dtu.dk.

Our Vasp module works natively with the ase-database. It is easy to write an entry to a database.

```python
from vasp import Vasp
from ase.db import connect
calc = Vasp('molecules/simple-co')
atoms = calc.get_atoms()
print calc.results
con = connect('example-1.db')
con.write(atoms)
```

Open the python script (dft-scripts/script-241.py).

```
{'magmom': 0, 'stress': array([ 0.0414556 ,  0.01094971,  0.01094971, -0.        , -0.        , -0.
       [-5.09138064,  0.        ,  0.        ]])}
```

```
ase-db example-1.db
```

Open the python script (dft-scripts/script-242.py).

```
id|age|user    |formula|calculator| energy| fmax|pbc| volume|charge|  mass| smax|magmom
 1| 5s|jkitchin|CO     |vasp      |-14.691|5.091|TTT|216.000| 0.000|28.010|0.041| 0.000
Rows: 1
```

9 Acknowledgments

I would like to thank Zhongnan Xu for sending me some examples on magnetism. Alan McGaughey and Lars Grabow for sending me some NEB examples. Matt Curnan for examples of phonons.

Many thanks to students in my class who have pointed out typos, places of confusion, etc... These include Bruno Calfa, Matt Curnan, Charlie Janini, Feng Cao, Gamze Gumuslu, Nicholas Chisholm, Prateek Mehta, Qiyang Duan, Shubhaditya Majumdar, Steven Illes, Wee-Liat Ong, Ye Wang, Yichun Sun, Yubing Lu, and Zhongnan Xu.

10 Appendices

10.1 Recipes

10.1.1 Modifying Atoms by deleting atoms

Sometimes it is convenient to create an Atoms object by deleting atoms from an existing object. Here is a recipe to delete all the hydrogen atoms in a molecule. The idea is to make a list of indices of which atoms to delete using list comprehension, then use list deletion to delete those indices.

```python
import textwrap
from ase.structure import molecule

atoms = molecule('CH3CH2OH')
print(atoms)

# delete all the hydrogens
ind2del = [atom.index for atom in atoms if atom.symbol == 'H']
print('Indices to delete: ', ind2del)

del atoms[ind2del]

# now print what is left
print(atoms)
```

Open the python script (dft-scripts/script-243.py).

```
Atoms(symbols='C2OH6', positions=..., cell=[1.0, 1.0, 1.0], pbc=[False, False, False])
Indices to delete:  [3, 4, 5, 6, 7, 8]
Atoms(symbols='C2O', positions=..., cell=[1.0, 1.0, 1.0], pbc=[False, False, False])
```

10.1.2 Advanced tagging

We can label atoms with integer tags to help identify them later, e.g. which atoms are adsorbates, or surface atoms, or near an adsorbate, etc... We might want to refer to those atoms later for electronic structure, geometry analysis, etc...

The method uses integer tags that are powers of two, and then uses binary operators to check for matches. & is a bitwise AND. The key to understanding this is to look at the tags in binary form. The tags [1 2 4 8] can be represented by a binary string:

```
1 = [1 0 0 0]
2 = [0 1 0 0]
4 = [0 0 1 0]
8 = [0 0 0 1]
```

So, an atom tagged with 1 and 2 would have a tag of [1 1 0 0] or equivalently in decimal numbers, a tag of 3.

```python
'''
adapted from https://listserv.fysik.dtu.dk/pipermail/campos/2004-September/001155.html
'''

from ase import *
from ase.io import write
from ase.lattice.surface import bcc111, add_adsorbate
from ase.constraints import FixAtoms

# the bcc111 function automatically tags atoms
slab = bcc111('W',
              a=3.92,        # W lattice constant
              size=(2, 2, 6),  # 6-layer slab in 2x2 configuration
              vacuum=10.0)

# reset tags to be powers of two so we can use binary math
slab.set_tags([2**a.get_tag() for a in slab])

# we had 6 layers, so we create new tags starting at 7
# Note you must use powers of two for all the tags!
LAYER1 = 2
ADSORBATE = 2**7
FREE = 2**8
NEARADSORBATE = 2**9

# let us tag LAYER1 atoms to be FREE too. we can address it by LAYER1 or FREE
tags = slab.get_tags()
for i, tag in enumerate(tags):
    if tag == LAYER1:
        tags[i] += FREE
slab.set_tags(tags)

# create a CO molecule
co=Atoms([Atom('C', [0., 0., 0.], tag=ADSORBATE),
          # we will relax only O
          Atom('O', [0., 0., 1.1], tag=ADSORBATE + FREE)])

add_adsorbate(slab, co, height=1.2, position='hollow')

# the adsorbate is centered between atoms 20, 21 and 22 (use
# view(slab)) and over atom12 let us label those atoms, so it is easy to
# do electronic structure analysis on them later.
tags = slab.get_tags()  # len(tags) changed, so we reget them.
tags[12] += NEARADSORBATE
tags[20] += NEARADSORBATE
tags[21] += NEARADSORBATE
tags[22] += NEARADSORBATE
slab.set_tags(tags)
```

```python
# update the tags
slab.set_tags(tags)

# extract pieces of the slab based on tags
# atoms in the adsorbate
ads = slab[(slab.get_tags() & ADSORBATE) == ADSORBATE]

# atoms in LAYER1
layer1 = slab[(slab.get_tags() & LAYER1) == LAYER1]

# atoms defined as near the adsorbate
nearads = slab[(slab.get_tags() & NEARADSORBATE) == NEARADSORBATE]

# atoms that are free
free = slab[(slab.get_tags() & FREE) == FREE]

# atoms that are FREE and part of the ADSORBATE
freeads = slab[(slab.get_tags() & FREE+ADSORBATE) == FREE+ADSORBATE]

# atoms that are NOT FREE
notfree = slab[(slab.get_tags() & FREE) != FREE]

constraint = FixAtoms(mask=(slab.get_tags() & FREE) != FREE)
slab.set_constraint(constraint)
write('images/tagged-bcc111.png', slab, rotation='-90x', show_unit_cell=2)
from ase.visualize import view; view(slab)
```

Open the python script (dft-scripts/script-244.py).

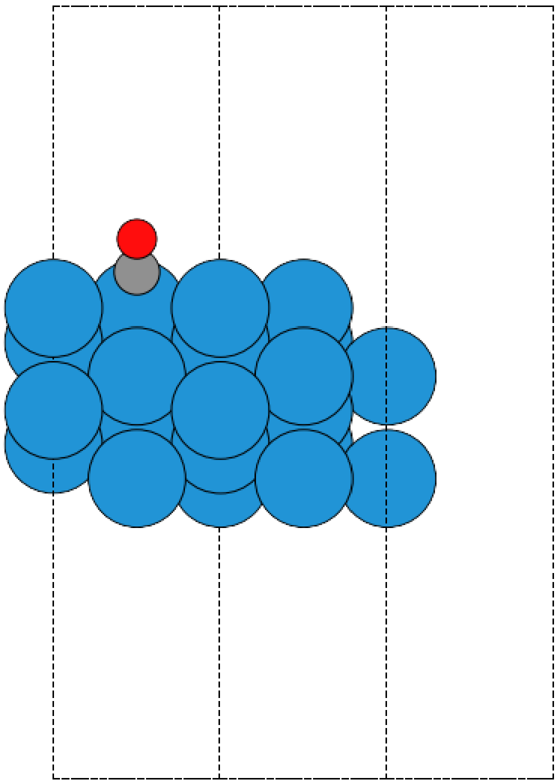


Figure 97: The tagged bcc(111) structure created above. Unfortunately, the frozen atoms do not show up in the figure.

10.1.3 Using units in ase

ase uses a base set of atomic units.These are eV for energy, Å for distance, seconds for time, and amu for mass. Other units are defined in terms of those units, and you can easily convert to alternative units by dividing your quantity in atomic units by the units you want.

Not too many units are defined: ['A', 'AUT', 'Ang', 'Angstrom', 'Bohr', 'C', 'Debye', 'GPa', 'Ha', 'Hartree', 'J', 'Pascal', 'Ry', 'Rydberg', 'alpha', 'cm', 'eV', 'erg', 'fs', 'kB', 'kJ', 'kcal', 'kg', 'm', 'meV', 'mol', 'nm', 's', 'second']

It is not that hard to define your own derived units though. Note these are only conversion factors. No units algebra is enforced (i.e. it will be ok to add a m and a kg)!

```python
from ase.units import *

d = 1 * Angstrom
print(' d = {0} nm'.format(d / nm))

print('1 eV = {0} Hartrees'.format(eV / Hartree))
print('1 eV = {0} Rydbergs'.format(eV / Rydberg))
print('1 eV = {0} kJ/mol'.format(eV / (kJ / mol)))
print('1 eV = {0} kcal/mol'.format(eV / (kcal / mol)))

print('1 Hartree = {0} kcal/mol'.format(1 * Hartree / (kcal / mol)))
print('1 Rydberg = {0} eV'.format(1 * Rydberg / eV))

# derived units
minute = 60 * s
hour = 60 * minute

# convert 10 hours to minutes
print('10 hours = {0} minutes'.format(10 * hour / minute))
```

Open the python script (dft-scripts/script-245.py).

```
 d = 0.1 nm
1 eV = 0.036749309468 Hartrees
1 eV = 0.0734986189359 Rydbergs
1 eV = 96.485308989 kJ/mol
1 eV = 23.0605423014 kcal/mol
1 Hartree = 627.509540594 kcal/mol
1 Rydberg = 13.6056978278 eV
10 hours = 600.0 minutes
```

10.1.4 Extracting parts of an array

See http://www.scipy.org/Cookbook/BuildingArrays for examples of making numpy arrays.

When analyzing numerical data you may often want to analyze only a part of the data. For example, suppose you have x and y data, (x=time, y=signal) and you want to integrate the date between a particular time interval. You can slice a numpy array to extract parts of it. See http://www.scipy.org/Cookbook/Indexing for several examples of this.

In this example we show how to extract the data in an interval. We have x data in the range of 0 to 6, and y data that is the $\cos(x)$. We want to extract the x and y data for $2 < x < 4$, and the corresponding y-data. To do this, we utilize the numpy capability of slicing with a boolean array. We also show some customization of matplotlib.

```python
import numpy as np
import matplotlib as mpl
# http://matplotlib.sourceforge.net/users/customizing.html
mpl.rcParams['legend.numpoints'] = 1  # default is 2
import matplotlib.pyplot as plt

x = np.linspace(0, 6, 100)
y = np.cos(x)

plt.plot(x, y, label='full')

```

```
ind = (x > 2) & (x < 4)

subx = x[ind]
suby = y[ind]

plt.plot(subx, suby, 'bo', label='sliced')
xlabel('x')
ylabel('cos(x)')
plt.legend(loc='lower right')
plt.savefig('images/np-array-slice.png')
```

Open the python script (dft-scripts/script-246.py).

```
None
```

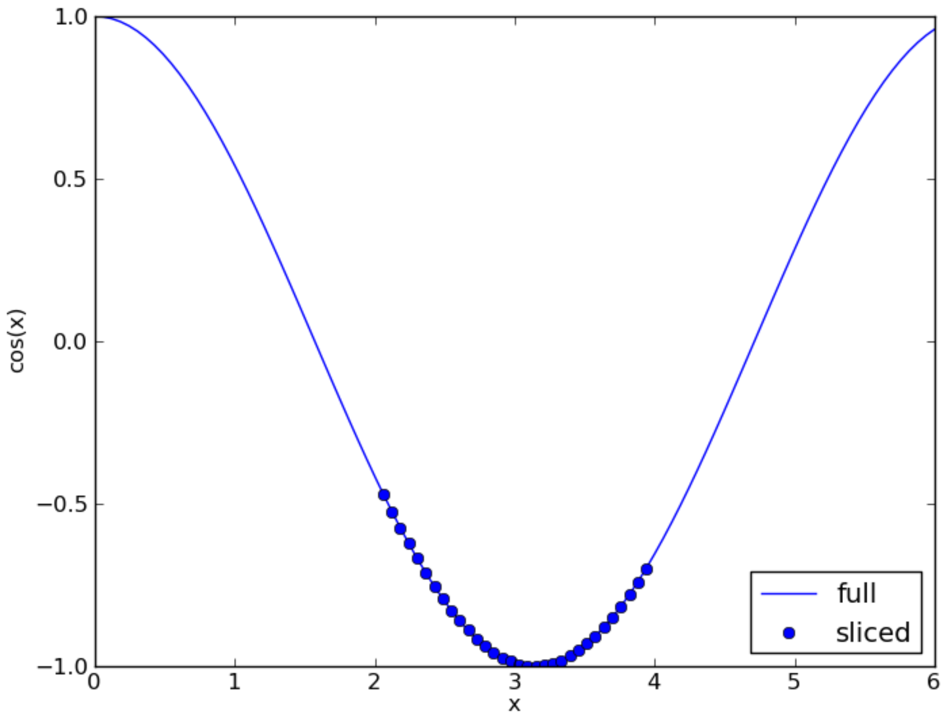


Figure 98: Example of slicing out part of an array. The solid line represents the whole array, and the symbols are the array between $2 < x < 4$.

The expression $x > 2$ returns an array of booleans (True where the element of x is greater than 2, and False where it is not) equal in size to x. Similarly $x < 4$ returns a boolean array where x is less than 4. We take the logical `and` of these two boolean arrays to get another boolean array where both conditions are True (i.e. $x < 2$ and $x > 4$). This final boolean array is `True` for the part of the arrays we are interested in, and we can use it to extract the subarrays we want.

10.1.5 Statistics

Confidence intervals `scipy` has a statistical package available for getting statistical distributions. This is useful for computing confidence intervals using the student-t tables. Here is an example of computing a 95% confidence interval on an average.

```python
import numpy as np
from scipy.stats.distributions import  t

n = 10  # number of measurements
dof = n - 1  # degrees of freedom
avg_x = 16.1  # average measurement
std_x = 0.01  # standard deviation of measurements

# Find 95% prediction interval for next measurement

alpha = 1.0 - 0.95

pred_interval = t.ppf(1 - alpha / 2., dof) * std_x * np.sqrt(1. + 1. / n)

s = ['We are 95% confident the next measurement',
       ' will be between {0:1.3f} and {1:1.3f}']
print(''.join(s).format(avg_x - pred_interval, avg_x + pred_interval))
```

Open the python script (dft-scripts/script-247.py).

```
We are 95% confident the next measurement will be between 16.076 and 16.124
```

10.1.6 Curve fitting

Linear fitting

```python
# examples of linear curve fitting using least squares
import numpy as np

xdata = np.array([0., 1., 2., 3., 4., 5., 6.])
ydata = np.array([0.1, 0.81, 4.03, 9.1, 15.99, 24.2, 37.2])

# fit a third order polynomial
from pylab import polyfit, plot, xlabel, ylabel, show, legend, savefig
pars = polyfit(xdata, ydata, 3)
print('pars from polyfit: {0}'.format(pars))

# numpy method returns more data
A = np.column_stack([xdata**3,
                     xdata**2,
                     xdata,
                     np.ones(len(xdata), np.float)])

pars_np, resids, rank,s = np.linalg.lstsq(A, ydata)
print('pars from np.linalg.lstsq: {0}'.format(pars_np))

'''
we are trying to solve Ax = b for x in the least squares sense. There
are more rows in A than elements in x so, we can left multiply each
side by A^T, and then solve for x with an inverse.

A^TAx = A^Tb
x = (A^TA)^-1 A^T b
'''
# not as pretty but equivalent!
pars_man = np.dot(np.linalg.inv(np.dot(A.T, A)), np.dot(A.T, ydata))
print('pars from linear algebra: {0}'.format(pars_man))

# but, it is easy to fit an exponential function to it!
# y = a*exp(x)+b
Aexp = np.column_stack([np.exp(xdata), np.ones(len(xdata), np.float)])
pars_exp = np.dot(np.linalg.inv(np.dot(Aexp.T, Aexp)), np.dot(Aexp.T, ydata))

plot(xdata, ydata, 'ro')
fity = np.dot(A, pars)
plot(xdata, fity, 'k-', label='poly fit')
plot(xdata, np.dot(Aexp, pars_exp), 'b-', label='exp fit')
xlabel('x')
ylabel('y')
legend()
savefig('images/curve-fit-1.png')
```

Open the python script (dft-scripts/script-248.py).

```
pars from polyfit: [ 0.04861111  0.63440476  0.61365079 -0.08928571]
pars from np.linalg.lstsq: [ 0.04861111  0.63440476  0.61365079 -0.08928571]
pars from linear algebra: [ 0.04861111  0.63440476  0.61365079 -0.08928571]
```

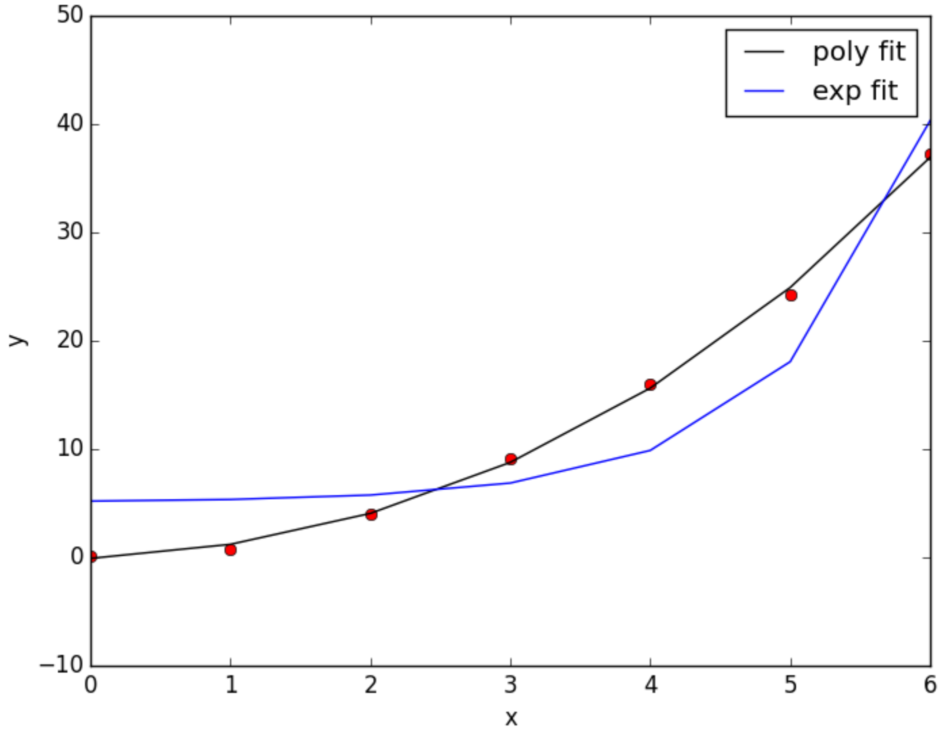


Figure 99: Example of linear least-squares curve fitting.

10.1.7 Nonlinear curve fitting

```python
from scipy.optimize import leastsq
import numpy as np

vols = np.array([13.71, 14.82, 16.0, 17.23, 18.52])

energies = np.array([-56.29, -56.41, -56.46, -56.463, -56.41])


def Murnaghan(parameters, vol):
    'From Phys. Rev. B 28, 5480 (1983)'
    E0 = parameters[0]
    B0 = parameters[1]
    BP = parameters[2]
    V0 = parameters[3]

    E = (E0 + B0*vol / BP*(((V0 / vol)**BP) / (BP - 1) + 1)
         - V0 * B0 / (BP - 1.))

    return E


def objective(pars, y, x):
    # we will minimize this function
    err = y - Murnaghan(pars, x)
    return err

```

```python
x0 = [-56., 0.54, 2., 16.5]  # initial guess of parameters

plsq = leastsq(objective, x0, args=(energies, vols))

print('Fitted parameters = {0}'.format(plsq[0]))

import matplotlib.pyplot as plt
plt.plot(vols, energies, 'ro')

# plot the fitted curve on top
x = np.linspace(min(vols), max(vols), 50)
y = Murnaghan(plsq[0], x)
plt.plot(x, y, 'k-')
plt.xlabel('Volume')
plt.ylabel('energy')
plt.savefig('images/nonlinear-curve-fitting.png')
```

Open the python script (dft-scripts/script-249.py).

```
Fitted parameters = (array([-56.46839641,   0.57233217,   2.7407944 ,  16.55905648]), 1)
```

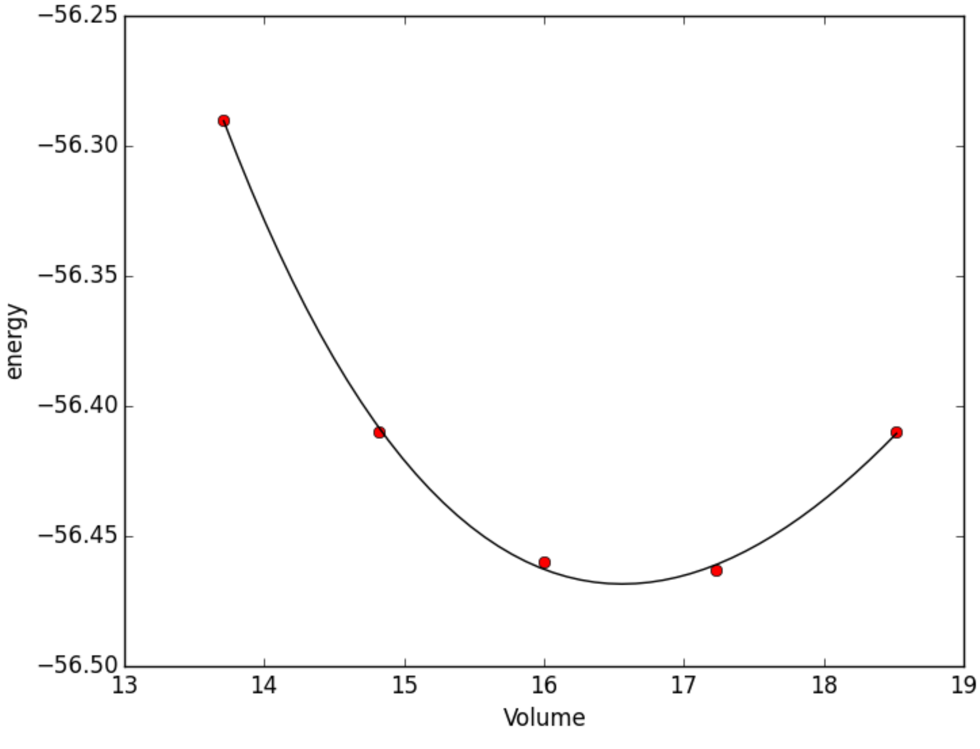


Figure 100: Example of least-squares non-linear curve fitting.

See additional examples at http://docs.scipy.org/doc/scipy/reference/tutorial/optimize.html.

10.1.8 Nonlinear curve fitting by direct least squares minimization

```python
from scipy.optimize import fmin
import numpy as np

```

```python
volumes = np.array([13.71, 14.82, 16.0, 17.23, 18.52])

energies = np.array([-56.29, -56.41, -56.46, -56.463, -56.41])


def Murnaghan(parameters, vol):
    'From PRB 28,5480 (1983'
    E0 = parameters[0]
    B0 = parameters[1]
    BP = parameters[2]
    V0 = parameters[3]

    E = E0 + B0*vol/BP*(((V0/vol)**BP)/(BP-1)+1) - V0*B0/(BP-1.)

    return E


def objective(pars, vol):
    # we will minimize this function
    err = energies - Murnaghan(pars, vol)
    return np.sum(err**2)  # we return the summed squared error directly

x0 = [-56., 0.54, 2., 16.5]  # initial guess of parameters

plsq = fmin(objective, x0, args=(volumes,))  # note args is a tuple

print('parameters = {0}'.format(plsq))

import matplotlib.pyplot as plt
plt.plot(volumes, energies, 'ro')

# plot the fitted curve on top
x = np.linspace(min(volumes), max(volumes), 50)
y = Murnaghan(plsq, x)
plt.plot(x, y, 'k-')
plt.xlabel(r'Volume ($\AA^3$)')
plt.ylabel('Total energy (eV)')
plt.savefig('images/nonlinear-fitting-lsq.png')
```

Open the python script (dft-scripts/script-250.py).

```
Optimization terminated successfully.
         Current function value: 0.000020
         Iterations: 137
         Function evaluations: 240
parameters = [-56.46932645   0.59141447   1.9044796   16.59341303]
```

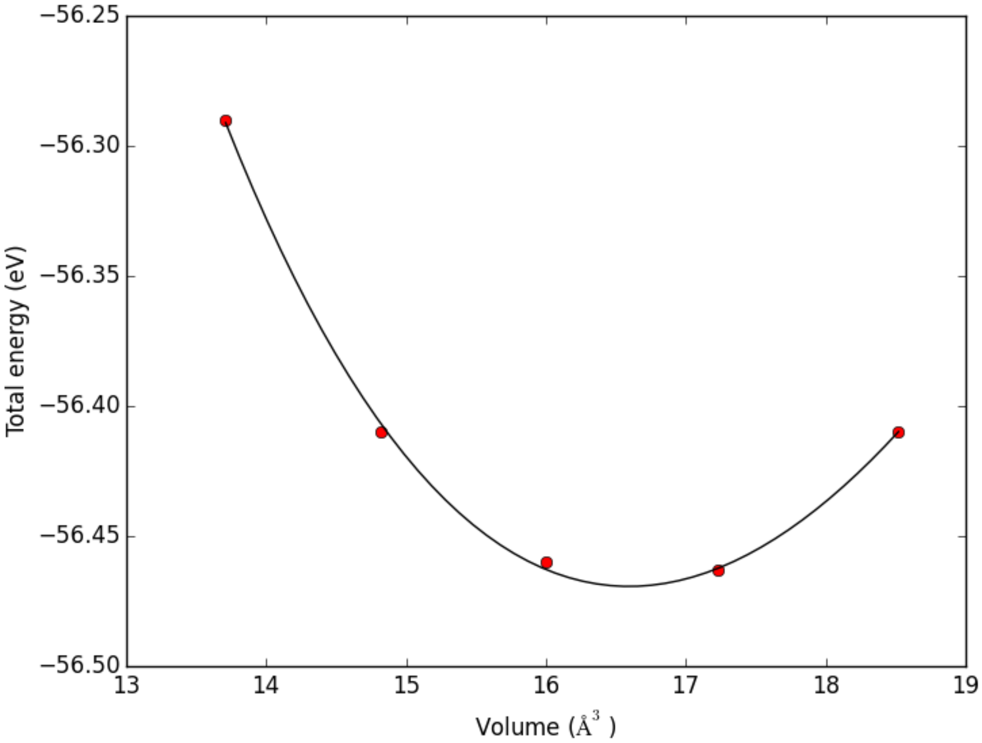


Figure 101: Fitting a nonlinear function.

10.1.9 Nonlinear curve fitting with confidence intervals

```python
# Nonlinear curve fit with confidence interval
import numpy as np
from scipy.optimize import curve_fit
from scipy.stats.distributions import  t

'''
fit this equation to data
y = c1 exp(-x) + c2*x

this is actually a linear regression problem, but it is convenient to
use the nonlinear fitting routine because it makes it easy to get
confidence intervals. The downside is you need an initial guess.

from Matlab
b =

    4.9671
    2.1100


bint =

    4.6267    5.3075
    1.7671    2.4528
'''

x = np.array([ 0.1,  0.2,  0.3,  0.4,  0.5,  0.6,  0.7,  0.8,  0.9,  1. ])
y = np.array([ 4.70192769,  4.46826356,  4.57021389,  4.29240134,  3.88155125,
            3.78382253,  3.65454727,  3.86379487,  4.16428541,  4.06079909])

# this is the function we want to fit to our data
def func(x,c0, c1):
    return c0 * np.exp(-x) + c1*x
```

```
pars, pcov = curve_fit(func, x, y, p0=[4.96, 2.11])

alpha = 0.05 # 95% confidence interval

n = len(y)    # number of data points
p = len(pars) # number of parameters

dof = max(0, n-p) # number of degrees of freedom

tval = t.ppf(1.0-alpha/2., dof) # student-t value for the dof and confidence level

for i, p,var in zip(range(n), pars, np.diag(pcov)):
    sigma = var**0.5
    print('c{0}: {1} [{2}  {3}]'.format(i, p,
                                  p - sigma*tval,
                                  p + sigma*tval))

import matplotlib.pyplot as plt
plt.plot(x,y,'bo ')
xfit = np.linspace(0,1)
yfit = func(xfit, pars[0], pars[1])
plt.plot(xfit,yfit,'b-')
plt.legend(['data','fit'],loc='best')
plt.savefig('images/nonlin-fit-ci.png')
```

Open the python script (dft-scripts/script-251.py).

```
c0: 4.96713966439 [4.62674476321  5.30753456558]
c1: 2.10995112628 [1.76711622067  2.45278603188]
```

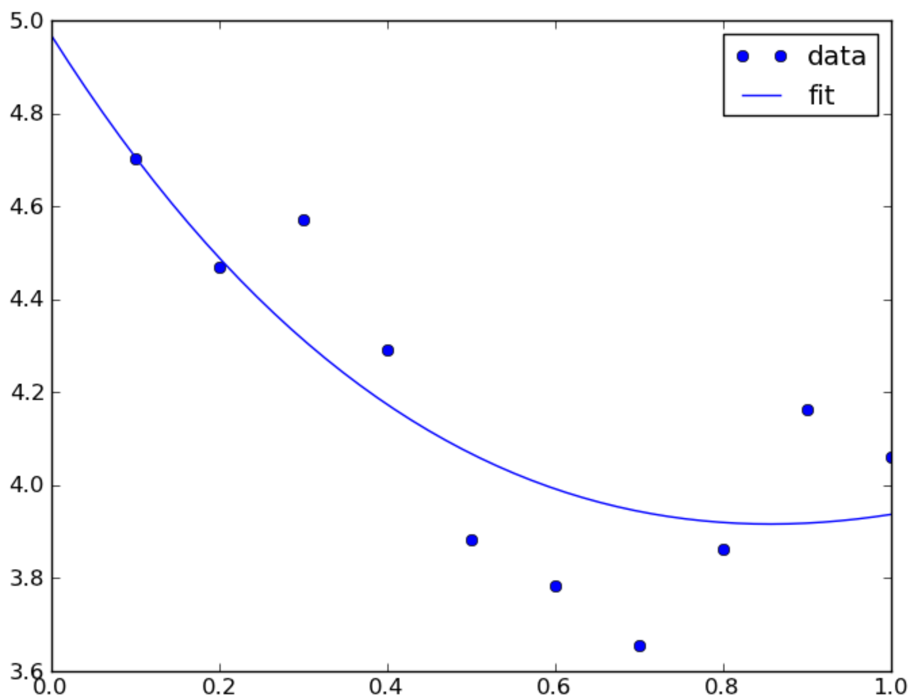


Figure 102: Nonlinear fit to data.

10.1.10 Interpolation with splines

When you do not know the functional form of data to fit an equation, you can still fit/interpolate with splines.

```
# use splines to fit and interpolate data
from scipy.interpolate import interp1d
from scipy.optimize import fmin
import numpy as np
import matplotlib.pyplot as plt

x = np.array([ 0,      1,      2,      3,      4    ])
y = np.array([ 0.,     0.308,  0.55,   0.546,  0.44 ])

# create the interpolating function
f = interp1d(x, y, kind='cubic', bounds_error=False)

# to find the maximum, we minimize the negative of the function. We
# cannot just multiply f by -1, so we create a new function here.
f2 = interp1d(x, -y, kind='cubic')
xmax = fmin(f2, 2.5)

xfit = np.linspace(0,4)

plt.plot(x,y,'bo')
plt.plot(xfit, f(xfit),'r-')
plt.plot(xmax, f(xmax),'g*')
plt.legend(['data','fit','max'], loc='best', numpoints=1)
plt.xlabel('x data')
plt.ylabel('y data')
plt.title('Max point = ({0:1.2f}, {1:1.2f})'.format(float(xmax),
                                                    float(f(xmax))))
plt.savefig('images/splinefit.png')
```

Open the python script (dft-scripts/script-252.py).

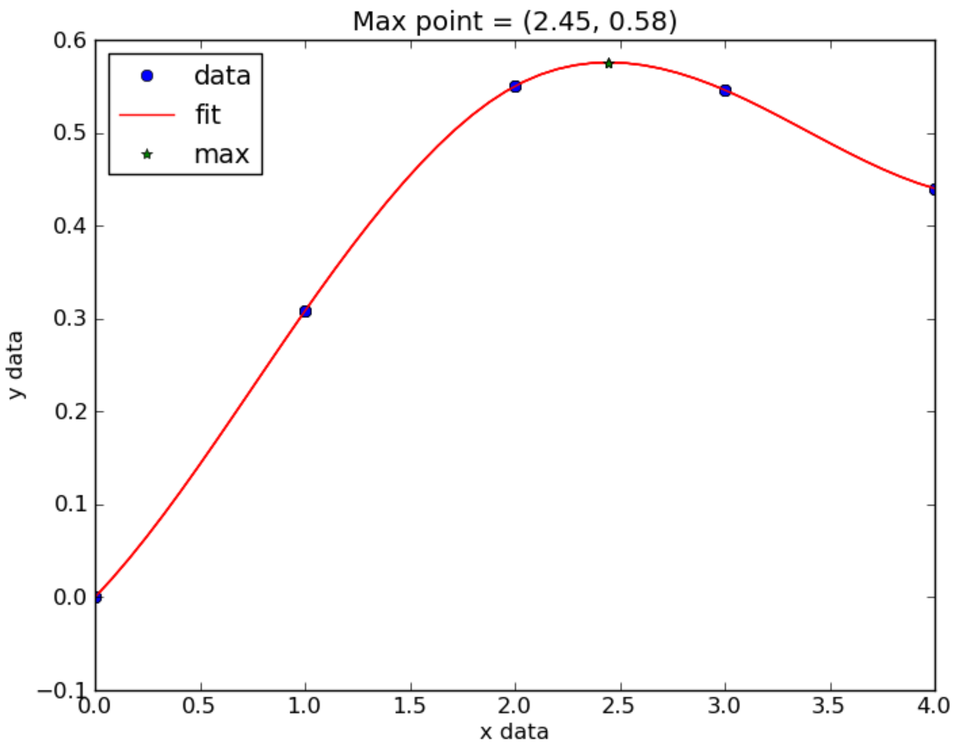


Figure 103: Illustration of a spline fit to data and finding the maximum point.

There are other good examples at http://docs.scipy.org/doc/scipy/reference/tutorial/interpolate.html

10.1.11 Interpolation in 3D

You might ask, why would I need to interpolate in 3D? Suppose you want to plot the charge density along a line through a unit cell that does not correspond to grid points. What are you to do? Interpolate. In contrast to an abundance of methods for 1D and 2D interpolation, I could not find any standard library methods for 3D interpolation.

The principle we will use to develop an interpolation function in 3D is called trilinear interpolation, where we use multiple linear 1D interpolations to compute the value of a point inside a cube. As developed here, this solution only applies to rectangular grids. Later we will generalize the approach. We state the problem as follows:

We know a scalar field inside a unit cell on a regularly spaced grid. In VASP these fields may be the charge density or electrostatic potential for example, and they are known on the fft grids. We want to estimate the value of the scalar field at a point not on the grid, say P=(a,b,c).

Solution: Find the cube that contains the point, and is defined by points P1-P8 as shown in Figure 104.

We use 1D interpolation formulas to compute the value of the scalar field at points I1 by interpolating between P1 and P2, and the value of the scalar field at I2 by interpolating between P3 and P4. In these points the only variable changing is x, so it is a simple 1D interpolation. We can then compute the value of the scalar field at I5 by interpolating between I1 and I2. We repeat the process on the top of the cube, to obtain points I3, I4 and I5. Finally, we compute the value of the scalar field at point P by interpolating between points I5 and I6. Note that the point I5 has coordinates (a,b,z1) and I6 is at

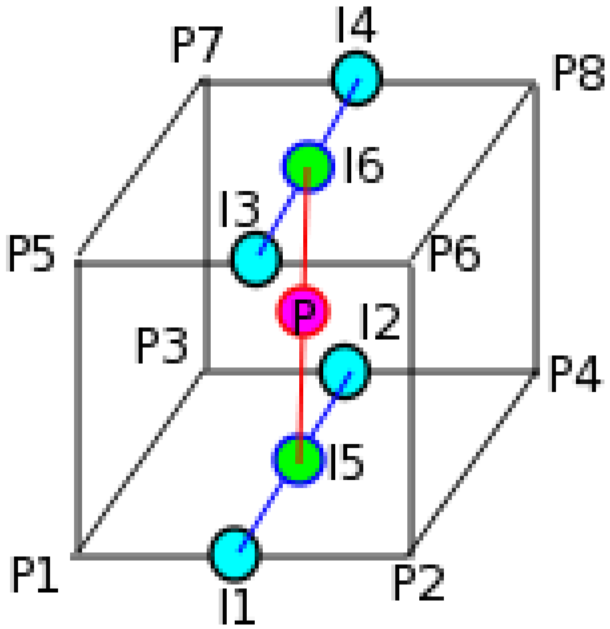


Figure 104: Trilinear interpolation scheme.

(a,b,z2), so the final interpolation is again a 1D interpolation along z evaluated at z=c to get the final value of the scalar field at P=(a,b,c).

```
from vasp import Vasp
import numpy as np

calc = Vasp('molecules/co-centered')
atoms = calc.get_atoms()
x, y, z, cd = calc.get_charge_density()

def interp3d(x,y,z,cd,xi,yi,zi):
    '''
    interpolate a cubic 3D grid defined by x,y,z,cd at the point
    (xi,yi,zi)
    '''

    def get_index(value,vector):
        '''
        assumes vector ordered decreasing to increasing. A bisection
        search would be faster.
        '''
```

```
        for i,val in enumerate(vector):
            if val > value:
                return i-1
        return None

    xv = x[:,0,0]
    yv = y[0,:,0]
    zv = z[0,0,:]

    a,b,c = xi, yi, zi

    i = get_index(a,xv)
    j = get_index(b,yv)
    k = get_index(c,zv)

    x1 = x[i,j,k]
    x2 = x[i+1,j,k]
    y1 = y[i,j,k]
    y2 = y[i,j+1,k]
    z1 = z[i,j,k]
    z2 = z[i,j,k+1]

    u1 = cd[i, j, k]
    u2 = cd[i+1, j, k]
    u3 = cd[i, j+1, k]
    u4 = cd[i+1, j+1, k]
    u5 = cd[i, j, k+1]
    u6 = cd[i+1, j, k+1]
    u7 = cd[i, j+1, k+1]
    u8 = cd[i+1, j+1, k+1]

    w1 = u2 + (u2-u1)/(x2-x1)*(a-x2)
    w2 = u4 + (u4-u3)/(x2-x1)*(a-x2)
    w3 = w2 + (w2-w1)/(y2-y1)*(b-y2)
    w4 = u5 + (u6-u5)/(x2-x1)*(a-x1)
    w5 = u7 + (u8-u7)/(x2-x1)*(a-x1)
    w6 = w4 + (w5-w4)/(y2-y1)*(b-y1)
    w7 = w3 + (w6-w3)/(z2-z1)*(c-z1)
    u = w7

    return u

pos = atoms.get_positions()

P1 = np.array([0.0, 5.0, 5.0])
P2 = np.array([9.0, 5.0, 5.0])

npoints = 60

points = [P1 + n*(P2-P1)/npoints for n in range(npoints)]

R = [np.linalg.norm(p-P1) for p in points]

# interpolated line
icd = [interp3d(x,y,z,cd,p[0],p[1],p[2]) for p in points]

import matplotlib.pyplot as plt

plt.plot(R, icd)
cR = np.linalg.norm(pos[0] - P1)
oR = np.linalg.norm(pos[1] - P1)
plt.plot([cR, cR], [0, 2], 'r-') #markers for where the nuclei are
plt.plot([oR, oR], [0, 8], 'r-')
plt.xlabel('|R| ($\AA$)')
plt.ylabel('Charge density (e/$\AA^3$)')
plt.savefig('images/CO-charge-density.png')
plt.show()
```

Open the python script (dft-scripts/script-253.py).

```
None
```

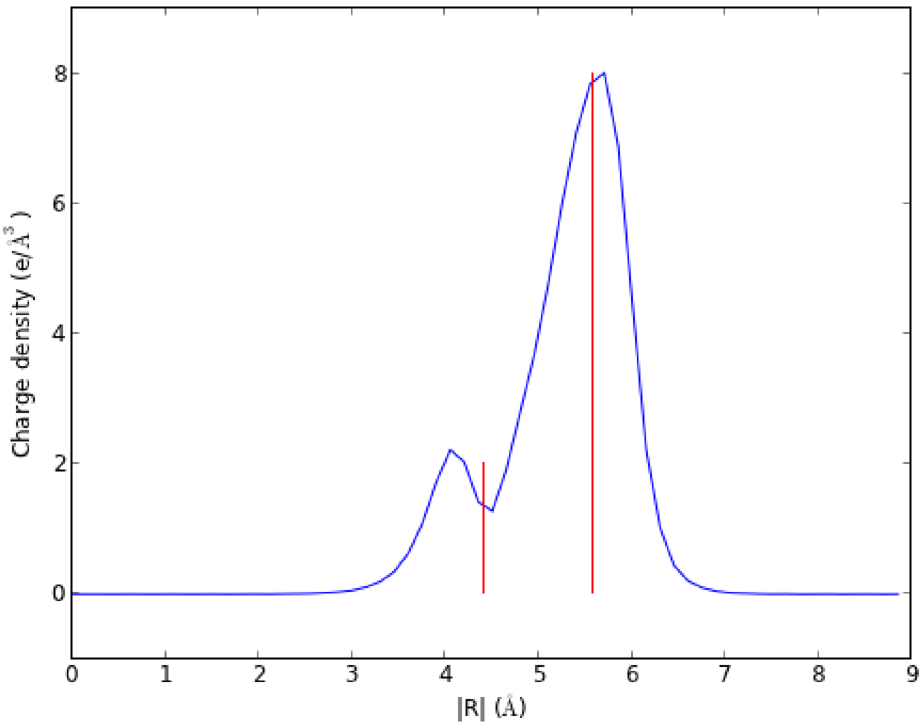


Figure 105: An example of interpolated charge density of a CO molecule along the axis of molecule.

To generalize this to non-cubic cells, we need to do interpolation along arbitrary vectors. The overall strategy is the same:

Find the cell that contains the point (a,b,c). compute the scaled coordinates (sa,sb,sc) of the point inside the cell. Do the interpolations along the basis vectors. Given u1 at P1(x1,y1,z1) and u2 at P2(x2,y2,z2) where (P2-P1) is a cell basis vector a, u = u1 + sa*(u2-u1). There are still 7 interpolations to do.

Below is an example of this code, using a the python library bisect to find the cell.

```
'''
3D vector interpolation in non-cubic unit cells with vector
interpolation.

This function should work for any shape unit cell.
'''
from vasp import Vasp
import bisect
import numpy as np
from pylab import plot, xlabel, ylabel, savefig, show

calc = Vasp('molecules/co-centered')
atoms = calc.get_atoms()
x,y,z,cd = calc.get_charge_density()

def vinterp3d(x, y, z, u, xi, yi, zi):

    p = np.array([xi, yi, zi])

    #1D arrays of cooridinates
    xv = x[:, 0, 0]
    yv = y[0, :, 0]
    zv = z[0, 0, :]

```

```python
    # we subtract 1 because bisect tells us where to insert the
    # element to maintain an ordered list, so we want the index to the
    # left of that point
    i = bisect.bisect_right(xv, xi) - 1
    j = bisect.bisect_right(yv, yi) - 1
    k = bisect.bisect_right(zv, zi) - 1

    #points at edge of cell. We only need P1, P2, P3, and P5
    P1 = np.array([x[i, j, k], y[i, j, k], z[i,j,k]])
    P2 = np.array([x[i + 1, j, k], y[i + 1, j, k], z[i + 1, j, k]])
    P3 = np.array([x[i, j + 1, k], y[i, j + 1, k], z[i, j + 1, k]])
    P5 = np.array([x[i, j, k + 1], y[i, j, k + 1], z[i, j, k + 1]])

    #values of u at edge of cell
    u1 = u[i, j, k]
    u2 = u[i + 1, j, k]
    u3 = u[i, j + 1, k]
    u4 = u[i + 1, j + 1, k]
    u5 = u[i, j, k + 1]
    u6 = u[i + 1, j, k + 1]
    u7 = u[i, j + 1, k + 1]
    u8 = u[i + 1, j + 1, k + 1]

    #cell basis vectors, not the unit cell, but the voxel cell containing the point
    cbasis = np.array([P2 - P1,
                       P3 - P1,
                       P5 - P1])

    #now get interpolated point in terms of the cell basis
    s = np.dot(np.linalg.inv(cbasis.T), np.array([xi, yi, zi]) - P1)

    #now s = (sa, sb, sc) which are fractional coordinates in the vector space
    #next we do the interpolations
    ui1 = u1 + s[0] * (u2 - u1)
    ui2 = u3 + s[0] * (u4 - u3)

    ui3 = u5 + s[0] * (u6 - u5)
    ui4 = u7 + s[0] * (u8 - u7)

    ui5 = ui1 + s[1] * (ui2 - ui1)
    ui6 = ui3 + s[1] * (ui4 - ui3)

    ui7 = ui5 + s[2] * (ui6 - ui5)

    return ui7

# compute a line with 60 points in it through these two points
P1 = np.array([0.0, 5.0, 5.0])
P2 = np.array([10.0, 5.0, 5.0])

npoints = 60

points = [P1 + n * (P2 - P1) / npoints for n in range(npoints)]

# compute the distance along the line
R = [np.linalg.norm(p - P1) for p in points]

icd = [vinterp3d(x, y, z, cd, p[0], p[1], p[2]) for p in points]

plot(R, icd)
pos = atoms.get_positions()
cR = np.linalg.norm(pos[0] - P1)
oR = np.linalg.norm(pos[1] - P1)
plot([cR, cR], [0, 2], 'r-') #markers for where the nuclei are
plot([oR, oR], [0, 8], 'r-')
xlabel('|R| ($\AA$)')
ylabel('Charge density (e/$\AA^3$)')
savefig('images/interpolated-charge-density.png')
show()
```

Open the python script (dft-scripts/script-254.py).

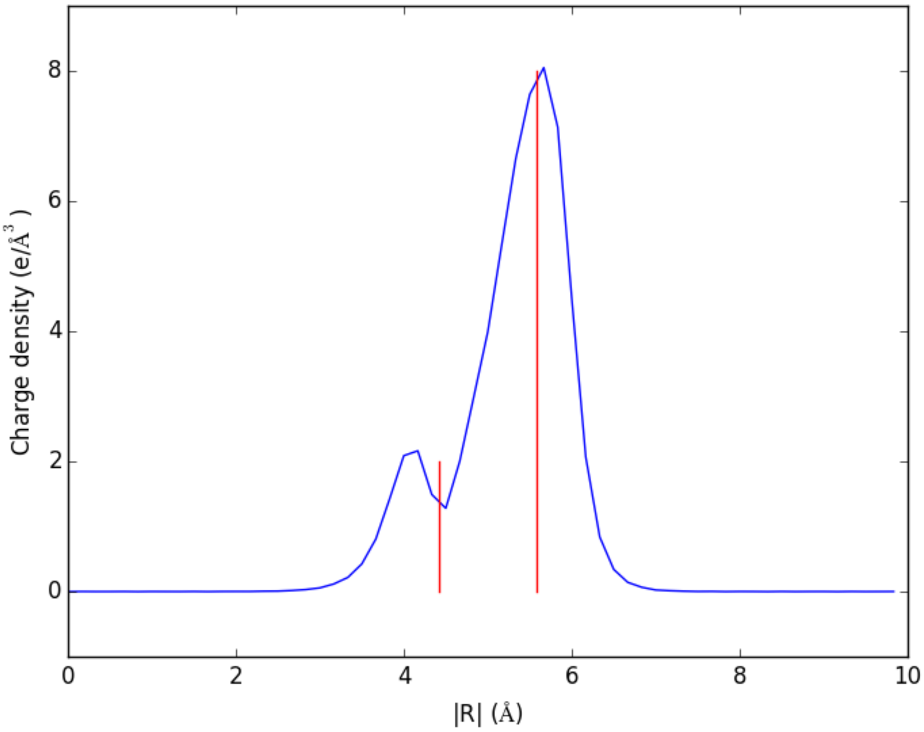


Figure 106: Interpolated charge density for a CO molecule.

10.1.12 Reading and writing data

Built-in io modules pylab has two convenient and powerful functions for saving and reading data, pylab.save and pylab.load.

```
pylab.save('pdat.dat',(x,y))
```

Open the python script (dft-scripts/script-255.py).
and later you can read these arrays back in with:

```
x,y = pylab.load('pdat.dat')
```

Open the python script (dft-scripts/script-256.py).
see also pylab.csv2rec and pylab.loadtxt and pylab.savetxt.
See http://www.scipy.org/Cookbook/InputOutput for examples of numpy io.

From scratch You can save data in many ways from scratch. Basically, just open a file and write data to it. Likewise, any datafile that has some structure to it can probably be read by python.

Let us consider a datafile with these contents:

```
#header
#ignore these lines
john, 4
robert, 5
terry, 5
```

A standard approach would be to read in all the lines, skip the first two lines, split each line (remember each line is a string) at the ',', and append the first field to one variable, and append the second field to another variable as an integer. For example:

```
v1 = []
v2 = []
lines = open('somefile','r').readlines()

for line in lines[2:]: #skip the first two lines
    fields = line.split(',')
        v1.append(fields[0]) #names
        v2.append(int(fields[1])) #number
```

Open the python script (dft-scripts/script-257.py).

Writing datafiles is easy too.

```
v1 = ['john', 'robert', 'terry']
v2 = [4,5,6]
f = open('somefile', 'w') #note 'w' = write mode
f.write('#header\n')
f.write('#ignore these lines\n')
for a,b in zip(v1,v2):
        f.write('{0}, {1}\n'.format(a,b))
f.close()
```

Open the python script (dft-scripts/script-258.py).

Some notes:

1. opening a file in 'w' mode clobbers any existing file, so do that

with care!

1. when writing to a file you have to add a carriage return to each line.
2. Manually writing and reading files is pretty tedious. Whenever

possible you should use the built-in methods of numpy or pylab.

10.1.13 Integration

Numerical integrations is easy with the numpy.trapz() method. Use it like this: numpy.trapz(y,x). Note that y comes first. y and x must be the same length.

Integration can be used to calculate average properties of continuous distributions. Suppose for example, we have a density of states, ρ as a function of energy E. We can integrate the density of states to find the total number of states:

$N_{states} = \int \rho dE$

or, in python:

```
Nstates = np.trapz(rho,E)
```

Open the python script (dft-scripts/script-259.py).

where rho is a vector that contains the density of states at each energy in the vector E (vector here means a list of numbers).

The average energy of distribution is:

$E_{avg} = \frac{\int \rho E dE}{\int \rho dE}$

or, in python:

```
e_avg = np.trapz(rho*E,E)/np.trapz(rho,E)
```

Open the python script (dft-scripts/script-260.py).

These last two examples are the zeroth and first moments of the density of states. The second moment is related to the width squared of the distribution, and the third and fourth moements are related to skewness and kurtosis of the distribution.

The nth moment is defined by:

$m_n = \frac{\int \rho * E^n dE}{\int \rho dE}$

To get the second moment of the density of states in python, we use::

```
n = 2
mom_2 = np.trapz(rho*E**n,E)/np.trapz(rho,E)
```

Open the python script (dft-scripts/script-261.py).

10.1.14 Numerical differentiation

numpy has a function called `numpy.diff` that is similar to the one found in Matlab. It calculates the differences between the elements in your list, and returns a list that is one element shorter, which makes it unsuitable for plotting the derivative of a function.

Simple loops to define finite difference derivatives Loops in python are pretty slow (relatively speaking) but they are usually trivial to understand. In this script we show some simple ways to construct derivative vectors using loops. It is implied in these formulas that the data points are equally spaced.

```
import numpy as np
import matplotlib.pyplot as plt
import time

'''
These are the brainless way to calculate numerical derivatives. They
work well for very smooth data. they are surprisingly fast even up to
10000 points in the vector.
'''

x = np.linspace(0.78, 0.79, 100) # 100 points between 0.78 and 0.79
y = np.sin(x)
dy_analytical = np.cos(x)
'''
let us use a forward difference method:
that works up until the last point, where there is not
a forward difference to use. there, we use a backward difference.
'''

tf1 = time.time()
dyf = [0.0]*len(x)
for i in range(len(y)-1):
    dyf[i] = (y[i+1] - y[i])/(x[i+1]-x[i])
# set last element by backwards difference
dyf[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

print(' Forward difference took {0:1.1f} seconds'.format(time.time() - tf1))

# and now a backwards difference
tb1 = time.time()
dyb = [0.0]*len(x)
# set first element by forward difference
dyb[0] = (y[0] - y[1])/(x[0] - x[1])
for i in range(1,len(y)):
    dyb[i] = (y[i] - y[i-1])/(x[i]-x[i-1])

print(' Backward difference took {0:1.1f} seconds'.format(time.time() - tb1))

# and now, a centered formula
tc1 = time.time()
dyc = [0.0]*len(x)
dyc[0] = (y[0] - y[1])/(x[0] - x[1])
for i in range(1,len(y)-1):
```

```
    dyc[i] = (y[i+1] - y[i-1])/(x[i+1]-x[i-1])
dyc[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

print(' Centered difference took {0:1.1f} seconds'.format(time.time() - tc1))

# the centered formula is the most accurate formula here


plt.plot(x,dy_analytical, label='analytical derivative')
plt.plot(x,dyf,'--', label='forward')
plt.plot(x,dyb,'--', label='backward')
plt.plot(x,dyc,'--', label='centered')

plt.legend(loc='lower left')
plt.savefig('images/simple-diffs.png')
```

Open the python script (dft-scripts/script-262.py).

```
Forward difference took 0.0 seconds
Backward difference took 0.0 seconds
Centered difference took 0.0 seconds
```

Obviously, all of these evaluations are very fast.

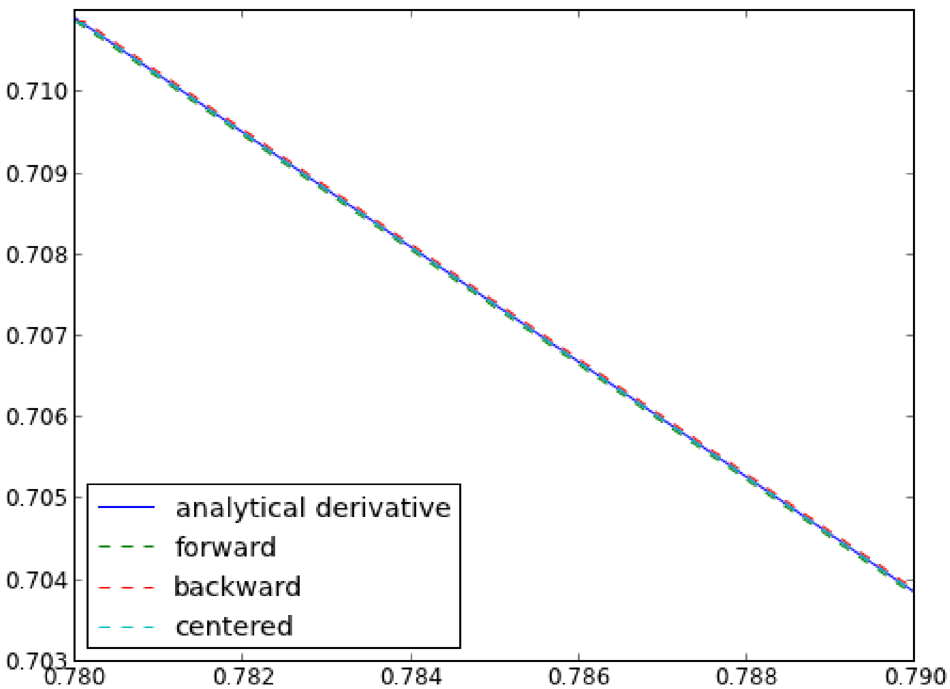


Figure 107: Comparison of different numerical derivatives.

Loops are usually not great for performance. Numpy offers some vectorized methods that allow us to compute derivatives without loops, although this comes at the mental cost of harder to understand syntax:

```
import numpy as np
import matplotlib.pyplot as plt
```

```

x = np.linspace(0,2*np.pi,100)
y = np.sin(x)
dy_analytical = np.cos(x)

# we need to specify the size of dy ahead because diff returns
#an array of n-1 elements
dy = np.zeros(y.shape,np.float) #we know it will be this size
dy[0:-1] = np.diff(y)/np.diff(x)
dy[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])


'''
calculate dy by center differencing using array slices
'''

dy2 = np.zeros(y.shape,np.float) #we know it will be this size
dy2[1:-1] = (y[2:] - y[0:-2])/(x[2:] - x[0:-2])
dy2[0] = (y[1]-y[0])/(x[1]-x[0])
dy2[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

plt.plot(x,y)
plt.plot(x,dy_analytical,label='analytical derivative')
plt.plot(x,dy,label='forward diff')
plt.plot(x,dy2,'k--',lw=2,label='centered diff')
plt.legend(loc='lower left')
plt.savefig('images/vectorized-diffs.png')
```

Open the python script (dft-scripts/script-263.py).

```
None
```

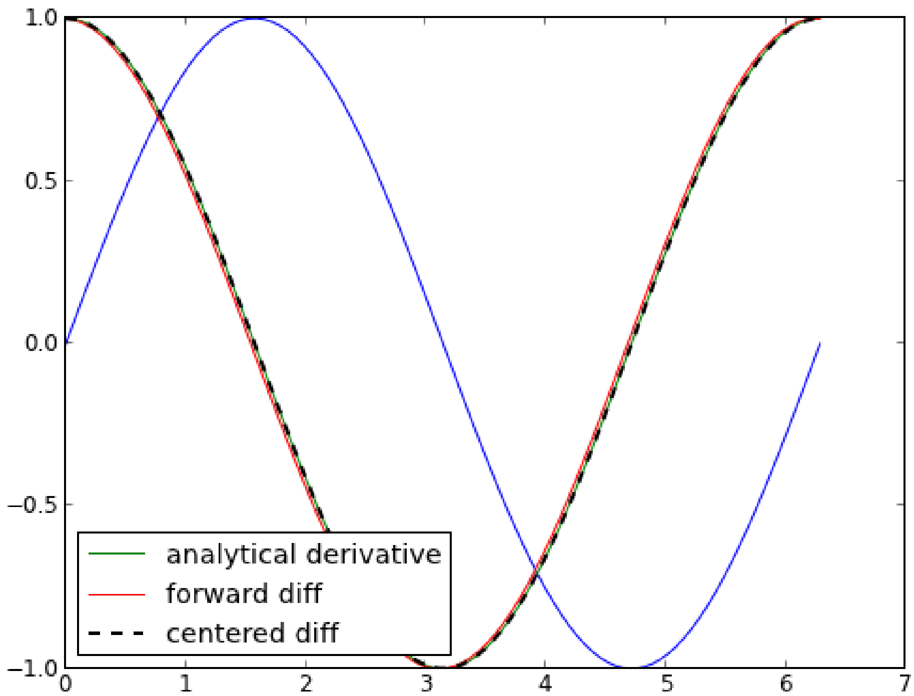


Figure 108: Comparison of different numerical derivatives.

If your data is very noisy, you will have a hard time getting good derivatives; derivatives tend to magnify noise. In these cases, you have to employ smoothing techniques, either implicitly by using a multipoint derivative formula, or explicitly by smoothing the data yourself, or taking the derivative of a function that has been fit to the data in the neighborhood you are interested in.

Here is an example of a 4-point centered difference of some noisy data:

```
import numpy as np
import matplotlib.pyplot as plt

x = np.linspace(0,2*np.pi,100)
y = np.sin(x) + 0.1*np.random.random(size=x.shape)
dy_analytical = np.cos(x)

#2-point formula
dyf = [0.0]*len(x)
for i in range(len(y)-1):
    dyf[i] = (y[i+1] - y[i])/(x[i+1]-x[i])
#set last element by backwards difference
dyf[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

'''
calculate dy by 4-point center differencing using array slices

\frac{y[i-2] - 8y[i-1] + 8[i+1] - y[i+2]}{12h}

y[0] and y[1] must be defined by lower order methods
and y[-1] and y[-2] must be defined by lower order methods
'''

dy = np.zeros(y.shape,np.float) #we know it will be this size
h = x[1]-x[0] #this assumes the points are evenely spaced!
dy[2:-2] = (y[0:-4] - 8*y[1:-3] + 8*y[3:-1] - y[4:])/(12.*h)

dy[0] = (y[1]-y[0])/(x[1]-x[0])
dy[1] = (y[2]-y[1])/(x[2]-x[1])
dy[-2] = (y[-2] - y[-3])/(x[-2] - x[-3])
dy[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])

plt.plot(x,y)
plt.plot(x,dy_analytical,label='analytical derivative')
plt.plot(x,dyf,'r-',label='2pt-forward diff')
plt.plot(x,dy,'k--',lw=2,label='4pt-centered diff')
plt.legend(loc='lower left')
plt.savefig('images/multipt-diff.png')
```

Open the python script (dft-scripts/script-264.py).

```
None
```

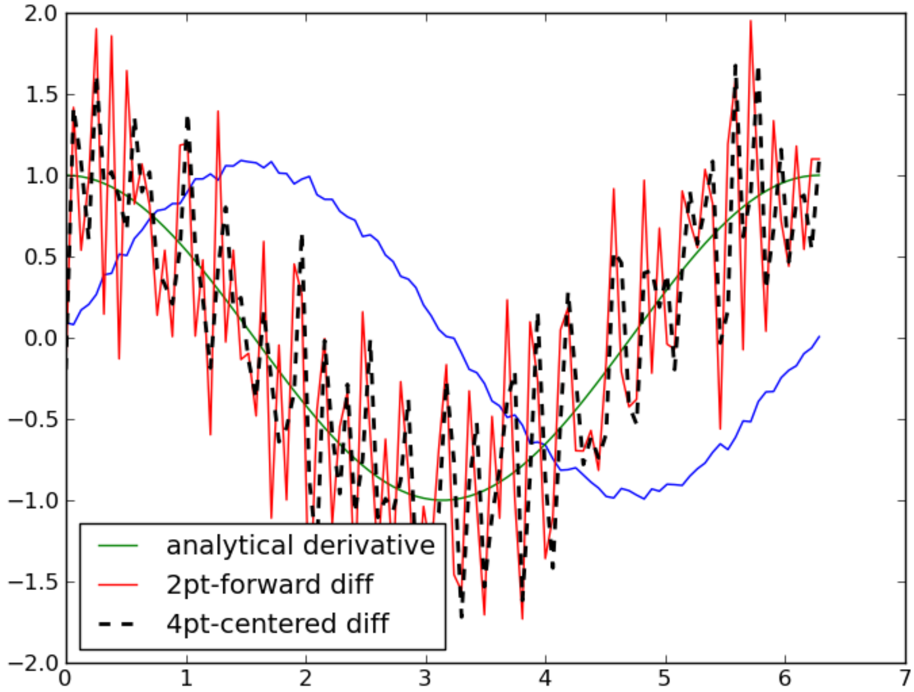


Figure 109: Comparison of 2 point and 4 point numerical derivatives.

The derivative is still noisy, but the four-point derivative is a little better than the two-pt formula.

FFT derivatives It is possible to perform derivatives using fast fourier transforms (FFT):

```
import numpy as np
import matplotlib.pyplot as plt

N = 101 #number of points
L = 2*np.pi #interval of data

x = np.arange(0.0,L,L/float(N)) #this does not include the endpoint

#add some random noise
y = np.sin(x) + 0.05*np.random.random(size=x.shape)
dy_analytical = np.cos(x)

'''
http://sci.tech-archive.net/Archive/sci.math/2008-05/msg00401.html

you can use fft to calculate derivatives!
'''

if N % 2 == 0:
    k = np.asarray(range(0,N/2)+[0] + range(-N/2+1,0))
else:
    k = np.asarray(range(0,(N-1)/2) +[0] + range(-(N-1)/2,0))

k *= 2*np.pi/L

fd = np.fft.ifft(1.j*k * np.fft.fft(y))

plt.plot(x,y)
plt.plot(x,dy_analytical,label='analytical der')
plt.plot(x,fd,label='fft der')
```

```
plt.legend(loc='lower left')

plt.savefig('images/fft-der.png')
```

Open the python script (dft-scripts/script-265.py).

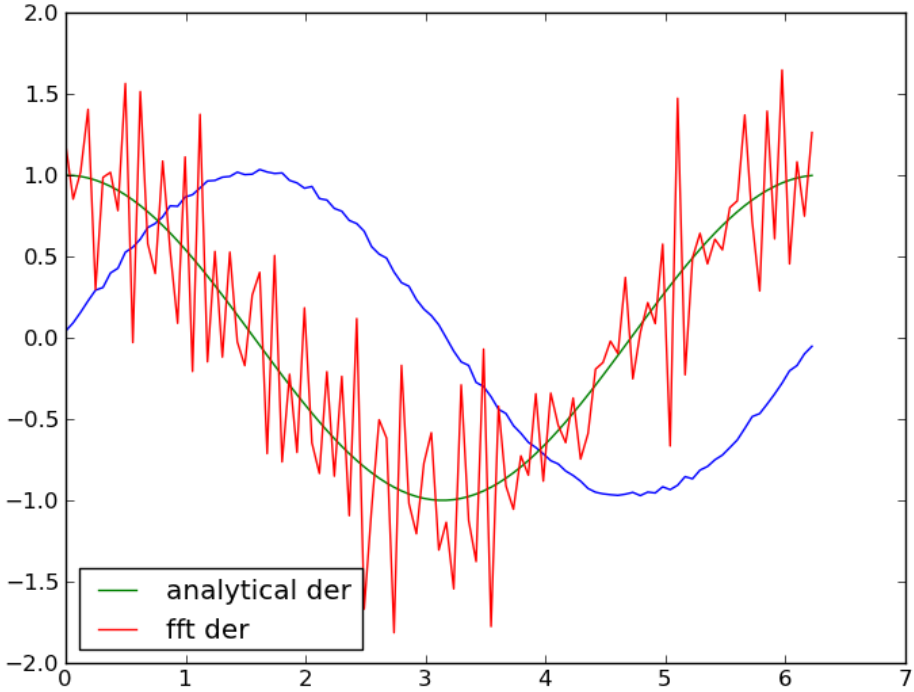


Figure 110: Comparison of FFT numerical derivatives.

This example does not show any major advantage in the quality of the derivative, and it is almost certain I would never remember how to do this off the top of my head.

10.1.15 NetCDF files

NetCDF is a binary, but cross-platform structured data format. The input file and output file for Dacapo is the NetCDF format. On creating a NetCDF file you must define the dimensions and variables before you can store data in them. You can create and read NetCDF files in python using one of the following modules:

`Scientific.IO.NetCDF` (http://dirac.cnrs-orleans.fr/plone/software/scientificpython/)

`netCDF3` (http://netcdf4-python.googlecode.com/svn/trunk/docs/netCDF3-module.html)

`pycdf` (http://pysclint.sourceforge.net/pycdf/) this is a very low level module modelled after the C-api. I am not sure it is completely bug-free (I have problems with character variables)

10.1.16 Python modules

The comma separated values (`csv`) module in python allows you to easily create datafiles:

csv writing:

```python
import numpy as np

x = np.linspace(0.0,6.0,100)
y = np.cos(x)

import csv
writer = csv.writer(open("some.csv", "w"))
writer.writerows(zip(x,y))
```

Open the python script (dft-scripts/script-266.py).

It is not so easy to read the data back in though because the module only returns strings, so you must turn the strings back into floats (or whatever other format they should be).

csv reading:

```python
import csv
reader = csv.reader(open("some.csv",'r'),delimiter=',')

x,y = [],[]
for row in reader:
#csv returns strings that must be cast as floats
    a,b = [float(z) for z in row]
    x.append(a)
    y.append(b)
```

Open the python script (dft-scripts/script-267.py).

This is almost as much work as manually reading the data though. The module is more powerful than I have shown here, so one day checkout `pydoc csv`.

The `pickle` and `shelve` modules of python also offer some data storage functionality. Check them out some day too.

10.1.17 Writing and reading Excel files

Writing Excel files It is sometimes convenient to do some analysis in Excel. We can create Excel files in python with `xlwt`. Google this module if you need to do this a lot.

```python
import numpy as np
import xlwt

wbk = xlwt.Workbook()
sheet = wbk.add_sheet('sheet 1')

volumes = np.array([13.72, 14.83, 16.0, 17.23, 18.52])
energies = np.array([-56.29, -56.41, -56.46, -56.46, -56.42])

for i, pair in enumerate(zip(volumes, energies)):
    vol = pair[0]
    energy = pair[1]
    sheet.write(i,0,vol)
    sheet.write(i,1,energy)
wbk.save('images/test-write.xls')
```

Open the python script (dft-scripts/script-268.py).

Reading Excel files We can also read Excel files (even on Linux!) with `xlrd`. Let us read in the data we just wrote. We wrote 5 volumes to column 0, and 5 energies to column 1.

```python
import xlrd
wbk = xlrd.open_workbook('images/test-write.xls')
sheet1 = wbk.sheet_by_name('sheet 1')
print(sheet1.col_values(0))
print(sheet1.col_values(1))
```

Open the python script (dft-scripts/script-269.py).

```
[13.72, 14.83, 16.0, 17.23, 18.52]
[-56.29, -56.41, -56.46, -56.46, -56.42]
```

10.1.18 TODO making movies

1. using animate
2. using swftools (png2swf, pdf2swf)

#http://wiki.swftools.org/wiki/Main_Page#SWF_Tools_0.9.2_.28_Current_Stable_Version_.29_Documentation

10.2 Computational geometry

10.2.1 Changing coordinate systems

Let A, B, C be the unit cell vectors

$$A = A1x + A2y + A3z \tag{9}$$
$$B = B1x + B2y + B3z \tag{10}$$
$$C = C1x + C2y + C3z \tag{11}$$

and we want to find the vector $[s1, s2, s3]$ so that $P = s1A + s2B + s3C$
if we expand this, we get:

$$\begin{aligned} &s1A1x + s1A2y + s1A3z \\ &+ s2B1x + s2B2y + s2B3z \\ &+ s3C1x + s3C2y + s3C3z = p1x + p2y + p3z \end{aligned}$$

If we now match coefficients on x, y, and z, we can write a set of linear equations as:

$$\begin{bmatrix} A1 & B1 & C1 \\ A2 & B2 & C2 \\ A3 & B3 & C3 \end{bmatrix} \begin{bmatrix} s1 \\ s2 \\ s3 \end{bmatrix} = \begin{bmatrix} p1 \\ p2 \\ p3 \end{bmatrix} \tag{12}$$

or, in standard form:
$A^T s = p$
and we need to solve for s as:
$s = (A^T)^{-1} \cdot p$
p must be a column vector, so we will have to transpose the positions provided by the atoms class, and then transpose the final result to get the positions back into row-vector form:
$s = ((A^T)^{-1} p^T)^T$
Here we implement that in code:

```
from ase.lattice.surface import fcc111
import numpy as np
np.set_printoptions(precision=3,suppress=True)

slab = fcc111('Pd',
              a=3.92,       # Pd lattice constant
              size=(2,2,3), #3-layer slab in 1x1 configuration
              vacuum=10.0)

pos = slab.get_positions() #these positions use x,y,z vectors as a basis

# we want to see the atoms in terms of the unitcell vectors
newbasis = slab.get_cell()

s = np.dot(np.linalg.inv(newbasis.T),pos.T).T
print('Coordinates in new basis are: \n',s)

# what we just did is equivalent to the following atoms method
print('Scaled coordinates from ase are: \n',slab.get_scaled_positions())
```

Open the python script (dft-scripts/script-270.py).

```
Coordinates in new basis are:
[[ 0.167  0.167  0.408]
 [ 0.667  0.167  0.408]
 [ 0.167  0.667  0.408]
 [ 0.667  0.667  0.408]
 [-0.167  0.333  0.5  ]
 [ 0.333  0.333  0.5  ]
 [-0.167  0.833  0.5  ]
 [ 0.333  0.833  0.5  ]
 [ 0.     0.     0.592]
 [ 0.5    0.     0.592]
 [ 0.     0.5    0.592]
 [ 0.5    0.5    0.592]]
Scaled coordinates from ase are:
[[ 0.167  0.167  0.408]
 [ 0.667  0.167  0.408]
 [ 0.167  0.667  0.408]
 [ 0.667  0.667  0.408]
 [ 0.833  0.333  0.5  ]
 [ 0.333  0.333  0.5  ]
 [ 0.833  0.833  0.5  ]
 [ 0.333  0.833  0.5  ]
 [ 0.     0.     0.592]
 [ 0.5    0.     0.592]
 [ 0.     0.5    0.592]
 [ 0.5    0.5    0.592]]
```

The method shown above is general to all basis set transformations. We examine another case next. Sometimes it is nice if all the coordinates are integers. For this example, we will use the bcc primitive lattice vectors and express the positions of each atom in terms of them. By definition each atomic position should be an integer combination of the primitive lattice vectors (before relaxation, and assuming one atom is at the origin, and the unit cell is aligned with the primitive basis!)

```python
from ase.lattice.cubic import BodyCenteredCubic
import numpy as np
bulk = BodyCenteredCubic(directions=[[1,0,0],
                                     [0,1,0],
                                     [0,0,1]],
                         size=(2,2,2),
                         latticeconstant=2.87,
                         symbol='Fe')


newbasis = 2.87*np.array([[-0.5, 0.5, 0.5],
                          [0.5, -0.5, 0.5],
                          [0.5, 0.5, -0.5]])

pos = bulk.get_positions()

s = np.dot(np.linalg.inv(newbasis.T), pos.T).T
print('atom positions in primitive basis')
print(s)

# let us see the unit cell in terms of the primitive basis too
print('unit cell in terms of the primitive basis')
print(np.dot(np.linalg.inv(newbasis.T), bulk.get_cell().T).T)
```

Open the python script (dft-scripts/script-271.py).

```
atom positions in primitive basis
[[ 0.  0.  0.]
 [ 1.  1.  1.]
 [ 0.  1.  1.]
 [ 1.  2.  2.]
 [ 1.  0.  1.]
 [ 2.  1.  2.]
 [ 1.  1.  2.]
 [ 2.  2.  3.]
 [ 1.  1.  0.]
 [ 2.  2.  1.]
 [ 1.  2.  1.]
 [ 2.  3.  2.]
 [ 2.  1.  1.]
 [ 3.  2.  2.]
 [ 2.  2.  2.]
 [ 3.  3.  3.]]
unit cell in terms of the primitive basis
[[ 0.  2.  2.]
 [ 2.  0.  2.]
 [ 2.  2.  0.]]
```

10.2.2 Simple distances, angles

`Scientific.Geometry` contains several useful functions for performing vector algebra including computing lengths and angles.

```python
import numpy as np
from Scientific.Geometry import Vector

A = Vector([1, 1, 1])   # Scientfic
a = np.array([1, 1, 1])  # numpy

B = Vector([0.0, 1.0, 0.0])

print('|A| = ', A.length())        # Scientific Python way
print('|a| = ', np.sum(a**2)**0.5)  # numpy way
print('|a| = ', np.linalg.norm(a))  # numpy way 2

print('ScientificPython angle = ', A.angle(B))  # in radians
print ('numpy angle = {}',
       np.arccos(np.dot(a / np.linalg.norm(a),
                        B / np.linalg.norm(B))))

# cross products
print('Scientific A .cross. B = ', A.cross(B))

# you can use Vectors in numpy
print('numpy A .cross. B      = ', np.cross(A,B))
```

Open the python script (dft-scripts/script-272.py).

```
('|A| = ', 1.7320508075688772)
('|a| = ', 1.7320508075688772)
('|a| = ', 1.7320508075688772)
('ScientificPython angle = ', 0.9553166181245092)
('numpy angle = {}', 0.95531661812450919)
('Scientific A .cross. B = ', Vector(-1.000000,0.000000,1.000000))
('numpy A .cross. B      = ', array([-1.,  0.,  1.]))
```

10.2.3 Unit cell properties

The volume of a unit cell can be calculated from $V = (a_1 \times a_2) \cdot a_3$ where a_1, a_2 and a_3 are the unit cell vectors. It is more convenient, however, to simply evaluate that equation as the determinant of the matrix describing the unit cell, where each row of the matrix is a unit cell vector.

$V = |\det(ucell)|$

Why do we need to take the absolute value? The sign of the determinant depends on the handedness of the order of the unit cell vectors. If they are right-handed the determinant will be positive, and if they are left-handed the determinant will be negative. Switching any two rows will change the sign of the determinant and the handedness. `ase` implements a convenient function to get the volume of an `Atoms` object: `ase.Atoms.get_volume`.

Here are three equivalent ways to compute the unit cell volume.

```
import numpy as np

a1 = [2, 0, 0]
a2 = [1, 1, 0]
a3 = [0, 0, 10]

uc = np.array([a1, a2, a3])

print('V = {0} ang^3 from dot/cross'.format(np.dot(np.cross(a1,a2),a3)))
print('V = {0} ang^3 from det'.format(np.linalg.det(uc)))

from ase import Atoms

atoms = Atoms([],cell=uc) #empty list of atoms
print('V = {0} ang^3 from get_volume'.format(atoms.get_volume()))
```

Open the python script (dft-scripts/script-273.py).

```
V = 20 ang^3 from dot/cross
V = 20.0 ang^3 from det
V = 20.0 ang^3 from get_volume
```

10.2.4 d-spacing

If you like to set up the vacuum in your slab calculations in terms of equivalent layers of atoms, you need to calculate the d-spacing (which is the spacing between parallel planes of atoms) for the hkl plane you are using. The script below shows several ways to accomplish that.

```
import numpy as np
from ase.lattice.cubic import FaceCenteredCubic

ag = FaceCenteredCubic(directions=[[1, 0, 0],
                                   [0, 1, 0],
                                   [0, 0, 1]],
                       size=(1, 1, 1),
                       symbol='Ag',
                       latticeconstant=4.0)

# these are the reciprocal lattice vectors
b1, b2, b3 = np.linalg.inv(ag.get_cell())

'''
g(111) = 1*b1 + 1*b2 + 1*b3

and |g(111)| = 1/d_111
'''
h,k,l = (1, 1, 1)
d = 1./np.linalg.norm(h*b1 + k*b2 + l*b3)

print('d_111 spacing (method 1) = {0:1.3f} Angstroms'.format(d))

# method #2
hkl = np.array([h, k, l])
```

```python
G = np.array([b1, b2, b3])  # reciprocal unit cell

'''
Gstar is usually defined as this matrix of dot products:

Gstar = np.array([[dot(b1,b1), dot(b1,b2), dot(b1,b3)],
                  [dot(b1,b2), dot(b2,b2), dot(b2,b3)],
                  [dot(b1,b3), dot(b2,b3), dot(b3,b3)]])

but I prefer the notationally more compact:
Gstar = G .dot. transpose(G)

then, 1/d_hkl^2 = hkl .dot. Gstar .dot. hkl
'''

Gstar = np.dot(G, G.T)

id2 = np.dot(hkl, np.dot(Gstar, hkl))

print('d_111 spacing (method 2) =',np.sqrt(1 / id2))

# http://books.google.com/books?id=nJHSqEseuIUC&lpg=PA118&ots=YA9TBldoVH
# &dq=reciprocal%20metric%20tensor&pg=PA119#v=onepage
# &q=reciprocal%20metric%20tensor&f=false

'''Finally, many text books on crystallography use long algebraic
formulas for computing the d-spacing with sin and cos, vector lengths,
and angles. Below we compute these and use them in the general
triclinic structure formula which applies to all the structures.
'''
from Scientific.Geometry import Vector
import math

unitcell = ag.get_cell()
A = Vector(unitcell[0])
B = Vector(unitcell[1])
C = Vector(unitcell[2])

# lengths of the vectors
a = A.length()#*angstroms2bohr
b = B.length()#*angstroms2bohr
c = C.length()#*angstroms2bohr

# angles between the vectors in radians
alpha = B.angle(C)
beta = A.angle(C)
gamma = A.angle(B)

print('')
print('a   b   c   alpha beta gamma')
print('{0:1.3f} {1:1.3f} {2:1.3f} {3:1.3f} {4:1.3f} {5:1.3f}\n'.format(a,b,c,          a

h, k, l = (1, 1, 1)

from math import sin, cos

id2 = ((h**2 / a**2 * sin(alpha)**2
       + k**2 / b**2 * sin(beta)**2
       + l**2 / c**2 * sin(gamma)**2
       + 2 * k * l / b / c * (cos(beta) * cos(gamma) - cos(alpha))
       + 2 * h * l / a / c * (cos(alpha) * cos(gamma) - cos(beta))
       + 2 * h * k / a / b * (cos(alpha) * cos(beta) - cos(gamma)))
       / (1 - cos(alpha)**2 - cos(beta)**2 - cos(gamma)**2
         + 2 * cos(alpha) * cos(beta) * cos(gamma)))

d = 1 / math.sqrt(id2)

print('d_111 spacing (method 3) = {0}'.format(d))
```

Open the python script (dft-scripts/script-274.py).

```
d_111 spacing (method 1) = 2.309 Angstroms
('d_111 spacing (method 2) =', 2.3094010767585029)

a    b    c    alpha beta gamma
```

```
4.000 4.000 4.000 1.571 1.571 1.571

d_111 spacing (method 3) = 2.30940107676
```

10.3 Equations of State

The module ase.utils.eos uses a simple polynomial equation of state to find bulk unit cell equilibrium volumes and bulk modulus. There are several other choices you could use that are more standard in the literature. Here we summarize them and provide references to the relevant literature. In each of these cases we show equations for the energy as a function of volume, although sometimes the volume is transformed or normalized.

10.3.1 Birch-Murnaghan

This is probably the most common equation of state used most often, and is a modification of the original Murnaghan EOS described below. A current description of the equation is in reference.[102] You can also find the equations for the Vinet and Poirier-Tarantola equations of state in that reference.

Birch-Murnaghan EOS:

$E(\eta) = E_0 + \frac{9B_0V_0}{16}(\eta^2-1)^2(6+B_0'(\eta^2-1)-4\eta^2)$

where $\eta = (V/V_0)^{1/3}$, B_0 and B_0' are the bulk modulus and its pressure derivative at the equilibrium volume V_0. You may find other derivations of this equation in the literature too.

Two other equations of state in that reference are the Vinet EOS:

$E(\eta) = E_0 + \frac{2B_0V_0}{(B_0'-1)^2}(2-(5+3B_0'(\eta-1)e^{-3(B_0'-1)(\eta-1)/2})$

and the Poirier-Tarantola EOS:

$E(\varrho) = E_0 + \frac{B_0V_0\varrho^2}{6}(3+\varrho(B_0'-2))$

with $\varrho = -3\ln(\eta)$.

10.3.2 Murnaghan

The equation most often used in the Murnaghan[103] equation of state is described in[104].

$E = E_T + \frac{B_0V}{B_0'}\left[\frac{(V_0/V)^{B_0'}}{B_0'-1}+1\right] - \frac{V_0B_0}{B_0'-1}$

where V is the volume, B_0 and B_0' are the bulk modulus and its pressure derivative at the equilibrium volume V_0. All of these are parameters that are fitted to energy vs. unit cell volume (V) data. When fitting data to this equation a guess of 2-4 for B_0' is usually a good start.

10.3.3 Birch

The original Birch equation[105] is:

$E = E_0 + \frac{9}{8}B_0V_0\left(\left(\frac{V_0}{V}\right)^{\frac{2}{3}}-1\right)^2 + \frac{9}{16}B_0V_0(B_0'-4)\left(\left(\frac{V}{V_0}\right)^{2/3}-1\right)^3$

10.3.4 The Anton-Schmidt Equation of state[106]

$E(V) = E_\infty + \frac{BV_0}{n+1}\left(\frac{V}{V_0}\right)^{n+1}\left(\ln\frac{V}{V_0}-\frac{1}{n+1}\right)$

where E_∞ corresponds to the energy at infinite separation, although the model they use to derive this equation breaks down at large separations so this is usually not a good estimate of the cohesive energy. n is typically about -2.

10.3.5 Fitting data to these equations of state

To use these equations of state to find the equilibrium cell volume and bulk modulus we need a set of calculations that give us the energy of the unit cell as a function of the cell volume. We then fit that data to one of the above equations to extract the parameters we want. All of these equations of state are non-linear in the cell volume, which means you have to provide some initial guesses for the parameters.

Here we describe a strategy for getting some estimates of the parameters using a linear least squares fitting of a parabola to the data to estimate E_0, V_0, B and B_0' which are used as initial guess for a non-linear least squares fit of the equation of state to the data.

The following example illustrates one approach to this problem for the Murnaghan equation of state:

```python
'''Example of fitting the Birch-Murnaghan EOS to data'''

import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import leastsq

# raw data from 2.2.3-al-analyze-eos.py
v = np.array([13.72, 14.83, 16.0, 17.23, 18.52])
e = np.array([-56.29, -56.41, -56.46, -56.46, -56.42])

#make a vector to evaluate fits on with a lot of points so it looks smooth
vfit = np.linspace(min(v),max(v),100)

### fit a parabola to the data
# y = ax^2 + bx + c
a,b,c = np.polyfit(v,e,2) #this is from pylab

'''
the parabola does not fit the data very well, but we can use it to get
some analytical guesses for other parameters.

V0 = minimum energy volume, or where dE/dV=0
E = aV^2 + bV + c
dE/dV = 2aV + b = 0
V0 = -b/2a

E0 is the minimum energy, which is:
E0 = aV0^2 + bV0 + c

B is equal to V0*d^2E/dV^2, which is just 2a*V0

and from experience we know Bprime_0 is usually a small number like 4
'''

#now here are our initial guesses.
v0 = -b/(2*a)
e0 = a*v0**2 + b*v0 + c
b0 = 2*a*v0
bP = 4

#now we have to create the equation of state function
def Murnaghan(parameters,vol):
    '''
    given a vector of parameters and volumes, return a vector of energies.
    equation From PRB 28,5480 (1983)
    '''
    E0 = parameters[0]
    B0 = parameters[1]
    BP = parameters[2]
    V0 = parameters[3]

    E = E0 + B0*vol/BP*(((V0/vol)**BP)/(BP-1)+1) - V0*B0/(BP-1.)

    return E

# and we define an objective function that will be minimized
def objective(pars,y,x):
    #we will minimize this function
    err =  y - Murnaghan(pars,x)
    return err

x0 = [e0, b0, bP, v0] #initial guesses in the same order used in the Murnaghan function

```

```
murnpars, ier = leastsq(objective, x0, args=(e,v)) #this is from scipy

#now we make a figure summarizing the results
plt.plot(v,e,'ro')
plt.plot(vfit, a*vfit**2 + b*vfit + c,'--',label='parabolic fit')
plt.plot(vfit, Murnaghan(murnpars,vfit), label='Murnaghan fit')
plt.xlabel('Volume ($\AA^3$)')
plt.ylabel('Energy (eV)')
plt.legend(loc='best')

#add some text to the figure in figure coordinates
ax = plt.gca()
plt.text(0.4, 0.5, 'Min volume = {0:1.2f} $\AA^3$'.format(murnpars[3]),
     transform = ax.transAxes)
plt.text(0.4, 0.4, 'Bulk modulus = {0:1.2f} eV/$\AA^3$ = {1:1.2f} GPa'.format(murnpars[1],
                                                                           murnpars[1]*160.21773),
     transform = ax.transAxes)
plt.savefig('images/a-eos.png')

np.set_printoptions(precision=3)
print('initial guesses  : ', np.array(x0))  # array for easy printing
print('fitted parameters: ', murnpars)
```

Open the python script (dft-scripts/script-275.py).

```
initial guesses  :  [-56.472   0.631   4.     16.79 ]
fitted parameters:  [-56.466   0.49    4.753  16.573]
```

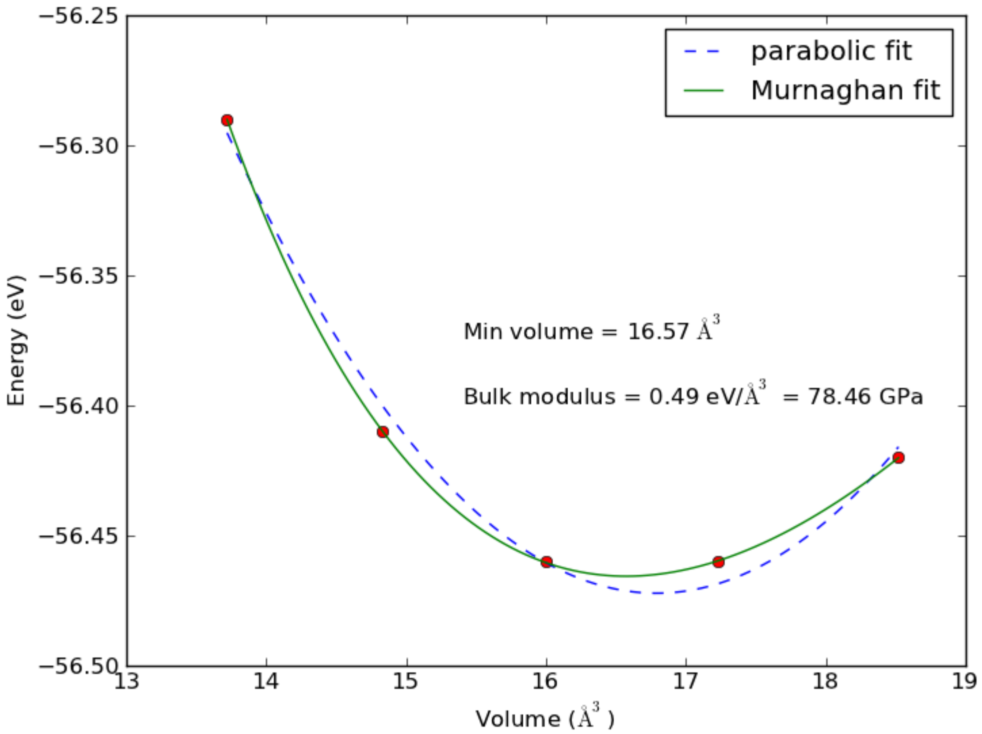


Figure 111: Fitted equation of state for bulk data. The initial fitted parabola is shown to illustrate how it is useful for making initial guesses of the minimum and bulk modulus.

You can see the Murnaghan equation of state fits the data better than the parabola.

Here is a comparison of the initial guesses and final parameters. You can see our guesses from the parabola were actually pretty good, and are the main reason we converged to a solution. If you try other guesses you will probably find the `scipy.optimize.leastsq` function does not converge.

10.4 Miscellaneous vasp/VASP tips

10.4.1 Using a special setup

VASP provides special setups for some elements. The following guidelines tell you what is in a potential: No extension means the standard potential. The following extensions mean:

Table 6: Meaning of extensions on POTCAR files for special setups.

extension	
_h	means the potential is harder than the standard (i.e. needs a higher cutoff energy)
_s	means the potential is softer than the standard (i.e. needs a lower cutoff energy)
_sv	s and p semi-core states are treated as valence states
_pv	p semi-core states are treated as valence states
_d	d semi-core states are treated as valence states

Here are some links to information in the VASP manual for the setups.

- 1st row elements
- Alkali and alkali-earth metals
- d-elements
- p-elements
- f-elements

Here we show how to select the O_sv potential in a calculation.

```python
from ase import Atoms, Atom
from vasp import Vasp

atoms = Atoms([Atom('O',[5, 5, 5], magmom=1)],
             cell=(6, 6, 6))

calc = Vasp('molecules/O_s',
          encut=300,
            xc='PBE',
            ispin=2,
            ismear=0,
            sigma=0.001,
            setups=[['O', '_s']], # specifies O_s potential
            atoms=atoms)

print calc.potential_energy
```

Open the python script (dft-scripts/script-276.py).

```
-1.50564364
```

How do you know you got the right special setup? We can look at the first line of the POTCAR file in the calculation directory to see.

```
head -n 1 molecules/O_sv/POTCAR
```

Open the python script (dft-scripts/script-277.py).

```
PAW_PBE O_sv 05Jul2007
```

This shows we indeed used the O_sv setup.

10.4.2 TODO Running vasp in parallel

vasp is smart. If you ask for more than one node, it will automatically try to run in parallel. On our cluster you have to use cores, i.e. (processor per node) not nodes due to a limitation in how vasp is compiled.

```python
from vasp import Vasp
from vasp.vasprc import VASPRC

VASPRC['queue.ppn']=4
from ase import Atom, Atoms
atoms = Atoms([Atom('O',[5, 5, 5], magmom=1)],
             cell=(6, 6, 6))

calc = Vasp('molecules/O_s-4nodes',
          encut=300,
          xc='PBE',
          ispin=2,
          ismear=0,
          sigma=0.001,
          setups=[['O', '_s']],  # specifies O_s potential
          atoms=atoms)

print calc.potential_energy
```

Open the python script (dft-scripts/script-278.py).
How do you know it ran on four nodes?

```
head molecules/O_s-4nodes/OUTCAR
```

Open the python script (dft-scripts/script-279.py).

```
vasp.5.3.5 31Mar14 (build Aug 04 2015 13:07:31) complex

executed on             LinuxIFC date 2016.05.11  15:58:14
running on    4 total cores
distrk:  each k-point on    4 cores,    1 groups
distr:  one band on NCORES_PER_BAND=   1 cores,    4 groups


--------------------------------------------------------------------------------------------------------
```

10.4.3 Running multiple instances of vasp in parallel

vasp was designed to enable asynchronous, parallel running processes through a queuing system. This is ideal for submitting large numbers of independent calculations in one script. The design uses exceptions to exit the script if the results are not available for subsequent analysis. The design expects that you run the script often, and the results are analyzed only when they are finally available.

Sometimes it is convenient to run a set of calculations and then wait for them to finish so that a second set of calculations that depend on the first results can be run. In this scenario, it is inconvenient to have to rerun your script again after the first set of calculations is done. The challenge is how to tell the computer to run a set of calculations in parallel, **and** wait for the calculations to finish. This can be achieved using the multiprocessing module in python.

The principle idea is to set up the calculations you want to run, and use multiprocessing to handle running them and waiting for you. To do this, you must instruct vasp to use a "run mode", and construct a script with a function that runs a calculation, and a section that only runs in the "main" script.

```python
import multiprocessing
from vasp import Vasp
from ase import Atom, Atoms
```

```
from ase.utils.eos import EquationOfState
import numpy as np

# this is the function that runs a calculation
def do_calculation(calc):
    """function to run a calculation through multiprocessing."""
    atoms = calc.get_atoms()
    e = atoms.get_potential_energy()
    v = atoms.get_volume()
    return v, e

# this only runs in the main script, not in processes on other cores
if __name__ == '__main__':
    NCORES = 6  # number of cores to run processes on

    # setup an atoms object
    a = 3.6
    atoms = Atoms([Atom('Cu',(0, 0, 0))],
                  cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
                                           [0.0, 1.0, 1.0],
                                           [1.0, 0.0, 1.0]]))
    v0 = atoms.get_volume()

    # Step 1
    COUNTER = 0
    calculators = []  # list of calculators to be run
    factors = [-0.1, 0.05, 0.0, 0.05, 0.1]
    for f in factors:
        newatoms = atoms.copy()
        newatoms.set_volume(v0*(1 + f))
        label = 'bulk/cu-mp/step1-{0}'.format(COUNTER)
        COUNTER += 1

        calc = Vasp(label,
                    xc='PBE',
                    encut=350,
                    kpts=[6, 6, 6],
                    isym=2,
                    atoms=newatoms)

        calculators.append(calc)

    # now we set up the Pool of processes
    pool = multiprocessing.Pool(processes=NCORES)

    # get the output from running each calculation
    out = pool.map(do_calculation, calculators)
    pool.close()
    pool.join() # this makes the script wait here until all jobs are done

    # now proceed with analysis
    V = [x[0] for x in out]
    E = [x[1] for x in out]

    eos = EquationOfState(V, E)
    v1, e1, B = eos.fit()
    print('step1: v1 = {v1}'.format(**locals()))

    ### ################################################################
    ## STEP 2, eos around the minimum
    ## #################################################################
    factors = [-0.06, -0.04, -0.02,
               0.0,
               0.02, 0.04, 0.06]

    calculators = [] # reset list
    for f in factors:
        newatoms = atoms.copy()
        newatoms.set_volume(v1*(1 + f))
        label = 'bulk/cu-mp/step2-{0}'.format(COUNTER)
        COUNTER += 1

        calc = Vasp(label,
                    xc='PBE',
                    encut=350,
                    kpts=[6, 6, 6],
                    isym=2,
                    atoms=newatoms)
```

```
        calculators.append(calc)

    pool = multiprocessing.Pool(processes=NCORES)

    out = pool.map(do_calculation, calculators)
    pool.close()
    pool.join() # wait here for calculations to finish

    # proceed with analysis
    V += [x[0] for x in out]
    E += [x[1] for x in out]

    V = np.array(V)
    E = np.array(E)

    f = np.array(V)/v1

    # only take points within +- 10% of the minimum
    ind = (f >=0.90) & (f <= 1.1)

    eos = EquationOfState(V[ind], E[ind])
    v2, e2, B = eos.fit()
    print('step2: v2 = {v2}'.format(**locals()))
    eos.plot('images/cu-mp-eos.png')
```

Open the python script (dft-scripts/script-280.py).

```
step1: v1 = 12.0218897111
step2: v2 = 12.0216094217
```

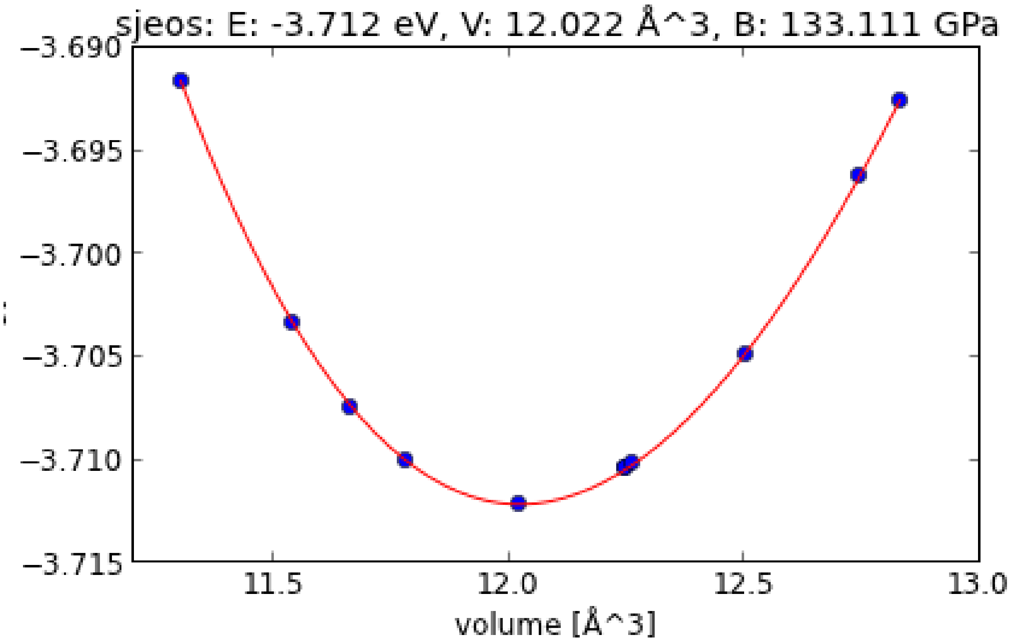


Figure 112: Equation of state for Cu using the multiprocessing module.

Note:
The first time you run this you will get all the VASP output. The second time you get the smaller output above.
Also, I have not figured out how to integrate this method with the queue system. At the moment, the runvasp.py script which ultimately runs VASP will run VASP in parallel, i.e. one process on multiple nodes/cores instead of a single job that runs multiple processes simultaneously on multiple nodes/cores.

Here is an example of running this through the queue. The main variations are you must set several variables in `VASPRC` that indicate you want to use `multiprocessing`, and you must save the script and submit manually to the queue with matching parameters. This is not 100% satisfying, but it is the best that I have found for now.

```python
#!/usr/bin/env python
import multiprocessing
from vasp import Vasp
from vasp.vasprc import VASPRC
from ase import Atom, Atoms
from ase.utils.eos import EquationOfState
import numpy as np

VASPRC['queue.nodes'] = 1

# Here we will be able to run three MPI jobs on 2 cores at a time.
VASPRC['queue.ppn'] = 6
VASPRC['multiprocessing.cores_per_process'] = 2

# to submit this script, save it as cu-mp.py
# qsub -l nodes=1:ppn=6,walltime=10:00:00 cu-mp.py
import os
if 'PBS_O_WORKDIR' in os.environ:
    os.chdir(os.environ['PBS_O_WORKDIR'])

# this is the function that runs a calculation
def do_calculation(calc):
    'function to run a calculation through multiprocessing'
    atoms = calc.get_atoms()
    e = atoms.get_potential_energy()
    v = atoms.get_volume()
    return v, e

# this only runs in the main script, not in processes on other cores
if __name__ == '__main__':

    # setup an atoms object
    a = 3.6
    atoms = Atoms([Atom('Cu',(0, 0, 0))],
                  cell=0.5 * a*np.array([[1.0, 1.0, 0.0],
                                         [0.0, 1.0, 1.0],
                                         [1.0, 0.0, 1.0]]))
    v0 = atoms.get_volume()

    # Step 1
    COUNTER = 0
    calculators = []  # list of calculators to be run
    factors = [-0.1, 0.05, 0.0, 0.05, 0.1]
    for f in factors:
        newatoms = atoms.copy()
        newatoms.set_volume(v0*(1 + f))
        label = 'bulk/cu-mp2/step1-{0}'.format(COUNTER)
        COUNTER += 1

        calc = Vasp(label,
                    xc='PBE',
                    encut=350,
                    kpts=[6, 6, 6],
                    isym=2,
                    debug=logging.DEBUG,
                    atoms=newatoms)

        calculators.append(calc)

```

```
    # now we set up the Pool of processes
    pool = multiprocessing.Pool(processes=3) # ask for 6 cores but run MPI on 2 cores

    # get the output from running each calculation
    out = pool.map(do_calculation, calculators)
    pool.close()
    pool.join() # this makes the script wait here until all jobs are done

    # now proceed with analysis
    V = [x[0] for x in out]
    E = [x[1] for x in out]

    eos = EquationOfState(V, E)
    v1, e1, B = eos.fit()
    print('step1: v1 = {v1}'.format(**locals()))

    ### ################################################################
    ## STEP 2, eos around the minimum
    ## #################################################################
    factors = [-0.06, -0.04, -0.02,
               0.0,
               0.02, 0.04, 0.06]

    calculators = [] # reset list
    for f in factors:
        newatoms = atoms.copy()
        newatoms.set_volume(v1*(1 + f))
        label = 'bulk/cu-mp2/step2-{0}'.format(COUNTER)
        COUNTER += 1

        calc = Vasp(label,
                    xc='PBE',
                    encut=350,
                    kpts=[6, 6, 6],
                    isym=2,
                    debug=logging.DEBUG,
                    atoms=newatoms)
        calculators.append(calc)

    pool = multiprocessing.Pool(processes=3)

    out = pool.map(do_calculation, calculators)
    pool.close()
    pool.join() # wait here for calculations to finish

    # proceed with analysis
    V += [x[0] for x in out]
    E += [x[1] for x in out]

    V = np.array(V)
    E = np.array(E)

    f = np.array(V)/v1

    # only take points within +- 10% of the minimum
    ind = (f >=0.90) & (f <= 1.1)

    eos = EquationOfState(V[ind], E[ind])
    v2, e2, B = eos.fit()
    print('step2: v2 = {v2}'.format(**locals()))
    eos.plot('images/cu-mp2-eos.png',show=True)
```

Open the python script (dft-scripts/script-281.py).

```
step1: v1 = 12.0218897111
step2: v2 = 12.0216189798
```

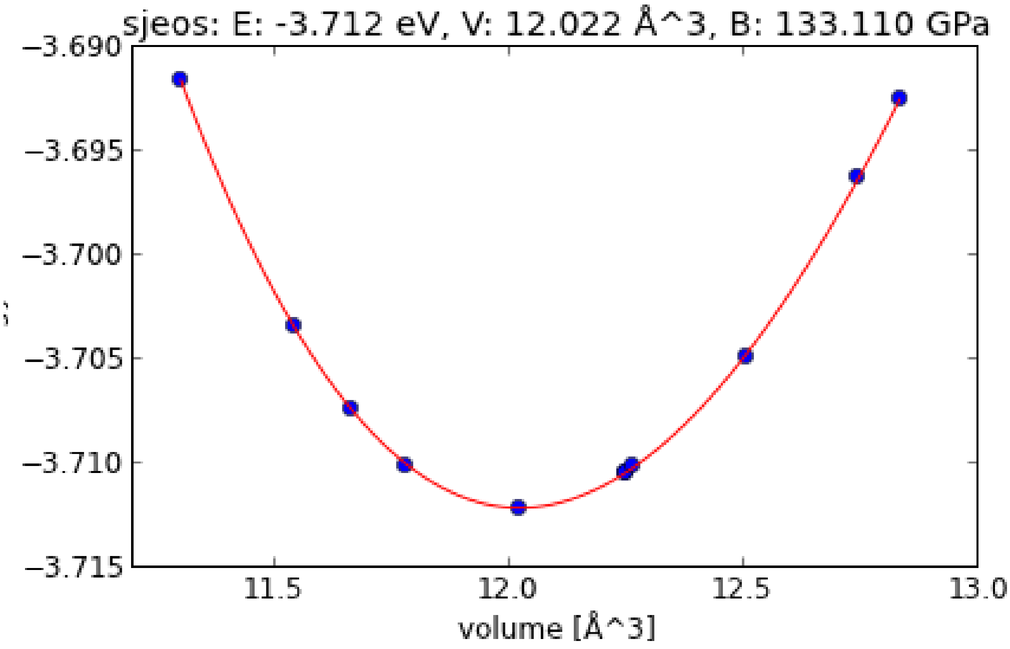


Figure 113: Second view of a Cu equation of state computed with multiprocessing.

10.4.4 Exporting data json, xml, python, sqlite

Vasp has some capability for representing a calculation result in an archival format.

json

```python
from vasp import Vasp

calc = Vasp('bulk/alloy/cu')
print(calc.json)
```

Open the python script (dft-scripts/script-282.py).


```
{"1": {
 "calculator": "vasp",
 "calculator_parameters": {"kpts": [13, 13, 13], "xc": "pbe", "encut": 350, "isif": 4, "ibrion": 2,
 "cell": [[1.818, 0.0, 1.818], [1.818, 1.818, 0.0], [0.0, 1.818, 1.818]],
 "charges": [null],
 "ctime": 16.38080562948716,
 "data": {"resort": [0], "ppp_list": [["Cu", "potpaw_PBE/Cu/POTCAR", 1]], "parameters": {"pp": "PBE"
 "energy": -3.73437124,
 "forces": [[0.0, 0.0, 0.0]],
 "key_value_pairs": {"path": "/home-research/jkitchin/dft-book-new-vasp/bulk/alloy/cu"},
 "magmom": 0,
 "magmoms": [0.0],
 "mtime": 16.38080562948716,
 "numbers": [29],
 "pbc": [true, true, true],
 "positions": [[0.0, 0.0, 0.0]],
```

```
 "stress": [0.006175314338977028, 0.006175314338977028, 0.006175314338977028, -0.0, -0.0, -0.0],
 "unique_id": "18c58fda5603fa5be9d99b5a7a4de74a",
 "user": "jkitchin"},
"ids": [1],
"nextid": 2}
```


10.4.5 Recommended values for ENCUT and valence electrons for different POTCAR files

The ENCUT tag and PREC tag affect the accuracy/convergence of your calculations.

```python
from vasp.POTCAR import get_ENMIN, get_ENMAX, get_ZVAL
from ase.data import chemical_symbols
import glob, os

print('#+ATTR_LaTeX: :environment longtable')
print('#+tblname: POTCAR')
print('#+caption: Parameters for POTPAW_PBE POTCAR files.')
print('| POTCAR | ENMIN | ENMAX | prec=high (eV) | # val. elect. |')
print('|-')

chemical_symbols.sort()
for symbol in chemical_symbols:

    potcars = glob.glob('{0}/potpaw_PBE/{1}*/POTCAR'.format(os.environ['VASP_PP_PATH'],
                                                         symbol))

    for potcar in potcars:

        POTCAR = os.path.relpath(potcar,
                                 os.environ['VASP_PP_PATH']+'/potpaw_PBE')[:-7]
        ENMIN = get_ENMIN(potcar)
        ENMAX = get_ENMAX(potcar)
        HIGH  = 1.3*ENMAX
        ZVAL  = get_ZVAL(potcar)
        print('|{POTCAR:30s}|{ENMIN}|{ENMAX}|{HIGH:1.3f}|{ZVAL}|'.format(**locals()))
```

Open the python script (dft-scripts/script-283.py).

Table 7: Parameters for POTPAW_PBE POTCAR files.

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Ac	129.263	172.351	224.056	11.0
Ag	187.383	249.844	324.797	11.0
Ag_GW	187.383	249.844	324.797	11.0
Ag_pv	223.399	297.865	387.225	17.0
Al_GW	180.225	240.3	312.390	3.0
Al_sv_GW	308.331	411.109	534.442	11.0
Al	180.225	240.3	312.390	3.0
Am	191.906	255.875	332.637	17.0
Ar	199.806	266.408	346.330	8.0
Ar_GW	199.806	266.408	346.330	8.0
As_GW	156.526	208.702	271.313	5.0
As	156.526	208.702	271.313	5.0
As_d	216.488	288.651	375.246	15.0
At_d	199.688	266.251	346.126	17.0
At	121.073	161.43	209.859	7.0
Au_pv_GW	186.258	248.344	322.847	17.0
Au_GW	186.258	248.344	322.847	11.0
Au	172.457	229.943	298.926	11.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Bi	78.777	105.037	136.548	5.0
Be_GW	185.657	247.543	321.806	2.0
Bi_d_GW	182.129	242.839	315.691	15.0
Be_sv	231.576	308.768	401.398	4.0
Ba_sv_GW	178.136	237.515	308.769	10.0
B_GW	238.96	318.614	414.198	3.0
B_s	201.934	269.245	350.019	3.0
Br_GW	162.214	216.285	281.171	7.0
Br	162.214	216.285	281.171	7.0
Bi_GW	109.897	146.53	190.489	5.0
Bi_d	182.129	242.839	315.691	15.0
B	238.96	318.614	414.198	3.0
Be_sv_GW	403.09	537.454	698.690	4.0
Be	185.658	247.543	321.806	2.0
B_h	500.0	700.0	910.000	3.0
Ba_sv	140.386	187.181	243.335	10.0
Ba_sv_GW	178.136	237.515	308.769	10.0
Ba_sv	140.386	187.181	243.335	10.0
Be_GW	185.657	247.543	321.806	2.0
Be_sv	231.576	308.768	401.398	4.0
Be_sv_GW	403.09	537.454	698.690	4.0
Be	185.658	247.543	321.806	2.0
Bi	78.777	105.037	136.548	5.0
Bi_d_GW	182.129	242.839	315.691	15.0
Bi_GW	109.897	146.53	190.489	5.0
Bi_d	182.129	242.839	315.691	15.0
Br_GW	162.214	216.285	281.171	7.0
Br	162.214	216.285	281.171	7.0
Cm	193.465	257.953	335.339	18.0
Cd_GW	190.534	254.045	330.258	12.0
Cu_pv_GW	350.498	467.331	607.530	17.0
Ce_h	224.925	299.9	389.870	12.0
C_s	205.433	273.911	356.084	4.0
Cd	205.752	274.336	356.637	12.0
Cr_sv_GW	246.211	328.282	426.767	14.0
Co_pv	203.281	271.042	352.355	15.0
Cs_sv_GW	148.575	198.101	257.531	9.0
Ca_sv	199.967	266.622	346.609	10.0
Cl_h	306.852	409.136	531.877	7.0
Ca_sv_GW	211.072	281.43	365.859	10.0
Cd_sv_GW	488.441	651.254	846.630	20.0
Cu	221.585	295.446	384.080	11.0
Cd_pv_GW	297.574	396.766	515.796	18.0
Cr_sv	296.603	395.471	514.112	14.0
C_GW_new	310.494	413.992	538.190	4.0
Cr	170.31	227.08	295.204	6.0
Co	200.976	267.968	348.358	9.0
Co_GW	242.55	323.4	420.420	9.0
C_h	500.0	700.0	910.000	4.0
Cr_pv	199.261	265.681	345.385	12.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Ce_GW	228.468	304.625	396.012	12.0
Cl_GW	196.854	262.472	341.214	7.0
C	300.0	400.0	520.000	4.0
Cu_pv	276.486	368.648	479.242	17.0
Ce_3	132.379	176.506	229.458	11.0
Cs_sv	165.238	220.318	286.413	9.0
Cl	196.854	262.472	341.214	7.0
Ca_pv	89.67	119.559	155.427	8.0
Co_sv_GW	272.827	363.77	472.901	17.0
Cu_GW	312.779	417.039	542.151	11.0
Co_sv	292.771	390.362	507.471	17.0
C_GW	310.494	413.992	538.190	4.0
Ce	204.781	273.042	354.955	12.0
Ca_sv	199.967	266.622	346.609	10.0
Ca_sv_GW	211.072	281.43	365.859	10.0
Ca_pv	89.67	119.559	155.427	8.0
Cd_GW	190.534	254.045	330.258	12.0
Cd	205.752	274.336	356.637	12.0
Cd_sv_GW	488.441	651.254	846.630	20.0
Cd_pv_GW	297.574	396.766	515.796	18.0
Ce_h	224.925	299.9	389.870	12.0
Ce_GW	228.468	304.625	396.012	12.0
Ce_3	132.379	176.506	229.458	11.0
Ce	204.781	273.042	354.955	12.0
Cl_h	306.852	409.136	531.877	7.0
Cl_GW	196.854	262.472	341.214	7.0
Cl	196.854	262.472	341.214	7.0
Cm	193.465	257.953	335.339	18.0
Co_pv	203.281	271.042	352.355	15.0
Co	200.976	267.968	348.358	9.0
Co_GW	242.55	323.4	420.420	9.0
Co_sv_GW	272.827	363.77	472.901	17.0
Co_sv	292.771	390.362	507.471	17.0
Cr_sv_GW	246.211	328.282	426.767	14.0
Cr_sv	296.603	395.471	514.112	14.0
Cr	170.31	227.08	295.204	6.0
Cr_pv	199.261	265.681	345.385	12.0
Cs_sv_GW	148.575	198.101	257.531	9.0
Cs_sv	165.238	220.318	286.413	9.0
Cu_pv_GW	350.498	467.331	607.530	17.0
Cu	221.585	295.446	384.080	11.0
Cu_pv	276.486	368.648	479.242	17.0
Cu_GW	312.779	417.039	542.151	11.0
Dy	191.601	255.467	332.107	20.0
Dy_3	116.785	155.713	202.427	9.0
Er_2	89.813	119.75	155.675	8.0
Er	223.587	298.116	387.551	22.0
Er_3	116.278	155.037	201.548	9.0
Eu_3	96.793	129.057	167.774	9.0
Eu	187.251	249.668	324.568	17.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Eu_2	74.496	99.328	129.126	8.0
F_s	217.378	289.837	376.788	7.0
Fr_sv	160.905	214.54	278.902	9.0
F	300.0	400.0	520.000	7.0
Fe_GW	240.755	321.007	417.309	8.0
Fe_sv	292.918	390.558	507.725	16.0
Fe	200.911	267.882	348.247	8.0
F_GW	365.773	487.698	634.007	7.0
F_h	500.0	700.0	910.000	7.0
F_GW_new	365.773	487.698	634.007	7.0
Fe_pv	219.928	293.238	381.209	14.0
Fe_sv_GW	273.539	364.719	474.135	16.0
Fe_GW	240.755	321.007	417.309	8.0
Fe_sv	292.918	390.558	507.725	16.0
Fe	200.911	267.882	348.247	8.0
Fe_pv	219.928	293.238	381.209	14.0
Fe_sv_GW	273.539	364.719	474.135	16.0
Fr_sv	160.905	214.54	278.902	9.0
Ga_sv_GW	377.564	503.418	654.443	21.0
Ga	101.009	134.678	175.081	3.0
Ga_GW	101.009	134.678	175.081	3.0
Ga_pv_GW	317.251	423.002	549.903	19.0
Ga_d_GW	303.451	404.602	525.983	13.0
Ga_h	303.451	404.601	525.981	13.0
Ga_d	212.018	282.691	367.498	13.0
Gd	192.354	256.472	333.414	18.0
Gd_3	115.749	154.332	200.632	9.0
Ge_GW	130.355	173.807	225.949	4.0
Ge	130.355	173.807	225.949	4.0
Ge_sv_GW	340.866	454.489	590.836	22.0
Ge_d	232.72	310.294	403.382	14.0
Ge_h	307.818	410.425	533.553	14.0
Ge_d_GW	232.72	310.294	403.382	14.0
H	200.0	250.0	325.000	1.0
H_h_GW	350.0	700.0	910.000	1.0
H_AE	400.0	1000.0	1300.000	1.0
Ho	192.876	257.168	334.318	21.0
H1.33	None	250.0	325.000	1.33
Ho_3	115.603	154.137	200.378	9.0
He_GW	304.335	405.78	527.514	2.0
H1.25	343.141	457.521	594.777	1.25
Hg	174.903	233.204	303.165	12.0
Hf	165.25	220.334	286.434	4.0
He	359.172	478.896	622.565	2.0
H.58	None	250.0	325.000	0.58
H.66	None	250.0	325.000	0.66
H.42	None	250.0	325.000	0.42
Hf_sv_GW	212.223	282.964	367.853	12.0
H1.5	200.0	250.0	325.000	1.5
H_h	350.0	700.0	910.000	1.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
H_GW	250.0	300.0	390.000	1.0
H_s	150.0	200.0	260.000	1.0
H1.66	None	250.0	325.000	1.66
H.5	200.0	250.0	325.000	0.5
H.25	None	250.0	325.000	0.25
Hf_pv	165.25	220.334	286.434	10.0
H.75	200.0	250.0	325.000	0.75
H.33	None	250.0	325.000	0.33
H1.75	None	250.0	325.000	1.75
Hf_sv	178.083	237.444	308.677	12.0
He_GW	304.335	405.78	527.514	2.0
He	359.172	478.896	622.565	2.0
Hf	165.25	220.334	286.434	4.0
Hf_sv_GW	212.223	282.964	367.853	12.0
Hf_pv	165.25	220.334	286.434	10.0
Hf_sv	178.083	237.444	308.677	12.0
Hg	174.903	233.204	303.165	12.0
Ho	192.876	257.168	334.318	21.0
Ho_3	115.603	154.137	200.378	9.0
In_d_GW	208.968	278.624	362.211	13.0
In_d	179.409	239.211	310.974	13.0
I_GW	131.735	175.647	228.341	7.0
I	131.735	175.647	228.341	7.0
Ir_sv_GW	239.882	319.843	415.796	17.0
Ir	158.148	210.864	274.123	9.0
In	71.951	95.934	124.714	3.0
In_d_GW	208.968	278.624	362.211	13.0
In_d	179.409	239.211	310.974	13.0
In	71.951	95.934	124.714	3.0
Ir_sv_GW	239.882	319.843	415.796	17.0
Ir	158.148	210.864	274.123	9.0
Kr	138.998	185.331	240.930	8.0
K_pv	87.548	116.731	151.750	7.0
K_sv	194.448	259.264	337.043	9.0
Kr_GW	138.998	185.331	240.930	8.0
K_sv_GW	186.749	248.998	323.697	9.0
Kr	138.998	185.331	240.930	8.0
Kr_GW	138.998	185.331	240.930	8.0
La	164.469	219.292	285.080	11.0
La_s	102.397	136.53	177.489	9.0
Li_sv_GW	325.274	433.699	563.809	3.0
Li_GW	84.078	112.104	145.735	1.0
Li_AE_GW	325.274	433.699	563.809	3.0
Li	100.0	140.0	182.000	1.0
Li_sv	374.276	499.034	648.744	3.0
Lu	191.771	255.695	332.404	25.0
Lu_3	116.244	154.992	201.490	9.0
Mg_pv_GW	302.947	403.929	525.108	8.0
Mg_GW	94.607	126.143	163.986	2.0
Mg_pv	302.947	403.929	525.108	8.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Mg	94.607	126.143	163.986	2.0
Mg_sv	371.417	495.223	643.790	10.0
Mg_sv_GW	322.42	429.893	558.861	10.0
Mn_sv_GW	268.458	357.944	465.327	15.0
Mn_pv	202.398	269.864	350.823	13.0
Mn	202.398	269.864	350.823	7.0
Mn_GW	208.85	278.466	362.006	7.0
Mn_sv	290.39	387.187	503.343	15.0
Mo_sv	182.007	242.676	315.479	14.0
Mo_sv_GW	233.929	311.905	405.476	14.0
Mo	168.438	224.584	291.959	6.0
Mo_pv	168.438	224.584	291.959	12.0
Nb_sv	219.927	293.235	381.206	13.0
Nb_pv	156.456	208.608	271.190	11.0
N_s_GW	222.371	296.495	385.444	5.0
Na_pv	194.671	259.561	337.429	7.0
N_GW	315.677	420.902	547.173	5.0
Np	190.695	254.26	330.538	15.0
Ni_sv_GW	310.107	413.475	537.518	18.0
Ne	257.704	343.606	446.688	8.0
N_GW_new	315.677	420.902	547.173	5.0
Na_sv	484.23	645.64	839.332	9.0
Ni	202.149	269.532	350.392	10.0
Ne_GW_soft	238.695	318.26	413.738	8.0
N	300.0	400.0	520.000	5.0
N_s	209.769	279.692	363.600	5.0
N_h	500.0	700.0	910.000	5.0
Nb_sv_GW	214.344	285.792	371.530	13.0
Na	76.476	101.968	132.558	1.0
Nd_3	136.964	182.619	237.405	11.0
Ne_GW	238.695	318.26	413.738	8.0
Ni_GW	267.992	357.323	464.520	10.0
Nd	189.892	253.189	329.146	14.0
Np_s	155.785	207.713	270.027	15.0
Na_sv_GW	195.049	260.065	338.084	9.0
Ni_pv	275.989	367.986	478.382	16.0
Na_pv	194.671	259.561	337.429	7.0
Na_sv	484.23	645.64	839.332	9.0
Na	76.476	101.968	132.558	1.0
Na_sv_GW	195.049	260.065	338.084	9.0
Nb_sv	219.927	293.235	381.206	13.0
Nb_pv	156.456	208.608	271.190	11.0
Nb_sv_GW	214.344	285.792	371.530	13.0
Nd_3	136.964	182.619	237.405	11.0
Nd	189.892	253.189	329.146	14.0
Ne	257.704	343.606	446.688	8.0
Ne_GW_soft	238.695	318.26	413.738	8.0
Ne_GW	238.695	318.26	413.738	8.0
Ni_sv_GW	310.107	413.475	537.518	18.0
Ni	202.149	269.532	350.392	10.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Ni_GW	267.992	357.323	464.520	10.0
Ni_pv	275.989	367.986	478.382	16.0
Np	190.695	254.26	330.538	15.0
Np_s	155.785	207.713	270.027	15.0
Os	171.017	228.022	296.429	8.0
O_s	212.14	282.853	367.709	6.0
O	300.0	400.0	520.000	6.0
O_h	500.0	700.0	910.000	6.0
Os_pv	171.017	228.022	296.429	14.0
O_s_GW	250.998	334.664	435.063	6.0
O_GW	310.976	414.635	539.025	6.0
Os_sv_GW	239.83	319.773	415.705	16.0
O_GW_new	325.824	434.431	564.760	6.0
Os	171.017	228.022	296.429	8.0
Os_pv	171.017	228.022	296.429	14.0
Os_sv_GW	239.83	319.773	415.705	16.0
Pt_pv_GW	186.537	248.716	323.331	16.0
Pm	193.97	258.627	336.215	15.0
P_h	292.651	390.202	507.263	5.0
Pb_d	178.376	237.835	309.186	14.0
Pa	189.145	252.193	327.851	13.0
Po_d	198.424	264.565	343.935	16.0
Pb_d_GW	178.357	237.809	309.152	14.0
P	191.28	255.04	331.552	5.0
Pt	172.712	230.283	299.368	10.0
Pd_GW	188.194	250.925	326.203	10.0
Po	119.78	159.707	207.619	6.0
Pd_pv	188.194	250.925	326.203	16.0
Pu	190.765	254.353	330.659	16.0
Pt_GW	186.537	248.716	323.331	10.0
Pb	73.48	97.973	127.365	4.0
Pm_3	132.719	176.959	230.047	11.0
Pr	204.706	272.941	354.823	13.0
Pr_3	136.289	181.719	236.235	11.0
Pt_sv_GW	242.752	323.669	420.770	18.0
P_GW	191.28	255.04	331.552	5.0
Pa_s	145.1	193.466	251.506	11.0
Pd	188.194	250.925	326.203	10.0
Pt_pv	220.955	294.607	382.989	16.0
Pu_s	155.873	207.83	270.179	16.0
Pa	189.145	252.193	327.851	13.0
Pa_s	145.1	193.466	251.506	11.0
Pb_d	178.376	237.835	309.186	14.0
Pb_d_GW	178.357	237.809	309.152	14.0
Pb	73.48	97.973	127.365	4.0
Pd_GW	188.194	250.925	326.203	10.0
Pd_pv	188.194	250.925	326.203	16.0
Pd	188.194	250.925	326.203	10.0
Pm	193.97	258.627	336.215	15.0
Pm_3	132.719	176.959	230.047	11.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Po_d	198.424	264.565	343.935	16.0
Po	119.78	159.707	207.619	6.0
Pr	204.706	272.941	354.823	13.0
Pr_3	136.289	181.719	236.235	11.0
Pt_pv_GW	186.537	248.716	323.331	16.0
Pt	172.712	230.283	299.368	10.0
Pt_GW	186.537	248.716	323.331	10.0
Pt_sv_GW	242.752	323.669	420.770	18.0
Pt_pv	220.955	294.607	382.989	16.0
Pu	190.765	254.353	330.659	16.0
Pu_s	155.873	207.83	270.179	16.0
Ra_sv	178.025	237.367	308.577	10.0
Rb_sv	165.084	220.112	286.146	9.0
Rb_sv_GW	165.898	221.197	287.556	9.0
Rb_pv	91.412	121.882	158.447	7.0
Re	169.662	226.216	294.081	7.0
Re_pv	169.662	226.216	294.081	13.0
Re_sv_GW	237.759	317.012	412.116	15.0
Rh_sv_GW	240.068	320.091	416.118	17.0
Rh_pv_GW	185.556	247.408	321.630	15.0
Rh_pv	185.556	247.408	321.630	15.0
Rh	171.747	228.996	297.695	9.0
Rh_GW	185.556	247.408	321.630	9.0
Rn	114.091	152.121	197.757	8.0
Ru	159.953	213.271	277.252	8.0
Ru_pv_GW	180.037	240.049	312.064	14.0
Ru_sv_GW	240.9	321.2	417.560	16.0
Ru_pv	180.037	240.049	312.064	14.0
Ru_sv	239.141	318.855	414.512	16.0
Sn_d_GW	195.049	260.066	338.086	14.0
S_h	301.827	402.436	523.167	6.0
Sn	77.427	103.236	134.207	4.0
Sr_sv_GW	168.613	224.817	292.262	10.0
Sc_sv_GW	213.799	285.066	370.586	11.0
Se_GW	158.666	211.555	275.022	6.0
Sm_3	132.815	177.087	230.213	11.0
S_GW	194.016	258.689	336.296	6.0
Si_sv_GW	410.683	547.578	711.851	12.0
Sc_sv	166.995	222.66	289.458	11.0
Se	158.666	211.555	275.022	6.0
S	194.016	258.689	336.296	6.0
Sb_d_GW	197.325	263.1	342.030	15.0
Sn_d	180.812	241.083	313.408	14.0
Sc	116.072	154.763	201.192	3.0
Sr_sv	172.014	229.353	298.159	10.0
Sb	129.052	172.069	223.690	5.0
Si	184.009	245.345	318.949	4.0
Sb_GW	129.052	172.069	223.690	5.0
Sm	193.136	257.515	334.769	16.0
Si_GW	184.009	245.345	318.949	4.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Sb_d_GW	197.325	263.1	342.030	15.0
Sb	129.052	172.069	223.690	5.0
Sb_GW	129.052	172.069	223.690	5.0
Sc_sv_GW	213.799	285.066	370.586	11.0
Sc_sv	166.995	222.66	289.458	11.0
Sc	116.072	154.763	201.192	3.0
Se_GW	158.666	211.555	275.022	6.0
Se	158.666	211.555	275.022	6.0
Si_sv_GW	410.683	547.578	711.851	12.0
Si	184.009	245.345	318.949	4.0
Si_GW	184.009	245.345	318.949	4.0
Sm_3	132.815	177.087	230.213	11.0
Sm	193.136	257.515	334.769	16.0
Sn_d_GW	195.049	260.066	338.086	14.0
Sn	77.427	103.236	134.207	4.0
Sn_d	180.812	241.083	313.408	14.0
Sr_sv_GW	168.613	224.817	292.262	10.0
Sr_sv	172.014	229.353	298.159	10.0
Ta_pv	167.75	223.667	290.767	11.0
Ta	167.75	223.667	290.767	5.0
Ta_sv_GW	214.506	286.008	371.810	13.0
Tb_3	116.709	155.613	202.297	9.0
Tb	198.618	264.824	344.271	19.0
Tc_pv	197.642	263.523	342.580	13.0
Tc_sv	239.028	318.703	414.314	15.0
Tc_sv_GW	238.582	318.11	413.543	15.0
Tc	171.521	228.694	297.302	7.0
Te	131.236	174.982	227.477	6.0
Te_GW	131.236	174.982	227.477	6.0
Th_s	127.022	169.363	220.172	10.0
Th	185.48	247.306	321.498	12.0
Ti	133.747	178.33	231.829	4.0
Ti_pv	166.751	222.335	289.036	10.0
Ti_sv_GW	214.498	285.998	371.797	12.0
Ti_sv	205.957	274.61	356.993	12.0
Tl_d	177.789	237.053	308.169	13.0
Tl	67.605	90.14	117.182	3.0
Tm	193.065	257.42	334.646	23.0
Tm_3	111.916	149.221	193.987	9.0
U_s	156.922	209.23	271.999	14.0
U	189.376	252.502	328.253	14.0
V_sv	197.755	263.673	342.775	13.0
V	144.408	192.543	250.306	5.0
V_sv_GW	242.302	323.07	419.991	13.0
V_pv	197.755	263.673	342.775	11.0
W	167.293	223.057	289.974	6.0
W_sv_GW	237.849	317.132	412.272	14.0
W_pv	167.293	223.057	289.974	12.0
Xe	114.839	153.118	199.053	8.0
Xe_GW	134.66	179.547	233.411	8.0

Continued on next page

Continued from previous page

POTCAR	ENMIN	ENMAX	prec=high (eV)	# val. elect.
Xe	114.839	153.118	199.053	8.0
Xe_GW	134.66	179.547	233.411	8.0
Y_sv	151.97	202.626	263.414	11.0
Y_sv_GW	171.957	229.276	298.059	11.0
Yb	189.771	253.028	328.936	24.0
Yb_2	84.433	112.578	146.351	8.0
Yb	189.771	253.028	328.936	24.0
Yb_2	84.433	112.578	146.351	8.0
Zn_GW	246.143	328.191	426.648	12.0
Zn_pv_GW	270.184	360.246	468.320	18.0
Zn_sv_GW	372.453	496.604	645.585	20.0
Zn	207.542	276.723	359.740	12.0
Zr_sv_GW	211.823	282.431	367.160	12.0
Zr_sv	172.424	229.898	298.867	12.0

10.5 Hy

Here is our prototypical python script.

```python
from ase import Atoms, Atom
from vasp import Vasp

co = Atoms([Atom('C', [0, 0, 0]),
            Atom('O', [1.2, 0, 0])],
           cell=(6., 6., 6.))

calc = Vasp('molecules/simple-co',  # output dir
            xc='pbe',  # the exchange-correlation functional
            nbands=6,    # number of bands
            encut=350,    # planewave cutoff
            ismear=1,    # Methfessel-Paxton smearing
            sigma=0.01,  # very small smearing factor for a molecule
            atoms=co)

print('energy = {0} eV'.format(co.get_potential_energy()))
print(co.get_forces())
```

Open the python script (dft-scripts/script-284.py).

```
energy = -14.69111507 eV
[[ 5.09138064  0.          0.        ]
 [-5.09138064  0.          0.        ]]
```

We can also use hy-lang for these scripts. Hy is a Lisp that works with Python. You need this in your Emacs setup (mile-hy is part of jmax).

```
(require 'auto-complete)
(require 'mile-hy)
```

Open the python script (dft-scripts/script-285.py).

```
mile-hy
```

And here is the same script in hy.

```
(import [ase [Atom Atoms]])
(import [vasp [Vasp]])
```

```

(setv co (Atoms [(Atom "C" [0.0 0.0 0.0])
                 (Atom "O" [1.2 0.0 0.0])]
                :cell [6.0 6.0 6.0]))

(setv calc (Vasp "molecules/simple-co-hy"
                 :xc "pbe"
                 :nbands 6
                 :encut 350
                 :ismear 1
                 :sigma 0.01
                 :atoms co))

(print (.format "energy = {0} eV"
                (.get_potential_energy co)))

(print (. calc potential_energy))
; (print (.potential_energy calc)) ;; not ok
(print (.get_forces co))
```

Open the python script (dft-scripts/script-286.py).

```
energy = -14.69111507 eV
-14.69111507
[[ 5.09138064  0.          0.        ]
 [-5.09138064  0.          0.        ]]
```

11 Python

11.1 pip as a user

pip is pretty easy to install as a user.

```
pip install --user some-package
```

Open the python script (dft-scripts/script-287.py).
For me this installs here:
~/.local/lib/python2.7/site-packages
That may or may not be on your Python path.

11.2 Integer division math gotchas

It pays to be careful when dividing by integers because you can get unexpected results if you do not know the integer division rules. In python 2.6, if you divide two integers, you get an integer! This is usually not a problem if there is no emainder in the division, e.g. 6/3=2. But, if there is a remainder, and that remainder is important, you will lose it. Here is an example of calculating the mole fraction of a species from integer numbers of atoms in the unit cell. If you are not careful, you get the wrong answer! You can convert (also called casting) a number to a float using the float command.

```
nPd = 4
nCu = 5
x_Cu = nCu/(nPd + nCu)
print('x_cu = {0} (integer division)'.format(x_Cu))

# now cast as floats
x_Cu = float(nCu)/float(nPd + nCu)
print('x_cu = {0} (float division)'.format(x_Cu))
```

Open the python script (dft-scripts/script-288.py).

```
x_cu = 0 (integer division)
x_cu = 0.555555555556 (float division)
```

Note that if one of the numbers is a float, python will automatically cast the integer as a float, and return a float.

```python
nPd = 4
nCu = 5

# now cast as floats
x_Cu = float(nCu)/(nPd + nCu)
print('x_cu = {0}'.format(x_Cu))
```

Open the python script (dft-scripts/script-289.py).

```
x_cu = 0.555555555556
```

Finally, you can tell python a number is a float by adding a decimal to it. You do not need to put a 0 after the decimal, but you can.

```python
nPd = 4.  # this is a float
nCu = 5

x_Cu = nCu / (nPd + nCu)
print('x_cu = {0}'.format(x_Cu))
```

Open the python script (dft-scripts/script-290.py).

```
x_cu = 0.555555555556
```

12 References

References

[1] David S. Sholl and Janice A. Steckel. *Density Functional Theory: A Practical Introduction*. Wiley, 2009.

[2] R. G. Parr and W. Yang. *Density-Functional Theory of Atoms and Molecules*. Oxford Science Publications, 1989.

[3] W. Koch and M. C. Holthausen. *A Chemist's Guide to Density Functional Theory*. Wiley-VCH, 2 edition, 2001.

[4] Charles Kittel. *Introduction to Solid State Physics*. Wiley, 8th edition, 2005.

[5] N. W. Ashcroft and N. David Mermin. *Solid State Physics*. Saunders College Publishing, 1976.

[6] Roald Hoffmann. How chemistry and physics meet in the solid state. *Angewandte Chemie International Edition in English*, 26(9):846–878, 1987. ISSN 1521-3773. doi: 10.1002/anie.198708461. URL http://dx.doi.org/10.1002/anie.198708461.

[7] Roald Hoffmann. A chemical and theoretical way to look at bonding on surfaces. *Rev. Mod. Phys.*, 60:601–628, Jul 1988. doi: 10.1103/RevModPhys.60.601. URL http://link.aps.org/doi/10.1103/RevModPhys.60.601.

[8] B. Hammer and J.K. Nørskov. Theoretical surface science and catalysiscalculations and concepts. In Helmut Knozinger Bruce C. Gates, editor, *Impact of Surface Science on Catalysis*, volume 45 of *Advances in Catalysis*, pages 71 – 129. Academic Press, 2000. doi: 10.1016/S0360-0564(02)45013-4. URL http://www.sciencedirect.com/science/article/pii/S0360056402450134.

[9] Jeff Greeley, Jens K. Nørskov, and Manos Mavrikakis. Electronic structure and catalysis on metal surfaces. *Annual Review of Physical Chemistry*, 53(1):319–348, 2002. doi: 10.1146/annurev.physchem.53.100301.131630. URL http://www.annualreviews.org/doi/abs/10.1146/annurev.physchem.53.100301.131630.

[10] A J Freeman and E Wimmer. Density functional theory as a major tool in computational materials science. *Annual Review of Materials Science*, 25(1):7–36, 1995. doi: 10.1146/annurev.ms.25.080195.000255.

[11] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos. Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients. *Rev. Mod. Phys.*, 64:1045–1097, Oct 1992. doi: 10.1103/RevModPhys.64.1045. URL http://link.aps.org/doi/10.1103/RevModPhys.64.1045.

[12] G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*, 6(1):15 – 50, 1996. ISSN 0927-0256. doi: 10.1016/0927-0256(96)00008-0. URL http://www.sciencedirect.com/science/article/pii/0927025696000080.

[13] T. Bligaard. Exchange and Correlation Functionals - a study toward improving the precision of electron density functional calculations of atomistic systems. Master's thesis, Technical University of Denmark, 2000. http://www.fysik.dtu.dk/~{}bligaard/masterthesis/masterdirectory/project/project.pdf.

[14] T. Bligaard. *Understanding Materials Properties on the Basis of Density Functional Theory Calculations*. PhD thesis, Technical University of Denmark, 2003. http://www.fysik.dtu.dk/~{}bligaard/phdthesis/phdproject.pdf.

[15] A. P. Seitsonen. *Theoretical Investigations into adsorption and co-adsorption on transition-metal surfaces as models to heterogeneous catalysis*. PhD thesis, Technical University of Berlin, School of Mathematics and Natural Sciences, 2000. http://edocs.tu-berlin.de/diss/2000/seitsonen_ari.pdf.

[16] R. Hirschl. *Binary Transition Metal Alloys and Their Surfaces*. PhD thesis, Institut für Materialphysik, University of Vienna, 2002. http://www.hirschl.at/download/diss_part1.pdf and http://www.hirschl.at/download/diss_part2.pdf.

[17] L. Pauling and E. B. Wilson, Jr. *Introduction to Quantum Mechanics with Applications to Chemistry*. Dover Publications, Inc., 1963.

[18] W. Kohn. Nobel lecture: Electronic structure of matter-wave functions and density functionals. *Rev. Mod. Phys.*, 71:1253–1266, Oct 1999. doi: 10.1103/RevModPhys.71.1253. URL http://link.aps.org/doi/10.1103/RevModPhys.71.1253.

[19] P. A. M. Dirac. Quantum mechanics of many-electron systems. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 123(792):pp. 714–733, 1929. ISSN 09501207. URL http://www.jstor.org/stable/95222.

[20] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:B864–B871, Nov 1964. doi: 10.1103/PhysRev.136.B864. URL http://link.aps.org/doi/10.1103/PhysRev.136.B864.

[21] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133–A1138, Nov 1965. doi: 10.1103/PhysRev.140.A1133. URL http://link.aps.org/doi/10.1103/PhysRev.140.A1133.

[22] John A. Pople. Nobel lecture: Quantum chemical models. *Rev. Mod. Phys.*, 71:1267–1274, Oct 1999. doi: 10.1103/RevModPhys.71.1267. URL http://link.aps.org/doi/10.1103/RevModPhys.71.1267.

[23] M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler. Pseudopotential study of binding properties of solids within generalized gradient approximations: The role of core-valence exchange correlation. *Phys. Rev. B*, 57:2134–2145, Jan 1998. doi: 10.1103/PhysRevB.57.2134. URL http://link.aps.org/doi/10.1103/PhysRevB.57.2134.

[24] John P. Perdew, Robert G. Parr, Mel Levy, and Jose L. Balduz. Density-functional theory for fractional particle number: Derivative discontinuities of the energy. *Phys. Rev. Lett.*, 49:1691–1694, Dec 1982. doi: 10.1103/PhysRevLett.49.1691. URL http://link.aps.org/doi/10.1103/PhysRevLett.49.1691.

[25] B. Hammer, L. B. Hansen, and J. K. Nørskov. Improved adsorption energetics within density-functional theory using revised perdew-burke-ernzerhof functionals. *Phys. Rev. B*, 59:7413–7421, Mar 1999. doi: 10.1103/PhysRevB.59.7413. URL http://link.aps.org/doi/10.1103/PhysRevB.59.7413.

[26] G. Makov and M. C. Payne. Periodic boundary conditions in *ab initio* calculations. *Phys. Rev. B*, 51:4014–4022, Feb 1995. doi: 10.1103/PhysRevB.51.4014. URL http://link.aps.org/doi/10.1103/PhysRevB.51.4014.

[27] D. J. Chadi and Marvin L. Cohen. Special points in the brillouin zone. *Phys. Rev. B*, 8:5747–5753, Dec 1973. doi: 10.1103/PhysRevB.8.5747. URL http://link.aps.org/doi/10.1103/PhysRevB.8.5747.

[28] Hendrik J. Monkhorst and James D. Pack. Special points for brillouin-zone integrations. *Phys. Rev. B*, 13:5188–5192, Jun 1976. doi: 10.1103/PhysRevB.13.5188. URL http://link.aps.org/doi/10.1103/PhysRevB.13.5188.

[29] N. Troullier and José Luriaas Martins. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B*, 43:1993–2006, Jan 1991. doi: 10.1103/PhysRevB.43.1993. URL http://link.aps.org/doi/10.1103/PhysRevB.43.1993.

[30] David Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B*, 41:7892–7895, Apr 1990. doi: 10.1103/PhysRevB.41.7892. URL http://link.aps.org/doi/10.1103/PhysRevB.41.7892.

[31] E. G. Moroni, G. Kresse, J. Hafner, and J. Furthmüller. Ultrasoft pseudopotentials applied to magnetic fe, co, and ni: From atoms to solids. *Phys. Rev. B*, 56:15629–15646, Dec 1997. doi: 10.1103/PhysRevB.56.15629. URL http://link.aps.org/doi/10.1103/PhysRevB.56.15629.

[32] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50:17953–17979, Dec 1994. doi: 10.1103/PhysRevB.50.17953. URL http://link.aps.org/doi/10.1103/PhysRevB.50.17953.

[33] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59:1758–1775, Jan 1999. doi: 10.1103/PhysRevB.59.1758. URL http://link.aps.org/doi/10.1103/PhysRevB.59.1758.

[34] M J Gillan. Calculation of the vacancy formation energy in aluminium. *Journal of Physics: Condensed Matter*, 1(4):689, 1989. URL http://stacks.iop.org/0953-8984/1/i=4/a=005.

[35] N. David Mermin. Thermal properties of the inhomogeneous electron gas. *Phys. Rev.*, 137:A1441–A1443, Mar 1965. doi: 10.1103/PhysRev.137.A1441. URL http://link.aps.org/doi/10.1103/PhysRev.137.A1441.

[36] G. Kresse and J. Furthmüller. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54:11169–11186, Oct 1996. doi: 10.1103/PhysRevB.54.11169. URL http://link.aps.org/doi/10.1103/PhysRevB.54.11169.

[37] G. Kresse and J. Hafner. *Ab initio* molecular-dynamics simulation of the liquid-metal/amorphous-semiconductor transition in germanium. *Phys. Rev. B*, 49:14251–14269, May 1994. doi: 10.1103/PhysRevB.49.14251. URL http://link.aps.org/doi/10.1103/PhysRevB.49.14251.

[38] G. Kresse and J. Hafner. *Ab initio* molecular dynamics for liquid metals. *Phys. Rev. B*, 47:558–561, Jan 1993. doi: 10.1103/PhysRevB.47.558. URL http://link.aps.org/doi/10.1103/PhysRevB.47.558.

[39] Joachim Paier, Robin Hirschl, Martijn Marsman, and Georg Kresse. The Perdew–Burke–Ernzerhof exchange-correlation functional applied to the G2-1 test set using a plane-wave basis set. *The Journal of Chemical Physics*, 122(23):234102, 2005. doi: 10.1063/1.1926272. URL http://link.aip.org/link/?JCP/122/234102/1.

[40] Larry A. Curtiss, Krishnan Raghavachari, Paul C. Redfern, and John A. Pople. Assessment of gaussian-2 and density functional theories for the computation of enthalpies of formation. *The Journal of Chemical Physics*, 106(3):1063–1079, 1997. doi: 10.1063/1.473182. URL http://link.aip.org/link/?JCP/106/1063/1.

[41] Graeme Henkelman, Andri Arnaldsson, and Hannes Jónsson. A fast and robust algorithm for bader decomposition of charge density. *Computational Materials Science*, 36(3):354 – 360, 2006. ISSN 0927-0256. doi: 10.1016/j.commatsci.2005.04.010. URL http://www.sciencedirect.com/science/article/pii/S0927025605001849.

[42] Thomas A. Manz and David S. Sholl. Chemically meaningful atomic charges that reproduce the electrostatic potential in periodic and nonperiodic materials. *Journal of Chemical Theory and Computation*, 6(8):2455–2468, 2010. doi: 10.1021/ct100125x. URL http://pubs.acs.org/doi/abs/10.1021/ct100125x.

[43] Jr. E. Bright Wilson, J.C. Decius, and Paul C. Cross. *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*. Dover Publications, 1955.

[44] Paolo Giannozzi and Stefano Baroni. Vibrational and dielectric properties of c_60 from density-functional perturbation theory. *The Journal of Chemical Physics*, 100(11):8537–8539, 1994. doi: 10.1063/1.466753. URL http://link.aip.org/link/?JCP/100/8537/1.

[45] David Karhánek, Tomáš Bučko, and Jürgen Hafner. A density-functional study of the adsorption of methane-thiol on the (111) surfaces of the Ni-group metals: II. vibrational spectroscopy. *Journal of Physics: Condensed Matter*, 22(26):265006, 2010. URL http://stacks.iop.org/0953-8984/22/i=26/a=265006.

[46] Antonio Fernández-Ramos, Benjamin Ellingson, Rubén Meana-Pañeda, Jorge Marques, and Donald Truhlar. Symmetry numbers and chemical reaction rates. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, 118:813–826, 2007. ISSN 1432-881X. URL http://dx.doi.org/10.1007/s00214-007-0328-0. 10.1007/s00214-007-0328-0.

[47] Daniel Sheppard, Rye Terrell, and Graeme Henkelman. Optimization methods for finding minimum energy paths. *The Journal of Chemical Physics*, 128(13):134106, 2008. doi: 10.1063/1.2841941. URL http://link.aip.org/link/?JCP/128/134106/1.

[48] R. A. Olsen, G. J. Kroes, G. Henkelman, A. Arnaldsson, and H. Jonsson. Comparison of methods for finding saddle points without knowledge of the final states. *The Journal of Chemical Physics*, 121(20):9776–9792, 2004. doi: 10.1063/1.1809574. URL http://link.aip.org/link/?JCP/121/9776/1.

[49] Ann E. Mattsson, Rickard Armiento, Joachim Paier, Georg Kresse, John M. Wills, and Thomas R. Mattsson. The am05 density functional applied to solids. *The Journal of Chemical Physics*, 128(8):084714, 2008. doi: 10.1063/1.2835596. URL http://link.aip.org/link/?JCP/128/084714/1.

[50] Yvon Le Page and Paul Saxe. Symmetry-general least-squares extraction of elastic data for strained materials from *ab initio* calculations of stress. *Phys. Rev. B*, 65:104104, Feb 2002. doi: 10.1103/PhysRevB.65.104104. URL http://link.aps.org/doi/10.1103/PhysRevB.65.104104.

[51] Shun-Li Shang, Yi Wang, DongEung Kim, and Zi-Kui Liu. First-principles thermodynamics from phonon and debye model: Application to ni and ni3al. *Computational Materials Science*, 47(4): 1040 – 1048, 2010. ISSN 0927-0256. doi: 10.1016/j.commatsci.2009.12.006. URL http://www.sciencedirect.com/science/article/pii/S0927025609004558.

[52] A. van de Walle, M. Asta, and G. Ceder. The alloy theoretic automated toolkit: A user guide. *Calphad*, 26(4):539 – 553, 2002. ISSN 0364-5916. doi: 10.1016/S0364-5916(02)80006-2. URL http://www.sciencedirect.com/science/article/pii/S0364591602800062.

[53] Axel van de Walle. Multicomponent multisublattice alloys, nonconfigurational entropy and other additions to the alloy theoretic automated toolkit. *Calphad*, 33(2):266 – 278, 2009. ISSN 0364-5916. doi: 10.1016/j.calphad.2008.12.005. URL http://www.sciencedirect.com/science/article/pii/S0364591608001314. <ce:title>Tools for Computational Thermodynamics</ce:title>.

[54] Lei Wang, Thomas Maxisch, and Gerbrand Ceder. Oxidation energies of transition metal oxides within the GGA + U framework. *Phys. Rev. B*, 73:195107, May 2006. doi: 10.1103/PhysRevB.73.195107. URL http://link.aps.org/doi/10.1103/PhysRevB.73.195107.

[55] Leonard Kleinman. Significance of the highest occupied Kohn-Sham eigenvalue. *Phys. Rev. B*, 56: 12042–12045, Nov 1997. doi: 10.1103/PhysRevB.56.12042. URL http://link.aps.org/doi/10.1103/PhysRevB.56.12042.

[56] John P. Perdew and Mel Levy. Comment on "Significance of the highest occupied Kohn-Sham eigenvalue". *Phys. Rev. B*, 56:16021–16028, Dec 1997. doi: 10.1103/PhysRevB.56.16021. URL http://link.aps.org/doi/10.1103/PhysRevB.56.16021.

[57] Leonard Kleinman. Reply to "Comment on 'Significance of the highest occupied Kohn-Sham eigenvalue' ". *Phys. Rev. B*, 56:16029–16030, Dec 1997. doi: 10.1103/PhysRevB.56.16029. URL http://link.aps.org/doi/10.1103/PhysRevB.56.16029.

[58] Ralf Stowasser and Roald Hoffmann. What do the Kohn-Sham Orbitals and Eigenvalues Mean? *Journal of the American Chemical Society*, 121(14):3414–3420, 1999. doi: 10.1021/ja9826892. URL http://pubs.acs.org/doi/abs/10.1021/ja9826892.

[59] O. V. Gritsenko and E. J. Baerends. The analog of Koopmans' theorem in spin-density functional theory. *The Journal of Chemical Physics*, 117(20):9154–9159, 2002. doi: 10.1063/1.1516800. URL http://link.aip.org/link/?JCP/117/9154/1.

[60] R. O. Jones and O. Gunnarsson. The density functional formalism, its applications and prospects. *Rev. Mod. Phys.*, 61:689–746, Jul 1989. doi: 10.1103/RevModPhys.61.689. URL http://link.aps.org/doi/10.1103/RevModPhys.61.689.

[61] J. P. Perdew and Alex Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, 23:5048–5079, May 1981. doi: 10.1103/PhysRevB.23.5048. URL http://link.aps.org/doi/10.1103/PhysRevB.23.5048.

[62] Daniel Sanchez-Portal, Emilio Artacho, and Jose M Soler. Projection of plane-wave calculations into atomic orbitals. *Solid State Communications*, 95(10):685 – 690, 1995. ISSN 0038-1098. doi: 10.1016/0038-1098(95)00341-X. URL http://www.sciencedirect.com/science/article/pii/003810989500341X.

[63] M. D. Segall, R. Shah, C. J. Pickard, and M. C. Payne. Population analysis of plane-wave electronic structure calculations of bulk materials. *Phys. Rev. B*, 54:16317–16320, Dec 1996. doi: 10.1103/PhysRevB.54.16317. URL http://link.aps.org/doi/10.1103/PhysRevB.54.16317.

[64] M. D. Segall, C. J. Pickard, R. Shah, and M. C. Payne. Population analysis in plane wave electronic structure calculations. *Mol. Phys.*, 89(2):571–577, 1996.

[65] A Ruban, B Hammer, P Stoltze, H.L Skriver, and J.K Nørskov. Surface electronic structure and reactivity of transition and noble metals. *Journal of Molecular Catalysis A: Chemical*, 115 (3):421 – 429, 1997. ISSN 1381-1169. doi: 10.1016/S1381-1169(96)00348-2. URL http://www.sciencedirect.com/science/article/pii/S1381116996003482.

[66] A. Cottrell. *Introduction to the Modern Theory of Metals*. The Institute of Metals, 1988.

[67] F. Ducastelle. *Order and Phase Stability in Alloys*. Elsevier Science Publishers, 1991.

[68] D. G. Pettifor and A. H. Cottrell, editors. *Electon Theory in Alloy Design*. The Institute of Materials, 1992.

[69] Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.*, 73:515–562, Jul 2001. doi: 10.1103/RevModPhys.73.515. URL http://link.aps.org/doi/10.1103/RevModPhys.73.515.

[70] Kyle J. Caspersen and Emily A. Carter. Finding transition states for crystalline solid/solid phase transformations. *Proceedings of the National Academy of Sciences of the United States of America*, 102(19):6738–6743, 2005. doi: 10.1073/pnas.0408127102. URL http://www.pnas.org/content/102/19/6738.abstract.

[71] Daniel Sheppard, Penghao Xiao, William Chemelewski, Duane D. Johnson, and Graeme Henkelman. A generalized solid-state nudged elastic band method. *The Journal of Chemical Physics*, 136 (7):074103, 2012. doi: 10.1063/1.3684549. URL http://link.aip.org/link/?JCP/136/074103/1.

[72] G. Ritz, M. Schmid, P. Varga, A. Borg, and M. Rønning. Pt(100) quasihexagonal reconstruction: A comparison between scanning tunneling microscopy data and effective medium theory simulation calculations. *Phys. Rev. B*, 56:10518–10525, Oct 1997. doi: 10.1103/PhysRevB.56.10518. URL http://link.aps.org/doi/10.1103/PhysRevB.56.10518.

[73] Paula Havu, Volker Blum, Ville Havu, Patrick Rinke, and Matthias Scheffler. Large-scale surface reconstruction energetics of pt(100) and au(100) by all-electron density functional theory. *Phys. Rev. B*, 82:161418, Oct 2010. doi: 10.1103/PhysRevB.82.161418. URL http://link.aps.org/doi/10.1103/PhysRevB.82.161418.

[74] Wei Chen, David Schmidt, William F. Schneider, and C. Wolverton. First-principles cluster expansion study of missing-row reconstructions of fcc (110) surfaces. *Phys. Rev. B*, 83:075415, Feb 2011. doi: 10.1103/PhysRevB.83.075415. URL http://link.aps.org/doi/10.1103/PhysRevB.83.075415.

[75] J. W. M. Frenken, R. L. Krans, J. F. van der Veen, E. Holub-Krappe, and K. Horn. Missing-row surface reconstruction of ag(110) induced by potassium adsorption. *Phys. Rev. Lett.*, 59:2307–2310, Nov 1987. doi: 10.1103/PhysRevLett.59.2307. URL http://link.aps.org/doi/10.1103/PhysRevLett.59.2307.

[76] J. C. Boettger. Nonconvergence of surface energies obtained from thin-film calculations. *Phys. Rev. B*, 49:16798–16800, Jun 1994. doi: 10.1103/PhysRevB.49.16798. URL http://link.aps.org/doi/10.1103/PhysRevB.49.16798.

[77] J. C. Boettger, John R. Smith, Uwe Birkenheuer, Notker Rösch, S. B. Trickey, John R. Sabin, and S. Peter Apell. Extracting convergent surface formation energies from slab calculations. *Journal of Physics: Condensed Matter*, 10(4):893, 1998. URL http://stacks.iop.org/0953-8984/10/i=4/a=017.

[78] Carlos Fiolhais, L.M. Almeida, and C. Henriques. Extraction of aluminium surface energies from slab calculations: perturbative and non-perturbative approaches. *Progress in Surface Science*, 74 (1–8):209 – 217, 2003. ISSN 0079-6816. doi: 10.1016/j.progsurf.2003.08.017. URL http://www.sciencedirect.com/science/article/pii/S0079681603000777.

[79] Fabien Tran, Robert Laskowski, Peter Blaha, and Karlheinz Schwarz. Performance on molecules, surfaces, and solids of the Wu-Cohen GGA exchange-correlation energy functional. *Phys. Rev. B*, 75:115131, Mar 2007. doi: 10.1103/PhysRevB.75.115131. URL http://link.aps.org/doi/10.1103/PhysRevB.75.115131.

[80] Jeong Woo Han, Liwei Li, and David S. Sholl. Density functional theory study of H and CO adsorption on alkali-promoted Mo_2C surfaces. *The Journal of Physical Chemistry C*, 115(14):6870–6876, 2011. doi: 10.1021/jp200950a. URL http://pubs.acs.org/doi/abs/10.1021/jp200950a.

[81] Nilay İnoğlu and John R. Kitchin. Atomistic thermodynamics study of the adsorption and the effects of water–gas shift reactants on cu catalysts under reaction conditions. *Journal of Catalysis*, 261(2):188 – 194, 2009. ISSN 0021-9517. doi: 10.1016/j.jcat.2008.11.020. URL http://www.sciencedirect.com/science/article/pii/S0021951708004314.

[82] L. Vitos, A.V. Ruban, H.L. Skriver, and J. Kollár. The surface energy of metals. *Surface Science*, 411(12):186 – 202, 1998. ISSN 0039-6028. doi: 10.1016/S0039-6028(98)00363-X. URL http://www.sciencedirect.com/science/article/pii/S003960289800363X.

[83] Jörg Neugebauer and Matthias Scheffler. Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111). *Phys. Rev. B*, 46:16067–16080, Dec 1992. doi: 10.1103/PhysRevB.46.16067. URL http://link.aps.org/doi/10.1103/PhysRevB.46.16067.

[84] Lennart Bengtsson. Dipole correction for surface supercell calculations. *Phys. Rev. B*, 59:12301–12304, May 1999. doi: 10.1103/PhysRevB.59.12301. URL http://link.aps.org/doi/10.1103/PhysRevB.59.12301.

[85] Yoshitada Morikawa. Adsorption geometries and vibrational modes of C_2H_2 on the si(001) surface. *Phys. Rev. B*, 63:033405, Jan 2001. doi: 10.1103/PhysRevB.63.033405. URL http://link.aps.org/doi/10.1103/PhysRevB.63.033405.

[86] Nilay İnoğlu and John R. Kitchin. Simple model explaining and predicting coverage-dependent atomic adsorption energies on transition metal surfaces. *Phys. Rev. B*, 82:045414, Jul 2010. doi: 10.1103/PhysRevB.82.045414. URL http://link.aps.org/doi/10.1103/PhysRevB.82.045414.

[87] Spencer D. Miller, Nilay Inoglu, and John R. Kitchin. Configurational correlations in the coverage dependent adsorption energies of oxygen atoms on late transition metal fcc(111) surfaces. *The Journal of Chemical Physics*, 134(10):104709, 2011. doi: 10.1063/1.3561287. URL http://link.aip.org/link/?JCP/134/104709/1.

[88] Spencer D. Miller and John R. Kitchin. Relating the coverage dependence of oxygen adsorption on Au and Pt fcc(111) surfaces through adsorbate-induced surface electronic structure effects. *Surface Science*, 603(5):794 – 801, 2009. ISSN 0039-6028. doi: 10.1016/j.susc.2009.01.021. URL http://www.sciencedirect.com/science/article/pii/S0039602809001186.

[89] John R. Kitchin. Correlations in coverage-dependent atomic adsorption energies on pd(111). *Phys. Rev. B*, 79:205412, May 2009. doi: 10.1103/PhysRevB.79.205412. URL http://link.aps.org/doi/10.1103/PhysRevB.79.205412.

[90] John R. Kitchin, Karsten Reuter, and Matthias Scheffler. Alloy surface segregation in reactive environments: First-principles atomistic thermodynamics study of $Ag_3Pd(111)$ in oxygen atmospheres. *Phys. Rev. B*, 77:075437, Feb 2008. doi: 10.1103/PhysRevB.77.075437. URL http://link.aps.org/doi/10.1103/PhysRevB.77.075437.

[91] Anand Udaykumar Nilekar, Jeff Greeley, and Manos Mavrikakis. A simple rule of thumb for diffusion on transition-metal surfaces. *Angewandte Chemie International Edition*, 45(42):7046–7049, 2006. ISSN 1521-3773. doi: 10.1002/anie.200602223. URL http://dx.doi.org/10.1002/anie.200602223.

[92] Graeme Henkelman, Blas P. Uberuaga, and Hannes Jonsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics*, 113(22):9901–9904, 2000. doi: 10.1063/1.1329672. URL http://link.aip.org/link/?JCP/113/9901/1.

[93] B. Meredig, A. Thompson, H. A. Hansen, C. Wolverton, and A. van de Walle. Method for locating low-energy solutions within DFT $+u$. *Phys. Rev. B*, 82:195128, Nov 2010. doi: 10.1103/PhysRevB.82.195128. URL http://link.aps.org/doi/10.1103/PhysRevB.82.195128.

[94] Anubhav Jain, Geoffroy Hautier, Shyue Ping Ong, Charles J. Moore, Christopher C. Fischer, Kristin A. Persson, and Gerbrand Ceder. Formation enthalpies by mixing GGA and GGA + U calculations. *Phys. Rev. B*, 84:045115, Jul 2011. doi: 10.1103/PhysRevB.84.045115. URL http://link.aps.org/doi/10.1103/PhysRevB.84.045115.

[95] Stefan Grimme. Semiempirical gga-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry*, 27(15):1787–1799, 2006. ISSN 1096-987X. doi: 10.1002/jcc.20495. URL http://dx.doi.org/10.1002/jcc.20495.

[96] Jiří Klimeš, David R. Bowler, and Angelos Michaelides. Van der waals density functionals applied to solids. *Physical Review B*, 83(19):nil, 2011. doi: 10.1103/physrevb.83.195131. URL http://dx.doi.org/10.1103/PhysRevB.83.195131.

[97] Alexandre Tkatchenko and Matthias Scheffler. Accurate molecular van der waals interactions from ground-state electron density and free-atom reference data. *Phys. Rev. Lett.*, 102(7):nil, 2009. doi: 10.1103/physrevlett.102.073005. URL http://dx.doi.org/10.1103/physrevlett.102.073005.

[98] B. Silvi and A Savin. Classification of chemical bonds based on topological analysis of electron localization functions. *Nature*, 371:683–686, 1994. URL http://dx.doi.org/10.1038/371683a0.

[99] Jess Wellendorff, Keld T. Lundgaard, Andreas Møgelhøj, Vivien Petzold, David D. Landis, Jens K. Nørskov, Thomas Bligaard, and Karsten W. Jacobsen. Density functionals for surface science: Exchange-correlation model development with bayesian error estimation. *Physical Review B*, 85 (23):nil, 2012. doi: 10.1103/physrevb.85.235149. URL http://dx.doi.org/10.1103/physrevb.85.235149.

[100] Matthew Fishman, Houlong L. Zhuang, Kiran Mathew, William Dirschka, and Richard G. Hennig. Accuracy of exchange-correlation functionals and effect of solvation on the surface energy of copper. *Physical Review B*, 87(24):nil, 2013. doi: 10.1103/physrevb.87.245402. URL http://dx.doi.org/10.1103/PhysRevB.87.245402.

[101] Kiran Mathew, Ravishankar Sundararaman, Kendra Letchworth-Weaver, T. A. Arias, and Richard G. Hennig. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *J. Chem. Phys.*, 140(8):084106, 2014. doi: 10.1063/1.4865107. URL http://dx.doi.org/10.1063/1.4865107.

[102] M. Hebbache and M. Zemzemi. *Ab initio* study of high-pressure behavior of a low compressibility metal and a hard material: osmium and diamond. *Phys. Rev. B*, 70:224107, Dec 2004. doi: 10.1103/PhysRevB.70.224107. URL http://link.aps.org/doi/10.1103/PhysRevB.70.224107.

[103] F. D. Murnaghan. The compressibility of media under extreme pressures. *Proceedings of the National Academy of Sciences of the United States of America*, 30(9):pp. 244–247, 1944. ISSN 00278424. URL http://www.jstor.org/stable/87468.

[104] C. L. Fu and K. M. Ho. First-principles calculation of the equilibrium ground-state properties of transition metals: Applications to Nb and Mo. *Phys. Rev. B*, 28:5480–5486, Nov 1983. doi: 10.1103/PhysRevB.28.5480. URL http://link.aps.org/doi/10.1103/PhysRevB.28.5480.

[105] Michael J. Mehl, Barry M. Klein, and Dimitri A. Papaconstantopoulos. *Intermetallic Compounds: Principles and Principles, Volume I: Principles*, volume I, chapter First principles calculations of elastic properties of metals, pages 195–210. John Wiley and Sons, 1995. URL http://cst-www.nrl.navy.mil/users/mehl/papers/cij453.pdf.

[106] B. Mayer, H. Anton, E. Bott, M. Methfessel, J. Sticht, J. Harris, and P.C. Schmidt. Ab-initio calculation of the elastic constants and thermal expansion coefficients of laves phases. *Intermetallics*, 11(1):23 – 32, 2003. ISSN 0966-9795. doi: 10.1016/S0966-9795(02)00127-9. URL http://www.sciencedirect.com/science/article/pii/S0966979502001279.

13 GNU Free Documentation License

GNU Free Documentation License
Version 1.3, 3 November 2008

Copyright (C) 2000, 2001, 2002, 2007, 2008 Free Software Foundation, Inc.
<http://fsf.org/>
Everyone is permitted to copy and distribute verbatim copies
of this license document, but changing it is not allowed.

0. PREAMBLE

The purpose of this License is to make a manual, textbook, or other functional and useful document "free" in the sense of freedom: to assure everyone the effective freedom to copy and redistribute it, with or without modifying it, either commercially or noncommercially. Secondarily, this License preserves for the author and publisher a way to get credit for their work, while not being considered responsible for modifications made by others.

This License is a kind of "copyleft", which means that derivative works of the document must themselves be free in the same sense. It complements the GNU General Public License, which is a copyleft license designed for free software.

We have designed this License in order to use it for manuals for free software, because free software needs free documentation: a free program should come with manuals providing the same freedoms that the software does. But this License is not limited to software manuals; it can be used for any textual work, regardless of subject matter or whether it is published as a printed book. We recommend this License principally for works whose purpose is instruction or reference.

1. APPLICABILITY AND DEFINITIONS

This License applies to any manual or other work, in any medium, that contains a notice placed by the copyright holder saying it can be distributed under the terms of this License. Such a notice grants a world-wide, royalty-free license, unlimited in duration, to use that work under the conditions stated herein. The "Document", below, refers to any such manual or work. Any member of the public is a licensee, and is addressed as "you". You accept the license if you copy, modify or distribute the work in a way requiring permission under copyright law.

A "Modified Version" of the Document means any work containing the Document or a portion of it, either copied verbatim, or with modifications and/or translated into another language.

A "Secondary Section" is a named appendix or a front-matter section of the Document that deals exclusively with the relationship of the publishers or authors of the Document to the Document's overall subject (or to related matters) and contains nothing that could fall directly within that overall subject. (Thus, if the Document is in part a textbook of mathematics, a Secondary Section may not explain any mathematics.) The relationship could be a matter of historical connection with the subject or with related matters, or of legal, commercial, philosophical, ethical or political position regarding them.

The "Invariant Sections" are certain Secondary Sections whose titles are designated, as being those of Invariant Sections, in the notice that says that the Document is released under this License. If a section does not fit the above definition of Secondary then it is not allowed to be designated as Invariant. The Document may contain zero Invariant Sections. If the Document does not identify any Invariant Sections then there are none.

The "Cover Texts" are certain short passages of text that are listed, as Front-Cover Texts or Back-Cover Texts, in the notice that says that the Document is released under this License. A Front-Cover Text may be at most 5 words, and a Back-Cover Text may be at most 25 words.

A "Transparent" copy of the Document means a machine-readable copy, represented in a format whose specification is available to the general public, that is suitable for revising the document straightforwardly with generic text editors or (for images composed of pixels) generic paint programs or (for drawings) some widely available drawing editor, and that is suitable for input to text formatters or for automatic translation to a variety of formats suitable for input to text formatters. A copy made in an otherwise Transparent file format whose markup, or absence of markup, has been arranged to thwart or discourage subsequent modification by readers is not Transparent. An image format is not Transparent if used for any substantial amount of text. A copy that is not "Transparent" is called "Opaque".

Examples of suitable formats for Transparent copies include plain ASCII without markup, Texinfo input format, LaTeX input format, SGML or XML using a publicly available DTD, and standard-conforming simple HTML, PostScript or PDF designed for human modification. Examples of transparent image formats include PNG, XCF and JPG. Opaque formats include proprietary formats that can be read and edited only by proprietary word processors, SGML or XML for which the DTD and/or processing tools are not generally available, and the machine-generated HTML, PostScript or PDF produced by some word processors for output purposes only.

The "Title Page" means, for a printed book, the title page itself, plus such following pages as are needed to hold, legibly, the material this License requires to appear in the title page. For works in formats which do not have any title page as such, "Title Page" means the text near the most prominent appearance of the work's title, preceding the beginning of the body of the text.

The "publisher" means any person or entity that distributes copies of the Document to the public.

A section "Entitled XYZ" means a named subunit of the Document whose title either is precisely XYZ or contains XYZ in parentheses following text that translates XYZ in another language. (Here XYZ stands for a specific section name mentioned below, such as "Acknowledgements", "Dedications", "Endorsements", or "History".) To "Preserve the Title" of such a section when you modify the Document means that it remains a section "Entitled XYZ" according to this definition.

The Document may include Warranty Disclaimers next to the notice which states that this License applies to the Document. These Warranty Disclaimers are considered to be included by reference in this License, but only as regards disclaiming warranties: any other implication that these Warranty Disclaimers may have is void and has no effect on the meaning of this License.

2. VERBATIM COPYING

You may copy and distribute the Document in any medium, either commercially or noncommercially, provided that this License, the copyright notices, and the license notice saying this License applies to the Document are reproduced in all copies, and that you add no other conditions whatsoever to those of this License. You may not use technical measures to obstruct or control the reading or further copying of the copies you make or distribute. However, you may accept compensation in exchange for copies. If you distribute a large enough number of copies you must also follow the conditions in section 3.

You may also lend copies, under the same conditions stated above, and you may publicly display copies.

3. COPYING IN QUANTITY

If you publish printed copies (or copies in media that commonly have printed covers) of the Document, numbering more than 100, and the Document's license notice requires Cover Texts, you must enclose the copies in covers that carry, clearly and legibly, all these Cover Texts: Front-Cover Texts on the front cover, and Back-Cover Texts on the back cover. Both covers must also clearly and legibly identify you as the publisher of these copies. The front cover must present the full title with all words of the title equally prominent and visible. You may add other material on the covers in addition. Copying with changes limited to the covers, as long as they preserve the title of the Document and satisfy these conditions, can be treated as verbatim copying in other respects.

If the required texts for either cover are too voluminous to fit legibly, you should put the first ones listed (as many as fit reasonably) on the actual cover, and continue the rest onto adjacent pages.

If you publish or distribute Opaque copies of the Document numbering more than 100, you must either include a machine-readable Transparent copy along with each Opaque copy, or state in or with each Opaque copy a computer-network location from which the general network-using public has access to download using public-standard network protocols a complete Transparent copy of the Document, free of added material. If you use the latter option, you must take reasonably prudent steps, when you begin distribution of Opaque copies in quantity, to ensure that this Transparent copy will remain thus accessible at the stated location until at least one year after the last time you distribute an Opaque copy (directly or through your agents or retailers) of that edition to the public.

It is requested, but not required, that you contact the authors of the Document well before redistributing any large number of copies, to give them a chance to provide you with an updated version of the Document.

4. MODIFICATIONS

You may copy and distribute a Modified Version of the Document under the conditions of sections 2 and 3 above, provided that you release the Modified Version under precisely this License, with the Modified Version filling the role of the Document, thus licensing distribution and modification of the Modified Version to whoever possesses a copy of it. In addition, you must do these things in the Modified Version:

A. Use in the Title Page (and on the covers, if any) a title distinct from that of the Document, and from those of previous versions (which should, if there were any, be listed in the History section of the Document). You may use the same title as a previous version if the original publisher of that version gives permission.
B. List on the Title Page, as authors, one or more persons or entities

responsible for authorship of the modifications in the Modified Version, together with at least five of the principal authors of the Document (all of its principal authors, if it has fewer than five), unless they release you from this requirement.

C. State on the Title page the name of the publisher of the Modified Version, as the publisher.
D. Preserve all the copyright notices of the Document.
E. Add an appropriate copyright notice for your modifications adjacent to the other copyright notices.
F. Include, immediately after the copyright notices, a license notice giving the public permission to use the Modified Version under the terms of this License, in the form shown in the Addendum below.
G. Preserve in that license notice the full lists of Invariant Sections and required Cover Texts given in the Document's license notice.
H. Include an unaltered copy of this License.
I. Preserve the section Entitled "History", Preserve its Title, and add to it an item stating at least the title, year, new authors, and publisher of the Modified Version as given on the Title Page. If there is no section Entitled "History" in the Document, create one stating the title, year, authors, and publisher of the Document as given on its Title Page, then add an item describing the Modified Version as stated in the previous sentence.
J. Preserve the network location, if any, given in the Document for public access to a Transparent copy of the Document, and likewise the network locations given in the Document for previous versions it was based on. These may be placed in the "History" section. You may omit a network location for a work that was published at least four years before the Document itself, or if the original publisher of the version it refers to gives permission.
K. For any section Entitled "Acknowledgements" or "Dedications", Preserve the Title of the section, and preserve in the section all the substance and tone of each of the contributor acknowledgements and/or dedications given therein.
L. Preserve all the Invariant Sections of the Document, unaltered in their text and in their titles. Section numbers or the equivalent are not considered part of the section titles.
M. Delete any section Entitled "Endorsements". Such a section may not be included in the Modified Version.
N. Do not retitle any existing section to be Entitled "Endorsements" or to conflict in title with any Invariant Section.
O. Preserve any Warranty Disclaimers.

If the Modified Version includes new front-matter sections or appendices that qualify as Secondary Sections and contain no material copied from the Document, you may at your option designate some or all of these sections as invariant. To do this, add their titles to the list of Invariant Sections in the Modified Version's license notice. These titles must be distinct from any other section titles.

You may add a section Entitled "Endorsements", provided it contains nothing but endorsements of your Modified Version by various parties--for example, statements of peer review or that the text has been approved by an organization as the authoritative definition of a standard.

You may add a passage of up to five words as a Front-Cover Text, and a passage of up to 25 words as a Back-Cover Text, to the end of the list of Cover Texts in the Modified Version. Only one passage of Front-Cover Text and one of Back-Cover Text may be added by (or through arrangements made by) any one entity. If the Document already includes a cover text for the same cover, previously added by you or by arrangement made by the same entity you are acting on behalf of, you may not add another; but you may replace the old one, on explicit permission from the previous publisher that added the old one.

The author(s) and publisher(s) of the Document do not by this License give permission to use their names for publicity for or to assert or imply endorsement of any Modified Version.

5. COMBINING DOCUMENTS

You may combine the Document with other documents released under this License, under the terms defined in section 4 above for modified versions, provided that you include in the combination all of the Invariant Sections of all of the original documents, unmodified, and list them all as Invariant Sections of your combined work in its license notice, and that you preserve all their Warranty Disclaimers.

The combined work need only contain one copy of this License, and multiple identical Invariant Sections may be replaced with a single copy. If there are multiple Invariant Sections with the same name but different contents, make the title of each such section unique by adding at the end of it, in parentheses, the name of the original author or publisher of that section if known, or else a unique number. Make the same adjustment to the section titles in the list of Invariant Sections in the license notice of the combined work.

In the combination, you must combine any sections Entitled "History" in the various original documents, forming one section Entitled "History"; likewise combine any sections Entitled "Acknowledgements", and any sections Entitled "Dedications". You must delete all sections Entitled "Endorsements".

6. COLLECTIONS OF DOCUMENTS

You may make a collection consisting of the Document and other documents released under this License, and replace the individual copies of this License in the various documents with a single copy that is included in the collection, provided that you follow the rules of this License for verbatim copying of each of the documents in all other respects.

otherwise to copy, modify, sublicense, or distribute it is void, and will automatically terminate your rights under this License.

However, if you cease all violation of this License, then your license from a particular copyright holder is reinstated (a) provisionally, unless and until the copyright holder explicitly and finally terminates your license, and (b) permanently, if the copyright holder fails to notify you of the violation by some reasonable means prior to 60 days after the cessation.

Moreover, your license from a particular copyright holder is reinstated permanently if the copyright holder notifies you of the violation by some reasonable means, this is the first time you have received notice of violation of this License (for any work) from that copyright holder, and you cure the violation prior to 30 days after your receipt of the notice.

Termination of your rights under this section does not terminate the licenses of parties who have received copies or rights from you under this License. If your rights have been terminated and not permanently reinstated, receipt of a copy of some or all of the same material does not give you any rights to use it.

10. FUTURE REVISIONS OF THIS LICENSE

The Free Software Foundation may publish new, revised versions of the GNU Free Documentation License from time to time. Such new versions will be similar in spirit to the present version, but may differ in detail to address new problems or concerns. See http://www.gnu.org/copyleft/.

Each version of the License is given a distinguishing version number. If the Document specifies that a particular numbered version of this License "or any later version" applies to it, you have the option of following the terms and conditions either of that specified version or of any later version that has been published (not as a draft) by the Free Software Foundation. If the Document does not specify a version number of this License, you may choose any version ever published (not as a draft) by the Free Software Foundation. If the Document specifies that a proxy can decide which future versions of this License can be used, that proxy's public statement of acceptance of a version permanently authorizes you to choose that version for the Document.

11. RELICENSING

"Massive Multiauthor Collaboration Site" (or "MMC Site") means any World Wide Web server that publishes copyrightable works and also provides prominent facilities for anybody to edit those works. A public wiki that anybody can edit is an example of such a server. A "Massive Multiauthor Collaboration" (or "MMC") contained in the site

14 Index

Index