

Contents

1	Introduction to this book	7
2	Introduction to DFT	8
2.1	Background	9
2.2	Exchange correlation functionals	10
2.3	Basis sets	10
2.4	Pseudopotentials	11
2.5	Fermi Temperature and band occupation numbers	12
2.6	Spin polarization and magnetism	12
2.7	TODO Recommended reading	13
3	Molecules	13
3.1	Defining and visualizing molecules	13
3.1.1	From scratch	13
3.1.2	Reading other data formats into a calculation	16
3.1.3	Predefined molecules	18
3.1.4	Combining Atoms objects	24
3.2	Simple properties	25
3.2.1	Getting cartesian positions	25
3.2.2	Molecular weight and molecular formula	26
3.2.3	Center of mass	27
3.2.4	Moments of inertia	27
3.2.5	Computing bond lengths and angles	29
3.3	Simple properties that require single computations	31
3.3.1	Energy and forces	31
3.3.2	Visualizing electron density	36
3.3.3	Visualizing electron density differences	39
3.3.4	Dipole moments	43
3.3.5	The density of states (DOS)	45
3.3.6	Atom-projected density of states on molecules	46
3.3.7	Electrostatic potential	48
3.3.8	Bader analysis	50
3.4	Geometry optimization	53
3.4.1	Manual determination of a bond length	53
3.4.2	Automatic geometry optimization with VASP	56
3.4.3	Relaxation of a water molecule	57
3.5	Vibrational frequencies	57
3.5.1	Manual calculation of vibrational frequency	57
3.5.2	Automated vibrational calculations	59
3.6	Simulated infrared spectra	61
3.7	Thermochemical properties of molecules	65
3.8	Molecular reaction energies	67
3.8.1	O ₂ dissociation	67
3.8.2	Water gas shift example	80
3.8.3	Temperature dependent water gas shift equilibrium constant	85
3.9	Molecular reaction barriers	89
3.9.1	Get initial and final states	89
3.9.2	Run band calculation	91
3.9.3	Make a movie of the animation	91

4	Bulk systems	92
4.1	Defining and visualizing bulk systems	92
4.1.1	Built-in functions in ase	92
4.1.2	Using http://materialsproject.org	100
4.2	Computational parameters that are important for bulk structures	103
4.2.1	k-point convergence	103
4.2.2	Effect of SIGMA	104
4.2.3	The number of bands	106
4.3	Determining bulk structures	110
4.3.1	fcc/bcc crystal structures	110
4.3.2	Optimizing the hcp lattice constant	115
4.3.3	Complex structures with internal degrees of freedom	118
4.3.4	Effect of XC on bulk properties	125
4.4	Using built-in ase optimization with jasp	126
4.5	Cohesive energy	129
4.6	Elastic properties	131
4.6.1	Fe elastic properties	131
4.6.2	Al elastic properties	133
4.7	Bulk thermodynamics	134
4.8	Effect of pressure on phase stability	135
4.9	Bulk reaction energies	140
4.9.1	Alloy formation energies	140
4.9.2	Metal oxide oxidation energies	148
4.10	Bulk density of states	152
4.11	Atom projected density of states	156
4.11.1	Effect of RWIGS on ADOS	159
4.12	Band structures	162
4.12.1	create example showing band dispersion with change in lattice constant	167
4.13	Magnetism	168
4.13.1	Determining if a magnetic solution is energetically favorable	168
4.13.2	Antiferromagnetic spin states	171
4.13.3	TODO NiO-FeO formation energies with magnetism	172
4.14	TODO phonons	172
4.15	TODO solid state NEB	172
5	Surfaces	172
5.1	Surface structures	172
5.1.1	Simple surfaces	172
5.1.2	Vicinal surfaces	173
5.2	Surface calculation parameters	176
5.3	Surface relaxation	177
5.4	Surface reconstruction	181
5.4.1	Au(110) missing row reconstruction	181
5.4.2	Ag(110) missing row reconstruction	186
5.4.3	Cu(110) missing row reconstruction	188
5.5	Surface energy	189
5.5.1	Advanced topics in surface energy	192
5.6	Work function	193
5.7	Dipole correction	194
5.7.1	Slab with no dipole correction	194
5.7.2	Slab with a dipole correction	197
5.7.3	Comparing no dipole correction with a dipole correction	197
5.8	Adsorption energies	199

5.8.1	Simple estimate of the adsorption energy	199
5.8.2	Coverage dependence	209
5.8.3	Effect of adsorption on the surface energy	211
5.9	Adsorbate vibrations	212
5.9.1	Vibrations of the bridge site	214
5.10	Surface Diffusion barrier	215
5.10.1	Standard nudged elastic band method	215
5.10.2	Climbing image NEB	217
5.10.3	Using vibrations to confirm a transition state	217
5.11	TODO Diffusion rates with transition state theory	217
5.12	TODO Effects of electric fields on adsorbates	217
5.13	TODO Simulating STM images	218
6	Atomistic thermodynamics	218
6.1	Bulk phase stability of oxides	221
6.2	Effect on adsorption	227
6.3	Atomistic therodynamics and multiple reactions	229
7	Advanced electronic structure methods	230
7.1	DFT+U	230
7.1.1	Metal oxide oxidation energies with DFT+U	230
7.2	Hybrid functionals	234
7.2.1	FCC Ni DOS	234
7.3	van der Waals forces	236
7.3.1	PBE	236
7.3.2	DFT-D2	238
7.4	Electron localization function	240
7.5	TODO Charge partitioning schemes	242
7.6	TODO Modeling Core level shifts	242
7.7	The BEEF functional in Vasp	244
7.8	TODO Solvation	246
8	TODO Databases in molecular simulations	250
9	Acknowledgments	250
10	Appendices	250
10.1	Recipes	250
10.1.1	Modifying Atoms by deleting atoms	250
10.1.2	Advanced tagging	250
10.1.3	Using units in ase	253
10.1.4	Extracting parts of an array	254
10.1.5	Statistics	255
10.1.6	Curve fitting	256
10.1.7	Nonlinear curve fitting	257
10.1.8	Nonlinear curve fitting by direct least squares minimization	258
10.1.9	Nonlinear curve fitting with confidence intervals	259
10.1.10	Interpolation with splines	261
10.1.11	Interpolation in 3D	262
10.1.12	Reading and writing data	266
10.1.13	Integration	268
10.1.14	Numerical differentiation	269
10.1.15	NetCDF files	275

10.1.16	Python modules	275
10.1.17	Writing and reading Excel files	275
10.1.18	TODO making movies	276
10.2	Computational geometry	276
10.2.1	Changing coordinate systems	276
10.2.2	Simple distances, angles	279
10.2.3	Unit cell properties	279
10.2.4	d-spacing	280
10.3	Equations of State	281
10.3.1	Birch-Murnaghan	281
10.3.2	Murnaghan	282
10.3.3	Birch	282
10.3.4	The Anton-Schmidt Equation of state ¹⁰⁸	282
10.3.5	Fitting data to these equations of state	282
10.4	Miscellaneous jasp /VASP tips	284
10.4.1	Using a special setup	284
10.4.2	Running jasp in parallel	286
10.4.3	Running multiple instances of jasp in parallel	286
10.4.4	Exporting data json, xml, python, sqlite	291
10.4.5	Recommended values for ENCUT and valence electrons for different POTCAR files	297
11	Python	300
11.1	easy_install as a user	300
11.2	pip as a user	300
11.3	Integer division math gotchas	300
12	References	301
13	GNU Free Documentation License	414
14	Index	422

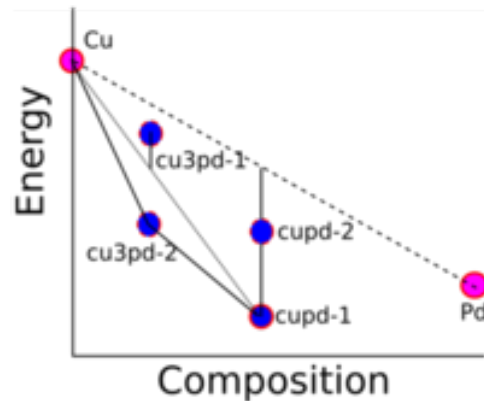
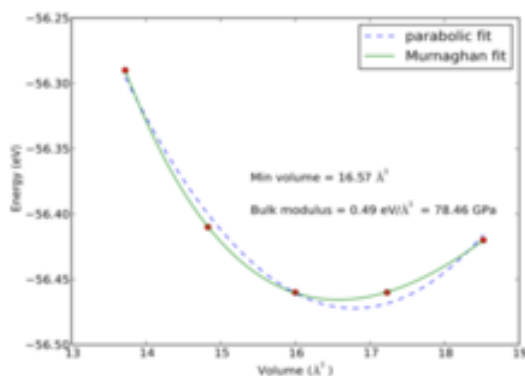
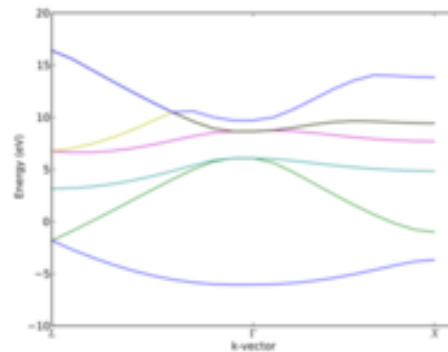
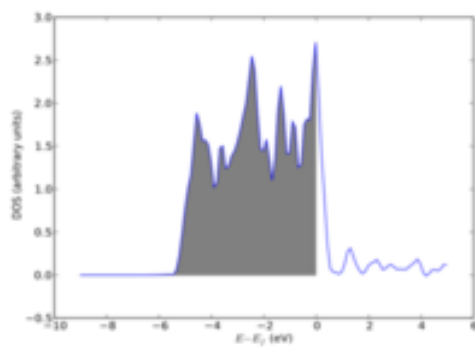
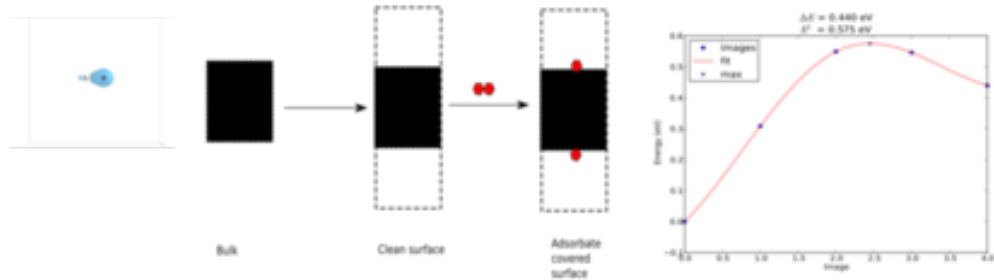
Modeling materials using density functional theory

John Kitchin

2012-07-11 Wed

Modeling materials using density functional theory

By John R. Kitchin



Copyright 2012 John Kitchin
All rights reserved

Copyright ©2012–2015\ John Kitchin

Permission is granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.3 or any later version published by the Free Software Foundation; with no Invariant Sections, no Front-Cover Texts, and no Back-Cover Texts. A copy of the license is included in the section entitled "GNU Free Documentation License".

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, as the comprehension of code is an integral part of its design. I believe that computational work should always be scripted. As a result, a written record of everything you have done will be available, allowing you to reproduce your code 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>
- [jasp](#)

[jasp](#) is a sophisticated wrapper to the [ase.calculators.vasp](#) python interface to the VASP calculator. It was written by me to facilitate writing this book and to develop the best possible way to run DFT calculations. The best way to learn to use jasp is from this book. It probably requires the latest svn version of ase to work since I have been adding new functionality to [ase.calculators.vasp](#) as [jasp](#) is developed. [jasp](#) is available at <https://github.com/jkitchin/jasp>.

The goal in writing [jasp](#) was to create a computational environment where you write one script to create, run and analyze your calculations. The code is smart, and submits jobs to a queue system when required, does not submit jobs more than once, allows many jobs to run in parallel, and gives you answers when available. [jasp](#) takes care of changing into VASP calculation directories, and then changing back to where you started from. [jasp](#) has an interface to sqlite, and to version control (git) software. [jasp](#) has some features that [ase.calculators.vasp](#) does not have yet. They may get incorporated into ase one day.

[jaspsum](#) is a utility program provided in jasp which prints a pretty representation of the state of a calculation, plots the relaxation trajectory, or prints a code representation of a VASP directory.

It is not critical that you use [jasp](#). You should be able to copy the actual VASP input files (which were generated by jasp) from a directory and simply run vasp. [jasp](#) is mostly compatible with [ase.calculators.vasp](#), so you can replace this kind of code:

```
1 with jasp('directory', lotsofkeywords, atoms=atoms) as calc:
2     #do stuff
```

Open the python script (dft-scripts/script-1.py).
with code similar to this:

```
1 CWD = os.getcwd()
2 os.chdir('directory')
3 calc=Vasp(lotsofkeywords)
4 atoms.set_calculator(calc)
5
6 try:
7     #do stuff
8 finally:
9     os.chdir(CWD)
```

Open the python script (dft-scripts/script-2.py).
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 DFT³ 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 Kittel⁴ 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 Reference¹⁰, 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 functionals¹³ 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:

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

with

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

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:

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

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:

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

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

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

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, \mathbf{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 \mathbf{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 \mathbf{k} points that are close together are similar, thus an interpolation scheme can be used with a finite number of \mathbf{k} points. This also converts the integral used to determine the energy into a sum over the \mathbf{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 \mathbf{k} , but these can be reduced and tested for convergence by using higher \mathbf{k} -point densities. An excellent discussion of this for aperiodic systems can be found in Ref. ²⁶.

The most common schemes for generating \mathbf{k} points are the Chadi-Cohen scheme, ²⁷ and the Monkhorst-Pack scheme. ²⁸ The use of these \mathbf{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 \mathbf{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

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 \mathbf{k} points) that defines the band energy converges very slowly with the number of \mathbf{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 Reference³ 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, respectively⁴ and are usually good initial guesses. See Reference³¹ 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 TODO Recommended reading

This section needs cleaning up.

Original papers on DFT^{20,21}

Kohn's Nobel Lecture,¹⁸ Pople's Nobel Lecture²²

⁷ Hoffman

PAW in GPAW³⁶

All calculations were performed using VASP^{12,37-39} with the projector augmented wave (PAW) potentials provided in VASP.

Monkhorst-Pack k-points²⁸

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 see⁴⁰.

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.

```
1 from ase import Atoms, Atom
2 from ase.io import write
3
4 # define an Atoms object
5 atoms = Atoms([Atom('C', [0., 0., 0.]),
6               Atom('O', [1.1, 0., 0.])],
7               cell=(10, 10, 10))
8
9 print('V = {0:1.0f} Angstrom^3'.format(atoms.get_volume()))
10
11 write('images/simple-cubic-cell.png', atoms, show_unit_cell=2)
```

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

V = 1000 Angstrom³

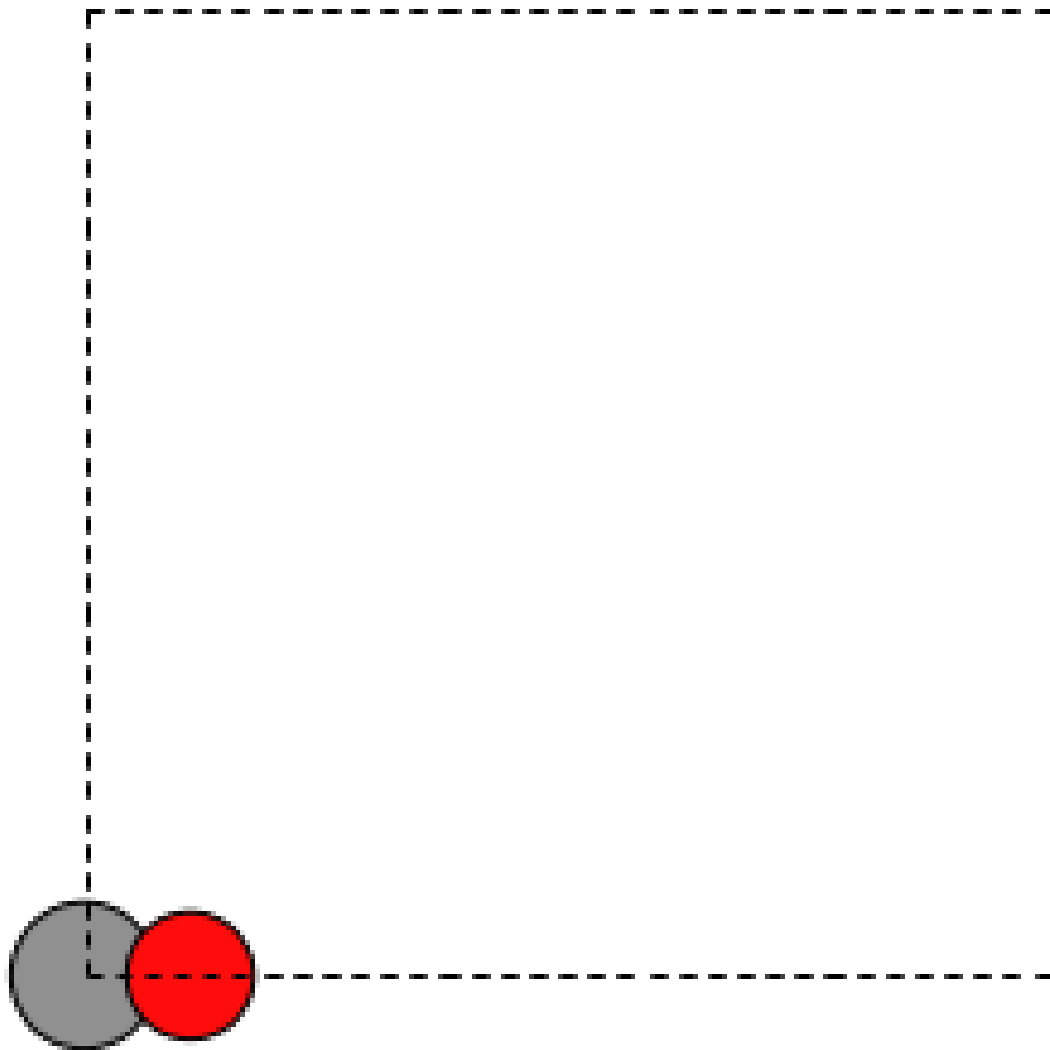


Figure 1: Image of a CO molecule with the C at the origin.

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 \AA away. The volume of the unit cell is 1000 \AA^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 \AA apart. Note the final volume is only about 715 \AA^3 , which is smaller than the cube. This will result in less computational time to compute properties.

```

1  from ase import Atoms, Atom
2  from ase.io import write
3
4  b = 7.1
5  atoms = Atoms([Atom('C', [0., 0., 0.]),
6                 Atom('O', [1.1, 0., 0.])],
7                cell=[[b, b, 0.],
8                      [b, 0., b],
9                      [0., b, b]])
10
11 print('V = {0:1.0f} Ang^3'.format(atoms.get_volume()))
12
13 atoms.center() # translate atoms to center of unit cell
14 write('images/fcc-cell.png', atoms, show_unit_cell=2)

```

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

$V = 716 \text{ Ang}^3$

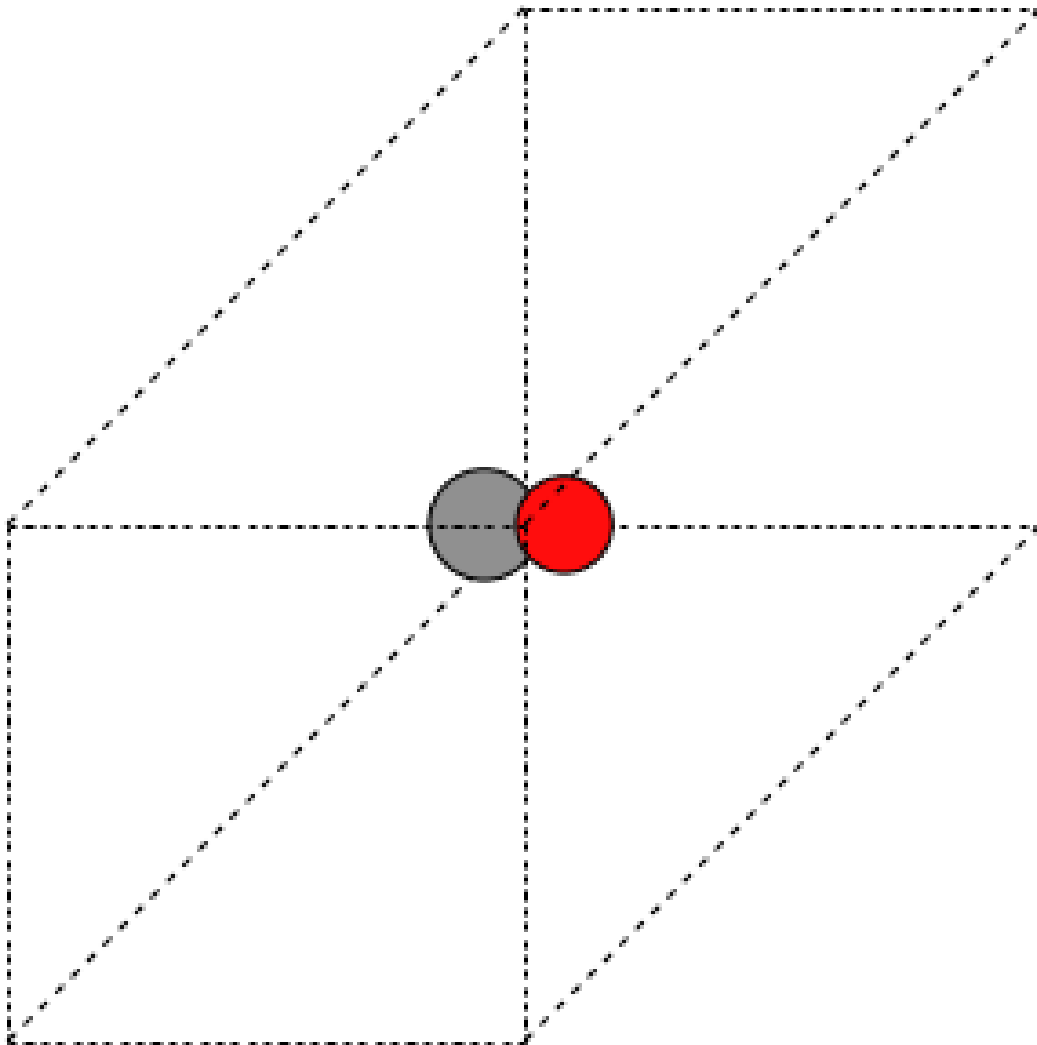


Figure 2: CO in a face-centered cubic unit cell.

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.

```

1  from ase import Atoms, Atom
2  import numpy as np
3
4  b = 7.1
5  atoms = Atoms([Atom('C', [0., 0., 0.]),
6                 Atom('O', [1.1, 0., 0.])],
7                cell=[[b, b, 0.],
8                      [b, 0., b],
9                      [0., b, b]])
10
11 # get unit cell vectors and their lengths
12 (a1, a2, a3) = atoms.get_cell()
13 print('|a1| = {0:1.2f} Ang'.format(np.sum(a1**2)**0.5))
14 print('|a2| = {0:1.2f} Ang'.format(np.linalg.norm(a2)))
15 print('|a3| = {0:1.2f} Ang'.format(np.sum(a3**2)**0.5))

```

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

```
1 from ase.io import read, write
2
3 atoms = read('molecules/isobutane.xyz')
4 atoms.center(vacuum=5)
5 write('images/isobutane-xyz.png', atoms, show_unit_cell=2)
```

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

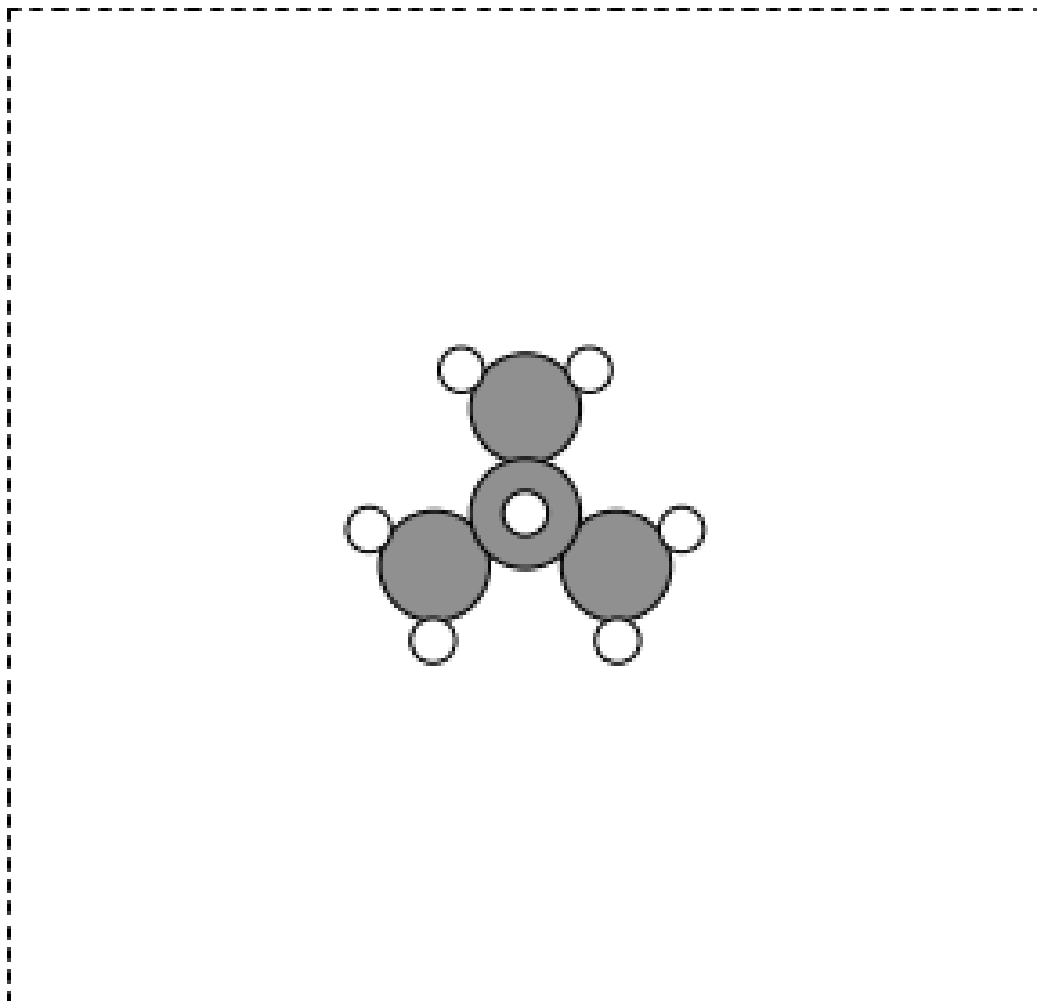


Figure 3: An isobutane molecule read in from an XYZ formatted data file.

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.⁴¹ 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.

```

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

```

Open the python script (dft-scripts/script-7.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
HC00H	CH3ONO	C5H8
2-butyne	SH	NF3
HOCl	CS2	P2
C	CH3S	O
C4H4S	S	C3H7Cl
H2CCHCl	C2H6	CH3CHO
C2H4	HCN	C2H2
C2Cl4	bicyclobutane	H2
C6H6	N2H4	C4H4NH
H2CCHCN	H2CCHF	cyclobutane
HCl	CH3OCH3	Li2
Na	CH3SiH3	NaCl
CH3CH2SH	OCHCHO	SiH4
C2H5	SiH3	NH
ClO	AlCl3	CCl4
NO	C2H3	ClF
HCO	CH3CONH2	CH2SCH2
CH3COCH3	C3H4_D2d	CH
CO	CN	F
CH3COC1	N	CH3Cl
Si	C3H8	CS
N2	Cl2	NCCN
F2	CO2	Cl
CH2OCH2	H2O	CH3CO
SO	HC00CH3	butadiene
ClF3	Li	PF3
B	CH3SH	CF4
C3H6_Cs	C2H6NH	N2O
LiF	H2COH	cyclobutene
LiH	SiO	Si2
C2H6SO	C5H5N	trans-butane
Na2	C4H4O	S02
NH3	NH2	CH2_s3B1d
ClNO	C3H6_D3h	Al

CH3SCH3	H2CO	CH3CN
isobutene	CH3CH2OH	CH3COOH
COF2	CH3NO2	CF3CN
CH3OH	CCH	CH3CH2NH2
PH3	Si2H6	O3
O2	BCl3	CH2_s1A1d
Be	H2CCl2	C3H9C
C3H9N	CH3CH2OCH3	BF3
CH3	CH4	S2
C2H6CHOH	SiH2_s1A1d	H3CNH2
CH3O	H	BeH
P	C3H4_C3v	C2F4
OH	methylenecyclopropane	F2O
SiCl4	HCF3	HCCl3
C3H7	CH3CH2O	AlF3
CH2NHCH2	SiH2_s3B1d	H2CF2
SiF4	H2CCO	PH2
OCS	HF	NO2
SH2	C3H4_C2v	H2O2
CH3CH2Cl	isobutane	CH3COF
HCOOH	CH3ONO	C5H8
2-butyne	SH	NF3
HOCl	CS2	P2
C	CH3S	O
C4H4S	S	C3H7Cl
H2CCHCl	C2H6	CH3CHO
C2H4	HCN	C2H2
C2Cl4	bicyclobutane	H2
C6H6	N2H4	C4H4NH
H2CCHCN	H2CCHF	cyclobutane
HCl	CH3OCH3	Li2
Na	CH3SiH3	NaCl
CH3CH2SH	OCHCHO	SiH4
C2H5	SiH3	NH
ClO	AlCl3	CCl4
NO	C2H3	ClF
HCO	CH3CONH2	CH2SCH2
CH3COCH3	C3H4_D2d	CH
CO	CN	F
CH3COCl	N	CH3Cl
Si	C3H8	CS
N2	Cl2	NCCN
F2	CO2	Cl
CH2OCH2	H2O	CH3CO
SO	HCOOCH3	butadiene
ClF3	Li	PF3
B	CH3SH	CF4
C3H6_Cs	C2H6NH	N2O
LiF	H2COH	cyclobutene
LiH	SiO	Si2
C2H6SO	C5H5N	trans-butane

Na2	C4H4O	S02
NH3	NH2	CH2_s3B1d
C1NO	C3H6_D3h	A1
CH3SCH3	H2CO	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 $1\text{\AA} \times 1\text{\AA} \times 1\text{\AA}$ 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.

```

1 from ase.structure import molecule
2 from ase.io import write
3
4 atoms = molecule('CH3CN')
5
6 atoms.center(vacuum=6)
7 print('unit cell')
8 print('-----')
9 print(atoms.get_cell())
10
11 write('images/ch3cn.png', atoms, show_unit_cell=2)

```

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

```

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

```

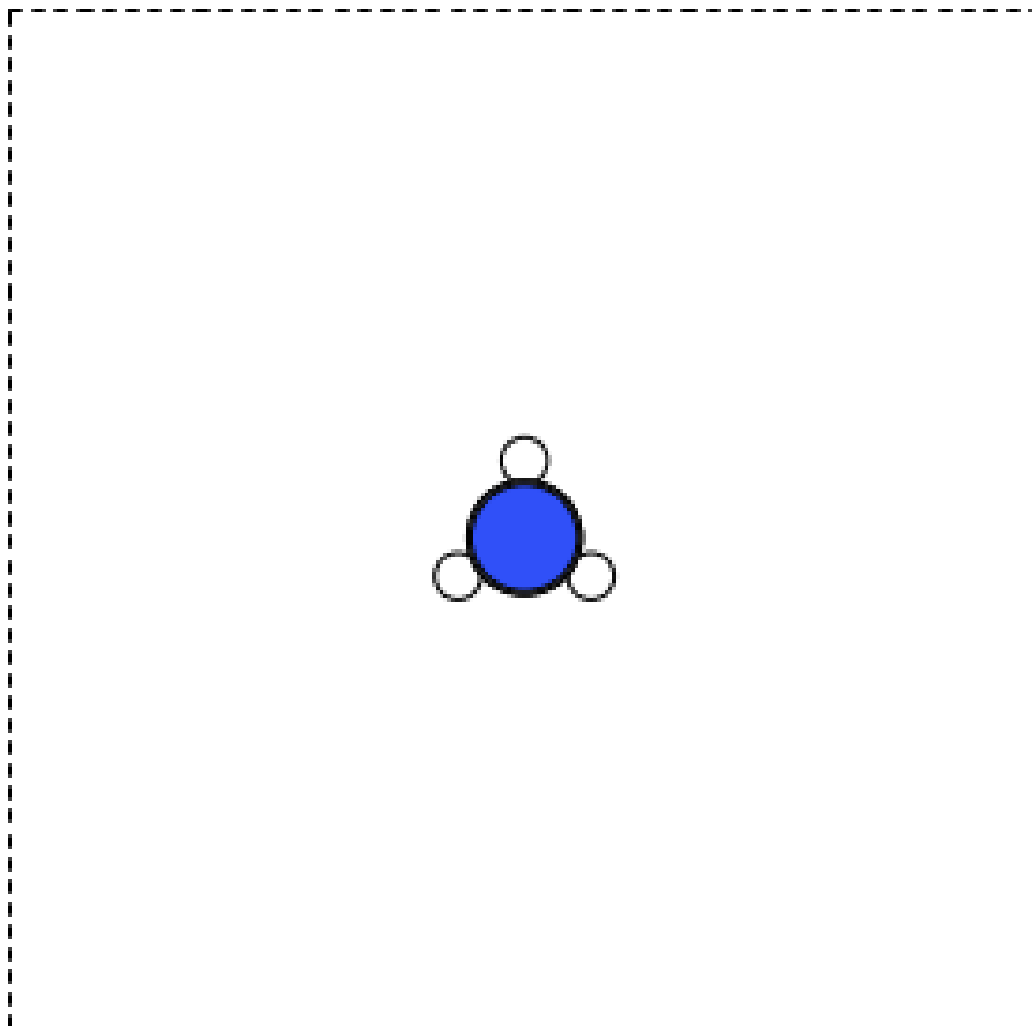


Figure 4: A CH_3CN molecule in a box.

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.

```
1 from ase.structure import molecule
2 from ase.io import write
3
4 atoms = molecule('CH3CN')
5
6 atoms.center(vacuum=6)
7 print('unit cell')
8 print('-----')
9 print(atoms.get_cell())
10
11 write('images/ch3cn-rotated.png', atoms,
12      show_unit_cell=2, rotation='45x,45y,0z')
```

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

unit cell

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

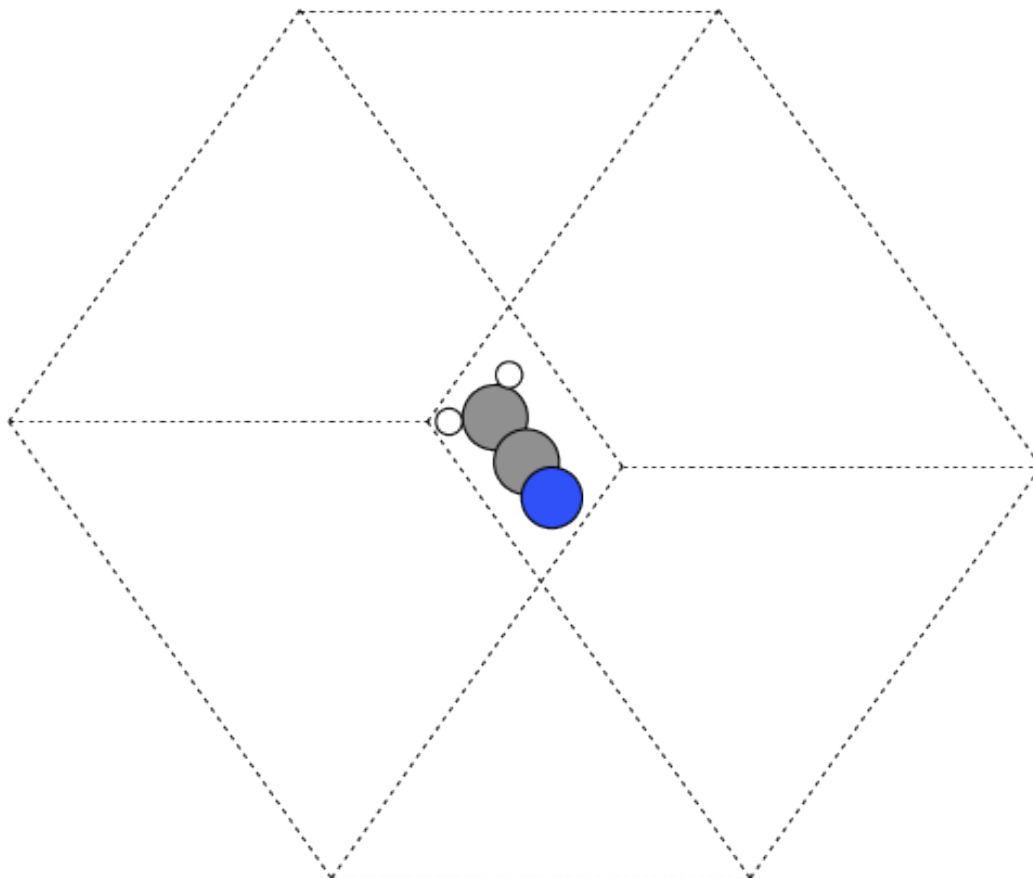


Figure 5: The rotated version of CH_3CN .

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.

```
1 from ase.structure import molecule
2 from ase.io import write
3 from numpy import pi
4
5 atoms = molecule('CH3CN')
6 atoms.center(vacuum=6)
7 p1 = atoms.get_positions()
8
9 atoms.rotate('x', pi/4, center='COM', rotate_cell=False)
10 atoms.rotate('y', pi/4, center='COM', rotate_cell=False)
11
12 write('images/ch3cn-rotated-2.png', atoms, show_unit_cell=2)
```

```

13 print('difference in positions after rotating')
14 print('atom    difference vector')
15 print('-----')
16 p2 = atoms.get_positions()
17
18 diff = p2 - p1
19 for i, d in enumerate(diff):
20     print('{0} {1}'.format(i, d))

```

Open the python script (dft-scripts/script-10.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 ]

```

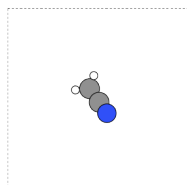


Figure 6: Rotated CH₃CN molecule

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.

```

1 from ase.structure import molecule
2 from ase.io import write
3
4 atoms1 = molecule('NH3')
5
6 atoms2 = molecule('O2')
7 atoms2.translate([3, 0, 0])
8
9 bothatoms = atoms1 + atoms2
10 bothatoms.center(5)
11
12 write('images/bothatoms.png', bothatoms, show_unit_cell=2, rotation='90x')

```

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

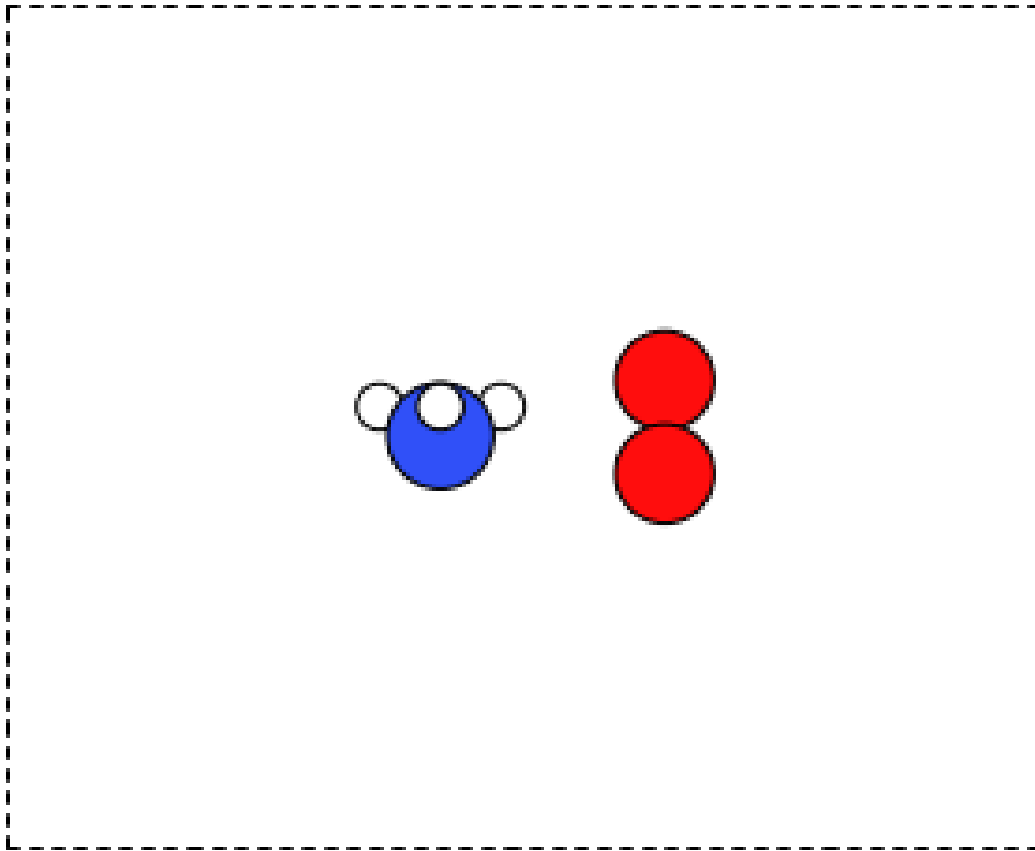


Figure 7: Image featuring ammonia and oxygen molecule in one unit cell.

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`.

```

1  from ase.structure import molecule
2
3  atoms = molecule('C6H6') # benzene
4
5  # access properties on each atom
6  print(' #   sym   p_x   p_y   p_z')
7  print('-----')
8  for i, atom in enumerate(atoms):
9      print('{0:3d}{1:^4s}{2:-8.2f}{3:-8.2f}{4:-8.2f}'.format(i,
10                                                             atom.symbol,
11                                                             atom.x,
12                                                             atom.y,
13                                                             atom.z))
14
15  # get all properties in arrays
16  sym = atoms.get_chemical_symbols()
17  pos = atoms.get_positions()
18  num = atoms.get_atomic_numbers()

```

```

19
20 atom_indices = range(len(atoms))
21
22 print()
23 print(' # sym    at#    p_x    p_y    p_z')
24 print('-----')
25 for i, s, n, p in zip(atom_indices, sym, num, pos):
26     px, py, pz = p
27     print('{0:3d}{1:>3s}{2:8d}{3:-8.2f}{4:-8.2f}{5:-8.2f}'.format(i, s, n,
28                                                                    px, py, pz))

```

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

```

1 from ase.structure import molecule
2
3 atoms = molecule('C6H6')
4 masses = atoms.get_masses()
5
6 molecular_weight = masses.sum()
7 molecular_formula = atoms.get_chemical_formula(mode='reduce')
8
9 # note use of two lines to keep length of line reasonable

```

```

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

```

Open the python script (dft-scripts/script-13.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:

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

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`.

```

1 from ase.structure import molecule
2 import numpy as np
3
4 # ammonia
5 atoms = molecule('NH3')
6
7 # cartesian coordinates
8 print('COM1 = {0}'.format(atoms.get_center_of_mass()))
9
10 # compute the center of mass by hand
11 pos = atoms.positions
12 masses = atoms.get_masses()
13
14 COM = np.array([0., 0., 0.])
15 for m, p in zip(masses, pos):
16     COM += m*p
17 COM /= masses.sum()
18
19 print('COM2 = {0}'.format(COM))
20
21 # one-line linear algebra definition of COM
22 print('COM3 = {0}'.format(np.dot(masses, pos) / np.sum(masses)))

```

Open the python script (dft-scripts/script-14.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 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.:

```

1 from ase.structure import molecule
2
3 print('linear rotors: I = [0 Ia Ia]')
4 atoms = molecule('CO2')

```

```

5  print(' CO2 moments of inertia: ', atoms.get_moments_of_inertia())
6  print()
7
8  print('symmetric rotors (Ia = Ib) < Ic')
9  atoms = molecule('NH3')
10 print(' NH3 moments of inertia: ', atoms.get_moments_of_inertia())
11
12 atoms = molecule('C6H6')
13 print(' C6H6 moments of inertia:', atoms.get_moments_of_inertia())
14 print()
15
16 print('symmetric rotors Ia < (Ib = Ic)')
17 atoms = molecule('CH3Cl')
18 print('CH3Cl moments of inertia: ', atoms.get_moments_of_inertia())
19 print()
20
21 print('spherical rotors Ia = Ib = Ic')
22 atoms = molecule('CH4')
23 print(' CH4 moments of inertia: ', atoms.get_moments_of_inertia())
24 print()
25
26 print('unsymmetric rotors Ia != Ib != Ic')
27 atoms = molecule('C3H7Cl')
28 print(' C3H7Cl moments of inertia: ', atoms.get_moments_of_inertia())

```

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

```

1  from ase.structure import molecule
2
3  atoms = molecule('CH3Cl')
4  moments, axes = atoms.get_moments_of_inertia(vectors=True)
5  print('Moments = {0}'.format(moments))
6  print('axes = {0}'.format(axes))

```

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

```
1 from ase.structure import molecule
2
3 # ammonia
4 atoms = molecule('NH3')
5
6 print('atom symbol')
7 print('=====')
8 for i, atom in enumerate(atoms):
9     print('{0:2d} {1:3s}'.format(i, atom.symbol))
10
11 # N-H bond length
12 s = 'The N-H distance is {0:1.3f} angstroms'
13 print(s.format(atoms.get_distance(0, 1)))
```

Open the python script (dft-scripts/script-17.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-H₁ and N-H₂. 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.

```
1 from ase.structure import molecule
2
3 # ammonia
4 atoms = molecule('NH3')
5
6 print('atom symbol')
7 print('=====')
8 for i, atom in enumerate(atoms):
9     print('{0:2d} {1:3s}'.format(i, atom.symbol))
10
11 a = atoms.positions[0] - atoms.positions[1]
12 b = atoms.positions[0] - atoms.positions[2]
13
14 from numpy import arccos, dot, pi
15 from numpy.linalg import norm
16
17 theta_rad = arccos(dot(a, b) / (norm(a) * norm(b))) # in radians
18
19 print('theta = {0:1.1f} degrees'.format(theta_rad * 180./pi))
```

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

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

```

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

```

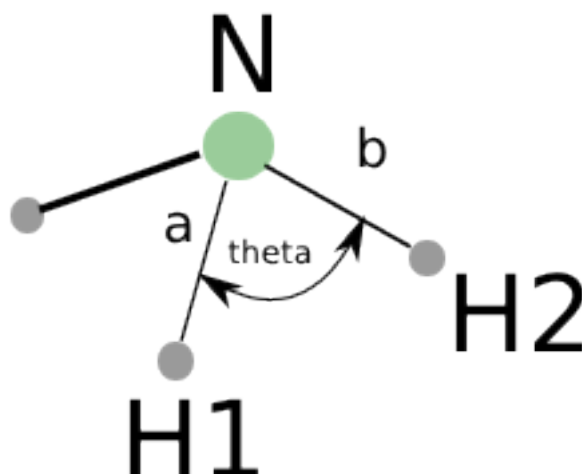


Figure 8: Schematic of the vectors defining the H-N-H angle.

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.

```

1 from ase.structure import molecule
2 from numpy import pi
3 # ammonia
4 atoms = molecule('NH3')
5
6 print('theta = {0} degrees'.format(atoms.get_angle([1, 0, 2]) * 180. / pi))

```

Open the python script (dft-scripts/script-19.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 60° (Figure 9).

```

1 # calculate an ethane dihedral angle
2 from ase.structure import molecule
3 import numpy as np

```

```

4
5 atoms = molecule('C2H6')
6
7 print('atom symbol')
8 print('=====')
9 for i, atom in enumerate(atoms):
10     print('{0:2d} {1:3s}'.format(i, atom.symbol))
11
12 da = atoms.get_dihedral([5, 1, 0, 4]) * 180. / np.pi
13 print('dihedral angle = {0:1.2f} degrees'.format(da))

```

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

```

1 from ase import Atoms, Atom
2 from jasp import *
3 import numpy as np
4 np.set_printoptions(precision=3, suppress=True)
5
6 co = Atoms([Atom('C', [0, 0, 0]),
7             Atom('O', [1.2, 0, 0])],
8            cell=(6., 6., 6.))
9
10 with jasp('molecules/simple-co', # output dir
11          xc='PBE', # the exchange-correlation functional
12          nbands=6, # number of bands
13          encut=350, # plane-wave cutoff
14          ismear=1, # Methfessel-Paxton smearing
15          sigma=0.01, # very small smearing factor for a molecule
16          atoms=co) as calc:
17     print('energy = {0} eV'.format(co.get_potential_energy()))
18     print(co.get_forces())

```

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

```

energy = -14.687906 eV
[[ 5.095  0.      0.   ]
 [-5.095  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.

```

1 from jasp import *
2 from ase import Atoms, Atom
3 import numpy as np
4 np.set_printoptions(precision=3, suppress=True)
5
6 atoms = Atoms([Atom('C', [0, 0, 0]),
7                 Atom('O', [1.2, 0, 0])])
8
9 L = [4, 5, 6, 8, 10]
10
11 energies = []
12 ready = True
13 for a in L:
14     atoms.set_cell([a, a, a], scale_atoms=False)
15     atoms.center()
16     with jasp('molecules/co-L-{0}'.format(a),
17             encut=350,
18             xc='PBE',
19             atoms=atoms) as calc:
20         try:
21             energies.append(atoms.get_potential_energy())
22         except (VaspSubmitted, VaspQueued):
23             ready = False
24
25 if not ready:
26     import sys; sys.exit()
27
28 import matplotlib.pyplot as plt
29 plt.plot(L, energies, 'bo-')
30 plt.xlabel('Unit cell length ($\AA$)')
31 plt.ylabel('Total energy (eV)')
32 plt.savefig('images/co-e-v.png')
33 plt.show()

```

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

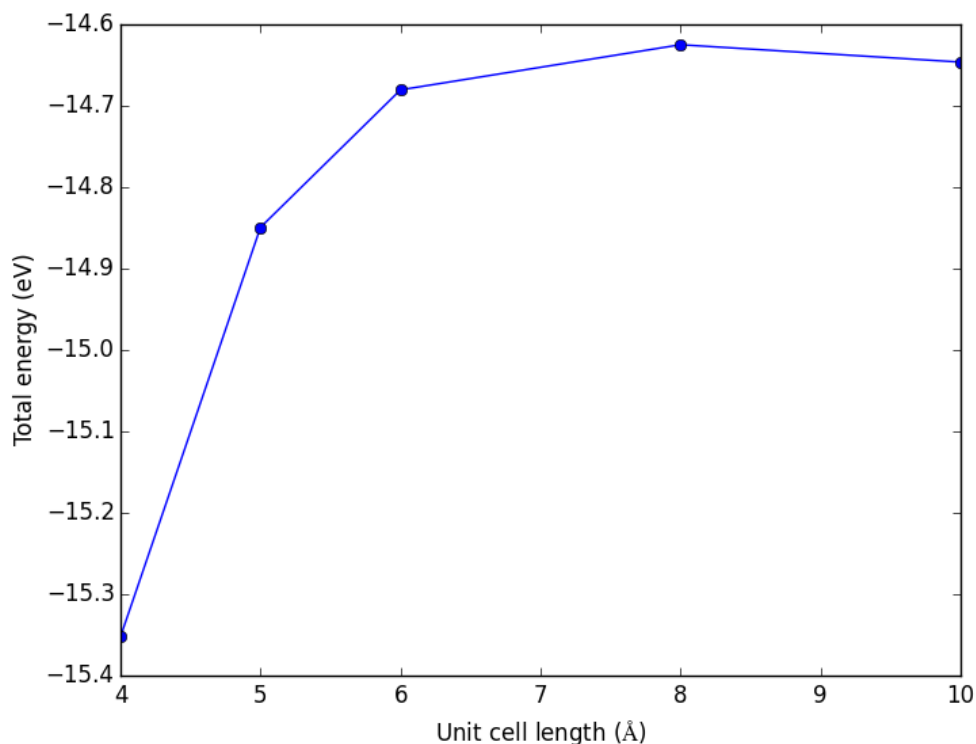


Figure 10: Total energy of a CO molecule as a function of the unit cell length.

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 plane waves that fit in the cube grows as the cube gets larger.

```

1 from jasp import *
2
3 L = [4, 5, 6, 8, 10]
4
5 for a in L:
6     with jasp('molecules/co-L-{}'.format(a)) as calc:
7         print('{0} {1} seconds'.format(a, calc.get_elapsed_time()))

```

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

```

4 1.601 seconds
5 3.932 seconds
6 6.543 seconds
8 19.678 seconds
10 36.013 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 .

```

1  from ase.units import kB, Pascal
2  import numpy as np
3  import matplotlib.pyplot as plt
4
5  atm = 101325 * Pascal
6
7  L = np.linspace(4, 10)
8  V = L**3
9
10 n = 1 # one atom/molecule per unit cell
11
12 for T in [298, 600, 1000]:
13     P = n / V * kB * T / atm # convert to atmospheres
14
15     plt.plot(V, P, label='{0}K'.format(T))
16
17 plt.xlabel('Unit cell volume ($\AA^3$)')
18 plt.ylabel('Pressure (atm)')
19 plt.legend(loc='best')
20 plt.savefig('images/ideal-gas-pressure.png')
21 plt.show()

```

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

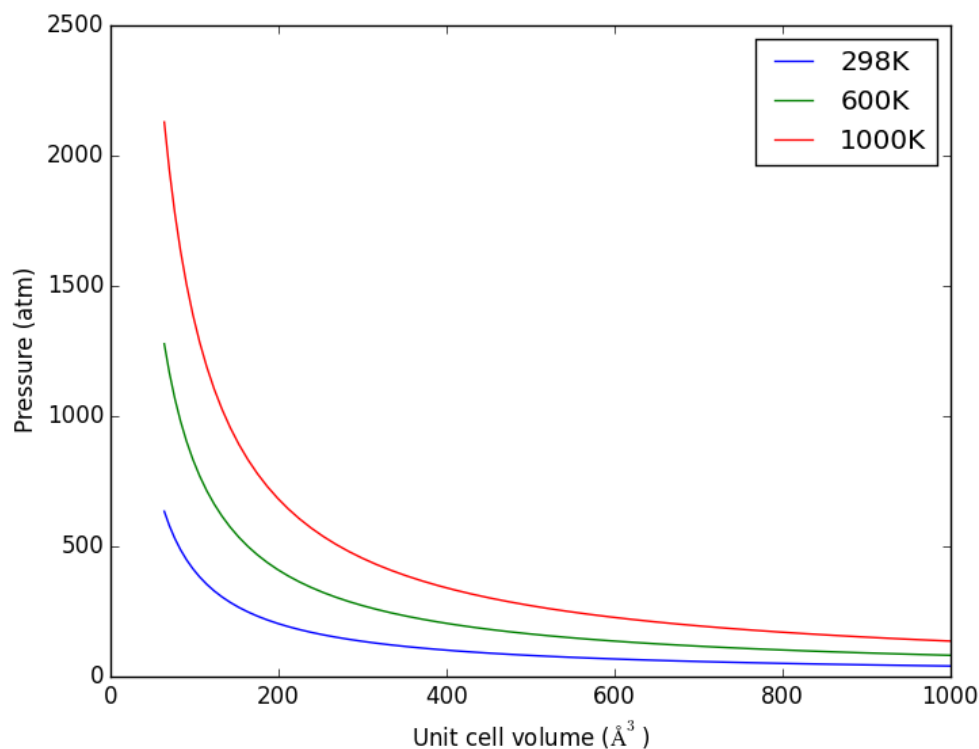


Figure 11: Ideal gas pressure dependence on temperature and unit cell volume.

Convergence of ENCUT The total energy and forces also depend on the computational parameters, notably [ENCUT](#).

```

1  from ase import Atoms, Atom
2  from jasp import *
3  import numpy as np
4  np.set_printoptions(precision=3, suppress=True)
5
6  atoms = Atoms([Atom('C', [0, 0, 0]),
7                 Atom('O', [1.2, 0, 0])],
8                cell=(6, 6, 6))
9  atoms.center()
10
11  ENCUTS = [250, 300, 350, 400, 450, 500]
12
13  energies = []
14  ready = True
15  for en in ENCUTS:
16      with jasp('molecules/co-en-{0}'.format(en),
17               encut=en,
18               xc='PBE',
19               atoms=atoms) as calc:
20          try:
21              energies.append(atoms.get_potential_energy())
22          except (VaspSubmitted, VaspQueued):
23              ready = False
24
25  if not ready:
26      import sys; sys.exit()
27
28  import matplotlib.pyplot as plt
29  plt.plot(ENCUTS, energies, 'bo-')
30  plt.xlabel('ENCUT (eV)')
31  plt.ylabel('Total energy (eV)')
32  plt.savefig('images/co-encut-v.png')

```

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

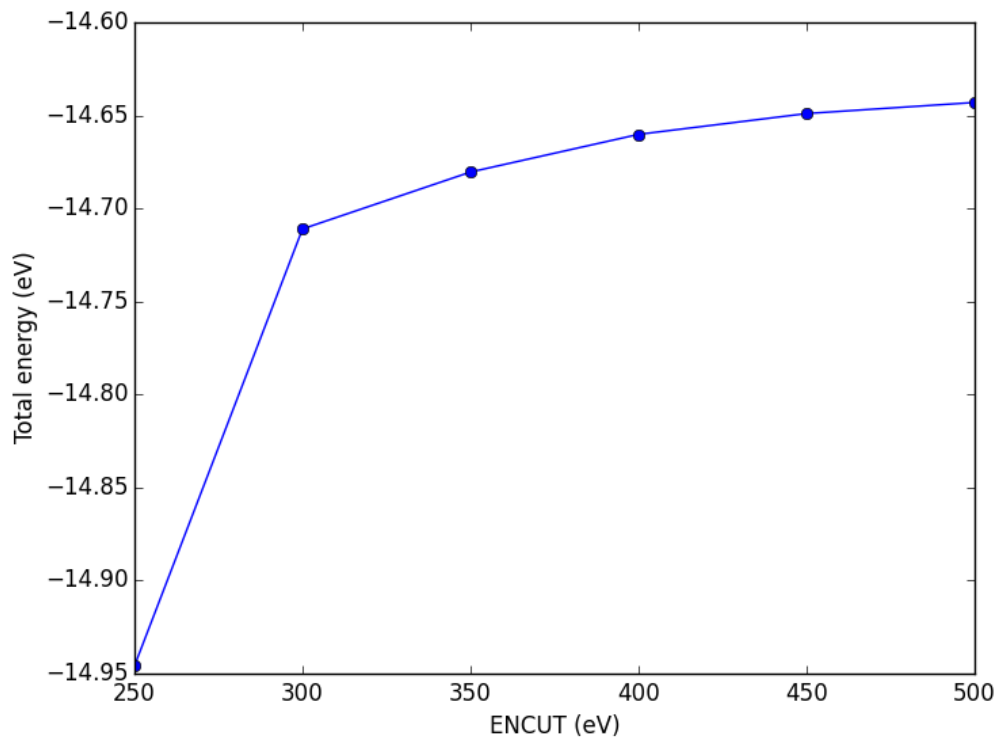


Figure 12: Dependence of the total energy of CO molecule on ENCUT.

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.

```
1 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):	3.590
molecules/co-en-300/OUTCAR:	Elapsed time (sec):	6.016
molecules/co-en-350/OUTCAR:	Elapsed time (sec):	6.014
molecules/co-en-400/OUTCAR:	Elapsed time (sec):	7.883
molecules/co-en-450/OUTCAR:	Elapsed time (sec):	12.421
molecules/co-en-500/OUTCAR:	Elapsed time (sec):	15.167

Although here the times do not seem that unreasonable, note we increased the time by a factor of three by simply doubling ENCUT. If the first time was a week, this is a significant increase in time!

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.

```
1 from jasp import *
2 from enthought.mayavi import mlab
3 from ase.data import vdw_radii
4 from ase.data.colors import cpk_colors
5
6 with jasp('molecules/simple-co') as calc:
7     atoms = calc.get_atoms()
8     x, y, z, cd = calc.get_charge_density()
9
10 # make a white figure
11 mlab.figure(1, bgcolor=(1, 1, 1))
12
13 # plot the atoms as spheres
14 for atom in atoms:
15     mlab.points3d(atom.x,
16                   atom.y,
17                   atom.z,
18                   #this determines the size of the atom
19                   scale_factor=vdw_radii[atom.number] / 5.,
20                   resolution=20,
21                   # a tuple is required for the color
22                   color=tuple(cpk_colors[atom.number]),
23                   scale_mode='none')
24
25 # draw the unit cell - there are 8 corners, and 12 connections
26 a1, a2, a3 = atoms.get_cell()
27 origin = [0, 0, 0]
28 cell_matrix = [[origin, a1],
29                [origin, a2],
30                [origin, a3],
31                [a1, a1 + a2],
32                [a1, a1 + a3],
33                [a2, a2 + a1],
34                [a2, a2 + a3],
35                [a3, a1 + a3],
36                [a3, a2 + a3],
37                [a1 + a2, a1 + a2 + a3],
38                [a2 + a3, a1 + a2 + a3],
39                [a1 + a3, a1 + a3 + a2]]
```

```

40
41 for p1, p2 in cell_matrix:
42     mlab.plot3d([p1[0], p2[0]], # x-positions
43                 [p1[1], p2[1]], # y-positions
44                 [p1[2], p2[2]], # z-positions
45                 tube_radius=0.02)
46
47 # Now plot the charge density
48 mlab.contour3d(x, y, z, cd)
49 mlab.view(azimuth=-90, elevation=90, distance='auto')
50
51 mlab.savefig('images/co-cd.png')
52 mlab.show()

```

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

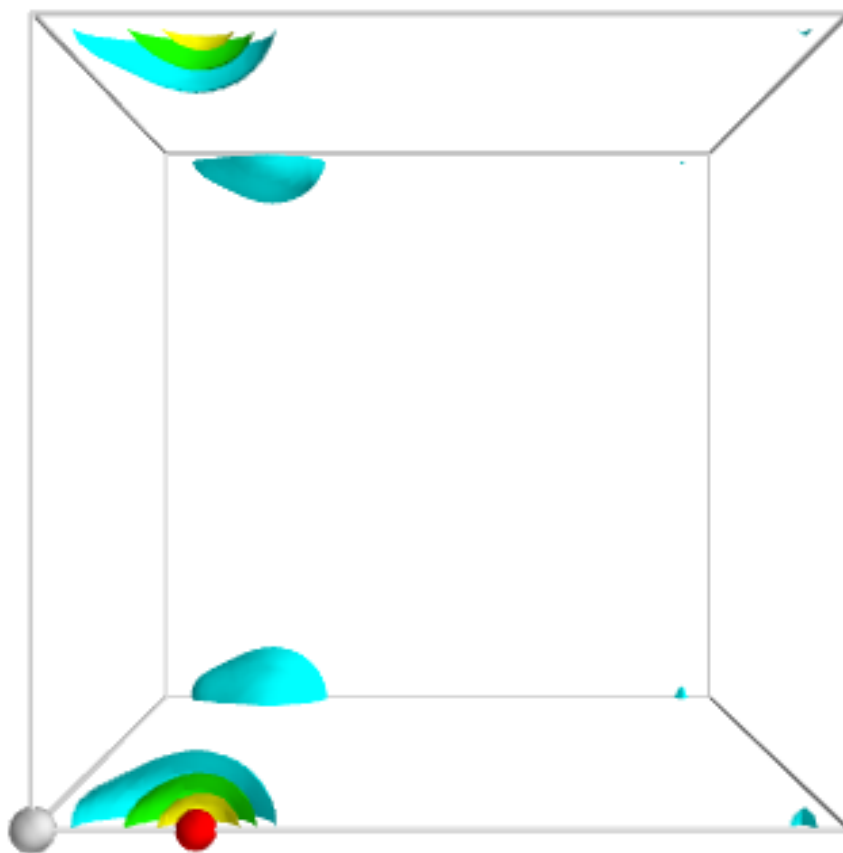


Figure 13: Charge density of a CO molecule that is located at the origin. The electron density that is outside the cell is wrapped around to the other corners.

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

```

1 from jasp import *
2 from enthought.mayavi import mlab
3 from ase.data import vdw_radii
4 from ase.data.colors import cpk_colors
5 from ase import Atom, Atoms
6
7 atoms = Atoms([Atom('C', [2.422, 0.0, 0.0]),
8                 Atom('O', [3.578, 0.0, 0.0])],
9               cell=(10,10,10))
10

```

```

11 atoms.center()
12
13 with jasp('molecules/co-centered',
14         encut=350,
15         xc='PBE',
16         atoms=atoms) as calc:
17
18     atoms = calc.get_atoms()
19     x, y, z, cd = calc.get_charge_density()
20
21 mlab.figure(bgcolor=(1, 1, 1))
22
23 # plot the atoms as spheres
24 for atom in atoms:
25     mlab.points3d(atom.x,
26                  atom.y,
27                  atom.z,
28                  scale_factor=vdw_radii[atom.number]/5.,
29                  resolution=20,
30                  # a tuple is required for the color
31                  color=tuple(cpk_colors[atom.number]),
32                  scale_mode='none')
33
34 # draw the unit cell - there are 8 corners, and 12 connections
35 a1, a2, a3 = atoms.get_cell()
36 origin = [0, 0, 0]
37 cell_matrix = [[origin, a1],
38               [origin, a2],
39               [origin, a3],
40               [a1, a1 + a2],
41               [a1, a1 + a3],
42               [a2, a2 + a1],
43               [a2, a2 + a3],
44               [a3, a1 + a3],
45               [a3, a2 + a3],
46               [a1 + a2, a1 + a2 + a3],
47               [a2 + a3, a1 + a2 + a3],
48               [a1 + a3, a1 + a3 + a2]]
49
50 for p1, p2 in cell_matrix:
51     mlab.plot3d([p1[0], p2[0]], # x-positions
52                [p1[1], p2[1]], # y-positions
53                [p1[2], p2[2]], # z-positions
54                tube_radius=0.02)
55
56
57 # Now plot the charge density
58 mlab.contour3d(x, y, z, cd, transparent=True)
59
60 # this view was empirically found by iteration
61 mlab.view(azimuth=-90, elevation=90, distance='auto')
62
63 mlab.savefig('images/co-centered-cd.png')
64 mlab.show()

```

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

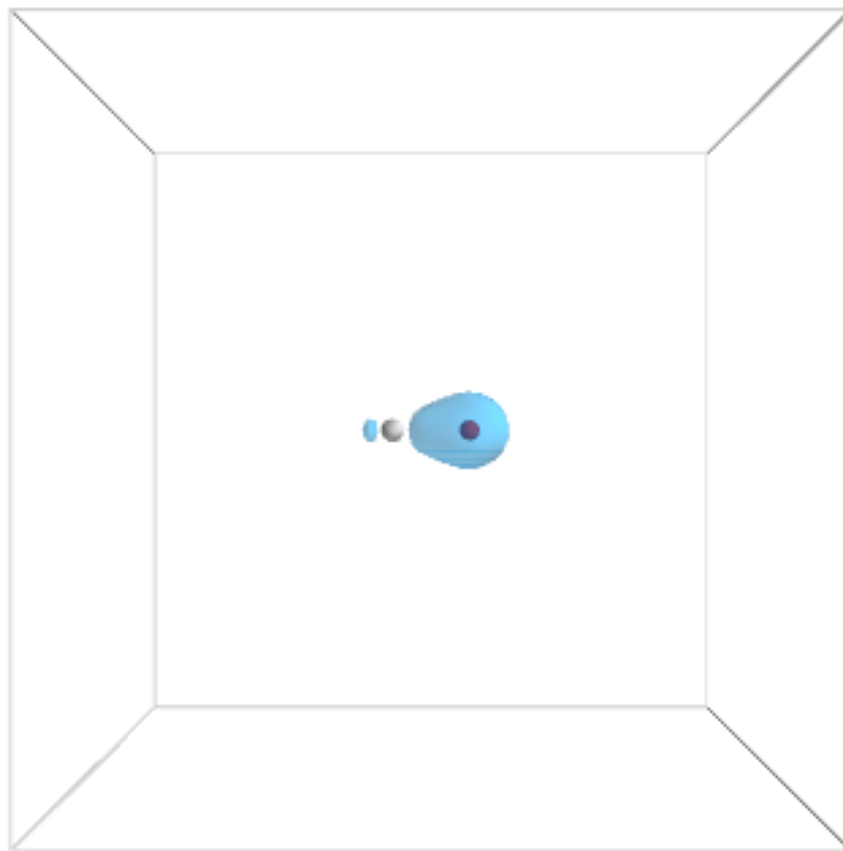


Figure 14: Charge density of a CO molecule centered in the unit cell. Now the electron density is centered in the unit cell.

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.

```

1  #!/usr/bin/env python
2  from ase import *
3  from ase.structure import molecule
4  from jasp import *
5
6  ### Setup calculators
7  benzene = molecule('C6H6')
8  benzene.set_cell([10, 10, 10])
9  benzene.center()
10
11 with jasp('molecules/benzene',
12          xc='PBE',
13          nbands=18,
14          encut=350,
15          atoms=benzene) as calc:
16
17     print(benzene.get_potential_energy())
18     x1, y1, z1, cd1 = calc.get_charge_density()
19
20 chlorobenzene = molecule('C6H5Cl')
```

```

21 chlorobenzene.set_cell([10, 10, 10])
22 chlorobenzene.center()
23 chlorobenzene[11].symbol = 'Cl'
24
25 with jasp('molecules/chlorobenzene',
26          xc='PBE',
27          nbands=18,
28          encut=350,
29          atoms=chlorobenzene) as calc:
30     chlorobenzene.get_potential_energy()
31     x2, y2, z2, cd2 = calc.get_charge_density()
32
33 cdiff = cd2 - cd1
34
35 print(cdiff.min(), cdiff.max())
36 #####
37
38
39 ##### set up visualization of charge difference
40 from enthought.mayavi import mlab
41 mlab.contour3d(x1, y1, z1, cdiff,
42              contours=[-0.02, 0.02])
43
44 mlab.savefig('images/cdiff.png')
45
46 mlab.show()

```

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

```

-75.99995466
(-2.08214499999999988, 2.96889999999999979)

```


./images/cdiff.png

```
1  #!/usr/bin/env python
2  from ase import *
3  from ase.structure import molecule
4  from jasp import *
5  import bisect
6
7  def vinterp3d(x, y, z, u, xi, yi, zi):
8      "Interpolate the point (xi, yi, zi) from the values at u(x, y, z)"
9      p = np.array([xi, yi, zi])
10
11     #1D arrays of coordinates
12     xv = x[:, 0, 0]
13     yv = y[0, :, 0]
14     zv = z[0, 0, :]
15
16     # we subtract 1 because bisect tells us where to insert the
17     # element to maintain an ordered list, so we want the index to the
18     # left of that point
19     i = bisect.bisect_right(xv, xi) - 1
20     j = bisect.bisect_right(yv, yi) - 1
21     k = bisect.bisect_right(zv, zi) - 1
22
23     if i == len(x) - 1:
24         i = len(x) - 2
25     elif i < 0:
26         i = 0
```

```

27
28     if j == len(y) - 1:
29         j = len(y) - 2
30     elif j < 0:
31         j = 0
32
33     if k == len(z) - 1:
34         k = len(z) - 2
35     elif k < 0:
36         k = 0
37
38     # points at edge of cell. We only need P1, P2, P3, and P5
39     P1 = np.array([x[i, j, k],
40                   y[i, j, k],
41                   z[i, j, k]])
42     P2 = np.array([x[i + 1, j, k],
43                   y[i + 1, j, k],
44                   z[i + 1, j, k]])
45     P3 = np.array([x[i, j + 1, k],
46                   y[i, j + 1, k],
47                   z[i, j + 1, k]])
48     P5 = np.array([x[i, j, k + 1],
49                   y[i, j, k + 1],
50                   z[i, j, k + 1]])
51
52     # values of u at edge of cell
53     u1 = u[i, j, k]
54     u2 = u[i+1, j, k]
55     u3 = u[i, j+1, k]
56     u4 = u[i+1, j+1, k]
57     u5 = u[i, j, k+1]
58     u6 = u[i+1, j, k+1]
59     u7 = u[i, j+1, k+1]
60     u8 = u[i+1, j+1, k+1]
61
62     # cell basis vectors, not the unit cell, but the voxel cell containing the point
63     cbasis = np.array([P2 - P1,
64                       P3 - P1,
65                       P5 - P1])
66
67     # now get interpolated point in terms of the cell basis
68     s = np.dot(np.linalg.inv(cbasis.T), np.array([xi, yi, zi]) - P1)
69
70     # now s = (sa, sb, sc) which are fractional coordinates in the vector space
71     # next we do the interpolations
72     ui1 = u1 + s[0] * (u2 - u1)
73     ui2 = u3 + s[0] * (u4 - u3)
74
75     ui3 = u5 + s[0] * (u6 - u5)
76     ui4 = u7 + s[0] * (u8 - u7)
77
78     ui5 = ui1 + s[1] * (ui2 - ui1)
79     ui6 = ui3 + s[1] * (ui4 - ui3)
80
81     ui7 = ui5 + s[2] * (ui6 - ui5)
82
83     return ui7
84
85     ### Setup calculators
86     with jasp('molecules/benzene') as calc:
87         benzene = calc.get_atoms()
88         x1, y1, z1, cd1 = calc.get_charge_density()
89
90     with jasp('molecules/chlorobenzene') as calc:
91         x2, y2, z2, cd2 = calc.get_charge_density()
92
93     cdiff = cd2 - cd1
94
95     #we need the x-y plane at z=5
96     import matplotlib.pyplot as plt
97     from scipy import mgrid
98
99     X, Y = mgrid[0: 10: 25j, 0: 10: 25j]
100
101     cdiff_plane = np.zeros(X.shape)
102     ni, nj = X.shape
103
104     for i in range(ni):

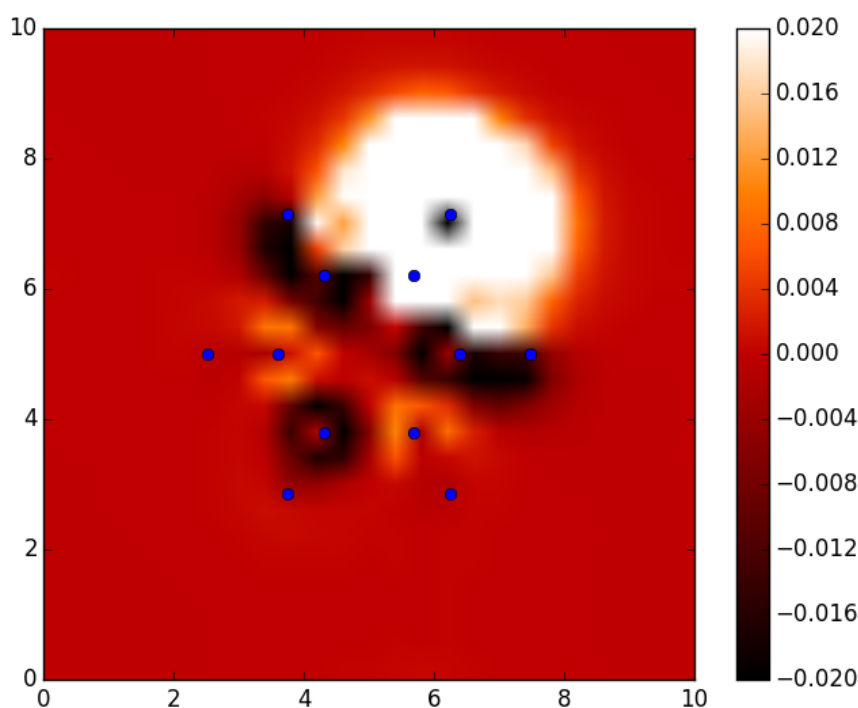
```

```

105     for j in range(nj):
106         cdiff_plane[i, j] = vinterp3d(x1, y1, z1, cdiff, X[i, j], Y[i, j], 5.0)
107
108 plt.imshow(cdiff_plane,
109           vmin=-0.02, # min charge diff to plot
110           vmax=0.02, # max charge diff to plot
111           cmap=plt.cm.gist_heat, # colormap
112           extent=(0., 10., 0., 10.)) # axes limits
113
114 # plot atom positions. It is a little tricky to see why we reverse the x and y coordinates. That is because imshow does that.
115 x = [a.y for a in benzene]
116 y = [a.x for a in benzene]
117 plt.plot(x, y, 'bo')
118
119 plt.colorbar() #add colorbar
120 plt.savefig('images/cdiff-imshow.png')
121
122 plt.figure()
123 plt.contourf(X, Y, cdiff_plane)
124 plt.plot(y, x, 'ko')
125 plt.axis('equal')
126 plt.show()

```

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

```

1 from jasp import *
2 from ase.units import Debye

```

```

3
4 with jasp('molecules/co-centered') as calc:
5     atoms = calc.get_atoms()
6     atoms.get_potential_energy()
7
8     vcd = VaspChargeDensity()
9
10    cd = np.array(vcd.chg[0])
11    n0, n1, n2 = cd.shape
12
13    s0 = 1.0 / n0
14    s1 = 1.0 / n1
15    s2 = 1.0 / n2
16
17    X, Y, Z = np.mgrid[0.0:1.0:s0,
18                        0.0:1.0:s1,
19                        0.0:1.0:s2]
20
21    C = np.column_stack([X.ravel(),
22                        Y.ravel(),
23                        Z.ravel()])
24
25    atoms = calc.get_atoms()
26    uc = atoms.get_cell()
27    real = np.dot(C, uc)
28
29    # now convert arrays back to unitcell shape
30    x = np.reshape(real[:, 0], (n0, n1, n2))
31    y = np.reshape(real[:, 1], (n0, n1, n2))
32    z = np.reshape(real[:, 2], (n0, n1, n2))
33
34    nelelements = n0 * n1 * n2
35    voxel_volume = atoms.get_volume() / nelelements
36    total_electron_charge = -cd.sum() * voxel_volume
37
38    electron_density_center = np.array([(cd * x).sum(),
39                                       (cd * y).sum(),
40                                       (cd * z).sum()])
41
42    electron_density_center *= voxel_volume
43    electron_density_center /= total_electron_charge
44
45    electron_dipole_moment = -electron_density_center * total_electron_charge
46
47    # now the ion charge center. We only need the Zval listed in the potcar
48    from jasp.POTCAR import get_ZVAL
49
50    LOP = calc.get_pseudopotentials()
51    ppp = os.environ['VASP_PP_PATH']
52
53    zval = {}
54    for sym, ppath, hash in LOP:
55        fullpath = os.path.join(ppp, ppath)
56        z = get_ZVAL(fullpath)
57        zval[sym] = z
58
59    ion_charge_center = np.array([0.0, 0.0, 0.0])
60    total_ion_charge = 0.0
61    for atom in atoms:
62        Z = zval[atom.symbol]
63        total_ion_charge += Z
64        pos = atom.position
65        ion_charge_center += Z*pos
66
67    ion_charge_center /= total_ion_charge
68    ion_dipole_moment = ion_charge_center * total_ion_charge
69
70    dipole_vector = (ion_dipole_moment + electron_dipole_moment)
71
72    dipole_moment = ((dipole_vector**2).sum())**0.5 / Debye
73
74    print('The dipole moment is {0:1.2f} Debye'.format(dipole_moment))

```

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

The dipole moment is 0.10 Debye

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

```

1 from jasp import *
2 from ase.units import Debye
3
4 with jasp('molecules/co-centered') as calc:
5     dipole_vector = calc.get_dipole_moment()
6     dipole_moment = ((dipole_vector**2).sum())**0.5/Debye
7     print('The dipole moment is {0:1.2f} Debye'.format(dipole_moment))

```

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

Warning:

One way that `jasp` is unintuitive is that whenever you are "inside" (indented) a `with` statement, the current working directory may be different than where your script started. In this example that can lead to your figure not being saved where you expect it to be saved!

```

1 from jasp import *
2 from ase.dft.dos import DOS
3 import matplotlib.pyplot as plt
4
5 with jasp('molecules/simple-co') as calc: # we already ran this!
6     dos = DOS(calc)
7     plt.plot(dos.get_energies(), dos.get_dos())
8     plt.xlabel('Energy - $E_f$ (eV)')
9     plt.ylabel('DOS')
10
11 # make sure you save the figure outside the with statement, or provide
12 # the correct relative or absolute path to where you want it.
13 plt.savefig('images/co-dos.png')

```

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

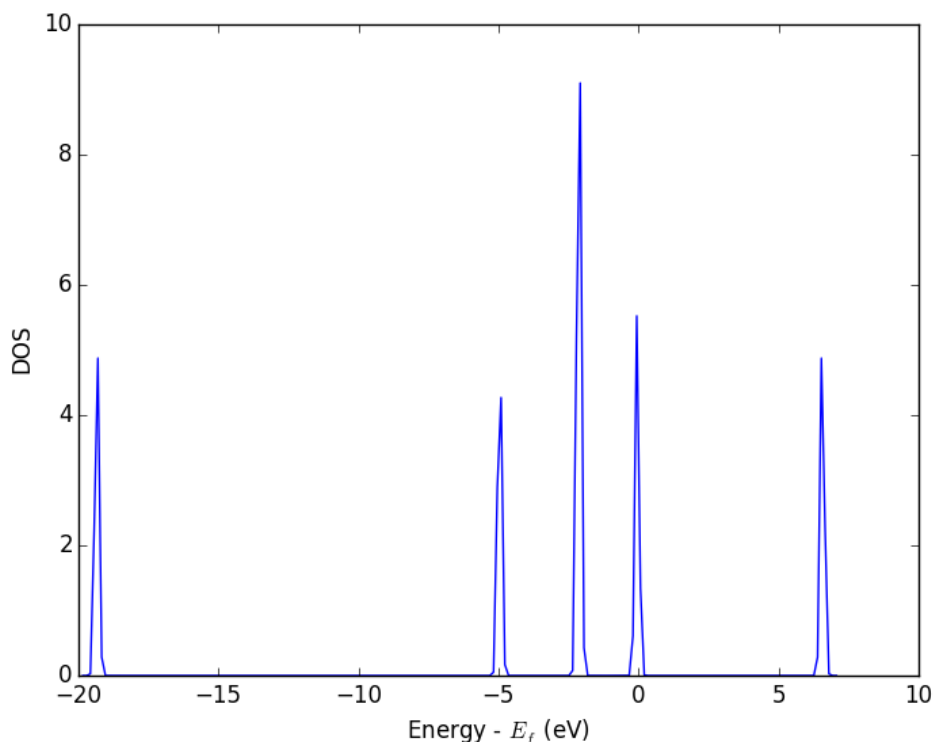


Figure 15: Density of states for a CO molecule.

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.

```

1  from jasp import *
2  from ase.dft.dos import DOS
3  import matplotlib.pyplot as plt
4
5  # get the geometry from another calculation
6  with jasp('molecules/simple-co') as calc:
7      atoms = calc.get_atoms()
8
9  with jasp('molecules/co-ados',
10          encut=300,
11          xc='PBE',
12          rwiggs=[1.0, 1.0], # these are the cutoff radii for projected states
13          atoms=atoms) as calc:
14      calc.calculate()
15
16      # now get results
17      dos = DOS(calc)
18      plt.plot(dos.get_energies(), dos.get_dos() + 10)
19
20      ados = VaspDos(efermi=calc.get_fermi_level())
21      energies = ados.energy
22
23      plt.plot(energies, ados.dos + 8, label='ADOS') # these are the total DOS
24
25      c_s = ados.site_dos(0, 's')
26      c_p = ados.site_dos(0, 'p')
27      o_s = ados.site_dos(1, 's')
28      o_p = ados.site_dos(1, 'p')
29
30      c_d = ados.site_dos(0, 'd')
31      o_d = ados.site_dos(1, 'd')
32
33      plt.plot(energies, c_s + 6, energies, o_s + 5)
34      plt.plot(energies, c_p + 4, energies, o_p + 3)
35      plt.plot(energies, c_d, energies, o_d + 2)
36      plt.xlabel('Energy -  $E_f$  (eV)')
37      plt.ylabel('DOS')
38      plt.legend(['DOS', 'ADOS',
39                 'Cs', 'Os',
40                 'Cp', 'Op',
41                 'Cd', 'Od'],
42                ncol=2, loc='best')
43  plt.savefig('images/co-ados.png')

```

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

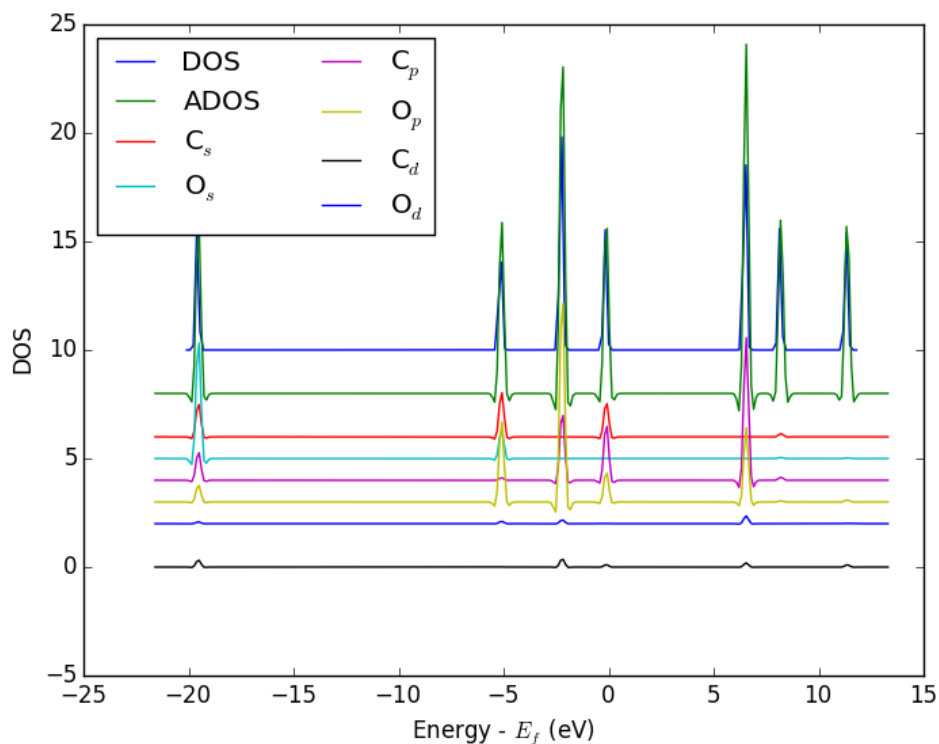


Figure 16: Atom-projected DOS for a CO molecule. The total density of states and the s , p and d states on the C and O are shown.

3.3.7 Electrostatic potential

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

```

1  from jasp import *
2  from ase import Atom, Atoms
3  from ase.io import write
4
5  from enthought.mayavi import mlab
6  from ase.data import vdw_radii
7  from ase.data.colors import cpk_colors
8
9  atoms = Atoms([Atom('C', [ 0.0000, 0.0000, -0.8088]),
10                Atom('Br', [ 0.0000, 0.0000, 1.1146]),
11                Atom('F', [ 0.0000, 1.2455, -1.2651]),
12                Atom('F', [ 1.0787, -0.6228, -1.2651]),
13                Atom('F', [-1.0787, -0.6228, -1.2651]),
14                cell=(10, 10, 10))
15  atoms.center()
16
17  with jasp('molecules/CF3Br',
18            encut=350,
19            xc='PBE',
20            ibrion=1,
21            nsw=50,
22            lvtot=True,
23            lvhar=True,
24            atoms=atoms) as calc:
25      calc.set_nbands(f=2)
26      calc.calculate()
27

```



```

28     x, y, z, lp = calc.get_local_potential()
29     x, y, z, cd = calc.get_charge_density()
30
31     mlab.figure(1, bgcolor=(1, 1, 1)) # make a white figure
32
33     # plot the atoms as spheres
34     for atom in atoms:
35         mlab.points3d(atom.x,
36                       atom.y,
37                       atom.z,
38                       scale_factor=vdw_radii[atom.number]/5.,
39                       resolution=20,
40                       # a tuple is required for the color
41                       color=tuple(cpk_colors[atom.number]),
42                       scale_mode='none')
43     # plot the bonds. We want a line from C-Br, C-F, etc...
44     # We create a bond matrix showing which atoms are connected.
45     bond_matrix = [[0, 1],
46                   [0, 2],
47                   [0, 3],
48                   [0, 4]]
49
50     for a1, a2 in bond_matrix:
51         mlab.plot3d(atoms.positions[[a1,a2], 0], # x-positions
52                   atoms.positions[[a1,a2], 1], # y-positions
53                   atoms.positions[[a1,a2], 2], # z-positions
54                   [2, 2],
55                   tube_radius=0.02,
56                   colormap='Reds')
57
58     mlab.contour3d(x, y, z, lp)
59     mlab.savefig('images/halogen-ep.png')
60     mlab.show()

```

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

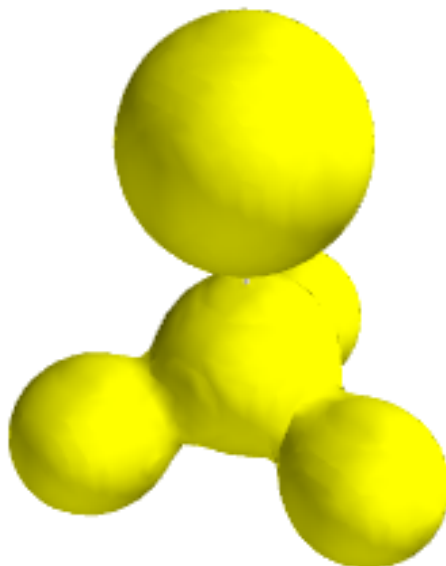


Figure 17: Plot of the electrostatic potential of CF_3Br . TODO: figure out how to do an isosurface of charge, colormapped by the local potential.

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

3.3.8 Bader analysis

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.^{42,43} 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.

```

1 from jasp import *
2 from ase.structure import molecule
3 atoms = molecule('H2O')
4 atoms.center(vacuum=6)
5
6 with jasp('molecules/h2o-bader',
7           xc='PBE',
8           encut=350,
9           atoms=atoms) as calc:
10     calc.calculate()
11
12     os.system('bader -p all_atom -p atom_index CHG')
```

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

GRID BASED BADER ANALYSIS (Version 0.27e 05/09/11)

OPEN ... CHG
VASP-STYLE INPUT FILE
VASP5 format
FFT-grid: 112 x 128 x 120
CLOSE ... CHG

RUN TIME: 0.74 SECONDS

CALCULATING BADER CHARGE DISTRIBUTION
0 10 25 50 75 100
PERCENT DONE: *****

REFINING AUTOMATICALLY

ITERATION: 1
EDGE POINTS: 1400048
REASSIGNED POINTS: 111247
ITERATION: 2
CHECKED POINTS: 913174
REASSIGNED POINTS: 1424
ITERATION: 3
CHECKED POINTS: 15784
REASSIGNED POINTS: 362
ITERATION: 4
CHECKED POINTS: 3190
REASSIGNED POINTS: 176
ITERATION: 5
CHECKED POINTS: 1228
REASSIGNED POINTS: 99
ITERATION: 6
CHECKED POINTS: 688
REASSIGNED POINTS: 21
ITERATION: 7
CHECKED POINTS: 267
REASSIGNED POINTS: 1
ITERATION: 8
CHECKED POINTS: 26
REASSIGNED POINTS: 0

RUN TIME: 26.40 SECONDS

CALCULATING MINIMUM DISTANCES TO ATOMS
0 10 25 50 75 100
PERCENT DONE: *****

RUN TIME: 1.29 SECONDS

WRITING BADER ATOMIC CHARGES TO ACF.dat
WRITING BADER VOLUME CHARGES TO BCF.dat

NUMBER OF BADER MAXIMA FOUND: 5407

SIGNIFICANT MAXIMA FOUND: 10
NUMBER OF ELECTRONS: 7.99999

WRITING ATOMIC VOLUMES

0 10 25 50 75 100

PERCENT DONE: *****

RUN TIME: 3.96 SECONDS

WRITING BADER ATOMIC INDEX TO AtIndex.dat

1 cat ACF.dat

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

#	X	Y	Z	CHARGE	MIN DIST	ATOMIC VOL
1	6.0000	6.7632	6.5963	7.9990	2.2193	644.5831
2	6.0000	7.5265	6.0000	0.0007	1.6422	759.8654
3	6.0000	6.0000	6.0000	0.0003	1.6422	640.1559
VACUUM CHARGE:			0.0000			
VACUUM VOLUME:			0.0000			
NUMBER OF ELECTRONS:			8.0000			

This script should work, but only if displacement is set to None or we convert the positions to Bohr. Otherwise, the positions do not match because of a Bohr/Angstrom units problem in the code. Note the sorting that has to be done, because the order of atoms in the Atoms object is not the same as in the POSCAR file.

```

1 from jasp import *
2 from ase.io.bader import attach_charges
3 from ase.units import Bohr
4
5 with jasp('molecules/h2o-bader') as calc:
6     atoms = calc.get_atoms()
7
8     symbols = np.array(atoms.get_chemical_symbols())[calc.sort]
9     pos = atoms.positions[calc.sort] * Bohr
10    newatoms = Atoms(symbols, positions=pos, cell=atoms.get_cell())
11
12    attach_charges(newatoms, 'ACF.dat')
13
14    print('##tblname: bader')
15    print('##caption: Bader charges for a water molecule')
16    print('| atom | Bader charge|')
17    print('|-|')
18    for atom in newatoms:
19        print('{0} | {1} |'.format(atom.symbol, atom.charge))

```

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

Table 2: Bader charges for a water molecule

atom	Bader charge
O	0.001
H	0.9993
H	0.9997

It looks like not much has been transferred. This may be an artifact of using the valence electron density, or a lack of convergence. See <https://wiki.fysik.dtu.dk/ase/ase/dft/bader.html#example-the-water-molecule> for a comparison.

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. `jasp` 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4
5  bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
6  energies = []
7
8  for d in bond_lengths: # possible bond lengths
9
10     co = Atoms([Atom('C', [0, 0, 0]),
11                Atom('O', [d, 0, 0])],
12                cell=(6, 6, 6))
13
14     with jasp('molecules/co-{0}'.format(d), # output dir
15              xc='PBE',
16              nbands=6,
17              encut=350,
18              ismear=1,
19              sigma=0.01,
20              atoms=co):
21         try:
22             e = co.get_potential_energy()
23             energies.append(e)
24             print('d = {0:1.2f} ang'.format(d))
25             print('energy = {0:1.3f} eV'.format(e))
26             print('forces = (eV/ang)\n {0}'.format(co.get_forces()))
27             print('') # blank line
28         except (VaspSubmitted, VaspQueued):
29             energies.append(None)
30             pass
31
32 if None not in energies:
33     import matplotlib.pyplot as plt
34     plt.plot(bond_lengths, energies, 'bo-')
35     plt.xlabel(r'Bond length ($\text{\AA}$)')
36     plt.ylabel('Total energy (eV)')
37     plt.savefig('images/co-bondlengths.png')

```

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

```

d = 1.05 ang
energy = -14.215 eV
forces = (eV/ang)
[[-14.903  0.      0.   ]
 [ 14.903  0.      0.   ]]

```

```

d = 1.10 ang
energy = -14.720 eV
forces = (eV/ang)

```

```

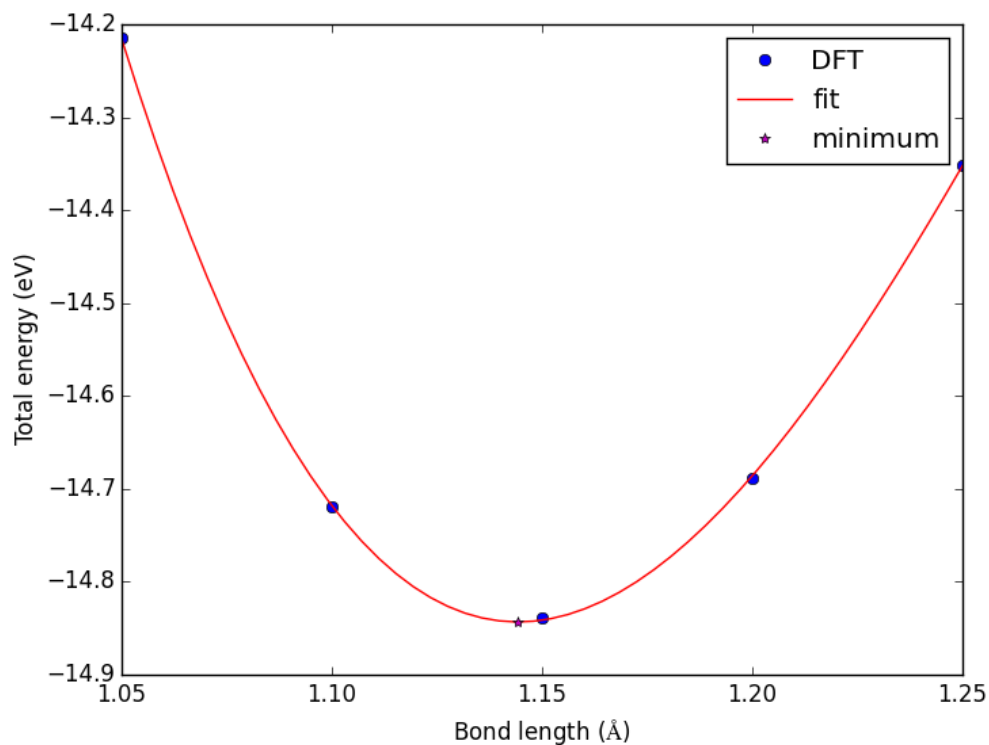
[[-5.8  0.   0. ]
 [ 5.8  0.   0. ]]

d = 1.15 ang
energy = -14.838 eV
forces = (eV/ang)
[[ 0.645  0.   0. ]
 [-0.645  0.   0. ]]

d = 1.20 ang
energy = -14.688 eV
forces = (eV/ang)
[[ 5.095  0.   0. ]
 [-5.095  0.   0. ]]

d = 1.25 ang
energy = -14.352 eV
forces = (eV/ang)
[[ 8.141  0.   0. ]
 [-8.141  0.   0. ]]

```



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.

```

1 from jasp import *
2 import numpy as np
3 import matplotlib.pyplot as plt
4 np.set_printoptions(precision=3, suppress=True)
5

```

```

6  bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
7  energies = []
8
9  for d in bond_lengths: # possible bond lengths
10
11      with jasp('molecules/co-{0}'.format(d)) as calc:
12          atoms = calc.get_atoms()
13          energies.append(atoms.get_potential_energy())
14
15      # Now we fit an equation - cubic polynomial
16      pp = np.polyfit(bond_lengths, energies, 3)
17      dp = np.polyder(pp) # first derivative - quadratic
18
19      # we expect two roots from the quadratic eqn. These are where the
20      # first derivative is equal to zero.
21      roots = np.roots(dp)
22
23      # The minimum is where the second derivative is positive.
24      dpp = np.polyder(dp) # second derivative - line
25      secd = np.polyval(dpp, roots)
26
27      minV = roots[secd > 0]
28      minE = np.polyval(pp, minV)
29
30      print('The minimum energy is {0} eV at V = {1} Ang^3'.format(minE, minV))
31
32      # plot the fit
33      x = np.linspace(1.05, 1.25)
34      fit = np.polyval(pp, x)
35
36      plt.plot(bond_lengths, energies, 'bo ')
37      plt.plot(x, fit, 'r-')
38      plt.plot(minV, minE, 'm* ')
39      plt.legend(['DFT', 'fit', 'minimum'], numpoints=1)
40      plt.xlabel(r'Bond length ($\AA$)')
41      plt.ylabel('Total energy (eV)')
42      plt.savefig('images/co-bondlengths.png')
43      plt.show()

```

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

The minimum energy is [-14.843] eV at V = [1.144] Ang³

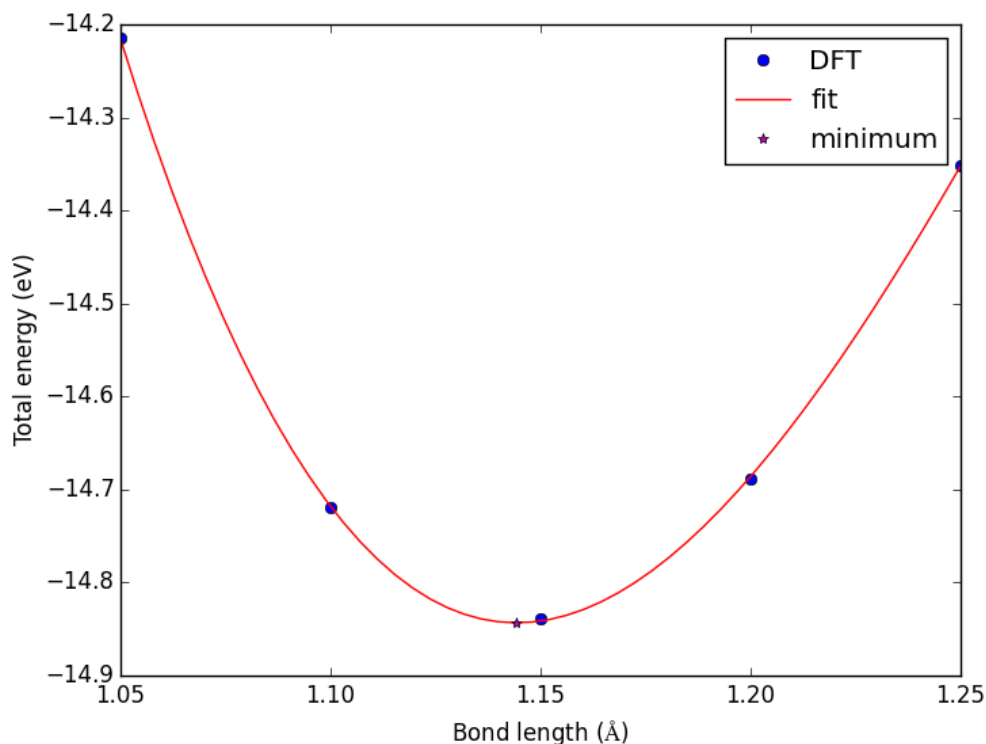


Figure 18: Energy vs CO bond length.

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 $10 \times \text{EDIFF}$), the relaxation is stopped. This criteria is controlled by the [EDIFFG](#) tag. If you prefer to stop based on forces, set $\text{EDIFFG} = -0.05$, 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.

```

1 from ase import Atom, Atoms
2 from jasp import *
3
4 co = Atoms([Atom('C', [0, 0, 0]),
5             Atom('O', [1.2, 0, 0])],
6            cell=(6, 6, 6))

```

```

7
8 with jasp('molecules/co-cg',
9         xc='PBE',
10        nbands=6,
11        encut=350,
12        ismear=1,
13        sigma=0.01, # this is small for a molecule
14        ibrion=2,   # conjugate gradient optimizer
15        nsw=5,     # do at least 5 steps to relax
16        atoms=co) as calc:
17
18     print('Forces')
19     print('=====')
20     print(co.get_forces())
21
22     pos = co.get_positions()
23     d = ((pos[0] - pos[1])**2).sum()**0.5
24     print('Bondlength = {0:1.2f} angstroms'.format(d))

```

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

```

Forces
=====
[[ 0.013  0.      0.   ]
 [-0.013  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.

```

1 from ase import Atoms, Atom
2 from jasp import *
3 JASPRC['queue.ppn'] = 4
4
5 atoms = Atoms([Atom('H', [0.5960812, -0.7677068, 0.0000000]),
6                Atom('O', [0.0000000, 0.0000000, 0.0000000]),
7                Atom('H', [0.5960812, 0.7677068, 0.0000000])],
8               cell=(8, 8, 8))
9
10 atoms.center()
11
12 with jasp('molecules/h2o-relax-centered',
13         xc='PBE', debug=logging.DEBUG,
14         encut=400,
15         ismear=0, # Gaussian smearing
16         ibrion=2,
17         ediff=1e-8,
18         nsw=10,
19         atoms=atoms) as calc:
20
21     print("forces")
22     print('=====')
23     print(atoms.get_forces())

```

Open the python script (dft-scripts/script-42.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`.

```

1  from jasp import *
2  from ase.units import *
3
4  bond_lengths = [1.05, 1.1, 1.15, 1.2, 1.25]
5  energies = []
6
7  for d in bond_lengths:
8      with jasp('molecules/co-{0}'.format(d)) as calc:
9          atoms = calc.get_atoms()
10         energies.append(atoms.get_potential_energy())
11
12  # fit the data
13  pars = np.polyfit(bond_lengths, energies, 3)
14  xfit = np.linspace(1.05, 1.25)
15  efit = np.polyval(pars, xfit)
16
17  # first derivative
18  dpars = np.polyder(pars)
19  # find where the minimum is. chose the second one because it is the
20  # minimum we need.
21  droots = np.roots(dpars)
22
23  # second derivative
24  ddpars = np.polyder(dpars)
25
26  d_min = droots[np.polyval(ddpars, droots) > 0]
27
28  # curvature at minimum = force constant in SI units
29  k = np.polyval(ddpars, d_min) / (J / m**2)
30
31  # mu, reduced mass
32  from ase.data import atomic_masses
33  C_mass = atomic_masses[6] / kg
34  O_mass = atomic_masses[8] / kg
35
36  mu = 1.0 / (1.0 / C_mass + 1.0 / O_mass)
37
38  frequency = 1. / (2. * np.pi) * np.sqrt(k / mu)
39  print('The CO vibrational frequency is {0} Hz'.format(*frequency))
40  print('The CO vibrational frequency is {0} cm^{-1}'.format(frequency / 3e10))
41
42  import matplotlib.pyplot as plt
43  plt.plot(bond_lengths, energies, 'bo ')
44  plt.plot(xfit, efit, 'b-')
45  plt.xlabel('Bond length ($\AA$)')
46  plt.ylabel('Total energy (eV)')
47  plt.show()

```

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

The CO vibrational frequency is 6.43082289837e+13 Hz

The CO vibrational frequency is [2143.608] 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.⁴⁴ 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).

```

1 c = 3e10 # speed of light cm/s
2 h = 4.135667516e-15 # eV*s
3
4 nu = 2143.6076625*c # 1/s
5
6 E_zpe = 0.5*h*nu
7
8 print('E_ZPE = {0:1.3f} eV'.format(E_zpe))

```

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

```

1 # <<water-vib>>
2 # adapted from http://cms.mpi.univie.ac.at/wiki/index.php/H2O_vibration
3 from ase import Atoms, Atom
4 from jasp import *
5 import ase.units
6
7 atoms = Atoms([Atom('H', [0.5960812, -0.7677068, 0.0000000]),
8                 Atom('O', [0.0000000, 0.0000000, 0.0000000]),
9                 Atom('H', [0.5960812, 0.7677068, 0.0000000])],
10              cell=(8, 8, 8))
11 atoms.center()
12
13 with jasp('molecules/h2o_vib',
14          xc='PBE',
15          encut=400,
16          ismear=0, # Gaussian smearing
17          ibrion=6, # finite differences with symmetry
18          nfree=2, # central differences (default)
19          potim=0.015, # default as well
20          ediff=1e-8, # for vibrations you need precise energies
21          nsrw=1, # Set to 1 for vibrational calculation
22          atoms=atoms) as calc:
23
24     print('Forces')
25     print('====')
26     print(atoms.get_forces())
27     print()
28     # vibrational energies are in eV
29     energies, modes = calc.get_vibrational_modes()
30     print('energies\n=====')
31     for i, e in enumerate(energies):
32         print('{0:02d}: {1} eV'.format(i, e))

```

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

Forces
=====

```

[[ 0.018 -0.032 -0.001]
 [-0.035  0.      0.003]
 [ 0.018  0.032 -0.001]]
()
energies
=====
00: 0.475824705 eV
01: 0.461734211 eV
02: 0.19618999 eV
03: 0.007093876 eV
04: 0.002459836 eV
05: (0.000291856+0j) eV
06: (0.012642767+0j) eV
07: (0.012959493+0j) eV
08: (0.015883929+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

```

1 # <<h2o-vib-vis>>
2 from jasp import *
3 import numpy as np
4 with jasp('molecules/h2o_vib') as calc:
5     energies, modes = calc.get_vibrational_modes(mode=3, massweighted=True,
6                                                    show=True)

```

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

```

1 from jasp import *
2 import numpy as np
3 c = 3e10 # speed of light cm/s
4 h = 4.135667516e-15 # eV/s
5
6 # first, get the frequencies.
7 with jasp('molecules/h2o_vib') as calc:
8     freq = calc.get_vibrational_frequencies()
9
10 ZPE = 0.0
11 for f in freq:
12     if not isinstance(f, float):
13         continue # skip complex numbers
14     nu = f * c # convert to frequency
15     ZPE += 0.5 * h * nu
16
17 print('The ZPE of water is {0:1.3f} eV'.format(ZPE))
18
19 # one liner
20 ZPE = np.sum([0.5 * h * f * c for f in freq if isinstance(f, float)])
21 print('The ZPE of water is {0:1.3f} eV'.format(ZPE))

```

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

The ZPE of water is 0.572 eV

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.

```

1 from ase import Atoms, Atom
2 from jasp import *
3
4 atoms = Atoms([Atom('H', [0.5960812, -0.7677068, 0.0000000]),
5               Atom('O', [0.0000000, 0.0000000, 0.0000000]),
6               Atom('H', [0.5960812, 0.7677068, 0.0000000])],
7               cell=(8, 8, 8))
8
9 with jasp('molecules/h2o_relax',
10         xc='PBE',
11         encut=400,

```

```

12         ismear=0, # Gaussian smearing
13         ibrion=2,
14         ediff=1e-8,
15         nsw=10,
16         atoms=atoms) as calc:
17     print('Forces')
18     print('=====')
19     print(atoms.get_forces())

```

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

Forces

```

=====
[[ 0.    -0.    0.   ]
 [-0.001 0.    0.   ]
 [ 0.     0.    0.   ]]

```

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.

```

1  from jasp import *
2
3  # read in relaxed geometry
4  with jasp('molecules/h2o_relax') as calc:
5      atoms = calc.get_atoms()
6
7  # now define a new calculator
8  with jasp('molecules/h2o_vib_dfpt',
9          xc='PBE',
10         encut=400,
11         ismear=0, # Gaussian smearing
12         ibrion=7, # switches on the DFPT vibrational analysis (with
13                 # no symmetry constraints)
14         nfree=2,
15         potim=0.015,
16         lepsilon=True, # enables to calculate and to print the BEC
17                       # tensors
18         lreal=False,
19         nsw=1,
20         nwrite=3, # affects OUTCAR verbosity: explicitly forces
21                 # SQR(mass)-divided eigenvectors to be printed
22         atoms=atoms) as calc:
23      calc.calculate(atoms)

```

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

To analyze the results, this [shell script](#) was provided to extract the results.

```

1  #!/bin/bash
2  # A utility for calculating the vibrational intensities from VASP output (OUTCAR)
3  # (C) David Karhanek, 2011-03-25, ICIQ Tarragona, Spain (www.iciq.es)
4
5  # extract Born effective charges tensors
6  printf "..reading OUTCAR"
7  BORN_NROWS=$(grep NIONS OUTCAR | awk '{print $12*4+1}');
8  if [ $(grep 'BORN' OUTCAR | wc -l) = 0 ] ; then \
9      printf " .. FAILED! Born effective charges missing! Bye! \n\n" ; exit 1 ; fi
10  grep "in e, cumulative" -A $BORN_NROWS OUTCAR > born.txt
11
12  # extract Eigenvectors and eigenvalues
13  if [ $(grep 'SQR(mass)' OUTCAR | wc -l) != 1 ] ; then \
14      printf " .. FAILED! Restart VASP with NWRITE=3! Bye! \n\n" ; exit 1 ; fi
15  EIG_NVIBS=$(grep -A 2000 'SQR(mass)' OUTCAR | grep 'cm-1' | wc -l)
16  EIG_NIONS=$(grep NIONS OUTCAR | awk '{print $12}');
17  EIG_NROWS=$(echo "(${EIG_NIONS}*3)*${EIG_NVIBS}+3" | bc)
18  grep -A $((EIG_NROWS+2)) 'SQR(mass)' OUTCAR | tail -n $((EIG_NROWS+1)) | sed 's/f/i/fi/g' > eigenvectors.txt
19  printf " ..done\n"
20
21  # set up a new directory, split files - prepare for parsing
22  printf "..splitting files"
23  mkdir intensities ; mv born.txt eigenvectors.txt intensities/

```

```

24 cd intensities/
25 let NBORN_NROWS=BORN_NROWS-1
26 let NEIG_NROWS=EIG_NROWS-3
27 let NBORN_STEP=4
28 let NEIG_STEP=EIG_NIONS+3
29 tail -n $NBORN_NROWS born.txt > temp.born.txt
30 tail -n $NEIG_NROWS eigenvectors.txt > temp.eige.txt
31 mkdir inputs ; mv born.txt eigenvectors.txt inputs/
32 split -a 3 -d -l $NEIG_STEP temp.eige.txt temp.ei.
33 split -a 3 -d -l $NBORN_STEP temp.born.txt temp.bo.
34 mkdir temps01 ; mv temp.born.txt temp.eige.txt temps01/
35 for nu in `seq 1 $EIG_NVIBS` ; do
36   let nud=nu-1 ; ei=`printf "%03u" $nu` ; eid=`printf "%03u" $nud` ; mv temp.ei.$eid eigens.vib.$ei
37 done
38 for s in `seq 1 $EIG_NIONS` ; do
39   let sd=s-1 ; bo=`printf "%03u" $s` ; bod=`printf "%03u" $sd` ; mv temp.bo.$bod borncs.$bo
40 done
41 printf " ..done\n"
42
43 # parse deviation vectors (eig)
44 printf "..parsing eigenvectors"
45 let sad=$EIG_NIONS+1
46 for nu in `seq 1 $EIG_NVIBS` ; do
47   nuu=`printf "%03u" $nu`
48   tail -n $sad eigens.vib.$nuu | head -n $EIG_NIONS | awk '{print $4,$5,$6}' > e.vib.$nuu.allions
49   split -a 3 -d -l 1 e.vib.$nuu.allions temp.e.vib.$nuu.ion.
50   for s in `seq 1 $EIG_NIONS` ; do
51     let sd=s-1 ; bo=`printf "%03u" $s` ; bod=`printf "%03u" $sd` ; mv temp.e.vib.$nuu.ion.$bod e.vib.$nuu.ion.$bo
52   done
53 done
54 printf " ..done\n"
55
56 # parse born effective charge matrices (born)
57 printf "..parsing eff.charges"
58 for s in `seq 1 $EIG_NIONS` ; do
59   ss=`printf "%03u" $s`
60   awk '{print $2,$3,$4}' borncs.$ss | tail -3 > bornch.$ss
61 done
62 mkdir temps02 ; mv eigens.* borncs.* temps02/
63 printf " ..done\n"
64
65 # parse matrices, multiply them and collect squares (giving intensities)
66 printf "..multiplying matrices, summing "
67 for nu in `seq 1 $EIG_NVIBS` ; do
68   nuu=`printf "%03u" $nu`
69   int=0.0
70   for alpha in 1 2 3 ; do # summing over alpha coordinates
71     sumpol=0.0
72     for s in `seq 1 $EIG_NIONS` ; do # summing over atoms
73       ss=`printf "%03u" $s`
74       awk -v a="$alpha" '(NR==a){print}' bornch.$ss > z.ion.$ss.alpha.$alpha
75       # summing over beta coordinates and multiplying Z(s,alpha)*e(s) done by the following awk script
76       paste z.ion.$ss.alpha.$alpha e.vib.$nuu.ion.$ss | \
77       awk '{pol=$((1*$4+$2*$5+$3*$6); print $0," ",pol)}' > matr-vib-{$nuu}-alpha-{$alpha}-ion-{$ss}
78     done
79     sumpol=`cat matr-vib-{$nuu}-alpha-{$alpha}-ion-* | awk '{sum+=$7} END {print sum}'`
80     int=`echo "$int+($sumpol)^2" | sed 's/[eE]/*10~/g' | bc -l`
81   done
82   freq=`awk '(NR==1){print $8}' temps02/eigens.vib.$nuu`
83   echo "$nuu $freq $int">> exact.res.txt
84   printf "."
85 done
86 printf " ..done\n"
87
88 # format results, normalize intensities
89 printf "..normalizing intensities"
90 max=`awk '(NR==1){max=$3} $3>max {max=$3} END {print max}' exact.res.txt`
91 awk -v max="$max" '{printf "%03u %6.1f %5.3f\n",$1,$2,$3/max}' exact.res.txt > results.txt
92 printf " ..done\n"
93
94 # clean up, display results
95 printf "..finalizing:\n"
96 mkdir temps03 ; mv bornch.* e.vib.*.allions temps03/
97 mkdir temps04 ; mv z.ion.* e.vib.*.ion.* temps04/
98 mkdir temps05 ; mv matr-* temps05/
99 mkdir results ; mv *res.txt results/
100 let NMATRIX=$EIG_NVIBS**2
101 printf "%5u atoms found\n%5u vibrations found\n%5u matrices evaluated" \

```

```

102     $EIG_NIONS $EIG_NVIBS $NMATRIX > results/statistics.txt
103     # fast switch to clean up all temporary files
104     rm -r temps*
105     cat results/results.txt

```

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

```

..reading OUTCAR ..done
..splitting files ..done
..parsing eigenvectors ..done
..parsing eff.charges ..done
..multiplying matrices, summing ..... ..done
..normalizing intensities ..done
..finalizing:
001 3827.3 0.227
002 3713.0 0.006
003 1587.2 0.312
004 235.5 1.000
005 19.1 0.006
006 2.3 0.000
007 16.6 0.005
008 45.0 0.000
009 136.1 0.345

```

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.

```

1  #!/bin/bash
2  # reformat intensities, just normal modes: 3N -> (3N-6)
3  printf "..reformatting and normalizing intensities"
4  cd intensities/results/
5  nlms=$(wc -l exact.res.txt | awk '{print $1}' ); let bodylns=nlms-6
6  head -n $bodylns exact.res.txt > temp.reform.res.txt
7  max=$(awk ' (NR==1){max=$3} $3>max {max=$3} END {print max}' temp.reform.res.txt)
8  awk -v max="$max" '{print $1,$2,$3/max}' temp.reform.res.txt > exact.reform.res.txt
9  awk -v max="$max" '{printf "%03u %6.1f %5.3f\n",$1,$2,$3/max}' temp.reform.res.txt > reform.res.txt
10 printf " ..done\n..normal modes:\n"
11 rm temp.reform.res.txt
12 cat reform.res.txt
13 cd ../../

```

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

```

..reformatting and normalizing intensities ..done
..normal modes:
001 3827.3 0.726
002 3713.0 0.019
003 1587.2 1.000

```

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. ⁴⁵ For HREELS simulations see. ⁴⁶

The shell script above has been translated to a convenient python function in [jasp](#).

```

1  from jasp import *
2  with jasp('molecules/h2o_vib_dfpt') as calc:

```

```

3     print('mode Relative intensity')
4     for i, intensity in enumerate(calc.get_infrared_intensities()):
5         print('{0:02d} {1:1.3f}'.format(i, intensity))

```

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

```

mode Relative intensity
00      0.227
01      0.006
02      0.312
03      1.000
04      0.006
05      0.000
06      0.005
07      0.000
08      0.345

```

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 N₂ molecule.

The symmetry numbers are determined by the molecular point group.⁴⁷ Here is a table of the most common ones.

Table 3: Symmetry numbers for common point groups

point group	σ	examples
C ₁	1	
C _s	1	
C ₂	2	
C _{2v}	2	H ₂ O
C _{3v}	3	NH ₃
C _{∞v}	1	CO
D _{2h}	4	
D _{3h}	6	
D _{5h}	10	
D _{∞h}	2	CO ₂ , H ₂
D _{3d}	6	
T _d	12	CH ₄
O _h	24	

```

1  from ase.structure import molecule
2  from ase.thermochemistry import IdealGasThermo
3  from jasp import *
4
5  atoms = molecule('N2')
6  atoms.set_cell((10,10,10), scale_atoms=False)
7
8  # first we relax a molecule
9  with jasp('molecules/n2-relax',
10          xc='PBE',
11          encut=300,
12          ibrion=2,
13          nsw=5,
14          atoms=atoms) as calc:
15      electronicenergy = atoms.get_potential_energy()
16

```

```

17 # next, we get vibrational modes
18 with jasp('molecules/n2-vib',
19         xc='PBE',
20         encut=300,
21         ibrion=6,
22         nfree=2,
23         potim=0.15,
24         nsw=1,
25         atoms=atoms) as calc:
26     calc.calculate()
27     vib_freq = calc.get_vibrational_frequencies() # in cm^-1
28
29     #convert wavenumbers to energy
30     h = 4.1356675e-15 # eV*s
31     c = 3.0e10 #cm/s
32     vib_energies = [h*c*nu for nu in vib_freq]
33     print('vibrational energies\n=====')
34     for i,e in enumerate(vib_energies):
35         print('{0:02d}: {1} eV'.format(i,e))
36
37 # # now we can get some properties. Note we only need one vibrational
38 # energy since there is only one mode. This example does not work if
39 # you give all the energies because one energy is zero.
40 thermo = IdealGasThermo(vib_energies=vib_energies[0:0],
41                         electronicenergy=electronicenergy, atoms=atoms,
42                         geometry='linear', symmetrynumber=2, spin=0)
43
44 # temperature in K, pressure in Pa, G in eV
45 G = thermo.get_free_energy(temperature=298.15, pressure=101325.)

```

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

vibrational energies

=====

```

00: 0.29159234324 eV
01: 0.0169775241059 eV
02: 0.0169775241059 eV
03: 2.853610575e-09 eV
04: 8.68490175e-10 eV
05: 0.0 eV

```

Enthalpy components at T = 298.15 K:

=====

```

E_elec          -16.478 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              -16.388 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	0.0007870 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              0.0023449 eV/K      0.699 eV

```

=====

Free energy components at T = 298.15 K and P = 101325.0 Pa:

=====

H	-16.388 eV
-T*S	-0.699 eV

G	-17.087 eV

=====

Let us compare this to what is in the [Nist webbook](#) via the Shomate equations.

```
1 import numpy as np
2 A = 28.98641
3 B = 1.853978
4 C = -9.647459
5 D = 16.63537
6 E = 0.000117
7 F = -8.671914
8 G = 226.4168
9 H = 0.0
10
11 T = 298.15
12 t = T/1000.
13
14 S = A*np.log(t) + B*t + C*t**2/2 + D*t**3/3 - E/(2*t**2) + G
15 print('-T*S = {0:1.3f} eV'.format(-T*S/1000/96.4853))
```

Open the python script (dft-scripts/script-54.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 O₂ dissociation

The first reaction we consider is a simple dissociation of oxygen molecule into two oxygen atoms: O₂ → 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 O₂ dissociation energy

```
1 from jasp import *
2 from ase import Atom, Atoms
3
4 atoms = Atoms([Atom('O', [5, 5, 5])],
5               cell=(10, 10, 10))
6
7 with jasp('molecules/0',
8           xc='PBE',
9           encut=400,
10          ismear=0,
11          atoms=atoms) as calc:
12     try:
13         E_O = atoms.get_potential_energy()
14     except (VaspSubmitted, VaspQueued):
15         E_O = None
16
17 # now relaxed O2 dimer
18 atoms = Atoms([Atom('O', [5, 5, 5])],
```

```

19         Atom('O', [6.22, 5, 5]),
20         cell=(10, 10, 10))
21
22 with jasp('molecules/O2',
23         xc='PBE',
24         encut=400,
25         ismear=0,
26         ibrion=2,
27         nsw=10,
28         atoms=atoms) as calc:
29     try:
30         E_O2 = atoms.get_potential_energy()
31     except (VaspSubmitted, VaspQueued):
32         E_O2 = None
33
34 if None not in (E_O, E_O2):
35     print('O2 -> 20 D = {0:1.3f} eV'.format(2 * E_O - E_O2))

```

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

O2 -> 20 D = 8.521 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 O₂ 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 O₂ 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  atoms = Atoms([Atom('O', [5, 5, 5], magmom=2)],
5               cell=(10, 10, 10))
6
7  with jasp('molecules/O-sp-triplet',
8         xc='PBE',
9         encut=400,
10         ismear=0,
11         ispin=2, # turn spin-polarization on
12         atoms=atoms) as calc:
13     try:
14         E_O = atoms.get_potential_energy()
15     except (VaspSubmitted, VaspQueued):
16         E_O = None
17
18     print('Magnetic moment on O = {0} Bohr'
19           ' magnetons'.format(atoms.get_magnetic_moment()))
20
21 # now relaxed O2 dimer
22 atoms = Atoms([Atom('O', [5, 5, 5], magmom=1),
23               Atom('O', [6.22, 5, 5], magmom=1)],
24               cell=(10, 10, 10))
25
26 with jasp('molecules/O2-sp-triplet',
27         xc='PBE',
28         encut=400,
29         ismear=0,
30         ispin=2, # turn spin-polarization on
31         ibrion=2, # make sure we relax the geometry
32         nsw=10,
33         atoms=atoms) as calc:

```

```

34     try:
35         E_O2 = atoms.get_potential_energy()
36     except (VaspSubmitted, VaspQueued):
37         E_O2 = None
38
39     # verify magnetic moment
40     print('Magnetic moment on O2 = {0} Bohr'
41           ' magnetons'.format(atoms.get_magnetic_moment()))
42
43     if None not in (E_O, E_O2):
44         print('O2 -> 20   D = {0:1.3f} eV'.format(2 * E_O - E_O2))

```

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

```

Magnetic moment on O = 2.0000072 Bohr magnetons
Magnetic moment on O2 = 2.0000084 Bohr magnetons
O2 -> 20   D = 6.668 eV

```

This is much closer to accepted literature values for the DFT-GGA O₂ 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.

TODO: show what "hard or soft" is in the pseudopotential.

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.

```

1  from jasp import *
2  from ase.dft.dos import *
3
4  with jasp('molecules/O2-sp-triplet') as calc:
5      dos = DOS(calc, width=0.2)
6      d_up = dos.get_dos(spin=0)
7      d_down = dos.get_dos(spin=1)
8      e = dos.get_energies()
9
10     ind = e <= 0.0
11     # integrate up to 0eV
12     print('number of up states = {0}'.format(np.trapz(d_up[ind], e[ind])))
13     print('number of down states = {0}'.format(np.trapz(d_down[ind], e[ind])))
14
15     import pylab as plt
16     plt.plot(e, d_up,
17             e, -d_down)
18     plt.xlabel('energy [eV]')
19     plt.ylabel('DOS')
20     plt.legend(['up', 'down'])
21     plt.savefig('images/O2-sp-dos.png')

```

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

```

number of up states = 5.95489738902
number of down states = 5.00001754136

```

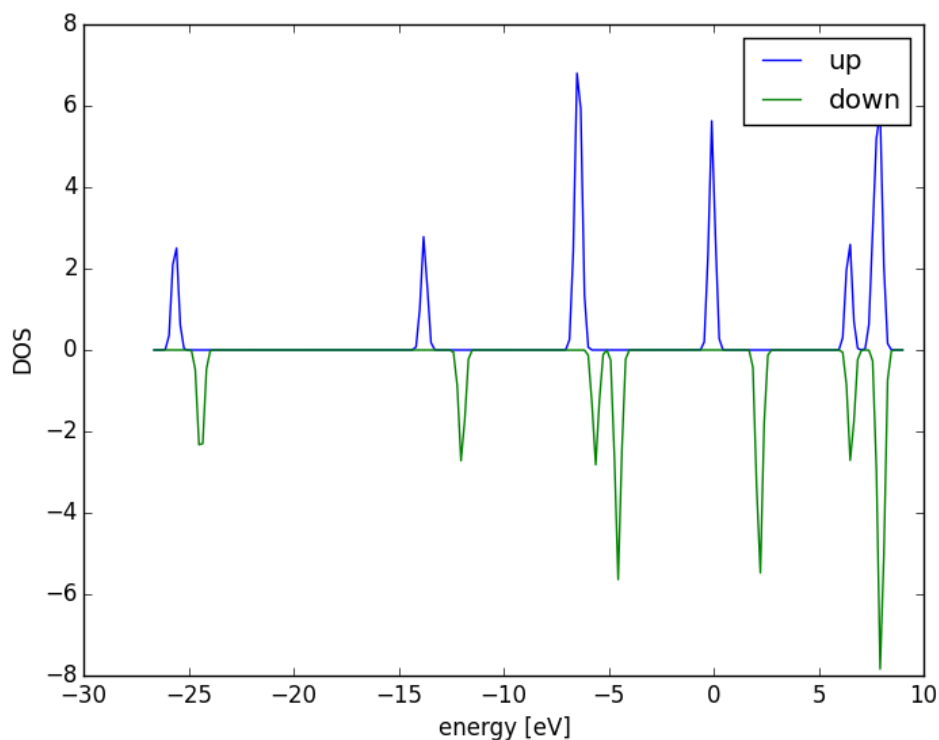


Figure 19: Spin-polarized DOS for the O₂ molecule.

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, whereas the blue peak between -5 and -10 eV corresponds to three electrons.

Convergence study of the O₂ dissociation energy

```

1  from jasp import *
2  from ase import Atom, Atoms
3  encuts = [250, 300, 350, 400, 450, 500, 550]
4
5  D = []
6  for encut in encuts:
7      atoms = Atoms([Atom('O', [5, 5, 5], magmom=2)],
8                    cell=(10, 10, 10))
9
10     with jasp('molecules/O-sp-triplet-{0}'.format(encut),
11              xc='PBE',
12              encut=encut,
13              ismear=0,
14              ispin=2,
15              atoms=atoms) as calc:
16         try:
17             E_0 = atoms.get_potential_energy()
18         except (VaspSubmitted, VaspQueued):
19             E_0 = None
20
21     # now relaxed O2 dimer

```

```

22     atoms = Atoms([Atom('O', [5, 5, 5], magmom=1),
23                   Atom('O', [6.22, 5, 5], magmom=1)],
24                   cell=(10, 10, 10))
25
26     with jasp('molecules/O2-sp-triplet-{0}'.format(encut),
27              xc='PBE',
28              encut=encut,
29              ismear=0,
30              ispin=2, # turn spin-polarization on
31              ibrion=2, # this turns relaxation on
32              nsw=10,
33              atoms=atoms) as calc:
34         try:
35             E_O2 = atoms.get_potential_energy()
36         except (VaspSubmitted, VaspQueued):
37             E_O2 = None
38
39     if None not in (E_O, E_O2):
40         d = 2*E_O - E_O2
41         D.append(d)
42         print('O2 -> 2O encut = {0} D = {1:1.3f} eV'.format(encut, d))
43
44 import matplotlib.pyplot as plt
45 plt.plot(encuts, D)
46 plt.xlabel('ENCUT (eV)')
47 plt.ylabel('O2 -> 2O dissociation energy (eV)')
48 plt.savefig('images/O2-dissociation-convergence.png')

```

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

```

O2 -> 2O encut = 250 D = 6.696 eV
O2 -> 2O encut = 300 D = 6.727 eV
O2 -> 2O encut = 350 D = 6.708 eV
O2 -> 2O encut = 400 D = 6.668 eV
O2 -> 2O encut = 450 D = 6.650 eV
O2 -> 2O encut = 500 D = 6.648 eV
O2 -> 2O encut = 550 D = 6.650 eV

```

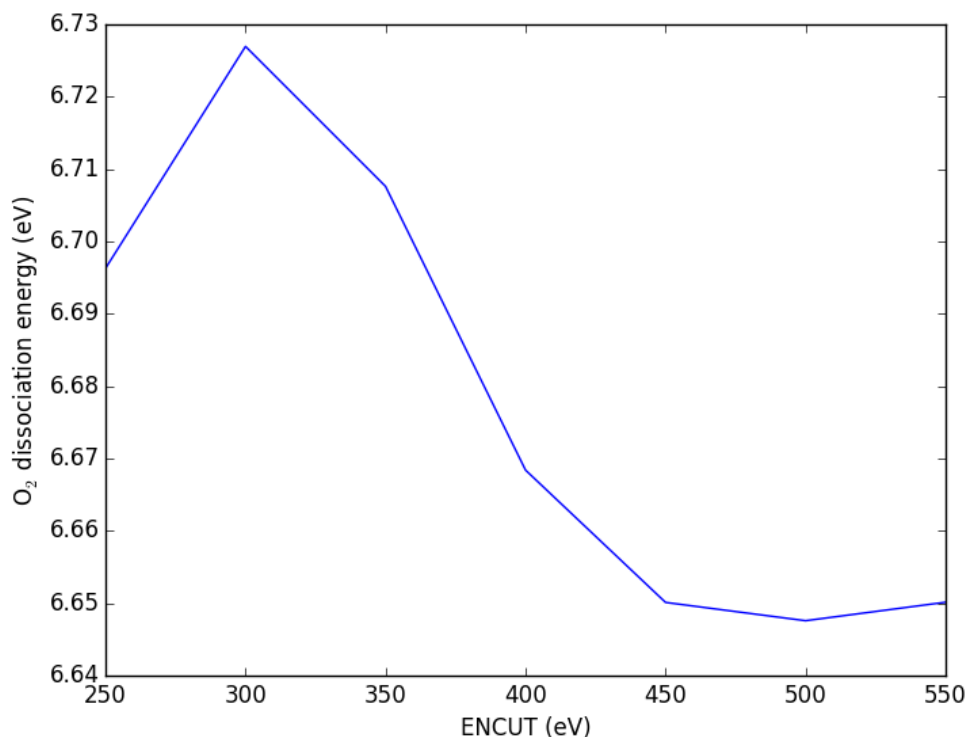


Figure 20: Convergence study of the O₂ dissociation energy as a function of ENCUT.

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.

```

1 encuts = [250, 300, 350, 400, 450, 500, 550]
2 print('encut (eV)          Total CPU time')
3 print('-----')
4
5 for encut in encuts:
6     OUTCAR = 'molecules/O2-sp-triplet-{0}/OUTCAR'.format(encut)
7     f = open(OUTCAR, 'r')
8     for line in f:
9         if 'Total CPU time used (sec)' in line:
10             print('{0} eV: {1}'.format(encut, line))
11     f.close()

```

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

encut (eV)	Total CPU time

250 eV:	Total CPU time used (sec): 67.926
300 eV:	Total CPU time used (sec): 121.296
350 eV:	Total CPU time used (sec): 150.808

400 eV:	Total CPU time used (sec):	307.465
450 eV:	Total CPU time used (sec):	199.381
500 eV:	Total CPU time used (sec):	240.705
550 eV:	Total CPU time used (sec):	266.318

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 O₂ 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  sigmas = [0.2, 0.1, 0.05, 0.02, 0.01, 0.001]
5
6  D = []
7  for sigma in sigmas:
8      atoms = Atoms([Atom('O',[5, 5, 5], magmom=2)],
9                    cell=(10, 10, 10))
10
11     with jasp('molecules/0-sp-triplet-sigma-{}'.format(sigma),
12              xc='PBE',
13              encut=400,
14              ismear=0,
15              sigma=sigma,
16              ispin=2,
17              atoms=atoms) as calc:
18         try:
19             E_0 = atoms.get_potential_energy()
20         except (VaspSubmitted, VaspQueued):
21             E_0 = None
22
23     # now relaxed O2 dimer
24     atoms = Atoms([Atom('O',[5, 5, 5],magmom=1),
25                   Atom('O',[6.22, 5, 5],magmom=1)],
26                  cell=(10, 10, 10))
27
28     with jasp('molecules/O2-sp-triplet-sigma-{}'.format(sigma),
29              xc='PBE',
30              encut=400,
31              ismear=0,
32              sigma=sigma,
33              ispin=2, # turn spin-polarization on
34              ibrion=2, # make sure we relax the geometry
35              nsw=10,
36              atoms=atoms) as calc:
37         try:
38             E_O2 = atoms.get_potential_energy()

```

```

39         except (VaspSubmitted, VaspQueued):
40             E_O2 = None
41
42     if None not in (E_O, E_O2):
43         d = 2 * E_O - E_O2
44         D.append(d)
45         print('O2 -> 2O sigma = {0} D = {1:1.3f} eV'.format(sigma, d))
46
47 import matplotlib.pyplot as plt
48 plt.plot(sigmas, D, 'bo-')
49 plt.xlabel('SIGMA (eV)')
50 plt.ylabel('O2 dissociation energy (eV)')
51 plt.savefig('images/O2-dissociation-sigma-convergence.png')

```

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

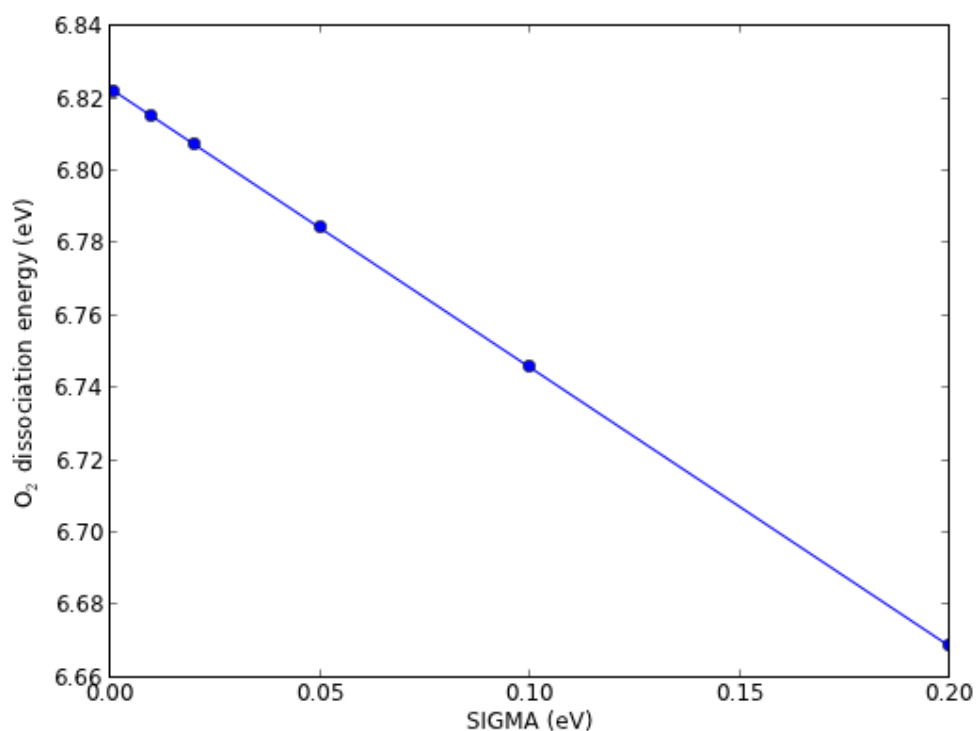


Figure 21: Effect of SIGMA on the oxygen dissociation energy.

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.

```

1 from jasp import *
2 from ase import Atom, Atoms
3
4 atoms = Atoms([Atom('O', [5, 5, 5], magmom=0)],
5               cell=(10, 10, 10))
6
7 with jasp('molecules/O-sp-singlet',
8           xc='PBE',

```

```

9         encut=400,
10        ismear=0,
11        ispin=2,
12        atoms=atoms) as calc:
13    try:
14        E_0 = atoms.get_potential_energy()
15    except (VaspSubmitted, VaspQueued):
16        E_0 = None
17
18    print('Magnetic moment on O = {0} Bohr'
19          ' magnetons'.format(atoms.get_magnetic_moment()))
20
21    # now relaxed O2 dimer
22    atoms = Atoms([Atom('O', [5, 5, 5], magmom=1),
23                  Atom('O', [6.22, 5, 5], magmom=-1)],
24                  cell=(10, 10, 10))
25
26    with jasp('molecules/O2-sp-singlet',
27              xc='PBE',
28              encut=400,
29              ismear=0,
30              ispin=2, # turn spin-polarization on
31              ibrion=2, # make sure we relax the geometry
32              nsw=10,
33              atoms=atoms) as calc:
34    try:
35        E_02 = atoms.get_potential_energy()
36    except (VaspSubmitted, VaspQueued):
37        E_02 = None
38
39    # verify magnetic moment
40    print('O2 molecule magnetic moment = ', atoms.get_magnetic_moment())
41
42    if None not in (E_0, E_02):
43        print('O2 -> 20 D = {0:1.3f} eV'.format(2*E_0 - E_02))

```

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

```

Magnetic moment on O = 1.9998232 Bohr magnetons
('O2 molecule magnetic moment = ', 0.0)
O2 -> 20 D = 5.650 eV

```

Interestingly, VASP still found a triplet spin state on the oxygen atom, even though we guessed an initial magnetic moment of 0. This highlights a difficulty in computing magnetic moments: you provide an initial guess and a solution is found. The magnetic moment of a singlet state is zero, so the molecule is correct. Also interesting is that the dissociation energy is almost equal to the experimental value. This is probably a coincidence, and may reflect the fact that the singlet oxygen state is less stable than the triplet state. Let us directly compare their total energies:

```

1 from jasp import *
2
3 with jasp('molecules/O2-sp-singlet') as calc:
4     print('singlet: {0} eV'.format(calc.get_atoms().get_potential_energy()))
5
6 with jasp('molecules/O2-sp-triplet') as calc:
7     print('triplet: {0} eV'.format(calc.get_atoms().get_potential_energy()))

```

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

```

singlet: -8.830101 eV
triplet: -9.848238 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  # square box origin
5  atoms = Atoms([Atom('O', [0, 0, 0], magmom=2)],
6                cell=(10, 10, 10))
7
8  with jasp('molecules/0-square-box-origin',
9            xc='PBE',
10           encut=400,
11           ismear=0,
12           sigma=0.01,
13           ispin=2,
14           atoms=atoms) as calc:
15      try:
16          print('Square box (origin): E = {0} eV'.format(atoms.get_potential_energy()))
17      except (VaspSubmitted, VaspQueued):
18          pass
19
20  # square box center
21  atoms = Atoms([Atom('O', [5, 5, 5], magmom=2)],
22                cell=(10, 10, 10))
23
24  with jasp('molecules/0-square-box-center',
25            xc='PBE',
26           encut=400,
27           ismear=0,
28           sigma=0.01,
29           ispin=2,
30           atoms=atoms) as calc:
31      try:
32          print('Square box (center): E = {0} eV'.format(atoms.get_potential_energy()))
33      except (VaspSubmitted, VaspQueued):
34          pass
35
36  # square box random
37  atoms = Atoms([Atom('O', [2.13, 7.32, 1.11], magmom=2)],
38                cell=(10, 10, 10))
39
40  with jasp('molecules/0-square-box-random',
41            xc='PBE',
42           encut=400,
43           ismear=0,
44           sigma=0.01,
45           ispin=2,
46           atoms=atoms) as calc:
47      try:
48          print('Square box (random): E = {0} eV'.format(atoms.get_potential_energy()))
49      except (VaspSubmitted, VaspQueued):
50          pass

```

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

Square box (origin): E = -1.516623 eV

Square box (center): E = -1.516623 eV

Square box (random): E = -1.515359 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.

```

1  # calculate O atom energy in orthorhombic boxes
2  from jasp import *
3  from ase import Atom, Atoms
4
5  # orthorhombic box origin
6  atoms = Atoms([Atom('O', [0, 0, 0], magmom=2)],
7                cell=(8, 9, 10))
8
9  with jasp('molecules/0-orthorhombic-box-origin',
10           xc='PBE',
11           encut=400,

```

```

12         ismear=0,
13         sigma=0.01,
14         ispin=2,
15         atoms=atoms) as calc:
16     try:
17         print('Orthorhombic box (origin): E = {0} eV'.format(atoms.get_potential_energy()))
18     except (VaspSubmitted, VaspQueued):
19         pass
20
21     # orthorhombic box center
22     atoms = Atoms([Atom('O', [4, 4.5, 5], magmom=2)],
23                   cell=(8, 9, 10))
24
25     with jasp('molecules/0-orthorhombic-box-center',
26              xc='PBE',
27              encut=400,
28              ismear=0,
29              sigma=0.01,
30              ispin=2,
31              atoms=atoms) as calc:
32     try:
33         print('Orthorhombic box (center): E = {0} eV'.format(atoms.get_potential_energy()))
34     except (VaspSubmitted, VaspQueued):
35         pass
36
37     # orthorhombic box random
38     atoms = Atoms([Atom('O', [2.13, 7.32, 1.11], magmom=2)],
39                   cell=(8, 9, 10))
40
41     with jasp('molecules/0-orthorhombic-box-random',
42              xc='PBE',
43              encut=400,
44              ismear=0,
45              sigma=0.01,
46              ispin=2,
47              atoms=atoms) as calc:
48     try:
49         print('Orthorhombic box (random): E = {0} eV'.format(atoms.get_potential_energy()))
50     except (VaspSubmitted, VaspQueued):
51         pass

```

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

```

Orthorhombic box (origin): E = -1.8941 eV
Orthorhombic box (center): E = -1.894124 eV
Orthorhombic box (random): E = -1.494285 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  atoms = Atoms([Atom('O', [5.1, 4.2, 6.1], magmom=2)],
5                cell=(8, 9, 10))
6
7  with jasp('molecules/0-sp-triplet-lowsym',
8           xc='PBE',
9           encut=400,
10          ismear=0,
11          sigma=0.01,
12          ispin=2,
13          atoms=atoms) as calc:
14  try:
15      E_0 = atoms.get_potential_energy()
16      print('Magnetic moment on O = {0} Bohr magnetons'.format(atoms.get_magnetic_moment()))
17  except (VaspSubmitted, VaspQueued):
18      E_0 = None
19
20  # now relaxed O2 dimer

```

```

21 atoms = Atoms([Atom('O', [5, 5, 5], magmom=1),
22               Atom('O', [6.22, 5, 5], magmom=1)],
23               cell=(10, 10, 10))
24
25 with jasp('molecules/O2-sp-triplet',
26          xc='PBE',
27          encut=400,
28          ismear=0,
29          sigma=0.01,
30          ispin=2, # turn spin-polarization on
31          ibrion=2, # make sure we relax the geometry
32          nsw=10,
33          atoms=atoms) as calc:
34     try:
35         E_O2 = atoms.get_potential_energy()
36         # verify magnetic moment
37         print('Magnetic moment on O2 = {0} Bohr magnetons'.format(atoms.get_magnetic_moment()))
38
39     except (VaspSubmitted, VaspQueued):
40         E_O2 = None
41
42 if None not in (E_O, E_O2):
43     print('E_O: ', E_O)
44     print('O2 -> 20 D = {0:1.3f} eV'.format(2 * E_O - E_O2))

```

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

```

Magnetic moment on O = 2.0000016 Bohr magnetons
Magnetic moment on O2 = 2.0000084 Bohr magnetons
E_O: -1.893571
O2 -> 20 D = 6.061 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.

```

1 from jasp import *
2
3 with jasp('molecules/O2-sp-singlet') as calc:
4     calc.clone('molecules/O2-sp-singlet-magmoms')
5
6 with jasp('molecules/O2-sp-singlet-magmoms') as calc:
7     calc.set(lorbit=11)
8     atoms = calc.get_atoms()
9     magmoms = atoms.get_magnetic_moments()
10
11     print('singlet ground state')
12     for i, atom in enumerate(atoms):
13         print('atom {0}: magmom = {1}'.format(i, magmoms[i]))
14     print(atoms.get_magnetic_moment())
15
16 with jasp('molecules/O2-sp-triplet') as calc:
17     calc.clone('molecules/O2-sp-triplet-magmoms')
18
19 with jasp('molecules/O2-sp-triplet-magmoms') as calc:
20     calc.set(lorbit=11)
21     atoms = calc.get_atoms()
22     magmoms = atoms.get_magnetic_moments()
23     print()
24     print('triplet ground state')
25     for i, atom in enumerate(atoms):

```

```

26     print('atom {0}: magmom = {1}'.format(i, magmoms[i]))
27     print(atoms.get_magnetic_moment())

```

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

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!

```

1  grep ENMIN $VASP_PP_PATH/potpw_PBE/O_sv/POTCAR

```

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

ENMAX = 1421.493; ENMIN = 1066.119 eV

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

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  atoms = Atoms([Atom('O', [4, 4.5, 5], magmom=2)],
5               cell=(8, 9, 10))
6
7  with jasp('molecules/O-sp-triplet-lowsym-sv',
8           xc='PBE',
9           ismear=0,
10          ispin=2,
11          sigma=0.01,
12          setups={'O': '_sv'},
13          atoms=atoms) as calc:
14
15      try:
16          E_0 = atoms.get_potential_energy()
17      except (VaspSubmitted, VaspQueued):
18          E_0 = None
19
20  print('Magnetic moment on O = {0} Bohr'
21        ' magnetons'.format(atoms.get_magnetic_moment()))
22
23  # now relaxed O2 dimer
24  atoms = Atoms([Atom('O', [5, 5, 5], magmom=1),
25               Atom('O', [6.22, 5, 5], magmom=1)],
26               cell=(10, 10, 10))
27
28  with jasp('molecules/O2-sp-triplet-sv',
29           xc='PBE',
30           ismear=0,
31           sigma=0.01,
32           ispin=2, # turn spin-polarization on
33           ibrion=2, # make sure we relax the geometry
34           nsr=10,
35           setups={'O': '_sv'},
36           atoms=atoms) as calc:
37
38      try:
39          E_02 = atoms.get_potential_energy()
40      except (VaspSubmitted, VaspQueued):
41          E_02 = None
42
43  # verify magnetic moment
44  print('Magnetic moment on O2 = {0} Bohr'
45        ' magnetons'.format(atoms.get_magnetic_moment()))
46
47  if None not in (E_0, E_02):
48      print('O2 -> 2O D = {0:1.3f} eV'.format(2*E_0 - E_02))

```

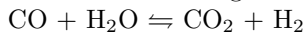
Open the python script (dft-scripts/script-68.py).

Magnetic moment on O = 2.0000001 Bohr magnetons
Magnetic moment on O2 = 1.9999996 Bohr magnetons
O2 -> 2O D = 6.299 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 O₂ 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.



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

$$\Delta E = E_{\text{CO}_2} + E_{\text{H}_2} - E_{\text{CO}} - E_{\text{H}_2\text{O}}$$

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.

```

1  from ase.structure import molecule
2  from jasp import *
3
4  # first we define our molecules. These will automatically be at the coordinates from the G2 database.
5
6  CO = molecule('CO')
7  CO.set_cell([8, 8, 8], scale_atoms=False)
8
9  H2O = molecule('H2O')
10 H2O.set_cell([8, 8, 8], scale_atoms=False)
11
12 CO2 = molecule('CO2')
13 CO2.set_cell([8, 8, 8], scale_atoms=False)
14
15 H2 = molecule('H2')
16 H2.set_cell([8, 8, 8], scale_atoms=False)
17
18 # now the calculators to get the energies
19 with jasp('molecules/wgs/CO',
20          xc='PBE',
21          encut=350,
22          ismear=0,
23          ibrion=2,
24          nsw=10,
25          atoms=CO) as calc:
26     try:
27         eCO = CO.get_potential_energy()
28     except (VaspSubmitted, VaspQueued):
29         eCO = None
30
31 with jasp('molecules/wgs/CO2',
32          xc='PBE',
33          encut=350,
34          ismear=0,
35          ibrion=2,
36          nsw=10,
37          atoms=CO2) as calc:
38     try:
39         eCO2 = CO2.get_potential_energy()
40     except (VaspSubmitted, VaspQueued):
41         eCO2 = None
42
43 with jasp('molecules/wgs/H2',
44          xc='PBE',
45          encut=350,
46          ismear=0,
47          ibrion=2,
48          nsw=10,
49          atoms=H2) as calc:
50     try:
51         eH2 = H2.get_potential_energy()

```



```

52     except (VaspSubmitted, VaspQueued):
53         eH2 = None
54
55 with jasp('molecules/wgs/H2O',
56         xc='PBE',
57         encut=350,
58         ismear=0,
59         ibrion=2,
60         nsw=10,
61         atoms=H2O) as calc:
62     try:
63         eH2O = H2O.get_potential_energy()
64     except (VaspSubmitted, VaspQueued):
65         eH2O = None
66
67 if None in (eCO2, eH2, eCO, eH2O):
68     pass
69 else:
70     dE = eCO2 + eH2 - eCO - eH2O
71     print('Delta E = {0:1.3f} eV'.format(dE))
72     print('Delta E = {0:1.3f} kcal/mol'.format(dE * 23.06035))
73     print('Delta E = {0:1.3f} kJ/mol'.format(dE * 96.485))

```

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

```

Delta E = -0.720 eV
Delta E = -16.614 kcal/mol
Delta E = -69.514 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.

```

1  from jasp import *
2
3  print('**** Calculation summaries')
4  print('***** CO')
5  with jasp('molecules/wgs/CO') as calc:
6      print('##begin_example')
7      print(calc)
8      print('##end_example')
9
10 print('***** CO2')
11 with jasp('molecules/wgs/CO2') as calc:
12     print('##begin_example')
13     print(calc)
14     print('##end_example')
15
16 print('***** H2')
17 with jasp('molecules/wgs/H2') as calc:
18     print('##begin_example')
19     print(calc)
20     print('##end_example')
21
22 print '***** H2O'
23 with jasp('molecules/wgs/H2O') as calc:
24     print('##begin_example')
25     print(calc)
26     print('##end_example')

```

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

Calculation summaries

CO

```
: -----
VASP calculation from /home-research/jkitchin/dft-book2/molecules/wgs/CO
converged: True
Energy = -14.789536 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 8.000  0.000  0.000] 8.000
a1 [ 0.000  8.000  0.000] 8.000
a2 [ 0.000  0.000  8.000] 8.000
a,b,c,alpha,beta,gamma (deg):8.000 8.000 8.000 90.0 90.0 90.0
Unit cell volume = 512.000 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              0.005  0.005  0.005-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
   0    O  [0.000      0.000      0.490]  0  0.01      T T T
   1    C  [0.000      0.000      7.346]  0  0.01      T T T
-----
```

INCAR Parameters:

```
-----
nbands: 9
ismear: 0
nsw: 10
ibrion: 2
encut: 350.0
magmom: None
prec: Normal
kpts: [1, 1, 1]
reciprocal: False
xc: PBE
txt: -
gamma: False
```

Pseudopotentials used:

```
-----
C: potpaw_PBE/C/POTCAR (git-hash: 2272d6745da89a3d872983542cef1d18750fc952)
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)
```

CO2

```
: -----
VASP calculation from /home-research/jkitchin/dft-book2/molecules/wgs/CO2
converged: True
Energy = -22.959572 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 8.000  0.000  0.000] 8.000
a1 [ 0.000  8.000  0.000] 8.000
a2 [ 0.000  0.000  8.000] 8.000
```

```

a,b,c,alpha,beta,gamma (deg):8.000 8.000 8.000 90.0 90.0 90.0
Unit cell volume = 512.000 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
                0.009  0.009  0.008-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
   0    C    [0.000    0.000    0.000]  0  0.00      T T T
   1    O    [0.000    0.000    1.177]  0  0.01      T T T
   2    O    [0.000    0.000    6.823]  0  0.01      T T T
-----

```

INCAR Parameters:

```

-----
nbands: 12
ismear: 0
  nsw: 10
ibrion: 2
encut: 350.0
magmom: None
prec: Normal
kpts: [1, 1, 1]
reciprocal: False
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
C: potpaw_PBE/C/POTCAR (git-hash: 2272d6745da89a3d872983542cef1d18750fc952)
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)

```

H2

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/molecules/wgs/H2
converged: True
Energy = -6.744001 eV

```

```

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 8.000  0.000  0.000] 8.000
a1 [ 0.000  8.000  0.000] 8.000
a2 [ 0.000  0.000  8.000] 8.000
a,b,c,alpha,beta,gamma (deg):8.000 8.000 8.000 90.0 90.0 90.0
Unit cell volume = 512.000 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
                0.000  0.000  0.000-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
   0    H    [0.000    0.000    0.376]  0  0.00      T T T
   1    H    [0.000    0.000    7.624]  0  0.00      T T T
-----

```

INCAR Parameters:

```

-----

```

```

nbands: 5
ismear: 0
  nsw: 10
ibrion: 2
  encut: 350.0
magmom: None
  prec: Normal
  kpts: [1, 1, 1]
reciprocal: False
  xc: PBE
  txt: -
  gamma: False

```

Pseudopotentials used:

H: potpaw_PBE/H/POTCAR (git-hash: fbc0773b08b32f553234b0b50cc6ad6f5085c816)

H2O

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/molecules/wgs/H2O
converged: True
Energy = -14.193569 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 8.000  0.000  0.000] 8.000
a1 [ 0.000  8.000  0.000] 8.000
a2 [ 0.000  0.000  8.000] 8.000
a,b,c,alpha,beta,gamma (deg):8.000 8.000 8.000 90.0 90.0 90.0
Unit cell volume = 512.000 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              0.005  0.004  0.005-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    O    [0.000      0.000      0.122]  0  0.06      T T T
  1    H    [0.000      0.766      7.522]  0  0.04      T T T
  2    H    [0.000      7.234      7.522]  0  0.04      T T T
-----

```

INCAR Parameters:

```

-----
nbands: 8
ismear: 0
  nsw: 10
ibrion: 2
  encut: 350.0
magmom: None
  prec: Normal
  kpts: [1, 1, 1]
reciprocal: False
  xc: PBE
  txt: -
  gamma: False

```

Pseudopotentials used:

H: potpaw_PBE/H/POTCAR (git-hash: fbc0773b08b32f553234b0b50cc6ad6f5085c816)

O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)

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

```
1 from jasp import *
2
3 # get relaxed geometry
4 with jasp('molecules/wgs/CO') as calc:
5     CO = calc.get_atoms()
6
7 # now do the vibrations
8 with jasp('molecules/wgs/CO-vib',
9         xc='PBE',
10        encut=350,
11        ismear=0,
12       ibrion=6,
13        nfree=2,
14        potim=0.02,
15        nsw=1,
16        atoms=CO) as calc:
17     calc.calculate()
18     vib_freq = calc.get_vibrational_frequencies()
19     for i, f in enumerate(vib_freq):
20         print('{0:02d}: {1} cm(-1)'.format(i, f))
```

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

```
00: 2115.528894 cm(-1)
01: 60.594878 cm(-1)
02: 60.594878 cm(-1)
03: (0.987178+0j) cm(-1)
04: (17.958586+0j) cm(-1)
05: (17.958586+0j) cm(-1)
```

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

CO₂ vibrations

```
1 from jasp import *
2
3 # get relaxed geometry
4 with jasp('molecules/wgs/CO2') as calc:
5     CO2 = calc.get_atoms()
6
7 # now do the vibrations
8 with jasp('molecules/wgs/CO2-vib',
9         xc='PBE',
10        encut=350,
11        ismear=0,
12        ibrion=6,
```

```

13         nfree=2,
14         potim=0.02,
15         nsw=1,
16         atoms=CO2) as calc:
17     calc.calculate()
18     vib_freq = calc.get_vibrational_frequencies()
19     for i, f in enumerate(vib_freq):
20         print('{0:02d}: {1} cm-1'.format(i, f))

```

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

```

00: 2352.901285 cm-1
01: 1316.689504 cm-1
02: 635.015913 cm-1
03: 635.015913 cm-1
04: (0.344306+0j) cm-1
05: (1.763867+0j) cm-1
06: (1.763867+0j) cm-1
07: (62.700411+0j) cm-1
08: (62.700411+0j) cm-1

```

CO₂ is a linear molecule with $3N-5 = 4$ vibrational modes. They are the first four frequencies in the output above.

H₂ vibrations

```

1  from jasp import *
2
3  # get relaxed geometry
4  with jasp('molecules/wgs/H2') as calc:
5      H2 = calc.get_atoms()
6
7  # now do the vibrations
8  with jasp('molecules/wgs/H2-vib',
9          xc='PBE',
10         encut=350,
11         ismear=0,
12         ibrion=6,
13         nfree=2,
14         potim=0.02,
15         nsw=1,
16         atoms=H2) as calc:
17     calc.calculate()
18     vib_freq = calc.get_vibrational_frequencies()
19     for i, f in enumerate(vib_freq):
20         print('{0:02d}: {1} cm-1'.format(i, f))

```

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

```

00: 4281.917749 cm-1
01: 129.146855 cm-1
02: 129.146855 cm-1
03: 0.0 cm-1
04: 0.0 cm-1
05: (1e-05+0j) cm-1

```

There is only one frequency of importance (the one at 4281 cm⁻¹) for the linear H₂ molecule.

H₂O vibrations

```

1  from jasp import *
2
3  # get relaxed geometry

```

```

4  with jasp('molecules/wgs/H2O') as calc:
5      H2O = calc.get_atoms()
6
7  # now do the vibrations
8  with jasp('molecules/wgs/H2O-vib',
9          xc='PBE',
10         encut=350,
11         ismear=0,
12         ibrion=6,
13         nfree=2,
14         potim=0.02,
15         nsw=1,
16         atoms=H2O) as calc:
17      calc.calculate()
18      vib_freq = calc.get_vibrational_frequencies()
19      for i, f in enumerate(vib_freq):
20          print('{0:02d}: {1} cm-1'.format(i, f))

```

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

```

00: 3782.062213 cm-1
01: 3672.1246 cm-1
02: 1586.23055 cm-1
03: 135.82763 cm-1
04: 16.280411 cm-1
05: (0.208582+0j) cm-1
06: (26.297061+0j) cm-1
07: (106.869518+0j) cm-1
08: (131.286732+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`](#)

```

1  from ase.thermochemistry import IdealGasThermo
2  from jasp import *
3  import numpy as np
4  import matplotlib.pyplot as plt
5
6  # first we get the electronic energies
7  with jasp('molecules/wgs/CO') as calc:
8      CO = calc.get_atoms()
9      E_CO = CO.get_potential_energy()
10
11  with jasp('molecules/wgs/CO2') as calc:
12      CO2 = calc.get_atoms()
13      E_CO2 = CO2.get_potential_energy()
14
15  with jasp('molecules/wgs/H2') as calc:
16      H2 = calc.get_atoms()
17      E_H2 = H2.get_potential_energy()
18
19  with jasp('molecules/wgs/H2O') as calc:
20      H2O = calc.get_atoms()
21      E_H2O = H2O.get_potential_energy()
22
23  # now we get the vibrational energies
24  h = 4.1356675e-15 # eV * s
25  c = 3.0e10 # cm / s
26
27  with jasp('molecules/wgs/CO-vib') as calc:
28      vib_freq = calc.get_vibrational_frequencies()
29      CO_vib_energies = [h * c * nu for nu in vib_freq]
30
31  with jasp('molecules/wgs/CO2-vib') as calc:
32      vib_freq = calc.get_vibrational_frequencies()
33      CO2_vib_energies = [h * c * nu for nu in vib_freq]
34
35  with jasp('molecules/wgs/H2-vib') as calc:

```

```

36     vib_freq = calc.get_vibrational_frequencies()
37     H2_vib_energies = [h * c * nu for nu in vib_freq]
38
39 with jasp('molecules/wgs/H2O-vib') as calc:
40     vib_freq = calc.get_vibrational_frequencies()
41     H2O_vib_energies = [h * c * nu for nu in vib_freq]
42
43 # now we make a thermo object for each molecule
44 CO_t = IdealGasThermo(vib_energies=CO_vib_energies[0:0],
45                       electronicenergy=E_CO, atoms=CO,
46                       geometry='linear', symmetrynumber=1,
47                       spin=0)
48
49 CO2_t = IdealGasThermo(vib_energies=CO2_vib_energies[0:4],
50                       electronicenergy=E_CO2, atoms=CO2,
51                       geometry='linear', symmetrynumber=2,
52                       spin=0)
53
54 H2_t = IdealGasThermo(vib_energies=H2_vib_energies[0:0],
55                       electronicenergy=E_H2, atoms=H2,
56                       geometry='linear', symmetrynumber=2,
57                       spin=0)
58
59 H2O_t = IdealGasThermo(vib_energies=H2O_vib_energies[0:3],
60                       electronicenergy=E_H2O, atoms=H2O,
61                       geometry='nonlinear', symmetrynumber=2,
62                       spin=0)
63
64 # now we can compute G_rxn for a range of temperatures from 298 to 1000 K
65 Trange = np.linspace(298, 1000, 20) # K
66 P = 101325. # Pa
67 Grxn = np.array([(CO2_t.get_free_energy(temperature=T, pressure=P)
68                 + H2_t.get_free_energy(temperature=T, pressure=P)
69                 - H2O_t.get_free_energy(temperature=T, pressure=P)
70                 - CO_t.get_free_energy(temperature=T, pressure=P)) * 96.485 for T in Trange])
71
72 Hrxn = np.array([(CO2_t.get_enthalpy(temperature=T)
73                 + H2_t.get_enthalpy(temperature=T)
74                 - H2O_t.get_enthalpy(temperature=T)
75                 - CO_t.get_enthalpy(temperature=T)) * 96.485
76                 for T in Trange])
77
78 plt.plot(Trange, Grxn, 'bo-', label='$\Delta G_{rxn}$')
79 plt.plot(Trange, Hrxn, 'ro:', label='$\Delta H_{rxn}$')
80 plt.xlabel('Temperature (K)')
81 plt.ylabel(r'$\Delta G_{rxn}$ (kJ/mol)')
82 plt.legend(loc='best')
83 plt.savefig('images/wgs-dG-T.png')
84
85 plt.figure()
86 R = 8.314e-3 # gas constant in kJ/mol/K
87
88 Keq = np.exp(-Grxn/R/Trange)
89 plt.plot(Trange, Keq)
90 plt.ylim([0, 100])
91 plt.xlabel('Temperature (K)')
92 plt.ylabel('$K_{eq}$')
93 plt.savefig('images/wgs-Keq.png')
94 plt.show()

```

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

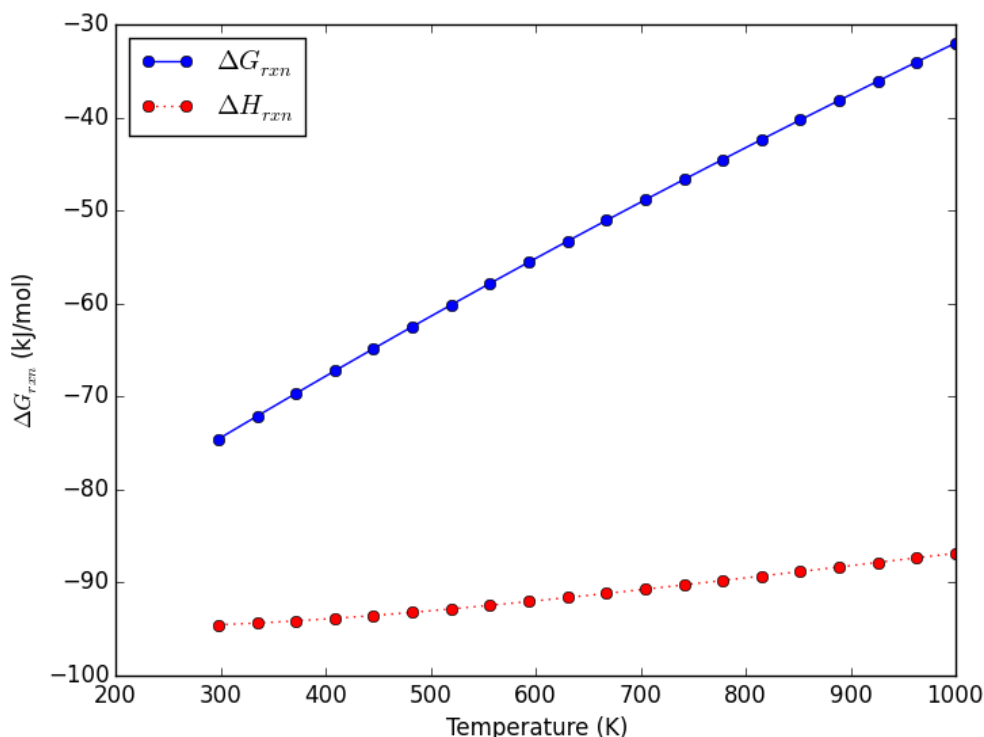


Figure 22: Thermodynamic energies of the water gas shift reaction as a function of temperature.

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.

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 method⁴⁸ 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.⁴⁹

3.9.1 Get initial and final states

```

1  # compute initial and final states
2  from ase import Atoms
3  from ase.structure import molecule
4  import numpy as np
5  from jasp import *
6  from ase.constraints import FixAtoms
7
8  atoms = molecule('NH3')
9  constraint = FixAtoms(mask=[atom.symbol == 'N' for atom in atoms])
10 atoms.set_constraint(constraint)
11
12 Npos = atoms.positions[0]
13
```

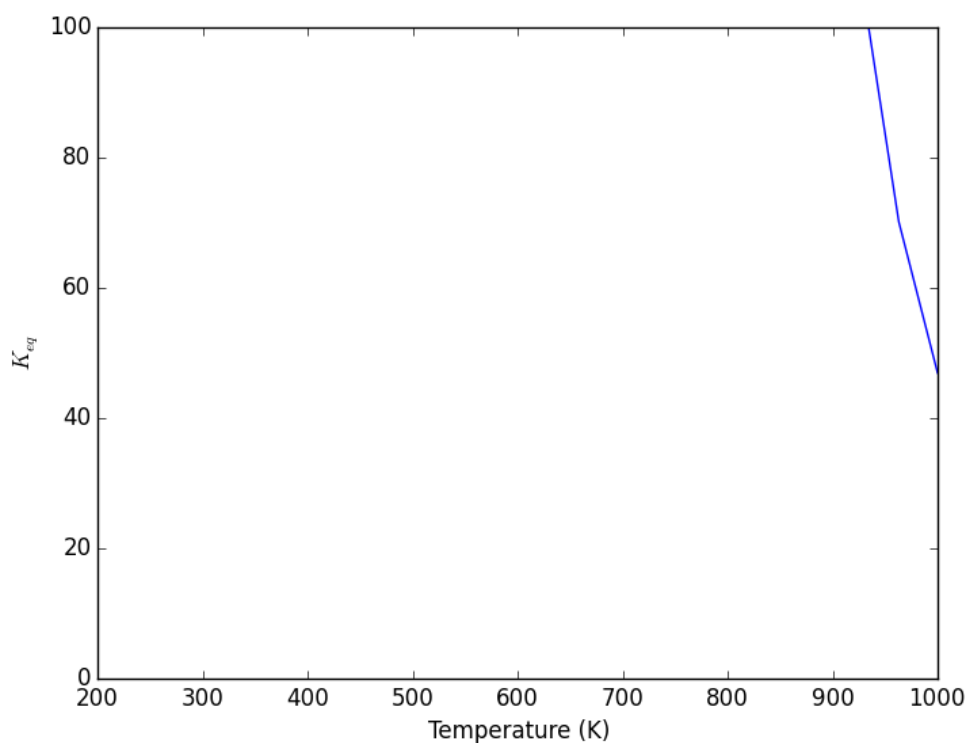


Figure 23: Temperature dependence of the equilibrium constant.

```

14 # move N to origin
15 atoms.translate(-Npos)
16 atoms.set_cell((10, 10, 10), scale_atoms=False)
17
18 atoms2 = atoms.copy()
19 pos2 = atoms2.positions
20
21 for i,atom in enumerate(atoms2):
22     if atom.symbol == 'H':
23         # reflect through z
24         pos2[i] *= np.array([1, 1, -1])
25 atoms2.positions = pos2
26
27 #now move N to center of box
28 atoms.translate([5, 5, 5])
29 atoms2.translate([5, 5, 5])
30
31 with jasp('molecules/nh3-initial',
32         xc='PBE',
33         encut=350,
34         ibrion=1,
35         nsw=10,
36         atoms=atoms) as calc:
37     try:
38         calc.calculate()
39     except (VaspSubmitted, VaspQueued):
40         pass
41
42 with jasp('molecules/nh3-final',
43         xc='PBE',
44         encut=350,
45         ibrion=1,
46         nsw=10,
47         atoms=atoms2) as calc:
48     try:

```

```
49         calc.calculate()
50     except (VaspSubmitted, VaspQueued):
51         pass
```

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

3.9.2 Run band calculation

Now we do the band calculation.

```
1  # Run NH3 NEB calculations
2  from jasp import *
3  from ase.neb import NEB
4
5  with jasp('molecules/nh3-initial') as calc:
6      atoms = calc.get_atoms()
7
8  with jasp('molecules/nh3-final') as calc:
9      atoms2 = calc.get_atoms()
10
11  # 5 images including endpoints
12  images = [atoms] # initial state
13  images += [atoms.copy() for i in range(3)]
14  images += [atoms2] # final state
15
16  neb = NEB(images)
17  neb.interpolate()
18
19  with jasp('molecules/nh3-neb',
20          xc='PBE',
21          ibrion=1,
22          ns=90,
23          spring=-5, debug=logging.DEBUG,
24          atoms=images) as calc:
25      images, energies = calc.get_neb()
26
27      calc.plot_neb(show=False)
28  import matplotlib.pyplot as plt
29  plt.savefig('images/nh3-neb.png')
30  plt.show()
```

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

Optimization terminated successfully.

Current function value: -0.223946

Iterations: 15

Function evaluations: 30

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

```
1  # make neb movie
2  from ase.io import write
3  from ase.visualize import view
4  from jasp import *
5
6  with jasp('molecules/nh3-neb') as calc:
7      images, energies = calc.get_neb()
8
9  # this rotates the atoms 90 degrees about the y-axis
10 [atoms.rotate('y', np.pi/2.) for atoms in images]
11
12 for i, atoms in enumerate(images):
13     write('images/00{0}-nh3.png'.format(i), atoms, show_unit_cell=2)
14
```

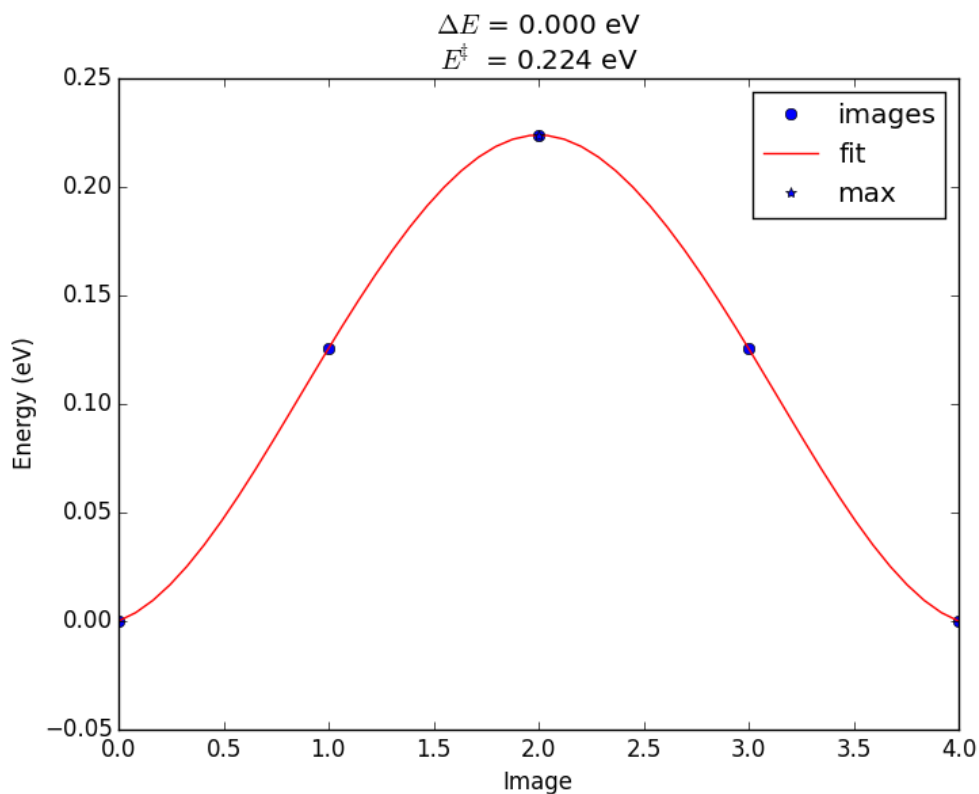


Figure 24: Nudged elastic band results for ammonia flipping.

```

15 # animated gif
16 os.system('convert -delay 50 -loop 0 images/00*-nh3.png images/nh3-neb.gif')
17
18 # Shockwave flash
19 os.system('png2swf -o images/nh3-neb.swf images/00*-nh3.png ')

```

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

```

1 from ase.io import write
2 from ase.lattice.cubic import FaceCenteredCubic
3
4 atoms = FaceCenteredCubic('Ag')
5
6 write('images/Ag-fcc.png', atoms, show_unit_cell=2)
7
8 print(atoms)

```

Open the python script (dft-scripts/script-79.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 an `ase.atoms.Atoms` object.

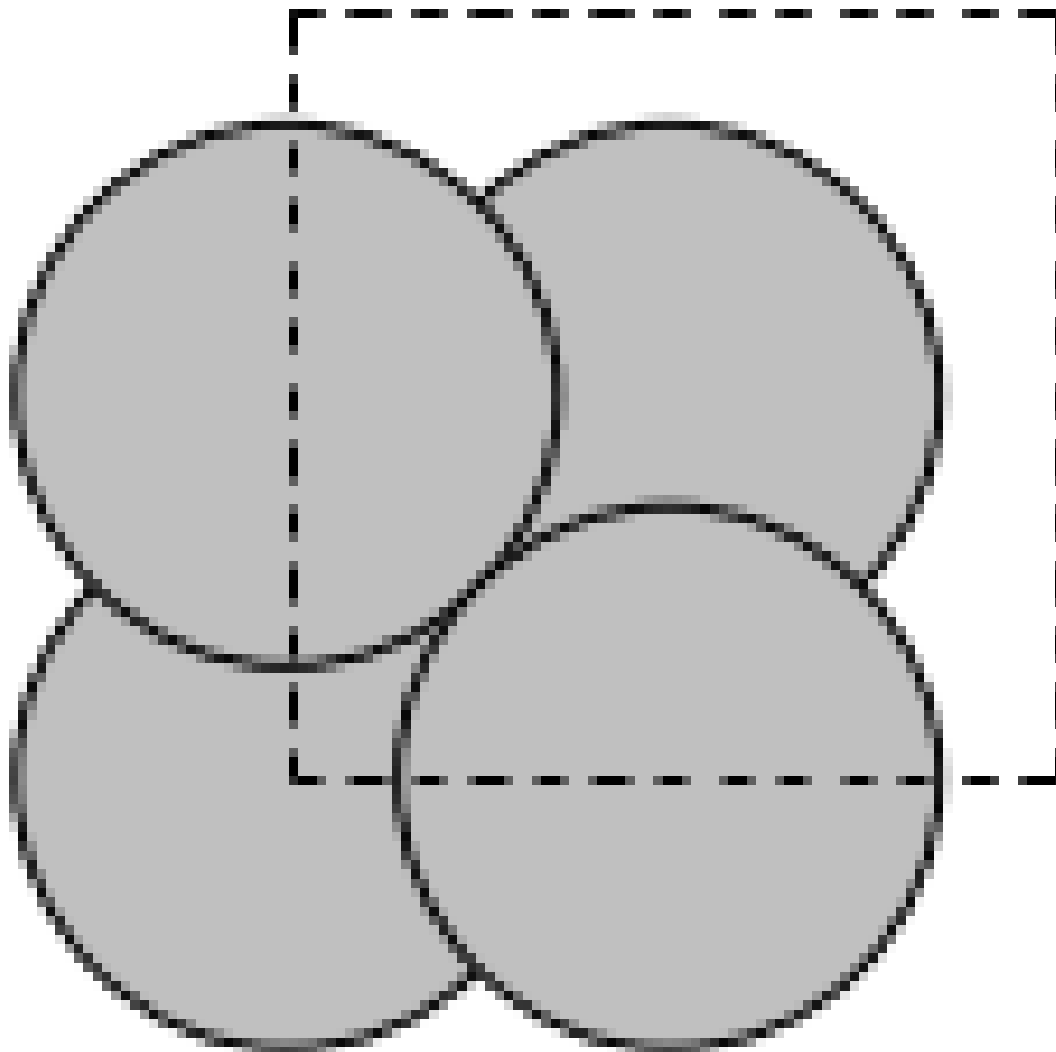


Figure 25: A simple fcc Ag bulk structure in the primitive unit cell.

Here we specify the primitive unit cell, which only has one atom in it.

```

1 from ase.io import write
2 from ase.lattice.cubic import FaceCenteredCubic
3
4 atoms = FaceCenteredCubic('Ag', directions=[[0, 1, 1],
5                                             [1, 0, 1],
6                                             [1, 1, 0]])
7
8 write('images/Ag-fcc-primitive.png', atoms, show_unit_cell=2)
9
10 print atoms

```

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

```
Lattice(symbols='Ag', positions=..., cell=[[2.892066735052979, 0.0, 0.0], [1.4460333675264898, 2.504
```

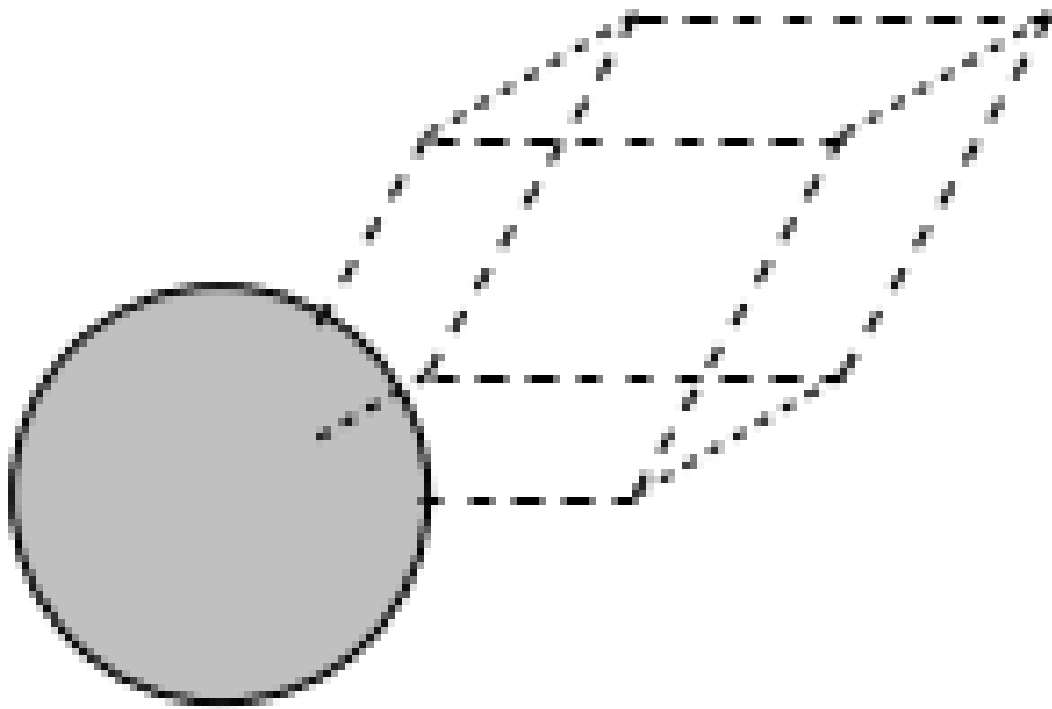


Figure 26: A simple fcc Ag bulk structure in the primitive unit cell.

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.

```

1  from ase.io import write
2  from ase.lattice.cubic import FaceCenteredCubic
3
4  atoms = FaceCenteredCubic(directions=[[1, 0, 0],
5                                     [0, 1, 0],
6                                     [0, 0, 1]],
7                           size=(1, 1, 1),
8                           symbol='Ag',
9                           latticeconstant=4.0)
10
11 write('images/Ag-bulk.png', atoms, show_unit_cell=2)
12
13 # to make an alloy, we can replace one atom with another kind
14 atoms[0].symbol = 'Pd'
15 write('images/AgPd-bulk.png', atoms, show_unit_cell=2)

```

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

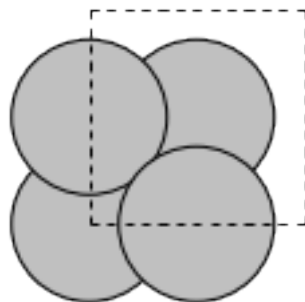


Figure 27: A simple fcc Ag bulk structure in the traditional unit cell.

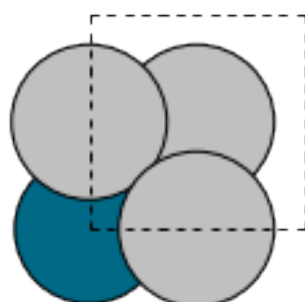


Figure 28: A simple Ag_3Pd bulk structure.

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.

```

1 from ase.lattice.hexagonal import Graphite
2 from ase.io import write
3
4 atoms = Graphite('C', latticeconstant={'a': 2.4612,
5                                       'c': 6.7079})
6 write('images/graphite.png',
7       atoms.repeat((2, 2, 1)),
8       rotation='115x', show_unit_cell=2)
9
10 write('images/graphite-top.png',
11       atoms.repeat((2, 2, 1)),
12       show_unit_cell=2)

```

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

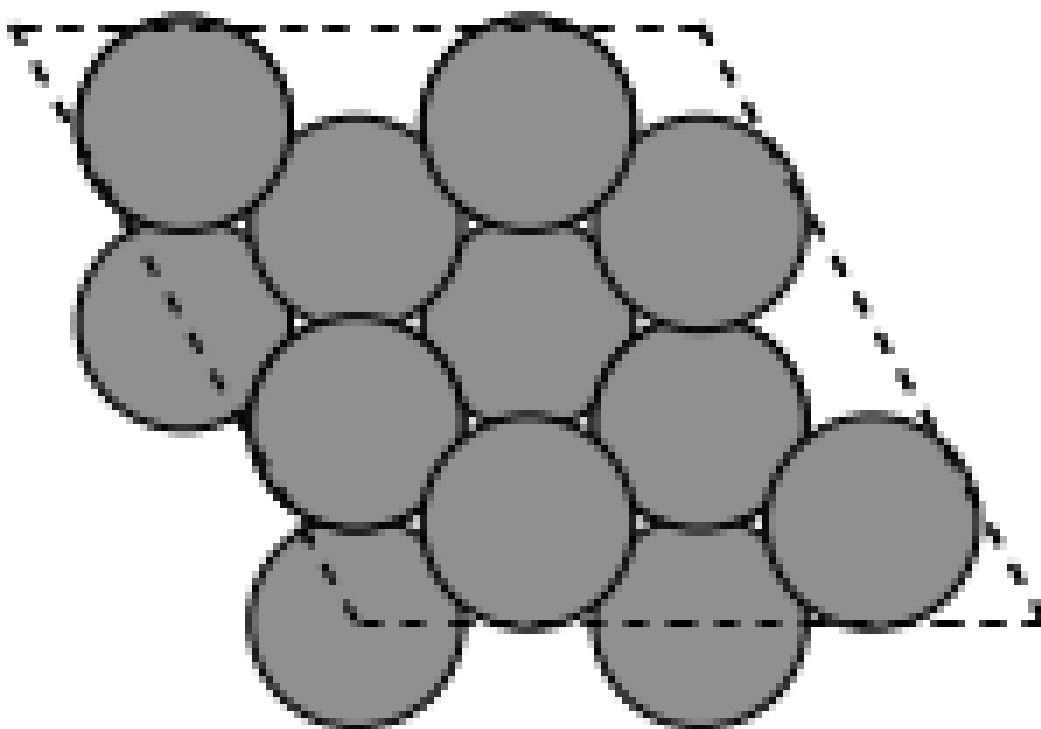


Figure 29: A top view of graphite.

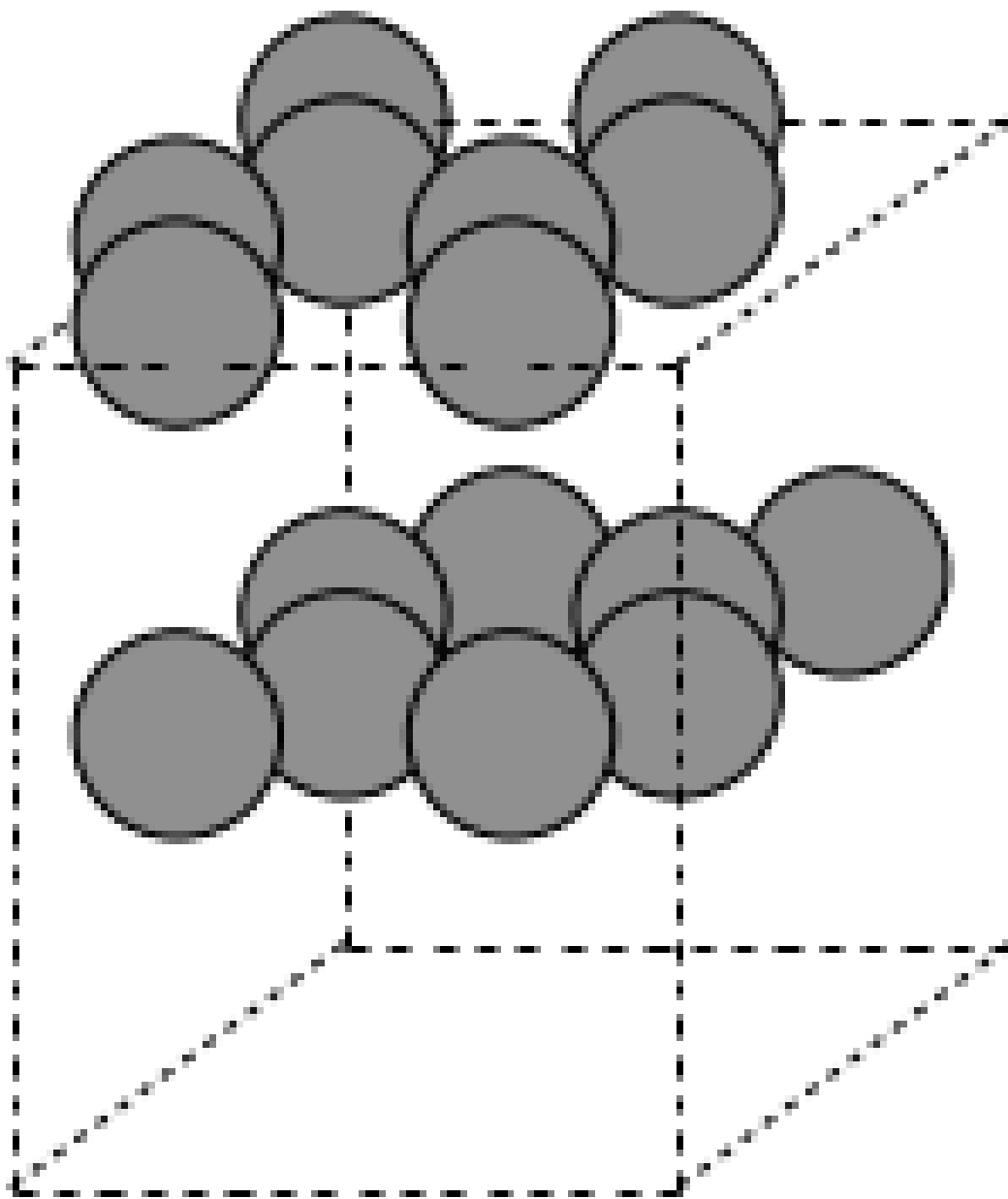


Figure 30: A side view of graphite.

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).

```

1 from ase.lattice.compounds import NaCl
2 from ase.io import write
3
4 atoms = NaCl(['Na', 'Cl'], latticeconstant=5.65)
5 write('images/NaCl.png', atoms, show_unit_cell=2, rotation='45x,45y,45z')
```

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

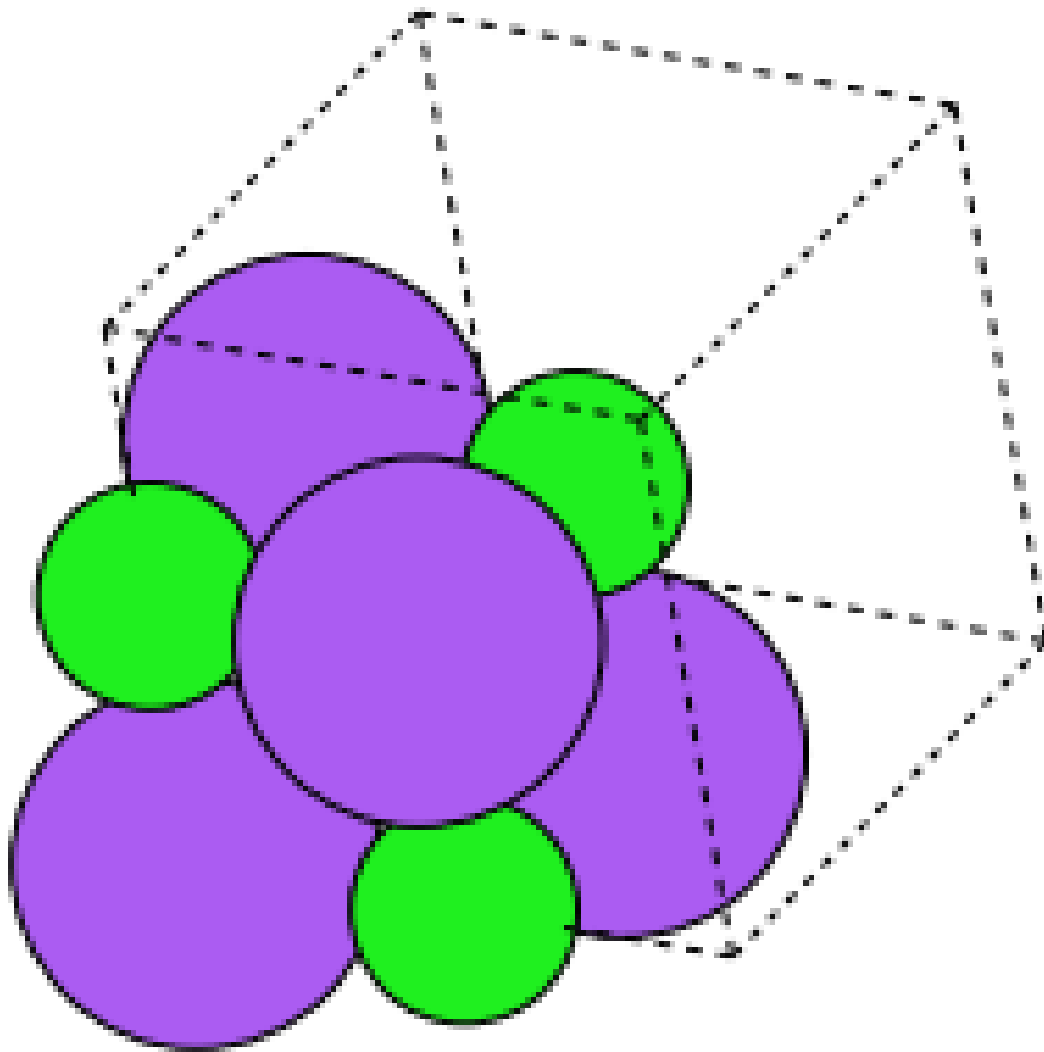


Figure 31: A view of a NaCl crystal structure.

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)

```

1 from ase.lattice.spacegroup import crystal
2 # FCC aluminum
3 a = 4.05
4 al = crystal('Al', [(0, 0, 0)],
5             spacegroup=225,
6             cellpar=[a, a, a, 90, 90, 90])
7 print(al)

```

Open the python script (dft-scripts/script-84.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 .

```
1 from ase.lattice.spacegroup import crystal
2
3 a = 4.6
4 c = 2.95
5 rutile = crystal(['Ti', 'O'], basis=[(0, 0, 0), (0.3, 0.3, 0.0)],
6                 spacegroup=136, cellpar=[a, a, c, 90, 90, 90])
7 print rutile
```

Open the python script (dft-scripts/script-85.py).

```
Atoms(symbols='Ti2O4', positions=..., cell=[[4.6, 0.0, 0.0], [2.816687638038912e-16, 4.6, 0.0], [1.8
```

4.1.2 Using <http://materialsproject.org>

The [Materials Project](http://materialsproject.org) 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](http://pymatgen.org) project (which requires python 2.7+).

For example, I downloaded this cif file for a RuO_2 structure (Material ID 825).

```
1 #\#CIF1.1
2 #####
3 # Crystallographic Information Format file
4 # Produced by PyCifRW module
5 #
6 # This is a CIF file. CIF has been adopted by the International
7 # Union of Crystallography as the standard for data archiving and
8 # transmission.
9 #
10 # For information on this file format, follow the CIF links at
11 # http://www.iucr.org
12 #####
13
14 data_RuO2
15 _symmetry_space_group_name_H-M 'P 1'
16 _cell_length_a 3.13970109
17 _cell_length_b 4.5436378
18 _cell_length_c 4.5436378
19 _cell_angle_alpha 90.0
20 _cell_angle_beta 90.0
21 _cell_angle_gamma 90.0
22 _chemical_name_systematic 'Generated by pymatgen'
23 _symmetry_Int_Tables_number 1
24 _chemical_formula_structural RuO2
25 _chemical_formula_sum 'Ru2 O4'
26 _cell_volume 64.8180127062
27 _cell_formula_units_Z 2
28 loop_
29 _symmetry_equiv_pos_site_id
30 _symmetry_equiv_pos_as_xyz
31 1 'x, y, z'
32
33 loop_
34 _atom_site_type_symbol
35 _atom_site_label
36 _atom_site_symmetry_multiplicity
37 _atom_site_fract_x
38 _atom_site_fract_y
39 _atom_site_fract_z
40 _atom_site_attached_hydrogens
41 _atom_site_B_iso_or_equiv
```

```

42 _atom_site_occupancy
43 0 01 1 0.000000 0.694330 0.694330 0 . 1
44 0 02 1 0.500000 0.805670 0.194330 0 . 1
45 0 03 1 0.000000 0.305670 0.305670 0 . 1
46 0 04 1 0.500000 0.194330 0.805670 0 . 1
47 Ru Ru5 1 0.500000 0.500000 0.500000 0 . 1
48 Ru Ru6 1 0.000000 0.000000 0.000000 0 . 1

```

Open the python script (dft-scripts/script-86.py).

We can read this file in with [ase.io.read](#). That function automatically recognizes the file type by the extension.

```

1 from ase.io import read, write
2
3 atoms = read('bulk/Ru2O4_1.cif')
4
5 write('images/Ru2O4.png', atoms, show_unit_cell=2)

```

Open the python script (dft-scripts/script-87.py).

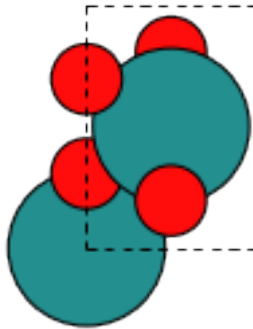


Figure 32: An RuO₂ unit cell prepared from a cif file.

You can also download the VASP files. I have copied these files (INCAR, POSCAR, KPOINTS) to a directory (bulk/Ru2O4), and now we can run a calculation like this:

```

1 from jasp import *
2
3 with jasp('bulk/Ru2O4',
4         xc='PBE',
5         setups={'Ru': '_pv'}) as calc:
6     calc.calculate()
7     print calc

```

Open the python script (dft-scripts/script-88.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/Ru2O4
converged: True
Energy = -44.302690 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 3.137  0.000  0.000] 3.137
a1 [ 0.000  4.541  0.000] 4.541
a2 [ 0.000  0.000  4.541] 4.541
a,b,c,alpha,beta,gamma (deg):3.137 4.541 4.541 90.0 90.0 90.0

```

```

Unit cell volume = 64.694 Ang^3
Stress (GPa):xx,   yy,   zz,   yz,   xz,   xy
               -0.002 -0.000 -0.000-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Ru  [1.569      2.270      2.270]  0  0.00      T T T
  1    Ru  [0.000      0.000      0.000]  0  0.00      T T T
  2    O   [0.000      3.153      3.153]  0  0.00      T T T
  3    O   [1.569      3.659      0.882]  0  0.00      T T T
  4    O   [0.000      1.388      1.388]  0  0.00      T T T
  5    O   [1.569      0.882      3.659]  0  0.00      T T T

```

INCAR Parameters:

```

-----
nbands: 31
ismear: 1
nelmin: 3
icharg: 1
nelm: 100
nsw: 99
ibrion: 2
npar: 1
isif: 3
encut: 520.0
sigma: 0.2
ediff: 0.0003
lwave: True
magmom: [0.6, 0.6, 0.6, 0.6, 0.6, 0.6]
prec: Normal
algo: Fast
lreal: Auto
kpts: [8, 6, 6]
reciprocal: False
setups: {'Ru': '_pv'}
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
Ru: potpaw_PBE/Ru_pv/POTCAR (git-hash: c29610ef9b7bfa353e710b09dfadcd2b0fb0d274)
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)

```

Some notes: we had to specify the PBE functional. That is good habit, since the default may be something else. We also had to specify the special setups used, since those were not defaults either.

We get exactly the same result as the website! Why is this helpful then? Well, we could use this as a starting point to look at an equation of state, or to plot some interesting electronic structure, etc... Or we can gain a little confidence that our version of VASP is working like the one they used.

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-Pack²⁸ 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 $n_1 \times n_2 \times n_3$ grids, and the total number of k-points is $n_1 \cdot n_2 \cdot n_3$. 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.

```
1 from ase.lattice.cubic import FaceCenteredCubic
2 from jasp import *
3
4 atoms = FaceCenteredCubic('Ag')
5
6 KPTS = [2, 3, 4, 5, 6, 8, 10]
7
8 TE = []
9
10 ready = True
11 for k in KPTS:
12     with jasp('bulk/Ag-kpts-{}'.format(k),
13              xc='PBE',
14              kpts=(k, k, k), # specifies the Monkhorst-Pack grid
15              encut=300,
16              atoms=atoms) as calc:
17         try:
18             TE.append(atoms.get_potential_energy())
19         except (VaspSubmitted, VaspQueued):
20             ready = False
21
22 if not ready:
23     import sys; sys.exit()
24
25 import matplotlib.pyplot as plt
26
27 # consider the change in energy from lowest energy state
28 TE = np.array(TE)
29 TE -= TE.min()
30
31 plt.plot(KPTS, TE)
32 plt.xlabel('number of k-points in each dimension')
33 plt.ylabel('Total Energy (eV)')
34 plt.savefig('images/Ag-kpt-convergence.png')
35 plt.show()
```

Open the python script (dft-scripts/script-89.py).

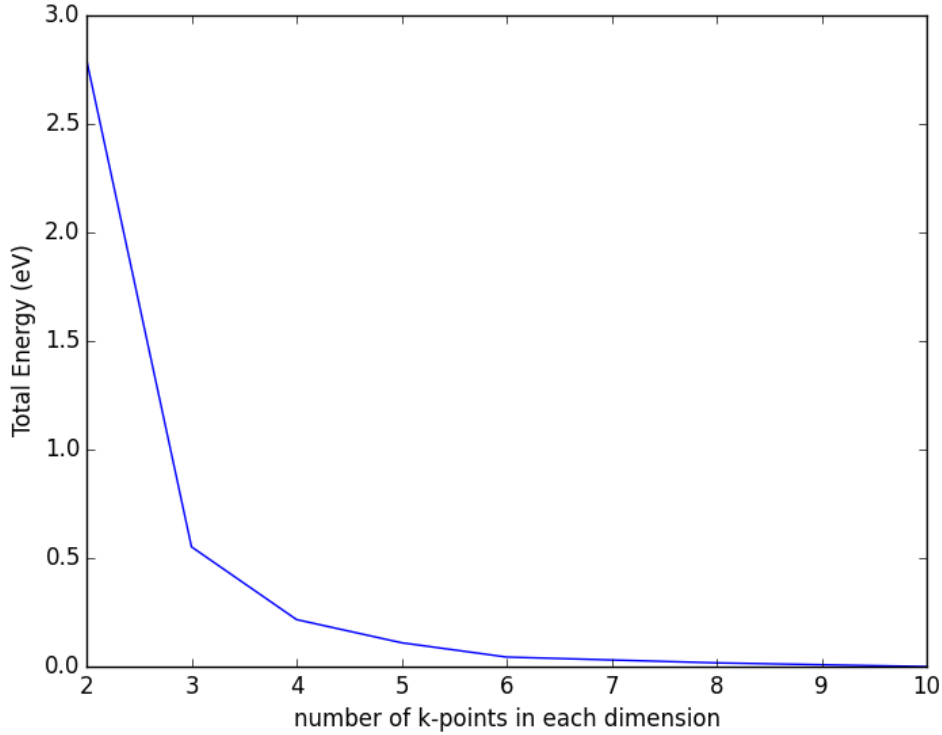


Figure 33: k-point convergence of the total energy of fcc Ag.

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 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3  import matplotlib.pyplot as plt
4
5  a = 3.61
6  atoms = Atoms([Atom('Cu', (0, 0, 0))],
7                cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
8                                          [0.0, 1.0, 1.0],
9                                          [1.0, 0.0, 1.0]]).repeat((2, 2, 2))
10
11  SIGMA = [0.001, 0.05, 0.1, 0.2, 0.5]
12
13  for sigma in SIGMA:
14
15      with jasp('bulk/Cu-sigma-{}'.format(sigma),
16              xc='PBE',
17              encut=350,
18              kpts=(4, 4, 4),
19              ismear=-1,
20              sigma=sigma,
21              nbands=9 * 8,
22              atoms=atoms) as calc:
23          e = atoms.get_potential_energy()
24
25          nbands = calc.nbands
26          nkpts = len(calc.get_ibz_k_points())
27
28          occ = np.zeros((nkpts, nbands))
29          for i in range(nkpts):
30              occ[i,:] = calc.get_occupation_numbers(kpt=i)
31
32          max_occ = np.max(occ,axis=0) #axis 0 is columns
33
34          plt.plot(range(nbands), max_occ, label='$\sigma = {}'.format(sigma))
35
36  plt.xlabel('band number')
37  plt.ylabel('maximum occupancy (electrons)')
38  plt.ylim([-0.1, 2.1])
39  plt.legend(loc='best')
40  plt.savefig('images/occ-sigma.png')
41  plt.show()

```

Open the python script (dft-scripts/script-90.py).

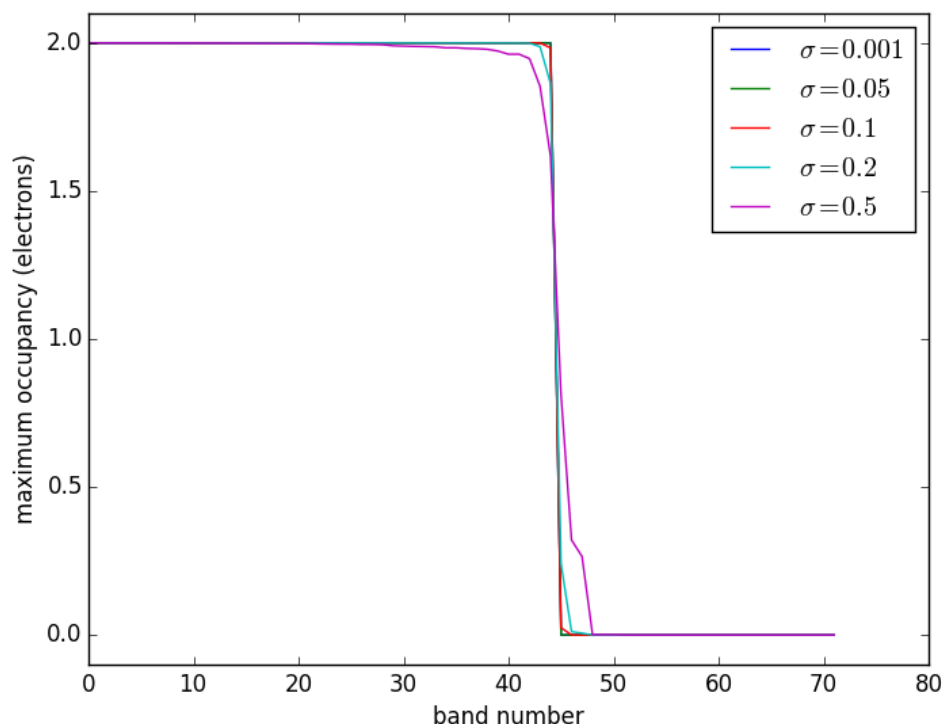


Figure 34: Effects of SIGMA on the occupancies of the Cu system.

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.

```

1  import numpy as np
2
3  print int(np.ceil(50 / 2.))
4  print int(np.ceil(51 / 2.))

```

Open the python script (dft-scripts/script-91.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	$\text{NELECT}/2 + \text{NIONS}/2$
spin-polarized	$0.6 * \text{NELECT} + \text{NMAGIONS}$

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 $2 * \text{NIONS}$ extra bands.

To figure out how many bands you need, it is necessary to know how many electrons are in your calculation. The [jasp.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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000])],
5                cell= [[1.818, 0.000, 1.818],
6                      [1.818, 1.818, 0.000],
7                      [0.000, 1.818, 1.818]])
8
9  with jasp('bulk/alloy/cu',
10           xc='PBE',
11           encut=350,
12           kpts=(13, 13, 13),
13           nbands=9,
14           ibrion=2,
15           isif=4,
16           nsw=10,
17           atoms=atoms) as calc:
18      print calc.get_valence_electrons()

```

Open the python script (dft-scripts/script-92.py).

```

11.0

```

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 `jasp.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 $n_{\text{bands}} = \text{int}(n_{\text{electrons}}/2 + \text{len}(\text{atoms}) * f)$. 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 `jasp.set_nbands`.

```

1 from jasp import *
2 from ase import Atom, Atoms
3
4 atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000])],
5               cell=[[1.818, 0.000, 1.818],
6                    [1.818, 1.818, 0.000],
7                    [0.000, 1.818, 1.818]])
8
9 with jasp('bulk/alloy/cu',
10          xc='PBE',
11          encut=350,
12          kpts=(13, 13, 13),
13          ibrion=2,
14          isif=4,
15          nsw=10,
16          atoms=atoms) as calc:
17     calc.set_nbands(9)
18     print calc

```

Open the python script (dft-scripts/script-93.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/alloy/cu
converged: True
Energy = -3.723306 eV

```

Unit cell vectors (angstroms)

	x	y	z	length
a0	[1.818	0.000	1.818]	2.571
a1	[1.818	1.818	0.000]	2.571
a2	[0.000	1.818	1.818]	2.571

a,b,c,alpha,beta,gamma (deg):2.571 2.571 60.0 60.0 60.0
Unit cell volume = 12.017 Ang³

Stress (GPa):xx, yy, zz, yz, xz, xy
0.006 0.006 0.006-0.000 -0.000 -0.000

Atom#	sym	position [x,y,z]	tag	rmsForce	constraints
0	Cu	[0.000 0.000 0.000]	0	0.00	T T T

INCAR Parameters:

```

-----
nbands: 9
nsw: 10
ibrion: 2
isif: 4
encut: 350.0
magmom: None
prec: Normal

```

```

kpts: (13, 13, 13)
reciprocal: False
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

Cu: potpaw_PBE/Cu/POTCAR (git-hash: a44c591415026f53deb16a99ca3f06b1e69be10b)

```

1 from jasp import *
2 from ase import Atom, Atoms
3
4 atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000])],
5               cell=[[1.818, 0.000, 1.818],
6                     [1.818, 1.818, 0.000],
7                     [0.000, 1.818, 1.818]])
8
9 with jasp('bulk/alloy/cu-setnbands',
10          xc='PBE',
11          encut=350,
12          kpts=(13, 13, 13),
13          ibrion=2,
14          isif=4,
15          nsw=10,
16          atoms=atoms) as calc:
17     calc.set_nbands(f=3)
18     print calc

```

Open the python script (dft-scripts/script-94.py).

False

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/alloy/cu-setnbands
converged: None
Energy = nan eV

```

Unit cell vectors (angstroms)

	x	y	z	length
a0	[1.818	0.000	1.818]	2.571
a1	[1.818	1.818	0.000]	2.571
a2	[0.000	1.818	1.818]	2.571

a,b,c,alpha,beta,gamma (deg):2.571 2.571 2.571 60.0 60.0 60.0
Unit cell volume = 12.017 Ang³

Stress was not computed

Atom#	sym	position [x,y,z]	tag	rmsForce	constraints
0	Cu	[0.000 0.000 0.000]	0	nan	T T T

INCAR Parameters:

```

-----
nbands: 9
nsw: 10
ibrion: 2
isif: 4
encut: 350
magmom: None
prec: Normal

```

```

        kpts: (13, 13, 13)
reciprocal: False
        xc: PBE
        txt: -
        gamma: False

```

Pseudopotentials used:

None: None (git-hash: None)

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. $\text{NBANDS} = 0.65 \cdot \text{NELECT} + 10$
2. $\text{NBANDS} = 0.5 \cdot \text{NELECT} + 15$
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 Kittel⁴ (Chapter 1).

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  # fcc
5  LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
6  fcc_energies = []
7  ready = True
8  for a in LC:
9      atoms = Atoms([Atom('Cu', (0, 0, 0))],
10                    cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
11                                              [0.0, 1.0, 1.0],
12                                              [1.0, 0.0, 1.0]]))
13
14      with jasp('bulk/Cu-{0}'.format(a),
15                xc='PBE',
16                encut=350,
17                kpts=(8, 8, 8),
18                atoms=atoms) as calc:
19
20          try:
21              e = atoms.get_potential_energy()
22              fcc_energies.append(e)
23          except (VaspSubmitted, VaspQueued):

```

```

24         ready = False
25
26     if not ready:
27         import sys; sys.exit()
28
29     import matplotlib.pyplot as plt
30     plt.plot(LC, fcc_energies)
31     plt.xlabel('Lattice constant ($\AA$)')
32     plt.ylabel('Total energy (eV)')
33     plt.savefig('images/Cu-fcc.png')
34
35     print '#+tblname: cu-fcc-energies'
36     print r'| lattice constant ($\AA$) | Total Energy (eV) |'
37     for lc, e in zip(LC, fcc_energies):
38         print '| {0} | {1} |'.format(lc, e)

```

Open the python script (dft-scripts/script-95.py).

lattice constant (\AA)	Total Energy (eV)
3.5	-3.649238
3.55	-3.696204
3.6	-3.719946
3.65	-3.723951
3.7	-3.711284
3.75	-3.68426

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.

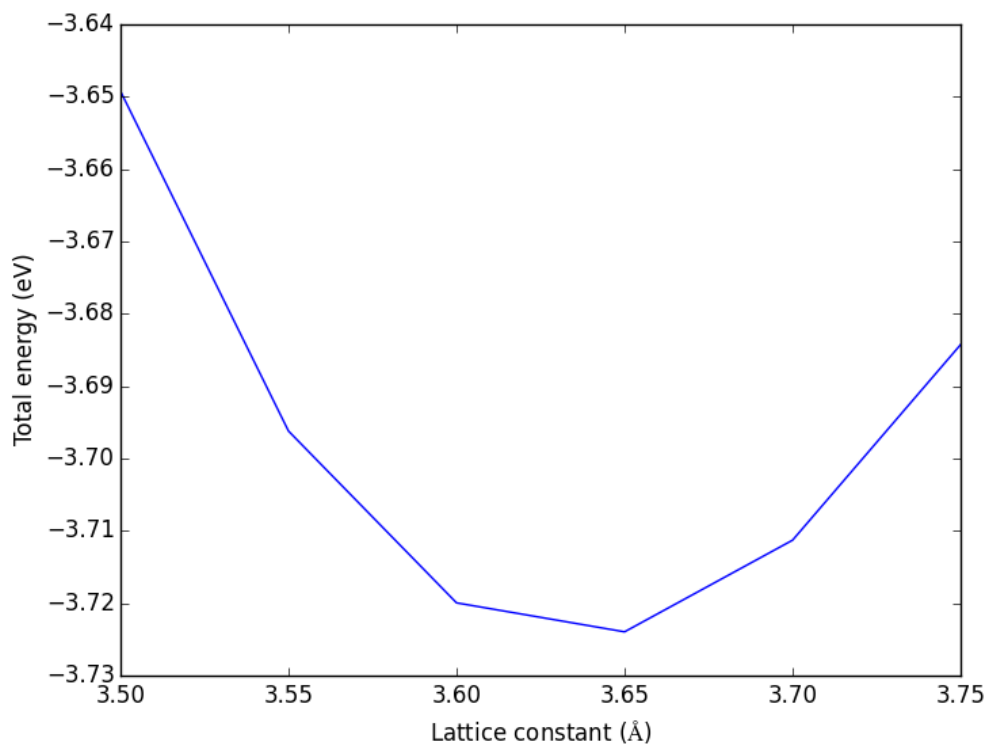


Figure 35: Total energy vs. fcc lattice constant for Cu. It appears the minimum is near 3.65 Å.

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](#).

```

1  from jasp import *
2  from ase.utils.eos import EquationOfState
3  LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
4  energies = []
5  volumes = []
6  for a in LC:
7      with jasp('bulk/Cu-{}'.format(a)) as calc:
8          atoms = calc.get_atoms()
9          volumes.append(atoms.get_volume())
10         energies.append(atoms.get_potential_energy())
11
12  eos = EquationOfState(volumes, energies)
13  v0, e0, B = eos.fit()
14
15  print '''
16  v0 = {0} A^3
17  E0 = {1} eV
18  B = {2} eV/A^3'''.format(v0, e0, B)
19
20  eos.plot('images/Cu-fcc-eos.png')
```

Open the python script (dft-scripts/script-96.py).

```

v0 = 12.0167118546 A^3
E0 = -3.7246811445 eV
B = 0.859009528171 eV/A^3
```


3.63585568663

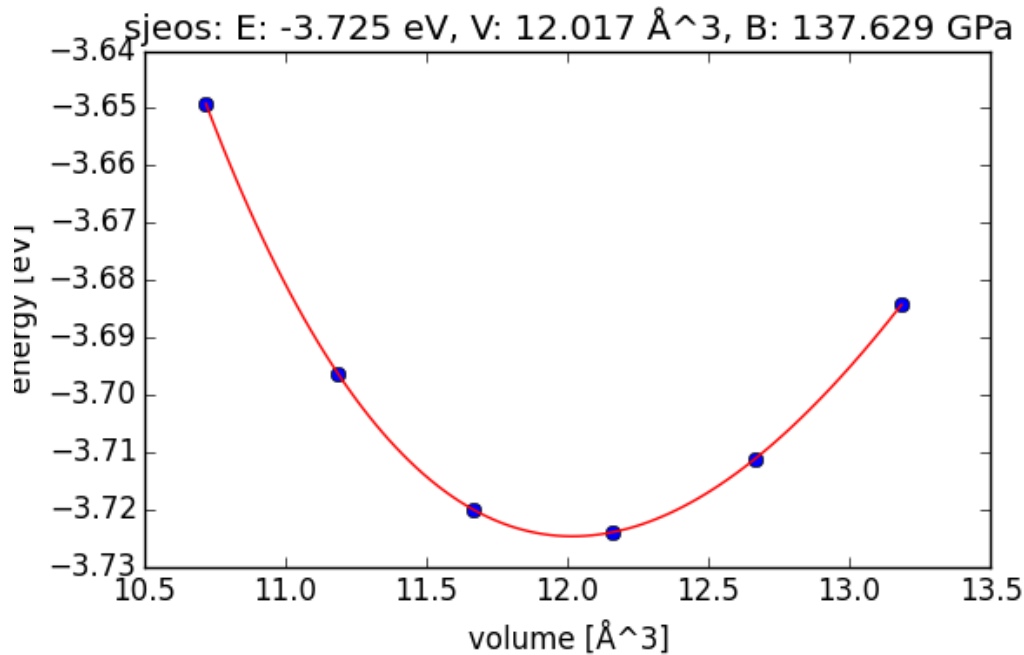


Figure 36: Total energy vs. volume for fcc Cu with fitted cubic polynomial equation of state.

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 $11.8 \text{ Å}^3/\text{atom}$. 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.

```

1 from ase import Atom, Atoms
2 import numpy as np
3 a = 3.61 # lattice constant
4
5 atoms = Atoms([Atom('Cu', [0,0,0])],
6               cell=0.5 * a*np.array([[ 1.0,  1.0, -1.0],
7                                     [-1.0,  1.0,  1.0],
8                                     [ 1.0, -1.0,  1.0]]))
9
10 print 'BCC lattice constant = {0} Ang'.format(a * (11.8 / atoms.get_volume())**(1./3.))

```

Open the python script (dft-scripts/script-97.py).

BCC lattice constant = 2.86838428403 Ang

Now we run the equation of state calculations.

```

1 from jasp import *
2 from ase import Atom, Atoms
3
4 LC = [2.75, 2.8, 2.85, 2.9, 2.95, 3.0]
5
6 for a in LC:
7     atoms = Atoms([Atom('Cu', [0, 0, 0])],

```

```

8         cell=0.5 * a * np.array([[ 1.0,  1.0, -1.0],
9                                   [-1.0,  1.0,  1.0],
10                                  [ 1.0, -1.0,  1.0]])
11
12     with jasp('bulk/Cu-bcc-{}'.format(a),
13              xc='PBE',
14              encut=350,
15              kpts=(8, 8, 8),
16              atoms=atoms) as calc:
17         calc.calculate()

```

Open the python script (dft-scripts/script-98.py).
Finally, we will compare the two crystal structures.

```

1  from jasp import *
2
3  # bcc energies and volumes
4  bcc_LC = [2.75, 2.8, 2.85, 2.9, 2.95, 3.0]
5  bcc_volumes = []
6  bcc_energies = []
7  for a in bcc_LC:
8      with jasp('bulk/Cu-bcc-{}'.format(a)) as calc:
9          atoms = calc.get_atoms()
10         bcc_volumes.append(atoms.get_volume())
11         bcc_energies.append(atoms.get_potential_energy())
12
13  # fcc energies and volumes
14  fcc_LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
15  fcc_volumes = []
16  fcc_energies = []
17  for a in fcc_LC:
18      with jasp('bulk/Cu-fcc-{}'.format(a)) as calc:
19          atoms = calc.get_atoms()
20          fcc_volumes.append(atoms.get_volume())
21          fcc_energies.append(atoms.get_potential_energy())
22
23  import matplotlib.pyplot as plt
24  plt.plot(fcc_volumes, fcc_energies, label='fcc')
25  plt.plot(bcc_volumes, bcc_energies, label='bcc')
26
27  plt.xlabel('Atomic volume (Å³/atom)')
28  plt.ylabel('Total energy (eV)')
29  plt.legend()
30  plt.savefig('images/Cu-bcc-fcc.png')
31
32  # print table of data
33  print '#+tblname: bcc-data'
34  print '#+caption: Total energy vs. lattice constant for BCC Cu.'
35  print '| Lattice constant (Å³) | Total energy (eV) |'
36  print '|-'
37  for lc, e in zip(bcc_LC, bcc_energies):
38      print '| {} | {} |'.format(lc, e)

```

Open the python script (dft-scripts/script-99.py).

Table 4: Total energy vs. lattice constant for BCC Cu.

Lattice constant (Å ³)	Total energy (eV)
2.75	-3.587523
2.8	-3.668112
2.85	-3.708699
2.9	-3.716496
2.95	-3.697781
3.0	-3.657913

Exercise 4.3

Use the data for FCC and BCC Cu to plot the total energy as a function of the lattice constant.

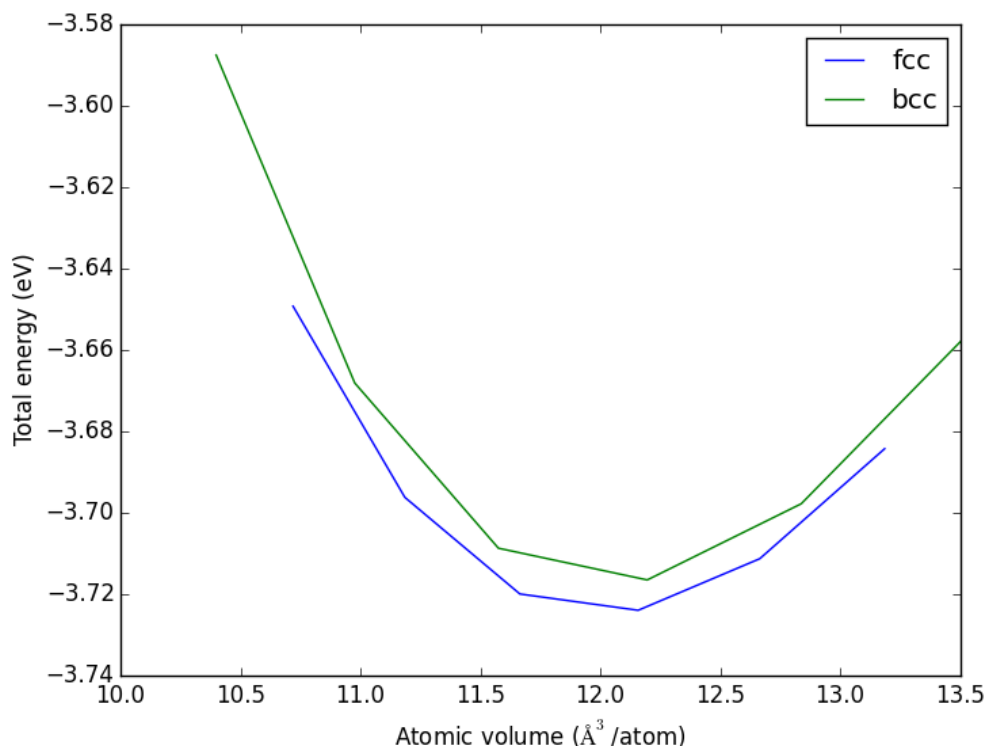


Figure 37: Comparison of energies between fcc and bcc Cu. The fcc structure is lower in energy.

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.

```

1 from ase.lattice.hexagonal import HexagonalClosedPacked
2 from jasp import *
3 import matplotlib.pyplot as plt
4
5 atoms = HexagonalClosedPacked(symbol='Ru',
6                               latticeconstant={'a': 2.7,
7                                               'c/a': 1.584})

```

```

8
9 a_list = [2.5, 2.6, 2.7, 2.8, 2.9]
10 covera_list = [1.4, 1.5, 1.6, 1.7, 1.8]
11
12 for a in a_list:
13     energies = []
14     for covera in covera_list:
15
16         atoms = HexagonalClosedPacked(symbol='Ru',
17                                       latticeconstant={'a': a,
18                                                       'c/a': covera})
19
20         wd = 'bulk/Ru/{0:1.2f}-{1:1.2f}'.format(a, covera)
21
22         with jasp(wd,
23                 xc='PBE',
24                 # the c-axis is longer than the a-axis, so we use
25                 # fewer kpoints.
26                 kpts=(6, 6, 4),
27                 encut=350,
28                 atoms=atoms) as calc:
29             try:
30                 energies.append(atoms.get_potential_energy())
31             except (VaspSubmitted, VaspQueued):
32                 pass
33     plt.plot(covera_list, energies, label=r'a={0} Å'.format(a))
34
35 plt.xlabel('$c/a$')
36 plt.ylabel('Energy (eV)')
37 plt.legend()
38 plt.savefig('images/Ru-covera-scan.png')
39 plt.show()

```

Open the python script (dft-scripts/script-100.py).

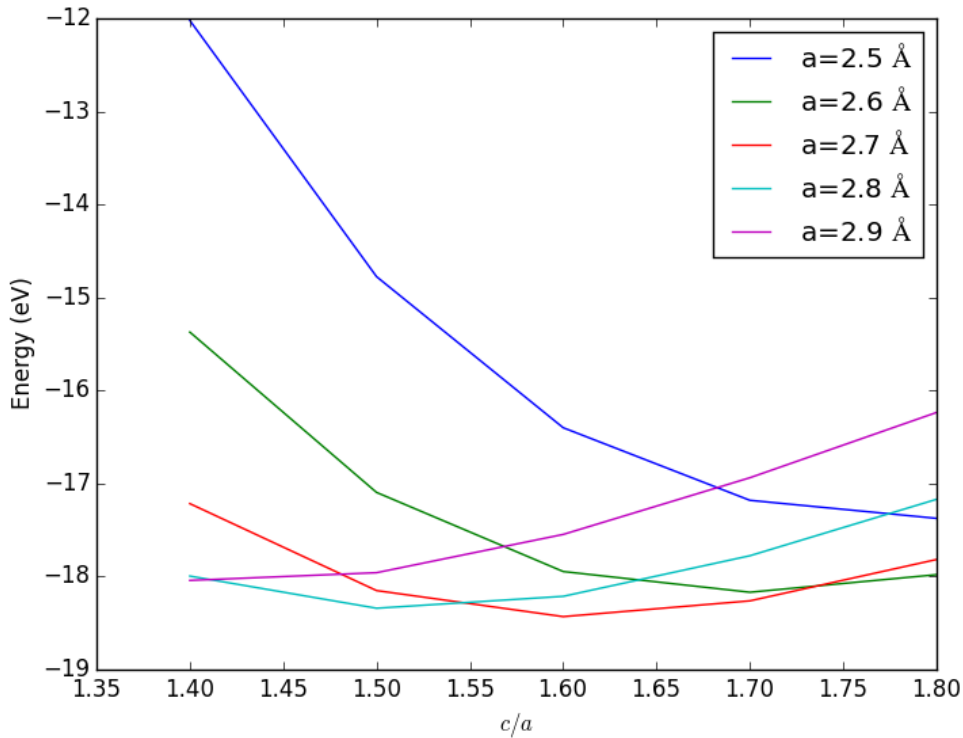


Figure 38: Total energy vs. c/a for different values of a .

It looks like there is a minimum in the $a=2.7 \text{ \AA}$ 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).

```

1  from jasp import *
2  import matplotlib.pyplot as plt
3
4  x = [2.5, 2.6, 2.7, 2.8, 2.9]
5  y = [1.4, 1.5, 1.6, 1.7, 1.8]
6
7  X,Y = np.meshgrid(x, y)
8  Z = np.zeros(X.shape)
9
10 for i,a in enumerate(x):
11     for j,covera in enumerate(y):
12
13         wd = 'bulk/Ru/{0:1.2f}-{1:1.2f}'.format(a,covera)
14
15         with jasp(wd) as calc:
16             atoms = calc.get_atoms()
17             try:
18                 Z[i][j] = atoms.get_potential_energy()
19             except (VaspSubmitted, VaspQueued):
20                 pass
21
22 cf = plt.contourf(X, Y, Z, 20,
23                  cmap=plt.cm.jet)
24
25 cbar = plt.colorbar(cf)
26 cbar.ax.set_ylabel('Energy (eV)')
27
28 plt.xlabel('$a$ ($\text{\AA}$)')
29 plt.ylabel('$c/a$')
30
31 plt.legend()
32 plt.savefig('images/ru-contourf.png')
33 plt.show()

```

Open the python script (dft-scripts/script-101.py).

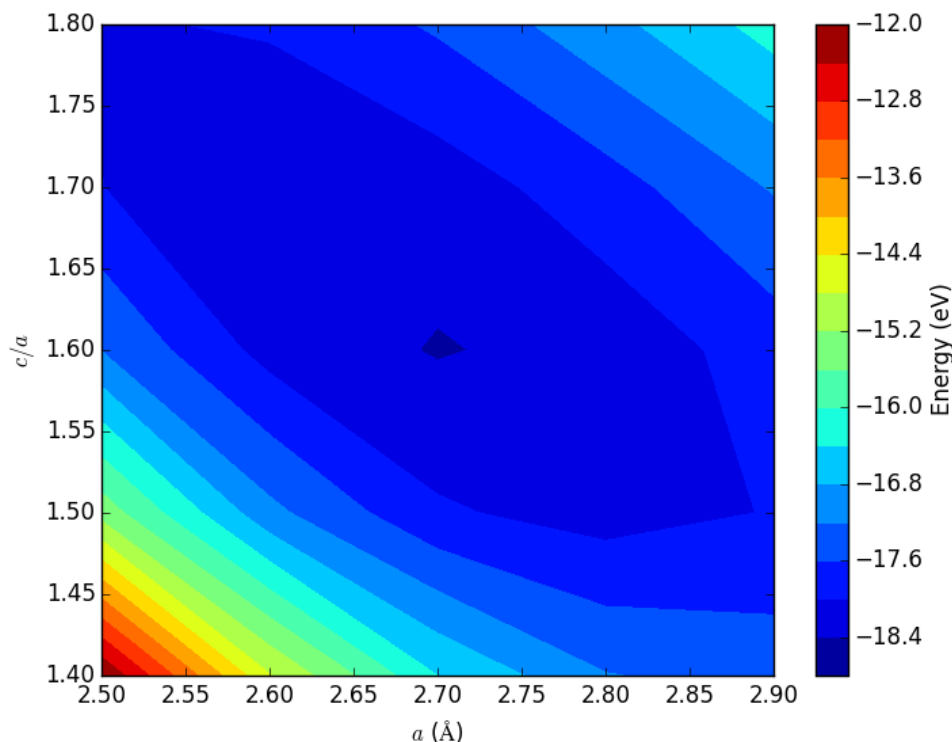


Figure 39: Contour plot of the total energy of hcp Ru for different values of a and c/a .

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 $1.3 \times \max(\text{ENMAX})$ 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 .

```
1 grep ENMAX $VASP_PP_PATH/POTPAW_PBE/Ti/POTCAR
2 grep ENMAX $VASP_PP_PATH/POTPAW_PBE/O/POTCAR
```

Open the python script (dft-scripts/script-102.py).

```
ENMAX = 178.330; ENMIN = 133.747 eV
ENMAX = 400.000; ENMIN = 300.000 eV
```

According to the manual, we should use $\text{ENCUT} = 1.3 \times 400 = 520$ 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.

```
1 # step 1 frozen atoms and shape at different volumes
2 from ase import Atom, Atoms
3 import numpy as np
4 from jasp import *
5 import matplotlib.pyplot as plt
6
7 '''
8 create a TiO2 structure from the lattice vectors at
9 http://cst-www.nrl.navy.mil/lattice/struk/c4.html
10 This site does not exist anymore.
11 '''
12 a = 4.59 # experimental degrees of freedom.
13 c = 2.96
14 u = 0.3 # internal degree of freedom!
15
16 #primitive vectors
17 a1 = a * np.array([1.0, 0.0, 0.0])
18 a2 = a * np.array([0.0, 1.0, 0.0])
19 a3 = c * np.array([0.0, 0.0, 1.0])
20
21 atoms = Atoms([Atom('Ti', [0., 0., 0.]),
22               Atom('Ti', 0.5 * a1 + 0.5 * a2 + 0.5 * a3),
23               Atom('O', u * a1 + u * a2),
24               Atom('O', -u * a1 - u * a2),
25               Atom('O', (0.5 + u) * a1 + (0.5 - u) * a2 + 0.5 * a3),
26               Atom('O', (0.5 - u) * a1 + (0.5 + u) * a2 + 0.5 * a3)],
27              cell=[a1, a2, a3])
28
29 KPOINTS = [2, 3, 4, 5, 6, 7, 8]
30 energies = []
31
32 ready = True
33 for k in KPOINTS:
34     with jasp('bulk/tio2/kpts-{}'.format(k),
35             encut=520,
36             kpts=(k, k, k),
37             xc='PBE',
38             sigma=0.05,
39             atoms=atoms) as calc:
40         try:
41             energies.append(atoms.get_potential_energy())
42         except (VaspSubmitted, VaspQueued):
43             ready = False
44
45 if not ready:
46     import sys; sys.exit()
47
48 plt.plot(KPOINTS, energies)
```

```

49 plt.xlabel('number of k-points in each vector')
50 plt.ylabel('Total energy (eV)')
51 plt.savefig('images/tio2-kpt-convergence.png')
52 plt.show()

```

Open the python script (dft-scripts/script-103.py).

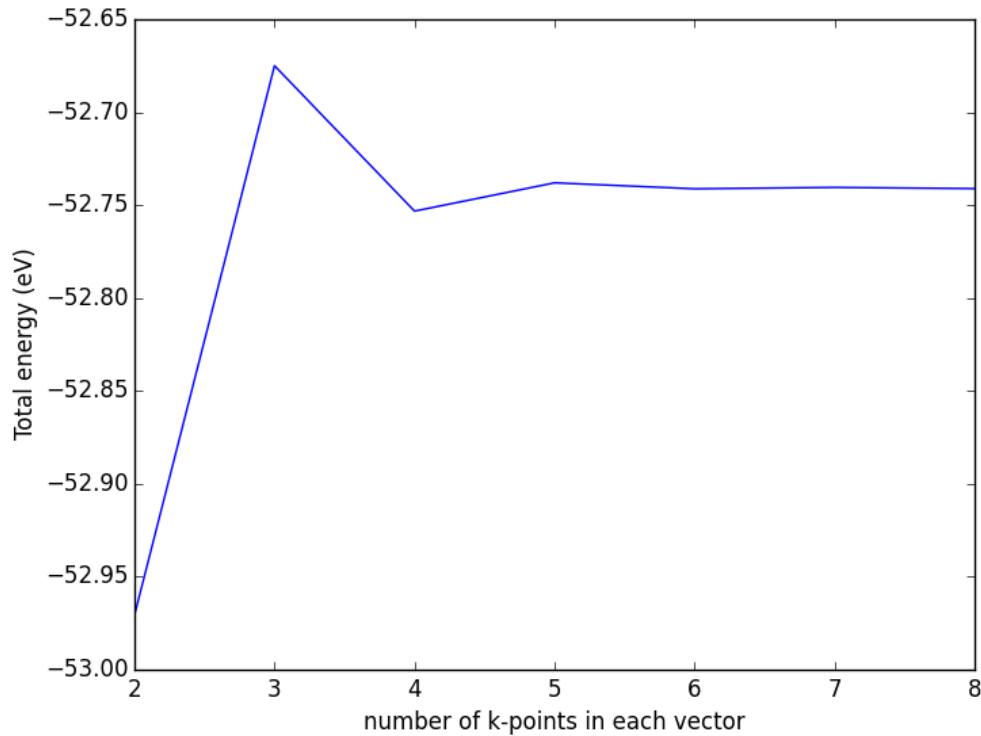


Figure 40: k-point convergence of rutile TiO_2 .

A k-point grid of $5 \times 5 \times 5$ 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.

```

1  # step 1 frozen atoms and shape at different volumes
2  from ase import Atom, Atoms
3  import numpy as np
4  from jasp import *
5  import matplotlib.pyplot as plt
6
7  '''
8  create a TiO2 structure from the lattice vectors at
9  http://cst-www.nrl.navy.mil/lattice/struk/c4.html
10  '''
11  a = 4.59 # experimental degrees of freedom.
12  c = 2.96
13  u = 0.3 # internal degree of freedom!
14
15  #primitive vectors
16  a1 = a * np.array([1.0, 0.0, 0.0])
17  a2 = a * np.array([0.0, 1.0, 0.0])
18  a3 = c * np.array([0.0, 0.0, 1.0])
19
20  atoms = Atoms([Atom('Ti', [0., 0., 0.]),

```



```

21         Atom('Ti', 0.5 * a1 + 0.5 * a2 + 0.5 * a3),
22         Atom('O', u * a1 + u * a2),
23         Atom('O', -u * a1 - u * a2),
24         Atom('O', (0.5 + u) * a1 + (0.5 - u) * a2 + 0.5 * a3),
25         Atom('O', (0.5 - u) * a1 + (0.5 + u) * a2 + 0.5 * a3)],
26         cell=[a1, a2, a3])
27
28 v0 = atoms.get_volume()
29 cell0 = atoms.get_cell()
30
31 factors = [0.9, 0.95, 1.0, 1.05, 1.1] #to change volume by
32
33 energies, volumes = [], []
34
35 ready = True
36 for f in factors:
37     v1 = f * v0
38     cell_factor = (v1 / v0)**(1. / 3.)
39
40     atoms.set_cell(cell0 * cell_factor, scale_atoms=True)
41
42     with jasp('bulk/tio2/step1-{:0:1.2f}'.format(f),
43             encut=520,
44             kpts=(5,5,5),
45             isif=2, # relax internal degrees of freedom
46             ibrion=1,
47             nsw=50,
48             xc='PBE',
49             sigma=0.05,
50             atoms=atoms) as calc:
51         try:
52             energies.append(atoms.get_potential_energy())
53             volumes.append(atoms.get_volume())
54         except (VaspSubmitted, VaspQueued):
55             ready = False
56
57 if not ready:
58     import sys; sys.exit()
59
60 plt.plot(volumes, energies)
61 plt.xlabel('Vol. (Å3)')
62 plt.ylabel('Total energy (eV)')
63 plt.savefig('images/tio2-step1.png')
64
65 print '#+tblname: tio2-vol-ene'
66 print '#+caption: Total energy of TiO2 vs. volume.'
67 print '| Volume (Å3) | Energy (eV) |'
68 print '|-'
69 for v, e in zip(volumes, energies):
70     print '| {0} | {1} |'.format(v, e)

```

Open the python script (dft-scripts/script-104.py).

Table 5: Total energy of TiO₂ vs. volume.

Volume (Å ³)	Energy (eV)
56.1254184	-51.820427
59.2434972	-52.462241
62.361576	-52.761097
65.4796548	-52.801329
68.5977336	-52.64715

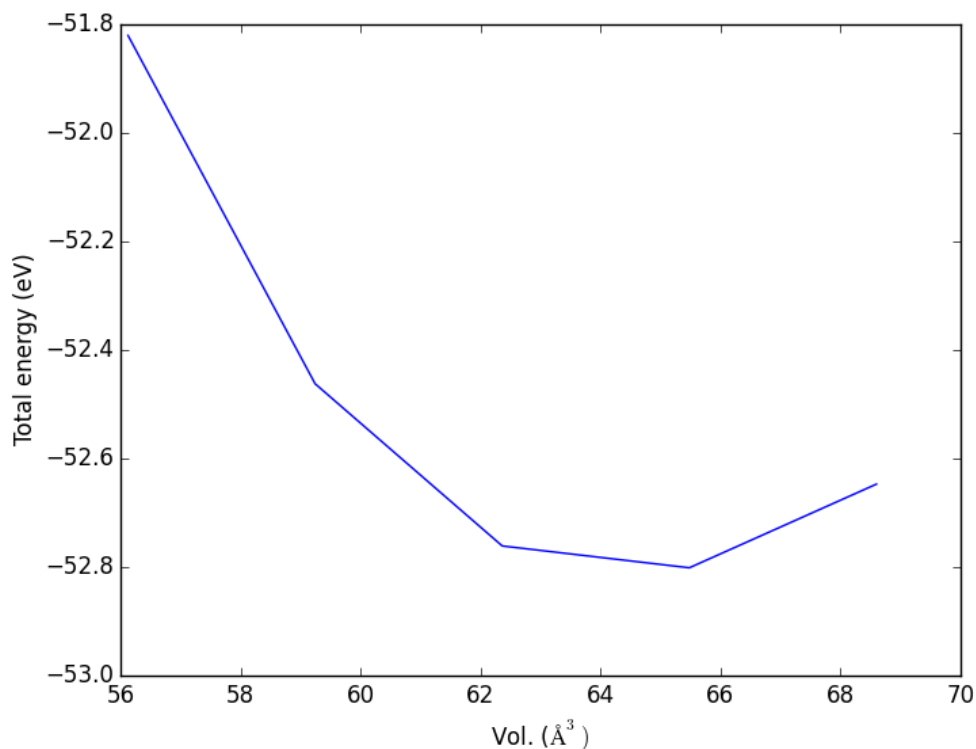


Figure 41: Total energy vs. volume for rutile TiO_2 in step 1 of the optimization.

Now, we know the minimum energy volume is near 64 \AA^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.

```

1  from jasp import *
2
3  factors = [0.9, 0.95, 1.0, 1.05, 1.1] # to change volume by
4
5  energies1, volumes1 = [], [] # from step 1
6  energies, volumes = [], [] # for step 2
7  ready = True
8  for f in factors:
9      with jasp('bulk/tio2/step1-{0:1.2f}'.format(f)) as calc:
10         atoms = calc.get_atoms()
11         energies1.append(atoms.get_potential_energy())
12         volumes1.append(atoms.get_volume())
13         calc.clone('bulk/tio2/step2-{0:1.2f}'.format(f))
14
15     # now set ISIF=4 and run
16     with jasp('bulk/tio2/step2-{0:1.2f}'.format(f),
17             isif=4) as calc:
18         atoms = calc.get_atoms()
19         try:
20             energies.append(atoms.get_potential_energy())
21             volumes.append(atoms.get_volume())
22         except (VaspSubmitted, VaspQueued):
23             ready = False
24
25 if not ready:
26     import sys; sys.exit()
27
28 import matplotlib.pyplot as plt
29 plt.plot(volumes1, energies1, volumes, energies)
30 plt.xlabel('Vol. ($\text{\AA}^3$)')
```

```

31 plt.ylabel('Total energy (eV)')
32 plt.legend(['step 1', 'step 2'], loc='best')
33 plt.savefig('images/tio2-step2.png')
34 plt.show()

```

Open the python script (dft-scripts/script-105.py).

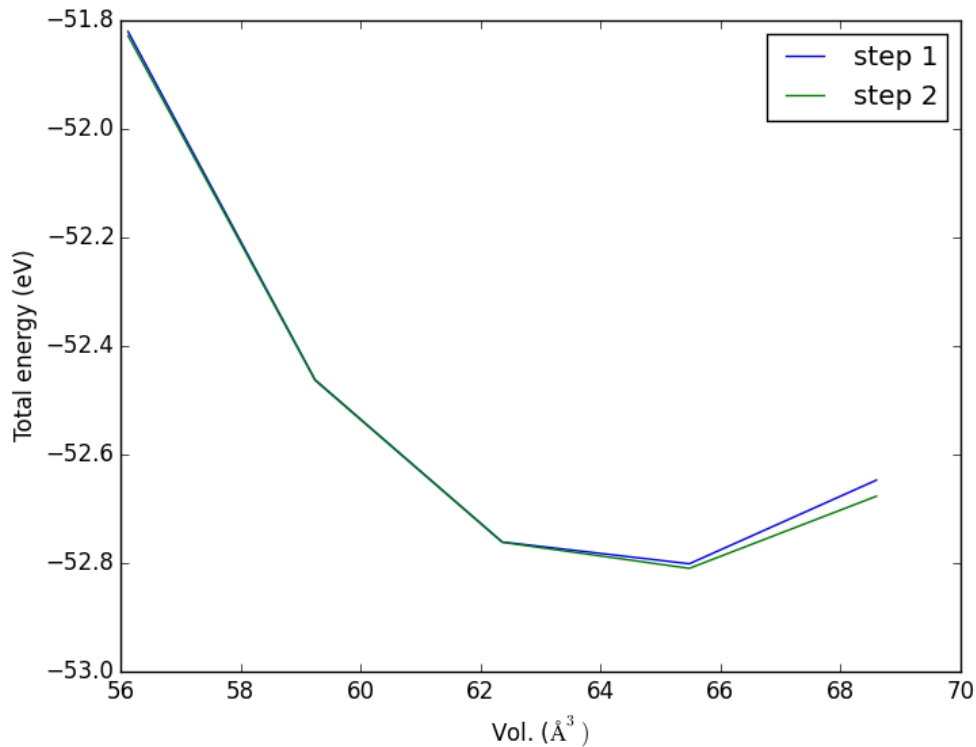


Figure 42: Total energy vs. volume for step 2 of the unit cell optimization.

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.

```

1 from jasp import *
2
3 with jasp('bulk/tio2/step2-1.05') as calc:
4     calc.clone('bulk/tio2/step3')
5
6 with jasp('bulk/tio2/step3',
7     isif=3) as calc:
8     calc.calculate()
9     atoms = calc.get_atoms()
10    print calc
11
12 from pyspilib import spglib
13 print '\n\nThe spacegroup is {0}'.format(spglib.get_spacegroup(atoms))

```

Open the python script (dft-scripts/script-106.py).

```
: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/tio2/step3
converged: True
Energy = -52.818610 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 4.661  0.000  0.000] 4.661
a1 [ 0.000  4.661  0.000] 4.661
a2 [ 0.000  0.000  2.970] 2.970
a,b,c,alpha,beta,gamma (deg):4.661 4.661 2.970 90.0 90.0 90.0
Unit cell volume = 64.515 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              -0.000 -0.000 -0.000-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Ti  [0.000      0.000      0.000] 0  0.00      T T T
  1    Ti  [2.331      2.331      1.485] 0  0.00      T T T
  2     O  [1.420      1.420      0.000] 0  0.00      T T T
  3     O  [3.241      3.241      0.000] 0  0.00      T T T
  4     O  [3.751      0.910      1.485] 0  0.00      T T T
  5     O  [0.910      3.751      1.485] 0  0.00      T T T
-----
```

INCAR Parameters:

```
-----
nbands: 20
nsw: 50
ibrion: 1
isif: 3
encut: 520.0
sigma: 0.05
magmom: None
prec: Normal
kpts: [5, 5, 5]
reciprocal: False
xc: PBE
txt: -
gamma: False
```

Pseudopotentials used:

```
-----
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)
Ti: potpaw_PBE/Ti/POTCAR (git-hash: a29a4f0f14083cf90544a3cf1ae7fc220b31829c)
```

The spacegroup is P4₂/mmn (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.

```

1 from jasp import *
2
3 with jasp('bulk/tio2/step3') as calc:
4     atoms = calc.get_atoms()
5     print 'default ismear: ', atoms.get_potential_energy()
6     calc.clone('bulk/tio2/step4')
7
8 with jasp('bulk/tio2/step4',
9     ismear=-5,
10    nsw=0) as calc:
11     atoms = calc.get_atoms()
12     print 'ismear=-5: ', atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-107.py).

```

default ismear:  -52.81861
ismear=-5:      -52.817345

```

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.⁵⁰ We examine several functionals. The `xc` keyword in `jasp` is used to select the POTCARs. The value of `xc` can be 'LDA', 'PW91' or 'PBE'. Let us consider the LDA functional first.

```

1 from jasp import *
2 from ase import Atom, Atoms
3 from ase.utils.eos import EquationOfState
4
5 LC = [3.75, 3.80, 3.85, 3.90, 3.95, 4.0, 4.05, 4.1]
6
7 volumes, energies = [], []
8 for a in LC:
9     atoms = Atoms([Atom('Pd', (0, 0, 0))],
10                  cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
11                                           [0.0, 1.0, 1.0],
12                                           [1.0, 0.0, 1.0]]))
13     with jasp('bulk/Pd-LDA-{0}'.format(a),
14              encut=350,
15              kpts=(12, 12, 12),
16              xc='LDA',
17              atoms=atoms):
18         try:
19             e = atoms.get_potential_energy()
20             energies.append(e)
21             volumes.append(atoms.get_volume())
22         except (VaspSubmitted, VaspQueued):
23             pass
24
25 if len(energies) == len(LC):
26     eos = EquationOfState(volumes, energies)
27     v0, e0, B = eos.fit()
28     print 'LDA lattice constant is {0:1.3f} Ang^3'.format((4*v0)**(1./3.))

```

Open the python script (dft-scripts/script-108.py).

```
LDA lattice constant is 3.855 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3  from ase.utils.eos import EquationOfState
4
5  LC = [3.75, 3.80, 3.85, 3.90, 3.95, 4.0, 4.05, 4.1]
6
7  GGA = {'AM': 'AM05',
8         'PE': 'PBE',
9         'PS': 'PBEsol',
10        'RP': 'RPBE'}
11
12  for key in GGA:
13      volumes, energies = [], []
14      for a in LC:
15          atoms = Atoms([Atom('Pd', (0, 0, 0))],
16                        cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
17                                                  [0.0, 1.0, 1.0],
18                                                  [1.0, 0.0, 1.0]]))
19          with jasp('bulk/Pd-GGA-{1}-{0}'.format(a, key),
20                  encut=350,
21                  kpts=(12, 12, 12),
22                  xc='LDA',
23                  gga=key,
24                  atoms=atoms):
25              try:
26                  e = atoms.get_potential_energy()
27                  energies.append(e)
28                  volumes.append(atoms.get_volume())
29              except (VaspSubmitted, VaspQueued):
30                  pass
31
32      if len(energies) == len(LC):
33          eos = EquationOfState(volumes, energies)
34          v0, e0, B = eos.fit()
35          print '{1:6s} lattice constant is {0:1.3f} Ang^3'.format((4*v0)**(1./3.),
36                                                                GGA[key])
37      else:
38          print energies, LC
39          print '{0} is not ready'.format(GGA[key])

```

Open the python script (dft-scripts/script-109.py).

```

PBEsol lattice constant is 3.885 Ang^3
AM05   lattice constant is 3.882 Ang^3
RPBE   lattice constant is 3.990 Ang^3
PBE    lattice constant is 3.952 Ang^3

```

These results compare very favorably to those in.⁵⁰ 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 Using built-in ase optimization with jasp

ASE has some nice optimization tools built into it. We can use them in jasp 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.

```

1  from jasp import *
2  from ase.lattice import bulk
3
4  Al = bulk('Al', 'fcc', a=4.5, cubic=True)
5  with jasp('bulk/Al-lda-vasp',
6          xc='LDA', isif=7, ns=5,
7          ibrion=1, ediffg=-1e-3,

```

```

8         lwave=False, lcharg=False,
9         atoms=Al) as calc:
10     calc.calculate(Al)
11     print calc

```

Open the python script (dft-scripts/script-110.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/Al-lda-vasp
converged: True
Energy = -10.128461 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 4.186  0.000  0.000] 4.186
a1 [ 0.000  4.186  0.000] 4.186
a2 [ 0.000  0.000  4.186] 4.186
a,b,c,alpha,beta,gamma (deg):4.186 4.186 4.186 90.0 90.0 90.0
Unit cell volume = 73.351 Ang^3
Stress (GPa):xx,   yy,   zz,   yz,   xz,   xy
              0.000  0.000  0.000-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Al  [0.000      0.000      0.000] 0  0.00      T T T
  1    Al  [0.000      2.093      2.093] 0  0.00      T T T
  2    Al  [2.093      0.000      2.093] 0  0.00      T T T
  3    Al  [2.093      2.093      0.000] 0  0.00      T T T
-----

```

INCAR Parameters:

```

-----
nbands: 10
nsw: 5
ibrion: 1
isif: 7
ediffg: -0.001
lcharg: False
lwave: False
magmom: None
kpts: [1, 1, 1]
reciprocal: False
xc: LDA
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
Al: potpaw/Al/POTCAR (git-hash: 654467a983b98bde034bc5918ee7817209863fe4)

```

```

1 from jasp import *
2 from ase.lattice import bulk
3 from ase.optimize import BFGS as QuasiNewton
4
5 Al = bulk('Al', 'fcc', a=4.5, cubic=True)
6
7 with jasp('bulk/Al-lda-ase',
8         xc='LDA',

```

```

9         atoms=Al) as calc:
10
11     from ase.constraints import StrainFilter
12     sf = StrainFilter(Al)
13     qn = QuasiNewton(sf, logfile='relaxation.log')
14     qn.run(fmax=0.1, steps=5)
15     print 'Stress:\n', calc.read_stress()
16     print 'Al post ASE volume relaxation\n', calc.get_atoms().get_cell()
17     print calc

```

Open the python script (dft-scripts/script-111.py).

```

Stress:
[ 0.  0.  0. -0. -0. -0.]
Al post ASE volume relaxation
[[ 4.187  0.  0.  ]
 [ 0.    4.187  0.  ]
 [ 0.    0.    4.187]]
: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/Al-lda-ase
converged: True
Energy = -10.111043 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 4.187  0.000  0.000] 4.187
a1 [ 0.000  4.187  0.000] 4.187
a2 [ 0.000  0.000  4.187] 4.187
a,b,c,alpha,beta,gamma (deg):4.187 4.187 90.0 90.0 90.0
Unit cell volume = 73.417 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              0.000  0.000  0.000-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Al  [0.000      0.000      0.000]  0  0.00      T T T
  1    Al  [0.000      2.094      2.094]  0  0.00      T T T
  2    Al  [2.094      0.000      2.094]  0  0.00      T T T
  3    Al  [2.094      2.094      0.000]  0  0.00      T T T
-----

```

INCAR Parameters:

```

-----
nbands: 10
magmom: None
kpts: [1, 1, 1]
reciprocal: False
xc: LDA
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
Al: potpaw/Al/POTCAR (git-hash: 654467a983b98bde034bc5918ee7817209863fe4)

```

Now for a detailed comparison:

```

1  from jasp import *
2
3  with jasp('bulk/Al-lda-vasp') as calc:
4      atoms = calc.get_atoms()
5
6  with jasp('bulk/Al-lda-ase') as calc:
7      atoms2 = calc.get_atoms()
8
9  import numpy as np
10
11  cellA = atoms.get_cell()
12  cellB = atoms2.get_cell()
13
14  print (np.abs(cellA - cellB) < 0.01).all()

```

Open the python script (dft-scripts/script-112.py).

True

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.

```

1  from jasp import *
2  from ase.lattice.cubic import FaceCenteredCubic
3  from ase import Atoms, Atom
4
5  # bulk system
6  atoms = FaceCenteredCubic(directions=[[0, 1, 1],
7                                         [1, 0, 1],
8                                         [1, 1, 0]],
9                               size=(1, 1, 1),
10                               symbol='Rh')
11
12  with jasp('bulk/bulk-rh',
13            xc='PBE',
14            encut=350,
15            kpts=(4, 4, 4),
16            isif=3,
17            ibrion=2,
18            nsw=10,
19            atoms=atoms) as calc:
20      bulk_energy = atoms.get_potential_energy()
21
22  # atomic system
23  atoms = Atoms([Atom('Rh', [5, 5, 5])],
24                cell=(7, 8, 9))
25
26  with jasp('bulk/atomic-rh',
27            xc='PBE',
28            encut=350,
29            kpts=(1, 1, 1),
30            atoms=atoms) as calc:
31      atomic_energy = atoms.get_potential_energy()
32
33  cohesive_energy = atomic_energy - bulk_energy
34  print 'The cohesive energy is {0:1.3f} eV'.format(cohesive_energy)

```

Open the python script (dft-scripts/script-113.py).

The cohesive energy is 6.187 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.

```

1 from jasp import *
2
3 with jasp('bulk/atomic-rh') as calc:
4     atoms = calc.get_atoms()
5     atomic_energy = atoms.get_potential_energy()
6
7 with jasp('bulk/bulk-rh') as calc:
8     atoms = calc.get_atoms()
9
10 kpts = [3, 4, 6, 9, 12, 15, 18]
11
12 for k in kpts:
13     with jasp('bulk/bulk-rh-kpts-{}'.format(k),
14             xc='PBE',
15             encut=350,
16             kpts=(k, k, k),
17             atoms=atoms) as calc:
18         e = atoms.get_potential_energy()
19
20 print('{0:2d}, {0:2d}, {0:2d}: cohesive energy = {1} eV'.format(k,e-atomic_energy))

```

Open the python script (dft-scripts/script-114.py).

```

( 3,  3,  3): cohesive energy = -4.837472 eV
( 4,  4,  4): cohesive energy = -6.189573 eV
( 6,  6,  6): cohesive energy = -6.210668 eV
( 9,  9,  9): cohesive energy = -6.208576 eV
(12, 12, 12): cohesive energy = -6.215367 eV
(15, 15, 15): cohesive energy = -6.215319 eV
(18, 18, 18): cohesive energy = -6.216032 eV

```

Using only 1 k-point for the bulk energy is a terrible approximation! It takes at least a $6 \times 6 \times 6$ 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.

```

1 from jasp import *
2 from ase.lattice.cubic import FaceCenteredCubic
3 from ase import Atoms, Atom
4 # bulk system
5 atoms = FaceCenteredCubic(directions=[[0, 1, 1],
6                                     [1, 0, 1],
7                                     [1, 1, 0]],
8                           size=(1, 1, 1),
9                           symbol='Rh')
10
11 with jasp('bulk/bulk-rh',
12         xc='PBE',
13         encut=350,
14         kpts=(4, 4, 4),
15         isif=3,
16         ibrion=2,
17         nsf=10,
18         atoms=atoms) as calc:
19     bulk_energy = atoms.get_potential_energy()
20

```

```

21 # atomic system
22 atoms = Atoms([Atom('Rh',[5, 5, 5], magmom=1)],
23               cell=(7, 8, 9))
24
25 with jasp('bulk/atomic-rh-sp',
26           xc='PBE',
27           encut=350,
28           kpts=(1, 1, 1),
29           ispin=2,
30           atoms=atoms) as calc:
31     atomic_energy = atoms.get_potential_energy()
32
33 cohesive_energy = atomic_energy - bulk_energy
34 print 'The cohesive energy is {0:1.3f} eV'.format(cohesive_energy)

```

Open the python script (dft-scripts/script-115.py).

The cohesive energy is 5.887 eV

Again, the value in Kittel⁴ 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.⁵¹

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.

```

1 from jasp import *
2 from ase.lattice.cubic import BodyCenteredCubic
3
4 atoms = BodyCenteredCubic(symbol='Fe')
5 for atom in atoms:
6     atom.magmom = 3.0
7
8 with jasp('bulk/Fe-bulk',
9           xc='PBE',
10          kpts=(6, 6, 6),
11          encut=350,
12          ispin=2,
13          isif=3,
14          nsr=30,
15          ibrion=1,
16          atoms=atoms) as calc:
17     print atoms.get_potential_energy()
18     print atoms.get_stress()

```

Open the python script (dft-scripts/script-116.py).

```

-16.604623
[-0.001 -0.001 -0.001 -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)

```

1 from jasp import *
2
3 with jasp('bulk/Fe-bulk') as calc:

```

```

4     calc.clone('bulk/Fe-elastic')
5
6 with jasp('bulk/Fe-elastic',
7         ibrion=6,      #
8         isif=3,       # gets elastic constants
9         potim=0.05,   # displacements
10        nsw=1,
11        nfree=2) as calc:
12     atoms = calc.get_atoms()
13     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-117.py).

-16.592189

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.

```

1 import numpy as np
2 EM = []
3
4 with open('bulk/Fe-elastic/OUTCAR') as f:
5     lines = f.readlines()
6     for i, line in enumerate(lines):
7         if line.startswith(' TOTAL ELASTIC MODULI (kBar)'):
8             j = i + 3
9             data = lines[j:j+6]
10            break
11
12 for line in data:
13     EM += [[float(x) for x in line.split()[1:]]]
14
15 print np.array(EM)

```

Open the python script (dft-scripts/script-118.py).

```

[[ 2803.5081  1622.6085  1622.6085    0.         0.         0.        ]
 [ 1622.6085  2803.5081  1622.6085    0.         0.         0.        ]
 [ 1622.6085  1622.6085  2803.5081    0.         0.         0.        ]
 [    0.         0.         0.        866.8792    0.         0.        ]
 [    0.         0.         0.         0.        866.8792    0.        ]
 [    0.         0.         0.         0.         0.        866.8792]]

```

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 jasp.

4.6.2 Al elastic properties

First, the relaxed geometry.

```

1 from jasp import *
2 from ase.lattice.cubic import FaceCenteredCubic
3
4 atoms = FaceCenteredCubic(symbol='Al')
5
6 with jasp('bulk/Al-bulk',
7          xc='PBE',
8          kpts=(12, 12, 12),
9          encut=350,
10         prec='High',
11         isif=3,
12         nsf=30,
13         ibrion=1,
14         atoms=atoms) as calc:
15     print atoms.get_potential_energy()
16     print atoms.get_stress()

```

Open the python script (dft-scripts/script-119.py).

```

-14.96989
[-0.127 -0.127 -0.127  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.

```

1 from jasp import *
2 from jasp.elastic_moduli import *
3
4 with jasp('bulk/Al-bulk') as calc:

```

```

5     calc.clone('bulk/Al-elastic')
6
7 with jasp('bulk/Al-elastic',
8         ibrion=6,      #
9         isif=3,        # gets elastic constants
10        potim=0.015,   # displacements
11        nsw=1,
12        nfree=2) as calc:
13     atoms = calc.get_atoms()
14     print atoms.get_potential_energy()
15     EM = calc.get_elastic_moduli()
16     print EM
17
18 c11 = EM[0,0]
19 c12 = EM[0,1]
20 B = (c11 + 2 * c12) / 3.0
21 print B

```

Open the python script (dft-scripts/script-120.py).

```

-14.969509
[[ 98.944  66.153  66.153   0.      0.      0.   ]
 [ 66.153  98.944  66.153   0.      0.      0.   ]
 [ 66.153  66.153  98.944   0.      0.      0.   ]
 [   0.      0.      0.      1.687   0.      0.   ]
 [   0.      0.      0.      0.      1.687   0.   ]
 [   0.      0.      0.      0.      0.      1.687]]
77.08309

```

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.

4.7 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 Reference⁵² 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.

```

1 from jasp import *
2 from ase import Atom, Atoms
3
4 # fcc
5 LC = [3.5, 3.55, 3.6, 3.65, 3.7, 3.75]
6 volumes, energies = [], []
7 for a in LC:
8     atoms = Atoms([Atom('Ni', (0, 0, 0), magmom=2.5)],
9                  cell=0.5 * a * np.array([[1.0, 1.0, 0.0],
10                                           [0.0, 1.0, 1.0],
11                                           [1.0, 0.0, 1.0]]))
12
13     with jasp('bulk/Ni-{}'.format(a),
14             xc='PBE',
15             encut=350,
16             kpts=(12,12,12),
17             ispin=2,
18             atoms=atoms) as calc:
19         try:
20             e = atoms.get_potential_energy()
21             energies.append(e)
22             volumes.append(atoms.get_volume())
23         except:
24             pass
25
26 if len(energies) != len(LC):

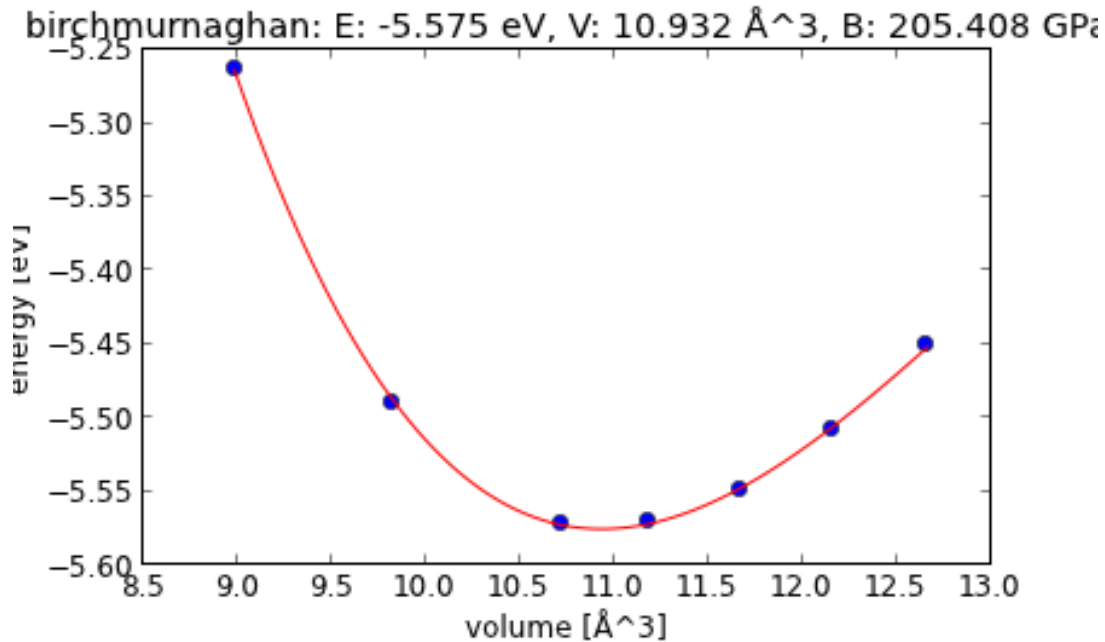
```

```

27     import sys; sys.exit()
28
29 import matplotlib.pyplot as plt
30 plt.plot(LC, fcc_energies)
31 plt.xlabel('Lattice constant ($\AA$)')
32 plt.ylabel('Total energy (eV)')
33 plt.savefig('images/Ni-fcc.png')

```

Open the python script (dft-scripts/script-121.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 TiO₂ 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 $E_{\text{rutile}}(V)$ and $E_{\text{anatase}}(V)$.

```

1  # run the rutile calculations
2  from jasp import *
3  from ase import Atom, Atoms
4
5  B = 'Ti'; X = 'O'; a = 4.59; c = 2.958; u = 0.305;
6  '''
7  create a rutile structure from the lattice vectors at
8  http://cst-www.nrl.navy.mil/lattice/struk/c4.html
9
10 spacegroup: 136 P4_2/mmm
11 '''
12 a1 = a * np.array([1.0, 0.0, 0.0])
13 a2 = a * np.array([0.0, 1.0, 0.0])
14 a3 = c * np.array([0.0, 0.0, 1.0])
15
16 atoms = Atoms([Atom(B, [0., 0., 0.]),
17               Atom(B, 0.5*a1 + 0.5*a2 + 0.5*a3),

```

```

18         Atom(X, u*a1 + u*a2),
19         Atom(X, -u*a1 - u*a2),
20         Atom(X, (0.5+u)*a1 + (0.5-u)*a2 + 0.5*a3),
21         Atom(X, (0.5-u)*a1 + (0.5+u)*a2 + 0.5*a3)],
22         cell=[a1, a2, a3])
23
24 nTiO2 = len(atoms) / 3.
25 v0 = atoms.get_volume()
26 cell0 = atoms.get_cell()
27
28 volumes = [28., 30., 32., 34., 36.] #vol of one TiO2
29
30 for v in volumes:
31     atoms.set_cell(cell0 * ((nTiO2 * v / v0)**(1. / 3.)),
32                     scale_atoms=True)
33
34     with jasp('bulk/TiO2/rutile/rutile-{0}'.format(v),
35              encut=350,
36              kpts=(6, 6, 6),
37              xc='PBE',
38              smear=0,
39              sigma=0.001,
40              isif=2,
41              ibrion=2,
42              nsw=20,
43              atoms=atoms) as calc:
44         try:
45             calc.calculate()
46         except (VaspSubmitted, VaspQueued):
47             pass

```

Open the python script (dft-scripts/script-122.py).

```

1  # run the anatase calculations
2  from jasp import *
3  from ase import Atom, Atoms
4  # http://cst-www.nrl.navy.mil/lattice/struk/c5.html
5
6  B = 'Ti'; X = 'O'; a = 3.7842; c = 2*4.7573; z = 0.0831;
7
8  a1 = a * np.array([1.0, 0.0, 0.0])
9  a2 = a * np.array([0.0, 1.0, 0.0])
10 a3 = np.array([0.5 * a, 0.5 * a, 0.5 * c])
11
12 atoms = Atoms([Atom(B, -0.125 * a1 + 0.625 * a2 + 0.25 * a3),
13               Atom(B, 0.125 * a1 + 0.375 * a2 + 0.75 * a3),
14               Atom(X, -z*a1 + (0.25-z)*a2 + 2.*z*a3),
15               Atom(X, -(0.25+z)*a1 + (0.5-z)*a2 + (0.5+2*z)*a3),
16               Atom(X, z*a1 - (0.25 - z)*a2 + (1-2*z)*a3),
17               Atom(X, (0.25 + z)*a1 + (0.5 + z)*a2 + (0.5-2*z)*a3)],
18               cell=[a1,a2,a3])
19
20 nTiO2 = len(atoms) / 3.
21 v0 = atoms.get_volume()
22 cell0 = atoms.get_cell()
23
24 volumes = [30., 33., 35., 37., 39.] #vol of one TiO2
25
26 for v in volumes:
27     atoms.set_cell(cell0 * ((nTiO2*v/v0)**(1./3.)),
28                     scale_atoms=True)
29
30     with jasp('bulk/TiO2/anatase/anatase-{0}'.format(v),
31              encut=350,
32              kpts=(6, 6, 6),
33              xc='PBE',
34              smear=0,
35              sigma=0.001,
36              isif=2,
37              ibrion=2,
38              nsw=20,
39              atoms=atoms) as calc:
40         try:
41             calc.calculate()
42         except (VaspSubmitted, VaspQueued):
43             pass

```

Open the python script (dft-scripts/script-123.py).
Now we will fit cubic polynomials to the data.

```

1  # fit cubic polynomials to E(V) for rutile and anatase
2  from jasp import *
3  import matplotlib.pyplot as plt
4  import numpy as np
5  np.set_printoptions(precision=2)
6
7  # anatase equation of state
8  volumes = [30., 33., 35., 37., 39.] # vol of one TiO2 formula unit
9  a_volumes, a_energies = [], []
10 for v in volumes:
11     with jasp('bulk/TiO2/anatase/anatase-{0}'.format(v)) as calc:
12         atoms = calc.get_atoms()
13         nTiO2 = len(atoms) / 3.0
14         a_volumes.append(atoms.get_volume() / nTiO2)
15         a_energies.append(atoms.get_potential_energy() / nTiO2)
16
17 # rutile equation of state
18 volumes = [28., 30., 32., 34., 36.] # vol of one TiO2
19 r_volumes, r_energies = [], []
20 for v in volumes:
21     with jasp('bulk/TiO2/rutile/rutile-{0}'.format(v)) as calc:
22         atoms = calc.get_atoms()
23         nTiO2 = len(atoms) / 3.0
24         r_volumes.append(atoms.get_volume() / nTiO2)
25         r_energies.append(atoms.get_potential_energy() / nTiO2)
26
27 # cubic polynomial fit to equation of state E(V) = pars*[V^3 V^2 V^1 V^0]
28 apars = np.polyfit(a_volumes, a_energies, 3)
29 rpars = np.polyfit(r_volumes, r_energies, 3)
30
31 print 'E_anatase(V) = {0:1.2f}*V^3 + {1:1.2f}*V^2 + {2:1.2f}*V + {3:1.2f}'.format(*apars)
32 print 'E_rutile(V) = {0:1.2f}*V^3 + {1:1.2f}*V^2 + {2:1.2f}*V + {3:1.2f}'.format(*rpars)
33 print 'anatase epars: {0!r}'.format(apars)
34 print 'rutile epars: {0!r}'.format(rpars)
35 # get pressure parameters P(V) = -dE/dV
36 dapars = -np.polyder(apars)
37 drpars = -np.polyder(rpars)
38
39 print 'anatase ppars: {0!r}'.format(dapars)
40 print 'rutile ppars: {0!r}'.format(drpars)
41
42 print
43 print 'P_anatase(V) = {0:1.2f}*V^2 + {1:1.2f}*V + {2:1.2f}'.format(*dapars)
44 print 'P_rutile(V) = {0:1.2f}*V^2 + {1:1.2f}*V + {2:1.2f}'.format(*drpars)
45
46 vfit = np.linspace(28, 40)
47
48 # plot the equations of state
49 plt.plot(a_volumes, a_energies, 'bo ', label='Anatase')
50 plt.plot(vfit, np.polyval(apars, vfit), 'b-')
51
52 plt.plot(r_volumes, r_energies, 'gs ', label='Rutile')
53 plt.plot(vfit, np.polyval(rpars, vfit), 'g-')
54
55 plt.xlabel('Volume ($\text{\AA}^3/\text{f.u.}$)')
56 plt.ylabel('Total energy (eV/f.u.)')
57 plt.legend()
58 plt.xlim([25, 40])
59 plt.ylim([-27, -26])
60 plt.savefig('images/rutile-anatase-eos.png')

```

Open the python script (dft-scripts/script-124.py).

```

E_anatase(V) = -0.00*V^3 + 0.13*V^2 + -5.23*V + 42.47
E_rutile(V) = -0.00*V^3 + 0.14*V^2 + -5.33*V + 38.59
anatase epars: array([-0. ,  0.13, -5.23, 42.47])
rutile epars: array([-0. ,  0.14, -5.33, 38.59])
anatase ppars: array([ 0. , -0.26,  5.23])
rutile ppars: array([ 0. , -0.29,  5.33])

```

$$P_{\text{anatase}}(V) = 0.00 \cdot V^2 + -0.26 \cdot V + 5.23$$

$$P_{\text{rutile}}(V) = 0.00 \cdot V^2 + -0.29 \cdot V + 5.33$$

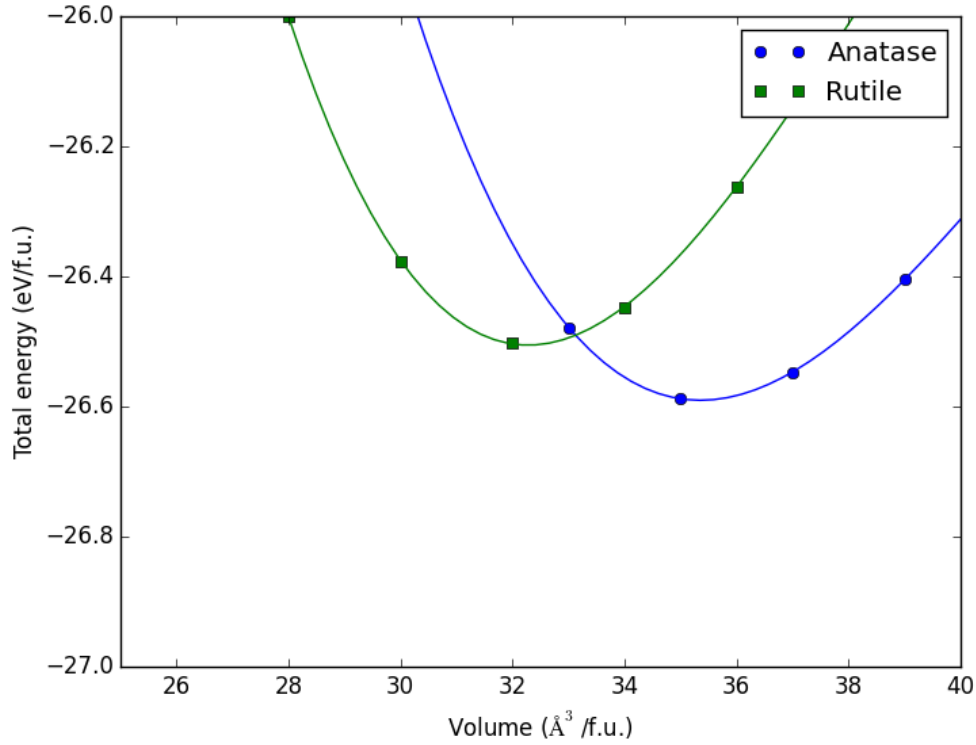


Figure 43: Equations of state ($E(V)$) for anatase and rutile TiO_2 .

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:

$$(E_{\text{anatase}}(V1) - E_{\text{rutile}}(V2)) / (V1 - V2) = P_{\text{anatase}}(V1)$$

$$(E_{\text{anatase}}(V1) - E_{\text{rutile}}(V2)) / (V1 - V2) = P_{\text{rutile}}(V2)$$

This is a nonlinear algebra problem. We use the `scipy.optimize.fsolve` to solve this problem.

```

1 from ase.units import GPa
2 from numpy import array, linspace, polyval
3
4 # copied from polynomial fit above
5 anatase_epars = array([-1.06049246e-03,  1.30279404e-01, -5.23520055e+00,
6                        4.25202869e+01])
7 rutile_epars = array([-1.24680208e-03,  1.42966536e-01, -5.33239733e+00,
8                        3.85903670e+01])
9
10 # polynomial fits for pressures
11 anatase_ppars = array([3.18147737e-03, -2.60558808e-01,  5.23520055e+00])
12 rutile_ppars = array([3.74040625e-03, -2.85933071e-01,  5.33239733e+00])
13
14
15 def func(V):
16     V1 = V[0] # rutile volume
17     V2 = V[1] # anatase volume
18
19     E_rutile = polyval(rutile_epars, V1)
```

```

20     E_anatase = polyval(anatase_epars, V2)
21
22     P_rutile = polyval(rutile_ppars, V1)
23     P_anatase = polyval(anatase_ppars, V2)
24
25     return [(E_anatase - E_rutile) / (V1 - V2) - P_anatase,
26            (E_anatase - E_rutile) / (V1 - V2) - P_rutile]
27
28 from scipy.optimize import fsolve
29 x0 = fsolve(func, [28, 34])
30 print 'The solutions are at V = {0}'.format(x0)
31 print 'Anatase pressure: {0} GPa'.format(polyval(anatase_ppars, x0[1]) / GPa)
32 print 'Rutile pressure: {0} GPa'.format(polyval(rutile_ppars, x0[0]) / GPa)
33
34 # illustrate the common tangent
35 import matplotlib.pyplot as plt
36
37 vfit = linspace(28, 40)
38 plt.plot(vfit, polyval(anatase_epars, vfit), label='anatase')
39 plt.plot(vfit, polyval(rutile_epars, vfit), label='rutile')
40 plt.plot(x0, [polyval(rutile_epars, x0[0]),
41               polyval(anatase_epars, x0[1])], 'ko-', label='common tangent')
42 plt.legend()
43 plt.xlabel('Volume ($\AA^3$/f.u.)')
44 plt.ylabel('Total energy (eV/f.u.)')
45 plt.savefig('images/eos-common-tangent.png')

```

Open the python script (dft-scripts/script-125.py).

```

The solutions are at V = [ 31.67490656  34.60893508]
Anatase pressure: 4.52495142656 GPa
Rutile pressure: 4.5249514267 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.

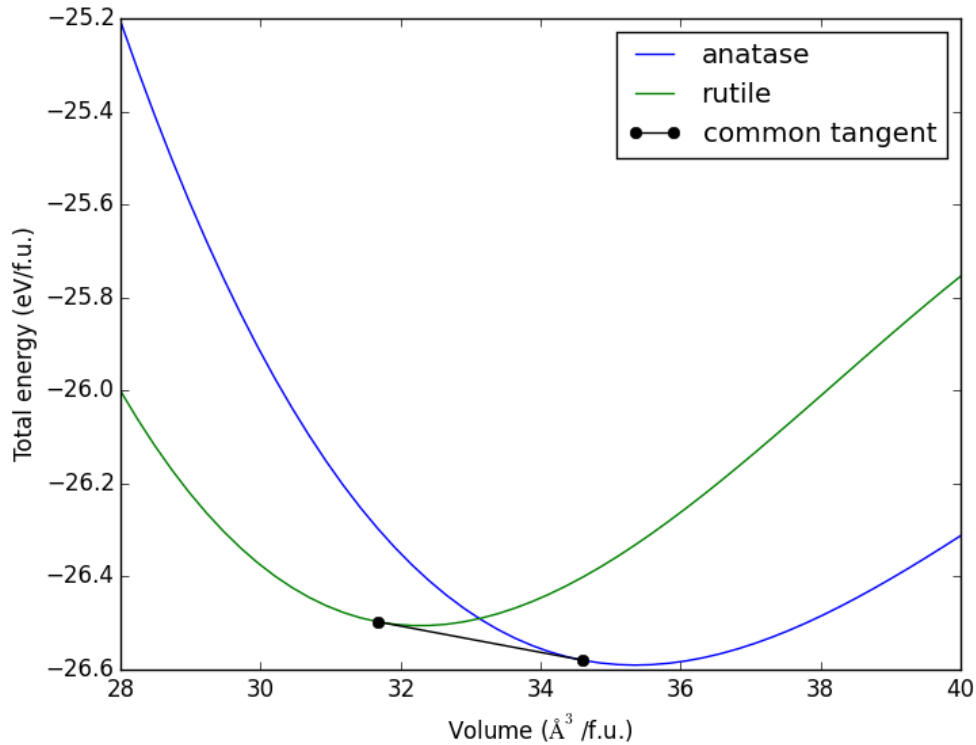


Figure 44: Illustration of the common tangent that shows the pressure where anatase and rutile coexist before anatase converts to rutile.

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

```
1 # get bulk Cu and Pd energies. <<pure-metal-components>>
2 from jasp import *
3 from ase import Atom, Atoms
4
5 atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000])),
6               cell= [[ 1.818, 0.000, 1.818],
7                     [ 1.818, 1.818, 0.000],
8                     [ 0.000, 1.818, 1.818]])
9
10 with jasp('bulk/alloy/cu',
11          xc='PBE',
12          encut=350,
13          kpts=(13, 13, 13),
14          nbands=9,
15          ibrion=2,
16          isif=3,
17          nsw=10,
18          atoms=atoms) as calc:
19     cu = atoms.get_potential_energy()
20
21 atoms = Atoms([Atom('Pd', [0.000, 0.000, 0.000])),
22               cell= [[ 1.978, 0.000, 1.978],
23                     [ 1.978, 1.978, 0.000],
24                     [ 0.000, 1.978, 1.978]])
25
26 with jasp('bulk/alloy/pd',
27          xc='PBE',
28          encut=350,
29          kpts=(13, 13, 13),
30          nbands=9,
31          ibrion=2,
32          isif=3,
33          nsw=10,
34          atoms=atoms) as calc:
35     pd = atoms.get_potential_energy()
36
37 print 'Cu energy = {0} eV'.format(cu)
38 print 'Pd energy = {0} eV'.format(pd)
```

Open the python script (dft-scripts/script-126.py).

Cu energy = -3.723352 eV

Pd energy = -5.18438 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.

```
1 from jasp import *
2 from ase import Atom, Atoms
3
4 atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000]),
5                 Atom('Pd', [-1.652, 0.000, 2.039])),
6               cell= [[0.000, -2.039, 2.039],
7                     [0.000, 2.039, 2.039],
8                     [-3.303, 0.000, 0.000]])
9
10 with jasp('bulk/alloy/cupd-1',
11          xc='PBE',
12          encut=350,
13          kpts=(12, 12, 8),
14          nbands=17,
15          ibrion=2,
```

```

16         isif=3,
17         nsw=10,
18         atoms=atoms) as calc:
19     cupd1 = atoms.get_potential_energy()
20
21     atoms = Atoms([Atom('Cu', [-0.049, 0.049, 0.049]),
22                     Atom('Cu', [-11.170, 11.170, 11.170]),
23                     Atom('Pd', [-7.415, 7.415, 7.415]),
24                     Atom('Pd', [-3.804, 3.804, 3.804])],
25                   cell=[[-5.629, 3.701, 5.629 ],
26                         [-3.701, 5.629, 5.629 ],
27                         [-5.629, 5.629, 3.701 ]])
28
29     with jasp('bulk/alloy/cupd-2',
30              xc='PBE',
31              encut=350,
32              kpts=(8,8,8),
33              nbands=34,
34              ibrion=2,
35              isif=3,
36              nsw=10,
37              atoms=atoms) as calc:
38     cupd2 = atoms.get_potential_energy()
39
40     print 'cupd-1 = {0} eV'.format(cupd1)
41     print 'cupd-2 = {0} eV'.format(cupd2)

```

Open the python script (dft-scripts/script-127.py).

```

cupd-1 = -9.148409 eV
cupd-2 = -17.979436 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.

```

1  from jasp import *
2
3  with jasp('bulk/alloy/cupd-1') as calc:
4      atoms = calc.get_atoms()
5      e1 = atoms.get_potential_energy()/len(atoms)
6
7  with jasp('bulk/alloy/cupd-2') as calc:
8      atoms = calc.get_atoms()
9      e2 = atoms.get_potential_energy()/len(atoms)
10
11  print 'cupd-1: {0} eV/atom'.format(e1)
12  print 'cupd-2: {0} eV/atom'.format(e2)

```

Open the python script (dft-scripts/script-128.py).

```

cupd-1: -4.5742045 eV/atom
cupd-2: -4.494859 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:

$\text{Cu} + \text{Pd} \rightarrow \text{CuPd}$ 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.

```

1  from jasp import *
2
3  # bulk energy 1

```

```

4  with jasp('bulk/alloy/cu') as calc:
5      atoms = calc.get_atoms()
6      cu = atoms.get_potential_energy()/len(atoms)
7
8  # bulk energy 2
9  with jasp('bulk/alloy/pd') as calc:
10     atoms = calc.get_atoms()
11     pd = atoms.get_potential_energy()/len(atoms)
12
13  with jasp('bulk/alloy/cupd-1') as calc:
14     atoms = calc.get_atoms()
15     e1 = atoms.get_potential_energy()
16     # subtract bulk energies off of each atom in cell
17     for atom in atoms:
18         if atom.symbol == 'Cu':
19             e1 -= cu
20         else:
21             e1 -= pd
22     e1 /= len(atoms) # normalize by number of atoms in cell
23
24  with jasp('bulk/alloy/cupd-2') as calc:
25     atoms = calc.get_atoms()
26     e2 = atoms.get_potential_energy()
27     for atom in atoms:
28         if atom.symbol == 'Cu':
29             e2 -= cu
30         else:
31             e2 -= pd
32     e2 /= len(atoms)
33
34  print 'Delta Hf cupd-1 = {0:1.2f} eV/atom'.format(e1)
35  print 'Delta Hf cupd-2 = {0:1.2f} eV/atom'.format(e2)

```

Open the python script (dft-scripts/script-129.py).

Delta Hf cupd-1 = -0.12 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.

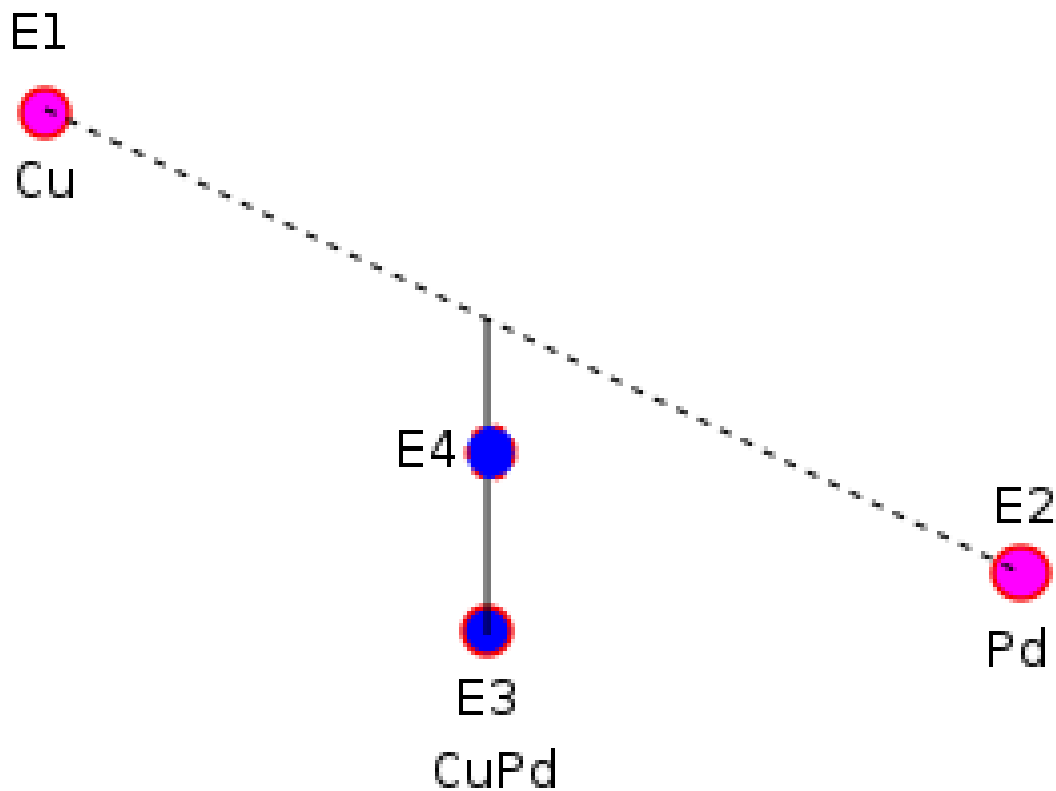


Figure 45: Conceptual picture of two alloys with exothermic formation energies. The dashed line represents a composition weighted average energy of the parent metals. E4 and E3 are energies associated with two different alloy structures at the same composition. Both structures are more stable than a 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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  # parent metals
5  with jasp('bulk/alloy/cu') as calc:
6      atoms = calc.get_atoms()
7      cu = atoms.get_potential_energy()/len(atoms)
8
9  with jasp('bulk/alloy/pd') as calc:
10     atoms = calc.get_atoms()
11     pd = atoms.get_potential_energy()/len(atoms)
12
13  atoms = Atoms([Atom('Cu', [-3.672, 3.672, 3.672]),
14                Atom('Cu', [0.000, 0.000, 0.000]),
15                Atom('Cu', [-10.821, 10.821, 10.821]),
16                Atom('Pd', [-7.246, 7.246, 7.246])],

```



```

17         cell=[[-5.464,  3.565,  5.464],
18               [-3.565,  5.464,  5.464],
19               [-5.464,  5.464,  3.565]])
20
21 with jasp('bulk/alloy/cu3pd-1',
22          xc='PBE',
23          encut=350,
24          kpts=(8, 8, 8),
25          nbands=34,
26          ibrion=2,
27          isif=3,
28          nsw=10,
29          atoms=atoms) as calc:
30     e3 = atoms.get_potential_energy()
31     for atom in atoms:
32         if atom.symbol == 'Cu':
33             e3 -= cu
34         else:
35             e3 -= pd
36     e3 /= len(atoms)
37 print 'Delta Hf cu3pd-1 = {0:1.2f} eV/atom'.format(e3)

```

Open the python script (dft-scripts/script-130.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:

$$H_{f,Cu} = 0.0 \text{ eV/atom}, x_0 = 0, H_{f,cupd-1} = -0.12 \text{ eV/atom}, x_3 = 0.5.$$

The composition weighted average at $x_{Pd} = 0.25$ is:

$$H_f = H_{f,Cu} + \frac{x_0 - x}{x_0 - x_3} (H_{f,cupd-1} - H_{f,Cu})$$

```

1 x0 = 0.0; x3 = 0.5; x = 0.25;
2 Hf1 = 0.0; Hf3 = -0.12;
3
4 print 'Composition weighted average = {0} eV'.format(Hf1 +
5               (x0 - x)
6               / (x0 - x3)
7               * (Hf3 - Hf1))

```

Open the python script (dft-scripts/script-131.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.

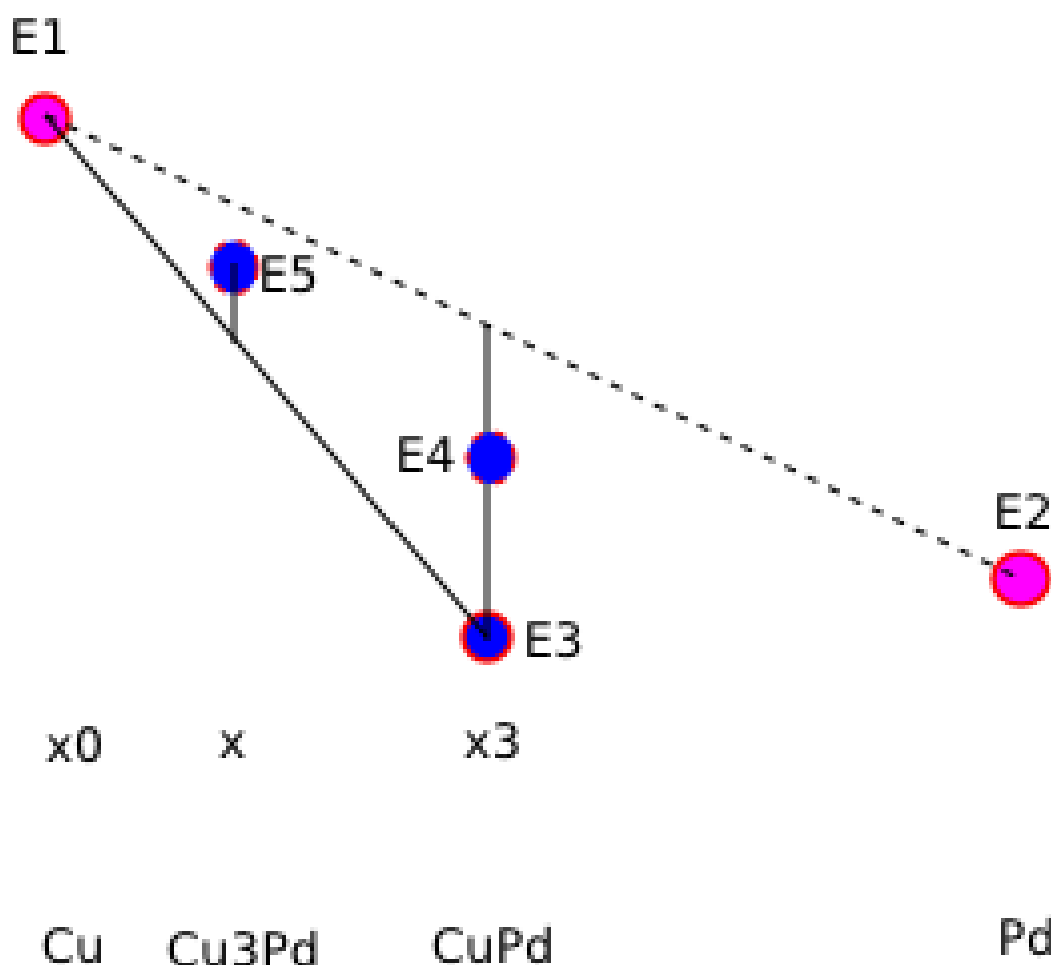


Figure 46: Illustration of of an alloy structure with an exothermic formation energy that is not stable with respect to phase separation. The solid line shows the composition weighted average energy of a mixture of Cu and cupd-2. Since the energy of cu3pd-1 is above the solid line, it is less favorable than a mixture of Cu and cupd-2 with the same composition.

Finally, let us consider one more structure with the Cu₃Pd stoichiometry.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  # parent metals
5  with jasp('bulk/alloy/cu') as calc:
6      atoms = calc.get_atoms()
7      cu = atoms.get_potential_energy()/len(atoms)
8
9  with jasp('bulk/alloy/pd') as calc:
10     atoms = calc.get_atoms()
11     pd = atoms.get_potential_energy()/len(atoms)
12
13  atoms = Atoms([Atom('Cu', [-1.867, 1.867, 0.000]),
14                Atom('Cu', [0.000, 0.000, 0.000]),
15                Atom('Cu', [0.000, 1.867, 1.867]),
16                Atom('Pd', [-1.867, 0.000, 1.867])],

```

```

17         cell=[[-3.735, 0.000, 0.000],
18               [0.000, 0.000, 3.735],
19               [0.000, 3.735, 0.000]])
20
21 with jasp('bulk/alloy/cu3pd-2',
22          xc='PBE',
23          encut=350,
24          kpts=(8, 8, 8),
25          nbands=34,
26          ibrion=2,
27          isif=3,
28          nsw=10,
29          atoms=atoms) as calc:
30     e4 = atoms.get_potential_energy()
31     for atom in atoms:
32         if atom.symbol == 'Cu':
33             e4 -= cu
34         else:
35             e4 -= pd
36     e4 /= len(atoms)
37 print 'Delta Hf cu3pd-2 = {0:1.2f} eV/atom'.format(e4)

```

Open the python script (dft-scripts/script-132.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.

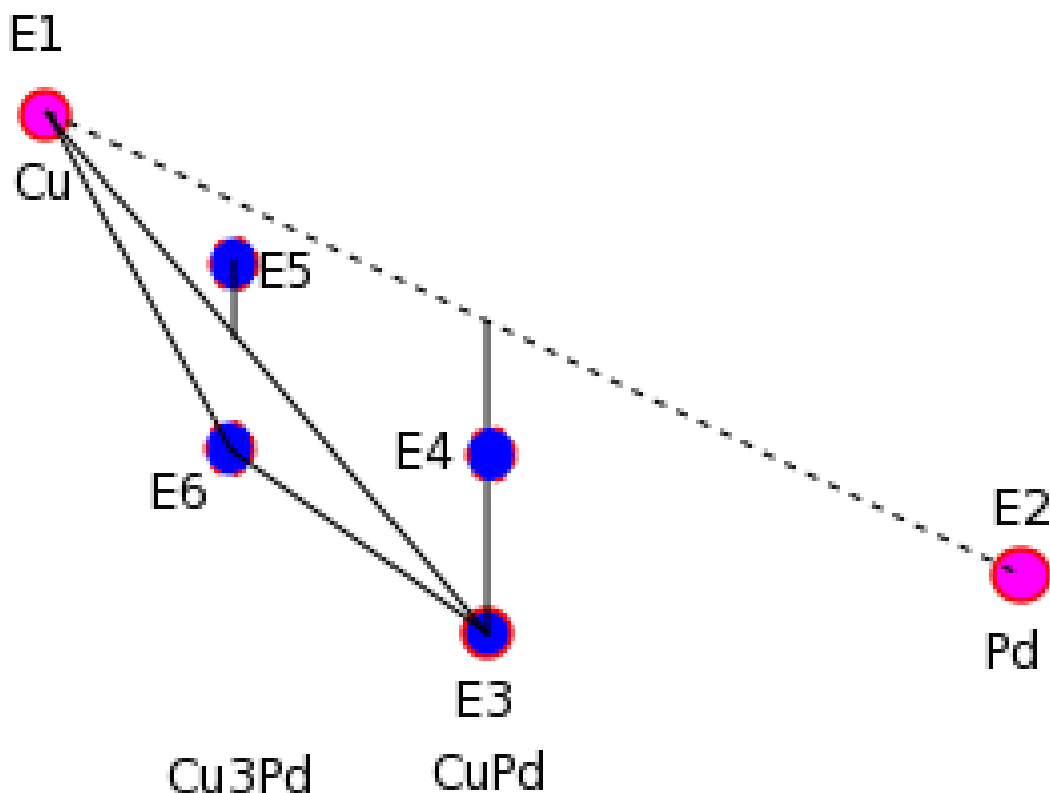


Figure 47: Illustration that cu3pd-2 is more stable than cu3pd-1 and that it is more stable than a composition weighted mixture of Cu and cupd-1. The dotted line shows the energy of a composition weighted average energy of a mixture of Cu and cupd-1. Since cu3pd-2 is below the dotted line, it is more 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](#))^{53,54} which uses a cluster expansion methodology.

4.9.2 Metal oxide oxidation energies

We will consider here the reaction $2 \text{Cu}_2\text{O} + \text{O}_2 \rightleftharpoons 4 \text{CuO}$. The reaction energy is:

$$\Delta E = 4E_{\text{CuO}} - 2E_{\text{Cu}_2\text{O}} - E_{\text{O}_2}.$$

We need to compute the energy of each species.

Cu₂O calculation

```

1  # run Cu2O calculation
2  from jasp import *
3  from ase import Atom, Atoms
4
5  # http://phycomp.technion.ac.il/~ira/types.html#Cu2O
6  a = 4.27
7
8  atoms = Atoms([Atom('Cu', [0, 0, 0]),
9                 Atom('Cu', [0.5, 0.5, 0.0]),
10                 Atom('Cu', [0.5, 0.0, 0.5]),
11                 Atom('Cu', [0.0, 0.5, 0.5]),
12                 Atom('O', [0.25, 0.25, 0.25]),
13                 Atom('O', [0.75, 0.75, 0.75])])
14
15  atoms.set_cell((a, a, a), scale_atoms=True)
16
17  with jasp('bulk/Cu2O',
18            encut=400,
19            kpts=(8, 8, 8),
20            ibrion=2,
21            isif=3,
22            nsw=30,
23            xc='PBE',
24            atoms=atoms) as calc:
25      calc.set_nbands()
26      calc.calculate()
27      print calc

```

Open the python script (dft-scripts/script-133.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/Cu2O
converged: True
Energy = -27.204590 eV

```

Unit cell vectors (angstroms)

	x	y	z	length
a0	[4.270	0.000	0.000]	4.270
a1	[0.000	4.270	0.000]	4.270
a2	[0.000	0.000	4.270]	4.270

a,b,c,alpha,beta,gamma (deg):4.270 4.270 4.270 90.0 90.0 90.0
Unit cell volume = 77.854 Ang³

Stress (GPa):xx, yy, zz, yz, xz, xy
0.000 0.000 0.000-0.000 -0.000 -0.000

Atom#	sym	position [x,y,z]	tag	rmsForce	constraints
0	Cu	[0.000 0.000 0.000]	0	0.00	T T T
1	Cu	[2.135 2.135 0.000]	0	0.00	T T T
2	Cu	[2.135 0.000 2.135]	0	0.00	T T T
3	Cu	[0.000 2.135 2.135]	0	0.00	T T T
4	O	[1.067 1.067 1.067]	0	0.00	T T T
5	O	[3.202 3.202 3.202]	0	0.00	T T T

INCAR Parameters:

```

-----
nbands: 37
nsw: 30
ibrion: 2
isif: 3
encut: 400.0
magmom: None
prec: Normal

```

```

        kpts: (8, 8, 8)
reciprocal: False
        xc: PBE
        txt: -
        gamma: False

```

Pseudopotentials used:

```

-----
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5f5be3a3b1dfa)
Cu: potpaw_PBE/Cu/POTCAR (git-hash: a44c591415026f53deb16a99ca3f06b1e69be10b)

```

CuO calculation

```

1  # run CuO calculation
2  from jasp import *
3  from ase import Atom, Atoms
4
5  # CuO
6  # http://cst-www.nrl.navy.mil/lattice/struk/b26.html
7  # http://www.springermaterials.com/docs/info/10681727_51.html
8  a = 4.6837
9  b = 3.4226
10 c = 5.1288
11 beta = 99.54/180*np.pi
12 y = 0.5819
13
14 a1 = np.array([0.5*a, -0.5*b, 0.0])
15 a2 = np.array([0.5*a, 0.5*b, 0.0])
16 a3 = np.array([c*np.cos(beta), 0.0, c*np.sin(beta)])
17
18 atoms = Atoms([Atom('Cu', 0.5*a2),
19                Atom('Cu', 0.5*a1 + 0.5*a3),
20                Atom('O', -y*a1 + y*a2 + 0.25*a3),
21                Atom('O', y*a1 - y*a2 - 0.25*a3)],
22               cell=(a1, a2, a3))
23
24 with jasp('bulk/CuO',
25           encut=400,
26           kpts=(8, 8, 8),
27           ibrion=2,
28           isif=3,
29           nsw=30,
30           xc='PBE',
31           atoms=atoms) as calc:
32     calc.set_nbands()
33     calc.calculate()
34     print calc

```

Open the python script (dft-scripts/script-134.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/CuO
converged: True
Energy = -19.509498 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 2.302 -1.776  0.046] 2.908
a1 [ 2.302  1.776  0.046] 2.908
a2 [-0.762  0.000  5.087] 5.144
a,b,c,alpha,beta,gamma (deg):2.908 2.908 5.144 95.8 95.8 95.8
Unit cell volume = 41.730 Ang^3
Stress (GPa):xx,   yy,   zz,   yz,   xz,   xy
              0.008  0.013  0.009-0.000  0.000 -0.000

```

Atom#	sym	position [x,y,z]	tag	rmsForce	constraints
0	Cu	[1.151 0.888 0.023]	0	0.00	T T T
1	Cu	[0.770 -0.888 2.566]	0	0.00	T T T
2	O	[2.111 -0.168 1.318]	0	0.03	T T T
3	O	[1.730 0.168 3.861]	0	0.03	T T T

INCAR Parameters:

```

nbands: 23
nsw: 30
ibrion: 2
isif: 3
encut: 400.0
magmom: None
prec: Normal
kpts: (8, 8, 8)
reciprocal: False
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```

O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)
Cu: potpaw_PBE/Cu/POTCAR (git-hash: a44c591415026f53deb16a99ca3f06b1e69be10b)

```

Reaction energy calculation

```

1 from jasp import *
2
3 # don't forget to normalize your total energy to a formula unit. Cu2O
4 # has 3 atoms, so the number of formula units in an atoms is
5 # len(atoms)/3.
6 with jasp('bulk/Cu2O') as calc:
7     atoms = calc.get_atoms()
8     cu2o_energy = atoms.get_potential_energy()/(len(atoms)/3)
9
10 with jasp('bulk/CuO') as calc:
11     atoms = calc.get_atoms()
12     cuo_energy = atoms.get_potential_energy()/(len(atoms)/2)
13
14 # make sure to use the same cutoff energy for the O2 molecule!
15 with jasp('molecules/O2-sp-triplet-400') as calc:
16     atoms = calc.get_atoms()
17     o2_energy = atoms.get_potential_energy()
18
19 rxn_energy = 4.0*cuo_energy - o2_energy - 2.0*cu2o_energy
20 print 'Reaction energy = {0} eV'.format(rxn_energy)

```

Open the python script (dft-scripts/script-135.py).

Reaction energy = -1.966119 eV

This is the reaction energy for $2 \text{ Cu}_2\text{O} \rightarrow 4 \text{ CuO}$. In,⁵⁵ 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 3d orbitals.⁵⁵ The first error of incorrect O_2 dissociation error is a systematic error

that can be corrected empirically.⁵⁵ 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 $2\text{CuO} \rightleftharpoons \text{Cu}_2\text{O} + 1/2 \text{O}_2$.

```

1 from ase import Atoms
2 atoms = Atoms('Cu2O')
3 MW = atoms.get_masses().sum()
4
5 H = 1. # kJ/g
6 print 'rxn energy = {0:1.1f} eV'.format(-2 * H * MW / 96.4) # convert to eV

```

Open the python script (dft-scripts/script-136.py).

rxn energy = -3.0 eV

This is pretty close to the value in⁵⁵ 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,^{56–58} 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.⁵⁹ 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.⁶⁰

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)⁶¹ [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.⁶². The density of states can be calculated by a sum over the k-points:¹⁵

$$P(\epsilon) = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \beta(\epsilon - \epsilon_{\mathbf{k}}) \quad (7)$$

where $\omega_{\mathbf{k}}$ 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.

```

1 from jasp import *
2
3 npoints = 200
4 width = 0.5
5
6 def gaussian(energies, eik):
7     x = ((energies - eik) / width)
8     return np.exp(-x**2) / np.sqrt(np.pi) / width

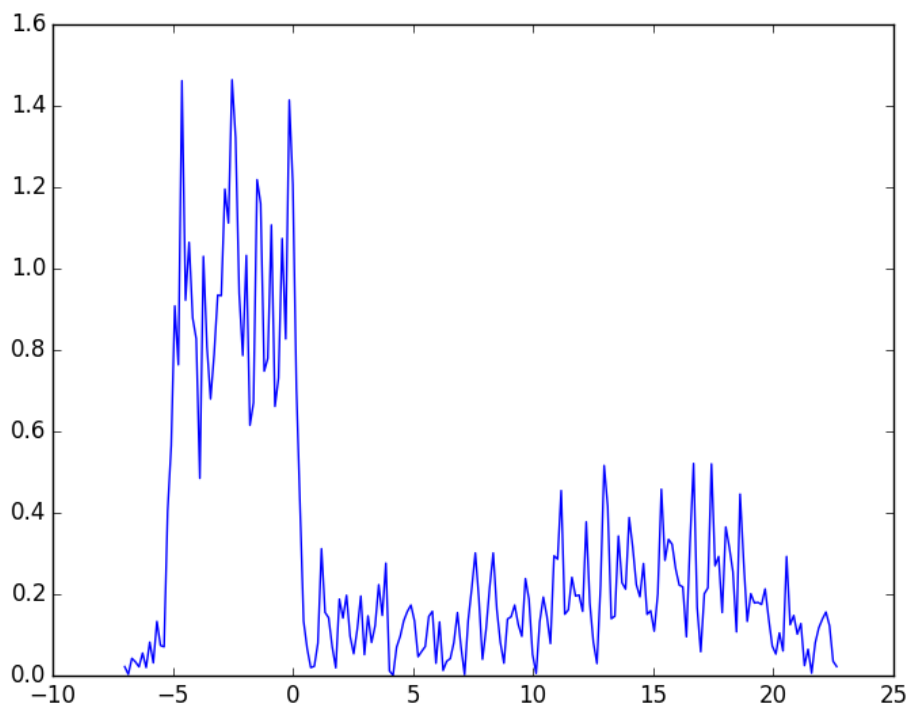
```

```

9
10 with jasp('bulk/pd-dos') as calc:
11
12     # kpt weights
13     wk = calc.get_k_point_weights()
14
15     # for each k-point there are a series of eigenvalues
16     # here we get all the eigenvalues for each k-point
17     e_kn = []
18     for i, k in enumerate(wk):
19         e_kn.append(calc.get_eigenvalues(kpt=i))
20
21     e_kn = np.array(e_kn) - calc.get_fermi_level()
22
23     # these are the energies we want to evaluate the dos at
24     energies = np.linspace(e_kn.min(), e_kn.max(), npoints)
25
26     # this is where we build up the dos
27     dos = np.zeros(npoints)
28
29     for j in range(npoints):
30         for k in range(len(wk)): # loop over all kpoints
31             for i in range(len(e_kn[k])): # loop over eigenvalues in each k
32                 dos[j] += wk[k] * gaussian(energies[j], e_kn[k][i])
33
34 import matplotlib.pyplot as plt
35 plt.plot(energies, dos)
36 plt.savefig('images/manual-dos.png')
37 plt.show()

```

Open the python script (dft-scripts/script-137.py).



Here is a more convenient way to compute the DOS using [ase.dft](#).

```

1 from jasp import *
2 import matplotlib.pyplot as plt
3 from ase.dft import DOS
4

```

```

5  with jasp('bulk/pd-dos') as calc:
6      dos = DOS(calc, width=0.2)
7      d = dos.get_dos()
8      e = dos.get_energies()
9
10 import pylab as plt
11 plt.plot(e, d)
12 plt.xlabel('energy (eV)')
13 plt.ylabel('DOS')
14 plt.savefig('images/pd-dos.png')

```

Open the python script (dft-scripts/script-138.py).

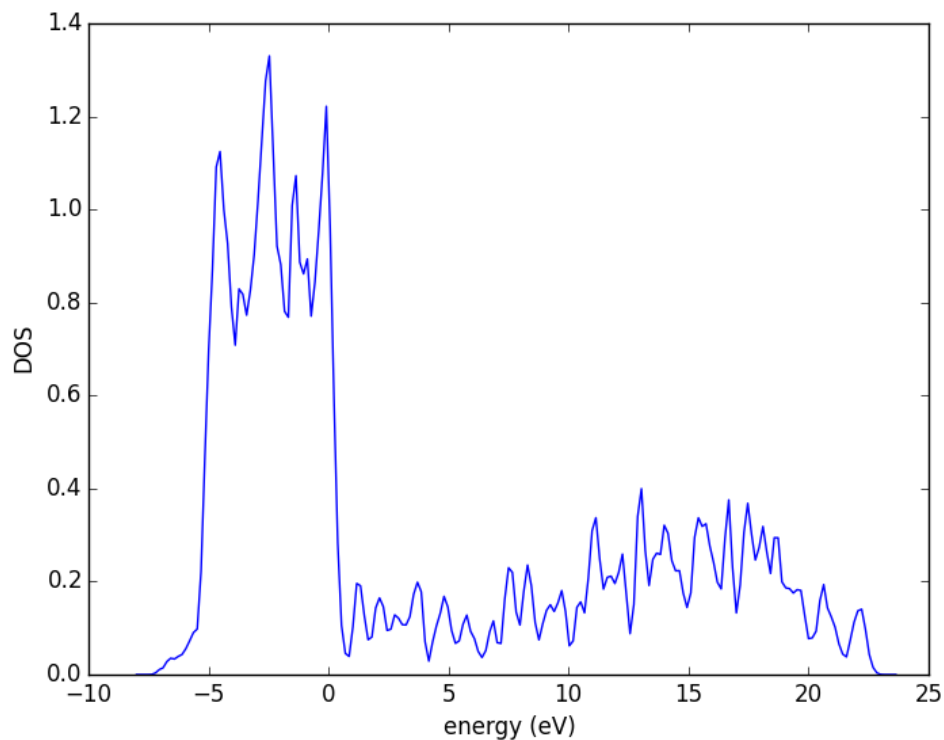


Figure 48: Total DOS for bulk Pd.

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 Blöchl corrections.

```

1  from jasp import *
2  from ase.dft import DOS
3  with jasp('bulk/pd-dos') as calc:
4      calc.clone('bulk/pd-dos-ismear-5')
5
6  with jasp('bulk/pd-dos-ismear-5') as calc:
7      bulk = calc.get_atoms()
8      calc.set(ismear=-5)
9
10     bulk.get_potential_energy()
11     dos = DOS(calc, width=0.2)
12     d = dos.get_dos()
13     e = dos.get_energies()
14

```

```

15 import pylab as plt
16 plt.plot(e, d)
17 plt.xlabel('energy [eV]')
18 plt.ylabel('DOS')
19 plt.savefig('images/pd-dos-ismear-5.png')

```

Open the python script (dft-scripts/script-139.py).
This not notably different to me.

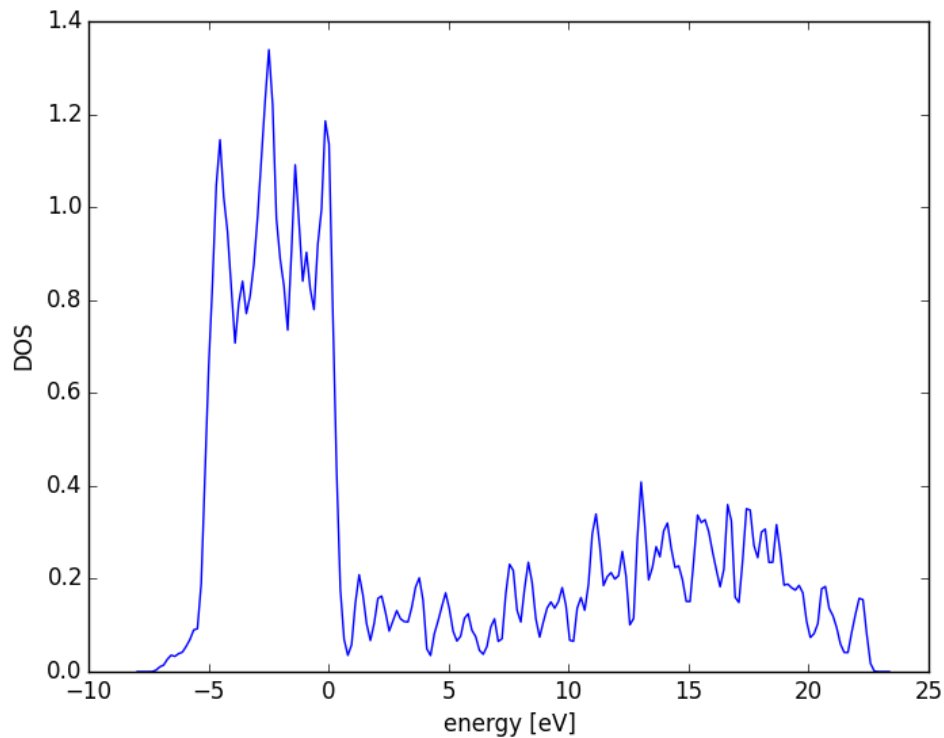


Figure 49: Total DOS for Pd computed with ISMEAR=-5

We can test for convergence of the DOS. The k-points are most important.

```

1  from ase import Atoms, Atom
2  from jasp import *
3  import sys
4
5  import matplotlib.pyplot as plt
6  import numpy as np
7  from ase.dft import DOS
8  import pylab as plt
9
10 a = 3.9 # approximate lattice constant
11 b = a / 2.
12 bulk = Atoms([Atom('Pd', (0.0, 0.0, 0.0))],
13              cell=[(0, b, b),
14                    (b, 0, b),
15                    (b, b, 0)])
16
17 kpts = [8, 10, 12, 14, 16, 18, 20]
18
19 for k in kpts:
20     with jasp('bulk/pd-dos-k{0}-ismear-5'.format(k),
21              encut=300,

```

```

22         xc='PBE',
23         kpts=(k, k, k),
24         atoms=bulk) as calc:
25
26     # this runs the calculation
27     try:
28         bulk.get_potential_energy()
29         dos = DOS(calc, width=0.2)
30         d = dos.get_dos() + k / 4.0
31         e = dos.get_energies()
32
33         plt.plot(e,d, label='k={0}'.format(k))
34     except:
35         pass
36 plt.xlabel('energy (eV)')
37 plt.ylabel('DOS')
38 plt.legend()
39 plt.savefig('images/pd-dos-k-convergence-ismear-5.png')
40 plt.show()

```

Open the python script (dft-scripts/script-140.py).

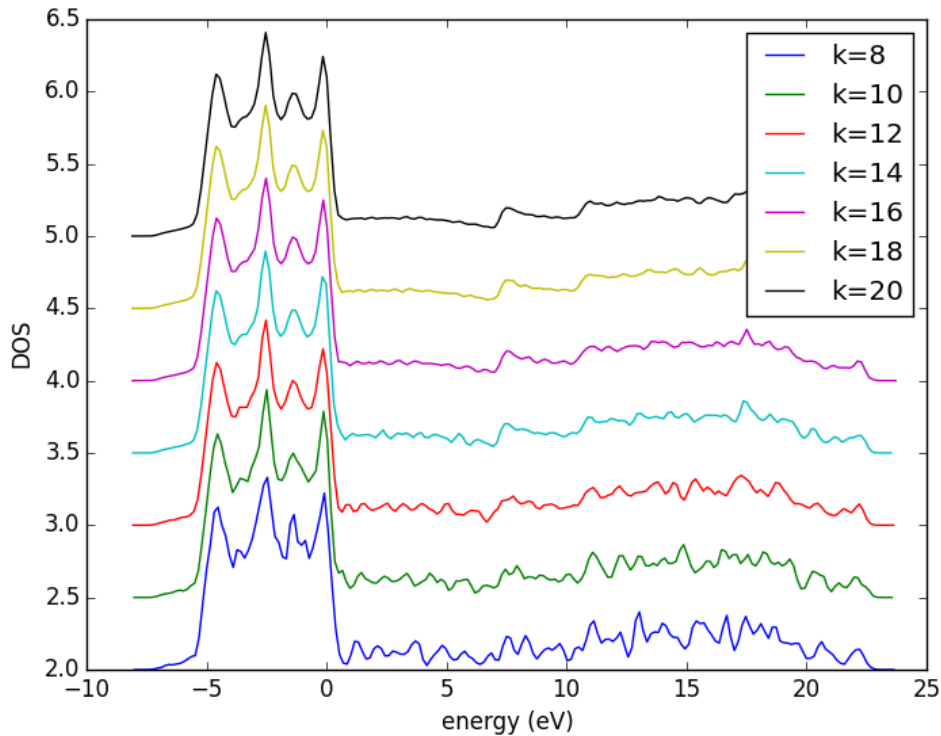


Figure 50: Convergence of the total DOS with k-points

4.11 Atom projected density of states

One major disadvantage of a plane-wave basis set is that it is difficult to relate the completely delocalized plane-waves 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.^{63–65} 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 Hückel theory,⁷ and linear muffin tin orbital theory.⁶⁶ 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.⁶⁷ and Chapter 6 in Refs.⁶⁸ and⁶⁹). The n^{th} order moment, μ_n , of a distribution of states $\rho(\epsilon)$ with respect to a reference ϵ_o is defined by

$$\mu_n = \frac{\int_{-\infty}^{\infty} \epsilon^n \rho(\epsilon - \epsilon_o) d\epsilon}{\int_{-\infty}^{\infty} \rho(\epsilon - \epsilon_o) d\epsilon} \quad (8)$$

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.

```

1  from ase import Atoms, Atom
2  from jasp import *
3  from ase.calculators.vasp import VaspDos
4
5  import matplotlib.pyplot as plt
6  import numpy as np
7
8  a = 3.9 # approximate lattice constant
9  b = a / 2.
10 bulk = Atoms([Atom('Pd', (0.0, 0.0, 0.0))],
11              cell=[(0, b, b),
12                   (b, 0, b),
13                   (b, b, 0)])
14
15 with jasp('bulk/pd-ados',
16          encut=300,
```

```

17         xc='PBE',
18         lreal=False,
19         rwigs=[1.5], # wigner-seitz radii for ados
20         kpts=(8, 8, 8),
21         atoms=bulk) as calc:
22
23     # this runs the calculation
24     bulk.get_potential_energy()
25
26     # now get results
27     ados = VaspDos(efermi=calc.get_fermi_level())
28
29     energies = ados.energy # energy is an attribute, not a function
30     dos = ados.site_dos(0, 'd') # this is a function, get d-orbitals on atom 0
31
32     # we will select energies in the range of -10, 5
33     ind = (energies < 5) & (energies > -10)
34
35     energies = energies[ind]
36     dos = dos[ind]
37
38     Nstates = np.trapz(dos, energies)
39     occupied = energies <= 0.0
40     N_occupied_states = np.trapz(dos[occupied], energies[occupied])
41     # first moment
42     ed = np.trapz(energies * dos, energies) / Nstates
43
44     # second moment
45     wd2 = np.trapz(energies**2 * dos, energies) / Nstates
46
47     print 'Total # states = {0:1.2f}'.format(Nstates)
48     print 'number of occupied states = {0:1.2f}'.format(N_occupied_states)
49     print 'd-band center = {0:1.2f} eV'.format(ed)
50     print 'd-band width = {0:1.2f} eV'.format(np.sqrt(wd2))
51
52     # plot the d-band
53     plt.plot(energies, dos, label='$d$-orbitals')
54
55     # plot the occupied states in shaded gray
56     plt.fill_between(x=energies[occupied],
57                     y1=dos[occupied],
58                     y2=np.zeros(dos[occupied].shape),
59                     color='gray', alpha=0.25)
60
61     plt.xlabel('$E - E_f$ (eV)')
62     plt.ylabel('DOS (arbitrary units)')
63
64     plt.savefig('images/pd-ados.png')
65     plt.show()

```

Open the python script (dft-scripts/script-141.py).

```

Total # states = 9.29
number of occupied states = 8.18
d-band center = -2.00 eV
d-band width = 2.72 eV

```

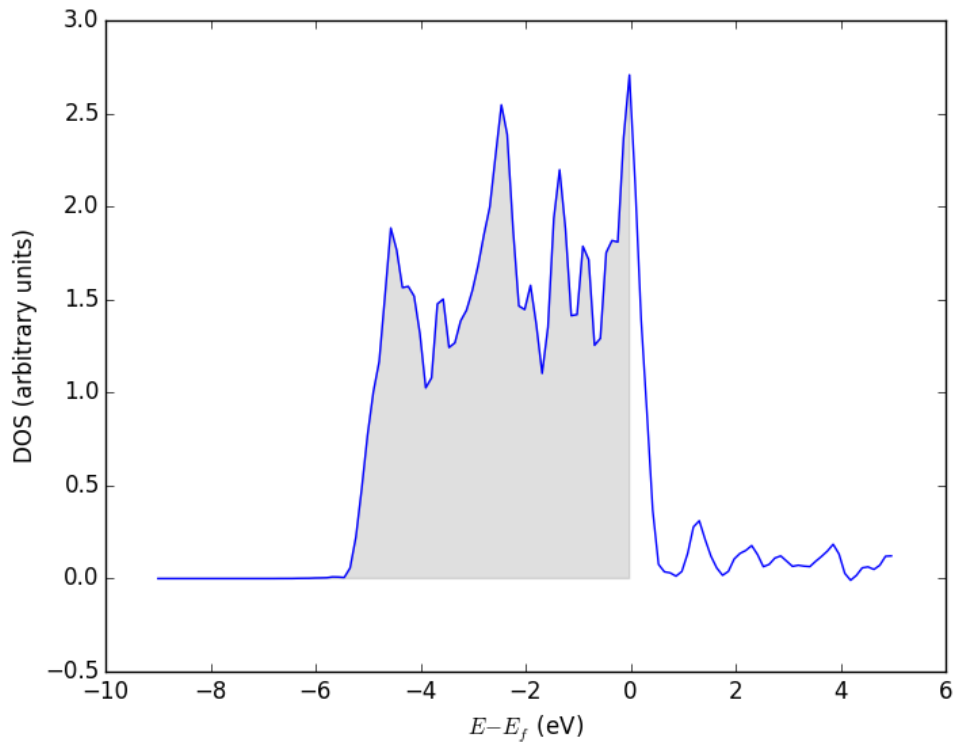


Figure 51: Atom projected d -band for bulk Pd. The shaded area corresponds to the occupied states below the Fermi level.

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.

```

1  from ase import Atoms, Atom
2  from jasp import *
3  from ase.calculators.vasp import VaspDos
4  import sys
5
6  import matplotlib.pyplot as plt
7  import numpy as np
8
9  a = 3.9 # approximate lattice constant
10 b = a / 2.
11 bulk = Atoms([Atom('Pd', (0.0, 0.0, 0.0))],
12              cell=[(0, b, b),
13                    (b, 0, b),
14                    (b, b, 0)])
15
16 RWIGS = [1.0, 1.1, 1.25, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 ]
17
18 ED, WD, N = [], [], []
19
20 for rwigs in RWIGS:
21     with jasp('bulk/pd-ados') as calc:
22         calc.clone('bulk/pd-ados-rwigs-{}'.format(rwigs))
23
24     with jasp('bulk/pd-ados-rwigs-{}'.format(rwigs)) as calc:
25         calc.set(rwigs=[rwigs])
26
27     try:

```

```

28         calc.calculate()
29     except (VaspSubmitted, VaspQueued):
30         continue
31
32     # now get results
33     ados = VaspDos(efermi=calc.get_fermi_level())
34
35     energies = ados.energy
36     dos = ados.site_dos(0, 'd')
37
38     #we will select energies in the range of -10, 5
39     ind = (energies < 5) & (energies > -10)
40
41     energies = energies[ind]
42     dos = dos[ind]
43
44     Nstates = np.trapz(dos, energies)
45     occupied = energies <= 0.0
46     N_occupied_states = np.trapz(dos[occupied], energies[occupied])
47     ed = np.trapz(energies * dos, energies) / np.trapz(dos, energies)
48     wd2 = np.trapz(energies**2 * dos, energies) / np.trapz(dos, energies)
49
50     N.append(N_occupied_states)
51     ED.append(ed)
52     WD.append(wd2**0.5)
53
54     plt.plot(RWIGS, N, 'bo', label='N. occupied states')
55     plt.legend(loc='best')
56     plt.xlabel('RWIGS ($\AA$)')
57     plt.ylabel('# occupied states')
58     plt.savefig('images/ados-rwigs-occupation.png')
59
60
61     fig, ax1 = plt.subplots()
62     ax1.plot(RWIGS, ED, 'bo', label='d-band center (eV)')
63     ax1.set_xlabel('RWIGS ($\AA$)')
64     ax1.set_ylabel('d-band center (eV)', color='b')
65     for t1 in ax1.get_yticklabels():
66         t1.set_color('b')
67
68     ax2 = ax1.twinx()
69     ax2.plot(RWIGS, WD, 'gs', label='d-band width (eV)')
70     ax2.set_ylabel('d-band width (eV)', color='g')
71     for t1 in ax2.get_yticklabels():
72         t1.set_color('g')
73
74     plt.savefig('images/ados-rwigs-moments.png')
75     plt.show()

```

Open the python script (dft-scripts/script-142.py).

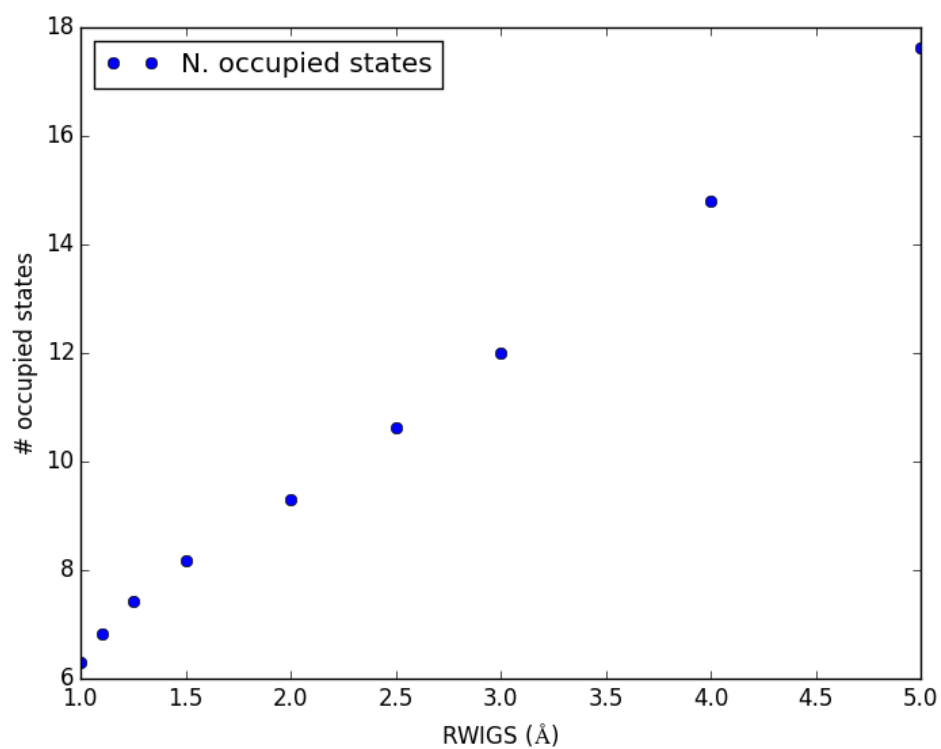


Figure 52: Effect of the RWIGS on the number of occupied d -states.

You can see the number of occupied states increases approximately linearly here with RWIGS. This is due to overcounting of neighboring electrons.

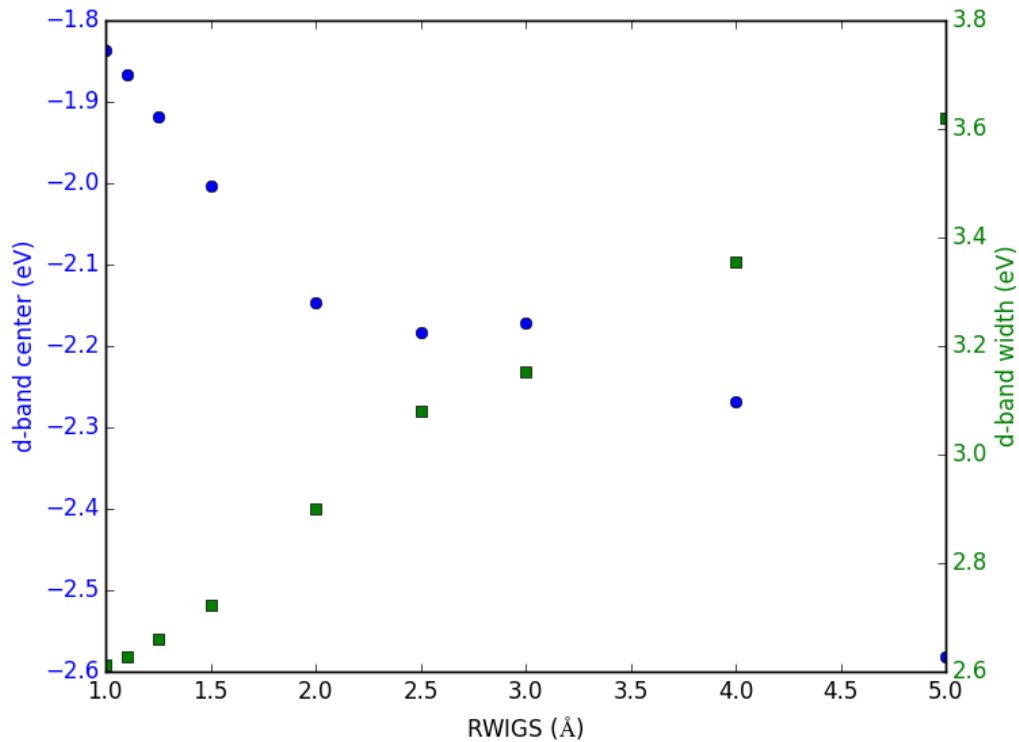


Figure 53: Effect of the RWIGS on the d -band center and width.

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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3  from ase.visualize import view
4
5  a = 5.38936
6  atoms = Atoms([Atom('Si', [0, 0, 0]),
7                 Atom('Si', [0.25, 0.25, 0.25])])
8
9  atoms.set_cell([[a / 2., a / 2., 0.0],
10                [0.0, a / 2., a / 2.],
11                [a / 2., 0.0, a / 2.]], scale_atoms=True)
12
13  with jasp('bulk/Si-selfconsistent',
14            xc='PBE',
15            prec='Medium',
16            istsart=0,
17            icharg=2,
18            ediff=0.1e-03,
19            kpts=(4, 4, 4), debug=logging.DEBUG,
20            atoms=atoms) as calc:

```

```

21 atoms.get_potential_energy()
22 print calc

```

Open the python script (dft-scripts/script-143.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/Si-selfconsistent
converged: True
Energy = -10.799983 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 2.695  2.695  0.000] 3.811
a1 [ 0.000  2.695  2.695] 3.811
a2 [ 2.695  0.000  2.695] 3.811
a,b,c,alpha,beta,gamma (deg):3.811 3.811 3.811 60.0 60.0 60.0
Unit cell volume = 39.134 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              -0.026 -0.026 -0.026-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag rmsForce constraints
  0    Si  [0.000      0.000      0.000] 0  0.00      T T T
  1    Si  [1.347      1.347      1.347] 0  0.00      T T T
-----

INCAR Parameters:
-----
      nbands: 8
      istart: 0
      icharg: 2
      ediff: 0.0001
      magmom: None
      prec: Medium
      kpts: (4, 4, 4)
reciprocal: False
      xc: PBE
      txt: -
      gamma: False

```

Pseudopotentials used:

Si: potpaw_PBE/Si/POTCAR (git-hash: ae2291fdf186a34272463039fb5a87cde0e50174)

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.

```

1 from jasp import *
2
3 wd = 'bulk/Si-bandstructure'
4
5 with jasp('bulk/Si-selfconsistent') as calc:
6     calc.clone(wd)
7
8 kpts = [[0.5, 0.5, 0.0], # L
9         [0, 0, 0],      # Gamma

```

```

10         [0, 0, 0],
11         [0.5, 0.5, 0.5]] # X
12
13 with jasp(wd,
14           kpts=kpts,
15           reciprocal=True,
16           kpts_nintersections=10,
17           icharg=11) as calc:
18     calc.calculate()
19     print(calc)

```

Open the python script (dft-scripts/script-144.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/bulk/Si-bandstructure
converged: True
Energy = -3.620909 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 2.695  2.695  0.000] 3.811
a1 [ 0.000  2.695  2.695] 3.811
a2 [ 2.695  0.000  2.695] 3.811
a,b,c,alpha,beta,gamma (deg):3.811 3.811 3.811 60.0 60.0 60.0
Unit cell volume = 39.134 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              -0.205 -0.205 -0.205-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Si  [0.000      0.000      0.000] 0  0.00      T T T
  1    Si  [1.347      1.347      1.347] 0  0.00      T T T
-----

INCAR Parameters:
-----
nbands: 8
istart: 0
icharg: 11
ediff: 0.0001
magmom: None
prec: Medium
kpts: [[0.5, 0.5, 0.0], [0, 0, 0], [0, 0, 0], [0.5, 0.5, 0.5]]
kpts_nintersections: 10
reciprocal: True
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```
-----
Si: potpaw_PBE/Si/POTCAR (git-hash: ae2291fdf186a34272463039fb5a87cde0e50174)
```

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:

```
1 head -n 20 bulk/Si-bandstructure/EIGENVAL
```

Open the python script (dft-scripts/script-145.py).

```

      2      2      1      1
0.1956688E+02  0.3810853E-09  0.3810853E-09  0.3810853E-09  0.5000000E-15
1.0000000000000000E-004
CAR
unknown system
      8      20      8

0.5000000E+00  0.5000000E+00  0.0000000E+00  0.5000000E-01
1          -1.826311
2          -1.826306
3           3.153690
4           3.153716
5           6.744294
6           6.744321
7          16.392989
8          16.405965

0.4444444E+00  0.4444444E+00  0.0000000E+00  0.5000000E-01
1          -2.669062
2          -0.918013

```

We can ignore the first five lines.

```

1  f = open('bulk/Si-bandstructure/EIGENVAL', 'r')
2
3  line1 = f.readline()
4  line2 = f.readline()
5  line3 = f.readline()
6  line4 = f.readline()
7  comment = f.readline()
8  unknown, nkpoints, nbands = [int(x) for x in f.readline().split()]
9
10 blankline = f.readline()
11
12 band_energies = [[] for i in range(nbands)]
13
14 for i in range(nkpoints):
15     x, y, z, weight = [float(x) for x in f.readline().split()]
16
17     for j in range(nbands):
18         fields = f.readline().split()
19         id, energy = int(fields[0]), float(fields[1])
20         band_energies[id - 1].append(energy)
21     blankline = f.readline()
22 f.close()
23
24 import matplotlib.pyplot as plt
25
26 for i in range(nbands):
27     plt.plot(range(nkpoints), band_energies[i])
28
29 ax = plt.gca()
30 ax.set_xticks([]) # no tick marks
31 plt.xlabel('k-vector')
32 plt.ylabel('Energy (eV)')
33 ax.set_xticks([0, 10, 19])
34 ax.set_xticklabels(['L$', '$\Gamma$', 'X$'])
35 plt.savefig('images/Si-bandstructure.png')

```

Open the python script (dft-scripts/script-146.py).

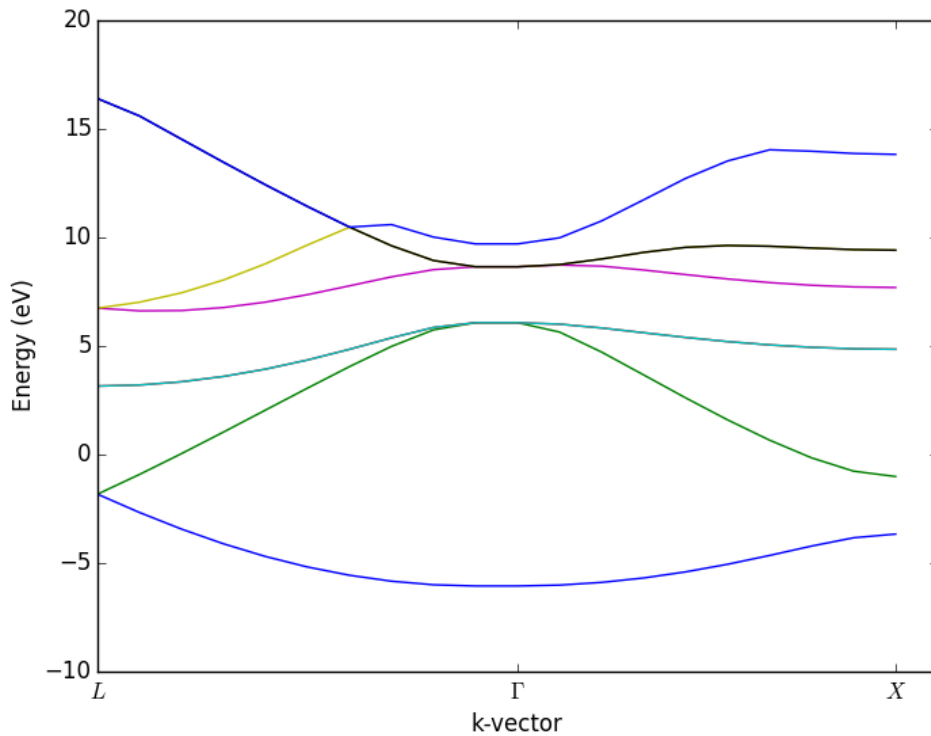


Figure 54: Calculated band-structure for Si.

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 [jasp](#) to do the analysis described above.

```

1 from jasp import *
2 from jasp.jasp_bandstructure import *
3
4 with jasp('bulk/tio2/step3') as calc:
5     n, bands, p = calc.get_bandstructure(kpts_path=[('$\Gamma$', [0.0, 0.0, 0.0]),
6     ('X', [0.5, 0.5, 0.0]),
7     ('X', [0.5, 0.5, 0.0]),
8     ('M', [0.0, 0.5, 0.5]),
9     ('M', [0.0, 0.5, 0.5]),
10    ('$\Gamma$', [0.0, 0.0, 0.0])])
11
12 p.savefig('images/tio2-bandstructure-dos.png')
```

Open the python script (dft-scripts/script-147.py).

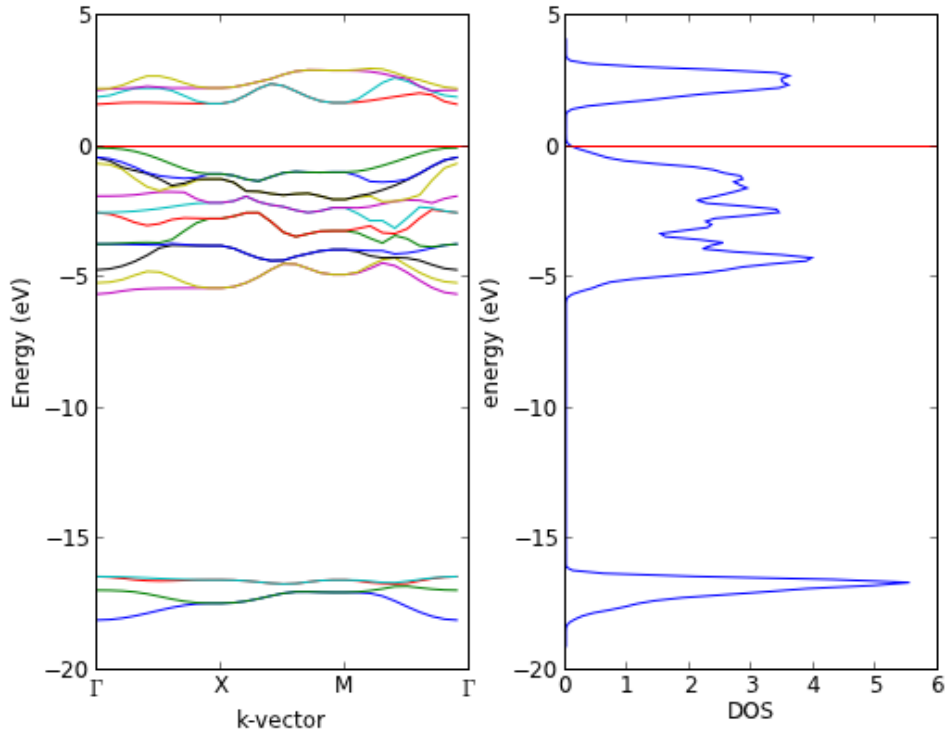


Figure 55: Band structure and total density of states for TiO_2 .

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.

```

1  from jasp import *
2  from jasp.jasp_bandstructure import *
3
4  from ase import Atom, Atoms
5  ready = True
6  for i,a in enumerate([4.7, 5.38936, 6.0]):
7
8      atoms = Atoms([Atom('Si', [0, 0, 0]),
9                    Atom('Si', [0.25, 0.25, 0.25])])
10
11     atoms.set_cell([[a/2., a/2., 0.0],
12                   [0.0, a/2., a/2.],
13                   [a/2., 0.0, a/2.]], scale_atoms=True)
14
15     with jasp('bulk/Si-bs-{0}'.format(i),
16              xc='PBE',
17              prec='Medium',
18              istsart=0,
19              icharg=2,
20              ediff=0.1e-03,
21              kpts=(4, 4, 4),
22              atoms=atoms) as calc:
23         try:
24             n,bands,p = calc.get_bandstructure(kpts_path=[('L', [0.5,0.5,0.0]),
25                                                           ('$\Gamma$', [0, 0, 0])],

```

```

26                                     ('$\Gamma$', [0, 0, 0]),
27                                     ('X', [0.5, 0.5, 0.5])),
28                                     kpts_nintersections=10)
29     except (VaspSubmitted, VaspQueued):
30         print 'not ready {0}'.format(i)
31         ready = False
32
33     if not ready:
34         import sys; sys.exit()
35
36
37     p.savefig('images/Si-bs-{0}.png'.format(i))
38     p.show()

```

Open the python script (dft-scripts/script-148.py).

not ready 0

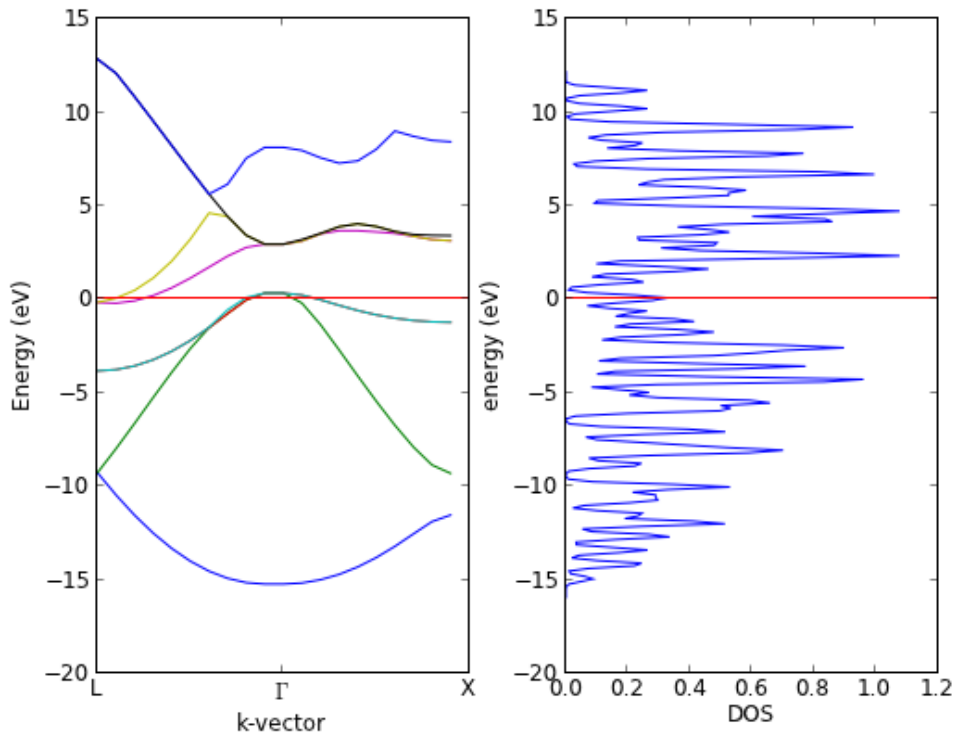


Figure 56: Si band structure for a=4.7

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.

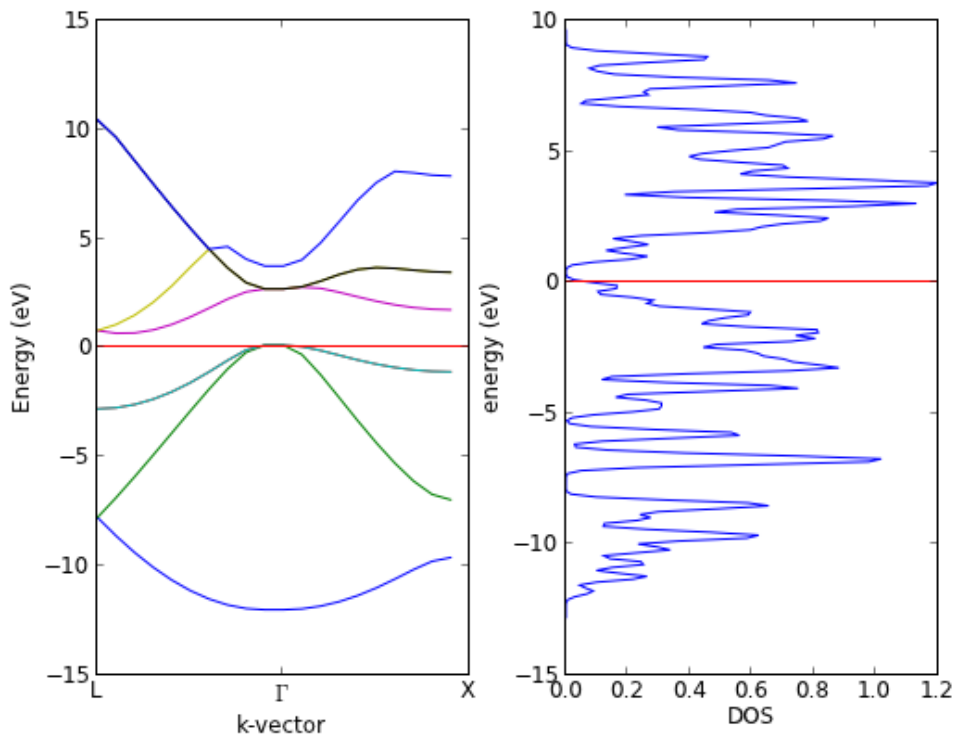


Figure 57: Si band structure for $a=5.38936$

```

1  from jasp import *
2  from ase.lattice.cubic import BodyCenteredCubic
3
4  atoms = BodyCenteredCubic(directions=[[1, 0, 0],
5                                         [0, 1, 0],
6                                         [0, 0, 1]],
7                               size=(1, 1, 1),
8                               symbol='Fe')
9
10 NUPDOWNS = [0.0, 2.0, 4.0, 5.0, 6.0, 8.0]
11 energies = []
12 for B in NUPDOWNS:
13     with jasp('bulk/Fe-bcc-fixedmagmom-{0:1.2f}'.format(B),
14               xc='PBE',
15               encut=300,
16               kpts=(4, 4, 4),
17               ispin=2,
18               nupdown=B,
19               atoms=atoms) as calc:
20         try:
21             e = atoms.get_potential_energy()
22             energies.append(e)
23         except (VaspSubmitted, VaspQueued):
24             pass
25
26 import matplotlib.pyplot as plt
27 plt.plot(NUPDOWNS, energies)
28 plt.xlabel('Total Magnetic Moment')
29 plt.ylabel('Energy (eV)')
30 plt.savefig('images/Fe-fixedmagmom.png')
31 plt.show()

```

Open the python script (dft-scripts/script-149.py).

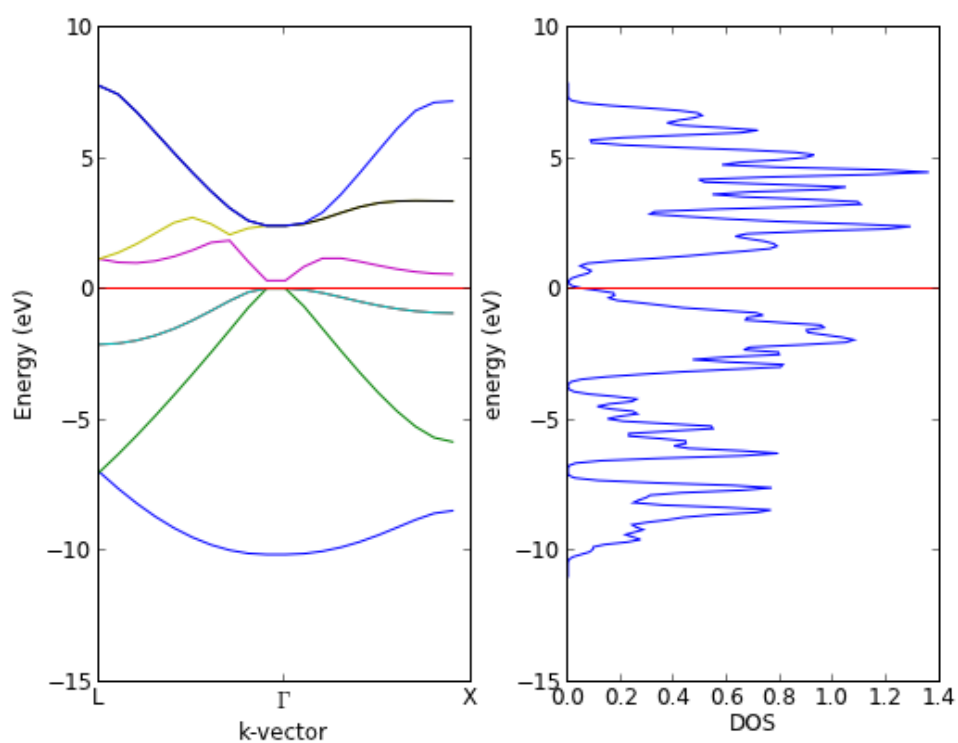
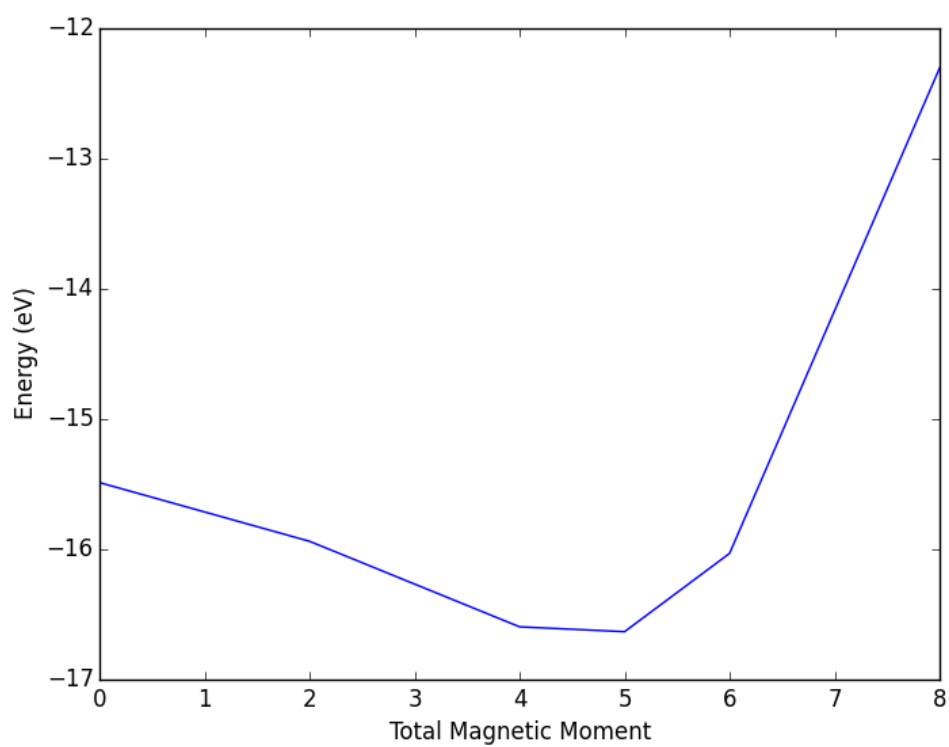


Figure 58: Si band structure for $a=6.0$



170
Figure 59: 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.

```

1  from jasp import *
2  from ase.lattice.cubic import BodyCenteredCubic
3
4  atoms = BodyCenteredCubic(directions=[[1, 0, 0],
5                                         [0, 1, 0],
6                                         [0, 0, 1]],
7                               size=(1, 1, 1),
8                               symbol='Fe')
9
10 # set magnetic moments on each atom
11 for atom in atoms:
12     atom.magmom = 2.5
13
14 with jasp('bulk/Fe-bcc-sp-1',
15           xc='PBE',
16           encut=300,
17           kpts=(4, 4, 4),
18           ispin=2,
19           lorbit=11, # you need this for individual magnetic moments
20           atoms=atoms) as calc:
21     try:
22         e = atoms.get_potential_energy()
23         B = atoms.get_magnetic_moment()
24         magmoms = atoms.get_magnetic_moments()
25     except (VaspSubmitted, VaspQueued):
26         pass
27
28 print 'Total magnetic moment is {0:1.2f} Bohr-magnetons'.format(B)
29 print 'Individual moments are {0} Bohr-magnetons'.format(magmoms)

```

Open the python script (`dft-scripts/script-150.py`).

```

Total magnetic moment is 4.25 Bohr-magnetons
Individual moments are [ 2.134  2.134] 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](#)

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  atoms = Atoms([Atom('Fe', [0.00, 0.00, 0.00], magmom=5),
5                 Atom('Fe', [4.3, 4.3, 4.3], magmom=-5),
6                 Atom('O', [2.15, 2.15, 2.15], magmom=0),
7                 Atom('O', [6.45, 6.45, 6.45], magmom=0)],
8               cell=[[4.3, 2.15, 2.15],
9                     [2.15, 4.3, 2.15],
10                    [2.15, 2.15, 4.3]])
11
12 with jasp('bulk/afm-feo',
13           encut=350,
14           prec='Normal',
15           ispin=2,
16           nupdown=0, # this forces a non-magnetic solution
17           lorbit=11, # to get individual moments
18           lreal=False,
19           atoms=atoms) as calc:

```

```
20 print 'Magnetic moments = ', atoms.get_magnetic_moments()
21 print 'Total magnetic moment = ', atoms.get_magnetic_moment()
```

Open the python script (dft-scripts/script-151.py).

```
Magnetic moments = [ 2.652 -2.652  0.      0.    ]
Total magnetic moment = 0.0
```

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

70

phonopy

4.15 TODO solid state NEB

⁷¹ Carter paper ⁷² 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.

```
1 from ase.lattice.surface import fcc111
2 from ase.io import write
3 from ase.visualize import view
4
5 slab = fcc111('Al', size=(2, 2, 3), vacuum=10.0)
6 from ase.constraints import FixAtoms
7 constraint = FixAtoms(mask=[atom.tag >= 2 for atom in slab])
8 slab.set_constraint(constraint)
9
10 view(slab)
11 write('images/Al-slab.png', slab, rotation='90x', show_unit_cell=2)
```

Open the python script (dft-scripts/script-152.py).

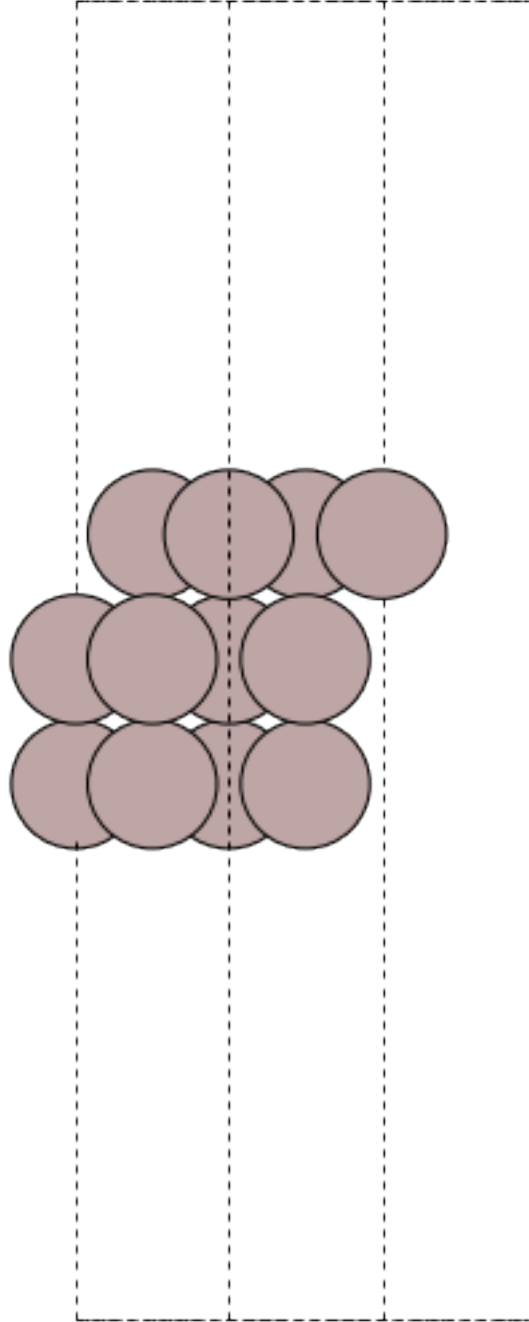


Figure 60: An Al(111) slab with three layers and 20 Å of vacuum.

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 coordination 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.

```
1 from ase.lattice.surface import surface
2 from ase.io import write
3
4 # Au(211) with 9 layers
5 s1 = surface('Au', (2, 1, 1), 9)
6 s1.center(vacuum=10, axis=2)
7
8 write('images/Au-211.png',
9       s1.repeat((3, 3, 1)),
10      rotation='-30z,90x', # change the orientation for viewing
11      show_unit_cell=2)
```

Open the python script (dft-scripts/script-153.py).

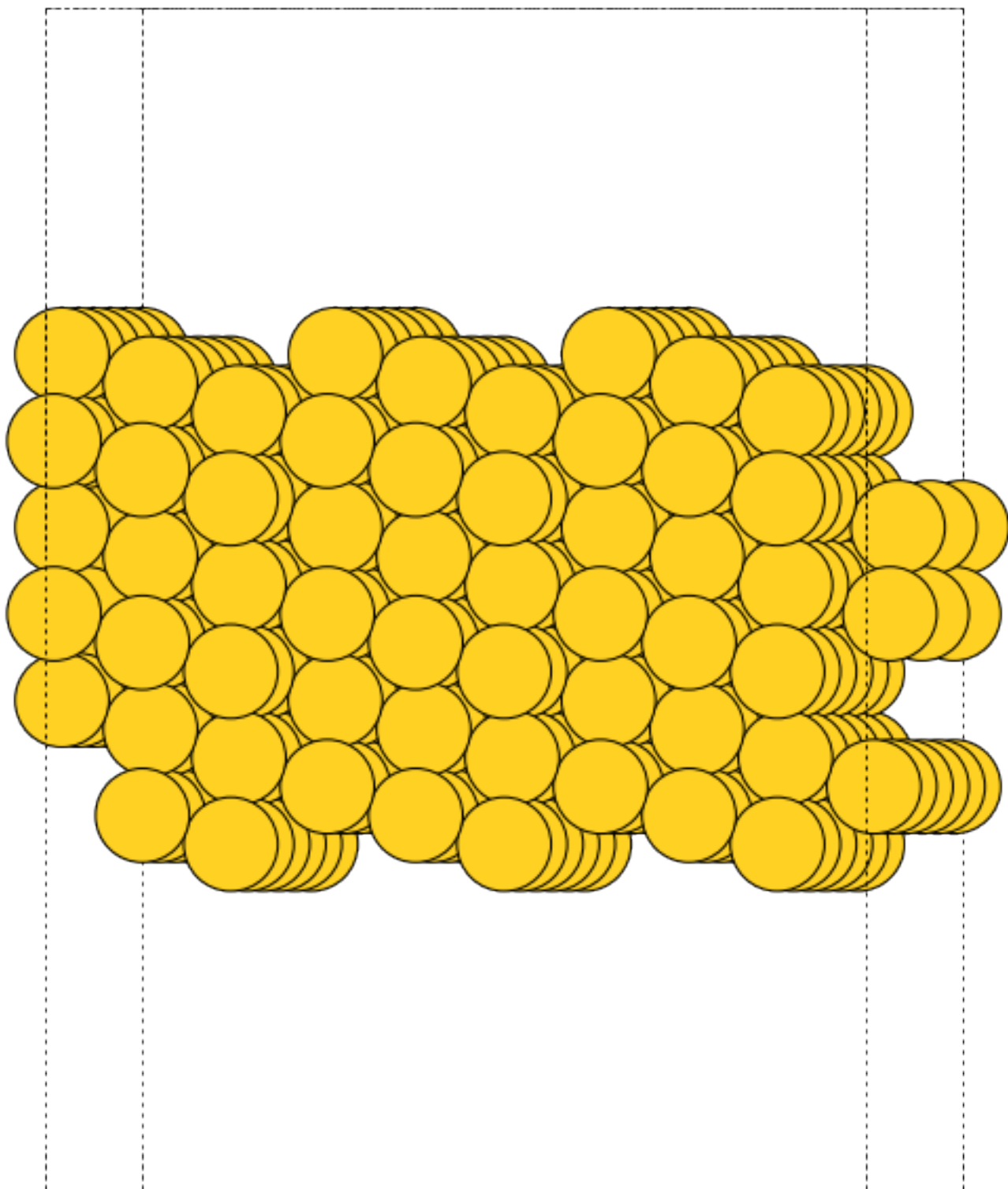


Figure 61: An Au(211) surface constructed with `ase`.

5.2 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:

```
1 from ase.lattice.surface import fcc111
2 from ase.io import write
3 from jasp import *
4 from jasp.jasp_bandstructure import *
5 slab = fcc111('Al', size=(1, 1, 4), vacuum=10.0)
6
7 with jasp('surfaces/Al-bandstructure',
8         xc='PBE',
9         encut=300,
10        kpts=(6, 6, 6),
11        atoms=slab) as calc:
12     n, bands, p = calc.get_bandstructure(kpts_path=[(r'$\Gamma$', [0, 0, 0]),
13             ('$K1$', [0.5, 0.0, 0.0]),
14             ('$K1$', [0.5, 0.0, 0.0]),
15             ('$K2$', [0.5, 0.5, 0.0]),
16             ('$K2$', [0.5, 0.5, 0.0]),
17             (r'$\Gamma$', [0, 0, 0]),
18             (r'$\Gamma$', [0, 0, 0]),
19             ('$K3$', [0.0, 0.0, 1.0])],
20     kpts_nintersections=10)
21
22 p.savefig('images/Al-slab-bandstructure.png')
23 p.show()
```

Open the python script (dft-scripts/script-154.py).

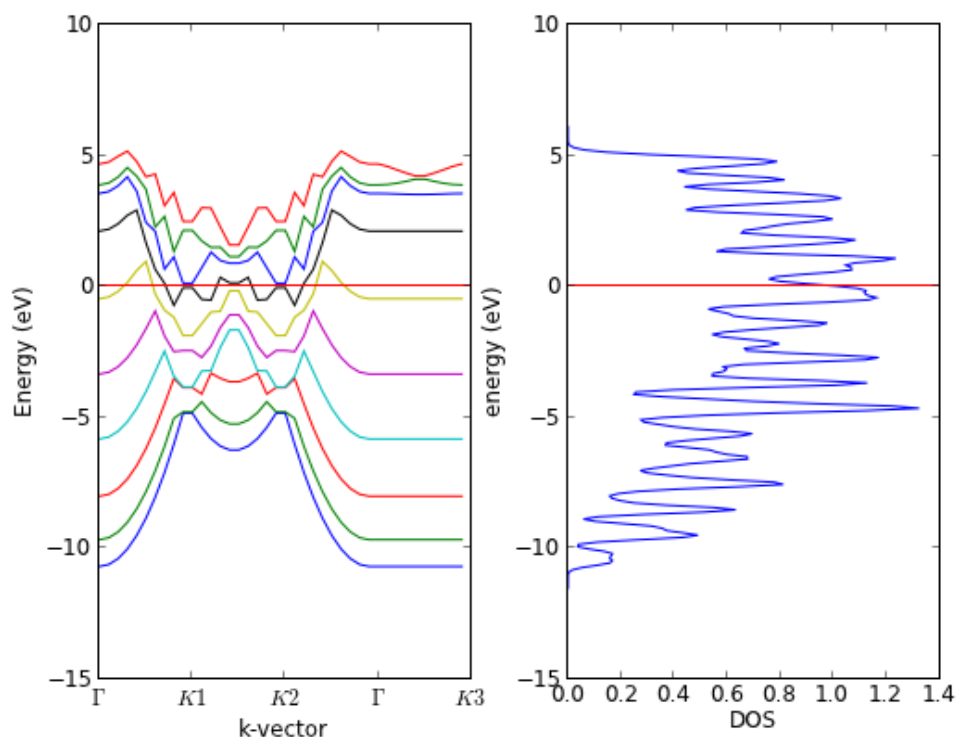


Figure 62: Band structure of an Al slab in the plane (path from Gamma to K1 to K2 to Gamma) and normal to the surface (Gamma to K3). Note the bands are flat in the direction normal to the surface, hence only one k-point is needed in this direction.

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.

```

1 from jasp import *
2 from ase.lattice.surface import fcc111
3
4 atoms = fcc111('Al', size=(1, 1, 4), vacuum=10.0)
5
6 with jasp('surfaces/Al-slab-unrelaxed',
7          xc='PBE',
8          kpts=(6, 6, 1),
9          encut=350,
10         atoms=atoms) as calc:
11     atoms.get_forces()
12     print calc

```

Open the python script (dft-scripts/script-155.py).

```

: -----
VASP calculation from /home-research/jkitchin/dft-book2/surfaces/Al-slab-unrelaxed
converged: True
Energy = -14.177069 eV

```

```

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 2.864  0.000  0.000] 2.864
a1 [ 1.432  2.480  0.000] 2.864
a2 [ 0.000  0.000 27.015] 27.015
a,b,c,alpha,beta,gamma (deg):2.864 2.864 27.015 90.0 90.0 90.0
Unit cell volume = 191.872 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              0.007  0.007  0.002-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Al  [0.000      0.000    10.000]  0   0.01      T T T
  1    Al  [1.432      0.827    12.338]  0   0.18      T T T
  2    Al  [2.864      1.653    14.677]  0   0.18      T T T
  3    Al  [0.000      0.000    17.015]  0   0.01      T T T

```

INCAR Parameters:

```

-----
nbands: 10
encut: 350.0
magmom: None
prec: Normal
kpts: (6, 6, 1)
reciprocal: False
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
Al: potpaw_PBE/Al/POTCAR (git-hash: c8d9ecb0b6ebec0256c5f5072cee4de6a046dac2)

```

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.

```

1 from jasp import *
2
3 with jasp('surfaces/Al-slab-unrelaxed') as calc:
4     atoms = calc.get_atoms()
5     print 'Total energy: {0:1.3f} eV'.format(atoms.get_potential_energy())
6
7     for i in range(1, len(atoms)):
8         print '{0}  deltaz = {1:1.3f} angstroms'.format(i, atoms[i].z - atoms[i-1].z)

```

Open the python script (dft-scripts/script-156.py).

```

Total energy: -14.177 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 `jasp`. 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.

```
1 from ase.lattice.surface import fcc111
2 atoms = fcc111('Al', size=(2, 2, 4), vacuum=10.0)
3 print([atom.z for atom in atoms])
4 print [atom.z <= 13 for atom in atoms]
```

Open the python script (dft-scripts/script-157.py).

```
[9.999999999999982, 9.999999999999982, 9.999999999999982, 9.999999999999982, 12.338268590217982,
[True, True, True, True, True, True, True, True, False, False, False, False, False, False, False, Fa
```

```

1 from jasp import *
2 from ase.lattice.surface import fcc111
3 from ase.constraints import FixAtoms
4
5 atoms = fcc111('Al', size=(1, 1, 4), vacuum=10.0)
6
7 constraint = FixAtoms(mask=[atom.tag >= 3 for atom in atoms])
8 atoms.set_constraint(constraint)
9
10 with jasp('surfaces/Al-slab-relaxed',
11          xc='PBE',
12          kpts=(6, 6, 1),
13          encut=350,
14          ibrion=2,
15          isif=2,
16          nsw=10,
17          atoms=atoms) as calc:
18     calc.calculate()
19     print calc

```

Open the python script (dft-scripts/script-158.py).

```

:
VASP calculation from /home-research/jkitchin/dft-book2/surfaces/Al-slab-relaxed
converged: True
Energy = -14.181417 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 2.864  0.000  0.000] 2.864
a1 [ 1.432  2.480  0.000] 2.864
a2 [ 0.000  0.000 27.015] 27.015
a,b,c,alpha,beta,gamma (deg):2.864 2.864 27.015 90.0 90.0 90.0
Unit cell volume = 191.872 Ang^3
Stress (GPa):xx,   yy,   zz,   yz,   xz,   xy
              0.006  0.006  0.001-0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]tag  rmsForce constraints
  0    Al  [0.000      0.000      10.000]  4   0.00      F F F
  1    Al  [1.432      0.827      12.338]  3   0.00      F F F
  2    Al  [2.864      1.653      14.637]  2   0.05      T T T
  3    Al  [0.000      0.000      16.982]  1   0.02      T T T

```

INCAR Parameters:

```
nbands: 10
  nsw: 10
ibrion: 2
  isif: 2
  encut: 350.0
magmom: None
  kpts: (6, 6, 1)
reciprocal: False
  xc: PBE
  txt: -
gamma: False
```

Pseudopotentials used:

Al: potpaw_PBE/Al/POTCAR (git-hash: c8d9ecb0b6ebec0256c5f5072cee4de6a046dac2)

You can see that atoms 2 and 3 (the ones we relaxed, because they 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`

```
1 from jasp import *
2
3 with jasp('surfaces/Al-slab-relaxed') as calc:
4     atoms = calc.get_atoms()
5
6     print 'Constraints = True: ', atoms.get_forces(apply_constraint=True)
7
8     print 'Constraints = False: ', atoms.get_forces(apply_constraint=False)
```

Open the python script (dft-scripts/script-159.py).

```
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]]
```

```
1 from jasp import *
2 from ase.lattice.surface import fcc111
3
4 with jasp('surfaces/Al-slab-relaxed') as calc:
5     atoms = calc.get_atoms()
6     print 'Total energy: {0:1.3f}'.format(atoms.get_potential_energy())
7
8     for i in range(1, len(atoms)):
9         print 'd_{0},{1} = {2:1.3f} angstroms'.format(i, i-1,
10               atoms[i].z - atoms[i-1].z)
```

Open the python script (dft-scripts/script-160.py).

```
Total energy: -14.181
d_(1,0) = 2.338 angstroms
d_(2,1) = 2.299 angstroms
d_(3,2) = 2.345 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,^{73,74} and the Au(111) herringbone reconstruction.

We will consider the (110) missing row reconstruction.⁷⁵ 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:

slab₁₁₀ \rightarrow slab_{missing row} + bulk

Thus, if this change in energy: $E_{\text{bulk}} + E_{\text{slab}_{\text{missing row}}} - E_{\text{slab}_{110}}$ 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

```
1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.io import write
4 from ase.constraints import FixAtoms
5 from ase.visualize import view
6
7 atoms = fcc110('Au', size=(2, 1, 6), vacuum=10.0)
8 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
9 atoms.set_constraint(constraint)
10 view(atoms)
```

Open the python script (dft-scripts/script-161.py).

```
1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.io import write
4 from ase.constraints import FixAtoms
5
6 atoms = fcc110('Au', size=(2, 1, 6), vacuum=10.0)
7 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
8 atoms.set_constraint(constraint)
9
```

```
10 write('images/Au-110.png', atoms.repeat((2, 2, 1)), rotation='-90x', show_unit_cell=2)
11
12 with jasp('surfaces/Au-110',
13          xc='PBE',
14          kpts=(6, 6, 1),
15          encut=350,
16          ibrion=2,
17          isif=2,
18          nsw=10,
19          atoms=atoms) as calc:
20     calc.calculate()
```

Open the python script (dft-scripts/script-162.py).

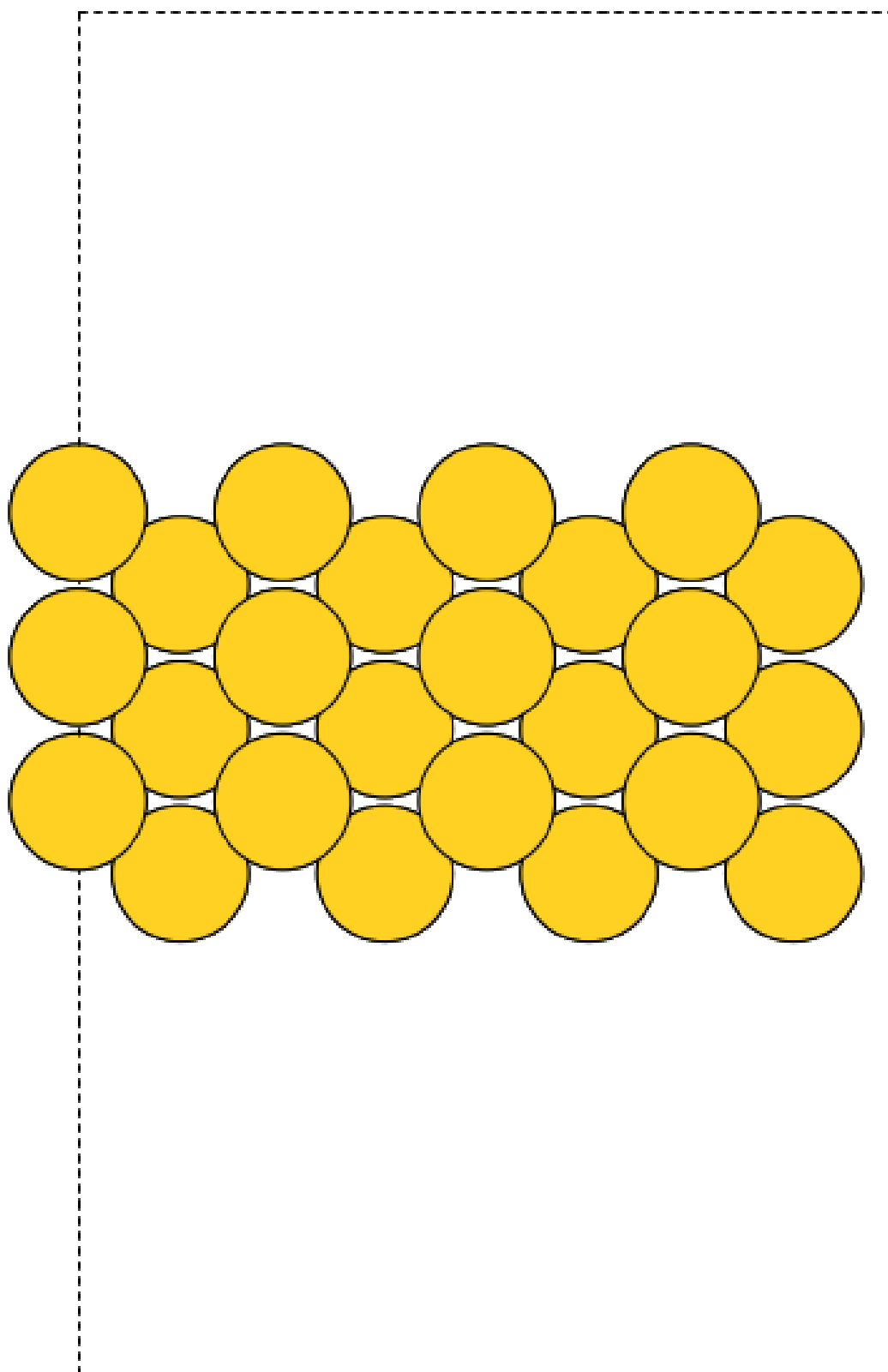


Figure 63: The unreconstructed Au(110) surface viewed from the side.

Missing row in Au(110)

```
1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.io import write
4 from ase.constraints import FixAtoms
5
6 atoms = fcc110('Au', size=(2, 1, 6), vacuum=10.0)
7 del atoms[11] # delete surface row
8
9 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
10 atoms.set_constraint(constraint)
11
12 write('images/Au-110-missing-row.png',
13       atoms.repeat((2, 2, 1)),
14       rotation='-90x',
15       show_unit_cell=2)
16
17 with jasp('surfaces/Au-110-missing-row',
18          xc='PBE',
19          kpts=(6, 6, 1),
20          encut=350,
21          ibrion=2,
22          isif=2,
23          nsr=10,
24          atoms=atoms) as calc:
25     calc.calculate()
```

Open the python script (dft-scripts/script-163.py).

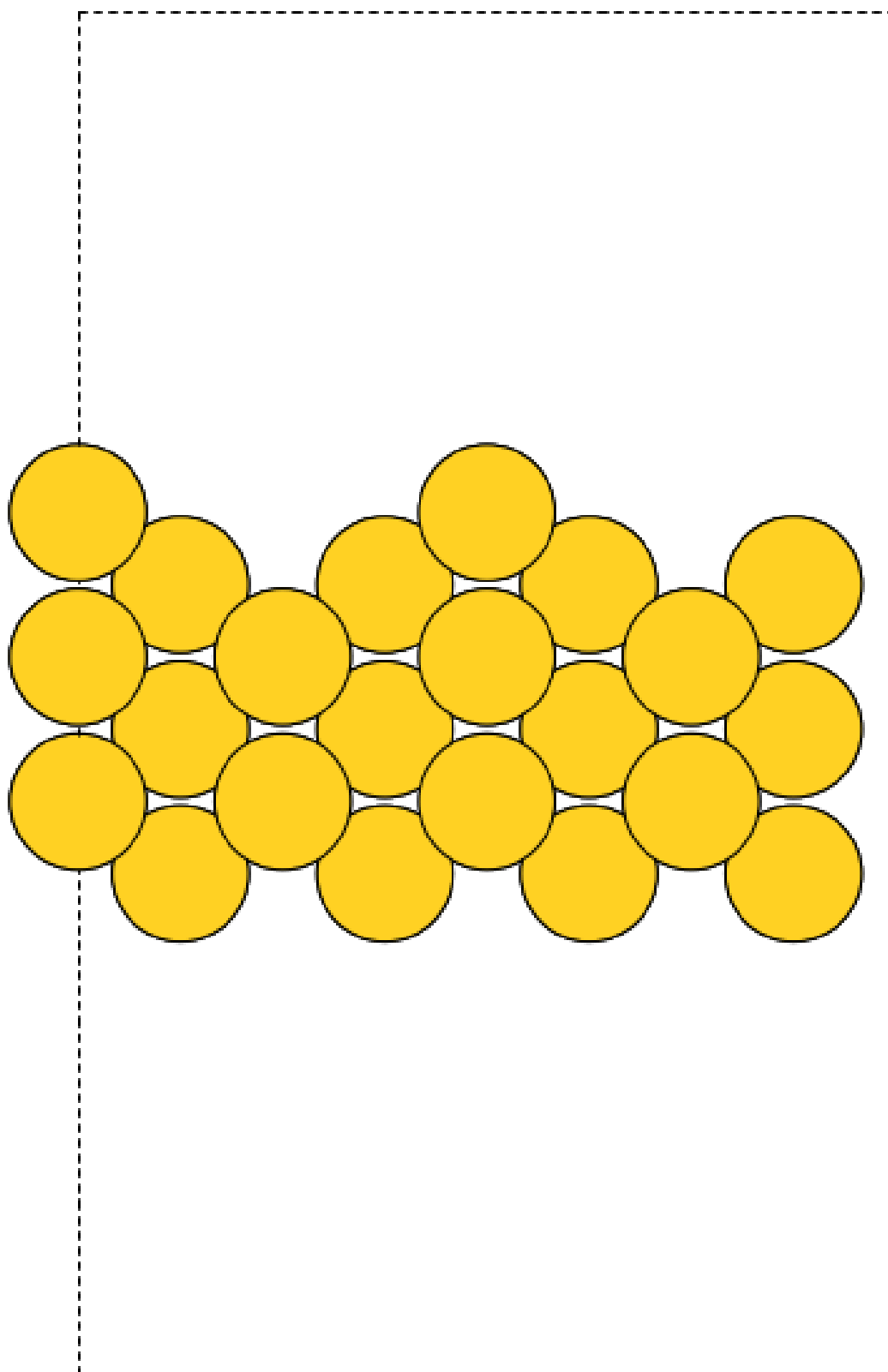


Figure 64: Au(110) with the missing row reconstruction.

Bulk Au

```
1 from jasp import *
2 from ase.visualize import view
3 from ase.lattice.cubic import FaceCenteredCubic
4
5 atoms = FaceCenteredCubic(directions=[[0, 1, 1],
6                                     [1, 0, 1],
7                                     [1, 1, 0]],
8                             size=(1, 1, 1),
9                             symbol='Au')
10
11 with jasp('bulk/Au-fcc',
12          xc='PBE',
13          encut=350,
14          kpts=(12, 12, 12),
15          atoms=atoms) as calc:
16     calc.calculate()
```

Open the python script (dft-scripts/script-164.py).

Analysis of energies

```
1 from jasp import *
2
3 with jasp('surfaces/Au-110') as calc:
4     slab = calc.get_atoms()
5     eslab = slab.get_potential_energy()
6
7 with jasp('surfaces/Au-110-missing-row') as calc:
8     missingrow = calc.get_atoms()
9     emissingrow = missingrow.get_potential_energy()
10
11 with jasp('bulk/Au-fcc') as calc:
12     bulk = calc.get_atoms()
13     ebulk = bulk.get_potential_energy()
14
15 print 'natoms slab          = {0}'.format(len(slab))
16 print 'natoms missing row = {0}'.format(len(missingrow))
17 print 'natoms bulk         = {0}'.format(len(bulk))
18
19 print 'dE = {0:1.3f} eV'.format(emissingrow + ebulk - eslab)
```

Open the python script (dft-scripts/script-165.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 is 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

```
1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.io import write
4 from ase.constraints import FixAtoms
5
```

```

6 atoms = fcc110('Ag', size=(2, 1, 6), vacuum=10.0)
7 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
8 atoms.set_constraint(constraint)
9
10 with jasp('surfaces/Ag-110',
11           xc='PBE',
12           kpts=(6, 6, 1),
13           encut=350,
14           ibrion=2,
15           isif=2,
16           nsw=10,
17           atoms=atoms) as calc:
18     calc.calculate()

```

Open the python script (dft-scripts/script-166.py).

Missing row in Ag(110)

```

1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.io import write
4 from ase.constraints import FixAtoms
5
6 atoms = fcc110('Ag', size=(2, 1, 6), vacuum=10.0)
7 del atoms[11] # delete surface row
8
9 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
10 atoms.set_constraint(constraint)
11
12 with jasp('surfaces/Ag-110-missing-row',
13           xc='PBE',
14           kpts=(6, 6, 1),
15           encut=350,
16           ibrion=2,
17           isif=2,
18           nsw=10,
19           atoms=atoms) as calc:
20     calc.calculate()

```

Open the python script (dft-scripts/script-167.py).

Bulk Ag

```

1 from jasp import *
2 from ase.visualize import view
3 from ase.lattice.cubic import FaceCenteredCubic
4
5 atoms = FaceCenteredCubic(directions=[[0, 1, 1],
6                                       [1, 0, 1],
7                                       [1, 1, 0]],
8                             size=(1, 1, 1),
9                             symbol='Ag')
10
11 with jasp('bulk/Ag-fcc',
12           xc='PBE',
13           encut=350,
14           kpts=(12, 12, 12),
15           atoms=atoms) as calc:
16     calc.calculate()

```

Open the python script (dft-scripts/script-168.py).

Analysis of energies

```

1 from jasp import *
2
3 with jasp('surfaces/Ag-110') as calc:
4     slab = calc.get_atoms()
5     eslab = slab.get_potential_energy()

```

```

6
7 with jasp('surfaces/Ag-110-missing-row') as calc:
8     missingrow = calc.get_atoms()
9     emissingrow = missingrow.get_potential_energy()
10
11 with jasp('bulk/Ag-fcc') as calc:
12     bulk = calc.get_atoms()
13     ebulk = bulk.get_potential_energy()
14
15 print 'natoms slab'      = {0}'.format(len(slab))
16 print 'natoms missing row = {0}'.format(len(missingrow))
17 print 'natoms bulk'      = {0}'.format(len(bulk))
18
19 print 'dE = {0:1.3f} eV'.format(emissingrow + ebulk - eslab)

```

Open the python script (dft-scripts/script-169.py).

```

natoms slab      = 12
natoms missing row = 11
natoms bulk      = 1
dE = -0.008 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.⁷⁶

5.4.3 Cu(110) missing row reconstruction

Clean Cu(110) slab

```

1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.constraints import FixAtoms
4
5 atoms = fcc110('Cu', size=(2, 1, 6), vacuum=10.0)
6 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
7 atoms.set_constraint(constraint)
8
9 with jasp('surfaces/Cu-110',
10         xc='PBE',
11         kpts=(6, 6, 1),
12         encut=350,
13         ibrion=2,
14         isif=2,
15         nsw=10,
16         atoms=atoms) as calc:
17     calc.calculate()

```

Open the python script (dft-scripts/script-170.py).

Missing row in Cu(110)

```

1 from jasp import *
2 from ase.lattice.surface import fcc110
3 from ase.constraints import FixAtoms
4
5 atoms = fcc110('Cu', size=(2, 1, 6), vacuum=10.0)
6 del atoms[11] # delete surface row
7
8 constraint = FixAtoms(mask=[atom.tag > 2 for atom in atoms])
9 atoms.set_constraint(constraint)
10 with jasp('surfaces/Cu-110-missing-row',
11         xc='PBE',
12         kpts=(6, 6, 1),
13         encut=350,
14         ibrion=2,
15         isif=2,

```

```

16         nsw=10,
17         atoms=atoms) as calc:
18     calc.calculate()

```

Open the python script (dft-scripts/script-171.py).

Bulk Cu

```

1  from jasp import *
2  from ase.visualize import view
3  from ase.lattice.cubic import FaceCenteredCubic
4
5  atoms = FaceCenteredCubic(directions=[[0, 1, 1],
6                                       [1, 0, 1],
7                                       [1, 1, 0]],
8                               size=(1, 1, 1),
9                               symbol='Cu')
10
11  with jasp('bulk/Cu-fcc',
12            xc='PBE',
13            encut=350,
14            kpts=(12, 12, 12),
15            atoms=atoms) as calc:
16      calc.calculate()

```

Open the python script (dft-scripts/script-172.py).

Analysis

```

1  from jasp import *
2
3  with jasp('surfaces/Cu-110') as calc:
4      slab = calc.get_atoms()
5      eslab = slab.get_potential_energy()
6
7  with jasp('surfaces/Cu-110-missing-row') as calc:
8      missingrow = calc.get_atoms()
9      emissingrow = missingrow.get_potential_energy()
10
11  with jasp('bulk/Cu-fcc') as calc:
12      bulk = calc.get_atoms()
13      ebulk = bulk.get_potential_energy()
14
15  print 'natoms slab      = {0}'.format(len(slab))
16  print 'natoms missing row = {0}'.format(len(missingrow))
17  print 'natoms bulk      = {0}'.format(len(bulk))
18
19  print 'dE = {0:1.3f} eV'.format(emissingrow + ebulk - eslab)

```

Open the python script (dft-scripts/script-173.py).

```

natoms slab      = 12
natoms missing row = 11
natoms bulk      = 1
dE = -0.011 eV

```

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:

$$\sigma = \frac{1}{2} \left(E_{slab} - \frac{N_{slab}}{N_{bulk}} E_{bulk} \right)$$

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.

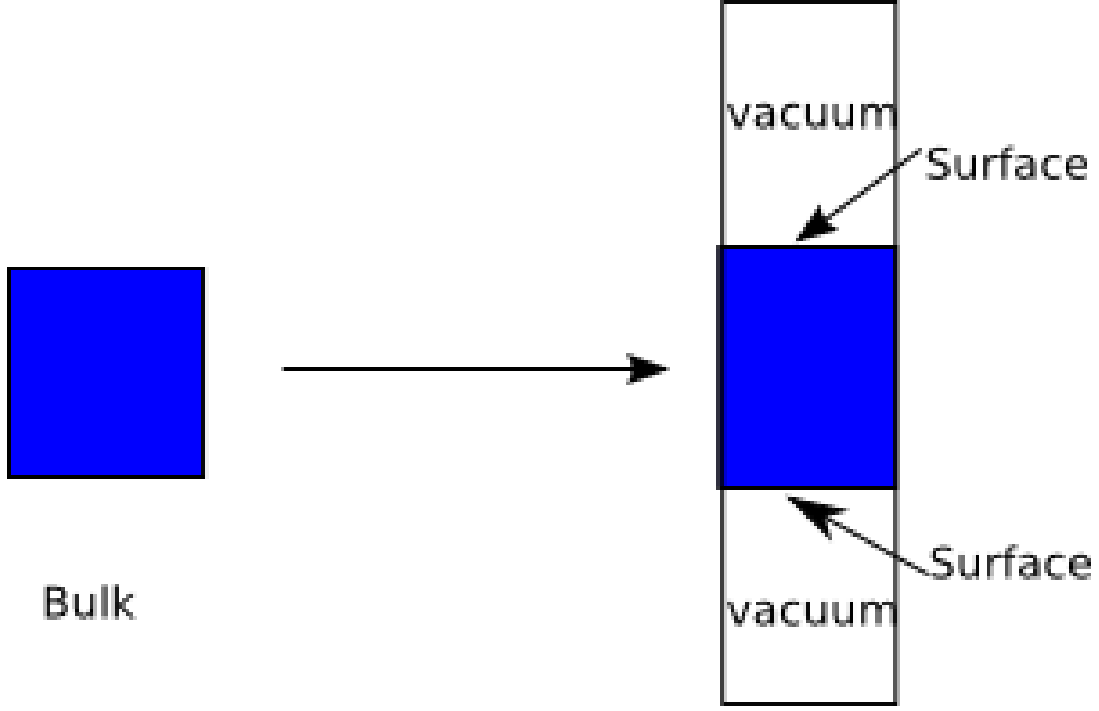


Figure 65: Schematic figure illustrating the calculation of a surface energy.

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.⁷⁷

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.^{77,78}

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.⁷⁸ 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.

$$\sigma = \lim_{N \rightarrow \infty} \frac{1}{2} (E_{\text{slab}}^N - N \Delta E_N)$$

where $\Delta E_N = E_{\text{slab}}^N - E_{\text{slab}}^{N-1}$.

We will examine this approach here. We will use unrelaxed slabs for computational efficiency.

```

1  from jasp import *
2  from ase.lattice.surface import fcc111
3  import matplotlib.pyplot as plt
4
5  Nlayers = [3, 4, 5, 6, 7, 8, 9, 10, 11]
6  energies = []
7  sigmas = []
8
9  for n in Nlayers:
10
11     slab = fcc111('Cu', size=(1, 1, n), vacuum=10.0)
12     slab.center()
13
14     with jasp('bulk/Cu-layers/{0}'.format(n),
15              xc='PBE',
16              encut=350,
17              kpts=(8, 8, 1),
18              atoms=slab) as calc:
19         calc.set_nbands(f=2) # the default nbands in VASP is too low for Cu
20         try:
21             energies.append(slab.get_potential_energy())
22         except (VaspSubmitted, VaspQueued):
23             pass
24
25  for i in range(len(Nlayers) - 1):
26     N = Nlayers[i]
27     DeltaE_N = energies[i + 1] - energies[i]
28     sigma = 0.5 * (-N * energies[i + 1] + (N + 1) * energies[i])
29     sigmas.append(sigma)
30     print 'nlayers = {1:2d} sigma = {0:1.3f} eV/atom'.format(sigma, N)
31
32  plt.plot(Nlayers[0:-1], sigmas, 'bo-')
33  plt.xlabel('Number of layers')
34  plt.ylabel('Surface energy (eV/atom)')
35  plt.savefig('images/Cu-unrelaxed-surface-energy.png')

```

Open the python script (dft-scripts/script-174.py).

```

nlayers = 3 sigma = 0.551 eV/atom
nlayers = 4 sigma = 0.399 eV/atom
nlayers = 5 sigma = 0.590 eV/atom
nlayers = 6 sigma = 0.319 eV/atom
nlayers = 7 sigma = 0.578 eV/atom
nlayers = 8 sigma = 0.322 eV/atom
nlayers = 9 sigma = 0.592 eV/atom
nlayers = 10 sigma = 0.403 eV/atom

```

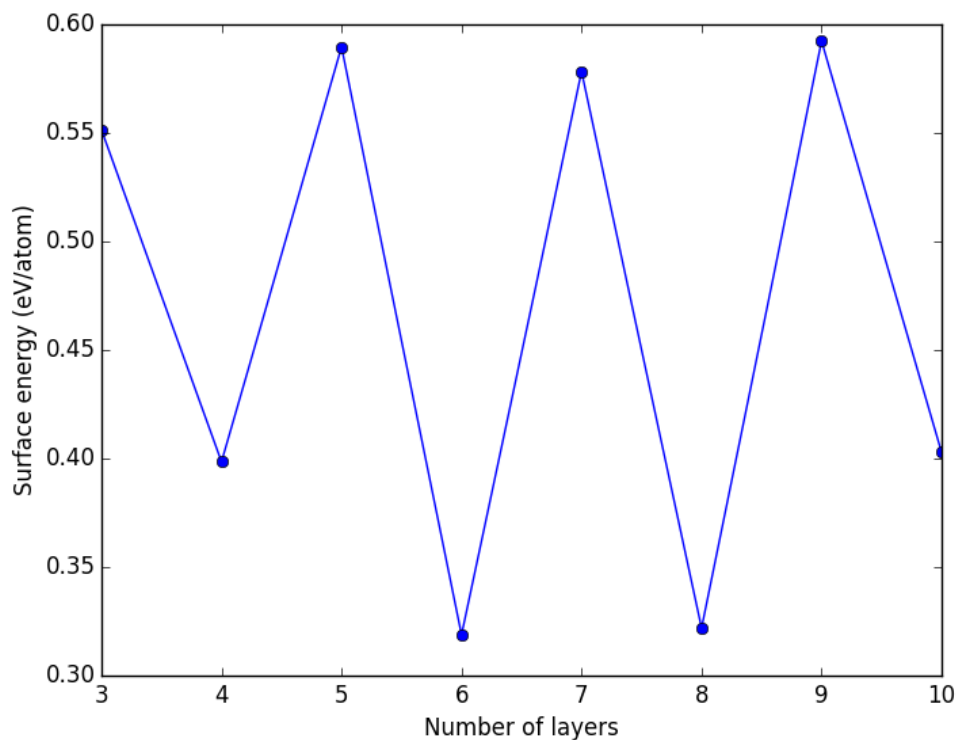


Figure 66: Surface energy of a Cu(111) slab as a function of thickness.

One reason for the oscillations may be quantum size effects.⁷⁹ In⁸⁰ the surface energy of Cu(111) is reported as 0.48 eV/atom, or 1.36 J/m². 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.

```

1 from ase.lattice.surface import fcc111
2 from ase.units import J, m
3 import numpy as np
4
5 slab = fcc111('Cu', size=(1, 1, 3), vacuum=10.0)
6 cell = slab.get_cell()
7
8 area = np.linalg.norm(np.cross(cell[0], cell[1])) # area per atom
9
10 sigma = 0.48 # eV/atom
11
12 print 'sigma = {0} J/m^2'.format(sigma / area / (J / m**2))

```

Open the python script (dft-scripts/script-175.py).

`sigma = 1.3628146074 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. See⁸¹ for an example of computing Mo₂C surface energies and particle shapes, and⁸² 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.⁸³

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.

```
1 from jasp import *
2 import matplotlib.pyplot as plt
3
4 with jasp('surfaces/Al-slab-relaxed') as calc:
5     atoms = calc.get_atoms()
6
7 with jasp('surfaces/Al-slab-locpot',
8         xc='PBE',
9         kpts=(6, 6, 1),
10        encut=350,
11        lvtot=True, # write out local potential
12        lvhar=True, # write out only electrostatic potential, not xc pot
13        atoms=atoms) as calc:
14
15     calc.calculate()
16     ef = calc.get_fermi_level()
17
18     atoms = calc.get_atoms()
19
20     x, y, z, lp = calc.get_local_potential()
21
22 nx, ny, nz = lp.shape
23
24 axy = np.array([np.average(lp[:, :, z]) for z in range(nz)])
25 # setup the x-axis in realspace
26 uc = atoms.get_cell()
27 xaxis = np.linspace(0, uc[2][2], nz)
28
29 plt.plot(xaxis, axy)
30 plt.plot([min(xaxis), max(xaxis)], [ef, ef], 'k:')
31 plt.xlabel('Position along z-axis')
32 plt.ylabel('x-y averaged electrostatic potential')
33 plt.savefig('images/Al-wf.png')
34
35 ind = (xaxis > 0) & (xaxis < 5)
36 wf = np.average(axy[ind]) - ef
37 print 'The workfunction is {0:1.2f} eV'.format(wf)
```

Open the python script (dft-scripts/script-176.py).

The workfunction is 4.04 eV

The workfunction of Al is listed as 4.08 at <http://hyperphysics.phy-astr.gsu.edu/hbase/tables/photoelec.html>.

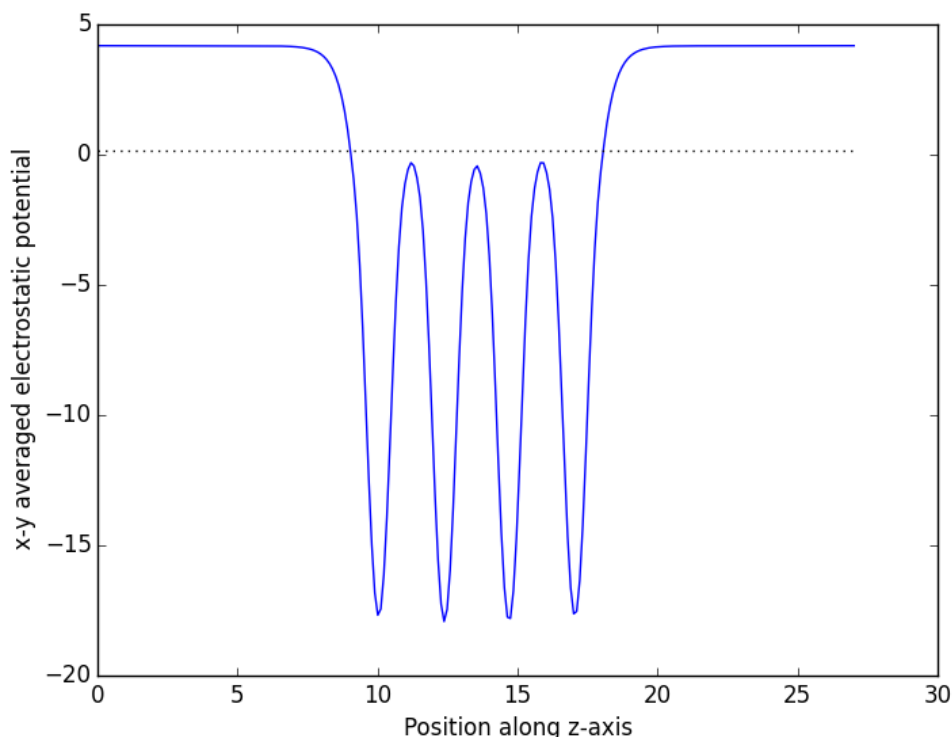


Figure 67: xy averaged local electrostatic potential of an Al(111) slab.

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 Scheffler⁸⁴ and later corrected by Bengtsson.⁸⁵ 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.⁸⁶ Nevertheless, in the literature the use of this correction is fairly standard, and it is typical to at least consider the correction.

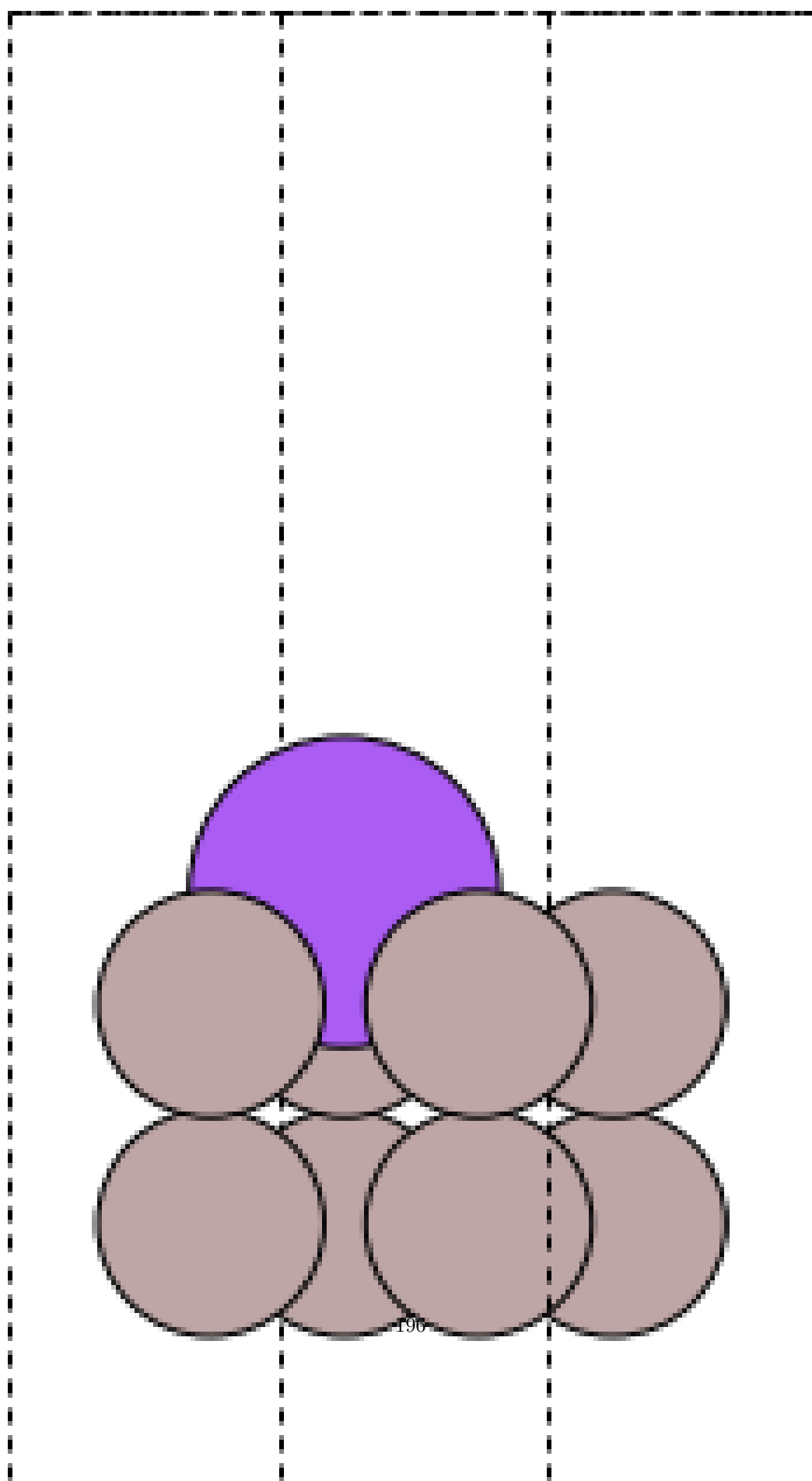
Here we will just illustrate the effect.

5.7.1 Slab with no dipole correction

We simply run the calculation here, and compare the results later.

```
#+BEGIN_SRC python from ase.lattice.surface import fcc111, add_adsorbate from jasp import *
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)
```

```
with jasp('surfaces/Al-Na-nodip', xc='PBE', encut=340, kpts=(2, 2, 1), lvtot=True, # write out
local potential lvhar=True, # write out only electrostatic potential, not xc pot atoms=slab) as calc:
calc.calculate() #+END_SRCb
```



5.7.2 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.

```
1  # compute local potential with dipole calculation on
2  from ase.lattice.surface import fcc111, add_adsorbate
3  from jasp import *
4
5  slab = fcc111('Al', size=(2, 2, 2), vacuum=10.0)
6  add_adsorbate(slab, 'Na', height=1.2, position='fcc')
7
8  slab.center()
9
10 with jasp('surfaces/Al-Na-dip',
11          xc='PBE',
12          encut=340,
13          kpts=(2, 2, 1),
14          idipol=3, # only along z-axis
15          lvtot=True, # write out local potential
16          lvhar=True, # write out only electrostatic potential, not xc pot
17          atoms=slab) as calc:
18
19     calc.calculate()
20
21     x, y, z, cd = calc.get_charge_density()
22     n0, n1, n2 = cd.shape
23     nelements = n0 * n1 * n2
24     voxel_volume = slab.get_volume() / nelements
25     total_electron_charge = cd.sum() * voxel_volume
26
27     electron_density_center = np.array([(cd * x).sum(),
28                                         (cd * y).sum(),
29                                         (cd * z).sum()])
30     electron_density_center *= voxel_volume
31     electron_density_center /= total_electron_charge
32
33     print 'electron-density center = {0}'.format(electron_density_center)
34     uc = slab.get_cell()
35
36     # get scaled electron charge density center
37     sedc = np.dot(np.linalg.inv(uc.T), electron_density_center.T).T
38
39     # we only write 4 decimal places out to the INCAR file, so we round here.
40     sedc = np.round(sedc, 4)
41
42     calc.clone('surfaces/Al-Na-dip-step2')
43
44 # now run step 2 with dipole set at scaled electron charge density center
45 with jasp('surfaces/Al-Na-dip-step2',
46          ldipol=True, dipol=sedc) as calc:
47     calc.calculate()
```

Open the python script (dft-scripts/script-177.py).

```
electron-density center = [ 4.212  2.419 10.657]
```

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.

```

1  from jasp import *
2  import matplotlib.pyplot as plt
3
4  with jasp('surfaces/Al-Na-nodip') as calc:
5      atoms = calc.get_atoms()
6
7      x, y, z, lp = calc.get_local_potential()
8      nx, ny, nz = lp.shape
9
10     axy_1 = [np.average(lp[:, :, z]) for z in range(nz)]
11     # setup the x-axis in realspace
12     uc = atoms.get_cell()
13     xaxis_1 = np.linspace(0, uc[2][2], nz)
14
15     e1 = atoms.get_potential_energy()
16
17 with jasp('surfaces/Al-Na-dip-step2') as calc:
18     atoms = calc.get_atoms()
19
20     x, y, z, lp = calc.get_local_potential()
21     nx, ny, nz = lp.shape
22
23     axy_2 = [np.average(lp[:, :, z]) for z in range(nz)]
24     # setup the x-axis in realspace
25     uc = atoms.get_cell()
26     xaxis_2 = np.linspace(0, uc[2][2], nz)
27
28     ef2 = calc.get_fermi_level()
29     e2 = atoms.get_potential_energy()
30
31 print 'The difference in energy is {0} eV.'.format(e2-e1)
32
33 plt.plot(xaxis_1, axy_1, label='no dipole correction')
34 plt.plot(xaxis_2, axy_2, label='dipole correction')
35 plt.plot([min(xaxis_2), max(xaxis_2)], [ef2, ef2], 'k:', label='Fermi level')
36 plt.xlabel('z ($\AA$)')
37 plt.ylabel('xy-averaged electrostatic potential')
38 plt.legend(loc='best')
39 plt.savefig('images/dip-vs-nodip-esp.png')

```

Open the python script (dft-scripts/script-178.py).

The difference in energy is 3.867888 eV.

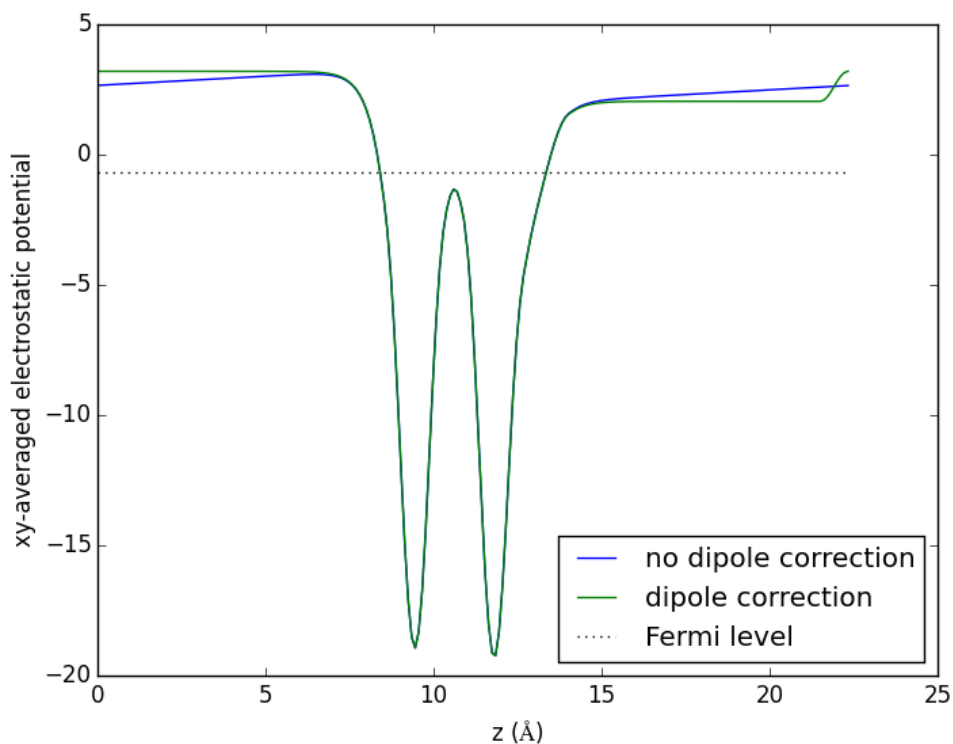


Figure 69: Comparison of the electrostatic potentials with a dipole correction and without it.

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:

$$\text{slab} + \text{gas-phase molecule} \rightarrow \text{slab_adsorbate} + \text{products}$$

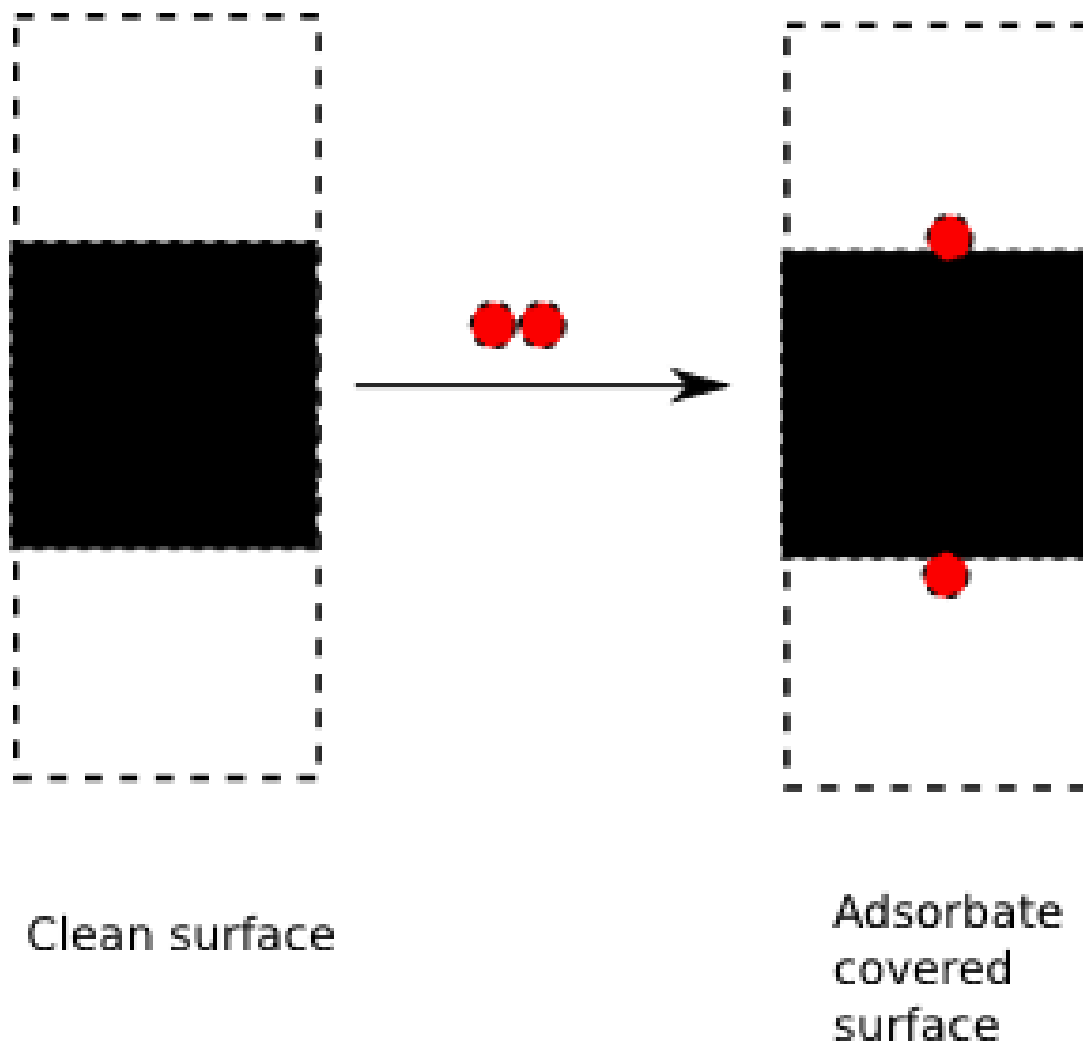


Figure 70: Schematic of an adsorption process.

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

```

1 from jasp import *
2 from ase.lattice.surface import fcc111
3 from ase.constraints import FixAtoms
4
```



```

5 atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)
6 constraint = FixAtoms(mask=[True for atom in atoms])
7 atoms.set_constraint(constraint)
8
9 from ase.io import write
10 write('images/Pt-fcc-ori.png', atoms, show_unit_cell=2)
11
12 with jasp('surfaces/Pt-slab',
13          xc='PBE',
14          kpts=(4, 4, 1),
15          encut=350,
16          atoms=atoms) as calc:
17     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-179.py).

-67.711178

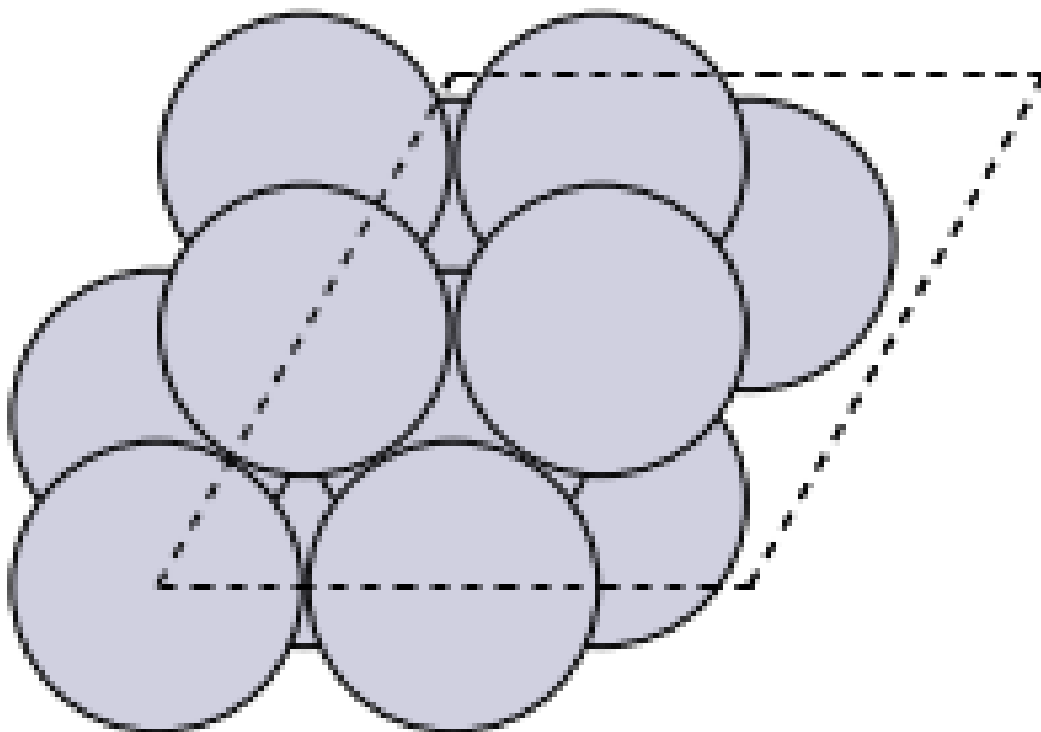


Figure 71: Pt(111) fcc surface

fcc site

```

1 from jasp import *
2
3 from ase.lattice.surface import fcc111, add_adsorbate
4 from ase.constraints import FixAtoms
5
6 atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)
7
8 # note this function only works when atoms are created by the surface module.
9 add_adsorbate(atoms, 'O', height=1.2, position='fcc')
10
11 constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
12 atoms.set_constraint(constraint)

```

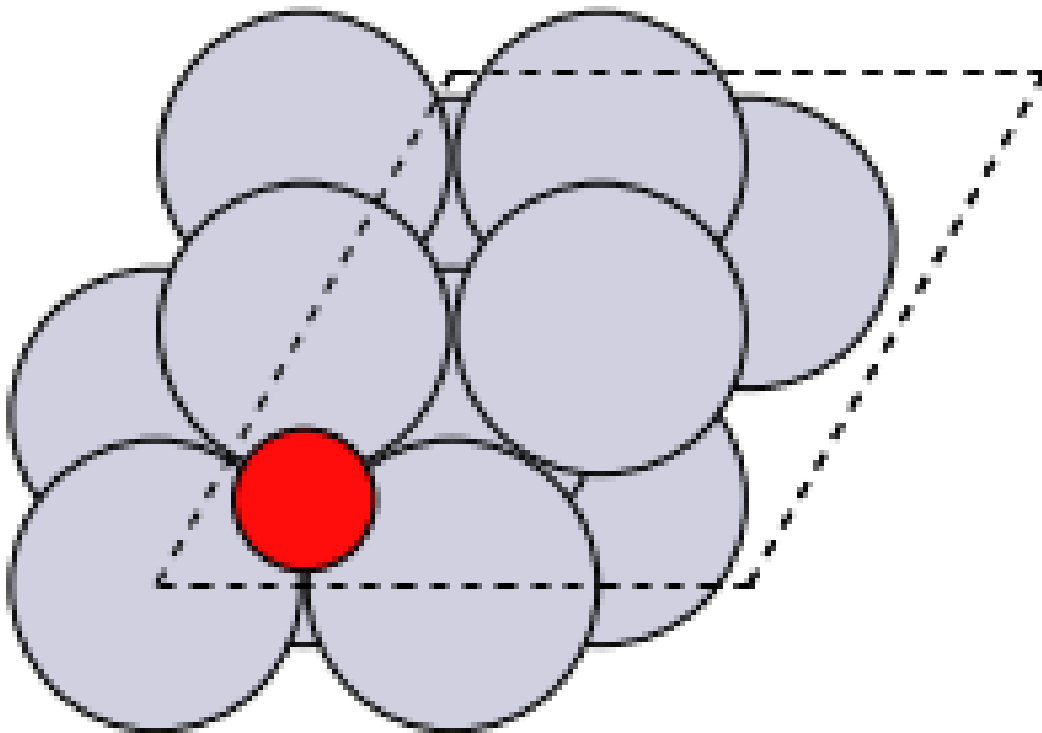
```

13
14 from ase.io import write
15 write('images/Pt-fcc-site.png', atoms, show_unit_cell=2)
16
17 with jasp('surfaces/Pt-slab-0-fcc',
18         xc='PBE',
19         kpts=[4, 4, 1],
20         encut=350,
21         ibrion=2,
22         nsw=25,
23         atoms=atoms) as calc:
24
25     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-180.py).

-73.663924



O atom on the bridge site

```

1 from jasp import *
2 from ase.lattice.surface import fcc111, add_adsorbate
3 from ase.constraints import FixAtoms
4
5 atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)
6
7 # note this function only works when atoms are created by the surface module.
8 add_adsorbate(atoms, 'O', height=1.2, position='bridge')
9
10 constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
11 atoms.set_constraint(constraint)
12
13 with jasp('surfaces/Pt-slab-0-bridge',
14         xc='PBE',
15         kpts=(4, 4, 1),
16         encut=350,
17         ibrion=2,
18         nsw=25,

```

```

19         atoms=atoms) as calc:
20
21     calc.calculate()
22     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-181.py).

-73.663615

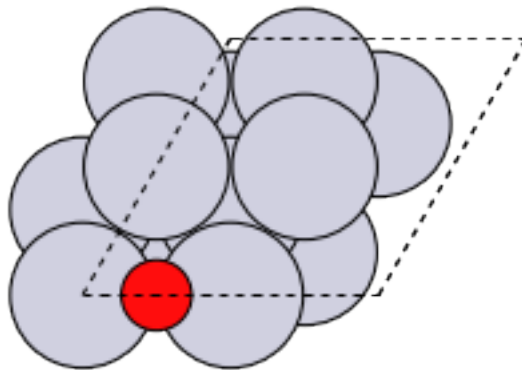


Figure 72: Initial geometry of the bridge site. It is definitely on the bridge.

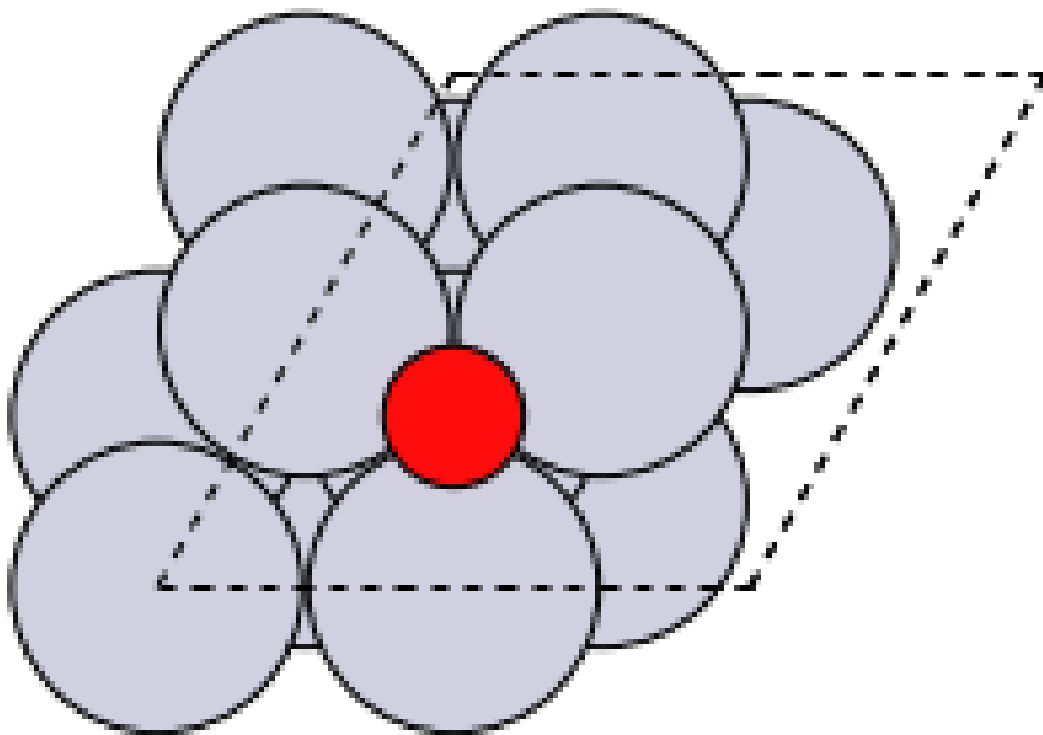
hcp site

```

1  from jasp import *
2  from ase.lattice.surface import fcc111, add_adsorbate
3  from ase.constraints import FixAtoms
4
5  atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)
6
7  # note this function only works when atoms are created by the surface module.
8  add_adsorbate(atoms, 'O', height=1.2, position='hcp')
9
10 constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
11 atoms.set_constraint(constraint)
12
13 from ase.io import write
14 write('images/Pt-hcp-o-site.png', atoms, show_unit_cell=2)
15
16 with jasp('surfaces/Pt-slab-0-hcp',
17           xc='PBE',
18           kpts=(4, 4, 1),
19           encut=350,
20           ibrion=2,
21           nsw=25,
22           atoms=atoms) as calc:
23     calc.calculate()

```

Open the python script (dft-scripts/script-182.py).



Analysis of adsorption energies

```

1  from jasp import *
2  from ase.io import write
3
4  with jasp('surfaces/Pt-slab') as calc:
5      atoms = calc.get_atoms()
6      e_slab = atoms.get_potential_energy()
7      write('images/pt-slab.png', atoms, show_unit_cell=2)
8
9  with jasp('surfaces/Pt-slab-0-fcc') as calc:
10     atoms = calc.get_atoms()
11     e_slab_o_fcc = atoms.get_potential_energy()
12     write('images/pt-slab-fcc-o.png', atoms, show_unit_cell=2)
13
14  with jasp('surfaces/Pt-slab-0-hcp') as calc:
15     atoms = calc.get_atoms()
16     e_slab_o_hcp = atoms.get_potential_energy()
17     write('images/pt-slab-hcp-o.png', atoms, show_unit_cell=2)
18
19  with jasp('surfaces/Pt-slab-0-bridge') as calc:
20     atoms = calc.get_atoms()
21     e_slab_o_bridge = atoms.get_potential_energy()
22     write('images/pt-slab-bridge-o.png', atoms, show_unit_cell=2)
23
24  with jasp('molecules/O2-sp-triplet-350') as calc:
25     atoms = calc.get_atoms()
26     e_O2 = atoms.get_potential_energy()
27
28  Hads_fcc = e_slab_o_fcc - e_slab - 0.5 * e_O2
29  Hads_hcp = e_slab_o_hcp - e_slab - 0.5 * e_O2
30  Hads_bridge = e_slab_o_bridge - e_slab - 0.5 * e_O2
31
32  print 'Hads (fcc)      = {0} eV/0'.format(Hads_fcc)
33  print 'Hads (hcp)      = {0} eV/0'.format(Hads_hcp)
34  print 'Hads (bridge) = {0} eV/0'.format(Hads_bridge)

```

Open the python script (dft-scripts/script-183.py).

Hads (fcc) = -1.0384925 eV/0

Hads (hcp) = -0.5986145 eV/0
Hads (bridge) = -1.0381835 eV/0

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 73) and hcp (Figure 74) sites, which look like we expect.

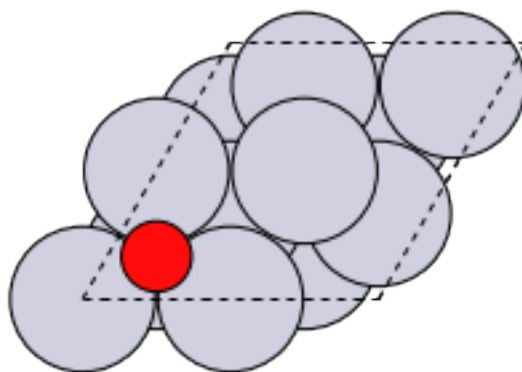


Figure 73: Final geometry of the fcc site.

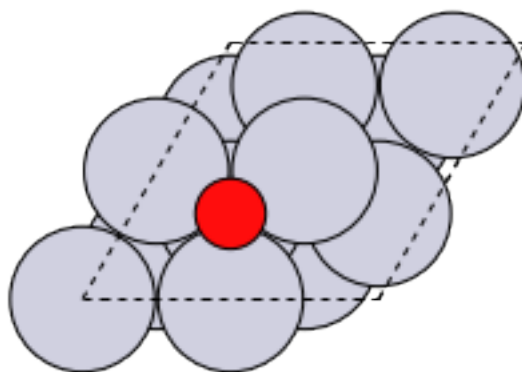


Figure 74: Final geometry of the hcp site.

The bridge site (Figure 75, however, is clearly not at a bridge site!

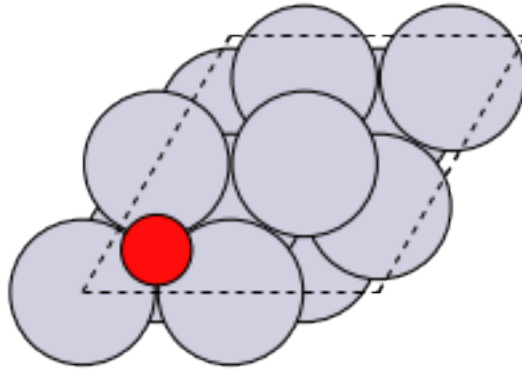


Figure 75: Final geometry of the bridge site. You can see that the oxygen atom ended up in the fcc site.

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.

```

1  from ase.io import read, write
2
3  atoms = read('surfaces/Pt-slab-0-bridge/POSCAR')
4  write('images/Pt-o-brige-ori.png', atoms, show_unit_cell=2)
5
6  atoms = read('surfaces/Pt-slab-0-bridge/CONTCAR')
7  write('images/Pt-o-brige-final.png', atoms, show_unit_cell=2)

```

Open the python script (dft-scripts/script-184.py).

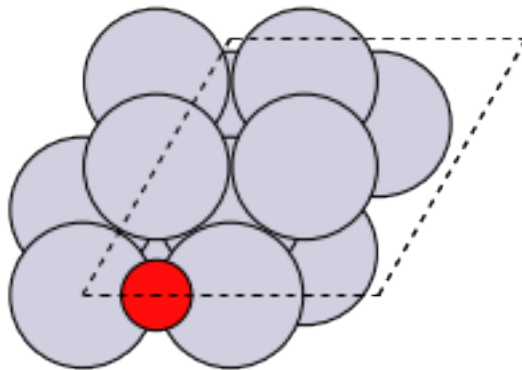


Figure 76: Initial geometry of the bridge site. It is definitely on the bridge.

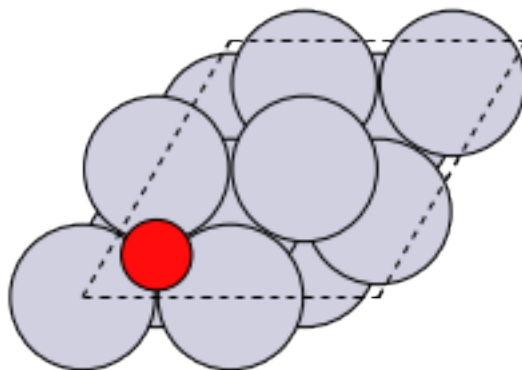


Figure 77: Final geometry of the bridge site. It has fallen into the fcc site.

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).

```

1  from jasp import *
2
3  from ase.lattice.surface import fcc111, add_adsorbate
4  from ase.constraints import FixAtoms, FixScaled
5  from ase.io import write
6
7  atoms = fcc111('Pt', size=(2, 2, 3), vacuum=10.0)
8
9  # note this function only works when atoms are created by the surface module.
10 add_adsorbate(atoms, 'O', height=1.2, position='bridge')
11 constraint1 = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
12 # fix in xy-direction, free in z. actually, freeze movement in surface
13 # unit cell, and free along 3rd lattice vector
14 constraint2 = FixScaled(atoms.get_cell(), 12, [True, True, False])
15
16 atoms.set_constraint([constraint1, constraint2])
17 write('images/Pt-O-bridge-constrained-initial.png', atoms, show_unit_cell=2)
18 print 'Initial O position: {0}'.format(atoms.positions[-1])
19
20 with jasp('surfaces/Pt-slab-O-bridge-xy-constrained',
```

```

21         xc='PBE',
22         kpts=(4, 4, 1),
23         encut=350,
24         ibrion=2,
25         nsw=25,
26         atoms=atoms) as calc:
27     e_bridge = atoms.get_potential_energy()
28
29 write('images/Pt-O-bridge-constrained-final.png', atoms, show_unit_cell=2)
30 print 'Final O position : {0}'.format(atoms.positions[-1])
31
32 # now compute Hads
33 with jasp('surfaces/Pt-slab') as calc:
34     atoms = calc.get_atoms()
35     e_slab = atoms.get_potential_energy()
36
37
38 with jasp('molecules/O2-sp-triplet-350') as calc:
39     atoms = calc.get_atoms()
40     e_O2 = atoms.get_potential_energy()
41
42 Hads_bridge = e_bridge - e_slab - 0.5*e_O2
43
44 print 'Hads (bridge) = {0:1.3f} eV/O'.format(Hads_bridge)

```

Open the python script (dft-scripts/script-185.py).

```

Initial O position: [  1.386   0.   15.726]
Final O position  : [  1.386   0.   15.977]
Hads (bridge) = -0.488 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.

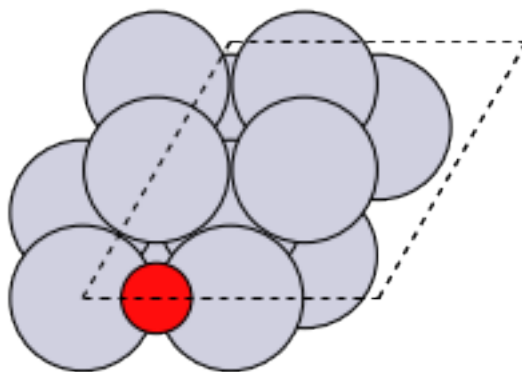


Figure 78: Initial state of the O atom on the bridge site.

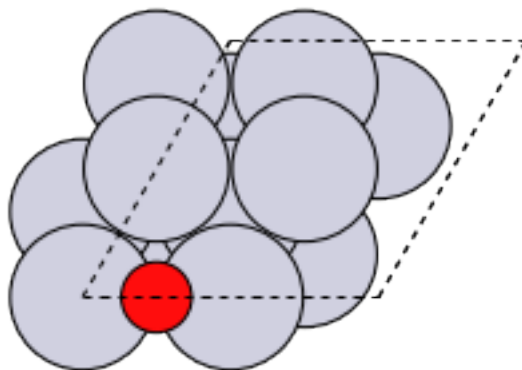


Figure 79: Final state of the constrained O atom, still on the bridge site.

5.8.2 Coverage dependence

The adsorbates on the surface can interact with each other which results in coverage dependent adsorption energies.⁸⁷ 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^{88,89}
- Coverage effects of atomic adsorbates on Pd(111)⁹⁰
- Simple model for estimating coverage dependence⁸⁷
- Coverage effects on alloys⁹¹

clean slab calculation

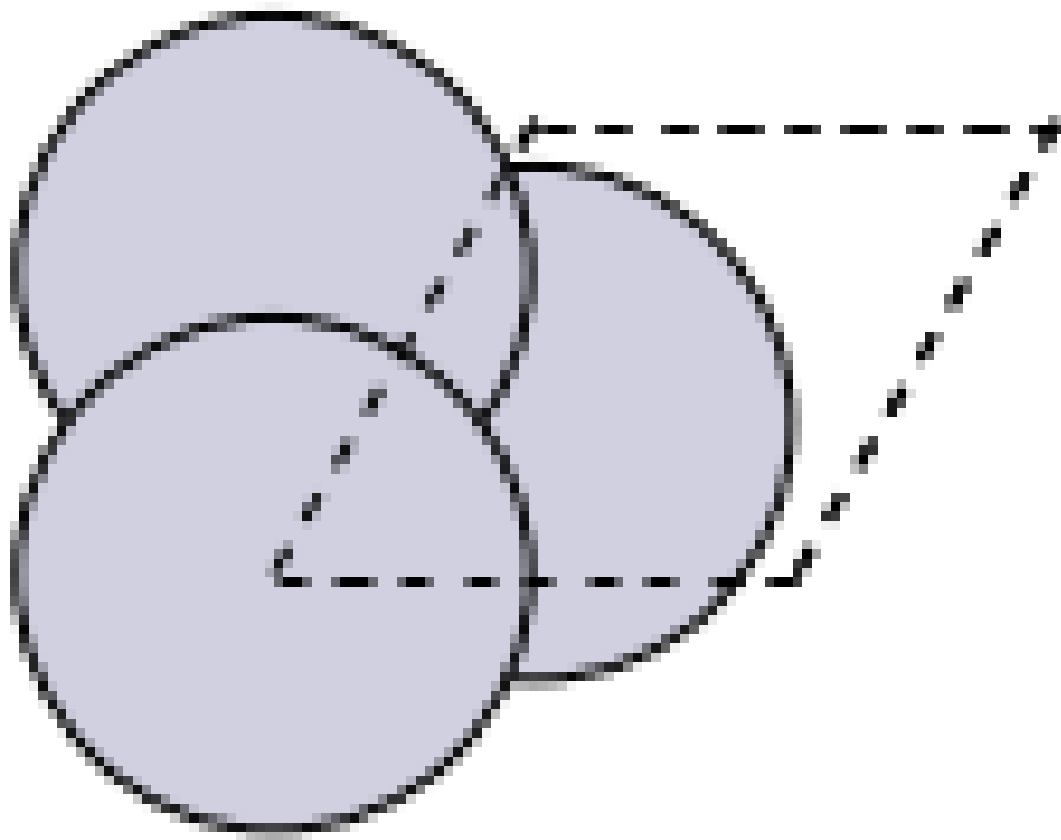
```

1  from jasp import *
2  from ase.lattice.surface import fcc111
3  from ase.constraints import FixAtoms
4
5  atoms = fcc111('Pt', size=(1, 1, 3), vacuum=10.0)
6  constraint = FixAtoms(mask=[True for atom in atoms])
7  atoms.set_constraint(constraint)
8
9  write('images/Pt-fcc-1ML.png', atoms, show_unit_cell=2)
10
11 with jasp('surfaces/Pt-slab-1x1',
12          xc='PBE',
13          kpts=(8, 8, 1),
14          encut=350,
15          atoms=atoms) as calc:
16     slab_e = atoms.get_potential_energy()
17     print slab_e

```

Open the python script (dft-scripts/script-186.py).

-16.927696



fcc site at 1 ML coverage

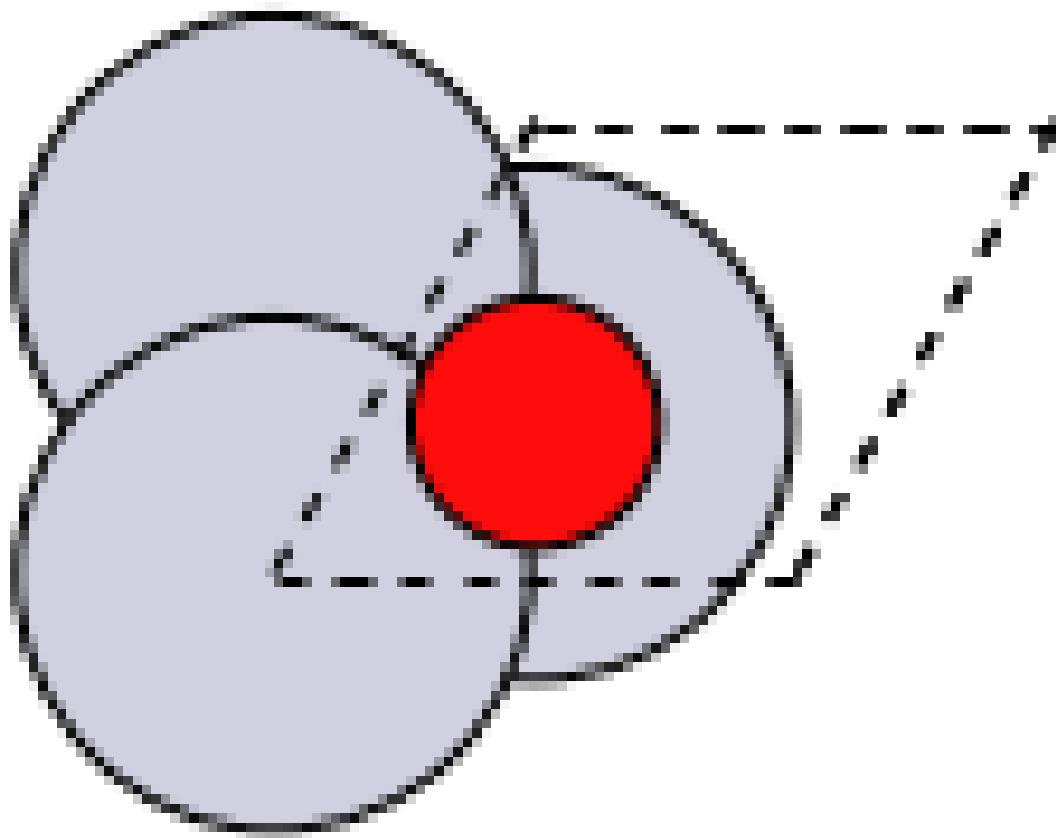
```

1  from jasp import *
2
3  from ase.lattice.surface import fcc111, add_adsorbate
4  from ase.constraints import FixAtoms
5  from ase.io import write
6
7  atoms = fcc111('Pt', size=(1, 1, 3), vacuum=10.0)
8
9  # note this function only works when atoms are created by the surface module.
10 add_adsorbate(atoms, 'O', height=1.2, position='fcc')
11
12 constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
13 atoms.set_constraint(constraint)
14
15
16 write('images/Pt-o-fcc-1ML.png', atoms, show_unit_cell=2)
17
18
19 with jasp('surfaces/Pt-slab-1x1-0-fcc',
20         xc='PBE',
21         kpts=(8, 8, 1),
22         encut=350,
23         ibrion=2,
24         nsw=25,
25         atoms=atoms) as calc:
26     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-187.py).

-21.941003



Adsorption energy at 1ML

```

1 from jasp import *
2
3 with jasp('surfaces/Pt-slab-1x1-0-fcc') as calc:
4     atoms = calc.get_atoms()
5     e_slab_o = atoms.get_potential_energy()
6
7 # clean slab
8 with jasp('surfaces/Pt-slab-1x1') as calc:
9     atoms = calc.get_atoms()
10    e_slab = atoms.get_potential_energy()
11
12 with jasp('molecules/O2-sp-triplet-350') as calc:
13     atoms = calc.get_atoms()
14     e_O2 = atoms.get_potential_energy()
15
16 hads = e_slab_o - e_slab - 0.5 * e_O2
17 print 'Hads (1ML) = {0:1.3f} eV'.format(hads)

```

Open the python script (dft-scripts/script-188.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:

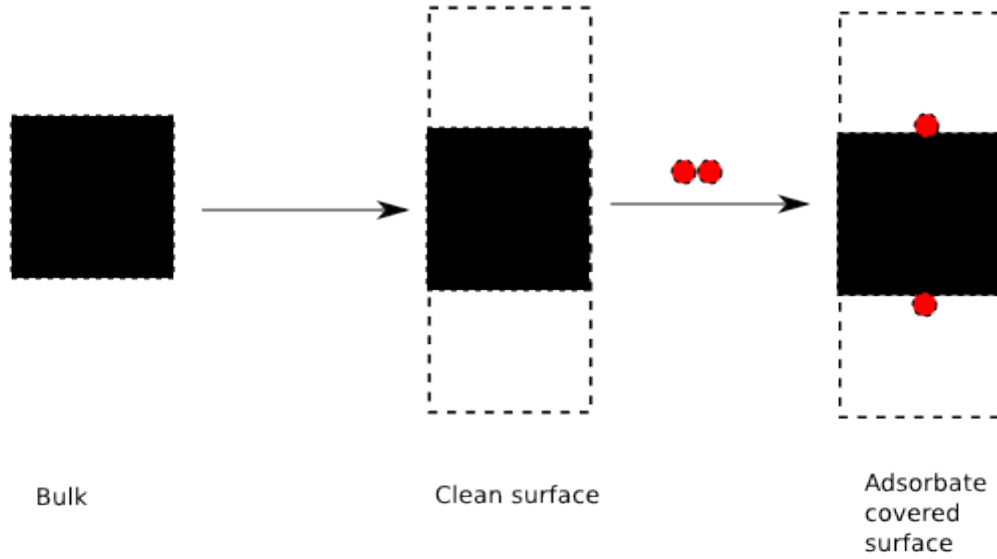


Figure 80: Schematic of forming a surface with adsorbates. First we form two clean surfaces by cleaving the bulk, then allow adsorption to occur on the surfaces.

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 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).

```

1 from jasp import *
2
3 with jasp('surfaces/Pt-slab-0-fcc') as calc:
4     calc.clone('surfaces/Pt-slab-0-fcc-vib')
5
6 with jasp('surfaces/Pt-slab-0-fcc-vib') as calc:
7     calc.set(ibrion=5,      # finite differences with selective dynamics
8             nfree=2,      # central differences (default)
9             potim=0.015,   # default as well
10            ediff=1e-8,
11            nsw=1)
12     atoms = calc.get_atoms()
13     f, v = calc.get_vibrational_modes(0)
14     print 'Elapsed time = {0} seconds'.format(calc.get_elapsed_time())
15     allfreq = calc.get_vibrational_modes()[0]
16
17 from ase.units import meV
18 c = 3e10 # cm/s
19 h = 4.135667516e-15 # eV*s
20
21 print 'vibrational energy = {0} eV'.format(f)
22 print 'vibrational energy = {0} meV'.format(f/meV)
23 print 'vibrational freq  = {0} 1/s'.format(f/h)
24 print 'vibrational freq  = {0} cm^{{-1}}'.format(f/(h*c))
25 print
26 print 'All energies = ', allfreq

```

Open the python script (dft-scripts/script-189.py).

```

Elapsed time = 14269.345 seconds
vibrational energy = 0.061606647 eV
vibrational energy = 61.606647 meV
vibrational freq  = 1.48964216204e+13 1/s
vibrational freq  = 496.547387346 cm^{{-1}}

```

```
All energies = [0.061606647, 0.044346362, 0.044344470000000004]
```

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.

```

1 from jasp import *
2
3 with jasp('surfaces/Pt-slab-0-fcc') as calc:
4     calc.clone('Pt-slab-0-fcc-vib-ibrion=6')
5
6 with jasp('surfaces/Pt-slab-0-fcc-vib-ibrion=6') as calc:
7     calc.set(ibrion=6, # finite differences with symmetry
8             nfree=2, # central differences (default)
9             potim=0.015, # default as well
10            ediff=1e-8,
11            nsw=1)
12     atoms = calc.get_atoms()
13     print 'Elapsed time = {0} seconds'.format(calc.get_elapsed_time())
14
15     f, m = calc.get_vibrational_modes(0)
16     allfreq = calc.get_vibrational_modes()[0]
17
18 from ase.units import meV

```

```

19 c = 3e10 # cm/s
20 h = 4.135667516e-15 # eV*s
21
22 print 'For mode 0:'
23 print 'vibrational energy = {0} eV'.format(f)
24 print 'vibrational energy = {0} meV'.format(f / meV)
25 print 'vibrational freq = {0} 1/s'.format(f / h)
26 print 'vibrational freq = {0} cm-1'.format(f / (h * c))
27 print
28 print 'All energies = ', allfreq

```

Open the python script (dft-scripts/script-190.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.

```

1 print 77000 / 3600.0

```

Open the python script (dft-scripts/script-191.py).

21.3888888889

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.

```

1 from jasp import *
2 from ase.constraints import FixAtoms
3
4 # clone calculation so we do not overwrite previous results
5 with jasp('surfaces/Pt-slab-0-bridge-xy-constrained') as calc:
6     calc.clone('surfaces/Pt-slab-0-bridge-vib')
7
8 with jasp('surfaces/Pt-slab-0-bridge-vib') as calc:
9     calc.set(ibrion=5, # finite differences with selective dynamics
10             nfree=2, # central differences (default)
11             potim=0.015, # default as well
12             ediff=1e-8,
13             nsw=1)
14     atoms = calc.get_atoms()
15     del atoms.constraints
16     constraint = FixAtoms(mask=[atom.symbol != 'O' for atom in atoms])
17     atoms.set_constraint([constraint])
18
19     f, v = calc.get_vibrational_modes(2)
20     print calc.get_vibrational_modes()[0]
21
22 from ase.units import meV
23 c = 3e10 # cm/s
24 h = 4.135667516e-15 # eV*s

```

```

25
26 print 'vibrational energy = {0} eV'.format(f)
27 print 'vibrational energy = {0} meV'.format(f/meV)
28 print 'vibrational freq   = {0} 1/s'.format(f/h)
29 print 'vibrational freq   = {0} cm-1'.format(f/(h*c))

```

Open the python script (dft-scripts/script-192.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 review⁹² 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.

```

1  from jasp import *
2  from ase.neb import NEB
3  import matplotlib.pyplot as plt
4
5  with jasp('surfaces/Pt-slab-0-fcc') as calc:
6      initial_atoms = calc.get_atoms()
7
8  with jasp('surfaces/Pt-slab-0-hcp') as calc:
9      final_atoms = calc.get_atoms()
10
11  # here is our estimated transition state. we use vector geometry to
12  # define the bridge position, and add 1.451 Ang to z based on our
13  # previous bridge calculation. The bridge position is half way between
14  # atoms 9 and 10.
15  ts = initial_atoms.copy()
16  ts.positions[-1] = 0.5 * (ts.positions[9] + ts.positions[10]) + [0, 0, 1.451]
17
18  # construct the band
19  images = [initial_atoms]
20  images += [initial_atoms.copy()]
21  images += [ts.copy()] # this is the TS
22
23  neb = NEB(images)
24  # Interpolate linearly the positions of these images:
25  neb.interpolate()
26
27  # now add the second half
28  images2 = [ts.copy()]
29  images2 += [ts.copy()]
30  images2 += [final_atoms]
31
32  neb2 = NEB(images2)
33  neb2.interpolate()
34
35  # collect final band. Note we do not repeat the TS in the second half
36  final_images = images + images2[1:]
37
38  with jasp('surfaces/Pt-0-fcc-hcp-neb',

```

```

39         ibrion=1,
40         nsr=90,
41         spring=-5,
42         atoms=final_images) as calc:
43
44     try:
45         images, energies = calc.get_neb()
46         p = calc.plot_neb(show=False)
47
48         # remember you are in surfaces/Pt-O-fcc-hcp-neb, so to save in
49         # the images directory you need ../../ in the path to get you
50         # back up.
51         plt.savefig('../../images/pt-o-fcc-hcp-neb.png')
52     except (VaspSubmitted, VaspQueued):
53         pass

```

Open the python script (dft-scripts/script-193.py).

Optimization terminated successfully.

Current function value: -0.575224

Iterations: 12

Function evaluations: 24

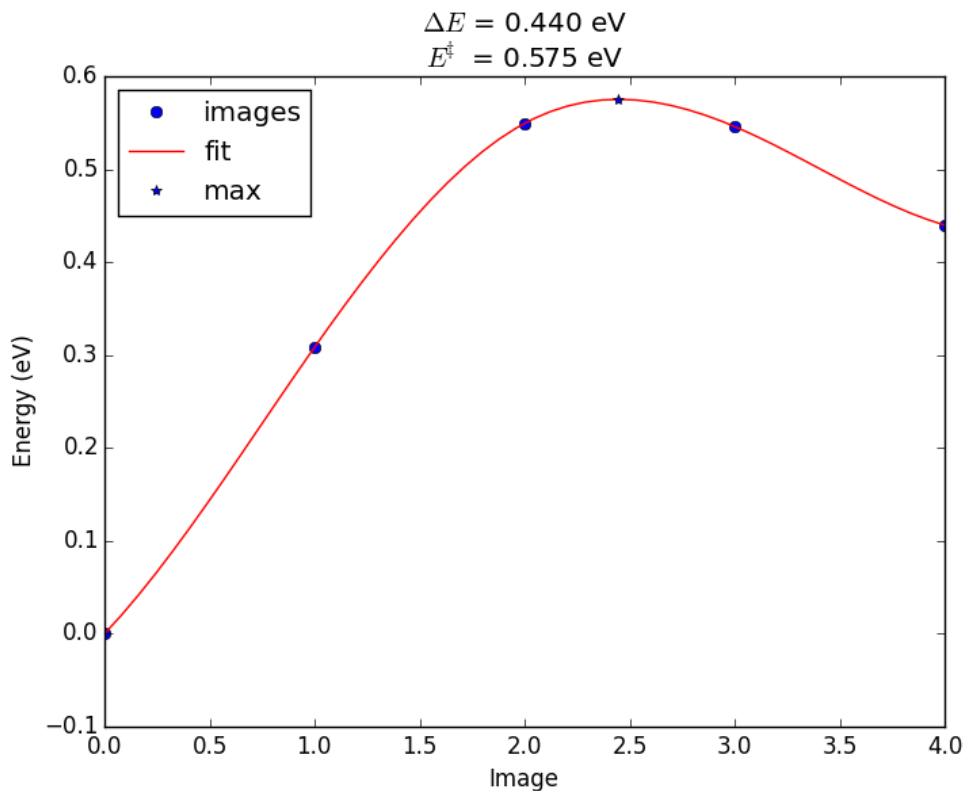


Figure 81: Energy pathway for O diffusion from an fcc to hcp site with a spline fit to determine the barrier.

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 method⁹³ solves that problem by making one image climb to the top. You set `LCLIMB==True` in `jasp` to turn on the climbing image method. Here we use the previous calculation as a starting point and turn on the climbing image method.

```

1  # perform a climbing image NEB calculation
2  from jasp import *
3  with jasp('surfaces/Pt-0-fcc-hcp-neb') as calc:
4      calc.clone('surfaces/Pt-0-fcc-hcp-cineb')
5
6  with jasp('surfaces/Pt-0-fcc-hcp-cineb',
7          debug=logging.DEBUG) as calc:
8      calc.set(ichain=0, lclimb=True)
9
10     images, energies = calc.get_neb()
11     calc.plot_neb(show=False)
12 import matplotlib.pyplot as plt
13 plt.savefig('images/pt-o-cineb.svg')
14 plt.show()

```

Open the python script (dft-scripts/script-194.py).

Optimization terminated successfully.

Current function value: -46.519590

Iterations: 12

Function evaluations: 24

Climbing image NEB.

[width=.9]./images/pt-o-cineb

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.

5.11 TODO Diffusion rates with transition state theory

5.12 TODO Effects of electric fields on adsorbates

Electric fields can polarize adsorbates, i.e. shift their electron density around, which changes their stability. We can model this to some extent in VASP. We have to set the `EFIELD` parameter to specify the field strength (in V/Å), and `LDIPOL` to `True`, and finally specify which lattice vector the field should be applied to with `IDIPOL`. Usually, `IDIPOL` will be set to 3 for surfaces so it points in the direction of the third lattice vector, which is conventionally in the z-direction and normal to the surface.

We will illustrate the effect using an example from⁹⁴ for the effect of electric field on the adsorption energy of a CO molecule on Pt(111) at 0.25 ML. For simplicity, we will use a frozen slab, with the CO molecule in the geometry reported in that reference.

```

1  from jasp import *
2  from ase.lattice.surface import fcc111
3
4  atoms = fcc111('Pt', size=(2, 2, 4), vacuum=10.0, a=3.986)

```

```

5  atoms.append(Atom('C', [atoms[12].x, atoms[12].y, atoms[12].z + 1.851]))
6  atoms.append(Atom('O', [atoms[-1].x, atoms[-1].y, atoms[-1].z + 1.157]))
7
8  for field in [-0.5, 0.0, 0.5]:
9      with jasp('surfaces/Pt-co-field-{0}'.format(field),
10               xc='PBE',
11               encut=350,
12               kpts=(6, 6, 1),
13               efield=field, # set the field
14               ldipol=True,  # turn dipole correction on
15               idipol=3,     # set field in z-direction
16               atoms=atoms) as calc:
17          try:
18              print '{0}: {1:1.3f}'.format(field, atoms.get_potential_energy())
19          except (VaspSubmitted, VaspQueued):
20              pass

```

Open the python script (dft-scripts/script-195.py).

0.0: -108.077

These energies are crazy different, and the forces on the atoms with the field on are insanely high. This section is on hold until I figure that out.

5.13 TODO Simulating STM images

this link seems to be nonexistent now: http://cst-www.nrl.navy.mil/users/sullivan/stm_backup/stm2.html

see <http://vaspnotes.blogspot.com/2013/09/simulated-stm.html>

adapted from <https://wiki.fysik.dtu.dk/gpaw/tutorials/stm/stm.html>

jasp needs this function for STM to work: `get_pseudo_wave_function`

```

1  from jasp import *
2  from ase.dft.stm import STM
3  import matplotlib.pyplot as plt
4
5
6  with jasp('surfaces/Al-slab-relaxed') as calc:
7      atoms = calc.get_atoms()
8
9      stm = STM(atoms)
10     z = 8.0
11     bias = 1.0
12     c = stm.get_averaged_current(bias, z)
13     x, y, h = stm.scan(bias, c, repeat=(3, 5))
14
15
16     plt.gca(aspect='equal')
17     plt.contourf(x, y, h, 40)
18     plt.hot()
19     plt.colorbar()
20     plt.show()

```

Open the python script (dft-scripts/script-196.py).

6 Atomistic thermodynamics

Let us consider how much the Gibbs free energy of an O₂ 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](http://webbook.nist.gov) for O₂.

```

1  from ase.units import *
2  K = 1.0
3

```

```

4 print J, mol, K
5
6 print 0.100 * kJ / mol / K
7
8 print 1 * eV / (kJ / mol)

```

Open the python script (dft-scripts/script-197.py).

```

6.24150636309e+18 6.0221367e+23 1.0
0.00103642721413
96.485308989

```

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3 from ase.units import *
4 K = 1. # Kelvin not defined in ase.units!
5
6 # Shomate parameters
7 A = 31.32234; B = -20.23531; C = 57.86644
8 D = -36.50624; E = -0.007374; F = -8.903471
9 G = 246.7945; H = 0.0
10
11
12 def entropy(T):
13     '''entropy returned as eV/K
14     T in K
15     '''
16     t = T / 1000.
17     s = (A * np.log(t) + B * t + C * (t**2) / 2.
18         + D * (t**3) / 3. - E / (2. * t**2) + G)
19     return s * J / mol / K
20
21
22 def enthalpy(T):
23     '''H - H(298.15) returned as eV/molecule'''
24     t = T / 1000.
25     h = (A * t + B * (t**2) / 2. + C * (t**3) / 3.
26         + D * (t**4) / 4. - E / t + F - H)
27     return h * kJ / mol
28
29 T = np.linspace(10, 700)
30
31 G = enthalpy(T) - T * entropy(T)
32
33 plt.plot(T, G)
34 plt.xlabel('Temperature (K)')
35 plt.ylabel(r'$\Delta G^\circ$ (eV)')
36 plt.savefig('images/02-mu.png')

```

Open the python script (dft-scripts/script-198.py).

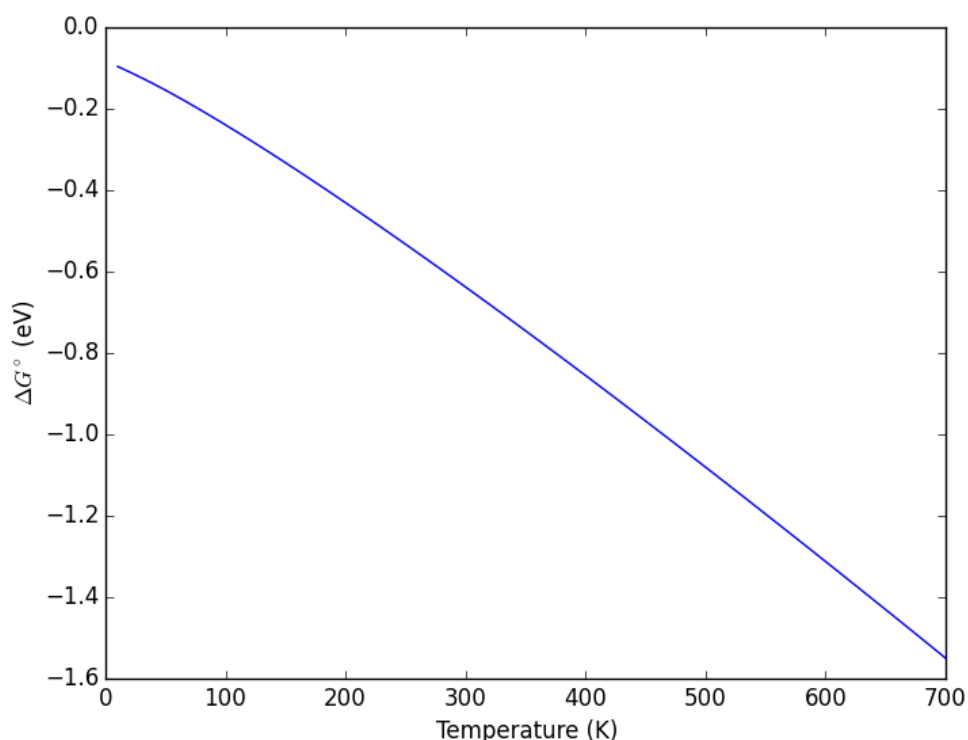


Figure 82: Effect of temperature on the Gibbs free energy of an O₂ molecule at standard state (1 atm).

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.

```

1  import matplotlib.pyplot as plt
2  import numpy as np
3  from ase.units import *
4
5  atm = 101325 * Pascal #atm is not defined in units
6  K = 1 # Kelvin
7
8  # examine range over 10-10 to 1010 atm
9  P = np.logspace(-10, 10) * atm
10
11 plt.semilogx(P / atm, kB * (300 * K) * np.log(P / (1 * atm)), label='300K')
12 plt.semilogx(P / atm, kB * (600 * K) * np.log(P / (1 * atm)), label='600K')
13 plt.xlabel('Pressure (atm)')
14 plt.ylabel(r'$\Delta G$ (eV)')
15 plt.legend(loc='best')
16 plt.savefig('images/O2-g-p.png')

```

Open the python script (dft-scripts/script-199.py).

None

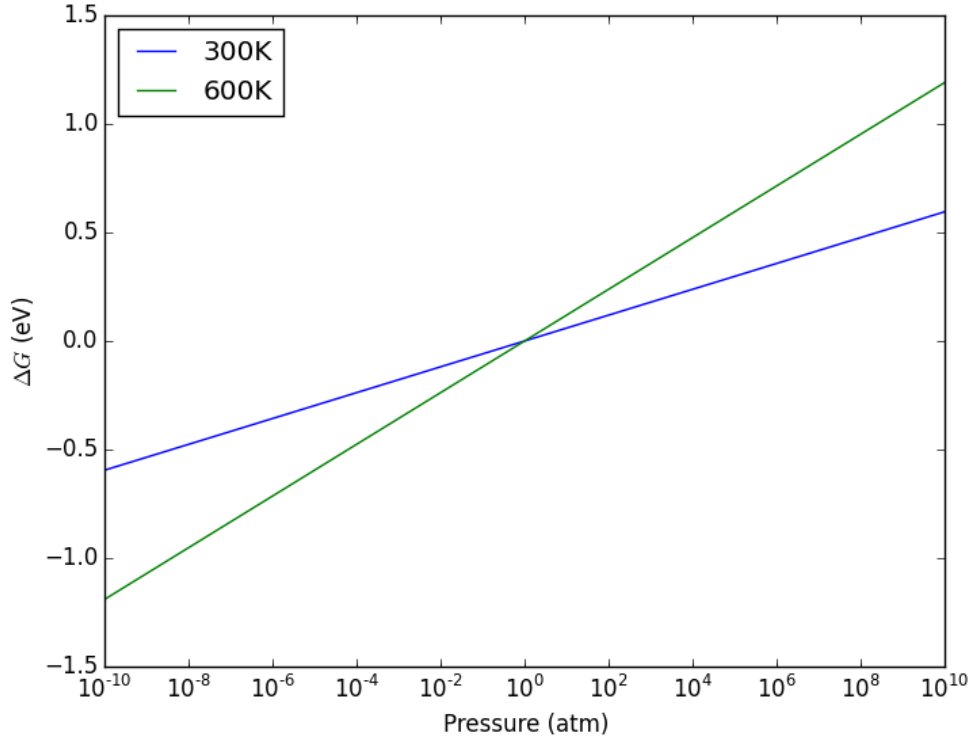


Figure 83: Effects of pressure on the ideal gas Gibbs free energy of O_2 .

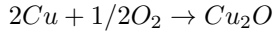
Similarly, you can see that simply changing the pressure has a large effect on the Gibbs free energy of an ideal gas through the term: $kT \ln(P/P_0)$, and that this effect is also temperature dependent. This leads us to the final formula we will use for the chemical potential of oxygen:

$$\mu_{O_2} = E_{O_2}^{DFT} + E_{O_2}^{ZPE} + \Delta\mu(T) + kT \ln(P/P_0)$$

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.



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
vi-
bra-
tional
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.

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3  from ase.units import *
4  from scipy.optimize import fsolve
5
6  K = 1. #not defined in ase.units!
7  atm = 101325 * Pascal
8
9  # Shomate parameters valid from 100-700K
10 A = 31.32234; B = -20.23531; C = 57.86644
11 D = -36.50624; E = -0.007374; F = -8.903471
12 G = 246.7945; H = 0.0
13
14
15 def entropy(T):
16     '''entropy returned as eV/K
17     T in K
18     '''
19     t = T/1000.
20     s = (A * np.log(t) + B * t + C * (t**2) / 2.
21         + D * (t**3) / 3. - E / (2. * t**2) + G)
22     return s * J / mol / K
23
24
25 def enthalpy(T):
26     ''' H - H(298.15) returned as eV/molecule'''
27     t = T / 1000.
28     h = (A * t + B * (t**2) / 2. + C * (t**3) / 3.
29         + D * (t**4) / 4. - E / t + F - H)
30     return h * kJ / mol
31
32
33 def DeltaMu(T, P):
34     '''
35     returns delta chemical potential of oxygen at T and P
36     T in K
37     P in atm
38     '''
39     return enthalpy(T) - T * entropy(T) + kB * T * np.log(P / atm)
40
41 P = 1e-10*atm
42
43
44 def func(T):
45     'Cu2O'
46     return -1.95 - 0.5*DeltaMu(T, P)
47
48 print 'Cu2O decomposition temperature is {0:1.0f} K'.format(fsolve(func,
49                                                                 900)[0])
50
51 def func(T):
52     'Ag2O'
53     return -0.99 - 0.5 * DeltaMu(T, P)
54
55 print 'Ag2O decomposition temperature is {0:1.0f} K'.format(fsolve(func,
```

```

56
57
58
59 T = np.linspace(100, 1000)
60 # Here we plot delta mu as a function of temperature at different pressures
61 # you have use \\times to escape the first \ in pyplot
62 plt.plot(T, DeltaMu(T, 1e10*atm), label=r'1$\times 10^{10}$ atm')
63 plt.plot(T, DeltaMu(T, 1e5*atm), label=r'1$\times 10^5$ atm')
64 plt.plot(T, DeltaMu(T, 1*atm), label='1 atm')
65 plt.plot(T, DeltaMu(T, 1e-5*atm), label=r'1$\times 10^{-5}$ atm')
66 plt.plot(T, DeltaMu(T, 1e-10*atm), label=r'1$\times 10^{-10}$ atm')
67
68 plt.xlabel('Temperature (K)')
69 plt.ylabel(r'$\Delta \mu_{O_2}(T,p)$ (eV)')
70 plt.legend(loc='best')
71 plt.savefig('images/02-mu-diff-p.png')

```

Open the python script (dft-scripts/script-200.py).

Cu₂O decomposition temperature is 917 K

Ag₂O decomposition temperature is 478 K

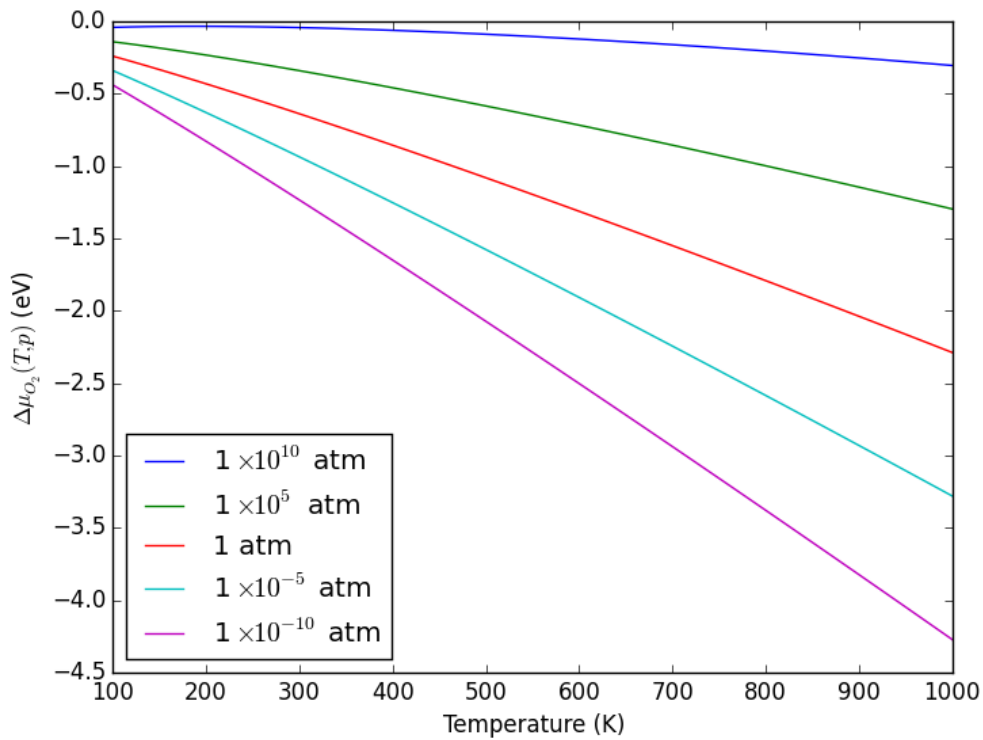


Figure 84: $\Delta \mu_{O_2}(T,p)$ at different pressures and temperatures.

Now, let us make a phase diagram that shows the boundary between silver oxide, and silver metal in P and T space.

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3 from ase.units import *
4 from scipy.optimize import fsolve

```



```

5
6 K = 1. #not defined in ase.units!
7 atm = 101325*Pascal
8
9 # Shomate parameters valid from 100-700K
10 A = 31.32234; B = -20.23531; C = 57.86644
11 D = -36.50624; E = -0.007374; F = -8.903471
12 G = 246.7945; H = 0.0
13
14
15 def entropy(T):
16     '''entropy returned as eV/K
17     T in K
18     '''
19     t = T/1000.
20     s = (A*np.log(t) + B*t + C*(t**2)/2.
21         + D*(t**3)/3. - E/(2.*t**2) + G)
22     return s*J/mol/K
23
24
25 def enthalpy(T):
26     ''' H - H(298.15) returned as eV/molecule'''
27     t = T/1000.
28     h = (A*t + B*(t**2)/2. + C*(t**3)/3.
29         + D*(t**4)/4. - E/t + F - H)
30     return h*kJ/mol
31
32
33 def DeltaMu(T, P):
34     '''
35     T in K
36     P in atm
37     '''
38     return enthalpy(T) - T * entropy(T) + kB * T * np.log(P / atm)
39
40 P = np.logspace(-11, 1, 10) * atm
41 T = []
42 for p in P:
43
44     def func(T):
45         return -0.99 - 0.5 * DeltaMu(T, p)
46     T.append(fsolve(func, 450)[0])
47
48 plt.semilogy(T, P / atm)
49 plt.xlabel('Temperature (K)')
50 plt.ylabel('Pressure (atm)')
51 plt.text(800, 1e-7, 'Ag')
52 plt.text(600, 1e-3, 'Ag$_{2}$O')
53 plt.savefig('images/Ag2O-decomposition.png')

```

Open the python script (dft-scripts/script-201.py).

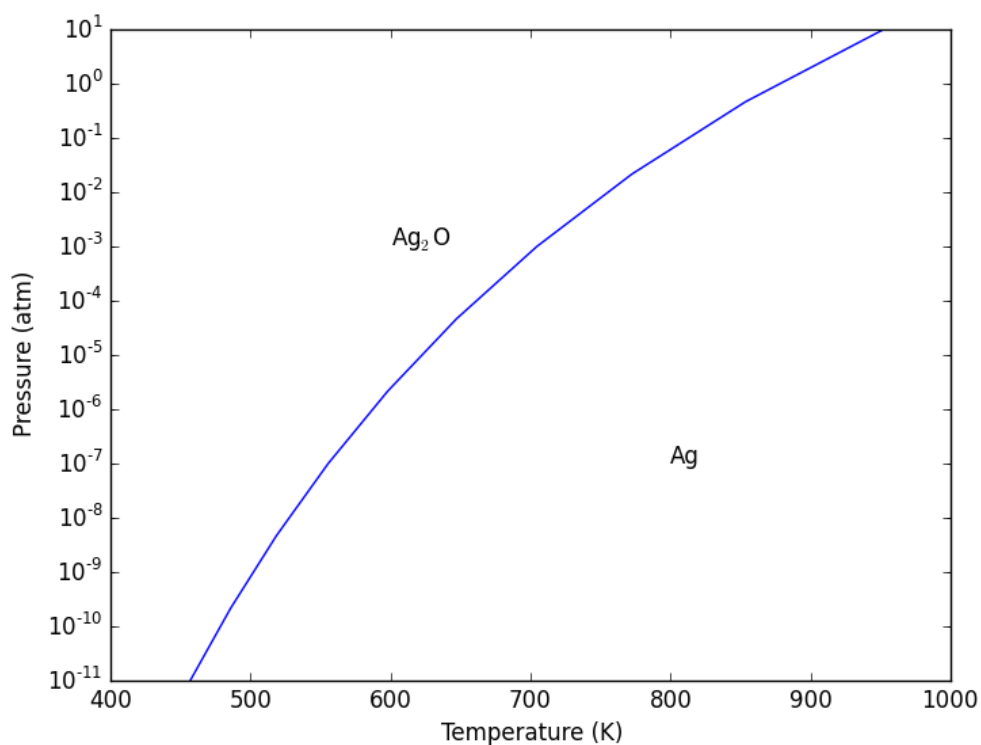


Figure 85: Temperature dependent decomposition pressure for Ag_2O .

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.

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3  from ase.units import *
4
5  K = 1. # not defined in ase.units!
6  atm = 101325*Pascal
7  Hf = -0.99
8
9  P = 1 * atm
10
11 Dmu = np.linspace(-4, 0)
12
13 Hf = -0.99 - 0.5*Dmu
14
15 plt.plot(Dmu, Hf, label='Ag$_2$O')
16 plt.plot(Dmu, np.zeros(Hf.shape), label='Ag')
17 plt.xlabel(r'$\Delta \mu_{\text{O}_2}$ (eV)')
18 plt.ylabel('$H_f$ (eV)')
19 plt.savefig('images/atomistic-thermo-hf-mu.png')

```

Open the python script (dft-scripts/script-202.py).

None

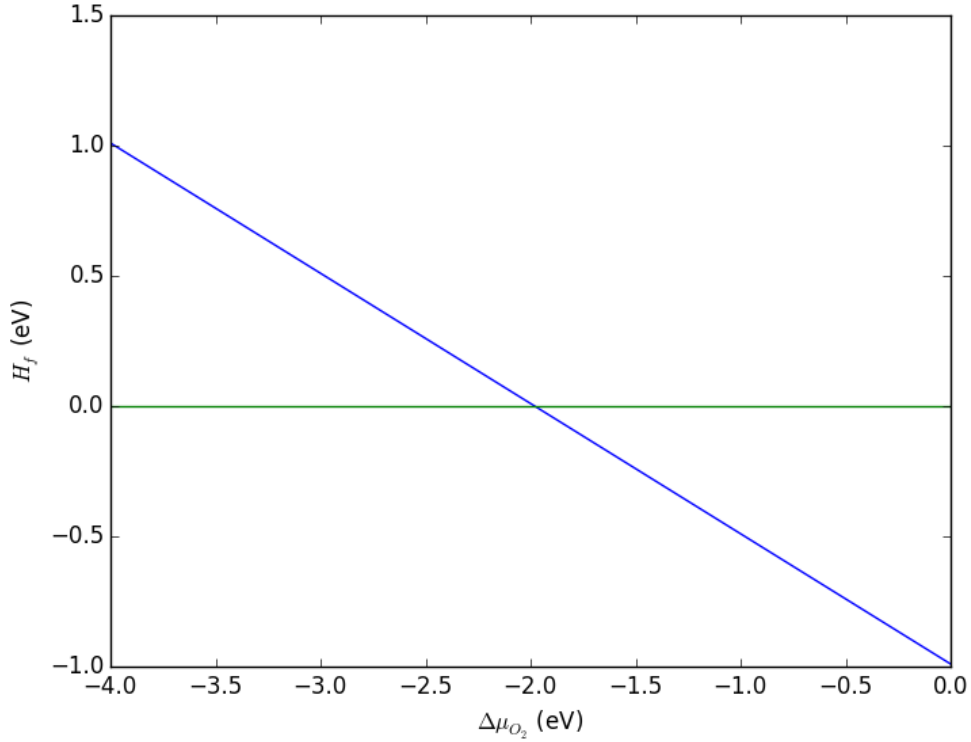


Figure 86: Dependence of the formation energy on the oxygen chemical potential.

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 84): About 500K at 1×10^{-10} atm, 600K at 1×10^{-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 also 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 6: 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

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 fcc25 = -1.04
5 hcp25 = -0.60
6 bridge25 = -0.49
7 fcc1 = -0.10
8
9 Dmu = np.linspace(-4, 2)
10
11 plt.plot(Dmu, np.zeros(Dmu.shape), label='Pt(111)')
12 plt.plot(Dmu, 0.25 * (fcc25 - 0.5*Dmu), label='fcc - 0.25 ML')
13 plt.plot(Dmu, 0.25 * (hcp25 - 0.5*Dmu), label='hcp - 0.25 ML')
14 plt.plot(Dmu, 0.25 * (bridge25 - 0.5*Dmu), label='bridge - 0.25 ML')
15 plt.plot(Dmu, 1.0 * (fcc1 - 0.5*Dmu), label='fcc - 1.0 ML')
16
17 plt.xlabel(r'$\Delta \mu_{O_2}$ (eV)')
18 plt.ylabel(r'$\Delta G_{ads}$ (eV/O)')
19 plt.legend(loc='best')
20 plt.savefig('images/atomistic-thermo-adsorption.png')
21 plt.show()

```

Open the python script (dft-scripts/script-203.py).

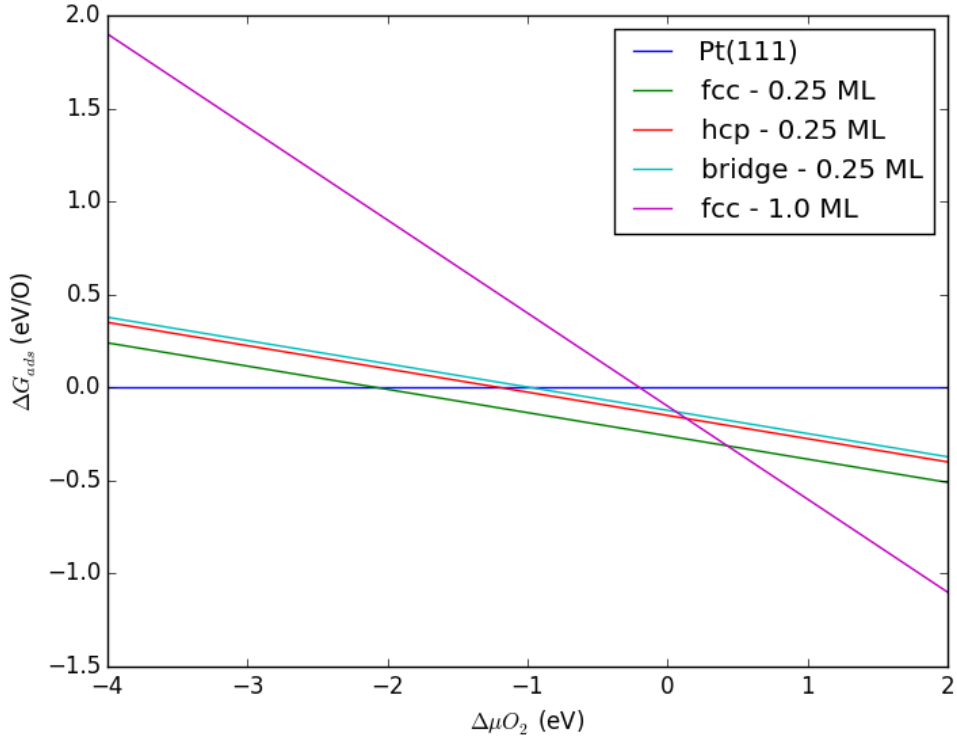


Figure 87: Effect of oxygen chemical potential on the adsorption energy.

6.3 Atomistic therodynamics and multiple reactions

In ⁸² 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.

$$\begin{array}{l} H_2 + \\ 2* \rightleftharpoons \\ 2H* \end{array}$$
2.

$$\begin{array}{l} H_2S + \\ 2* \rightleftharpoons \\ H* \\ + SH* \end{array}$$
3.

$$\begin{array}{l} SH* \\ + * \rightleftharpoons \\ S* \\ + H* \end{array}$$

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, preferably 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:

$$\mu_{H*} + \mu_{SH*} = \mu_{H_2S} \text{ and } \mu_{H*} + \mu_{S*} = \mu_{SH*}.$$

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:

$\mu_{gas}(T, p) = E_{gas}(0K) + \delta\mu + kT \ln(p/p^0)$, 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.⁹⁵

7.1.1 Metal oxide oxidation energies with DFT+U

We will reconsider here the reaction (see [Metal oxide oxidation energies](#)) $2 \text{ Cu}_2\text{O} + \text{O}_2 \rightleftharpoons 4 \text{ CuO}$. We need to compute the energy of each species, now with DFT+U. In⁵⁵ they use a U parameter of 4 eV for Cu which gave the best agreement with the experimental value. We will also try that.

Cu₂O calculation with U=4.0

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  with jasp('bulk/Cu2O') as calc:
5      calc.clone('bulk/Cu2O-U=4.0')
6
7  with jasp('bulk/Cu2O-U=4.0') as calc:
8      calc.set(ldau=True,      # turn DFT+U on
9              ldautype=2,      # select simplified rotationally invariant option
10             ldau_luj={'Cu':{'L':2, 'U':4.0, 'J':0.0},
11                      'O':{'L':-1, 'U':0.0, 'J':0.0}},
12             ldaprint=1,
13             ibrion=-1, #do not relax
14             nsw=0)
15      calc.calculate()
16      print calc

```

Open the python script (dft-scripts/script-204.py).

```

: -----
VASP calculation from /home/jkitchin/dft-org/bulk/Cu2O-U=4.0
converged: True
Energy = -22.228203 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 4.270  0.000  0.000] 4.270
a1 [ 0.000  4.270  0.000] 4.270
a2 [ 0.000  0.000  4.270] 4.270
a,b,c,alpha,beta,gamma (deg): 4.270 4.270 4.270 90.0 90.0 90.0

```

```

Unit cell volume = 77.854 Ang^3
Stress (GPa):xx,   yy,   zz,   yz,   xz,   xy
                0.018  0.018  0.018 -0.000 -0.000 -0.000
Atom#  sym      position [x,y,z]      tag  rmsForce constraints
  0    Cu  [0.000    0.000    0.000]    0   0.00      T T T
  1    Cu  [2.135    2.135    0.000]    0   0.00      T T T
  2    Cu  [2.135    0.000    2.135]    0   0.00      T T T
  3    Cu  [0.000    2.135    2.135]    0   0.00      T T T
  4    O   [1.067    1.067    1.067]    0   0.00      T T T
  5    O   [3.202    3.202    3.202]    0   0.00      T T T

```

INCAR Parameters:

```

-----
nbands: 37
nsw: 0
ibrion: -1
ldautype: 2
isif: 3
ldauprint: 1
encut: 400.0
ldau: True
magmom: None
ldaul: [-1.0, 2.0]
ldauj: [0.0, 0.0]
ldauu: [0.0, 4.0]
ldau_luj: {'O': {'J': 0.0, 'U': 0.0, 'L': -1}, 'Cu': {'J': 0.0,
              'U': 4.0, 'L': 2}}
prec: Normal
kpts: [8, 8, 8]
reciprocal: False
xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5fbe3a3b1dfa)
Cu: potpaw_PBE/Cu/POTCAR (git-hash: a44c591415026f53deb16a99ca3f06b1e69be10b)

```

```

1  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-205.py).

```

LDA+U is selected, type is set to LDAUTYPE = 2
angular momentum for each species LDAUL =   -1   2
U (eV)            for each species LDAUU =   0.0  4.0
J (eV)            for each species LDAUJ =   0.0  0.0

```

CuO calculation with U=4.0

```

1  from jasp import *
2  from ase import Atom, Atoms

```

```

3
4 with jasp('bulk/CuO') as calc:
5     calc.clone('bulk/CuO-U=4.0')
6
7 with jasp('bulk/CuO-U=4.0') as calc:
8     calc.set(ldau=True, # turn DFT+U on
9               ldautype=2, # select simplified rotationally invariant option
10              ldau_luj={'Cu':{'L':2, 'U':4.0, 'J':0.0},
11                       'O':{'L':-1, 'U':0.0, 'J':0.0}},
12              ldauprint=1,
13              ibrion=-1, #do not rerelex
14              nsw=0)
15     calc.calculate()
16     print calc

```

Open the python script (dft-scripts/script-206.py).

```

: -----
VASP calculation from /home/jkitchin/dft-org/bulk/CuO-U=4.0
converged: True
Energy = -16.870130 eV

Unit cell vectors (angstroms)
      x      y      z      length
a0 [ 2.302 -1.776  0.046] 2.908
a1 [ 2.302  1.776  0.046] 2.908
a2 [-0.762  0.000  5.087] 5.144
a,b,c,alpha,beta,gamma (deg): 2.908 2.908 5.144 95.8 95.8 95.8
Unit cell volume = 41.730 Ang^3
Stress (GPa):xx,  yy,  zz,  yz,  xz,  xy
              0.030  0.018  0.027 -0.000 -0.007 -0.000
Atom#  sym      position [x,y,z]      tag  rmsForce constraints
  0    Cu  [1.151    0.888    0.023]    0    0.00      T T T
  1    Cu  [0.770   -0.888    2.566]    0    0.00      T T T
  2     O  [2.111   -0.168    1.318]    0    0.04      T T T
  3     O  [1.730    0.168    3.861]    0    0.04      T T T
-----

```

INCAR Parameters:

```

-----
nbands: 23
nsw: 0
ibrion: -1
ldautype: 2
isif: 3
ldauprint: 1
encut: 400.0
ldau: True
magmom: None
ldaul: [-1.0, 2.0]
ldauj: [0.0, 0.0]
ldauu: [0.0, 4.0]
ldau_luj: {'O': {'J': 0.0, 'U': 0.0, 'L': -1}, 'Cu': {'J': 0.0,
              'U': 4.0, 'L': 2}}
prec: Normal
kpts: [8, 8, 8]
reciprocal: False

```



```

xc: PBE
txt: -
gamma: False

```

Pseudopotentials used:

```

-----
O: potpaw_PBE/O/POTCAR (git-hash: 9a0489b46120b0cad515d935f44b5f3e3a3b1dfa)
Cu: potpaw_PBE/Cu/POTCAR (git-hash: a44c591415026f53deb16a99ca3f06b1e69be10b)

```

Reaction energy calculation with DFT+U

```

1 from jasp import *
2
3 # don't forget to normalize your total energy to a formula unit. Cu2O
4 # has 3 atoms, so the number of formula units in an atoms is
5 # len(atoms)/3.
6 with jasp('bulk/Cu2O-U=4.0') as calc:
7     atoms = calc.get_atoms()
8     cu2o_energy = atoms.get_potential_energy()/(len(atoms)/3)
9
10 with jasp('bulk/CuO-U=4.0') as calc:
11     atoms = calc.get_atoms()
12     cuo_energy = atoms.get_potential_energy()/(len(atoms)/2)
13
14 # make sure to use the same cutoff energy for the O2 molecule!
15 with jasp('molecules/O2-sp-triplet-400') as calc:
16     atoms = calc.get_atoms()
17     o2_energy = atoms.get_potential_energy()
18
19 rxn_energy = 4.0*cuo_energy - o2_energy - 2.0*cu2o_energy
20 print 'Reaction energy = {0} eV'.format(rxn_energy)
21 print 'Corrected energy = {0} eV'.format(rxn_energy - 1.36)

```

Open the python script (dft-scripts/script-207.py).

```

Reaction energy = -1.663819 eV
Corrected energy = -3.023819 eV

```

This is still not in quantitative agreement with the result in,⁵⁵ which at U=4 eV is about -3.14 eV (estimated from a graph). We have not applied the O₂ correction here yet. In that paper, they apply a constant shift of -1.36 eV per O₂. 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.

```

1 from jasp import *
2 for U in [2.0, 4.0, 6.0]:
3     ## Cu2O #####
4     with jasp('bulk/Cu2O') as calc:
5         calc.clone('bulk/Cu2O-U={0}'.format(U))
6
7     with jasp('bulk/Cu2O-U={0}'.format(U)) as calc:
8         calc.set(ldau=True, # turn DFT+U on
9                 ldautype=2, # select simplified rotationally invariant option
10                ldau_luj={'Cu':{'L':2, 'U':U, 'J':0.0},
11                        'O':{'L':-1, 'U':0.0, 'J':0.0}},
12                ldauprint=1,
13                ibrion=-1, #do not rerelex
14                nsw=0)
15         atoms = calc.get_atoms()
16         cu2o_energy = atoms.get_potential_energy()/(len(atoms)/3)
17
18     ## CuO #####
19     with jasp('bulk/CuO') as calc:
20         calc.clone('bulk/CuO-U={0}'.format(U))

```

```

21
22     with jasp('bulk/CuO-U={0}'.format(U)) as calc:
23         calc.set(ldau=True, # turn DFT+U on
24                  ldautype=2, # select simplified rotationally invariant option
25                  ldauluj={'Cu':{'L':2, 'U':U, 'J':0.0},
26                           'O':{'L':-1, 'U':0.0, 'J':0.0}},
27                  ldauprint=1,
28                  ibrion=-1, #do not rerelex
29                  nsw=0)
30         atoms = calc.get_atoms()
31         cuo_energy = atoms.get_potential_energy()/(len(atoms)/2)
32
33     ## O2 #####
34     # make sure to use the same cutoff energy for the O2 molecule!
35     with jasp('molecules/O2-sp-triplet-400') as calc:
36         atoms = calc.get_atoms()
37         o2_energy = atoms.get_potential_energy()
38
39     rxn_energy = 4.0*cuo_energy - o2_energy - 2.0*cu2o_energy
40     print 'U = {0} reaction energy = {1}'.format(U,rxn_energy - 1.99)

```

Open the python script (dft-scripts/script-208.py).

```

U = 2.0 reaction energy = -3.876906
U = 4.0 reaction energy = -3.653819
U = 6.0 reaction energy = -3.397605

```

In,⁵⁵ 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 O₂ binding energy. In⁵⁵ the authors tried to get the O₂ binding energy correction from oxide calculations where U is not important, so that it is decoupled from the non-cancelling errors that U fixes. See⁹⁶ 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

```

1  from jasp import *
2  from ase.lattice.cubic import FaceCenteredCubic
3  from ase.dft import DOS
4
5  atoms = FaceCenteredCubic(directions=[[0, 1, 1],
6                                       [1, 0, 1],
7                                       [1, 1, 0]],
8                              size=(1, 1, 1),
9                              symbol='Ni')
10 atoms[0].magmom = 1
11
12 with jasp('bulk/Ni-PBE',
13          ismear=-5,
14          kpts=(5, 5, 5),
15          xc='PBE',
16          ispin=2,lorbit=11,
17          atoms=atoms) as calc:
18     print('PBE energy: ',atoms.get_potential_energy())
19     dos = DOS(calc, width=0.2)
20     e_pbe = dos.get_energies()
21     d_pbe = dos.get_dos()
22
23     calc.clone('bulk/Ni-PBE0')

```

```

24     calc.clone('bulk/Ni-HSE06')
25
26 with jasp('bulk/Ni-PBE0') as calc:
27     calc.set(lhfcalc=True,
28             algo='D',
29             time=0.4)
30     atoms = calc.get_atoms()
31     print('PBE0 energy: ', atoms.get_potential_energy())
32     dos = DOS(calc, width=0.2)
33     e_pbe0 = dos.get_energies()
34     d_pbe0 = dos.get_dos()
35
36 with jasp('bulk/Ni-HSE06') as calc:
37     calc.set(lhfcalc=True,
38             hfscreen=0.2,
39             algo='D', time=0.4)
40     atoms = calc.get_atoms()
41     print('HSE06 energy: ', atoms.get_potential_energy())
42     dos = DOS(calc, width=0.2)
43     e_hse06 = dos.get_energies()
44     d_hse06 = dos.get_dos()
45
46 import pylab as plt
47 plt.plot(e_pbe, d_pbe, label='PBE')
48 plt.plot(e_pbe0, d_pbe0, label='PBE0')
49 plt.plot(e_hse06, d_hse06, label='HSE06')
50 plt.xlabel('energy [eV]')
51 plt.ylabel('DOS')
52 plt.legend()
53 plt.savefig('images/ni-dos-pbe-pbe0-hse06.png')

```

Open the python script (dft-scripts/script-209.py).

```

PBE energy:      -5.530247
PBE0 energy:     -6.848931
HSE06 energy:    -6.293369

```

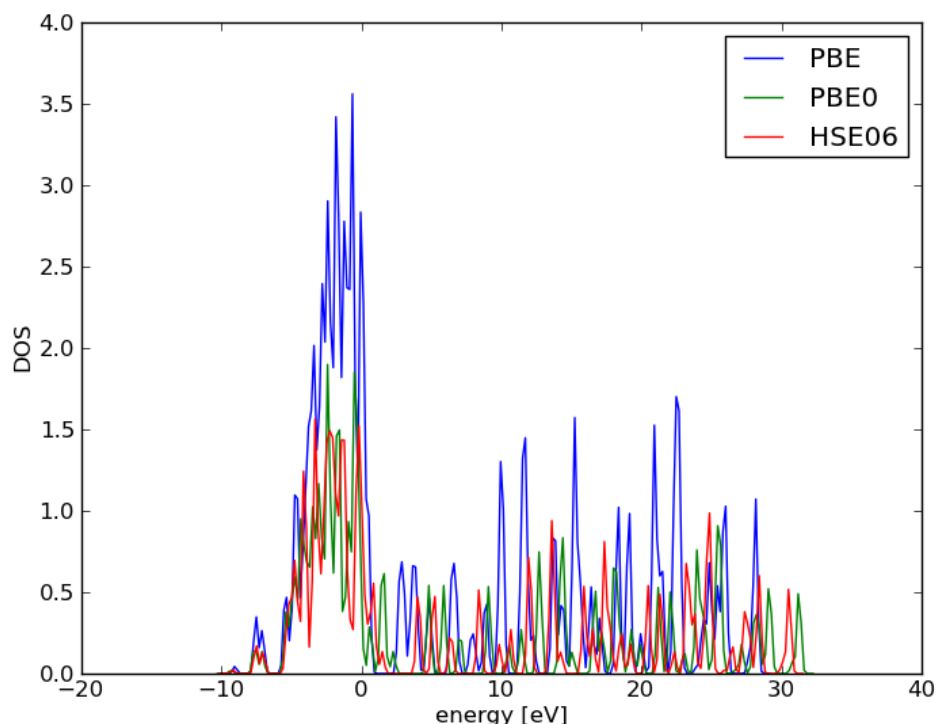


Figure 88: Comparison of DOS from GGA, and two hybrid GGAs (PBE0 and HSE06).

7.3 van der Waals forces

Older versions (5.2.11+) implement DFT+D2⁹⁷ with the `LVDW` tag.

The vdW-DF⁹⁸ 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 ⁹⁹ (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

```

1 from jasp import *
2 from ase.structure import molecule
```

```

3
4 benzene = molecule('C6H6')
5 benzene.center(vacuum=5)
6
7 with jasp('molecules/benzene-pbe',
8           xc='PBE',
9           encut=350,
10          kpts=(1,1,1),
11          ibrion=1,
12          nsw=100,
13          atoms=benzene) as calc:
14     print benzene.get_potential_energy()

```

Open the python script (dft-scripts/script-210.py).

-76.011625

clean slab

```

1  # the clean gold slab
2  from jasp import *
3  from ase.lattice.surface import fcc111, add_adsorbate
4  from ase.constraints import FixAtoms
5
6  atoms = fcc111('Au', size=(3,3,3), vacuum=10)
7
8  # now we constrain the slab
9  c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
10 atoms.set_constraint(c)
11
12 #from ase.visualize import view; view(atoms)
13
14 with jasp('surfaces/Au-pbe',
15          xc='PBE',
16          encut=350,
17          kpts=(4,4,1),
18          ibrion=1,
19          nsw=100,
20          atoms=atoms) as calc:
21     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-211.py).

-82.419513

benzene on Au(111)

```

1  # Benzene on the slab
2  from jasp import *
3  from ase.lattice.surface import fcc111, add_adsorbate
4  from ase.structure import molecule
5  from ase.constraints import FixAtoms
6
7  atoms = fcc111('Au', size=(3,3,3), vacuum=10)
8  benzene = molecule('C6H6')
9  benzene.translate(-benzene.get_center_of_mass())
10
11 # I want the benzene centered on the position in the middle of atoms
12 # 20, 22, 23 and 25
13 p = (atoms.positions[20] +
14      atoms.positions[22] +
15      atoms.positions[23] +
16      atoms.positions[25])/4.0 + [0.0, 0.0, 3.05]
17
18 benzene.translate(p)
19 atoms += benzene
20
21 # now we constrain the slab
22 c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
23 atoms.set_constraint(c)
24

```

```

25 #from ase.visualize import view; view(atoms)
26
27 with jasp('surfaces/Au-benzene-pbe',
28         xc='PBE',
29         encut=350,
30         kpts=(4,4,1),
31         ibrion=1,
32         nsw=100,
33         atoms=atoms) as calc:
34     print atoms.get_potential_energy()

```

Open the python script (dft-scripts/script-212.py).

-158.360082

```

1 from jasp import *
2
3 with jasp('surfaces/Au-benzene-pbe') as calc:
4     e1 = calc.get_atoms().get_potential_energy()
5
6 with jasp('surfaces/Au-pbe') as calc:
7     e2 = calc.get_atoms().get_potential_energy()
8
9 with jasp('molecules/benzene-pbe') as calc:
10    e3 = calc.get_atoms().get_potential_energy()
11
12 print('PBE adsorption energy = {} eV'.format(e1 - e2 - e3))

```

Open the python script (dft-scripts/script-213.py).

PBE adsorption energy = 0.071056 eV

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 corrections⁹⁷ we set `LVDW` to `True`.

gas-phase benzene

```

1 from jasp import *
2 from ase.structure import molecule
3
4 benzene = molecule('C6H6')
5 benzene.center(vacuum=5)
6
7 with jasp('molecules/benzene-pbe-d2',
8         xc='PBE',
9         encut=350,
10        kpts=(1,1,1),
11        ibrion=1,
12        nsw=100,
13        lvdw=True,
14        atoms=benzene) as calc:
15    print(benzene.get_potential_energy())

```

Open the python script (dft-scripts/script-214.py).

-76.157947

clean slab

```
1 # the clean gold slab
2 from jasp import *
3 from ase.lattice.surface import fcc111, add_adsorbate
4 from ase.constraints import FixAtoms
5
6 atoms = fcc111('Au', size=(3, 3, 3), vacuum=10)
7
8 # now we constrain the slab
9 c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
10 atoms.set_constraint(c)
11
12 with jasp('surfaces/Au-pbe-d2',
13          xc='PBE',
14          encut=350,
15          kpts=(4, 4, 1),
16          ibrion=1,
17          nsw=100,
18          lvdw=True,
19          atoms=atoms) as calc:
20     print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-215.py).

-106.34078774

benzene on Au(111)

```
1 # Benzene on the slab
2 from jasp import *
3 from ase.lattice.surface import fcc111, add_adsorbate
4 from ase.structure import molecule
5 from ase.constraints import FixAtoms
6
7 atoms = fcc111('Au', size=(3,3,3), vacuum=10)
8 benzene = molecule('C6H6')
9 benzene.translate(-benzene.get_center_of_mass())
10
11 # I want the benzene centered on the position in the middle of atoms
12 # 20, 22, 23 and 25
13 p = (atoms.positions[20] +
14      atoms.positions[22] +
15      atoms.positions[23] +
16      atoms.positions[25])/4.0 + [0.0, 0.0, 3.05]
17
18 benzene.translate(p)
19 atoms += benzene
20
21 # now we constrain the slab
22 c = FixAtoms(mask=[atom.symbol=='Au' for atom in atoms])
23 atoms.set_constraint(c)
24
25 #from ase.visualize import view; view(atoms)
26
27 with jasp('surfaces/Au-benzene-pbe-d2',
28          xc='PBE',
29          encut=350,
30          kpts=(4, 4, 1),
31          ibrion=1,
32          nsw=100,
33          lvdw=True,
34          atoms=atoms) as calc:
35     print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-216.py).

-184.07043811

```
1 from jasp import *
2
```

```

3  with jasp('surfaces/Au-benzene-pbe-d2') as calc:
4      e1 = calc.get_atoms().get_potential_energy()
5
6  with jasp('surfaces/Au-pbe-d2') as calc:
7      e2 = calc.get_atoms().get_potential_energy()
8
9  with jasp('molecules/benzene-pbe-d2') as calc:
10     e3 = calc.get_atoms().get_potential_energy()
11
12  print('Adsorption energy = {0:1.2f} eV'.format(e1 - e2 - e3))

```

Open the python script (dft-scripts/script-217.py).

Adsorption energy = -1.57 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.¹⁰⁰ Here we reproduce an example from Ref. 100. We compute and plot the ELF for tetrafluoromethane. The [LELF](#) tag turns this on.

```

1  # compute ELF for CF4
2  from jasp import *
3  from ase.structure import molecule
4  from enthought.mayavi import mlab
5
6  atoms = molecule('CF4')
7  atoms.center(vacuum=5)
8
9  with jasp('molecules/cf4-elf',
10         encut=350,
11         prec='high',
12         ismear=0,
13         sigma=0.01,
14         xc='PBE',
15         lelf=True,
16         atoms=atoms) as calc:
17     calc.calculate()
18
19     x, y, z, elf = calc.get_elf()
20     mlab.contour3d(x, y, z, elf, contours=[0.3])
21     mlab.savefig('../images/cf4-elf-3.png')
22
23     mlab.figure()
24     mlab.contour3d(x, y, z, elf, contours=[0.75])
25     mlab.savefig('../images/cf4-elf-75.png')

```

Open the python script (dft-scripts/script-218.py).

None

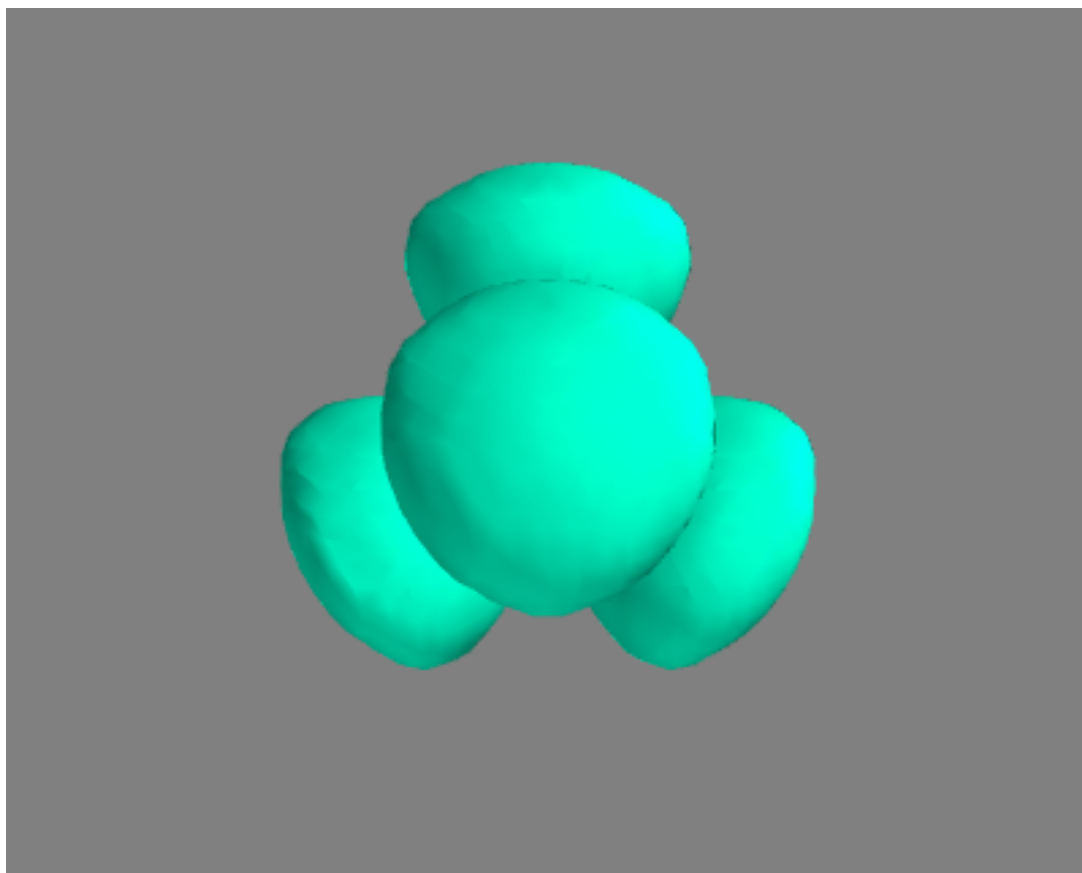


Figure 89: ELF for an isosurface of 0.3 for CF₄.

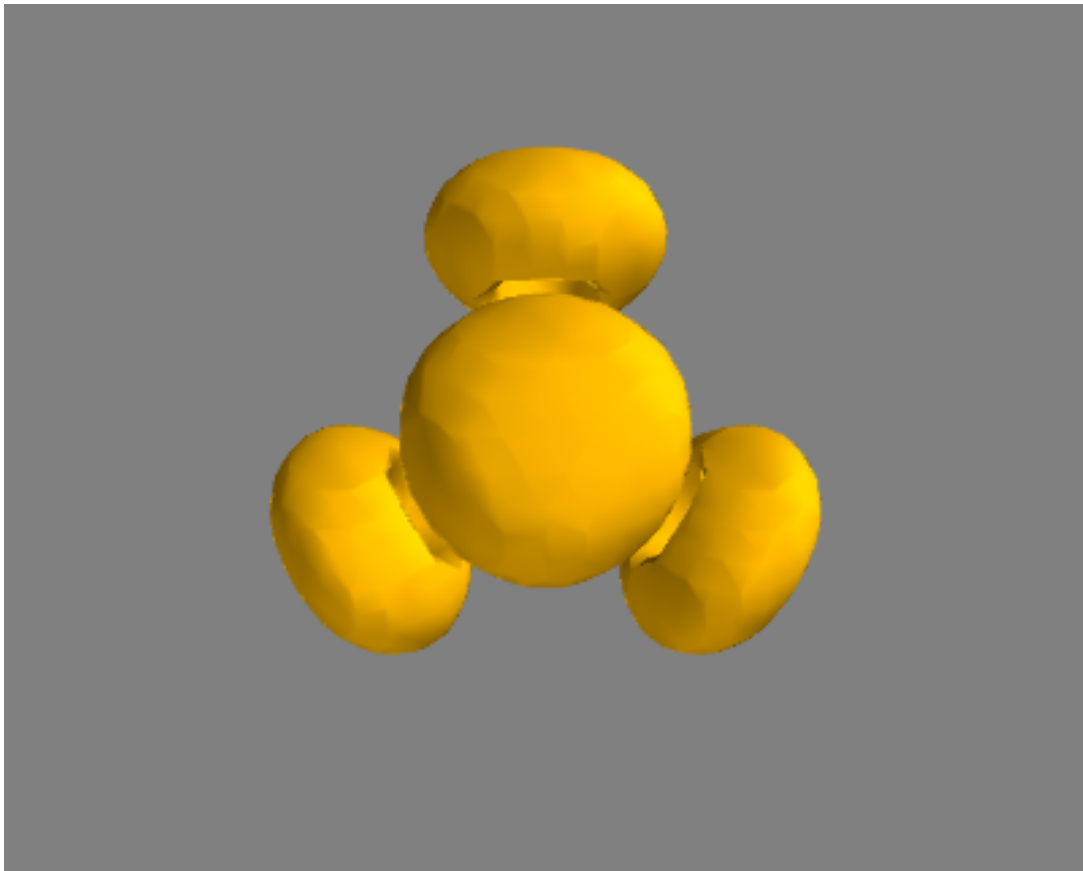


Figure 90: ELF for an isosurface of 0.75 for CF_4 .

These images (Figure 89 and 90) are basically consistent with those in Reference.¹⁰⁰

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.

```

1  from jasp import *
2  from ase import Atom, Atoms
3
4  atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000]),
5                  Atom('Cu', [-1.652, 0.000, 2.039])],
6               cell= [[0.000, -2.039, 2.039],
7                     [0.000, 2.039, 2.039],
8                     [-3.303, 0.000, 0.000]])
9
10 atoms = atoms.repeat((2, 2, 2))
11 print atoms[0]
12
13 with jasp('bulk/Cu-cls-0',
14          xc='PBE',
15          encut=350,
16          kpts=(4, 4, 4),
17          ibrion=2,
18          isif=3,
19          nsw=40,
20          atoms=atoms) as calc:
21     print(atoms.get_potential_energy())

```

Open the python script (dft-scripts/script-219.py).
Here, we setup the alloy calculation.

```
1 from jasp import *
2 from ase import Atom, Atoms
3
4 atoms = Atoms([Atom('Cu', [0.000, 0.000, 0.000]),
5                 Atom('Pd', [-1.652, 0.000, 2.039])],
6               cell= [[0.000, -2.039, 2.039],
7                     [0.000, 2.039, 2.039],
8                     [-3.303, 0.000, 0.000]])
9
10 atoms = atoms.repeat((2, 2, 2))
11
12 with jasp('bulk/CuPd-cls-0',
13          xc='PBE',
14          encut=350,
15          kpts=(4, 4, 4),
16          ibrion=2,
17          isif=3,
18          nsw=40,
19          atoms=atoms) as calc:
20     print(atoms.get_potential_energy())
```

Open the python script (dft-scripts/script-220.py).

```
Atom('Cu', [0.0, 0.0, 0.0], index=0)
-73.53338426
```

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.

```
1 from jasp import *
2
3 with jasp('bulk/Cu-cls-0') as calc:
4     calc.clone('bulk/Cu-cls-1')
5
6 with jasp('bulk/Cu-cls-1') as calc:
7     calc.set(ibrion=None,
8             isif=None,
9             nsw=None,
10            setups={'0': 'Cu'}, # Create separate entry in POTCAR for atom index 0
11            icorelevel=2,      # Perform core level shift calculation
12            clnt=0,            # Excite atom index 0
13            cln=2,             # 2p3/2 electron for Cu core level shift
14            cll=1,
15            clz=1)
16
17 print(calc.get_atoms().get_potential_energy())
```

Open the python script (dft-scripts/script-221.py).

```
-345.05440951
```

```
1 from jasp import *
2
3 with jasp('bulk/CuPd-cls-0') as calc:
4     calc.clone('bulk/CuPd-cls-1')
5
6 with jasp('bulk/CuPd-cls-1') as calc:
7     calc.set(ibrion=None,
8             isif=None,
9             nsw=None,
10            setups={'0': 'Cu'}, # Create separate entry in POTCAR for atom index 0
11            icorelevel=2,      # Perform core level shift calculation
12            clnt=0,            # Excite atom index 0
13            cln=2,             # 2p3/2 electron for Cu core level shift
14            cll=1,
15            clz=1)
16
17 print(calc.get_atoms().get_potential_energy())
```

Open the python script (dft-scripts/script-222.py).

-359.87250408

Finally we calculate the CLS:

```
1 from jasp import *
2
3 with jasp('bulk/CuPd-cls-0') as calc:
4     alloy_0 = calc.get_atoms().get_potential_energy()
5
6 with jasp('bulk/CuPd-cls-1') as calc:
7     alloy_1 = calc.get_atoms().get_potential_energy()
8
9 with jasp('bulk/Cu-cls-0') as calc:
10    ref_0 = calc.get_atoms().get_potential_energy()
11
12 with jasp('bulk/Cu-cls-1') as calc:
13    ref_1 = calc.get_atoms().get_potential_energy()
14
15 CLS = (alloy_1 - alloy_0) - (ref_1 - ref_0)
16
17 print('CLS = {} eV'.format(CLS))
```

Open the python script (dft-scripts/script-223.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.¹⁰¹

In jasp, we just specify `gga='BF'`, and jasp takes care of the rest. This includes setting some additional variables to setup van der Waals and to get the BEEF ensemble energies. Let us consider the dissociation energy of H₂.

```
1 from jasp import *
2 from ase.structure import molecule
3 import matplotlib.pyplot as plt
4
5 H2 = molecule('H2')
6 H2.set_cell([8, 8, 8], scale_atoms=False)
7
8 with jasp('molecules/H2-beef',
9         xc='PBE', gga='BF',
10        encut=350,
11        ismear=0,
12        ibrion=2,
13        nsr=10,
14        atoms=H2) as calc:
15    try:
16        eH2 = H2.get_potential_energy()
17        print(eH2)
18    except (VaspSubmitted, VaspQueued):
19        eH2 = None
```

Open the python script (dft-scripts/script-224.py).

/home-research/jkitchin/kitchin-python/jasp2/jasp/__init__.pyc
-7.13332059

Next, we get an H atom.

```

1 from jasp import *
2 from ase.structure import molecule
3
4 H = molecule('H')
5 H.set_cell([8, 8, 8], scale_atoms=False)
6
7 with jasp('molecules/H-beef',
8          xc='PBE', gga='BF',
9          encut=350,
10         ismear=0,
11         atoms=H) as calc:
12     try:
13         eH = H.get_potential_energy()
14         print(eH)
15     except (VaspSubmitted, VaspQueued):
16         print('running or queued')
17         eH = None

```

Open the python script (dft-scripts/script-225.py).

-1.15994056

Now, the dissociation energy.

```

1 from jasp import *
2
3 with jasp('molecules/H-beef') as calc:
4     H = calc.get_atoms()
5     eH = H.get_potential_energy()
6
7 with jasp('molecules/H2-beef') as calc:
8     H2 = calc.get_atoms()
9     eH2 = H2.get_potential_energy()
10
11 print('D = {} eV'.format(2 * eH - eH2))

```

Open the python script (dft-scripts/script-226.py).

-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 `jasp.jasp_extensions.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

```

1 from jasp import *
2
3 with jasp('molecules/H-beef') as calc:
4     ensH = calc.get_beefens()
5
6 with jasp('molecules/H2-beef') as calc:
7     ensH2 = calc.get_beefens()
8
9 ensD = 2 * ensH - ensH2
10
11 print('mean = {} eV'.format(ensD.mean()))
12 print('std = {} eV'.format(ensD.std()))
13
14 import matplotlib.pyplot as plt
15 plt.hist(ensD, 20)
16 plt.xlabel('Deviation')
17 plt.ylabel('frequency')
18 plt.savefig('images/beef-ens.png')

```

Open the python script (dft-scripts/script-227.py).

```
mean = 0.000755737994073 eV
std = 0.183590801736 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.

This seems to be the canonical way to do this in ASE. Note you have to get the ensemble energies in the jasp context manager, because they try to read the OUTCAR.

```
1 from jasp import *
2 from ase.dft.bee import BEEFEnsemble
3
4 with jasp('molecules/H-beef') as calc:
5     BE1 = BEEFEnsemble(calc.get_atoms()).get_ensemble_energies()
6
7 with jasp('molecules/H2-beef') as calc:
8     BE2 = BEEFEnsemble(calc.get_atoms()).get_ensemble_energies()
9
10 print((2 * BE1 - BE2).mean())
11 print((2 * BE1 - BE2).std())
```

Open the python script (dft-scripts/script-228.py).

```
beefvdw ensemble started
beefvdw ensemble finished
beefvdw ensemble started
beefvdw ensemble finished
4.81945187253
0.185505941434
```

7.8 TODO Solvation

See <http://vaspsol.mse.ufl.edu/download/>,^{102,103}

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 Vasp 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.

```
1 from jasp import *
2 from ase.structure import molecule
3
4 atoms = molecule('CO')
5 atoms.center(vacuum=5)
6
7 with jasp('molecules/CO-vacuum',
8         encut=600,
9         prec='Accurate',
10        ismear=0,
11        sigma=0.05,
12        ibrion=2,
13        nsw=0,
14        ediff=1e-6,
15        atoms=atoms) as calc:
16     print(atoms.get_potential_energy())
17     print(atoms.get_forces())
18     print('Calculation time: {} seconds'.format(calc.get_elapsed_time()))
```

Open the python script (dft-scripts/script-229.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.

```
1 from jasp import *
2
3 with jasp('molecules/CO-vacuum') as calc:
4     calc.clone('molecules/CO-solvated')
5
6 with jasp('molecules/CO-solvated',
7         istart=1, #
8         lsol=True) as calc:
9     print(calc.get_atoms().get_potential_energy())
10    print(calc.get_atoms().get_forces())
11    print('Calculation time: {} seconds'.format(calc.get_elapsed_time()))
```

Open the python script (dft-scripts/script-230.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:

```
1 grep -A 5 Solvation molecules/CO-solvated/OUTCAR
```

Open the python script (dft-scripts/script-231.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 TODO 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>.

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.

```
1 import textwrap
2 from ase.structure import molecule
3
4 atoms = molecule('CH3CH2OH')
5 print(atoms)
6
7 # delete all the hydrogens
8 ind2del = [atom.index for atom in atoms if atom.symbol == 'H']
9 print('Indices to delete: ', ind2del)
10
11 del atoms[ind2del]
12
13 # now print what is left
14 print(atoms)
```

Open the python script (dft-scripts/script-232.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.

```

1  '''
2  adapted from https://listserv.fysik.dtu.dk/pipermail/campos/2004-September/001155.html
3  '''
4
5  from ase import *
6  from ase.io import write
7  from ase.lattice.surface import bcc111, add_adsorbate
8  from ase.constraints import FixAtoms
9
10 # the bcc111 function automatically tags atoms
11 slab = bcc111('W',
12              a=3.92,          # W lattice constant
13              size=(2, 2, 6),  # 6-layer slab in 2x2 configuration
14              vacuum=10.0)
15
16 # reset tags to be powers of two so we can use binary math
17 slab.set_tags([2**a.get_tag() for a in slab])
18
19 # we had 6 layers, so we create new tags starting at 7
20 # Note you must use powers of two for all the tags!
21 LAYER1 = 2
22 ADSORBATE = 2**7
23 FREE = 2**8
24 NEARADSORBATE = 2**9
25
26 # let us tag LAYER1 atoms to be FREE too. we can address it by LAYER1 or FREE
27 tags = slab.get_tags()
28 for i, tag in enumerate(tags):
29     if tag == LAYER1:
30         tags[i] += FREE
31 slab.set_tags(tags)
32
33 # create a CO molecule
34 co=Atoms([Atom('C', [0., 0., 0.], tag=ADSORBATE),
35          # we will relax only O
36          Atom('O', [0., 0., 1.1], tag=ADSORBATE + FREE)])
37
38 add_adsorbate(slab, co, height=1.2, position='hollow')
39
40 # the adsorbate is centered between atoms 20, 21 and 22 (use
41 # view(slab)) and over atom12 let us label those atoms, so it is easy to
42 # do electronic structure analysis on them later.
43 tags = slab.get_tags() # len(tags) changed, so we reget them.
44 tags[12] += NEARADSORBATE
45 tags[20] += NEARADSORBATE
46 tags[21] += NEARADSORBATE
47 tags[22] += NEARADSORBATE
48 slab.set_tags(tags)
49 # update the tags
50 slab.set_tags(tags)
51
52 # extract pieces of the slab based on tags
53 # atoms in the adsorbate
54 ads = slab[(slab.get_tags() & ADSORBATE) == ADSORBATE]
55
56 # atoms in LAYER1
57 layer1 = slab[(slab.get_tags() & LAYER1) == LAYER1]
58
59 # atoms defined as near the adsorbate
60 nearads = slab[(slab.get_tags() & NEARADSORBATE) == NEARADSORBATE]
61
62 # atoms that are free
63 free = slab[(slab.get_tags() & FREE) == FREE]
64
65 # atoms that are FREE and part of the ADSORBATE
66 freeads = slab[(slab.get_tags() & FREE+ADSORBATE) == FREE+ADSORBATE]
67

```

```
68 # atoms that are NOT FREE
69 notfree = slab[(slab.get_tags() & FREE) != FREE]
70
71 constraint = FixAtoms(mask=(slab.get_tags() & FREE) != FREE)
72 slab.set_constraint(constraint)
73 write('images/tagged-bcc111.png', slab, rotation='-90x', show_unit_cell=2)
74 from ase.visualize import view; view(slab)
```

Open the python script (dft-scripts/script-233.py).

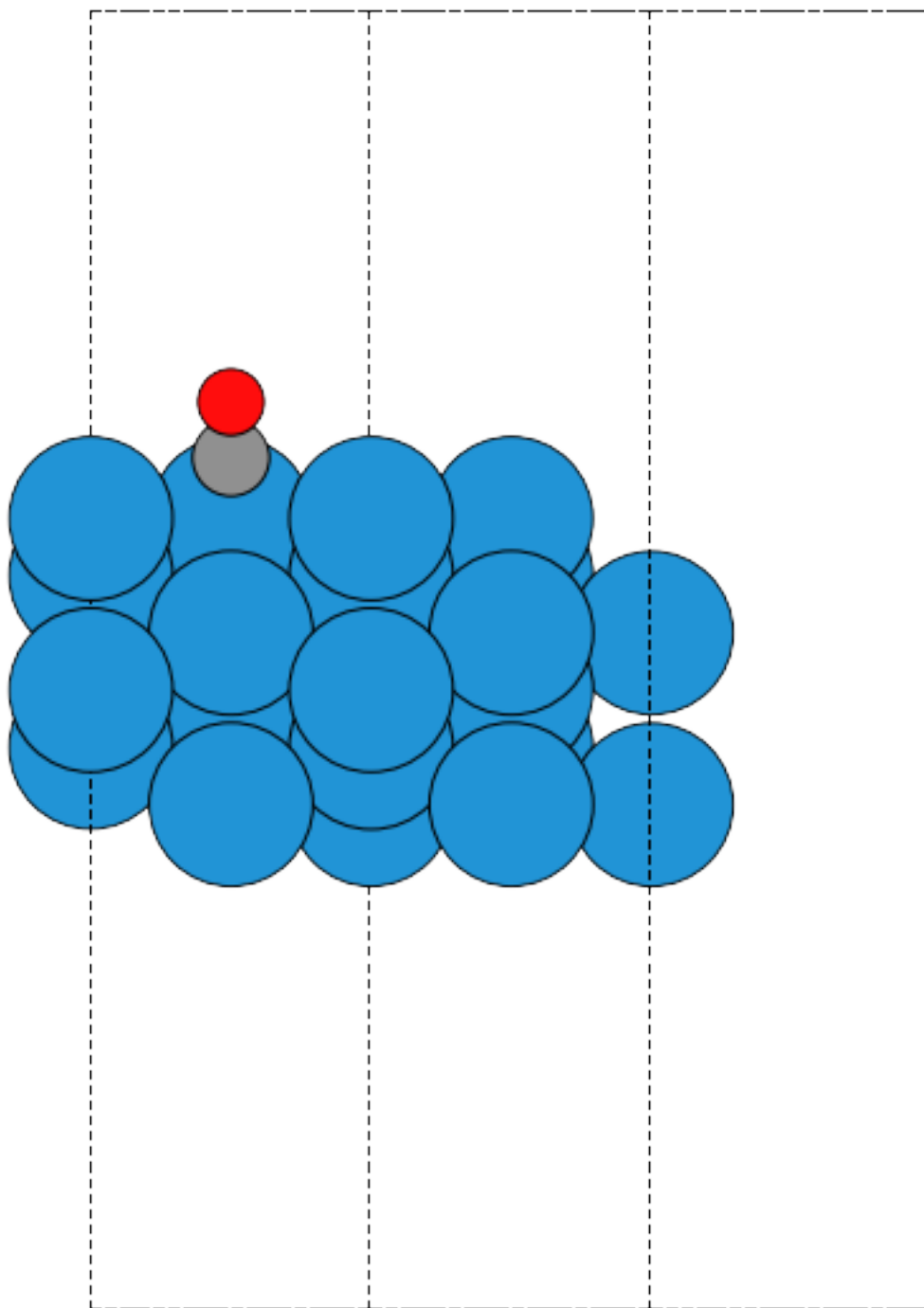


Figure 91: The tagged bcc(111) structure created above. Unfortunately, the frozen atoms do not show up in the figure.

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)!

```
1 from ase.units import *
2
3 d = 1 * Angstrom
4 print(' d = {0} nm'.format(d / nm))
5
6 print('1 eV = {0} Hartrees'.format(eV / Hartree))
7 print('1 eV = {0} Rydbergs'.format(eV / Rydberg))
8 print('1 eV = {0} kJ/mol'.format(eV / (kJ / mol)))
9 print('1 eV = {0} kcal/mol'.format(eV / (kcal / mol)))
10
11 print('1 Hartree = {0} kcal/mol'.format(1 * Hartree / (kcal / mol)))
12 print('1 Rydberg = {0} eV'.format(1 * Rydberg / eV))
13
14 # derived units
15 minute = 60 * s
16 hour = 60 * minute
17
18 # convert 10 hours to minutes
19 print('10 hours = {0} minutes'.format(10 * hour / minute))
```

Open the python script (dft-scripts/script-234.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 data 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.

```
1 import numpy as np
2 import matplotlib as mpl
3 # http://matplotlib.sourceforge.net/users/customizing.html
4 mpl.rcParams['legend.numpoints'] = 1 # default is 2
5 import matplotlib.pyplot as plt
6
7 x = np.linspace(0, 6, 100)
8 y = np.cos(x)
9
10 plt.plot(x, y, label='full')
11
12 ind = (x > 2) & (x < 4)
13
```

```

14 subx = x[ind]
15 suby = y[ind]
16
17 plt.plot(subx, suby, 'bo', label='sliced')
18 xlabel('x')
19 ylabel('cos(x)')
20 plt.legend(loc='lower right')
21 plt.savefig('images/np-array-slice.png')

```

Open the python script (dft-scripts/script-235.py).

None

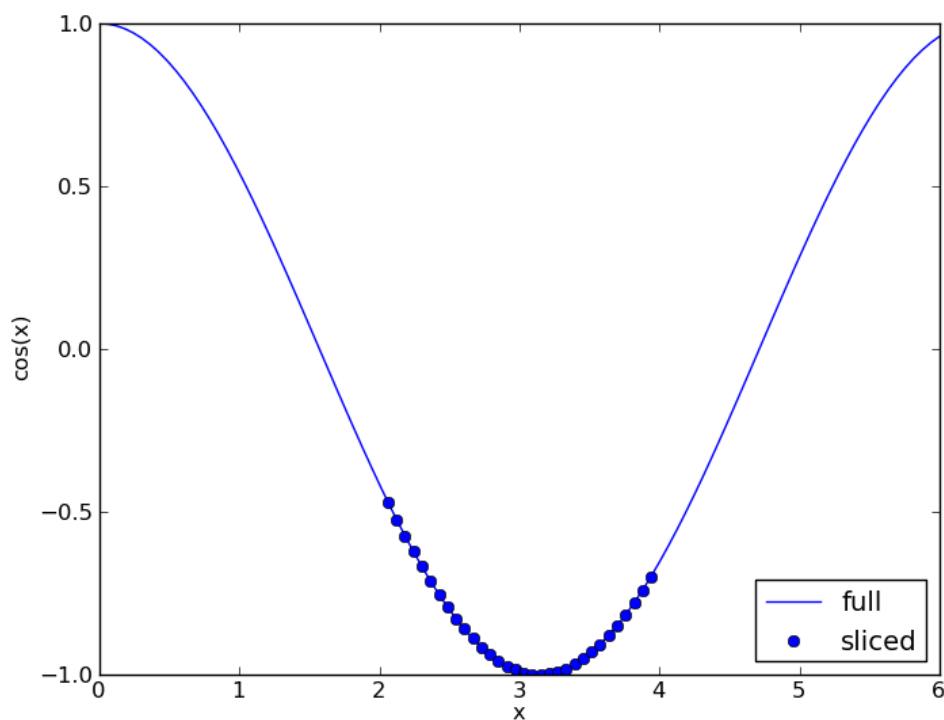


Figure 92: Example of slicing out part of an array. The solid line represents the whole array, and the symbols are the array between $2 < x < 4$.

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.

```

1 import numpy as np
2 from scipy.stats.distributions import t
3
4 n = 10 # number of measurements
5 dof = n - 1 # degrees of freedom
6 avg_x = 16.1 # average measurement
7 std_x = 0.01 # standard deviation of measurements
8
9 # Find 95% prediction interval for next measurement
10
11 alpha = 1.0 - 0.95
12
13 pred_interval = t.ppf(1 - alpha / 2., dof) * std_x * np.sqrt(1. + 1. / n)
14
15 s = ['We are 95% confident the next measurement',
16      ' will be between {0:1.3f} and {1:1.3f}']
17 print(''.join(s).format(avg_x - pred_interval, avg_x + pred_interval))

```

Open the python script (dft-scripts/script-236.py).

We are 95% confident the next measurement will be between 16.076 and 16.124

10.1.6 Curve fitting

Linear fitting

```

1 # examples of linear curve fitting using least squares
2 import numpy as np
3
4 xdata = np.array([0., 1., 2., 3., 4., 5., 6.])
5 ydata = np.array([0.1, 0.81, 4.03, 9.1, 15.99, 24.2, 37.2])
6
7 # fit a third order polynomial
8 from pylab import polyfit, plot, xlabel, ylabel, show, legend, savefig
9 pars = polyfit(xdata, ydata, 3)
10 print('pars from polyfit: {0}'.format(pars))
11
12 # numpy method returns more data
13 A = np.column_stack([xdata**3,
14                     xdata**2,
15                     xdata,
16                     np.ones(len(xdata), np.float)])
17
18 pars_np, resids, rank, s = np.linalg.lstsq(A, ydata)
19 print('pars from np.linalg.lstsq: {0}'.format(pars_np))
20
21 '''
22 we are trying to solve Ax = b for x in the least squares sense. There
23 are more rows in A than elements in x so, we can left multiply each
24 side by A^T, and then solve for x with an inverse.
25
26 A^T A x = A^T b
27 x = (A^T A)^-1 A^T b
28 '''
29 # not as pretty but equivalent!
30 pars_man = np.dot(np.linalg.inv(np.dot(A.T, A)), np.dot(A.T, ydata))
31 print('pars from linear algebra: {0}'.format(pars_man))
32
33 # but, it is easy to fit an exponential function to it!
34 # y = a*exp(x)+b
35 Aexp = np.column_stack([np.exp(xdata), np.ones(len(xdata), np.float)])
36 pars_exp = np.dot(np.linalg.inv(np.dot(Aexp.T, Aexp)), np.dot(Aexp.T, ydata))
37
38 plot(xdata, ydata, 'ro')
39 fity = np.dot(A, pars)
40 plot(xdata, fity, 'k-', label='poly fit')
41 plot(xdata, np.dot(Aexp, pars_exp), 'b-', label='exp fit')
42 xlabel('x')
43 ylabel('y')
44 legend()
45 savefig('images/curve-fit-1.png')

```

Open the python script (dft-scripts/script-237.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]

```

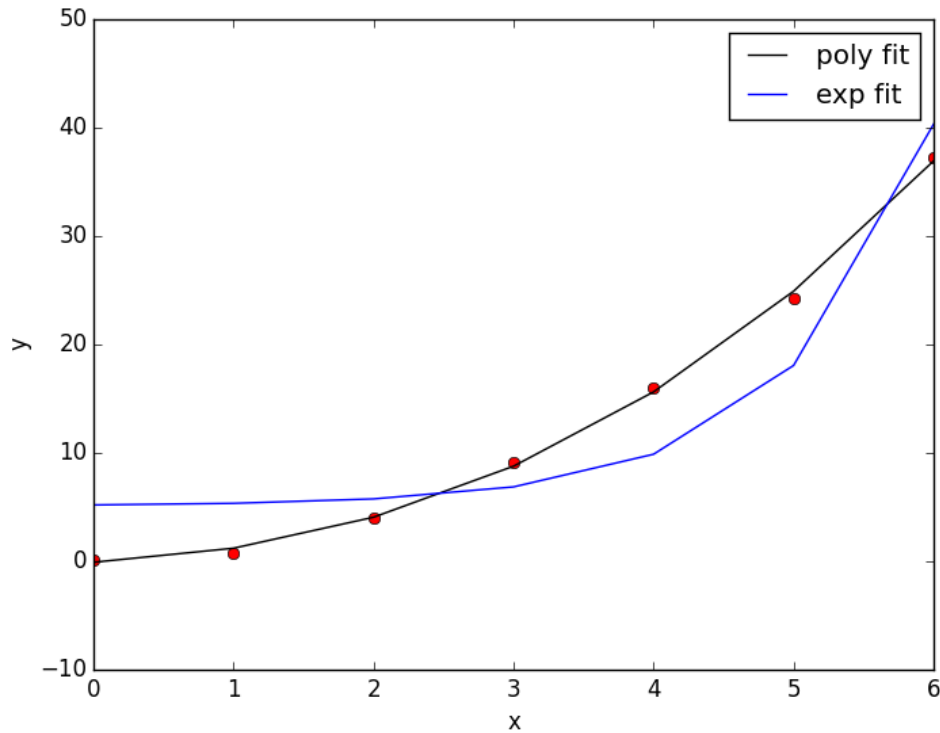


Figure 93: Example of linear least-squares curve fitting.

10.1.7 Nonlinear curve fitting

```

1  from scipy.optimize import leastsq
2  import numpy as np
3
4  vols = np.array([13.71, 14.82, 16.0, 17.23, 18.52])
5
6  energies = np.array([-56.29, -56.41, -56.46, -56.463, -56.41])
7
8
9  def Murnaghan(parameters, vol):
10     'From Phys. Rev. B 28, 5480 (1983)'
11     E0 = parameters[0]
12     B0 = parameters[1]
13     BP = parameters[2]
14     V0 = parameters[3]
15
16     E = (E0 + B0*vol / BP*(((V0 / vol)**BP) / (BP - 1) + 1)
17         - V0 * B0 / (BP - 1.))
18
19     return E
20
21
22  def objective(pars, y, x):
23     # we will minimize this function
24     err = y - Murnaghan(pars, x)

```

```

25     return err
26
27     x0 = [-56., 0.54, 2., 16.5] # initial guess of parameters
28
29     plsq = leastsq(objective, x0, args=(energies, vols))
30
31     print('Fitted parameters = {0}'.format(plsq[0]))
32
33     import matplotlib.pyplot as plt
34     plt.plot(vols, energies, 'ro')
35
36     # plot the fitted curve on top
37     x = np.linspace(min(vols), max(vols), 50)
38     y = Murnaghan(plsq[0], x)
39     plt.plot(x, y, 'k-')
40     plt.xlabel('Volume')
41     plt.ylabel('energy')
42     plt.savefig('images/nonlinear-curve-fitting.png')

```

Open the python script (dft-scripts/script-238.py).

Fitted parameters = (array([-56.46839641, 0.57233217, 2.7407944 , 16.55905648]), 1)

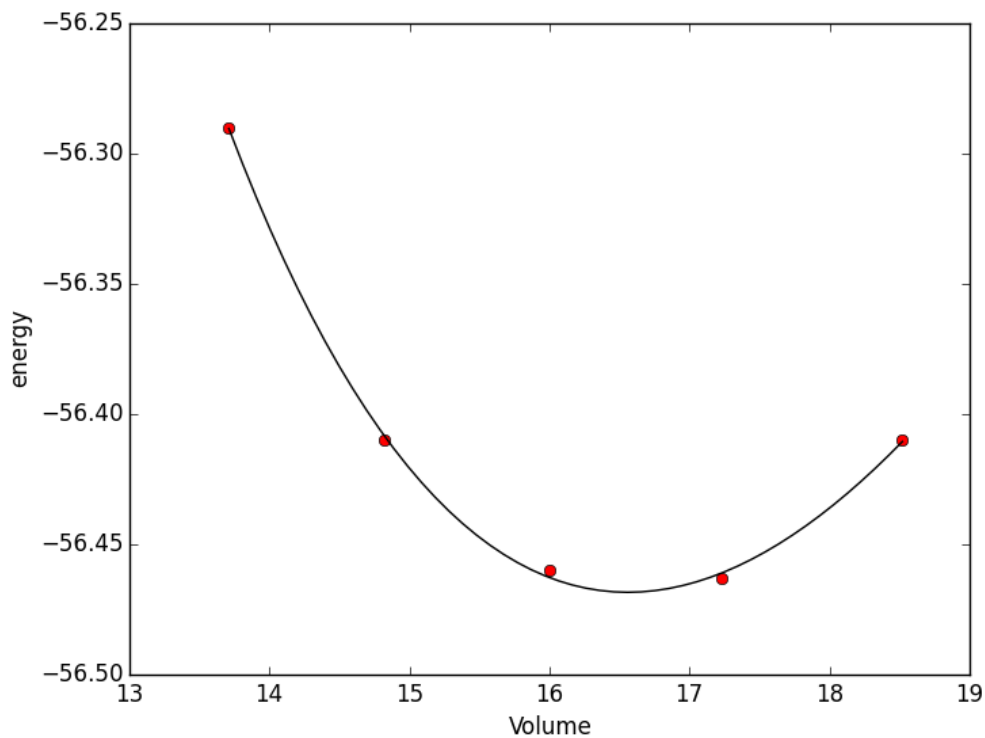


Figure 94: Example of least-squares non-linear curve fitting.

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

```

1 from scipy.optimize import fmin
2 import numpy as np

```

```

3
4 volumes = np.array([13.71, 14.82, 16.0, 17.23, 18.52])
5
6 energies = np.array([-56.29, -56.41, -56.46, -56.463, -56.41])
7
8
9 def Murnaghan(parameters, vol):
10     'From PRB 28,5480 (1983'
11     E0 = parameters[0]
12     B0 = parameters[1]
13     BP = parameters[2]
14     V0 = parameters[3]
15
16     E = E0 + B0*vol/BP*((V0/vol)**BP)/(BP-1)+1) - V0*B0/(BP-1.)
17
18     return E
19
20
21 def objective(pars, vol):
22     # we will minimize this function
23     err = energies - Murnaghan(pars, vol)
24     return np.sum(err**2) # we return the summed squared error directly
25
26 x0 = [-56., 0.54, 2., 16.5] # initial guess of parameters
27
28 plsq = fmin(objective, x0, args=(volumes,)) # note args is a tuple
29
30 print('parameters = {0}'.format(plsq))
31
32 import matplotlib.pyplot as plt
33 plt.plot(volumes, energies, 'ro')
34
35 # plot the fitted curve on top
36 x = np.linspace(min(volumes), max(volumes), 50)
37 y = Murnaghan(plsq, x)
38 plt.plot(x, y, 'k-')
39 plt.xlabel(r'Volume ($\AA^3$)')
40 plt.ylabel('Total energy (eV)')
41 plt.savefig('images/nonlinear-fitting-lsq.png')

```

Open the python script (dft-scripts/script-239.py).

Optimization terminated successfully.

Current function value: 0.000020

Iterations: 137

Function evaluations: 240

parameters = [-56.46932645 0.59141447 1.9044796 16.59341303]

10.1.9 Nonlinear curve fitting with confidence intervals

```

1 # Nonlinear curve fit with confidence interval
2 import numpy as np
3 from scipy.optimize import curve_fit
4 from scipy.stats.distributions import t
5
6 '''
7 fit this equation to data
8 y = c1 exp(-x) + c2*x
9
10 this is actually a linear regression problem, but it is convenient to
11 use the nonlinear fitting routine because it makes it easy to get
12 confidence intervals. The downside is you need an initial guess.
13
14 from Matlab
15 b =
16
17 4.9671
18 2.1100
19
20
21 bint =
22

```

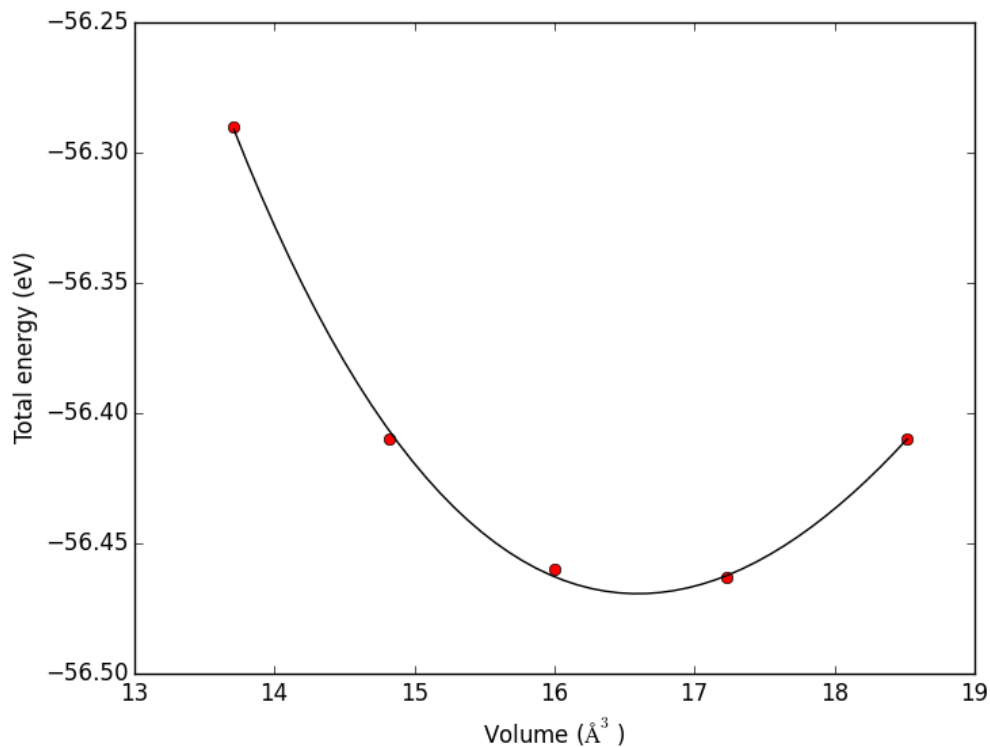


Figure 95: Fitting a nonlinear function.

```

23     4.6267    5.3075
24     1.7671    2.4528
25     ',,'
26
27 x = np.array([ 0.1,  0.2,  0.3,  0.4,  0.5,  0.6,  0.7,  0.8,  0.9,  1. ])
28 y = np.array([ 4.70192769,  4.46826356,  4.57021389,  4.29240134,  3.88155125,
29               3.78382253,  3.65454727,  3.86379487,  4.16428541,  4.06079909])
30
31 # this is the function we want to fit to our data
32 def func(x,c0, c1):
33     return c0 * np.exp(-x) + c1*x
34
35 pars, pcov = curve_fit(func, x, y, p0=[4.96, 2.11])
36
37 alpha = 0.05 # 95% confidence interval
38
39 n = len(y) # number of data points
40 p = len(pars) # number of parameters
41
42 dof = max(0, n-p) # number of degrees of freedom
43
44 tval = t.ppf(1.0-alpha/2., dof) # student-t value for the dof and confidence level
45
46 for i, p, var in zip(range(n), pars, np.diag(pcov)):
47     sigma = var**0.5
48     print('c{0}: {1} [{2} {3}]'.format(i, p,
49                                         p - sigma*tval,
50                                         p + sigma*tval))
51
52 import matplotlib.pyplot as plt
53 plt.plot(x,y,'bo ')
54 xfit = np.linspace(0,1)
55 yfit = func(xfit, pars[0], pars[1])
56 plt.plot(xfit,yfit,'b-')
57 plt.legend(['data','fit'],loc='best')

```

```
58 plt.savefig('images/nonlin-fit-ci.png')
```

Open the python script (dft-scripts/script-240.py).

```
c0: 4.96713966439 [4.62674476321 5.30753456558]
c1: 2.10995112628 [1.76711622067 2.45278603188]
```

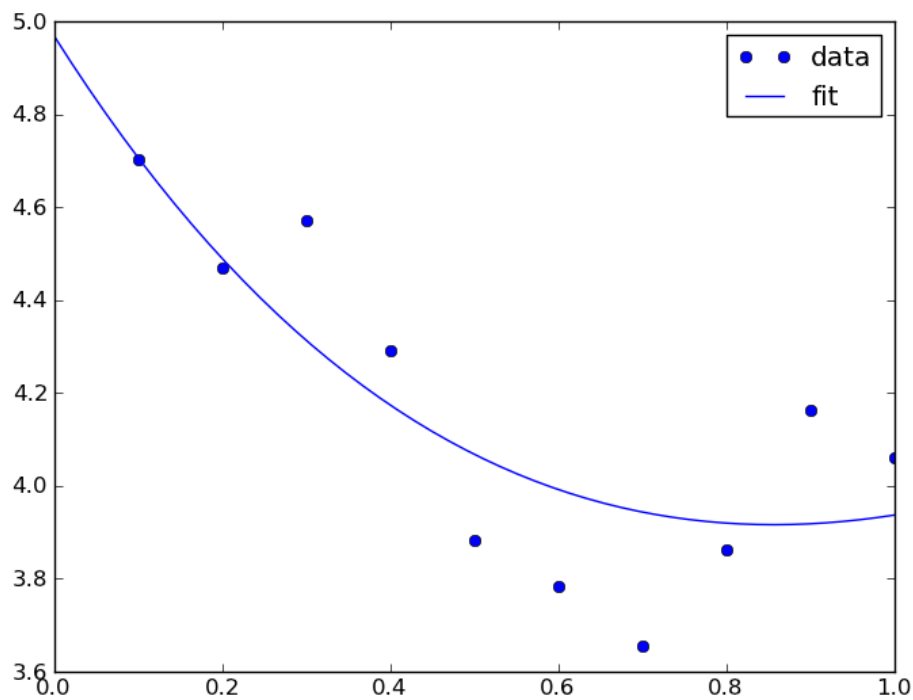


Figure 96: Nonlinear fit to data.

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.

```
1 # use splines to fit and interpolate data
2 from scipy.interpolate import interp1d
3 from scipy.optimize import fmin
4 import numpy as np
5 import matplotlib.pyplot as plt
6
7 x = np.array([ 0,    1,    2,    3,    4 ])
8 y = np.array([ 0.,   0.308, 0.55, 0.546, 0.44 ])
9
10 # create the interpolating function
11 f = interp1d(x, y, kind='cubic', bounds_error=False)
12
13 # to find the maximum, we minimize the negative of the function. We
14 # cannot just multiply f by -1, so we create a new function here.
15 f2 = interp1d(x, -y, kind='cubic')
16 xmax = fmin(f2, 2.5)
17
```

```

18 xfit = np.linspace(0,4)
19
20 plt.plot(x,y,'bo')
21 plt.plot(xfit, f(xfit),'r-')
22 plt.plot(xmax, f(xmax),'g*')
23 plt.legend(['data','fit','max'], loc='best', numpoints=1)
24 plt.xlabel('x data')
25 plt.ylabel('y data')
26 plt.title('Max point = ({0:1.2f}, {1:1.2f})'.format(float(xmax),
27                                                    float(f(xmax))))
28 plt.savefig('images/splinefit.png')

```

Open the python script (dft-scripts/script-241.py).

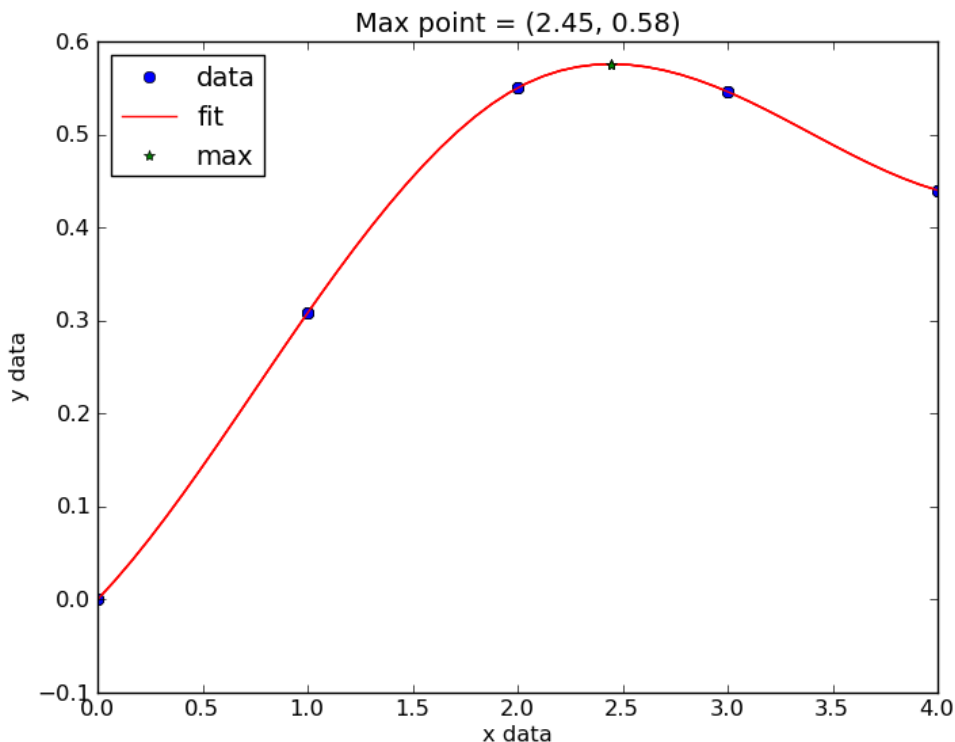


Figure 97: Illustration of a spline fit to data and finding the maximum point.

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 ??.

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 (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 $P=(a,b,c)$.

```

1  from jasp import jasp
2  import numpy as np
3
4  with jasp('molecules/co-centered') as calc:
5      atoms = calc.get_atoms()
6      x, y, z, cd = calc.get_charge_density()
7
8  def interp3d(x,y,z,cd,xi,yi,zi):
9      '''
10     interpolate a cubic 3D grid defined by x,y,z,cd at the point
11     (xi,yi,zi)
12     '''
13
14     def get_index(value,vector):
15         '''
16         assumes vector ordered decreasing to increasing. A bisection
17         search would be faster.
18         '''
19         for i,val in enumerate(vector):
20             if val > value:
21                 return i-1
22         return None
23
24     xv = x[:,0,0]
25     yv = y[0,:,0]
26     zv = z[0,0,:]
27
28     a,b,c = xi, yi, zi
29
30     i = get_index(a,xv)
31     j = get_index(b,yv)
32     k = get_index(c,zv)
33
34     x1 = x[i,j,k]
35     x2 = x[i+1,j,k]
36     y1 = y[i,j,k]
37     y2 = y[i,j+1,k]
38     z1 = z[i,j,k]
39     z2 = z[i,j,k+1]
40
41     u1 = cd[i, j, k]
42     u2 = cd[i+1, j, k]
43     u3 = cd[i, j+1, k]
44     u4 = cd[i+1, j+1, k]
45     u5 = cd[i, j, k+1]
46     u6 = cd[i+1, j, k+1]
47     u7 = cd[i, j+1, k+1]
48     u8 = cd[i+1, j+1, k+1]
49
50     w1 = u2 + (u2-u1)/(x2-x1)*(a-x1)
51     w2 = u4 + (u4-u3)/(x2-x1)*(a-x1)
52     w3 = w2 + (w2-w1)/(y2-y1)*(b-y1)
53     w4 = u5 + (u6-u5)/(x2-x1)*(a-x1)
54     w5 = u7 + (u8-u7)/(x2-x1)*(a-x1)
55     w6 = w4 + (w5-w4)/(y2-y1)*(b-y1)
56     w7 = w3 + (w6-w3)/(z2-z1)*(c-z1)

```

```

57     u = w7
58
59     return u
60
61 pos = atoms.get_positions()
62
63 P1 = np.array([0.0, 5.0, 5.0])
64 P2 = np.array([9.0, 5.0, 5.0])
65
66 npoints = 60
67
68 points = [P1 + n*(P2-P1)/npoints for n in range(npoints)]
69
70 R = [np.linalg.norm(p-P1) for p in points]
71
72 # interpolated line
73 icd = [interp3d(x,y,z,cd,p[0],p[1],p[2]) for p in points]
74
75 import matplotlib.pyplot as plt
76
77 plt.plot(R, icd)
78 cR = np.linalg.norm(pos[0] - P1)
79 oR = np.linalg.norm(pos[1] - P1)
80 plt.plot([cR, cR], [0, 2], 'r-') #markers for where the nuclei are
81 plt.plot([oR, oR], [0, 8], 'r-')
82 plt.xlabel('|R| ($AA$)')
83 plt.ylabel('Charge density (e/$AA^3$)')
84 plt.savefig('images/CO-charge-density.png')
85 plt.show()

```

Open the python script (dft-scripts/script-242.py).

None

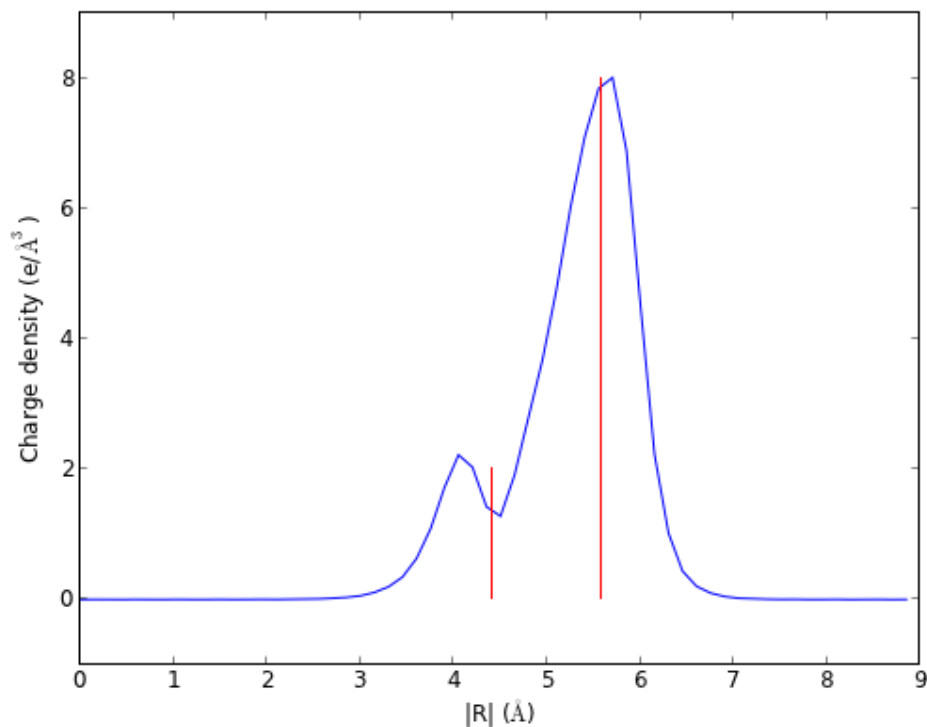


Figure 98: An example of interpolated charge density of a CO molecule along the axis of molecule.

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.

```

1  '''
2  3D vector interpolation in non-cubic unit cells with vector
3  interpolation.
4
5  This function should work for any shape unit cell.
6  '''
7  from jasp import *
8  import bisect
9  import numpy as np
10 from pylab import plot, xlabel, ylabel, savefig, show
11
12 with jasp('molecules/co-centered') as calc:
13     atoms = calc.get_atoms()
14     x,y,z,cd = calc.get_charge_density()
15
16 def vinterp3d(x,y,z,u,xi,yi,zi):
17
18     p = np.array([xi,yi,zi])
19
20     #1D arrays of coordinates
21     xv = x[:,0,0]
22     yv = y[0,:,0]
23     zv = z[0,0,:]
24
25     # we subtract 1 because bisect tells us where to insert the
26     # element to maintain an ordered list, so we want the index to the
27     # left of that point
28     i = bisect.bisect_right(xv,xi) - 1
29     j = bisect.bisect_right(yv,yi) - 1
30     k = bisect.bisect_right(zv,zi) - 1
31
32     #points at edge of cell. We only need P1, P2, P3, and P5
33     P1 = np.array([x[i,j,k],y[i,j,k],z[i,j,k]])
34     P2 = np.array([x[i+1,j,k],y[i+1,j,k],z[i+1,j,k]])
35     P3 = np.array([x[i,j+1,k],y[i,j+1,k],z[i,j+1,k]])
36     P5 = np.array([x[i,j,k+1],y[i,j,k+1],z[i,j,k+1]])
37
38     #values of u at edge of cell
39     u1 = u[i,j,k]
40     u2 = u[i+1,j,k]
41     u3 = u[i,j+1,k]
42     u4 = u[i+1,j+1,k]
43     u5 = u[i,j,k+1]
44     u6 = u[i+1,j,k+1]
45     u7 = u[i,j+1,k+1]
46     u8 = u[i+1,j+1,k+1]
47
48     #cell basis vectors, not the unit cell, but the voxel cell containing the point
49     cbasis = np.array([P2-P1,
50                        P3-P1,
51                        P5-P1])
52
53     #now get interpolated point in terms of the cell basis
54     s = np.dot(np.linalg.inv(cbasis.T),np.array([xi,yi,zi])-P1)
55
56     #now s = (sa, sb, sc) which are fractional coordinates in the vector space
57     #next we do the interpolations
58     ui1 = u1 + s[0]*(u2-u1)
59     ui2 = u3 + s[0]*(u4-u3)
60
61     ui3 = u5 + s[0]*(u6-u5)
62     ui4 = u7 + s[0]*(u8-u7)
63
64     ui5 = ui1 + s[1]*(ui2-ui1)
65     ui6 = ui3 + s[1]*(ui4-ui3)
66
67     ui7 = ui5 + s[2]*(ui6-ui5)

```

```

68
69     return ui7
70
71     # compute a line with 60 points in it through these two points
72     P1 = np.array([0.0, 5.0, 5.0])
73     P2 = np.array([10.0, 5.0, 5.0])
74
75     npoints = 60
76
77     points = [P1 + n*(P2-P1)/npoints for n in range(npoints)]
78
79     # compute the distance along the line
80     R = [np.linalg.norm(p-P1) for p in points]
81
82     icd = [vinterp3d(x,y,z,cd,p[0],p[1],p[2]) for p in points]
83
84     plot(R,icd)
85     pos = atoms.get_positions()
86     cR = np.linalg.norm(pos[0]-P1)
87     oR = np.linalg.norm(pos[1]-P1)
88     plot([cR,cR],[0,2], 'r-') #markers for where the nuclei are
89     plot([oR,oR],[0,8], 'r-')
90     xlabel('|R| (Å)')
91     ylabel('Charge density (e/Å3)')
92     savefig('images/interpolated-charge-density.png')
93     show()

```

Open the python script (dft-scripts/script-243.py).

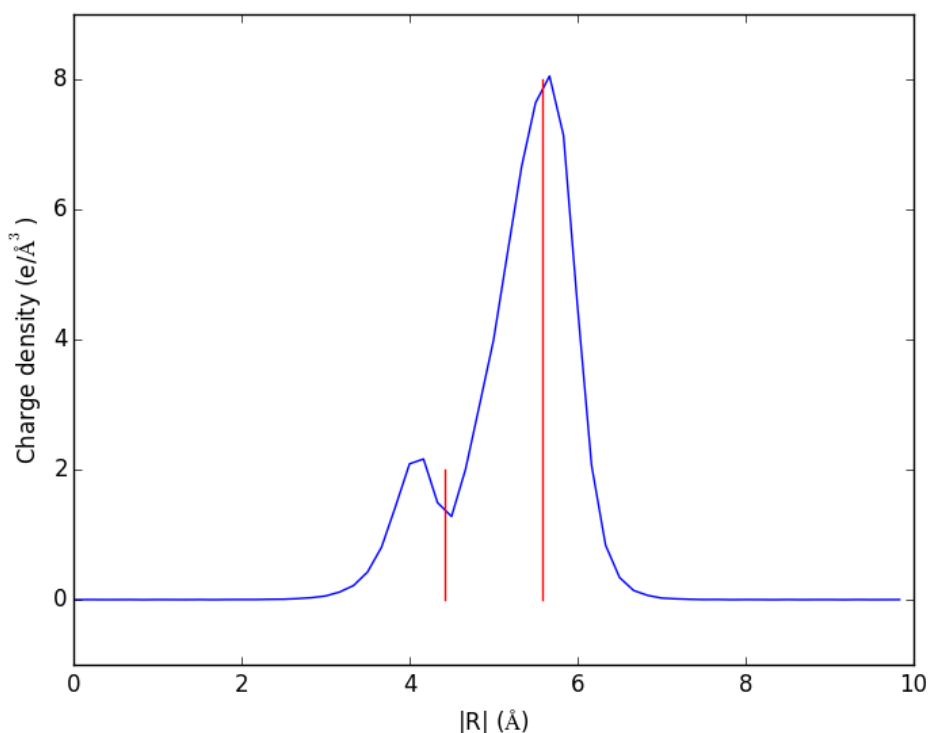


Figure 99: Interpolated charge density for a CO molecule.

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`.

```
1 pylab.save('pdat.dat', (x,y))
```

Open the python script (dft-scripts/script-244.py).
and later you can read these arrays back in with:

```
1 x,y = pylab.load('pdat.dat')
```

Open the python script (dft-scripts/script-245.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:

```
1 v1 = []
2 v2 = []
3 lines = open('somefile', 'r').readlines()
4
5 for line in lines[2:]: #skip the first two lines
6     fields = line.split(',')
7     v1.append(fields[0]) #names
8     v2.append(int(fields[1])) #number
```

Open the python script (dft-scripts/script-246.py).
Writing datafiles is easy too.

```
1 v1 = ['john', 'robert', 'terry']
2 v2 = [4,5,6]
3 f = open('somefile', 'w') #note 'w' = write mode
4 f.write('#header\n')
5 f.write('#ignore these lines\n')
6 for a,b in zip(v1,v2):
7     f.write('{0}, {1}\n'.format(a,b))
8 f.close()
```

Open the python script (dft-scripts/script-247.py).
Some notes:

1. opening
a
file
in
'w'
mode

clob-
bers
any
ex-
ist-
ing
file,
so
do
that

with care!

1.
when
writ-
ing
to
a
file
you
have
to
add
a
car-
riage
re-
turn
to
each
line.

2.
Manually
writ-
ing
and
read-
ing
files
is
pretty
te-
dious.
When-
ever

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:

```
1 Nstates = np.trapz(rho,E)
```

Open the python script (dft-scripts/script-248.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:

```
1 e_avg = np.trapz(rho*E,E)/np.trapz(rho,E)
```

Open the python script (dft-scripts/script-249.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 moments 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::

```
1 n = 2
2 mom_2 = np.trapz(rho*E**n,E)/np.trapz(rho,E)
```

Open the python script (dft-scripts/script-250.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.

```
1 import numpy as np
2 import matplotlib.pyplot as plt
3 import time
4
5 '''
6 These are the brainless way to calculate numerical derivatives. They
7 work well for very smooth data. they are surprisingly fast even up to
8 10000 points in the vector.
9 '''
10
11 x = np.linspace(0.78, 0.79, 100) # 100 points between 0.78 and 0.79
12 y = np.sin(x)
13 dy_analytical = np.cos(x)
14 '''
15 let us use a forward difference method:
```

```

16  that works up until the last point, where there is not
17  a forward difference to use. there, we use a backward difference.
18  '''
19
20  tf1 = time.time()
21  dyf = [0.0]*len(x)
22  for i in range(len(y)-1):
23      dyf[i] = (y[i+1] - y[i])/(x[i+1]-x[i])
24  # set last element by backwards difference
25  dyf[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])
26
27  print(' Forward difference took {0:1.1f} seconds'.format(time.time() - tf1))
28
29  # and now a backwards difference
30  tb1 = time.time()
31  dyb = [0.0]*len(x)
32  # set first element by forward difference
33  dyb[0] = (y[0] - y[1])/(x[0] - x[1])
34  for i in range(1,len(y)):
35      dyb[i] = (y[i] - y[i-1])/(x[i]-x[i-1])
36
37  print(' Backward difference took {0:1.1f} seconds'.format(time.time() - tb1))
38
39  # and now, a centered formula
40  tc1 = time.time()
41  dyc = [0.0]*len(x)
42  dyc[0] = (y[0] - y[1])/(x[0] - x[1])
43  for i in range(1,len(y)-1):
44      dyc[i] = (y[i+1] - y[i-1])/(x[i+1]-x[i-1])
45  dyc[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])
46
47  print(' Centered difference took {0:1.1f} seconds'.format(time.time() - tc1))
48
49  # the centered formula is the most accurate formula here
50
51
52  plt.plot(x,dy_analytical, label='analytical derivative')
53  plt.plot(x,dyf,'--', label='forward')
54  plt.plot(x,dyb,'--', label='backward')
55  plt.plot(x,dyc,'--', label='centered')
56
57  plt.legend(loc='lower left')
58  plt.savefig('images/simple-diffs.png')

```

Open the python script (dft-scripts/script-251.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.

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:

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  x = np.linspace(0,2*np.pi,100)
5  y = np.sin(x)
6  dy_analytical = np.cos(x)
7
8  # we need to specify the size of dy ahead because diff returns
9  #an array of n-1 elements
10 dy = np.zeros(y.shape,np.float) #we know it will be this size
11 dy[0:-1] = np.diff(y)/np.diff(x)
12 dy[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])
13
14
15 '''
16 calculate dy by center differencing using array slices
17 '''

```

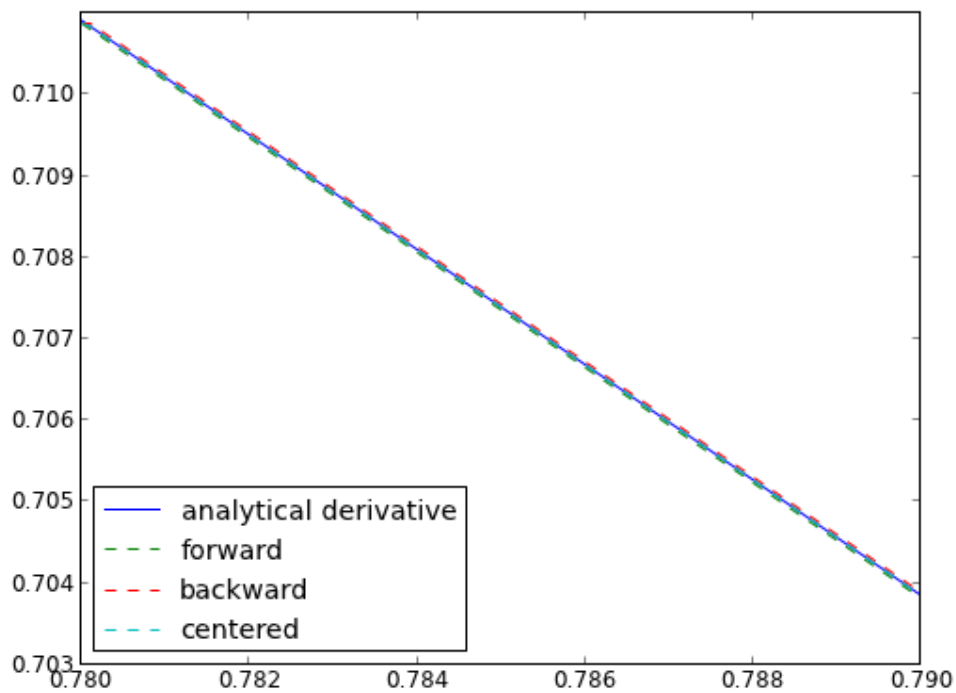


Figure 100: Comparison of different numerical derivatives.

```

18
19 dy2 = np.zeros(y.shape,np.float) #we know it will be this size
20 dy2[1:-1] = (y[2:] - y[0:-2])/(x[2:] - x[0:-2])
21 dy2[0] = (y[1]-y[0])/(x[1]-x[0])
22 dy2[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])
23
24 plt.plot(x,y)
25 plt.plot(x,dy_analytical,label='analytical derivative')
26 plt.plot(x,dy,label='forward diff')
27 plt.plot(x,dy2,'k--',lw=2,label='centered diff')
28 plt.legend(loc='lower left')
29 plt.savefig('images/vectorized-diffs.png')

```

Open the python script (dft-scripts/script-252.py).

None

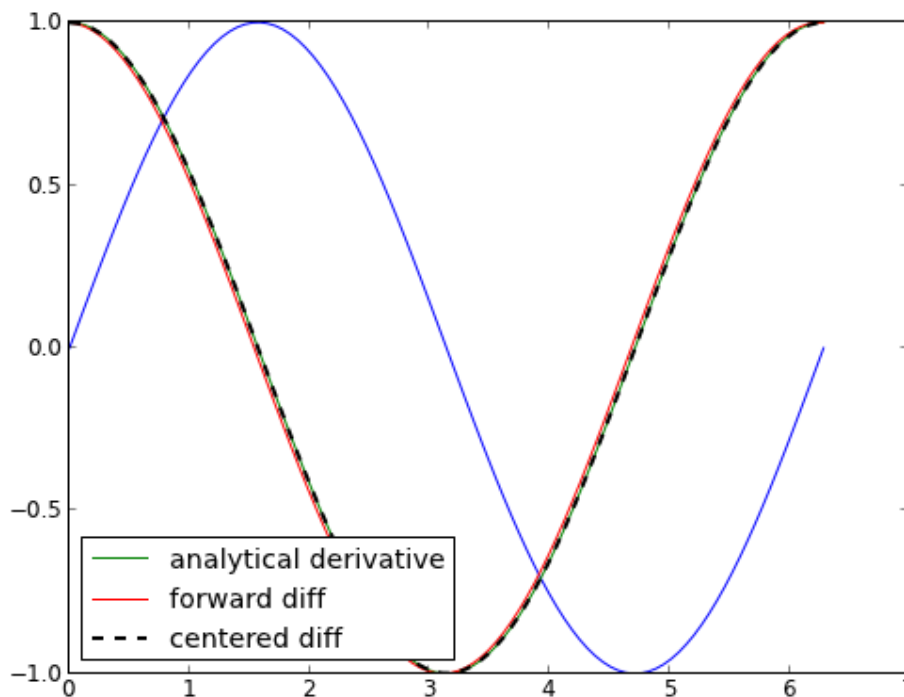


Figure 101: Comparison of different numerical derivatives.

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:

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  x = np.linspace(0, 2*np.pi, 100)
5  y = np.sin(x) + 0.1*np.random.random(size=x.shape)
6  dy_analytical = np.cos(x)
7
8  #2-point formula
9  dyf = [0.0]*len(x)
10 for i in range(len(y)-1):
11     dyf[i] = (y[i+1] - y[i])/(x[i+1]-x[i])
12 #set last element by backwards difference
13 dyf[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])
14
15 '''
16 calculate dy by 4-point center differencing using array slices
17
18 \frac{y[i-2] - 8y[i-1] + 8y[i+1] - y[i+2]}{12h}
19
20 y[0] and y[1] must be defined by lower order methods
21 and y[-1] and y[-2] must be defined by lower order methods
22 '''
23
24 dy = np.zeros(y.shape, np.float) #we know it will be this size
25 h = x[1]-x[0] #this assumes the points are evenly spaced!
26 dy[2:-2] = (y[0:-4] - 8*y[1:-3] + 8*y[3:-1] - y[4:])/ (12.*h)
27

```



```

28 dy[0] = (y[1]-y[0])/(x[1]-x[0])
29 dy[1] = (y[2]-y[1])/(x[2]-x[1])
30 dy[-2] = (y[-2] - y[-3])/(x[-2] - x[-3])
31 dy[-1] = (y[-1] - y[-2])/(x[-1] - x[-2])
32
33 plt.plot(x,y)
34 plt.plot(x,dy_analytical,label='analytical derivative')
35 plt.plot(x,dyf,'r-',label='2pt-forward diff')
36 plt.plot(x,dy,'k--',lw=2,label='4pt-centered diff')
37 plt.legend(loc='lower left')
38 plt.savefig('images/multipt-diff.png')

```

Open the python script (dft-scripts/script-253.py).

None

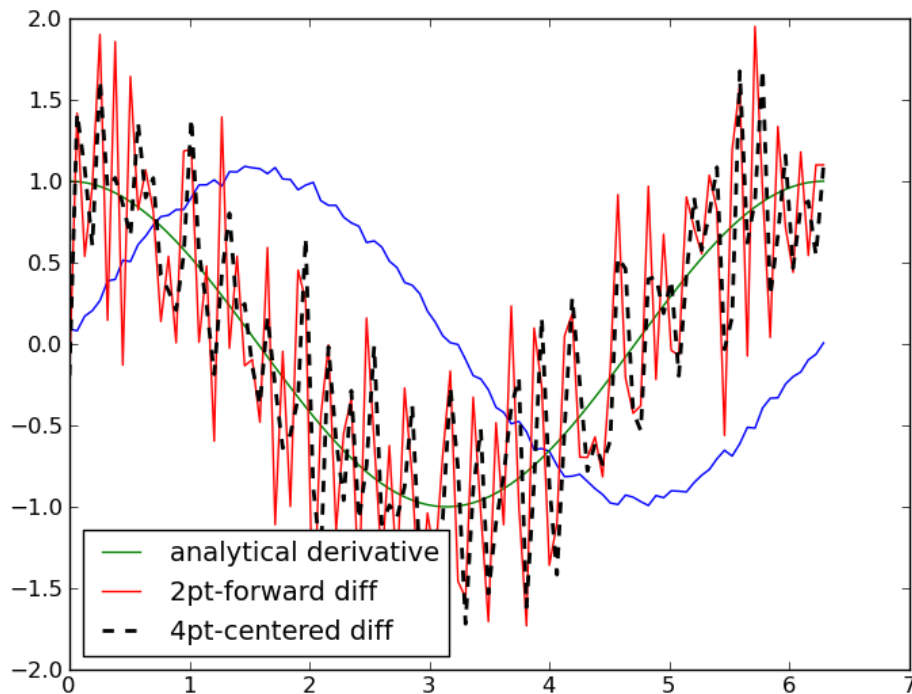


Figure 102: Comparison of 2 point and 4 point numerical derivatives.

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):

```

1 import numpy as np
2 import matplotlib.pyplot as plt
3
4 N = 101 #number of points
5 L = 2*np.pi #interval of data
6
7 x = np.arange(0.0,L,L/float(N)) #this does not include the endpoint
8
9 #add some random noise

```

```

10 y = np.sin(x) + 0.05*np.random.random(size=x.shape)
11 dy_analytical = np.cos(x)
12
13 '''
14 http://sci.tech-archive.net/Archive/sci.math/2008-05/msg00401.html
15
16 you can use fft to calculate derivatives!
17 '''
18
19 if N % 2 == 0:
20     k = np.arange(range(0,N/2)+[0] + range(-N/2+1,0))
21 else:
22     k = np.arange(range(0,(N-1)/2) + [0] + range(-(N-1)/2,0))
23
24 k *= 2*np.pi/L
25
26 fd = np.fft.ifft(1.j*k * np.fft.fft(y))
27
28 plt.plot(x,y)
29 plt.plot(x,dy_analytical,label='analytical der')
30 plt.plot(x,fd,label='fft der')
31 plt.legend(loc='lower left')
32
33 plt.savefig('images/fft-der.png')

```

Open the python script (dft-scripts/script-254.py).

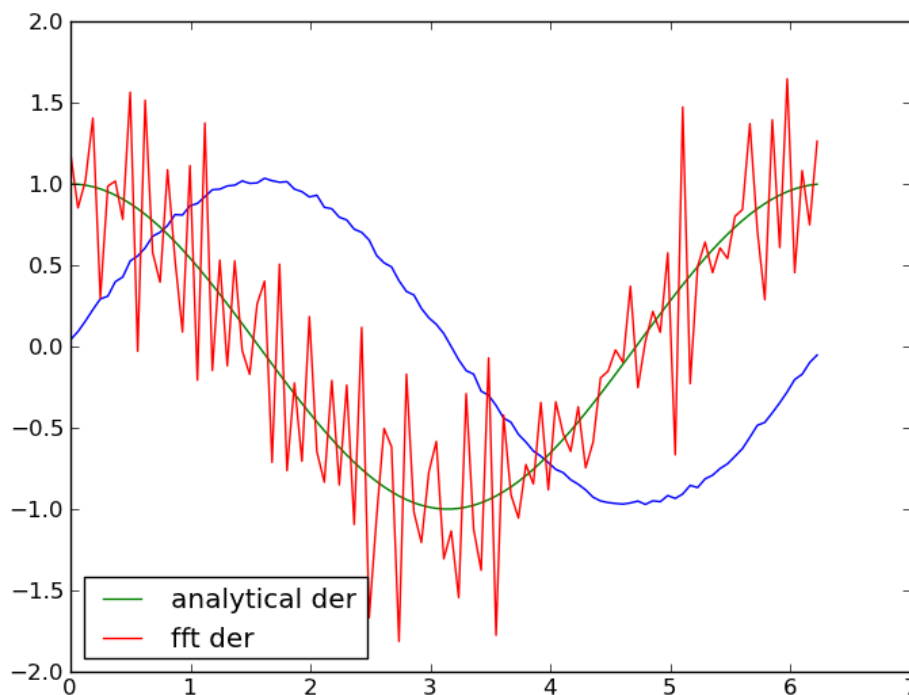


Figure 103: Comparison of FFT numerical derivatives.

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:

```
1 import numpy as np
2
3 x = np.linspace(0.0,6.0,100)
4 y = np.cos(x)
5
6 import csv
7 writer = csv.writer(open("some.csv", "w"))
8 writer.writerows(zip(x,y))
```

Open the python script (dft-scripts/script-255.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:

```
1 import csv
2 reader = csv.reader(open("some.csv", 'r'), delimiter=',')
3
4 x,y = [],[]
5 for row in reader:
6     #csv returns strings that must be cast as floats
7     a,b = [float(z) for z in row]
8     x.append(a)
9     y.append(b)
```

Open the python script (dft-scripts/script-256.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.

```
1 import numpy as np
2 import xlwt
3
4 wbk = xlwt.Workbook()
5 sheet = wbk.add_sheet('sheet 1')
6
7 volumes = np.array([13.72, 14.83, 16.0, 17.23, 18.52])
8 energies = np.array([-56.29, -56.41, -56.46, -56.46, -56.42])
9
10 for i, pair in enumerate(zip(volumes, energies)):
11     vol = pair[0]
```

```

12     energy = pair[1]
13     sheet.write(i,0,vol)
14     sheet.write(i,1,energy)
15 wbk.save('images/test-write.xls')

```

Open the python script (dft-scripts/script-257.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.

```

1 import xlrd
2 wbk = xlrd.open_workbook('images/test-write.xls')
3 sheet1 = wbk.sheet_by_name('sheet 1')
4 print(sheet1.col_values(0))
5 print(sheet1.col_values(1))

```

Open the python script (dft-scripts/script-258.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
 - an-
 - i-
 - mate
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

$$A = A1x + A2y + A3z \quad (9)$$

$$B = B1x + B2y + B3z \quad (10)$$

$$C = C1x + C2y + C3z \quad (11)$$

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:

$$\begin{bmatrix} A1 & B1 & C1 \\ A2 & B2 & C2 \\ A3 & B3 & C3 \end{bmatrix} \begin{bmatrix} s1 \\ s2 \\ s3 \end{bmatrix} = \begin{bmatrix} p1 \\ p2 \\ p3 \end{bmatrix} \quad (12)$$

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:

```

1  from ase.lattice.surface import fcc111
2  import numpy as np
3  np.set_printoptions(precision=3,suppress=True)
4
5  slab = fcc111('Pd',
6              a=3.92,          # Pd lattice constant
7              size=(2,2,3),    # 3-layer slab in 1x1 configuration
8              vacuum=10.0)
9
10 pos = slab.get_positions() #these positions use x,y,z vectors as a basis
11
12 # we want to see the atoms in terms of the unitcell vectors
13 newbasis = slab.get_cell()
14
15 s = np.dot(np.linalg.inv(newbasis.T),pos.T).T
16 print('Coordinates in new basis are: \n',s)
17
18 # what we just did is equivalent to the following atoms method
19 print('Scaled coordinates from ase are: \n',slab.get_scaled_positions())

```

Open the python script (dft-scripts/script-259.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!)

```
1 from ase.lattice.cubic import BodyCenteredCubic
2 import numpy as np
3 bulk = BodyCenteredCubic(directions=[[1,0,0],
4                                     [0,1,0],
5                                     [0,0,1]],
6                           size=(2,2,2),
7                           latticeconstant=2.87,
8                           symbol='Fe')
9
10
11 newbasis = 2.87*np.array([[ -0.5, 0.5, 0.5],
12                           [ 0.5, -0.5, 0.5],
13                           [ 0.5, 0.5, -0.5]])
14
15 pos = bulk.get_positions()
16
17 s = np.dot(np.linalg.inv(newbasis.T), pos.T).T
18 print('atom positions in primitive basis')
19 print(s)
20
21 # let us see the unit cell in terms of the primitive basis too
22 print('unit cell in terms of the primitive basis')
23 print(np.dot(np.linalg.inv(newbasis.T), bulk.get_cell().T).T)
```

Open the python script (dft-scripts/script-260.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.

```
1 import numpy as np
2 from Scientific.Geometry import Vector
3
4 A = Vector([1, 1, 1]) # Scientific
5 a = np.array([1, 1, 1]) # numpy
6
7 B = Vector([0.0, 1.0, 0.0])
8
9 print('|A| = ', A.length()) # Scientific Python way
10 print('|a| = ', np.sum(a**2)**0.5) # numpy way
11 print('|a| = ', np.linalg.norm(a)) # numpy way 2
12
13 print('ScientificPython angle = ', A.angle(B)) # in radians
14 print('numpy angle = {}'.format(
15     np.arccos(np.dot(a / np.linalg.norm(a),
16                   B / np.linalg.norm(B)))))
17
18 # cross products
19 print('Scientific A .cross. B = ', A.cross(B))
20
21 # you can use Vectors in numpy
22 print('numpy A .cross. B = ', np.cross(A,B))
```

Open the python script (dft-scripts/script-261.py).

```
('|A| = ', 1.7320508075688772)
('|a| = ', 1.7320508075688772)
('|a| = ', 1.7320508075688772)
('ScientificPython angle = ', 0.9553166181245092)
('numpy angle = {}'.format(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.

```
1 import numpy as np
2
3 a1 = [2, 0, 0]
4 a2 = [1, 1, 0]
5 a3 = [0, 0, 10]
6
7 uc = np.array([a1, a2, a3])
8
9 print('V = {0} ang^3 from dot/cross'.format(np.dot(np.cross(a1,a2),a3)))
10 print('V = {0} ang^3 from det'.format(np.linalg.det(uc)))
11
12 from ase import Atoms
```

```

13 atoms = Atoms([],cell=uc) #empty list of atoms
14 print('V = {0} ang^3 from get_volume'.format(atoms.get_volume()))
15

```

Open the python script (dft-scripts/script-262.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.

```

1  import numpy as np
2  from ase.lattice.cubic import FaceCenteredCubic
3
4  ag = FaceCenteredCubic(directions=[[1, 0, 0],
5                                     [0, 1, 0],
6                                     [0, 0, 1]],
7                           size=(1, 1, 1),
8                           symbol='Ag',
9                           latticeconstant=4.0)
10
11 # these are the reciprocal lattice vectors
12 b1, b2, b3 = np.linalg.inv(ag.get_cell())
13
14 '''
15 g(111) = 1*b1 + 1*b2 + 1*b3
16
17 and |g(111)| = 1/d_111
18 '''
19 h,k,l = (1, 1, 1)
20 d = 1./np.linalg.norm(h*b1 + k*b2 + l*b3)
21
22 print('d_111 spacing (method 1) = {0:1.3f} Angstroms'.format(d))
23
24 # method #2
25 hkl = np.array([h, k, l])
26 G = np.array([b1, b2, b3]) # reciprocal unit cell
27
28 '''
29 Gstar is usually defined as this matrix of dot products:
30
31 Gstar = np.array([[dot(b1,b1), dot(b1,b2), dot(b1,b3)],
32                   [dot(b1,b2), dot(b2,b2), dot(b2,b3)],
33                   [dot(b1,b3), dot(b2,b3), dot(b3,b3)])])
34
35 but I prefer the notationally more compact:
36 Gstar = G .dot. transpose(G)
37
38 then, 1/d_hkl^2 = hkl .dot. Gstar .dot. hkl
39 '''
40
41 Gstar = np.dot(G, G.T)
42
43 id2 = np.dot(hkl, np.dot(Gstar, hkl))
44
45 print('d_111 spacing (method 2) =',np.sqrt(1 / id2))
46
47 # http://books.google.com/books?id=nJHSqEseuIUC&pg=PA118&ots=YA9TBldoVH
48 # &dq=reciprocal%20metric%20tensor&pg=PA119#v=onepage
49 # &q=reciprocal%20metric%20tensor&f=false
50
51 '''Finally, many text books on crystallography use long algebraic
52 formulas for computing the d-spacing with sin and cos, vector lengths,
53 and angles. Below we compute these and use them in the general
54 triclinic structure formula which applies to all the structures.
55 '''
56 from Scientific.Geometry import Vector

```



```

57 import math
58
59 unitcell = ag.get_cell()
60 A = Vector(unitcell[0])
61 B = Vector(unitcell[1])
62 C = Vector(unitcell[2])
63
64 # lengths of the vectors
65 a = A.length()##angstroms2bohr
66 b = B.length()##angstroms2bohr
67 c = C.length()##angstroms2bohr
68
69 # angles between the vectors in radians
70 alpha = B.angle(C)
71 beta = A.angle(C)
72 gamma = A.angle(B)
73
74 print('')
75 print('a   b   c   alpha beta gamma')
76 print('{0:1.3f} {1:1.3f} {2:1.3f} {3:1.3f} {4:1.3f} {5:1.3f}\n'.format(a,b,c,
77
78 h, k, l = (1, 1, 1)
79
80 from math import sin, cos
81
82 id2 = ((h**2 / a**2 * sin(alpha)**2
83        + k**2 / b**2 * sin(beta)**2
84        + l**2 / c**2 * sin(gamma)**2
85        + 2 * k * l / b / c * (cos(beta) * cos(gamma) - cos(alpha))
86        + 2 * h * l / a / c * (cos(alpha) * cos(gamma) - cos(beta))
87        + 2 * h * k / a / b * (cos(alpha) * cos(beta) - cos(gamma)))
88        / (1 - cos(alpha)**2 - cos(beta)**2 - cos(gamma)**2
89           + 2 * cos(alpha) * cos(beta) * cos(gamma)))
90
91 d = 1 / math.sqrt(id2)
92
93 print('d_111 spacing (method 3) = {0}'.format(d))

```

Open the python script (dft-scripts/script-263.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.¹⁰⁴ 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 Murnaghan¹⁰⁵ equation of state is described in¹⁰⁶.

$$E = E_T + \frac{B_0V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0-1} + 1 \right] - \frac{V_0B_0}{B'_0-1}$$

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 equation¹⁰⁷ is:

$$E = E_0 + \frac{9}{8}B_0V_0 \left(\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right)^2 + \frac{9}{16}B_0V_0(B'_0-4) \left(\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right)^3$$

10.3.4 The Anton-Schmidt Equation of state¹⁰⁸

$$E(V) = E_\infty + \frac{BV_0}{n+1} \left(\frac{V}{V_0} \right)^{n+1} \left(\ln \frac{V}{V_0} - \frac{1}{n+1} \right)$$

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:

```

1  '''Example of fitting the Birch-Murnaghan EOS to data'''
2
3  import numpy as np
4  import matplotlib.pyplot as plt
5  from scipy.optimize import leastsq
6
7  # raw data from 2.2.3-al-analyze-eos.py
8  v = np.array([13.72, 14.83, 16.0, 17.23, 18.52])
9  e = np.array([-56.29, -56.41, -56.46, -56.46, -56.42])
10
11 #make a vector to evaluate fits on with a lot of points so it looks smooth
12 vfit = np.linspace(min(v),max(v),100)
13
14 ### fit a parabola to the data
15 # y = ax^2 + bx + c
16 a,b,c = np.polyfit(v,e,2) #this is from pylab
17

```

```

18 '''
19 the parabola does not fit the data very well, but we can use it to get
20 some analytical guesses for other parameters.
21
22 VO = minimum energy volume, or where dE/dV=0
23 E = aV2 + bV + c
24 dE/dV = 2aV + b = 0
25 VO = -b/2a
26
27 EO is the minimum energy, which is:
28 EO = aVO2 + bVO + c
29
30 B is equal to VO*d2E/dV2, which is just 2a*VO
31
32 and from experience we know Bprime_0 is usually a small number like 4
33 '''
34
35 #now here are our initial guesses.
36 v0 = -b/(2*a)
37 e0 = a*v0**2 + b*v0 + c
38 b0 = 2*a*v0
39 bP = 4
40
41 #now we have to create the equation of state function
42 def Murnaghan(parameters,vol):
43     '''
44     given a vector of parameters and volumes, return a vector of energies.
45     equation From PRB 28,5480 (1983)
46     '''
47     E0 = parameters[0]
48     B0 = parameters[1]
49     BP = parameters[2]
50     V0 = parameters[3]
51
52     E = E0 + B0*vol/BP*((V0/vol)**BP)/(BP-1)+1) - V0*B0/(BP-1.)
53
54     return E
55
56 # and we define an objective function that will be minimized
57 def objective(pars,y,x):
58     #we will minimize this function
59     err = y - Murnaghan(pars,x)
60     return err
61
62 x0 = [e0, b0, bP, v0] #initial guesses in the same order used in the Murnaghan function
63
64 murnpars, ier = leastsq(objective, x0, args=(e,v)) #this is from scipy
65
66 #now we make a figure summarizing the results
67 plt.plot(v,e,'ro')
68 plt.plot(vfit, a*vfit**2 + b*vfit + c,'--',label='parabolic fit')
69 plt.plot(vfit, Murnaghan(murnpars,vfit), label='Murnaghan fit')
70 plt.xlabel('Volume ($\AA^3$)')
71 plt.ylabel('Energy (eV)')
72 plt.legend(loc='best')
73
74 #add some text to the figure in figure coordinates
75 ax = plt.gca()
76 plt.text(0.4, 0.5, 'Min volume = {0:1.2f} $\AA^3$'.format(murnpars[3]),
77         transform = ax.transAxes)
78 plt.text(0.4, 0.4, 'Bulk modulus = {0:1.2f} eV/$\AA^3$ = {1:1.2f} GPa'.format(murnpars[1],
79         murnpars[1]*160.21773),
80         transform = ax.transAxes)
81 plt.savefig('images/a-eos.png')
82
83 np.set_printoptions(precision=3)
84 print('initial guesses : ', np.array(x0)) # array for easy printing
85 print('fitted parameters: ', murnpars)

```

Open the python script (dft-scripts/script-264.py).

```

initial guesses :  [-56.472  0.631  4.    16.79 ]
fitted parameters:  [-56.466  0.49   4.753 16.573]

```

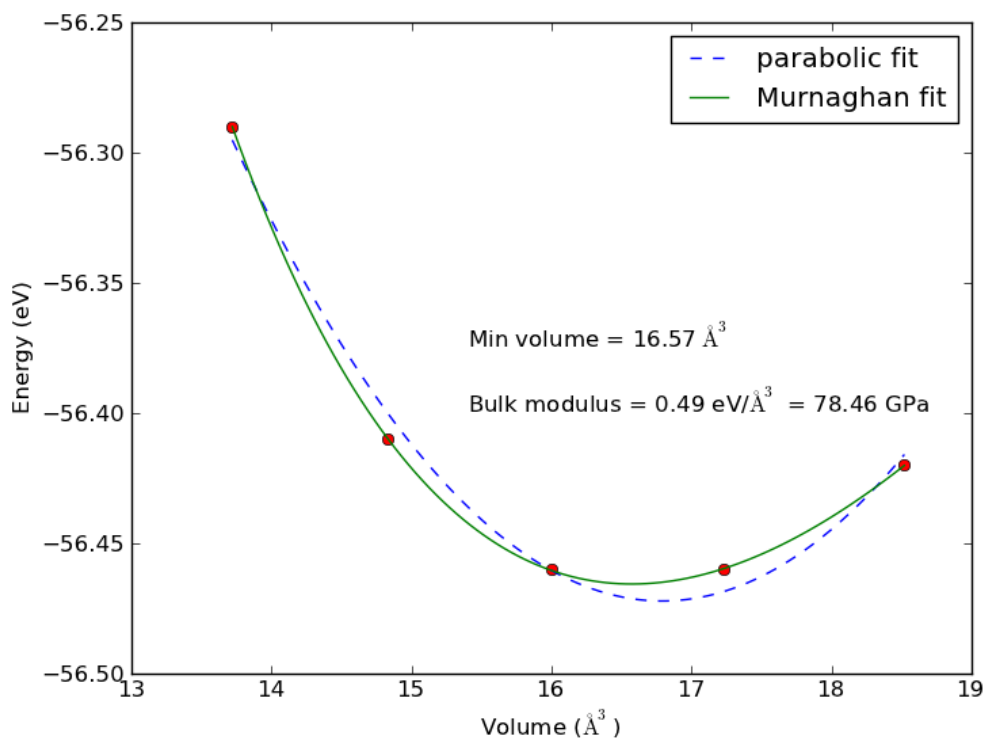


Figure 104: Fitted equation of state for bulk data. The initial fitted parabola is shown to illustrate how it is useful for making initial guesses of the minimum and bulk modulus.

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 jasp/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 7: Meaning of extensions on POTCAR files for special setups.

extension	
<code>_h</code>	means the potential is harder than the standard (i.e. needs a higher cutoff energy)
<code>_s</code>	means the potential is softer than the standard (i.e. needs a lower cutoff energy)
<code>_sv</code>	<i>s</i> and <i>p</i> semi-core states are treated as valence states
<code>_pv</code>	<i>p</i> semi-core states are treated as valence states
<code>_d</code>	<i>d</i> semi-core states are treated as valence states

Here are some links to information in the VASP manual for the setups.

- [1st](#)

row
el-
e-
ments

- Alkali
and
alkali-
earth
met-
als
- d-
elements
- p-
elements
- f-
elements

Here we show how to select the O_sv potential in a calculation.

```
1 from ase import Atoms, Atom
2 from jasp import *
3
4 atoms = Atoms([Atom('O',[5, 5, 5], magmom=1)],
5               cell=(6, 6, 6))
6
7 with jasp('molecules/O_sv',
8           encut=300,
9           xc='PBE',
10          ispin=2,
11          ismear=0,
12          sigma=0.001,
13          setups={'O':'_sv'}, # specifies O_sv potential
14          atoms=atoms) as calc:
15
16     print('Total energy = {0} eV'.format(atoms.get_potential_energy()))
```

Open the python script (dft-scripts/script-265.py).

Total energy = -1578.61345 eV

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.

```
1 head -n 1 molecules/O_sv/POTCAR
```

Open the python script (dft-scripts/script-266.py).

PAW_PBE O_sv 05Jul2007

This shows we indeed used the O_sv setup.

10.4.2 Running jasp in parallel

jasp is smart. If you ask for more than one node, it will automatically try to run in parallel.

```
1 from jasp import *
2 JASPRC['queue.nodes']=4
3 from ase import Atom, Atoms
4 atoms = Atoms([Atom('O',[5, 5, 5], magmom=1)],
5               cell=(6, 6, 6))
6
7 with jasp('molecules/O_s-4nodes',
8          encut=300,
9          xc='PBE',
10         ispin=2,
11         ismear=0,
12         sigma=0.001,
13         setups={'O':'_s'}, # specifies O_s potential
14         atoms=atoms) as calc:
15
16     calc.calculate()
```

Open the python script (dft-scripts/script-267.py).
How do you know it ran on four nodes?

```
1 head molecules/O_s-4nodes/OUTCAR
```

Open the python script (dft-scripts/script-268.py).

vasp.5.3.5 31Mar14 (build Jan 09 2015 15:20:38) complex

```
executed on           LinuxIFC date 2015.01.11 10:18:14
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 jasp in parallel

[jasp](#) 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 [jasp](#) 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.

```
1 import multiprocessing
2 from jasp import *
3 from ase import Atom, Atoms
4 from ase.utils.eos import EquationOfState
5 import numpy as np
6
7
8 # this is the function that runs a calculation
```

```

9  def do_calculation(calculator):
10     'function to run a calculation through multiprocessing'
11     with calculator as calc:
12         atoms = calc.get_atoms()
13         e = atoms.get_potential_energy()
14         v = atoms.get_volume()
15     return v, e
16
17 # this only runs in the main script, not in processes on other cores
18 if __name__ == '__main__':
19     Ncores = 6 # number of cores to run processes on
20
21     # setup an atoms object
22     a = 3.6
23     atoms = Atoms([Atom('Cu', (0, 0, 0))],
24                   cell=0.5 * a*np.array([[1.0, 1.0, 0.0],
25                                         [0.0, 1.0, 1.0],
26                                         [1.0, 0.0, 1.0]]))
27     v0 = atoms.get_volume()
28
29     # Step 1
30     COUNTER = 0
31     calculators = [] # list of calculators to be run
32     factors = [-0.1, 0.05, 0.0, 0.05, 0.1]
33     for f in factors:
34         newatoms = atoms.copy()
35         newatoms.set_volume(v0*(1 + f))
36         label = 'bulk/cu-mp/step1-{0}'.format(COUNTER)
37         COUNTER += 1
38
39         calc = jasp(label,
40                   xc='PBE',
41                   encut=350,
42                   kpts=(6,6,6),
43                   isym=2,
44                   atoms=newatoms)
45
46         calculators.append(calc)
47
48     # now we set up the Pool of processes
49     pool = multiprocessing.Pool(processes=Ncores)
50
51     # get the output from running each calculation
52     out = pool.map(do_calculation, calculators)
53     pool.close()
54     pool.join() # this makes the script wait here until all jobs are done
55
56     # now proceed with analysis
57     V = [x[0] for x in out]
58     E = [x[1] for x in out]
59
60     eos = EquationOfState(V, E)
61     v1, e1, B = eos.fit()
62     print('step1: v1 = {v1}'.format(**locals()))
63
64     ### #####
65     ## STEP 2, eos around the minimum
66     ## #####
67     factors = [-0.06, -0.04, -0.02,
68               0.0,
69               0.02, 0.04, 0.06]
70
71     calculators = [] # reset list
72     for f in factors:
73         newatoms = atoms.copy()
74         newatoms.set_volume(v1*(1 + f))
75         label = 'bulk/cu-mp/step2-{0}'.format(COUNTER)
76         COUNTER += 1
77
78         calc = jasp(label,
79                   xc='PBE',
80                   encut=350,
81                   kpts=(6,6,6),
82                   isym=2,
83                   atoms=newatoms)
84         calculators.append(calc)
85
86     pool = multiprocessing.Pool(processes=Ncores)

```

```

87
88 out = pool.map(do_calculation, calculators)
89 pool.close()
90 pool.join() # wait here for calculations to finish
91
92 # proceed with analysis
93 V += [x[0] for x in out]
94 E += [x[1] for x in out]
95
96 V = np.array(V)
97 E = np.array(E)
98
99 f = np.array(V)/v1
100
101 # only take points within +- 10% of the minimum
102 ind = (f >= 0.90) & (f <= 1.1)
103
104 eos = EquationOfState(V[ind], E[ind])
105 v2, e2, B = eos.fit()
106 print('step2: v2 = {v2}'.format(**locals()))
107 eos.plot('images/cu-mp-eos.png')

```

Open the python script (dft-scripts/script-269.py).

step1: v1 = 12.0218897111

step2: v2 = 12.0216094217

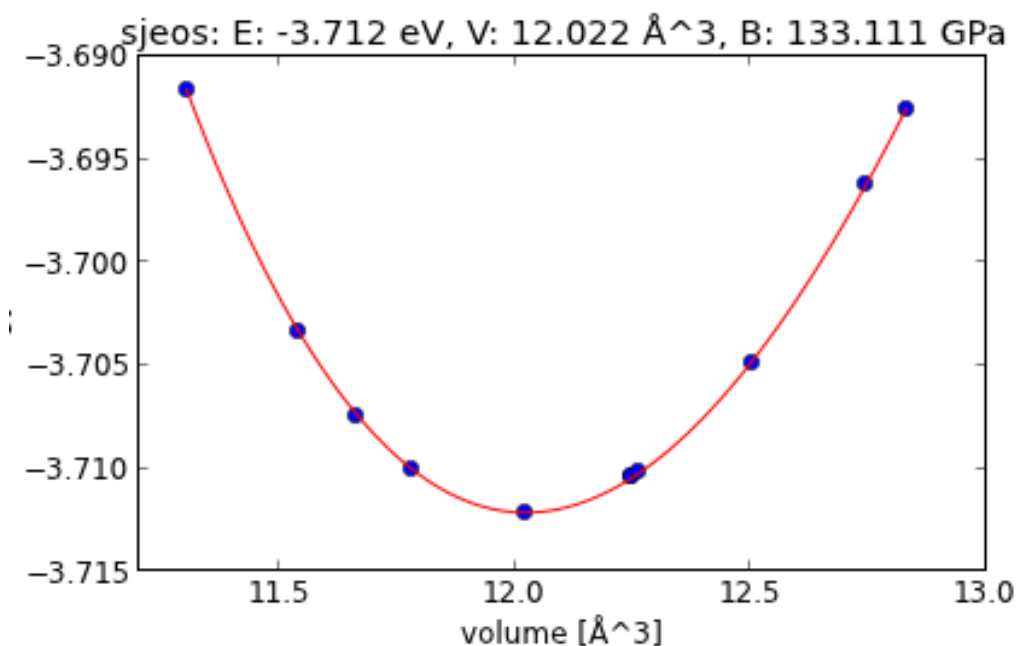


Figure 105: Equation of state for Cu using the multiprocessing module.

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 runjasp.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 JASPRC 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.

```

1  #!/usr/bin/env python
2  import multiprocessing
3  from jasp import *
4  from ase import Atom, Atoms
5  from ase.utils.eos import EquationOfState
6  import numpy as np
7
8  JASPRC['queue.nodes'] = 1
9
10 # Here we will be able to run three MPI jobs on 2 cores at a time.
11 JASPRC['queue.ppn'] = 6
12 JASPRC['multiprocessing.cores_per_process'] = 2
13
14 # to submit this script, save it as cu-mp.py
15 # qsub -l nodes=1:ppn=6,walltime=10:00:00 cu-mp.py
16 import os
17 if 'PBS_O_WORKDIR' in os.environ:
18     os.chdir(os.environ['PBS_O_WORKDIR'])
19
20 # this is the function that runs a calculation
21 def do_calculation(calculator):
22     'function to run a calculation through multiprocessing'
23     with calculator as calc:
24         atoms = calc.get_atoms()
25         e = atoms.get_potential_energy()
26         v = atoms.get_volume()
27     return v, e
28
29 # this only runs in the main script, not in processes on other cores
30 if __name__ == '__main__':
31
32     # setup an atoms object
33     a = 3.6
34     atoms = Atoms([Atom('Cu', (0, 0, 0))],
35                   cell=0.5 * a*np.array([[1.0, 1.0, 0.0],
36                                           [0.0, 1.0, 1.0],
37                                           [1.0, 0.0, 1.0]]))
38     v0 = atoms.get_volume()
39
40     # Step 1
41     COUNTER = 0
42     calculators = [] # list of calculators to be run
43     factors = [-0.1, 0.05, 0.0, 0.05, 0.1]
44     for f in factors:
45         newatoms = atoms.copy()
46         newatoms.set_volume(v0*(1 + f))
47         label = 'bulk/cu-mp2/step1-{0}'.format(COUNTER)
48         COUNTER += 1
49
50         calc = jasp(label,
51                    xc='PBE',
52                    encut=350,
53                    kpts=(6,6,6),
54                    isym=2,
55                    debug=logging.DEBUG,
56                    atoms=newatoms)
57
58         calculators.append(calc)
59
60     # now we set up the Pool of processes
61     pool = multiprocessing.Pool(processes=3) # ask for 6 cores but run MPI on 2 cores
62
63     # get the output from running each calculation
64     out = pool.map(do_calculation, calculators)
65     pool.close()
66     pool.join() # this makes the script wait here until all jobs are done
67
68     # now proceed with analysis
69     V = [x[0] for x in out]
70     E = [x[1] for x in out]
71

```

```

72 eos = EquationOfState(V, E)
73 v1, e1, B = eos.fit()
74 print('step1: v1 = {v1}'.format(**locals()))
75
76 ### #####
77 ## STEP 2, eos around the minimum
78 ## #####
79 factors = [-0.06, -0.04, -0.02,
80            0.0,
81            0.02, 0.04, 0.06]
82
83 calculators = [] # reset list
84 for f in factors:
85     newatoms = atoms.copy()
86     newatoms.set_volume(v1*(1 + f))
87     label = 'bulk/cu-mp2/step2-{0}'.format(COUNTER)
88     COUNTER += 1
89
90     calc = jasp(label,
91                xc='PBE',
92                encut=350,
93                kpts=(6,6,6),
94                isym=2,
95                debug=logging.DEBUG,
96                atoms=newatoms)
97     calculators.append(calc)
98
99 pool = multiprocessing.Pool(processes=3)
100
101 out = pool.map(do_calculation, calculators)
102 pool.close()
103 pool.join() # wait here for calculations to finish
104
105 # proceed with analysis
106 V += [x[0] for x in out]
107 E += [x[1] for x in out]
108
109 V = np.array(V)
110 E = np.array(E)
111
112 f = np.array(V)/v1
113
114 # only take points within +- 10% of the minimum
115 ind = (f >= 0.90) & (f <= 1.1)
116
117 eos = EquationOfState(V[ind], E[ind])
118 v2, e2, B = eos.fit()
119 print('step2: v2 = {v2}'.format(**locals()))
120 eos.plot('images/cu-mp2-eos.png', show=True)

```

Open the python script (dft-scripts/script-270.py).

```

step1: v1 = 12.0218897111
step2: v2 = 12.0216189798

```

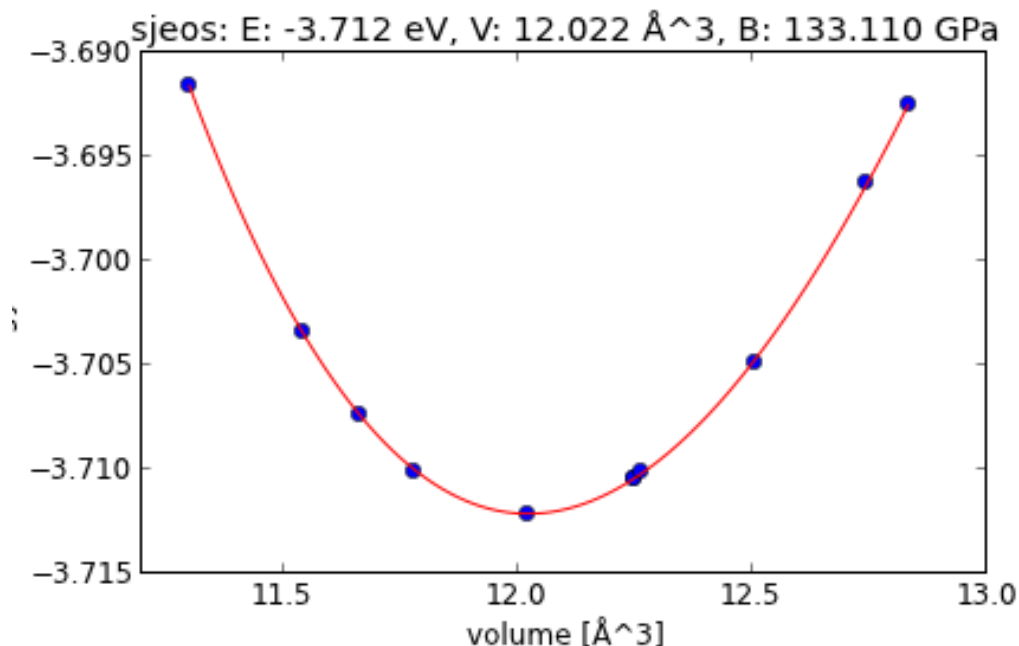


Figure 106: Second view of a Cu equation of state computed with multiprocessing.

10.4.4 Exporting data json, xml, python, sqlite

jasp has some capability for representing a calculation result in an archival format. The formats currently under development are json, xml, python and sqlite. The main point of these methods is to make it easy to create archive files that are machine readable for supplementary information in publications. These are under development.

python This is code that should reconstruct the python code needed to run a particular calculation. There are some limitations, e.g. it does not currently get magnetic moments on the atoms.

```

1 from jasp import *
2
3 with jasp('bulk/alloy/cu') as calc:
4     print(calc.python)

```

Open the python script (dft-scripts/script-271.py).

```

from numpy import array
from ase import Atom, Atoms
from jasp import *

atoms = Atoms([Atom('Cu', [0.0, 0.0, 0.0]),
               cell = [[1.818, 0.0, 1.818],
                       [1.818, 1.818, 0.0],
                       [0.0, 1.818, 1.818]])

with jasp('bulk/alloy/cu',
          nbands = 9,
          nsw = 10,

```

```

        ibrion = 2,
        isif = 4,
        encut = 350.0,
        prec = 'Normal',
        kpts = array([13, 13, 13]),
        reciprocal = False,
        xc = 'PBE',
        txt = '-',
        gamma = False,
        atoms=atoms) as calc:
# your code here

```

json

```

1 from jasp import *
2
3 with jasp('bulk/alloy/cu') as calc:
4     print(calc.pretty_json)

```

Open the python script (dft-scripts/script-272.py).

```

{
  "INCAR": {
    "addgrid": null,
    "aexx": null,
    "aggac": null,
    "aggax": null,
    "aldac": null,
    "algo": null,
    "amin": null,
    "amix": null,
    "amix_mag": null,
    "bmix": null,
    "bmix_mag": null,
    "ddr": null,
    "deper": null,
    "dfnmax": null,
    "dfnmin": null,
    "dipol": null,
    "drotmax": null,
    "ebreak": null,
    "ediff": null,
    "ediffg": null,
    "eint": null,
    "emax": null,
    "emin": null,
    "enaug": null,
    "encut": 350.0,
    "encutfock": null,
    "encutgw": null,
    "falpha": null,
    "falphadec": null,
    "fdstep": null,
    "ferdo": null,

```

```

"ferwe": null,
"fnmin": null,
"ftimedec": null,
"ftimeinc": null,
"ftimemax": null,
"gga": null,
"hfscreen": null,
"ialgo": null,
"iband": null,
"ibrion": 2,
"ichain": null,
"icharg": null,
"idipol": null,
"images": null,
"iniwav": null,
"invcurve": null,
"iopt": null,
"isif": 4,
"ismear": null,
"ispin": null,
"istart": null,
"isym": null,
"iwavpr": null,
"jacobian": null,
"kgamma": null,
"kpuse": null,
"kspacing": null,
"laechg": null,
"lasph": null,
"lasync": null,
"lbfgsmem": null,
"lcharg": null,
"lclimb": null,
"lcorr": null,
"ldau": null,
"ldau_luj": null,
"ldauj": null,
"ldaul": null,
"ldauprint": null,
"ldautype": null,
"ldauu": null,
"ldiag": null,
"ldipol": null,
"ldneb": null,
"lelf": null,
"lepsilon": null,
"lglobal": null,
"lhfcalc": null,
"llineopt": null,
"lmaxmix": null,
"lnebcell": null,
"loptics": null,

```

```

"lorbit": null,
"lpard": null,
"lplane": null,
"lscalapack": null,
"lscalu": null,
"lsepb": null,
"lsepk": null,
"ltangentold": null,
"lthomas": null,
"luse_vdw": null,
"lvdw": null,
"lvhar": null,
"lvtot": null,
"lwave": null,
"magmom": null,
"maxmix": null,
"maxmove": null,
"nbands": 9,
"nblk": null,
"nbmod": null,
"nelect": null,
"nelm": null,
"nelmdl": null,
"nelmin": null,
"nfree": null,
"ngx": null,
"ngxf": null,
"ngy": null,
"ngyf": null,
"ngz": null,
"ngzf": null,
"nkred": null,
"nkredx": null,
"nkredy": null,
"nkredz": null,
"nomega": null,
"nomegar": null,
"npar": null,
"nsim": null,
"nsw": 10,
"nupdown": null,
"nwrite": null,
"param1": null,
"param2": null,
"pomass": null,
"potim": null,
"prec": "Normal",
"precfock": null,
"ropt": null,
"rwigs": null,
"salpha": null,
"sdr": null,

```

```

    "sigma": null,
    "smass": null,
    "snl": null,
    "spring": null,
    "stol": null,
    "symprec": null,
    "system": null,
    "tebeg": null,
    "teend": null,
    "time": null,
    "timestep": null,
    "vdwgr": null,
    "vdwrn": null,
    "voskown": null,
    "weimin": null,
    "zab_vdw": null,
    "zval": null
  },
  "atoms": {
    "cell": [
      [
        1.818,
        0.0,
        1.818
      ],
      [
        1.818,
        1.818,
        0.0
      ],
      [
        0.0,
        1.818,
        1.818
      ]
    ],
    "pbc": [
      true,
      true,
      true
    ],
    "positions": [
      [
        0.0,
        0.0,
        0.0
      ]
    ],
    "symbols": [
      "Cu"
    ],
    "tags": [

```

```

        0
    ]
},
"input": {
    "gamma": false,
    "kpts": [
        13,
        13,
        13
    ],
    "kpts_nintersections": null,
    "reciprocal": false,
    "setups": null,
    "txt": "-",
    "xc": "PBE"
}
}

```

xml archive This relies on the pyxser module. I cannot get this to install anymore due to some unicode error.

```

1 from jasp import *
2
3 with jasp('bulk/alloy/cu') as calc:
4     print(calc.xml)

```

Open the python script (dft-scripts/script-273.py).

```

<?xml version="1.0" encoding="utf-8"?>
<pyx:obj xmlns:pyx="http://projects.coder.cl/pyxser/model/" version="1.0" type="vasp" module="jasp"
  <pyx:col type="dict" name="d">
    <pyx:col type="dict" name="INCAR">
      <pyx:prop type="str" name="prec">Normal</pyx:prop>
      <pyx:prop type="float" name="encut">350.0</pyx:prop>
      <pyx:prop type="int" name="nbands">9</pyx:prop>
      <pyx:prop type="int" name="isif">4</pyx:prop>
      <pyx:prop type="int" name="nsw">10</pyx:prop>
      <pyx:prop type="int" name="ibrion">2</pyx:prop>
    </pyx:col>
    <pyx:col type="dict" name="input">
      <pyx:col type="list" name="kpts">
        <pyx:prop type="int" name="kpts">13</pyx:prop>
        <pyx:prop type="int" name="kpts">13</pyx:prop>
        <pyx:prop type="int" name="kpts">13</pyx:prop>
      </pyx:col>
      <pyx:prop type="bool" name="reciprocal">False</pyx:prop>
      <pyx:prop type="str" name="xc">PBE</pyx:prop>
      <pyx:prop type="str" name="txt">-</pyx:prop>
      <pyx:prop type="bool" name="gamma">False</pyx:prop>
    </pyx:col>
    <pyx:col type="dict" name="atoms">
      <pyx:col type="list" name="cell">
        <pyx:col type="list" name="cell">
          <pyx:prop type="float" name="cell">1.818</pyx:prop>

```



```

    <pyx:prop type="float" name="cell">0.0</pyx:prop>
    <pyx:prop type="float" name="cell">1.818</pyx:prop>
  </pyx:col>
  <pyx:col type="list" name="cell">
    <pyx:prop type="float" name="cell">1.818</pyx:prop>
    <pyx:prop type="float" name="cell">1.818</pyx:prop>
    <pyx:prop type="float" name="cell">0.0</pyx:prop>
  </pyx:col>
  <pyx:col type="list" name="cell">
    <pyx:prop type="float" name="cell">0.0</pyx:prop>
    <pyx:prop type="float" name="cell">1.818</pyx:prop>
    <pyx:prop type="float" name="cell">1.818</pyx:prop>
  </pyx:col>
</pyx:col>
<pyx:col type="list" name="symbols">
  <pyx:prop type="str" name="symbols">Cu</pyx:prop>
</pyx:col>
<pyx:col type="list" name="pbc">
  <pyx:prop type="bool" name="pbc">True</pyx:prop>
  <pyx:prop type="bool" name="pbc">True</pyx:prop>
  <pyx:prop type="bool" name="pbc">True</pyx:prop>
</pyx:col>
<pyx:col type="list" name="positions">
  <pyx:col type="list" name="positions">
    <pyx:prop type="float" name="positions">0.0</pyx:prop>
    <pyx:prop type="float" name="positions">0.0</pyx:prop>
    <pyx:prop type="float" name="positions">0.0</pyx:prop>
  </pyx:col>
</pyx:col>
</pyx:col>
</pyx:col>
</pyx:obj>

```

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.

```

1  from jasp.POTCAR import *
2  from ase.data import chemical_symbols
3  import glob, os
4
5  print('#+tblname: POTCAR')
6  print('#+caption: Parameters for POTPAW_PBE POTCAR files.')
7  print('#+ATTR_LaTeX: longtable')
8  print('| POTCAR | ENMIN | ENMAX | prec=high (eV) | # val. elect. |')
9  print('|-'')
10
11  chemical_symbols.sort()
12  for symbol in chemical_symbols:
13
14      potcars = glob.glob('{0}/potpaw_PBE/{1}*/POTCAR'.format(os.environ['VASP_PP_PATH'],
15                                                                symbol))
16
17      for potcar in potcars:
18
19          POTCAR = os.path.relpath(potcar,
20                                  os.environ['VASP_PP_PATH']+'/potpaw_PBE')[:-7]
21          ENMIN = get_ENMIN(potcar)
22          ENMAX = get_ENMAX(potcar)

```

```
23     HIGH  = 1.3*ENMAX
24     ZVAL  = get_ZVAL(potcar)
25     print('{POTCAR:30s}|{ENMIN}|{ENMAX}|{HIGH:1.3f}|{ZVAL}|'.format(**locals()))
```

Open the python script (dft-scripts/script-274.py).

Table 8: 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
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	328.299	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

11 Python

11.1 easy_install as a user

`easy_install` is a python command-line utility that automatically installs python packages. Usually you need root access to install a python package, but you can also tell `easy_install` where to install a package. This usually works if the directory is on your `PYTHONPATH`

```
easy_install -d ~/lib/python2.6/site-packages/ pymatgen
```

11.2 pip as a user

`pip` is even better than `easy_install` these days.

```
1 pip install --user some-package
```

Open the python script (`dft-scripts/script-275.py`).

For me this installs here:

`~/local/lib/python2.7/site-packages`

That may or may not be on your Python path.

11.3 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 remainder 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.

```
1 nPd = 4
2 nCu = 5
3 x_Cu = nCu/(nPd + nCu)
4 print('x_cu = {0} (integer division)'.format(x_Cu))
5
6 # now cast as floats
7 x_Cu = float(nCu)/float(nPd + nCu)
8 print('x_cu = {0} (float division)'.format(x_Cu))
```

Open the python script (`dft-scripts/script-276.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.

```
1 nPd = 4
2 nCu = 5
3
4 # now cast as floats
5 x_Cu = float(nCu)/(nPd + nCu)
6 print('x_cu = {0}'.format(x_Cu))
```

Open the python script (`dft-scripts/script-277.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.

```
1 nPd = 4.  # this is a float
2 nCu = 5
3
4 x_Cu = nCu/(nPd + nCu)
5 print('x_cu = {0}'.format(x_Cu))
```

Open the python script (dft-scripts/script-278.py).

```
x_cu = 0.555555555556
```

12 References

References

[1]

David S.
Sholl
and
Jan-
ice A.
Steckel.
*Den-
sity
Func-
tional
The-
ory:
A
Prac-
ti-
cal
In-
tro-
duc-
tion.*
Wi-
ley,
2009.

[2]

R. G.
Parr
and
W. Yang.
*Density-
Functional
The-
ory
of
Atoms*

*and
Molecules.*
Ox-
ford
Sci-
ence
Pub-
li-
ca-
tions,
1989.

- [3] W. Koch
and
M. C.
Holthausen.
*A
Chemist's
Guide
to
Den-
sity
Func-
tional
The-
ory.*
Wiley-
VCH,
2
edi-
tion,
2001.

- [4] Charles
Kit-
tel.
*In-
tro-
duc-
tion
to
Solid
State
Physics.*
Wi-
ley,
8th
edi-
tion,
2005.

- [5]

N. W.
Ashcroft
and
N. David
Mer-
min.
*Solid
State
Physics.*
Saun-
ders
Col-
lege
Pub-
lish-
ing,
1976.

- [6] Roald
Hoff-
mann.
How
chem-
istry
and
physics
meet
in
the
solid
state.
*Ange-
wandte
Chemie
In-
ter-
na-
tional
Edi-
tion
in
En-
glish,*
26
(9):
846–
878,
1987.
ISSN
1521-
3773.
doi:

10.
1002/
anie.
198708461.
URL
[http://
dx.
doi.
org/
10.
1002/
anie.
198708461.](http://dx.doi.org/10.1002/anie.198708461)

[7]

Roald
Hoff-
mann.
A
chem-
i-
cal
and
the-
o-
ret-
i-
cal
way
to
look
at
bond-
ing
on
sur-
faces.
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.](http://link.aps.org/doi/10.1103/RevModPhys.60.601)

[8]

B. Ham-
mer
and
J.K.
Nørskov.
The-
o-
ret-
i-
cal
sur-
face
sci-
ence
and
catal-
y-
sis-
cal-
cu-
la-
tions
and
con-
cepts.
In
Hel-
mut Knozinger
Bruce
C. Gates,
ed-
i-
tor,
*Im-
pact
of
Sur-
face
Sci-
ence*

on
Catal-
y-
sis,
vol-
ume 45
of
Ad-
vances
in
Catal-
y-
sis,
pages
71
—

129.
Aca-
demic
Press,
2000.
doi:
10.
1016/
S0360-0564(02)
45013-4.
URL
[http:
//
www.
sciencedirect.
com/
science/
article/
pii/
S0360056402450134](http://www.sciencedirect.com/science/article/pii/S0360056402450134).

- [9]
Jeff
Gree-
ley,
Jens K.
Nørskov,
and
Manos
Mavrikakis.
Elec-
tronic
struc-
ture
and
catal-

y-
 sis
 on
 metal
 sur-
 faces.
*An-
 nual
 Re-
 view
 of
 Phys-
 i-
 cal
 Chem-
 istry,*
 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.](http://www.annualreviews.org/doi/abs/10.1146/annurev.physchem.53.100301.131630)

- [10] A J
 Free-
 man
 and
 E Wim-
 mer.
 Den-

sity
 func-
 tional
 the-
 ory
 as
 a
 ma-
 jor
 tool
 in
 com-
 pu-
 ta-
 tional
 ma-
 te-
 ri-
 als
 sci-
 ence.
*An-
 nual
 Re-
 view
 of
 Ma-
 te-
 ri-
 als
 Sci-
 ence,*
 25
 (1):
 7–
 36,
 1995.
 doi:
 10.
 1146/
 annurev.
 ms.
 25.
 080195.
 000255.

- [11]
 M. C.
 Payne,
 M. P.
 Teter,
 D. C.
 Al-

lan,
T. A.
Arias,
and
J. D.
Joannopou-
los.
It-
er-
a-
tive
min-
i-
miza-
tion
tech-
niques
for
ab
ini-
tio
total-
energy
cal-
cu-
la-
tions:
molec-
u-
lar
dy-
nam-
ics
and
con-
ju-
gate
gra-
di-
ents.
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.](http://link.aps.org/doi/10.1103/RevModPhys.64.1045)

- [12] G. Kresse
and
J. Furth-
müller.
Ef-
fi-
ciency
of
ab-
initio
to-
tal
en-
ergy
cal-
cu-
la-
tions
for
met-
als
and
semi-
con-
duc-
tors
us-
ing
a
plane-
wave
ba-
sis
set.
*Com-
pu-
ta-*

tiona
Ma-
te-
ri-
als
Sci-
ence,
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.](http://www.sciencedirect.com/science/article/pii/S0927025696000080)

- [13] T. Bli-
gaard.
Ex-
change
and
Cor-
re-
la-
tion
Func-
tion-
als
—

a
study
to-
ward
im-

proving
the
precision
of
electron
density
functional
calculations
of
atomic
systems.

Master's
thesis,
Technical
University
of
Denmark,
2000.

[http://
www.
fysik.
dtu.
dk/
~bligaard/
masterthesis/
masterdirectory/
project/
project.
pdf.](http://www.fysik.dtu.dk/~bligaard/masterthesis/masterdirectory/project/project.pdf)

[14]

T. Bligaard.
Un-

der-
stand-
ing
Ma-
te-
ri-
als
Prop-
er-
ties
on
the
Ba-
sis
of
Den-
sity
Func-
tional
The-
ory
Cal-
cu-
la-
tions.
 PhD
 the-
 sis,
 Tech-
 ni-
 cal
 Uni-
 ver-
 sity
 of
 Den-
 mark,
 2003.
[http://
 www.
 fysik.
 dtu.
 dk/
 ~{}bligaard/
 phdthesis/
 phdproject.
 pdf.](http://www.fysik.dtu.dk/~bligaard/phdthesis/phdproject.pdf)

- [15] A. P.
 Seit-
 so-

nen.
The-
o-
ret-
i-
cal
In-
ves-
ti-
ga-
tions
into
ad-
sorp-
tion
and
co-
adsorption
on
transition-
metal
sur-
faces
as
mod-
els
to
het-
ero-
ge-
neous
catal-
y-
sis.
PhD
the-
sis,
Tech-
ni-
cal
Uni-
ver-
sity
of
Berlin,
School
of
Math-
e-
mat-
ics
and

Nat-
u-
ral
Sci-
ences,
2000.
http://edocs.tu-berlin.de/diss/2000/seitsonen__ari.pdf.

[16]

R. Hirschl.

*Bi-
nary
Tran-
si-
tion
Metal
Al-
loys
and
Their
Sur-
faces.*

PhD

the-
sis,
In-
sti-
tut
für
Ma-
te-
ri-
al-
physik,

Uni-
ver-
sity
of

Vi-
enna,
2002.

[http:
//
www.
hirschl.
at/
download/
diss_
part1.
pdf](http://www.hirschl.at/download/diss_part1.pdf)
and

[http://
www.
hirschl.
at/
download/
diss_
part2.
pdf.](http://www.hirschl.at/download/diss_part2.pdf)

- [17] L. Paul-
ing
and
E. B.
Wil-
son,
Jr.
*In-
tro-
duc-
tion
to
Quan-
tum
Me-
chan-
ics
with
Ap-
pli-
ca-
tions
to
Chem-
istry.*
Dover
Pub-
li-
ca-
tions,
Inc.,
1963.

- [18] W. Kohn.
No-
bel
lec-
ture:
Elec-
tronic
struc-

ture
 of
 matter-
 wave
 func-
 tions
 and
 den-
 sity
 func-
 tion-
 als.
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.](http://link.aps.org/doi/10.1103/RevModPhys.71.1253)

- [19] P. A. M.
 Dirac.
 Quan-
 tum
 me-
 chan-
 ics
 of
 many-
 electron
 sys-
 tems.
Pro-

ceed-
ings
of
the
Royal
So-
ci-
ety
of
Lon-
don.
Se-
ries
A,
Con-
tain-
ing
Pa-
pers
of
a
Math-
e-
mat-
i-
cal
and
Phys-
i-
cal
Char-
ac-
ter,
123
(792):
pp.
714–
733,
1929.
ISSN
09501207.
URL
[http://
www.
jstor.
org/
stable/
95222.](http://www.jstor.org/stable/95222)

[20]
P. Ho-
hen-

berg
 and
 W. Kohn.
 In-
 ho-
 mo-
 ge-
 neous
 elec-
 tron
 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.](http://link.aps.org/doi/10.1103/PhysRev.136.B864)

- [21] W. Kohn
 and
 L. J.
 Sham.
 Self-
 consistent
 equa-
 tions
 in-
 clud-
 ing
 ex-
 change
 and
 cor-

re-
la-
tion
ef-
fects.
Phys.
Rev.,
140:
A1133–
A1138,
Nov
1965.
doi:
10.
1103/
PhysRev.
140.
A1133.
URL
[http://
link.
aps.
org/
doi/
10.
1103/
PhysRev.
140.
A1133.](http://link.aps.org/doi/10.1103/PhysRev.140.A1133)

- [22] John A.
Pople.
No-
bel
lec-
ture:
Quan-
tum
chem-
i-
cal
mod-
els.
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.](http://link.aps.org/doi/10.1103/RevModPhys.71.1267)

- [23] M. Fuchs,
M. Bock-
st-
edte,
E. Pehlke,
and
M. Schef-
fler.
Pseu-
dopo-
ten-
tial
study
of
bind-
ing
prop-
er-
ties
of
solids
within
gen-
er-
al-
ized
gra-
di-
ent
ap-
prox-
i-
ma-

tions:
The
role
of
core-
valence
ex-
change
cor-
re-
la-
tion.
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.](http://link.aps.org/doi/10.1103/PhysRevB.57.2134)

- [24]
John P.
Perdew,
Robert G.
Parr,
Mel
Levy,
and
Jose L.
Bal-
duz.
Density-
functional
the-

ory
 for
 frac-
 tional
 par-
 ti-
 cle
 num-
 ber:
 Deriva-
 tive
 dis-
 con-
 ti-
 nu-
 ities
 of
 the
 en-
 ergy.
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.](http://link.aps.org/doi/10.1103/PhysRevLett.49.1691)

- [25] B. Ham-
 mer,
 L. B.
 Hansen,
 and

J. K.
Nørskov.
Im-
proved
ad-
sorp-
tion
en-
er-
get-
ics
within
density-
functional
the-
ory
us-
ing
re-
vised
perdew-
burke-
ernzerhof
func-
tion-
als.
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.](http://link.aps.org/doi/10.1103/PhysRevB.59.7413)

[26]

G. Makov
and
M. C.
Payne.
Pe-
ri-
odic
bound-
ary
con-
di-
tions
in
ab
ini-
tio
cal-
cu-
la-
tions.
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.](http://link.aps.org/doi/10.1103/PhysRevB.51.4014)

[27]

D. J.
Chadi
and
Mar-

vin L.
Co-
hen.
Spe-
cial
points
in
the
bril-
louin
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.](http://link.aps.org/doi/10.1103/PhysRevB.8.5747)

- [28] Hendrik J.
Monkhorst
and
James D.
Pack.
Spe-
cial
points
for
brillouin-
zone
in-
te-
gra-

tions.
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.](http://link.aps.org/doi/10.1103/PhysRevB.13.5188)

- [29] N. Troul-
 lier
 and
 José Luri-
 aas
 Mar-
 tins.
 Ef-
 fi-
 cient
 pseu-
 dopo-
 ten-
 tials
 for
 plane-
 wave
 cal-
 cu-
 la-
 tions.
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.](http://link.aps.org/doi/10.1103/PhysRevB.43.1993)

- [30] David
 Van-
 der-
 bilt.
 Soft
 self-
 consistent
 pseu-
 dopo-
 ten-
 tials
 in
 a
 gen-
 er-
 al-
 ized
 eigen-
 value
 for-
 mal-
 ism.
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.](http://link.aps.org/doi/10.1103/PhysRevB.41.7892)

- [31] E. G.
Mo-
roni,
G. Kresse,
J. Hafner,
and
J. Furth-
müller.
Ul-
tra-
soft
pseu-
dopo-
ten-
tials
ap-
plied
to
mag-
netic
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.](http://link.aps.org/doi/10.1103/PhysRevB.56.15629)

- [32]
 P. E.
 Blöchl.
 Pro-
 jec-
 tor
 augmented-
 wave
 method.
Phys.
Rev.
B,
 50:
 17953–
 17979,
 Dec
 1994.
 doi:
 10.
 1103/
 PhysRevB.
 50.
 17953.
 URL
[http:
 //
 link.
 aps.
 org/](http://link.aps.org/)

[doi/
10.
1103/
PhysRevB.
50.
17953.](https://doi.org/10.1103/PhysRevB.50.17953)

[33]

G. Kresse
and
D. Joubert.
From
ultra-
soft
pseudo-
poten-
tials
to
the
pro-
jector
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.](http://link.aps.org/doi/10.1103/PhysRevB.59.1758)

1758.

[34]

M J
Gillan.
Cal-
cu-
la-
tion
of
the
va-
cancy
for-
ma-
tion
en-
ergy
in
alu-
minium.
*Jour-
nal
of
Physics:
Con-
densed
Mat-
ter*,
1
(4):
689,
1989.
URL
[http://
stacks.
iop.
org/
0953-8984/
1/
i=
4/
a=
005.](http://stacks.iop.org/0953-8984/1/i=4/a=005)

[35]

N. David
Mer-
min.
Ther-
mal
prop-

er-
ties
of
the
in-
ho-
mo-
ge-
neous
elec-
tron
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.](http://link.aps.org/doi/10.1103/PhysRev.137.A1441)

- [36]
J. J.
Mortensen,
L. B.
Hansen,
and
K. W.
Ja-
cob-
sen.
Real-
space
grid
im-
ple-

men-
 ta-
 tion
 of
 the
 pro-
 jec-
 tor
 aug-
 mented
 wave
 method.
Phys.
Rev.
B,
 71:
 035109,
 Jan
 2005.
 doi:
 10.
 1103/
 PhysRevB.
 71.
 035109.
 URL
[http:
 //
 link.
 aps.
 org/
 doi/
 10.
 1103/
 PhysRevB.
 71.
 035109.](http://link.aps.org/doi/10.1103/PhysRevB.71.035109)

- [37] G. Kresse
 and
 J. Furth-
 müller.
 Ef-
 fi-
 cient
 it-
 er-
 a-
 tive
 schemes
 for
ab

ini-
tio
 total-
 energy
 cal-
 cu-
 la-
 tions
 us-
 ing
 a
 plane-
 wave
 ba-
 sis
 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.](http://link.aps.org/doi/10.1103/PhysRevB.54.11169)

- [38] G. Kresse
 and
 J. Hafner.
Ab
ini-
tio
 molecular-
 dynamics
 sim-

u-
la-
tion
of
the
liquid-
metal/amorphous-
semiconductor
tran-
si-
tion
in
ger-
ma-
nium.
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.](http://link.aps.org/doi/10.1103/PhysRevB.49.14251)

- [39] G. Kresse
and
J. Hafner.
Ab
ini-
tio
molec-
u-
lar
dy-

nam-
ics
for
liq-
uid
met-
als.
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.](http://link.aps.org/doi/10.1103/PhysRevB.47.558)

- [40] Joachim
Paier,
Robin
Hirschl,
Mar-
tijn
Mars-
man,
and
Georg
Kresse.
The
Perdew–
Burke–
Ernzerhof
exchange-
correlation
func-

tional
ap-
plied
to
the
G2-
1
test
set
us-
ing
a
plane-
wave
ba-
sis
set.
The
Jour-
nal
of
Chem-
i-
cal
Physics,
122
(23):
234102,
2005.
doi:
10.
1063/
1.
1926272.
URL
[http://
link.
aip.
org/
link/
?JCP/
122/
234102/
1.](http://link.aip.org/link/?JCP/122/234102/1)

- [41] Larry A.
Cur-
tiss,
Kr-
ish-
nan

Raghavachari,
Paul C.
Red-
fern,
and
John A.
Pople.
As-
sess-
ment
of
gaussian-
2
and
den-
sity
func-
tional
the-
o-
ries
for
the
com-
pu-
ta-
tion
of
en-
thalpies
of
for-
ma-
tion.
The
Journal
of
Chem-
i-
cal
Physics,
106
(3):
1063–
1079,
1997.
doi:
10.
1063/
1.
473182.

URL
[http://
link.
aip.
org/
link/
?JCP/
106/
1063/
1.](http://link.aip.org/link/?JCP/106/1063/1)

- [42] Graeme
Henkel-
man,
An-
dri
Ar-
nalds-
son,
and
Hannes
Jóns-
son.
A
fast
and
ro-
bust
al-
go-
rithm
for
bader
de-
com-
po-
si-
tion
of
charge
den-
sity.
*Com-
pu-
ta-
tional
Ma-
te-
ri-
als
Sci-*

ence,
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](http://www.sciencedirect.com/science/article/pii/S0927025605001849).

- [43] Thomas A.
Manz
and
David S.
Sholl.
Chem-
i-
cally
mean-
ing-
ful
atomic
charges
that
re-
pro-
duce
the
elec-
tro-
static
po-

ten-
tial
in
pe-
ri-
odic
and
non-
pe-
ri-
odic
ma-
te-
ri-
als.

*Jour-
nal
of
Chem-
i-
cal
The-
ory
and
Com-
pu-
ta-
tion,*

6
(8):
2455–
2468,
2010.
doi:
10.
1021/
ct100125x.

URL

[http:
/
pubs.
acs.
org/
doi/
abs/
10.
1021/
ct100125x.](http://pubs.acs.org/doi/abs/10.1021/ct100125x)

[44]

Jr.
E. Bright Wil-
son,

J.C.
De-
cius,
and
Paul C.
Cross.
*Molec-
u-
lar
Vi-
bra-
tions:
The
The-
ory
of
In-
frared
and
Ra-
man
Vi-
bra-
tional
Spec-
tra.*
Dover
Pub-
li-
ca-
tions,
1955.

- [45] Paolo
Gi-
an-
nozzi
and
Ste-
fano
Ba-
roni.
Vi-
bra-
tional
and
di-
elec-
tric
prop-
er-
ties

of
 c_60
 from
 density-
 functional
 per-
 tur-
 ba-
 tion
 the-
 ory.
The
Jour-
nal
of
Chem-
i-
cal
Physics,
 100
 (11):
 8537–
 8539,
 1994.
 doi:
 10.
 1063/
 1.
 466753.
 URL
[http://
 link.
 aip.
 org/
 link/
 ?JCP/
 100/
 8537/
 1.](http://link.aip.org/link/?JCP/100/8537/1)

- [46] David
 Karhánek,
 Tomáš
 Bučko,
 and
 Jür-
 gen
 Hafner.
 A
 density-
 functional

study
of
the
ad-
sorp-
tion
of
methane-
thiol
on
the
(111)
sur-
faces
of
the
Ni-
group
met-
als:
II.
vi-
bra-
tional
spec-
troscopy.
*Jour-
nal
of
Physics:
Con-
densed
Mat-
ter,*
22
(26):
265006,
2010.
URL
[http:
/
stacks.
iop.
org/
0953-8984/
22/
i=
26/
a=
265006.](http://stacks.iop.org/0953-8984/22/i=26/a=265006)

[47]
Antonio

Fernández-
Ramos,
Ben-
jamin
Elling-
son,
Rubén
Meana-
Pañeda,
Jorge
Mar-
ques,
and
Don-
ald
Truh-
lar.
Sym-
me-
try
num-
bers
and
chem-
i-
cal
re-
ac-
tion
rates.
The-
o-
ret-
i-
cal
Chem-
istry
Ac-
counts:
The-
ory,
Com-
pu-
ta-
tion,
and
Mod-
el-
ing
(The-
o-
ret-

ica
Chim-
ica
Acta),
118:
813–
826,
2007.
ISSN
1432-
881X.
URL
[http://
dx.
doi.
org/
10.
1007/
s00214-007-0328-0](http://dx.doi.org/10.1007/s00214-007-0328-0).
10.1007/s00214-
007-
0328-
0.

- [48] Daniel
Shep-
pard,
Rye
Ter-
rell,
and
Graeme
Henkel-
man.
Op-
ti-
miza-
tion
meth-
ods
for
find-
ing
min-
i-
mum
en-
ergy
paths.
The
Jour-

nal
of
Chem-
i-
cal
Physics,
 128
 (13):
 134106,
 2008.
 doi:
 10.
 1063/
 1.
 2841941.
 URL
[http://
 link.
 aip.
 org/
 link/
 ?JCP/
 128/
 134106/
 1.](http://link.aip.org/link/?JCP/128/134106/1)

- [49] R. A. Olsen, G. J. Kroes, G. Henkelman, A. Arnaldsson, and H. Jonsson. Comparison of methods for finding saddle

points
with-
out
knowl-
edge
of
the
fi-
nal
states.
The
Jour-
nal
of
Chem-
i-
cal
Physics,
121
(20):
9776–
9792,
2004.
doi:
10.
1063/
1.
1809574.
URL
[http://
link.
aip.
org/
link/
?JCP/
121/
9776/
1.](http://link.aip.org/link/?JCP/121/9776/1)

- [50] Ann E.
Mattsson,
Rickard
Armiento,
Joachim
Paier,
Georg
Kresse,
John M.
Wills,
and

Thomas R.
 Matts-
 son.
 The
 am05
 den-
 sity
 func-
 tional
 ap-
 plied
 to
 solids.
The
Jour-
nal
of
Chem-
i-
cal
Physics,
 128
 (8):
 084714,
 2008.
 doi:
 10.
 1063/
 1.
 2835596.
 URL
[http://
 link.
 aip.
 org/
 link/
 ?JCP/
 128/
 084714/
 1.](http://link.aip.org/link/?JCP/128/084714/1)

- [51] Yvon
 Le Page
 and
 Paul
 Saxe.
 Symmetry-
 general
 least-
 squares
 ex-

traction
of
elastic
data
for
strained
ma-
te-
ri-
als
from
ab
ini-
tio
cal-
cu-
la-
tions
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.](http://link.aps.org/doi/10.1103/PhysRevB.65.104104)

[52]
Shun-
Li
Shang,
Yi Wang,

DongE-
ung
Kim,
and
Zi-
Kui
Liu.
First-
principles
ther-
mo-
dy-
nam-
ics
from
phonon
and
de-
bye
model:
Ap-
pli-
ca-
tion
to
ni
and
ni3al.
*Com-
pu-
ta-
tional
Ma-
te-
ri-
als
Sci-
ence*,
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](http://www.sciencedirect.com/science/article/pii/S0927025609004558).

[53]

A. van de
Walle,
M. Asta,
and
G. Ceder.
The
al-
loy
the-
o-
retic
au-
to-
mated
toolkit:
A
user
guide.
*Cal-
phad*,
26
(4):
539
—

553,
2002.
ISSN
0364-
5916.
doi:
10.
1016/
S0364-5916(02)
80006-2.
URL
[http:](http://)

//
www.
sciencedirect.
com/
science/
article/
pii/
S0364591602800062.

[54]

Axel
van de
Walle.
Mul-
ti-
com-
po-
nent
mul-
ti-
sub-
lat-
tice
al-
loys,
non-
con-
fig-
u-
ra-
tional
en-
tropy
and
other
ad-
di-
tions
to
the
al-
loy
the-
o-
retic
au-
to-
mated
toolkit.
Cal-
phad,
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](http://www.sciencedirect.com/science/article/pii/S0364591608001314).
<ce:title>Tools
for
Com-
pu-
ta-
tional
Ther-
mo-
dy-
nam-
ics</ce:title>.

[55]

Lei
Wang,
Thomas
Max-
isch,
and
Ger-
brand
Ceder.
Ox-
i-
da-
tion
en-

er-
 gies
 of
 tran-
 si-
 tion
 metal
 ox-
 ides
 within
 the
 the
 GGA+
 U
 frame-
 work.
Phys.
Rev.
B,
 73:
 195107,
 May
 2006.
 doi:
 10.
 1103/
 PhysRevB.
 73.
 195107.
 URL
[http://
 link.
 aps.
 org/
 doi/
 10.
 1103/
 PhysRevB.
 73.
 195107.](http://link.aps.org/doi/10.1103/PhysRevB.73.195107)

- [56] Leonard
 Klein-
 man.
 Sig-
 nif-
 i-
 cance
 of
 the
 high-
 est

oc-
cu-
pied
Kohn-
Sham
eigen-
value.
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.](http://link.aps.org/doi/10.1103/PhysRevB.56.12042)

- [57] John P.
Perdew
and
Mel
Levy.
Com-
ment
on
"Sig-
nif-
i-
cance
of
the
high-
est
oc-
cu-

pied
 Kohn-
 Sham
 eigen-
 value".
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.](http://link.aps.org/doi/10.1103/PhysRevB.56.16021)

- [58] Leonard
 Klein-
 man.
 Re-
 ply
 to
 "Com-
 ment
 on
 'Sig-
 nif-
 i-
 cance
 of
 the
 high-
 est
 oc-
 cu-
 pied

Kohn-
 Sham
 eigen-
 value'
 ".
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.](http://link.aps.org/doi/10.1103/PhysRevB.56.16029)

- [59] Ralf
 Stowasser
 and
 Roald
 Hoff-
 mann.
 What
 do
 the
 Kohn-
 Sham
 Or-
 bitals
 and
 Eigen-
 val-
 ues
 Mean?
*Jour-
 nal*

of
the
Amer-
i-
can
Chem-
i-
cal
So-
ci-
ety,
 121
 (14):
 3414–
 3420,
 1999.
 doi:
 10.
 1021/
 ja9826892.
 URL
[http://
 pubs.
 acs.
 org/
 doi/
 abs/
 10.
 1021/
 ja9826892.](http://pubs.acs.org/doi/abs/10.1021/ja9826892)

- [60] O. V.
 Grit-
 senko
 and
 E. J.
 Baerends.
 The
 ana-
 log
 of
 Koop-
 mans’
 the-
 o-
 rem
 in
 spin-
 density
 func-
 tional

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.](http://link.aip.org/link/?JCP/117/9154/1)

- [61] R. O.
 Jones
 and
 O. Gun-
 nars-
 son.
 The
 den-
 sity
 func-
 tional
 for-
 mal-
 ism,
 its
 ap-
 pli-
 ca-
 tions
 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.](http://link.aps.org/doi/10.1103/RevModPhys.61.689)

- [62] J. P.
 Perdew
 and
 Alex
 Zunger.
 Self-
 interaction
 cor-
 rec-
 tion
 to
 density-
 functional
 ap-
 prox-
 i-
 ma-
 tions
 for
 many-
 electron
 sys-
 tems.
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.](http://link.aps.org/doi/10.1103/PhysRevB.23.5048)

- [63] Daniel Sanchez-Portal, Emilio Artacho, and Jose M Soler. Projection of plane-wave calculations into atomic orbitals. *Solid State*

Com-
mu-
ni-
ca-
tions,
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](http://www.sciencedirect.com/science/article/pii/S003810989500341X).

[64]

M. D.
Segall,
R. Shah,
C. J.
Pickard,
and
M. C.
Payne.
Pop-
u-
la-
tion
anal-
y-
sis
of
plane-
wave
elec-
tronic
struc-

ture
cal-
cu-
la-
tions
of
bulk
ma-
te-
ri-
als.
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.](http://link.aps.org/doi/10.1103/PhysRevB.54.16317)

- [65]
M. D.
Segall,
C. J.
Pickard,
R. Shah,
and
M. C.
Payne.
Pop-
u-
la-
tion
anal-
y-

sis
in
plane
wave
elec-
tronic
struc-
ture
cal-
cu-
la-
tions.
Mol.
Phys.,
89
(2):
571–
577,
1996.

- [66] A Ruban,
B Ham-
mer,
P Stoltze,
H.L
Skriver,
and
J.K
Nørskov.
Sur-
face
elec-
tronic
struc-
ture
and
re-
ac-
tiv-
ity
of
tran-
si-
tion
and
no-
ble
met-
als.
*Jour-
nal
of*

Molec-
u-
lar
Catal-
y-
sis
A:
Chem-
i-
cal,
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.](http://www.sciencedirect.com/science/article/pii/S1381116996003482)

- [67] A. Cot-
trell.
In-
tro-
duc-
tion
to
the
Mod-
ern
The-
ory
of
Met-
als.
The

In-
sti-
tute
of
Met-
als,
1988.

- [68] F. Ducastelle.
*Or-
der
and
Phase
Sta-
bil-
ity
in
Al-
loys.*
El-
se-
vier
Sci-
ence
Pub-
lish-
ers,
1991.

- [69] D. G.
Pet-
ti-
for
and
A. H.
Cot-
trell,
ed-
i-
tors.
*Elec-
ton
The-
ory
in
Al-
loy
De-
sign.*
The
In-

stitute
of
Materials,
1992.

[70]

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.](http://link.aps.org/doi/10.1103/RevModPhys.73.515)

- [71] Kyle J.
Caspersen
and
Emily A.
Carter.
Find-
ing
tran-
si-
tion
states
for
crys-
talline
solid/solid
phase
trans-
for-
ma-
tions.
*Pro-
ceed-
ings
of
the
Na-
tional
Academy
of
Sci-
ences
of
the
United
States*

of
Amer-
ica,
 102
 (19):
 6738–
 6743,
 2005.
 doi:
 10.
 1073/
 pnas.
 0408127102.
 URL
[http://
 www.
 pnas.
 org/
 content/
 102/
 19/
 6738.
 abstract.](http://www.pnas.org/content/102/19/6738.abstract)

- [72] Daniel
 Shep-
 pard,
 Peng-
 hao
 Xiao,
 William
 Chemelewski,
 Du-
 ane D.
 John-
 son,
 and
 Graeme
 Henkel-
 man.
 A
 gen-
 er-
 al-
 ized
 solid-
 state
 nudged
 elas-
 tic
 band

method.

*The
Jour-
nal
of
Chem-
i-
cal
Physics,*
136
(7):
074103,
2012.
doi:
10.
1063/
1.
3684549.
URL
[http:
//
link.
aip.
org/
link/
?JCP/
136/
074103/
1.](http://link.aip.org/link/?JCP/136/074103/1)

[73]

G. Ritz,
M. Schmid,
P. Varga,
A. Borg,
and
M. Røn-
ning.
Pt(100)
quasi-
hexag-
o-
nal
re-
con-
struc-
tion:
A
com-
par-
i-
son
be-

tween
 scan-
 ning
 tun-
 nel-
 ing
 mi-
 croscopy
 data
 and
 ef-
 fec-
 tive
 medium
 the-
 ory
 sim-
 u-
 la-
 tion
 cal-
 cu-
 la-
 tions.
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.](http://link.aps.org/doi/10.1103/PhysRevB.56.10518)

[74]
 Paula

Havu,
Volker
Blum,
Ville
Havu,
Patrick
Rinke,
and
Matthias
Scheffler.
Large-scale
surface
re-construction
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.](#)

[75]

Wei
Chen,
David
Schmidt,
William F.
Schnei-
der,
and
C. Wolver-
ton.
First-
principles
clus-
ter
ex-
pan-
sion
study
of
missing-
row
re-
con-
struc-
tions
of
fcc
(110)
sur-
faces.
Phys.
Rev.
B,
83:
075415,
Feb
2011.
doi:
10.
1103/
PhysRevB.
83.

075415.
URL
[http://
link.
aps.
org/
doi/
10.
1103/
PhysRevB.
83.
075415.](http://link.aps.org/doi/10.1103/PhysRevB.83.075415)

[76]

J. W. M.
Frenken,
R. L.
Krans,
J. F.
van der
Veen,
E. Holub-
Krappe,
and
K. Horn.
Missing-
row
sur-
face
re-
con-
struc-
tion
of
ag(110)
in-
duced
by
potas-
sium
ad-
sorp-
tion.
*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.](http://link.aps.org/doi/10.1103/PhysRevLett.59.2307)

[77]

J. C.
Boettger.
Non-
con-
ver-
gence
of
sur-
face
en-
er-
gies
ob-
tained
from
thin-
film
cal-
cu-
la-
tions.
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.](http://link.aps.org/doi/10.1103/PhysRevB.49.16798)

[78]

J. C.
Boettger,
John R.
Smith,
Uwe
Birken-
heuer,
Notker
Rösch,
S. B.
Trickey,
John R.
Sabin,
and
S. Pe-
ter
Apell.
Ex-
tract-
ing
con-
ver-
gent
sur-
face
for-
ma-
tion
en-
er-
gies
from
slab
cal-
cu-
la-
tions.
Jour-

nal
of
Physics:
Con-
densed
Mat-
ter,
10
(4):
893,
1998.
URL
[http://
stacks.
iop.
org/
0953-8984/
10/
i=
4/
a=
017.](http://stacks.iop.org/0953-8984/10/i=4/a=017)

- [79] Carlos
Fi-
ol-
hais,
L.M.
Almeida,
and
C. Hen-
riques.
Ex-
trac-
tion
of
alu-
minium
sur-
face
en-
er-
gies
from
slab
cal-
cu-
la-
tions:
per-
tur-

ba-
tive
and
non-
perturbative
ap-
proaches.
Progress
in
Sur-
face
Sci-
ence,
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](http://www.sciencedirect.com/science/article/pii/S0079681603000777).

- [80]
Fabien
Tran,
Robert
Laskowski,
Pe-
ter
Blaha,
and
Karl-
heinz

Schwarz.
 Per-
 for-
 mance
 on
 molecules,
 sur-
 faces,
 and
 solids
 of
 the
 Wu-
 Cohen
 GGA
 exchange-
 correlation
 en-
 ergy
 func-
 tional.
Phys.
Rev.
B,
 75:
 115131,
 Mar
 2007.
 doi:
 10.
 1103/
 PhysRevB.
 75.
 115131.
 URL
[http://
 link.
 aps.
 org/
 doi/
 10.
 1103/
 PhysRevB.
 75.
 115131.](http://link.aps.org/doi/10.1103/PhysRevB.75.115131)

- [81]
 Jeong Woo
 Han,
 Li-
 wei
 Li,

and
David S.
Sholl.
Den-
sity
func-
tional
the-
ory
study
of
H
and
CO
ad-
sorp-
tion
on
alkali-
promoted
Mo₂C
sur-
faces.
The
Jour-
nal
of
Phys-
i-
cal
Chem-
istry
C,
115
(14):
6870–
6876,
2011.
doi:
10.
1021/
jp200950a.
URL
[http:
/
pubs.
acs.
org/
doi/
abs/
10.
1021/](http://pubs.acs.org/doi/abs/10.1021/)

[jp200950a.](#)

[82]

Nilay
In-
oğlu
and
John R.
Kitchin.
Atom-
istic
ther-
mo-
dy-
nam-
ics
study
of
the
ad-
sorp-
tion
and
the
ef-
fects
of
wa-
ter-gas
shift
re-
ac-
tants
on
cu
cat-
a-
lysts
un-
der
re-
ac-
tion
con-
di-
tions.
*Jour-
nal
of
Catal-
y-
sis,*
261

(2):
188

—

194,
2009.
ISSN
0021-
9517.

doi:
10.
1016/

j.
jcat.
2008.

11.
020.

URL

[http:](http://)
[//](http://)

[www.](http://www.sciencedirect.com/science/article/pii/S0021951708004314)
[sciencedirect.](http://www.sciencedirect.com/science/article/pii/S0021951708004314)
[com/](http://www.sciencedirect.com/science/article/pii/S0021951708004314)
[science/](http://www.sciencedirect.com/science/article/pii/S0021951708004314)
[article/](http://www.sciencedirect.com/science/article/pii/S0021951708004314)
[pii/](http://www.sciencedirect.com/science/article/pii/S0021951708004314)
[S0021951708004314.](http://www.sciencedirect.com/science/article/pii/S0021951708004314)

[83]

L. Vi-
tos,
A.V.
Ruban,
H.L.
Skriver,
and
J. Kol-
lár.
The
sur-
face
en-
ergy
of
met-
als.
*Sur-
face
Sci-
ence*,
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](http://www.sciencedirect.com/science/article/pii/S003960289800363X).

- [84]
Jörg
Neuge-
bauer
and
Matthias
Scheff-
ler.
Adsorbate-
substrate
and
adsorbate-
adsorbate
in-
ter-
ac-
tions
of
Na
and
K
ad-
lay-
ers
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.](http://link.aps.org/doi/10.1103/PhysRevB.46.16067)

- [85]
Lennart
Bengts-
son.
Dipole
cor-
rec-
tion
for
sur-
face
su-
per-
cell
cal-
cu-
la-
tions.
*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.](http://link.aps.org/doi/10.1103/PhysRevB.59.12301)

- [86] Yoshitada
Morikawa.
Ad-
sorp-
tion
ge-
ome-
tries
and
vi-
bra-
tional
modes
of
 C_2H_2
on
the
si(001)
sur-
face.
Phys.
Rev.
B,
63:
033405,
Jan
2001.
doi:
10.
1103/
PhysRevB.
63.
033405.
URL
[http://
link.](http://link.aps.org/doi/10.1103/PhysRevB.63.033405)

[aps.org/doi/10.1103/PhysRevB.63.033405](#).

[87]

Nilay
In-
oğlu
and
John R.
Kitchin.
Sim-
ple
model
ex-
plain-
ing
and
pre-
dict-
ing
coverage-
dependent
atomic
ad-
sorp-
tion
en-
er-
gies
on
tran-
si-
tion
metal
sur-
faces.
Phys.
Rev.
B,
82:
045414,
Jul
2010.
doi:
10.
1103/
PhysRevB.

82.
045414.
URL
[http://
link.
aps.
org/
doi/
10.
1103/
PhysRevB.
82.
045414.](http://link.aps.org/doi/10.1103/PhysRevB.82.045414)

- [88] Spencer D.
Miller,
Ni-
lay
In-
oglu,
and
John R.
Kitchin.
Con-
fig-
u-
ra-
tional
cor-
re-
la-
tions
in
the
cov-
er-
age
de-
pen-
dent
ad-
sorp-
tion
en-
er-
gies
of
oxy-
gen
atoms
on

late
tran-
si-
tion
metal
fcc(111)
sur-
faces.
The
Jour-
nal
of
Chem-
i-
cal
Physics,
134
(10):
104709,
2011.
doi:
10.
1063/
1.
3561287.
URL
[http://
link.
aip.
org/
link/
?JCP/
134/
104709/
1.](http://link.aip.org/link/?JCP/134/104709/1)

- [89] Spencer D.
Miller
and
John R.
Kitchin.
Re-
lat-
ing
the
cov-
er-
age
de-
pen-
dence

of
oxy-
gen
ad-
sorp-
tion
on
Au
and
Pt
fcc(111)
sur-
faces
through
adsorbate-
induced
sur-
face
elec-
tronic
struc-
ture
ef-
fects.
*Sur-
face
Sci-
ence*,
603
(5):
794

—

801,
2009.
ISSN
0039-
6028.
doi:
10.
1016/
j.
susc.
2009.
01.
021.
URL
[http:
//
www.
sciencedirect.
com/](http://www.sciencedirect.com/)

[science/
article/
pii/
S0039602809001186.](#)

[90]

John R.
Kitchin.
Cor-
re-
la-
tions
in
coverage-
dependent
atomic
ad-
sorp-
tion
en-
er-
gies
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.](#)

[91]

John R.
Kitchin,

Karsten
 Reuter,
 and
 Matthias
 Scheffler.
 Alloy
 surface
 segregation
 in
 reactive
 environments:
 First-principles
 atomistic
 thermodynamics
 study
 of
 Ag₃Pd(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.](http://link.aps.org/doi/10.1103/PhysRevB.77.075437)

- [92] Anand Udayku-
mar
Nilekar,
Jeff
Gree-
ley,
and
Manos
Mavrikakis.
A
sim-
ple
rule
of
thumb
for
dif-
fu-
sion
on
transition-
metal
sur-
faces.
*Ange-
wandte
Chemie
In-
ter-
na-
tional
Edi-
tion*,
45
(42):
7046–
7049,
2006.

ISSN
1521-
3773.
doi:
10.
1002/
anie.
200602223.
URL
[http:
//
dx.
doi.
org/
10.
1002/
anie.
200602223.](http://dx.doi.org/10.1002/anie.200602223)

- [93] Graeme
Henkel-
man,
Blas P.
Uberu-
aga,
and
Hannes
Jon-
s-
son.
A
climb-
ing
im-
age
nudged
elas-
tic
band
method
for
find-
ing
sad-
dle
points
and
min-
i-
mum
en-
ergy

paths.
The
Journal
of
Chem-
i-
cal
Physics,
113
(22):
9901–
9904,
2000.
doi:
10.
1063/
1.
1329672.
URL
[http://
link.
aip.
org/
link/
?JCP/
113/
9901/
1.](http://link.aip.org/link/?JCP/113/9901/1)

- [94] P. Desh-
lahra,
E. E.
Wolf,
and
W. F.
Schnei-
der.
A
pe-
ri-
odic
den-
sity
func-
tional
the-
ory
anal-
y-
sis

of
co
chemisorp-
tion
on
pt(111)
in
the
pres-
ence
of
uni-
form
elec-
tric
fields†.

*The
Jour-
nal
of
Phys-
i-
cal
Chem-
istry*

A,
113
(16):
4125–
4133,
2009.
doi:
10.
1021/
jp810518x.
URL

[http:
//
pubs.
acs.
org/
doi/
abs/
10.
1021/
jp810518x.](http://pubs.acs.org/doi/abs/10.1021/jp810518x)

- [95]
B. Meredig,
A. Thomp-
son,
H. A.
Hansen,

C. Wolver-
ton,
and
A. van de
Walle.
Method
for
lo-
cat-
ing
low-
energy
so-
lu-
tions
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.](http://link.aps.org/doi/10.1103/PhysRevB.82.195128)

- [96]
Anubhav
Jain,
Ge-
of-
froy
Hau-
tier,
Shyue Ping

Ong,
Charles J.
Moore,
Christo-
pher C.
Fis-
cher,
Kristin A.
Pers-
son,
and
Ger-
brand
Ceder.
For-
ma-
tion
en-
thalpies
by
mix-
ing
GGA
and
GGA
+
 U
cal-
cu-
la-
tions.
Phys.
Rev.
B,
84:
045115,
Jul
2011.
doi:
10.
1103/
PhysRevB.
84.
045115.
URL
[http:
//
link.
aps.
org/
doi/
10.](http://link.aps.org/doi/10.1103/PhysRevB.84.045115)

[1103/
PhysRevB.
84.
045115.](#)

[97]

Stefan
Grimme.
Semiempirical
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.](http://dx.doi.org/10.1002/jcc.20495)

[98]

Jiří
Klimeš,
David R.
Bowler,
and
An-
ge-
los
Michaelides.
Van
der
waals
den-
sity
func-
tion-
als
ap-
plied
to
solids.
*Phys-
i-
cal
Re-
view
B*,
83
(19):
nil,
2011.
doi:
10.
1103/
physrevb.
83.
195131.
URL
[http://
dx.
doi.](http://dx.doi.org/10.1103/physrevb.83.195131)

[org/](#)
[10.](#)
[1103/](#)
[PhysRevB.](#)
[83.](#)
[195131.](#)

[99]

Alexandre
Tkatchenko
and
Matthias
Scheff-
ler.
Ac-
cu-
rate
rate
molec-
u-
lar
van
der
waals
in-
ter-
ac-
tions
from
ground-
state
elec-
tron
den-
sity
and
free-
atom
ref-
er-
ence
data.
Phys.
Rev.
Lett.,
102
(7):
nil,
2009.
doi:
10.
1103/
physrevlett.
102.

073005.
URL
[http://
dx.
doi.
org/
10.
1103/
physrevlett.
102.
073005.](http://dx.doi.org/10.1103/physrevlett.102.073005)

[100]

B. Silvi
and
A Savin.
Clas-
si-
fi-
ca-
tion
of
chem-
i-
cal
bonds
based
on
topo-
log-
i-
cal
anal-
y-
sis
of
elec-
tron
lo-
cal-
iza-
tion
func-
tions.
*Na-
ture*,
371:
683–
686,
1994.
URL
[http:](http://)

//
dx.
doi.
org/
10.
1038/
371683a0.

[101]

Jess
Wellen-
dorff,
Keld T.
Lundgaard,
An-
dreas
Møgel-
høj,
Vivien
Pet-
zold,
David D.
Lan-
dis,
Jens K.
Nørskov,
Thomas
Bli-
gaard,
and
Karsten W.
Ja-
cob-
sen.
Den-
sity
func-
tion-
als
for
sur-
face
sci-
ence:
Exchange-
correlation
model
de-
vel-
op-
ment
with
bayesian

er-
ror
es-
ti-
ma-
tion.
Phys-
i-
cal
Re-
view
B,
85
(23):
nil,
2012.
doi:
10.
1103/
physrevb.
85.
235149.
URL
[http:
//
dx.
doi.
org/
10.
1103/
physrevb.
85.
235149.](http://dx.doi.org/10.1103/physrevb.85.235149)

- [102] Matthew
Fish-
man,
Hou-
long L.
Zhuang,
Ki-
ran
Mathew,
William
Dirschka,
and
Richard G.
Hen-
nig.
Ac-
cu-
racy

of
exchange-
correlation
func-
tion-
als
and
ef-
fect
of
sol-
va-
tion
on
the
sur-
face
en-
ergy
of
cop-
per.
*Phys-
i-
cal
Re-
view
B*,
87
(24):
nil,
2013.
doi:
10.
1103/
physrevb.
87.
245402.
URL
[http:
//
dx.
doi.
org/
10.
1103/
PhysRevB.
87.
245402.](http://dx.doi.org/10.1103/PhysRevB.87.245402)

[103]
Kiran
Mathew,

Rav-
is-
hankar
Sun-
darara-
man,
Kendra
Letchworth-
Weaver,
T. A.
Arias,
and
Richard G.
Hen-
nig.
Im-
plicit
sol-
va-
tion
model
for
density-
functional
study
of
nanocrys-
tal
sur-
faces
and
re-
ac-
tion
path-
ways.
J.
Chem.
Phys.,
140
(8):
084106,
2014.
doi:
10.
1063/
1.
4865107.
URL
[http://
dx.](http://dx.doi.org/10.1063/1.4865107)

[doi.
org/
10.
1063/
1.
4865107.](https://doi.org/10.1063/1.4865107)

[104]

M. Hebbache
and
M. Zemzemi.
*Ab
initio*
study
of
high-
pressure
be-
hav-
ior
of
a
low
com-
press-
ibil-
ity
metal
and
a
hard
ma-
te-
rial:
os-
mium
and
di-
a-
mond.
*Phys.
Rev.
B*,
70:
224107,
Dec
2004.
doi:
10.
1103/
PhysRevB.

70.
224107.
URL
[http://
link.
aps.
org/
doi/
10.
1103/
PhysRevB.
70.
224107.](http://link.aps.org/doi/10.1103/PhysRevB.70.224107)

[105]

F. D.
Mur-
naghan.
The
com-
press-
ibil-
ity
of
me-
dia
un-
der
ex-
treme
pres-
sures.
*Pro-
ceed-
ings
of
the
Na-
tional
Academy
of
Sci-
ences
of
the
United
States
of
Amer-
ica,*
30
(9):

pp.
244–
247,
1944.
ISSN
00278424.
URL
[http:
//
www.
jstor.
org/
stable/
87468.](http://www.jstor.org/stable/87468)

- [106] C. L.
Fu
and
K. M.
Ho.
First-
principles
cal-
cu-
la-
tion
of
the
equi-
lib-
rium
ground-
state
prop-
er-
ties
of
tran-
si-
tion
met-
als:
Ap-
pli-
ca-
tions
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.](http://link.aps.org/doi/10.1103/PhysRevB.28.5480)

- [107] Michael J. Mehl,
 Barry M. Klein,
 and
 Dimitri A. Papa-
 constantopoulos.
*Inter-metallic
 Compounds: Prin-
 ciples
 and Prin-
 ciples,*
 Vol-

ume
I:
Prin-
ci-
ples,
vol-
ume I,
chap-
ter
First
prin-
ci-
ples
cal-
cu-
la-
tions
of
elas-
tic
prop-
er-
ties
of
met-
als,
pages
195–
210.
John
Wi-
ley
and
Sons,
1995.
URL
[http:
//
cst-www.
nrl.
navy.
mil/
users/
mehl/
papers/
cij453.
pdf.](http://cst-www.nrl.navy.mil/users/mehl/papers/cij453.pdf)

- [108] B. Mayer,
H. An-
ton,
E. Bott,

M. Meth-
fes-
sel,
J. Sticht,
J. Har-
ris,
and
P.C.
Schmidt.
Ab-
initio
cal-
cu-
la-
tion
of
the
elas-
tic
con-
stants
and
ther-
mal
ex-
pan-
sion
co-
ef-
fi-
cients
of
laves
phases.
In-
ter-
metallics,

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.](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. Secondly, 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.

You may extract a single document from such a collection, and distribute it individually under this License, provided you insert a

copy of this License into the extracted document, and follow this License in all other respects regarding verbatim copying of that document.

7. AGGREGATION WITH INDEPENDENT WORKS

A compilation of the Document or its derivatives with other separate and independent documents or works, in or on a volume of a storage or distribution medium, is called an "aggregate" if the copyright resulting from the compilation is not used to limit the legal rights of the compilation's users beyond what the individual works permit. When the Document is included in an aggregate, this License does not apply to the other works in the aggregate which are not themselves derivative works of the Document.

If the Cover Text requirement of section 3 is applicable to these copies of the Document, then if the Document is less than one half of the entire aggregate, the Document's Cover Texts may be placed on covers that bracket the Document within the aggregate, or the electronic equivalent of covers if the Document is in electronic form. Otherwise they must appear on printed covers that bracket the whole aggregate.

8. TRANSLATION

Translation is considered a kind of modification, so you may distribute translations of the Document under the terms of section 4. Replacing Invariant Sections with translations requires special permission from their copyright holders, but you may include translations of some or all Invariant Sections in addition to the original versions of these Invariant Sections. You may include a translation of this License, and all the license notices in the Document, and any Warranty Disclaimers, provided that you also include the original English version of this License and the original versions of those notices and disclaimers. In case of a disagreement between the translation and the original version of this License or a notice or disclaimer, the original version will prevail.

If a section in the Document is Entitled "Acknowledgements", "Dedications", or "History", the requirement (section 4) to Preserve its Title (section 1) will typically require changing the actual title.

9. TERMINATION

You may not copy, modify, sublicense, or distribute the Document except as expressly provided under this License. Any attempt 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 means any set of copyrightable works thus published on the MMC site.

"CC-BY-SA" means the Creative Commons Attribution-Share Alike 3.0 license published by Creative Commons Corporation, a not-for-profit corporation with a principal place of business in San Francisco, California, as well as future copyleft versions of that license published by that same organization.

"Incorporate" means to publish or republish a Document, in whole or in part, as part of another Document.

An MMC is "eligible for relicensing" if it is licensed under this License, and if all works that were first published under this License somewhere other than this MMC, and subsequently incorporated in whole or in part into the MMC, (1) had no cover texts or invariant sections, and (2) were thus incorporated prior to November 1, 2008.

The operator of an MMC Site may republish an MMC contained in the site under CC-BY-SA on the same site at any time before August 1, 2009, provided the MMC is eligible for relicensing.

14 Index

Index

adsorption energy, [196](#)
animation, [88](#)
atomistic thermodynamics, [215](#)

bader, [47](#)
band structure, [159](#)

center of mass, [24](#)
cohesive energy, [126](#)
convergence
 ENCUT, [67](#)
 KPOINTS, [127](#)

DFT+U, [227](#)
dipole correction, [191](#)
dipole moment, [40](#)

HSE06, [231](#)

infrared intensity, [58](#)
ISMEAR, [101](#)

jasp, [4](#)

molecular weight, [23](#)
moment of inertia, [24](#)

nudged elastic band, [88](#)

reconstruction, [178](#)

SIGMA, [101](#)

thermochemistry, [62](#)

vibrations, [54](#)

work function, [190](#)