

# Open-Source Pseudopotential Interface/Unification Module (OPIUM): The Basic Ins and Outs of Operation

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## Learning Objectives

1. Determine necessary software to install.
2. Identify the keyblocks needed and what they should include.
3. Learn the commands used by OPIUM.
4. Understand how plotting works in OPIUM

## Installation and Necessary Software

To utilize OPIUM, one must install it on your desired platform along with Xmgrace. OPIUM is available as a precompiled binary for both Linux/x86 and MacOSX platforms, and will need to be compiled for other platforms. For this tutorial, we assume OPIUM has already been installed on the desired platform. If this is not the case, please see [opium.sourceforge.net](http://opium.sourceforge.net) for installation instructions and details.

Once OPIUM and Xmgrace have been installed, OPIUM can be used to create pseudopotentials and examine electronic structure. One should have a basic understanding of quantum numbers and electron configurations to get started. Typing `./opium -h` or `./opium` in the command line of the terminal without an argument will bring you directly to the help screen.

## Keyblocks

In order to utilize OPIUM to study basic electronic structure, we must be able to construct an input file in order to run calculations and determine the energies of our electrons. The input file for OPIUM is broken up into a series of "keyblocks" containing sets of related parameters. Some of these keyblocks are required in all input files while others are only required in certain instances.

[Atom]

C

6

100 2.00 -

200 2.00 -

210 2.00 -

[Atom] is the first of the required keyblocks. This keyblock tells OPIUM which specific atom a pseudopotential is being designed for, how many orbitals it has and how many electrons are in each of the orbitals for the given atom. The  $nlm$  number is used to reference the orbital, which are obtained from our principle quantum number (energy level), the angular quantum number (orbital or sublevel), and the magnetic quantum number, which OPIUM requires always be set to 0. By keeping the magnetic quantum number set to 0, this enforces spherical symmetry, making it easier to calculate. **Think about it, what's easier to calculate: the area of a sphere or the area of a figure eight?**

The  $nlm$  number is followed by its occupation (how many electrons are in each sublevel), and an eigenvalue guess of "--", which tells OPIUM to generate the guess. The configuration specified in the [Atom] keyblock is the reference configuration. This is used to construct the pseudopotential and will reproduce the valence electron properties of the all-electron atom in this configuration. The initial configuration will also provide us with the energies of our orbitals. The reference configuration does not need to be the same as that of a neutral atom. Why not? Atoms are very rarely found in their elemental form, which makes the neutral configuration a poor choice to use in the creation of a pseudopotential. **Are we likely to find aluminum as a cation or the neutral metal in nature?**

[Pseudo]

2 0.84 1.29

opt

The second keyblock, [Pseudo], lists the number of orbitals (usually the valence orbitals) to be contained in the pseudopotential. Required with this is the cut-off radii for each pseudo orbital. Since Carbon has 3 orbitals, we have to determine which ones are the valence orbitals (the ones with the highest principle quantum number), and the cut-off radius ( $r_c$ ) for each orbital. **How do**

**we decide what to use as  $r_c$ ?** As beginners, an acceptable approach is to start with  $r_c$  just under the atom's bohr radius (this turns out to be very close to the atom's diameter in angstroms). We can narrow it down as we look at our results. Typically though,  $r_c$  should be roughly 45% of the interatomic bond length in your target calculations. Remember  $r_c$  should be in bohr, not picometers! The radius of most neutral elements and a handful of ions can be obtained from within a first-year textbook or from some periodic tables, but may require a unit conversion. Also, 'opt' indicates we want to use the optimized pseudopotential method. Other norm-conserving options for pseudopotential design methods include kerker and troullier-martin (tm). More information on those methods can be found in the references. [7, 9]

The Optimized method is known as the RRKJ method in the literature [8], and optimizes the convergence with the basis size of quantities of interest, such as total energy, and allows the benefits of the planewave basis to be derived for a vast array of systems. This method is preferred since the total energy of solids with the planewave basis matches the convergence of the isolated pseudoatoms total energies [7]. When we use the Optimized method, we need to include another keyblock known as [Optinfo].

#### [Optinfo]

7.07 10

7.07 10

[Optinfo] consists of a minimum of two components:  $q_c$  and *bessel functions*. The first entry in [Optinfo] keyblock specifies the cutoff wavevector  $q_c$  for the pseudopotential construction.  $q_c$  should be larger than  $r_c$ ; a good starting point is  $q_c = 2 * r_c$ . The square of the cutoff wavevector in the input here will be your energy cutoff. Here if  $q_c$  is 7.07, our energy cutoff will be 50 Ry ( $q_c^2 = E$ ).

The second parameter is number of *bessel functions* being used to for a basis to use in the optimization. Bessel functions are the equations used to find the radial solutions of the Schrödinger equation. This value must be no smaller than 4, and will yield better convergence properties if raised to about 8-10. Raising the value beyond 10 is not recommended as it will only increase the time needed, with negligible improvements in convergence. Remember we want our pseudopotentials to be efficient as well as accurate!

We need to include cutoff wavevectors and *bessel functions* for *each* orbital in our pseudopo-

tential. As the Optimized approach constructs a pseudopotential which is optimized for the choice of  $q_c$ , this means choosing  $q_c$  to be too high or too low will result in a sub-optimal report file.

### [XC]

lda

[XC] is an optional key-block, and if not designated, will automatically utilize a local density approximation (LDA) [2] correlation functional. If this functional is not desired, it can be changed to Generalized Gradient Approximation (GGA) [6] functional. Each functional has its own pros and cons, parties interested in the difference between the types of exchange-correlation functionals can check out Axel Becke's perspective paper [14]. We need to make sure that we pick the functional that will be matching the calculation you will be using in your DFT calculations.

LDA functionals utilize only the electron density,  $\rho(r)$  at a spatial point  $\mathbf{r}$  to determine the exchange-correlation energy density at that point [1]. The exchange-correlation energy is accepted to be that of an invariable electron gas of the same density. The definition of the exchange portion of the functional is the exact expression derived for an invariable electron gas, i.e. the spin up electrons in your  $2p_x$ ,  $2p_y$ ,  $2p_z$  orbitals can be exchanged with each other. LDA correlation functionals vary in the representation of the correlation, which is how the electrons relate to each other due to repulsion. The varieties available for OPIUM are PZ81 [4] and PW92 [5]. One can change between between them by typing lda or pwlda.

GGA uses the electron density, but supplements it with a gradient containing information about the charge density. This is to help account for the non-homogeneity of the true electron density. The most commonly used variety in OPIUM is the PBE [6]. Reference 6 also contains more information on exchange-correlation energy if one is interested.

No matter which functional is chosen, they are all approximations, and their accuracy varies with the material property and system studied. While functionals have been found to work with oxides, surfaces, and bulk materials, scientists are continuously trying to design pseudopotentials which better match all-electron calculations—and for the entire periodic table, not just those elements which haven't had pseudopotentials designed yet. Functionals can be modified, but the modifications made may or may not work well for all materials and environments (solids, liquids, aqueous, gaseous).

### [Configs]

1

200 2.00 -

210 2.00 -

[**Configs**] is a key-block that allows us to take a look at various valence electron configurations for the element being examined. **Why is this important?**

**Transferability:** We want to create a single pseudopotential which will work for multiple configurations. Think of how many redox reactions you dealt with in just the first semester of first year chemistry. We know atoms are rarely found in the same configuration in different chemical environments. Electrons are shared, lost, and gained when chemical environments change. If we have to create a new pseudopotential for each configuration, we're not being efficient.

When utilizing the [Configs] keyblock, the valence orbitals must be listed in the same order they were in the reference state (see [**Atom**]), and the number of test configurations must be specified. OPIUM does not allow one to add more than one electron to an ion's configuration, so calculations for nitride and oxide ions found in our ionic compounds cannot be easily obtained. This is because Density Functional Theory (DFT) is a one electron method, so if we add more than one electron, it becomes difficult to predict what will happen to our results due to the increase in interactions between other electrons and the nucleus. For example, if electrons were flies, it would be fairly easy to keep track of one in the room. But if we have three in the room, how can we manage to keep track of all three at the same time? One electron is easy to make predictions for.

Electrons can easily be removed to create positively charged atoms and the periodic table contains far more atoms which form cations than anions. The configurations use the same *nlm*, occupation, eigenvalue guess set up as the [**Atom**] keyblock does.

There are some additional keyblocks which can be used when desired, and are as follows:

[**Pcc**] is a keyblock which is required in atoms or ions where distinguishing between the core and the valence electrons is difficult in magnetic systems. Initially, this was dealt with by constructing separate potentials for the spin up and spin down electrons—but this is not efficient! This issue is commonly observed when dealing with alkali and transition metals and cations in polar compounds. For the alkali metals, this occurs because the *p* state is empty, the *s* electrons are loosely bound (easily lost), and the *d* orbitals are empty but will soon be occupied.

Partial core corrections add a non-linear exchange-correlation interaction of the valence electrons with the semicore density. One needs to take care that any corrections made will work for the elemental form as well as the oxides. This correction also needs to be done for the transition metals in the  $3d$  block where the electrons are semicore. This is because any  $4s$  electrons we see are in the outermost level (valence electrons), but we can also remove the  $3d$  electrons. This means the  $3d$  electrons belong to neither the core electrons nor the valence electrons, leaving us with no other option than to make them semicore. Use of the [PCC] keyblock allows us to smooth out the core using one of two methods [17,18].

The first method, which is referred to as **lfc** in OPIUM utilizes spherical Bessel functions to replace the full core charge density with a partial core charge density. This partial core density needs to match the true charge density at the designated radius. More information on this method can be found in reference 17. The second method, **fuchs**, uses a similar method, but uses a polynomial instead of spherical Bessel functions.

**[Relativity]** is a keyblock which will allow one to switch for scalar-relativistic solving. Values are either **nrl** for non-relativistic scalar, or **srl** for scalar-relativistic solve. If this keyblock is unused, the default setting is **nrl**. This keyblock is required for all elements with  $Z > 54$ .

**[Loginfo]** is a keyblock necessary to explain which configuration will be utilized if one desires to plot logarithmic derivatives. Logarithmic derivatives are often used when doing transferability testing. One can simply add this keyblock to the param file. In the keyblock, you must specify the configuration number you want to consider, "0" means the reference state, "1" means the first test configuration and so on. The necessary radius, energy minimums and maximums to be plotted must be included in this keyblock for it to work properly. The radius in this keyblock needs to be larger than all of the cutoff radii, and we need to look at how the log of the radius changes with respect to changes in energy.

**[KBdesign]** is a keyblock which can be used to examine a local potential for a pseudopotential. It requires the symbol for the angular momentum component of the local potential for the KB construction, the number of functions necessary for the designed non-local procedure (this must be an integer), the units, and the coordinates for each box. These coordinates include the left edge, the right edge, and the depth. The units used will be either **au** or **gp**. **au** refers to the units of bohr, and **gp** to the coordinates specified by their grid points.

This keyblock essentially modulates the core potential to change how attractive it is to an electron. One is essentially putting in barriers for the electron.

### Commands in OPIUM

The following commands will be used in OPIUM. To use any of these, they should be prefaced by **.opiium Sy Sy.log** where Sy stands for the symbol of the atom of interest. One can string as many commands as one wants, as long as there is a space between each.

Command	Description
ae	All-electron solve of the atom
ps	Generates pseudopotential
nl	Pseudopotential solve of the atom for reference state
tc	Solves the all-electron and pseudo atom for all test configurations
ke	Solves a fictitious kinetic energy
all	Abbreviation for "ae ps nl tc"
rpt	Generates a report file
plot [plot type]	Make a plot of type [plot type]

### Plotting in OPIUM

OPIUM is set up to be create plots in a program called XmGrace. Useful graphs for first year students include those for both all-electron and pseudo wavefunctions, screened and ionic potentials, and densities. Those doing pseudopotential design will find all plots useful.

String (command abbreviation)	Plot Type
wa	All-electron wavefunctions
wp	Pseudo and all-electron wavefunctions
den	Core, valence, and partial core density
vs	Screened pseudopotentials
vi	Ionic (descreened) pseudopotentials
qp	Q-space pseudo-wavefunctions and potentials
logd	Log. deriv for state listed in [Loginfo] keyblock

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