

## Opium Tutorial 2: Aluminum

**Goal:** The purpose of this tutorial is to introduce the different pseudopotential construction methods and to discuss transferability testing.

Let's calculate the all-electron wavefunctions for aluminum to see what a reasonable cutoff radius could be. We will use the following param file as a starting point:

```
[Atom]
Al
5
100 2.00 -
200 2.00 -
210 6.00 -
300 2.00 -
310 1.00 -

[Pseudo]
2 2.5 2.5
kerker

[XC]
lda
```

```
%> ./opium al al.log ae plot wa
```

A cutoff radius of 2.5 a.u. seems like a very reasonable cutoff for aluminum based on the wavefunction peak positions. We must consider the environment that we wish to use this potential. Specifically, we want to avoid *core overlap* if possible. For example, let's say we are studying aluminum oxide. The smallest bond length in this system is the Al-O bond which can be as small as 3.2 a.u. If we already know that the oxygen cutoff radius is about 1.3 a.u. then we must construct the aluminium pseudopotential to have a cutoff radius of no more than 1.6 a.u. Let's choose 1.6 a.u. and take a look at the approximate cutoff energy:

```
%> ./opium al al.log ae ps nl ke rpt
```

Unlike the previous tutorial, we will concentrate on the output in the report file. Although, it is always a good idea to check the log file for errors and warnings.

```
%> cat al.rpt
```

```
.
.
.
### KE report #####

=== Ecut necessary for ~1 eV convergence error / electron ===
-----
                Ecut[Ry]      error [meV/e]
100                3          997.570
210                2          981.593
=== Ecut necessary for ~100 meV convergence error / electron ===
-----
                Ecut[Ry]      error [meV/e]
100                9           92.189
210               18           99.348

=== Ecut necessary for ~10 meV convergence error / electron ===
-----
                Ecut[Ry]      error [meV/e]
100               22            9.752
```

```

210          35          9.512

===  Ecut necessary for  ~1 meV convergence error / electron ===
-----
          Ecut[Ry]      error [meV/e]
100          46          0.995
210          85          0.962

```

Using the Kerker construction method the Al pseudopotential requires a cutoff energy of roughly 18-35 Ry to achieve a convergence error of between 10-100 meV/electron (the effective cutoff energy is the largest of all orbitals).

Let's remake the Al potential using the method of Troullier and Martins [1]. We do this by specifying `tm` in the param file:

```

[Atom]
Al
5
100 2.00 -
200 2.00 -
210 6.00 -
300 2.00 -
310 1.00 -

```

```

[Pseudo]
2 1.6 1.6
tm

```

```

[XC]
lda

```

```

%> ./opium al al.log ae ps nl ke rpt
%> cat al.rpt

```

```

.
.
.
### KE report #####

```

```

===  Ecut necessary for ~1    eV convergence error / electron ===
-----
          Ecut[Ry]      error [meV/e]
100          1          988.172
210          2          978.351
===  Ecut necessary for ~100 meV convergence error / electron ===
-----
          Ecut[Ry]      error [meV/e]
100          10          98.356
210          29          97.768

===  Ecut necessary for  ~10 meV convergence error / electron ===
-----
          Ecut[Ry]      error [meV/e]
100          31          9.701
210          41          9.822

===  Ecut necessary for  ~1 meV convergence error / electron ===
-----
          Ecut[Ry]      error [meV/e]
100          67          0.993

```

210

71

0.981

.  
.  
.

Using the Troullier-Martins method the kinetic energy convergence behavior is similar to the Kerker method for this atom.

An alternative to the Troullier-Martins and the Kerker method is the Optimized method [2] (sometimes referred to in the literature as *RRKJ*). This method should, at worst, give the same cutoff energy as Troullier-Martins and usually can do better.

The Optimized method requires two additional construction parameters for each valence state. These are specified in the [Optinfo] keyblock:

```
[Atom]
Al
5
100 2.00 -
200 2.00 -
210 6.00 -
300 2.00 -
310 1.00 -

[Pseudo]
2 1.6 1.6
opt

[Optinfo]
3.0 10
3.0 10

[XC]
lda
```

The first entry in the [Optinfo] keyblock specifies the cutoff wavevector ( $q_c$ ) for the pseudopotential construction. The square of this value is the desired cutoff energy for this valence state. The PS section of the report file will show the amount of convergence error resulting from this choice. The second parameter is the size of the basis used in the optimization. This value must be at least 4 and can yield better convergence properties if raised to about 8-10. Raising this value beyond 10 is not recommended.

Unlike the Kerker and Troullier-Martins methods, the Optimized approach constructs a pseudopotential which is “optimized” for the choice of  $q_c$ . This means that choosing  $q_c$  to be too high or too low will result in a sub-optimal potential. Fortunately, there is additional output which can guide the choice of  $q_c$ , this is in the PS section of the report file. Let’s try a guess of  $q_c = 3$  for both states and analyze the PS report output:

```
%> ./opium al al.log ae ps rpt
%> cat al.rpt
```

.  
.  
.

```
### PS report #####
```

```
=====Optimized pseudopotential method=====
```

Orbital	Pseudopotential convergence error				Ghost
	[mRy/e]	[meV/e]	[mRy]	[meV]	
300	6.101975	83.021637	12.203949	166.043275	no
310	1.345895	18.311848	1.345895	18.311848	no

Tot. error = 13.549845 184.355123

Using a  $q_c$  of 3.0 for both states, we see that the convergence error is about 83 meV/electron for the  $s$  state and about 18 meV/electron for the  $p$  state. The total convergence error (the sum of the convergence error/electron  $\times$  the number of electrons in that state) in this potential is about 184 meV. Let's adjust the  $q_c$  to get the total convergence error to be about 100 meV. Clearly, the  $s$  state could use some improvement.

After some tests, a  $q_c$  of 3.24 ( $\sqrt{10.5}$ ) is found to be acceptable:

```

.
.
.
### PS report #####
=====Optimized pseudopotential method=====

```

Orbital	Pseudopotential convergence error				Ghost
	[mRy/e]	[meV/e]	[mRy]	[meV]	
300	2.768383	37.665787	5.536766	75.331574	no
310	1.345895	18.311848	1.345895	18.311848	no
Tot. error =			6.882661	93.643422	

```

.
.
.

```

The  $p$  state  $q_c$  could also be adjusted, but it is not necessary since the  $p$  state is already well converged with a  $q_c$  of 3.

At this point, let's compare the convergence error results obtained with the Optimized method to that obtained from the other methods. The Optimized Al pseudopotential with a cutoff energy of 10.5 Ry in the  $s$  state has a convergence error of about 38 meV per electron and the  $p$  state has roughly 18 meV error per electron. This is a much lower error per electron compared to the other construction methods. In both the Kerker and Troullier-Martins case, at around 10 Ry, there is much more convergence error for both the  $s$  and especially the  $p$  states.

Of course one might want the convergence error to be smaller. Again, by adjusting the  $q_c$  values, we can directly control the convergence error in the Optimized method. For example, to achieve convergence error of less than 10 meV per electron, we would find that for the  $s$  state, a cutoff energy of 13 Ry is needed whereas for the  $p$  state, a cutoff energy of about 25 Ry is necessary. Therefore, this potential requires an overall cutoff of 25 Ry. This is much softer than the other methods. For instance, the Kerker potential required 35 Ry for a convergence error of 10 meV per electron and the Troullier-Martins required about 40 Ry.

Now, let's go back to the previous param file and add a section to test the *transferability* of the potential. This requires us to select a set of *test configurations* in order to compare the all-electron (AE) to the non-local pseudo- (NL) eigenvalues. Let's try the +1, +2, and +2.5 states:

```

[Atom]
Al
5
100 2.00 -
200 2.00 -
210 6.00 -
300 2.00 -
310 1.00 -

[Pseudo]
2 1.6 1.6

```

opt

[Optinfo]

3.24 10

3.00 10

[XC]

lda

[Configs]

3

300 1.00 -

310 1.00 -

300 1.00 -

310 0.00 -

300 0.50 -

310 0.00 -

With the [Configs] keyblock specified, the test configurations will be computed. Note that we will rerun the `ae ps nl` steps, then run the `tc` step to do run the test configurations and then end with a `rpt` step to get the report file. Rerunning the `ae ps nl` steps is actually not necessary if no changes have been made to the param file, however, it doesn't hurt to do this quick step to avoid confusion later.

```
%> ./opium al al.log ae ps nl tc rpt
```

The difference between the AE and NL eigenvalues are computed and written to the report file. Also, the total energy difference between each configuration is computed and the AE and NL values of these are subtracted, yield the second difference, sometimes called “delta,delta E”.

```
%> grep AE-NL al.rpt
```

AE-NL:Orbital Filling		Eigenvalues [mRy]	Norm[1e-3]
AE-NL-	-----		
AE-NL-	100 1.000	-4.5982455891	-1.3428860415
AE-NL-	210 1.000	-2.2377150108	1.1426541762
AE-NL-	total error =	6.8359605999	2.4855402177
AE-NL:Orbital Filling		Eigenvalues [mRy]	Norm[1e-3]
AE-NL-	-----		
AE-NL-	100 1.000	-13.9369754322	-3.3492860618
AE-NL-	210 0.000	-8.2407469767	2.8142654681
AE-NL-	total error =	22.1777224089	6.1635515299
AE-NL:Orbital Filling		Eigenvalues [mRy]	Norm[1e-3]
AE-NL-	-----		
AE-NL-	100 0.500	-33.6477246420	-8.7283576528
AE-NL-	210 0.000	-21.8008906486	0.5785512938
AE-NL-	total error =	55.4486152906	9.3069089467
AE-NL-	i j DD[mRy] DD[meV]		
AE-NL-	-----		
AE-NL-	0 1 -1.718698 -23.384089		
AE-NL-	0 2 -6.373866 -86.720907		
AE-NL-	0 3 -17.499787 -238.096853		
AE-NL-	1 2 -4.655168 -63.336818		
AE-NL-	1 3 -15.781089 -214.712764		
AE-NL-	2 3 -11.125921 -151.375946		

We see from the eigenvalue and tail norm errors that the transferability is getting worse as Al becomes more ionized. This is because the reference configuration is the neutral atom. This is not a very good choice for an aluminum oxide calculation. A charged reference configuration would probably do much better. Let's try the following param file:

[Atom]

```

A1
5
100 2.00 -
200 2.00 -
210 6.00 -
300 0.50 -
310 0.10 -

[Pseudo]
2 1.6 1.6
opt

[Optinfo]
3.24 10
3.00 10

[XC]
lda

[Configs]
3
300 1.00 -
310 1.00 -

300 1.00 -
310 0.00 -

300 0.50 -
310 0.00 -

```

This reference configuration can lead to much better transferability near more the positive charged aluminum species:

AE-NL:Orbital Filling	Eigenvalues [mRy]	Norm [1e-3]
AE-NL- 100 1.000	14.2169466969	6.0472831605
AE-NL- 210 1.000	7.5404291624	3.1439713755
AE-NL- total error =	21.7573758593	9.1912545360
AE-NL:Orbital Filling	Eigenvalues [mRy]	Norm [1e-3]
AE-NL- 100 1.000	12.3774080576	4.3497030850
AE-NL- 210 0.000	8.0982037680	3.0909271570
AE-NL- total error =	20.4756118256	7.4406302420
AE-NL:Orbital Filling	Eigenvalues [mRy]	Norm [1e-3]
AE-NL- 100 0.500	-3.5709710624	-1.0168880683
AE-NL- 210 0.000	-2.5661761925	-0.7632197974
AE-NL- total error =	6.1371472549	1.7801078657
AE-NL- i j	DD [mRy]	DD [meV]
AE-NL- 0 1	-11.687932	-159.022503
AE-NL- 0 2	-3.119241	-42.439458
AE-NL- 0 3	-0.122980	-1.673224
AE-NL- 1 2	8.568691	116.583044
AE-NL- 1 3	11.564953	157.349279
AE-NL- 2 3	2.996261	40.766234

Another way to qualitative check the transferability of the pseudopotential is to plot the logarithmic derviatives. This can easily be done by adding the [Loginfo] key block 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, etc. Also, you must specify the radius and energy range for the calculation. For instance, Let’s use the compute the

logarithmic derivatives over the range of -3.0 to +3.0 Ry at 1.7 a.u. (the radius must be larger than all of the cutoff radii).

```
[Atom]
Al
5
100 2.00 -
200 2.00 -
210 6.00 -
300 0.50 -
310 0.10 -

[Pseudo]
2 1.6 1.6
opt

[Optinfo]
6.3 10
6.3 10

[XC]
lda

[Configs]
3
300 1.00 -
310 1.00 -

300 1.00 -
310 0.00 -

300 0.50 -
310 0.00 -

[Loginfo]
0
1.7 -3.0 3.0
```

```
%> ./opium al al.log ae ps nl plot logd
```

Here, the vertical lines mark the location of the eigenvalues for this configuration. The hallmark of a pseudopotential with good transferability is to have the all-electron and pseudo logarithmic derivatives agree closely for a region of about 1-2 Ry around the eigenvalues. We can see that this is true for this potential.

**To Explore:** We just saw how selecting the reference state can really change the transferability properties of the pseudopotential. Using aluminum, investigate how different reference states effect the transferability over a specific range of ionization states. Is the pseudopotential more transferable when reference state is more ionized or neutral? How sensitive is this behavior for different cutoff radii?

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[1] N. Troullier and J. L. Martins, Phys.Rev.B **43** 1993 (1991).

[2] A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, Phys. Rev.B **41**, 1227 (1991).

## All electron wavefunctions for Al

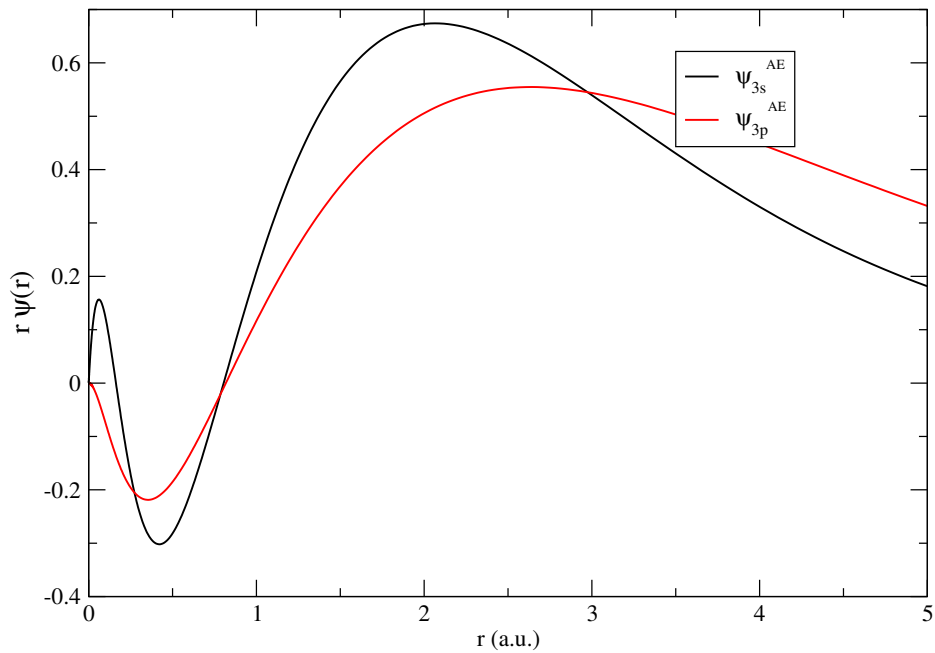


FIG. 1: Aluminum all-electron wavefunctions

Log\_derivs for Al at  $r_{\log} = 1.70$ 

Optimized Pseudopotential Method

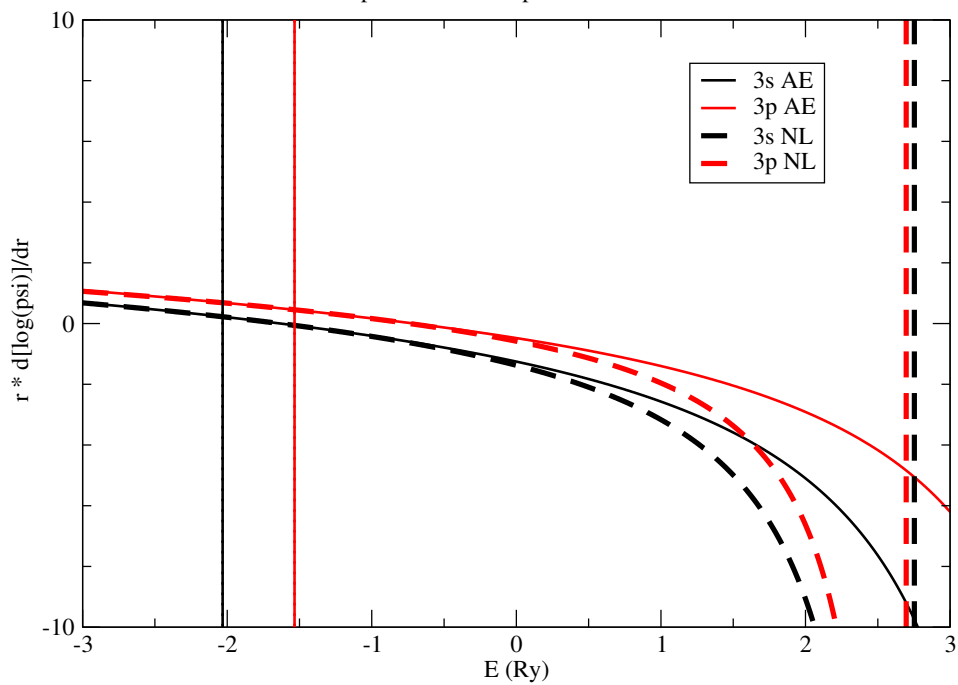


FIG. 2: Aluminum logarithmic derivatives