Opium Tutorial 3: Copper

Goal: The purpose of this tutorial is to introduce the concept of ghosts and the choice of the local potential.

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

```
[Atom]
Cu
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
310  6.00  -
400  0.10  -
410  0.10  -
320  9.80  -

[XC]
lda

[Pseudo]
3 2.20 2.20 2.20
opt

[Optinfo]
5.50 10
5.50 10
7.07 10

[Configs]
3
400  0.00  -
410  0.00  -
320 10.00  -

400  0.50  -
410  0.00  -
320  9.50  -

400  1.00  -
410  0.00  -
320  9.00  -
```

This is a reasonable starting guess for the cutoff radii since the interatomic distance of is about 2.55 Å(4.82 a.u.) in the fcc solid. Let's construct this potential, run the test configurations, and analyze the report file:

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

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

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

                        Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
```

```
    ------------------------------------------------------------------------
        400      0.010275      0.139794      0.001027      0.013979         no
        410      0.006933      0.094322      0.000693      0.009432         no
        320      0.024874      0.338427      0.243764      3.316582        yes

                  Tot. error =               0.245485      3.339994

        320 SHOULD NOT be used as the local potential

### NL report ########################################


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ------------------------------------------------------------------
        100      0.100        -0.9063858437       0.6167386735      no
        210      0.100        -0.5124462749       0.8177457148      no
        320      9.800        -1.1214340941       0.0485556830      no

         ========== No ghosts in potential!!==========

      E_tot =      -81.5567915983 Ry
.
.
.
```

The PS section shows that there is very small convergence error at 50 Ry (q_c^2). Also, clearly stated is the fact that the d potential can not be used as the local potential in the Kleinman-Bylander form. Either s or p is a possible choice. The default is always the s potential if an alternative is not specified in the [KBdesign] block.

Let's see how the transferability looks for s as the local potential:

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

```
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      0.000        -2.2134141587      -1.0426483517
 AE-NL- 210      0.000        -1.1629364086      -0.6419028506
 AE-NL- 320     10.000         0.1483779722       0.5374671553
 AE-NL-  total error =         3.5247285395       2.2220183576
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      0.500         2.9682975732       1.4511497784
 AE-NL- 210      0.000         1.3667767587       0.9211954180
 AE-NL- 320      9.500        -4.3912481717      -0.9258354236
 AE-NL-  total error =         8.7263225036       3.2981806200
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      1.000         6.3379012046       3.3986335790
 AE-NL- 210      0.000         2.3997799957       1.9173981438
 AE-NL- 320      9.000       -20.7896096228      -2.3438768499
 AE-NL-  total error =        29.5272908230       7.6599085727
 AE-NL-   i   j         DD[mRy]        DD[meV]
 AE-NL- ----------------------------------------
 AE-NL-   0   1        -0.196901      -2.678978
 AE-NL-   0   2        -1.106071     -15.048872
 AE-NL-   0   3        -9.248366    -125.830492
 AE-NL-   1   2        -0.909170     -12.369894
 AE-NL-   1   3        -9.051465    -123.151514
 AE-NL-   2   3        -8.142295    -110.781620
```

Let's specify the p channel as local and see how this affects the output:

```
[Atom]
```

```
Cu
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
310  6.00  -
400  0.10  -
410  0.10  -
320  9.80  -

[XC]
lda

[Pseudo]
3 2.20 2.20 2.20
opt

[Optinfo]
5.50 10
5.50 10
7.07 10

[KBdesign]
p

.
.
.
```

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

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

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

                      Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
        400      0.010275      0.139794      0.001027      0.013979         no
        410      0.006933      0.094322      0.000693      0.009432         no
        320      0.024874      0.338427      0.243764      3.316582        yes

                  Tot. error =               0.245485      3.339994

        320 SHOULD NOT be used as the local potential

### NL report ########################################


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ---------------------------------------------------------------
        100      0.100        -0.9063858437       0.6167386735      no
        210      0.100        -0.5124462749       0.8177457148      no
        320      9.800        -1.1214340941       0.0485556830      no

         ========== No ghosts in potential!!==========
```

```
      E_tot =      -81.5567915983 Ry
.
.
.
```

Notice that *the PS and NL output is independant of the local potential*. The only differences will occur in the transferability section:

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

```
AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
AE-NL- ------------------------------------------------------------
AE-NL- 100      0.000        -2.2875427618      -3.2341842610
AE-NL- 210      0.000        -1.2272016240      -0.7942157624
AE-NL- 320     10.000        -0.5832868859       0.5598991754
AE-NL-  total error =         4.0980312717       4.5882991988
AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
AE-NL- ------------------------------------------------------------
AE-NL- 100      0.500         2.8906600607       5.0170138322
AE-NL- 210      0.000         1.1359464819       1.0082096546
AE-NL- 320      9.500        -4.6464395788      -1.0110498468
AE-NL-  total error =         8.6730461215       7.0362733335
AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
AE-NL- ------------------------------------------------------------
AE-NL- 100      1.000         5.1852169822      15.7437947372
AE-NL- 210      0.000         0.3293516258       1.4717697721
AE-NL- 320      9.000       -27.5975860427      -2.7514802025
AE-NL-  total error =        33.1121546507      19.9670447118
AE-NL-   i   j         DD[mRy]        DD[meV]
AE-NL- -----------------------------------------
AE-NL-   0   1        -0.135678      -1.845999
AE-NL-   0   2        -1.095737     -14.908263
AE-NL-   0   3       -10.341000    -140.696549
AE-NL-   1   2        -0.960058     -13.062264
AE-NL-   1   3       -10.205322    -138.850550
AE-NL-   2   3        -9.245264    -125.788286
```

Using the s potential as the local potential yields moderately better transferability. But both could use some improvement. Therefore, let's stick with p as the local potential and try to improve the transferability. The most direct way to fix transferability is to simply reduce the cutoff radius. Let's try reducing the radius from 2.2 to 1.8 a.u. for the s and p states. For the d state we will try 2.0 a.u. since it is a much more localized orbital and, therefore, reducing the cutoff radius will increase the energy cutoff rapidly.

```
[Atom]
Cu
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
310  6.00  -
400  0.10  -
410  0.10  -
320  9.80  -

[XC]
lda

[Pseudo]
3 1.80 1.80 2.0
opt
```

```
.
.
.
```

```
  %> ./opium cu cu.log ae ps nl rpt
  %> cat cu.rpt
```

Again, let's check the PS and NL report:

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

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

                        Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
        400      0.014366      0.195463      0.001437      0.019546         no
        410      0.090536      1.231800      0.009054      0.123180        yes
        320      0.164605      2.239560      1.613125     21.947688        yes

                  Tot. error =              1.623615     22.090414

        410 SHOULD NOT be used as the local potential
        320 SHOULD NOT be used as the local potential

### NL report ########################################


NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ------------------------------------------------------------------
        100      0.100        -0.9063858437       0.7924724901     yes
        210      0.100        -0.5124462749       0.9145820216      no
        320      9.800        -1.1214340941       0.0679081466      no

  !!ERROR!! Ghosts are present in pseudopotential
  !!ERROR!! See log file for more information

      E_tot =      -83.0732014322 Ry
.
.
.
```

We see that by reducing the cutoff radii makes the s potential develop a *ghost* state. Remember that the PS report tells whether a particular state has ghosts if it is used as the local potential (notice that the only "no" is the s state). The NL section shows, for a given choice of local potential, whether a state has a ghost or not (notice that choosing p as local results in the s state having a ghost). To put it simply, *one* of the rows in the PS report needs to be "no", and *all* of the rows in the NL report need to be "no".

So, let's switch back to s as the local potential and check the transferability.

```
[Atom]
Cu
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
310  6.00  -
400  0.10  -
```

```
410  0.10  -
320  9.80  -

[XC]
lda

[Pseudo]
3 1.80 1.80 2.00
opt

[Optinfo]
5.50 10
5.50 10
7.07 10

[KBdesign]
s
.
.
.
```

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

```
AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
AE-NL- ------------------------------------------------------------
AE-NL- 100      0.000        -1.7218297632      -0.7345680920
AE-NL- 210      0.000        -0.9146979786      -0.4446581528
AE-NL- 320     10.000        -1.0984873723       0.5367412494
AE-NL-  total error =         3.7350151141       1.7159674942
AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
AE-NL- ------------------------------------------------------------
AE-NL- 100      0.500         2.5195280715       1.0950077643
AE-NL- 210      0.000         1.2218201840       0.6963348560
AE-NL- 320      9.500        -1.4355442651      -0.9647392378
AE-NL-  total error =         5.1768925207       2.7560818580
AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
AE-NL- ------------------------------------------------------------
AE-NL- 100      1.000         5.5879581699       2.8177084976
AE-NL- 210      0.000         2.4314762010       1.7614992801
AE-NL- 320      9.000       -11.2244344356      -2.5674015420
AE-NL-  total error =        19.2438688065       7.1466093197
AE-NL-   i   j         DD[mRy]        DD[meV]
AE-NL- ----------------------------------------
AE-NL-   0   1        -0.031779      -0.432382
AE-NL-   0   2        -0.602219      -8.193609
AE-NL-   0   3        -5.380415     -73.204314
AE-NL-   1   2        -0.570439      -7.761227
AE-NL-   1   3        -5.348636     -72.771932
AE-NL-   2   3        -4.778196     -65.010704
```

We see that the transferability has improved significatly, espescially in the s^1d^9 configuration.

To Explore: Can you find a reference state and cutoff radii that ever yield a ghostless pseuopotential for the d state being local?