Opium Tutorial 4: Titanium

Goal: The purpose of this tutorial is to demonstrate the construction of a pseudopotential with semicore states.

In many atoms, espescially towards the left of the periodic table, there are significant interactions between the valence and near-valence core states. These high-lying core states are often referred to as *semicore* states. Significant errors will occur in the target calculation if these orbitals are simply incorporated into the pseudopotential core. Therefore, it is necessary to explicitly include these states as part of the valence.

We will now demonstrate how to construct a semicore pseudopotential. Let's begin with the following param file:

```
[Atom]
Ti
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
310  6.00  -
320  0.00  -
400  0.00  -
410  0.00  -

[Pseudo]
5 1.7 1.6 1.9 1.7 1.6
opt

[XC]
lda

[Optinfo]
7.0 10
7.5 10
7.8 10
7.0 10
7.5 10

[Configs]
4
#
300  2.00  -
310  6.00  -
320  2.00  -
400  2.00  -
410  0.00  -
#
300  2.00  -
310  6.00  -
320  2.00  -
400  1.00  -
410  0.00  -
#
300  2.00  -
310  6.00  -
320  2.00  -
400  0.00  -
410  0.00  -
#
300  2.00  -
310  6.00  -
320  1.00  -
400  0.00  -
```

```
410  0.00  -
```

Here we have specified five valence states: $3s$,$3p$,$3d$,$4s$, and $4p$. Unlike other potentials, there are two s and two p states. The $3s$ and $3p$ are the semicore orbitals, the rest are valence.

We will construct one pseudopotential for each angular momemtum *type*, not for each valence orbital. Currently, OPIUM's functionality is limited to what is termed *single* projector pseudopotentials. Constructing multiple projectors per angular momemtum type can be done, but the target solid-state program must allow for this type of pseudopotential; not all do.

To clarify, the $4s$ and $4p$ orbitals are not used when constructing the pseudopotential. This is why these orbitals have no population in the reference state. The inclusion of these orbitals allows them to be considered in the transferability tests. Just as in the solid-state code, the $4s$ and $4p$ states will use the $3s$ and $3p$ potentials for transferability testing.

We have specified five cutoff radii as well as five entries in the `[Optinfo]` keyblock even though only three (one for s, p, and d) potentials will be constructed. These extra two entries are used for plotting and other output features. To reduce confusion, just keep the entries for a particular l value the same (notice that the reference state defines the order of the rest of the keyblocks).

Let's run this param file to see if we can continue onto transferability testing:

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

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

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

                      Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
        300      0.014566      0.198176      0.029131      0.396352         no
        310      0.009667      0.131528      0.058003      0.789168         no
        320      0.018412      0.250510      0.000000      0.000000         no

                  Tot. error =              0.087134      1.185520


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


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ------------------------------------------------------------------
        100      2.000        -8.2870763204       0.0414433365      no
        210      6.000        -6.5662526201       0.0943408885      no
        320      0.000        -3.8784059829       0.0879573998      no
        200      0.000        -2.9378838544       0.7387697202      no
        310      0.000        -2.3207879291       0.8687177944      no

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

      E_tot =     -109.3857318047 Ry
.
.
.
```

As we see, the potential is well converged for the given cutoff wavevectors and there are no ghosts at all. Let's move onto the transferability testing:

```
%> ./opium ti ti.log ae ps nl tc rpt
%> grep AE-NL ti.rpt
```

```
.
.
.
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000       -57.9266724784      -0.2337222836
 AE-NL- 210      6.000       -52.2842382626      -0.0115419383
 AE-NL- 320      2.000       -26.4340328700       8.6274515531
 AE-NL- 200      2.000        15.1027002621      29.6167845983
 AE-NL- 310      0.000       -13.3867989655       2.4042003989
 AE-NL-  total error =       165.1344428385      40.8937007721
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000       -25.6395070140       0.1101722815
 AE-NL- 210      6.000       -21.7153937207       0.7725263942
 AE-NL- 320      2.000        -0.0256058946      14.2604867865
 AE-NL- 200      1.000        39.5827899427      39.0560422065
 AE-NL- 310      0.000        -4.9784019867       6.7445401387
 AE-NL-  total error =        91.9416985587      60.9437678073
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000        27.5397990237       0.8249290981
 AE-NL- 210      6.000        28.0810962346       2.3654124477
 AE-NL- 320      2.000        43.3855119642      18.6077250860
 AE-NL- 200      0.000        81.3677820294      52.7043374015
 AE-NL- 310      0.000        17.1488582095      11.8748045916
 AE-NL-  total error =       197.5230474615      86.3772086249
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000        30.2278000049       0.5877158002
 AE-NL- 210      6.000        30.8743404960       1.6243663443
 AE-NL- 320      1.000        44.3311725724       8.1294589295
 AE-NL- 200      0.000       148.0416011340      79.1457976352
 AE-NL- 310      0.000        46.7399072857      21.6667024658
 AE-NL-  total error =       300.2148214930     111.1540411750
 AE-NL-   i   j          DD[mRy]         DD[meV]
 AE-NL- -----------------------------------------
 AE-NL-   0   1       -157.894305    -2148.262545
 AE-NL-   0   2       -131.483983    -1788.931632
 AE-NL-   0   3        -73.502902    -1000.058437
 AE-NL-   0   4        -26.474957     -360.210323
 AE-NL-   1   2         26.410322      359.330913
 AE-NL-   1   3         84.391403     1148.204109
 AE-NL-   1   4        131.419348     1788.052223
 AE-NL-   2   3         57.981081      788.873196
 AE-NL-   2   4        105.009026     1428.721309
 AE-NL-   3   4         47.027945      639.848114

.
.
```

The transferability tests considered here cover a range of 0 to +3 oxidation states, with the reference state being +4. An ionic reference state is *necessary* since the $4s$ and $4p$ states must be empty in the reference configuration.

The transferability is quite dissapointing. Let's try pulling in the cutoff radii.

```
[Atom]
Ti
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
```

```
310  6.00  -
320  0.00  -
400  0.00  -
410  0.00  -

[Pseudo]
5 1.3 1.3 1.3 1.3 1.3
opt

[XC]
lda

[Optinfo]
7.0 10
7.5 10
7.8 10
7.0 10
7.5 10
.
.
.
```

Again, we run the first section to check for ghosts and q-space convergence:

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

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

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

                        Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]          [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
        300     0.735787     10.010899      1.471574     20.021799         no
        310     0.027017      0.367589      0.162104      2.205537         no
        320    14.397956    195.894267      0.000000      0.000000         no

                    Tot. error =              1.633678     22.227336


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


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ---------------------------------------------------------------
        100     2.000        -8.2870763205       0.1863245872      no
        210     6.000        -6.5662526202       0.2353338125      no
        320     0.000        -3.8784059830       0.3323409071      no
        200     0.000        -2.8110650044       0.8812522328      no
        310     0.000        -2.2765746078       0.9043194766      no

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

      E_tot =     -109.1470757437 Ry
.
.
.
```

Again, there are no ghosts. The convergence looks good, but it is a little misleading. The first two columns of errors

in the PS report is the convergence error *per electron* the next two are absolute convergence errors. Therefore, the last two columns are weighted by the occupation of the reference state. So, as long as the *d*-occupation is strictly zero in the target calculation, the pseudopotential may do quite well with respect to convergence. However, any significant d-character will be unconverged at the estimated energy cutoff (61 Ry).

Because of the d-state convergence, we must either pull out the cutoff radius or increase the cutoff wavevector. Let's try pulling the d cutoff radius back out to 1.5 a.u. and check the convergence and the transferability:

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

```
[Atom]
Ti
8
100  2.00  -
200  2.00  -
210  6.00  -
300  2.00  -
310  6.00  -
320  0.00  -
400  0.00  -
410  0.00  -

[Pseudo]
5 1.3 1.3 1.5 1.3 1.3
opt
.
.
.



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

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

                        Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
        300      0.735787     10.010899      1.471574     20.021799         no
        310      0.027017      0.367589      0.162104      2.205537         no
        320      1.916903     26.080804      0.000000      0.000000         no

                  Tot. error =              1.633678     22.227336


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


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ---------------------------------------------------------------
        100      2.000        -8.2870763203       0.1863245871      no
        210      6.000        -6.5662526201       0.2353338125      no
        320      0.000        -3.8784059828       0.2242218457      no
        200      0.000        -2.8110650044       0.8812522328      no
        310      0.000        -2.2765746077       0.9043194766      no

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

      E_tot =     -109.1470757449 Ry
.
```

```
.
.

  %> grep AE-NL ti.rpt

.
.
.
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000       -24.7244298191      -0.1495660753
 AE-NL- 210      6.000       -23.0161219713       0.3511027409
 AE-NL- 320      2.000        -9.4245259552       9.0408510715
 AE-NL- 200      2.000         5.5851171878       8.6187475392
 AE-NL- 310      0.000        -5.8114572216       1.0370541139
 AE-NL-  total error =        68.5616521549      19.1973215408
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000       -11.2205015171       0.1503201208
 AE-NL- 210      6.000       -10.1367218648       0.8111021861
 AE-NL- 320      2.000         2.0207343089      11.4303655192
 AE-NL- 200      1.000        15.3860880889      11.2619929252
 AE-NL- 310      0.000        -2.4945207785       2.7473131360
 AE-NL-  total error =        41.2585665582      26.4010938873
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000        11.3650120939       0.7781255405
 AE-NL- 210      6.000        11.2088392994       1.7610572012
 AE-NL- 320      2.000        21.1532184971      13.9555742514
 AE-NL- 200      0.000        32.0592951281      14.9981107470
 AE-NL- 310      0.000         6.1742508854       4.6961382631
 AE-NL-  total error =        81.9606159039      36.1890060032
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      2.000        15.3070242896       0.6687820200
 AE-NL- 210      6.000        15.3141640096       1.3752676394
 AE-NL- 320      1.000        23.9941052750       7.6638939553
 AE-NL- 200      0.000        62.9879355577      23.1727245012
 AE-NL- 310      0.000        20.1828734229       8.5532727132
 AE-NL-  total error =       137.7861025548      41.4339408292
 AE-NL-   i   j         DD[mRy]        DD[meV]
 AE-NL- ----------------------------------------
 AE-NL-   0   1       -71.869310    -977.832270
 AE-NL-   0   2       -61.761760    -840.311982
 AE-NL-   0   3       -39.010837    -530.769739
 AE-NL-   0   4       -14.745177    -200.618449
 AE-NL-   1   2        10.107550     137.520288
 AE-NL-   1   3        32.858473     447.062531
 AE-NL-   1   4        57.124133     777.213821
 AE-NL-   2   3        22.750924     309.542242
 AE-NL-   2   4        47.016584     639.693533
 AE-NL-   3   4        24.265660     330.151290
.
.
.
```

We could continue the process of pulling descreasing the cutoff radii and increasing the cutoff wavevectors and obtain an even more accurate pseudopotential, at the cost of a harder pseudopotential. However, better results can be obtained by invoking the designed non-local approach [1] which will be left to a later tutorial.

[1] N. J. Ramer and A. M. Rappe, Phys. Rev. B **59**, 12471 (1999).