Opium Tutorial 5: Iron

Goal: The purpose of this tutorial is to demonstrate the construction of a pseudopotential with a partial core correction.

As in pseudopotentials with semicore orbitals, there are other cases in which it is important to include more than just the valence orbitals in the pseudopotential. Another common example is the inclusion of a *nonlinear* or *partial core correction*.

In a partial core correction, a static core charge is carried along with the pseudopotential. This extra charge reduces errors due to the *descreening* of the exchange-correlation potential. This is often applied to the case of spin-polarized solid-state calculations.

The core charge is termed a *partial* core correction due to the fact only part of the true core density is included in the pseudopotential. Including all of the core would be prohibitively expensive due to the sharply peaked regions near the nucleus. Therefore, *before* some cutoff radius (r_{pcc}) the core density is replaced by a smooth density.

Note: If the partial core correction radius is fairly small, additional covergence testing will need to be performed in the target calculation (the FFT mesh may need to be made more dense). Always check the convergence of parameters involving the charge density when including a partial core correction.

Including the partial core correction in OPIUM is quite simple, just add the `[pcc]` keyblock to the param file and specify (r_{pcc}) and the method to smooth the core.

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

[Pseudo]
3 2.30 2.30 2.30
opt

[Optinfo]
7.07  10
7.07  10
7.07  10

[XC]
lda

[Pcc]
1.2
lfc
.
.
.
```

As shown, the method to smooth the core is that of Louie, Froyen and Cohen[1]. Also avaliable is the method of Fuchs and Scheffler [2](by replacing `lfc` with `fuchs`). Let's construct the potential and plot the valence, core and partial core density.

```
%> ./opium fe fe.log ae ps nl plot den
```

As you can see, the large peaks from the core density are smoothed out in the region between r_{pcc} and the nucleus. An acceptable r_{pcc} should be small enough such that there is appreciable overlap between the partial core and the

valence density. But, as the partial core radius is made smaller, the partial density gets more strongly peaked. This increases the cost of faithfully representing the partial core.in the target calculation.

Now, we continue with this potential as we have before:

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

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

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

                        Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
400      0.006122      0.083295      0.012244      0.166590     no
410      0.000591      0.008043      0.000000      0.000000     no
320      0.025927      0.352749      0.155559      2.116494    yes

                 Tot. error =               0.167803      2.283084

320 SHOULD NOT be used as the local potential

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


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ---------------------------------------------------------------
100  2.000       -0.3965065480   0.7006851926     no
210  0.000       -0.1074863901   0.8934619782     no
320  6.000       -0.5896524124   0.0623617903     no

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

      E_tot =      -45.6060980561 Ry
.
.
.
```

We see that the convergence error is quite small and that there are no ghosts with the s potential chosen as local. What about the transferability?

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

```
.
.
.
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      1.000        -0.8562223210      -2.4084895280
 AE-NL- 210      0.000         0.8665798182      -0.2631166727
 AE-NL- 320      7.000        -9.8612973995       1.1613596499
 AE-NL-  total error =        11.5840995387       3.8329658506
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      0.000         3.6487417857      -2.2046999349
 AE-NL- 210      0.000         4.6943936295       0.7237461995
 AE-NL- 320      8.000       -10.8285874308      -0.4336429834
 AE-NL-  total error =        19.1717228460       3.3620891178
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
```

```
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      1.330        -0.8663210293      -1.7928347865
 AE-NL- 210      0.000         0.4803426596      -0.2693273743
 AE-NL- 320      6.670        -6.3801378782       1.0946108182
 AE-NL-  total error =         7.7268015671       3.1567729790
 AE-NL-   i   j         DD[mRy]        DD[meV]
 AE-NL- ----------------------------------------
 AE-NL-   0   1         3.983617      54.199898
 AE-NL-   0   2        16.516136     224.713587
 AE-NL-   0   3         1.571338      21.379153
 AE-NL-   1   2        12.532519     170.513689
 AE-NL-   1   3        -2.412279     -32.820745
 AE-NL-   2   3       -14.944798    -203.334434
.
.
.
```

The transferability looks adequate, but the cutoff radii are somewhat large (core overlap will occur in the bcc structure). Let's try reducing the core radii:

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

[Pseudo]
3 2.00 2.00 2.00
opt
.
.
.
```

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

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

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

                       Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]        [meV]        Ghost
    ------------------------------------------------------------------------
        400      0.002336      0.031779      0.004671      0.063558        yes
        410      0.009350      0.127210      0.000000      0.000000        yes
        320      0.119586      1.627046      0.717514      9.762275        yes

                  Tot. error =              0.722185      9.825833

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

```
        !!ERROR!! There are no choices for local potential

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


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ------------------------------------------------------------------
        100      2.000        -0.3965065480       0.8146375109      no
        210      0.000        -0.1074863901       0.9406500193     yes
        320      6.000        -0.5896524124       0.1014472799      no

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

      E_tot =      -46.0085239071 Ry
.
.
.
```

This is not good! Pulling in the cutoff radii results in having no channel avaliable as the local potential. However, looking at the `NL` section, we see that the p potential is the only channel with a ghost when s (the default) is chosen as the local potential. Therefore, we may be able to pull the p core radius back out and have a usable potential:

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

[Pseudo]
3 2.00 2.30 2.00
opt
.
.
.
```

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

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

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

                      Pseudopotential convergence error
    Orbital      [mRy/e]       [meV/e]         [mRy]         [meV]        Ghost
    ------------------------------------------------------------------------
        400      0.002336      0.031779      0.004671      0.063558         no
        410      0.000591      0.008043      0.000000      0.000000         no
        320      0.119586      1.627046      0.717514      9.762275        yes

                  Tot. error =              0.722185      9.825833
```

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

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


 NL:Orbital    Filling       Eigenvalues[Ry]          Norm       Ghost
    ------------------------------------------------------------------
        100      2.000        -0.3965065480       0.8146375109      no
        210      0.000        -0.1074863901       0.8934619782      no
        320      6.000        -0.5896524124       0.1014472790      no

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

      E_tot =      -46.0085239336 Ry
.
.
.
```

This removed the ghosts. Since we still have a low convergence error, we move onto check the transferability:

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

```
.
.
.
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      1.000         0.2853239332      -1.8680190378
 AE-NL- 210      0.000         1.4195696200       0.2976519978
 AE-NL- 320      7.000       -12.1514191833       1.2700832809
 AE-NL-  total error =        13.8563127365       3.4357543165
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      0.000         6.7878973445      -1.3438343854
 AE-NL- 210      0.000         6.2643883719       1.8731566380
 AE-NL- 320      8.000       -10.7633992225      -0.2436429537
 AE-NL-  total error =        23.8156849389       3.4606339770
 AE-NL:Orbital Filling       Eigenvalues[mRy]         Norm[1e-3]
 AE-NL- ------------------------------------------------------------
 AE-NL- 100      1.330        -0.2253601512      -1.4883638661
 AE-NL- 210      0.000         0.8025918312       0.0852035901
 AE-NL- 320      6.670        -8.6723596390       1.2366583176
 AE-NL-  total error =         9.7003116214       2.8102257738
 AE-NL-   i   j         DD[mRy]        DD[meV]
 AE-NL- ----------------------------------------
 AE-NL-   0   1         6.180204      84.085996
 AE-NL-   0   2        22.079085     300.401413
 AE-NL-   0   3         2.703022      36.776512
 AE-NL-   1   2        15.898882     216.315417
 AE-NL-   1   3        -3.477181     -47.309484
 AE-NL-   2   3       -19.376063    -263.624901
.
.
.
```

As expected, the transferability is quite similar to before.

To explore: What about simply including semicore states (such as $3s$ and $3p$) in the pseudopotential rather than adding the partial core correction? What are the pros and cons of such an approach?

[1] S.G.Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**,1738 (1982).
[2] M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).

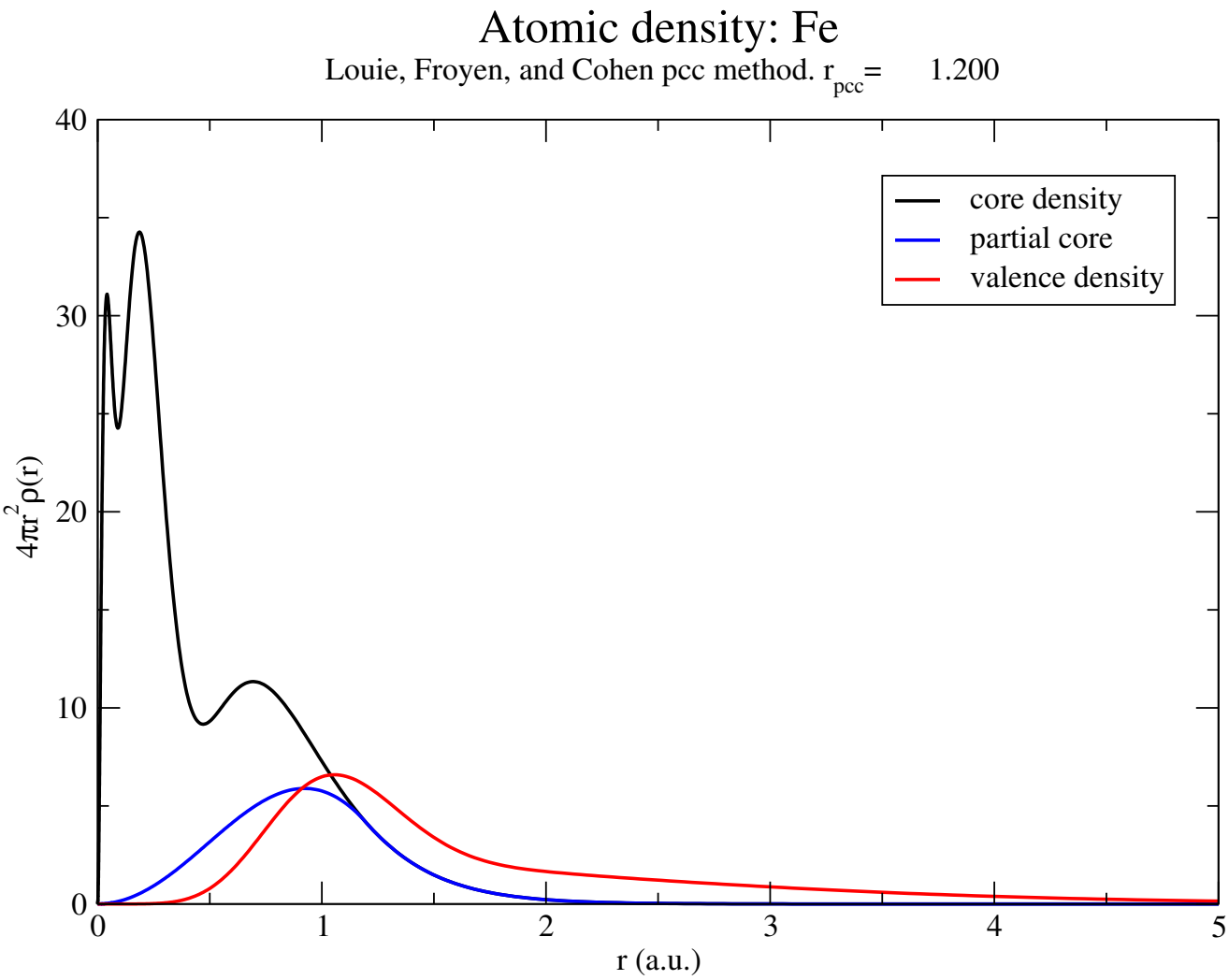

FIG. 1: LFC partial core correction for Iron