Opium Tutorial 6: Platinum

Goal: The goal of this tutorial is the demonstrate the process of constructing a scalar-relativistic pseudopotential.

The previous five tutorials have dealt only with non-relativistic pseudopotentials. For heavy atoms ($\sim$Z> 54), relativistic effects must be included in the pseudopotential. The valence states are only weakly perturbed by relativity directly. The majority of the change in the valence states comes from their interaction with the relativistic core. Therefore, relativistic effects can be incorporated into the pseudopotential for use in a non-relativistic target calculation.

The procedure that OPIUM uses for including relativity is as follows[1]. First, the Dirac-Slater equations are solved for the all-electron atom. The Dirac-Slater equations produce a pair of j-dependent wavefunctions for every state with $l > 0$ ($j = l \pm \frac{1}{2}$). Next, the j-dependent pairs of solutions must be transformed into single l-dependent states by performing a weighted average of $l + \frac{1}{2}$ and $l - \frac{1}{2}$. The j-averaged solutions are referred to as *scalar*-relativistic since they no longer contain the (vector) spin-orbit coupling terms that appear in the fully relativistic solutions. OPIUM uses the highly accurate relativistic j-averaging procedure of Grinberg *et. al.* [2].

From the user's point of view, only a minor modification is necessary for turning on the scalar-relativistic functionality. Only one keyblock, `[Relativity]` needs to be added to the param file and only the all-electron parts of the output are affected.

We will construct a platinum pseudopotential using the following param file as an example:

```
[Atom]
Pt
15
100 2.00  -
200 2.00  -
210 6.00  -
300 2.00  -
310 6.00  -
320 10.0  -
400 2.00  -
410 6.00  -
500 2.00  -
510 6.00  -
420 10.0  -
430 14.0  -
600 0.25  -
610 0.00  -
520 9.75  -

[Pseudo]
3 2.25 2.30 2.20
tm

[Relativity]
srl

[Configs]
2
#
600 1.00 -
610 0.00 -
520 9.00 -
#
600 0.00 -
610 0.00 -
520 9.00 -
#
600 1.00 -
610 0.00 -
520 8.00 -
```

Note that the *only* change to the param file compared to earlier tutorials is that we have added the keyblock `[Relativity]` and specified `srl` (the default setting is `nrl` meaning non-relativistic).

The only part of the pseudopotential construction is the all-electron step. Let's run this and analyze the output:

```
%> ./opium pt pt.log ae
%> more pt.log
```

```
.
.
.
 ========================================================================
 Begin AE calculation
 ========================================================================
 Performing relativistic AE calculation...
 XC functional is LDA (Perdew-Zunger)
 nuclear charge             = 78.000000
 number of core orbitals    = 19
 number of valence orbitals =  5
 electronic charge          = 78.000000
 ionic charge               =  0.000000


 input data for orbitals

  i    n    l    s     j     occ

  1    1    0   0.5   0.5    2.0000
  2    2    0   0.5   0.5    2.0000
  3    2    1  -0.5   0.5    2.0000
  4    2    1   0.5   1.5    4.0000
  5    3    0   0.5   0.5    2.0000
  6    3    1  -0.5   0.5    2.0000
  7    3    1   0.5   1.5    4.0000
  8    3    2  -0.5   1.5    4.0000
  9    3    2   0.5   2.5    6.0000
 10    4    0   0.5   0.5    2.0000
 11    4    1  -0.5   0.5    2.0000
 12    4    1   0.5   1.5    4.0000
 13    5    0   0.5   0.5    2.0000
 14    5    1  -0.5   0.5    2.0000
 15    5    1   0.5   1.5    4.0000
 16    4    2  -0.5   1.5    4.0000
 17    4    2   0.5   2.5    6.0000
 18    4    3  -0.5   2.5    6.0000
 19    4    3   0.5   3.5    8.0000
 20    6    0   0.5   0.5    0.2500
 21    6    1  -0.5   0.5    0.0000
 22    6    1   0.5   1.5    0.0000
 23    5    2  -0.5   1.5    3.9000
 24    5    2   0.5   2.5    5.8500


 radial grid parameters

 r(1) = .0 , r(2) =0.13E-05 , ... , r(  960) = 79.95
 aa = 4.00  bb = 70.00

 Converged in           36  iterations
    output data for orbitals
 ---------------------------
```

```
nl    s      occ         eigenvalue    kinetic energy      pot energy

1s   0.5    2.0000   -5714.77303661    7919.92396516  -14596.31709373
2s   0.5    2.0000   -1004.25283243    1879.93227771   -3580.69041019
2p  -0.5    2.0000    -963.17824162    1872.75593785   -3572.27517189
2p   0.5    4.0000    -837.78819306    1390.05271408   -2934.14836362
3s   0.5    2.0000    -235.88121797     596.18535674   -1315.00441796
3p  -0.5    2.0000    -217.33174514     586.77873733   -1301.66710078
3p   0.5    4.0000    -189.73978550     467.81427437   -1135.19417440
3d  -0.5    4.0000    -158.71550609     457.42319634   -1120.22517536
3d   0.5    6.0000    -152.73395885     431.81588125   -1081.84293603
4s   0.5    2.0000     -50.51849760     194.03498232    -556.30405412
4p  -0.5    2.0000     -42.63013963     184.54169912    -539.37166098
4p   0.5    4.0000     -36.03757750     148.53970007    -481.08985950
5s   0.5    2.0000      -7.32033733      46.64734201    -223.54340454
5p  -0.5    2.0000      -4.79378505      39.19975076    -203.41236550
5p   0.5    4.0000      -3.69985978      30.53721631    -181.67873373
4d  -0.5    4.0000     -23.07024994     132.58421060    -449.60979192
4d   0.5    6.0000     -21.83793072     125.07975923    -436.01371306
4f  -0.5    6.0000      -5.19702871      96.08310235    -375.64393315
4f   0.5    8.0000      -4.94307863      93.56888116    -370.27682840
6s   0.5    0.2500      -0.39495855       4.40073868     -66.53280277
6p  -0.5    0.0000      -0.07930806       1.73092395     -44.40555312
6p   0.5    0.0000      -0.04533286       1.12916384     -37.52000121
5d  -0.5    3.9000      -0.43627809      14.66664264    -124.03429411
5d   0.5    5.8500      -0.34280406      13.03699207    -117.32108640
```

So far, we see output similar to the non-relativistic case. The last part of the output in this section lists the orbital nl label, s quantum number $= \pm\frac{1}{2}$, occupation number, eigenvalue, and kinetic and potential energy contributions to the orbital.

```
Averaged Values

nl      occ        eigenvalue    kinetic energy      pot energy

1s    2.0000   -5714.77303661    7919.92396516  -14596.31709373
2s    2.0000   -1004.25283243    1879.93227771   -3580.69041019
2p    6.0000    -879.58487591    1550.95378867   -3146.85729971
3s    2.0000    -235.88121797     596.18535674   -1315.00441796
3p    6.0000    -198.93710538     507.46909535   -1190.68514986
3d   10.0000    -155.12657775     442.05880729   -1097.19583176
4s    2.0000     -50.51849760     194.03498232    -556.30405412
4p    6.0000     -38.23509821     160.54036642    -500.51712666
5s    2.0000      -7.32033733      46.64734201    -223.54340454
5p    6.0000      -4.06450154      33.42472780    -188.92327766
4d   10.0000     -22.33085841     128.08153978    -441.45214460
4f   14.0000      -5.05191438      94.64640453    -372.57701615
6s    0.2500      -0.39495855       4.40073868     -66.53280277
6p    0.0000      -0.05665793       1.32975054     -39.81518518
5d    9.7500      -0.38019367      13.68885230    -120.00636948


total energies
--------------

sum of eigenvalues        :   -22599.52812093
kinetic energy from ek    =    41948.79534591
el-ion interaction energy =   -92494.86917731
el-el  interaction energy =    14366.19465962
vxc    correction         :     -785.84361451
```

```
virial correction         :       11.96782803
exchange + corr energy    =     -618.27507182
kinetic energy from ev    :    41948.79535165
potential energy          :   -78746.94958951
---------------------------------------------
total energy              =   -36798.15424361   -36798.15423786
```

Once the relativistic orbitals are obtained, an average of $j+\frac{1}{2}$ and $j-\frac{1}{2}$ eigenvalues (weighted by the orbital occupation) is performed. This allows the j designation to be dropped and all orbitals are then referred to by the usual nl quantum numbers.

```
-----------------------------------------------
Starting j-averaging procedure
-----------------------------------------------
    Z atom                           : 78.000000
    Z valence                        : 10.000000
    Total valence charge             : 10.000000

6s  - eigenvalue                     : -0.394959
6p  - eigenvalue                     : -0.079308
5d  - eigenvalue                     : -0.436278
6s  + eigenvalue                     : -0.394959
6p  + eigenvalue                     : -0.045333
5d  + eigenvalue                     : -0.342804

6s  Norm rc->oo                      :  0.735962
6p  Norm rc->oo                      :  0.941377
5d  Norm rc->oo                      :  0.238649

    Converged in 101 iterations, residual: 0.213E-11

6s  Avg. eigenvalue                  : -0.394959
6p  Avg. eigenvalue                  : -0.056658
5d  Avg. eigenvalue                  : -0.380194

========================================================================
End AE calculation
========================================================================
```

Finally, in the last part of the `AE` log, the j-averaging procedure performed on the orbitals. This summarizes the changes to the logfile. There are no changes to the report file.

Naturally, there are also changes to the wavefunction plots. Let's plot the all-electron and pseudowavefunctions and see what has changed.

```
%> ./opium pt pt.log ae ps nl plot wp
```

There are *many* more things plotted compared to the non-relativistic case. The first thing to point out is the set of all-electron wavefunctions. These are labeled $\psi_{nl}^{AE}+$, $\psi_{nl}^{AE}-$, or just ψ_{nl}^{AE} for s states. The $+$ and $-$ refer to $j+\frac{1}{2}$ and $j-\frac{1}{2}$ relativistic states. In the case of platinum, there is a large difference between the $+$ and $-$ states for the p wavefunction, whereas the d orbitals are quite similar.

Next, the j-averaged wavefunctions are plotted *beyond* the cutoff radius. It is useless to average the all-electron wavefunctions before the cutoff radius since the construction of the pseudowavefunction and potential do not use this part.

Finally, the pseudowavefunctions are plotted. In a same spirit as the non-relativistic case the scalar-relativistic pseudowavefunctions agree with the j-averaged all-electron wavefunctions beyond the cutoff radius,

To explore: Just how much do the relativistic effects change the eigenvalues of the core orbitals? Using the platinum param file, investigate how the energy levels differ between relativistic and non-relativistic solutions. How does a more ionized atom compare to the neutral atom?

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[1] see G. B. Bachelet and M. Schlüter, Phys. Rev. B **25** 2103 (1982) and L. Kleinman, Phys. Rev. B **21** 2630 (1980) for more detailed information

[2] I. Grinberg, N. J. Ramer, and A. M. Rappe, Phys. Rev B **62** 2311 (2000).

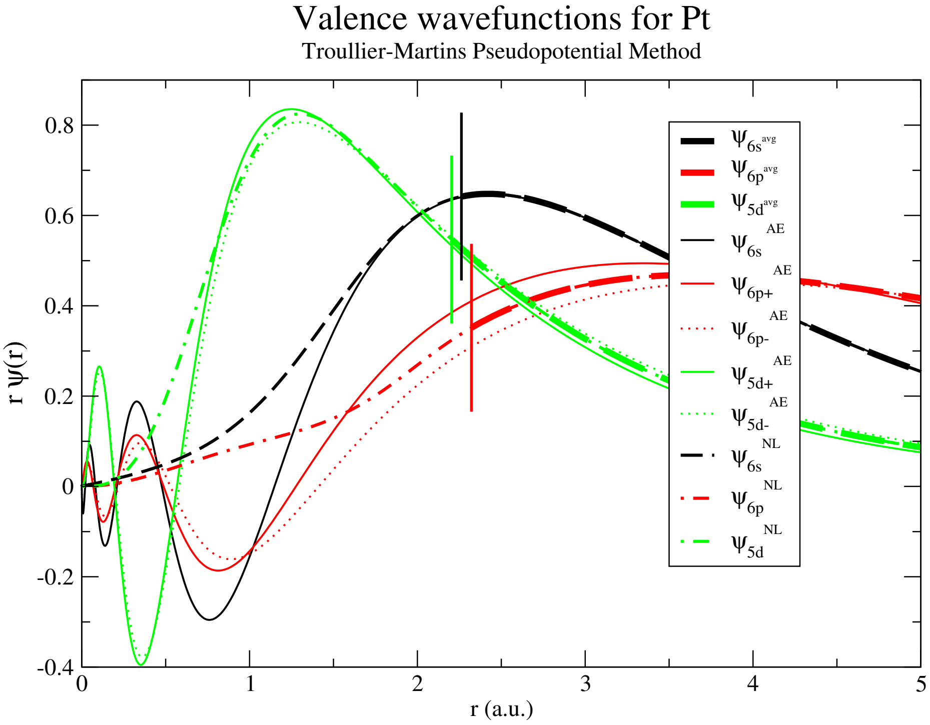

FIG. 1: Platinum all-electron and pseudowavefunctions