2025 제 6회 전자구조계산 여름학교

Lab Session: ATOM Simulations

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Contents

Program overview

❖ ATOM program

Written by Sverre Froyen @ University of California at Berkeley (1982)

- **Main functions:**

1) All-electron calculation (ae.sh)
2) Pseudopotential generation (pg.sh)
   – Norm-conserving pseudopotentials (NCPP) capable for psf, psml (SIESTA), vps (OpenMX)
3) Pseudopotential test (pt.sh)

- **Useful sources:**

(0) Installation: https://yhkimlab.github.io/YHKimLabWiki/site/build/build_atom/

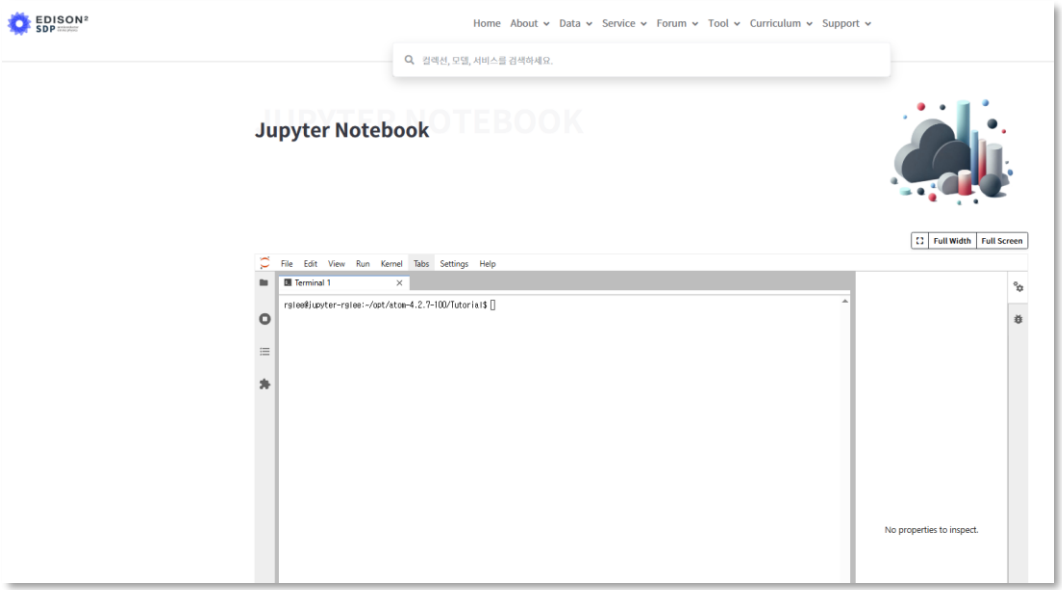
(1) ATOM manual (recommend): https://docs.siesta-project.org/projects/atom/en/latest/reference/atom.html

(2) ATOM wiki: https://docs.siesta-project.org/projects/atom/en/latest/index.html

(3) YHKLab wiki: https://yhkimlab.github.io/YHKimLabWiki/site/atom/atom_all_electron/

Program overview: preparation

1. Access the Jupyter Notebook terminal from Edison website



If you have not yet installed the ATOM program, please follow the Installation Tutorial before starting the tutorial

2. Main tutorial path: *<ATOM installation path>/atom-4.2.7-100/Tutorial*

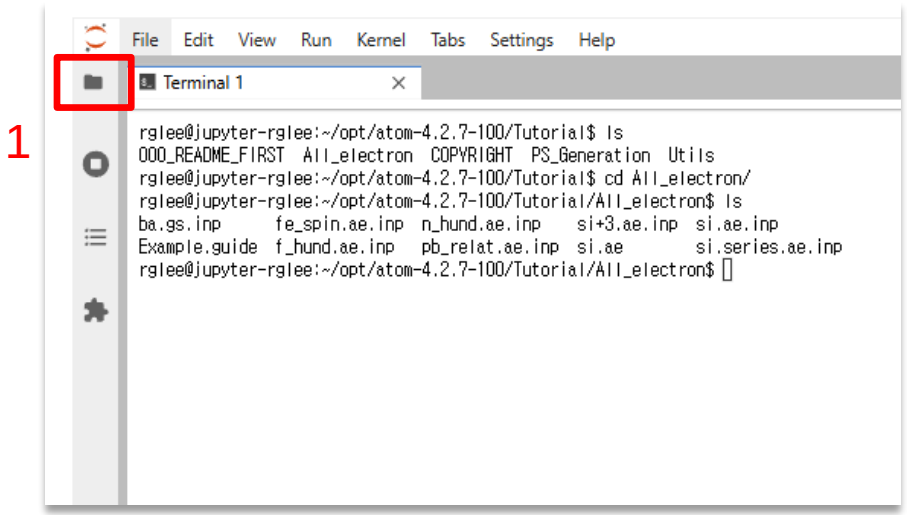
All-electron calculations

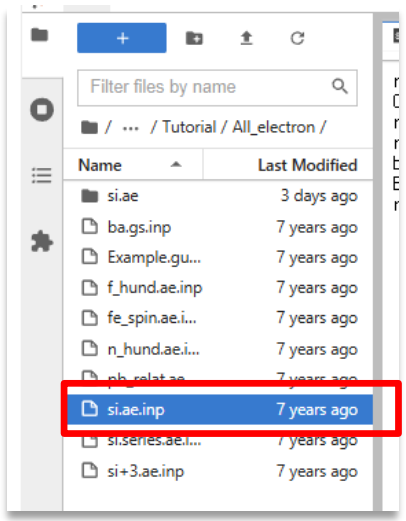
1. Access to *atom-4.2.7-100/Tutorial/All_electron*, *and open si.ae.inp file*

- *Vim (text editor)*

```
$ vi si.ae.inp
```

- *Jupyter notebook Browser,*





All-electron calculations

- ***si.ae.inp:***

```
1   ae Si Ground state all-electron
2   Si  ca
3       0.0
4    3   2
5    3   0        2.00
6    3   1        2.00
7
8  12345678901234567890123456789012345678901234567890      Ruler
9
10
```

Keep the line formatting (Ruler) in the input file
→ may cause the calculation to fail.

- **Fist line:** Calculation mode; “ae”: all-electron calculations
- **Second line:**

  (1st row) Atomic symbol ; “Si”

  (2nd row) Exchange-correlation flavor ; “ca” (LDA-CA)
- **Fourth line:**

  (1st row) Number of core electron shells; **3 (1s, 2s, 2p)**

  (2nd row) Number of valence electron shells; **2 (3s, 3p)**
- **Fifth & sixth lines:**

  (1st, 2nd ,3rd row) **Quantum number (n, l) and occupations** per each of valence electron shells (3s, 3p)

All-electron calculations

2. Perform the all-electron calculations

```
$ sh ../Utils/ae.sh si.ae.inp
==> Output data in directory si.ae
```

- Then, you will obtain,

```
$ cd si.ae
$ ls
AECHARGE  ae.gps   AEWFNR1  charge.gplot  INP       OUT  vcharge.gplot  vspin.gplot
ae.gplot  AEWFNR0  CHARGE   charge.gps    INP_COPY  RHO  vcharge.gps    vspin.gps
```

- **INP:** A copy of the input file for the calculation.
- **OUT:** Contains detailed information about the run.
- **AECHARGE:** Contains in four columns values of r, the “up” and “down” parts of the total charge density, and the total core charge density (multiplied by $4\pi r^2$)
- **RHO:** Like CHARGE, but without the $4\pi r^2$
- **AEWFNR0...AEWFNR3:** All-electron valence wavefunctions as function of radius (multiplied by r), for s, p, d, f valence

All-electron calculations

- ***OUT***:

```
Si output data for orbitals
---------------------------

nl    s      occ         eigenvalue     kinetic energy      pot energy

1s   0.0    2.0000    -130.36911240     183.01377616    -378.73491463
2s   0.0    2.0000     -10.14892694      25.89954259     -71.62102169
2p   0.0    6.0000      -7.02876268      24.42537874     -68.74331203
3s   0.0    2.0000      -0.79662742       3.23745215     -17.68692611  &v
3p   0.0    2.0000      -0.30705179       2.06135782     -13.62572515  &v
---------------------------- &v


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

sum of eigenvalues         =     -325.41601319
kinetic energy from ek     =      574.97652987
el-ion interaction energy  =    -1375.79704736
el-el  interaction energy  =      263.53000478
vxc    correction          =      -51.65548902
virial correction          =        1.40722950
exchange + corr energy     =      -39.09342414
kinetic energy from ev     =      574.97651364
potential energy           =    -1151.36046672
-------------------------------------------------
total energy               =     -576.38395308
```

Eigenvalue information (unit: Rydberg)

Total energy information (unit: Rydberg)

All-electron calculations

- Visualize the valence wavefunction

1. Modify the *ae.gps* file

```
$ vi ae.gps
#set terminal postscript enhanced color
#set output "ae.png"
set terminal pngcairo size 800,800 enhanced
set output "ae.png"
```

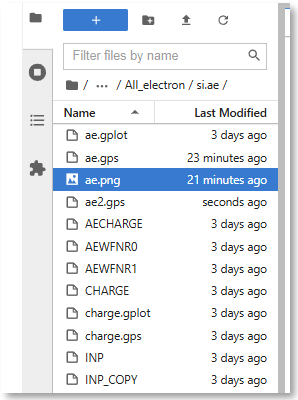
⇒ comment out

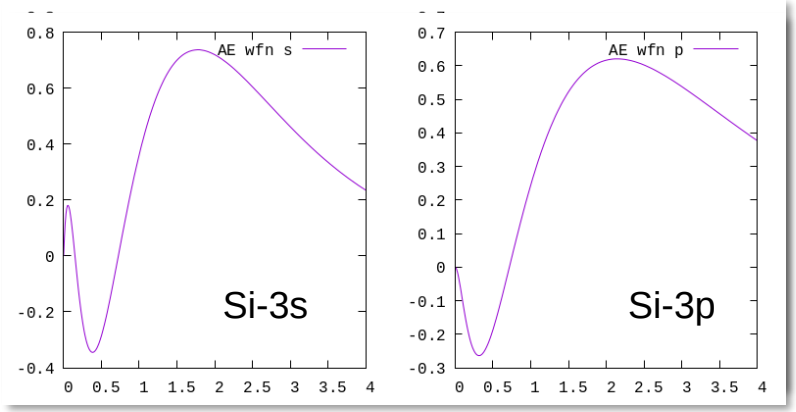
⇐ add new script

2. Run **gnuplot**

```
$ gnuplot ae.gps
```

⇒ ae.png file is generated





Pseudopotential generation

1. Access to *Tutorial/PS_Generation/Si, and open* Si.tm2.inp *file*

- *Vim (text editor)*

```
$ vi Si.tm2.inp
```

- *Jupyter notebook Browser,*

```
#
#  Pseudopotential generation for Silicon
#  pg: simple generation
#
   pg       Silicon
         tm2       3.0             # PS flavor, logder R
 n=Si c=car                        # Symbol, XC flavor,{ |r|s}
       0.0       0.0       0.0       0.0       0.0       0.0
     3    4                        # norbs_core, norbs_valence
     3    0       2.00      0.00   # 3s2
     3    1       2.00      0.00   # 3p2
     3    2       0.00      0.00   # 3d0
     4    3       0.00      0.00   # 4f0
      1.90      1.90      1.90      1.90      0.00      0.00
#
# Last line (above):
#    rc(s)     rc(p)     rc(d)     rc(f)   rcore_flag  rcore
#
#2345678901234567890123456789012345678901234567890123456789
```

- **Calculation mode = “pg”**

  Pseudopotential generation
- **Pseudopotential scheme = ‘’tm2”**

  Improved Troullier-Martins
- **Valence orbital information**

  Each orbital’s potentials will be generated
- **Pseudopotential cutoff radius for s, p, d, f orbital (in Bohr)**

Pseudopotential generation

2. Perform the pseudopotential generation calculation

```
$ sh ../../Utils/pg.sh Si.tm2.inp
==> Output data in directory Si.tm2
==> Pseudopotential in Si.tm2.vps, Si.tm2.psf, and Si.tm2.psml
```

- Then, you will obtain,

```
$ ls
Si.tm2.psf  Si.tm2.psml  Si.tm2.vps        ⇒ Pseudopotential input file (.psf)
$ cd Si.tm2                                for SIESTA
$ ls
```

⇒ (Output files)

- **PSCHARGE:** pseudo valence , and the pseudo core charge (multiplied by 4πr2)
- **PSWFNR0...PSWFNR3:** Valence pseudo wavefunctions as function of radius, for s, p, d, and f
- **PSWFNQ0...PSWFNQ3:** Fourier transform of the valence pseudo wavefunctions as a function of q
- **PSPOTR0...PSPOTR3:** Unscreened pseudopotentials as a function of r (in Bohr)
- **PSPOTQ0...PSPOTQ3:** Fourier transform of the unscreened pseudopotentials as a function of q

Pseudopotential generation

- Visualize the pseudopotentials

1. Modify the *pots.gps* file

```
$ vi pots.gps
set terminal postscript enhanced color
set output "pots.ps"

#
there_is_s=`test -f PSPOTR0 && echo 1 || echo 0`
there_is_p=`test -f PSPOTR1 && echo 1 || echo 0`
there_is_d=`test -f PSPOTR2 && echo 1 || echo 0`
there_is_f=`test -f PSPOTR3 && echo 1 || echo 0`
#
set style data lines

if (there_is_s == 0) print "No s pseudo... quiting..." ; quit
plot [0:4]  'PSPOTR0' title "V_s"
if (there_is_p == 1) replot  'PSPOTR1' title "V_p"
if (there_is_d == 1) replot  'PSPOTR2' title "V_d"
if (there_is_f == 1) replot  'PSPOTR3' title "V_f"

set terminal pngcairo size 800,800 enhanced
set output 'pot.png'
replot
```

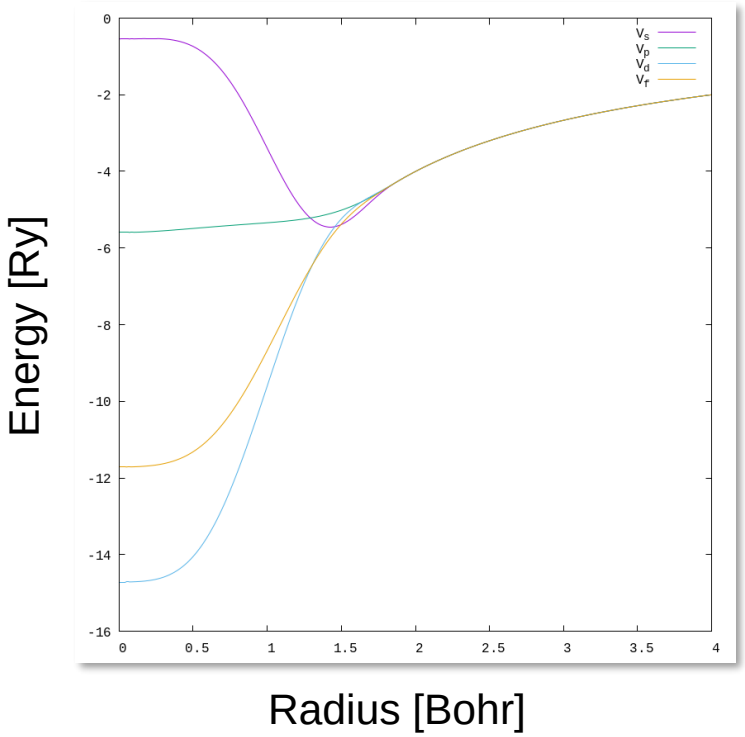
⇐ add new script

Pseudopotential generation

- Visualize the pseudopotentials

2. Run **gnuplot**

```
$ gnuplot pots.gps
⇒ pots.png file is generated
```



⇒ Unscreened pseudopotentials for valence orbitals (s, p, d, f) are generated

Beyond the largest cutoff radius, the unscreened pseudopotential tends to decay by –Z/r

Pseudopotential generation

- Check norm-conserving pseudopotential criteria

VOLUME 43, NUMBER 20 PHYSICAL REVIEW LETTERS 12 NOVEMBER 1979

Norm-Conserving Pseudopotentials

D. R. Hamann, M. Schlüter, and C. Chiang
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 1 August 1979)

(1) Real and pseudo valence eigenvalues agree for a chosen "prototype" atomic configuration.

(2) Real and pseudo atomic wave functions agree beyond a chosen "core radius" r_c

(3) The integrals from 0 to r of the real and pseudo charge densities agree for $r_c < r$, for each valence state (norm conservation).

(4) The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r_c < r$

Pseudopotential generation

- Check norm-conserving pseudopotential criteria

(1) Real and pseudo valence eigenvalues agree for a chosen "prototype" atomic configuration.

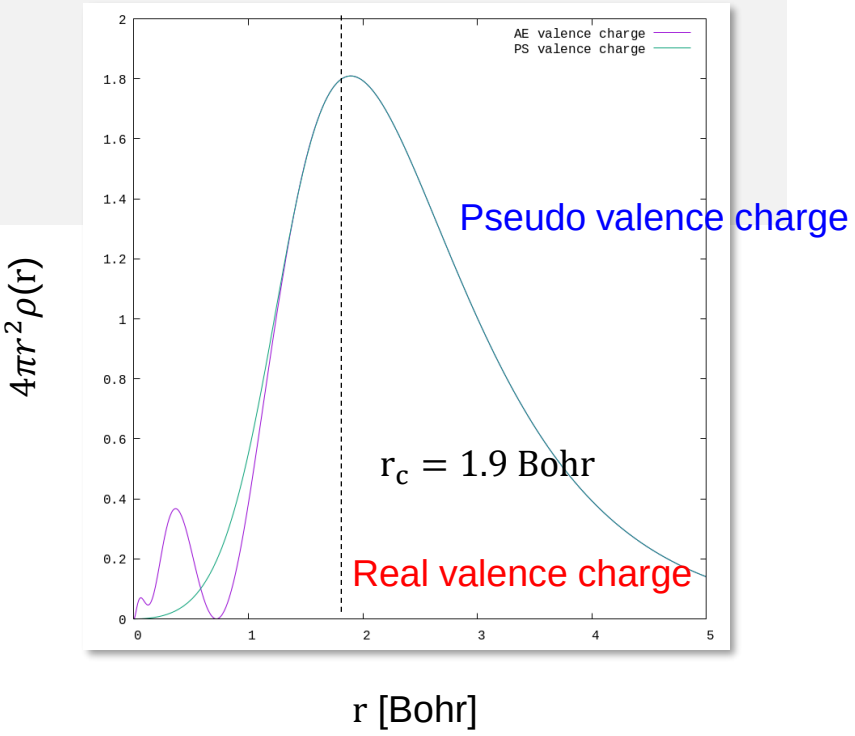
```
$ grep '&v' OUT

 ATM4.2.7  13-JUL-25       Silicon                          &v&d
 3s   0.5    2.0000     -0.79937161      0.00000000    -17.74263363  &v
 3p  -0.5    0.6667     -0.30807129      0.00000000    -13.66178958  &v
 3p   0.5    1.3333     -0.30567134      0.00000000    -13.60785822  &v
 3d  -0.5    0.0000      0.00000000      0.00000000     -0.27407047  &v
 3d   0.5    0.0000      0.00000000      0.00000000     -0.27407047  &v
 4f  -0.5    0.0000      0.00000000      0.00000000     -0.26482365  &v
 4f   0.5    0.0000      0.00000000      0.00000000     -0.26482365  &v
---------------------------- &v
                                        Real valence eigenvalues
 3s   0.5    2.0000     -0.79936061      0.50555315     -3.74113059  &v
 3p  -0.5    0.6667     -0.30804995      0.77243805     -3.26356669  &v
 3p   0.5    1.3333     -0.30565760      0.76702460     -3.25197500  &v
 3d  -0.5    0.0000      0.00000000      0.00140505     -0.07847269  &v
 3d   0.5    0.0000      0.00000000      0.00140505     -0.07847269  &v
 4f  -0.5    0.0000      0.00000000      0.00243411     -0.07586534  &v
 4f   0.5    0.0000      0.00000000      0.00243411     -0.07586534  &v
---------------------------- &v
                                        Pseudo valence eigenvalues
```

Pseudopotential generation

- Check norm-conserving pseudopotential criteria

(3) The integrals from 0 to r of the real and pseudo charge densities agree for r_c < r, for each valence state (norm conservation).

```
$ vi vcharge.gps
…
set terminal pngcairo size 800,800 enhanced
set output ‘vcharge.png'
replot
print "==> Postscript output in vcharge.ps"
quit
$ gnuplot vcharge.gps
```



➢ *Important criteria for chemical transferability*

Pseudopotential generation

- Check norm-conserving pseudopotential criteria

(2) Real and pseudo atomic wave functions agree beyond a chosen "core radius" r_c

(4) The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r_c < r$

```
$ vi pseudo.gps

#set terminal postscript enhanced color
#set output "pseudo.ps"
set terminal pngcairo size 800,800 enhanced
set output 'pseudo.png'
…
if (there_is_s == 1) call "subps.gplot" "0"
#if (there_is_p == 1) call "subps.gplot" "1"
#if (there_is_d == 1) call "subps.gplot" "2"
#if (there_is_f == 1) call "subps.gplot" "3"

$ gnuplot pseudo.gps
```

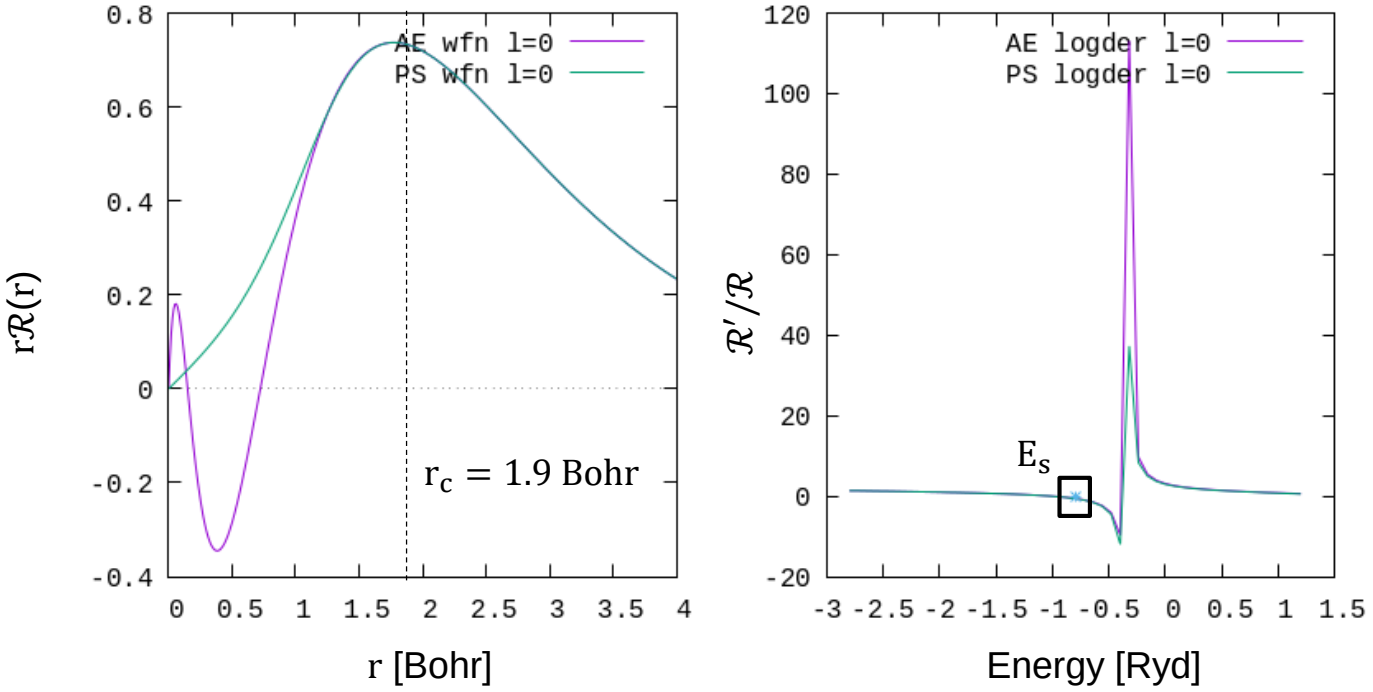
⇐ plot s orbital channel

Pseudopotential generation

- Check norm-conserving pseudopotential criteria

(2) Real and pseudo atomic wave functions agree beyond a chosen "core radius" r_c

(4) The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r_c < r$



Pseudopotential test

- Explicit evaluation of transferability of pseudopotential

1. Access to *Tutorial/PS_Generation/Si, and open* Si.test.inp *file*

- ***Si.test.inp:***

```
# All-electron calculations for a series of Si configurations
#
  ae Si Test -- GS 3s2 3p2
  Si   ca
      0.0
    3    2
    3    0      2.00
    3    1      2.00
  ae Si Test -- 3s2 3p1 3d1
  Si   ca
      0.0
    3    3
    3    0      2.00
    3    1      1.00
    3    2      1.00
  ae Si Test -- 3s1 3p3
  Si   ca
      0.0
    3    2
    3    0      1.00
    3    1      3.00
```

All electron calculations

Test electron configurations

```
# Pseudopotential test calculations
#
  pt Si Test -- GS 3s2 3p2
  Si   ca
      0.0
    3    2
    3    0      2.00
    3    1      2.00
  pt Si Test -- 3s2 3p1 3d1
  Si   ca
      0.0
    3    3
    3    0      2.00
    3    1      1.00
    3    2      1.00
  pt Si Test -- 3s1 3p3
  Si   ca
      0.0
    3    2
    3    0      1.00
    3    1      3.00
```

Corresponding pseudopotential calculations

$ sh ../../Utils/pt.sh Si.test.inp Si.tm2.vps (from previous Pseudopotential generation tutoria)

Pseudopotential test

- Explicit evaluation of transferability of pseudopotential

2. Check total energies difference

```
$ cd Si.test-Si.tm2
$ grep '&d' OUT
```

All-electron

```
ATM4.2.7  13-JUL-25   Si Test -- GS 3s2 3p2                          &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s2 3p1 3d1                        &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p3                            &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p2 3d1                        &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s0 3p3 3d1                        &v&d
&d total energy differences in series
&d          1       2       3       4       5
&d  1    0.0000
&d  2    0.4308   0.0000
&d  3    0.4961   0.0653   0.0000
&d  4    0.9613   0.5305   0.4652   0.0000
&d  5    1.4997   1.0689   1.0036   0.5384   0.0000
*----- End of series ----* spdfg &d&v
```

Pseudopotential

```
ATM4.2.7  13-JUL-25   Si Test -- GS 3s2 3p2                          &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s2 3p1 3d1                        &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p3                            &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p2 3d1                        &v&d
ATM4.2.7  13-JUL-25   Si Test -- 3s0 3p3 3d1                        &v&d
&d total energy differences in series
&d          1       2       3       4       5
&d  1    0.0000
&d  2    0.4299   0.0000
&d  3    0.4993   0.0694   0.0000
&d  4    0.9635   0.5336   0.4642   0.0000
&d  5    1.5044   1.0745   1.0051   0.5409   0.0000
*----- End of series ----* spdfg &d&v
```

3. Check eigenvalues difference

```
$ cd Si.test-Si.tm2
$ grep '&v' OUT
```

All-electron

```
ATM4.2.7  13-JUL-25   Si Test -- GS 3s2 3p2                          &v&d
3s   0.0    2.0000     -0.79662742      3.23745215    -17.68692611  &v
3p   0.0    2.0000     -0.30705179      2.06135782    -13.62572515  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s2 3p1 3d1                        &v&d
3s   0.0    2.0000     -1.08185979      3.53885995    -18.40569837  &v
3p   0.0    1.0000     -0.55548539      2.49959581    -14.93761602  &v
3d   0.0    1.0000     -0.04845556      0.32911715     -5.03432730  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p3                            &v&d
3s   0.0    1.0000     -0.85138783      3.35438895    -17.96219240  &v
3p   0.0    3.0000     -0.34906822      2.20374342    -14.05806014  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p2 3d1                        &v&d
3s   0.0    1.0000     -1.11431858      3.62997498    -18.60814710  &v
3p   0.0    2.0000     -0.57973855      2.59768801    -15.20572193  &v
3d   0.0    1.0000     -0.04775010      0.39529532     -5.51028818  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s0 3p3 3d1                        &v&d
3s   0.0    0.0000     -1.14358268      3.71462770    -18.79448683  &v
3p   0.0    3.0000     -0.60149474      2.68964512    -15.45326805  &v
3d   0.0    1.0000     -0.04725203      0.46423687     -5.97423039  &v
------------------------- &v
```

Pseudopotential

```
*----- End of series ----* spdfg &d&v
ATM4.2.7  13-JUL-25   Si Test -- GS 3s2 3p2                          &v&d
1s   0.0    2.0000     -0.79938037      0.50556261     -3.74114712  &v
2p   0.0    2.0000     -0.30646477      0.76884446     -3.25586617  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s2 3p1 3d1                        &v&d
1s   0.0    2.0000     -1.08384468      0.55070398     -3.81988817  &v
2p   0.0    1.0000     -0.55422979      0.90472233     -3.48042257  &v
3d   0.0    1.0000     -0.04849177      0.32471221     -1.43893301  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p3                            &v&d
1s   0.0    1.0000     -0.85392666      0.52020429     -3.76852577  &v
2p   0.0    3.0000     -0.34855995      0.81134430     -3.32927595  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s1 3p2 3d1                        &v&d
1s   0.0    1.0000     -1.11546464      0.56048425     -3.83646615  &v
2p   0.0    2.0000     -0.57808297      0.93152725     -3.52053672  &v
3d   0.0    1.0000     -0.04779711      0.38958693     -1.57676617  &v
------------------------- &v
ATM4.2.7  13-JUL-25   Si Test -- 3s0 3p3 3d1                        &v&d
1s   0.0    0.0000     -1.14353959      0.56945741     -3.85106049  &v
2p   0.0    3.0000     -0.59931810      0.95613808     -3.55643976  &v
3d   0.0    1.0000     -0.04733135      0.45664551     -1.71085893  &v
------------------------- &v
*----- End of series ----* spdfg &d&v
```

Advanced Topics

Topic 1. Non-linear exchange-correlation (XC) correction

Overlap between core and valence electron densities → problematic for (screened) XC potential

```
$ gnuplot charge.gps # to check charge overlapping
```

Solution:

- Non-linear core correlation S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B 26, 1738 (1982)

  Calculation mode “pg” → “pe”
- Inclusion of semicore state within the valence orbital

  e.g. Ba: $6s^2$ → Ba^{2+}: $5s^2\ 5p^6$

Topic 2. Relativistic effect

For heavy metal, one should consider **relativistic effect**

In exchange-correlation tag, “ca” → “ca**r**”

To check this effect on SIESTA calculation, refer to [Wiki]