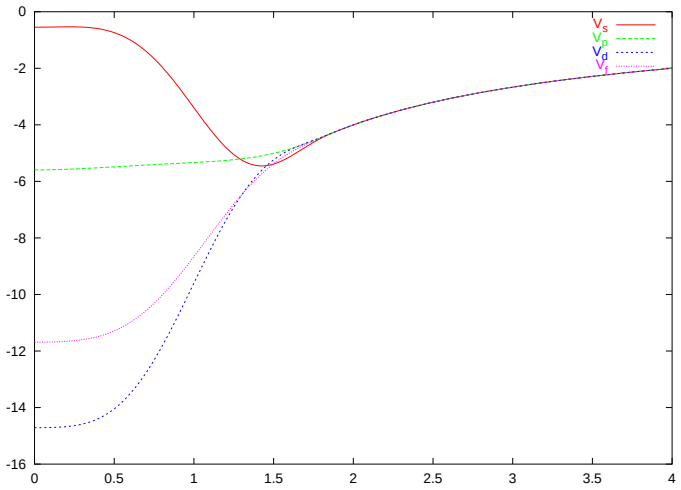
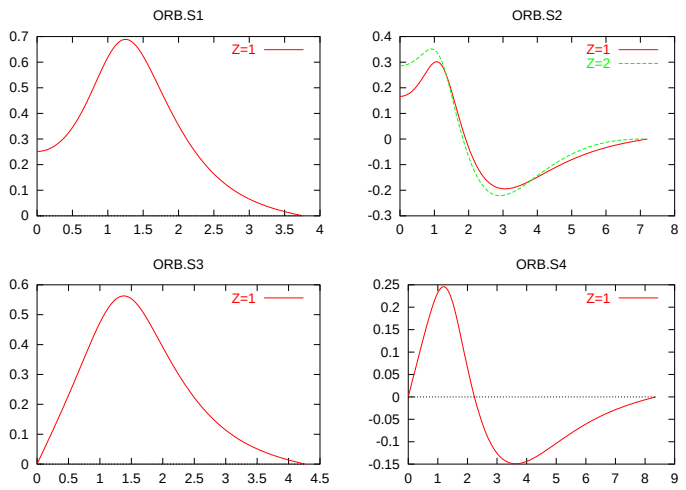
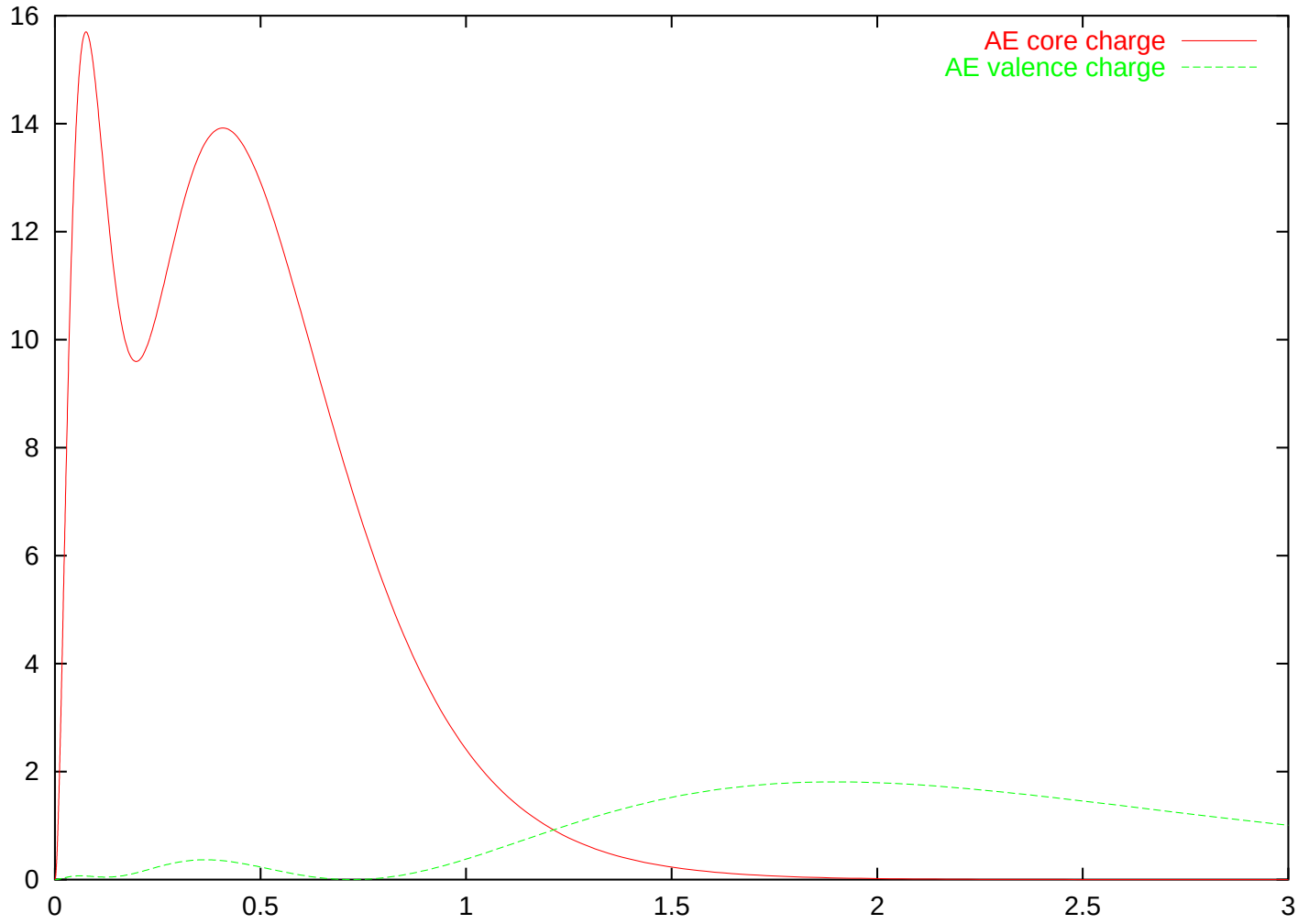
Pseudopotential and Basis Generation for SIESTA

Alberto García
Universidad del País Vasco, Bilbao, Spain



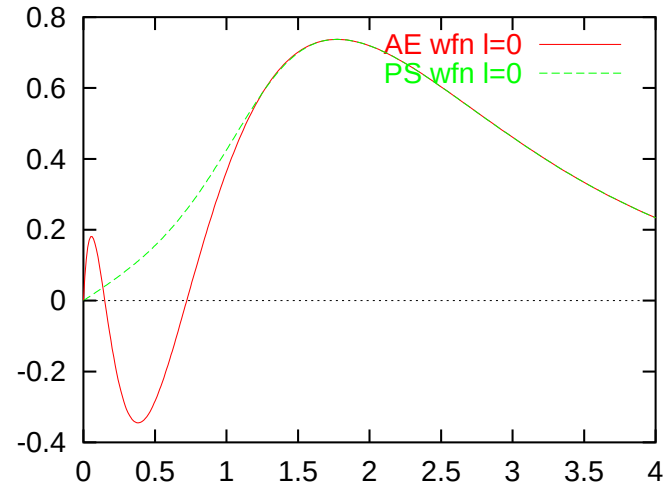


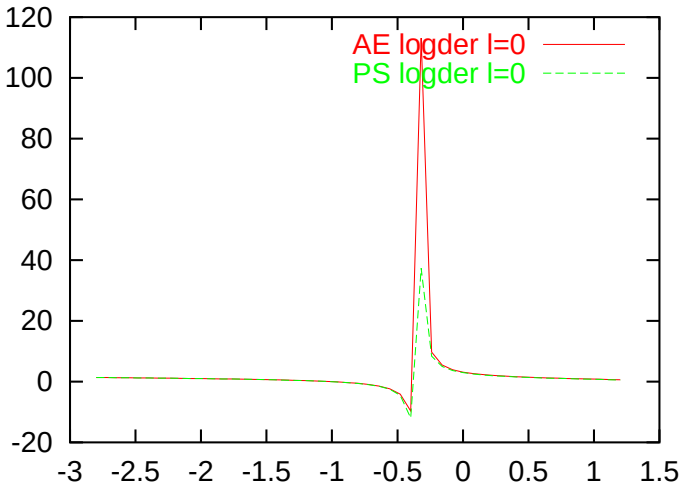

AE core charge
AE valence charge
16
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
3

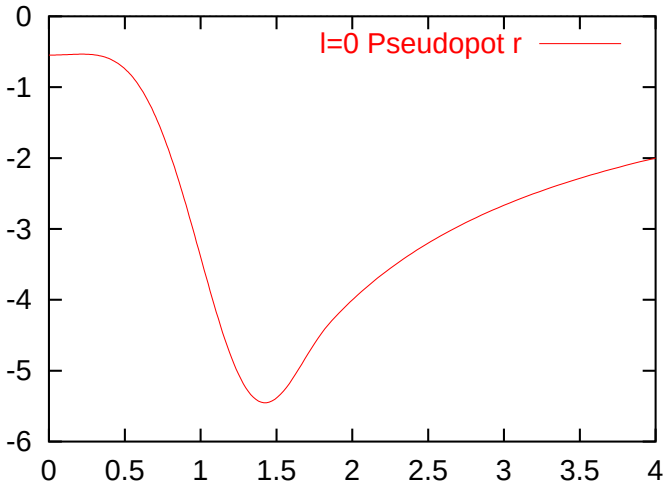
```
#
#  Pseudopotential generation for Silicon
#  pg: simple generation
#
   pg      Silicon
        tm2      3.0              # PS flavor, logder R
 n=Si c=car                       # Symbol, XC flavor,{ |r|s}
       0.0       0.0       0.0       0.0       0.0       0.0
    3    4                       # 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
```

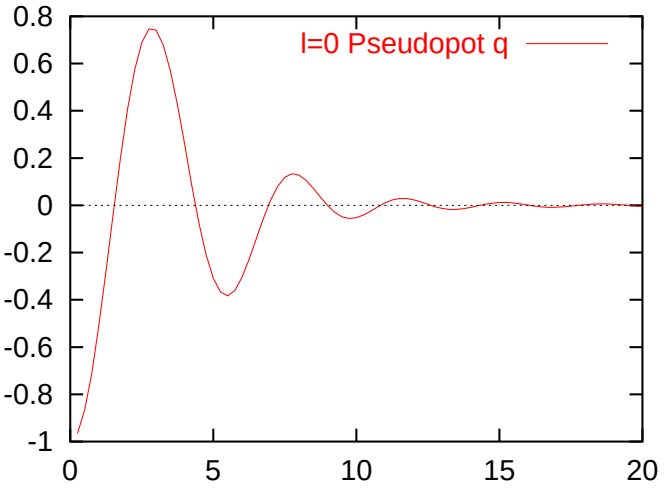
Generation Mechanics

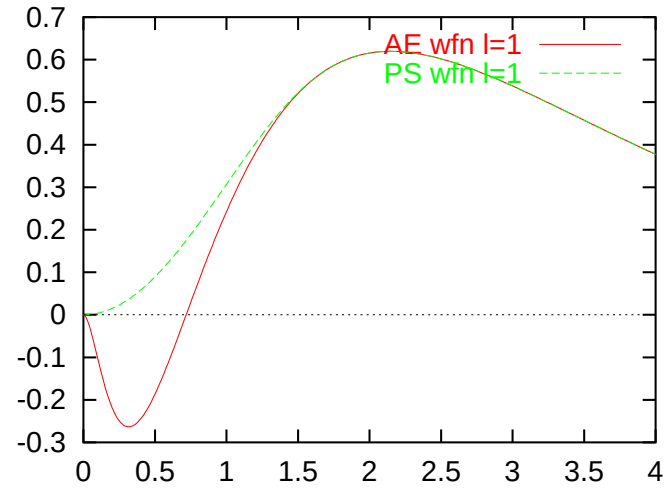
```
$ pg.sh Si.tm2.inp
Calculation for Si.tm2 completed. Output in directory Si.tm2
$ ls Si.tm2
AECHARGE  AEWFNR3   PSLOGD3  PSPOTR3  PSWFNR3     charge.gplot
AELOGD0   CHARGE    PSPOTQ0  PSWFNQ0  RHO         charge.gps
AELOGD1   INP       PSPOTQ1  PSWFNQ1  SCRPSPOTR0  pots.gplot
AELOGD2   OUT       PSPOTQ2  PSWFNQ2  SCRPSPOTR1  pots.gps
AELOGD3   PSCHARGE  PSPOTQ3  PSWFNQ3  SCRPSPOTR2  pseudo.gplot
AEWFNR0   PSLOGD0   PSPOTR0  PSWFNR0  SCRPSPOTR3  pseudo.gps
AEWFNR1   PSLOGD1   PSPOTR1  PSWFNR1  VPSFMT      pt.gplot
AEWFNR2   PSLOGD2   PSPOTR2  PSWFNR2  VPSOUT      pt.gps
$ cd Si.tm2
$
$ # PLOTTING
$
$ gnuplot pseudo.gps
==> Postscript output in pseudo.ps
```

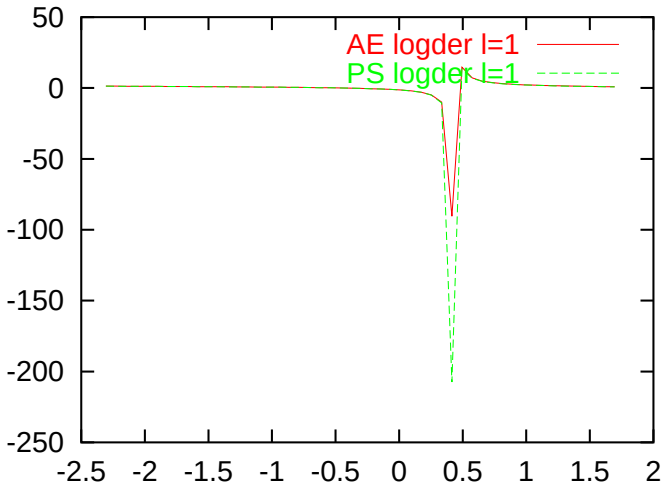

AE wfn l=0
PS wfn l=0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4

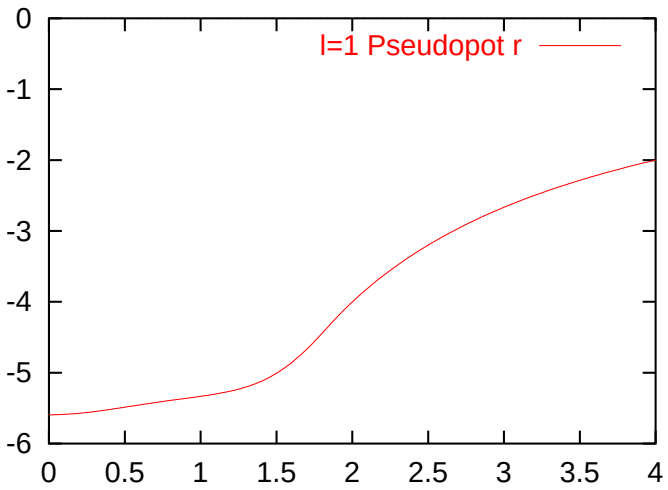

AE logder l=0
PS logder l=0
120
100
80
60
40
20
0
-20
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5

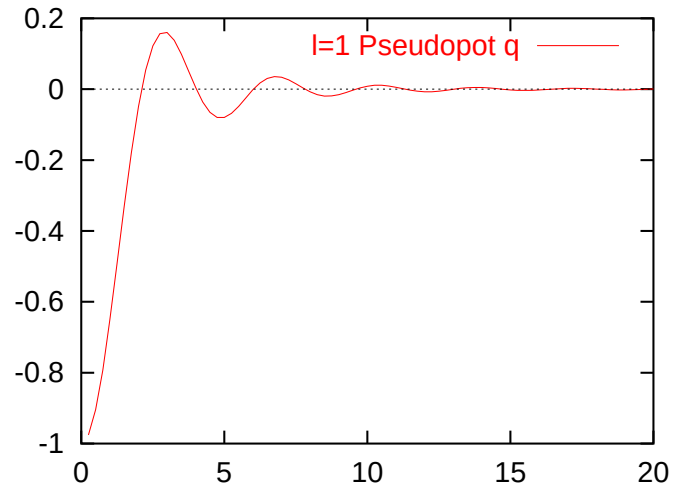

l=0 Pseudopot r
0
-1
-2
-3
-4
-5
-6
0
0.5
1
1.5
2
2.5
3
3.5
4

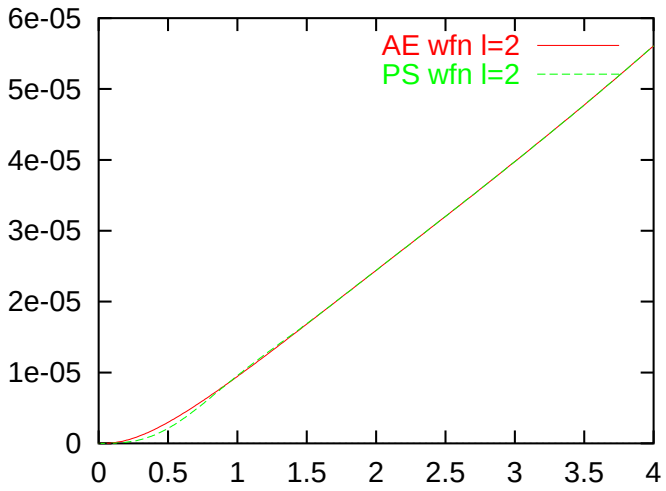

l=0 Pseudopot q
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
5
10
15
20

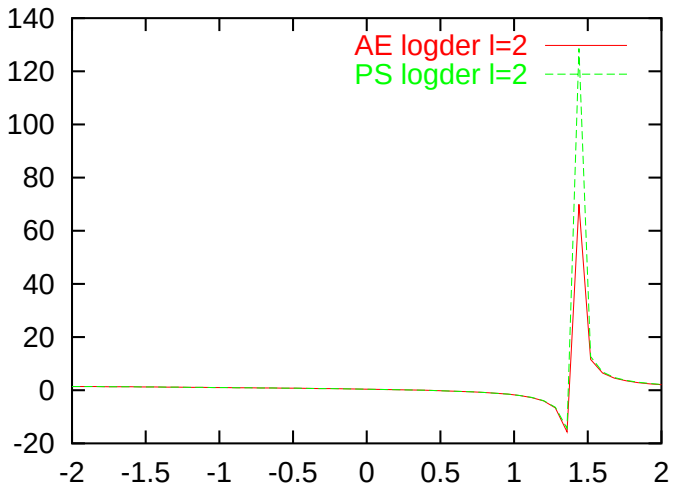

AE wfn l=1
PS wfn l=1
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
0
0.5
1
1.5
2
2.5
3
3.5
4

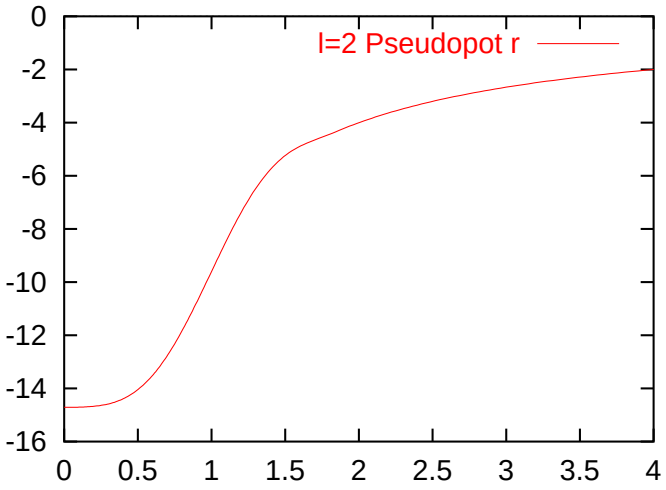

AE logder l=1
PS logder l=1
50
0
-50
-100
-150
-200
-250
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2

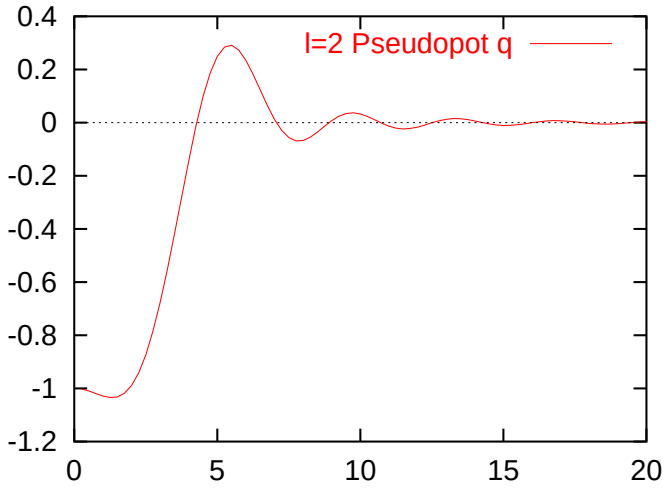

l=1 Pseudopot r
0
-1
-2
-3
-4
-5
-6
0
0.5
1
1.5
2
2.5
3
3.5
4

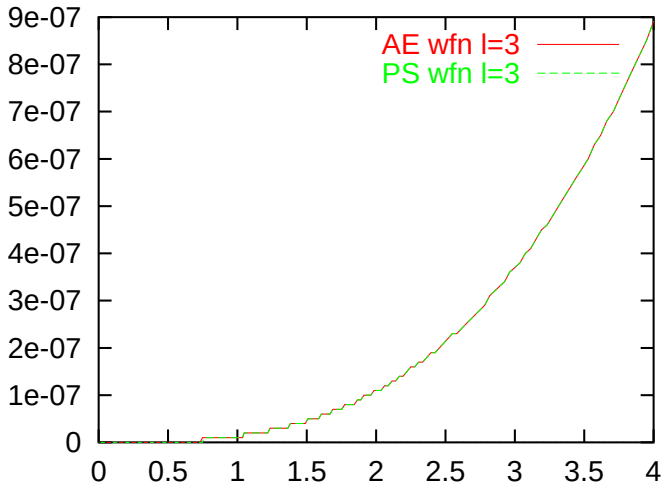

l=1 Pseudopot q
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
5
10
15
20

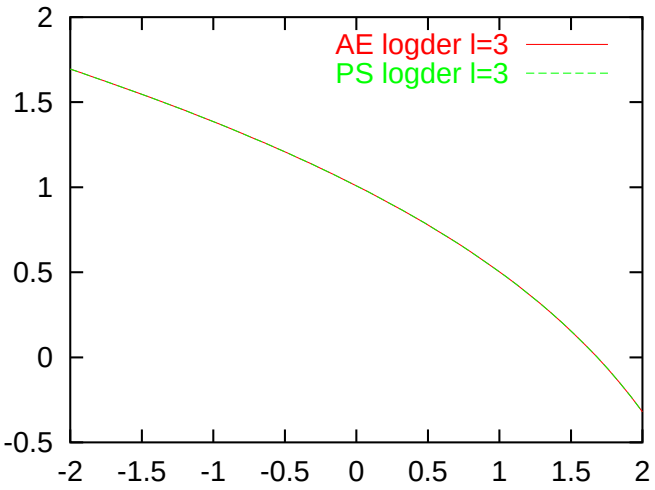

AE wfn l=2
PS wfn l=2
6e-05
5e-05
4e-05
3e-05
2e-05
1e-05
0
0 0.5 1 1.5 2 2.5 3 3.5 4

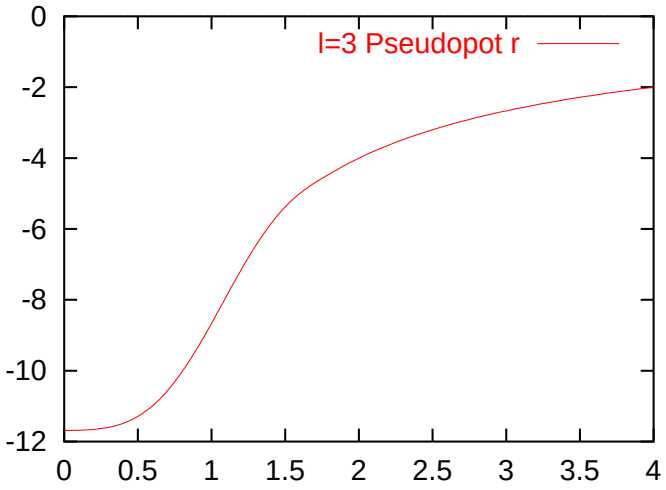

AE logder l=2
PS logder l=2
140
120
100
80
60
40
20
0
-20
-2 -1.5 -1 -0.5 0 0.5 1 1.5 2

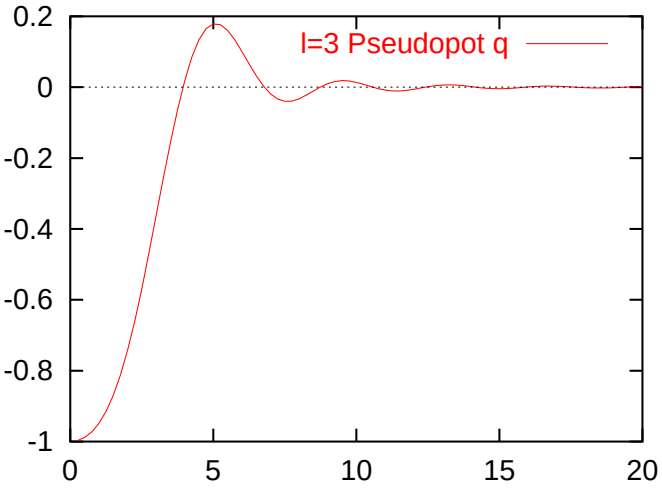

l=2 Pseudopot r
0
-2
-4
-6
-8
-10
-12
-14
-16
0 0.5 1 1.5 2 2.5 3 3.5 4

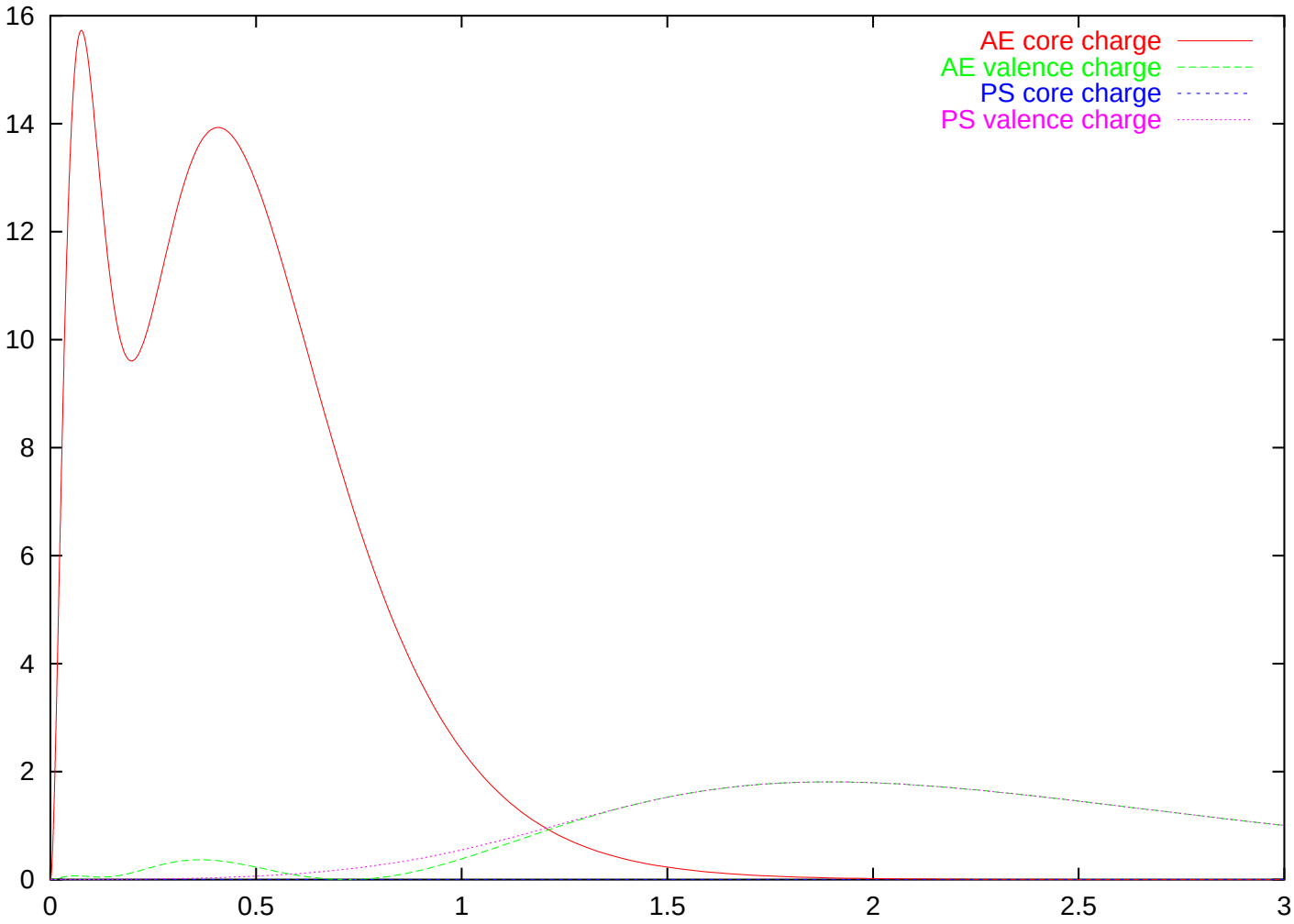

l=2 Pseudopot q
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0 5 10 15 20

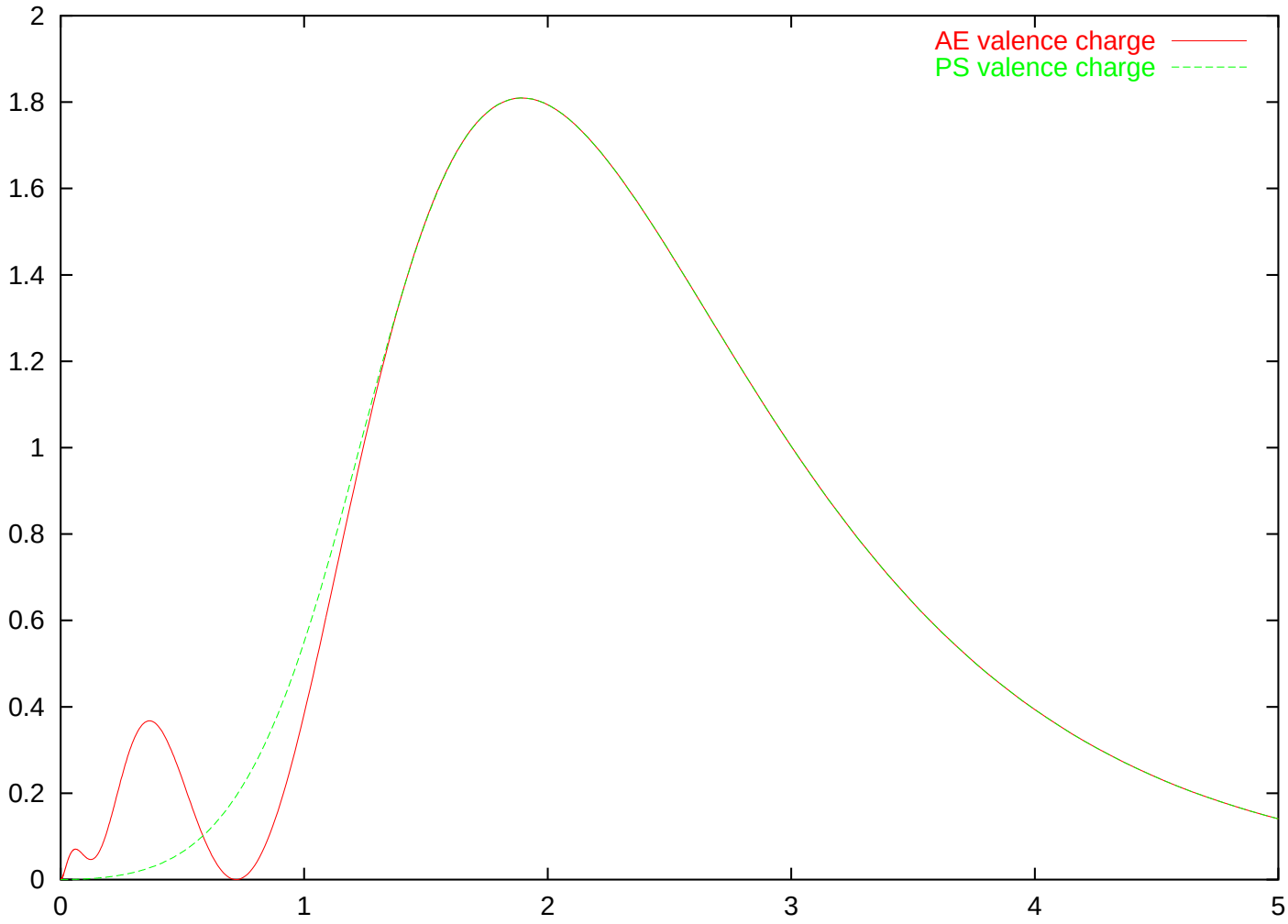

AE wfn l=3
PS wfn l=3
9e-07
8e-07
7e-07
6e-07
5e-07
4e-07
3e-07
2e-07
1e-07
0
0 0.5 1 1.5 2 2.5 3 3.5 4


AE logder l=3
PS logder l=3
2
1.5
1
0.5
0
-0.5
-2 -1.5 -1 -0.5 0 0.5 1 1.5 2


l=3 Pseudopot r
0
-2
-4
-6
-8
-10
-12
0 0.5 1 1.5 2 2.5 3 3.5 4


l=3 Pseudopot q
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0 5 10 15 20


AE core charge
AE valence charge
PS core charge
PS valence charge
16
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
3

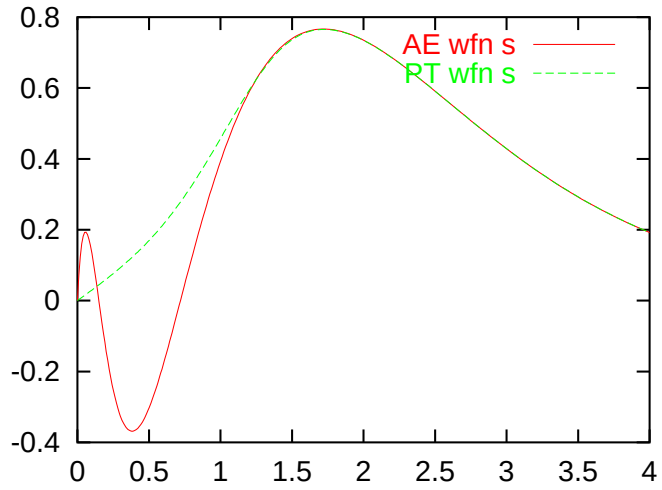

AE valence charge
PS valence charge
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5

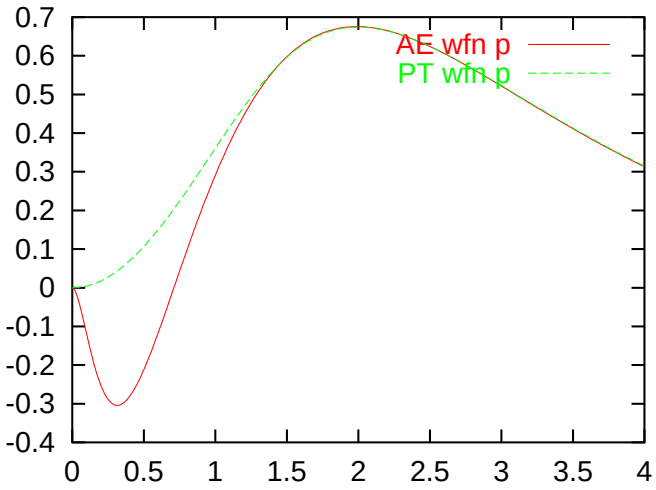
```
$ grep '&v' OUT
 ATM3       11-JUL-02           Silicon
 3s   0.5    2.0000       -0.79937161       0.00000000
 3p  -0.5    0.6667       -0.30807129       0.00000000
 3p   0.5    1.3333       -0.30567134       0.00000000
 3d  -0.5    0.0000        0.00000000       0.00000000
 3d   0.5    0.0000        0.00000000       0.00000000
 4f  -0.5    0.0000        0.00000000       0.00000000
 4f   0.5    0.0000        0.00000000       0.00000000
------------------------------ &v
 3s   0.5    2.0000       -0.79936061       0.50555315
 3p  -0.5    0.6667       -0.30804995       0.77243805
 3p   0.5    1.3333       -0.30565760       0.76702460
 3d  -0.5    0.0000        0.00000000       0.00140505
 3d   0.5    0.0000        0.00000000       0.00140505
 4f  -0.5    0.0000        0.00000000       0.00243411
 4f   0.5    0.0000        0.00000000       0.00243411
------------------------------ &v
```

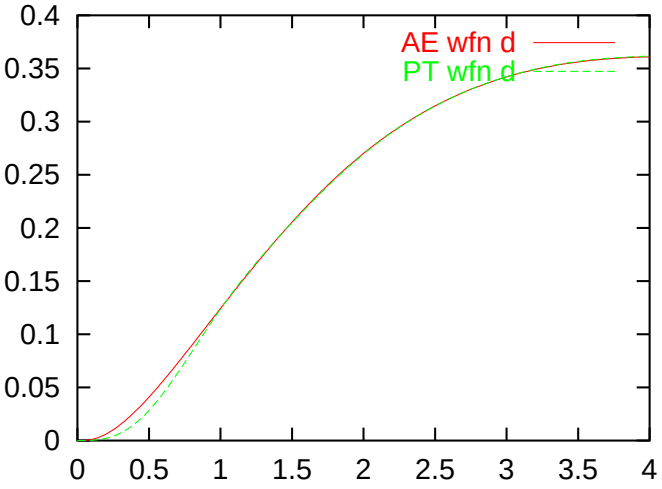
Testing Mechanics

```
   ae Si Test -- 3s0 3p3 3d1
   Si   ca
       0.0
    3    3
    3    0       0.00
    3    1       3.00
    3    2       1.00
#                                        (Same configuration)
   pt Si Test -- 3s0 3p3 3d1
   Si   ca
       0.0
    3    3
    3    0       0.00
    3    1       3.00
    3    2       1.00
```

```
sh ../pt.sh  Si.test.inp Si.tm2.vps
Output data in directory Si.test-Si.tm2...
$ cd Si.test-Si.tm2
$ ls [A-Z]*
AECHARGE  AEWFNR1  CHARGE  OUT       PTWFNR0  PTWFNR2  VPSIN
AEWFNR0   AEWFNR2  INP     PTCHARGE  PTWFNR1  RHO
$
$ ## EIGENVALUE TEST
$
$ grep '&v' OUT
 ATM3       11-JUL-02   Si Test -- 3s0 3p3 3d1
 3s   0.0    0.0000      -1.14358268       3.71462770
 3p   0.0    3.0000      -0.60149474       2.68964513
 3d   0.0    1.0000      -0.04725203       0.46423687
-----------------------------
 ATM3       11-JUL-02   Si Test -- 3s0 3p3 3d1
 1s   0.0    0.0000      -1.14353959       0.56945741
 2p   0.0    3.0000      -0.59931810       0.95613808
 3d   0.0    1.0000      -0.04733135       0.45664551
-----------------------------
```


AE wfn s
PT wfn s
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4


AE wfn p
PT wfn p
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4

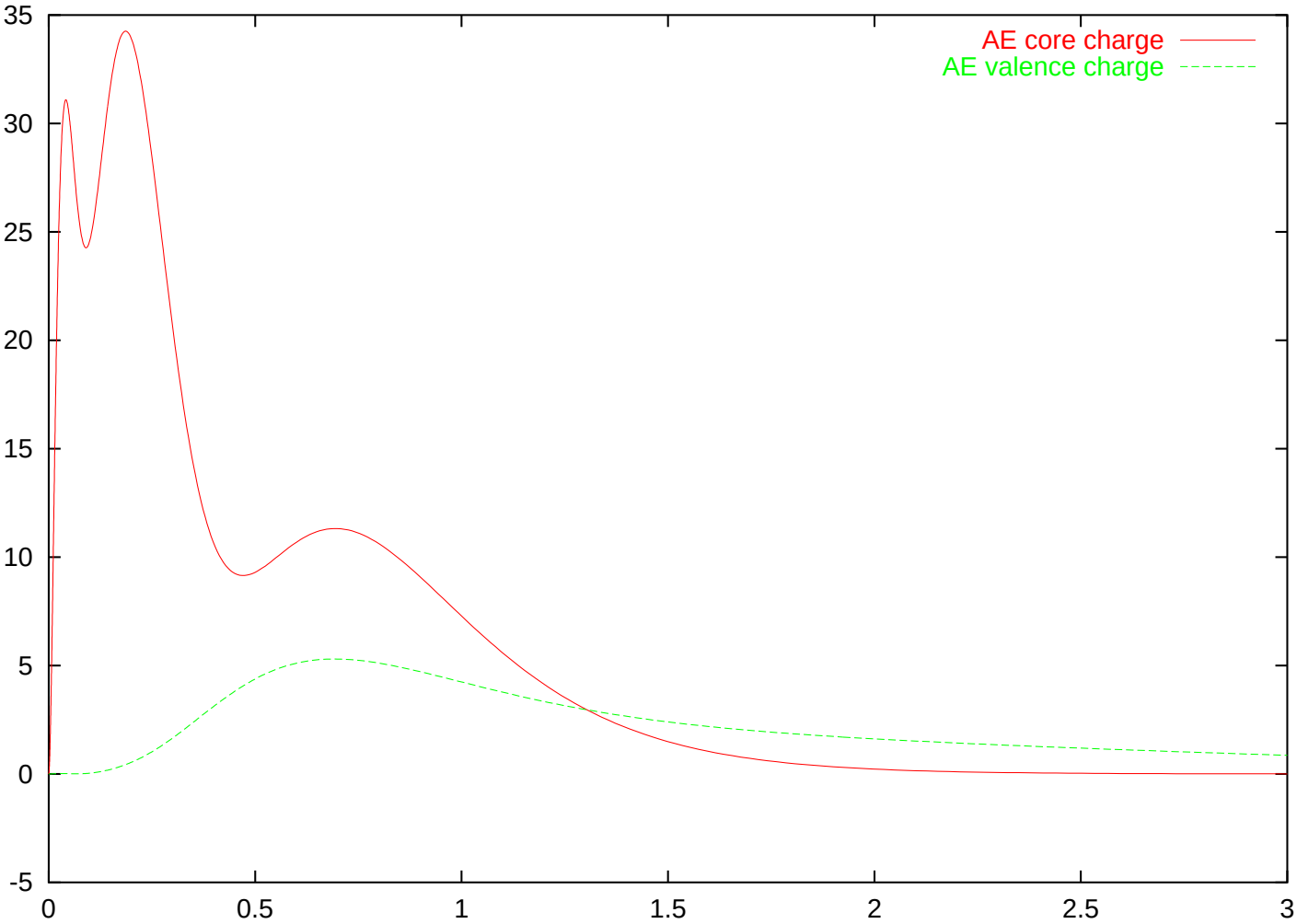

AE wfn d
PT wfn d
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.5
1
1.5
2
2.5
3
3.5
4

```
&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

ATM3       11-JUL-02   Si Test -- GS 3s2 3p2
ATM3       11-JUL-02   Si Test -- 3s2 3p1 3d1
ATM3       11-JUL-02   Si Test -- 3s1 3p3
ATM3       11-JUL-02   Si Test -- 3s1 3p2 3d1
ATM3       11-JUL-02   Si Test -- 3s0 3p3 3d1

&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
```

Large core-valence overlap



Standard pseudopotential unscreening:
Valence charge only

$$V^{ps}(r) = V^{ps}_{scr}[\rho_v](r) - V_H[\rho_v](r) - V_{xc}[\rho_v](r)$$

But

$$V_{xc}[\rho_v + \rho_c](r) \neq V_{xc}[\rho_v](r) + V_{xc}[\rho_c](r)$$

Error due to non-linearity of XC potential.

Corrected unscreening: Keep core charge in pseudopotential generation

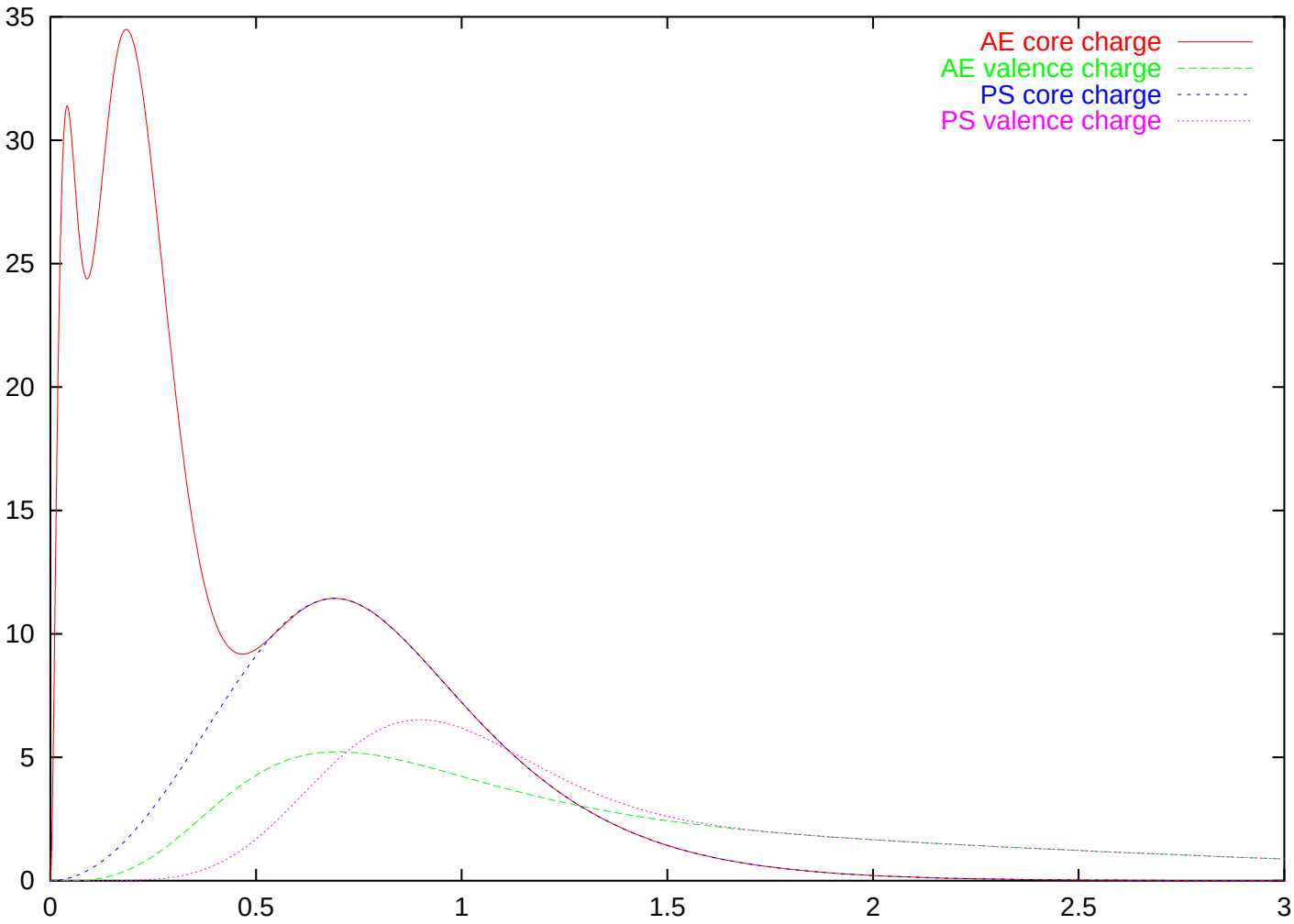
$$V^{ps}(r) = V^{ps}_{scr}[\rho_v + \rho_c](r) - V_H[\rho_v](r) - V_{xc}[\rho_v + \rho_c](r)$$

(Actually it is enough with a *pseudo core*)

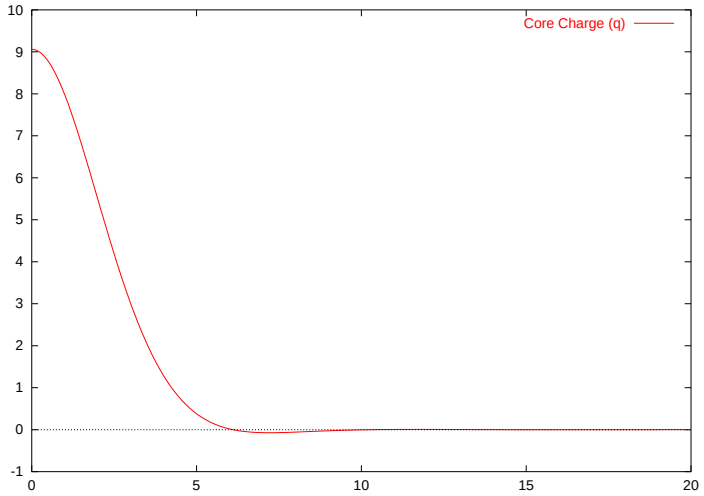
Non-linear core-corrections

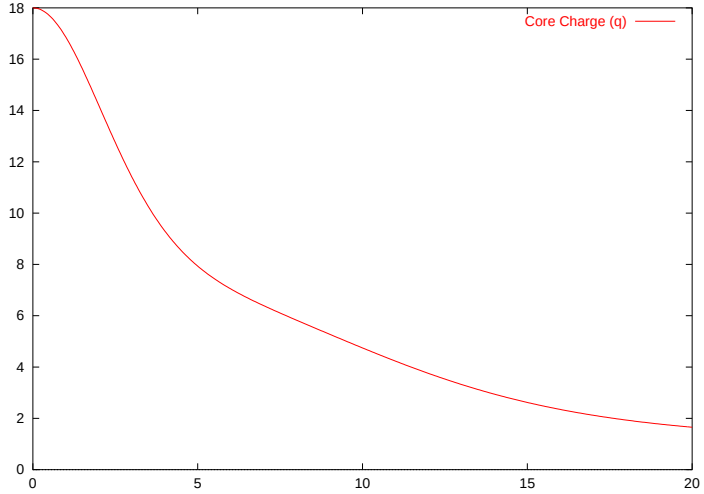
```
#
#  PS generation with core corrections
#  GGA (Perdew-Burke-Ernzerhof) XC , relativistic
#
   pe   Fe, GGA, rcore=0.70
        tm2      3.0
 n=Fe c=pbr
       0.0        0.0        0.0        0.0        0.0        0.0
    5    4
    4    0      2.00       0.00    # 4s2
    4    1      0.00       0.00    # 4p0
    3    2      6.00       0.00    # 3d6
    4    3      0.00       0.00    # 4f0
      2.00       2.00       2.00       2.00       0.00       0.70
#                                                              |
#                                                  Radius of pseudocore
```

Pseudo-core charge



Smooth Fourier Transform





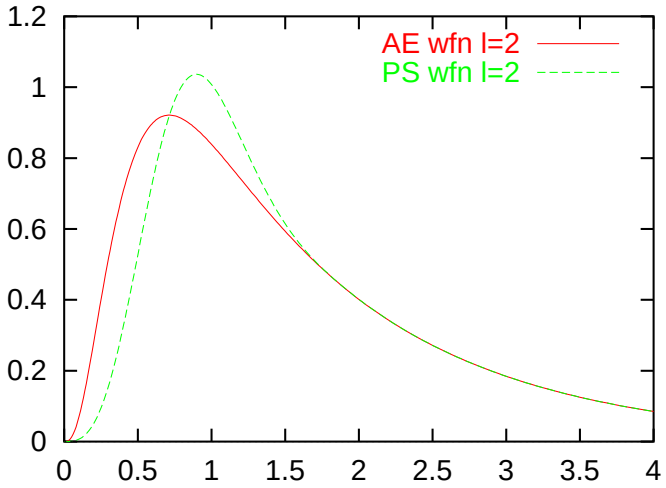
Real-Space Grid

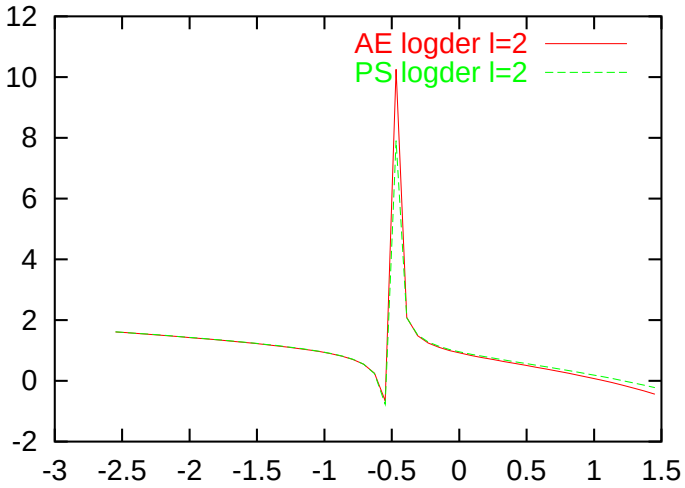
Charge density and local potentials are handled on a real-space grid, whose fineness is determined by the `MeshCutoff` parameter:

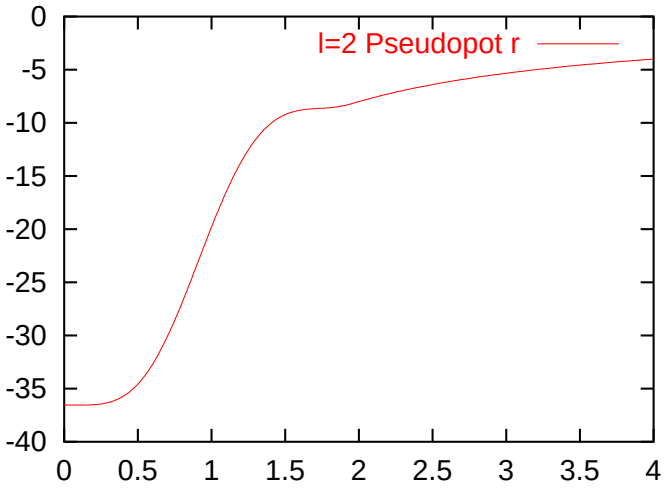
$$\text{Cutoff} \;=\; (q_{\max})^2$$

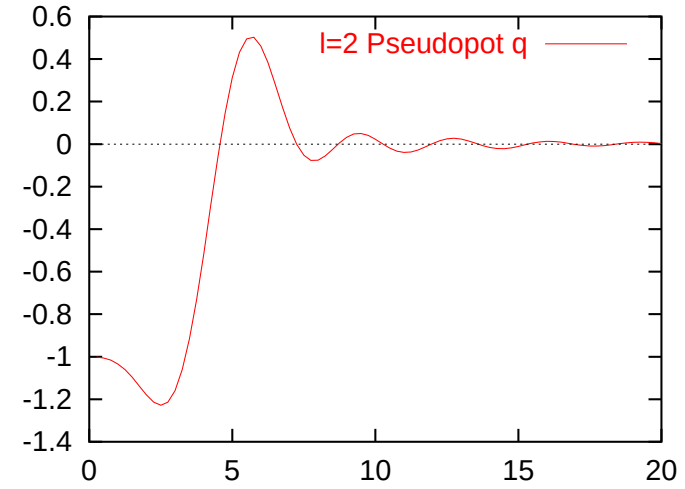
```
MeshCutoff 100 Ryd
```

Troullier-Martins $3d$ treatment

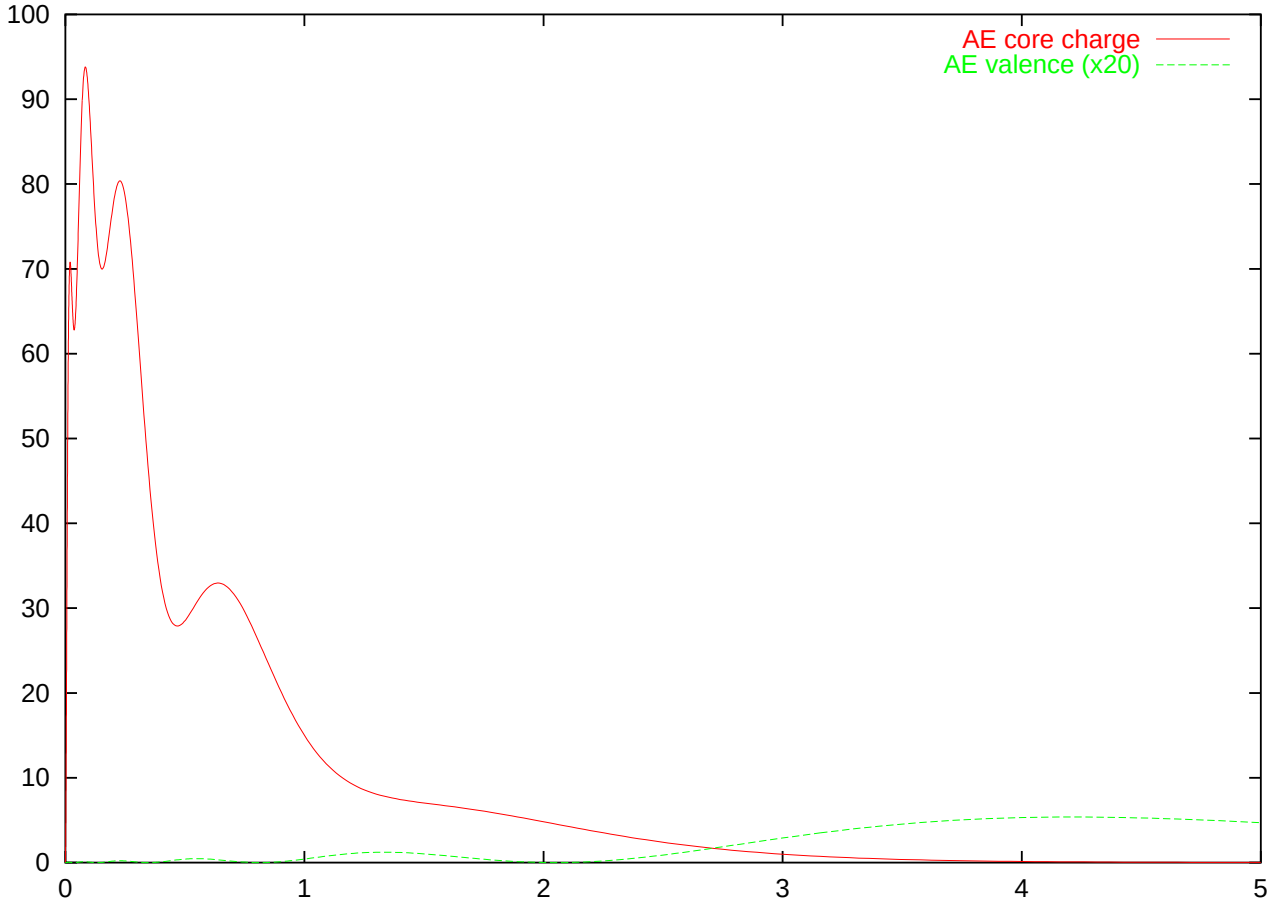








Ba: (Large core)$+6s^2$

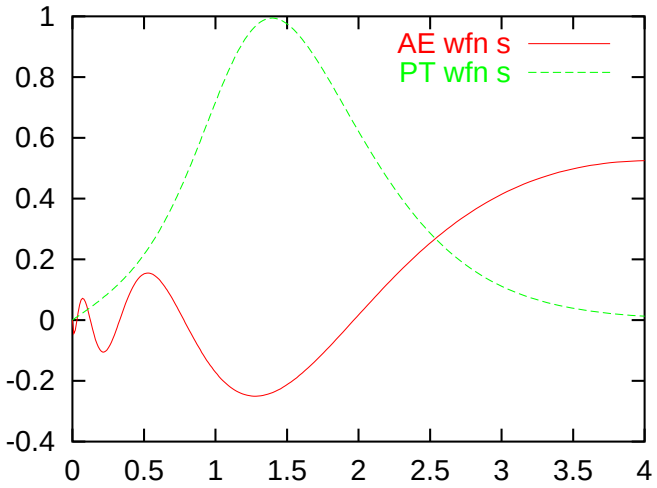


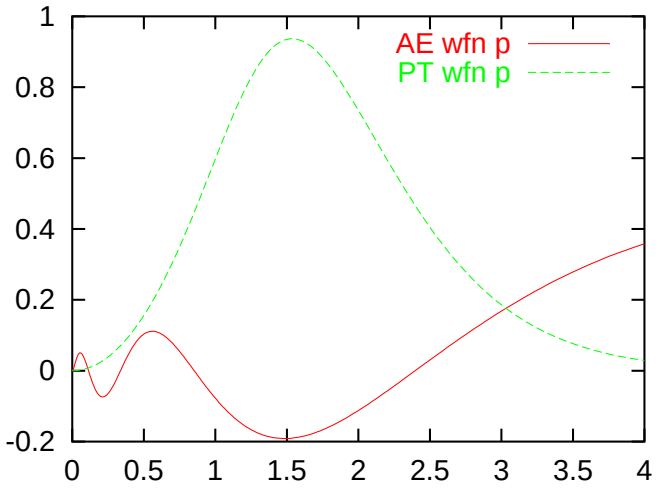
Put $5s^2$ and $5p^6$ in valence complex

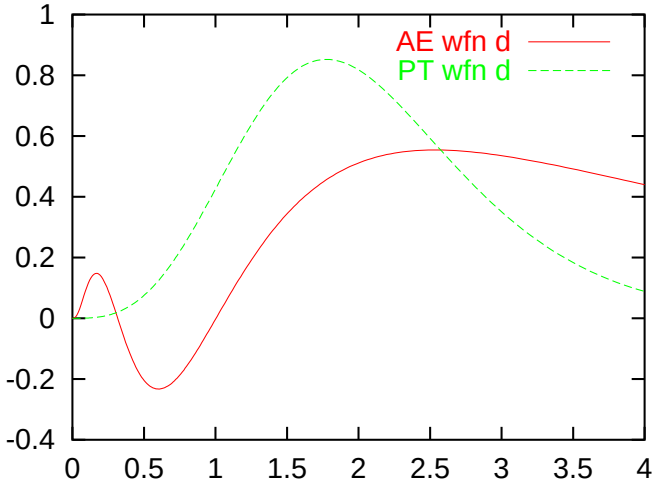
```
#
#  Note that this configuration is ionic (+2)
#
   pg Ba with 5s as semicore, 5p in valence -- soft Vf
        tm2     3.00
 n=Ba c=car
       0.0       0.0       0.0       0.0       0.0       0.0
    9    4
    5    0      2.00    # 5s2
    5    1      6.00    # 5p6
    5    2      0.00
    4    3      0.00
      1.75      2.00      2.50      2.50      0.00      0.00
```

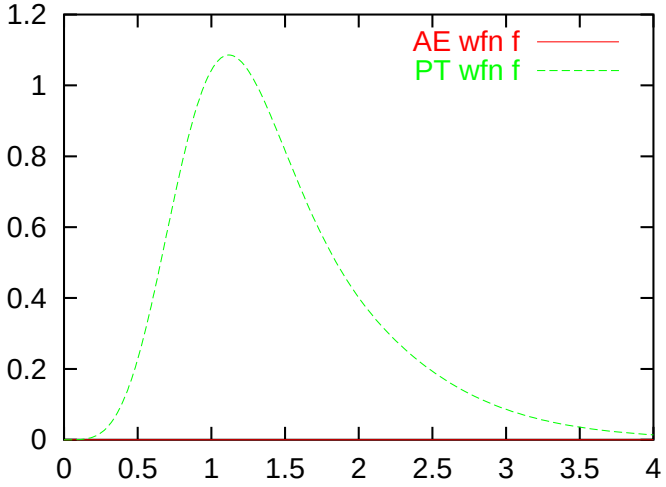
(Semicore States)

Pseudopotential reproduces semicore

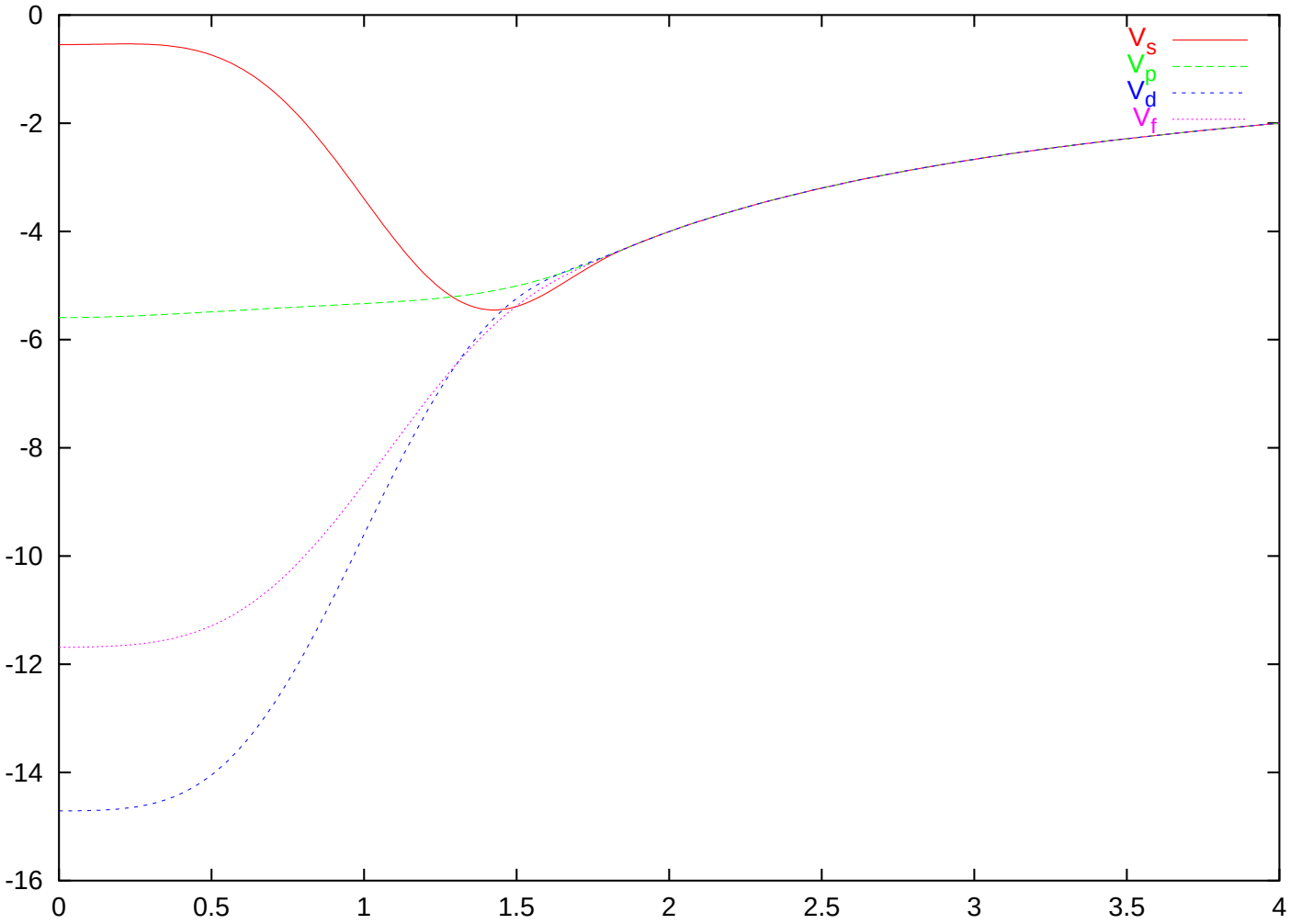


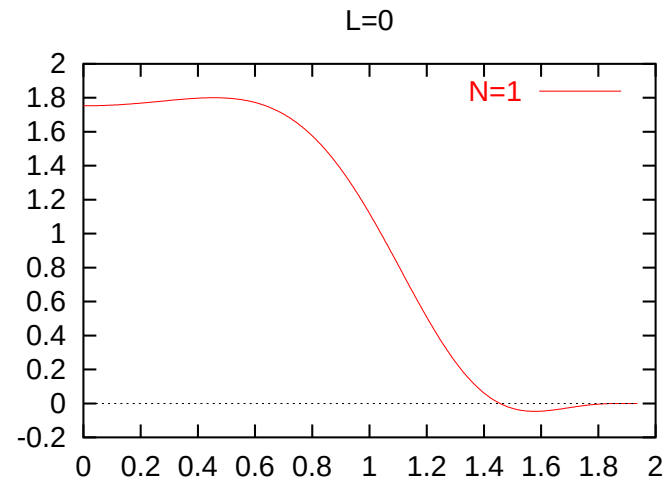


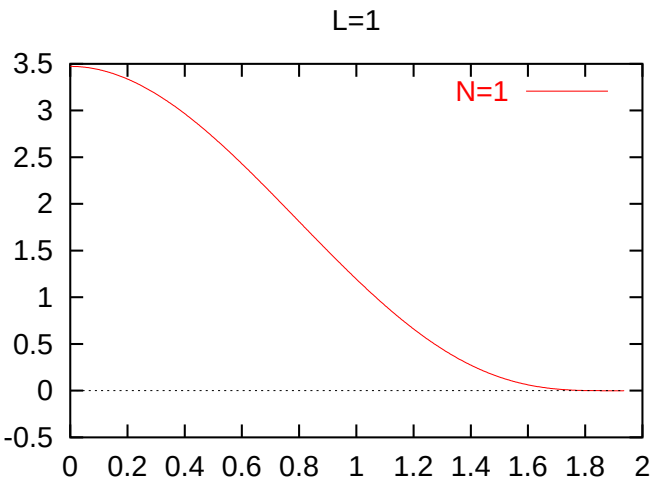


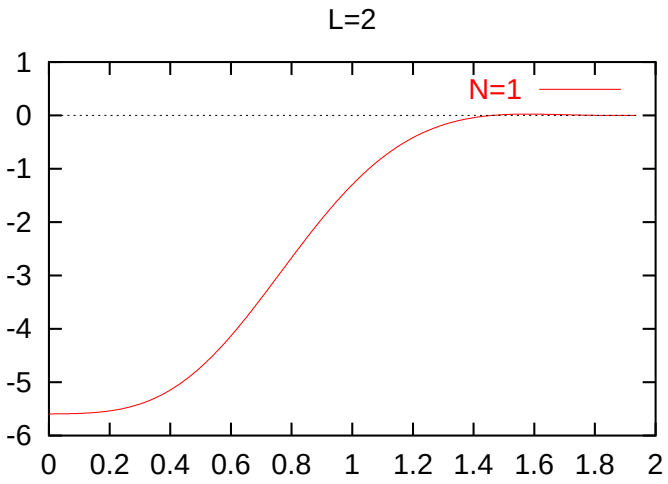


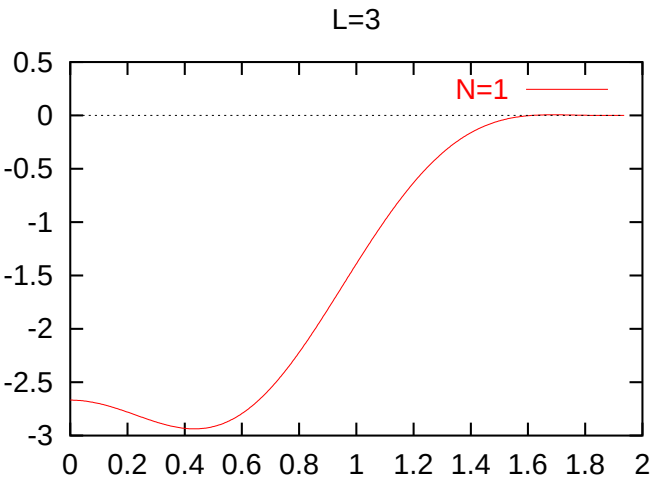
Constructing KB projectors

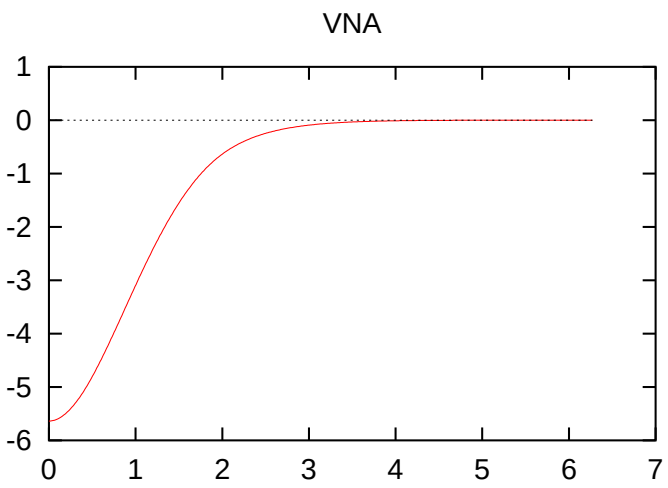


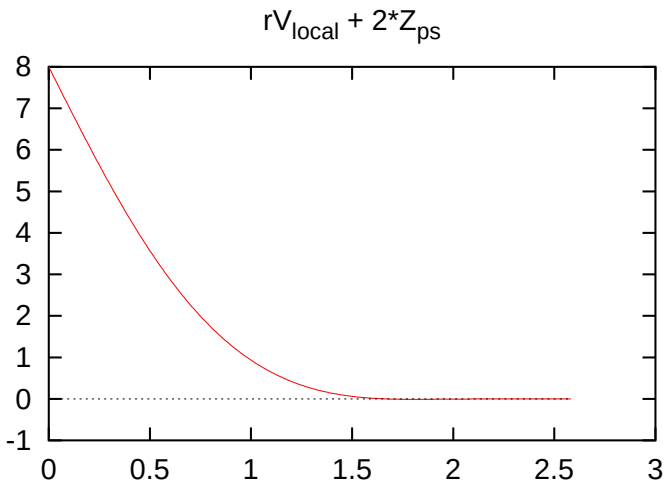

L=0
N=1
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2

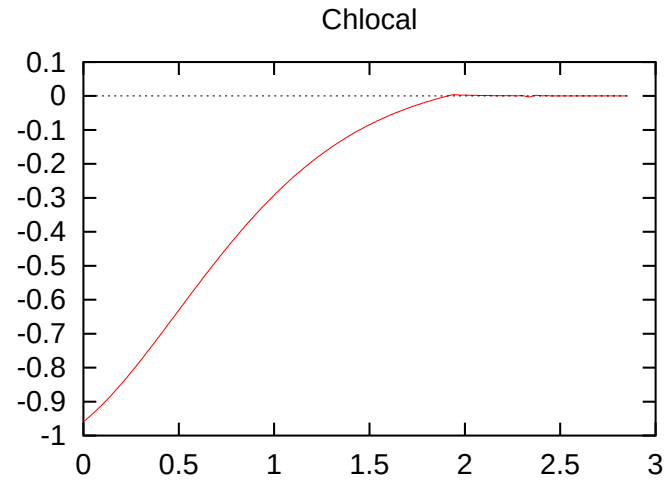

L=1
N=1
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2

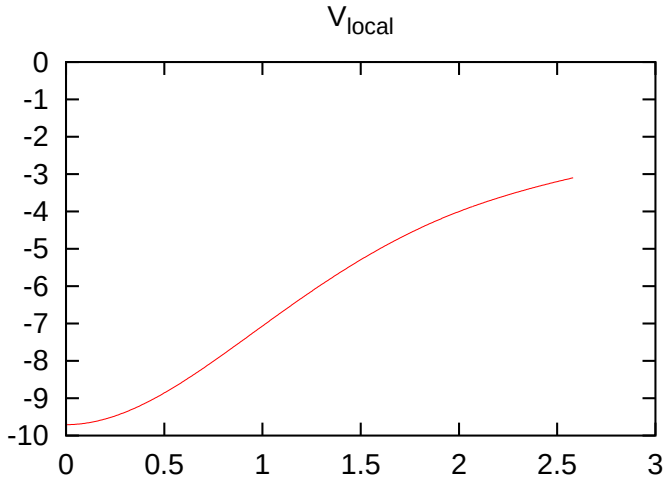

L=2
N=1
1
0
-1
-2
-3
-4
-5
-6
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2


L=3
N=1
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6 1.8 2

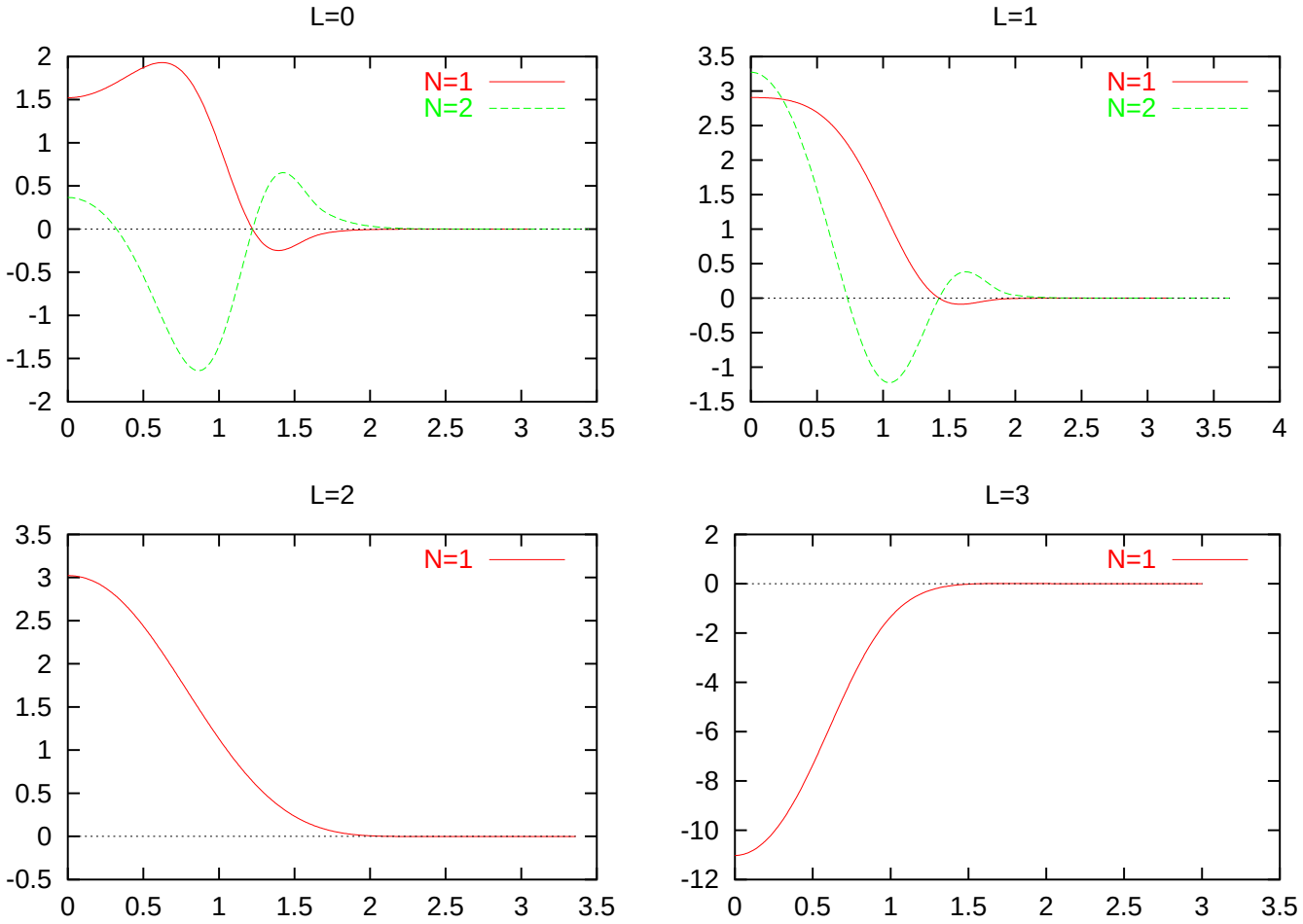

VNA
1
0
-1
-2
-3
-4
-5
-6
0
1
2
3
4
5
6
7


rV_local + 2*Z_ps
8
7
6
5
4
3
2
1
0
-1
0
0.5
1
1.5
2
2.5
3

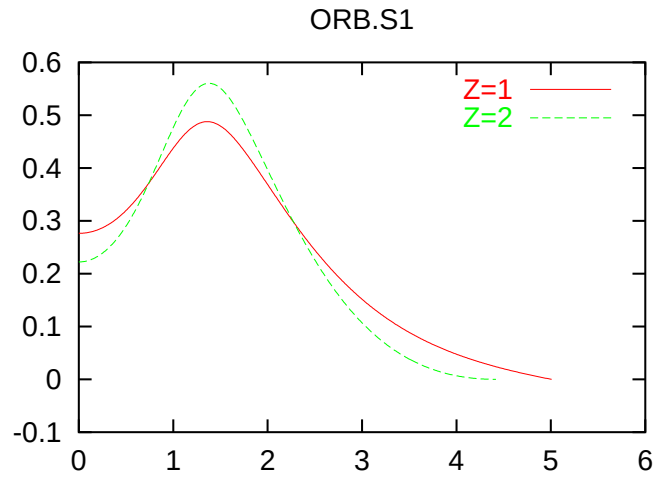

Chlocal
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0
0.5
1
1.5
2
2.5
3

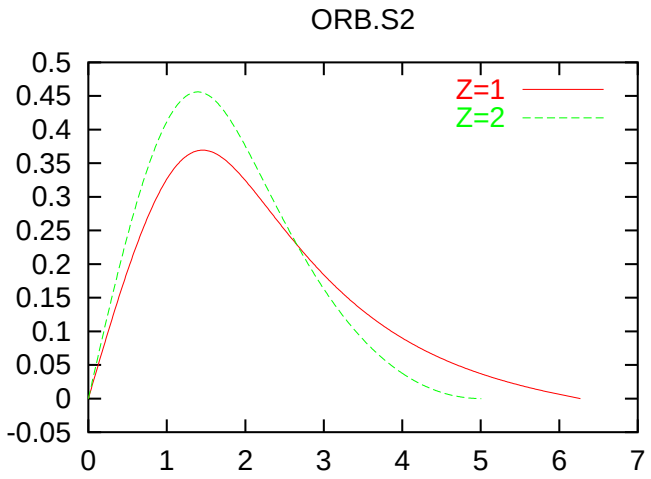

V_local
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
0.5
1
1.5
2
2.5
3

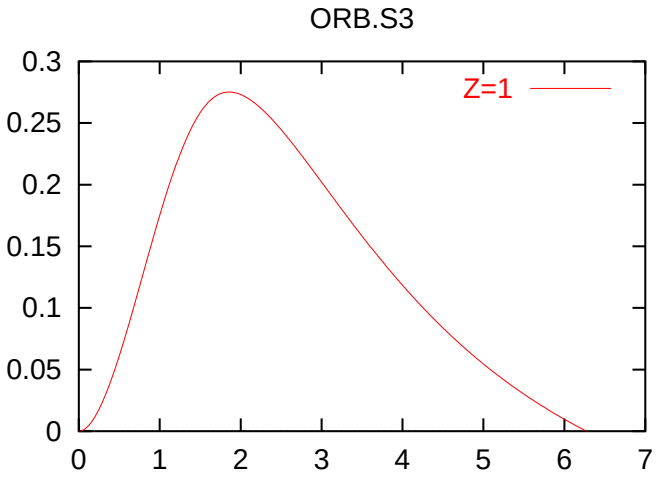
Ba: Semicore states in s and p



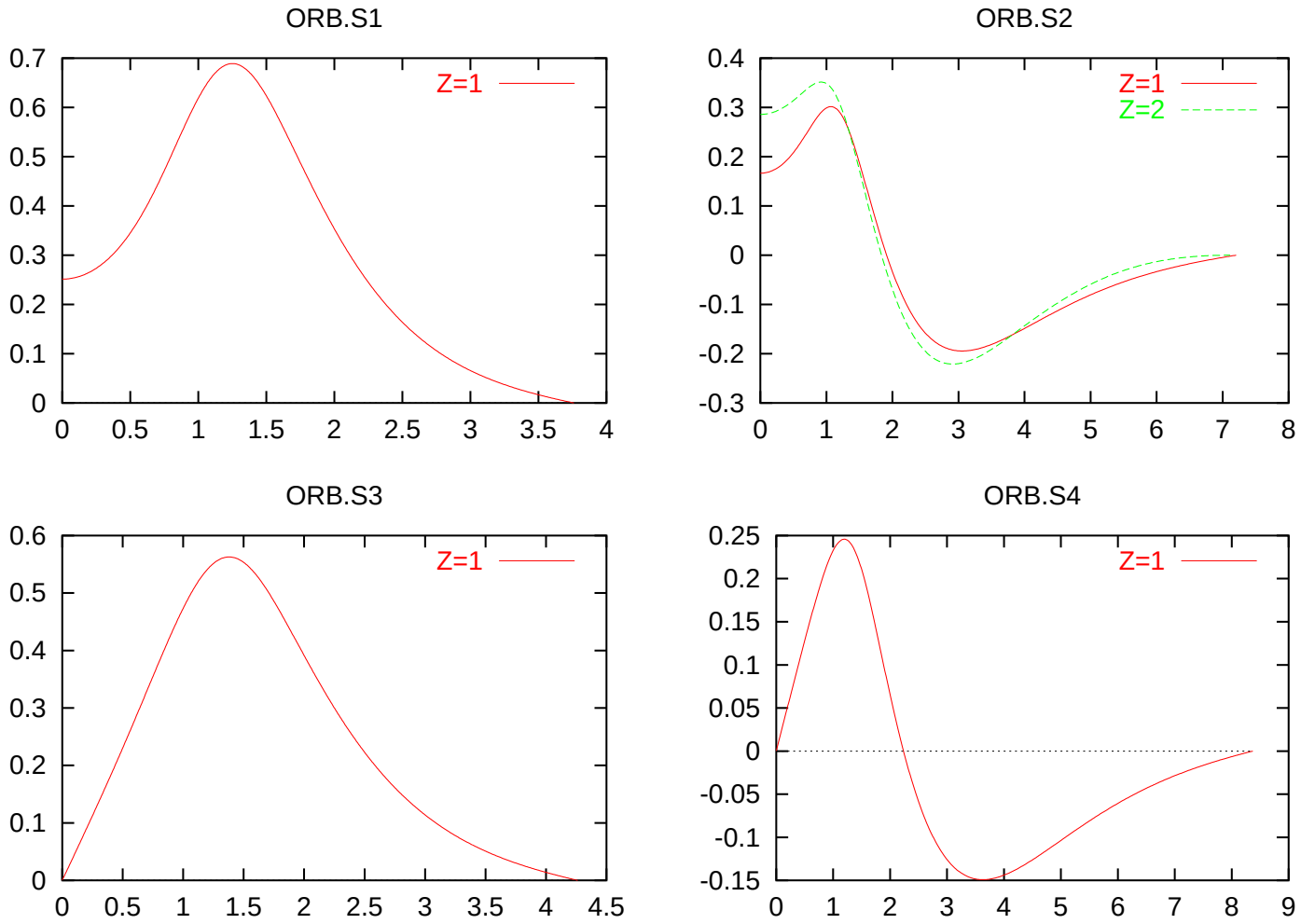
Si DZP: Pseudoatomic orbitals (PAOs)







Ba: $5s$, $6s$, $5p$, $6p$



```
NumberOfSpecies         1
%block ChemicalSpeciesLabel
      1      56     Ba_default
%endblock ChemicalSpeciesLabel

%block PAO.Basis
Ba_default    5
 n=5    0    1
   0.0
 n=6    0    2
   0.0 0.0
 n=5    1    1
   0.0
 n=5    2    1
   0.0
 n=6    1    1
   0.0
%endblock PAO.Basis
```

Sophisticated PAO specification

```
%block PS.lmax
   Ba_optim    3
%endblock PS.lmax

PAO.BasisType    split
%block PAO.Basis
Ba_optim    5       0.70
 n=5    0    1   E     98.95      5.90
   6.3989992009957 2
 n=6    0    2   E     97.95      6.50
   6.99956358549850         5.99949655050583
 n=5    1    1   E     96.95      6.09
   6.59922580635556
 n=5    2    1   E     95.95      6.60
   7.09995685034315
 n=6    1    1   E     94.96      6.60
   7.09996103032325
%endblock PAO.Basis
```

Ba optimized: $5s$, $6s$, $5p$, $6p$