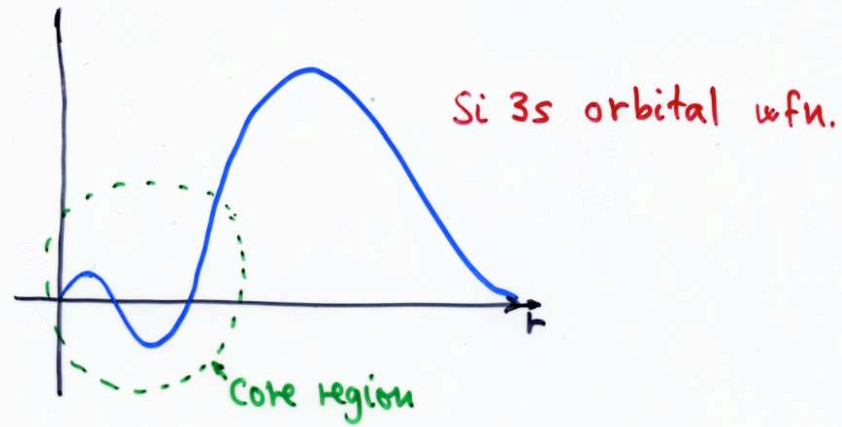


# How to generate and test pseudopotentials

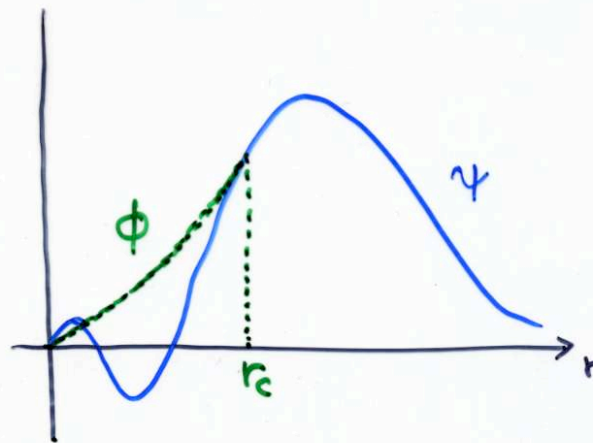
Alberto García  
ICMAB

CECAM--Siesta Tutorial -- June 2007



nodes: Imposed by orthogonality to the core states.

Idea: Eliminate the core electrons by "ironing out" the nodes:



$\phi$ : Pseudowavefunction

```

#
# 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
#
#23456789012345678901234567890123456789012345678901234567890

```

# 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
```

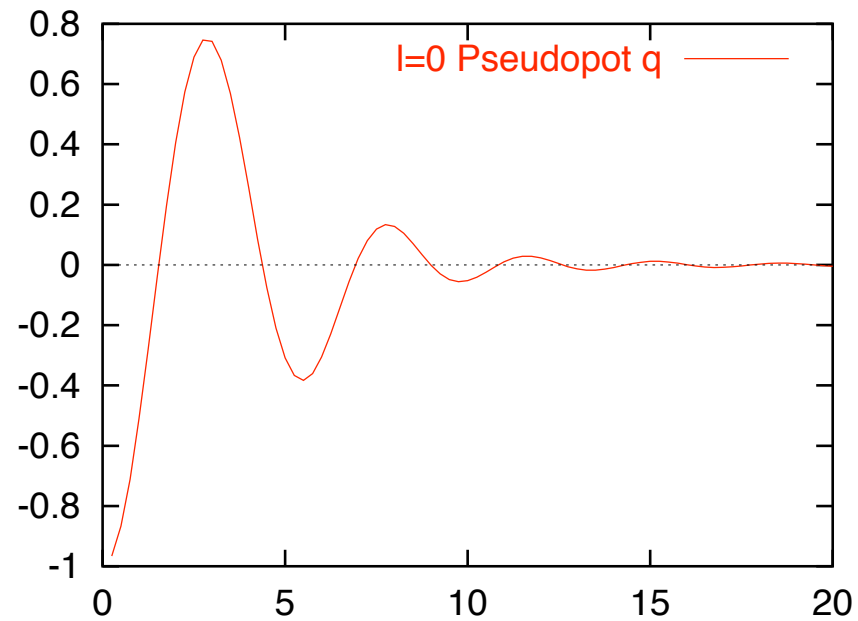
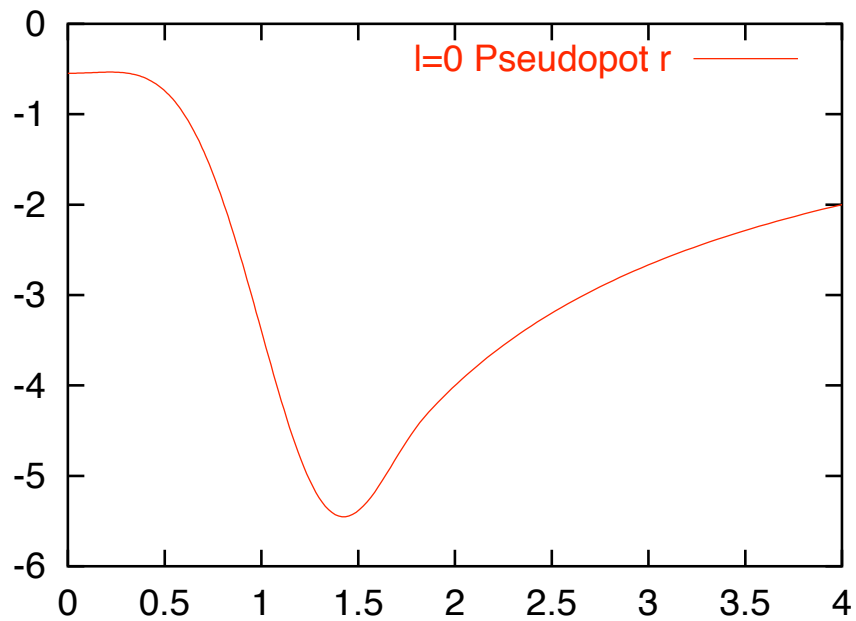
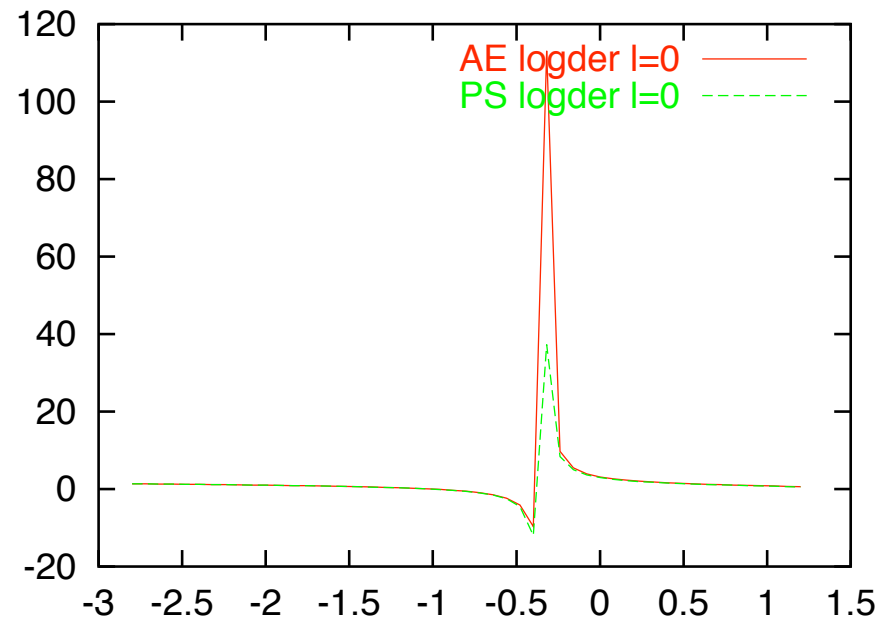
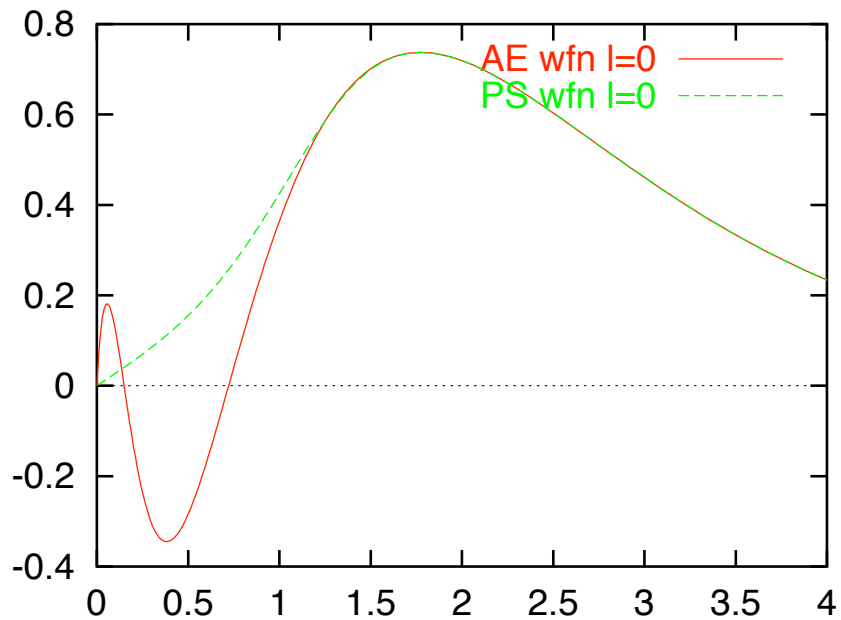
```
$
```

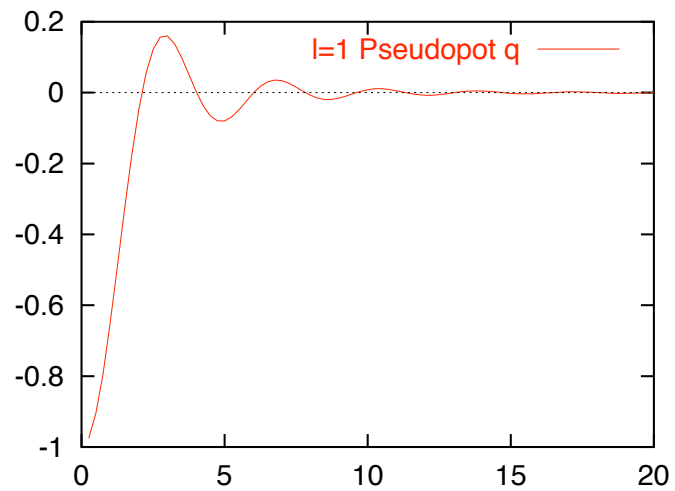
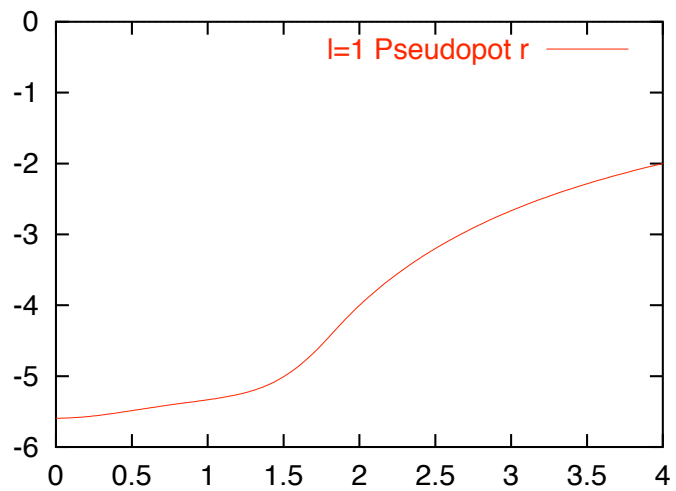
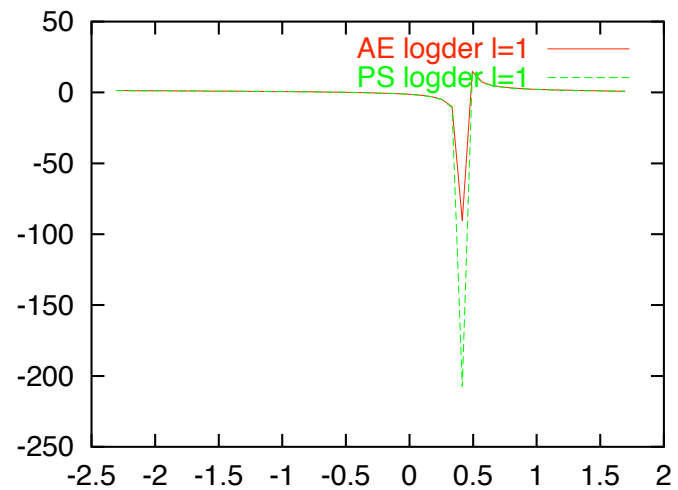
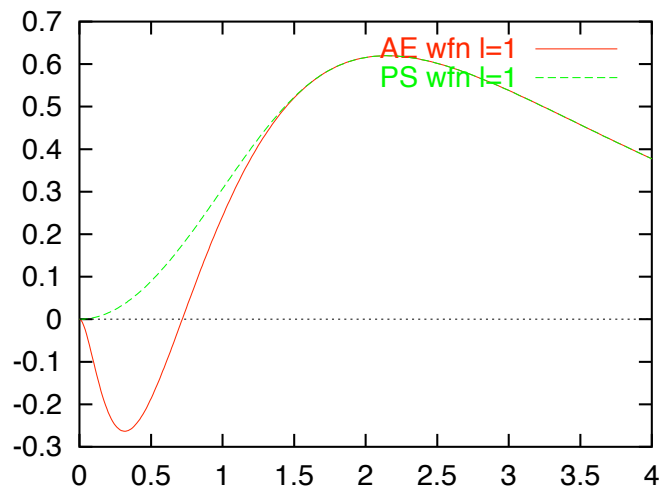
```
$ # PLOTTING
```

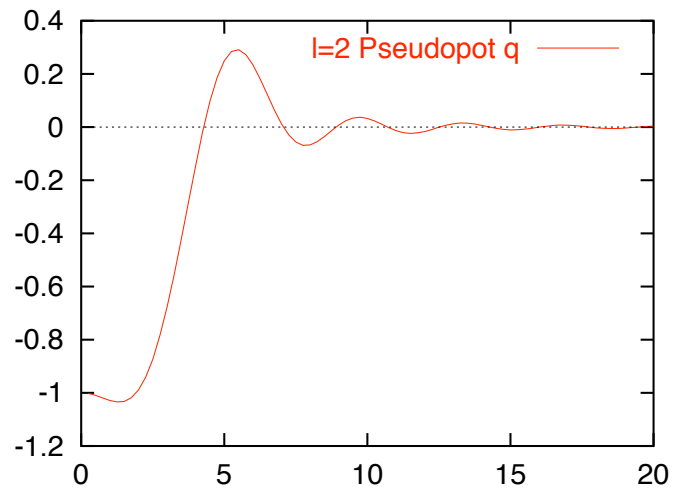
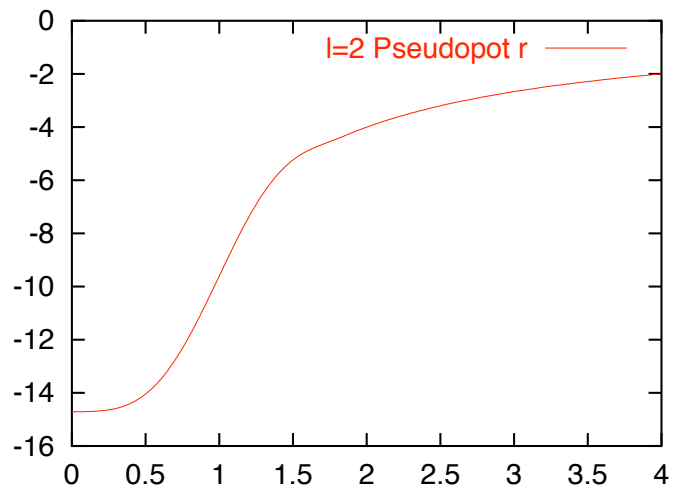
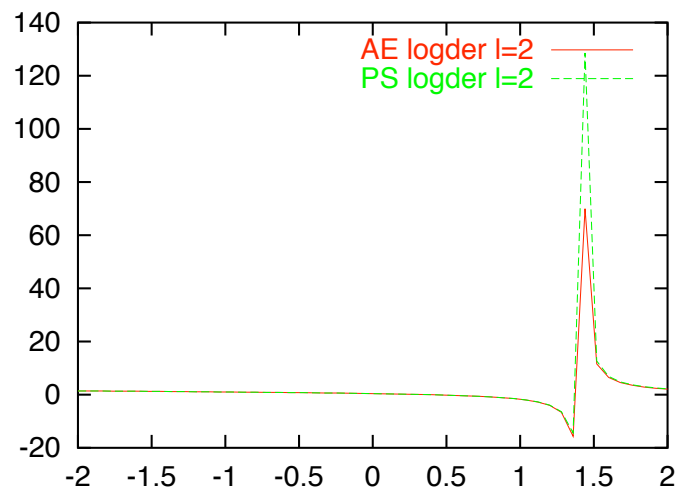
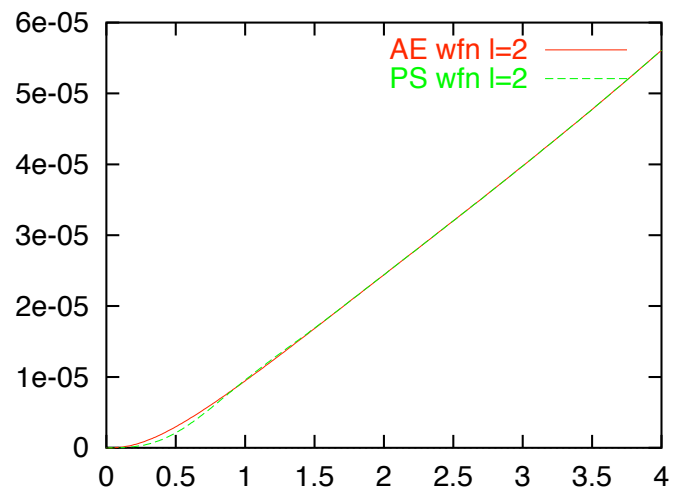
```
$
```

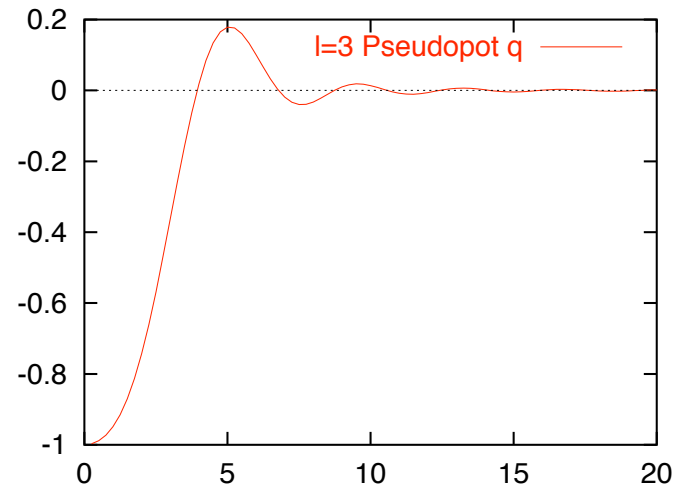
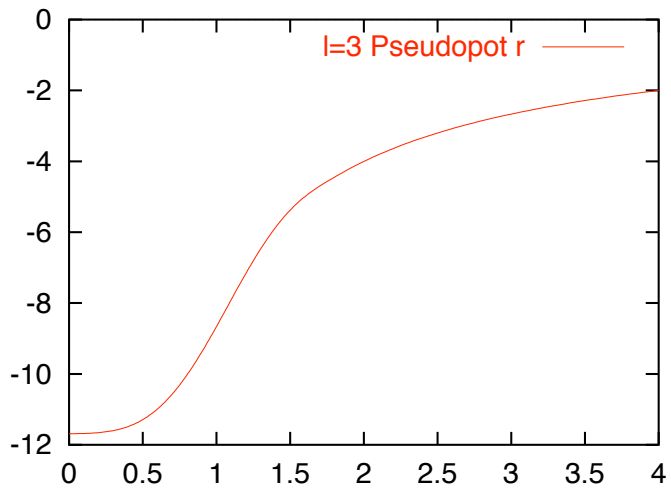
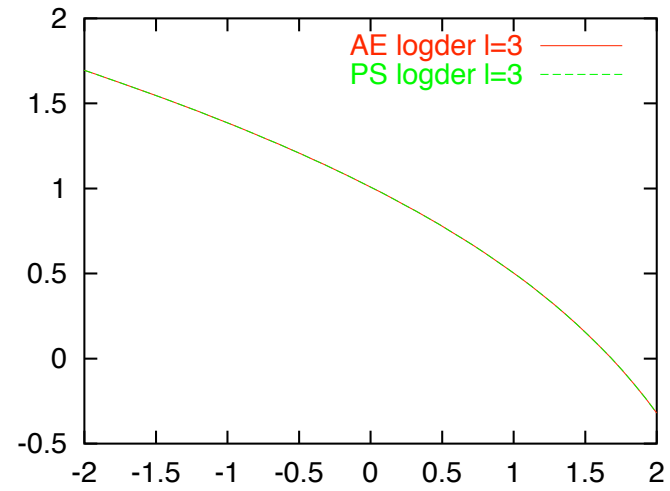
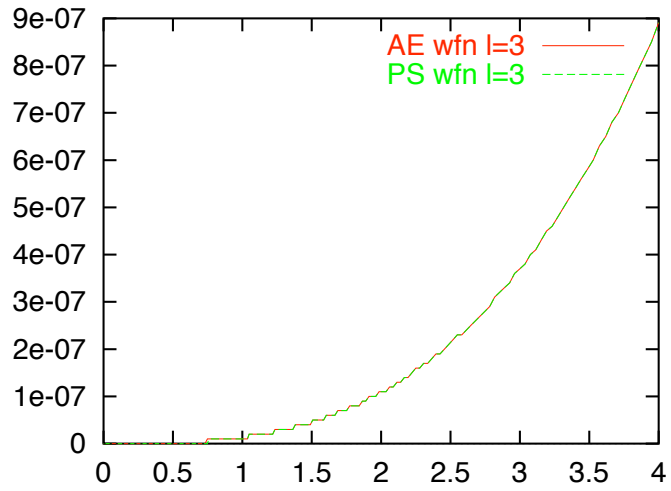
```
$ gnuplot pseudo.gps
```

```
==> Postscript output in pseudo.ps
```

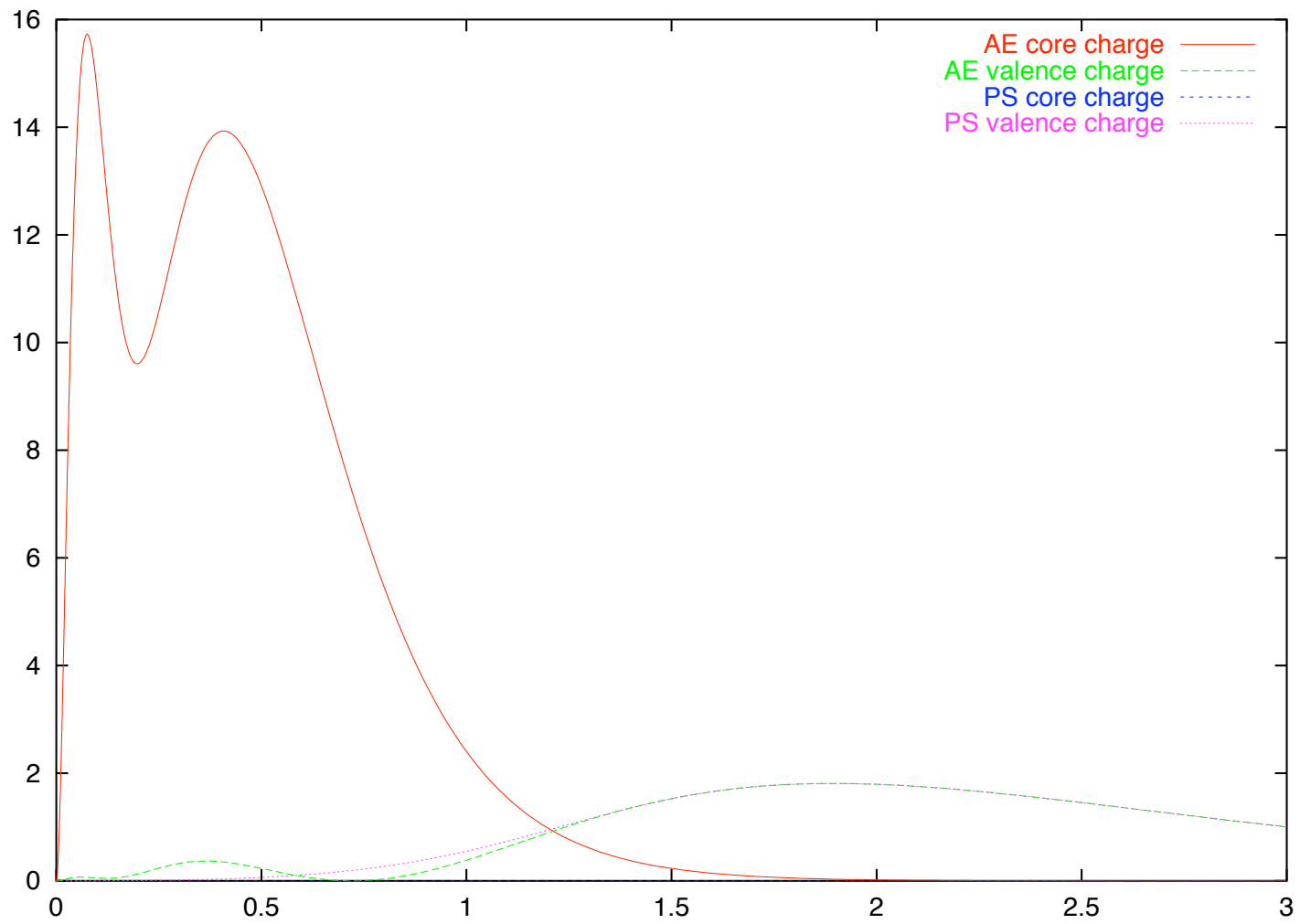


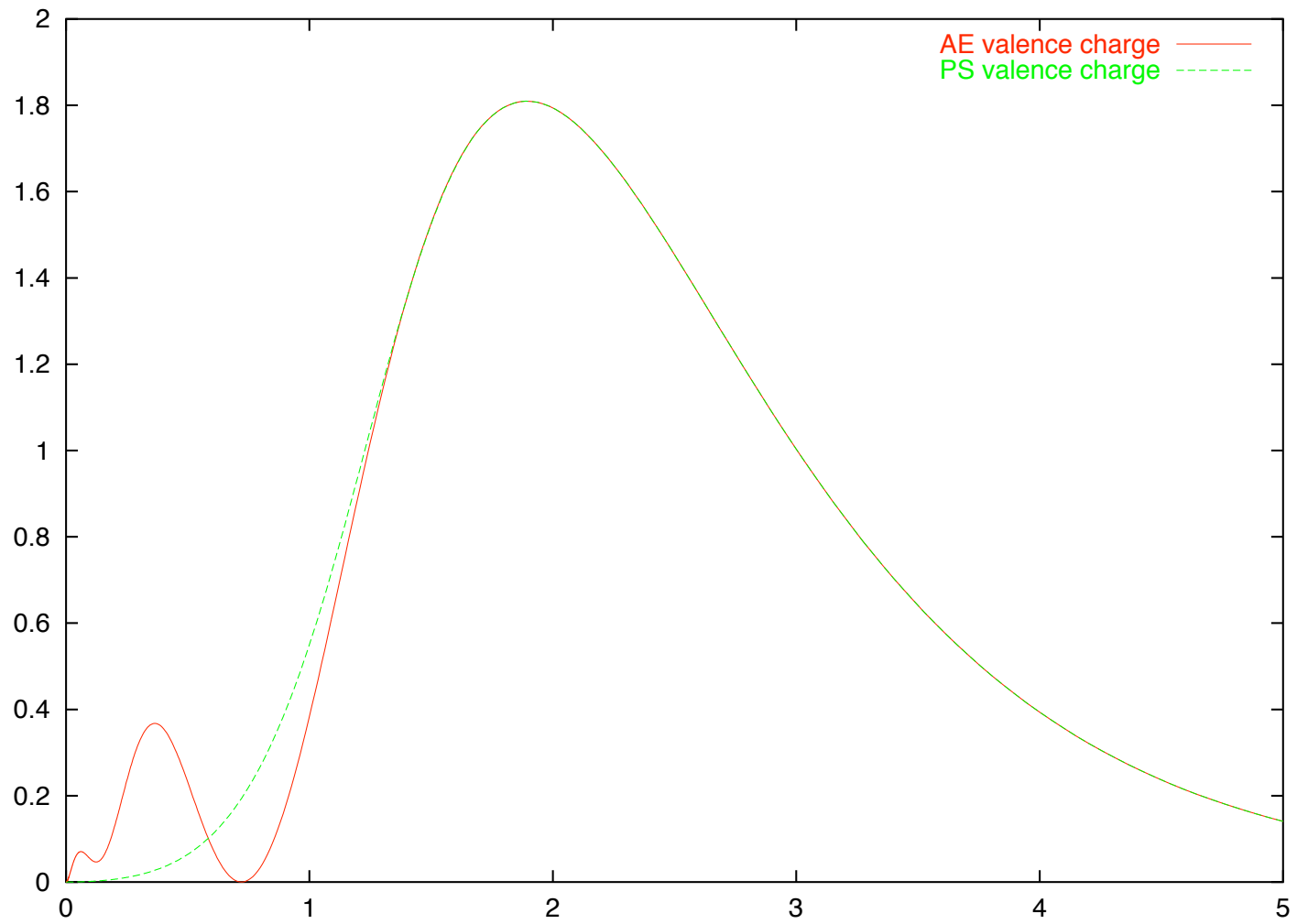












\$ grep '&v' OUT

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
```

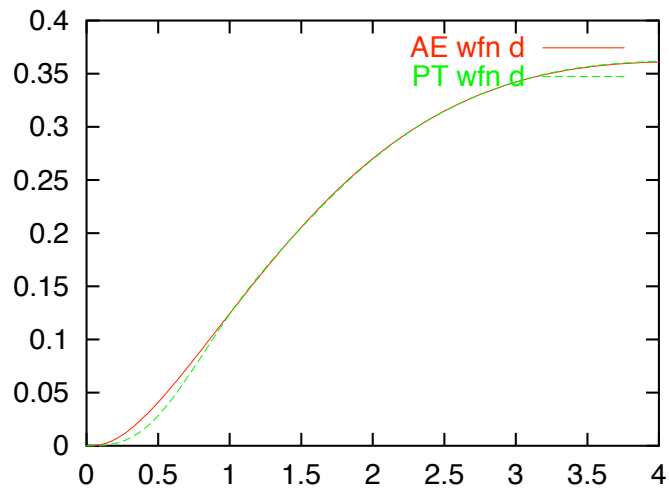
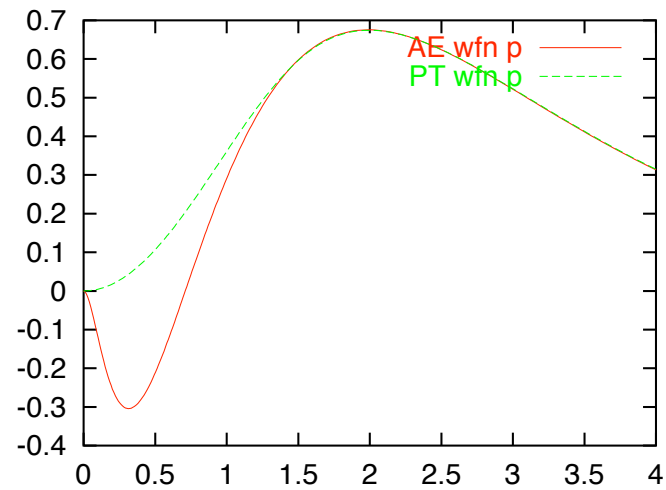
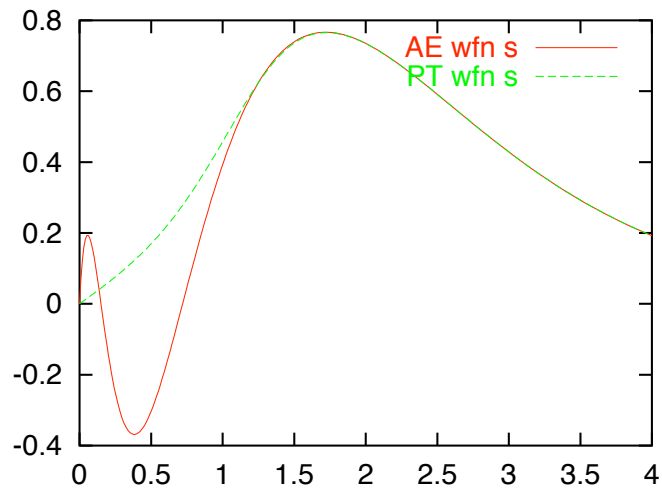
```
3 1 3.00
```

```
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  AEFNR1  CHARGE  OUT          PTWFNR0  PTWFNR2  VPSIN
AEWFNR0   AEFNR2  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
-----

```



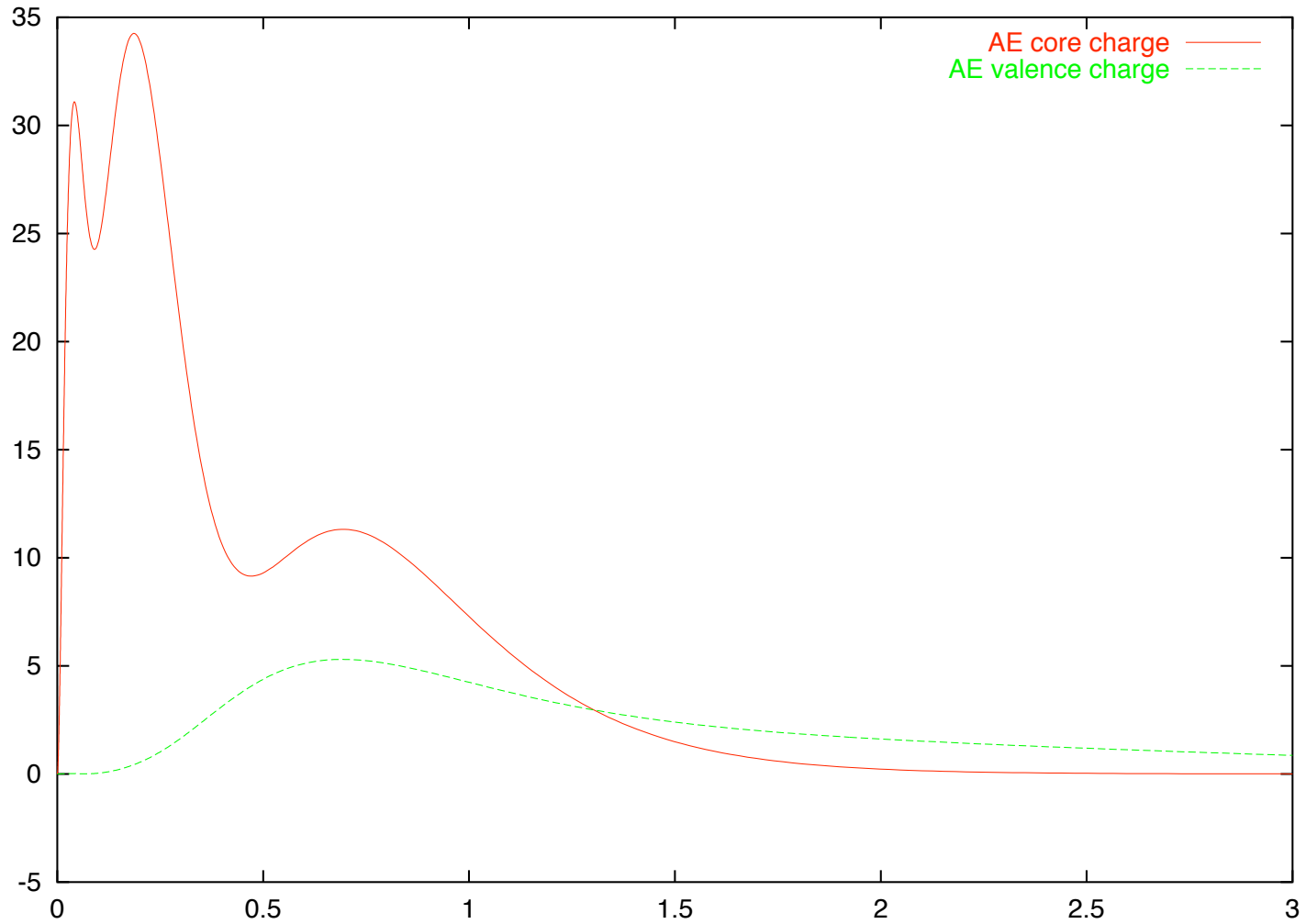
&d total energy differences in series

&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

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

But

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

Error due to non-linearity of XC potential.

Corrected unscreening: Keep core charge  
in pseudopotential generation

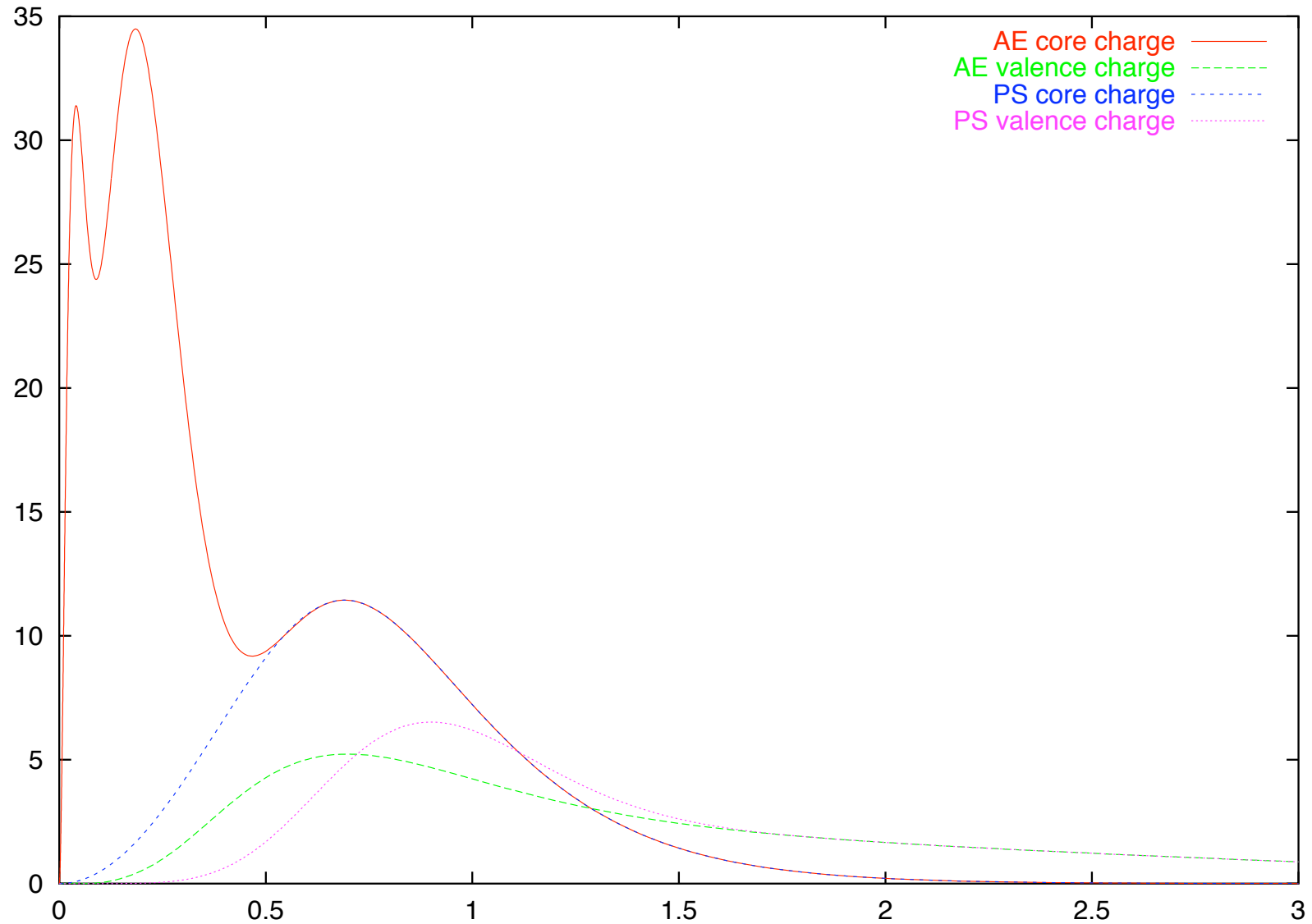
$$V^{ps}(r) = V_{scr}^{ps}[\rho_v + \rho_c](r) - V_H[\rho_v](r) - V_{xc}[\rho_v + \rho_c](r)$$

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

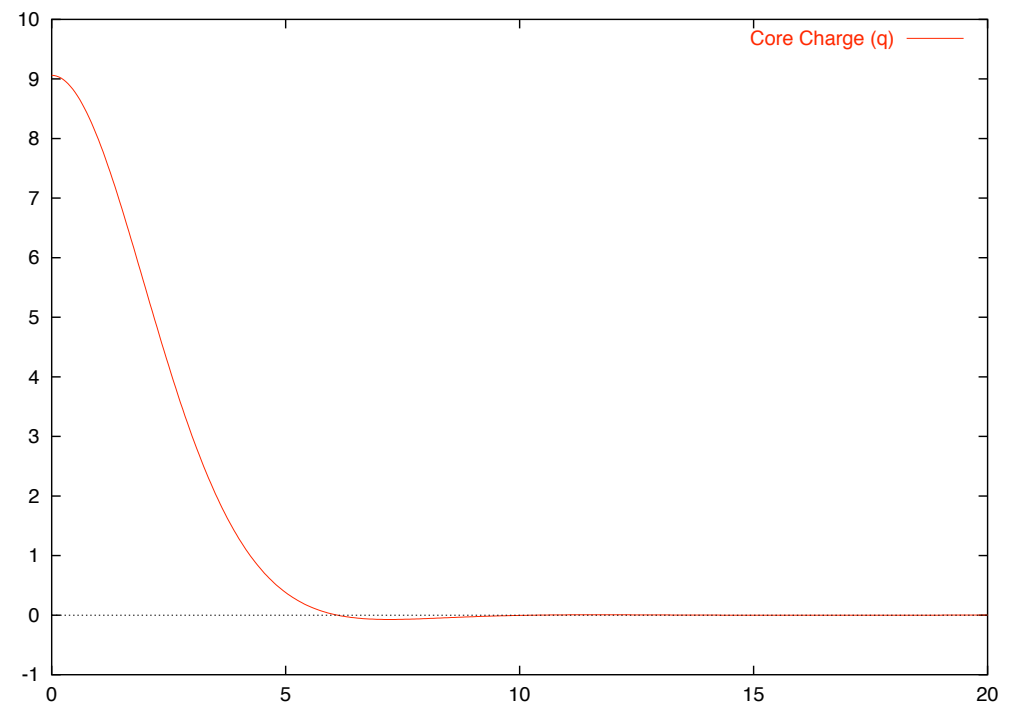
Non-linear core-corrections



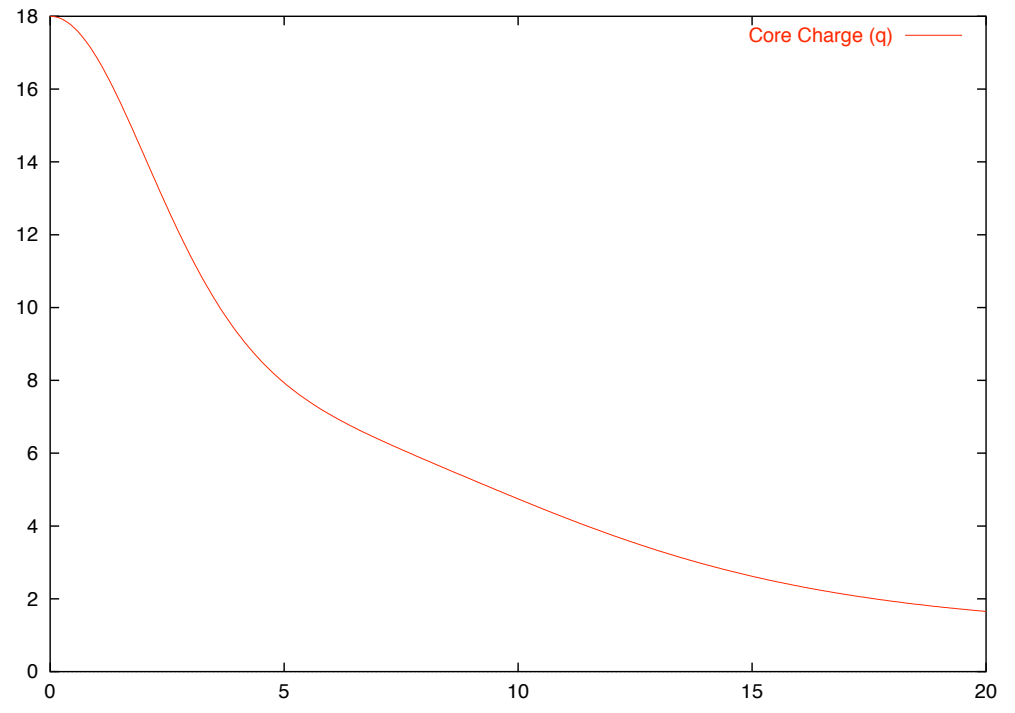
# Pseudo-core charge



Soft pseudo-core



Hard core



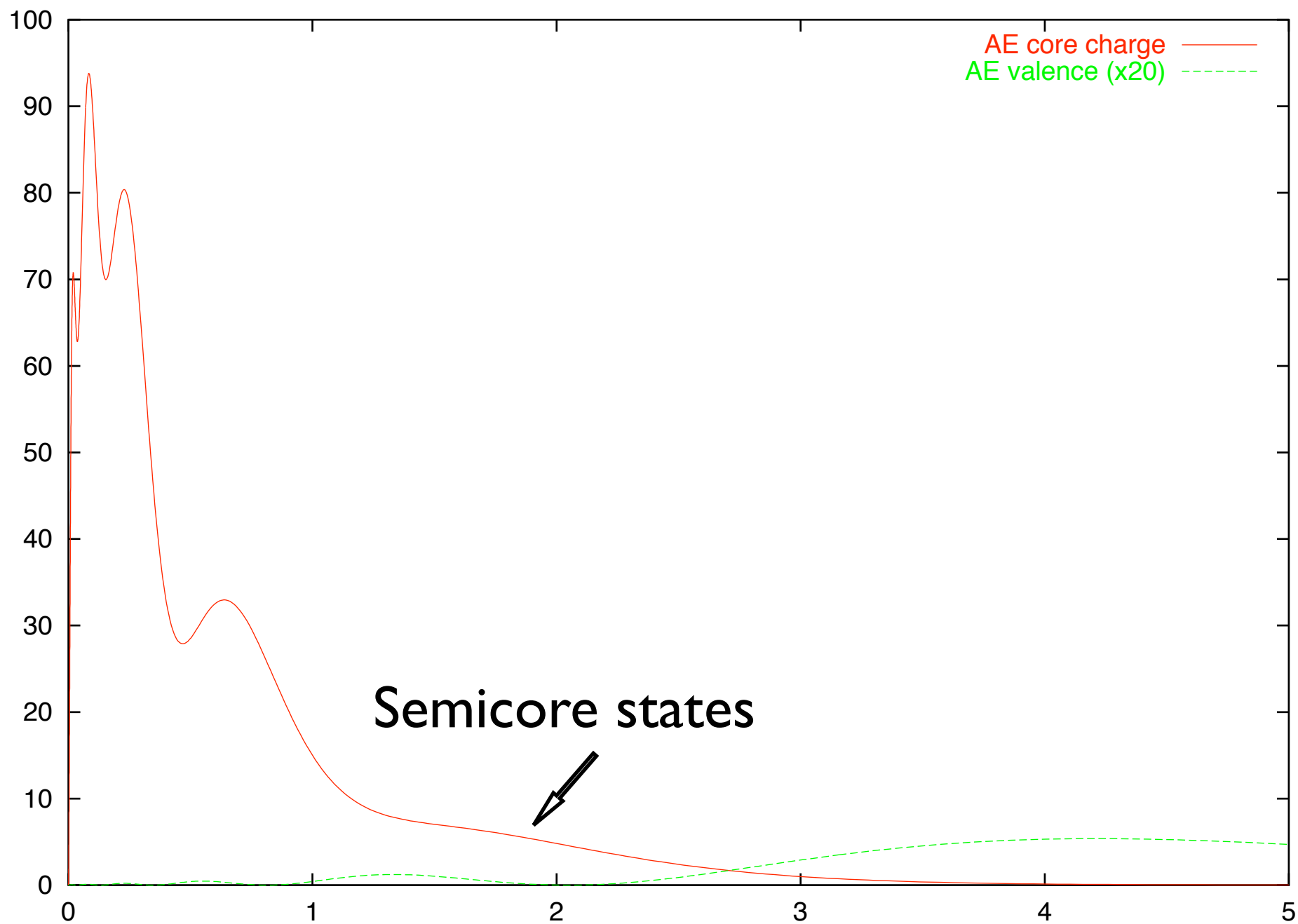
# Real-Space Grid

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

# Ba: Large core + 6s<sup>2</sup>



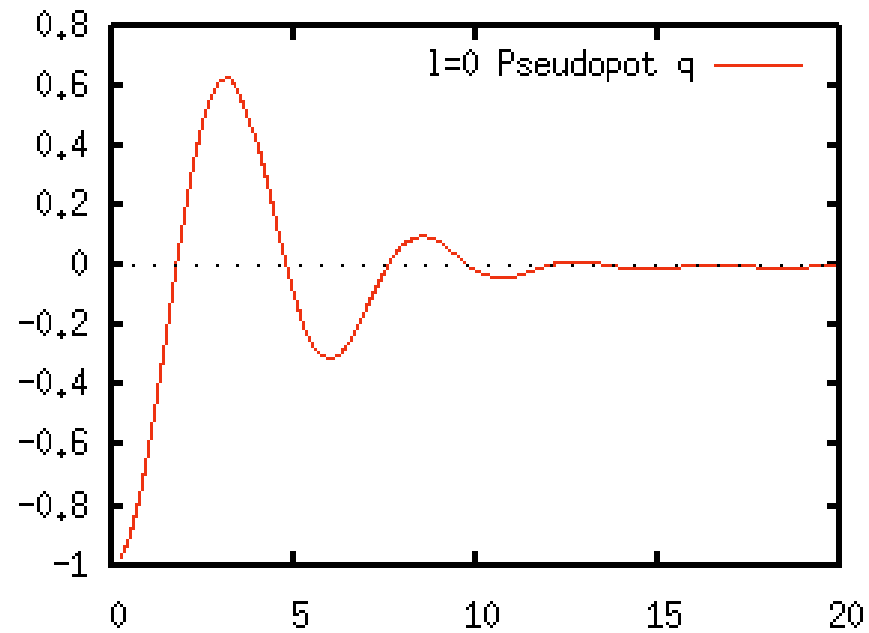
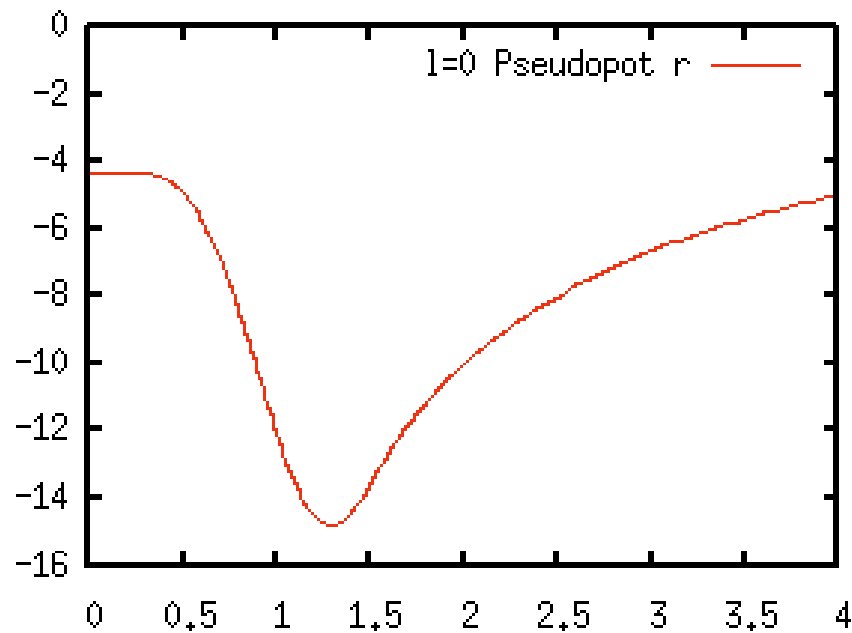
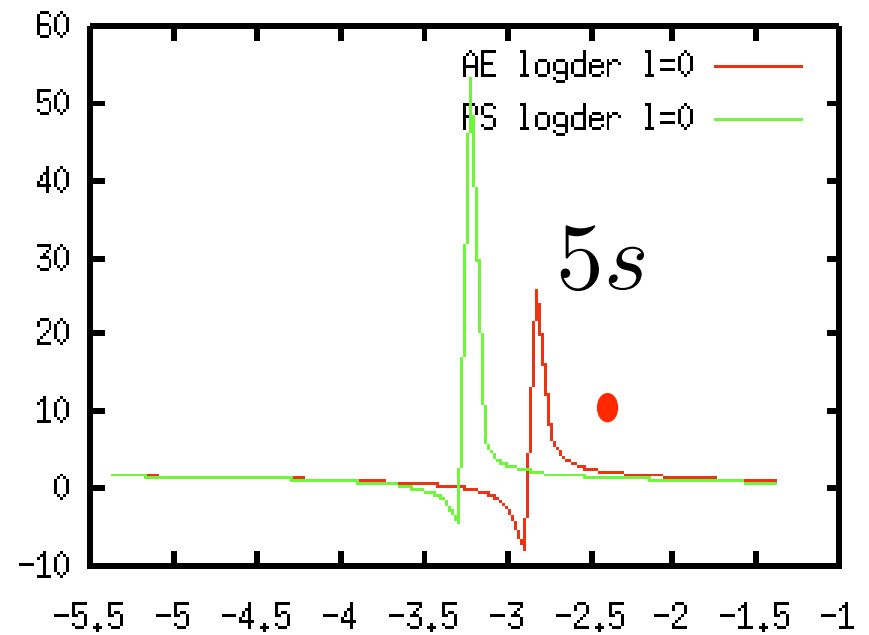
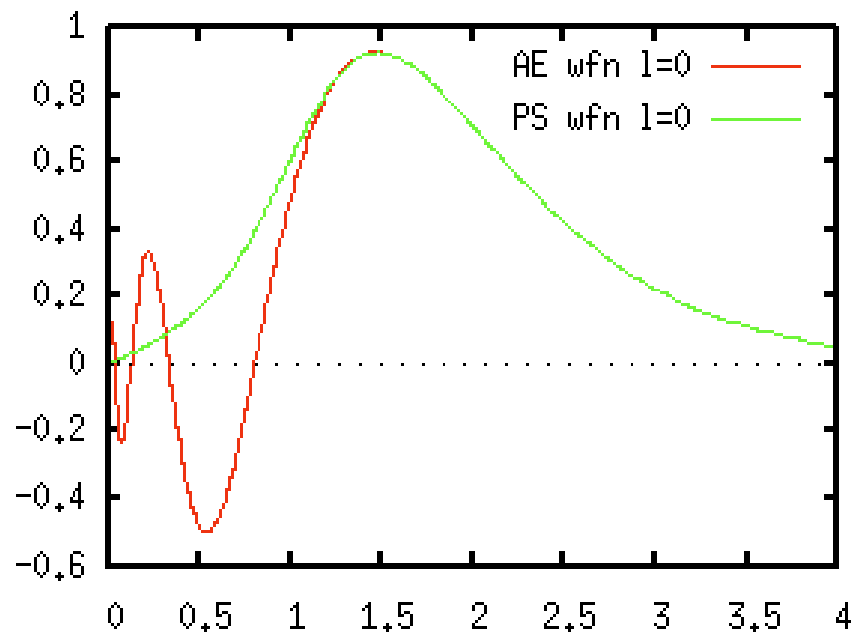
# Put $5s^2$ and $5p^6$ in valence complex

```
#
# 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
```

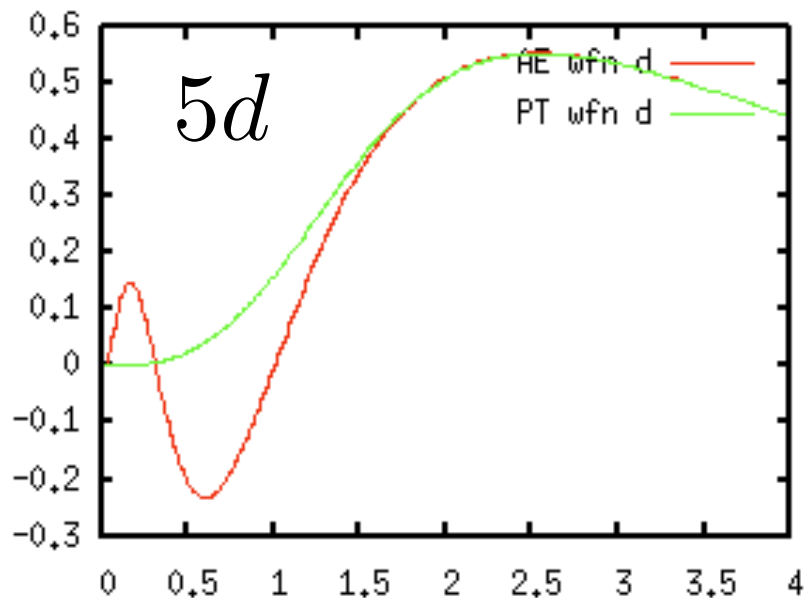
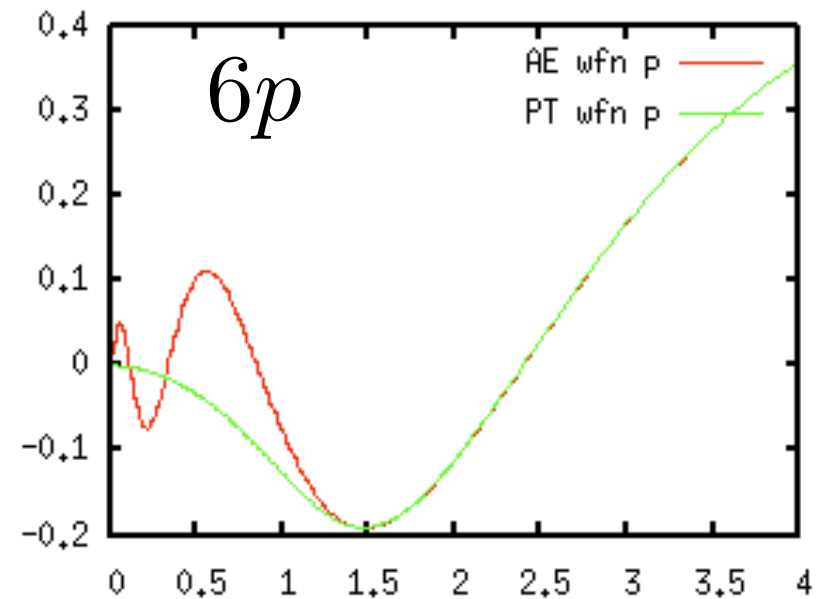
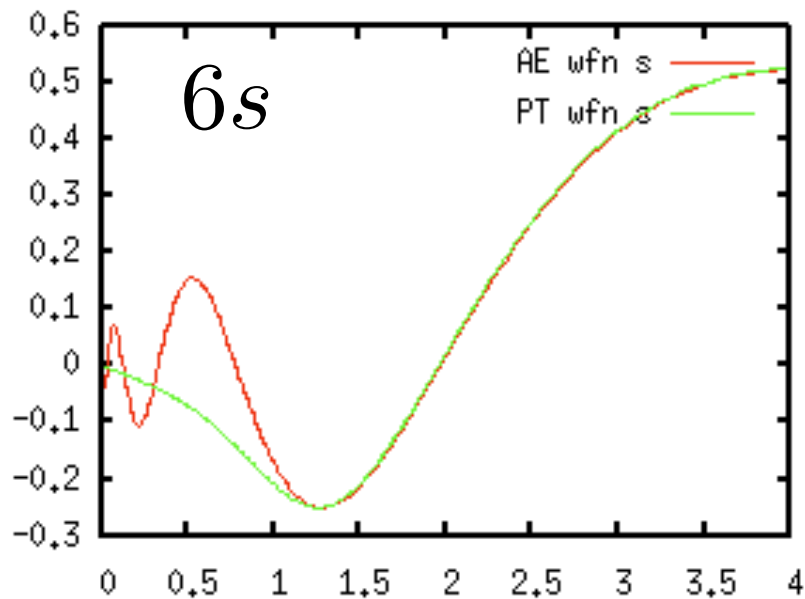
(Semicore States)



# Ba: s-channel pseudopotential construction

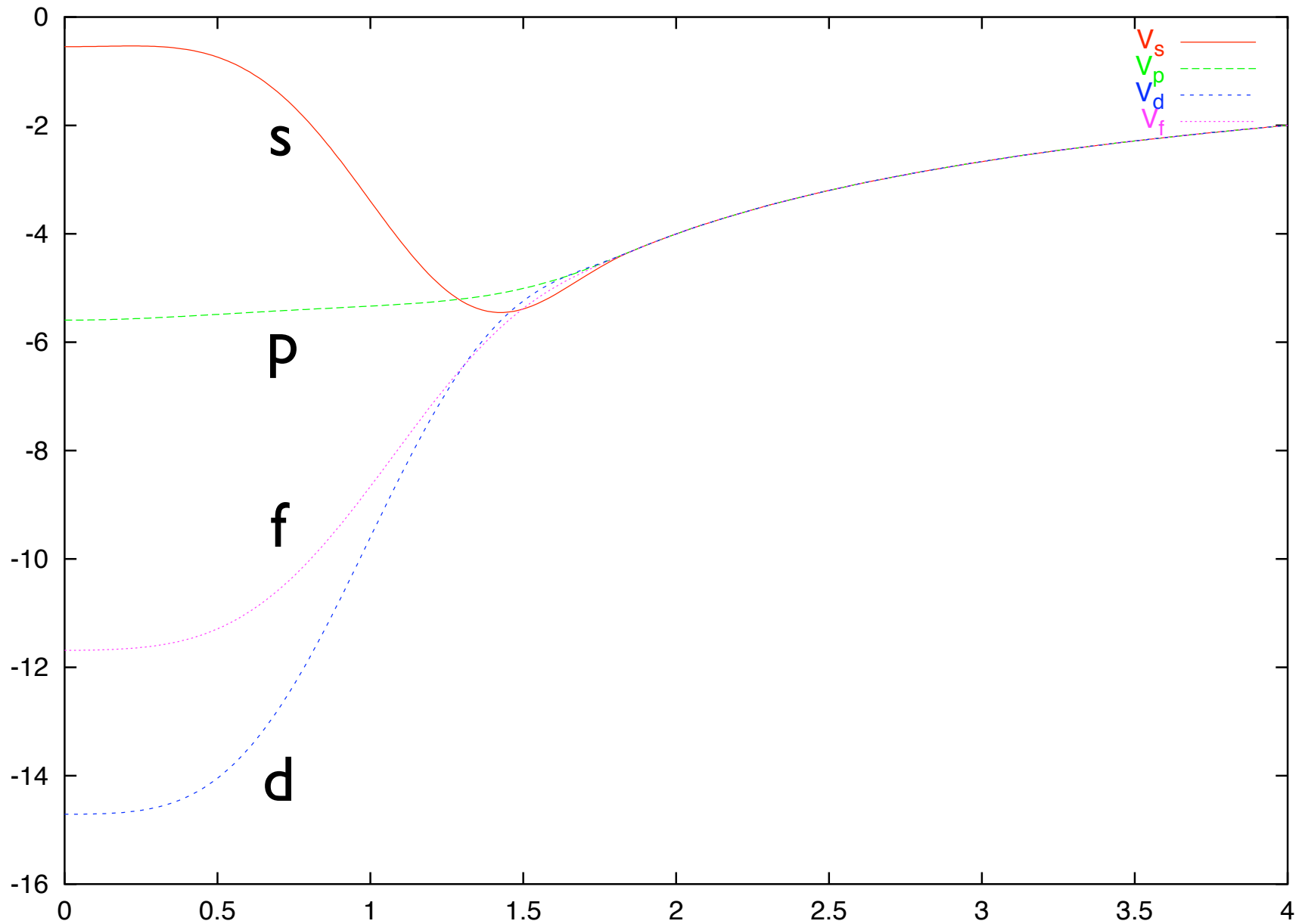


# Ba: The pseudopotential reproduces higher states



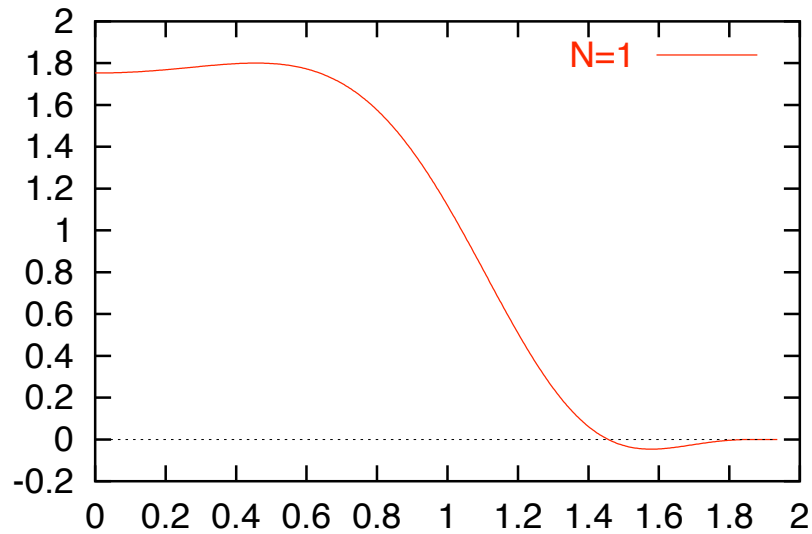
$6s$  and  $6p$  pseudo-orbitals  
have nodes

# Pseudopotential semi-local components

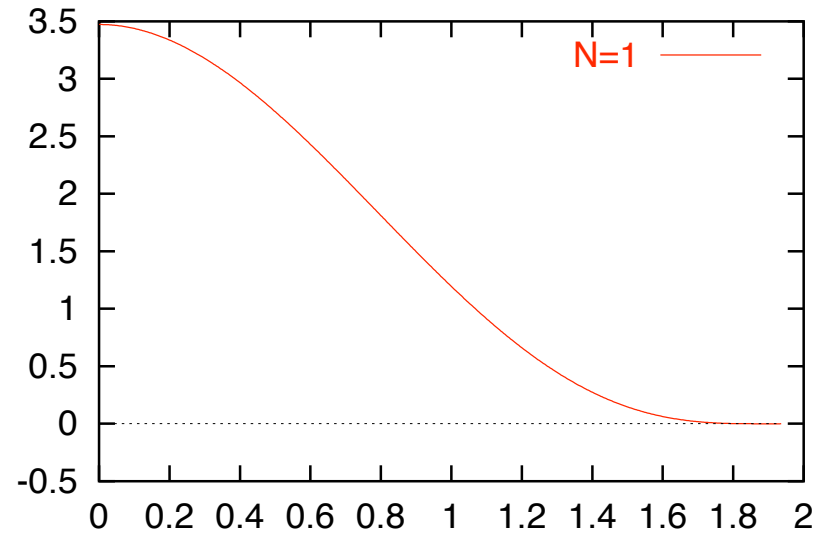


# Kleinman-Bylander projectors

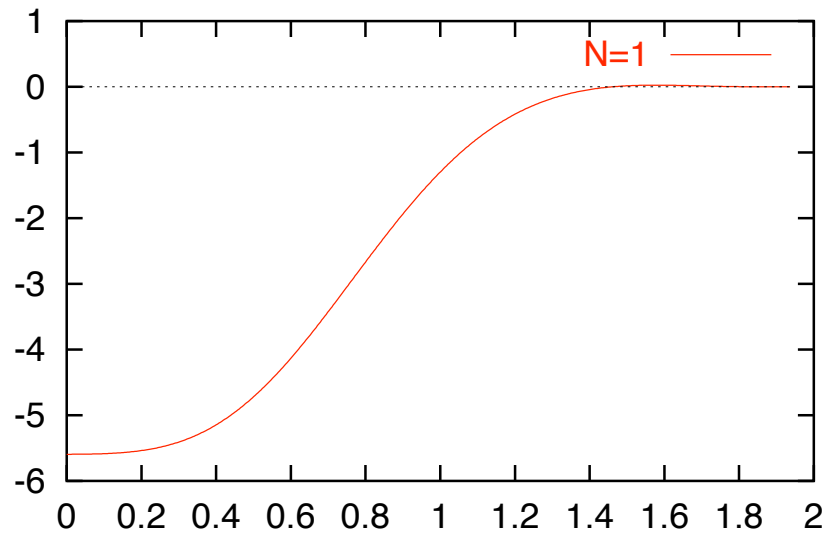
L=0



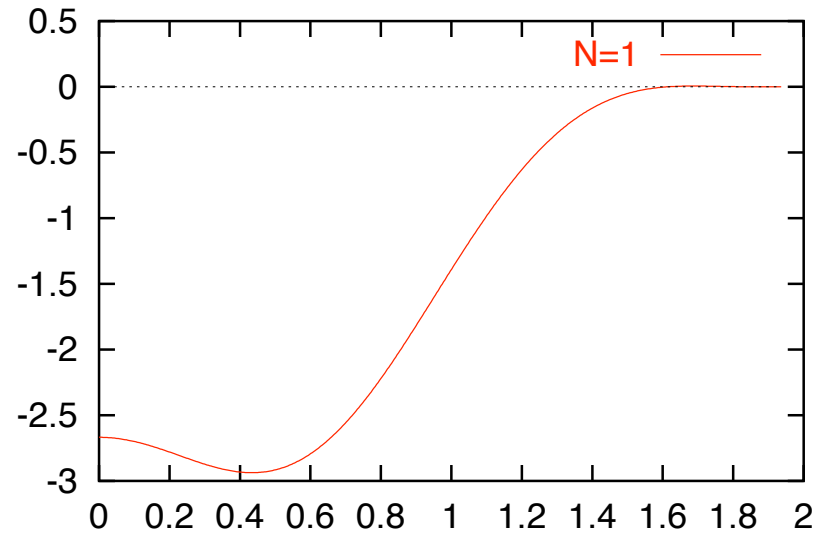
L=1



L=2

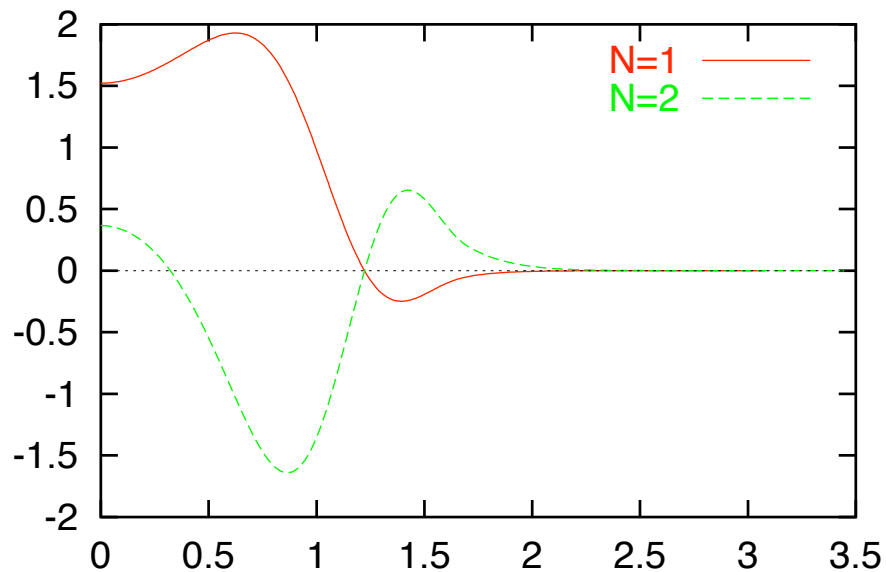


L=3

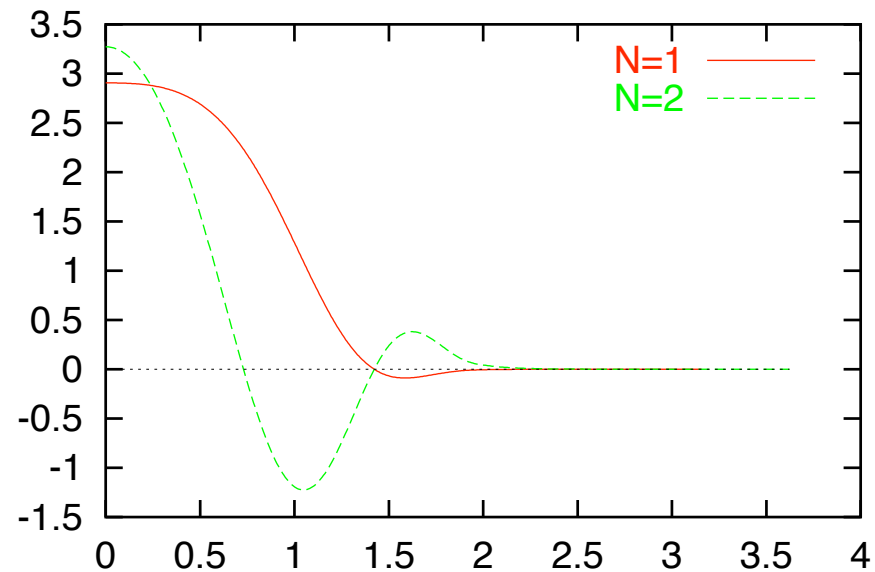


# Ba: Extra projectors for semicore states

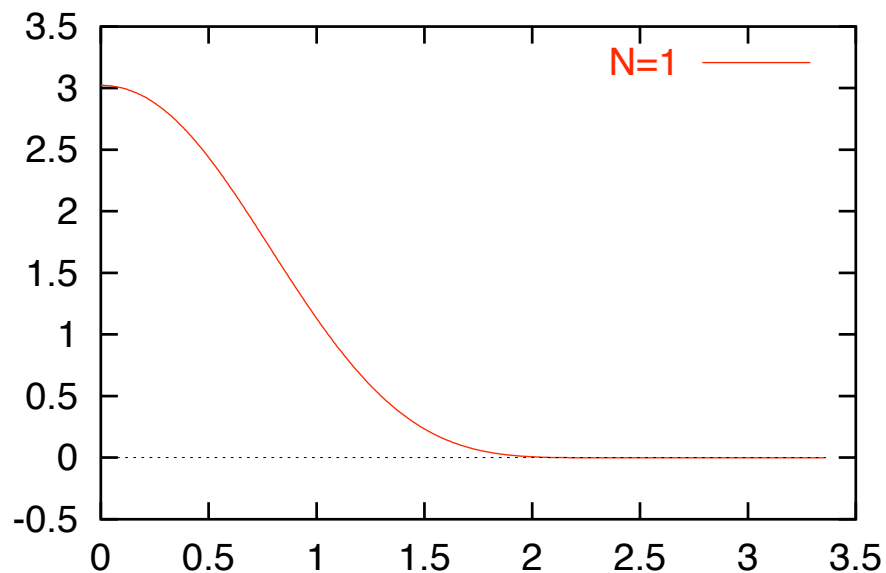
L=0



L=1



L=2



L=3

