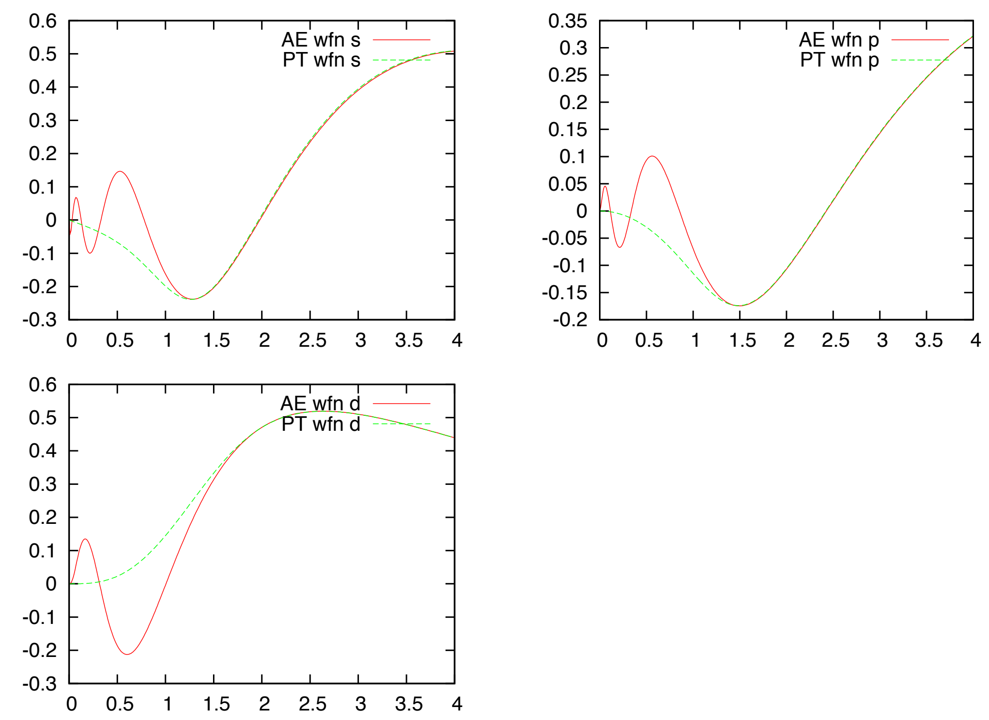
How to generate a pseudopotential with the semicore in the valence



Objectives

Check whether semicore states should be explicitly included in the valence and how it should be done

Generation of l-dependent norm-conserving pseudopotential

Choose an atomic reference configuration, i.e., a given distribution of electrons in the atomic energy levels (degree of freedom)

Solve the all-electron radial Schrödinger equation for the chosen atomic reference configuration

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V_{\text{eff}}[n](r)\right]u_{nl}^{\text{AE}}(r)=\varepsilon_{nl}u_{nl}^{\text{AE}}(r)$$

$$V_{\text{eff}}[n](r)=V_{\text{ext}}(r)+V_{\text{Hartree}}[n]+V_{xc}[n]=-\frac{Z}{r}+\int\frac{n(r')}{|r-r'|}dr'+V_{xc}[n]$$

$n(r)$ ≡ sum of electronic charges for occupied states

Z ≡bare nuclear charge

Parametrization of the pseudo-wave functions for $r<R_c$ according to any of the available prescriptions (degree of freedom)

Invert the radial Schrödinger equation for the screened pseudopotential

Subtract (unscreen) the Hartree and exchange-correlation potentials

Generation of *l*-dependent norm-conserving pseudo: unscreening of the pseudopotential

The pseudo-wave function obeys

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V^{\mathrm{PS}}_{(\mathrm{sc})l}(r)\right]u_l^{\mathrm{PS}}(r)=\varepsilon_l u_l^{\mathrm{PS}}(r)$$

Where the effective potential is computed in the atom

$V^{\mathrm{PS}}_{(\mathrm{sc})l}$ includes

- Bare nuclei-valence interaction
- Hartree interacion
- Exchange-correlation interacion

Computed with an atomic charge density

$$n_{\mathrm{atom}}(\vec{r})=n^{\mathrm{core}}_{\mathrm{atom}}(\vec{r})+n^{\mathrm{valence}}_{\mathrm{atom}}(\vec{r})$$

Blind to the chemical environment

Extremely dependent on the chemical environment

In the molecular system or condensed phase, we have to screen the (ion+core)-valence interaction with the valence charge density computed in the targeted system

Generation of l-dependent norm-conserving pseudo: unscreening of the pseudopotential

In the molecular system or condensed phase, we have to screen the (ion+core)-valence interaction with the valence charge density computed in the targeted sytem

So, the pseudopotential is finally obtained by subtracting (unscreening) the Hartree and exchange and correlation potential calculated only for the valence electrons (with the valence pseudo-wave function)

$$\begin{aligned} V_l^{\mathrm{PS}} &= V_{(\mathrm{sc})l}^{\mathrm{PS}} - V_{\mathrm{Hartree}}[n_v] - V_{xc}[n_v] \\ &= V_{(\mathrm{sc})l}^{\mathrm{PS}} - \int \frac{n_v(r')}{|r-r'|} dr' - V_{xc}[n_v] \end{aligned}$$

Where the pseudo-valence charge density is computed as

$$n_v(r) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} |u_{nl}^{\mathrm{PS}}(r)|^2$$

Exchange-correlation functional in the DFT all-electron calculation used to construct the pseudopotential has to be the same as in the target calculation

When there is a significant overlap of core and valence charge densities: problem with unscreening

The exchange and correlation potential and energy are not linear functions of the density

$$E_{xc}[n_{\text{atom}}(\vec{r})] \neq E_{xc}[n_{\text{atom}}^{\text{core}}(\vec{r})] + E_{xc}[n_{\text{atom}}^{\text{valence}}(\vec{r})]$$

In cases where the core and valence charge density overlap significantly:

- **In systems with few valence electrons (alkali atoms)**
- **In systems with extended core states**
- **In transition metals, where the valence d bands overlap spatially with the core s and p electrons**

the unscreening procedure as explained before is not fully justified.

$$\underbrace{V_{xc}[n_{\text{atom}}^{\text{core}}(\vec{r}) + n_{\text{atom}}^{\text{valence}}(\vec{r})]}_{\text{xc potential that appears in the unscreened potential}} = \underbrace{\left(V_{xc}\left[n_{\text{atom}}^{\text{core}}(\vec{r}) + n_{\text{atom}}^{\text{valence}}(\vec{r})\right] - V_{xc}[n_{\text{atom}}^{\text{valence}}(\vec{r})]\right)}_{\text{Since xc is not linear, if core and valence overlaps, the contribution from valence is not fully canceled}} + \underbrace{V_{xc}[n_{\text{atom}}^{\text{valence}}(\vec{r})]}_{\text{xc potential that is removed in the unscreening procedure}}$$

Then, the screening pseudopotentials are dependent on the valence configuration, a feature highly undesirable since it reduces the transferability of the potential.

When there is a significant overlap of core and valence charge densities: non-linear core correction

Solution 1: Include explicitly the extended core orbitals in the valence (semicore in valence)

Expensive since:

- We have to include explicitly more electrons in the simulation

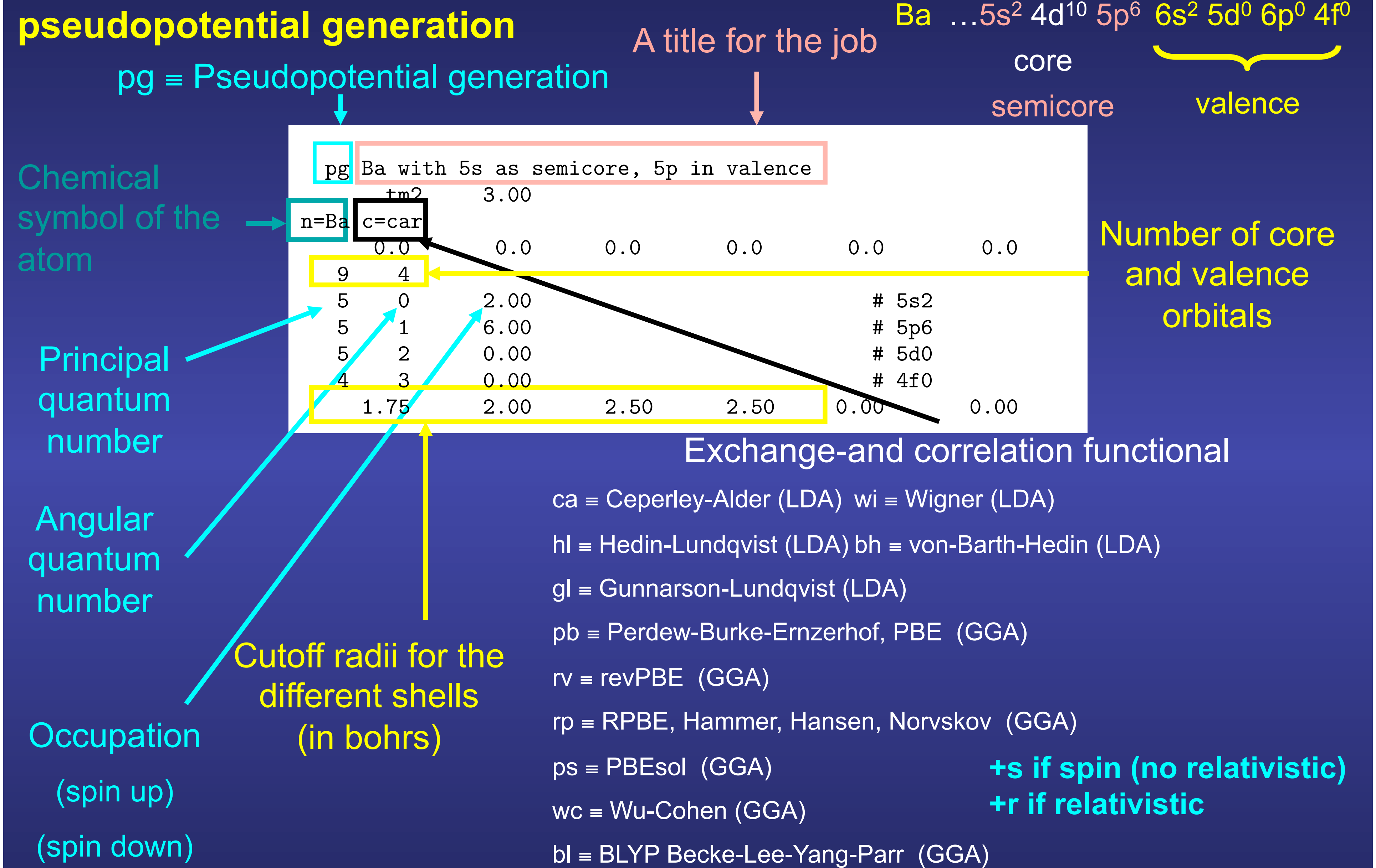
-The semicore orbitals tend to be very localized and hard, in the sense that high Fourier components are required

Description of the input file of the ATOM code for a pseudopotential generation

Ba …$5s^2$ $4d^{10}$ $5p^6$ $\underbrace{6s^2\ 5d^0\ 6p^0\ 4f^0}_{\text{valence}}$

core

semicore



pg ≡ Pseudopotential generation

A title for the job

Chemical symbol of the atom

Number of core and valence orbitals

Principal quantum number

Angular quantum number

Occupation

(spin up)

(spin down)

Cutoff radii for the different shells (in bohrs)

```
   pg Ba with 5s as semicore, 5p in valence
        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                              # 5d0
    4    3      0.00                              # 4f0
       1.75      2.00      2.50      2.50      0.00       0.00
```

Exchange-and correlation functional

ca ≡ Ceperley-Alder (LDA) wi ≡ Wigner (LDA)

hl ≡ Hedin-Lundqvist (LDA) bh ≡ von-Barth-Hedin (LDA)

gl ≡ Gunnarson-Lundqvist (LDA)

pb ≡ Perdew-Burke-Ernzerhof, PBE (GGA)

rv ≡ revPBE (GGA)

rp ≡ RPBE, Hammer, Hansen, Norvskov (GGA)

ps ≡ PBEsol (GGA)

wc ≡ Wu-Cohen (GGA)

bl ≡ BLYP Becke-Lee-Yang-Parr (GGA)

am≡ AM05 by Armiento and Mattson (GGA)

vw ≡ van der Waals functional

+s if spin (no relativistic)

+r if relativistic

Generate and test a pseudopotential for Ba with the semicore explicitly included in the valence

```
../../Utils/pg.sh Ba.semicore.inp
==> Output data in directory Ba.semicore
==> Pseudopotential in Ba.semicore.vps and Ba.semicore.psf (and maybe in Ba.semicore.xml)



../../Utils/pt.sh Ba.test.inp Ba.semicore.vps
==> Output data in directory Ba.test-Ba.semicore
```

See previous examples to understand how to generate and test norm-conserving pseudopotentials

Generate and test a pseudopotential for Ba with the semicore explicitly included in the valence

Both the 5*s* and 5*p* states are normally thought of as “core states”

But now, they have been included in the valence.

As the program can only deal with one pseudized state per angular momentum channel, this implies the elimination of the “genuinely valence” 6*s* state from the calculation

In other words, the pseudopotential has been generated for an ion

```
$ cd Ba.semicore

$ more OUT

Ba pseudopotential generation
 -----------------------------

 r e l a t i v i s t i c ! !

 correlation = ca       spin-polarized

 nuclear charge            = 56.000000
 number of core orbitals   = 14
 number of valence orbitals =  7
 electronic charge         = 54.000000
 ionic charge              =  2.000000
```

The semicore orbitals are very extended.
5s and 5p orbitals overlap strongly with 4d orbitals

The reason why the semicore orbitals have to be included in the valence is that they are very extended, and overlap a lot with the valence states

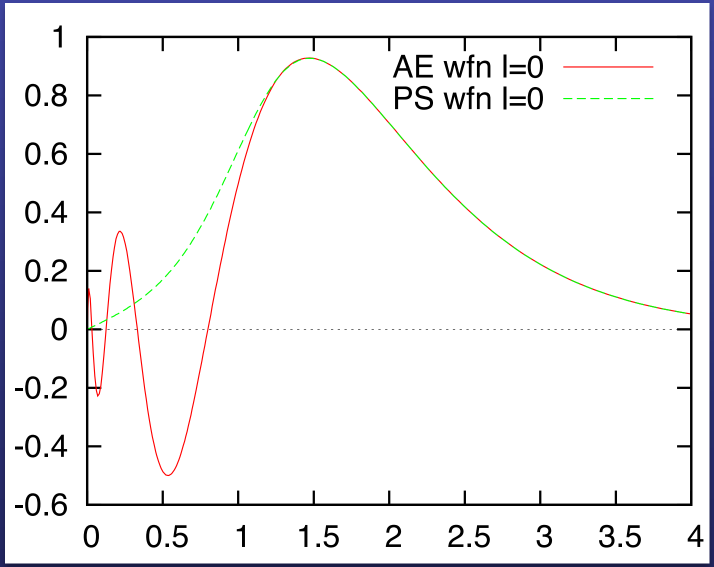
This can be seen plotting the semicore orbitals

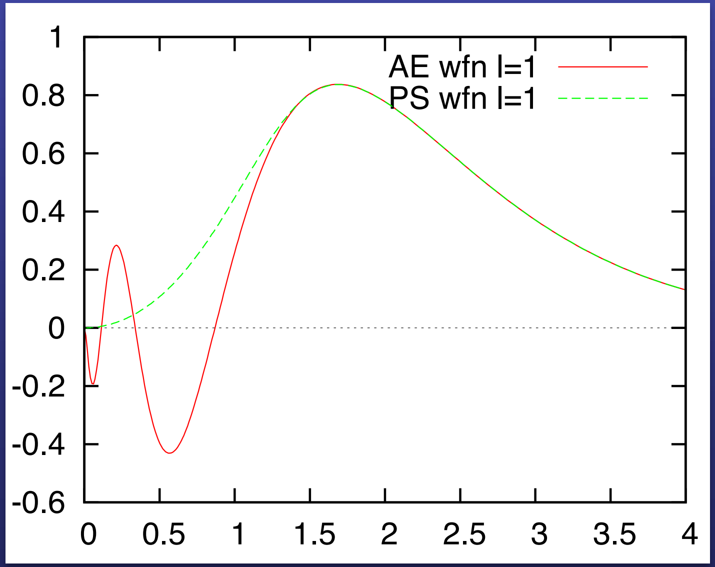
```
$ gnuplot –persist pseudo.gplot
```

(To generate a figure on the screen using gnuplot)

```
$ gnuplot pseudo.gps
```

(To generate a postscript file with the figure)





Generate and test a pseudopotential for Ba with the semicore explicitly included in the valence

The pseudopotential constructed is not expected to reproduce perfectly the 6*s* and 6*p* states, as their eigenvalues are more than 1 eV from those of the reference states 5*s* and 5*p*, but the actual results are not bad at all.

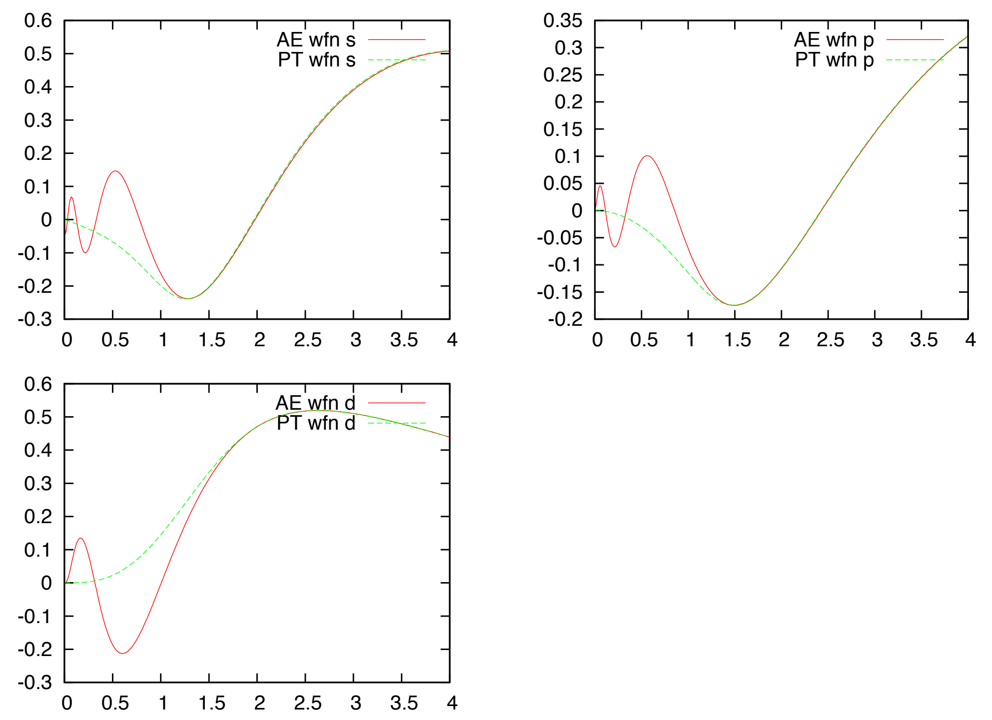
```
$ cd ..
$ cd Ba.test-Ba.semicore/
$ grep "&d" OUT
 ATM3.3    12-APR-13    Ba  True ground state (6s2)                             &v&d
 ATM3.3    12-APR-13    Ba  6s1 6p1 5d0                                         &v&d
 ATM3.3    12-APR-13    Ba  6s1 6p0 5d1                                         &v&d
 &d total energy differences in series
 &d           1        2        3
 &d  1    0.0000
 &d  2    0.1551   0.0000
 &d  3    0.0978  -0.0573   0.0000
*----- End of series ----* spdfg &d&v
 ATM3.3    12-APR-13    Ba  True ground state (6s2)                             &v&d
 ATM3.3    12-APR-13    Ba  6s1 6p1 5d0                                         &v&d
 ATM3.3    12-APR-13    Ba  6s1 6p0 5d1                                         &v&d
 &d total energy differences in series
 &d           1        2        3
 &d  1    0.0000
 &d  2    0.1569   0.0000
 &d  3    0.1011  -0.0558   0.0000
*----- End of series ----* spdfg &d&v
```

Generate and test a pseudopotential for Ba with the semicore explicitly included in the valence

Not only the differences in energies are well reproduced, but also the shape of the orbitals:

`$ gnuplot –persist pt.gplot` (To generate a figure on the screen using gnuplot)

`$ gnuplot pt.gps` (To generate a postscript file with the figure)



Note that the 6*s* and 6*p* states have a node, as they must be orthogonal to the 5*s* and 5*p* states, respectively.