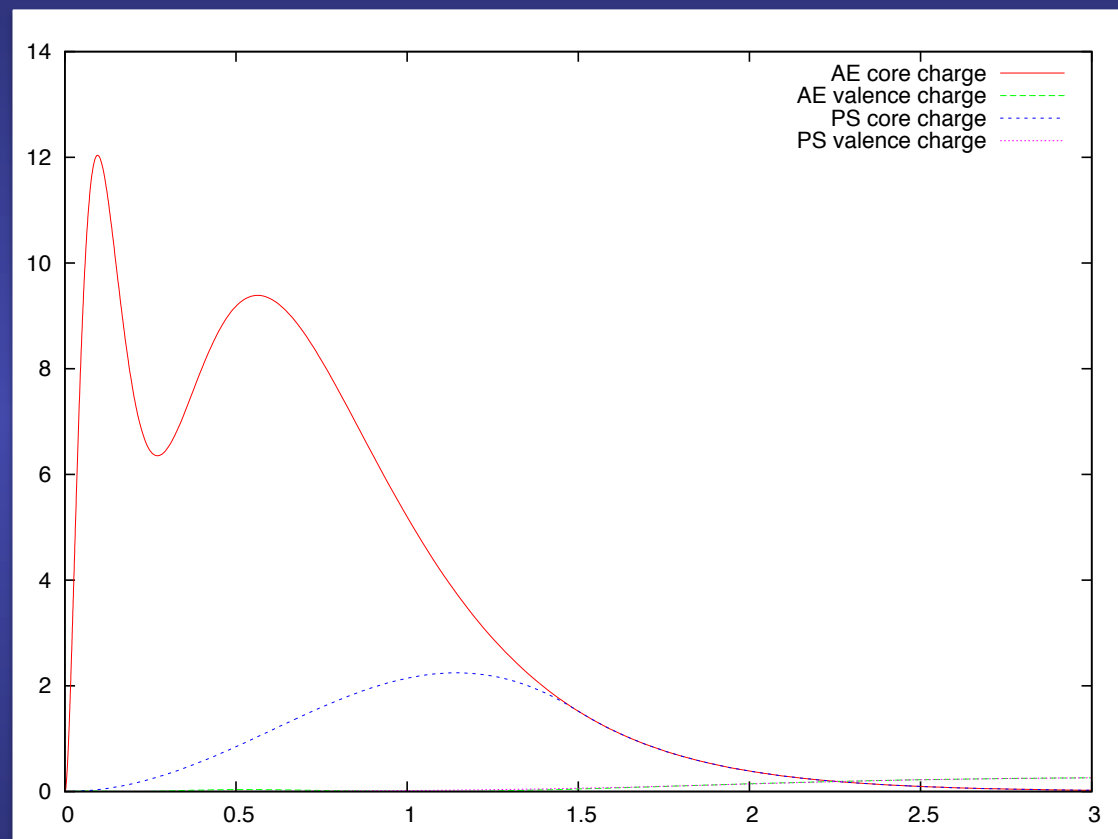


# How to generate a pseudopotential with non-linear core corrections



**Check whether the non-linear core-corrections are necessary and how to include them in the pseudopotential**

# 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

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

$n(r)$   $\equiv$  sum of electronic charges for occupied states       $Z$   $\equiv$  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

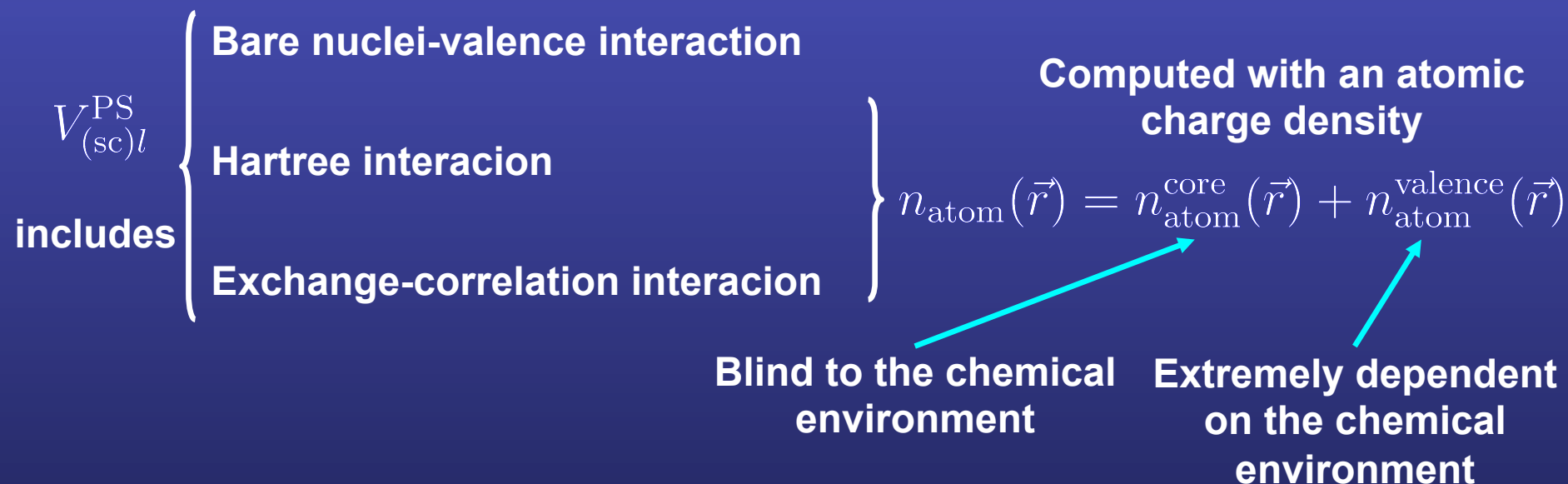
Subtract (unscreen) the Hartree and exchange-correlation potentials

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

The pseudo-wave function obeys

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

Where the **effective potential is computed in the atom**



**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 system

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)

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

Where the pseudo-valence charge density is computed as

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

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.

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

xc potential that  
appears in the  
unscreened potential

Since xc is not linear, if core  
and valence overlap, the  
contribution from valence is  
not fully canceled

xc potential that is  
removed in the  
unscreening  
procedure

Then, the screening pseudopotential 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**

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

## Solution 2: Include non-linear core corrections (NLCC)

S. Louie *et al.*, Phys. Rev. B 26, 1738 (1982)

Step 1: Replace the previous unscreening expression by

$$V_l^{\text{PS}}(r) = V_l^{(\text{sc})1}(r) - \int \frac{n_v(r')}{|r - r'|} dr' - V_{xc}[n_v + n_c]$$

Step 2: In the actual electronic structure calculations performed with this pseudopotential, the exchange and correlation distribution is computed from the full electronic charge,  $[n_v + n_c]$ , instead of the usual valence charge. The frozen core charge density of isolated atoms is used for  $n_c$

Step 3: The full core density, with its very high Fourier components, is impractical to use. However, the core charge has significant effect only where the core and valence charge densities are of similar magnitude. We can therefore, replace the full core charge density with a partial core charge density

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

## Solution 2: Include non-linear core corrections (NLCC)

### Models for the partial core

1. Original one proposed by S. Louie *et al.* (in ATOM, the default for LDA)

$$n_{\text{partial}}^{\text{core}}(r) = \begin{cases} \frac{a \sin(br)}{r}, & r < r_{\text{pc}} \\ n^{\text{core}}(r), & r > r_{\text{pc}} \end{cases}$$

Parameters  $a$  and  $b$  determined by the continuity of the partial core and its first derivative at  $r_{\text{pc}}$

2. New one that fixes some problems in the generation of GGA pseudos

$$n_{\text{partial}}^{\text{core}}(r) = \begin{cases} r^2 e^{(a+br^2+cr^4)}, & r < r_{\text{pc}} \\ n^{\text{core}}(r), & r > r_{\text{pc}} \end{cases}$$

Parameters  $a$ ,  $b$  and  $c$  determined by the continuity of the partial core and its first and second derivatives at  $r_{\text{pc}}$

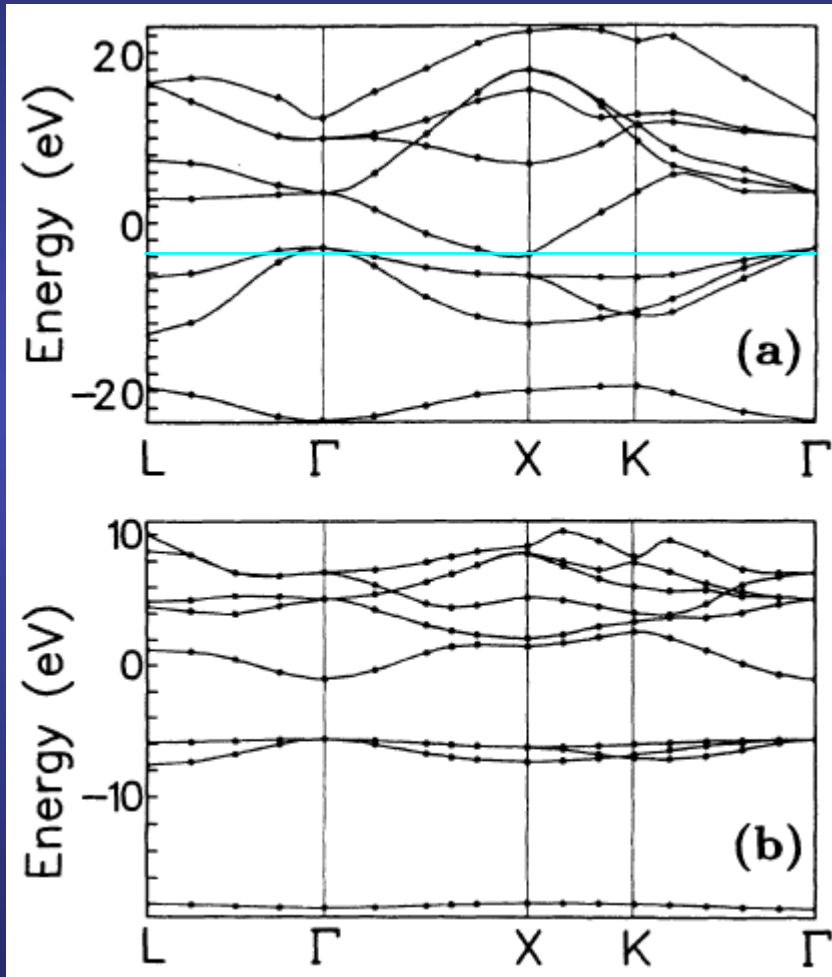
$r_{\text{pc}}$  has to be chosen such that the valence charge density is negligible compared to the core one for  $r < r_{\text{pc}}$ .

Tests show that it might be located where the core charge density is from 1 to 2 times larger than the valence charge density



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

Bulk NaCl (rocksalt structure)



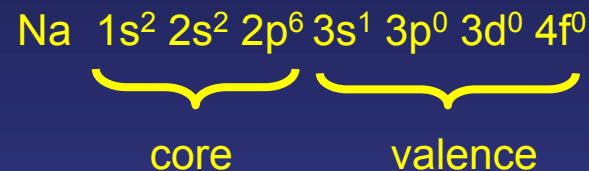
Without core corrections for Na:  
Semi metal

With core corrections for Na:  
Insulator

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

pe ≡ Pseudopotential generation with NLCC

A title for the job



Chemical symbol of the atom

Principal quantum number

Angular quantum number

Occupation  
(spin up)  
(spin down)

Cutoff radii for the different shells  
(in bohrs)

pe	Sodium NLCC rcore=1.50					
	tm2	4.0				
n=Na	c=ca	0.0	0.0	0.0	0.0	0.0
3	3					
3	0	1.00	0.00			
3	1	0.00	0.00			
3	2	0.00	0.00			
	2.95	2.95	2.95	2.95	0	1.50

Number of core and valence orbitals

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)

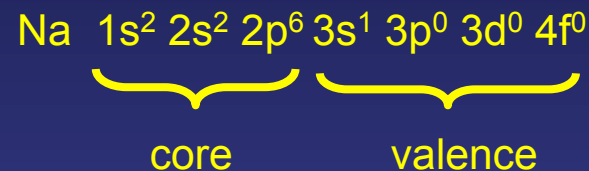
am ≡ AM05 by Armiento and Mattson (GGA)

vw ≡ van der Waals functional

**+s if spin (no relativistic)**  
**+r if relativistic**

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

pe ≡ Pseudopotential generation with NLCC



A title for the job

Chemical symbol of the atom

pe	Sodium NLCC rcore=1.50					
	tm2	4.0				
n=Na	c=ca	0.0	0.0	0.0	0.0	0.0
3	3					
3	0	1.00	0.00			
3	1	0.00	0.00			
3	2	0.00	0.00			
	2.95	2.95	2.95	2.95	0	1.50

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)

xc functional

$r_{pc}$  radius for the non-linear core correction  
Highly recommended to set an explicit value  
If it is zero, negative or blank, the radius is chosen from rcore\_flag

rcore\_flag:

At  $r_{pc}$  the core charge density equals  
(rcore\_flag)\*(valence charge density)

If negative, the full core charge is used

If zero, the sixth number is used

# Generate and test a pseudopotential for Na with and without non-linear core corrections

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

$ ../../Utils/pt.sh Na.test.inp Na.cc.vps
==> Output data in directory Na.test-Na.cc
$ ../../Utils/pt.sh Na.test.inp Na.vps
==> Output data in directory Na.test-Na
```

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

# Check that the transferability has improved with the non-linear core corrections

```
$ cd Na.test-Na.cc
$ grep "&d" OUT
ATM3.3      5-DEC-12      Sodium GS 3s1 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium   3s0.5 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p1 3d0      &v&d
&d total energy differences in series
&d          1          2          3          4
&d 1      0.0000
&d 2      0.1470      0.0000
&d 3      0.3798      0.2327      0.0000
&d 4      0.1553      0.0083     -0.2245      0.0000
*----- End of series -----* spdfg &d&v
ATM3.3      5-DEC-12      Sodium GS 3s1 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium   3s0.5 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p1 3d0      &v&d
&d total energy differences in series
&d          1          2          3          4
&d 1      0.0000
&d 2      0.1471      0.0000
&d 3      0.3809      0.2338      0.0000
&d 4      0.1557      0.0086     -0.2251      0.0000
*----- End of series -----* spdfg &d&v

$ cd ../Na.test-Na
$ grep "&d" OUT
ATM3.3      5-DEC-12      Sodium GS 3s1 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium   3s0.5 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p1 3d0      &v&d
&d total energy differences in series
&d          1          2          3          4
&d 1      0.0000
&d 2      0.1470      0.0000
&d 3      0.3798      0.2327      0.0000
&d 4      0.1553      0.0083     -0.2245      0.0000
*----- End of series -----* spdfg &d&v
ATM3.3      5-DEC-12      Sodium GS 3s1 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium   3s0.5 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p0 3d0      &v&d
ATM3.3      5-DEC-12      Sodium GS 3s0 3p1 3d0      &v&d
&d total energy differences in series
&d          1          2          3          4
&d 1      0.0000
&d 2      0.1461      0.0000
&d 3      0.3687      0.2226      0.0000
&d 4      0.1515      0.0054     -0.2172      0.0000
*----- End of series -----* spdfg &d&v
```

With non-linear core  
corrections

Without non-linear core  
corrections

# Plotting the core and pseudo-core charge density

```
$ cd Na.cc
```

```
$ gnuplot --persist charge.gplot
```

(To generate a figure on the screen using gnuplot)

```
$ gnuplot charge.gps
```

(To generate a postscript file with the figure)

