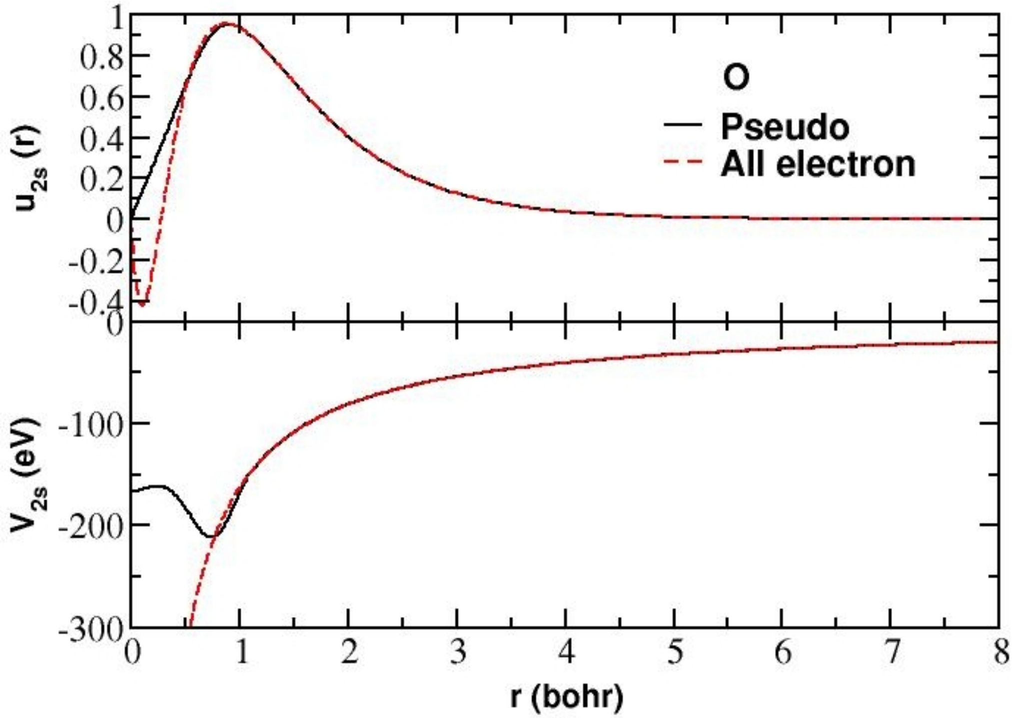
Norm-conserving pseudopotentials in electronic structure calculations



Javier Junquera

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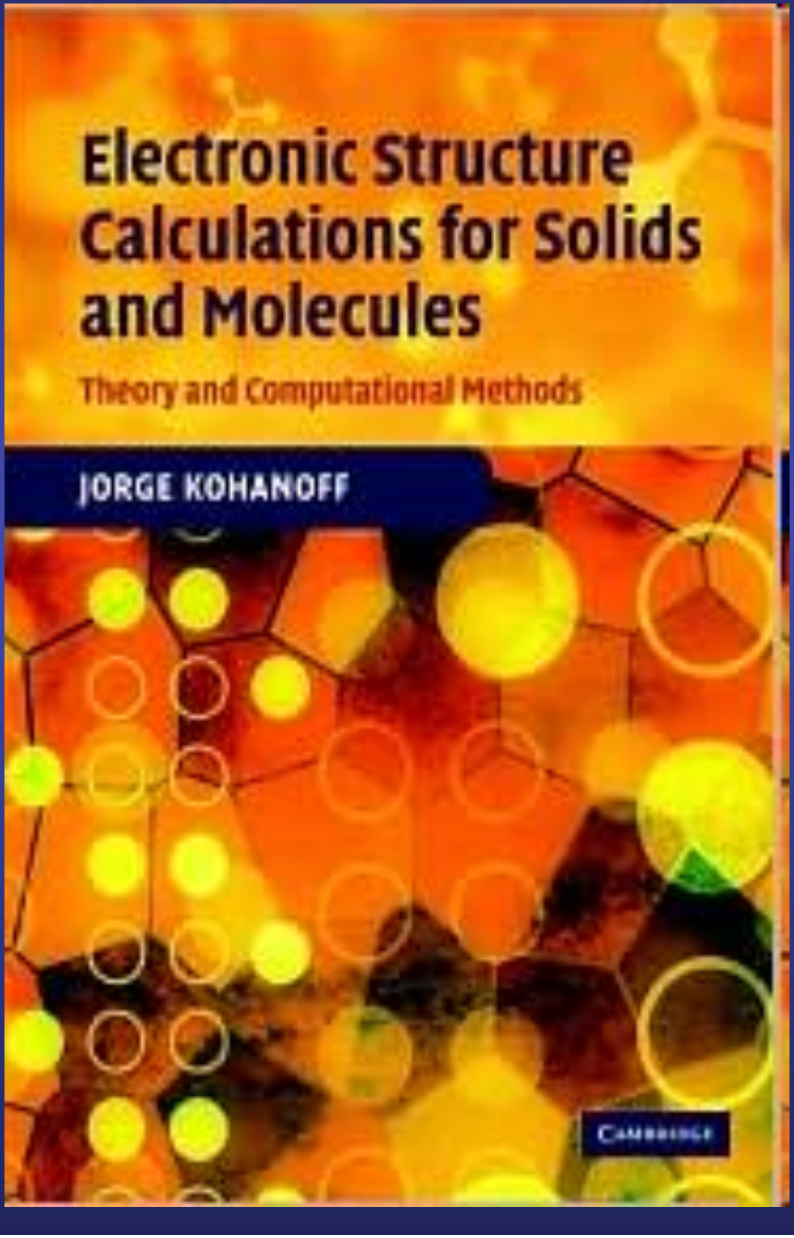
Alberto García

ICMAB

Bibliography used in the present lecture



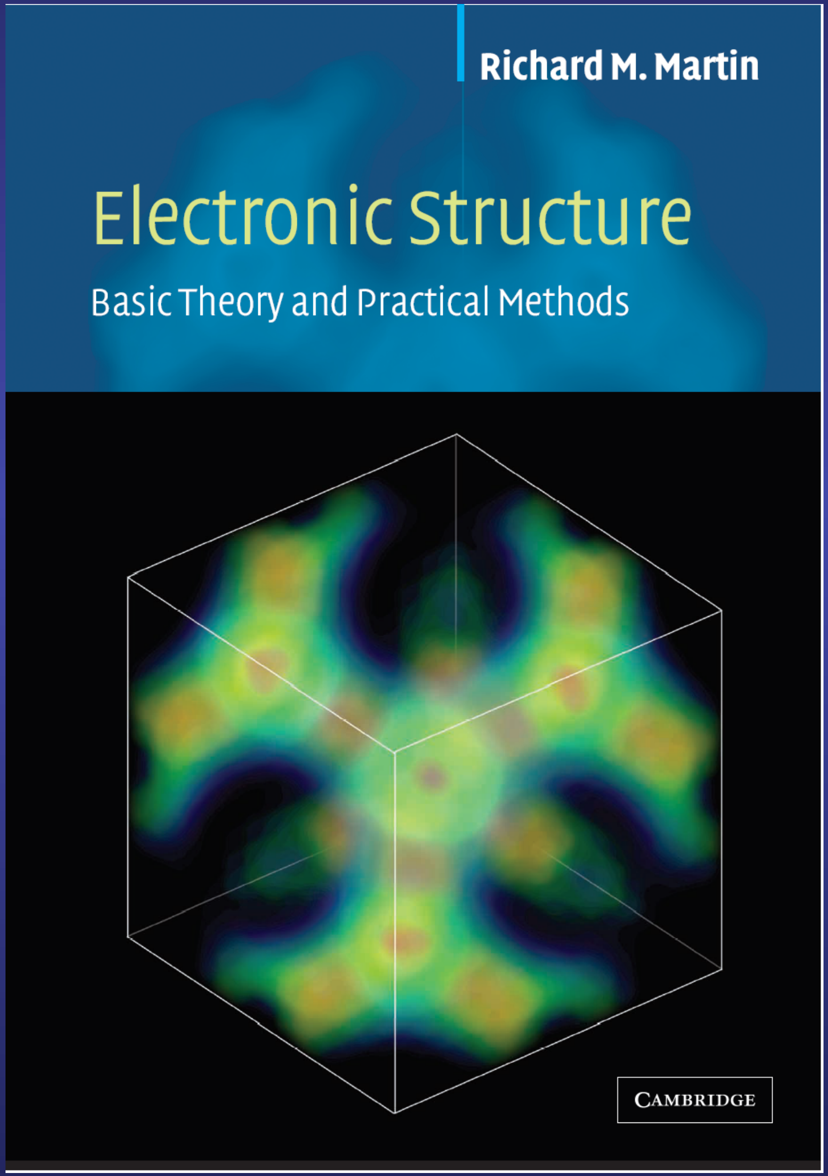
Electronic Structure Calculations for Solids and Molecules

Theory and Computational Methods

JORGE KOHANOFF

CAMBRIDGE

Bibliography used in the present lecture



Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods

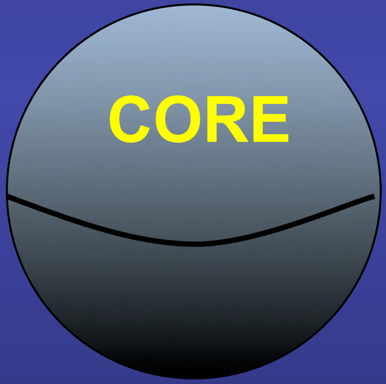
CAMBRIDGE

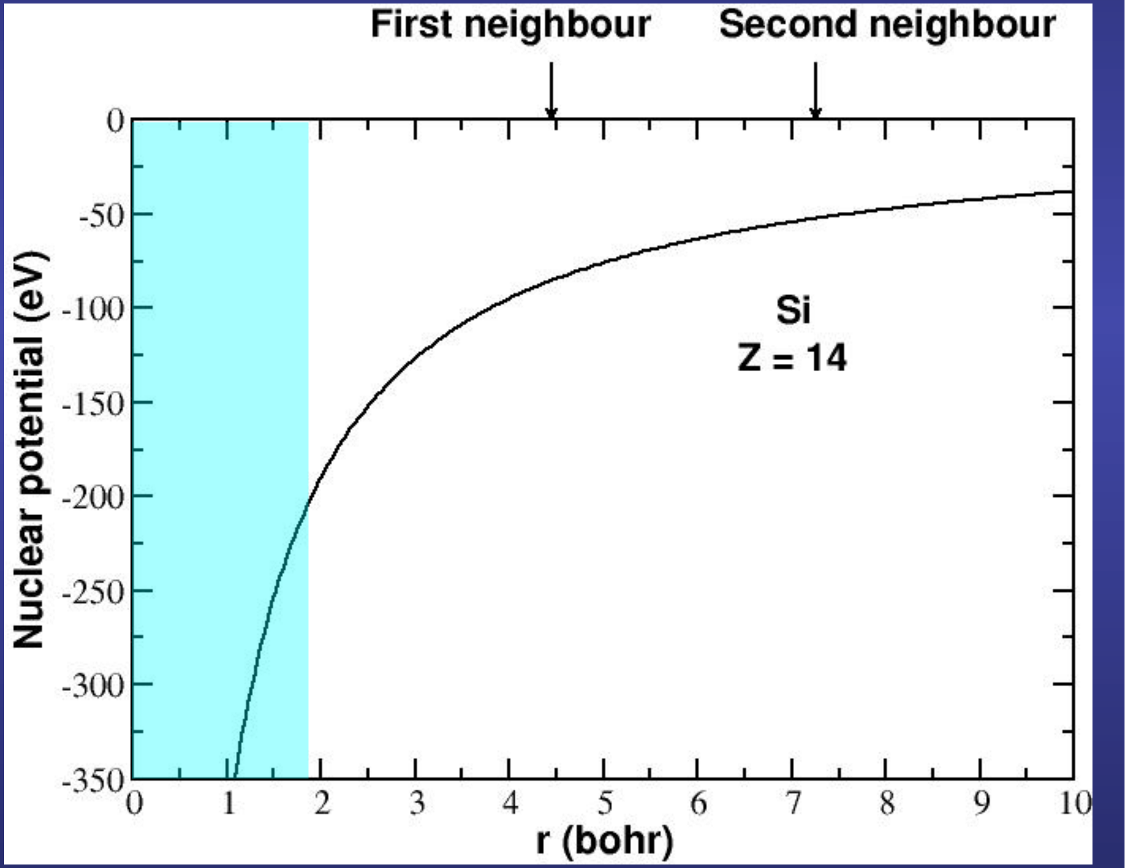
Atomic calculation using DFT: Solving the Schrodinger-like equation

One particle Kohn-Sham equations

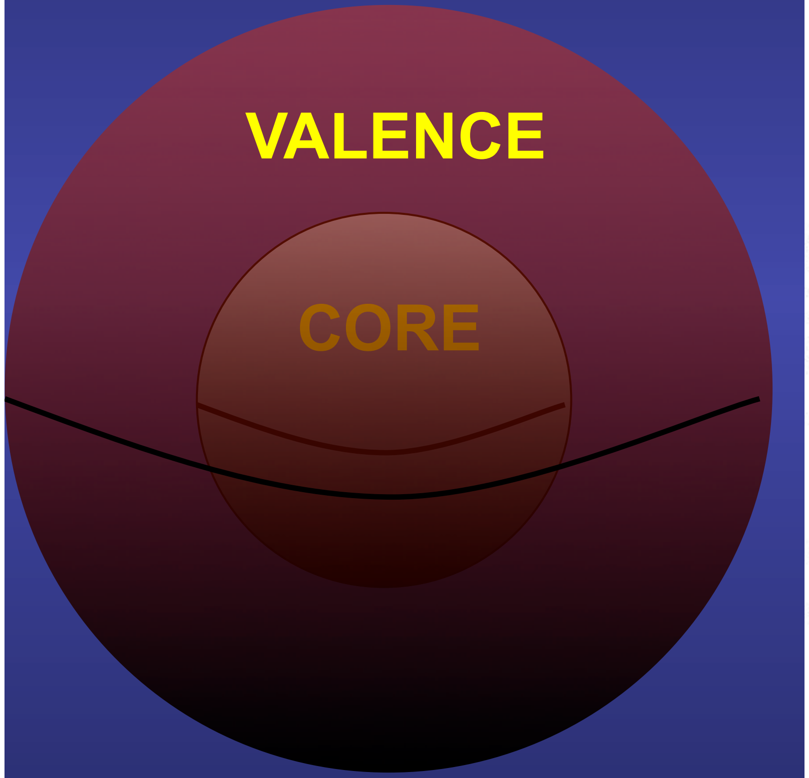
$$\left(\hat{T} + \underset{\underset{\displaystyle -\frac{Ze}{r}}{\Big\downarrow}}{\hat{V}_{ion-e}} + \hat{V}_H + \hat{V}_{xc}\right)\psi_i = \varepsilon_i \psi_i$$

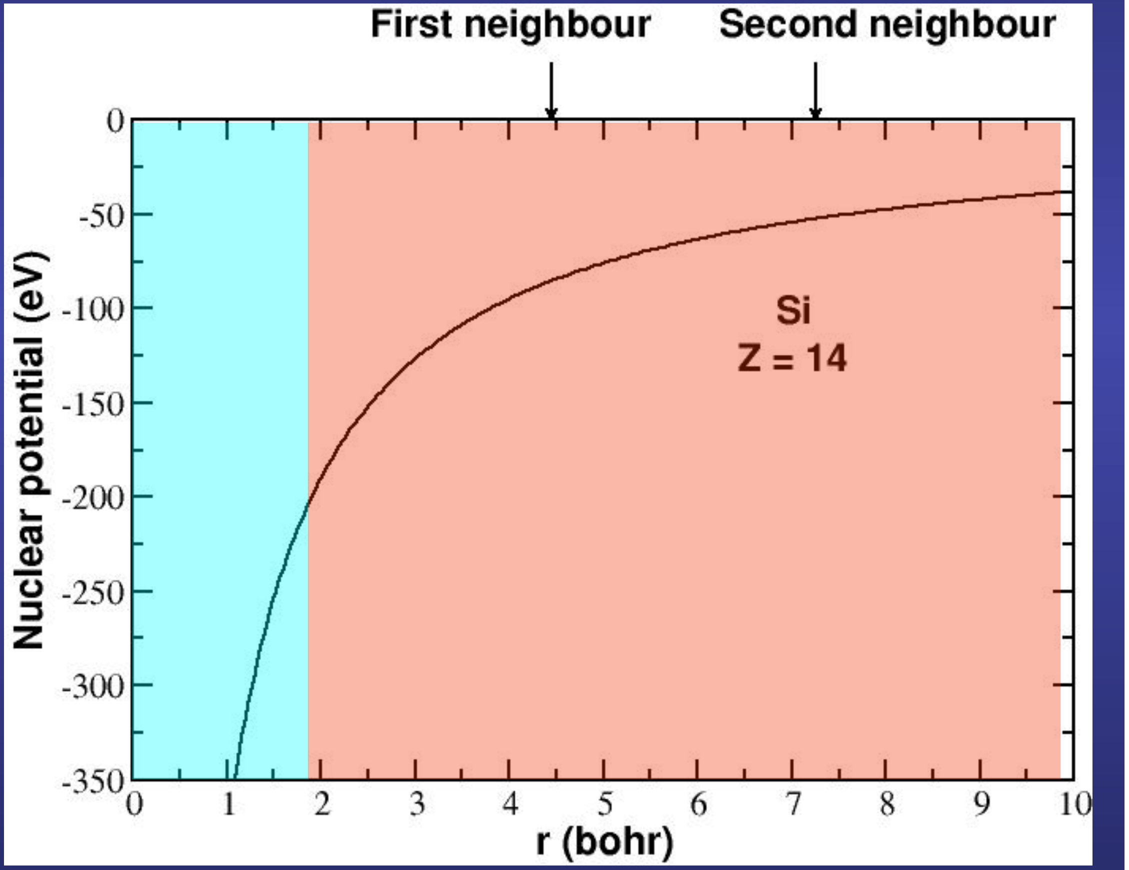
Difficulty: how to deal accurately with both the core and valence electrons



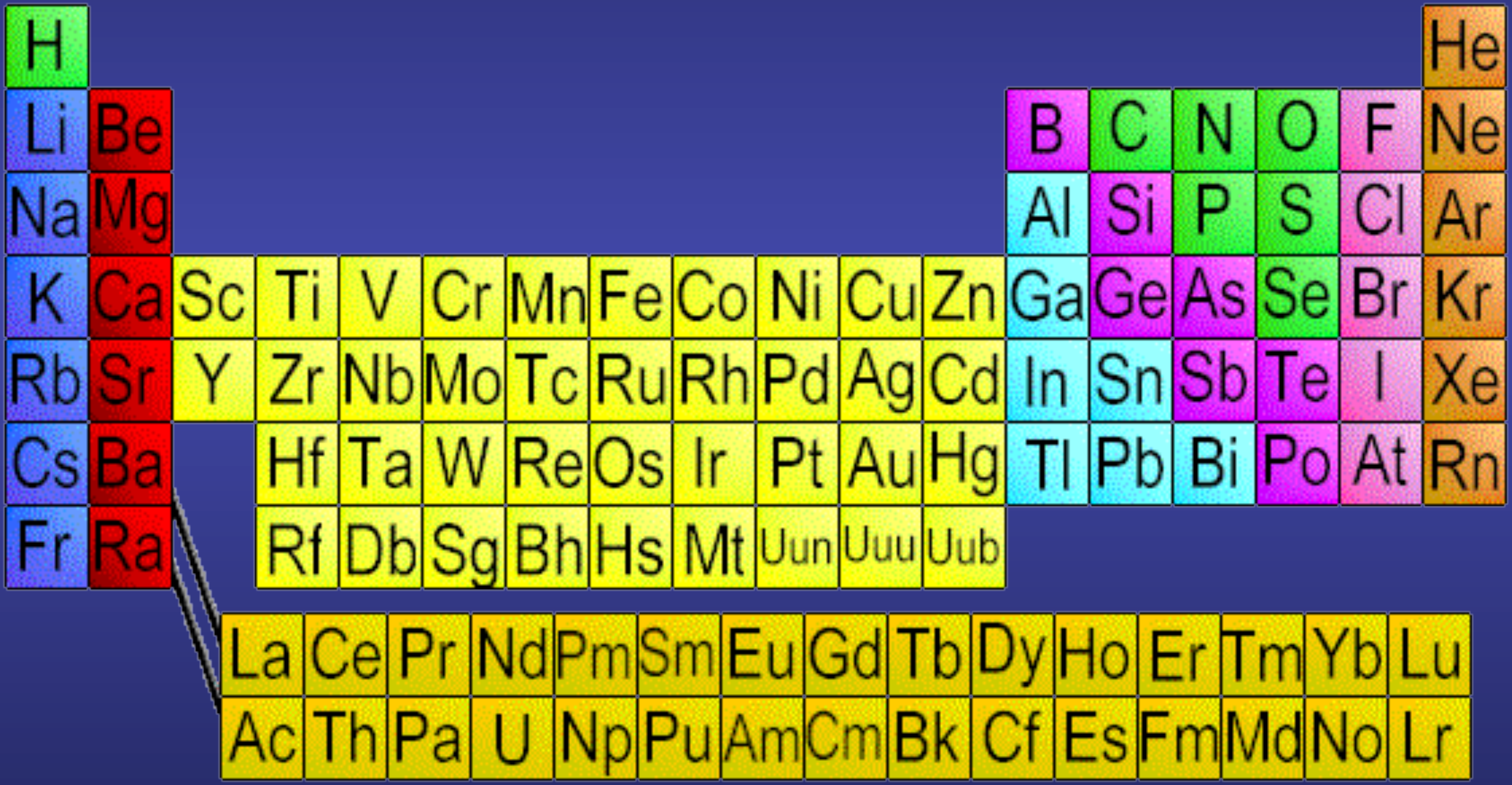


Difficulty: how to deal accurately with both the core and valence electrons



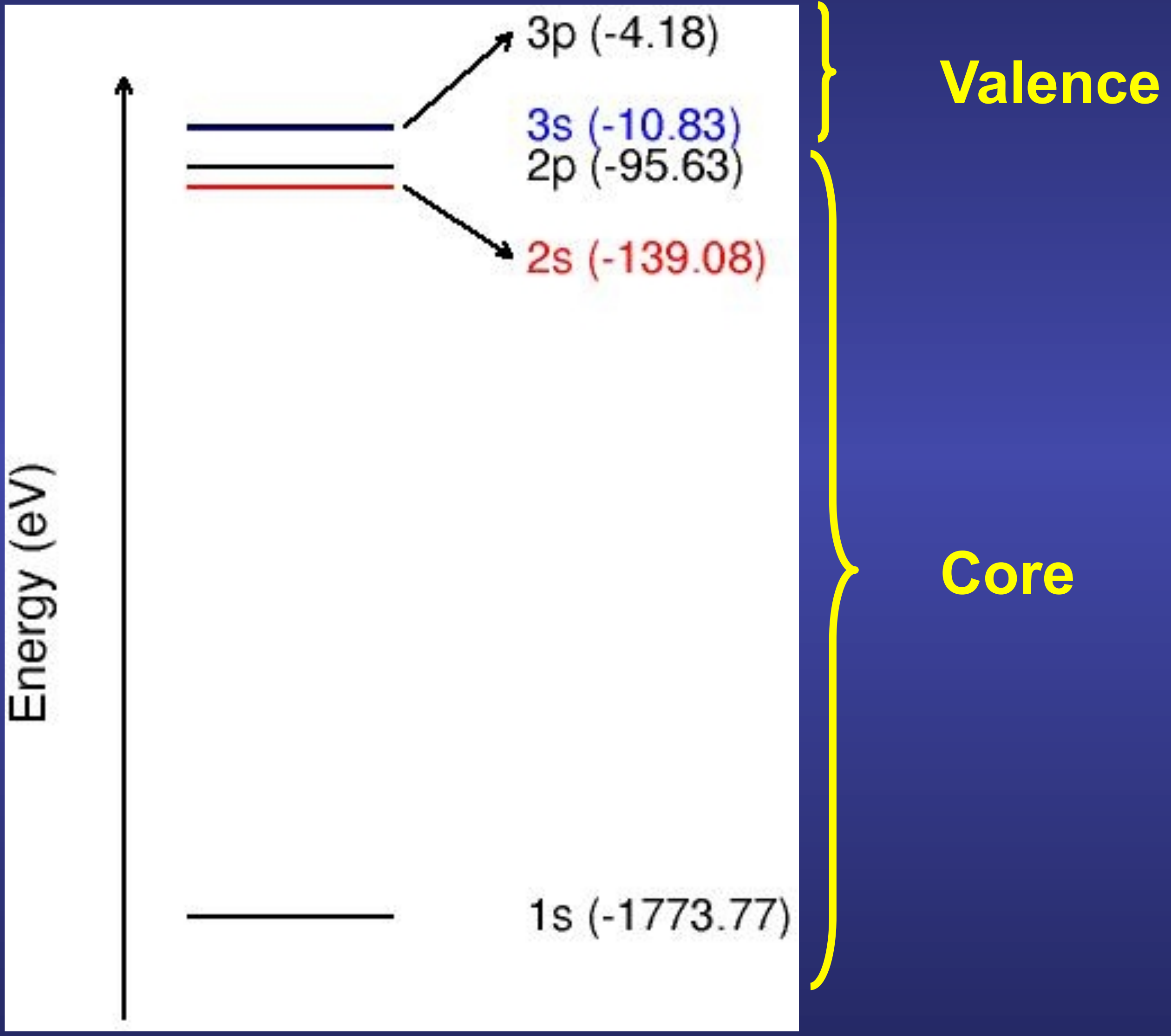


Si atomic configuration: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}} \qquad \underbrace{3s^2\ 3p^2}_{\text{valence}}$



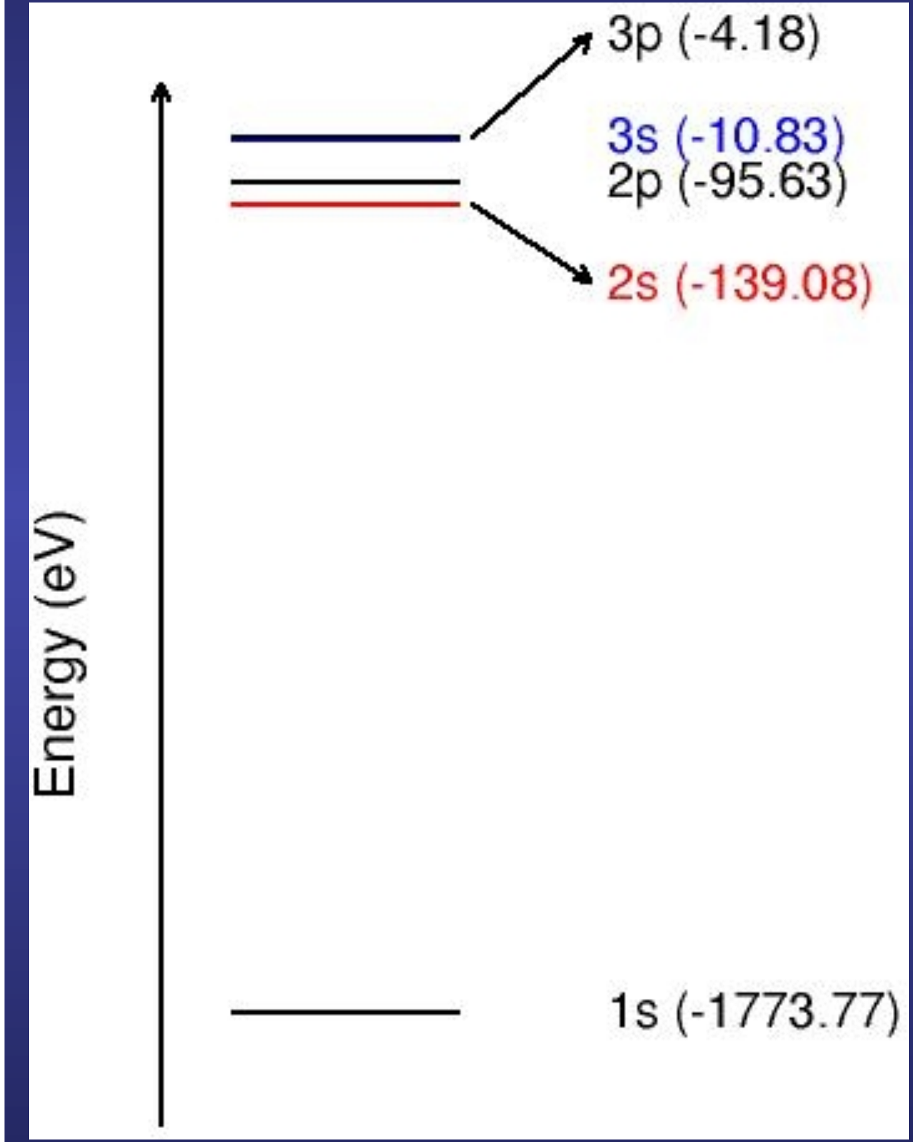
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub						
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Core eigenvalues are much deeper than valence eigenvalues

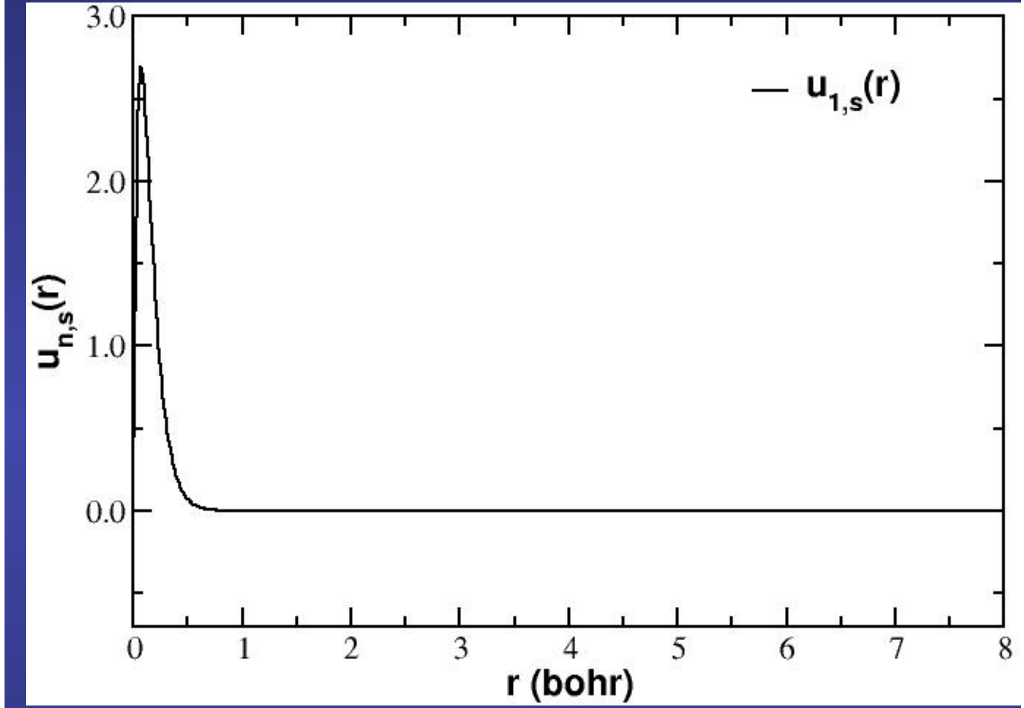


Atomic Si

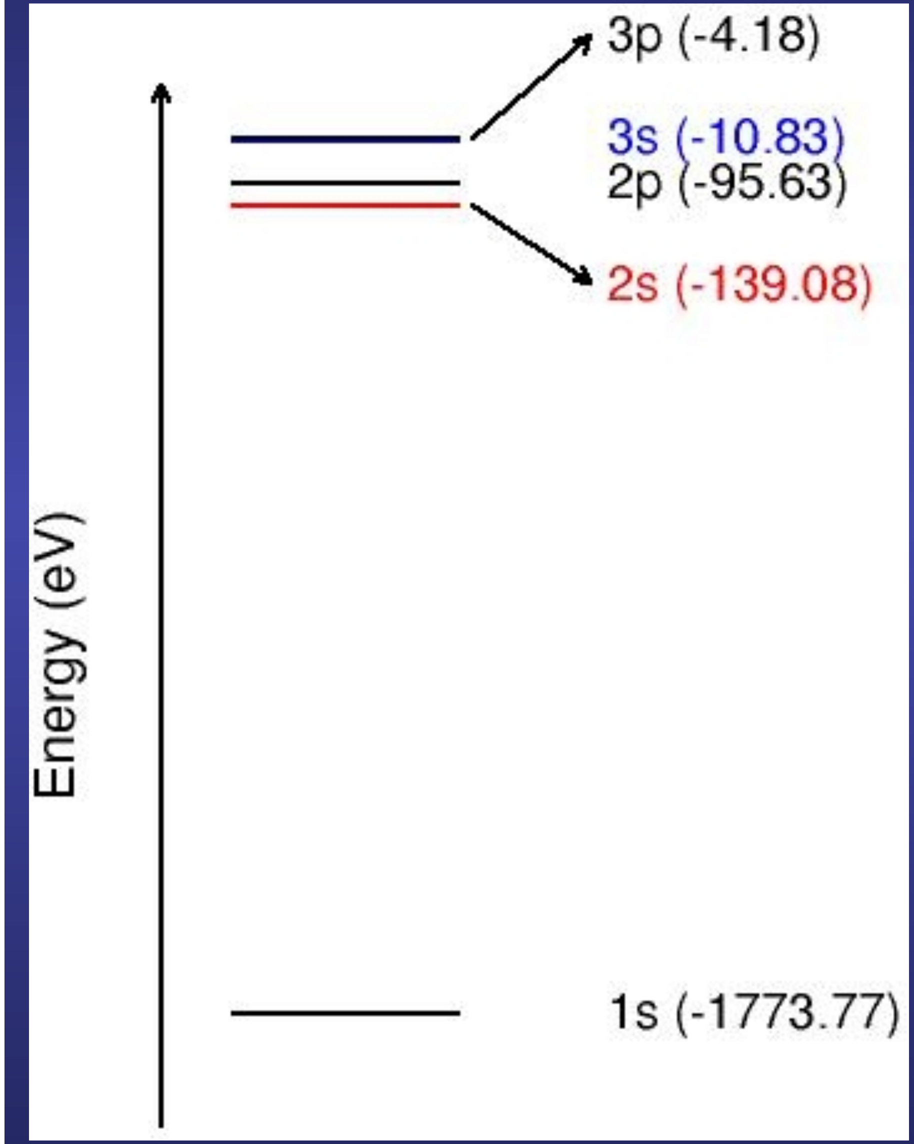
Core wavefunctions are very localized around the nuclei



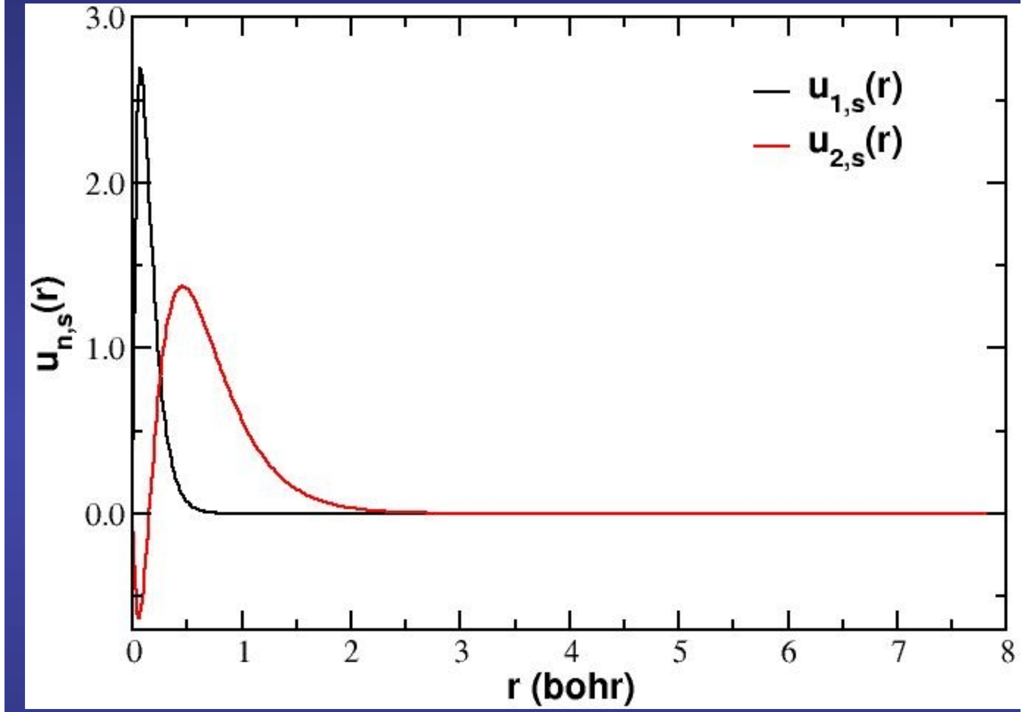
Atomic Si



Core wavefunctions are very localized around the nuclei



Atomic Si



Core electrons…

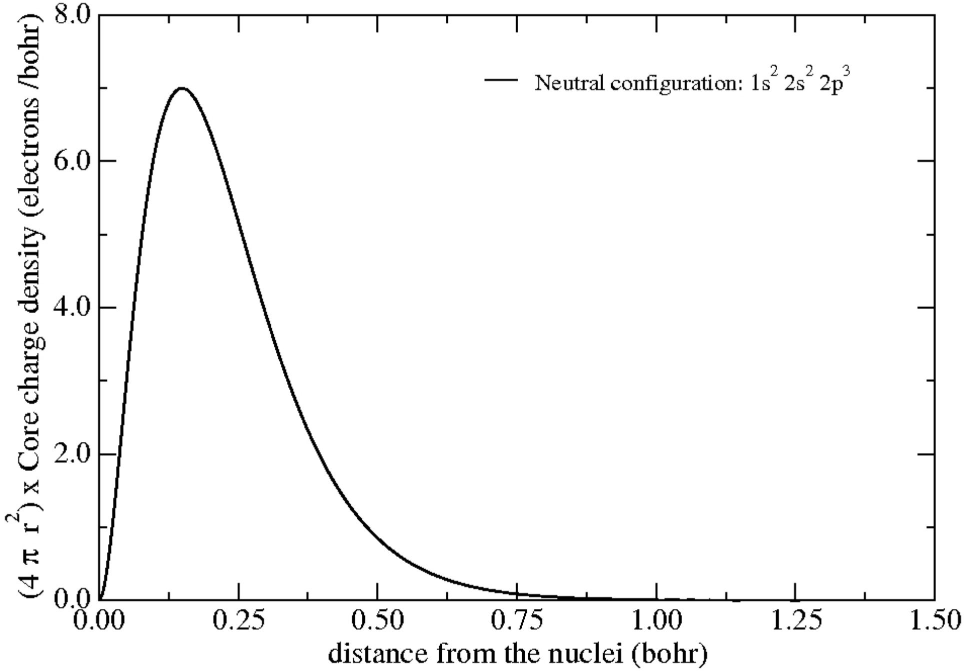
- highly localized
- very depth energy

… are chemically inert

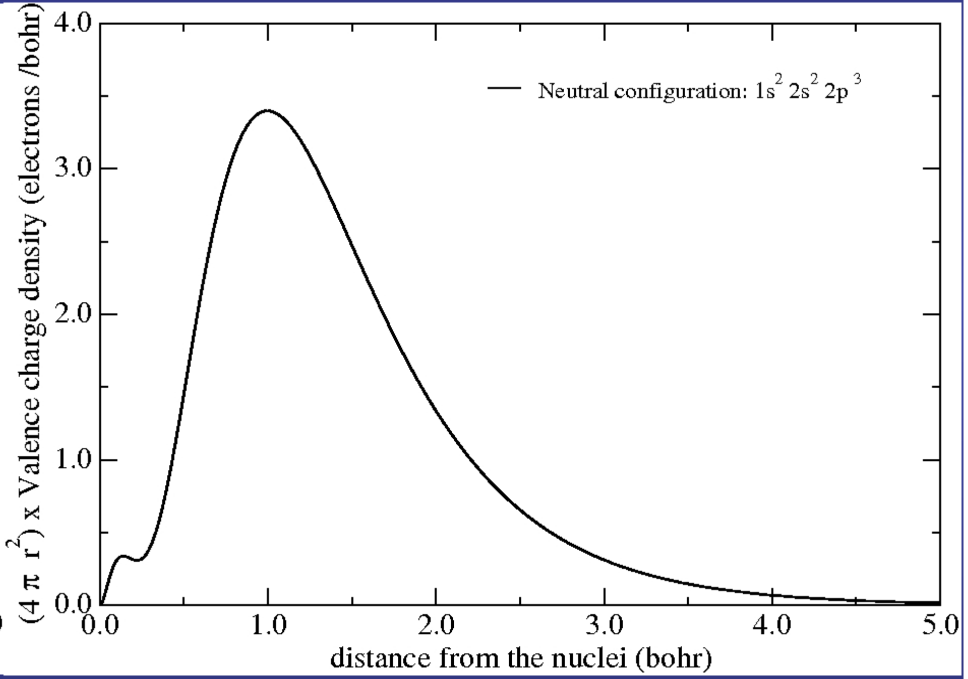
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



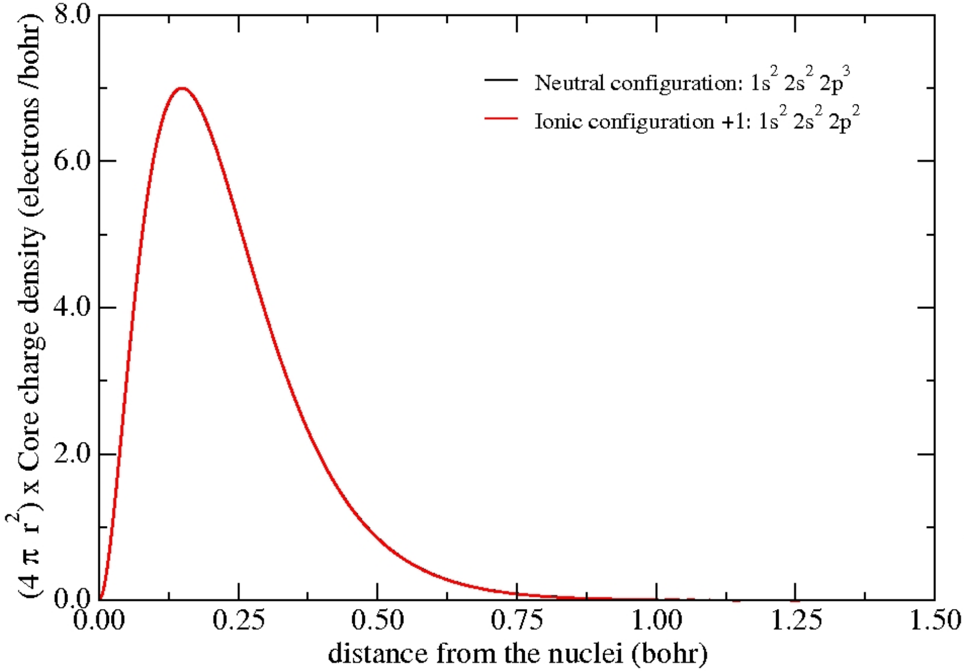
Valence charge density



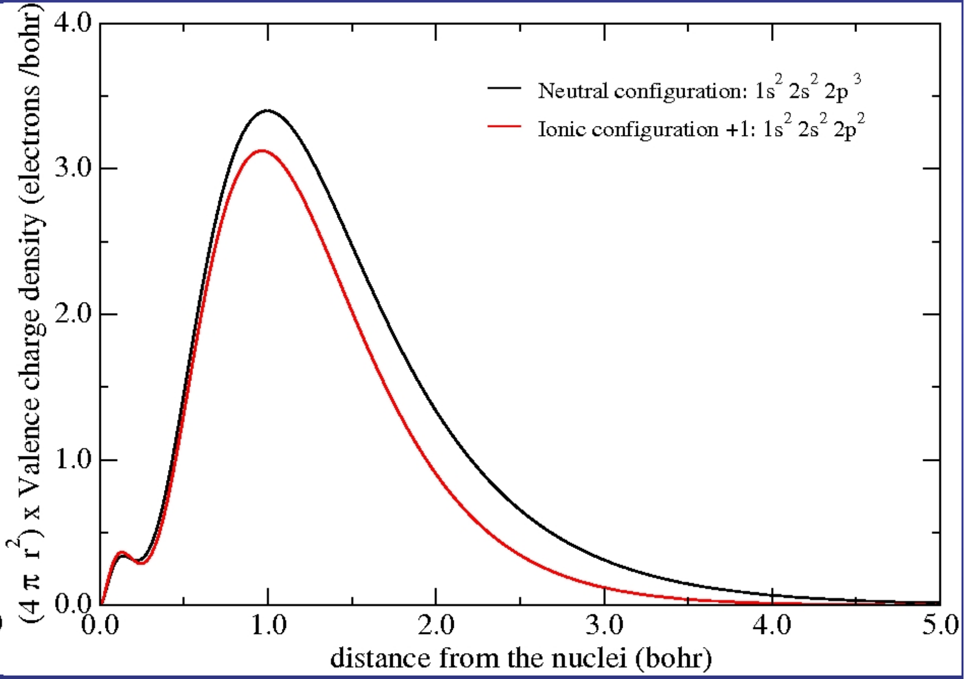
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



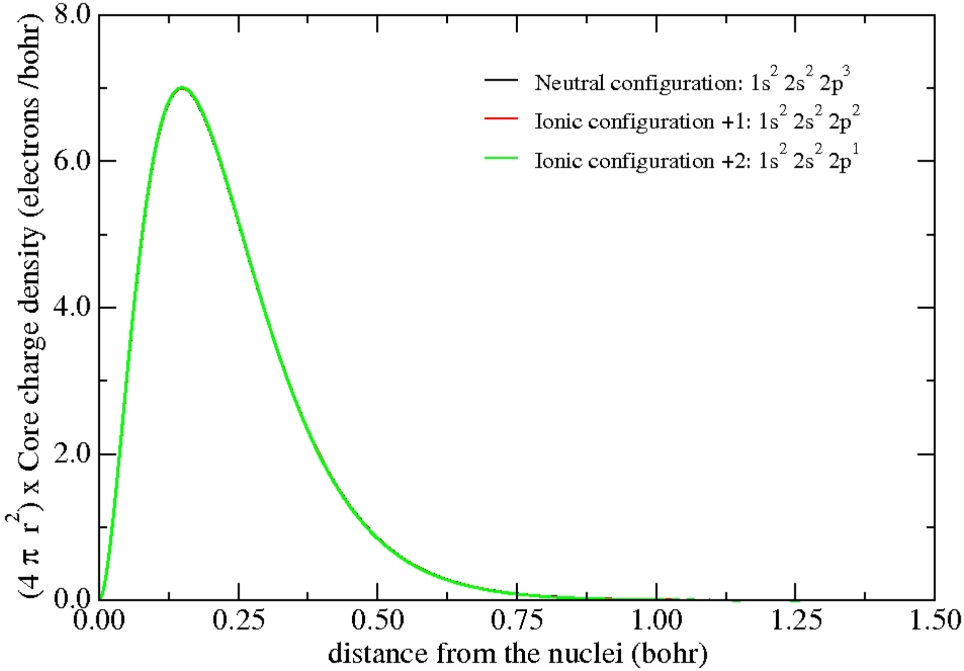
Valence charge density



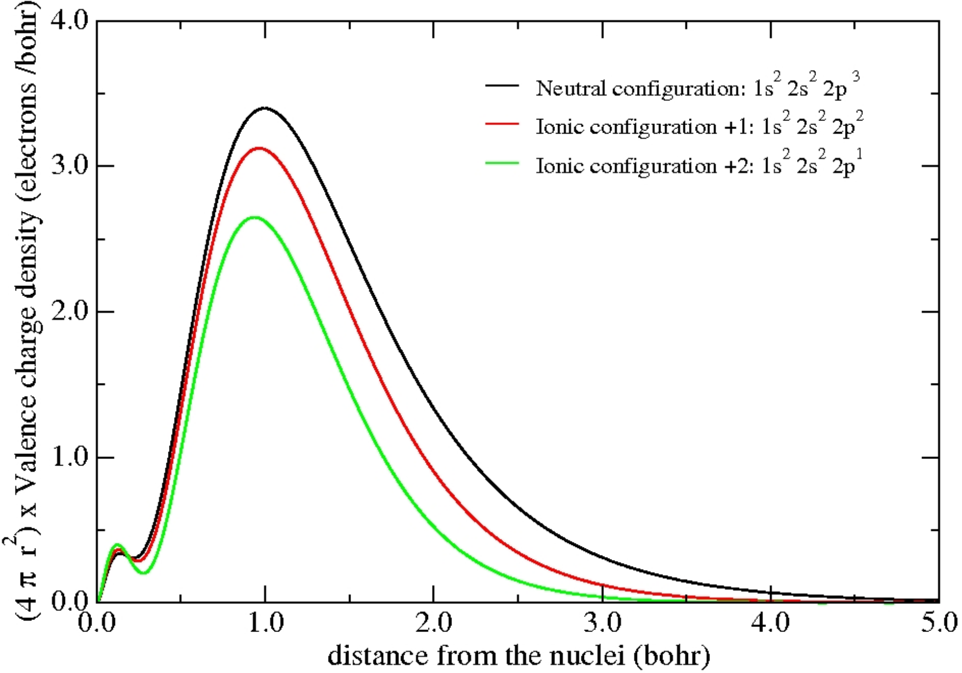
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density

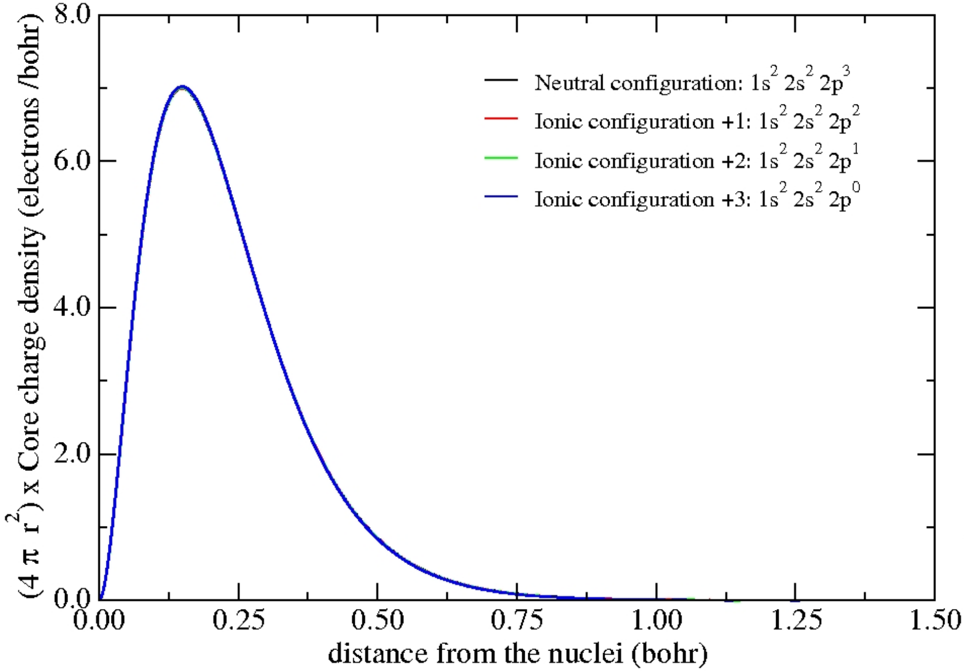


Valence charge density



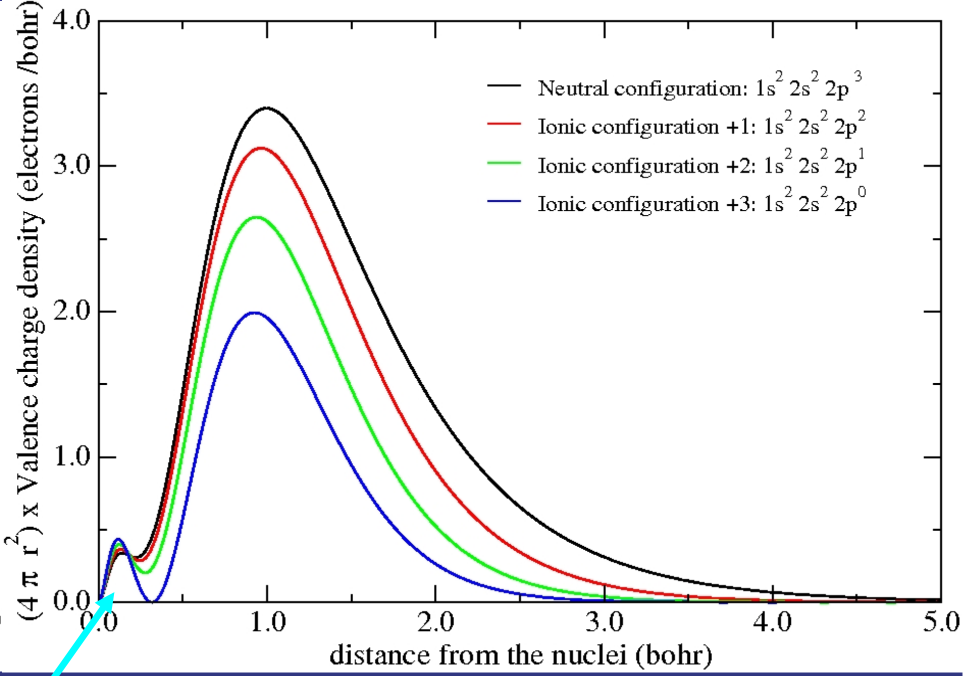
Core electrons are chemically inert

All electron calculation for an isolated N atom



Core charge density

The core charge density remains unperturbed



Valence charge density

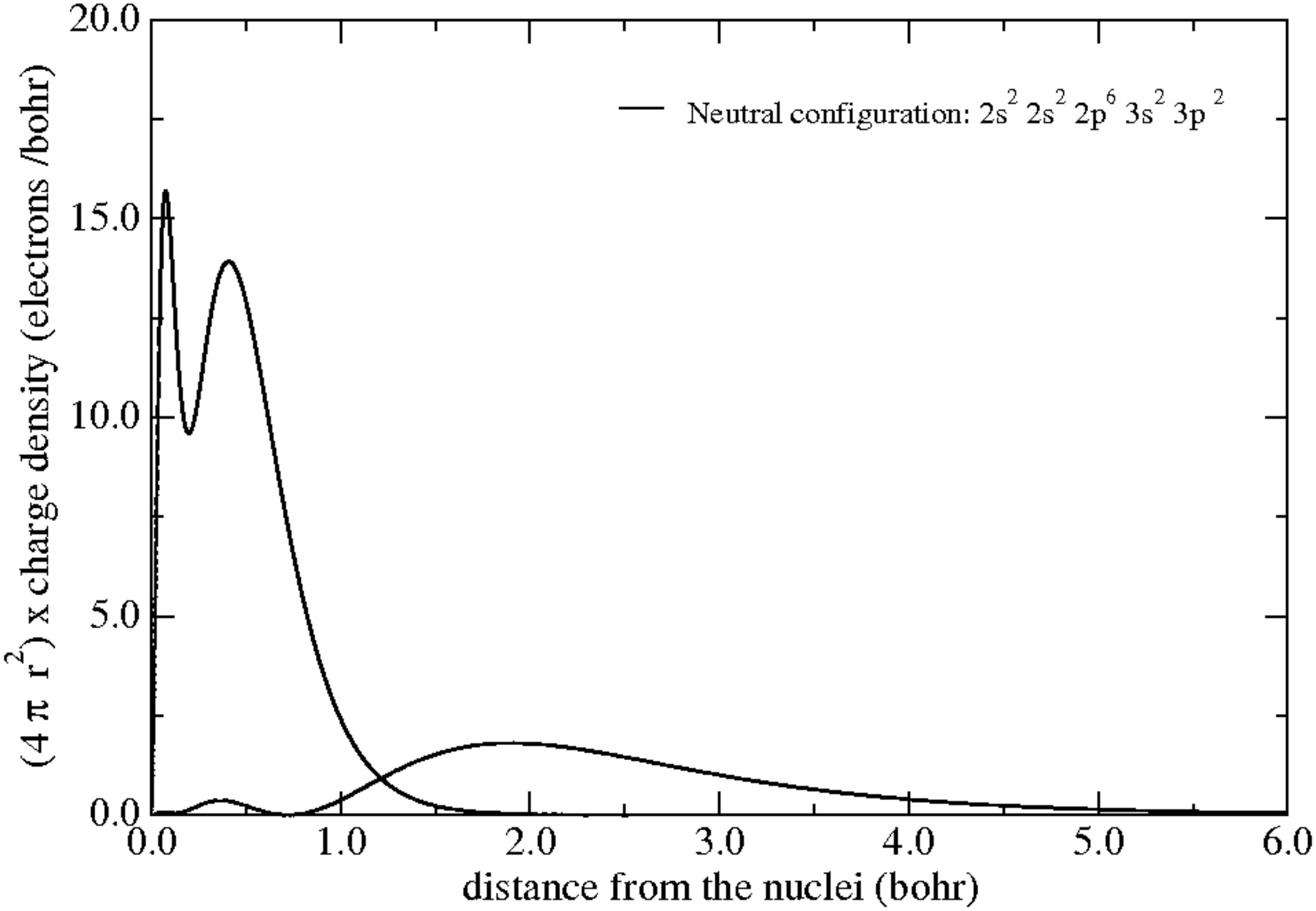
Although there are drastic modifications in the valence charge density

Peak due to the 2s all-electron orbitals of N,
(they have a node to be ortogonal with the 1s)

Core electrons are chemically inert

All electron calculation for an isolated Si atom

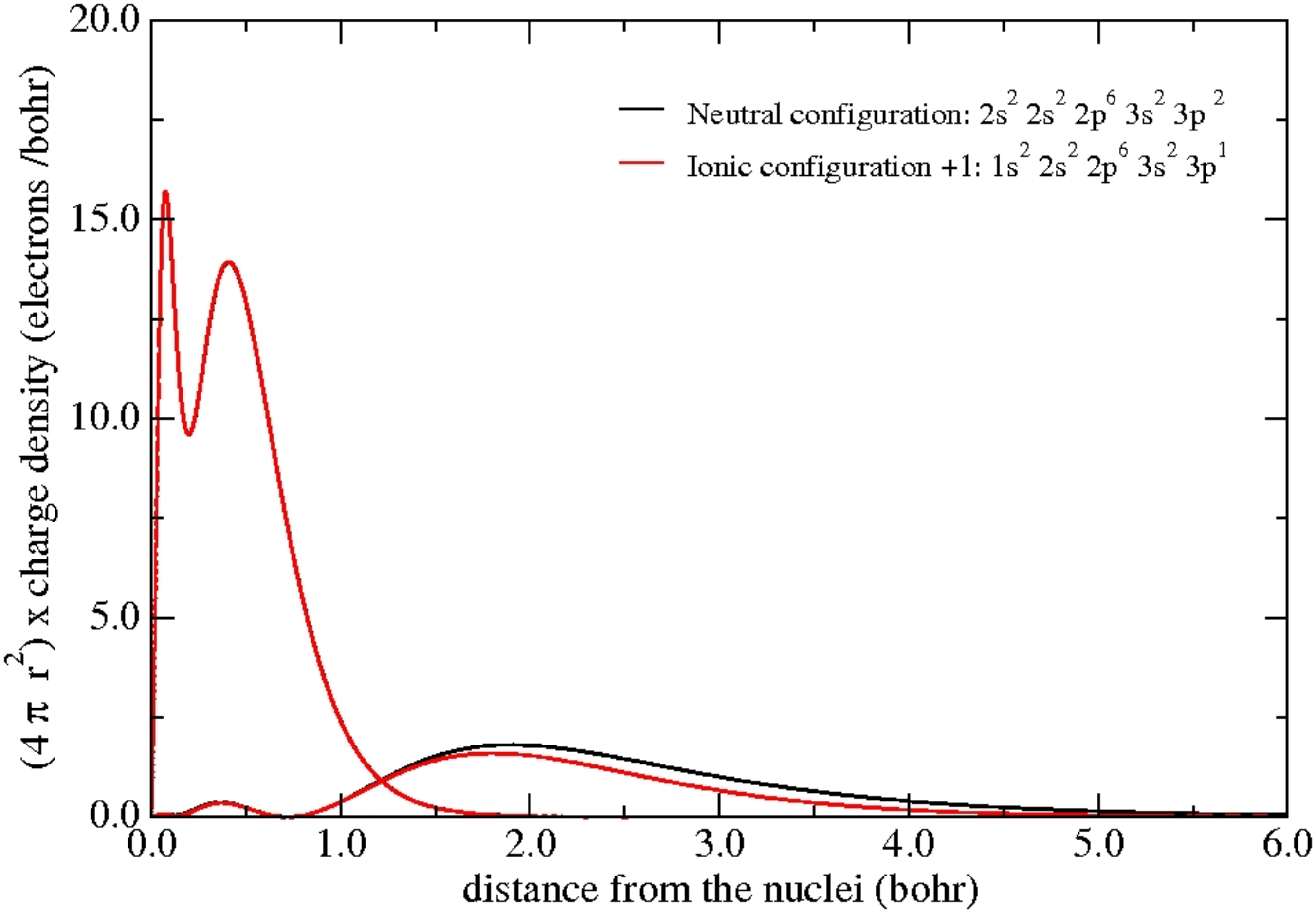
Angularly integrated core and valence charge densities



Core electrons are chemically inert

All electron calculation for an isolated Si atom

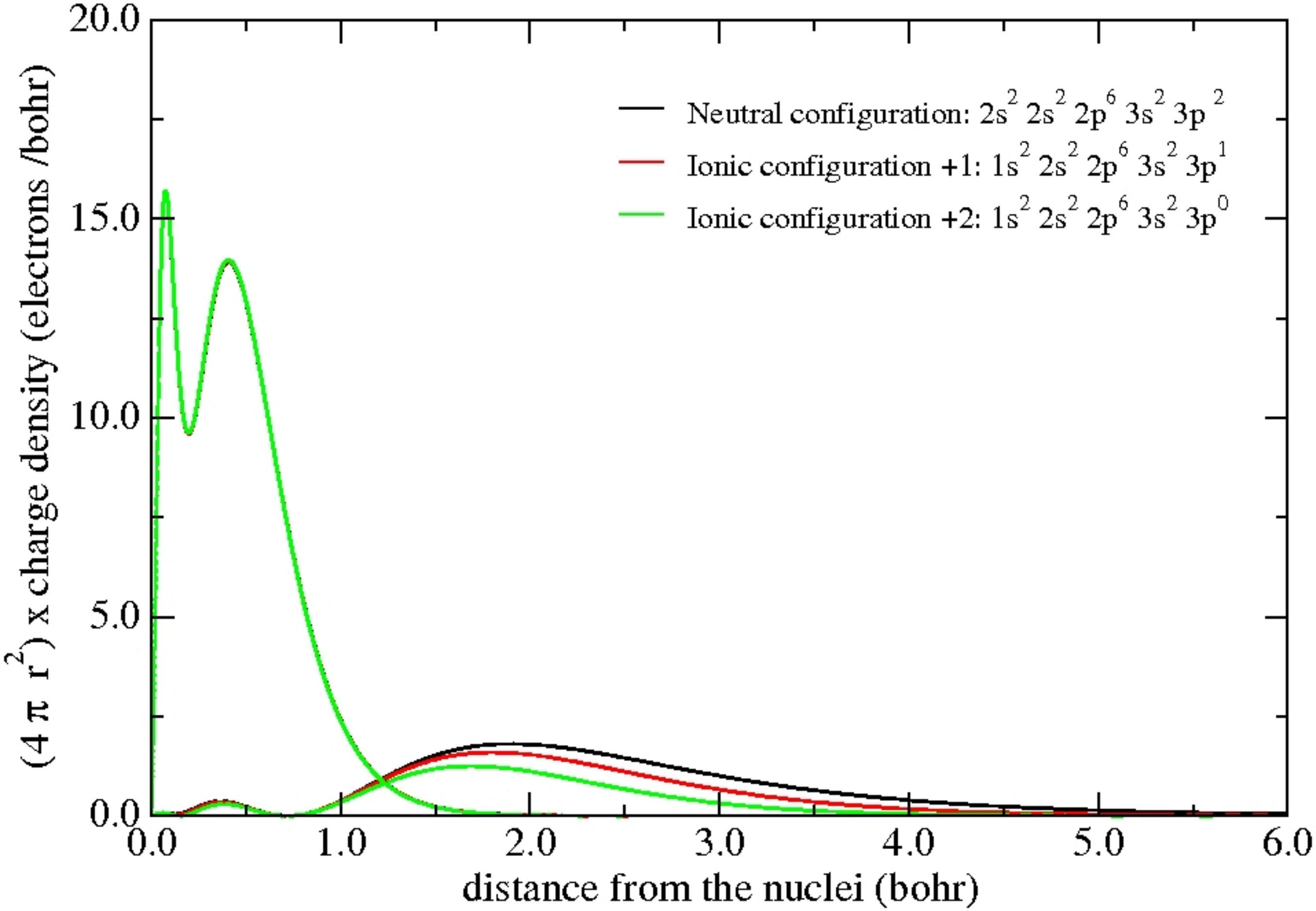
Angularly integrated core and valence charge densities



Core electrons are chemically inert

All electron calculation for an isolated Si atom

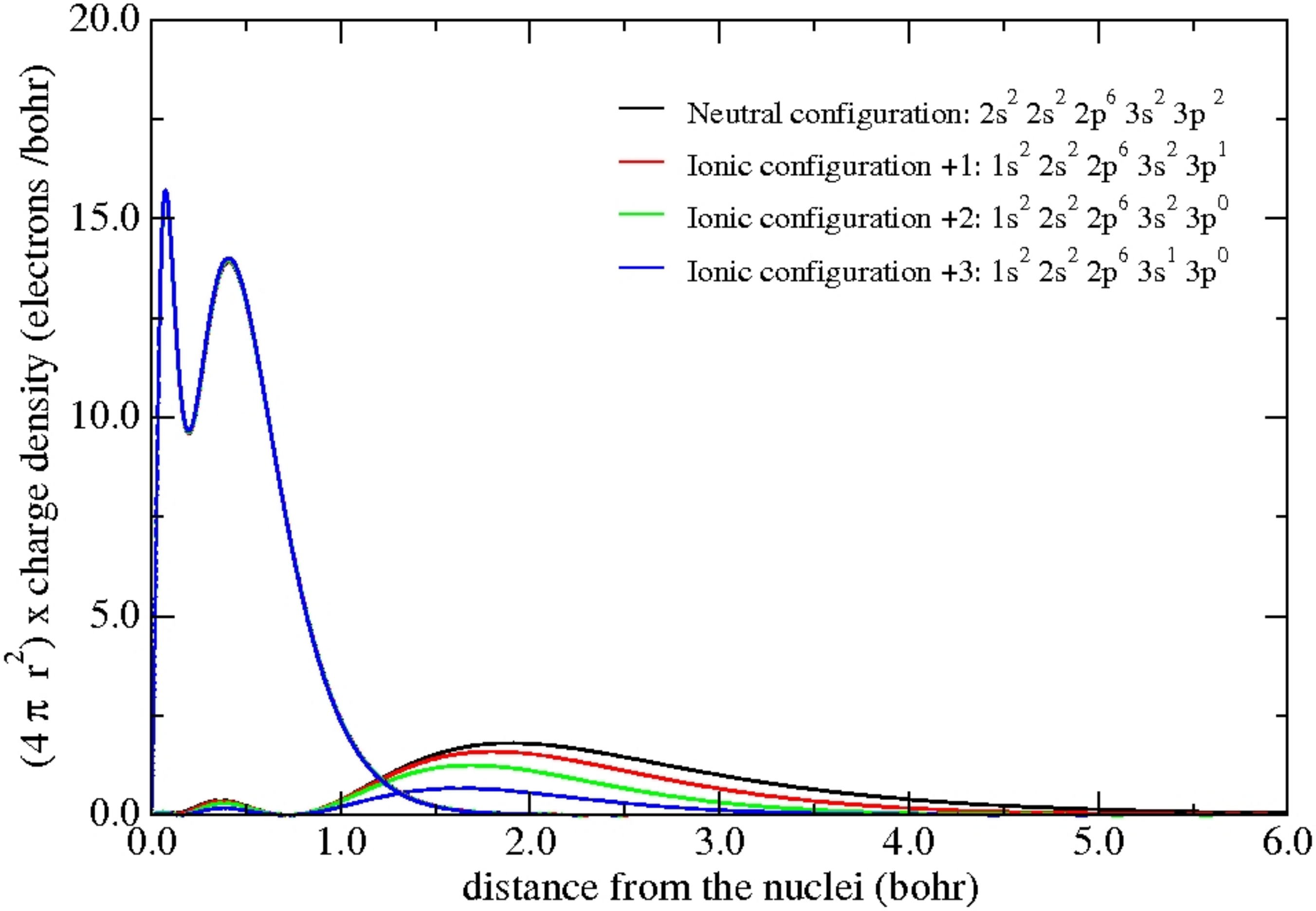
Angularly integrated core and valence charge densities



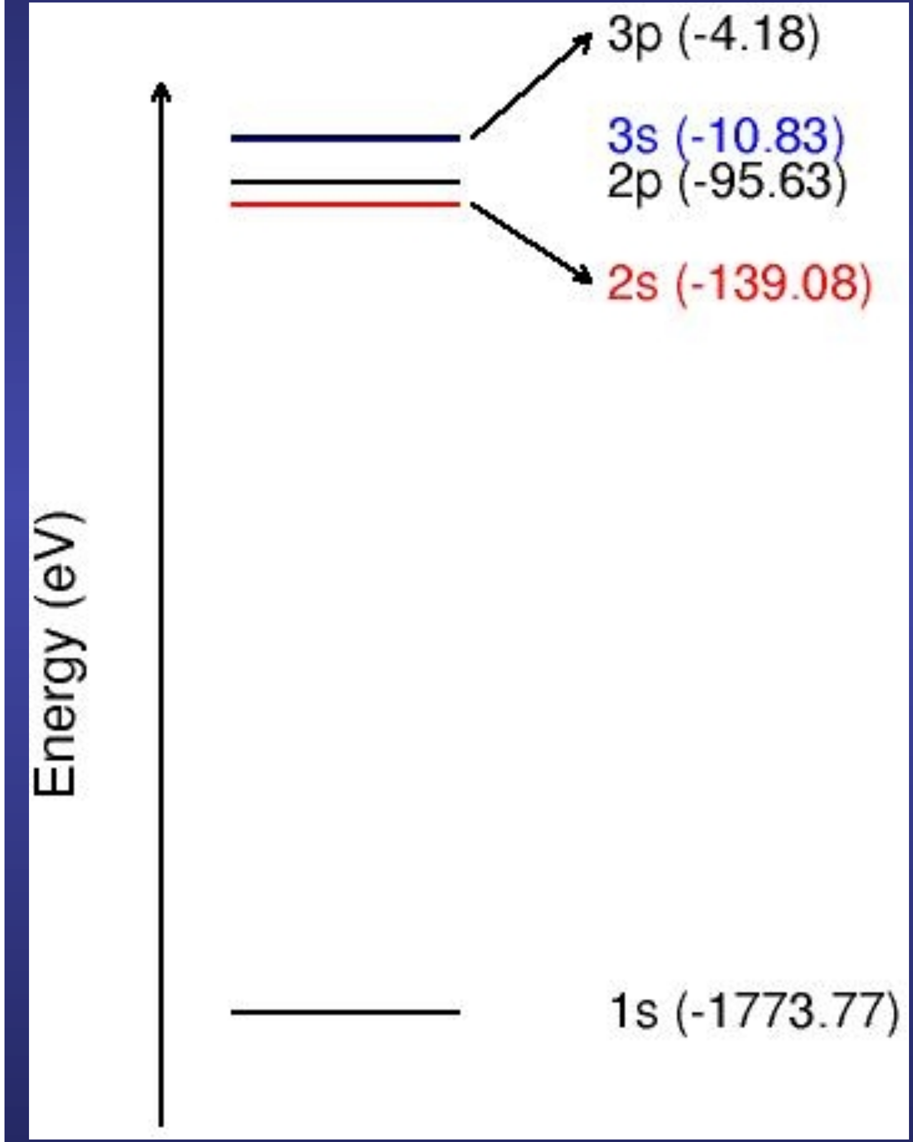
Core electrons are chemically inert

All electron calculation for an isolated Si atom

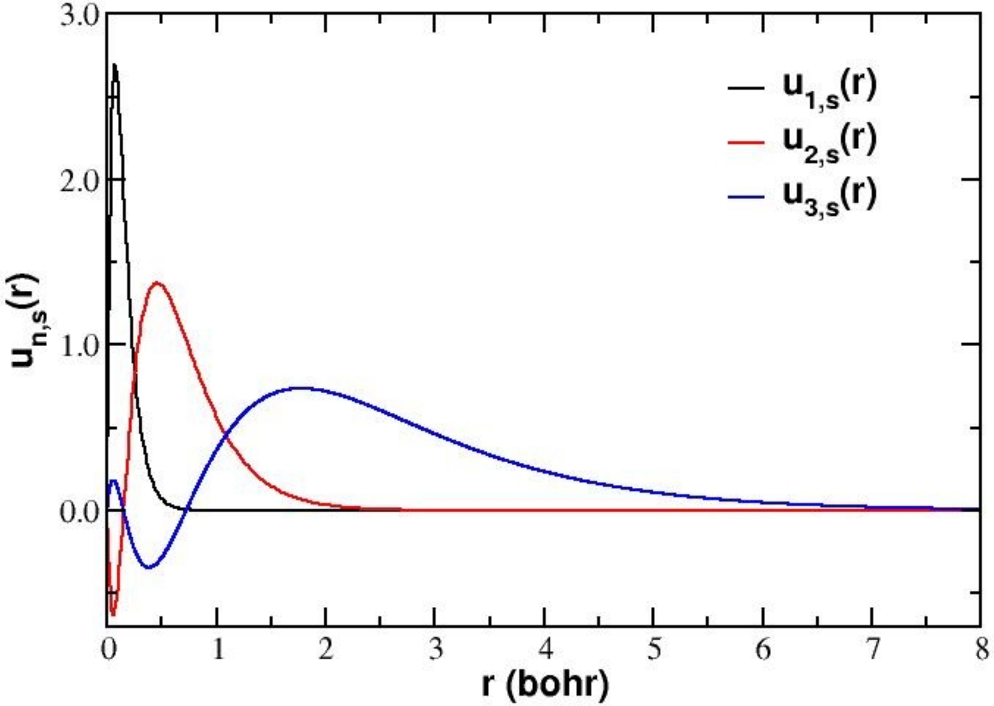
Angularly integrated core and valence charge densities



Valence wave functions must be orthogonal to the core wave functions



Atomic Si



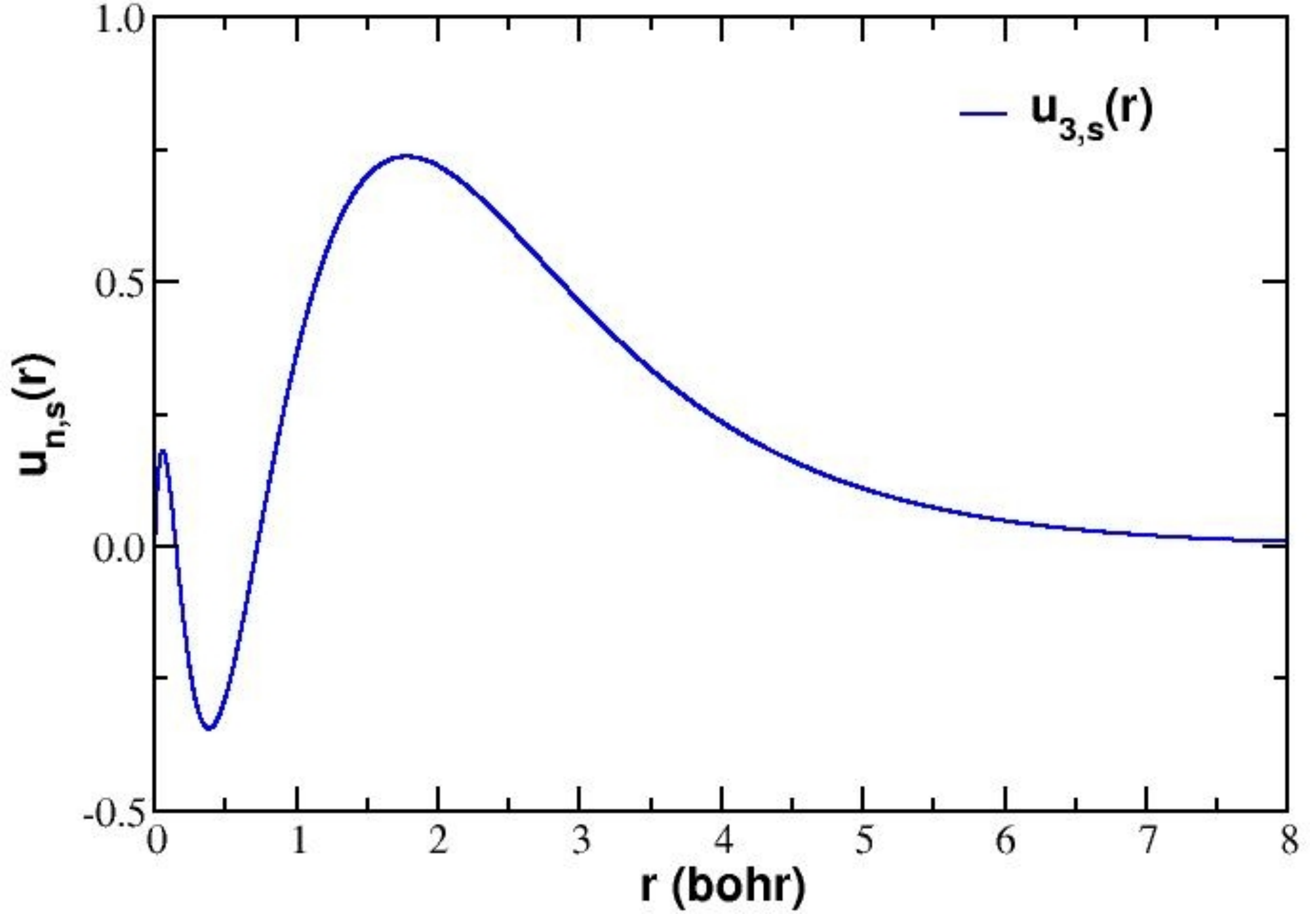
Core electrons…

highly localized

very depth energy

… are chemically inert

Fourier expansion of a valence wave function has a great contribution of short-wave length



To get a good approximation we would have to use a large number of plane waves.

Pseudopotential idea:

Core electrons are chemically inert

(only valence electrons involved in bonding)

Core electrons make the calculation more expensive

- more electrons to deal with
- orthogonality with valence ⇒ poor convergence in PW

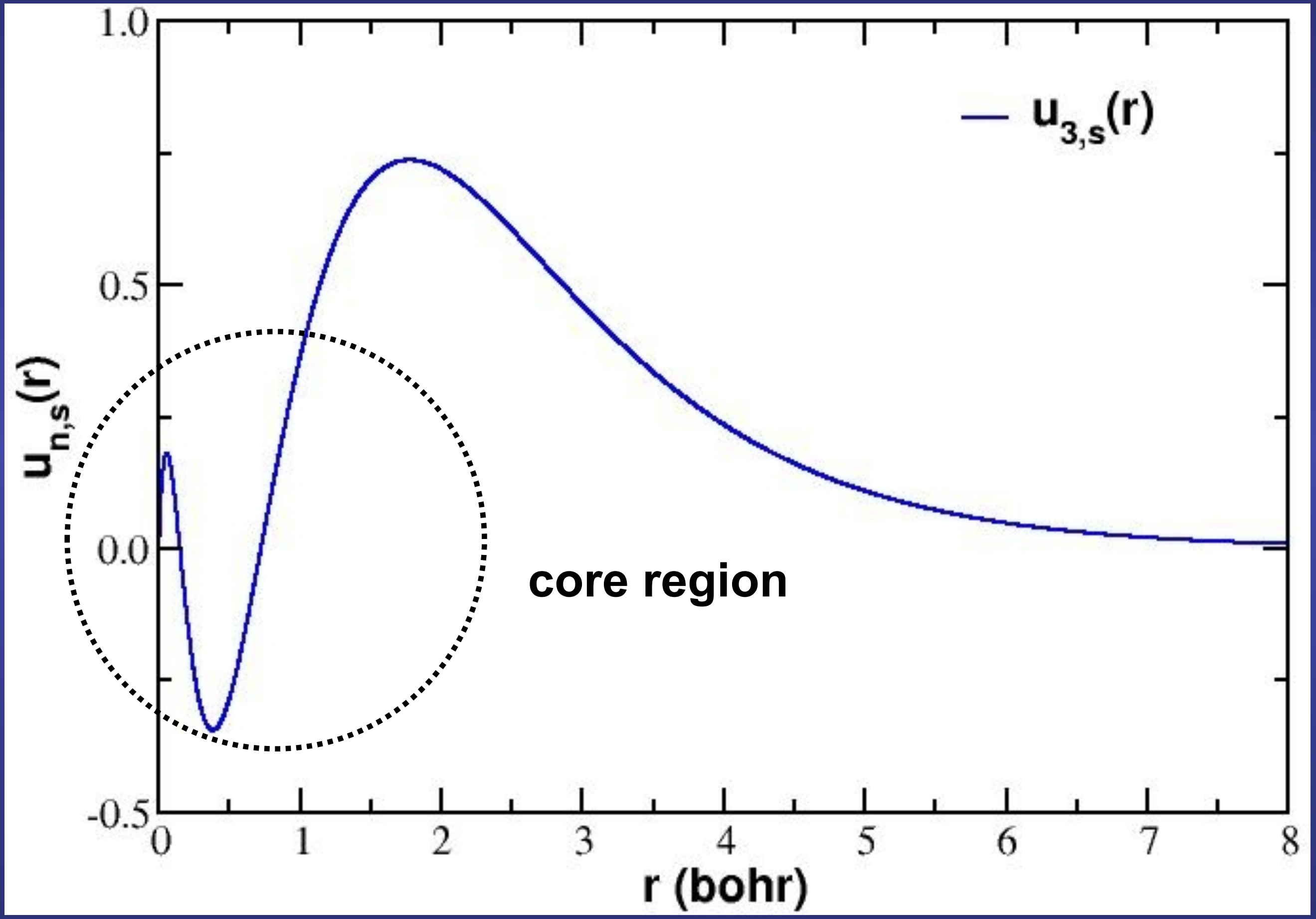
Core electrons main effect: screen nuclear potential

Idea:

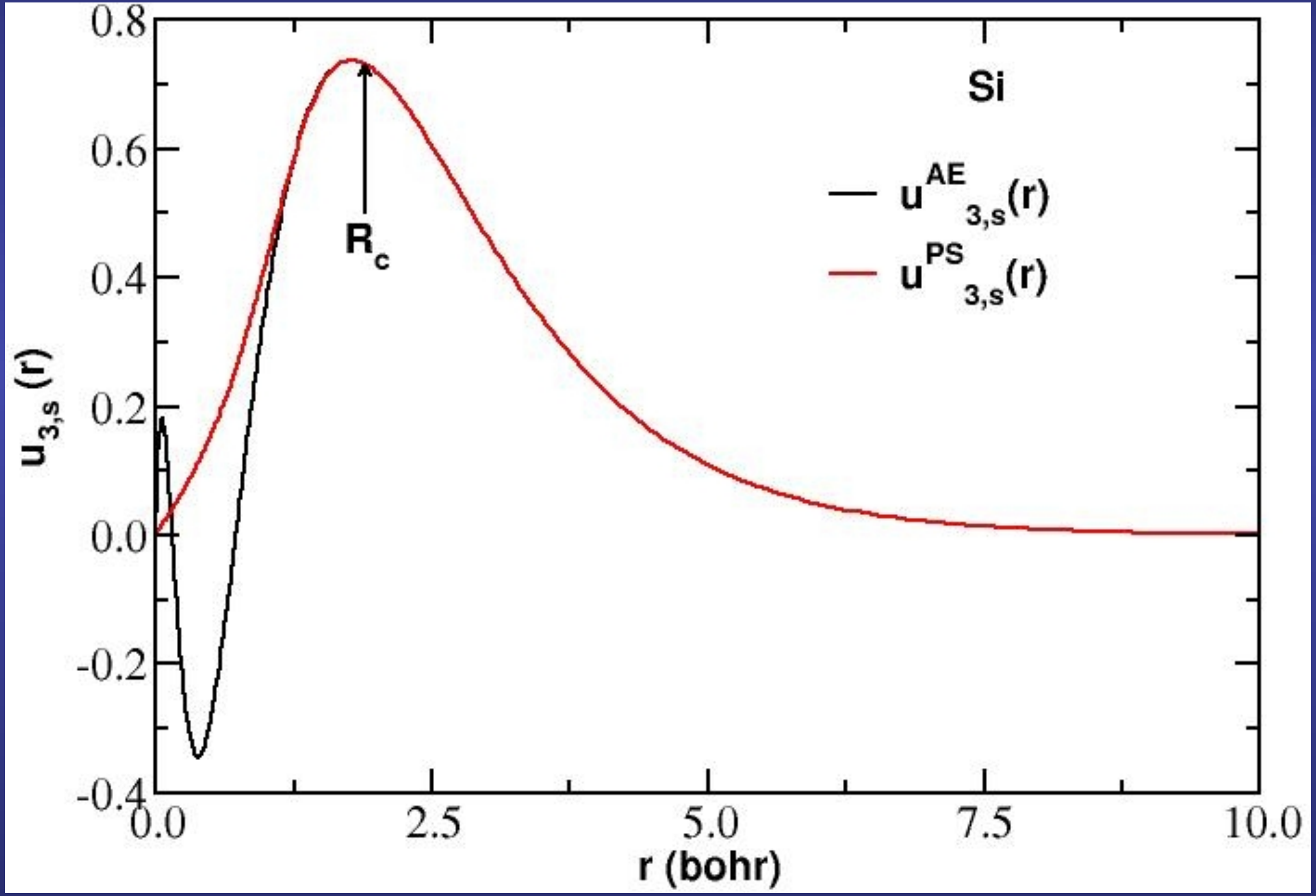
Ignore the dynamics of the core electrons (freeze them)

And replace their effects by an effective potential

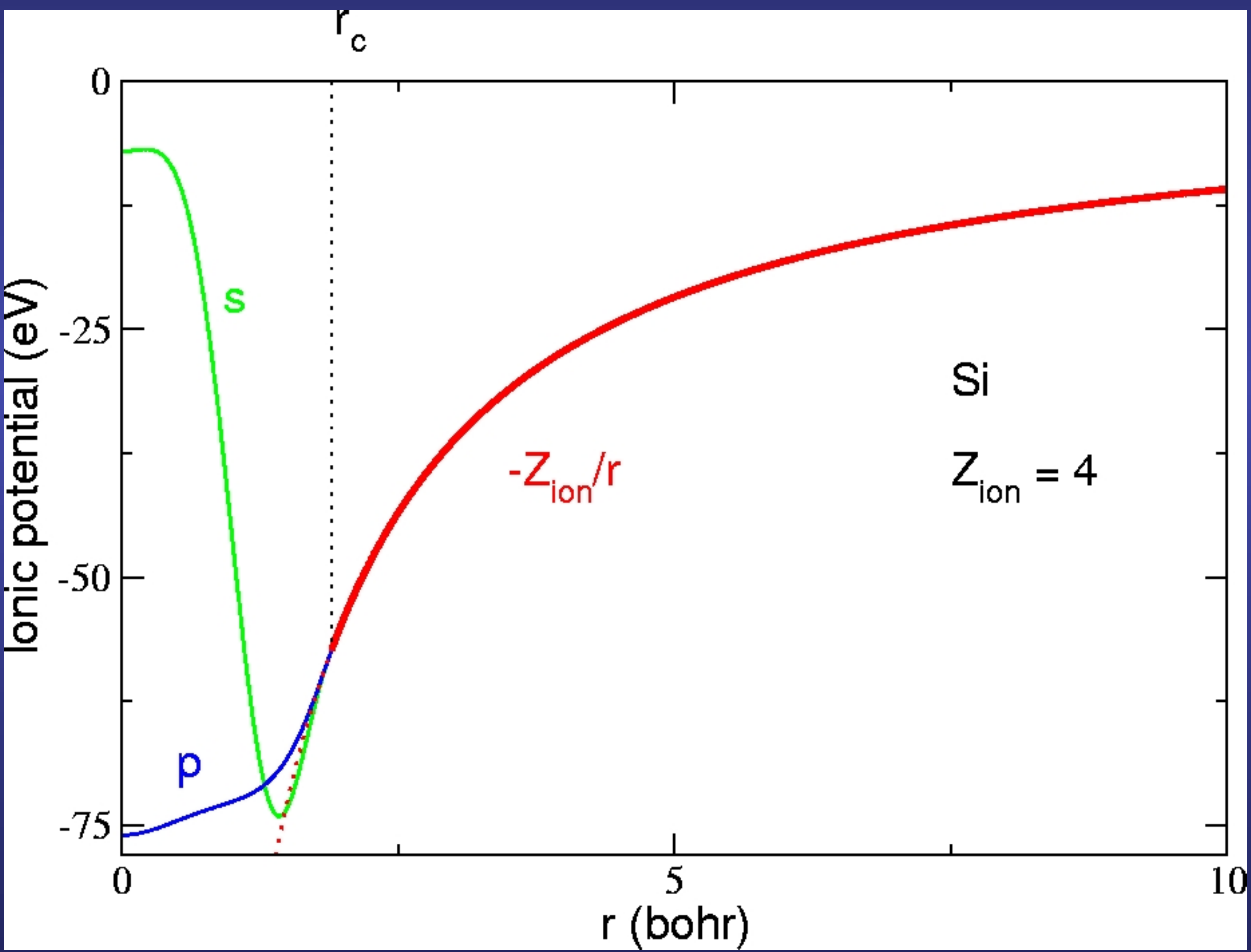
The nodes are imposed by orthogonality to the core states



Idea, eliminate the core electrons by ironing out the nodes



Ab-initio pseudopotential method: fit the valence properties calculated from the atom



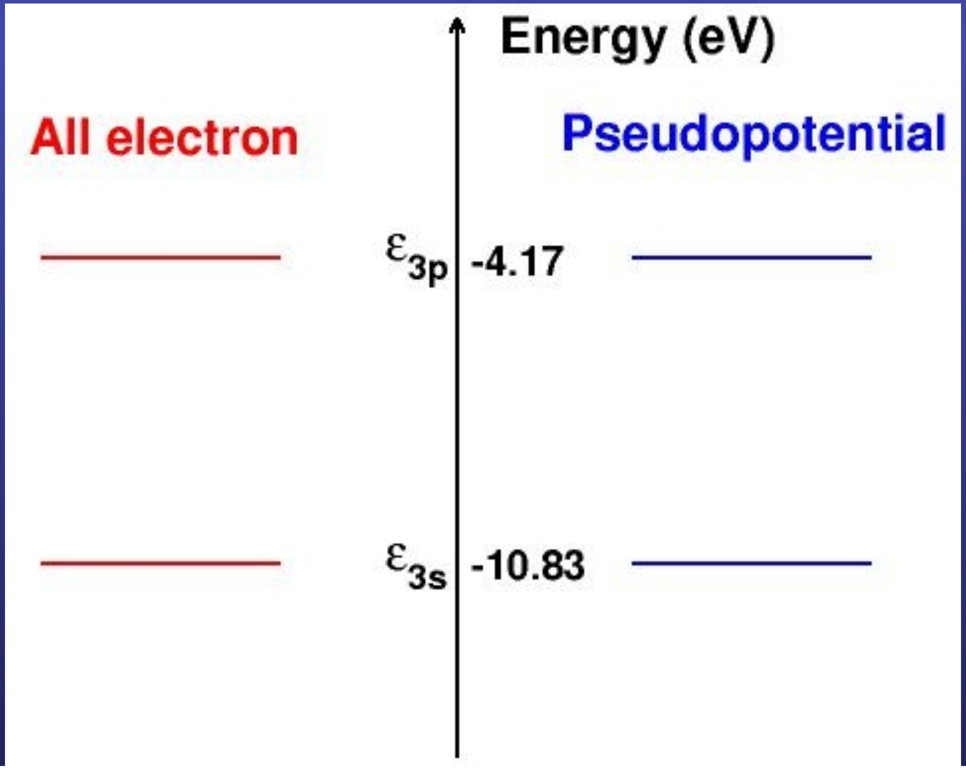
List of requirements for a good norm-conserving pseudopotential:

D. R. Hamann *et al.*, Phys. Rev. Lett. 43, 1494 (1979)

Choose an atomic reference configuration

Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$

1. All electron and pseudo valence eigenvalues agree for the chosen reference configuration

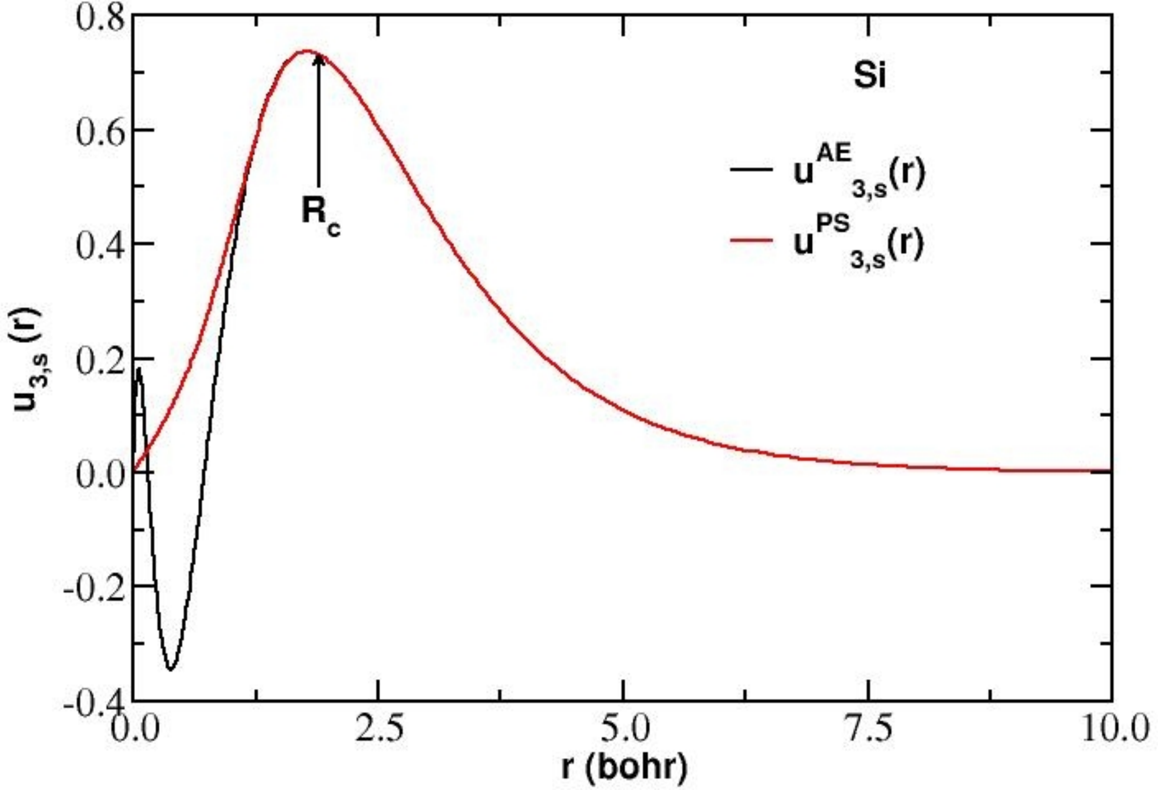


List of requirements for a good norm-conserving pseudopotential:

D. R. Hamann *et al.*, Phys. Rev. Lett. 43, 1494 (1979)

Choose an atomic reference configuration Si: $\underbrace{1s^2\,2s^2\,2p^6}_{\text{core}}\quad\underbrace{3s^2\,3p^2}_{\text{valence}}$

2. All electron and pseudo valence wavefunctions agree beyond a chosen cutoff radius R_c (might be different for each shell)



List of requirements for a good norm-conserving pseudopotential:

D. R. Hamann *et al.*, Phys. Rev. Lett. 43, 1494 (1979)

Choose an atomic reference configuration Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\ \underbrace{3s^2\ 3p^2}_{\text{valence}}$

3. The logarithmic derivatives of the all-electron and pseudowave functions agree at R_c

$$D_l(\varepsilon, r) \equiv r\frac{\psi_l'(\varepsilon, r)}{\psi_l(\varepsilon, r)} = r\frac{d}{dr} ln\left[\psi_l(\varepsilon, r)\right]$$

List of requirements for a good norm-conserving pseudopotential:

D. R. Hamann *et al.*, Phys. Rev. Lett. 43, 1494 (1979)

Choose an atomic reference configuration Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\quad\underbrace{3s^2\ 3p^2}_{\text{valence}}$

4. The integrals from 0 to *r* of the real and pseudo charge densities agree for $r > R_c$ for each valence state

$$Q_l = \int_0^{R_c} dr r^2 \left|\psi_l(r)\right|^2$$

Q_l is the same for ψ_l^{PS} as for the all electron radial orbital ψ_l

⇓

- Total charge in the core region is correct
- Normalized pseudoorbital is equal to the true orbital outside of R_c

List of requirements for a good norm-conserving pseudopotential:

D. R. Hamann *et al.*, Phys. Rev. Lett. 43, 1494 (1979)

Choose an atomic reference configuration Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\ \underbrace{3s^2\ 3p^2}_{\text{valence}}$

5. The first energy derivative of the logarithmic derivatives of the all-electron and pseudo wave functions agrees at R_c

Central point due to Hamann, Schlüter and Chiang:

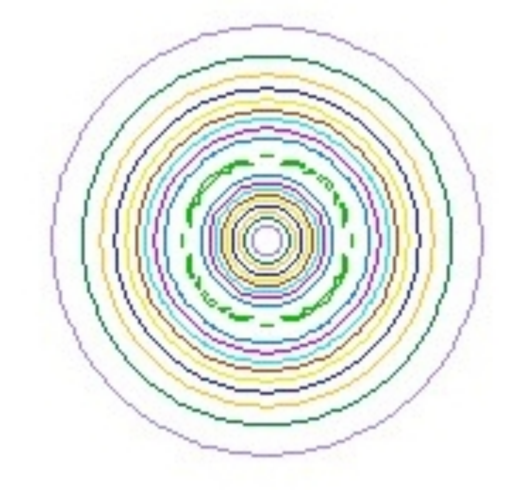
Norm conservation [(4)] ⇒ (5)

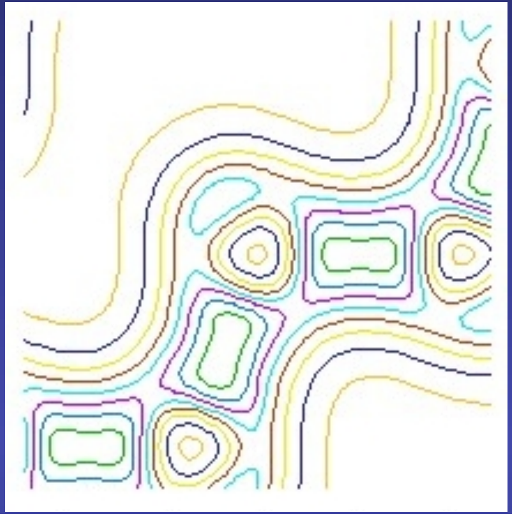
$$2\pi \left[(r\psi)^2 \frac{d}{d\varepsilon} \frac{d}{dr} ln\psi \right]_R = 4\pi \int_0^R r^2 \psi^2 dr$$

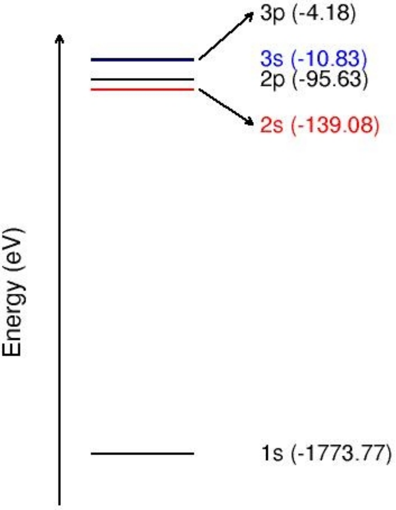
Equality of AE and PS energy derivatives of the logarithmic derivatives essential for transferability

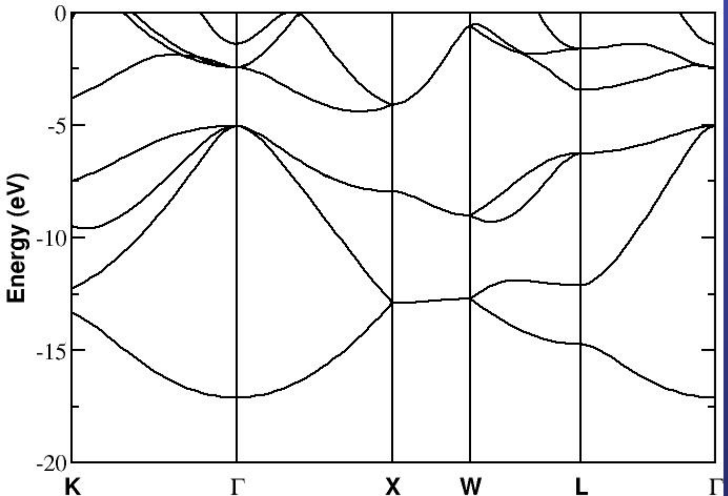
Atomic Si

Bulk Si









If condition 5 is satisfied, the change in the eigenvalues to linear order in the change in the potential is reproduced

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)

Generation of *l*-dependent norm-conserving pseudo: Step 1, choosing the reference configuration

Question: how to choose the electronic configuration of the isolated atom

(the reference atomic configuration)

so that the pseudopotential remains useful in molecular systems and solids

(the target system)

The reference configuration is arbitrary, the user has a degree of freedom here

If the pseudopotential is transferable enough, the choice is not so critical, but transferability tests are mandatory

Transferability is expected to work best for electronic configurations close to the reference one, but it is not obvious for rather different configurations (would a pseudopotential generated for neutral K work well in K^+?)

Generation of *l*-dependent norm-conserving pseudo: Step 1, choosing the reference configuration

Standard first choice: ground state configuration of the neutral isolated atom

However, states of angular momenta that are unoccupied in the neutral atom hibridize with the occupied states in the presence of a different environment, becoming partially occupied.

In these cases, it is necessary to include these angular momenta as non-local components of 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

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

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

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

Z **≡bare nuclear charge**

Generation of *l*-dependent norm-conserving pseudo: Step 2, solving the radial wave function

Since, in the isolated atom, the potential is spherically symmetric, the one electron wave functions can be decoupled as the product of a radial part times an spherical harmonic

$$\psi_{nlm}(\vec{r}) = \psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) = \frac{1}{r} u_{nl}(r) Y_{lm}(\theta,\phi)$$

The radial equation (in atomic units) reads

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

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

If, as in many textbooks, we redefine the radial part of the wave function, to simplify the differential operator

$$R_{nl}(r) = \frac{1}{r} u_{nl}(r)$$

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

Generation of l-dependent norm-conserving pseudo: Step 2, solving the radial wave function

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

The equation has to be solved subject to the following boundary conditions

$$\left.\begin{array}{r} u_{nl}(r)\propto r^{l+1} \\ \\ R_{nl}(r)=\dfrac{u_{nl}(r)}{r}\propto r^{l} \end{array}\right\} \quad \text{for} \quad r\to 0 \qquad \Rightarrow u_{nl}(r=0)=0$$

$$u_{nl}(r)\to 0 \quad \text{for} \quad r\to\infty$$

And the radial part of the wave function has to be normalized as

$$\int_0^\infty r^2|R_{nl}(r)|^2dr=\int_0^\infty |u_{nl}(r)|^2dr=1$$

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

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

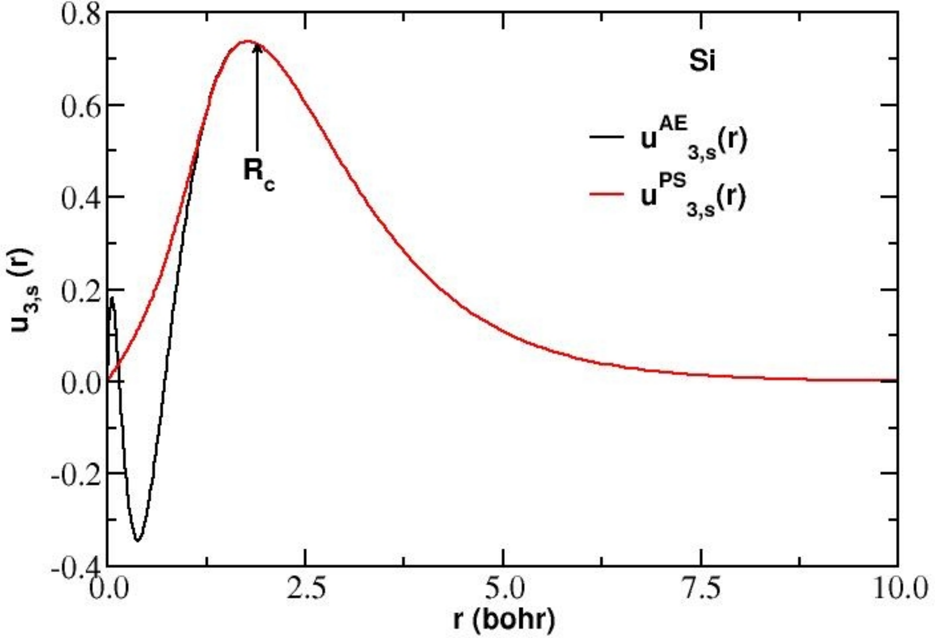
$$V_{\text{eff}}[n](r) = V_{\text{ext}}(r) + V_{\text{Hartree}}[n] + V_{xc}[n] = -\frac{Z}{r} + \int \frac{n(r')}{|r-r'|}dr' + V_{xc}[n]$$

$n(r)$ ≡ 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)

Generation of *l*-dependent norm-conserving pseudo: Step 3, parametrization of the pseudowave functions



Independently of the method, two conditions usually imposed:

-Smooth matching between the all electron and the pseudo wave function at the cutoff radius R_c

- Conservation of the norm of the pseudo wave function.

Degree of freedom in the choice of the flavour of the pseudopotential and R_c

Several schemes available in the literature for norm-conserving pseudopotentials

Hamann, Schlüter, and Chiang [D. R. Hamann *et al.*, Phys. Rev. Lett. 43, 1494 (1979)]

Kerker [G. P. Kerker, J. Phys. C 13, L189 (1980)]

Troullier-Martins [N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991)]

Rappe-Rabe-Kaxiras-Joannopoulos [A. M. Rappe et. al., Phys. Rev. B 41, 1227 (1990)]

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

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

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

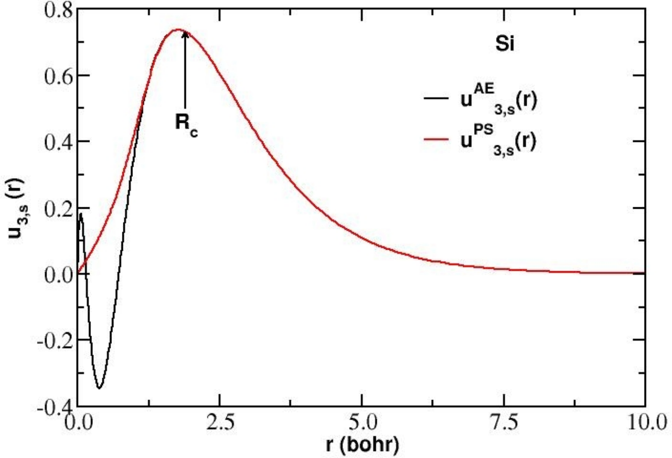
$n(r)$ ≡ sum of electronic charges for occupied states

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

Generation of *l*-dependent norm-conserving pseudo: Step 4, inversion of the radial Schrödinger equation



Search for the Schrödinger-like equation that would satisfy the pseudo-orbital

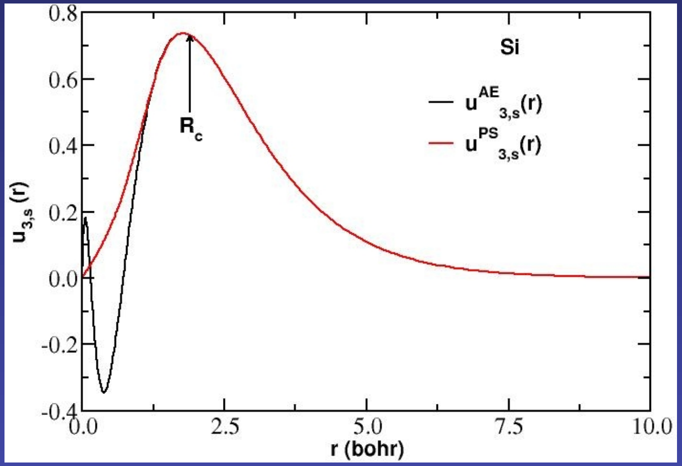
$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V^{\mathrm{PS}}_{(\mathrm{sc})l}(r)\right] u^{\mathrm{PS}}_l(r) = \varepsilon_l u^{\mathrm{PS}}_l(r)$$

$$-\frac{1}{2}\frac{d^2 u^{\mathrm{PS}}_l(r)}{dr^2} + \frac{l(l+1)}{2r^2} u^{\mathrm{PS}}_l(r) + V^{\mathrm{PS}}_{(\mathrm{sc})l}(r) u^{\mathrm{PS}}_l(r) = \varepsilon_l u^{\mathrm{PS}}_l(r)$$

$$-\frac{1}{2u^{\mathrm{PS}}_l(r)}\frac{d^2 u^{\mathrm{PS}}_l(r)}{dr^2} + \frac{l(l+1)}{2r^2} + V^{\mathrm{PS}}_{(\mathrm{sc})l}(r) = \varepsilon_l$$

$$V^{\mathrm{PS}}_{(\mathrm{sc})l}(r) = \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2u^{\mathrm{PS}}_l(r)}\frac{d^2 u^{\mathrm{PS}}_l(r)}{dr^2}$$

Generation of l-dependent norm-conserving pseudo: Step 4, inversion of the radial Schrödinger equation



Search for the Schrödinger-like equation that would satisfy the pseudo-orbital

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

The inversion can always be done because of the nodeless condition

Note that the principal quantum number has droped, because the pseudization is done for the lowest-lying valence state of each angular momentum

Higher lying valence states of the same angular momentum correspond to excited states of 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

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

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

$n(r)$ **≡ 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: Step 5, unscreening of the pseudopotential

The pseudo-wave function obeys

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

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: Step 5, 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)

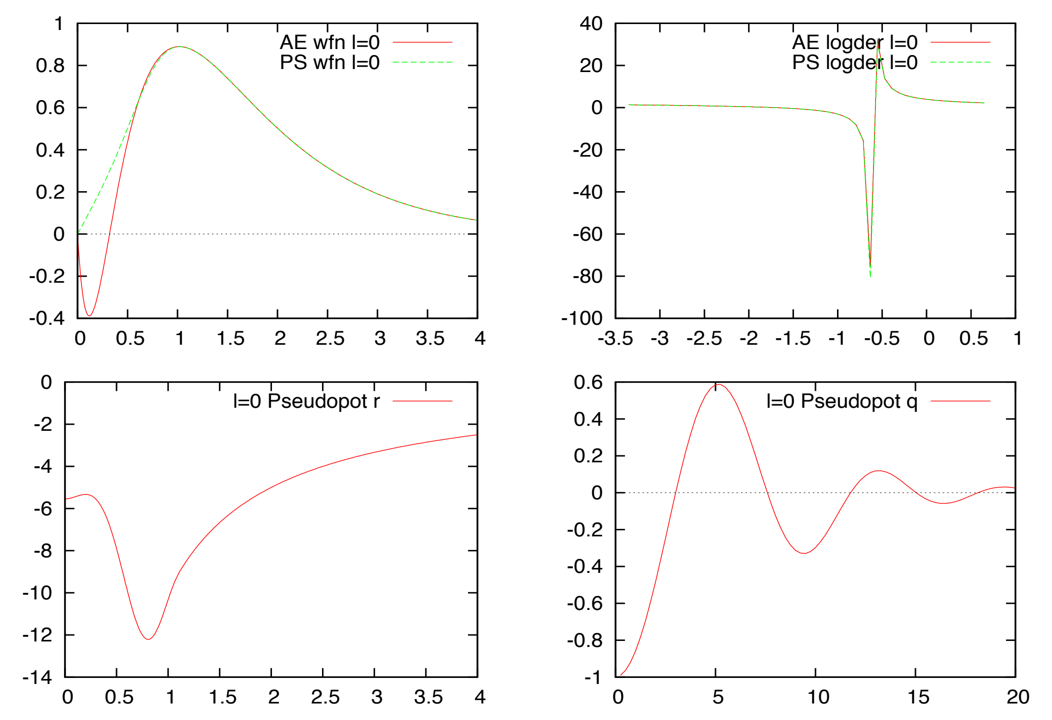
$$\begin{aligned} V_l^{\mathrm{PS}} &= V_{(\mathrm{sc})l}^{\mathrm{PS}} - V_{\mathrm{Hartree}}[n_v] - V_{xc}[n_v] \\ &= V_{(\mathrm{sc})l}^{\mathrm{PS}} - \int \frac{n_v(r')}{|r-r'|} dr' - V_{xc}[n_v] \end{aligned}$$

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

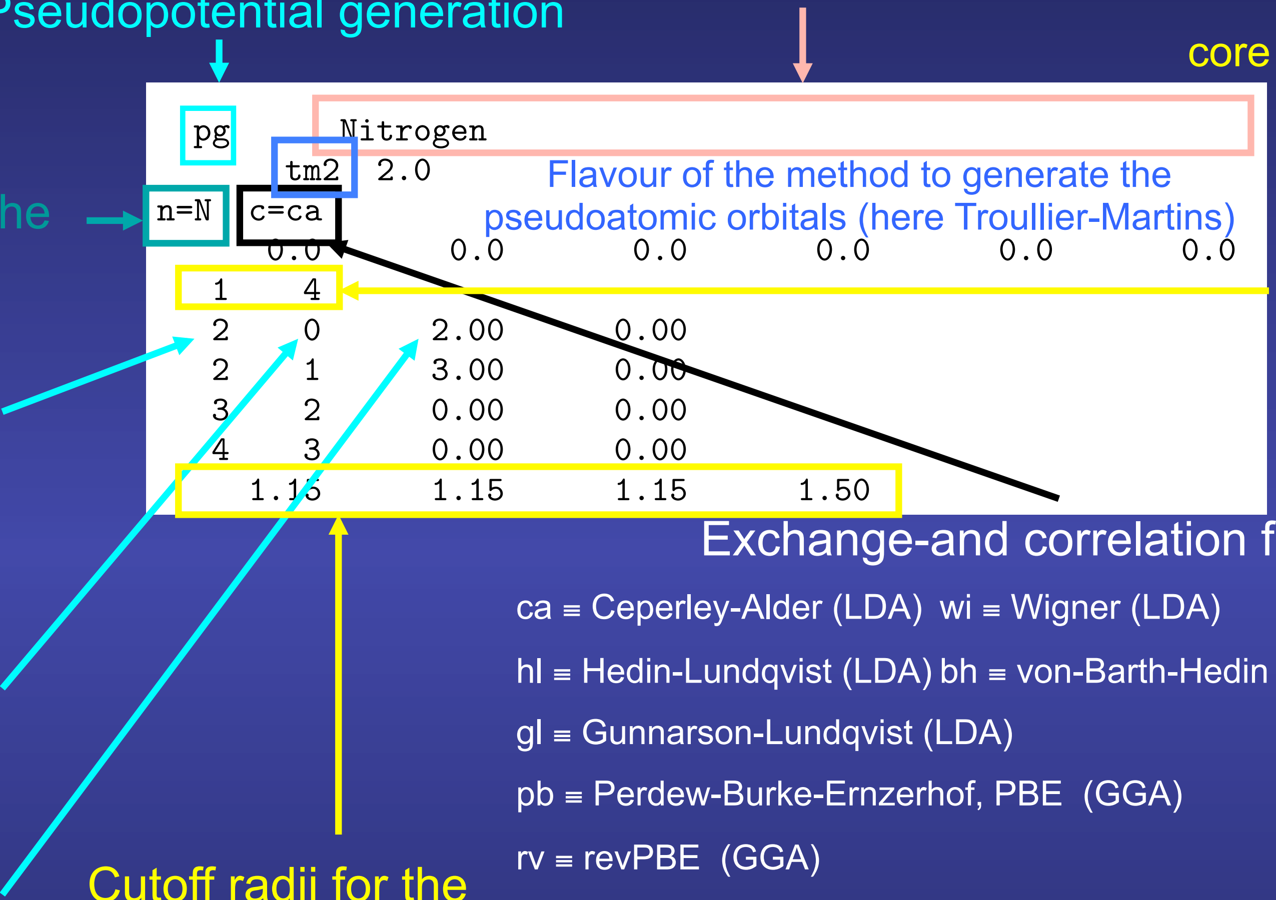
How to generate a pseudopotential



Objectives

Generate a norm-conserving pseudopotential using ATOM

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



```
   pg      Nitrogen
        tm2  2.0
 n=N  c=ca
        0.0      0.0      0.0      0.0      0.0      0.0
    1    4
    2    0      2.00     0.00
    2    1      3.00     0.00
    3    2      0.00     0.00
    4    3      0.00     0.00
        1.15     1.15     1.15     1.50
```

pg ≡ Pseudopotential generation

A title for the job

N $1s^2$ $\underbrace{2s^2\ 2p^3\ 3d^0\ 4f^0}$

core valence

Chemical symbol of the atom

Flavour of the method to generate the pseudoatomic orbitals (here Troullier-Martins)

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)

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

How to run a pseudopotential generation with ATOM

```
$ ../../Utils/pg.sh N.tm2.inp
==> Output data in directory N.tm2
==> Pseudopotential in N.tm2.vps and N.tm2.psf (and maybe in N.tm2.xml)

$ ls
N.test.inp N.tm2.inp N.tm2.vps
N.tm2 N.tm2.psf N.tm2.xml

$ cd N.tm2
$ ls
AECHARGE INP PSPOTR1 RHO pots.gplot
AELOGD0 OUT PSPOTR2 SCRPSPOTR0 pots.gps
AELOGD1 PSCHARGE PSPOTR3 SCRPSPOTR1 pseudo.gplot
AELOGD2 PSLOGD0 PSWFFMT SCRPSPOTR2 pseudo.gps
AELOGD3 PSLOGD1 PSWFNQ0 SCRPSPOTR3 scrpots.gplot
AEWFNR0 PSLOGD2 PSWFNQ1 VPSFMT scrpots.gps
AEWFNR1 PSLOGD3 PSWFNQ2 VPSOUT subps.gplot
AEWFNR2 PSPOTQ0 PSWFNQ3 VPSXML subps.gps
AEWFNR3 PSPOTQ1 PSWFNR0 charge.gplot vcharge.gplot
CHARGE PSPOTQ2 PSWFNR1 charge.gps vcharge.gps
FOURIER_AREA PSPOTQ3 PSWFNR2 coreq.gplot vspin.gplot
FOURIER_QMAX PSPOTR0 PSWFNR3 coreq.gps vspin.gps
$
```

Run the script

The pseudopotentials will be on the same parent directory:

.vps (unformatted)
.psf (formatted)
.xml (in XML format)

Different output files in a new directory (same name as the input file without the .inp extension)

An explanation of the different files can be found in the ATOM User's Guide (page 6)

Plotting the all electron and pseudo charge densities

```
$ gnuplot –persist charge.gplot
```

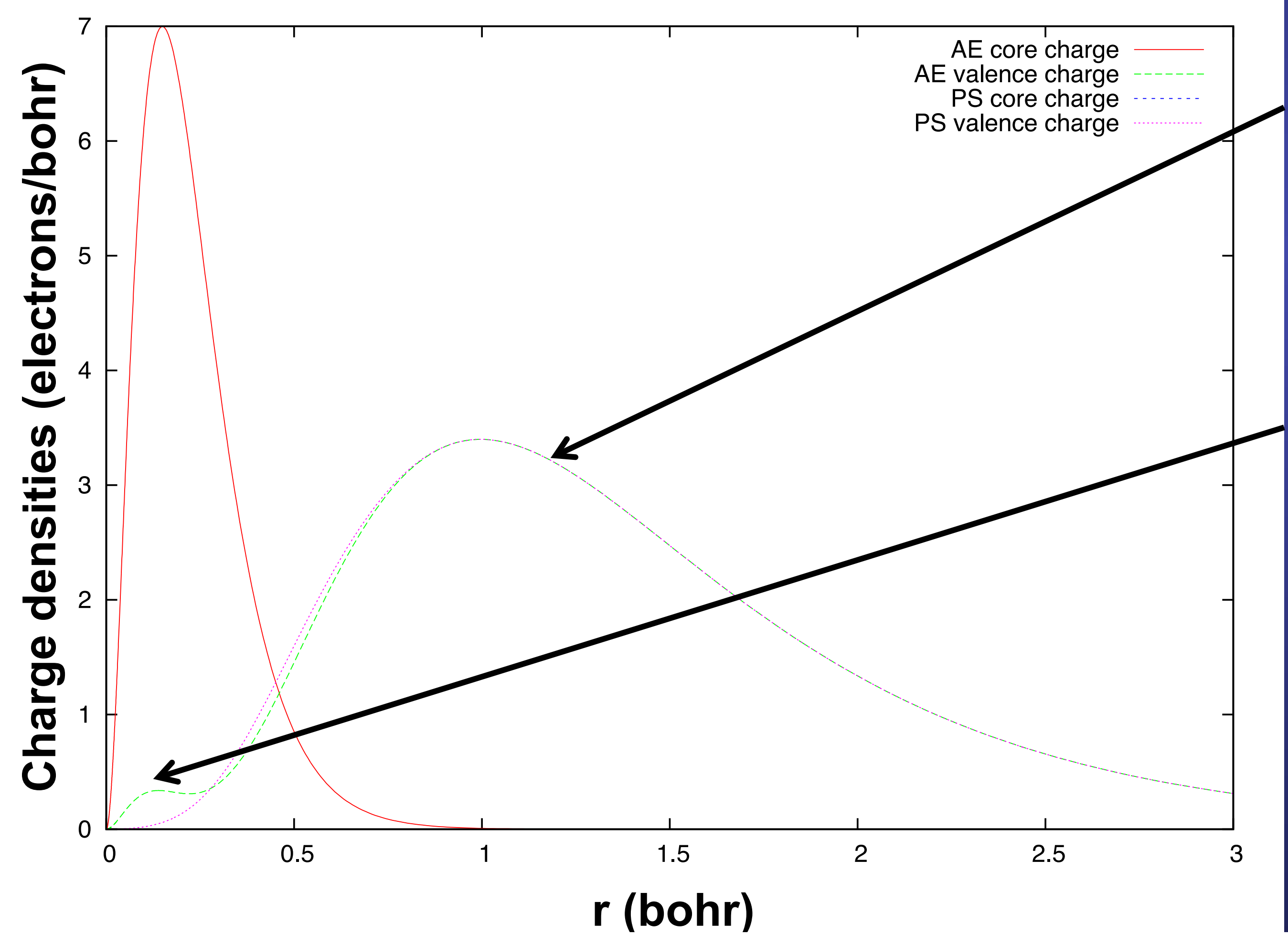
(To generate a figure on the screen using gnuplot)

```
$ gnuplot charge.gps
```

(To generate a postscript file with the figure)

The core and the charge densities are angularly integrated (multiplied by $4\pi r^2$)

$$\int_0^{\infty} \rho^{\mathrm{AE}}_{\mathrm{valence}} dr = \int_0^{\infty} \rho^{\mathrm{PS}}_{\mathrm{valence}} dr = \mathrm{Number\ \ valence\ \ electrons}$$



The PS and AE valence charge densities are equal beyond the cutoff radii

Small peak in the AE valence charge density due to orthogonality with AE core

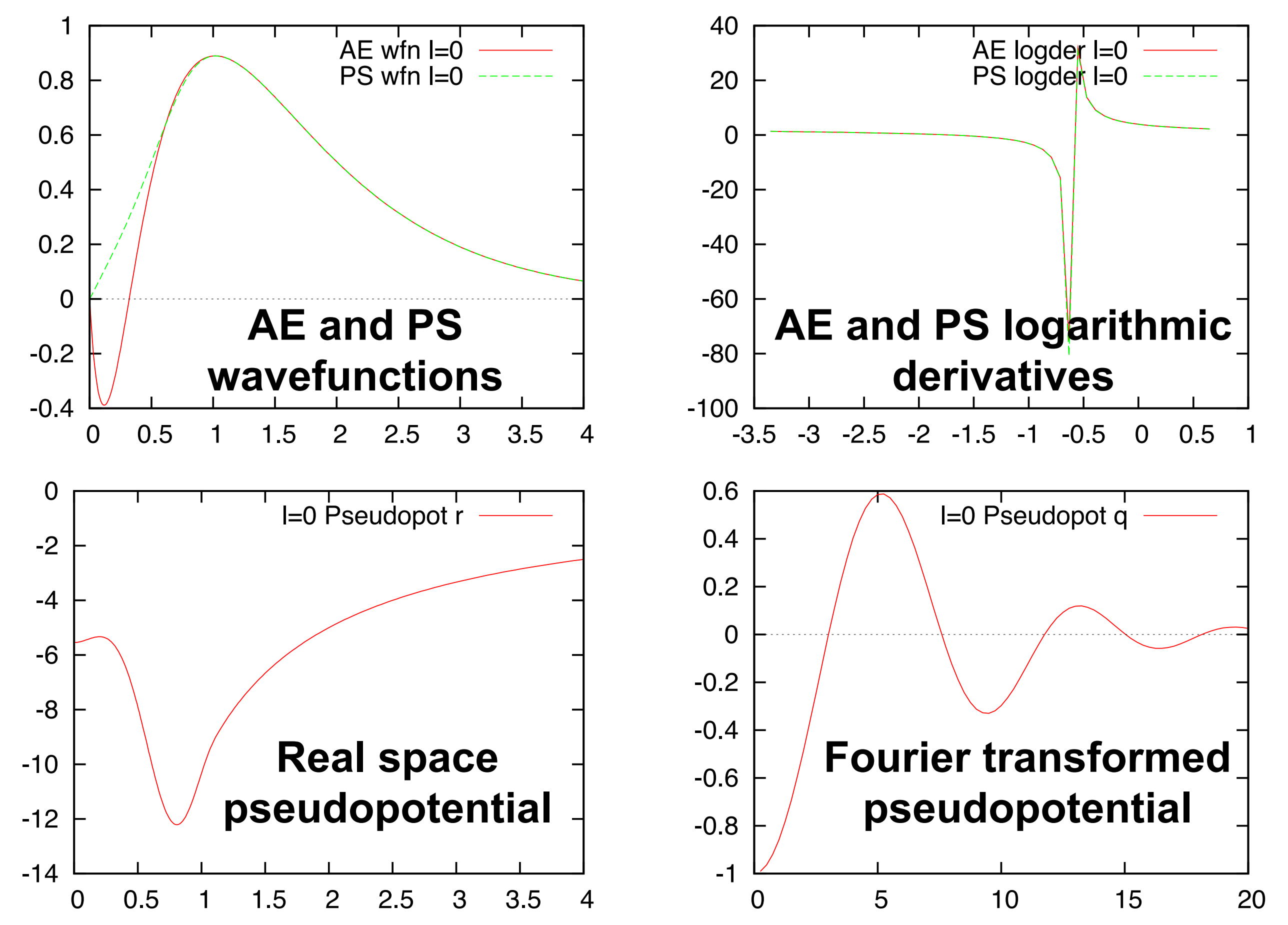
Plotting the all pseudopotenial information

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

(To generate a figure on the screen using gnuplot)

```
$ gnuplot pseudo.gps
```

(To generate a postscript file with the figure)



The more Fourier components, the harder the pseudopotential

A figure like this for each angular momentum shell in the valence

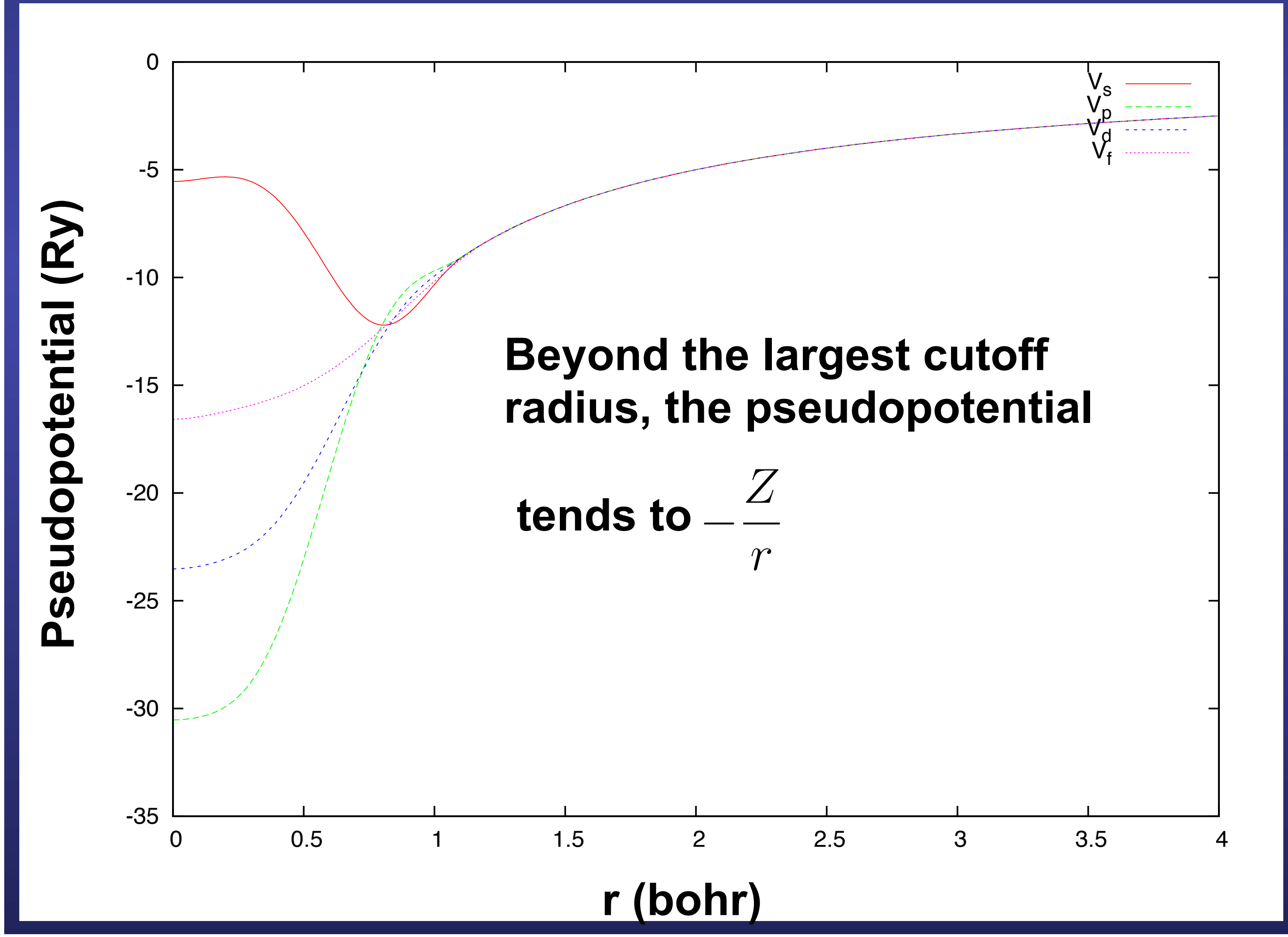
Plotting the real-space pseudopotentials

```
$ gnuplot –persist pots.gplot
```

(To generate a figure on the screen using gnuplot)

```
$ gnuplot pots.gps
```

(To generate a postscript file with the figure)



Beyond the largest cutoff radius, the pseudopotential tends to $-\frac{Z}{r}$

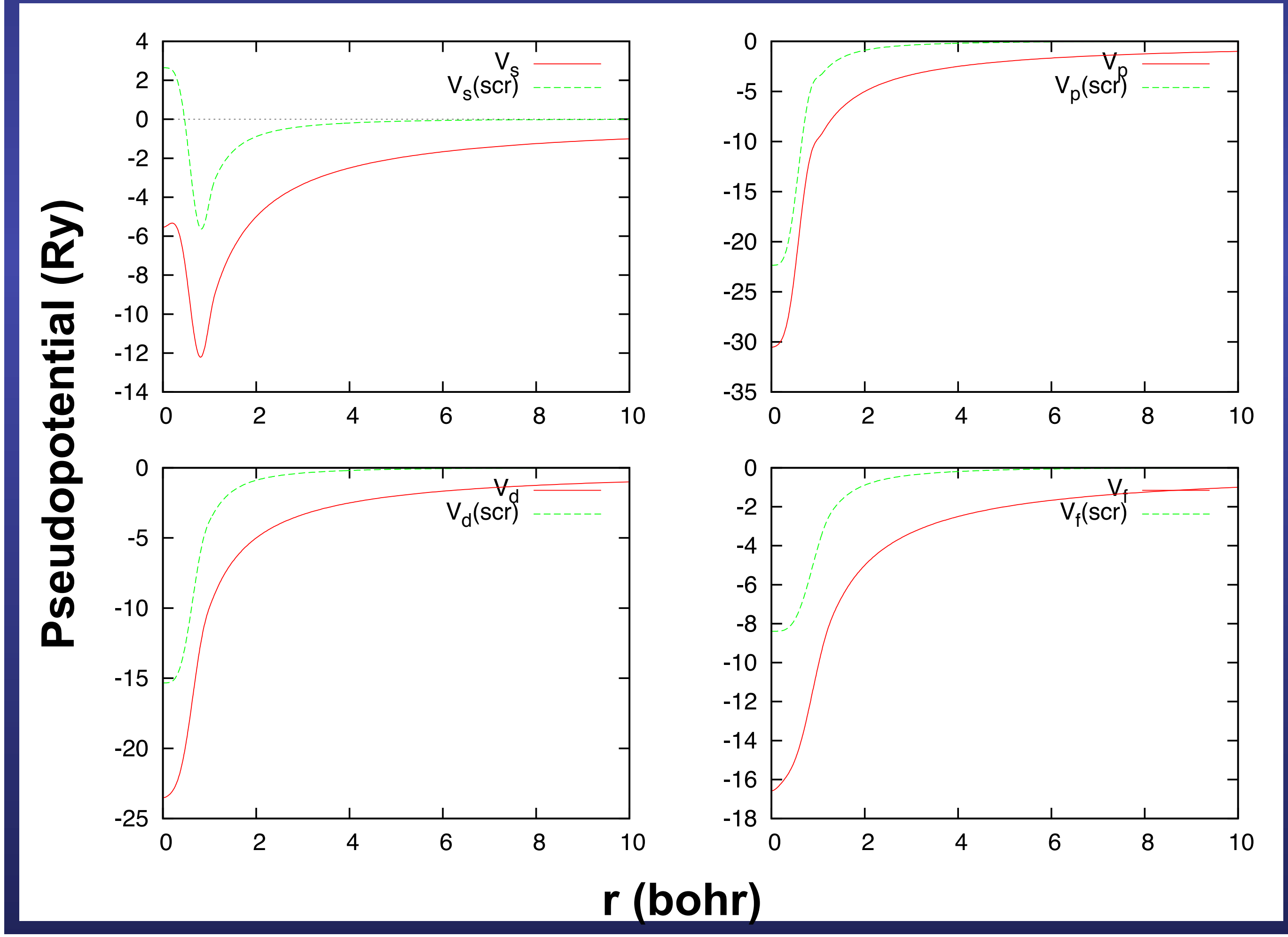
Plotting the unscreened and screened pseudopoten

```
$ gnuplot –persist scrpots.gplot
```

(To generate a figure on the screen using gnuplot)

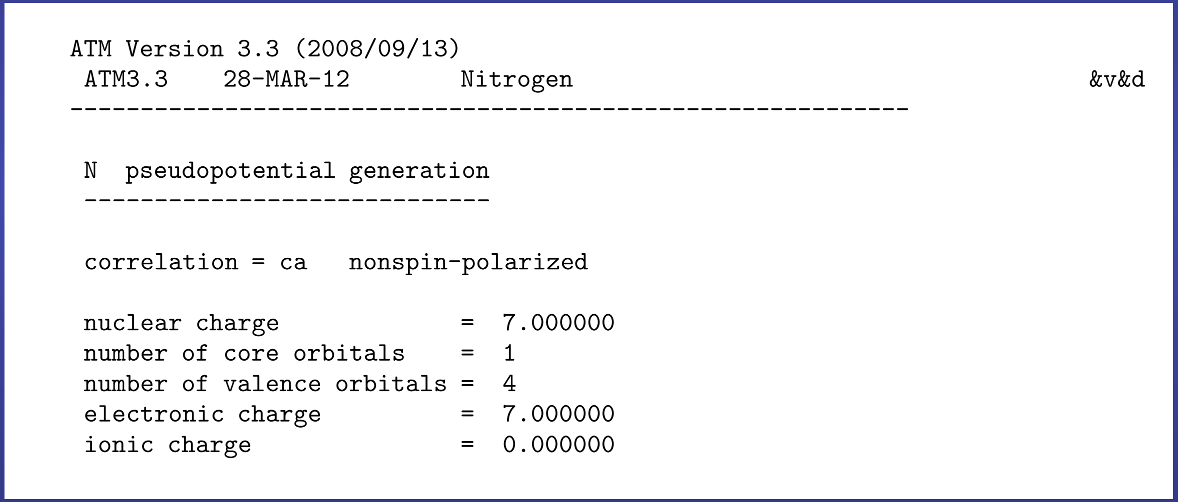
```
$ gnuplot scrpots.gps
```

(To generate a postscript file with the figure)



Exploring the output file

$ vi OUT

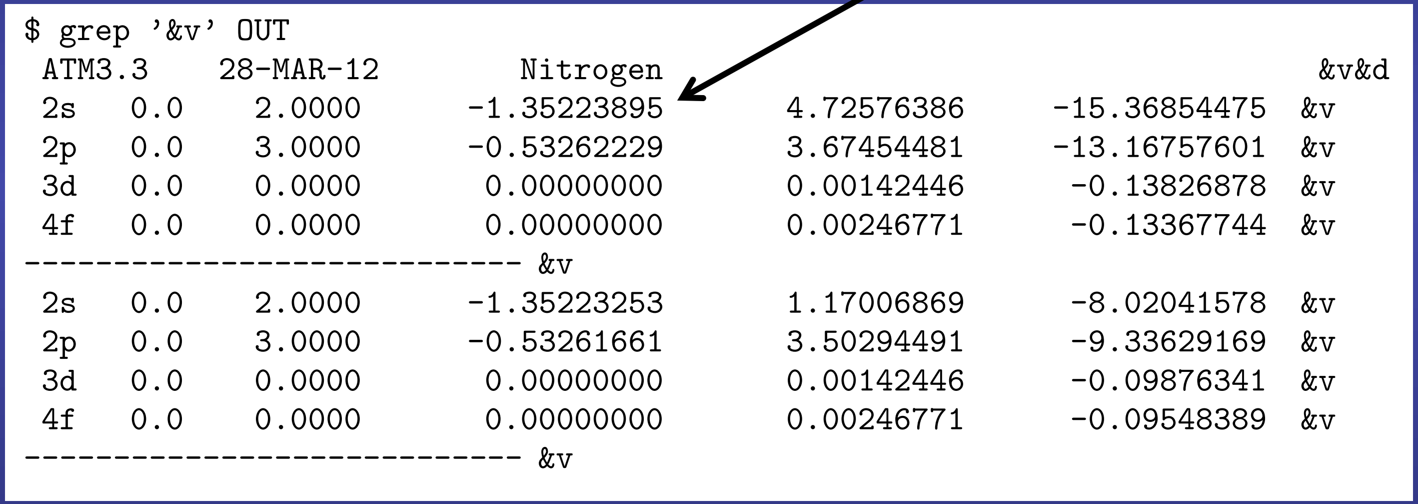


```
ATM Version 3.3 (2008/09/13)
 ATM3.3    28-MAR-12        Nitrogen                                    &v&d
------------------------------------------------------------

 N  pseudopotential generation
 -----------------------------

 correlation = ca   nonspin-polarized

 nuclear charge             =  7.000000
 number of core orbitals    =  1
 number of valence orbitals =  4
 electronic charge          =  7.000000
 ionic charge               =  0.000000
```

Comparing AE and PS eigenvalues

$ grep ‘&v’ OUT

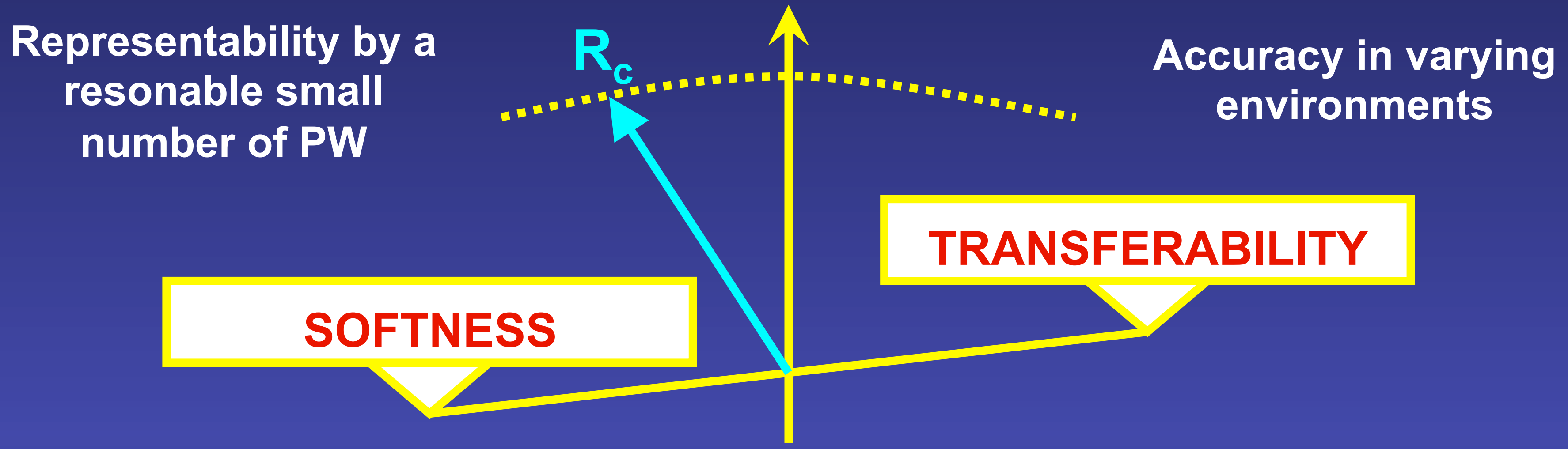
Eigenvalues (in Ry)



```
$ grep ’&v’ OUT
 ATM3.3    28-MAR-12        Nitrogen                                    &v&d
 2s    0.0     2.0000      -1.35223895       4.72576386      -15.36854475  &v
 2p    0.0     3.0000      -0.53262229       3.67454481      -13.16757601  &v
 3d    0.0     0.0000       0.00000000       0.00142446       -0.13826878  &v
 4f    0.0     0.0000       0.00000000       0.00246771       -0.13367744  &v
---------------------------- &v
 2s    0.0     2.0000      -1.35223253       1.17006869       -8.02041578  &v
 2p    0.0     3.0000      -0.53261661       3.50294491       -9.33629169  &v
 3d    0.0     0.0000       0.00000000       0.00142446       -0.09876341  &v
 4f    0.0     0.0000       0.00000000       0.00246771       -0.09548389  &v
---------------------------- &v
```

The AE and PS eigenvalues are not exactly identical because the pseudopotentials are changed slightly to make them approach their limit tails faster

Balance between softness and transferability controlled by R_c



Representability by a resonable small number of PW

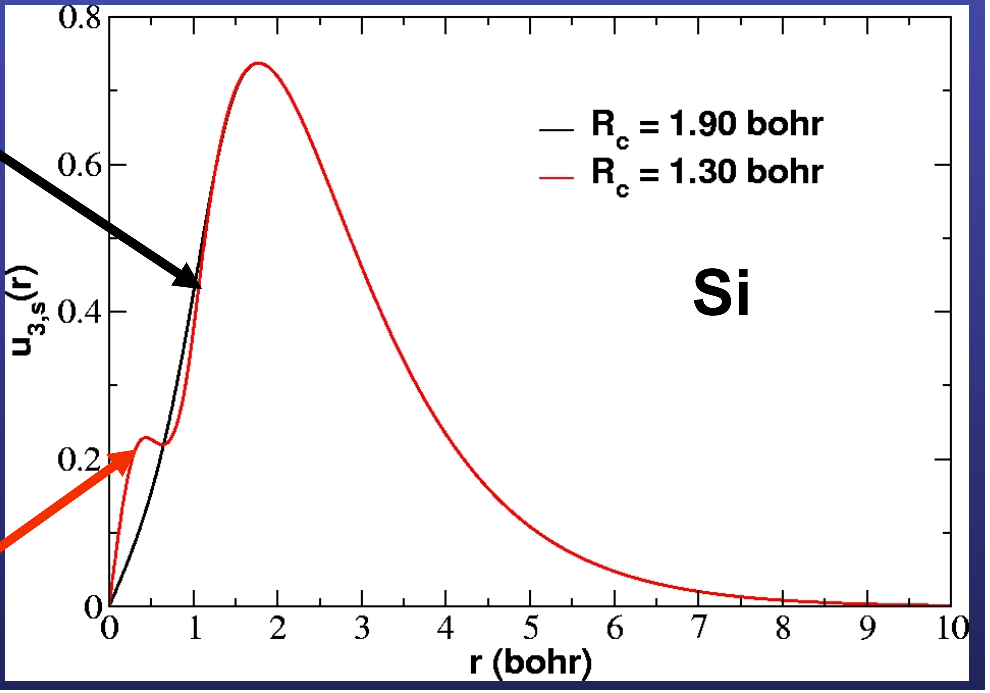
R_c

Accuracy in varying environments

TRANSFERABILITY

SOFTNESS

Larger R_c: softer pseudo



First guess: last peak of the all electron wave function

Shorter R_c: harder pseudo

How to test a norm-conserving pseudopotential

```
$ grep "&d" OUT
 ATM3.3    26-NOV-12   N Test -- GS 2s2 2p3                                &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.8 2p3.2                               &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.6 2p3.4                               &v&d
 ATM3.3    26-NOV-12   N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)  &v&d
 &d total energy differences in series
 &d          1        2        3        4
 &d  1    0.0000
 &d  2    0.1640   0.0000
 &d  3    0.3281   0.1641   0.0000
 &d  4   -0.1815  -0.3455  -0.5096   0.0000
*----- End of series ----* spdfg &d&v
 ATM3.3    26-NOV-12   N Test -- GS 2s2 2p3                                &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.8 2p3.2                               &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.6 2p3.4                               &v&d
 ATM3.3    26-NOV-12   N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)  &v&d
 &d total energy differences in series
 &d          1        2        3        4
 &d  1    0.0000
 &d  2    0.1640   0.0000
 &d  3    0.3280   0.1640   0.0000
 &d  4   -0.1815  -0.3454  -0.5094   0.0000
*----- End of series ----* spdfg &d&v
```

Objectives

Test a norm-conserving pseudopotential using ATOM

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

$\mathrm{N}\quad \underset{\text{core}}{1s^2}\quad \underbrace{2s^2\, 2p^3\, 3d^0\, 4f^0}_{\text{valence}}$

Concatenations of **all electron**

```
#
# All-electron calculations for a series of N configurations
#
   ae N Test -- GS 2s2 2p3
   N    ca
       0.0
    1    2
    2    0      2.00
    2    1      3.00
   ae N Test -- 2s1.8 2p3.2
   N    ca
       0.0
    1    2
    2    0      1.80
    2    1      3.20
   ae N Test -- 2s1.6 2p3.4
   N    ca
       0.0
    1    2
    2    0      1.60
    2    1      3.40
   ae N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)
   N    ca
       0.0
    1    2
    2    0      2.00
    2    1      3.70
#
#  Test
#
   pt N Test -- GS 2s2 2p3
   N    ca
       0.0
    1    2
    2    0      2.00
    2    1      3.00
   pt N Test -- 2s1.8 2p3.2
   N    ca
       0.0
    1    2
    2    0      1.80
    2    1      3.20
   pt N Test -- 2s1.6 2p3.4
   N    ca
       0.0
    1    2
    2    0      1.60
    2    1      3.40
   pt N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)
   N    ca
       0.0
    1    2
    2    0      2.00
    2    1      3.70
```

For each configuration, the block is the same as for an all electron calculations, replacing **pt instead of ae**

And **pseudopotential tests for the same configurations and in the same order**

How to run a pseudopotential test with ATOM

```
$ ../../Utils/pt.sh N.test.inp N.tm2.vps
==> Output data in directory N.test-N.tm2



$ cd N.test-N.tm2
$ ls
AECHARGE AEWFNR2 ECONF_DIFFS PTCHARGE PTWFNR2 VPSIN pt.gplot vcharge.gps
AEWFNR0 AE_ECONF INP PTWFNR0 PT_ECONF charge.gplot pt.gps vspin.gplot
AEWFNR1 CHARGE OUT PTWFNR1 RHO charge.gps vcharge.gplot vspin.gps
```

Run the script

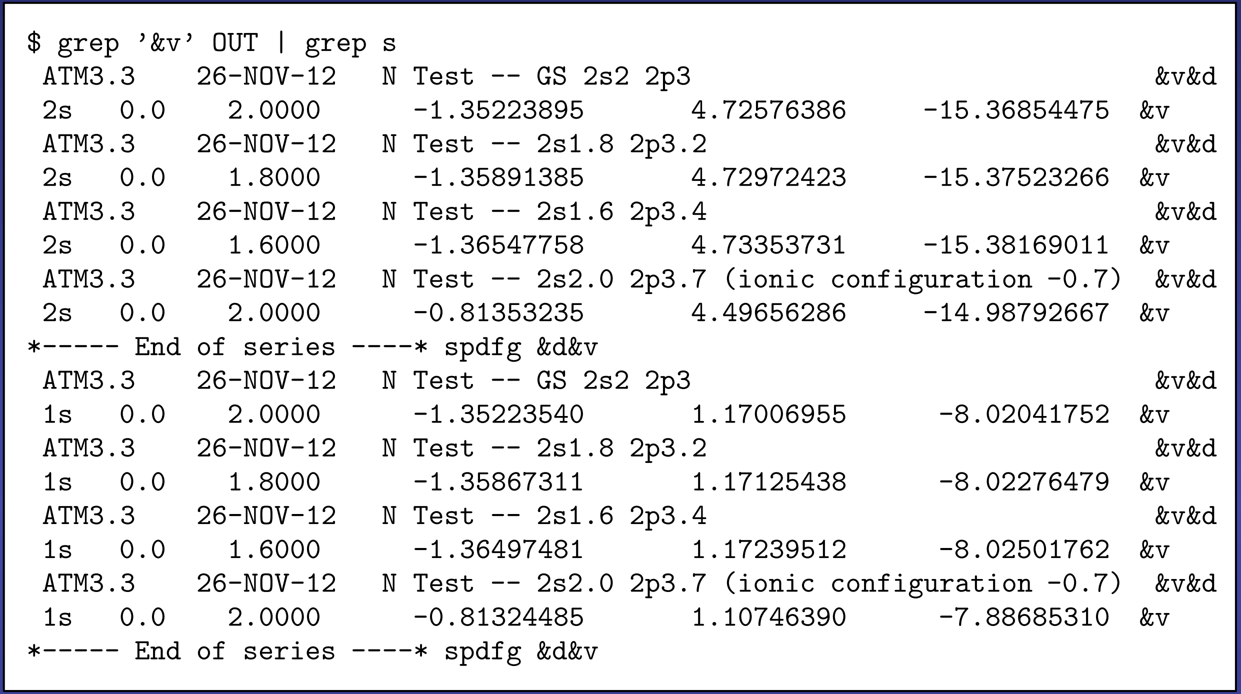
First, the name of the input
Second, the name of the pseudopotential in .vps (unformatted) format

Different output files in a new directory

The name of the directory is the concatenation of the name of the input file and the name of the pseudopotential file, both without the .inp and the .vps extensions

An explanation of the different files can be found in the ATOM User's Guide (page 6)

How to compare the AE and PS eigenvalues for different configurations



```
$ grep ’&v’ OUT | grep s
 ATM3.3    26-NOV-12   N Test -- GS 2s2 2p3                               &v&d
 2s    0.0    2.0000      -1.35223895       4.72576386     -15.36854475  &v
 ATM3.3    26-NOV-12   N Test -- 2s1.8 2p3.2                              &v&d
 2s    0.0    1.8000      -1.35891385       4.72972423     -15.37523266  &v
 ATM3.3    26-NOV-12   N Test -- 2s1.6 2p3.4                              &v&d
 2s    0.0    1.6000      -1.36547758       4.73353731     -15.38169011  &v
 ATM3.3    26-NOV-12   N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)  &v&d
 2s    0.0    2.0000      -0.81353235       4.49656286     -14.98792667  &v
*----- End of series ----* spdfg &d&v
 ATM3.3    26-NOV-12   N Test -- GS 2s2 2p3                               &v&d
 1s    0.0    2.0000      -1.35223540       1.17006955      -8.02041752  &v
 ATM3.3    26-NOV-12   N Test -- 2s1.8 2p3.2                              &v&d
 1s    0.0    1.8000      -1.35867311       1.17125438      -8.02276479  &v
 ATM3.3    26-NOV-12   N Test -- 2s1.6 2p3.4                              &v&d
 1s    0.0    1.6000      -1.36497481       1.17239512      -8.02501762  &v
 ATM3.3    26-NOV-12   N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)  &v&d
 1s    0.0    2.0000      -0.81324485       1.10746390      -7.88685310  &v
*----- End of series ----* spdfg &d&v
```

Repeat for the p, d, anf f shells

Units in Ry

The typical difference should be of around 1 mRyd for a ``good'' pseudopotential

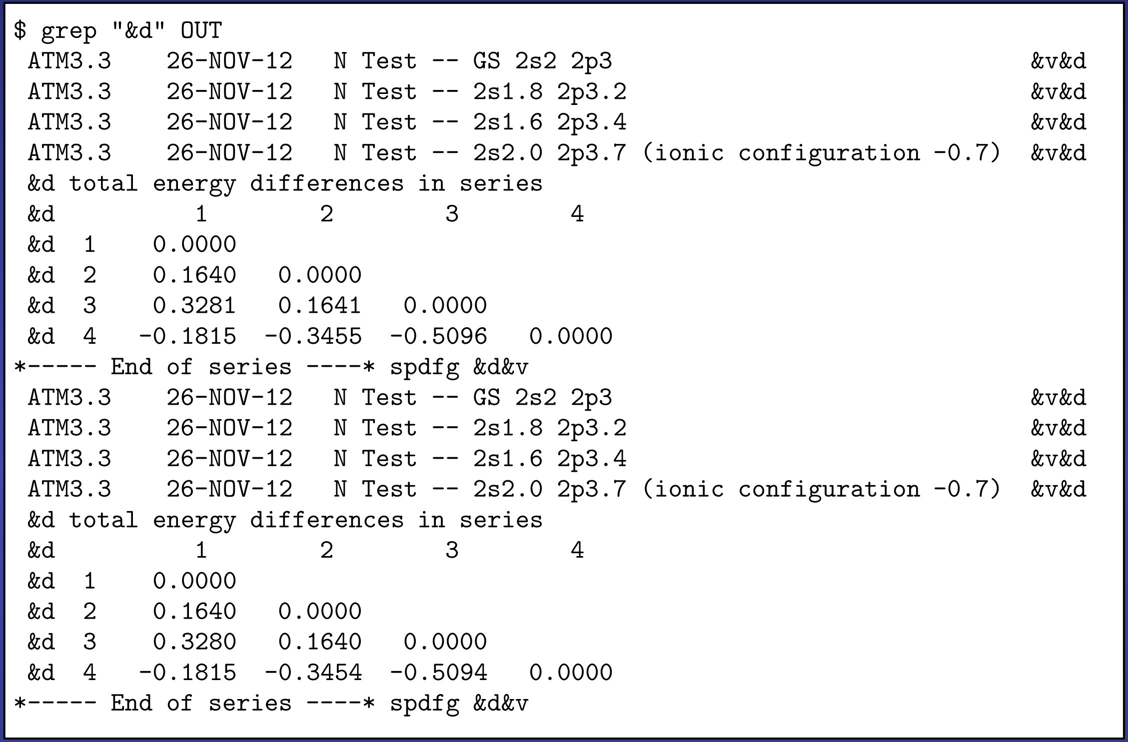
The real proof of good transferability, remember, can only come from a molecular or solid-state calculation

Note that the PT levels are labeled starting from principal quantum number 1

How to compare the differences in total energies between different configurations

All electron

Pseudoatom



```
$ grep "&d" OUT
 ATM3.3    26-NOV-12   N Test -- GS 2s2 2p3                                  &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.8 2p3.2                                 &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.6 2p3.4                                 &v&d
 ATM3.3    26-NOV-12   N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)      &v&d
 &d total energy differences in series
 &d           1        2        3        4
 &d  1     0.0000
 &d  2     0.1640   0.0000
 &d  3     0.3281   0.1641   0.0000
 &d  4    -0.1815  -0.3455  -0.5096   0.0000
*----- End of series ----* spdfg &d&v
 ATM3.3    26-NOV-12   N Test -- GS 2s2 2p3                                  &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.8 2p3.2                                 &v&d
 ATM3.3    26-NOV-12   N Test -- 2s1.6 2p3.4                                 &v&d
 ATM3.3    26-NOV-12   N Test -- 2s2.0 2p3.7 (ionic configuration -0.7)      &v&d
 &d total energy differences in series
 &d           1        2        3        4
 &d  1     0.0000
 &d  2     0.1640   0.0000
 &d  3     0.3280   0.1640   0.0000
 &d  4    -0.1815  -0.3454  -0.5094   0.0000
*----- End of series ----* spdfg &d&v
```

Cross excitations between different configurations

The typical difference should be of around 1 mRyd for a “good” 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

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

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

$n(r)$ ≡ 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

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 code s and p electrons

the unscreening procedure as explained before is not fully justified.

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

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 non-linear core corrections (NLCC)

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

Step 1: Replace the previous unscreening expression by

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

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)

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

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

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

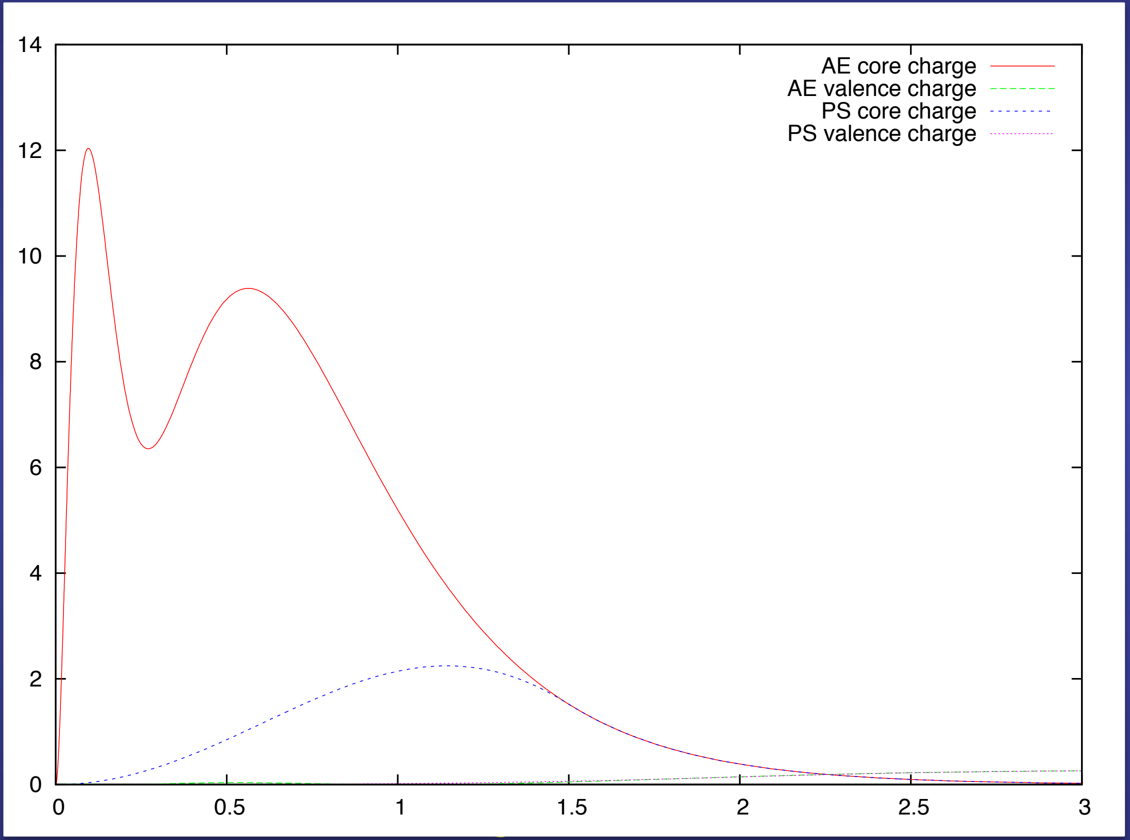
$$n^{\text{core}}_{\text{partial}}(r) = \begin{cases} r^2 e^{(a+br^2+cr^4)}, & r < r_{\text{pc}} \\ n^{\text{core}}(r), & r > r_{\text{pc}} \end{cases}$$

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

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

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

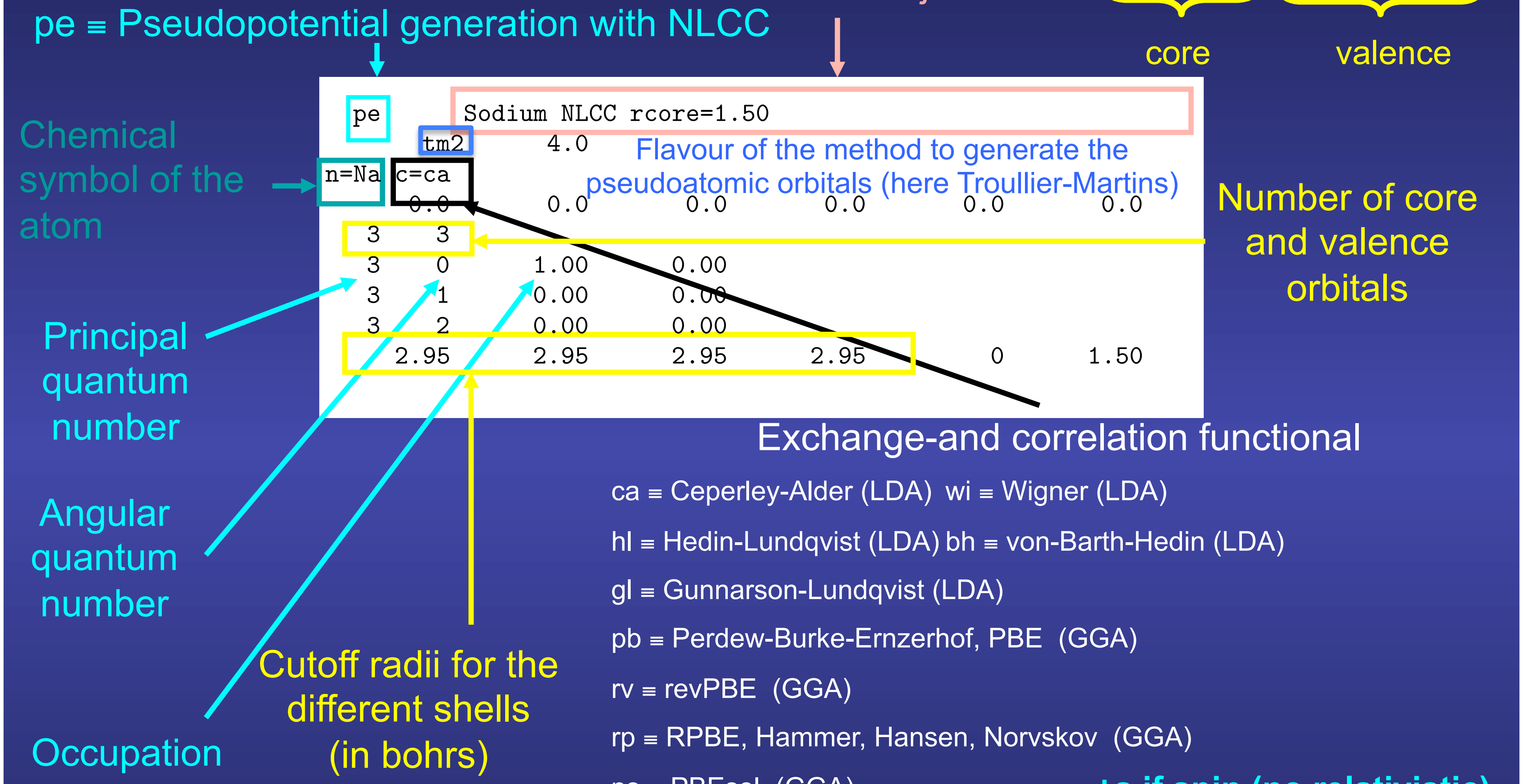
How to generate a pseudopotential with non-linear core corrections



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

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

$$\mathrm{Na}\ \underbrace{1s^2\,2s^2\,2p^6}_{\text{core}}\ \underbrace{3s^1\,3p^0\,3d^0\,4f^0}_{\text{valence}}$$



```
   pe      Sodium NLCC rcore=1.50
        tm2     4.0
n=Na c=ca
     0.0       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
```

pe ≡ Pseudopotential generation with NLCC

A title for the job

Chemical symbol of the atom

Flavour of the method to generate the pseudoatomic orbitals (here Troullier-Martins)

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)

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)

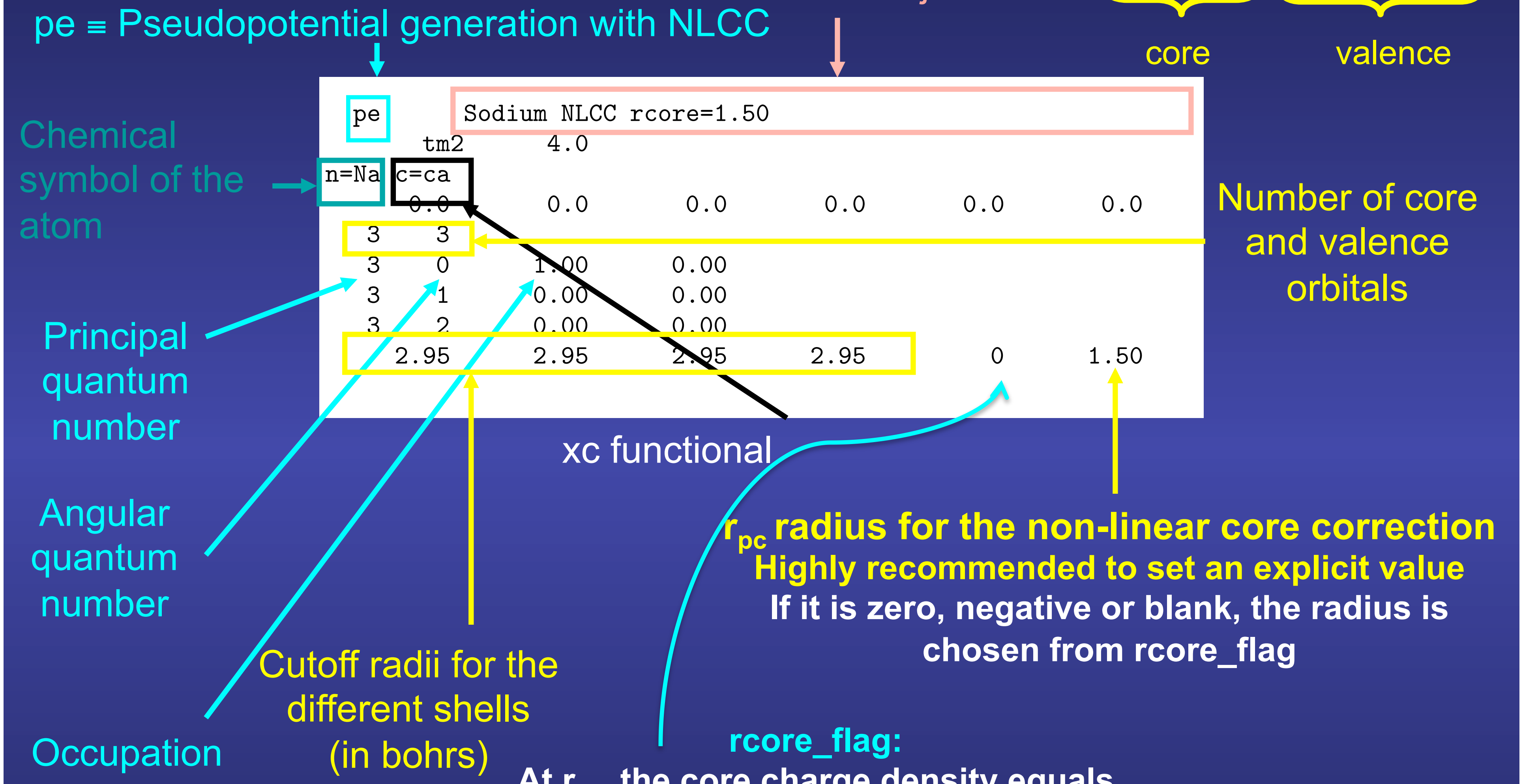
am≡ AM05 by Armiento and Mattson (GGA)

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

$$\text{Na}\ \underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\ \underbrace{3s^1\ 3p^0\ 3d^0\ 4f^0}_{\text{valence}}$$



```
 pe      Sodium NLCC rcore=1.50
        tm2      4.0
n=Na c=ca
        0.0      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
```

A title for the job

pe ≡ Pseudopotential generation with NLCC

Chemical symbol of the atom

Number of core and valence orbitals

Principal quantum number

Angular quantum number

Occupation

(spin up)

(spin down)

xc functional

Cutoff radii for the different shells (in bohrs)

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-lineal 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

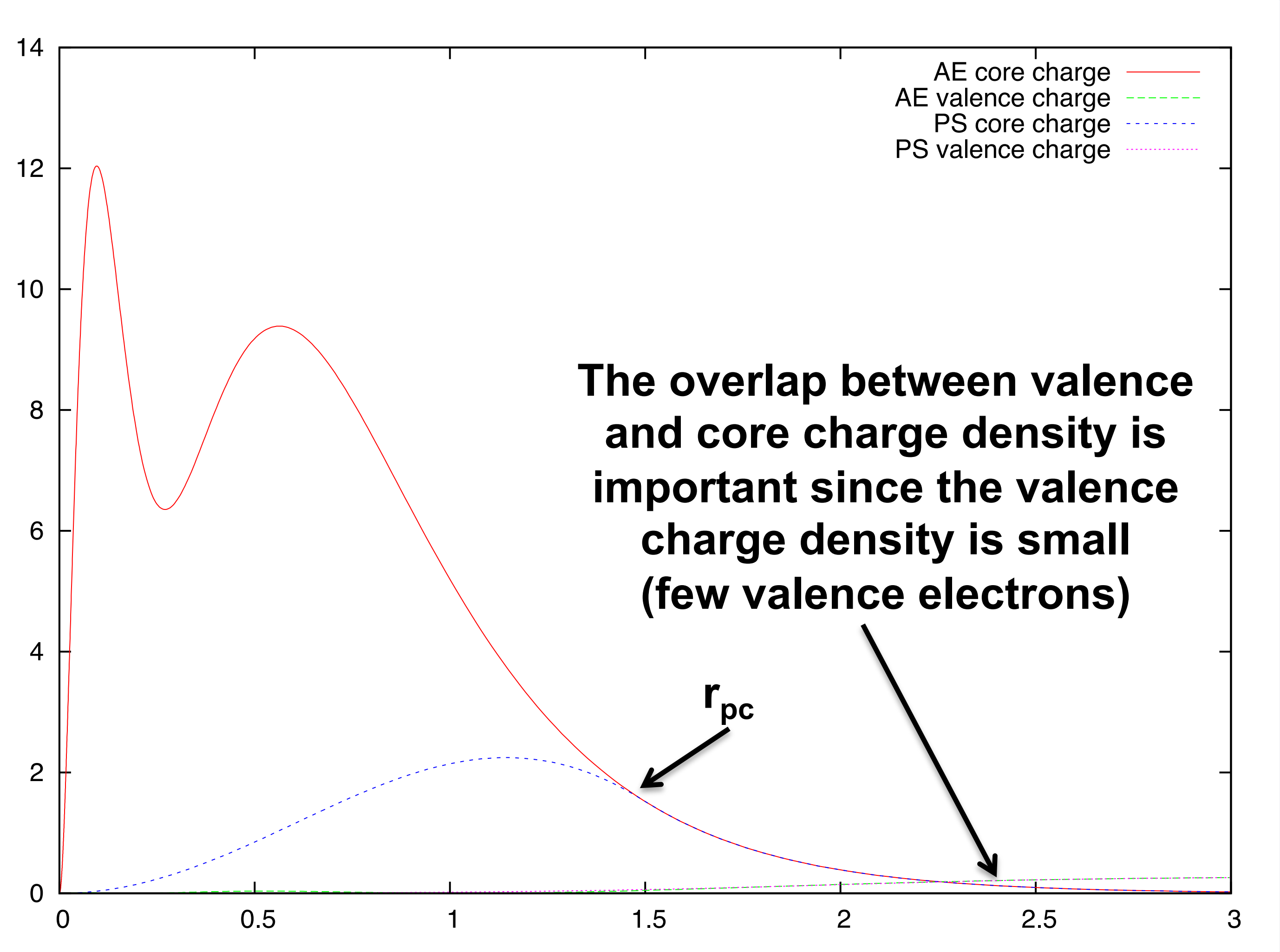
```
$ cd Na.cc
```

```
$ gnuplot –persist charge.gplot
```

(To generate a figure on the screen using gnuplot)

```
$ gnuplot charge.gps
```

(To generate a postscript file with the figure)

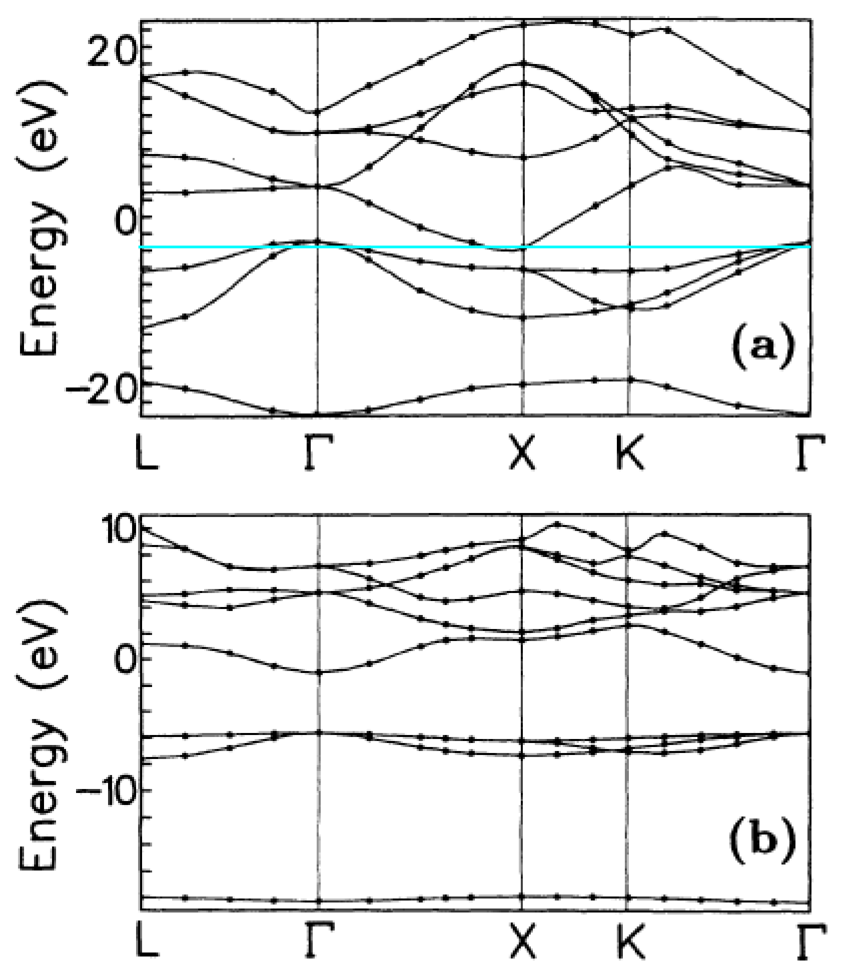


r_{pc}

The overlap between valence and core charge density is important since the valence charge density is small (few valence electrons)

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

Bulk NaCl (rocksalt structure)



J. Hebenstreit and M. Scheffler,
Phys. Rev. B 46, 10134 (1992)

Without core corrections for Na:

Semi metal

With core corrections for Na:

Insulator

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

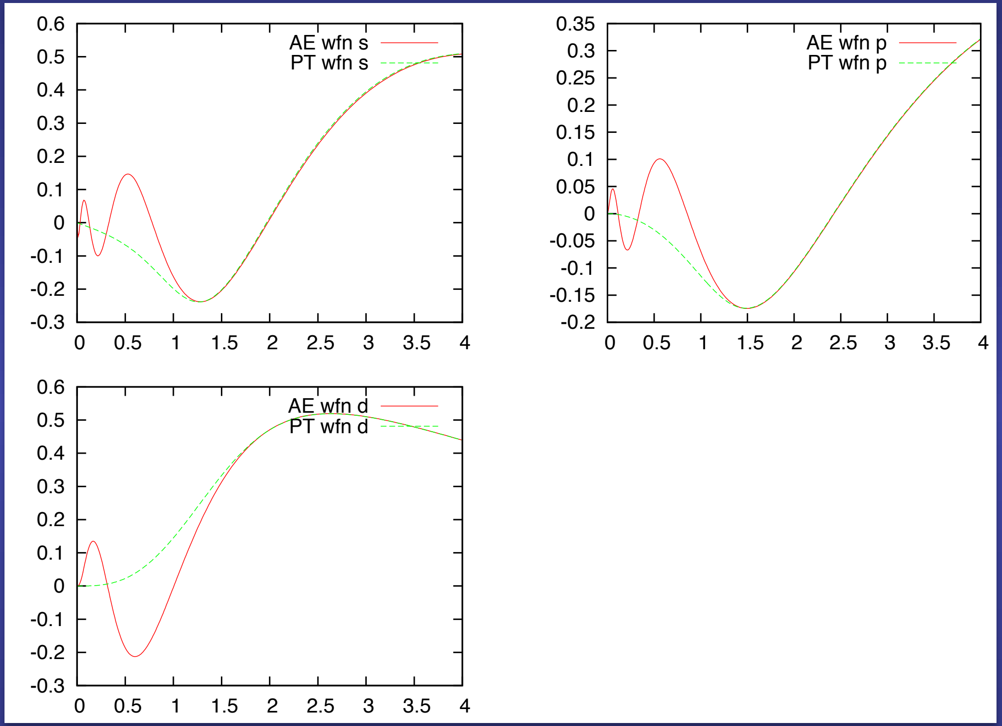
Solution 2: Include explicitly the extended core orbitals in the valence (semicore in valence)

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

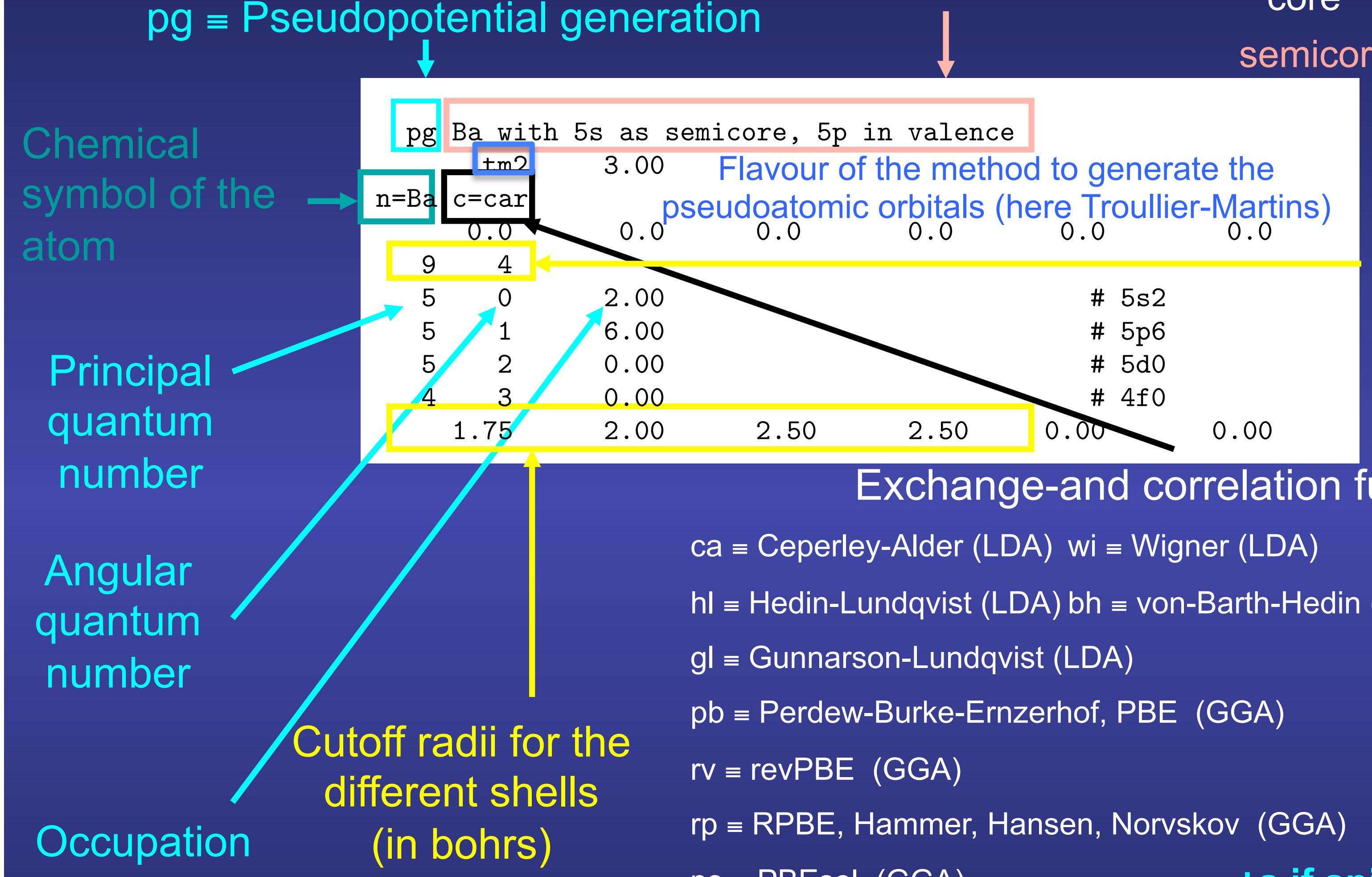
How to generate a pseudopotential with the semicore in the valence



Objectives

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

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

A title for the job

pg ≡ Pseudopotential generation

Chemical symbol of the atom

```
  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
```

Flavour of the method to generate the pseudoatomic orbitals (here Troullier-Martins)

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)

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

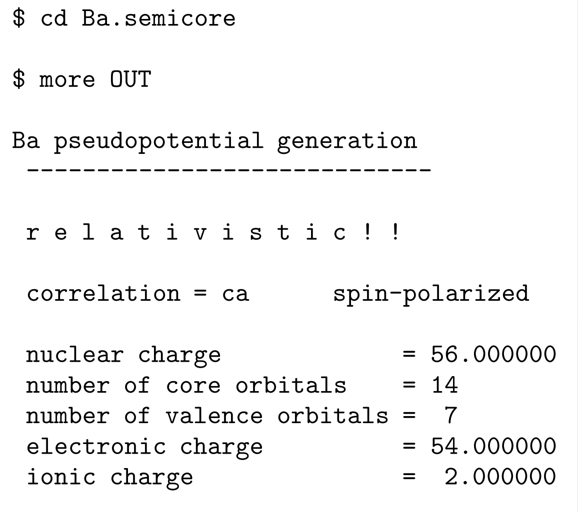
Generate and test a pseudopotential for Ba with the semicore explicitly included in the valence

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.
5*s* and 5*p* orbitals overlap strongly with 4*d* 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

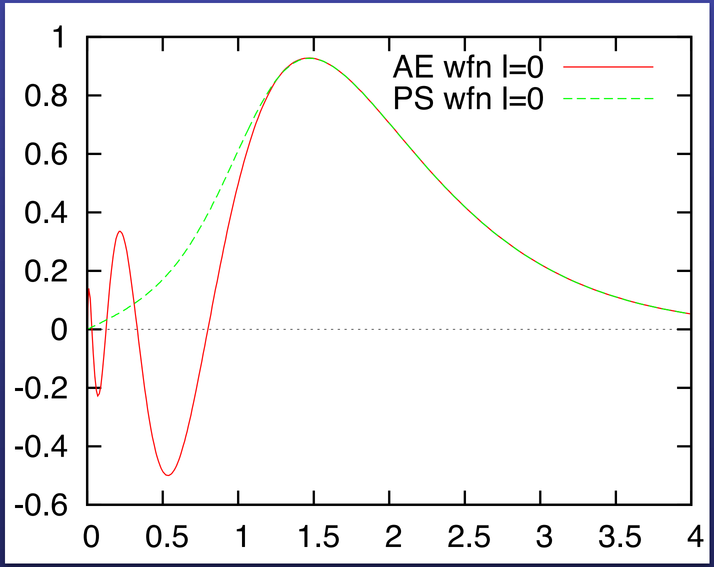
This can be seen plotting the semicore orbitals

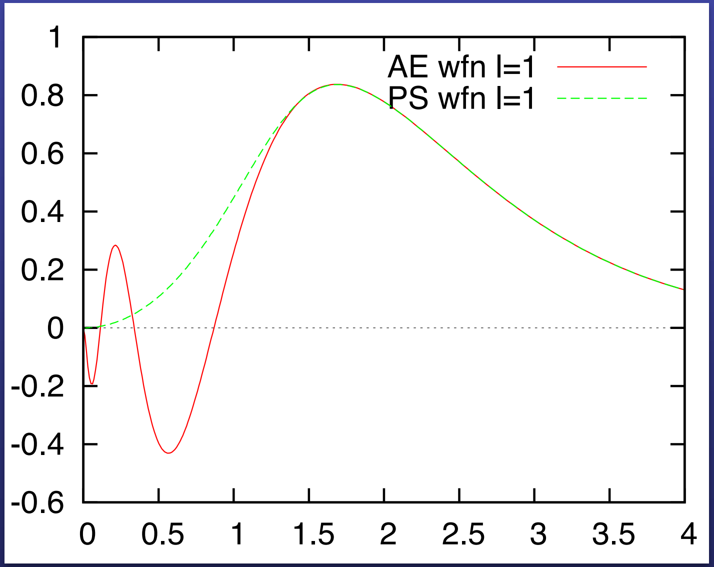
```
$ gnuplot –persist pseudo.gplot
```

(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

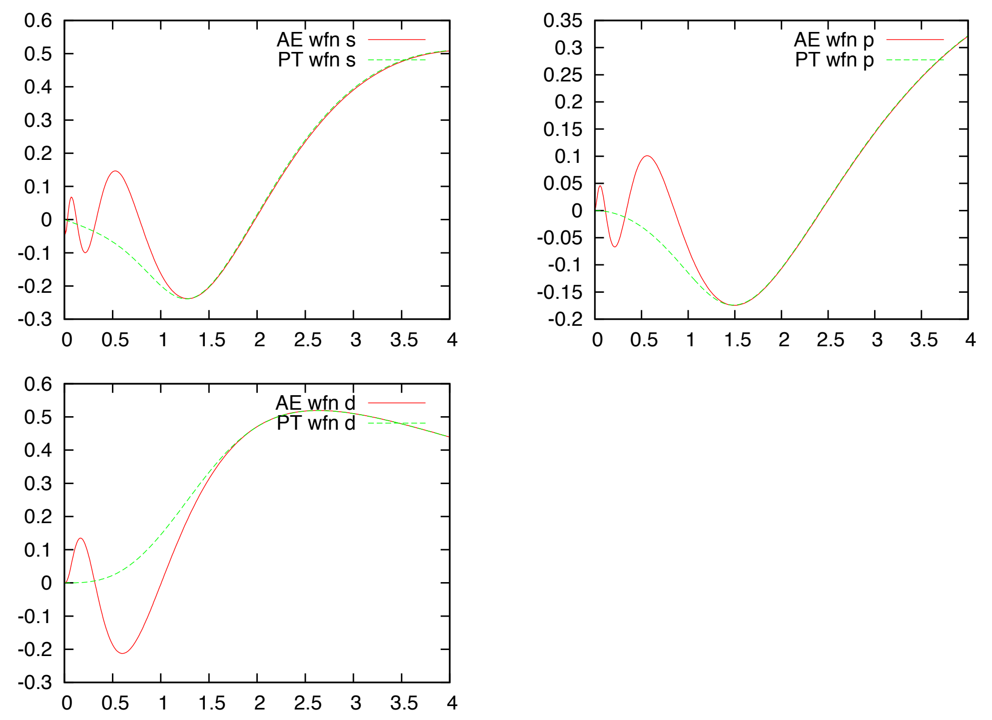
Not only the differences in energies are well reproduced, but also the shape of the orbitals:

```
$ 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 6s and 6p states have a node, as they must be orthogonal to the 5s and 5p states, respectively.

Conclusions

- Core electrons…

  highly localized and very depth energy

… are chemically inert

- Pseudopotential idea

  Ignore the dynamics of the core electrons (freeze them)

  And replace their effects by an effective potential

- Pseudopotentials are not unique

  there might be many “best choices”

- Two overall competing factors: transferability vs hardness

- Norm conservation helps transferability

- **Always test the pseudopotential in well-known situations**

Supplementary material for Kleinman-Bylander projectors

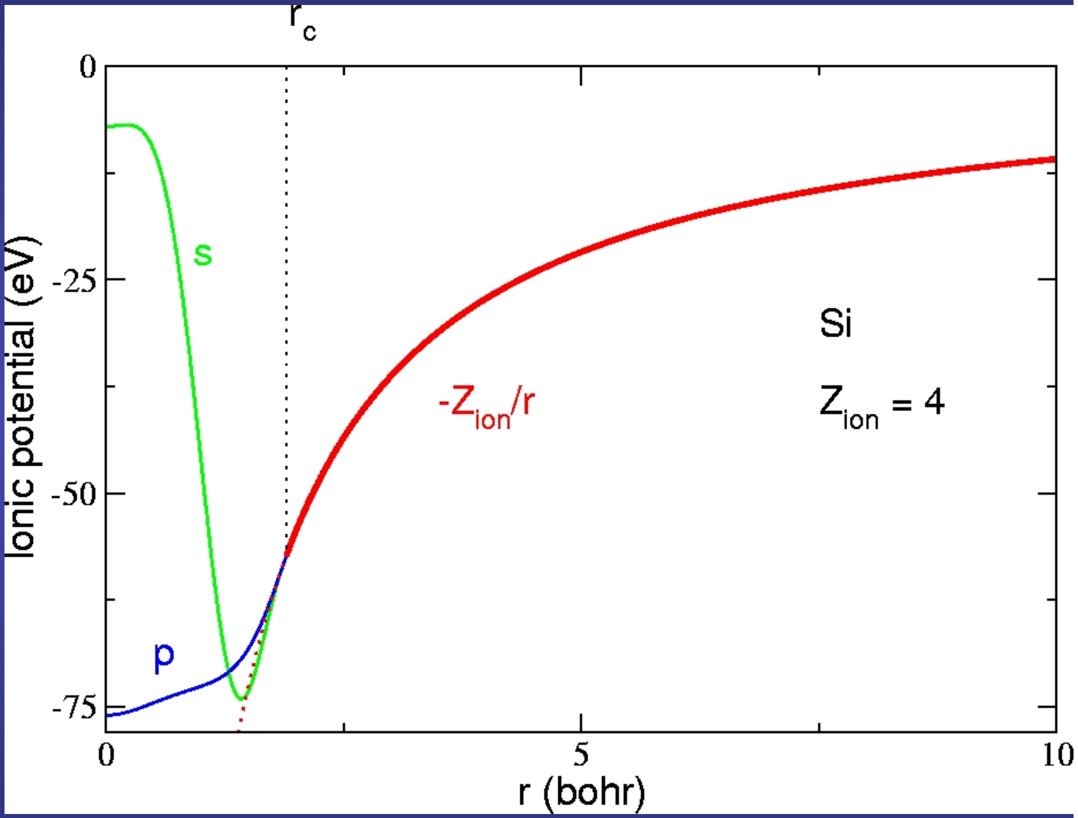
The screened potential depends on the angular momentum of the valence electron: is l-dependent

Reason for the l-dependency: different orthogonality conditions

For instance, in the Si atom

The $3s$ valence state has to be orthogonal with the $2s$ and $1s$ core states

The $3p$ valence state does not feel the orthogonality constraint with the $2s$ and $1s$ core states, because they have different angular momentum quantum numbers



Within the core region, these potentials feel different potentials from the ionic core.

At large distances (beyond R_c) the potential is $-Z_{ion}/r$, independently of l, because the ionic core is seen as a point charge of magnitude equal to the valence charge Z_{ion}

General form of a *l*-dependent pseudopotential

$$\hat{V}^{\mathrm{PS}}(\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} V_l^{\mathrm{PS}}(r) |Y_{lm}\rangle\langle Y_{lm}| = \sum_{l=0}^{\infty} V_l^{\mathrm{PS}}(r) \hat{P}_l$$

Where $\hat{P}_l$ is a projector operator onto the *l*-th angular momentum subspace

$$\hat{P}_l = \sum_{m=-l}^{l} |Y_{lm}\rangle\langle Y_{lm}|$$

Meaning of the previous expression:

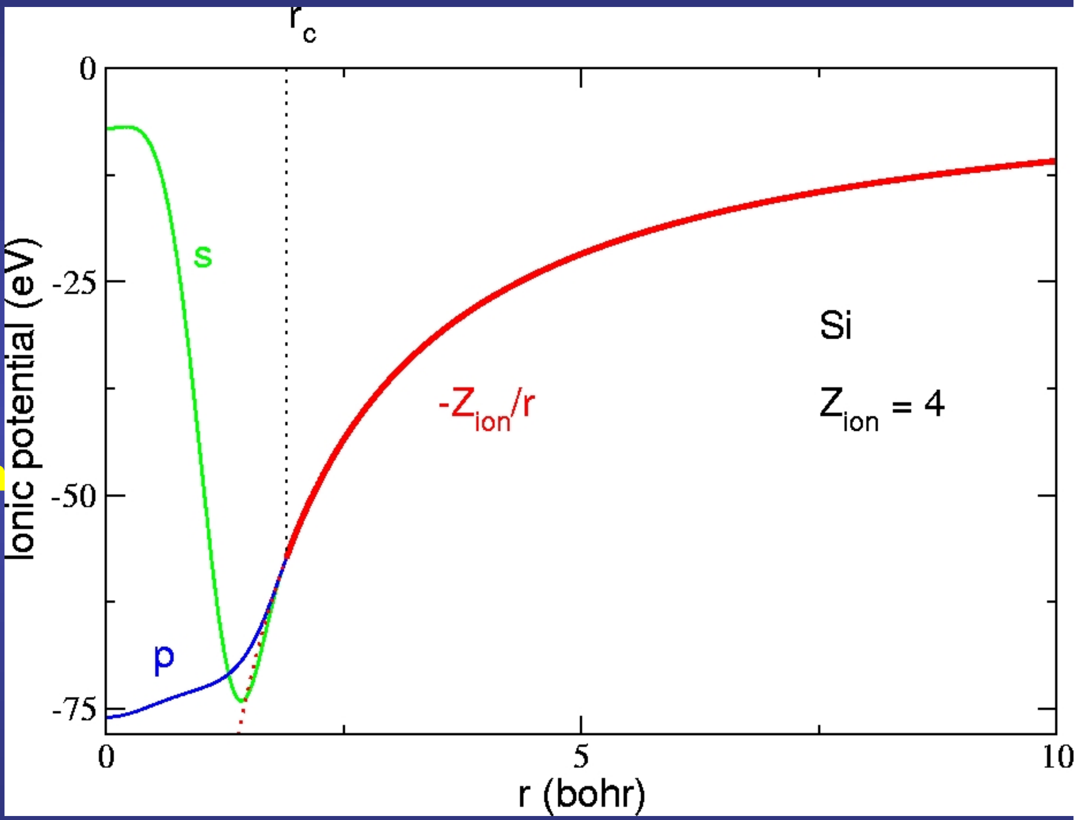
When the pseudopotential operator $\hat{V}^{\mathrm{PS}}$ acts on an electronic wave function, the projector operator $\hat{P}_l$ selects the different angular momentum components of the wave function, which are then multiplied by the corresponding pseudopotential.

The contributions of all the angular momentums are finally added up to form the total pseudopotential contribution to the Hamiltonian matrix elements that enter Schrödinger equation.

It is useful to separate the ionic pseudopotentials into a local (l-independent) part and non-local terms

$$V_l^{\mathrm{PS}}(r) = V_{\mathrm{local}}(r) + \delta V_l(r)$$

The local part of the pseudo $V_{\mathrm{local}}(r)$ is in principle arbitrary, but it must join the semilocal potentials $V_l(r)$, which by construccion, all become equal to the (unscreened) all electron potential beyond the pseupotential core radius R_c



Thus, the non-local part is short range

$$\delta V_l(r) = 0, \quad \text{for} \quad r > R_c$$

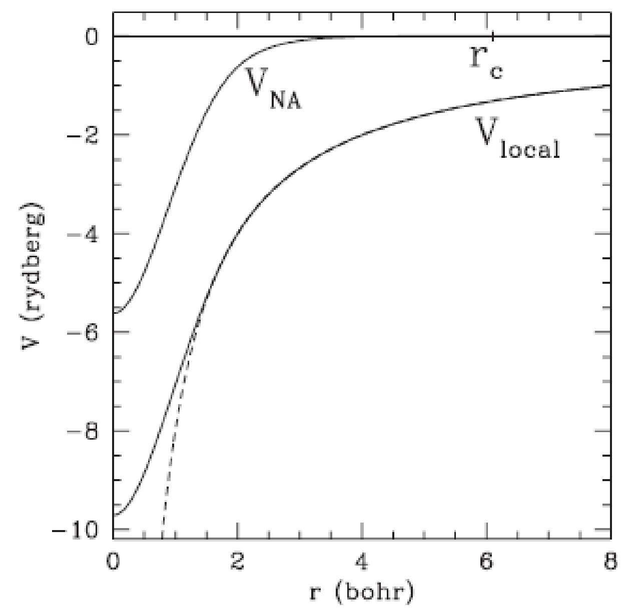
All the long-range effects of the Coulomb potential are included in the local part of the pseudopotential

It is useful to separate the ionic pseudopotentials into a local (*l*-independent) part and non-local terms

In Siesta, the local pseudopotential is optimized for smoothness, because it is represented in the real space grid

It is defined as the potential generated by a positive charge distribution of the form

$$n_{\rm local}(r) \propto e^{-\left(\frac{\sinh(abr)}{\sin b}\right)^2}$$



a and b are chosen to provide simultaneously optimal real-space localization and reciprocal-space convergence

$$b = 1 \qquad a = \frac{1.82}{R_c}$$

J. M. Soler *et al*., J. Phys.: Condens. Matter 14, 2745 (2002)

The pseudopotential operator in the semilocal form: local in radial variable, non-local in the angular variable

$$V_{\mathrm{SL}}^{\mathrm{PS}}(r) = V_{\mathrm{local}}(r) + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} |Y_{lm}\rangle \delta V_l(r) \langle Y_{lm}|$$

Matrix elements of the pseudopotential in some basis $|\phi_\alpha\rangle$ assume the form

$$V_{\mathrm{SL},\alpha\beta}^{\mathrm{PS}} = \langle \phi_\alpha | V_{\mathrm{SL}}^{\mathrm{PS}} | \phi_\beta \rangle = \langle \phi_\alpha | V_{\mathrm{local}}(r) | \phi_\beta \rangle + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \int r^2 dr \langle \phi_\alpha | Y_{lm} \rangle \delta V_l(r) \langle Y_{lm} | \phi_\beta \rangle$$

The most common basis functions:

- floating (plane waves) $e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l,m} i^l j_l(kr) Y_{lm}(\hat{k}) Y_{lm}^*(\hat{r})$

- atom-centered (product of radial function and spherical harmonics) $\phi_\alpha(\vec{r}) = \phi_\alpha(r) Y_{lm}(\theta, \phi)$

In either case, the above integral factorizes into two angular-dependent parts that can be integrated separately, and a radial integral of the form

$$G_{\alpha\beta} = \int r^2 \varphi_\alpha^*(r) \delta V_l(r) \varphi_\beta(r) dr$$

Local integral in the radial variable

Radial part of the basis function (for AO) or the spherical Bessel functions (for PW)

Replacing the semi-local operator by a fully non-local form separable in the radial variables

In the semilocal form, the matrix elements of the pseudopotential takes the form

$$\delta V_l^{\mathrm{PS}}(\alpha,\beta) = \langle \phi_\alpha | \delta V_l^{\mathrm{PS}}(r) \hat{P}_l | \phi_\beta \rangle$$

$$= \sum_{m=-l}^{l} \int \int \phi_\alpha^*(\vec{r}) Y_{lm}(\vec{r}) \delta V_l^{\mathrm{PS}}(r) Y_{lm}^*(\vec{r}^{\,\prime}) \phi_\beta(\vec{r}^{\,\prime}) d\vec{r} d\vec{r}^{\,\prime}$$

Where due to the semilocal character of the pseudopotential,
a factor $\delta(r - r^{\prime})$ is understood

Replacing the semi-local operator with a fully non-local form separable
in the radial variables, allows a factorization of the problem

$$\delta V_l(r) \longrightarrow \delta V_l^{\mathrm{sep}}(r, r^{\prime}) = \zeta_l(r) \zeta_l^*(r^{\prime})$$

$$\delta V_l^{\mathrm{sep}}(\alpha,\beta) = \sum_{m=-l}^{l} F_{\alpha l m}^* F_{\beta l m} \quad \textbf{with} \quad F_{\alpha l m} = \int \zeta_l^*(r) Y_{lm}(\vec{r}) \phi_\alpha(\vec{r}) d\vec{r}$$

Now, the non-local part can be cheaply and accurately computed as two-center intergrals

General expression for a separable non-local potential of the Kleinman-Bylander form

$$\delta V_l^{\text{sep}}(\alpha,\beta) = \sum_{m=-l}^{l} F^*_{\alpha l m} F_{\beta l m}$$ **with** $$F_{\alpha l m} = \int \zeta_l^*(r) Y_{lm}(\vec{r}) \phi_\alpha(\vec{r}) d\vec{r}$$

$$\delta \hat{V}_l^{\text{sep}} = \sum_{m=-l}^{l} \frac{|\zeta_{lm}\rangle\langle\zeta_{lm}|}{\langle\zeta_{lm}|\ \psi_{lm}^{\text{PS}}\rangle}$$

where $\psi_{lm}^{\text{PS}}(\vec{r})$ are the atomic, reference pseudo-wave function

The only relevant aspect is to reproduce the all-electron calculation for the reference configuration

Kleinman-Bylander fully non-local separable form

L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)

Request: the action of the fully non-local separable pseudopotential $\delta\hat{V}_l^{\mathrm{sep}}$ on the reference pseudo-wave function is the same as that of the original semi-local form

For that, they proposed

$$|\zeta_{lm}^{\mathrm{KB}}\rangle = |\delta\hat{V}_l(r)\psi_{lm}\rangle$$

so that

$$\delta\hat{V}_l^{\mathrm{sep}}|\psi_{lm}\rangle = \left[\frac{|\delta\hat{V}_l^{\mathrm{PS}}\psi_{lm}^{\mathrm{PS}}\rangle\langle\psi_{lm}^{\mathrm{PS}}\delta\hat{V}_l^{\mathrm{PS}}|}{\langle\psi_{lm}^{\mathrm{PS}}|\delta\hat{V}_l^{\mathrm{PS}}|\psi_{lm}^{\mathrm{PS}}\rangle}\right]|\psi_{lm}^{\mathrm{PS}}\rangle = \delta\hat{V}_l^{\mathrm{PS}}|\psi_{lm}^{\mathrm{PS}}\rangle$$

Kleinman-Bylander fully non-local separable form

L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)

The Kleinman–Bylander projector is then written as

$$\delta\hat{V}_l^{\mathrm{KB}} = \sum_{m=-l}^{l} |\xi_{lm}^{\mathrm{KB}}\rangle \, E_{lm}^{\mathrm{KB}} \langle \xi_{lm}^{\mathrm{KB}}|$$

Where the normalized projection functions are given by

$$|\xi_{lm}^{\mathrm{KB}}\rangle = \frac{|\zeta_{lm}^{\mathrm{KB}}\rangle}{\langle \zeta_{lm}^{\mathrm{KB}} | \zeta_{lm}^{\mathrm{KB}}\rangle} = \frac{|\delta\hat{V}_l \psi_{lm}^{\mathrm{PS}}\rangle}{\langle \psi_{lm}^{\mathrm{PS}} \delta\hat{V}_l | \delta\hat{V}_l \psi_{lm}^{\mathrm{PS}}\rangle}$$

Kleinman-Bylander fully non-local separable form

L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)

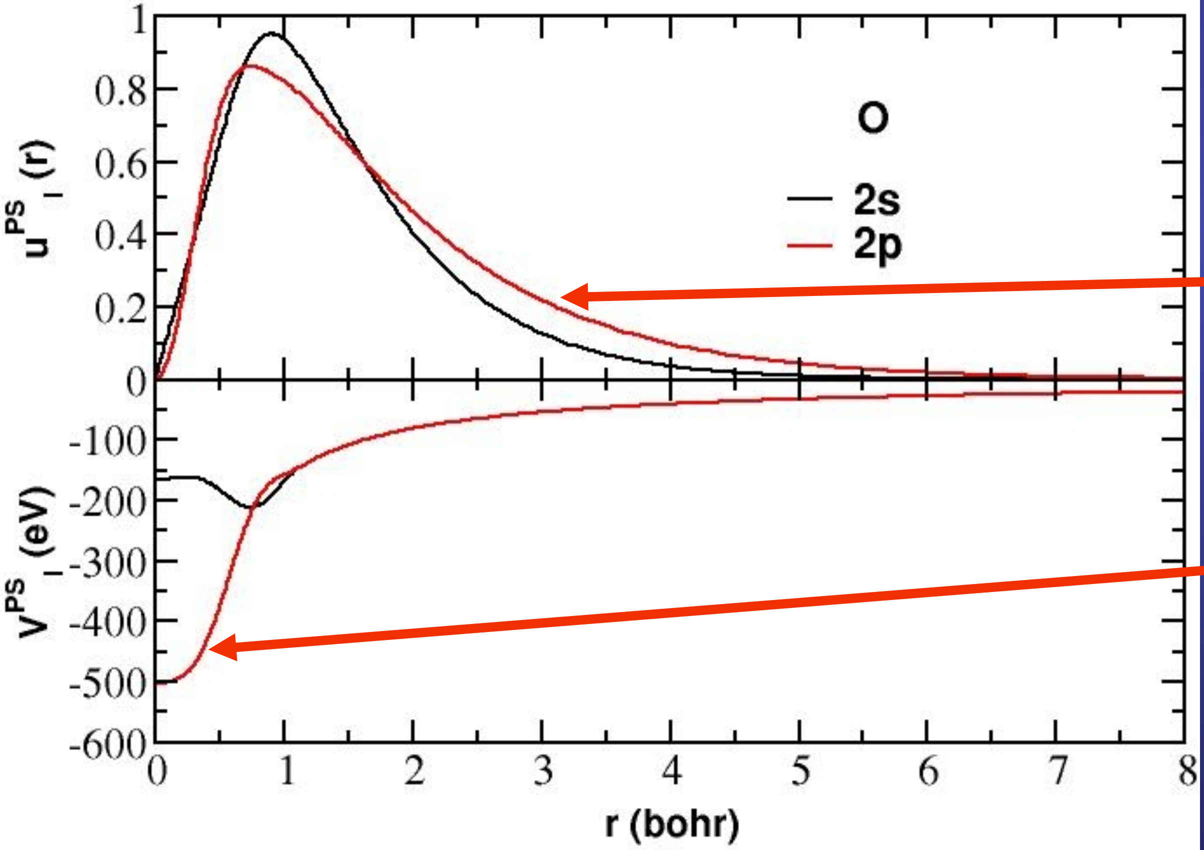
The strength of the non-locality is determined by

$$E_{lm}^{\mathrm{KB}} = \frac{\langle \psi_{lm}^{\mathrm{PS}} | (\delta \hat{V}_l^{\mathrm{PS}})^2 | \psi_{lm}^{\mathrm{PS}} \rangle}{\langle \psi_{lm}^{\mathrm{PS}} | \delta \hat{V}_l^{\mathrm{PS}} | \psi_{lm}^{\mathrm{PS}} \rangle}$$

Problematic cases: first row elements
2p and 3d elements

O: $1s^2 \underbrace{2s^2\ 2p^4}$

core valence



No nodes because there are no p states to be orthogonal to

pseudopotential is hard