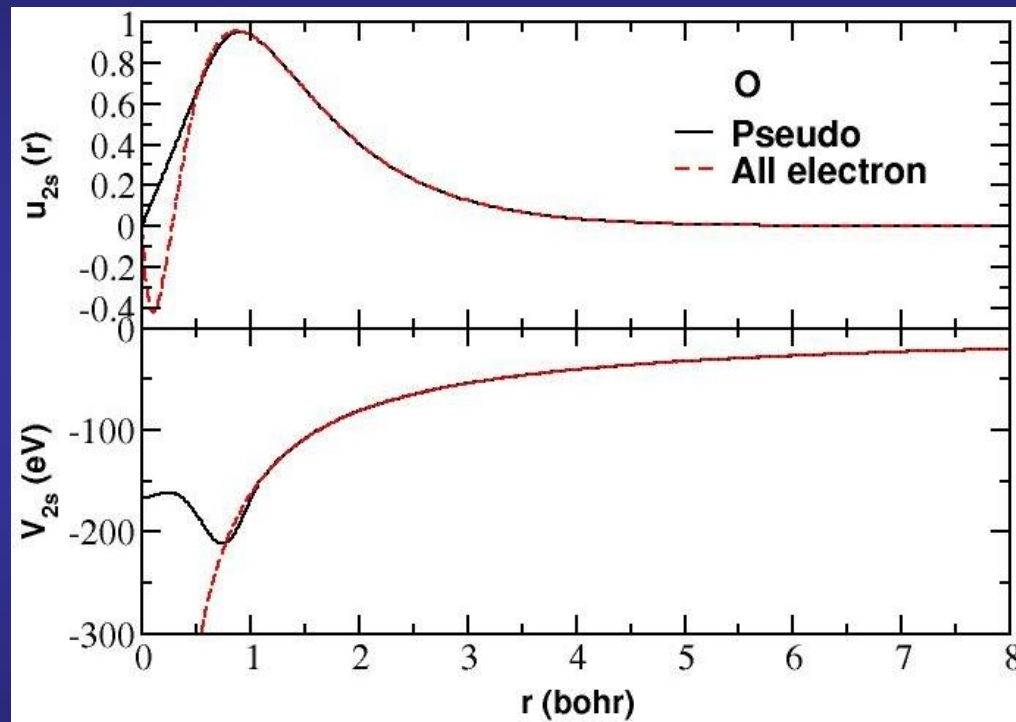# Norm-conserving pseudopotentials and basis sets in electronic structure calculations

Javier Junquera

Universidad de Cantabria

UC UNIVERSIDAD DE CANTABRIA

Outline

Pseudopotentials

Why pseudopotential approach is useful

Orthogonalized Plane Waves (1940)

Pseudopotential transformation (1959)

Norm-conserving pseudopotentials (1979)

Basis sets

Plane Waves

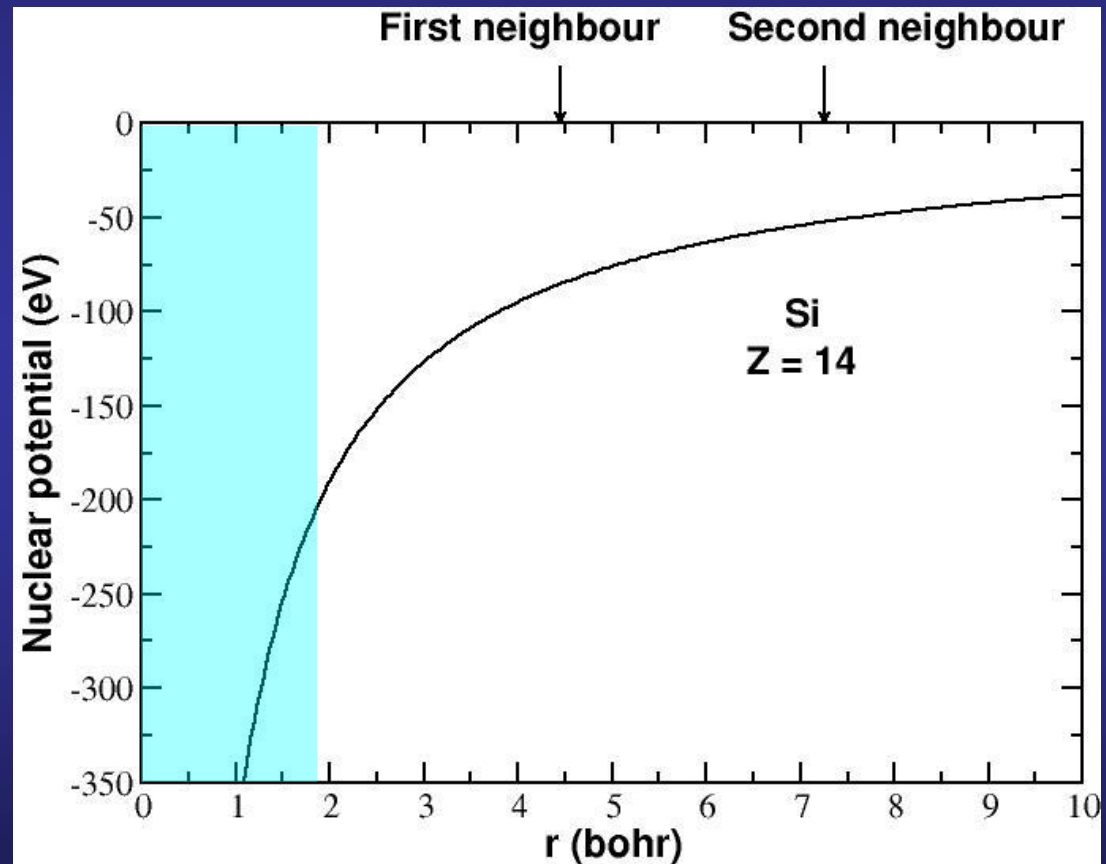Localized Orbitals

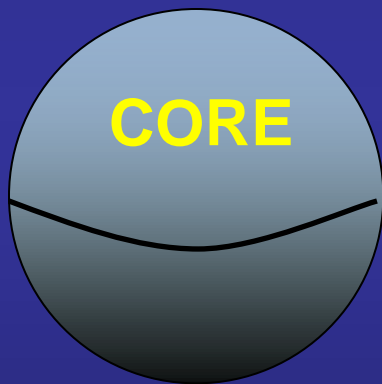Numerical Atomic Orbitals

Atomic calculation using DFT:
Solving the Schrodinger-like equation

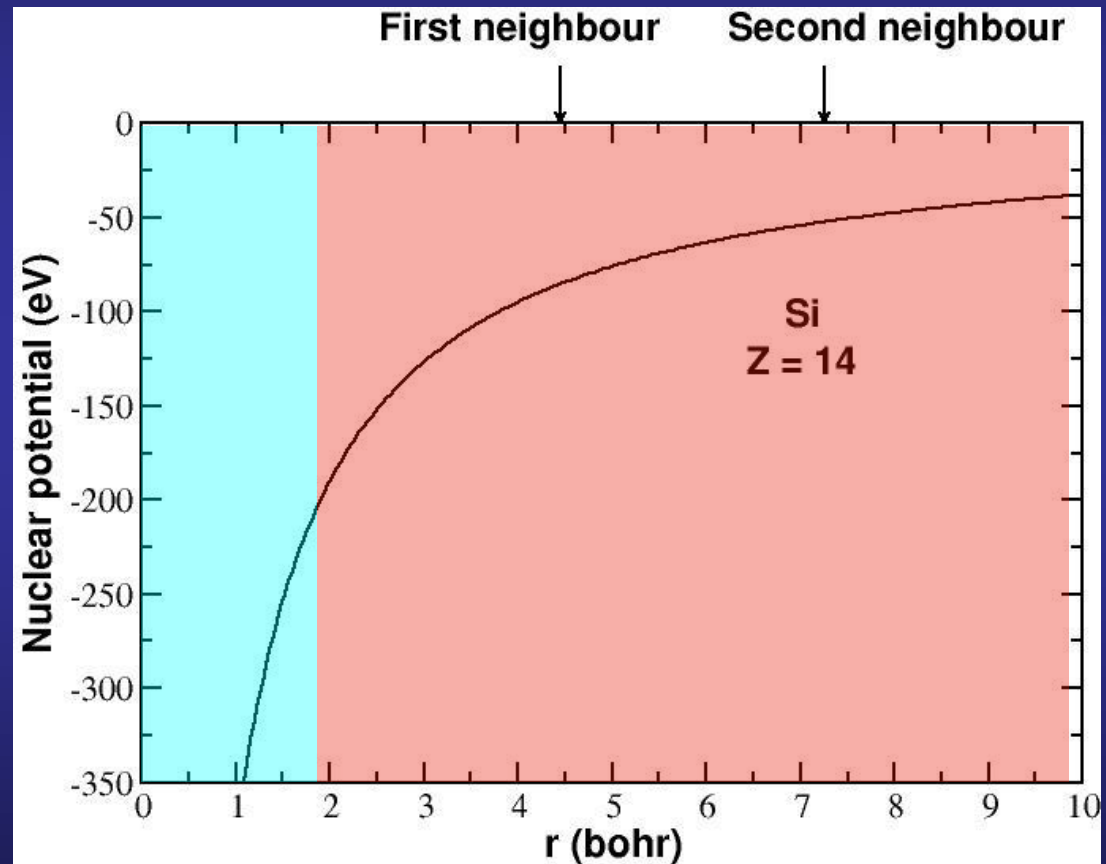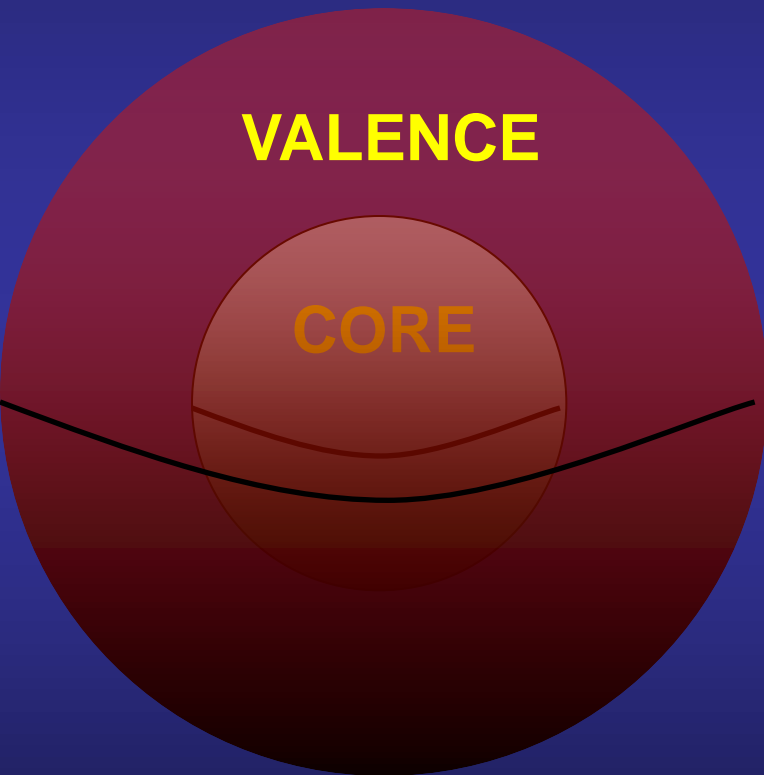**One particle Kohn-Sham equations**

$$\left(\hat{T} + \hat{V}_{ion-e} + \hat{V}_H + \hat{V}_{xc} \right) \psi_i = \varepsilon_i \psi_i$$

$$-\frac{Ze}{r}$$

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: $1s^2\ 2s^2\ 2p^6$ $\quad$ $3s^2\ 3p^2$

$$\underbrace{}_{\text{core}} \qquad \underbrace{}_{\text{valence}}$$

core $\qquad$ valence

Core eigenvalues are much deeper than valence eigenvalues
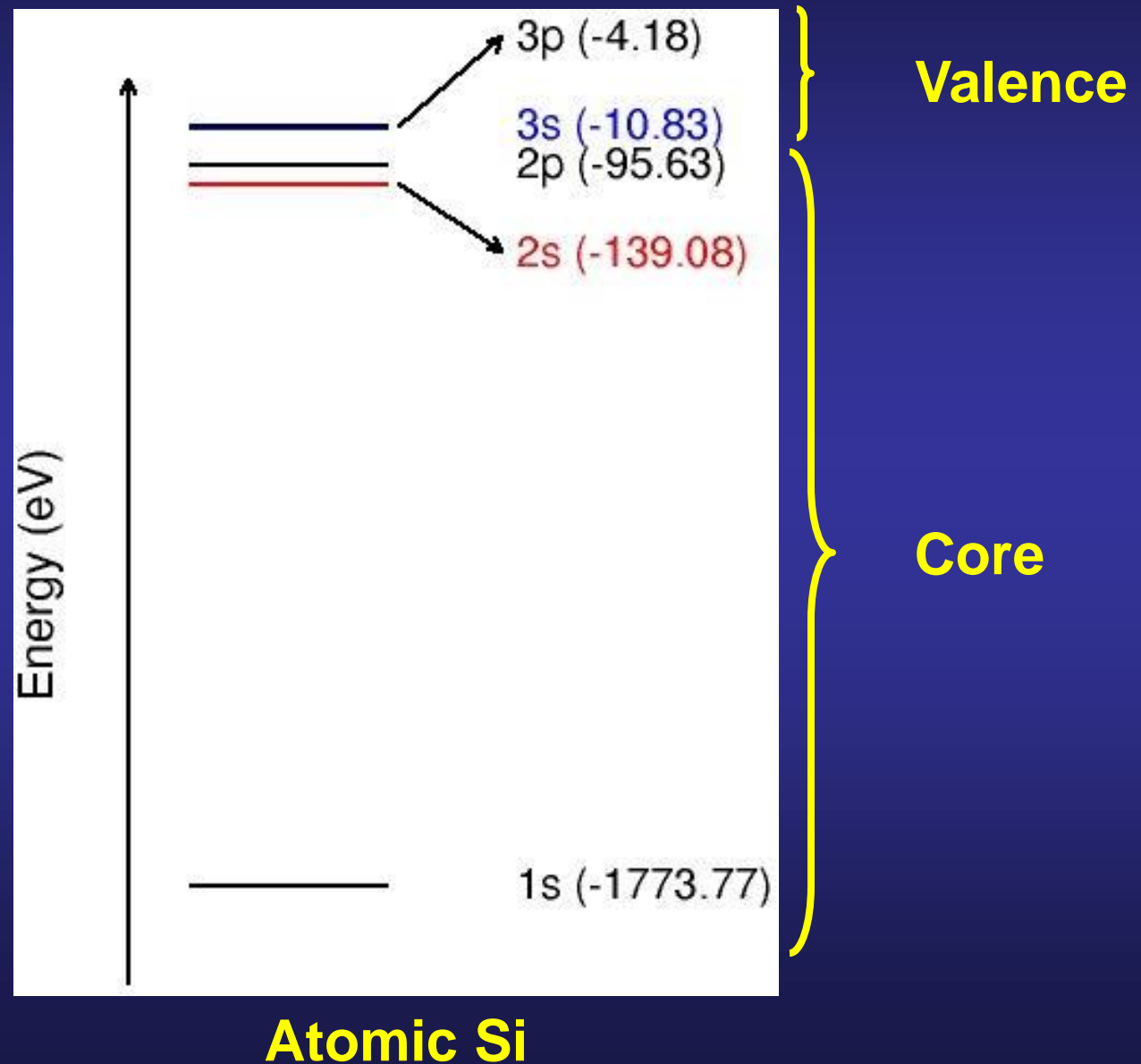
Atomic Si

Core wavefunctions are very localized around the nuclei
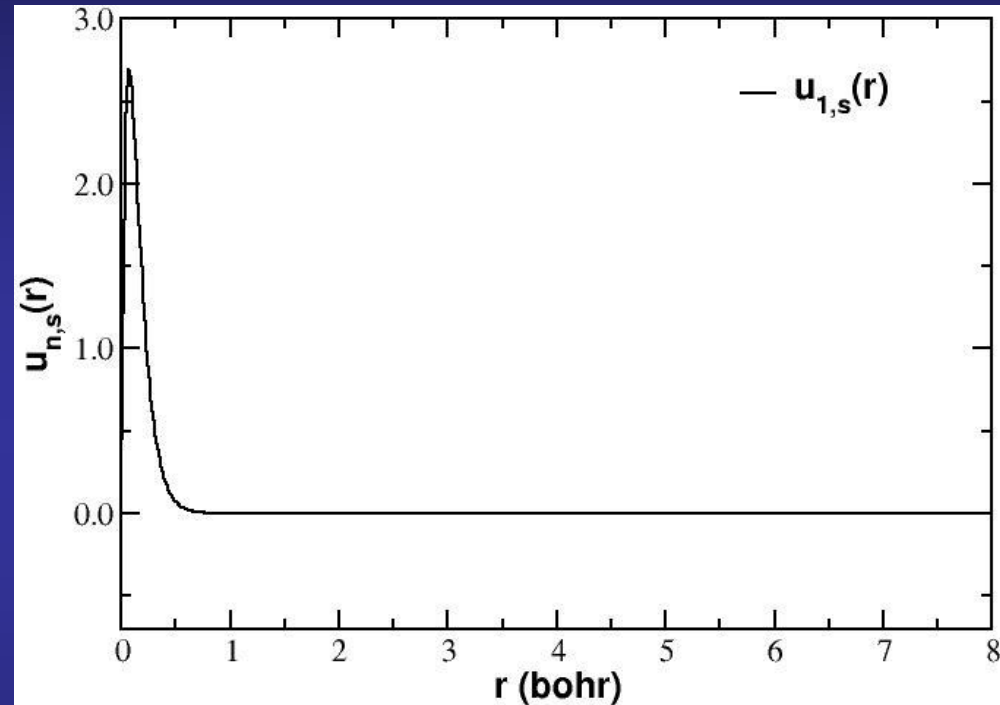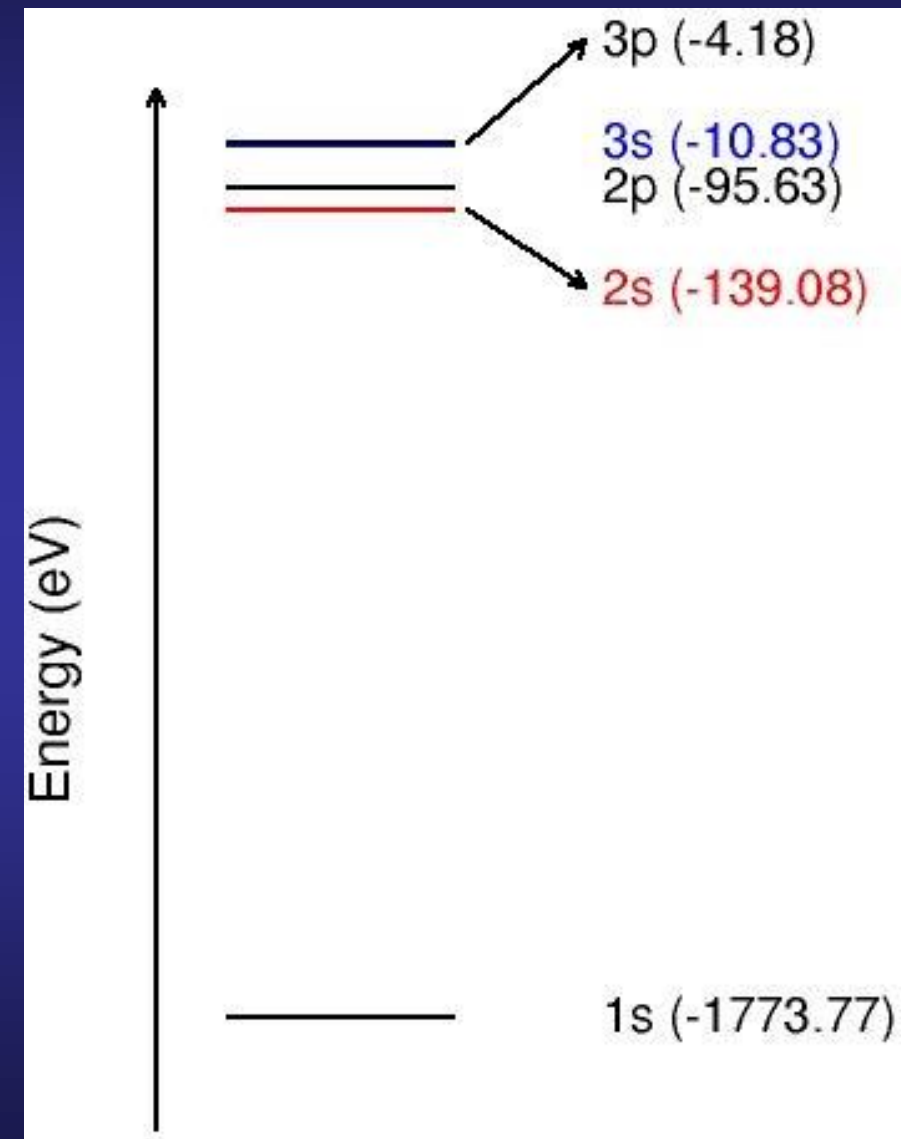
Atomic Si

Core wavefunctions are very localized around the nuclei
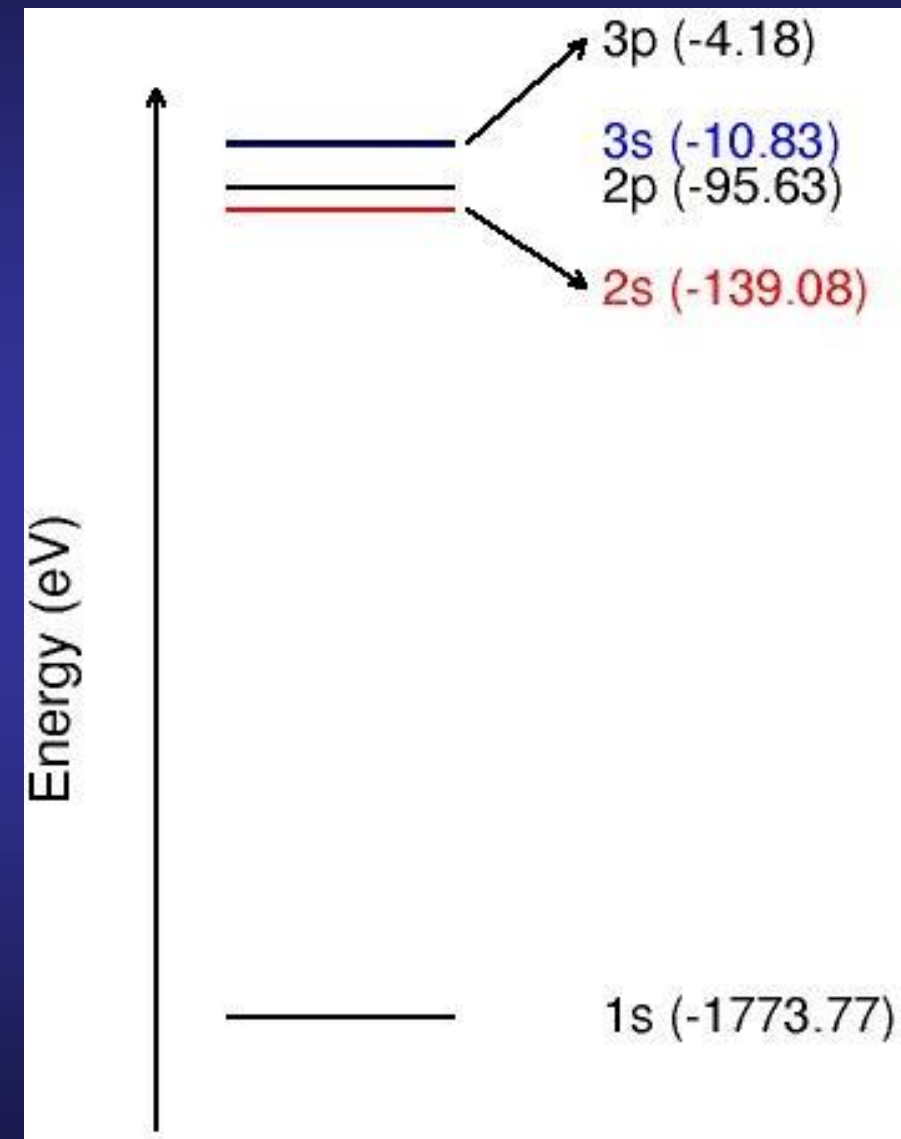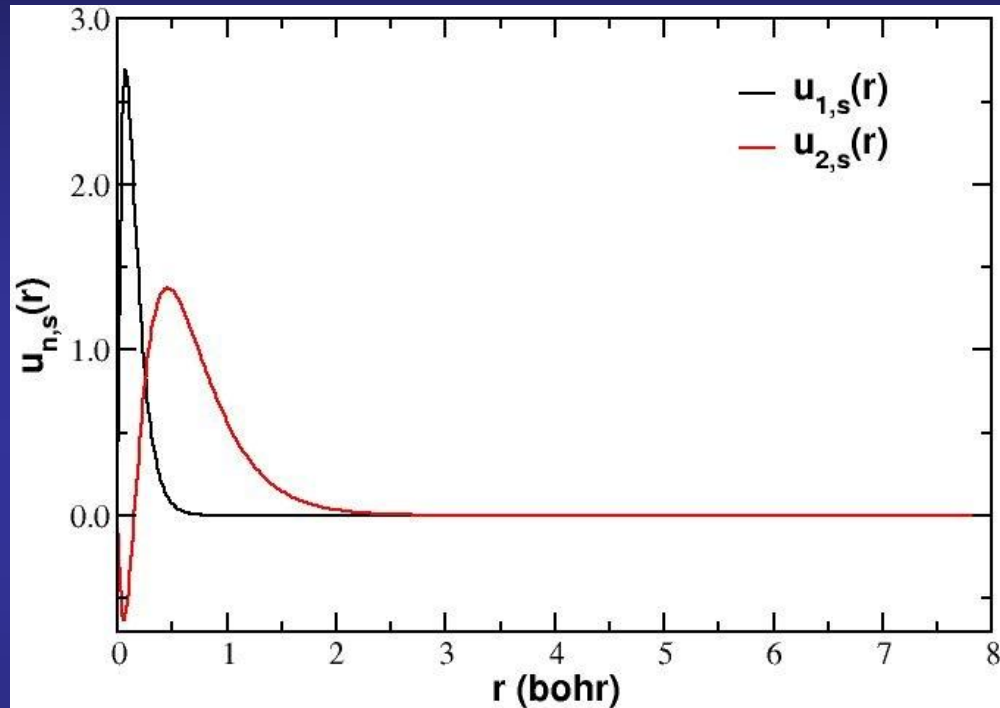
Atomic Si

Core electrons…

highly localized

very depth energy

… are chemically inert

Core electrons are chemically inert
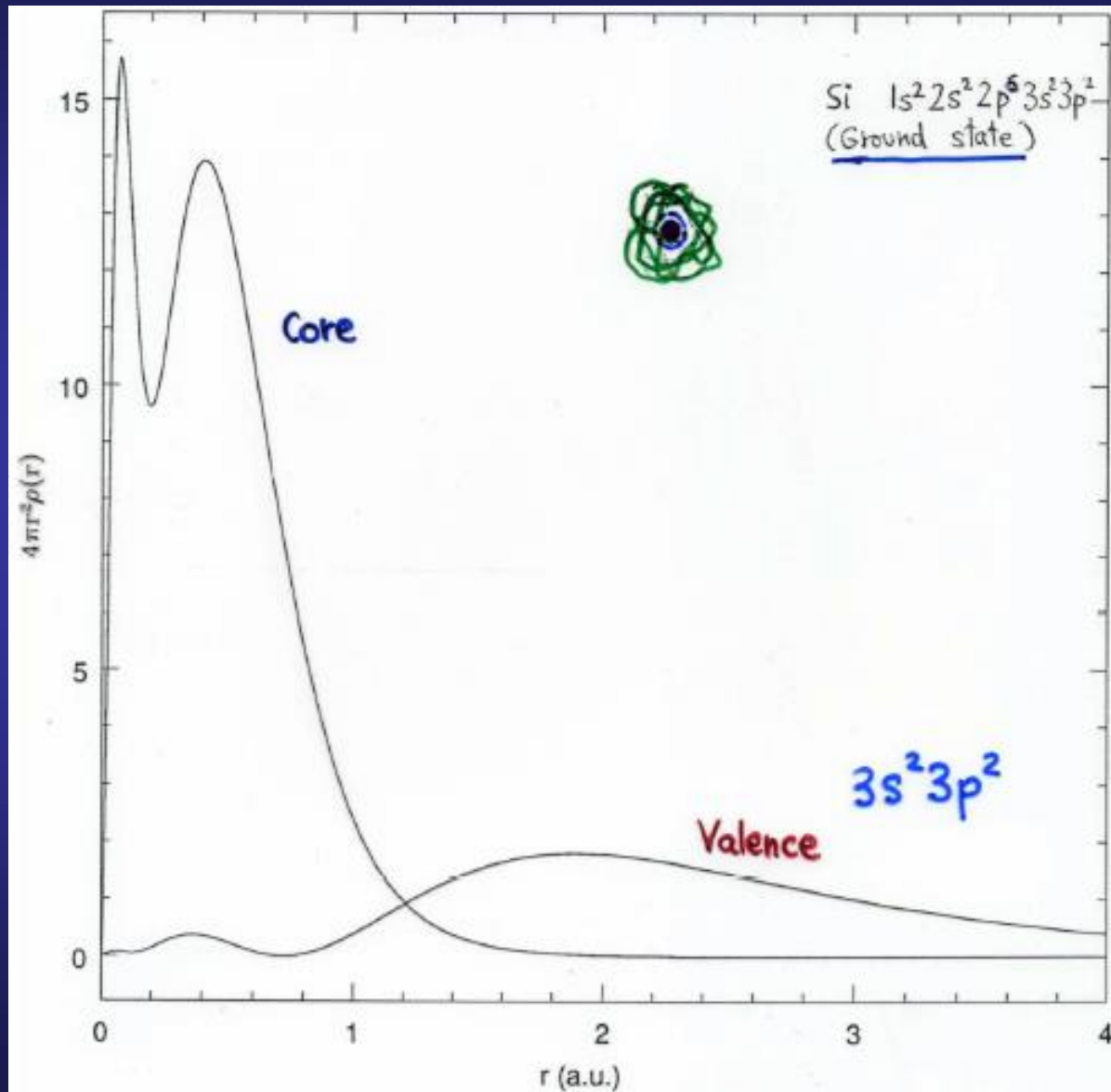
Core electrons are chemically inert
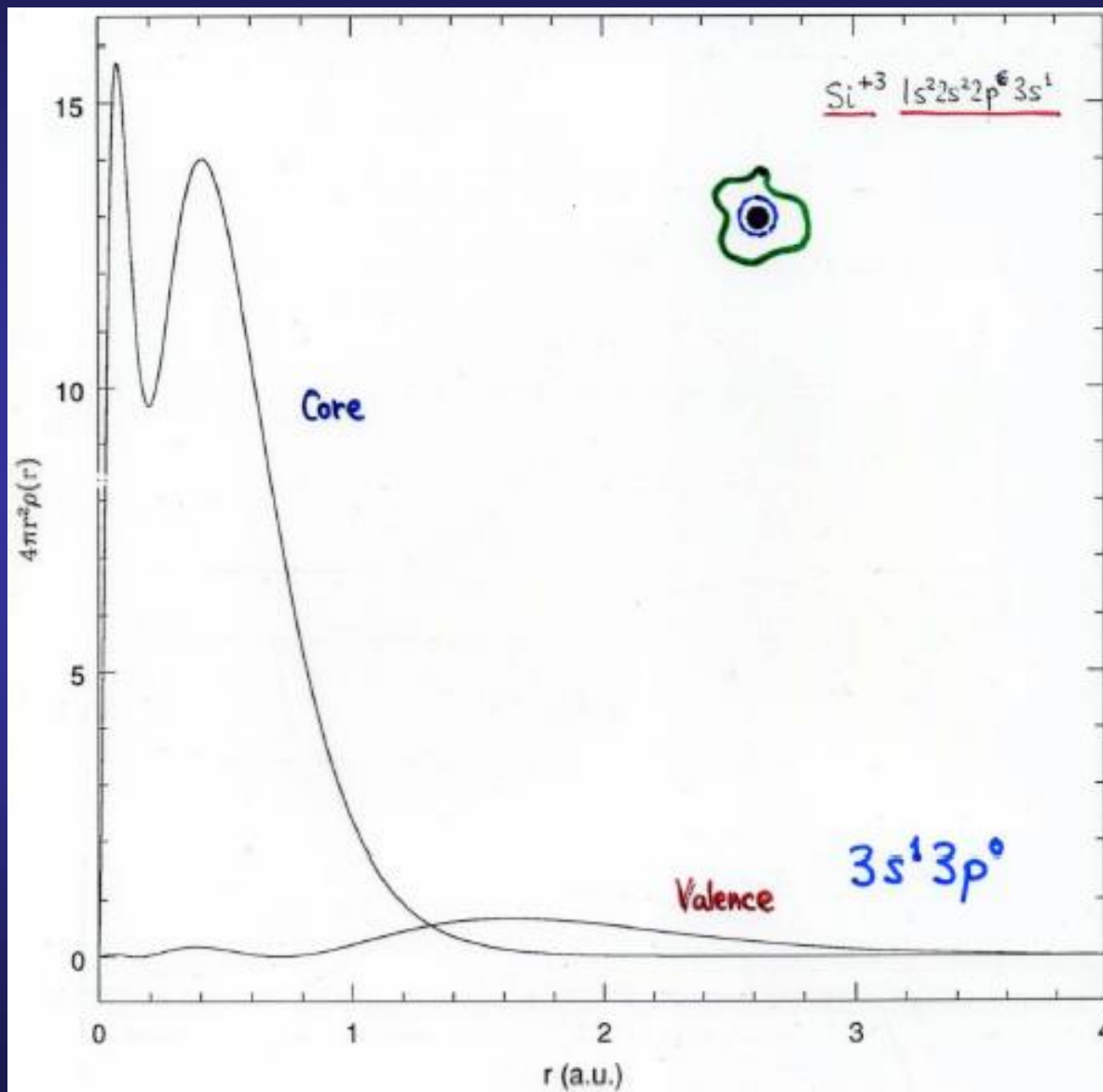
Valence wave functions must be orthogonal to the core wave functions
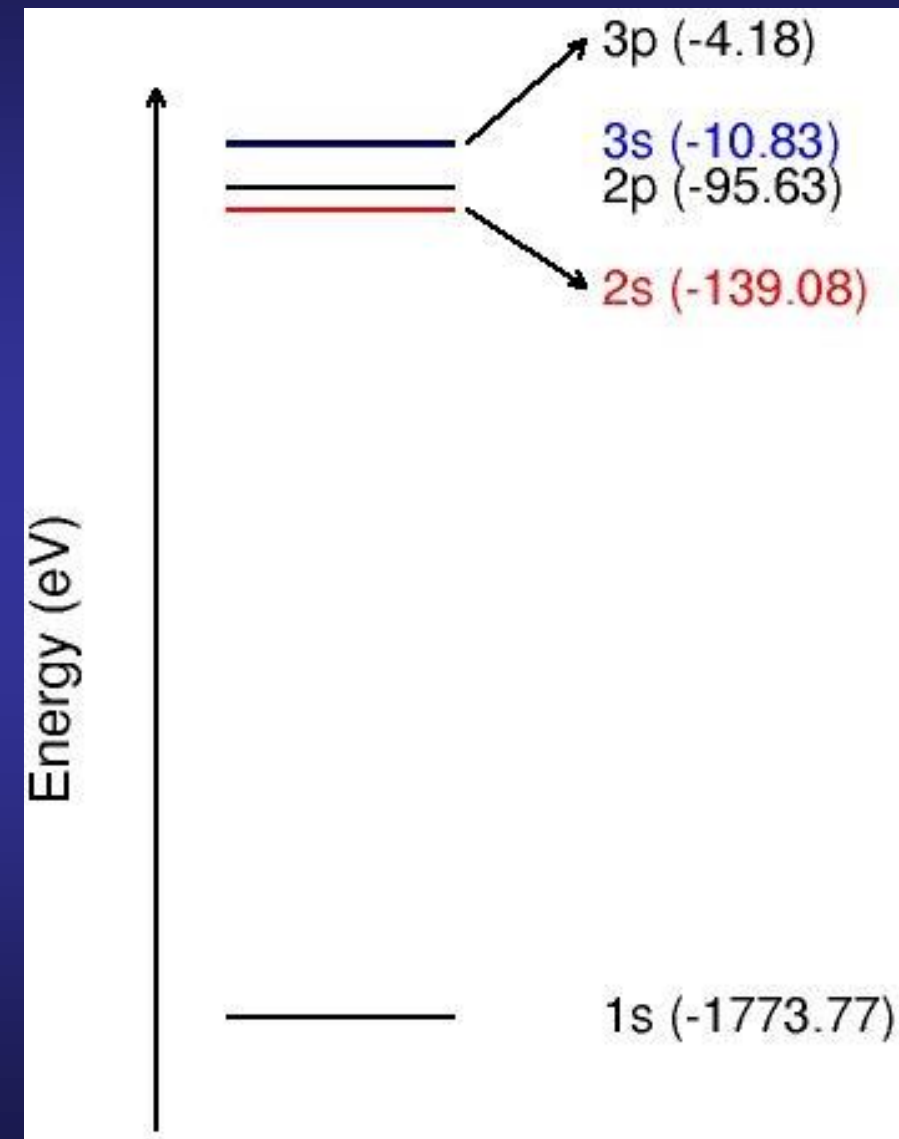
Atomic Si
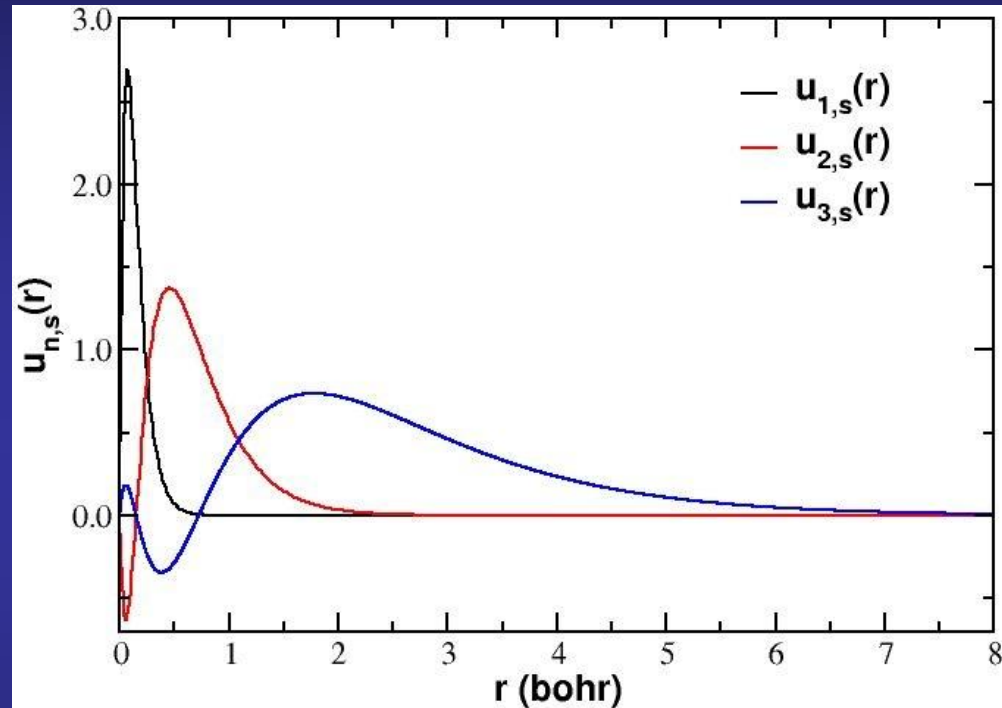
Core electrons…

highly localized

very depth energy

… are chemically inert

Fourier expansion of a valence wave function has a great contribution of short-wave length
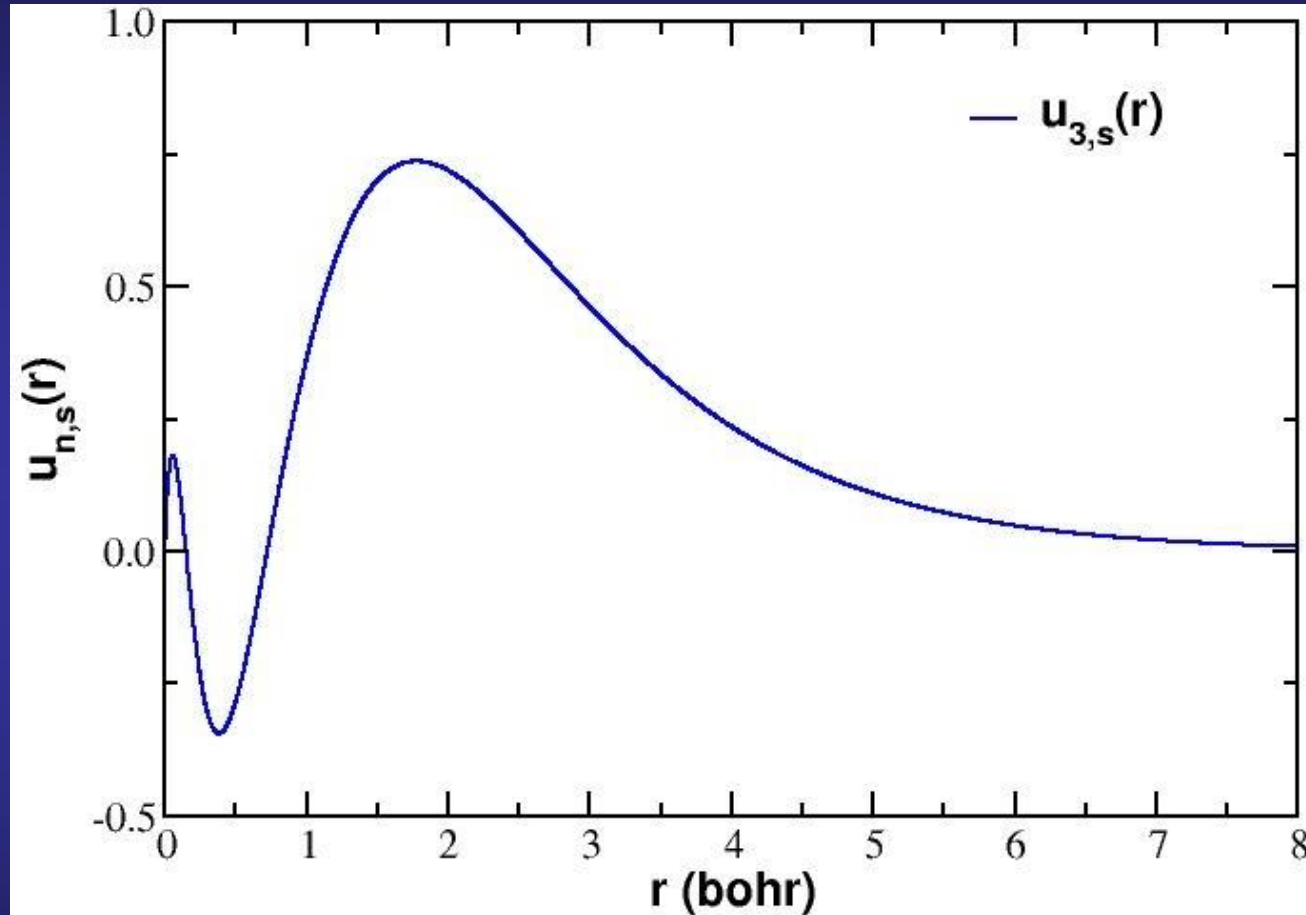
To get a good approximation we would have to use a large number of plane waves.

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 $\Rightarrow$ 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
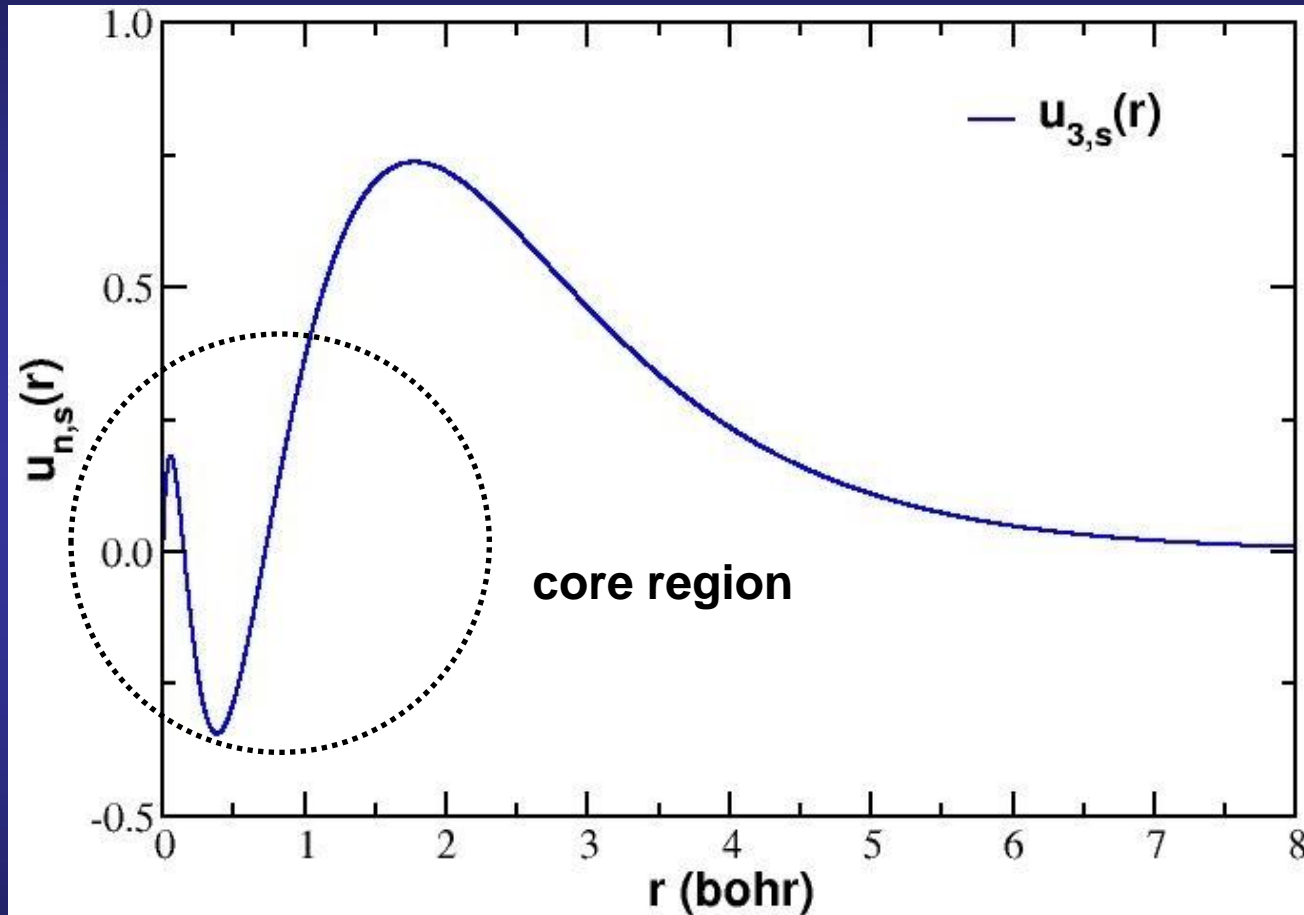
Idea, eliminate the core electrons by ironing out the nodes
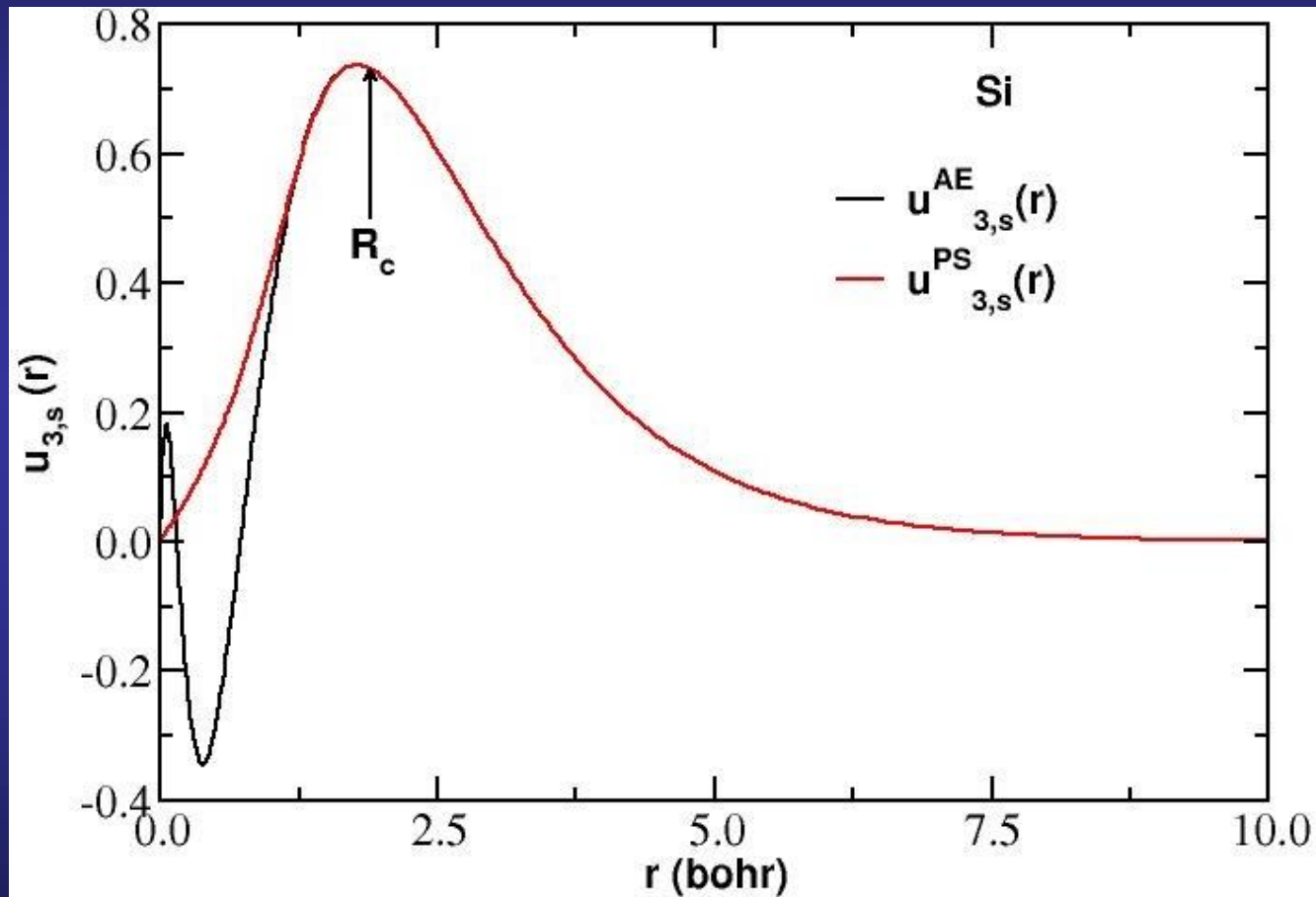
The pseudopotential transformation: Seeking for the wave equation of the "smooth"

Replace the OPW form of the wave function into the Schrödinger equation

$$\psi_i^v(\vec{r}) = \tilde{\psi}_i^v(\vec{r}) - \sum_j \left\langle \psi_j^c \middle| \tilde{\psi}_i^v \right\rangle \psi_j^c(\vec{r})$$

$$\hat{H}\psi_i^v(\vec{r}) = \left[-\frac{1}{2}\nabla^2 + V(\vec{r}) \right]\psi_i^v(\vec{r}) = \varepsilon_i^v \psi_i^v(\vec{r})$$

$$\Downarrow$$

Equation for the smooth part, with a non local operator

$$\hat{H}^{PKA}\tilde{\psi}_i^v(\vec{r}) \equiv \left[-\frac{1}{2}\nabla^2 + \hat{V}^{PKA} \right]\tilde{\psi}_i^v(\vec{r}) = \varepsilon_i^v \tilde{\psi}_i^v(\vec{r})$$

The original potential is replaced by a weaker non-local pseudopotential

J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959)

$$\hat{V}^{PKA} = V + \hat{V}^{R}$$

$$\hat{V}^{R}\tilde{\psi}_i^v(\vec{r}) = \sum_j (\varepsilon_i^v - \varepsilon_j^c)\left\langle\psi_j^c|\tilde{\psi}_i^v\right\rangle\psi_j^c(\vec{r})$$

Advantages

Repulsive

$$\varepsilon_i^v - \varepsilon_j^c > 0$$

$$\Downarrow$$

V^{PKA} is much weaker than the original potential V(r)

Spatially localized

vanishes where $\psi_j^c = 0$

Disadvantages

Non-local operator

$\tilde{\psi}_i^v$ **are not orthonormal**

$\hat{V}^{R}$ **is not smooth**

l-dependent

Ab-initio pseudopotential method:
fit the valence properties calculated from the atom
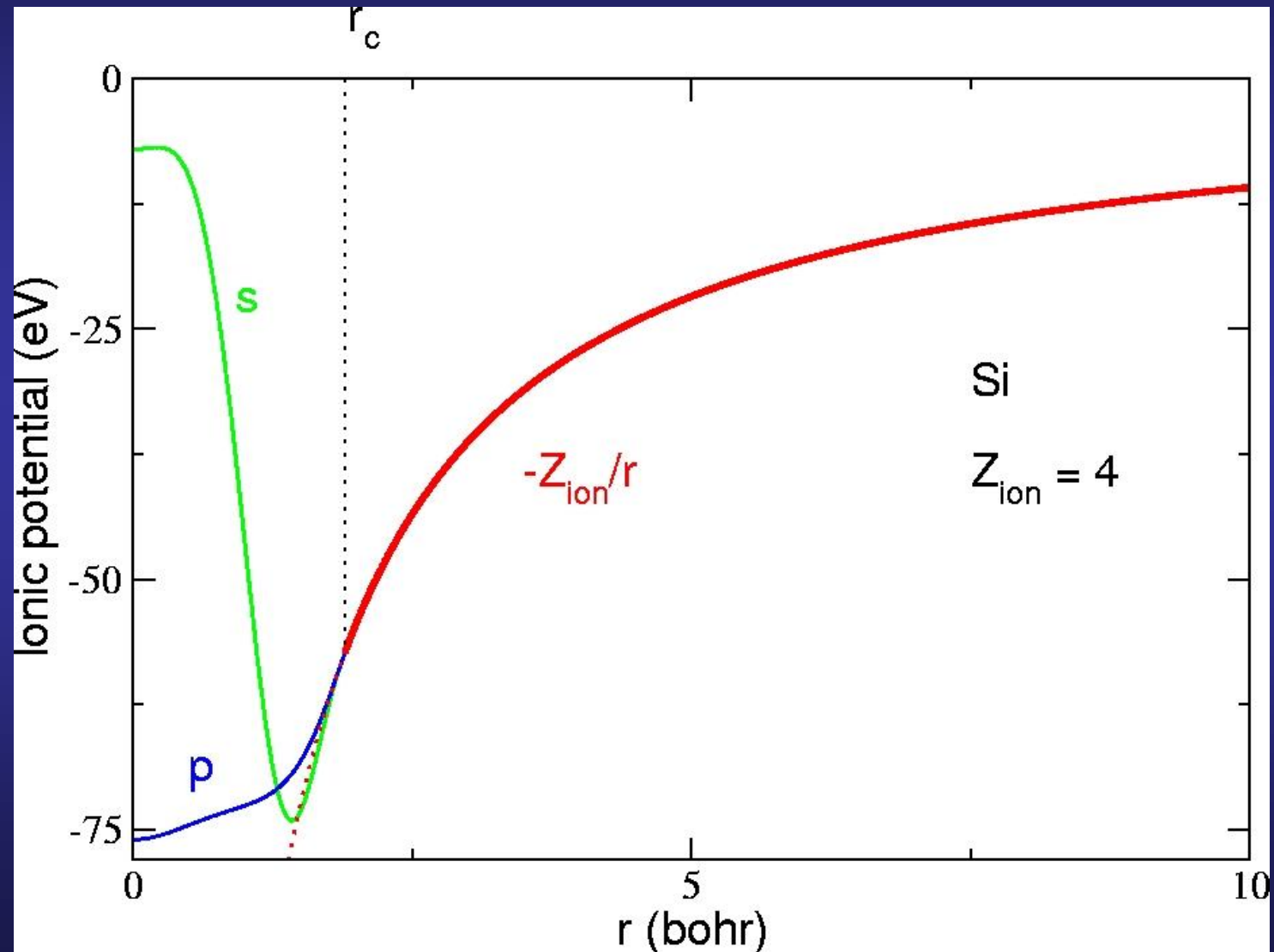
List of requirements for a good norm-conserving pseudopotential:

Choose an atomic reference configuration

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

1. All electron and pseudo valence eigenvalues agree for the chosen reference configuration
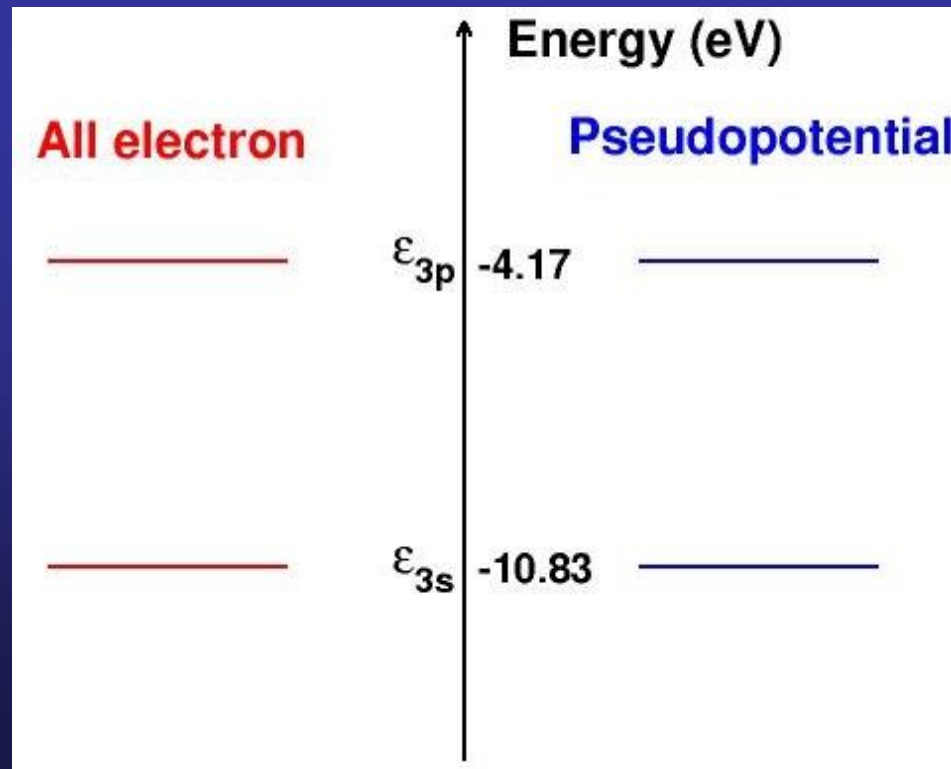
List of requirements for a good norm-conserving pseudopotential:

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

2. All electron and pseudo valence wavefunctions agree beyond a chosen cutoff radius R_c (might be different for each shell)
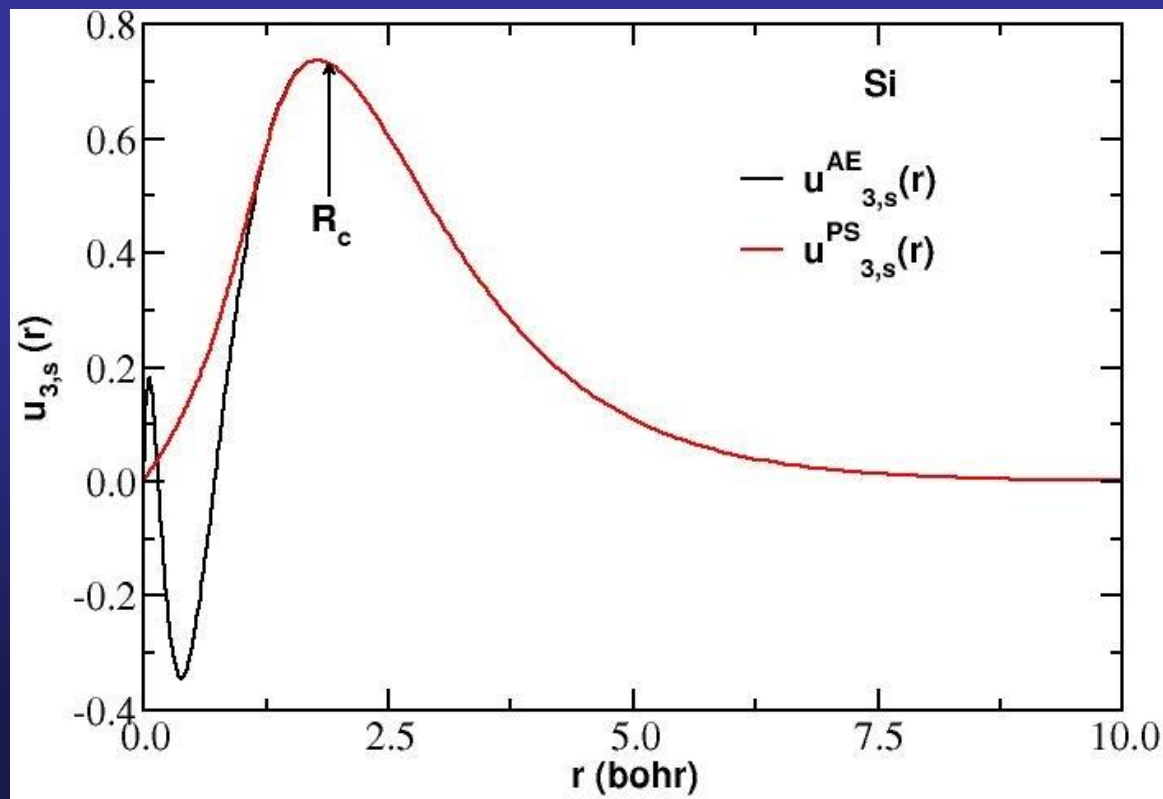
List of requirements for a good norm-conserving pseudopotential:

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:

Choose an atomic reference configuration

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

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:

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)] $\Rightarrow$ (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
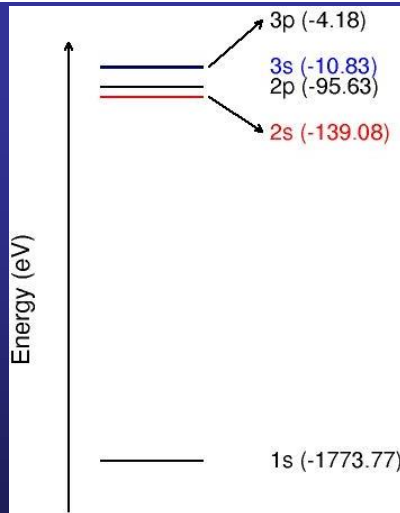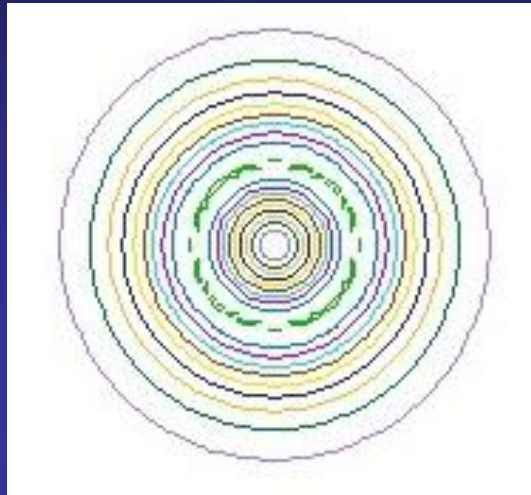
Bulk Si
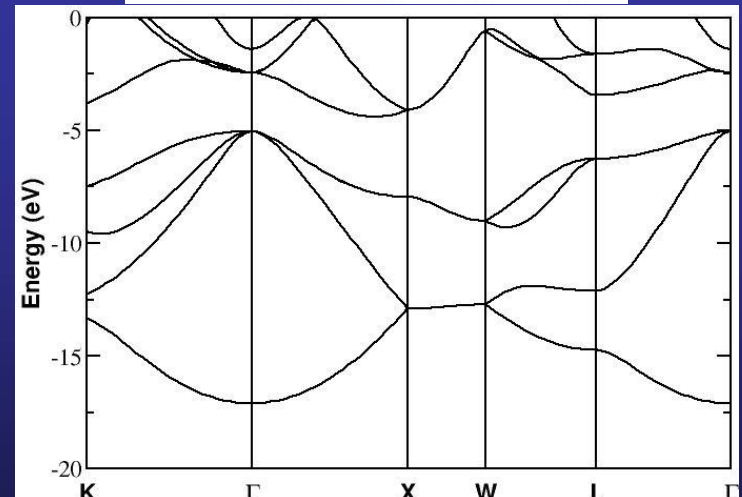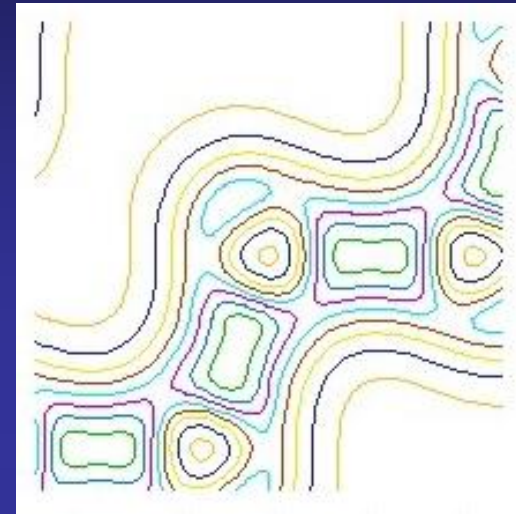
If condition 5 is satisfied, the change in the eigenvalues to linear order in the change in the potential is reproduced

Generation of *l*-dependent norm-conserving pseudopotential

All electron self consistent atomic calculation

Each state l,m treated independently

↓

Identify the valence states

Freedom (different approaches)

↓

Generate the pseudopotential $V_{l,total}(r)$ and pseudoorbitals $\psi_l^{PS}(r)$

$V_{l,total}(r)$ **screened pseudopotential acting on valence electrons**

↓

"Unscreened" by substracting from the total potential $V_{Hxc}^{PS}(r)$

$$V_l(\vec{r}) \equiv V_{l,total}(\vec{r}) - V_{Hxc}^{PS}(\vec{r})$$

Different methods to generate norm-conserving pseudopotential

Troullier-Martins   **Kerker**   **Haman-Schlüter-Chiang**   **Vanderbilt**
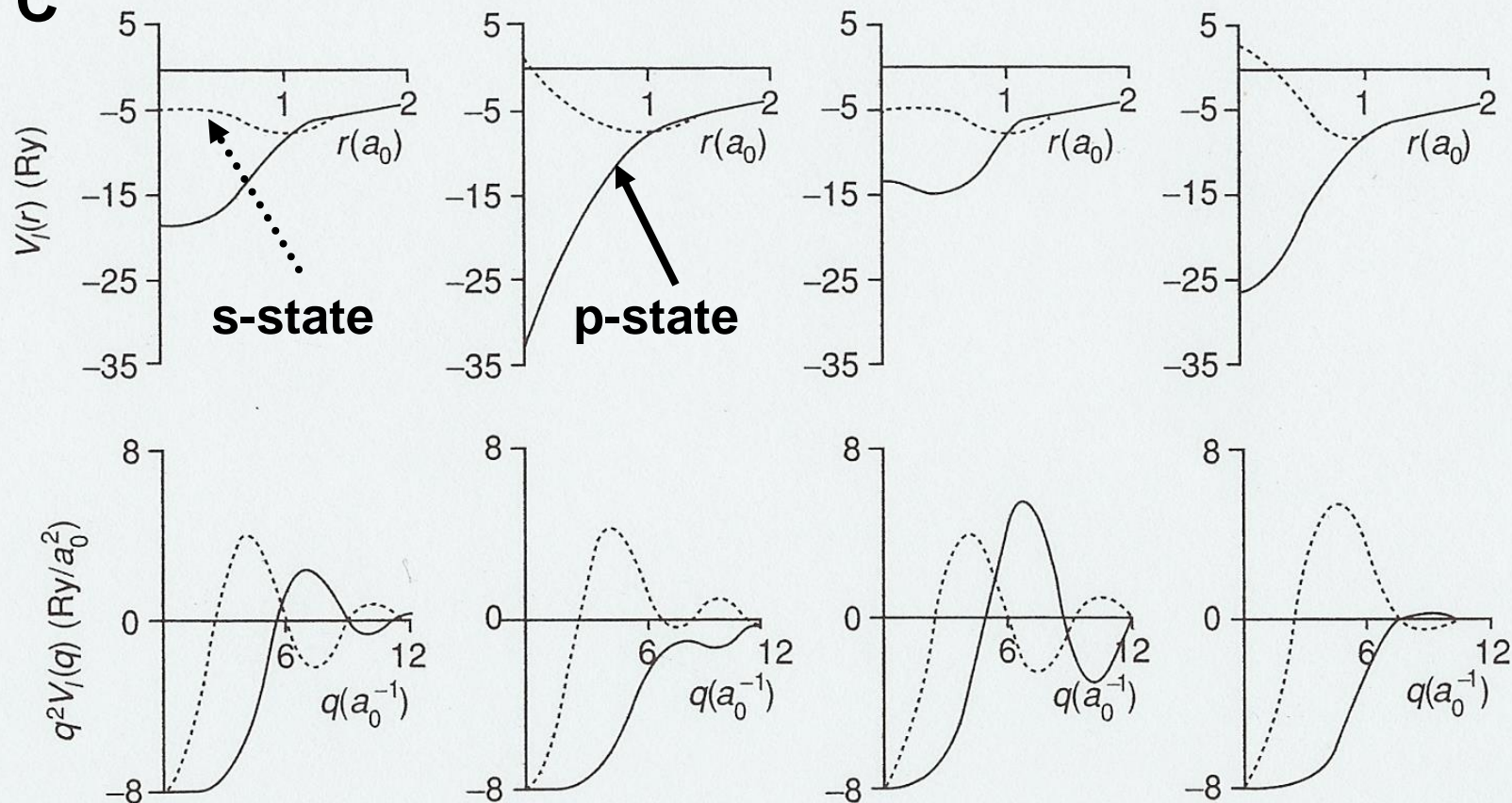
R. M. Martin, Electronic structure, Basic Theory and Practical Methods, Cambridge University Press, Cambridge, 2004

Separable fully non-local pseudopotentials. The Kleinam-Bylander projectors

The pseudopotential operator is *l*-dependent

$$\hat{V}_{ps} = \sum_{lm} V_l\left(r\right)\,|\,Y_{lm}\rangle\langle Y_{lm}|$$

Ab-initio pseudopotential method:
fit the valence properties calculated from the atom
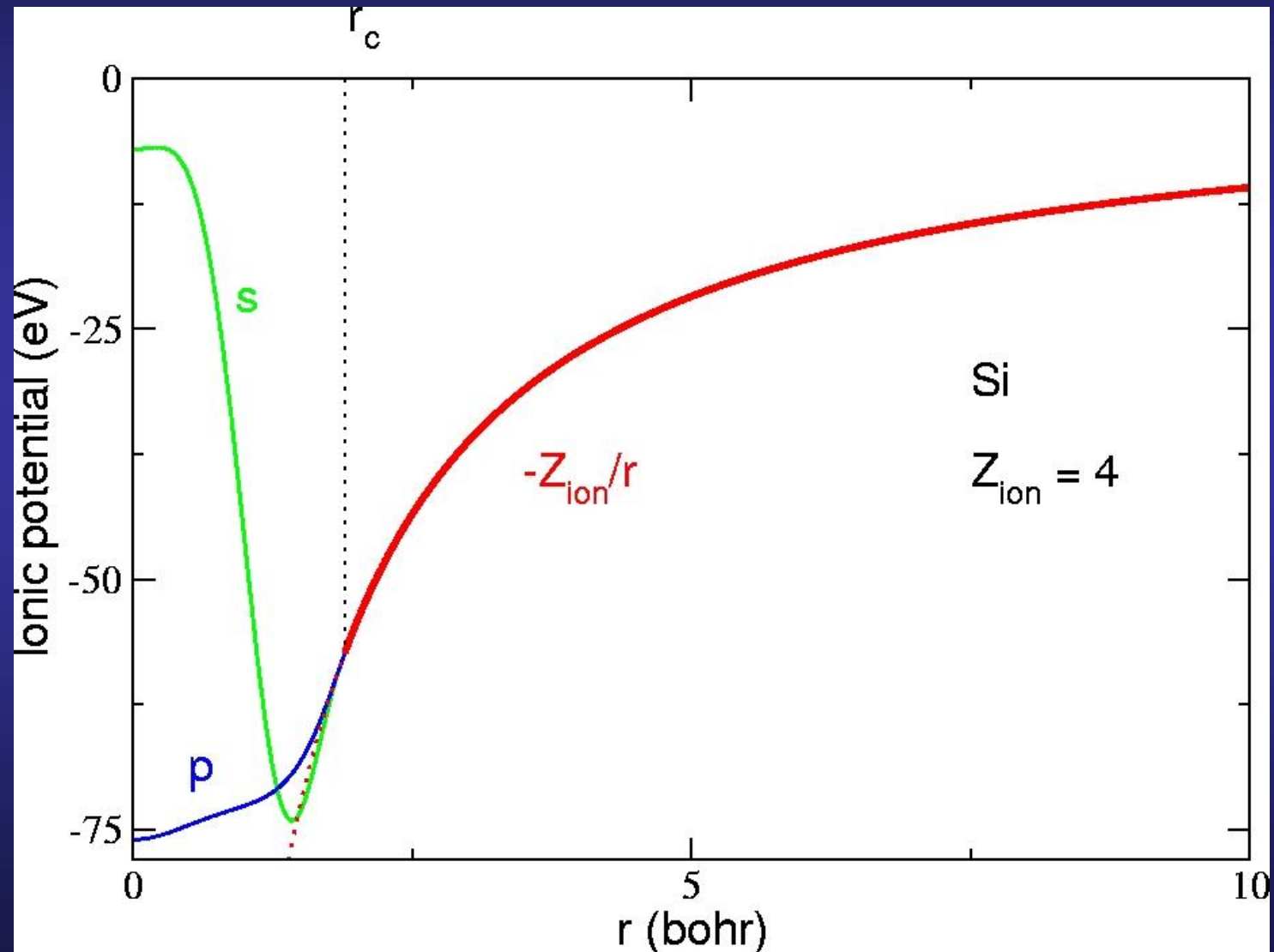
Separable fully non-local pseudopotentials. The Kleinam-Bylander projectors

The pseudopotential operator is _l_-dependent

$$\hat{V}_{ps} = \sum_{lm} V_l\left(r\right) \left| Y_{lm} \right\rangle \left\langle Y_{lm} \right|$$

It is useful to separate into a local (_l_-independent) plus a non-local term)

$$V_l\left(r\right) = V_{local}\left(r\right) + \delta V_l\left(r\right)$$

$$\hat{V}_{ps} = V_{local}\left(r\right) + \sum_{lm} \delta V_l\left(r\right) \left| Y_{lm} \right\rangle \left\langle Y_{lm} \right|$$

Kleinman-Bylander showed that the effect that the effect of the semilocal term can be replaced by a separable operator

$$\hat{V}_{ps} = V_{local}\left(r\right) + \sum_{lm} \frac{\left| \psi_{lm}^{ps} \delta V_l \right\rangle \left\langle \delta V_l \psi_{lm}^{ps} \right|}{\left\langle \psi_{lm}^{ps} \left| \delta V_l \right| \psi_{lm}^{ps} \right\rangle}$$

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

Shorter R_c: harder pseudo

Si

$R_c = 1.90$ bohr
$R_c = 1.30$ bohr

$u_{3,s}(r)$

r (bohr)
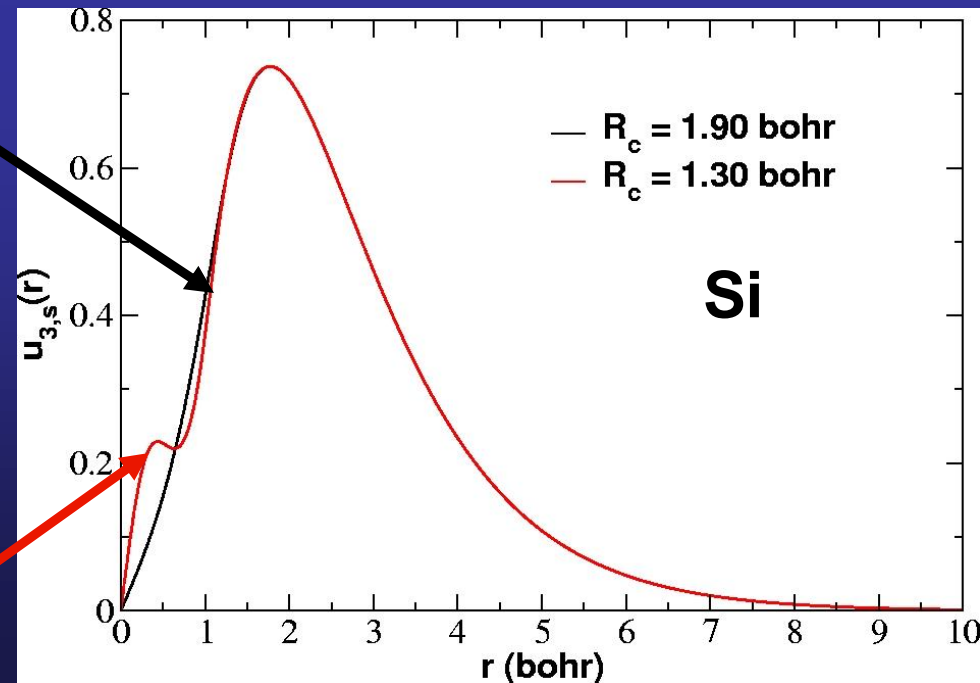
A transferable pseudo will reproduce the AE energy levels and wave functions in arbitrary environments

- Compute the energy of two different configurations E_{C1} E_{C2}
- Compute the difference in energy $\Delta E = E_{C2} - E_{C1}$
- For the pseudopotential to be transferible: $\Delta E^{AE} = \Delta E^{PS}$

```
total energy differences in series
          1         2         3         4         5
 1     0.0000
 2     0.4308    0.0000
 3     0.4961    0.0653    0.0000
 4     0.9613    0.5305    0.4652    0.0000
 5     1.4997    1.0689    1.0036    0.5384    0.0000
total energy differences in series
          1         2         3         4         5
 1     0.0000
 2     0.4304    0.0000
 3     0.4958    0.0654    0.0000
 4     0.9602    0.5297    0.4643    0.0000
 5     1.4970    1.0666    1.0012    0.5369    0.0000
```

ΔE^{AE}

ΔE^{PS}

$3s^2\, 3p^2$ (reference)
$3s^2\, 3p^1\, 3d^1$
$3s^1\, 3p^3$
$3s^1\, 3p^2\, 3d^1$
$3s^0\, 3p^3\, 3d^1$

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

O: $1s^2$ $2s^2$ $2p^4$

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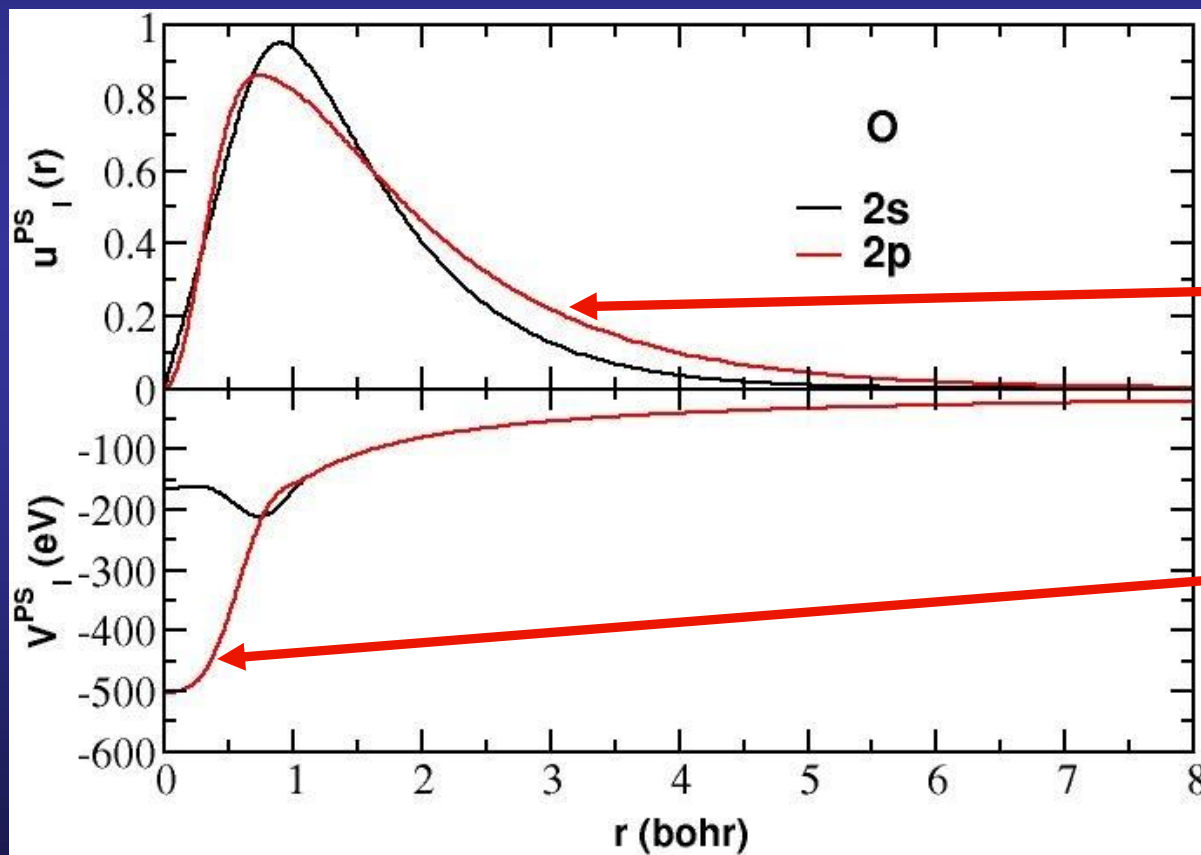
No nodes because there are no p states to be orthogonal to

pseudopotential is hard

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**

Howto: input file to generate the pseudopotential

```
#
#   Pseudopotential generation for Silicon
#   pg: simple generation
#

   pg        Silicon
        tm2        3.0                      # PS flavor, logder R
  n=Si c=car                               # Symbol, XC flavor,{ |r|s}
        0.0        0.0        0.0           0.0        0.0        0.0
     3     4                               # norbs_core, norbs_valence
     3     0     2.00        0.00    # 3s2
     3     1     2.00        0.00    # 3p2
     3     2     0.00        0.00    # 3d0
     4     3     0.00        0.00    # 4f0
        1.90       1.90       1.90        1.90       0.00       0.00
#
# Last line (above):
#    rc(s)      rc(p)      rc(d)      rc(f)    rcore_flag  rcore
#
#2345678901234567890123456789012345678901234567890123456789012345678901234567890
```

Generation Mechanics

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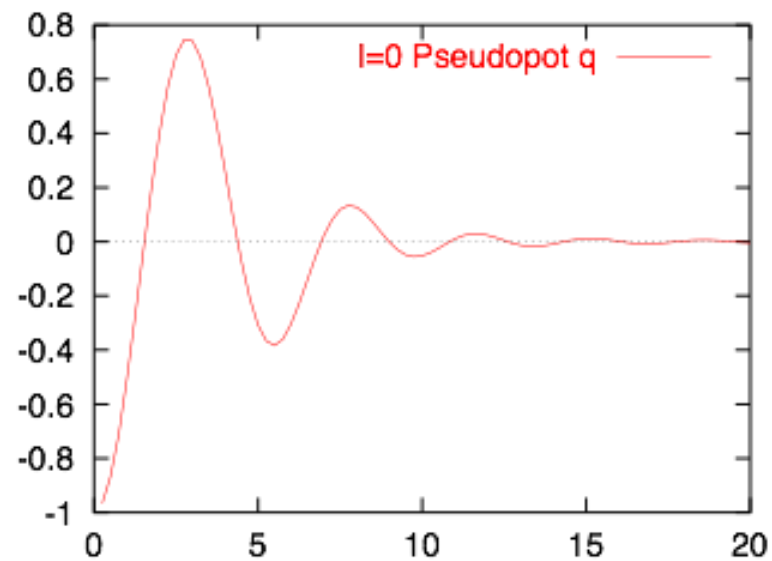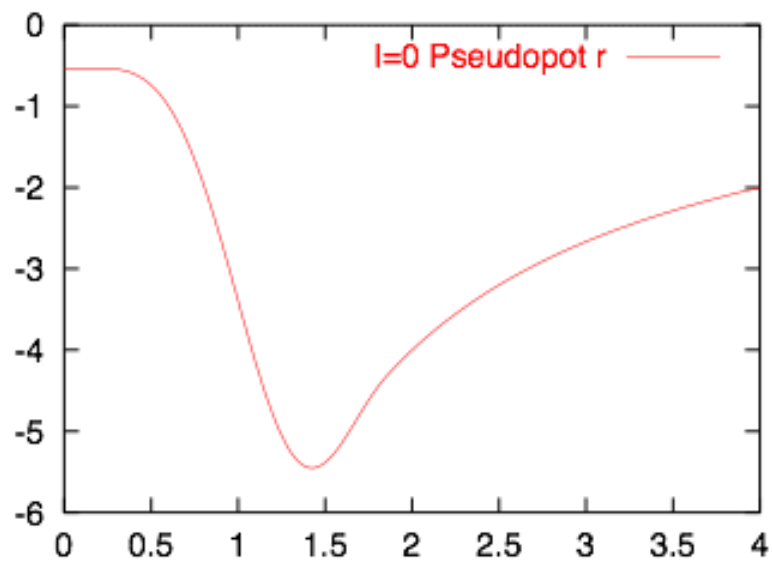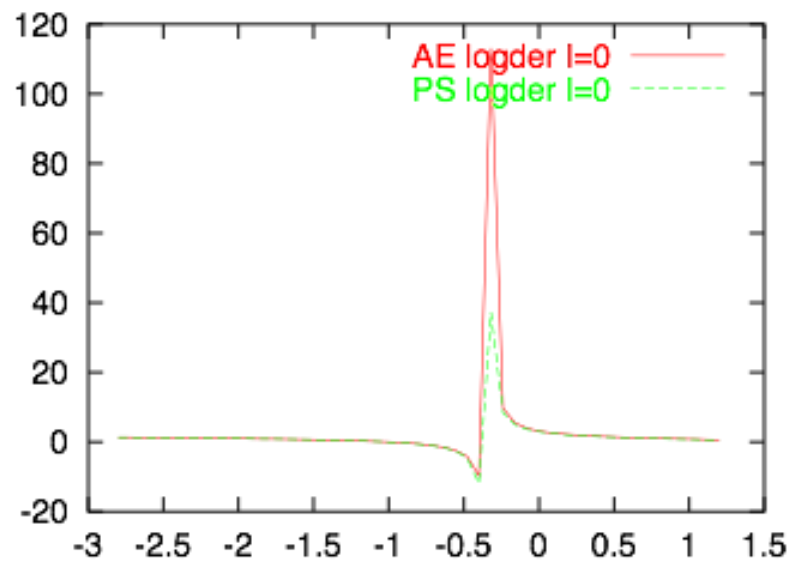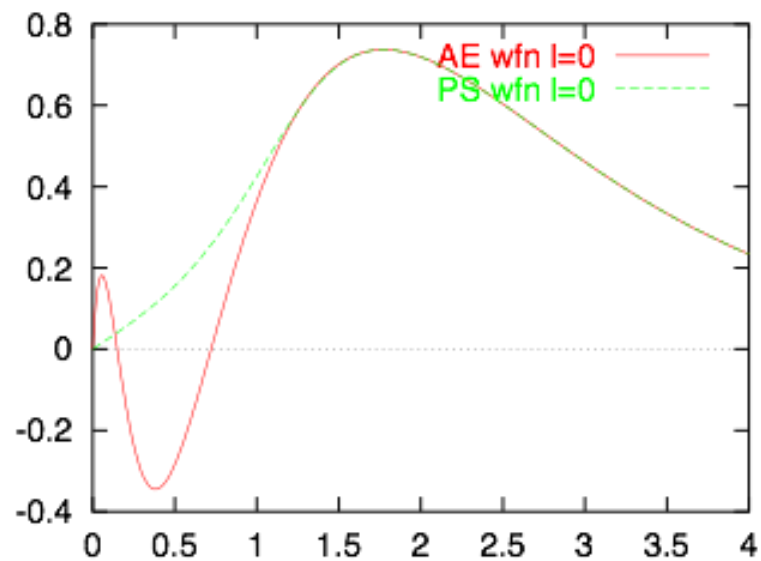
Testing Mechanics

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

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

```
&d total energy differences in series
&d              1          2          3          4          5
&d   1     0.0000
&d   2     0.4308     0.0000
&d   3     0.4961     0.0653     0.0000
&d   4     0.9613     0.5305     0.4652     0.0000
&d   5     1.4997     1.0689     1.0036     0.5384     0.0000


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


&d              1          2          3          4          5
&d   1     0.0000
&d   2     0.4299     0.0000
&d   3     0.4993     0.0694     0.0000
&d   4     0.9635     0.5336     0.4642     0.0000
&d   5     1.5044     1.0745     1.0051     0.5409     0.0000
```