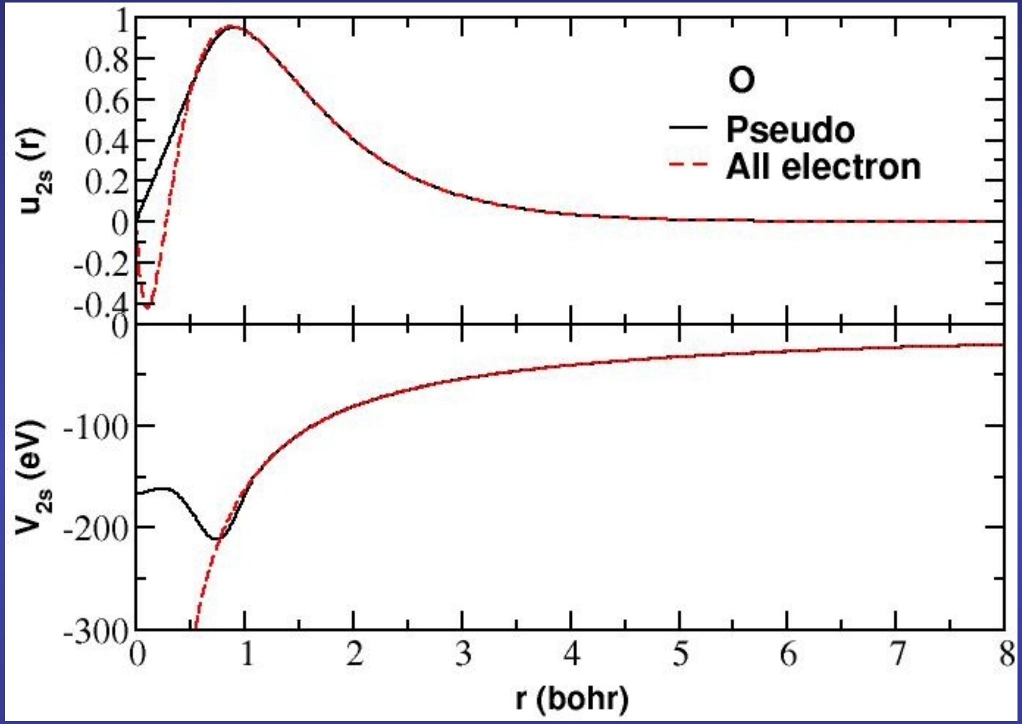
Norm-conserving pseudopotentials in electronic structure calculations



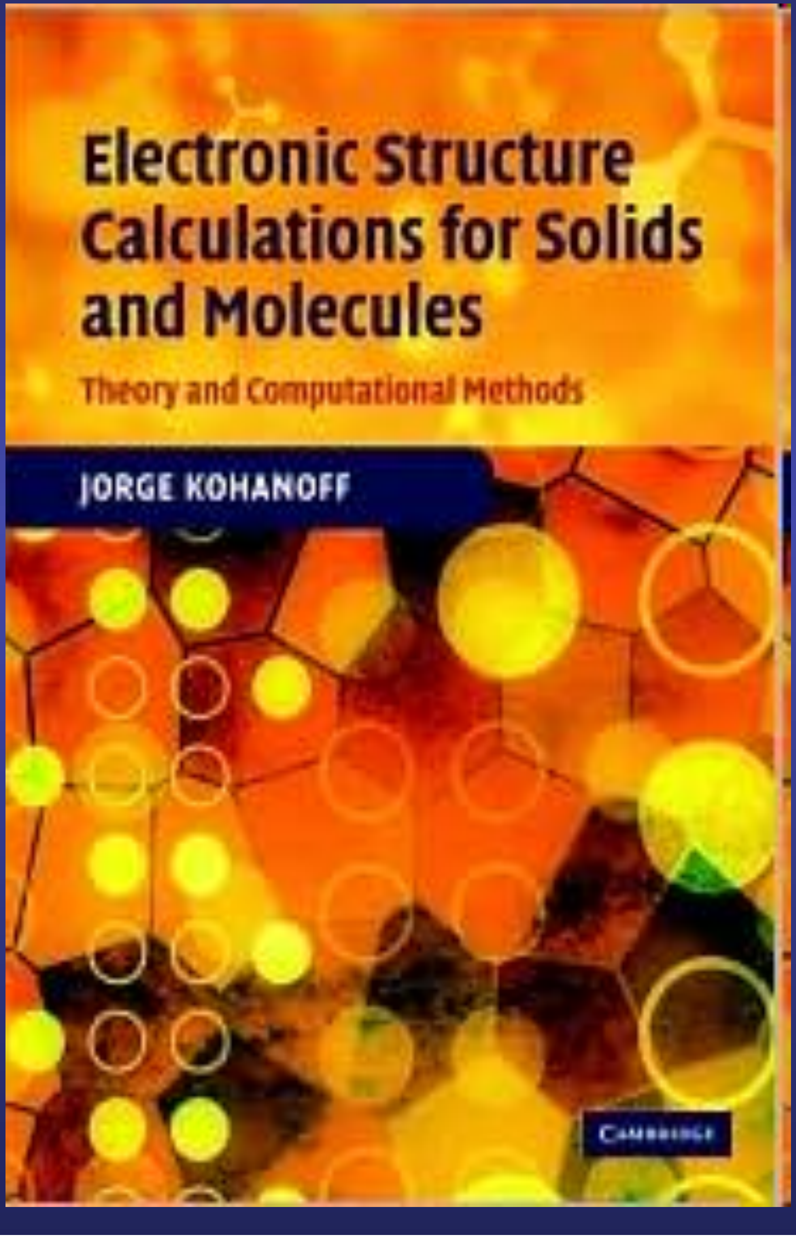
Javier Junquera

UNIVERSIDAD DE CANTABRIA

Alberto García

ICMAB

Bibliography used in the present lecture



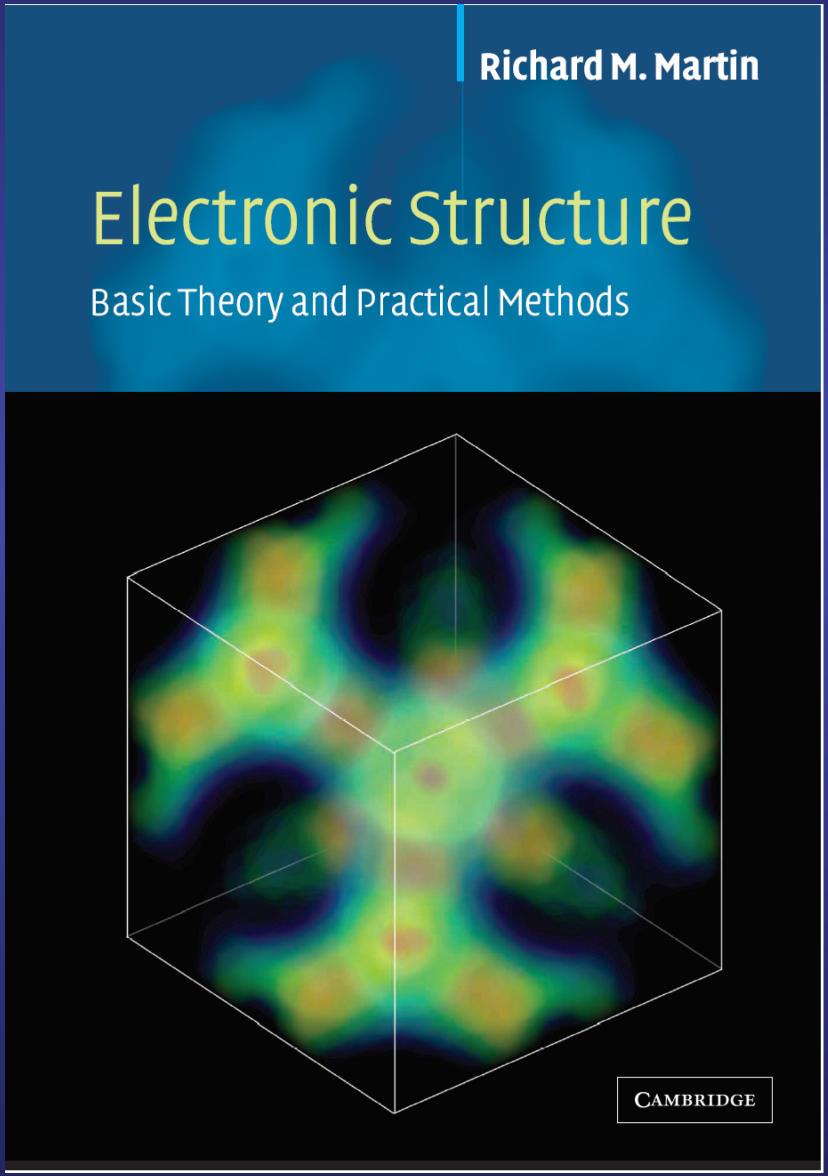
Electronic Structure Calculations for Solids and Molecules

Theory and Computational Methods

JORGE KOHANOFF

CAMBRIDGE

Bibliography used in the present lecture



Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods

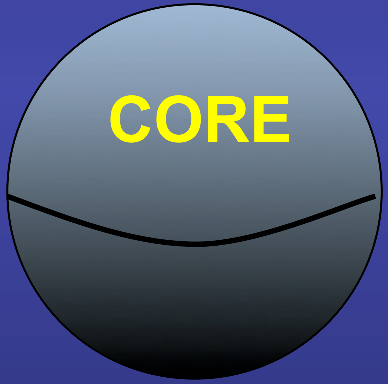
CAMBRIDGE

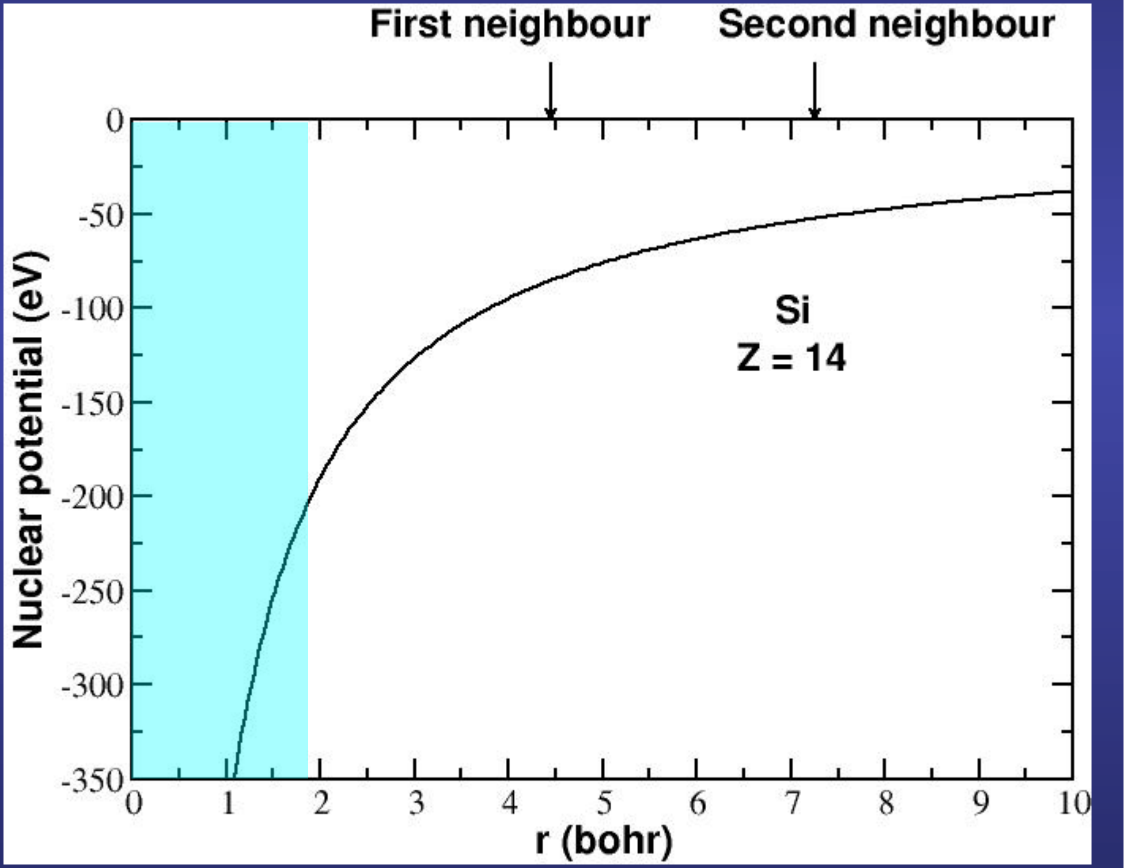
Atomic calculation using DFT:
Solving the Schrodinger-like equation

One particle Kohn-Sham equations

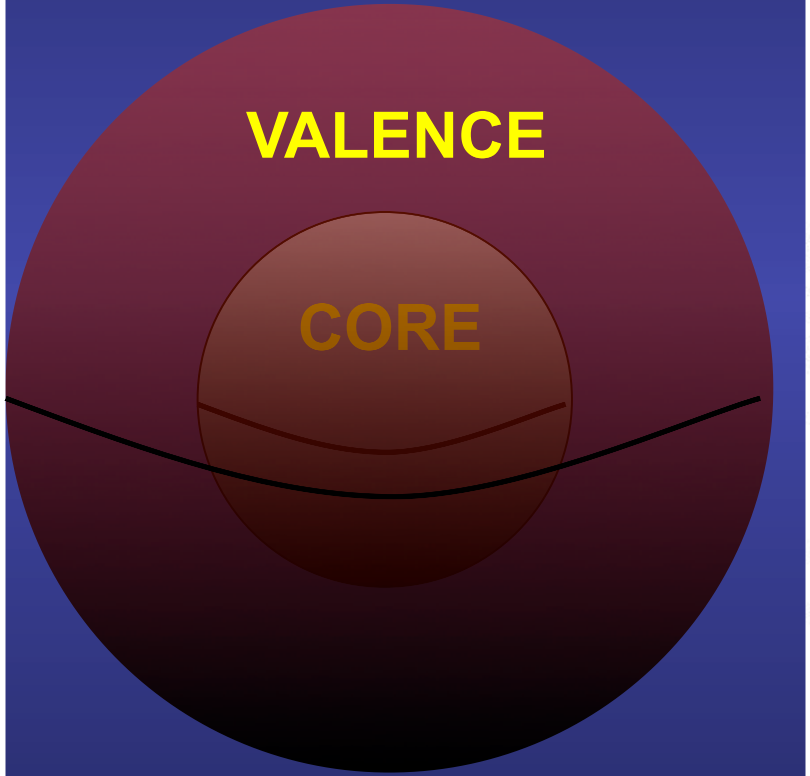
$$\left(\hat{T} + \underset{\substack{\Big\downarrow \\ -\dfrac{Ze}{r}}}{\hat{V}_{ion-e}} + \hat{V}_H + \hat{V}_{xc}\right)\psi_i = \varepsilon_i \psi_i$$

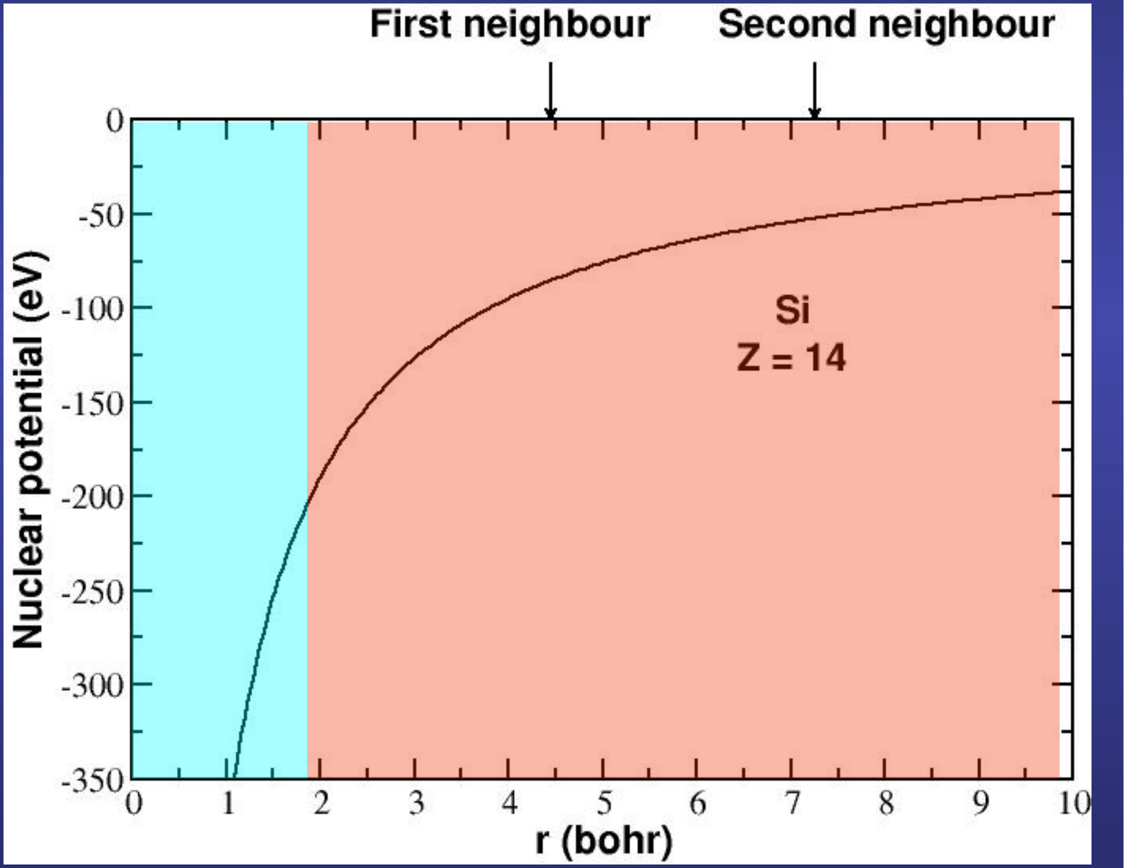
Difficulty: how to deal accurately with both the core and valence electrons



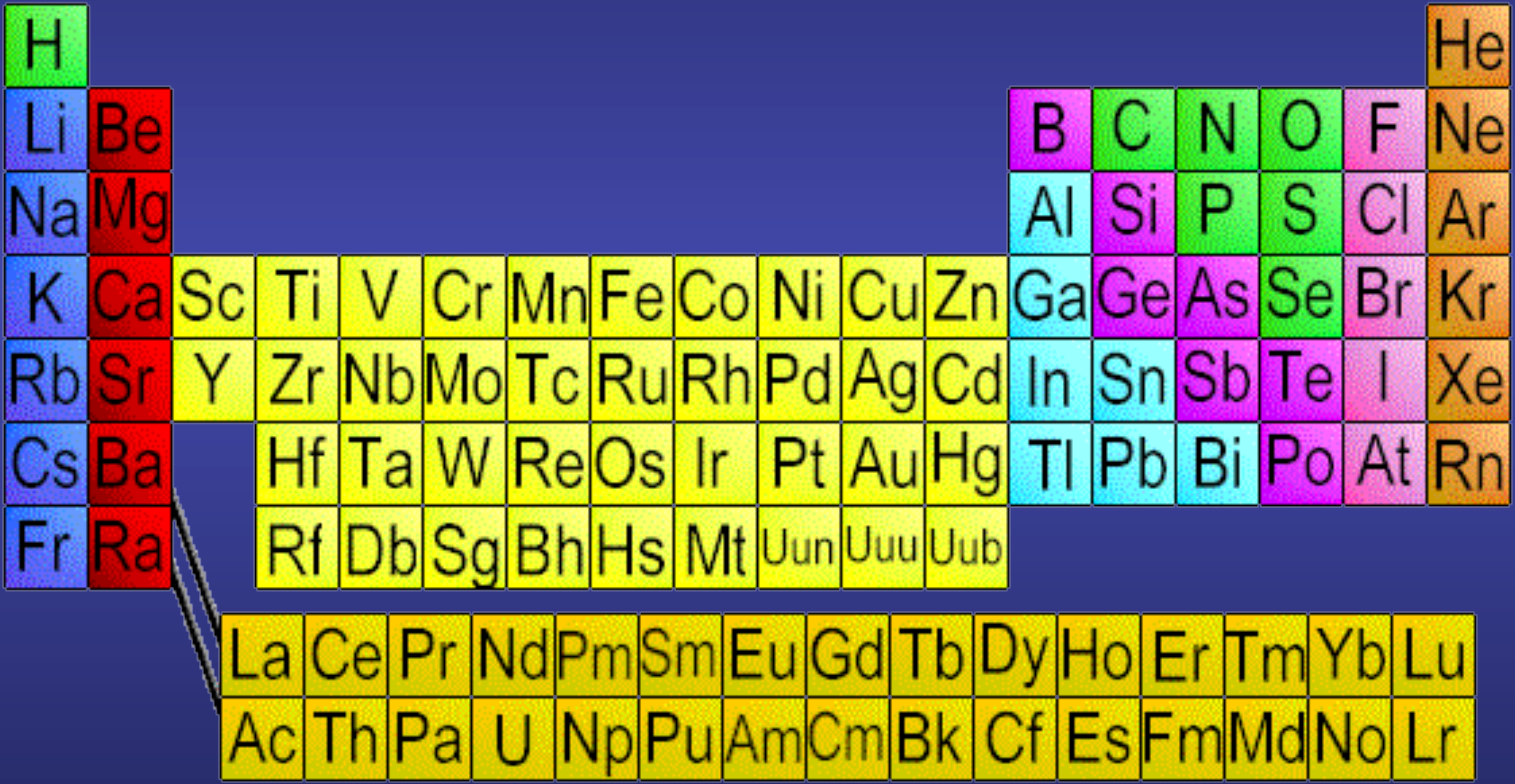


Difficulty: how to deal accurately with both the core and valence electrons





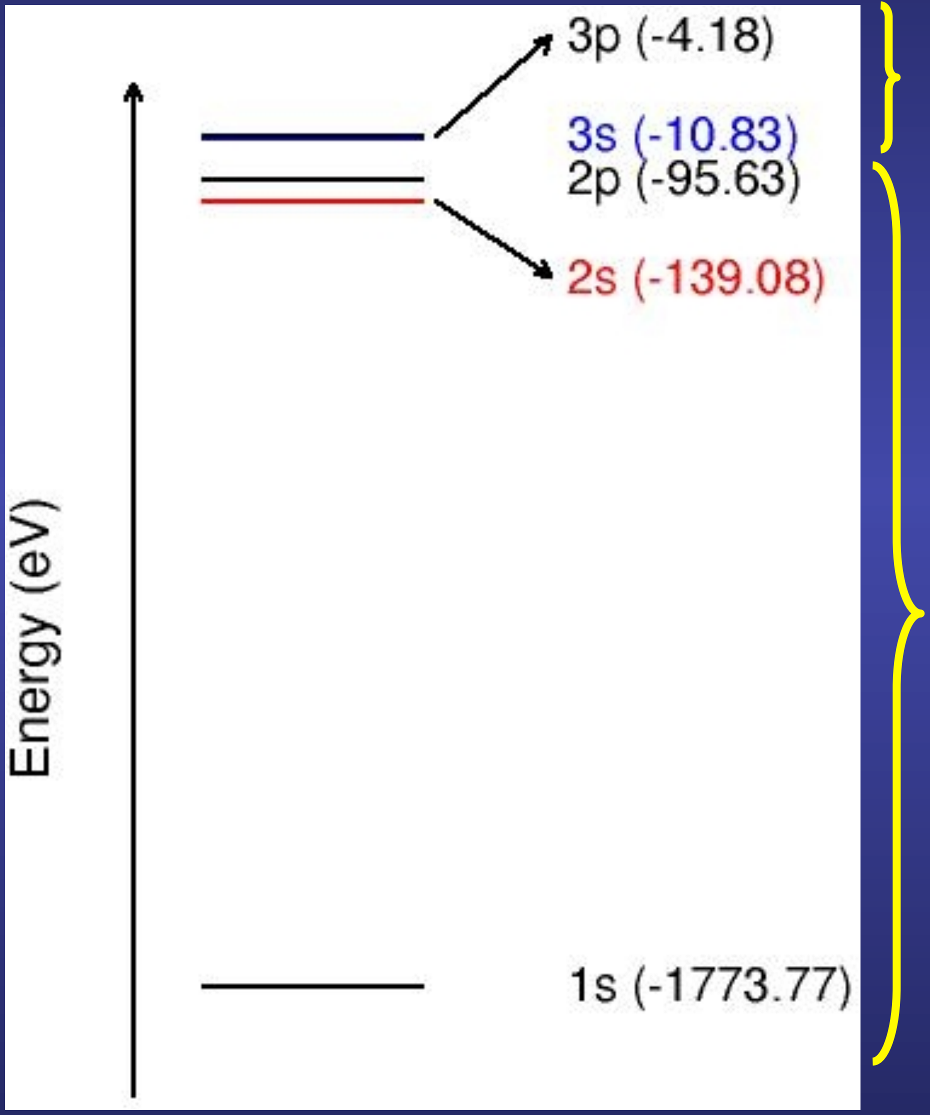
Si atomic configuration: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}\qquad\underbrace{3s^2\ 3p^2}_{\text{valence}}$



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

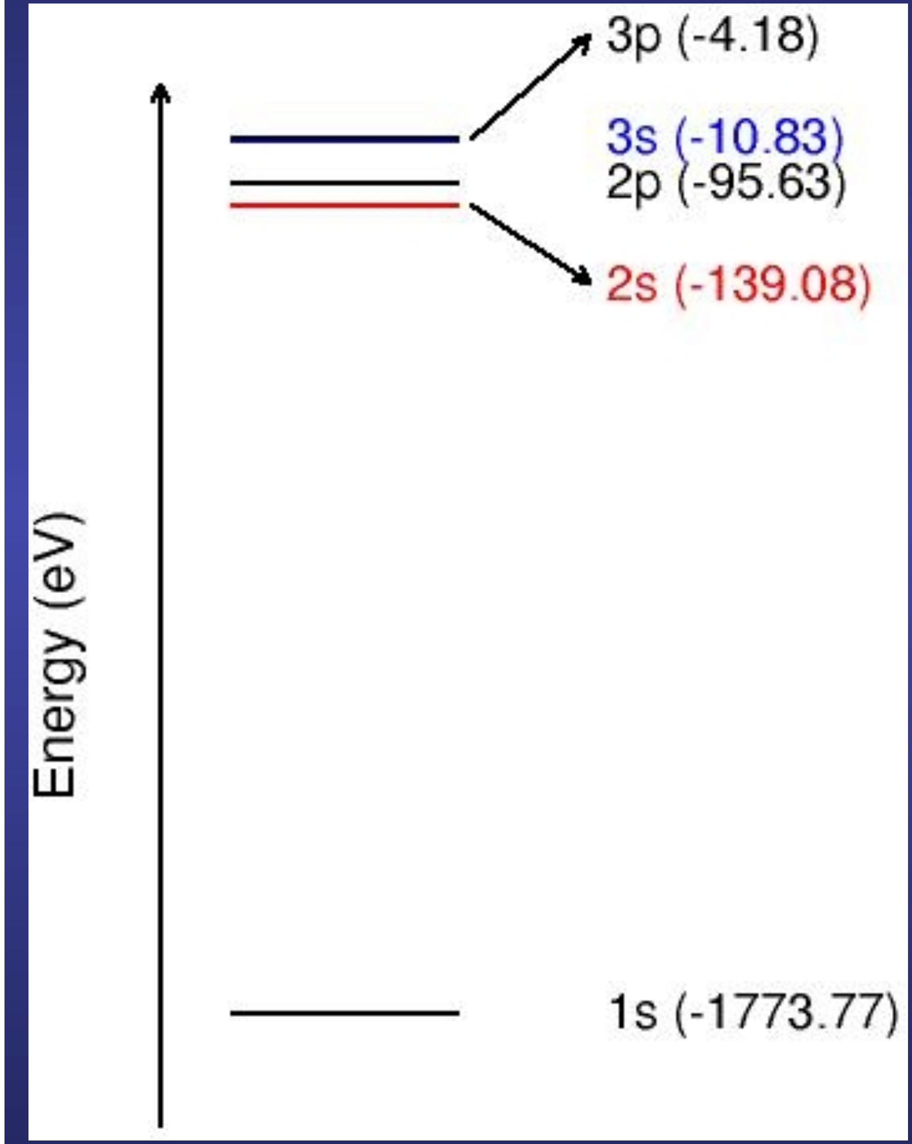


Valence

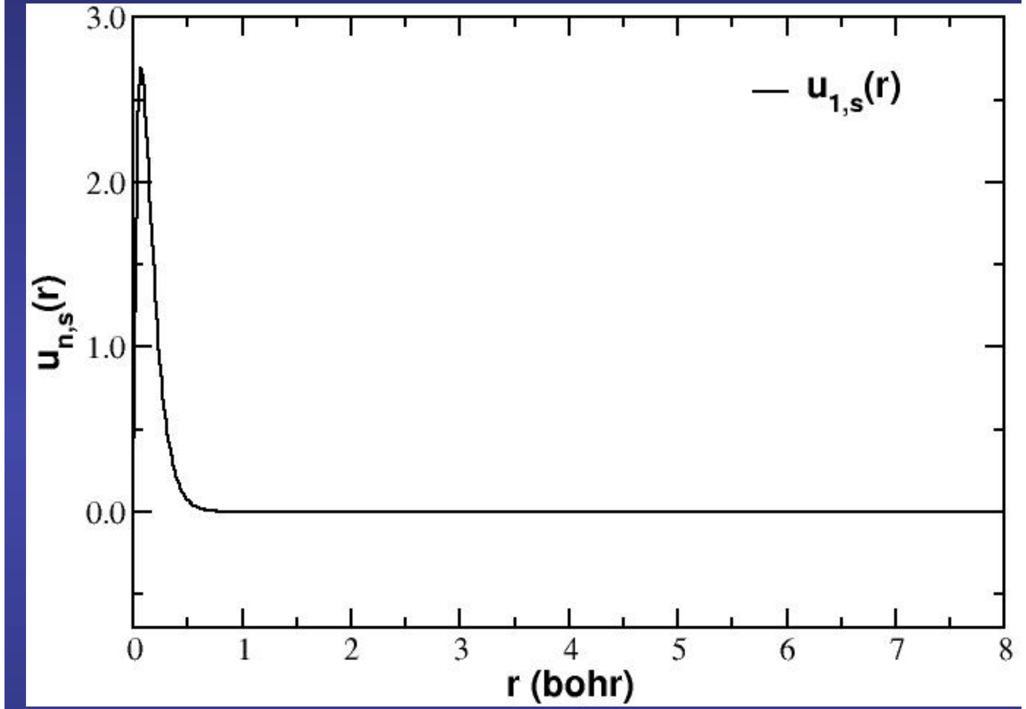
Core

Atomic Si

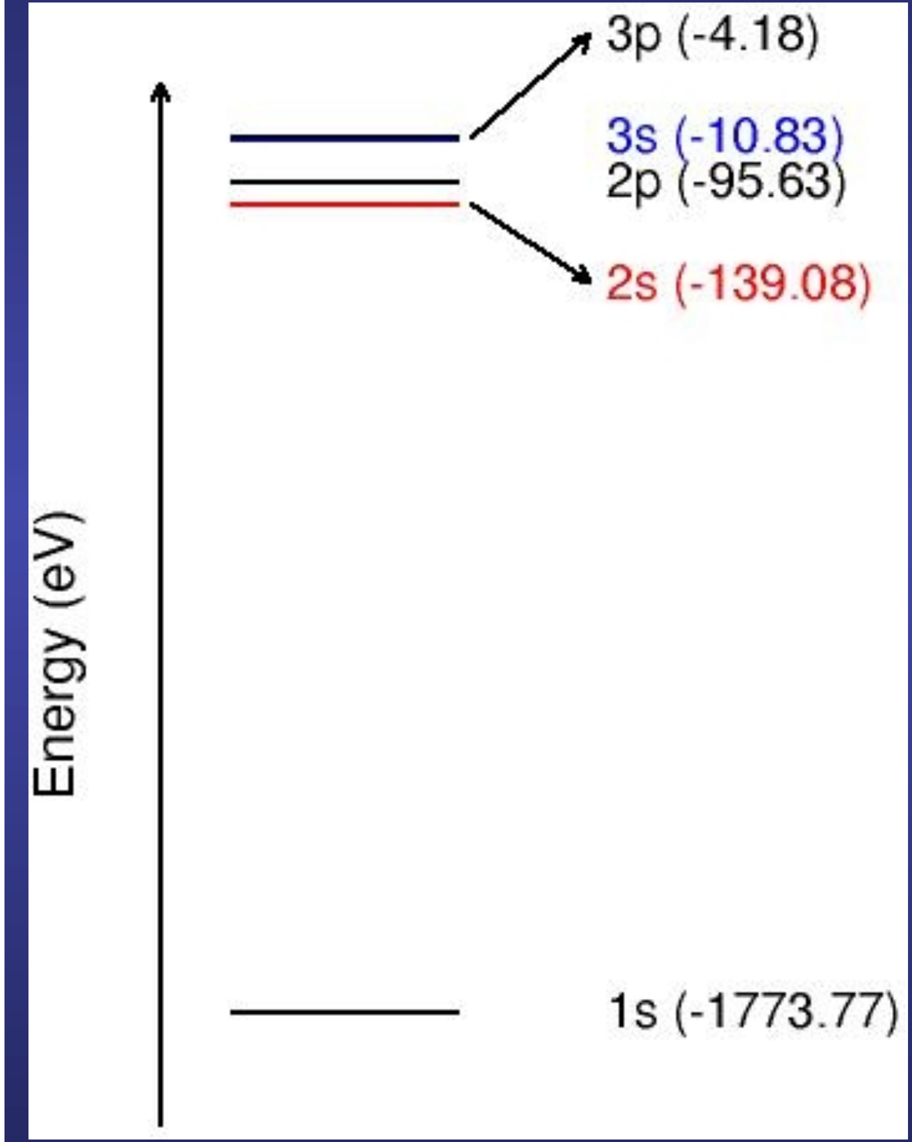
Core wavefunctions are very localized around the nuclei



Atomic Si



Core wavefunctions are very localized around the nuclei



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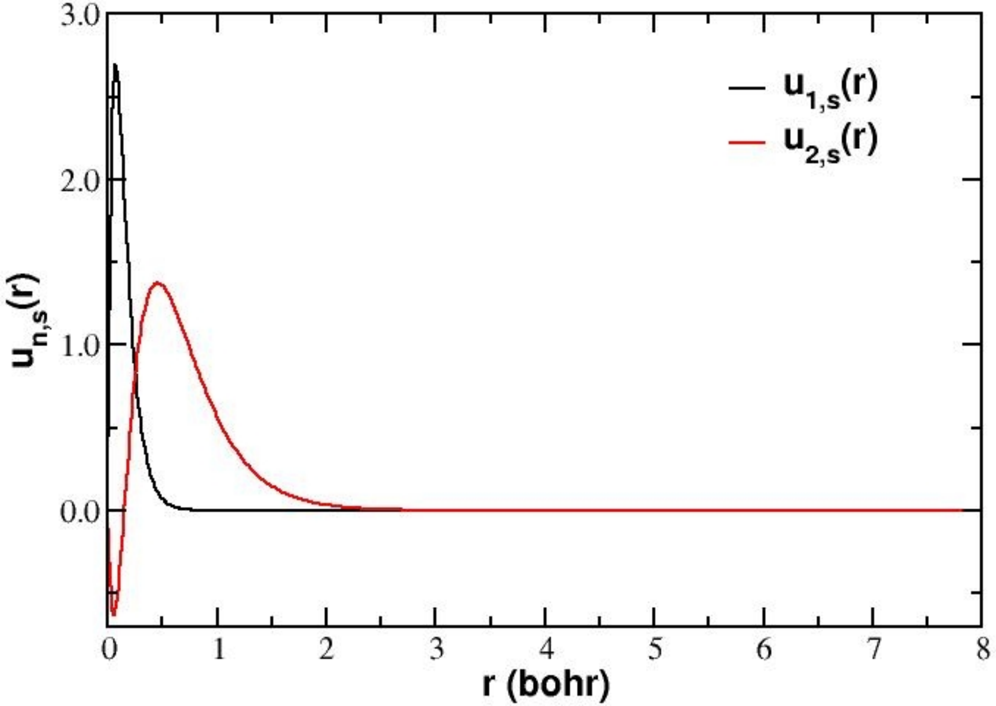


Core electrons…

highly localized

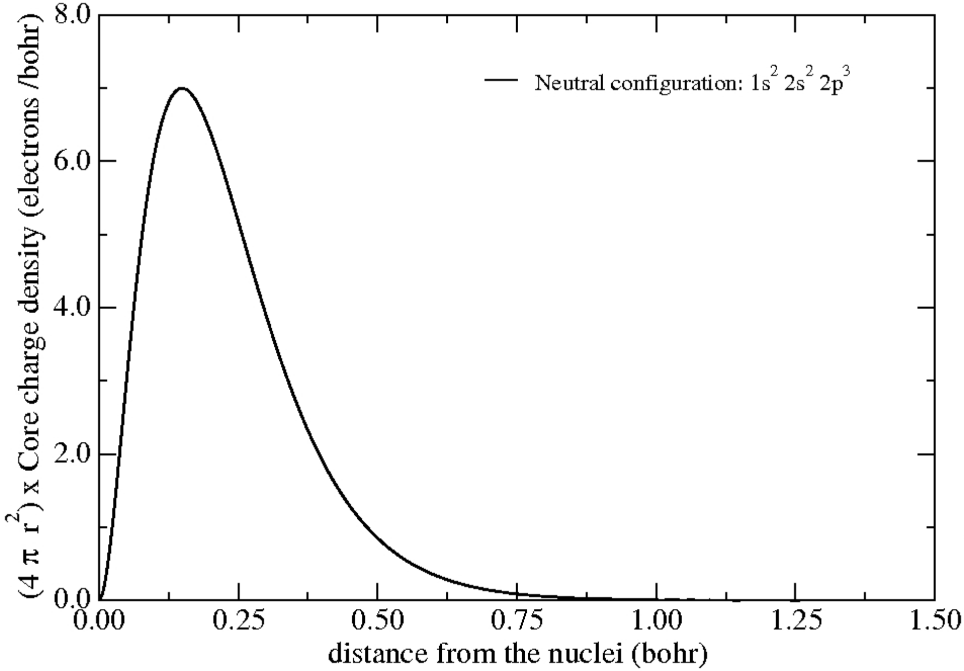
very depth energy

… are chemically inert

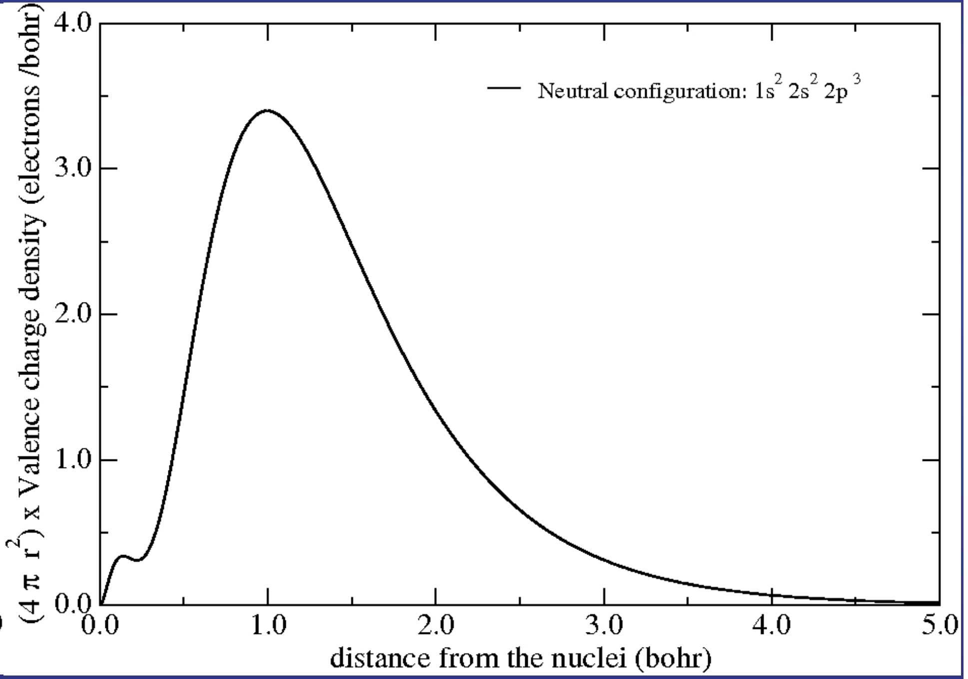
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



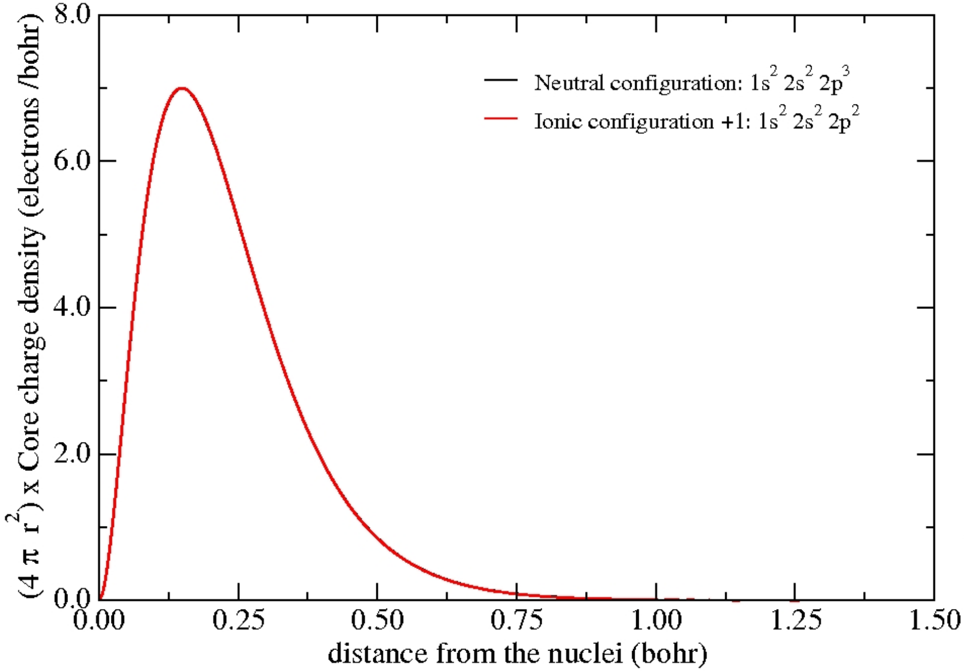
Valence charge density



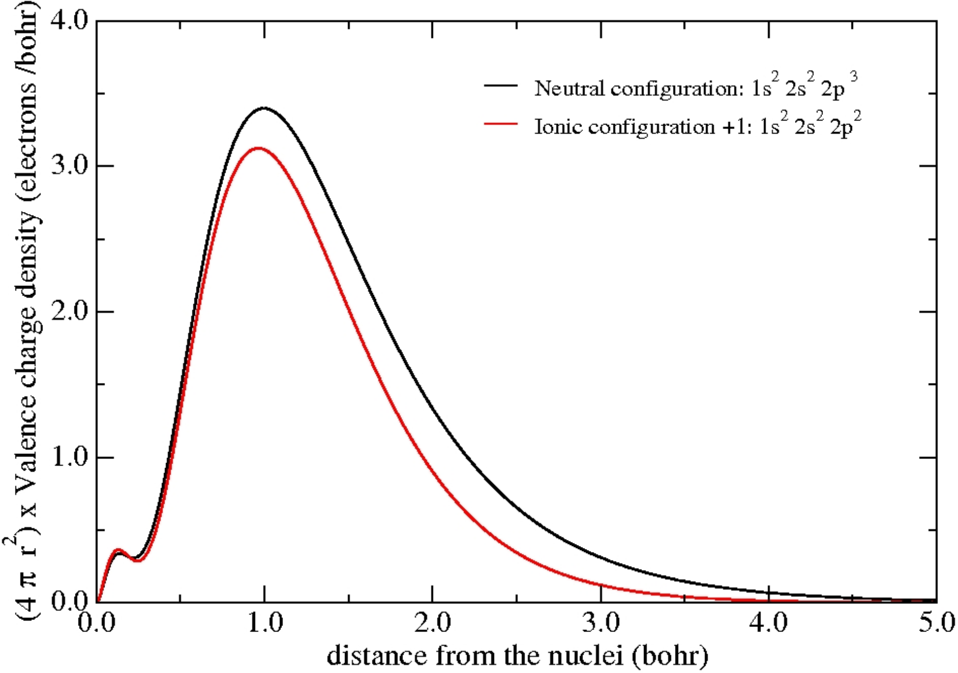
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



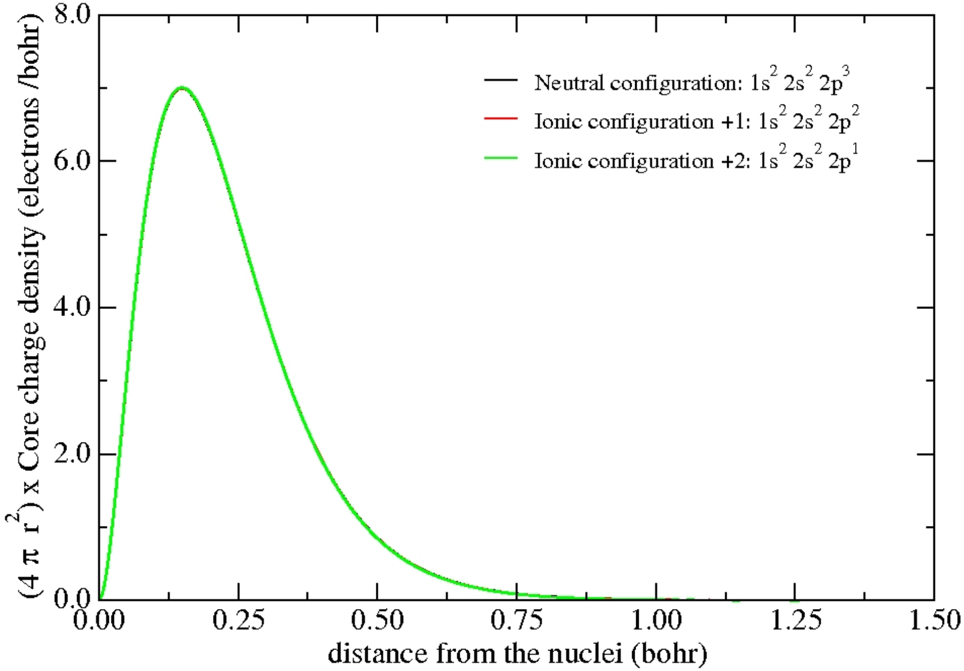
Valence charge density



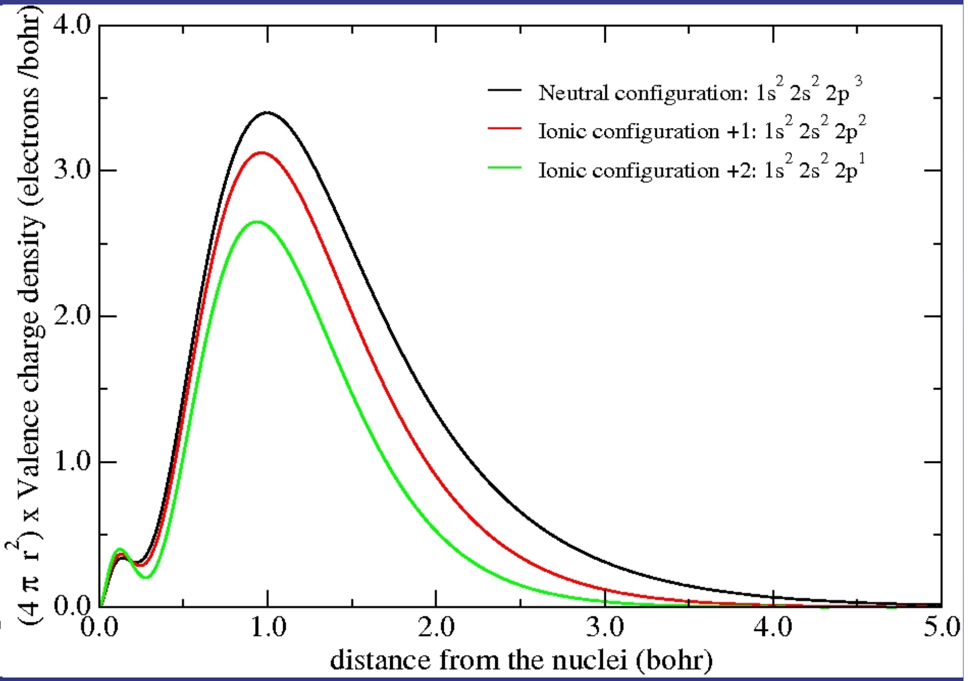
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



Valence charge density



Core electrons are chemically inert

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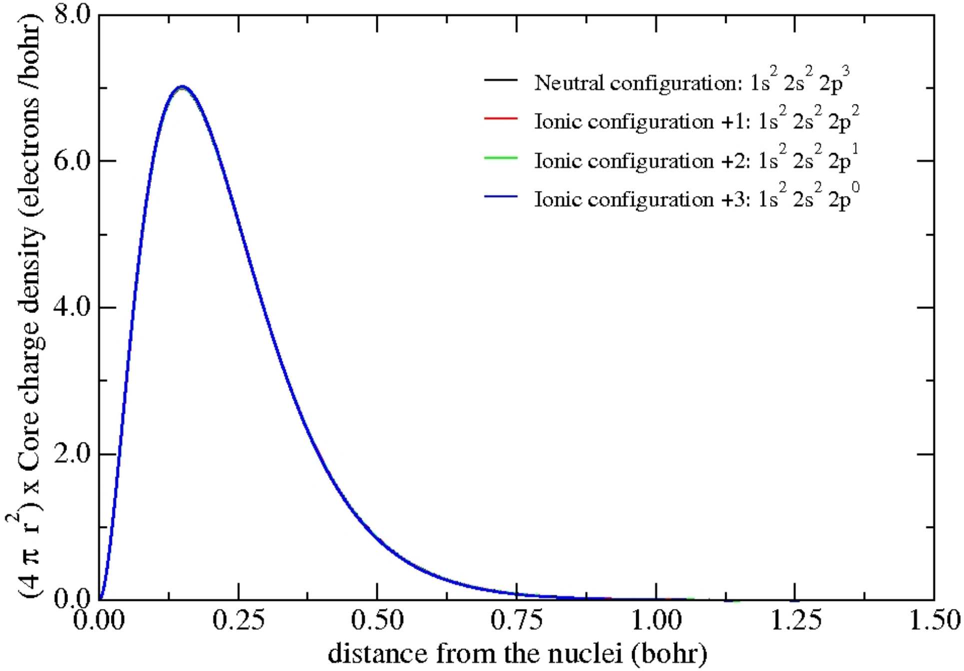
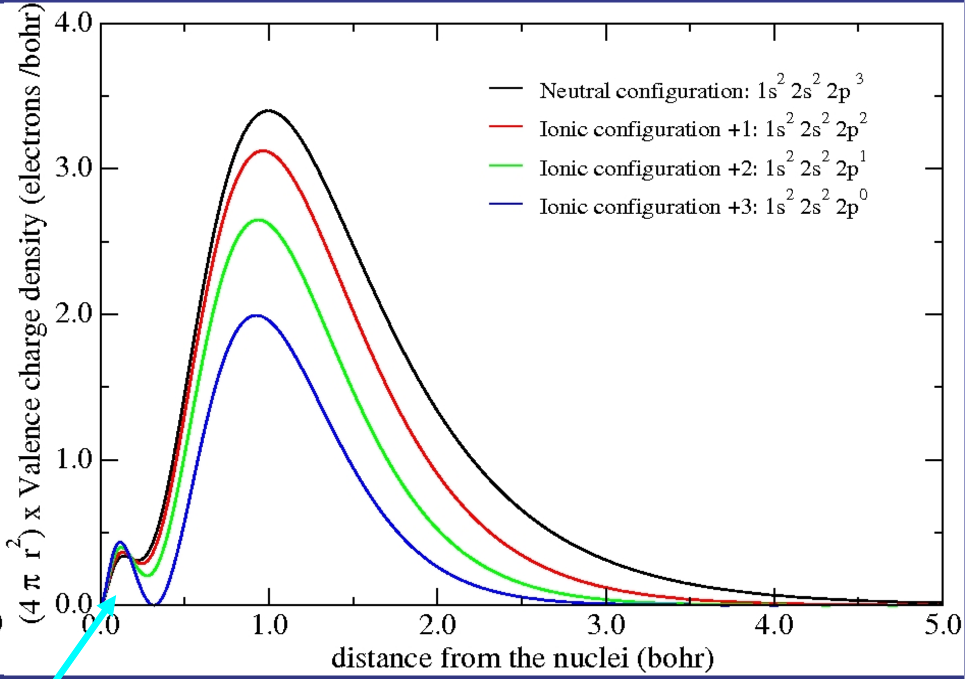
Core charge density



Valence charge density

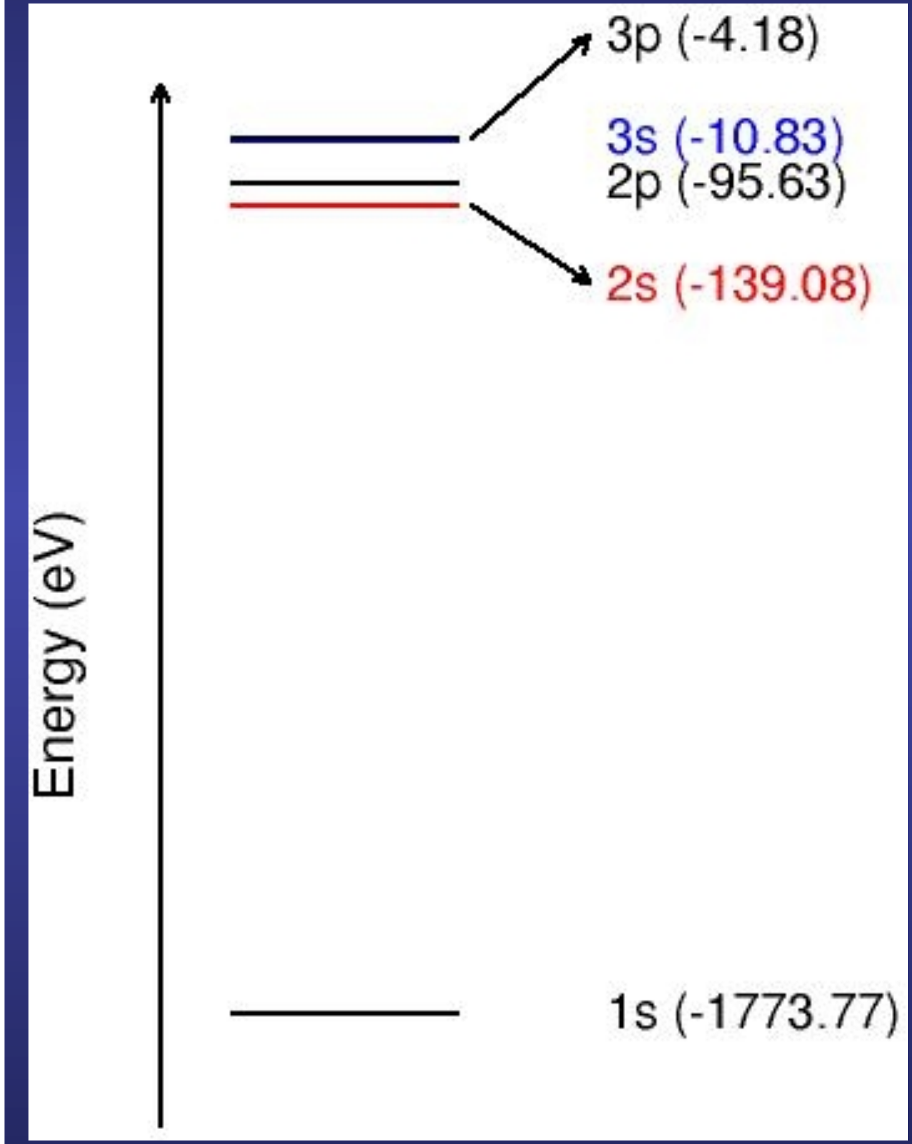


The core charge density remains unperturbed

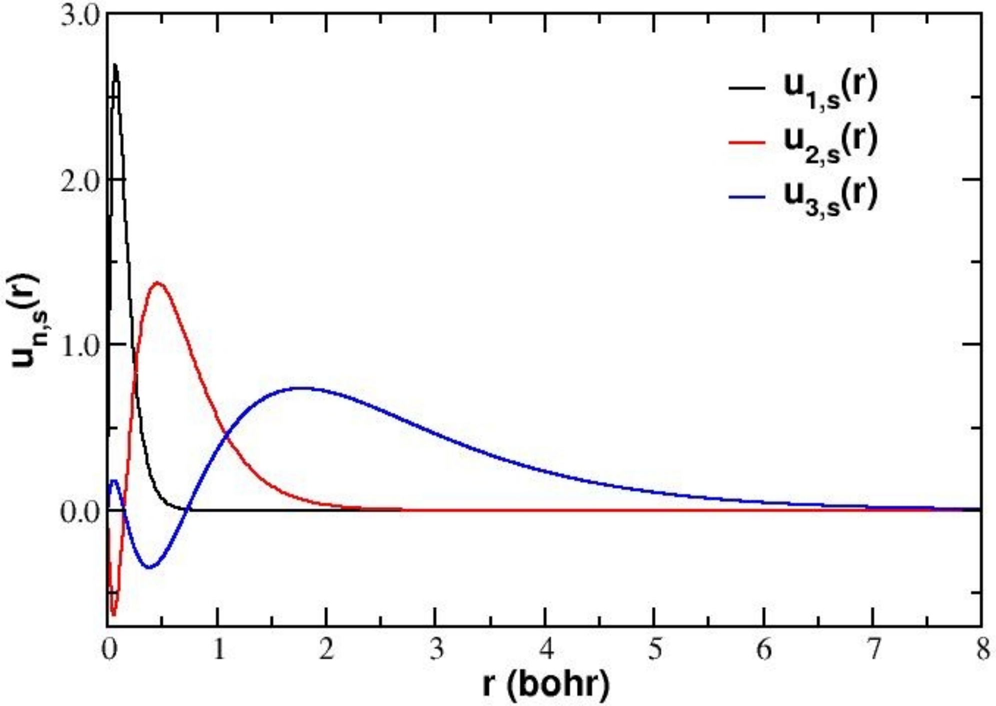
Although there are drastic modifications in the valence charge density

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

Valence wave functions must be orthogonal to the core wave functions



Atomic Si



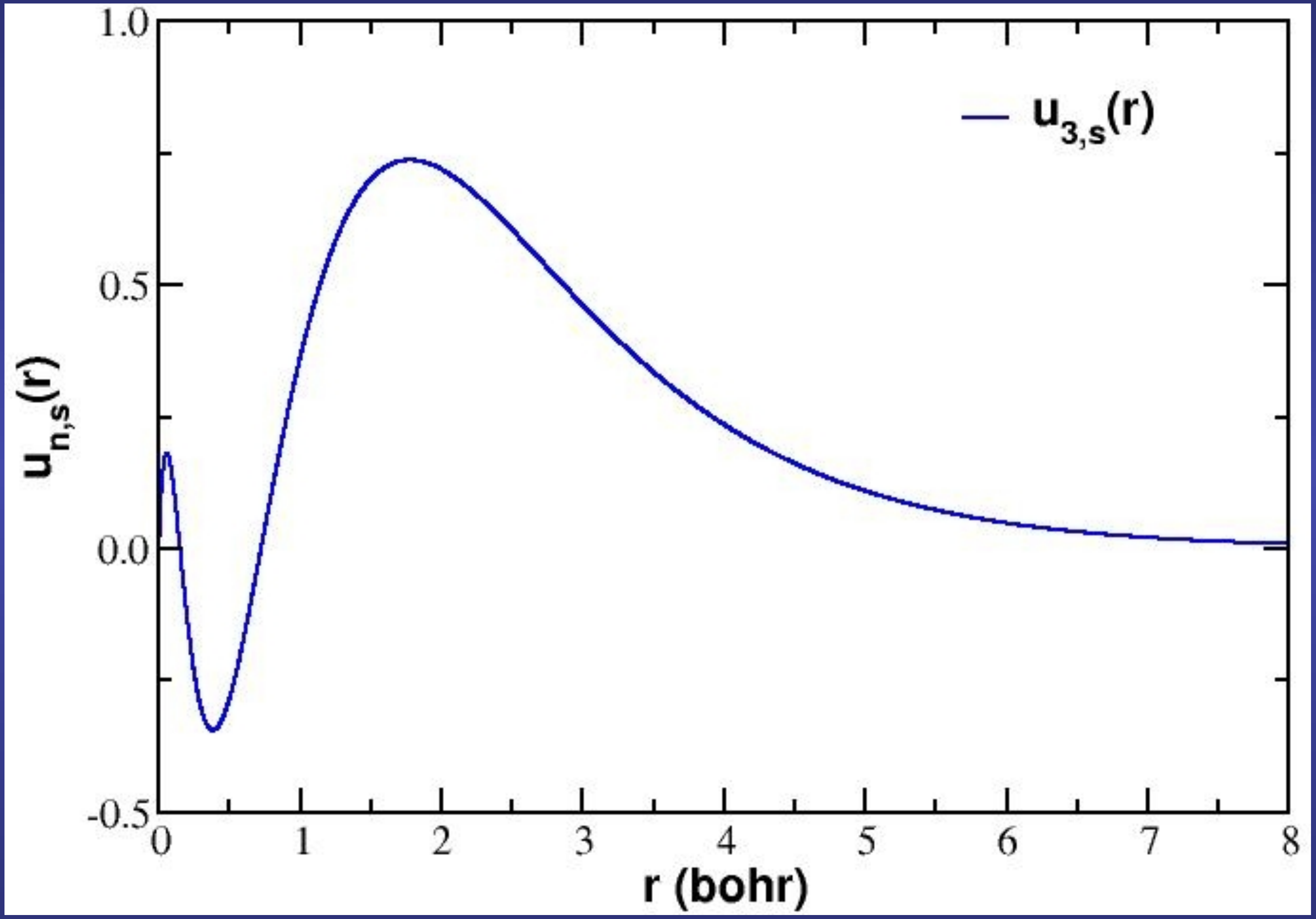
Core electrons…

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

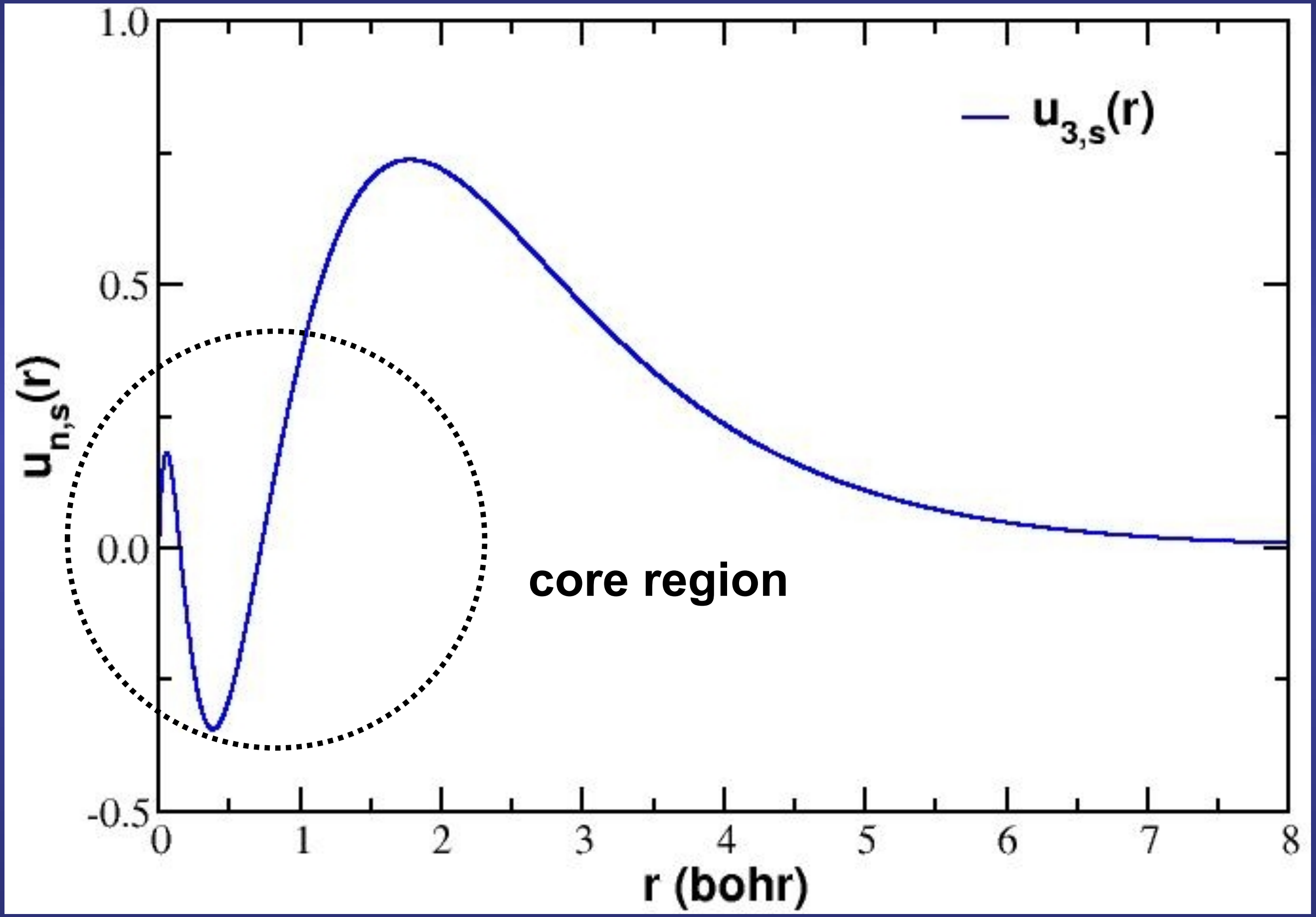
Core electrons main effect: screen nuclear potential

Idea:

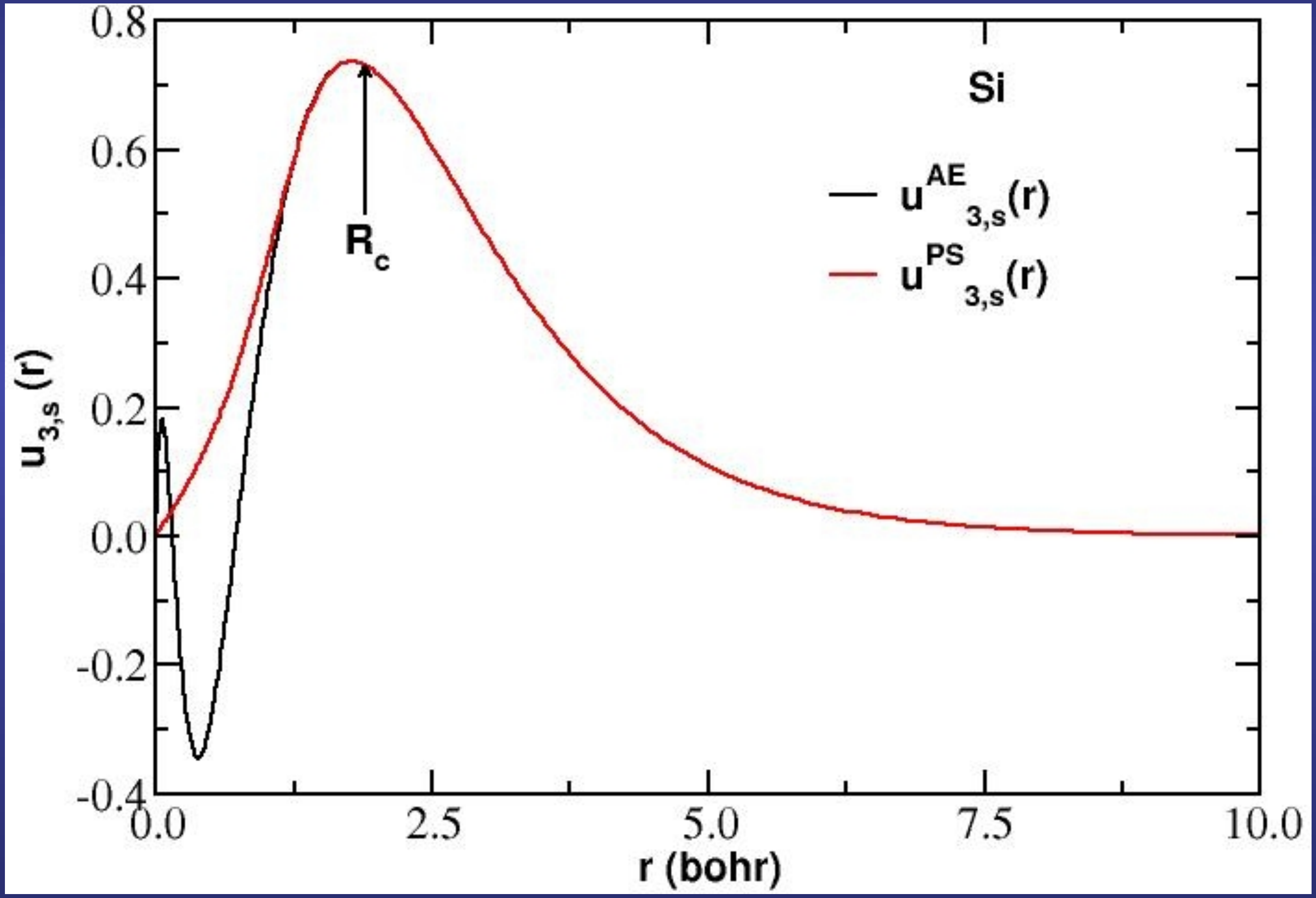
Ignore the dynamics of the core electrons (freeze them)

And replace their effects by an effective potential

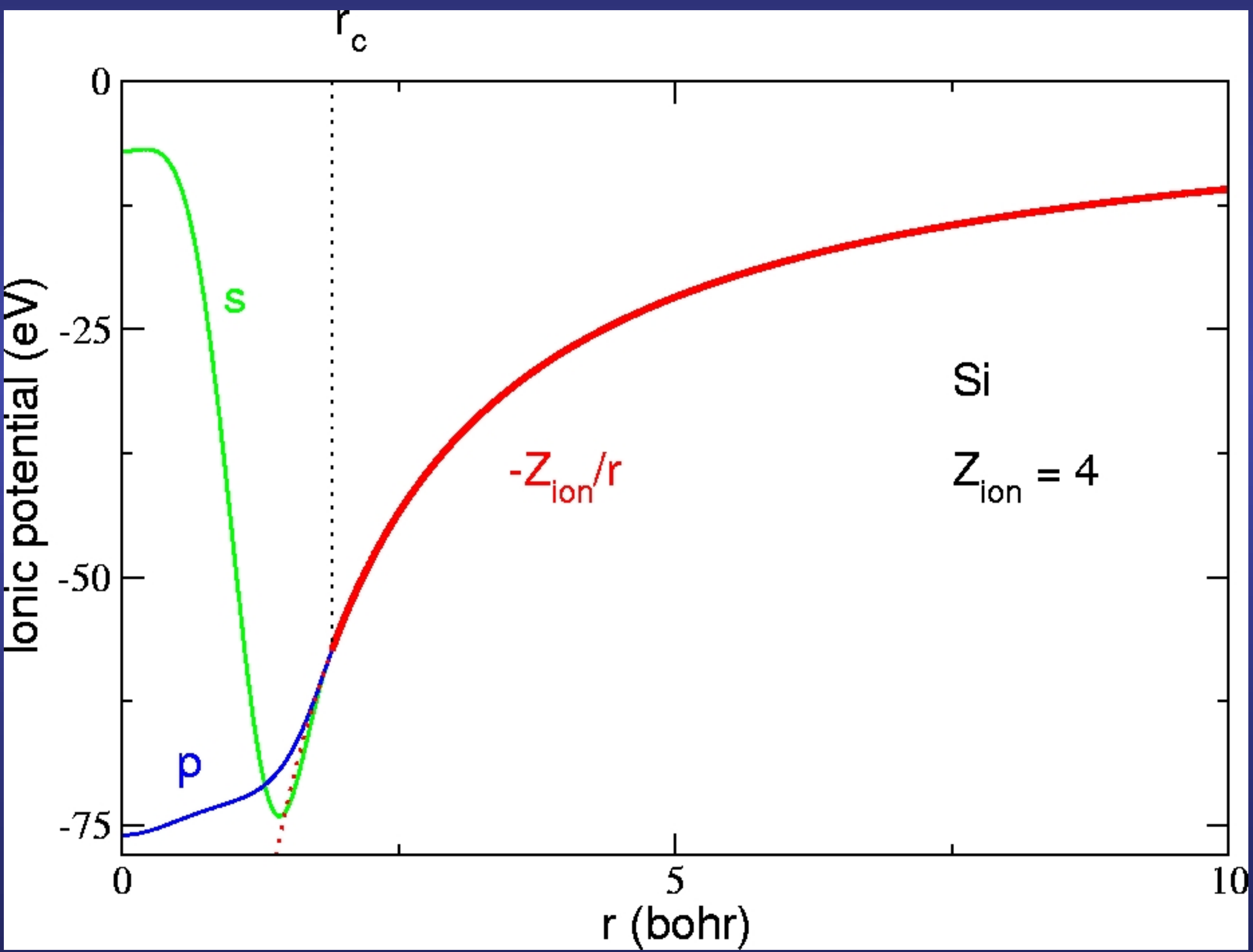
The nodes are imposed by orthogonality to the core states



Idea, eliminate the core electrons by ironing out the nodes



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

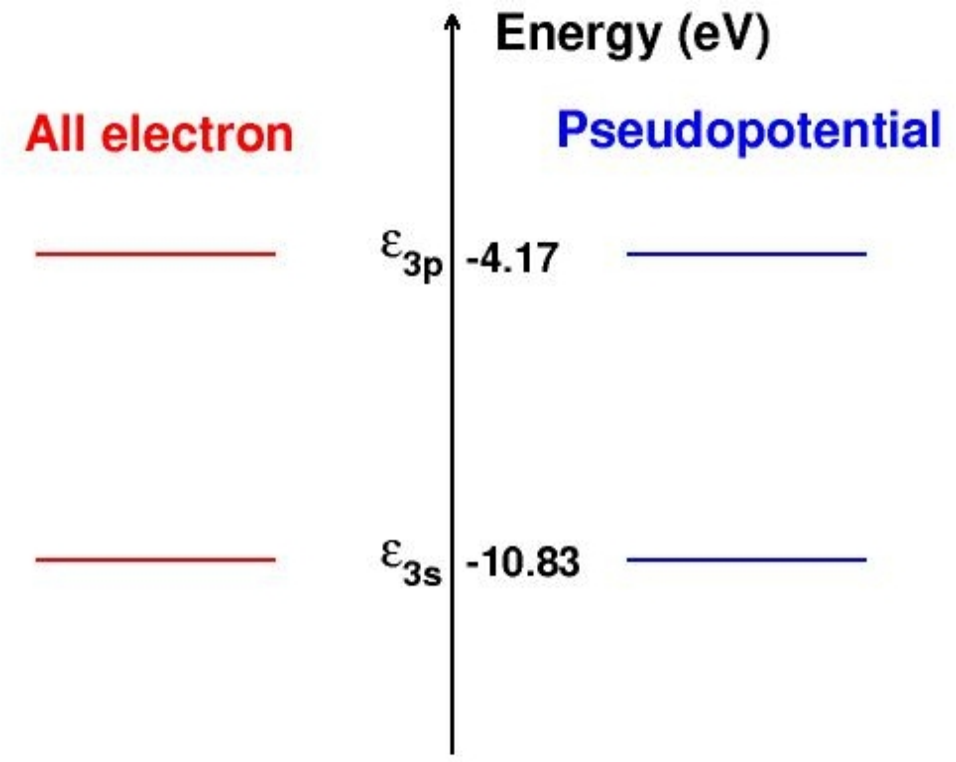


List of requirements for a good norm-conserving pseudopotential:

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

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

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



List of requirements for a good norm-conserving pseudopotential:

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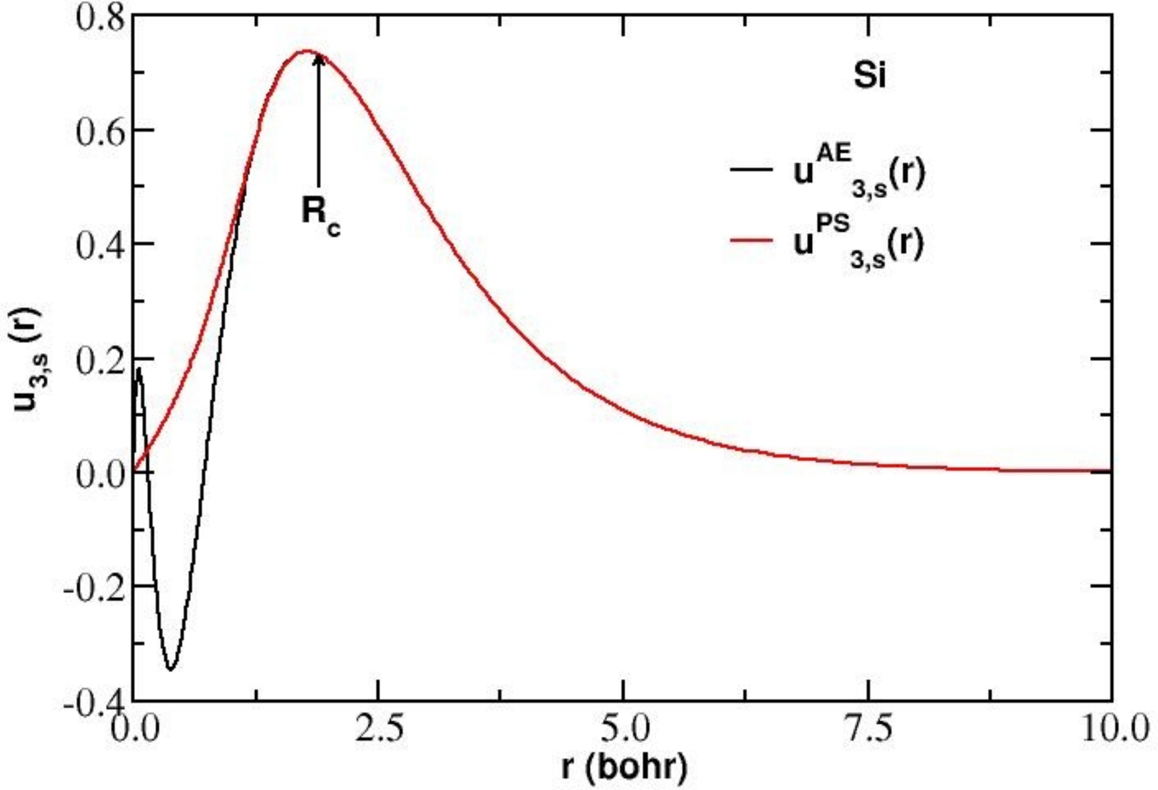
Choose an atomic reference configuration Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$

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

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

$\Downarrow$

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

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:

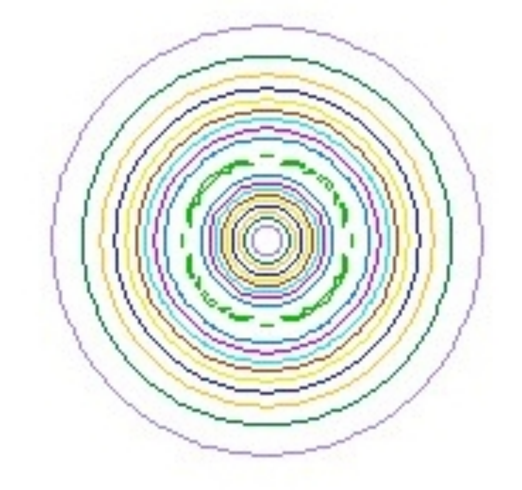
Norm conservation [(4)] ⇒ (5)

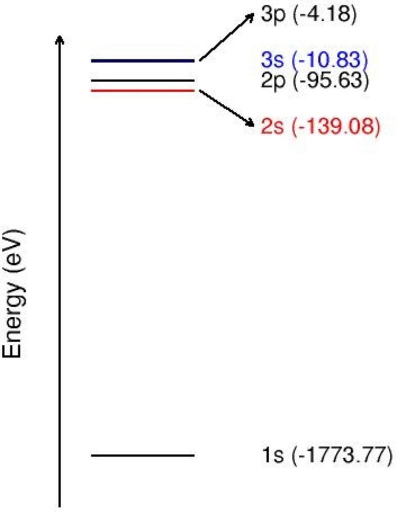
$$2\pi\left[(r\psi)^2\frac{d}{d\varepsilon}\frac{d}{dr}ln\psi\right]_R = 4\pi\int_0^R r^2\psi^2 dr$$

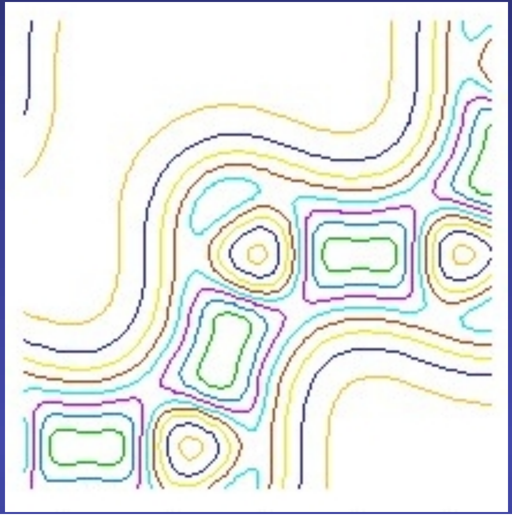
Equality of AE and PS energy derivatives of the logarithmic derivatives essential for transferability

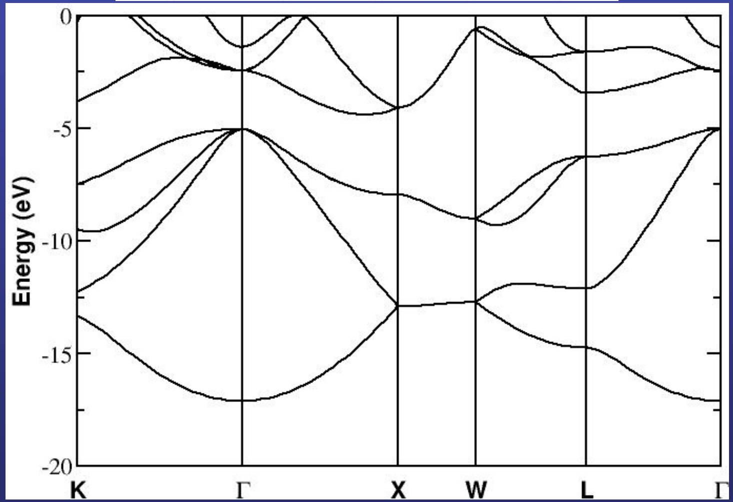
Atomic Si

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 pseudopotential

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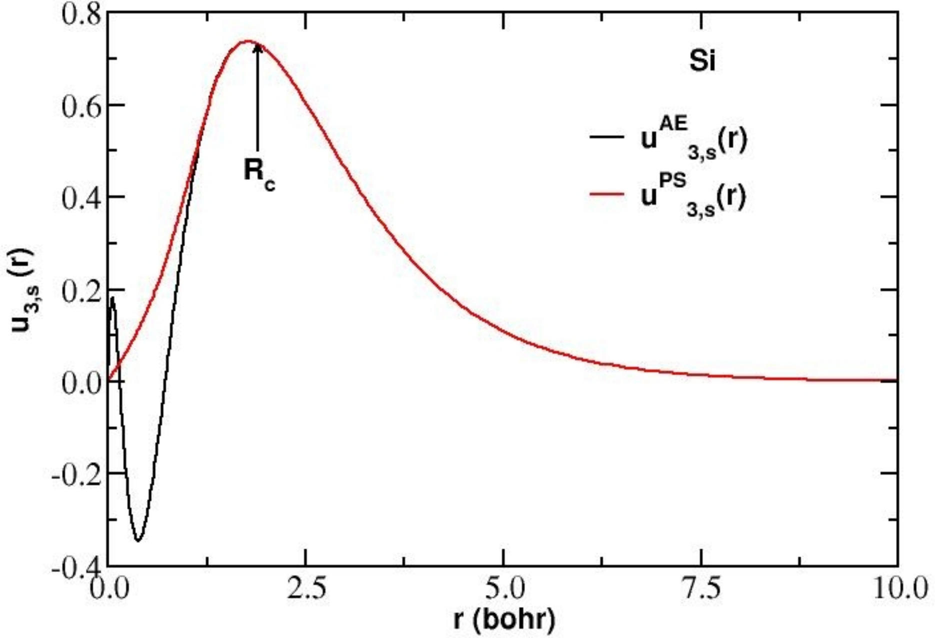
$$V_{\text{eff}}[n](r)=V_{\text{ext}}(r)+V_{\text{Hartree}}[n]+V_{xc}[n]=-\frac{Z}{r}+\int\frac{n(r^{'})}{|r-r^{'}|}dr^{'}+V_{xc}[n]$$

$n(r)$ ≡ 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)]

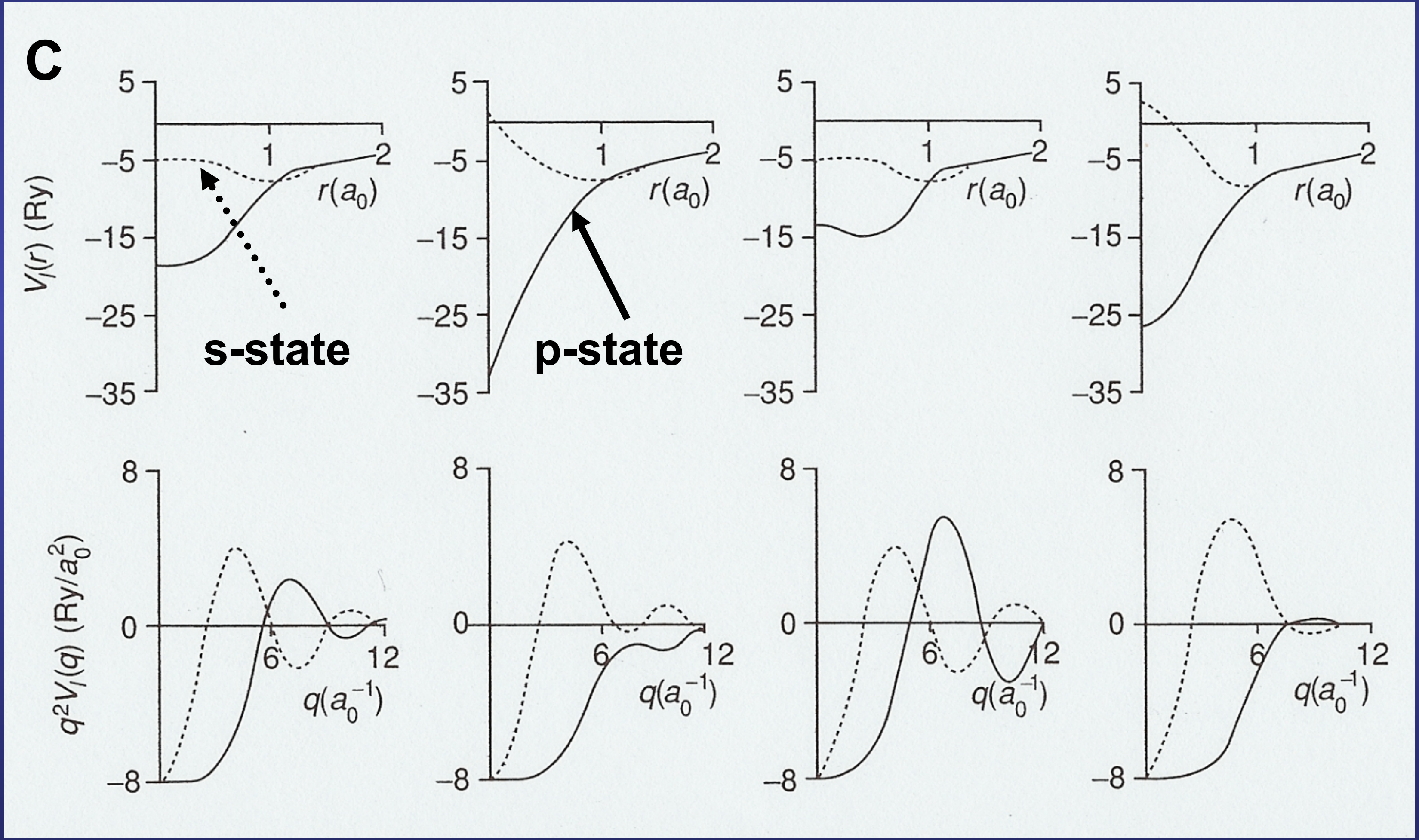
Kerker [G. P. Kerker, J. Phys. C 13, L189 (1980)]

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)]

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

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

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

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

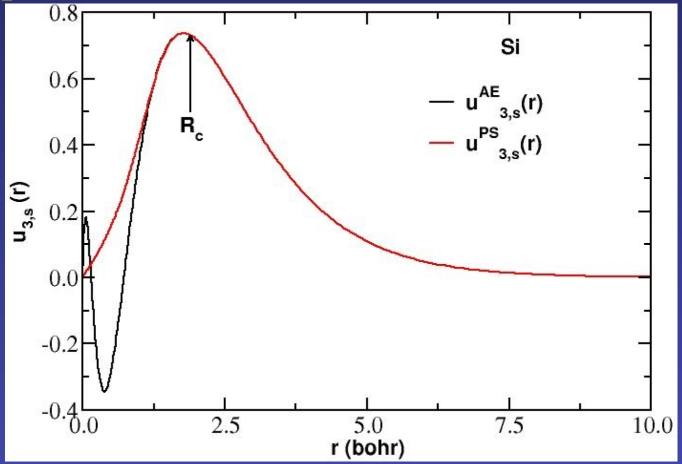
$n(r)$ **≡ sum of electronic charges for occupied states**

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

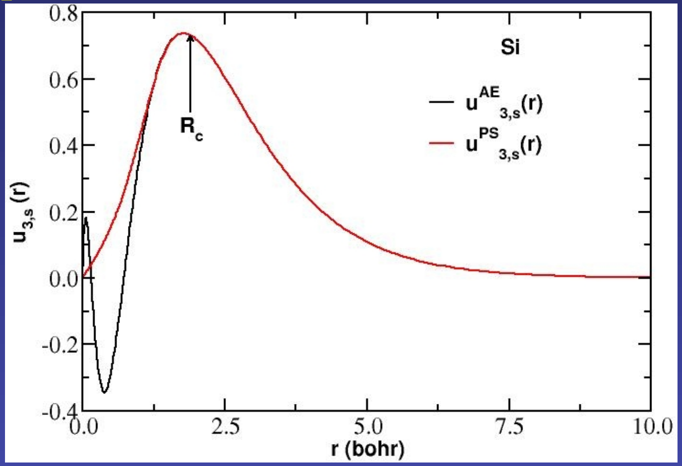
$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V^{\mathrm{PS}}_{(\mathrm{sc})l}(r)\right]u^{\mathrm{PS}}_l(r)=\varepsilon_l u^{\mathrm{PS}}_l(r)$$

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

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

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

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

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

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

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

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

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

Z ≡bare nuclear charge

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

Invert the radial Schrödinger equation for the screened pseudopotential

Subtract (unscreen) the Hartree and exchange-correlation potentials

Generation of l-dependent norm-conserving pseudo: Step 5, unscreening of the pseudopotential

The pseudo-wave function obeys

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

Where the effective potential is computed in the atom

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

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

Computed with an atomic charge density

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

Blind to the chemical environment

Extremely dependent on the chemical environment

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

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)

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

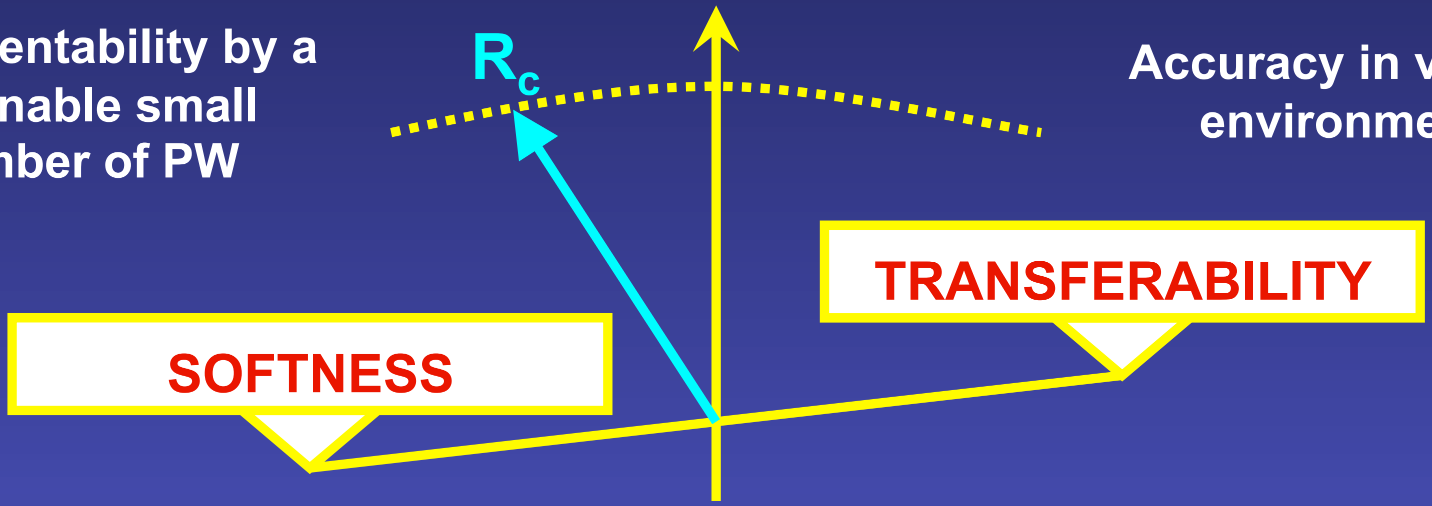
Where the pseudo-valence charge density is computed as

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

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

Balance between softness and transferability controlled by R_c

Representability by a resonable small number of PW



R_c

SOFTNESS

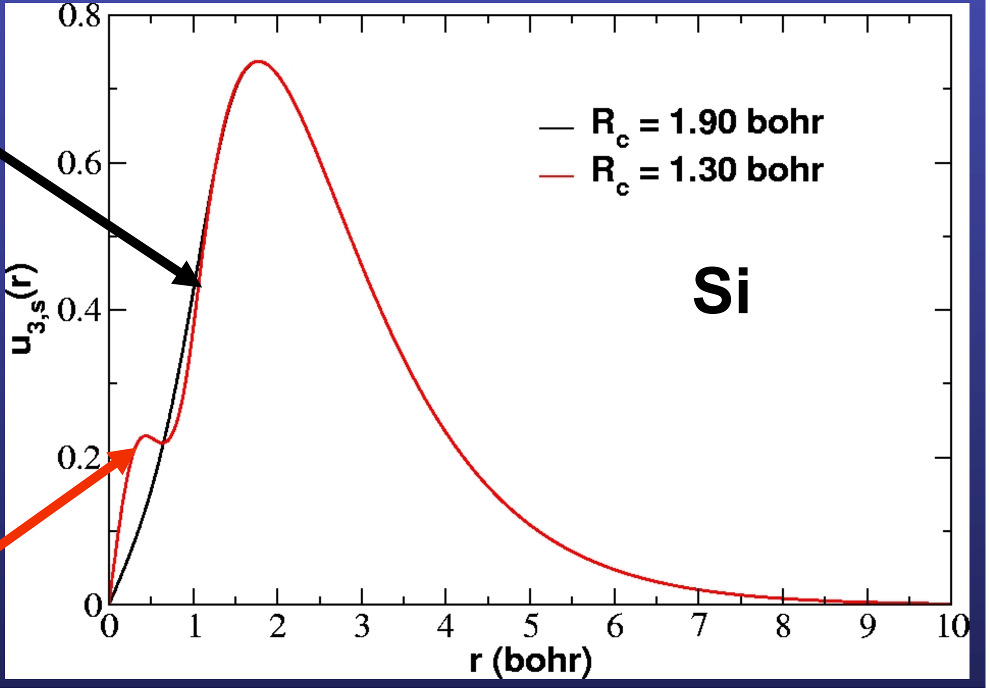
TRANSFERABILITY

Accuracy in varying environments

Larger R_c: softer pseudo

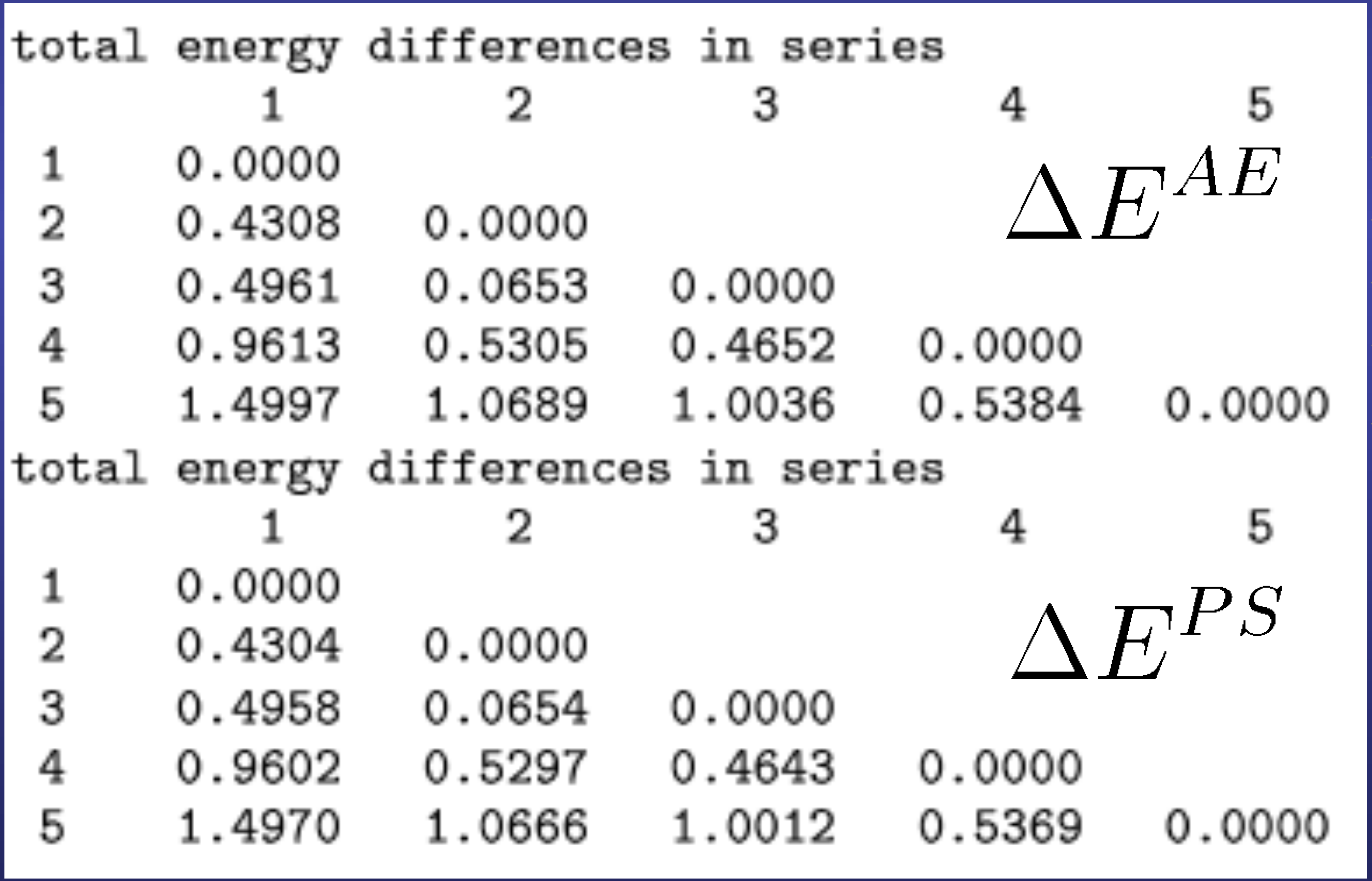
First guess: last peak of the all electron wave function

Shorter R_c: harder pseudo



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)

$3s^2\ 3p^1\ 3d^1$

$3s^1\ 3p^3$

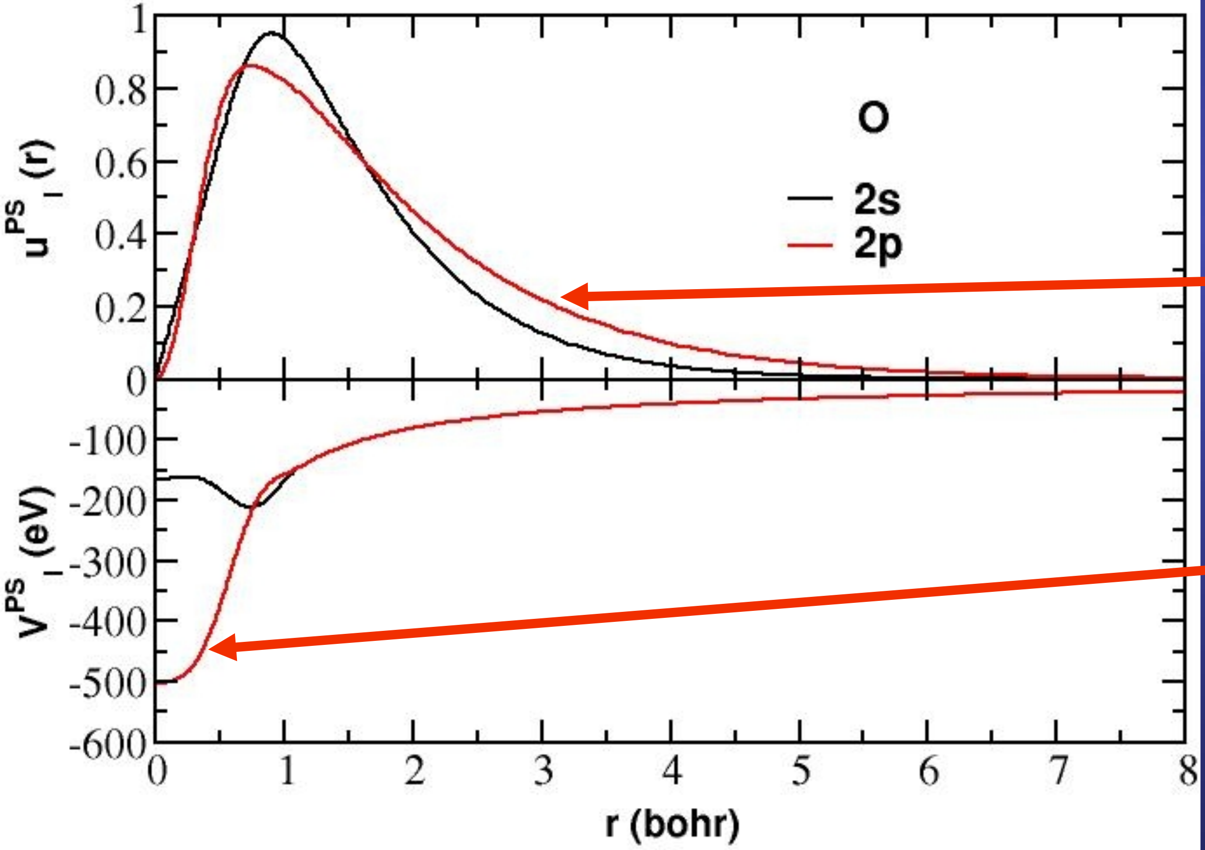
$3s^1\ 3p^2\ 3d^1$

$3s^0\ 3p^3\ 3d^1$

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

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

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**