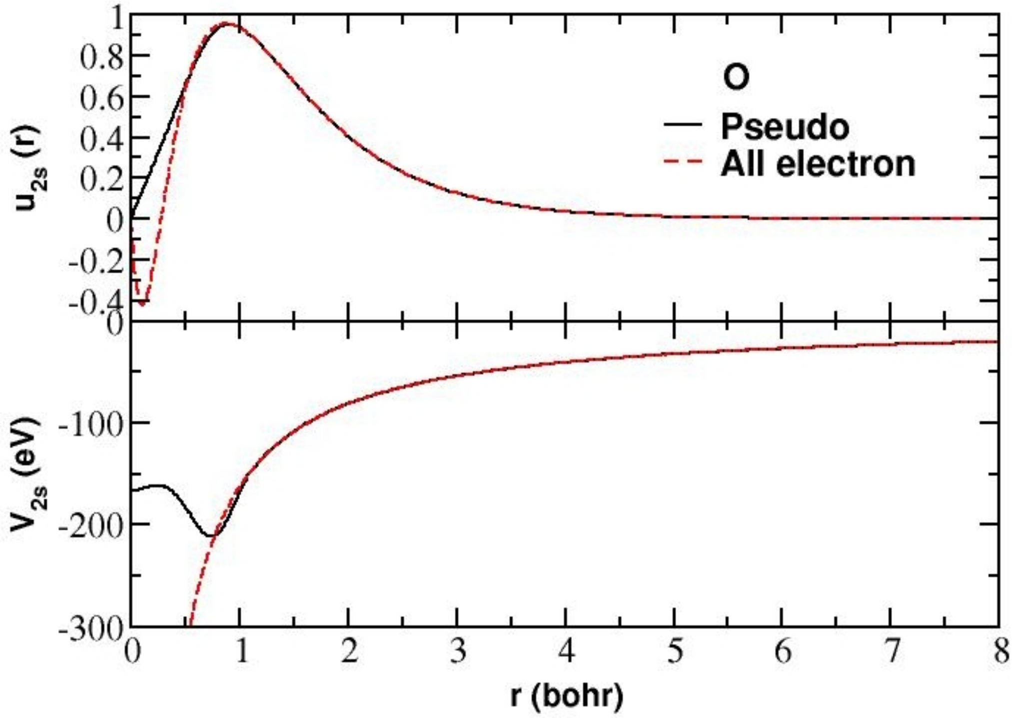
Norm-conserving pseudopotentials in electronic structure calculations



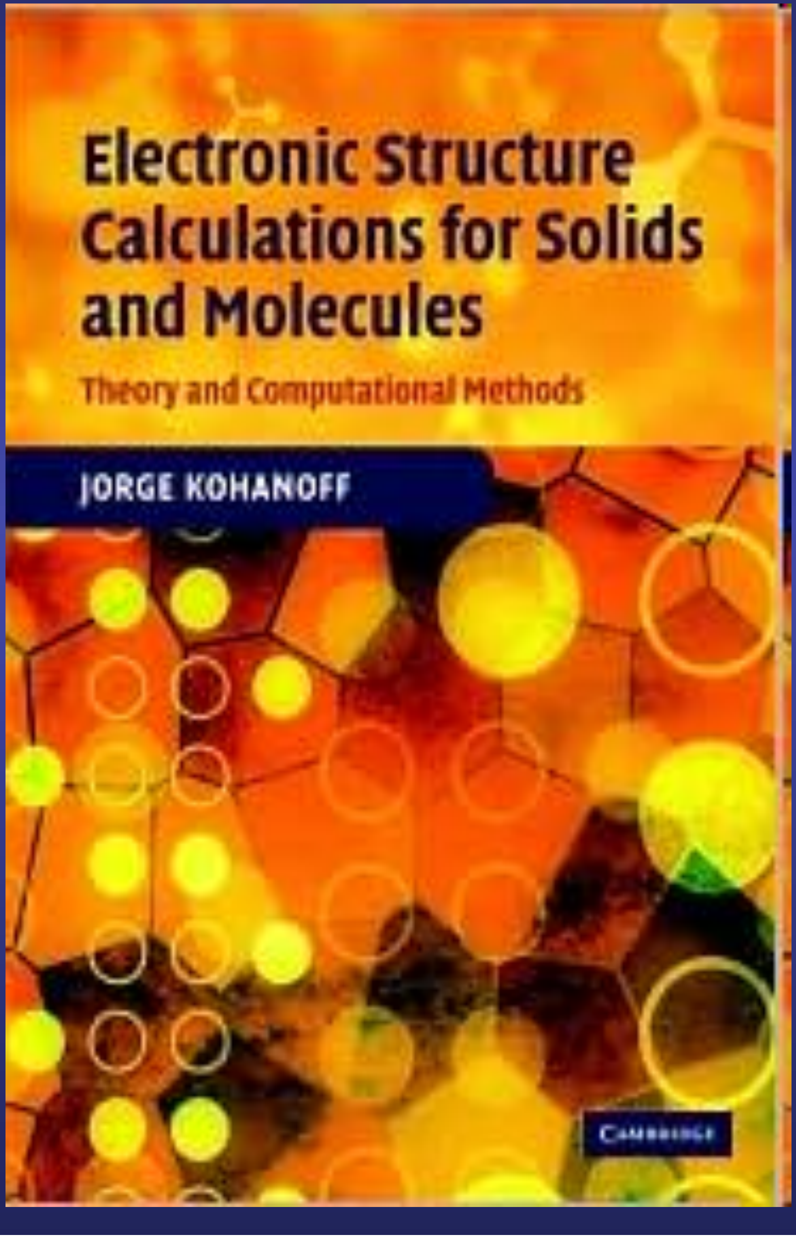
Javier Junquera

UNIVERSIDAD DE CANTABRIA

Alberto García

ICMAB

Bibliography used in the present lecture



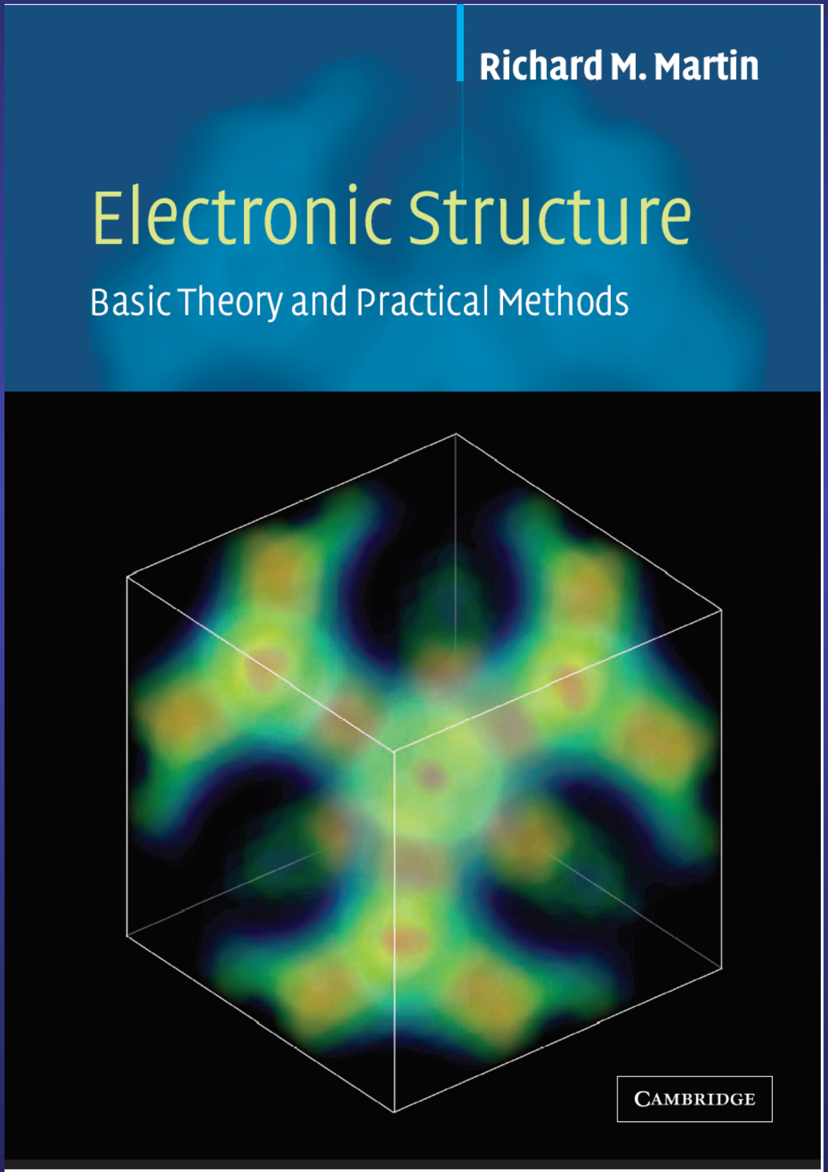
Electronic Structure Calculations for Solids and Molecules

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

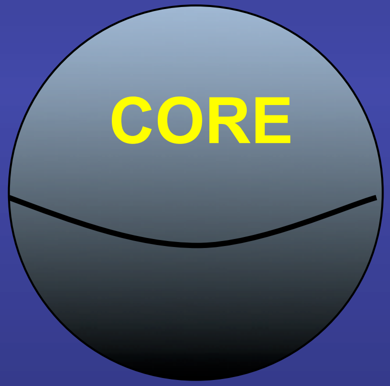
One particle Kohn-Sham equations

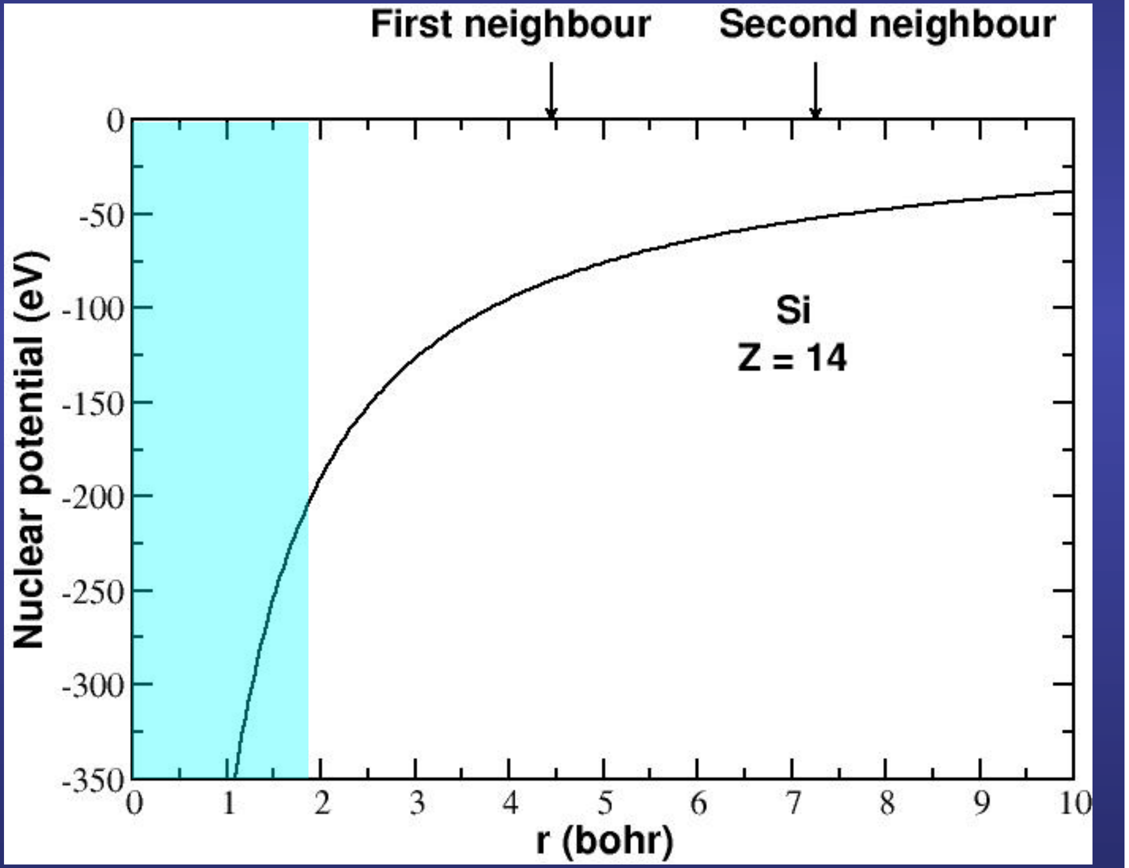
$$\left(\hat{T} + \hat{V}_{ion-e} + \hat{V}_{H} + \hat{V}_{xc}\right)\psi_i = \varepsilon_i \psi_i$$

$$\big\downarrow$$

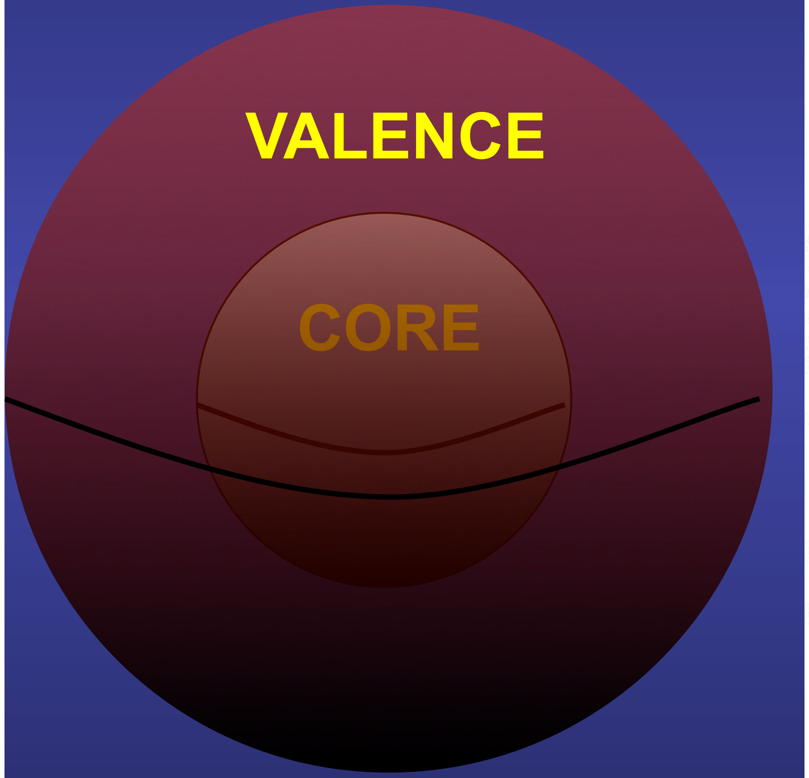
$$-\frac{Ze}{r}$$

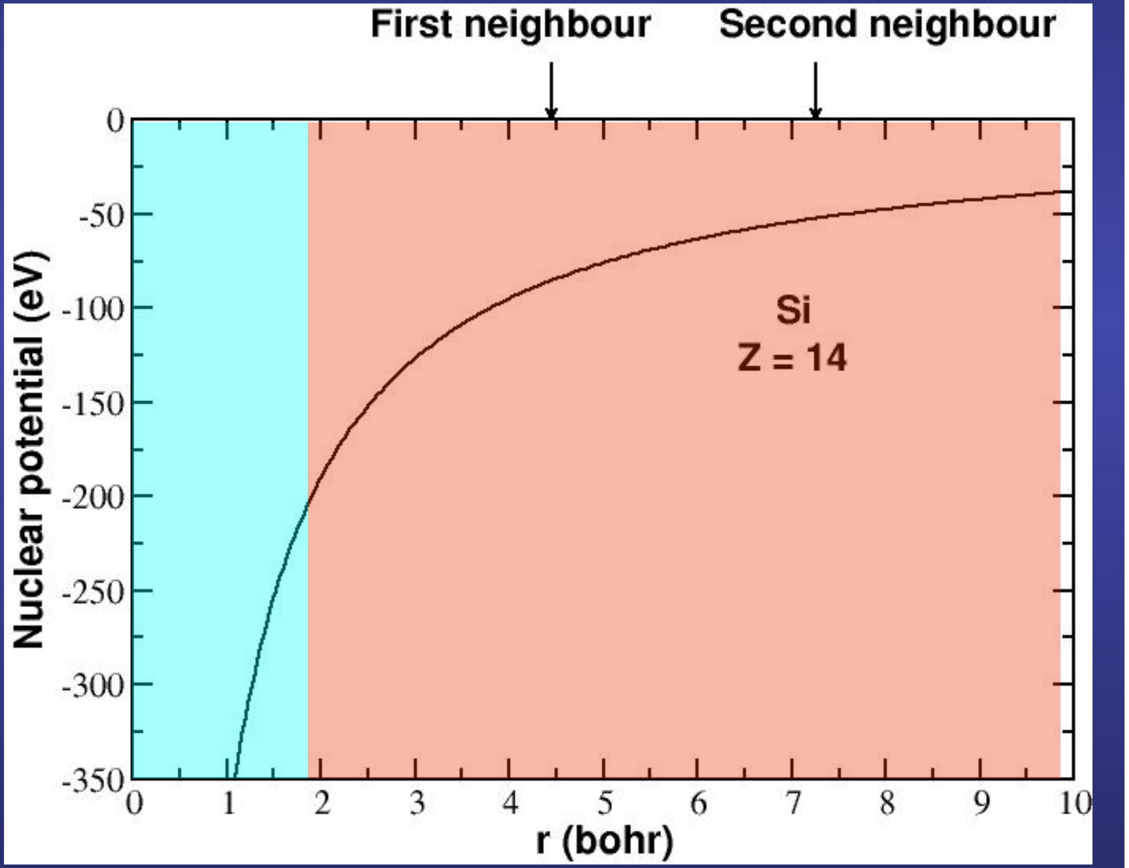
Difficulty: how to deal accurately with both the core and valence electrons



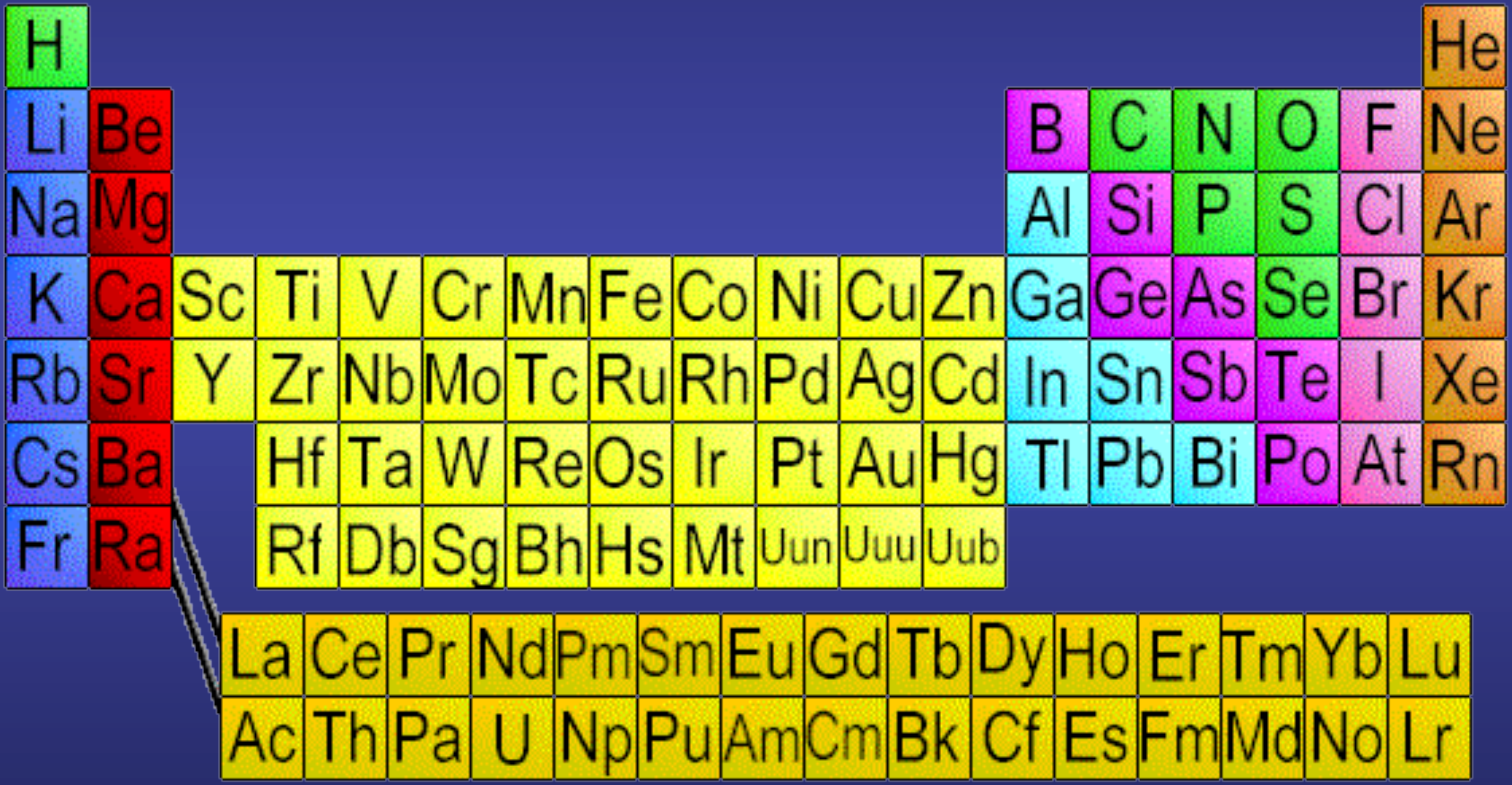


Difficulty: how to deal accurately with both the core and valence electrons





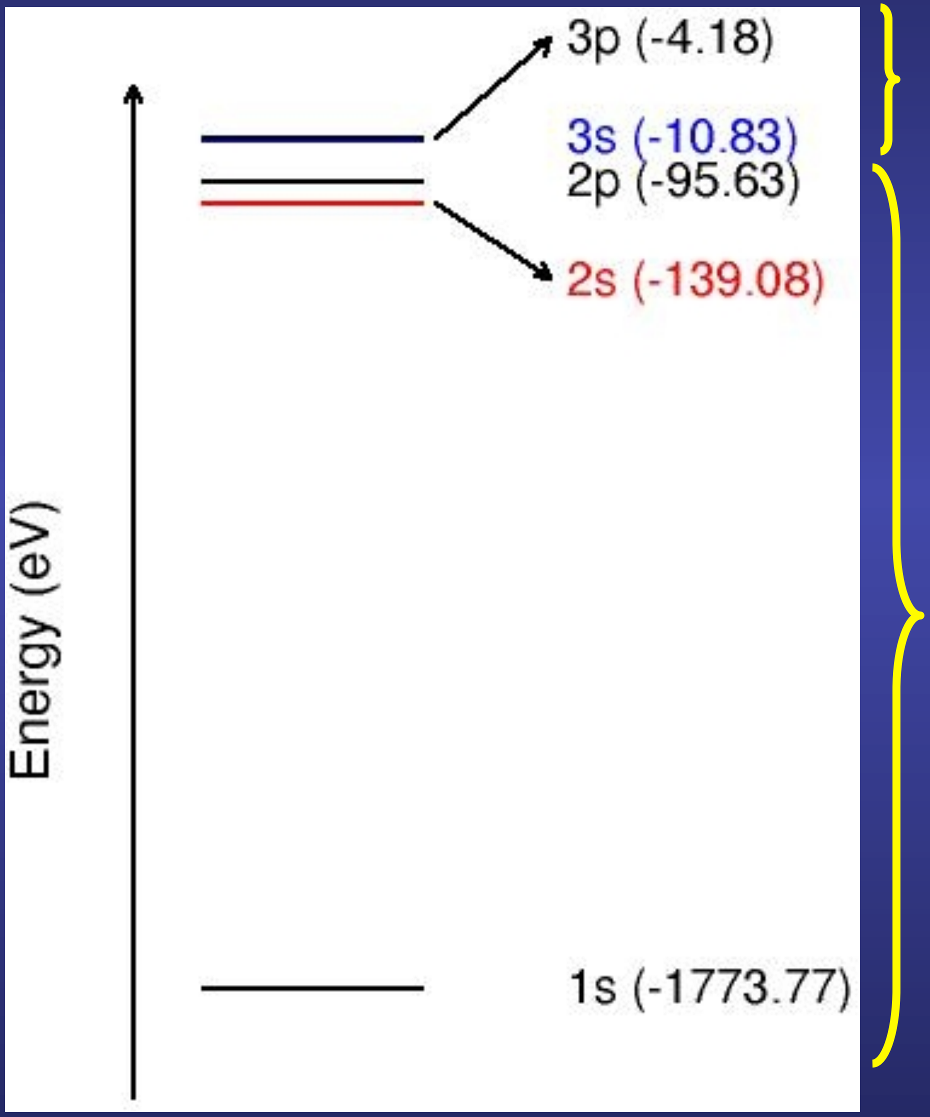
Si atomic configuration: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$



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

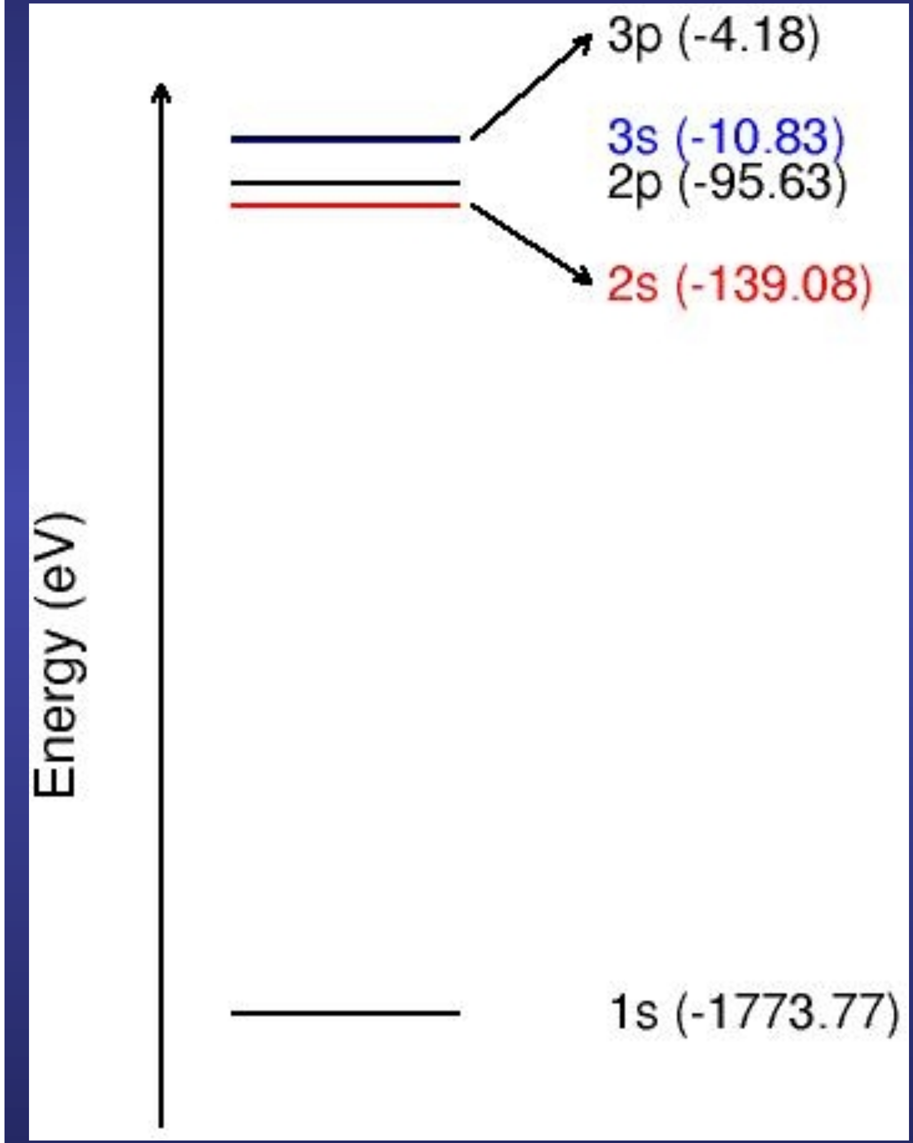


Valence

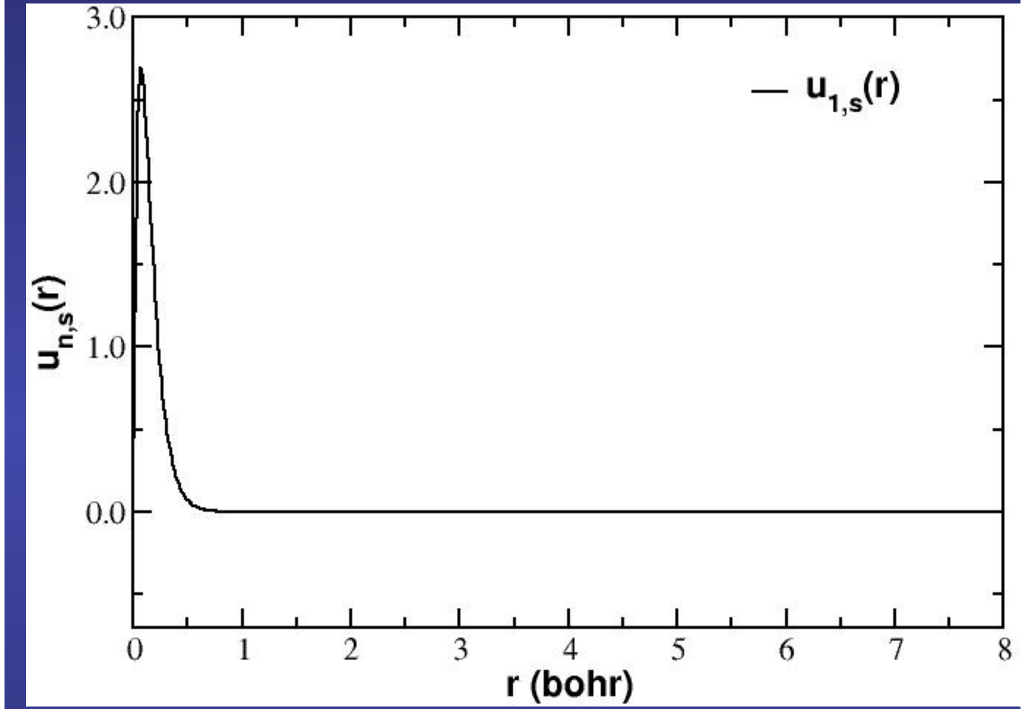
Core

Atomic Si

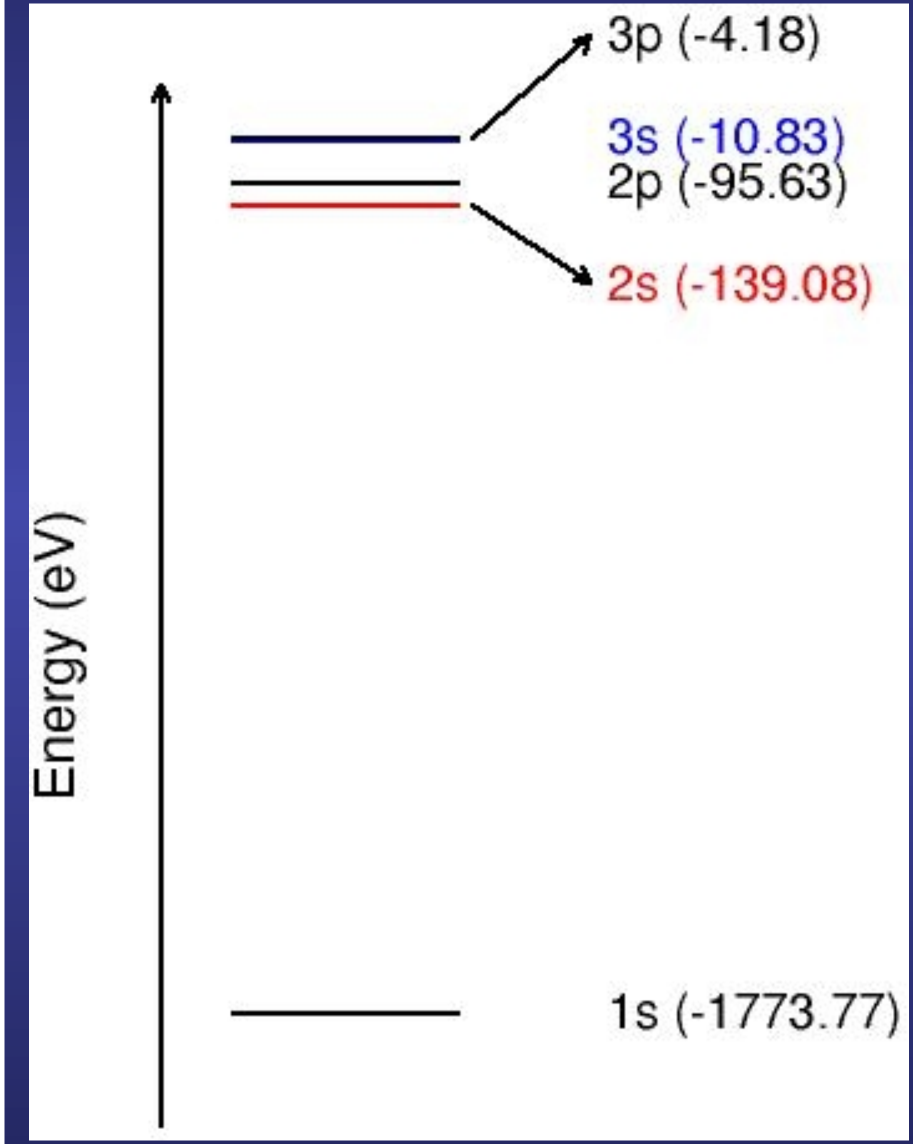
Core wavefunctions are very localized around the nuclei



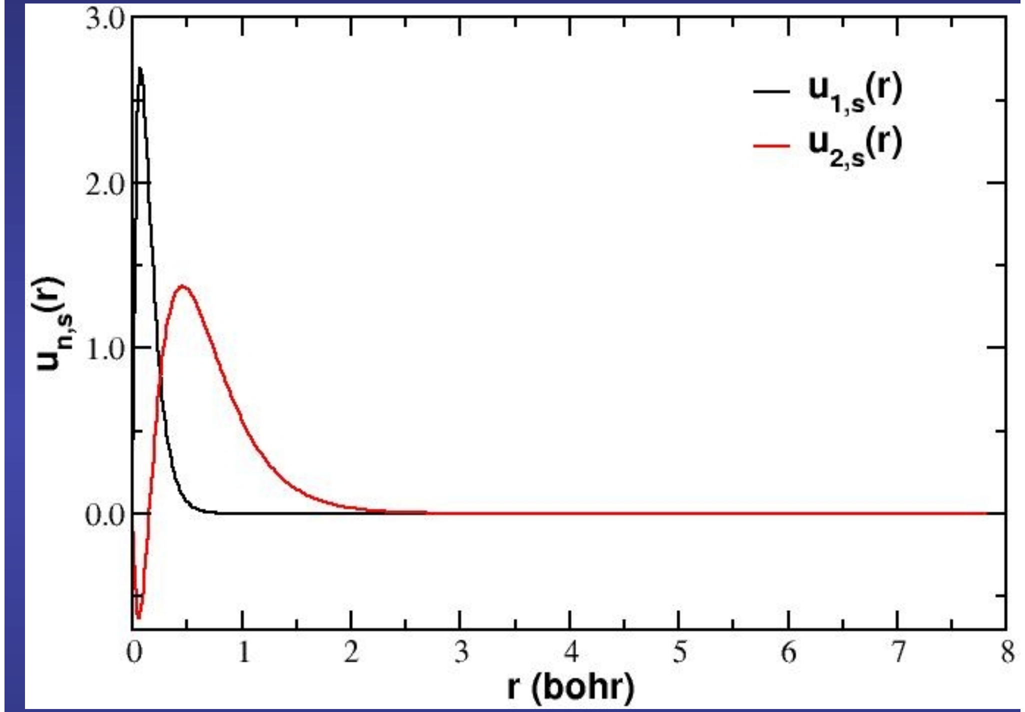
Atomic Si



Core wavefunctions are very localized around the nuclei



Atomic Si



Core electrons…

highly localized

very depth energy

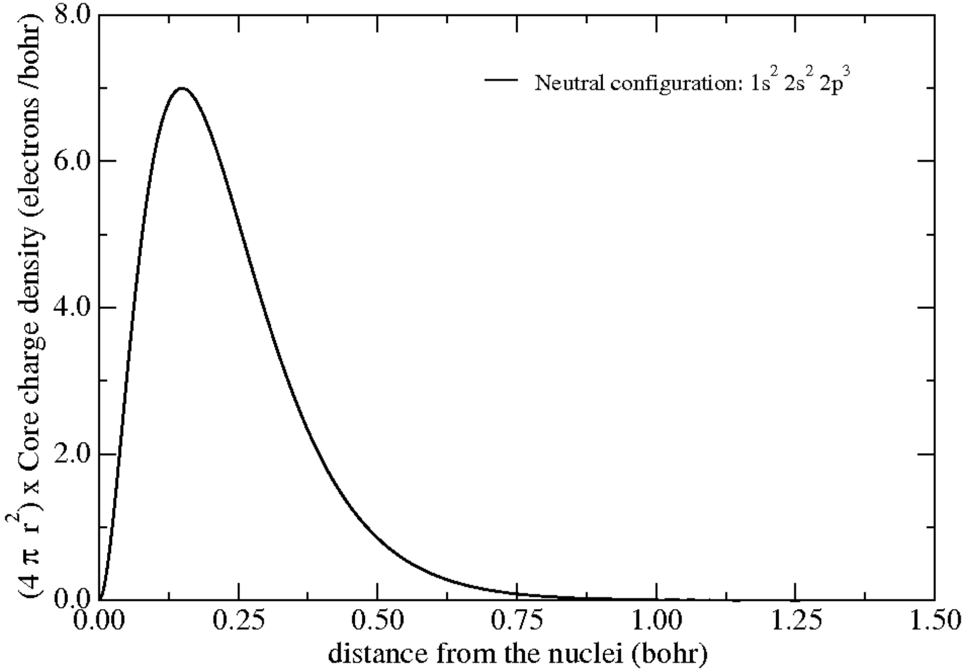
… are chemically inert

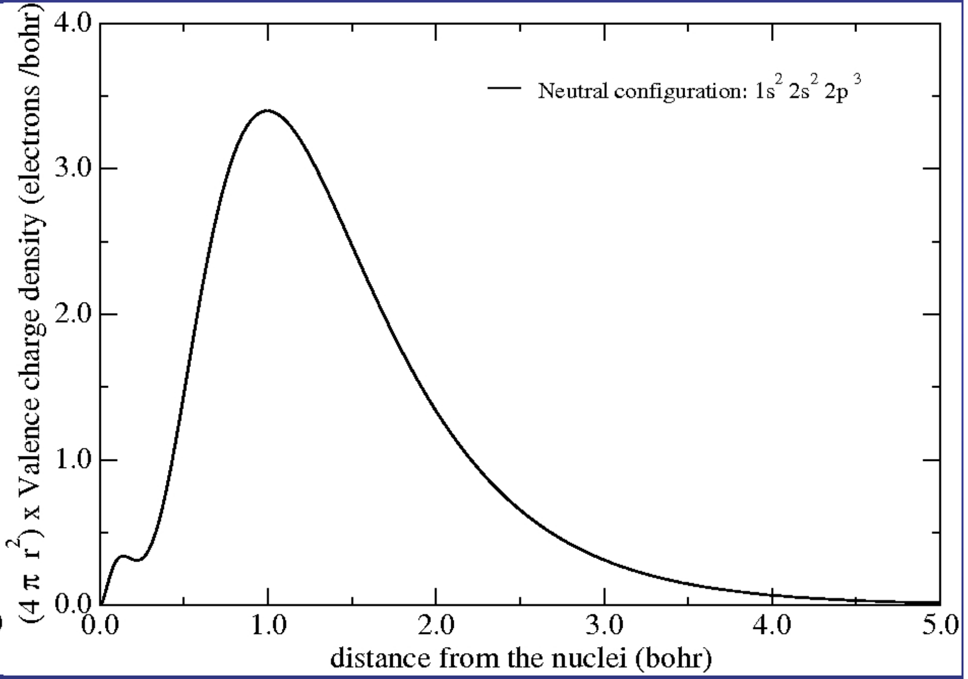
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density

Valence charge density

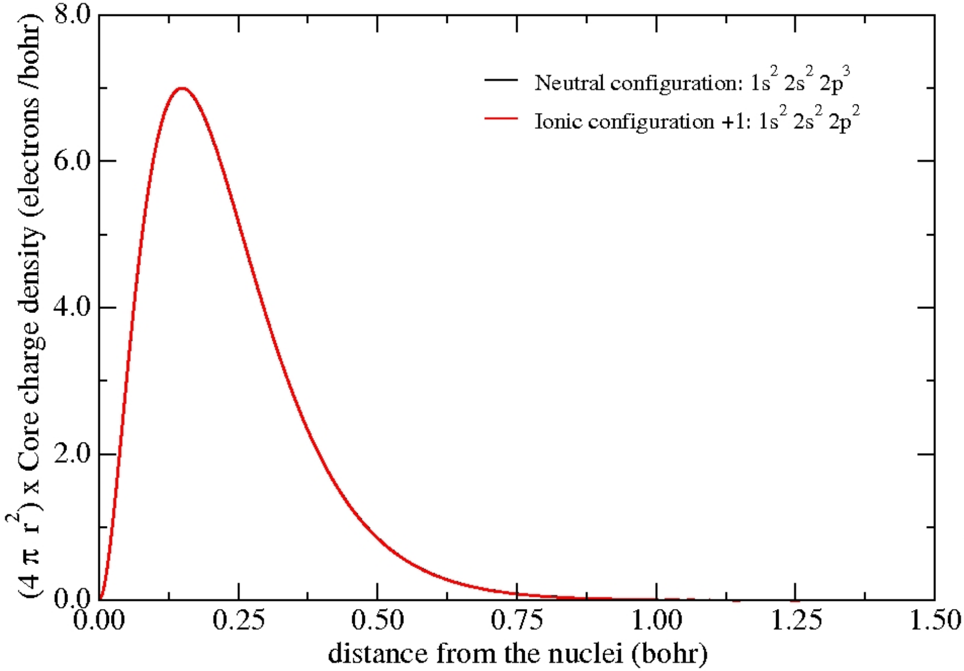




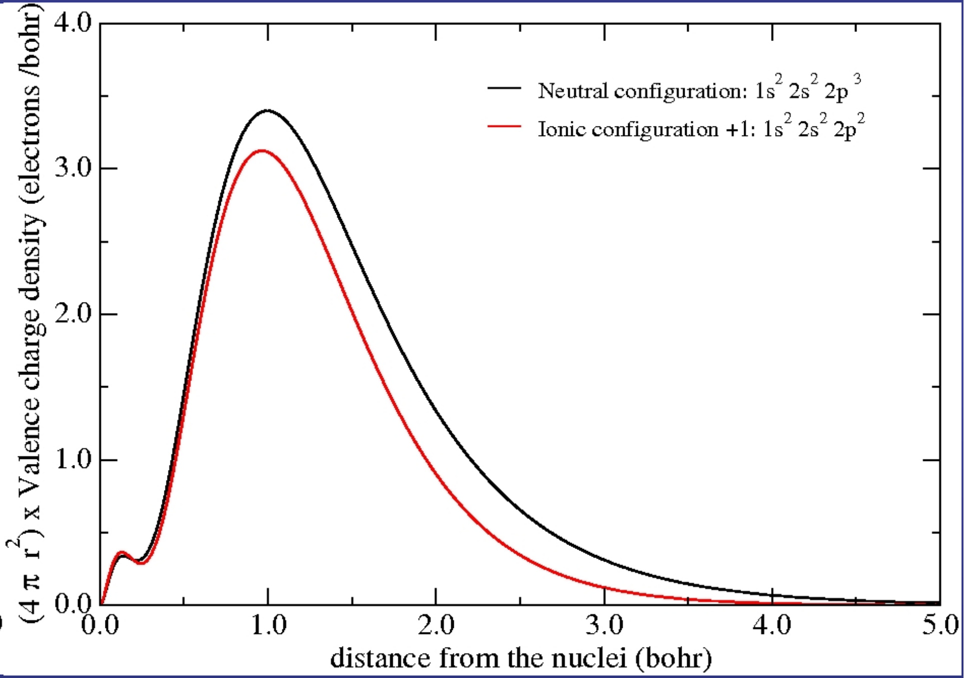
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



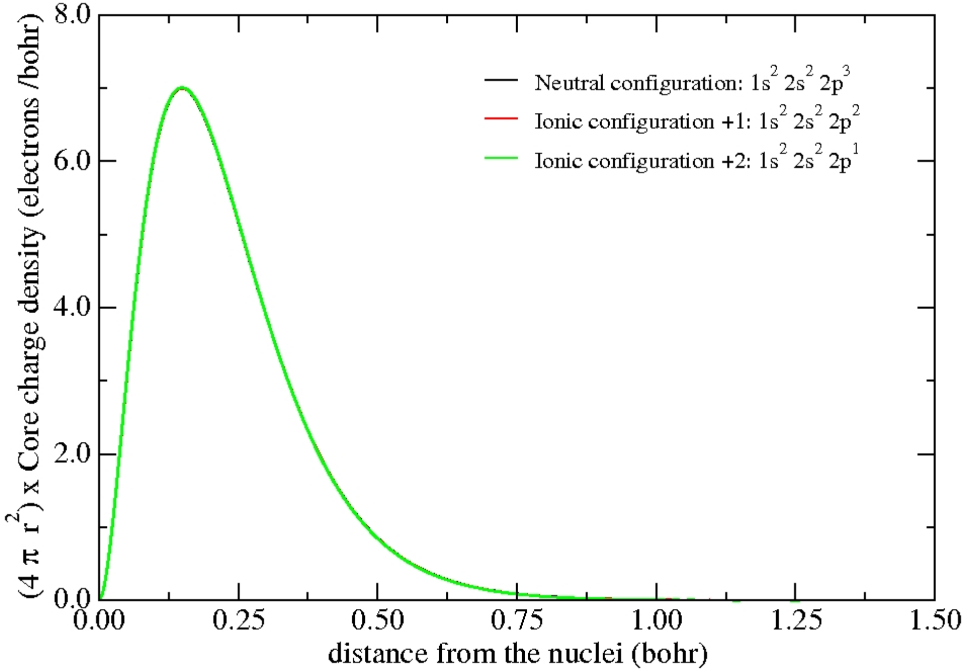
Valence charge density



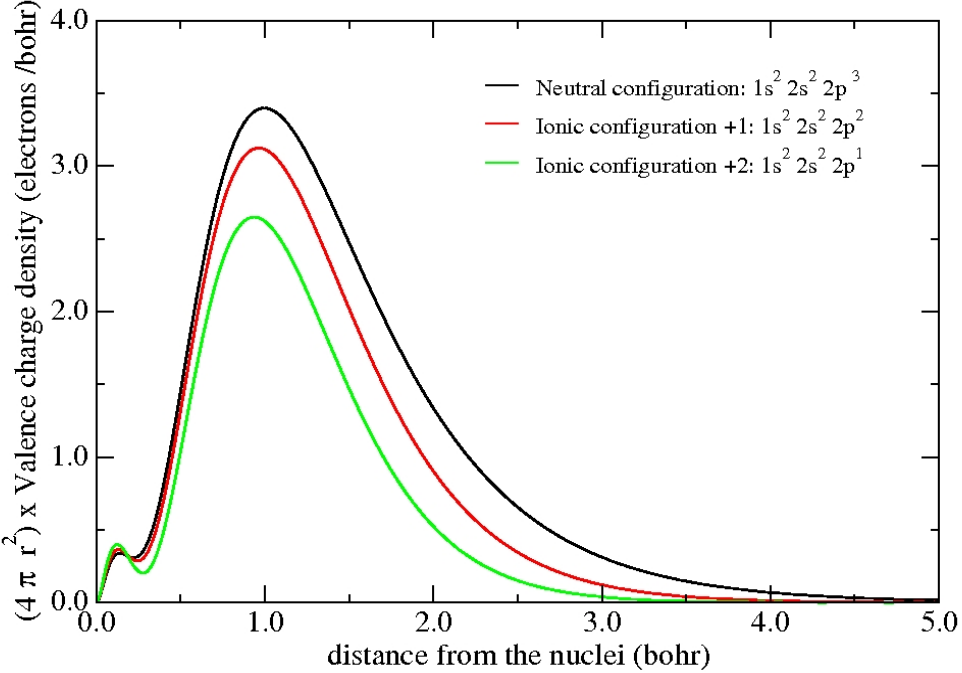
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



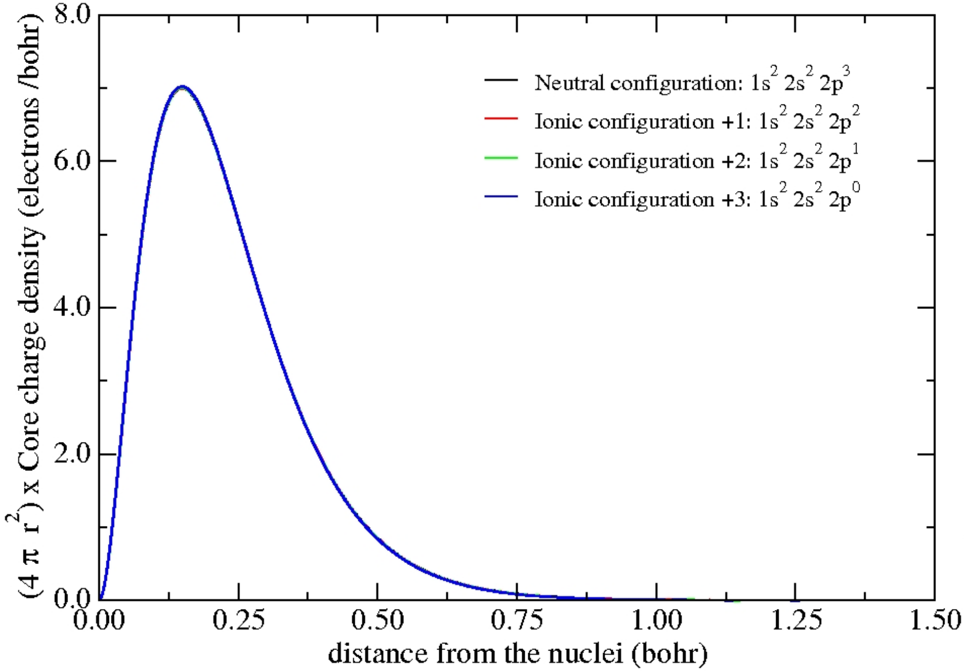
Valence charge density



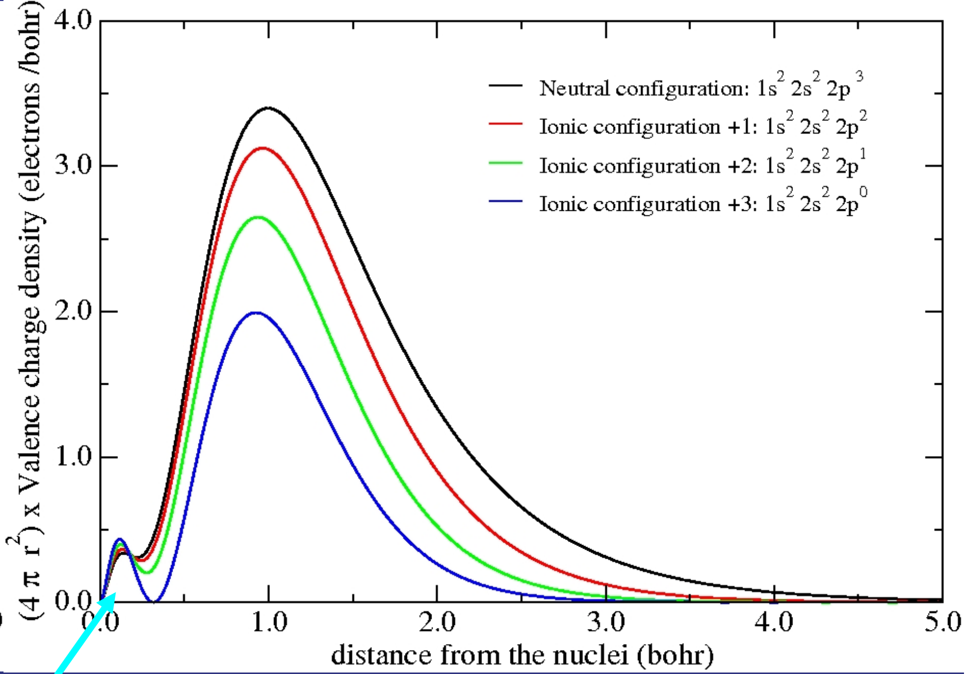
Core electrons are chemically inert

All electron calculation for an isolated N atom

Core charge density



Valence charge density



The core charge density remains unperturbed

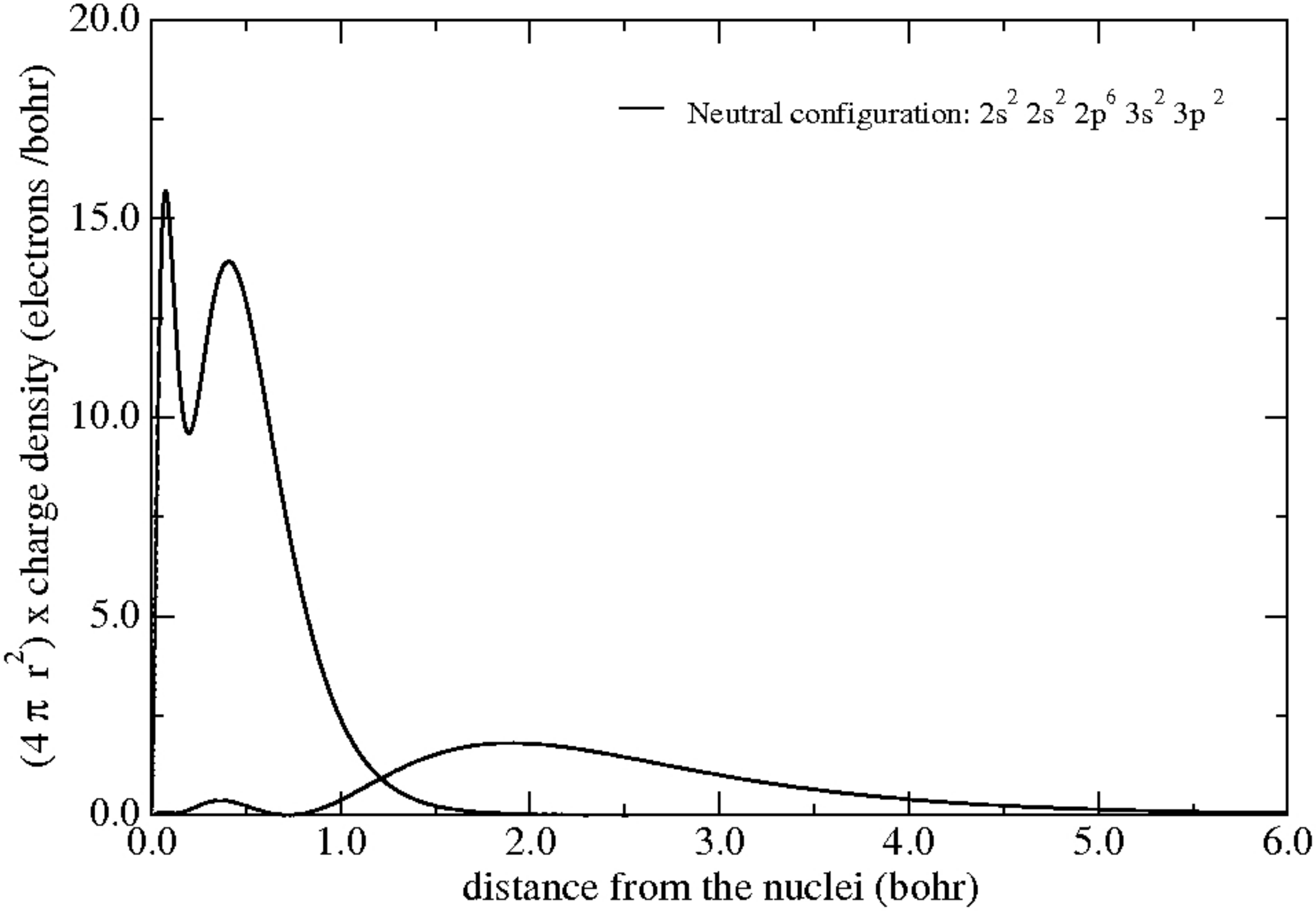
Although there are drastic modifications in the valence charge density

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

Core electrons are chemically inert

All electron calculation for an isolated Si atom

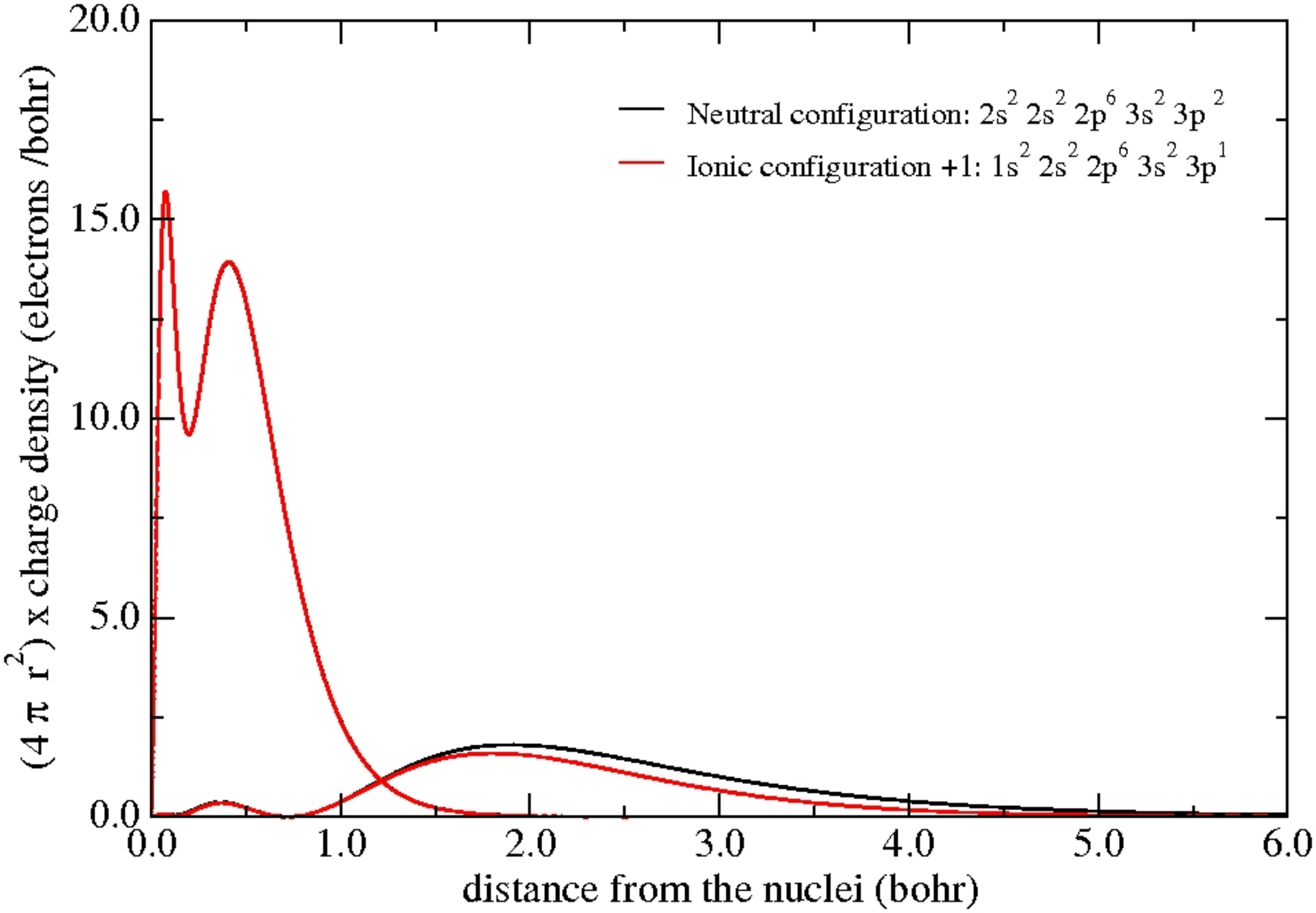
Angularly integrated core and valence charge densities



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

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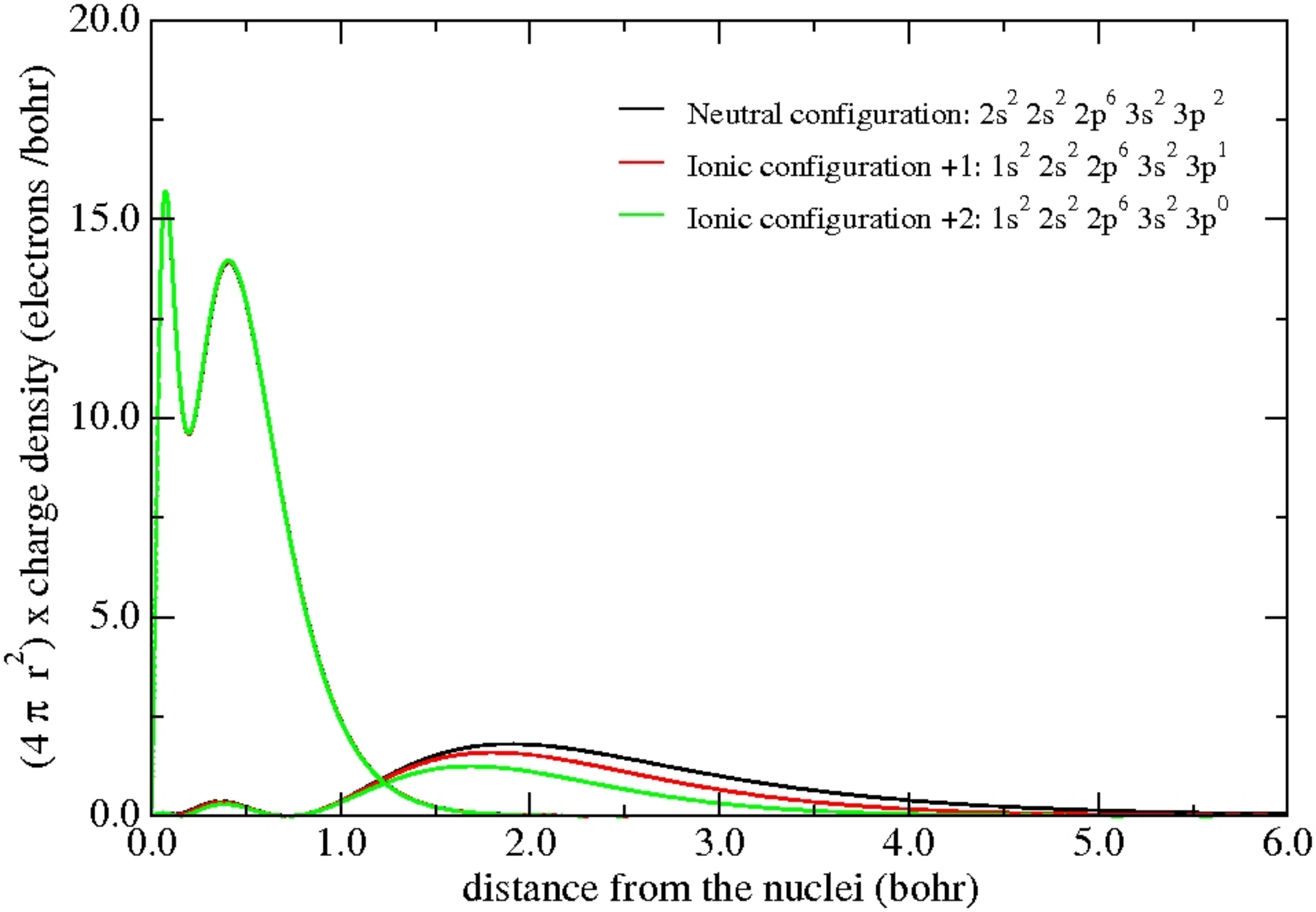
Angularly integrated core and valence charge densities



Core electrons are chemically inert

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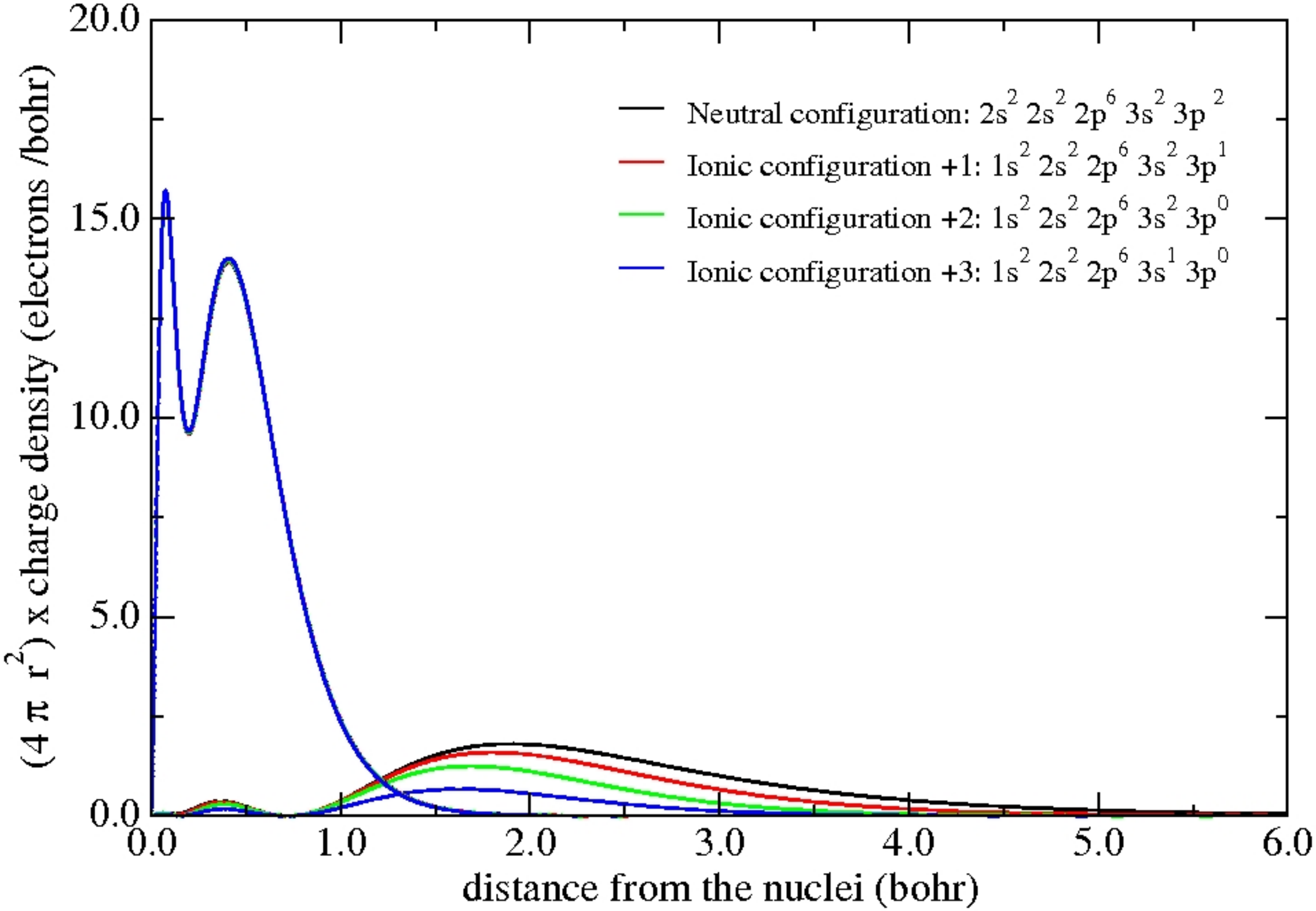
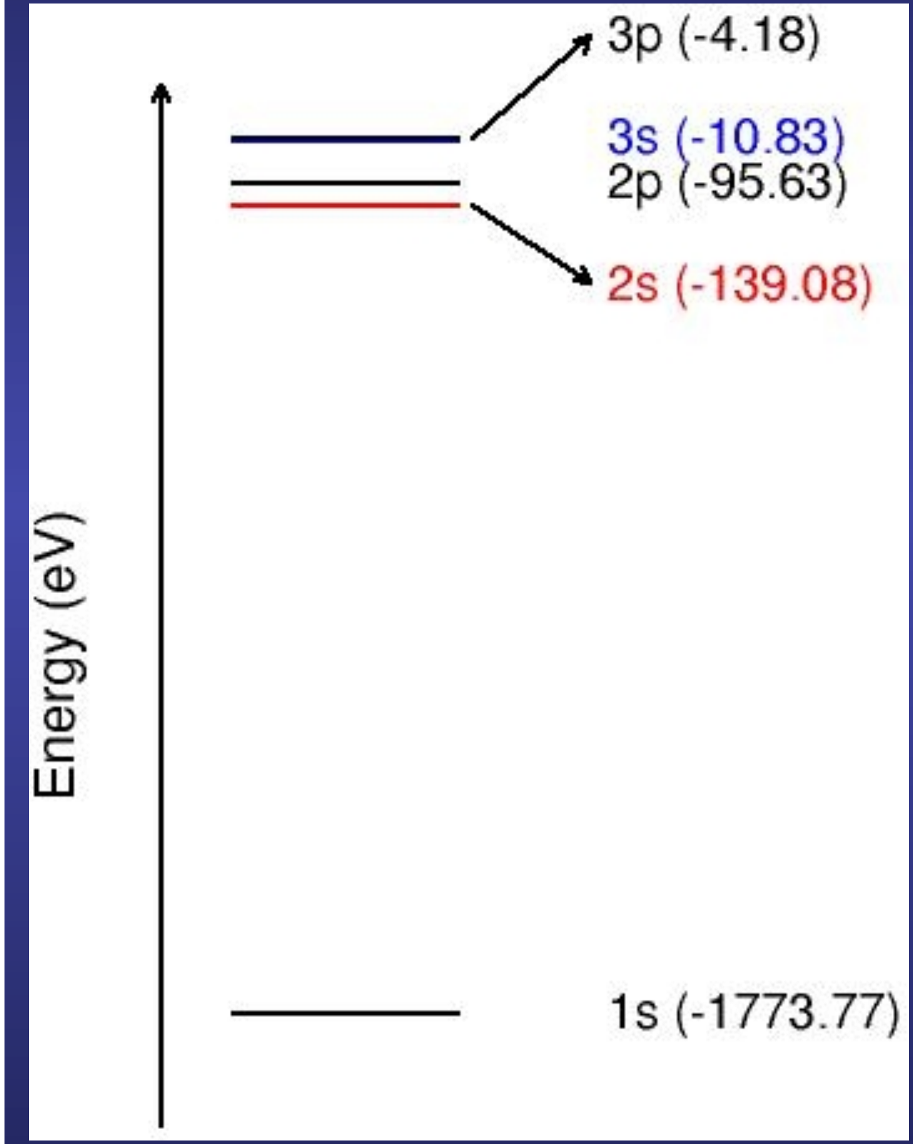
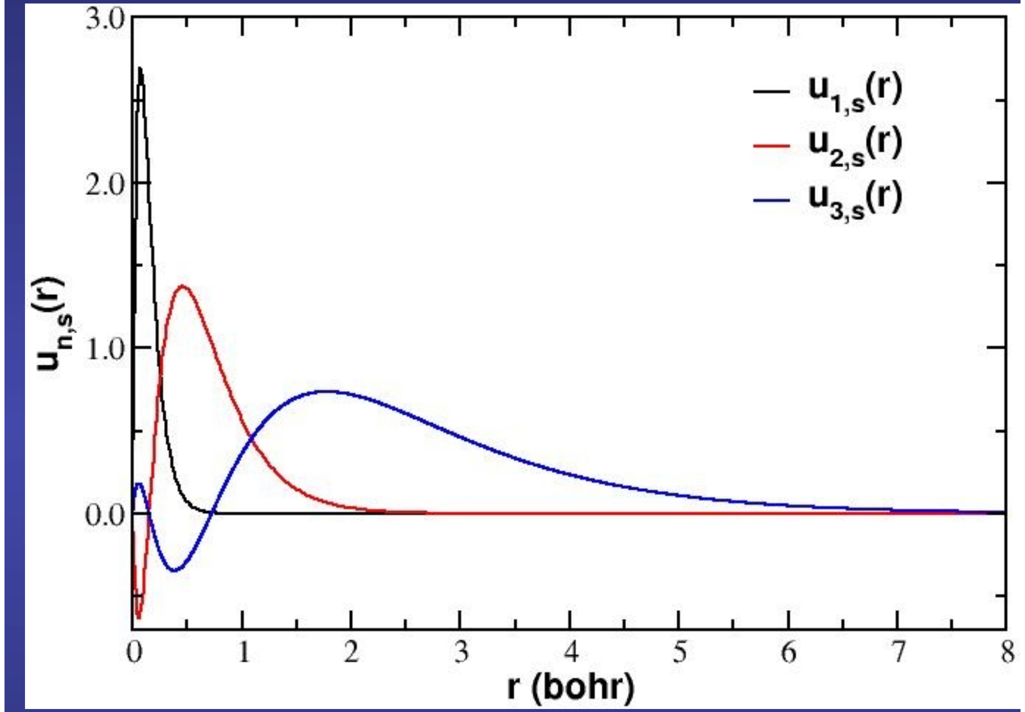
Angularly integrated core and valence charge densities



Valence wave functions must be orthogonal to the core wave functions



Atomic Si



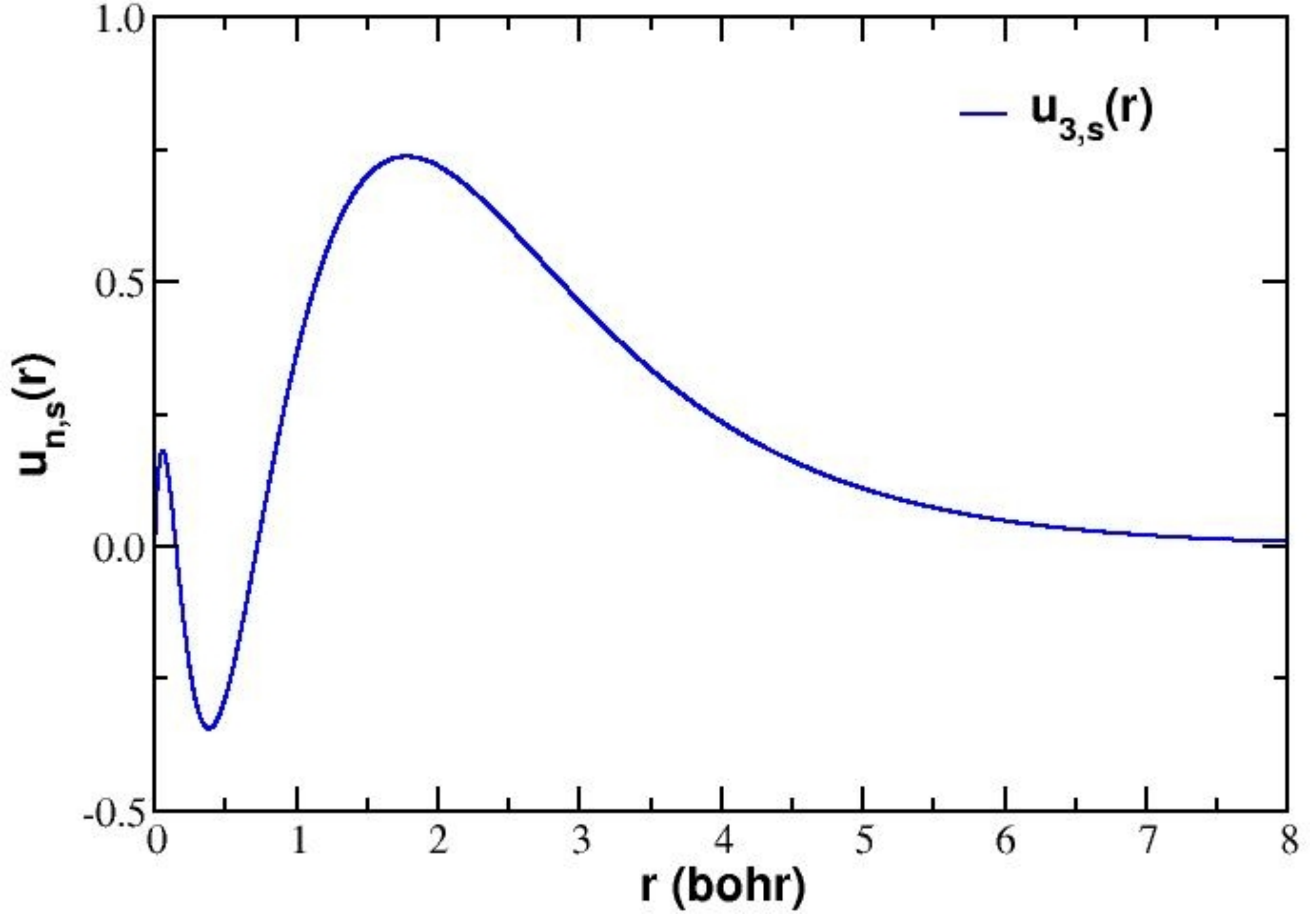
Core electrons…

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

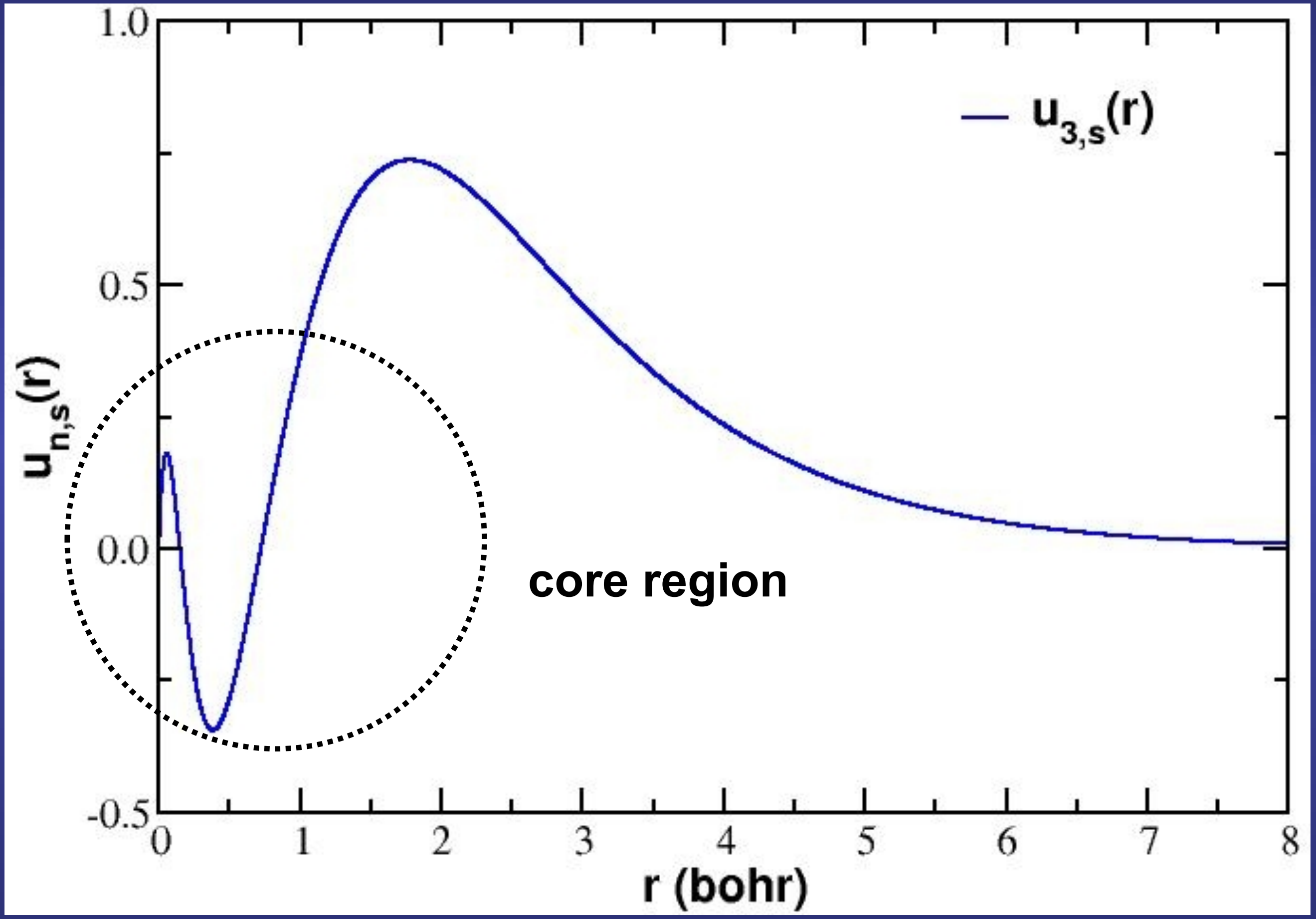
Core electrons main effect: screen nuclear potential

Idea:

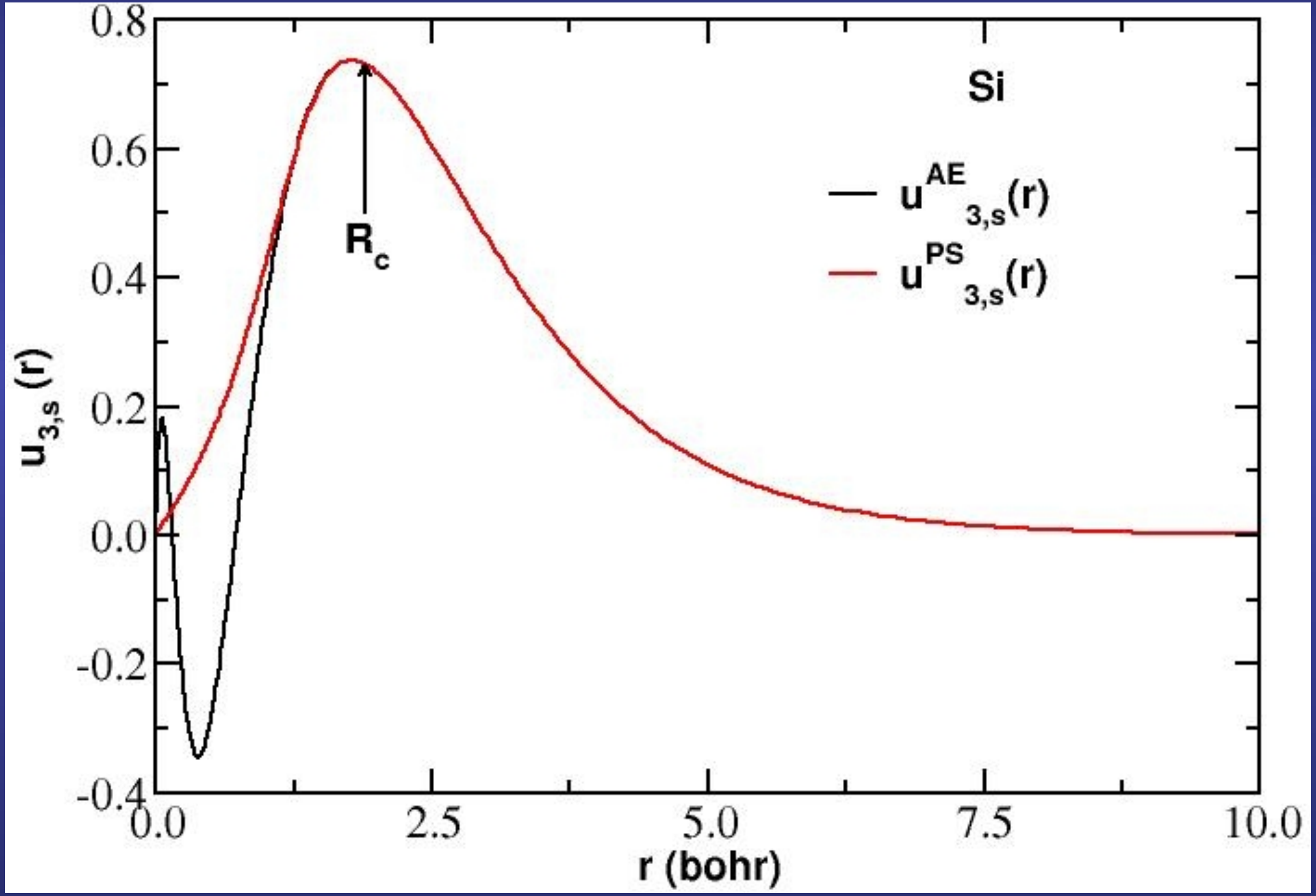
Ignore the dynamics of the core electrons (freeze them)

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



The pseudopotential transformation:
Seeking for the wave equation of the "smooth"

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

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

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

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

$$\Downarrow$$

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

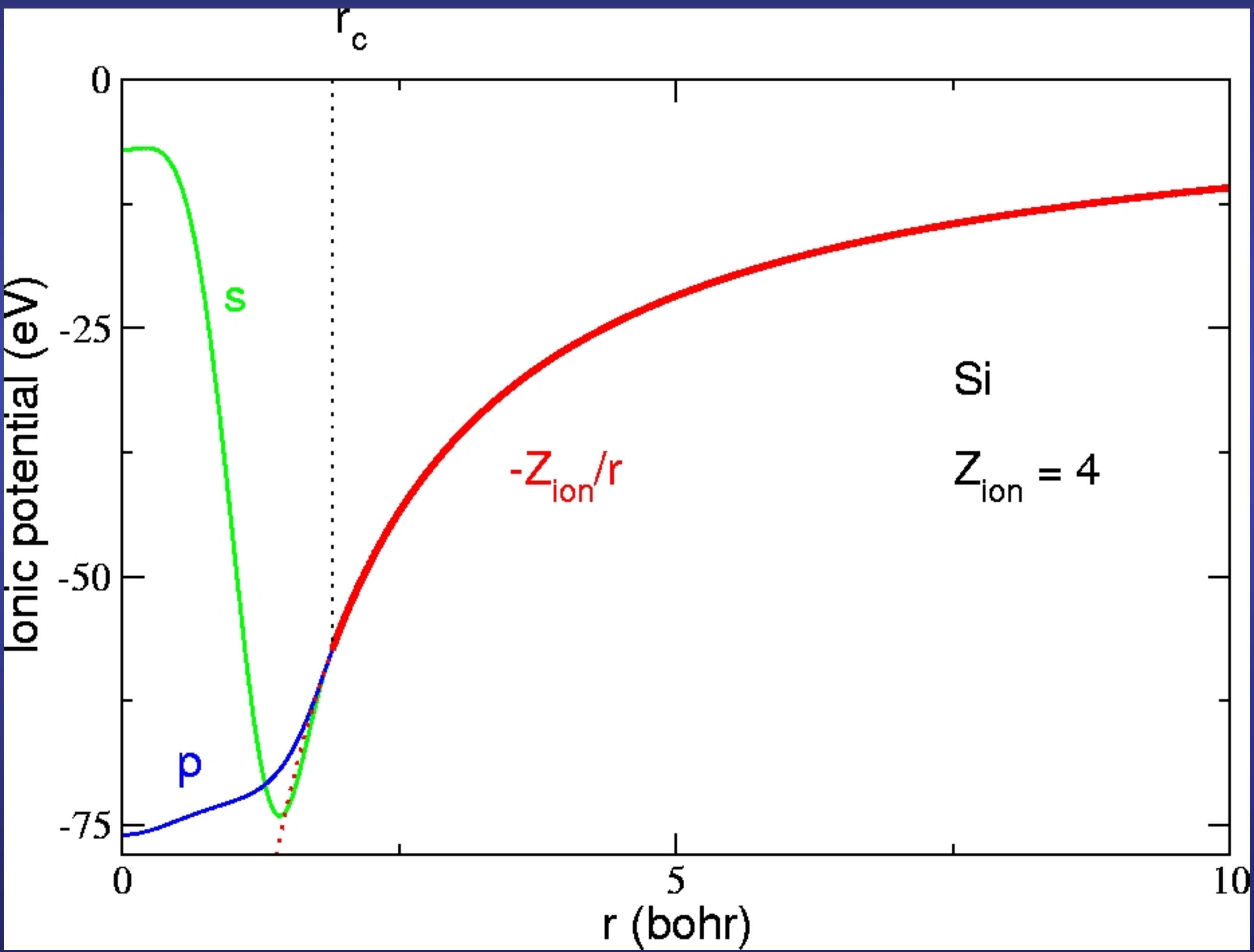
Non-local operator

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

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

l-dependent

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

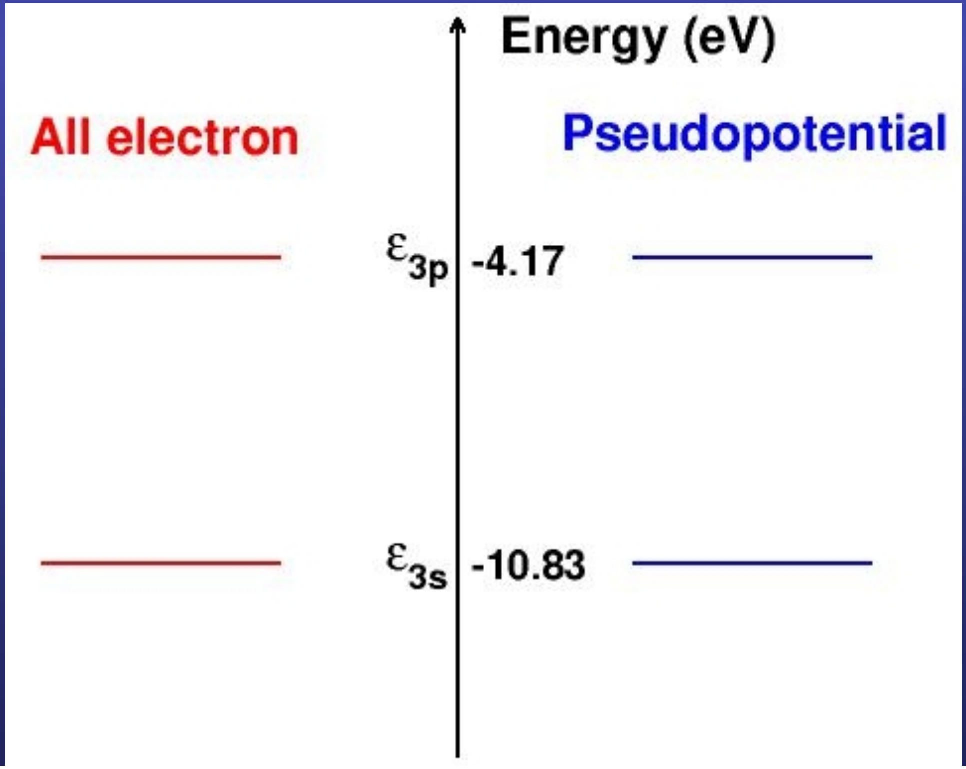


List of requirements for a good norm-conserving pseudopotential:

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



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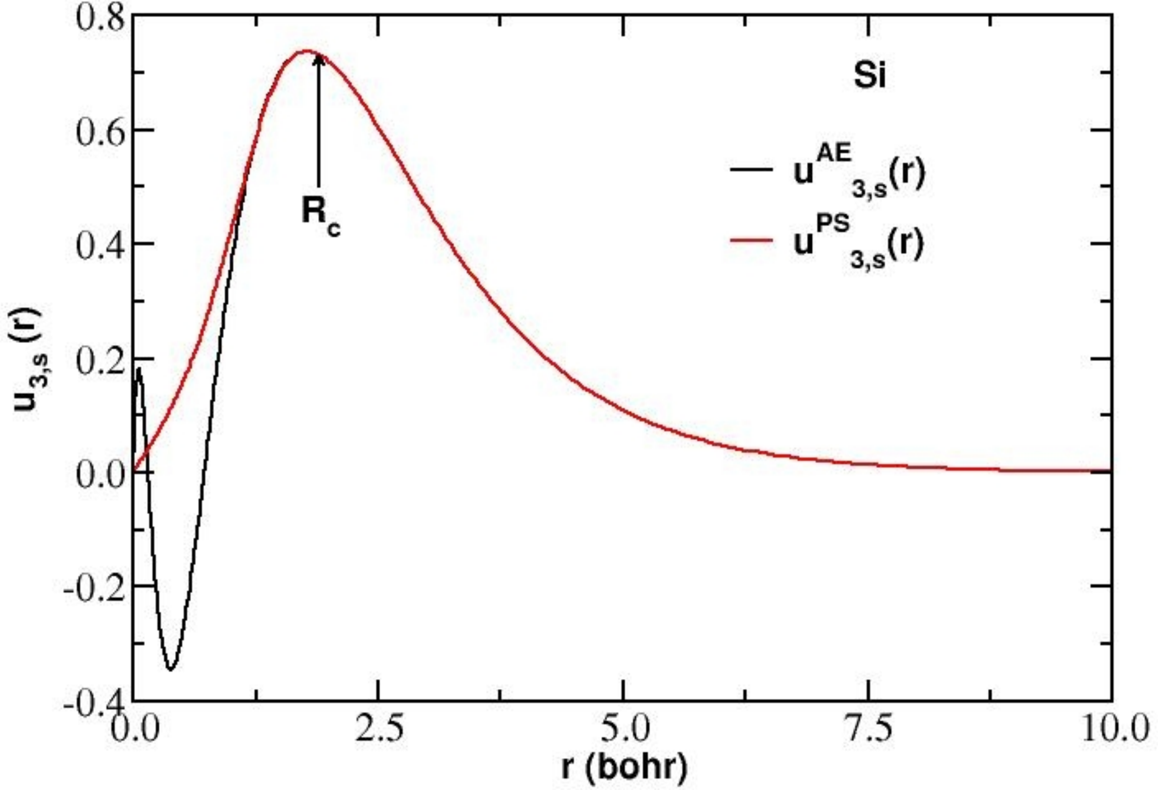
Choose an atomic reference configuration Si: $\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$

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



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

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

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

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

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

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

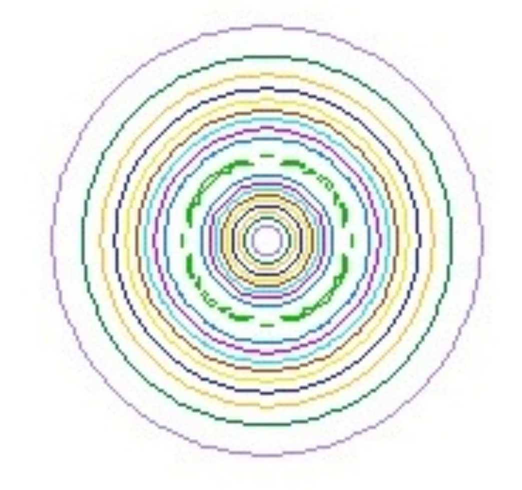
Central point due to Hamann, Schlüter and Chiang:

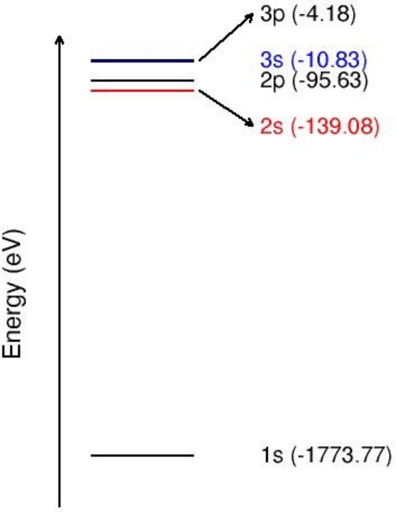
Norm conservation [(4)] ⇒ (5)

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

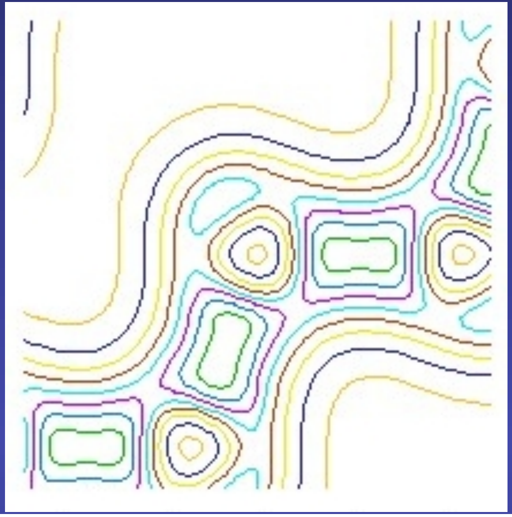
Equality of AE and PS energy derivatives of the logarithmic derivatives essential for transferability

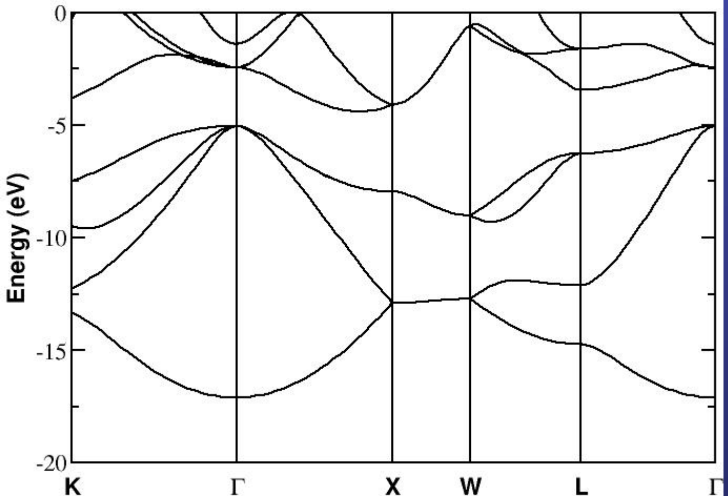
Atomic Si





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

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

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

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

Z **≡bare nuclear charge**

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

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

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

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

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

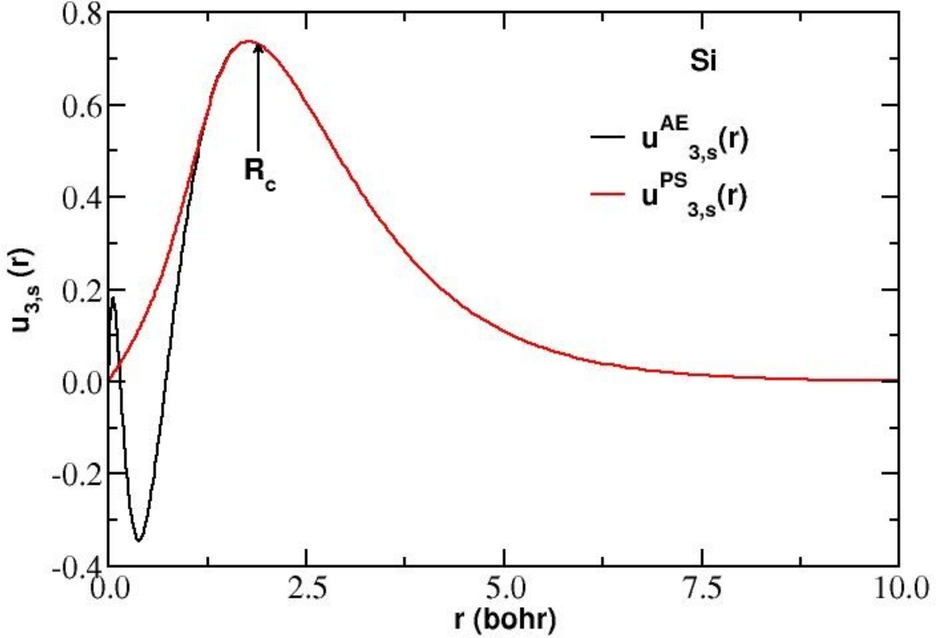
$$V_{\text{eff}}[n](r)=V_{\text{ext}}(r)+V_{\text{Hartree}}[n]+V_{xc}[n]=-\frac{Z}{r}+\int\frac{n(r')}{|r-r'|}dr'+V_{xc}[n]$$

$n(r)$ ≡ 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)]

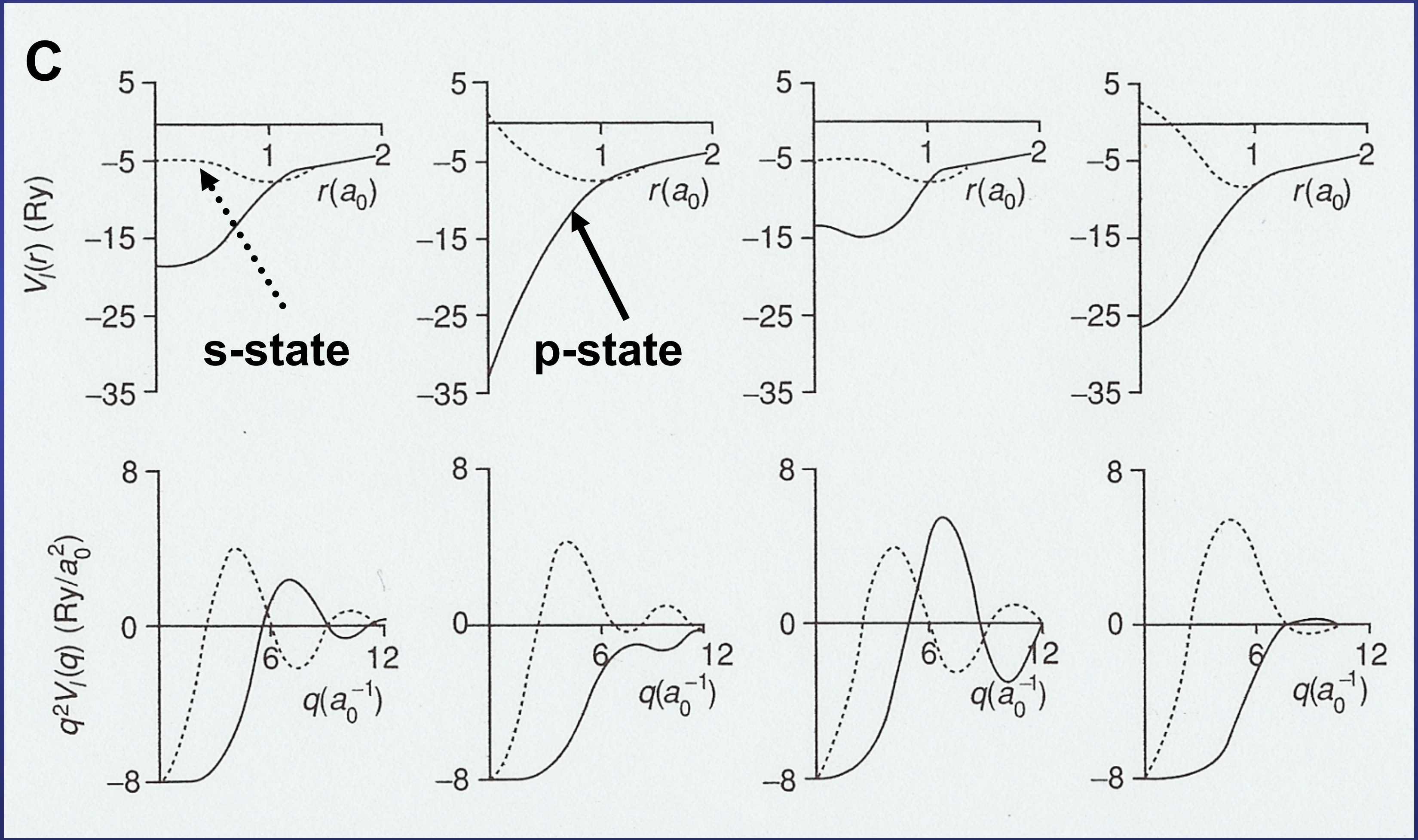
Kerker [G. P. Kerker, J. Phys. C 13, L189 (1980)]

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)]

Different methods to generate norm-conserving pseudopotential

Troullier-Martins **Kerker** **Haman-Schlüter-Chiang** **Vanderbilt**



s-state

p-state

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

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

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

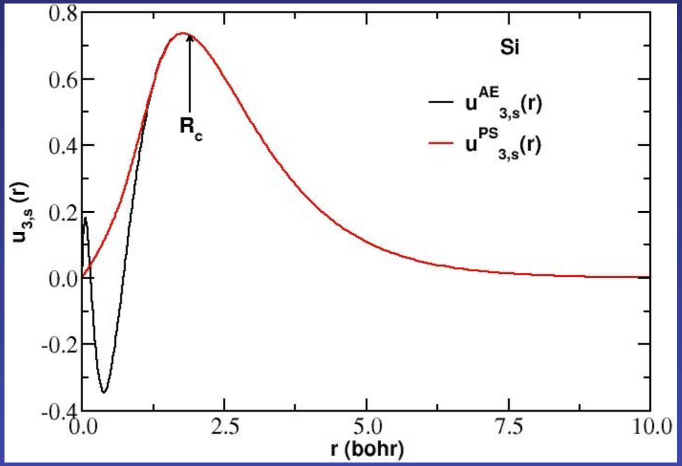
$n(r)$ ≡ sum of electronic charges for occupied states

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

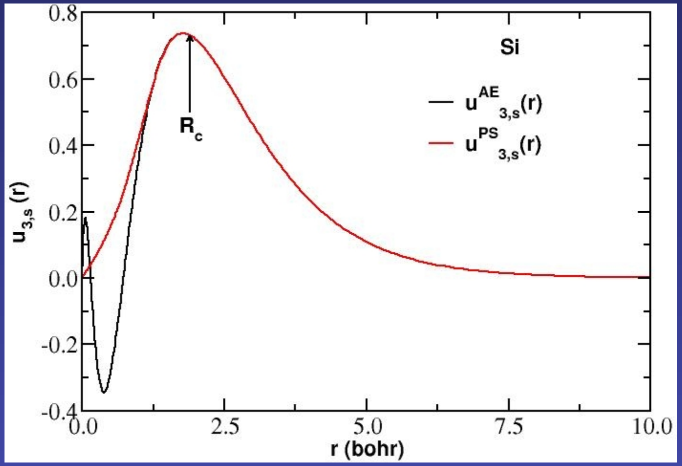
$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}+V^{\mathrm{PS}}_{(\mathrm{sc})l}(r)\right]u^{\mathrm{PS}}_l(r)=\varepsilon_l u^{\mathrm{PS}}_l(r)$$

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

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

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

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

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

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

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

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

$n(r)$ **≡ 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

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

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 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

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

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

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.

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

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 2: Include non-linear core corrections (NLCC)

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

Step 1: Replace the previous unscreening expression by

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

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

Expensive since:

- We have to include explicitly more electrons in the simulation

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

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

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

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

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

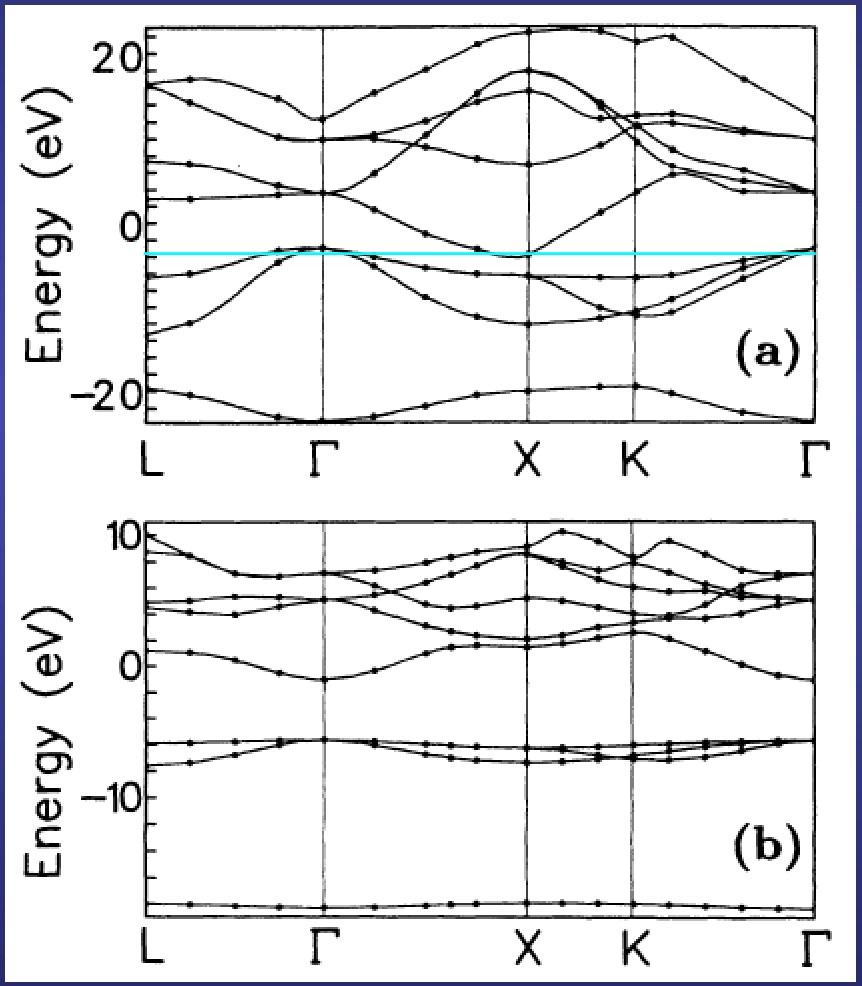
Parameters a, b and c determined by the continuity of the partial core and its first and second derivatives at r_{pc}

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

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

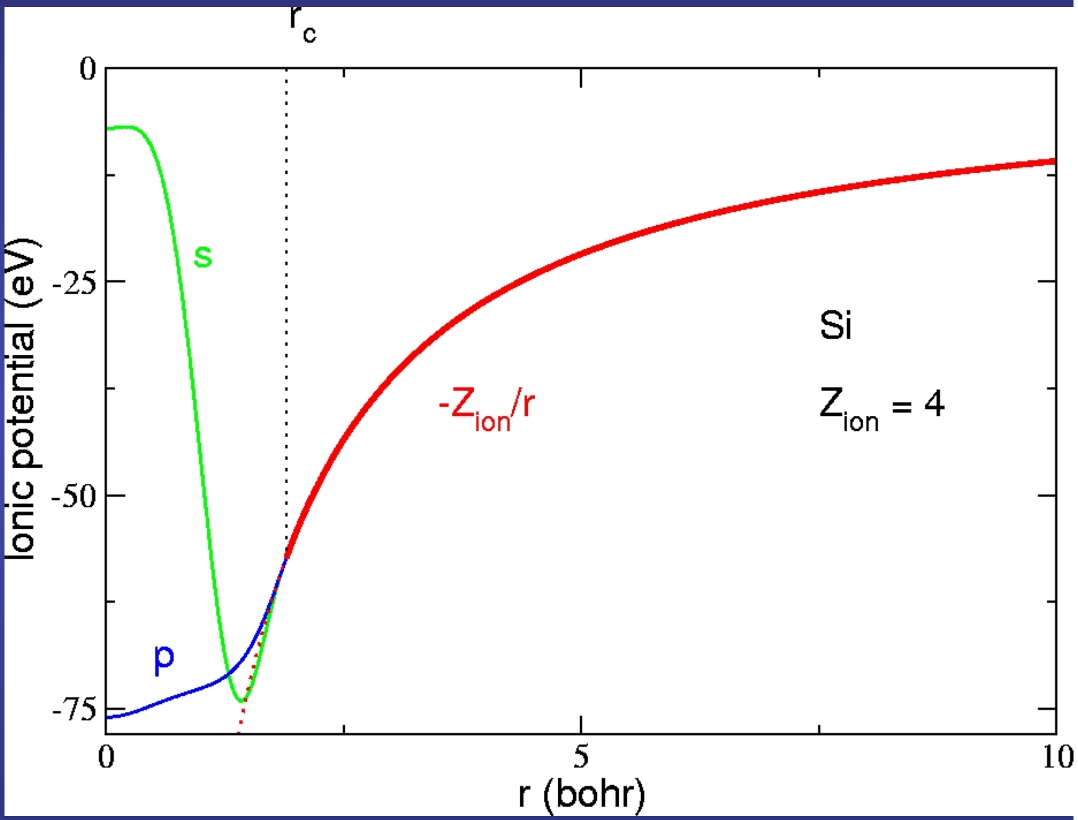
The screened potential depends on the angular momentum of the valence electron: is *l*-dependent

Reason for the *l*-dependency: different orthogonality conditions

For instance, in the Si atom

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

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



Within the core region, these electrons 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

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

$\hat{P}_l$ is spherically symmetric

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.

General form of a *l*-dependent pseudopotential

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

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$\hat{P}_l$ is spherically symmetric

This pseudopotential form is semilocal:

It is local in r but non-local in θ, ϕ

If we want to know the result of applying this operator to a function f in a point (r, θ, ϕ)

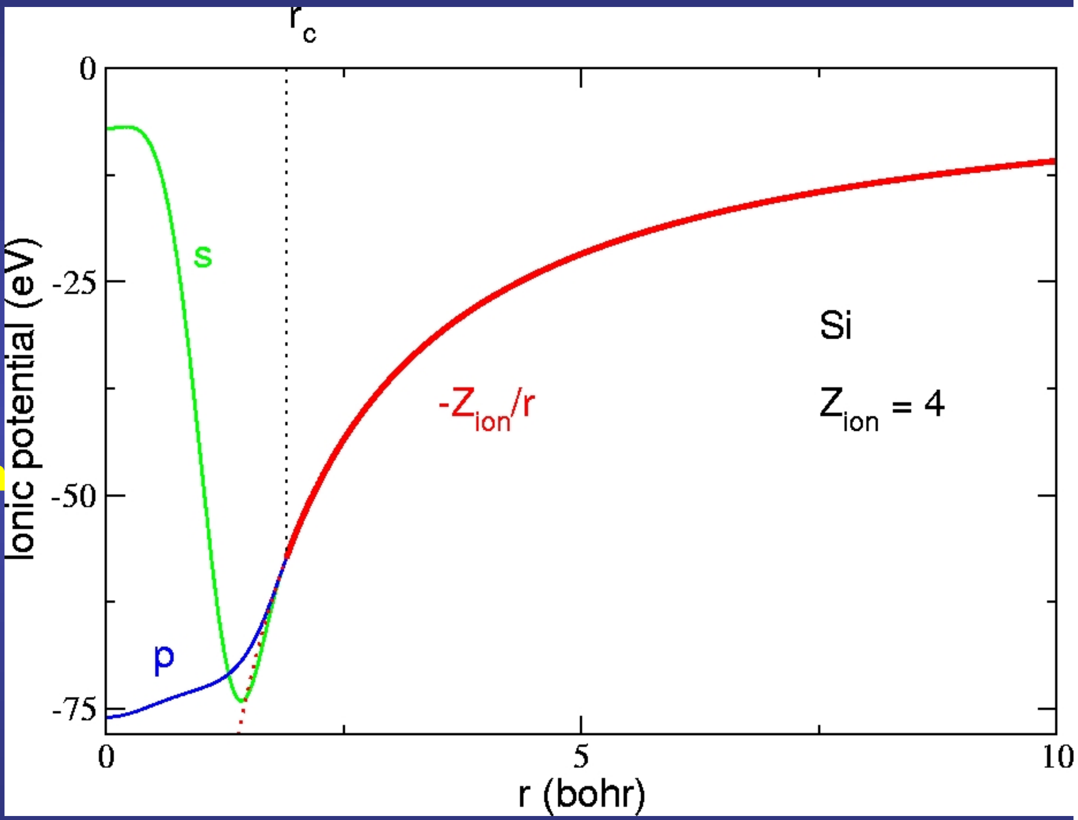
$$[\hat{V}^{\mathrm{PS}} f](r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} V_l^{\mathrm{PS}}(r) Y_{lm}(\theta, \phi) \int d(\cos\theta^{'}) d\phi^{'} Y_{lm}(\theta^{'}, \phi^{'}) f(r, \theta^{'}, \phi^{'})$$

We need to know the value of f at all the points $(r, \theta^{'}, \phi^{'})$

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
\delta V_l^{\mathrm{PS}}(\alpha,\beta) &= \sum_{m=-l}^{l} \langle \phi_\alpha | Y_{lm} \rangle \delta V_l(r) \langle Y_{lm} | \phi_\beta \rangle \\
&= \sum_{m=-l}^{l} \int\int \phi_\alpha^*(\vec{r}) Y_{lm}(\vec{r}) \delta V_l^{\mathrm{PS}}(r) Y_{lm}^*(\vec{r}\,') \phi_\beta(\vec{r}\,') d\vec{r} d\vec{r}\,'
\end{aligned}$$

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

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

Local integral in the radial variable

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

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

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

Local integral in the radial variable

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

The computation of these integrals is very expensive.
It scales as $\mathcal{O}(NM^2)$

M **Number of basis functions**

N **Number of atoms in the system (for every atom** δV_l **changes)**

Solution: replace the semilocal pseudopotential by a fully separable non-local pseudopotential (Kleinman-Bylander approach)

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

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

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

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

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

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

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

where $\psi_{lm}^{\mathrm{PS}}(\vec{r})$ 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

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

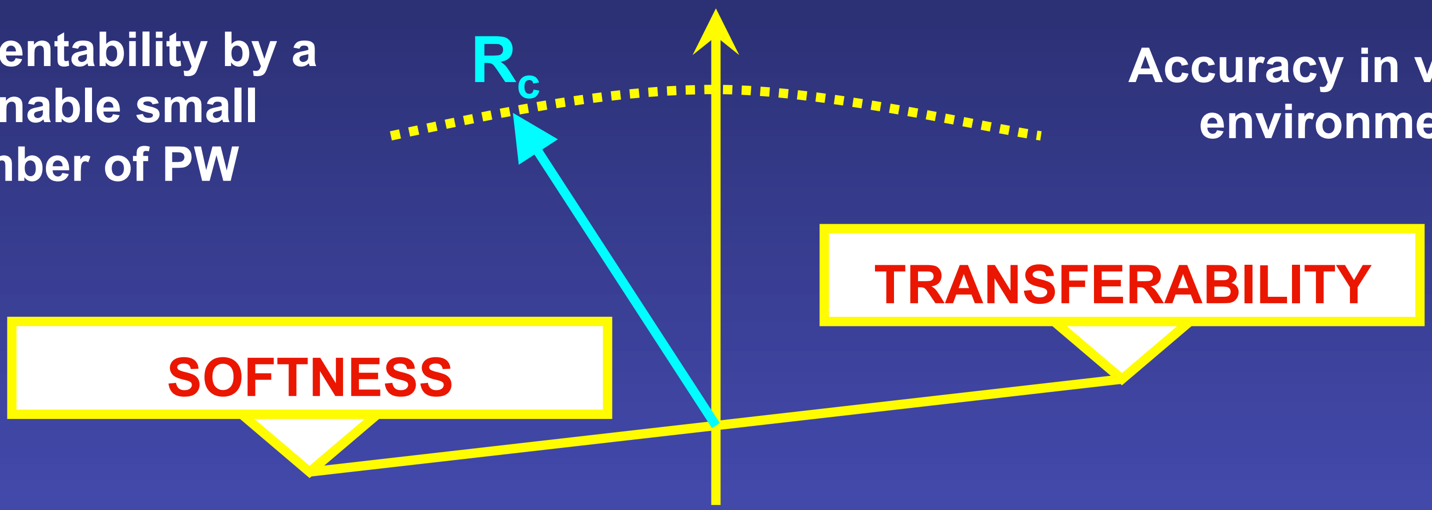
Kleinman-Bylander fully non-local separable form

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

The strength of the non-locality is determined by

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

Balance between softness and transferability controlled by R_c



Representability by a resonable small number of PW

R_c

Accuracy in varying environments

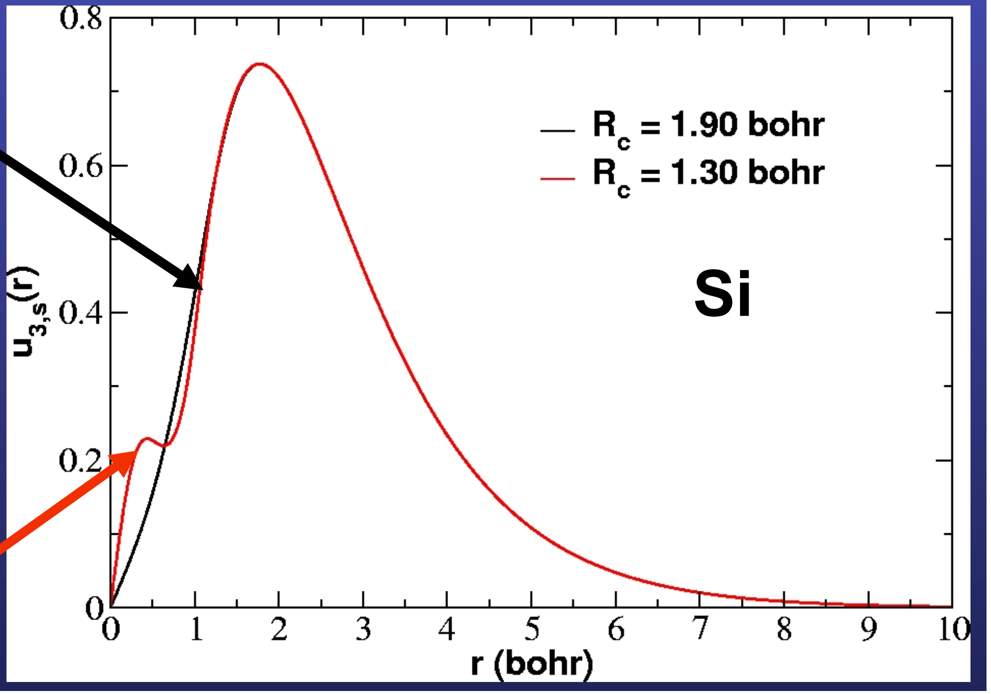
TRANSFERABILITY

SOFTNESS

Larger R_c: softer pseudo

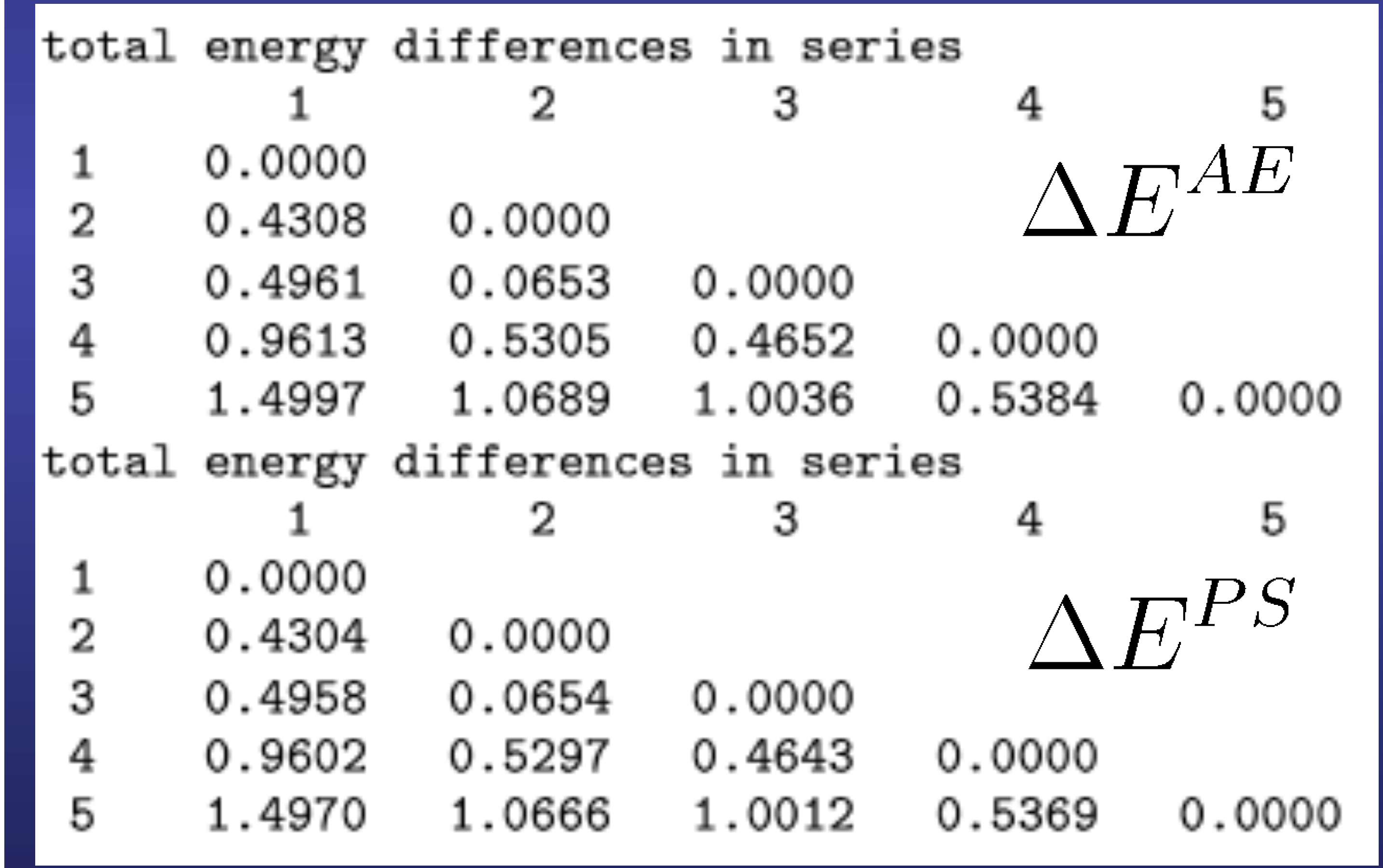
First guess: last peak of the all electron wave function

Shorter R_c: harder pseudo



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)

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

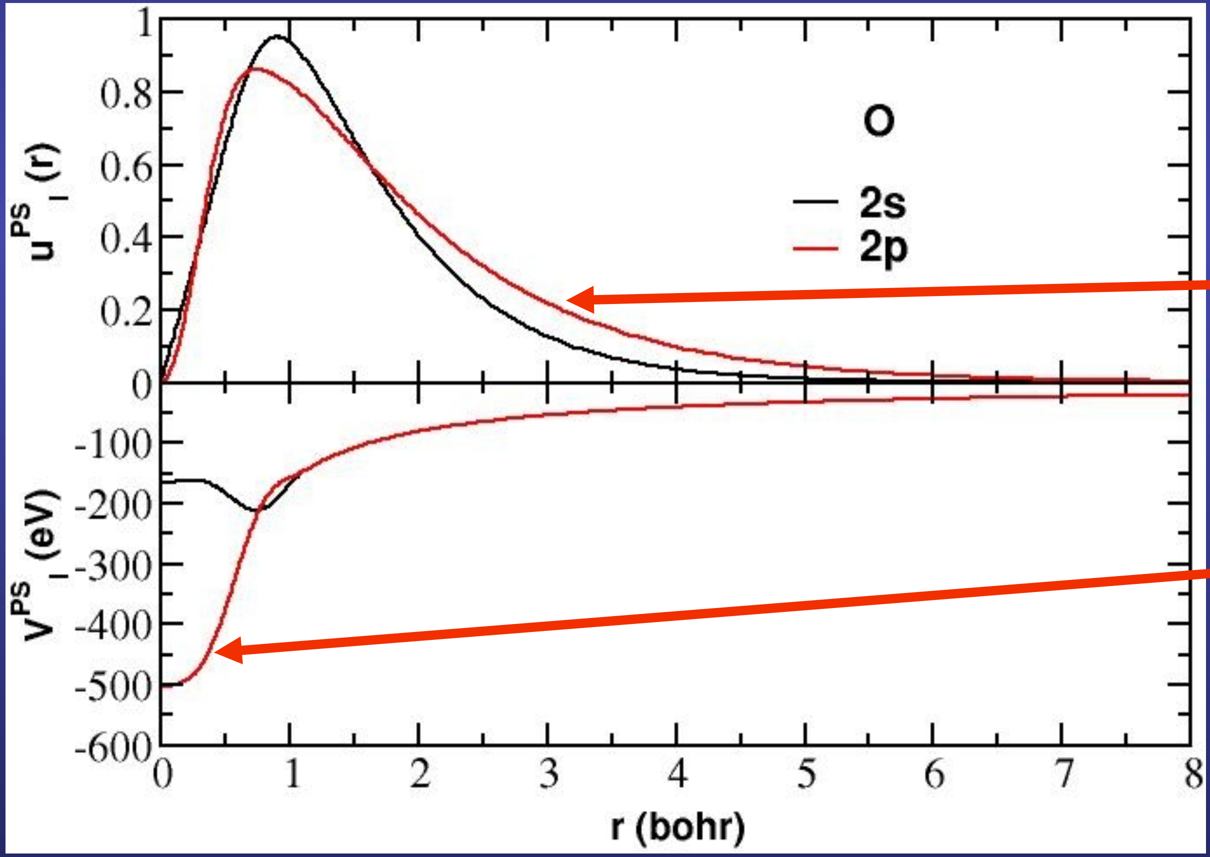
$3s^1\ 3p^3$

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

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

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

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



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

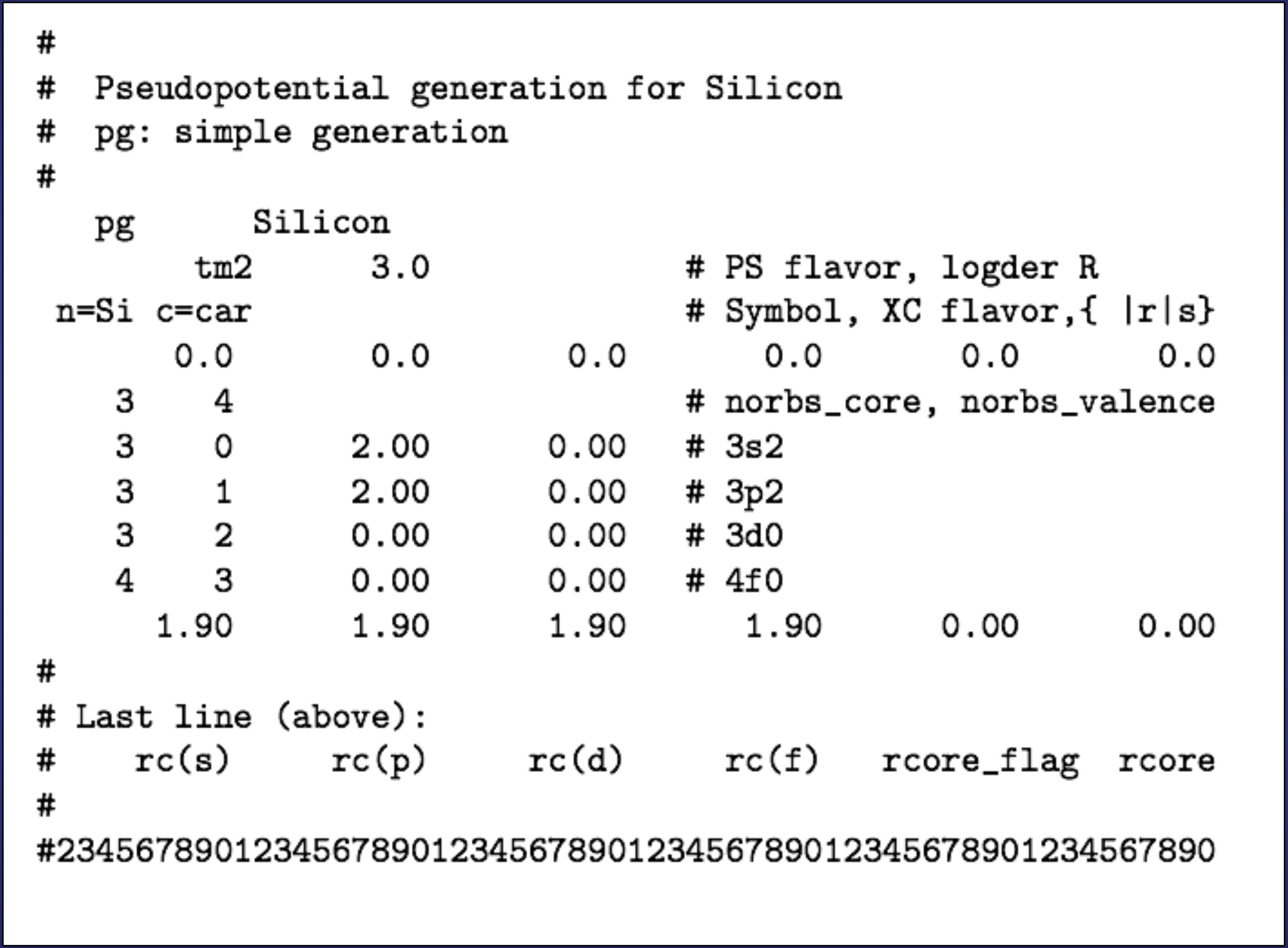
there might be many “best choices”

•Two overall competing factors: transferability vs hardness

•Norm conservation helps transferability

•Always test the pseudopotential in well-known situations

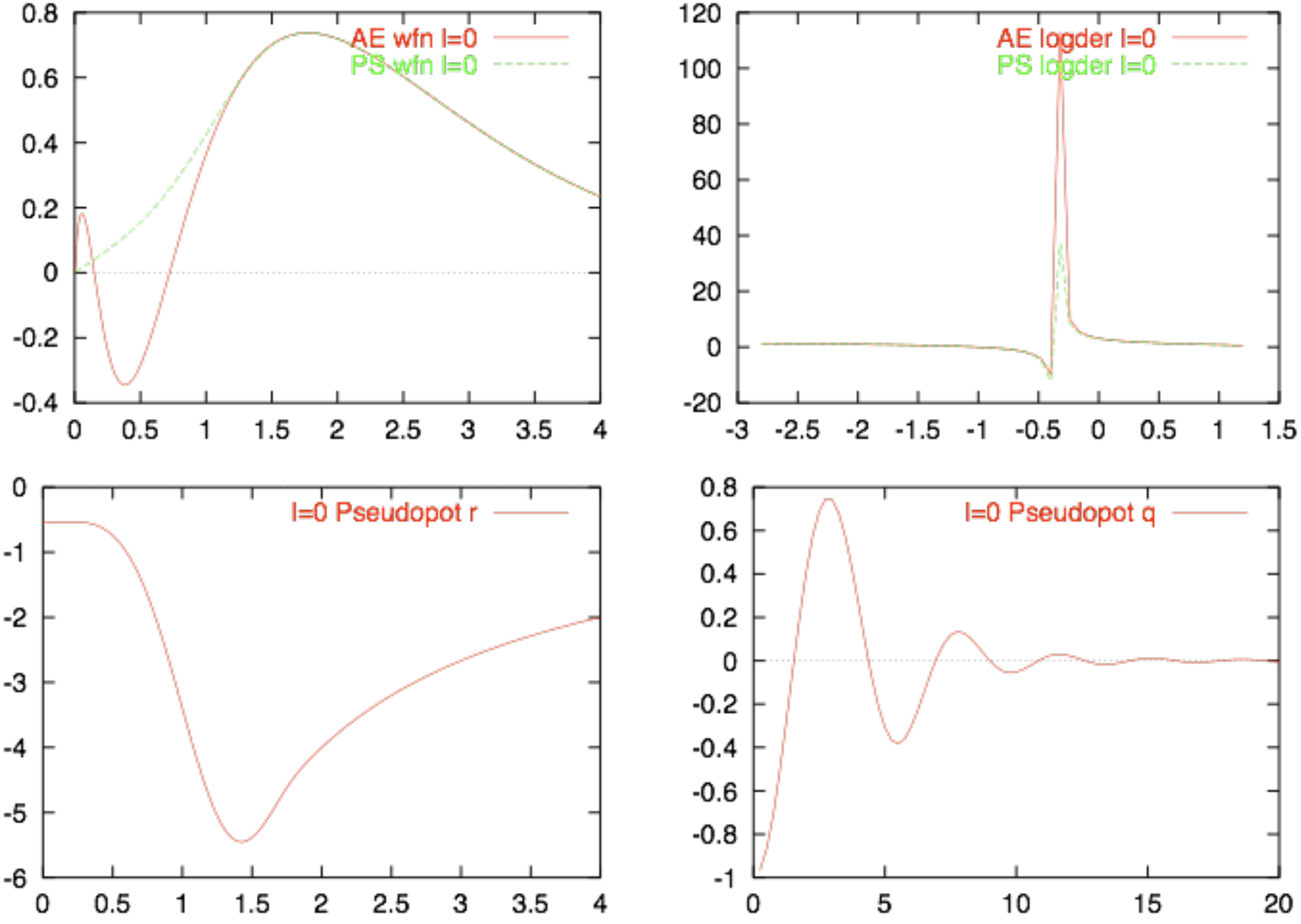
Howto: input file to generate the pseudopotential



```
#
#  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
#
#23456789012345678901234567890123456789012345678901234567890
```

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
```


AE wfn l=0
PS wfn l=0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
0
0.5
1
1.5
2
2.5
3
3.5
4
AE logder l=0
PS logder l=0
120
100
80
60
40
20
0
-20
-3
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
l=0 Pseudopot r
0
-1
-2
-3
-4
-5
-6
0
0.5
1
1.5
2
2.5
3
3.5
4
l=0 Pseudopot q
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
0
5
10
15
20

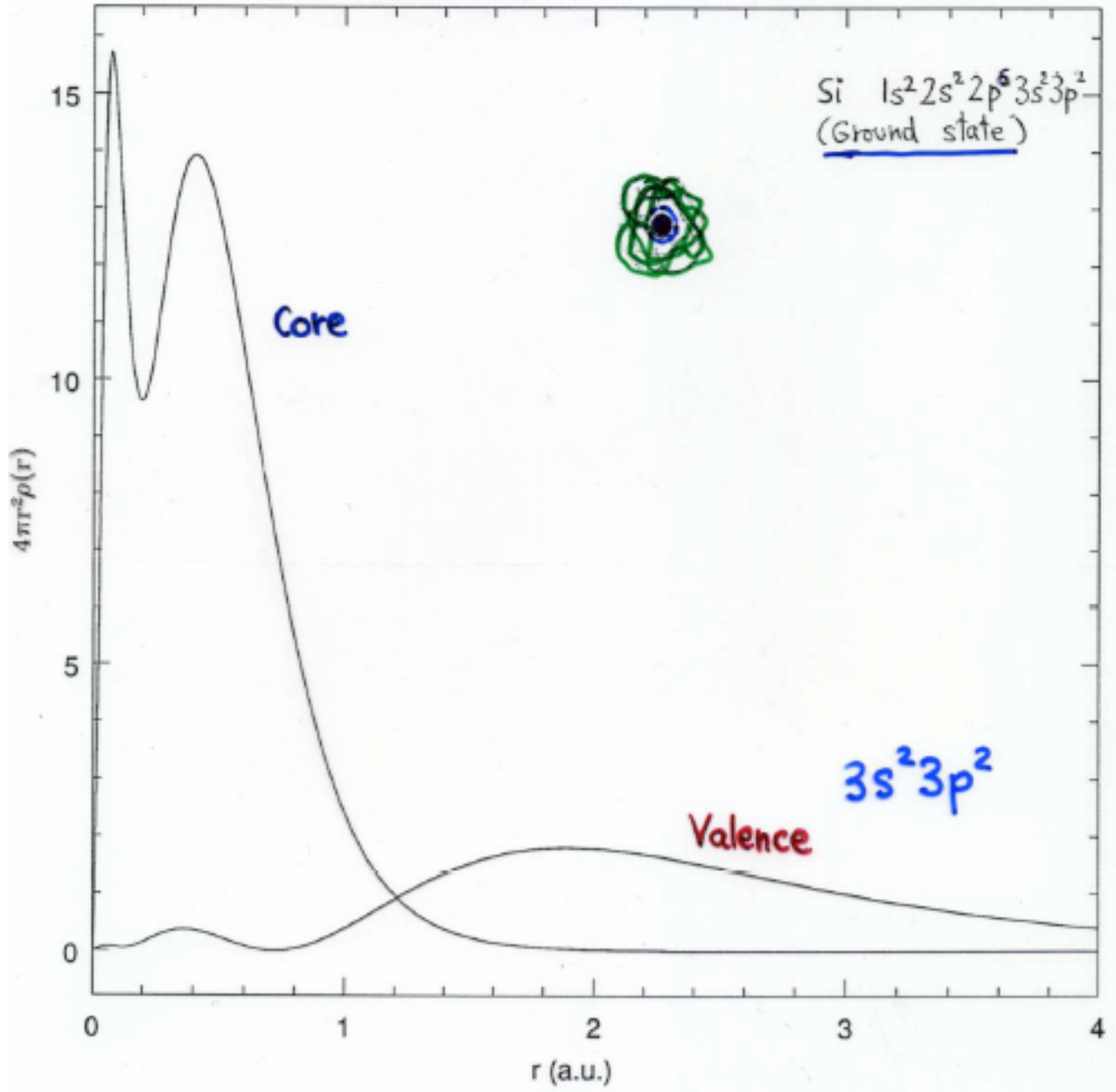
Testing Mechanics

```
   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
```

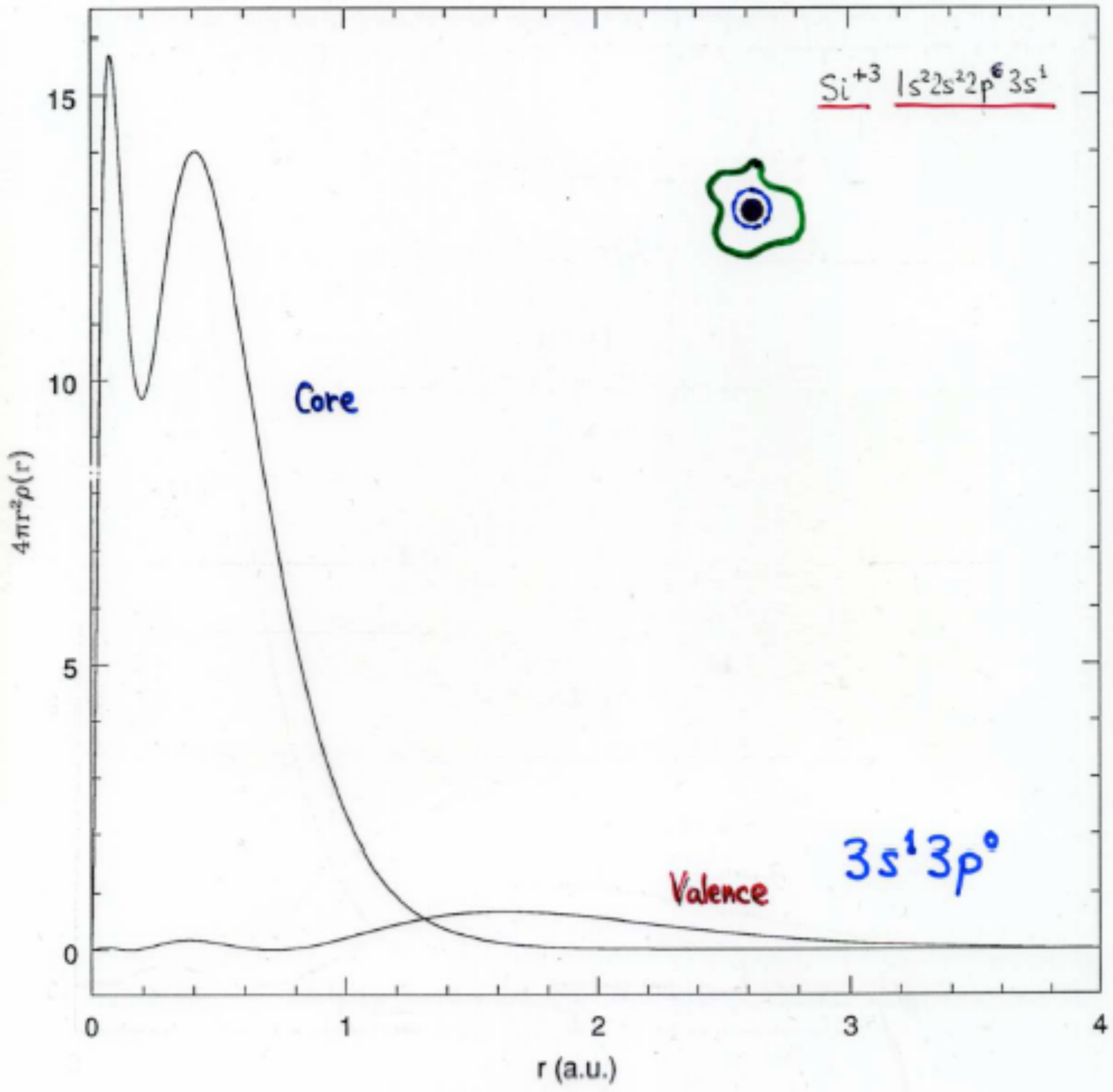
```
sh ../pt.sh  Si.test.inp Si.tm2.vps
Output data in directory Si.test-Si.tm2...
$ cd Si.test-Si.tm2
$ ls [A-Z]*
AECHARGE  AEWFNR1  CHARGE  OUT       PTWFNR0  PTWFNR2  VPSIN
AEWFNR0   AEWFNR2  INP     PTCHARGE  PTWFNR1  RHO
$
$ ## EIGENVALUE TEST
$
$ grep ’&v’ OUT
 ATM3      11-JUL-02   Si Test -- 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
```

Core electrons are chemically inert



Core electrons are chemically inert



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 $V_{Hxc}^{PS}(r)$

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