The pseudopotential concept

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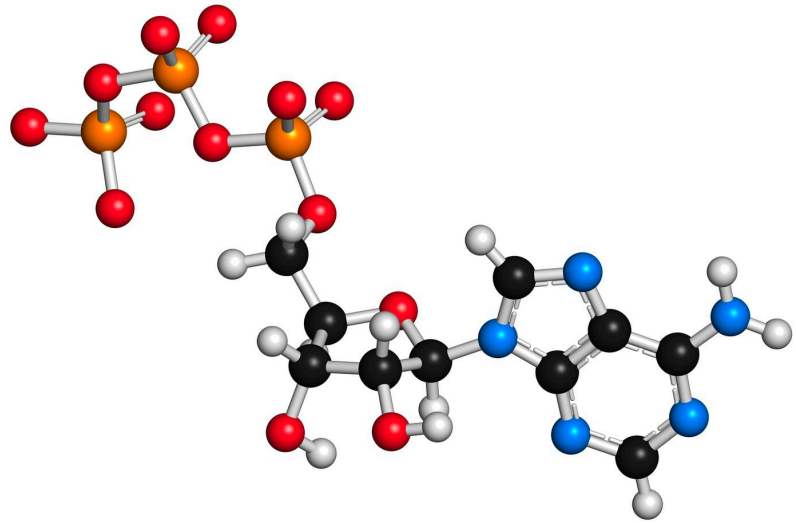
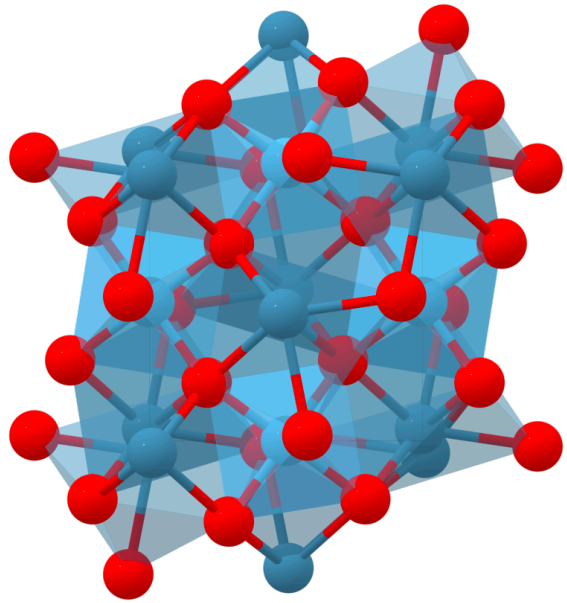
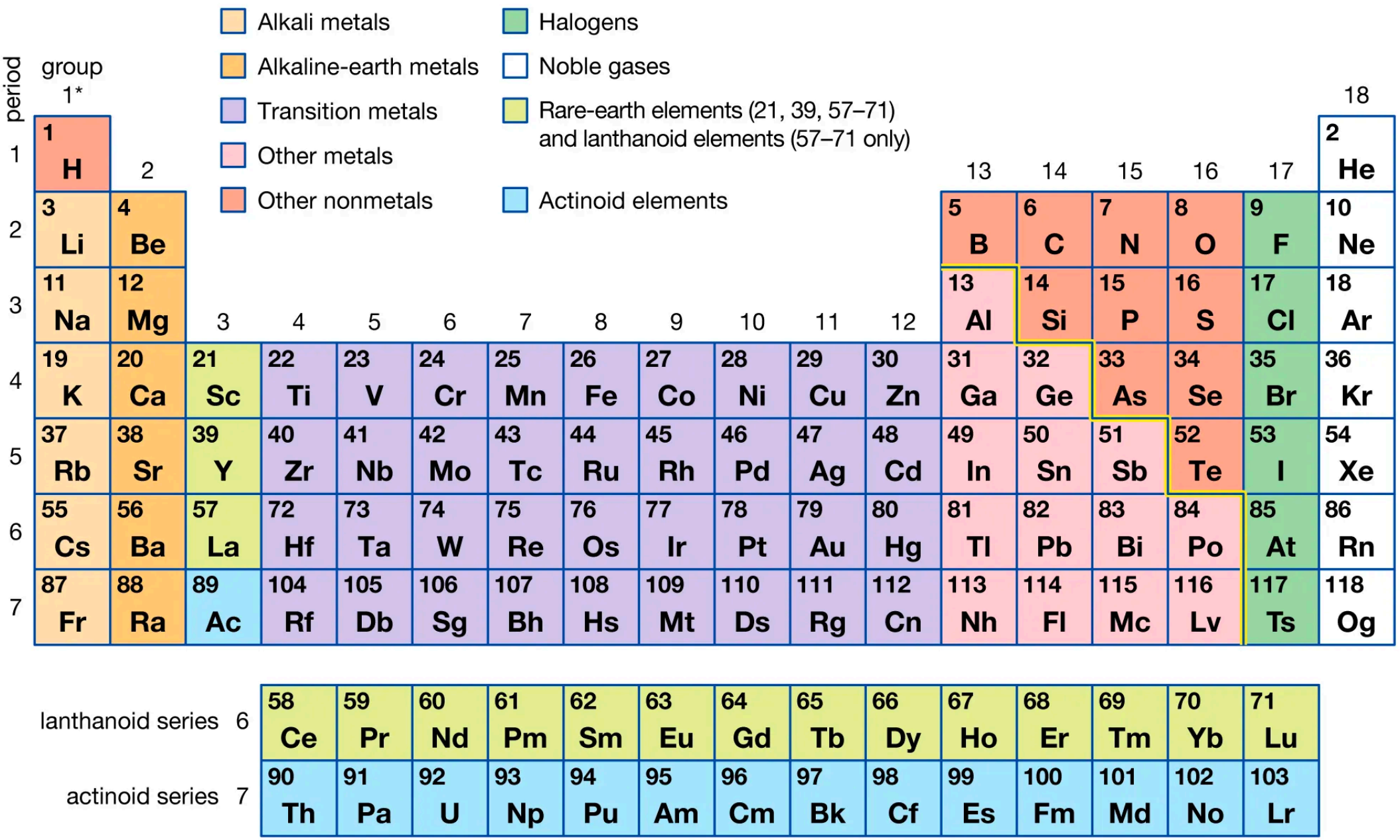
…using the work of many others!





Bonding
(the ‘glue’ in matter)
is determined
by the valence electrons

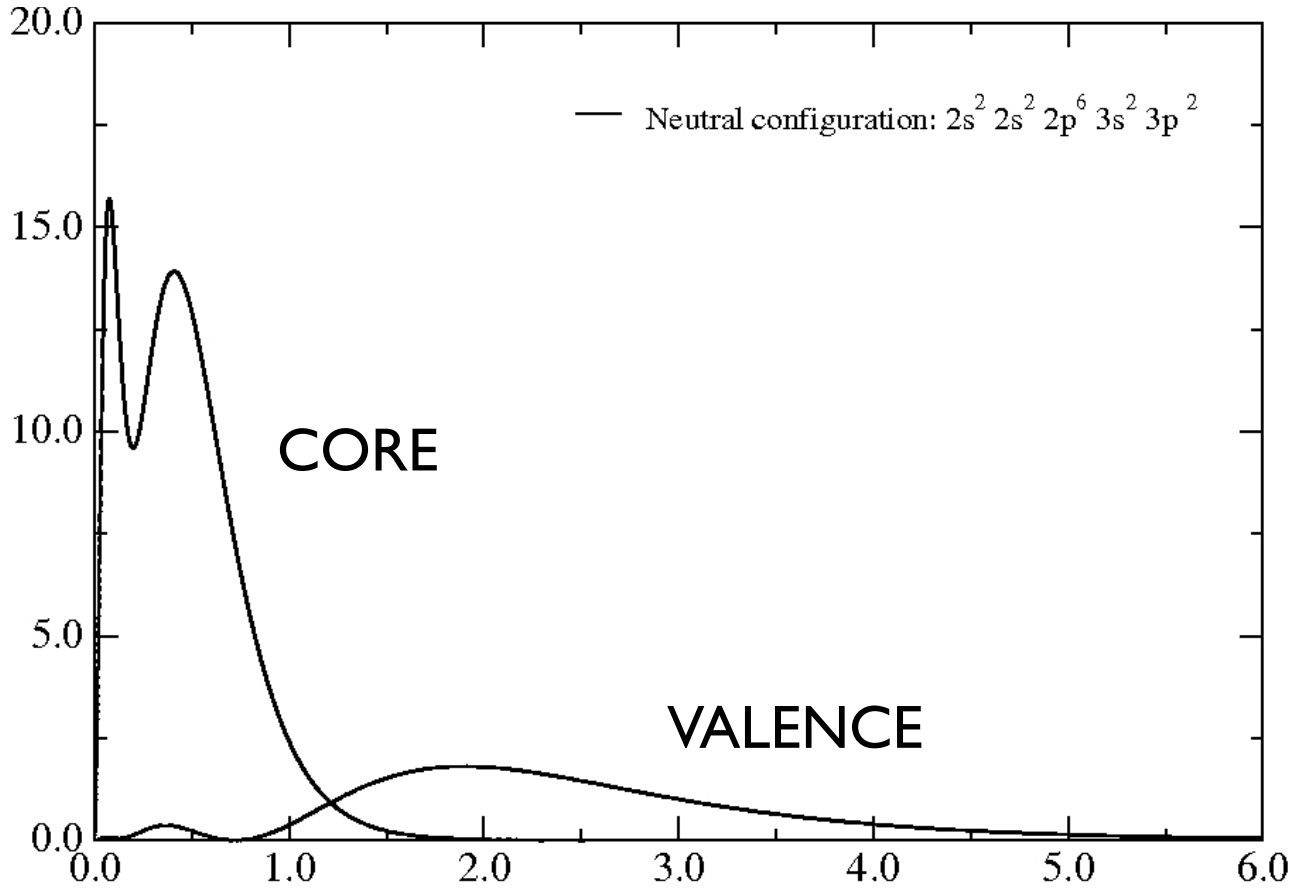
Periodic table of the elements



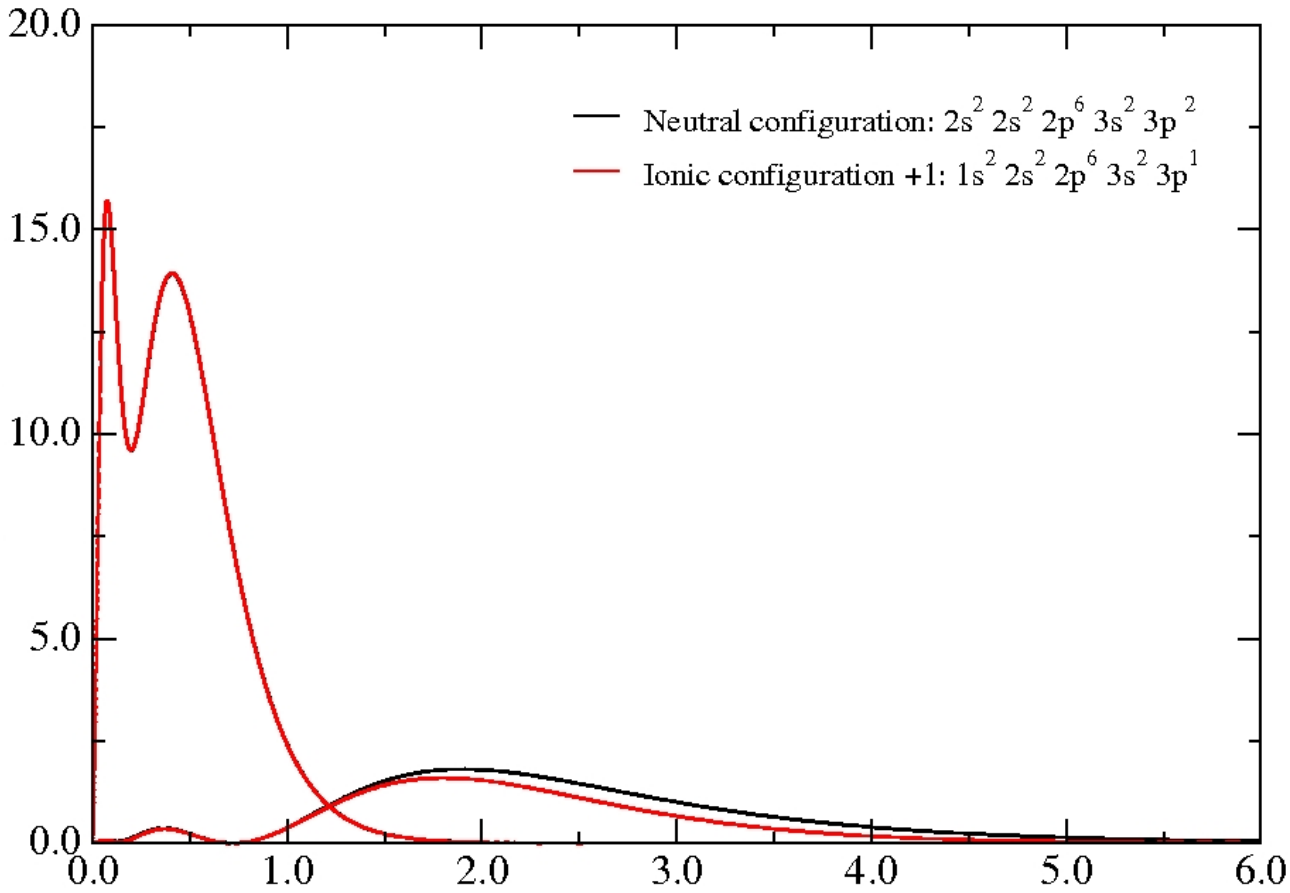
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

Radial profile of charge density for Si atom

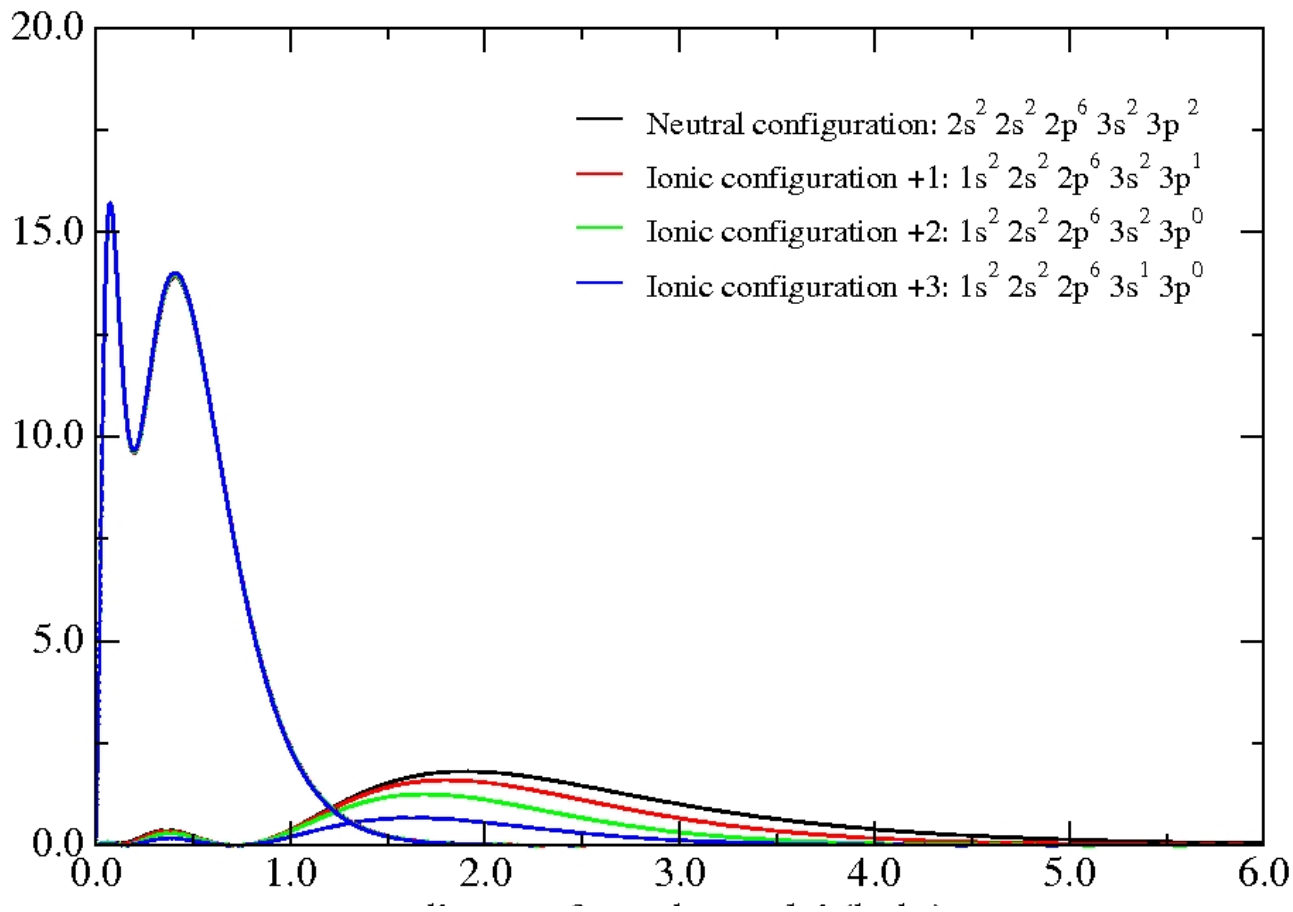
$$1s^2 2s^2 2p^6 3s^2 3p^2$$



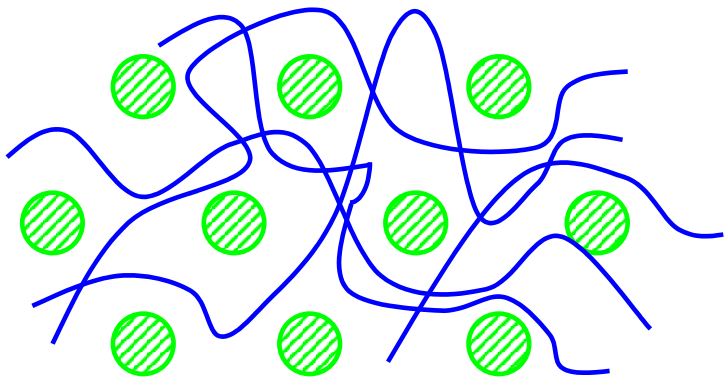
Radial profile of charge density for Si atom

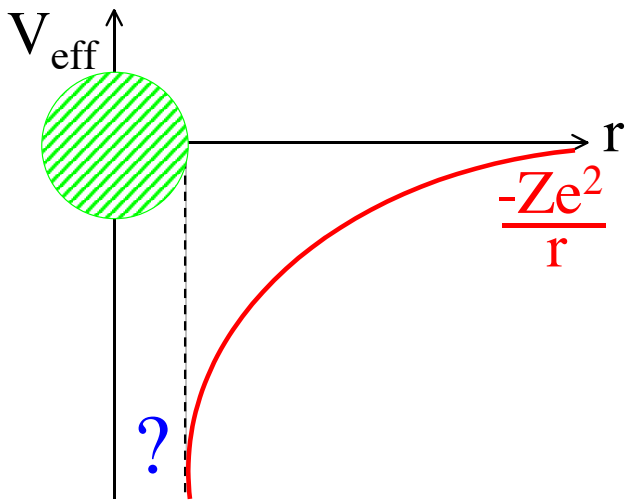


Radial profile of charge density for Si atom



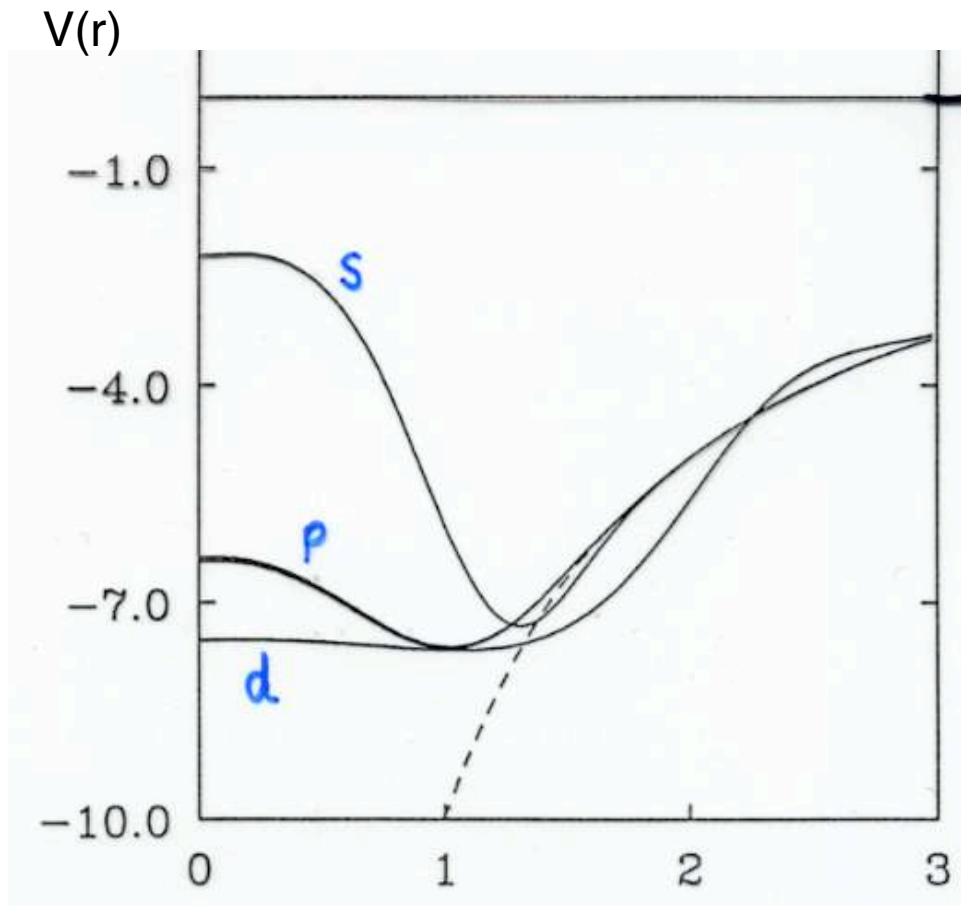
Internal electrons are inert, and do not participate in the chemical bond



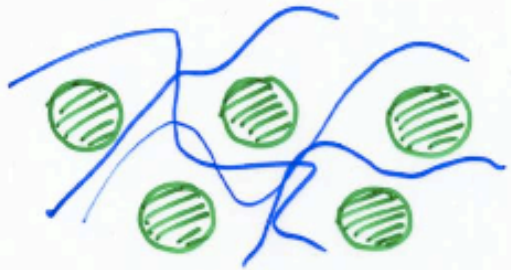


Effective potential for valence electrons

Pseudopotential



Orthogonalized plane-wave method (Herring, 1940)



Valence states: $|\vec{k}, OPW\rangle = |\vec{k}\rangle - \sum_c |\Psi_c\rangle\langle\Psi_c|\vec{k}\rangle$

orthogonal to the core states $|\Psi_c\rangle$

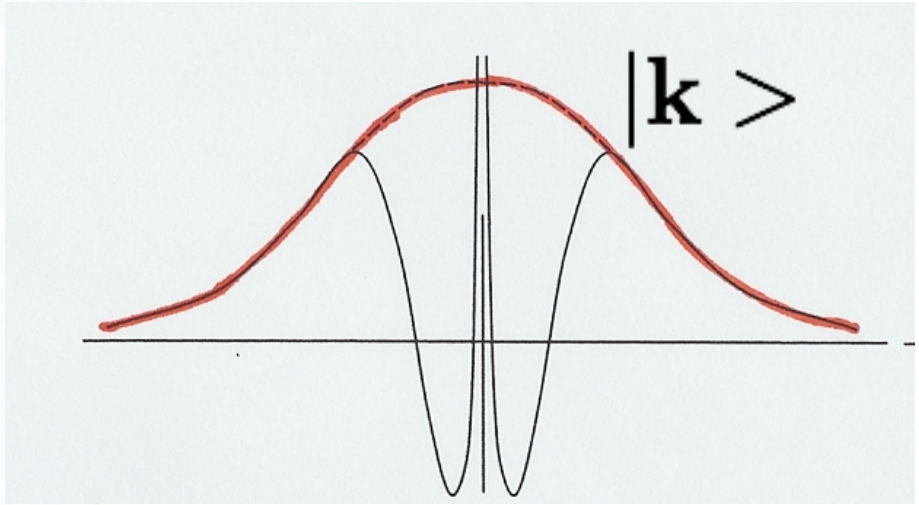
$\hat{H}\,|OPW\rangle = \varepsilon\,|OPW\rangle \Rightarrow$

$\Rightarrow (\hat{H} + \hat{V}_{Rep})\,|\vec{k}\rangle = \varepsilon\,|\vec{k}\rangle$

where: $\hat{V}_{Rep} = \sum_c (\varepsilon - \varepsilon_c)\,|\Psi_c\rangle\langle\Psi_c|$

is a repulsive potential

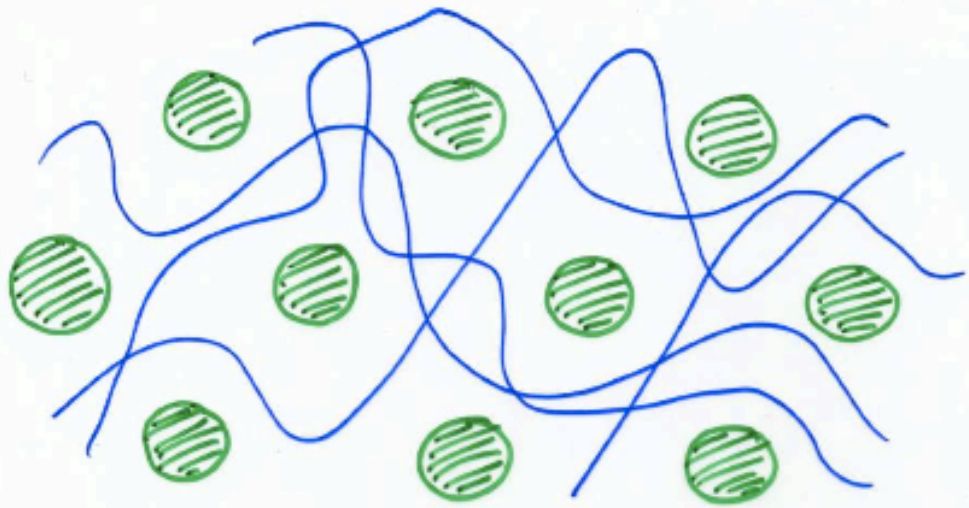
$\hat{H} = \hat{T} + \hat{V} \Rightarrow \hat{V}_{eff} = \hat{V} + \hat{V}_{Rep}$ is a "soft" pseudopotential

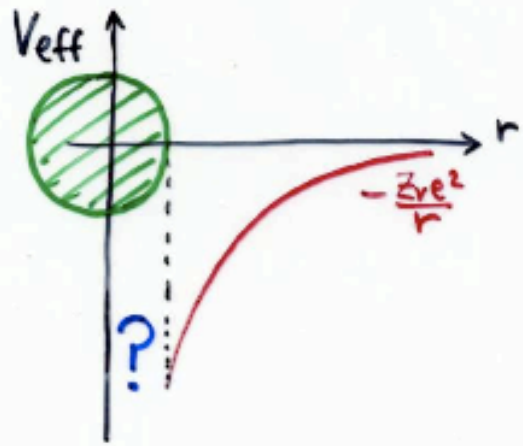


Phillips-Kleinman cancellation theorem (1959)

Common metal: Na

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





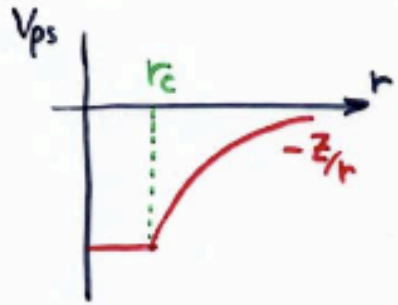
In the core zone, the effective potential will be <u>softer</u> than the coulomb $-\frac{Ze^2}{r}$ pot.

Empirical pseudopotentials

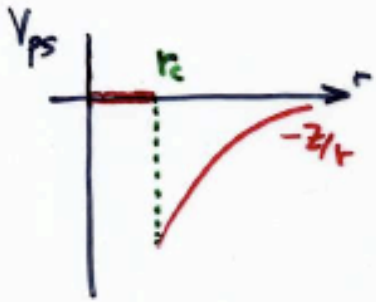
- Pseudopotential (pre) history

- Fermi (1934)

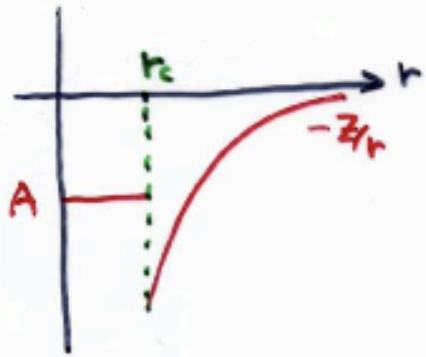
- Simple empirically-adjustable pseudopotentials



r_c adjusted to reproduce the valence eigenvalue



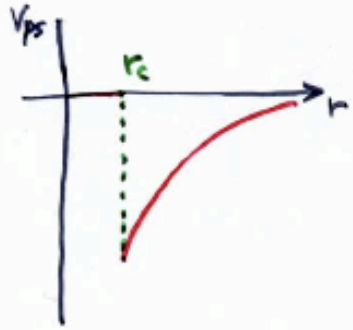
"Empty-core" pseudopotential
Ashcroft (1966)

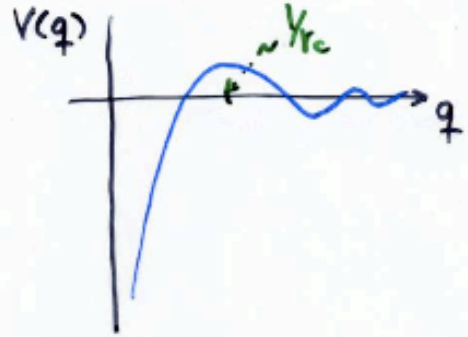


Heine - Abarenkov (~1964)

A = A(ℓ) : angular-momentum-dependent

A = A(E, ℓ) : energy-dependent



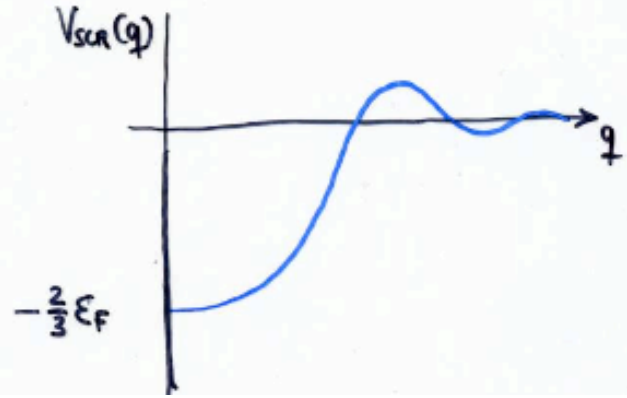


Fourier transform : $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

- Screening

$\frac{1}{r} \rightarrow \frac{1}{r} e^{-K_{TF} \cdot r}$ $\quad K_{TF}$: Thomas-Fermi wave vector

$$V_{scr}(q) = -\frac{4\pi e^2}{q^2 + K_{TF}^2} \cos q \cdot r_c$$



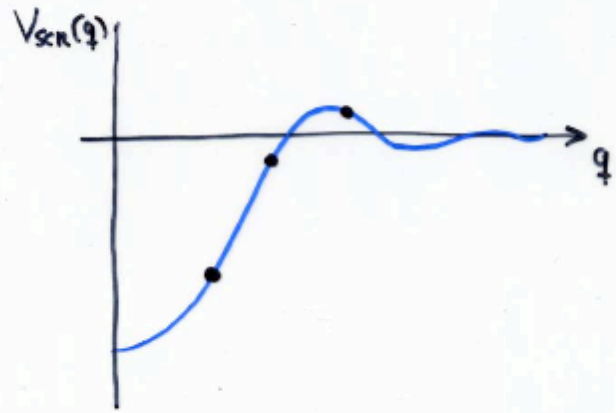
- In a periodic solid :

$$V(\vec{G}) = S(\vec{G}) \cdot V(q = |\vec{G}|)$$

$$S(\vec{G}) = \frac{1}{N_a} \sum_i e^{-i\vec{G}\cdot\vec{\tau}_i}$$ structure factor

For highly symmetric structures,
$S(\vec{G}) \neq 0$ for only relatively few $\vec{G}$'s

Diamond / Zinc Blende : $G^2 = 3, 8, 11, \ldots \left(\times \left(\frac{2\pi}{a}\right)^2\right)$



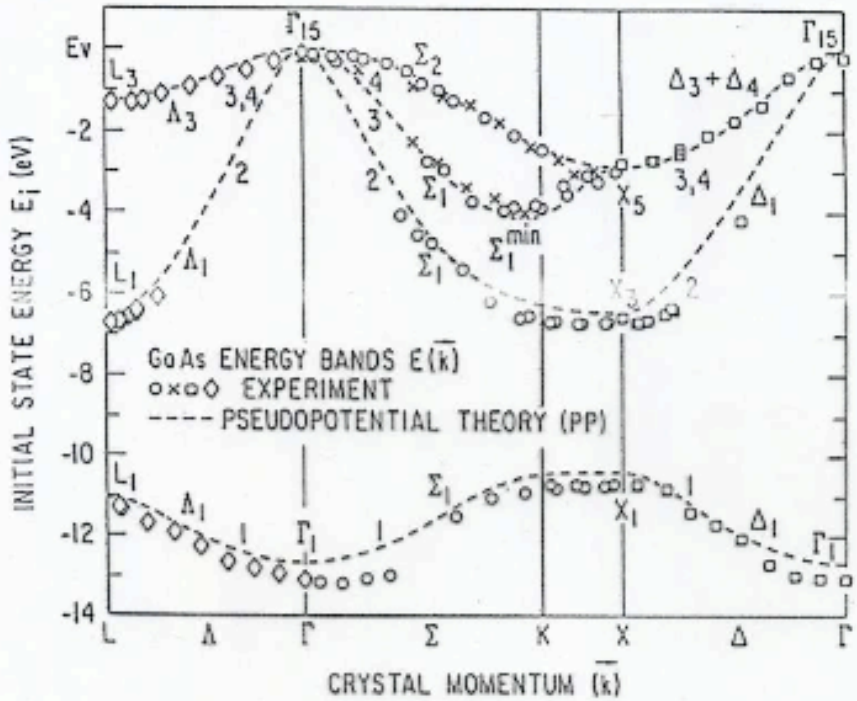
ONLY three parameters are needed for a reasonably good description

$$\left\{ -\nabla^2 + \underbrace{V_{ion} + V_H + V_{xc}}_{V_{eff}} \right\} \psi = \varepsilon \psi$$

$V_{eff}(G)$ fitted !

Empirical Pseudopotential Method (EPM)

(Marvin L. Cohen et al. ~ 1962)



Band structure of GaAs

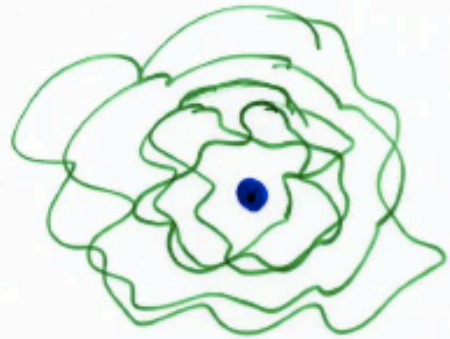
EPM needs a few experimental inputs

(absorption edge, reflectivity features...)

and provides the whole band structure

The modern era of pseudopotentials

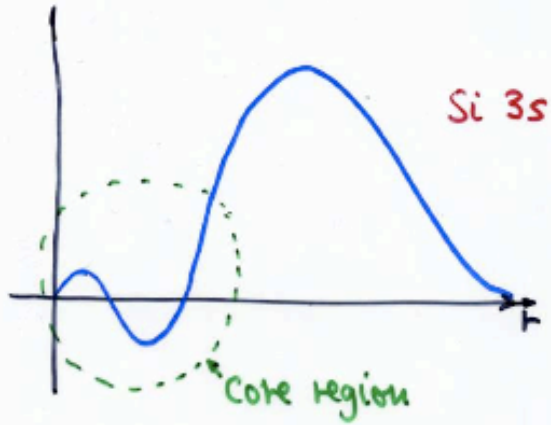
- Atomic calculations using DFT



$$\left\{ -\nabla^2 + V_{nucleus} + V_H + V_{xc} \right\} \psi_i = \varepsilon_i \psi_i$$

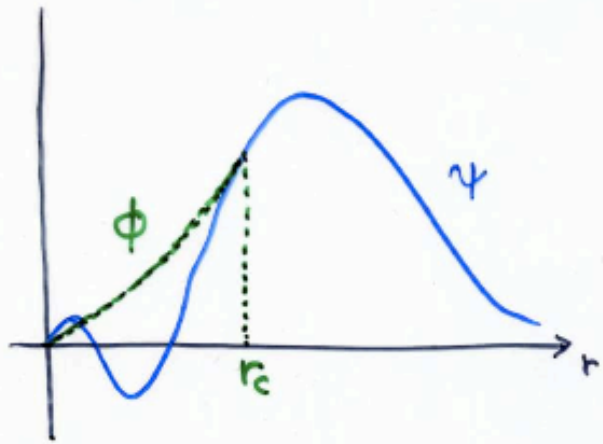
$$V_{nucleus} \rightarrow -\frac{Ze^2}{r}$$

$$n_{el}(\vec{r}) = \sum_i |\psi_i|^2$$

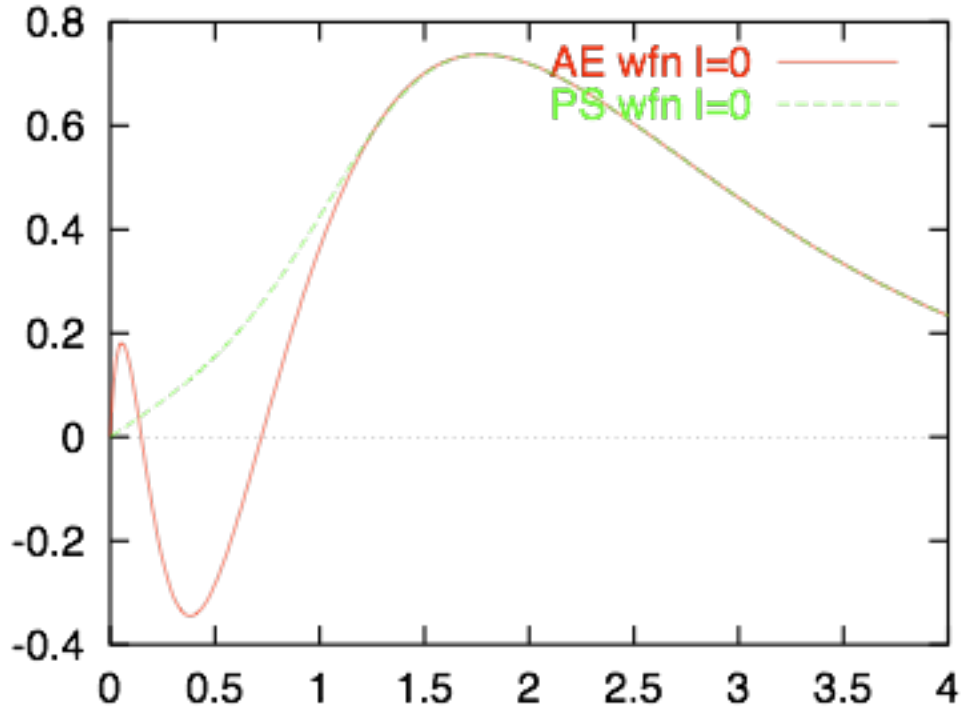


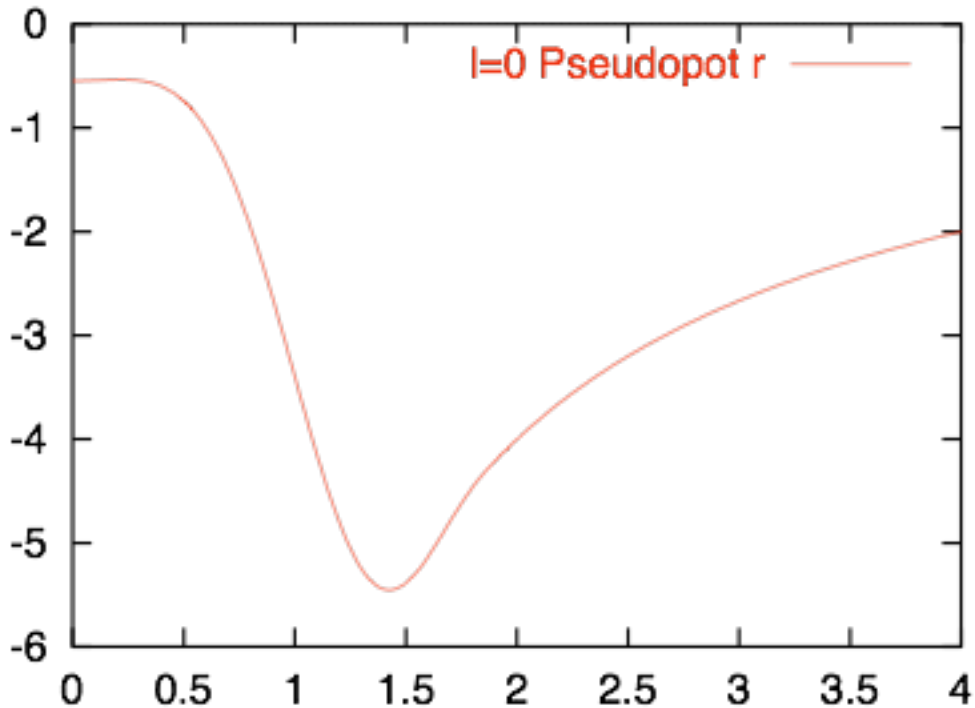
nodes : Imposed by orthogonality to the core states.

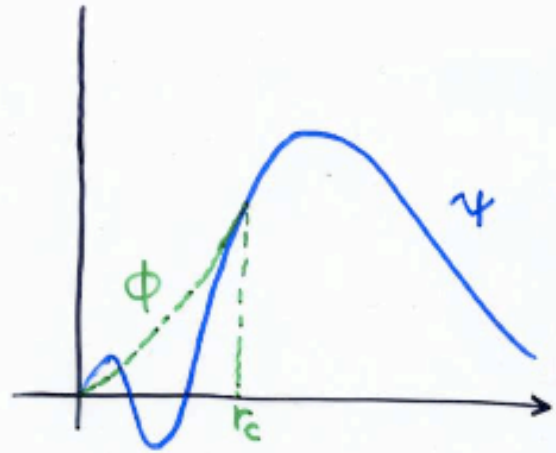
Idea : Eliminate the core electrons by "ironing out" the nodes :



ϕ: Pseudo wavefunction


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


l=0 Pseudopot r
0
-1
-2
-3
-4
-5
-6
0
0.5
1
1.5
2
2.5
3
3.5
4

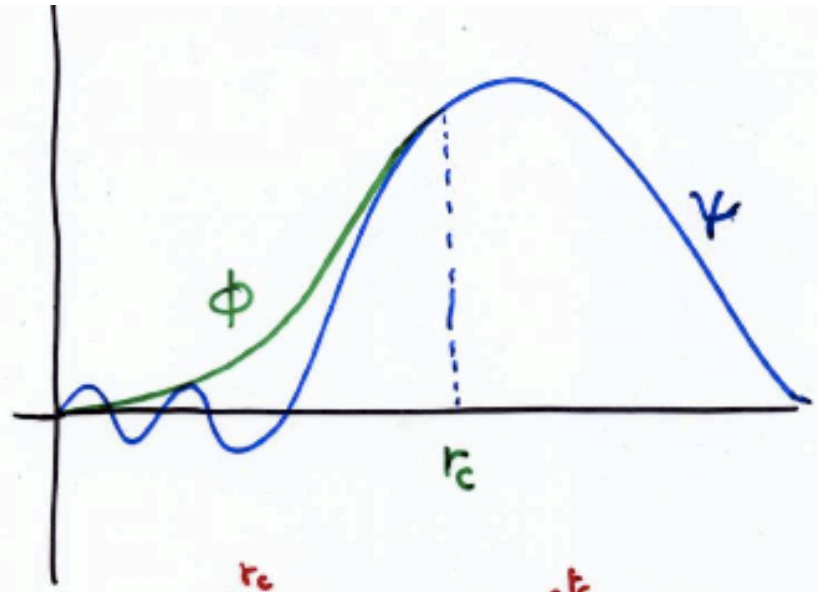


HOW does one get ϕ from ψ ?

Essential steps:

- Pick r_c (typically between the last node and the maximum)
- Match ϕ and ψ at or near r_c.
- Conserve the norm:

$$\int |\phi^{\bullet}|^2 dV = \int |\psi^{\bullet}|^2 dV$$



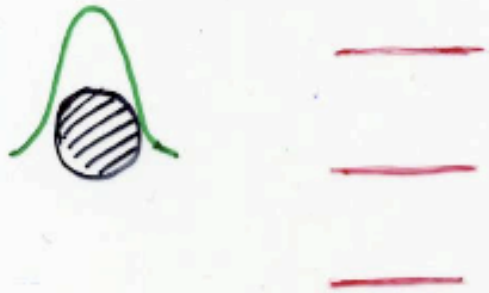
$$\int_0^{r_c} |\phi|^2 r^2 dr = \int_0^{r_c} |\psi|^2 r^2 dr$$

Norm – conservation

- Preserves electrostatic potential outside r_c
- $$\frac{d}{d\varepsilon}\left(\frac{d}{dr}\ln(r\phi)\right)\Big|_R \propto \frac{1}{(r\phi)^2}\int_0^R (r\phi)^2 dr$$

Preserves scattering properties (and their first energy derivative)

Isolated atom

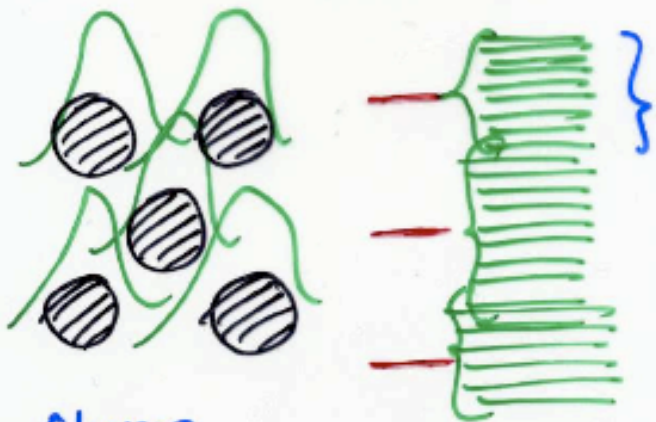


Atomic eigenvalues

V_{ps} "perfect"

TRANSFERABILITY

Solid



Bands

V_{ps} ?

Charge Transfer...

$$\{-\nabla^2 + \hat{V}_{AE}\}\,\Psi = \varepsilon\,\Psi$$

$$\hat{V}_{AE} = V_{nuc}(r) + V_H^{[n]}(r) + V_{xc}^{[n]}(r)$$

$$\{-\nabla^2 + \hat{V}_{ps}^{[n]}\}\,\phi = \varepsilon\,\phi$$

$\hat{V}_{ps}^{[n]}$: Screened pseudopotential

$$V_{ps}^{[n]} = \varepsilon + \frac{1}{\phi}\nabla^2\phi$$

"Bare" or ionic pseudopotential:

$$V_{ps}(r) = V_{ps}^{[n]} - V_H^{[n]} - V_{xc}^{[n]}$$

n: Valence charge density

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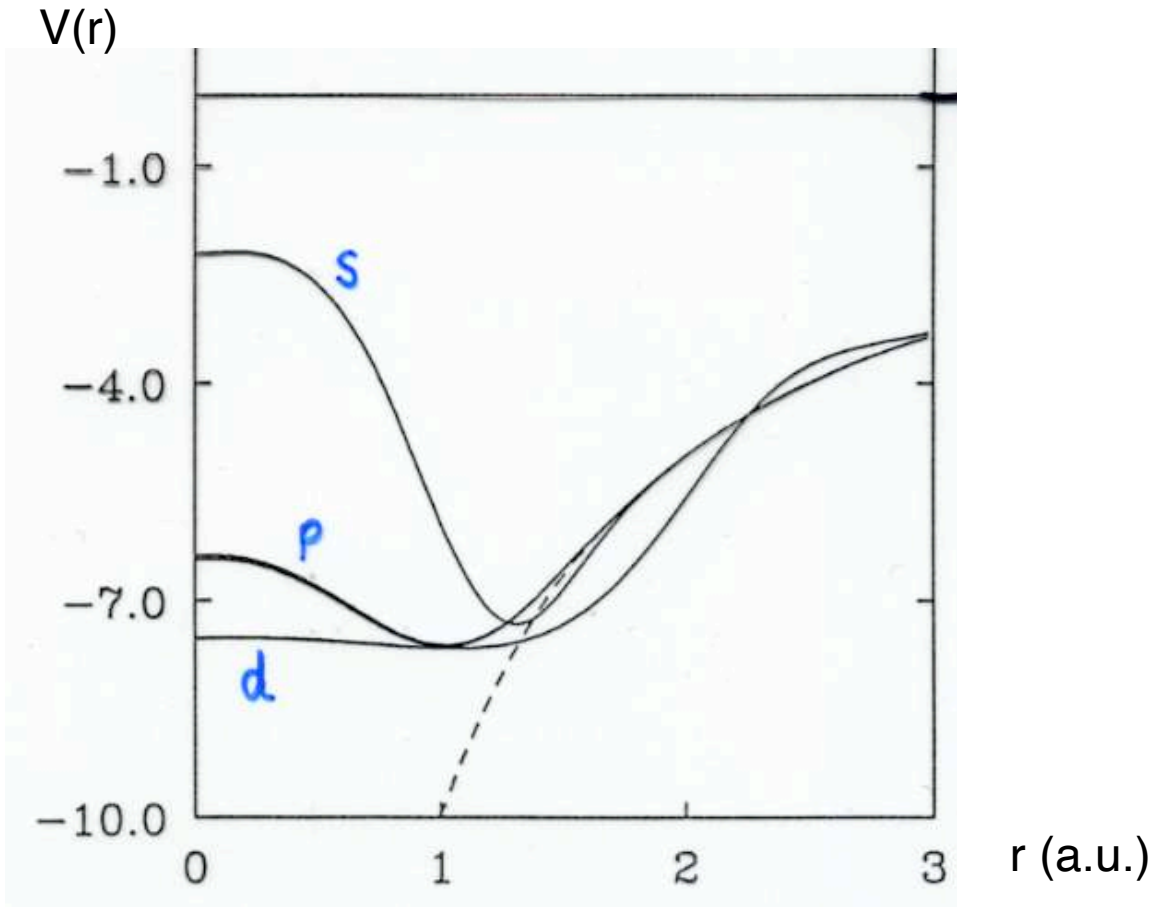
non-linear core corrections

n : Valence charge density

Ab-initio pseudopotentials



Semi-local form:

$$\hat{V}_{ps} = \sum_{\ell} V_{\ell}(r) \underbrace{|\ell><\ell|}_{\text{Projector for } \ell}$$

$$= V_{LOCAL}(r) + \sum_{\ell} \underbrace{\Delta V_{\ell}(r)}_{\text{Short ranged}} |\ell><\ell|$$

Kleinman-Bylander form:

$$\hat{V}_{ps} = V_{LOCAL}(r) + \sum_{\ell m} \frac{|\Delta V_{\ell} \phi_{\ell m}><\phi_{\ell m} \Delta V_{\ell}|}{<\phi_{\ell m}|\Delta V_{\ell}|\phi_{\ell m}>}$$

(Fully non-local form)

(Many) newer developments to address transferability and cost issues

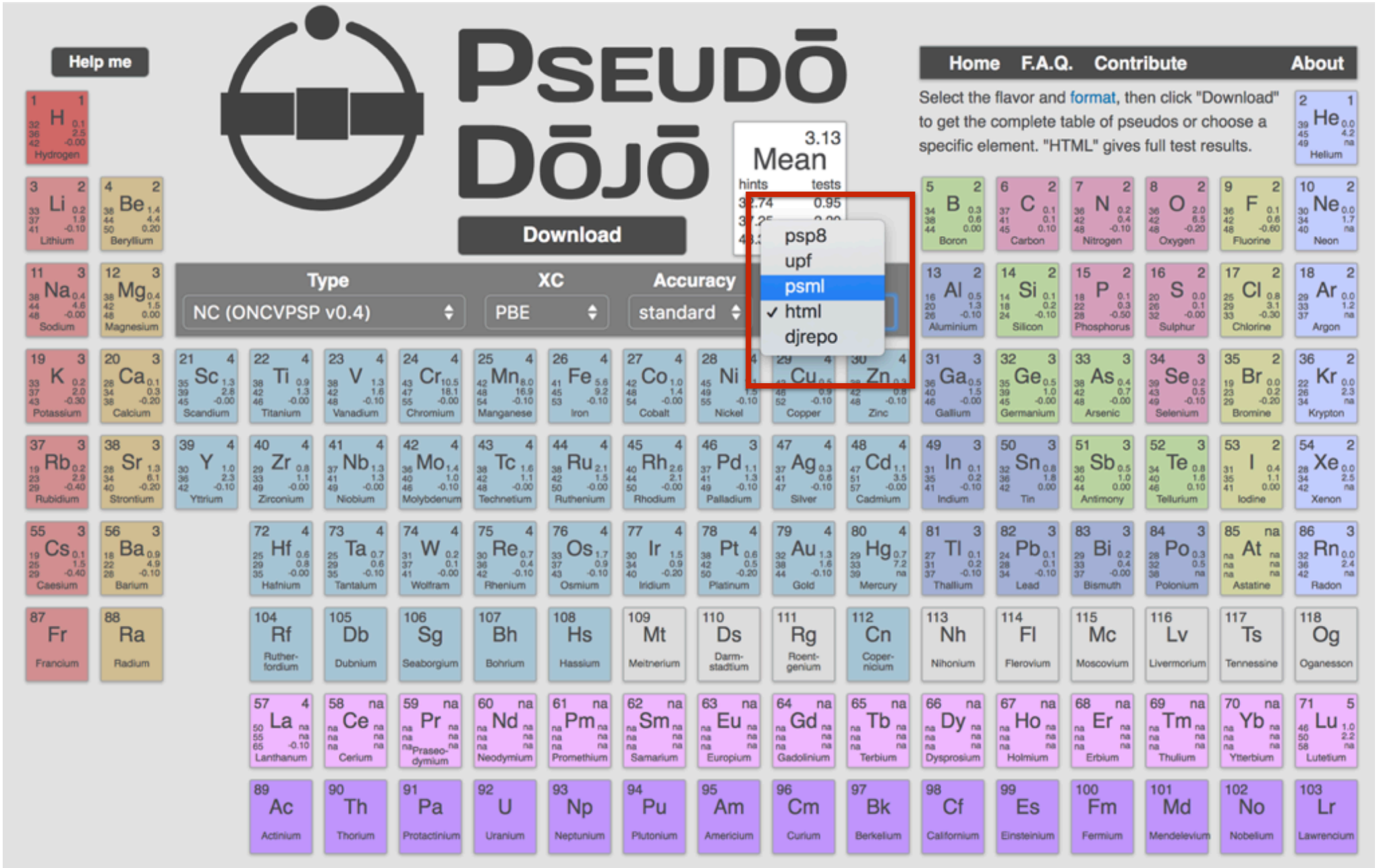
- Refinements of the "node ironing" and inversion procedures.
- Ultrasoft pseudopotentials
- Norm-conserving schemes using multiple projectors

More…

- Find out how your favorite materials simulation code uses pseudopotentials.
- Become familiar with the available databases.
- (Remember to test your pseudopotentials!)

Databases of curated pseudopotentials

http://www.pseudo-dojo.org/



Practical issues in Siesta

PS use in Siesta

- Legacy format: .psf extension
- PSML format: .psml extension
  - Richer metadata
  - Can use Pseudo-Dojo database

Generation of pseudopotentials:

- ATOM program: https://docs.siesta-project.org/projects/atom
- ONCV program: See https://www.pseudo-dojo.org