# The pseudopotential concept

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…using the work of many others!

siesta

MAX DRIVING THE EXASCALE TRANSITION

CSIC

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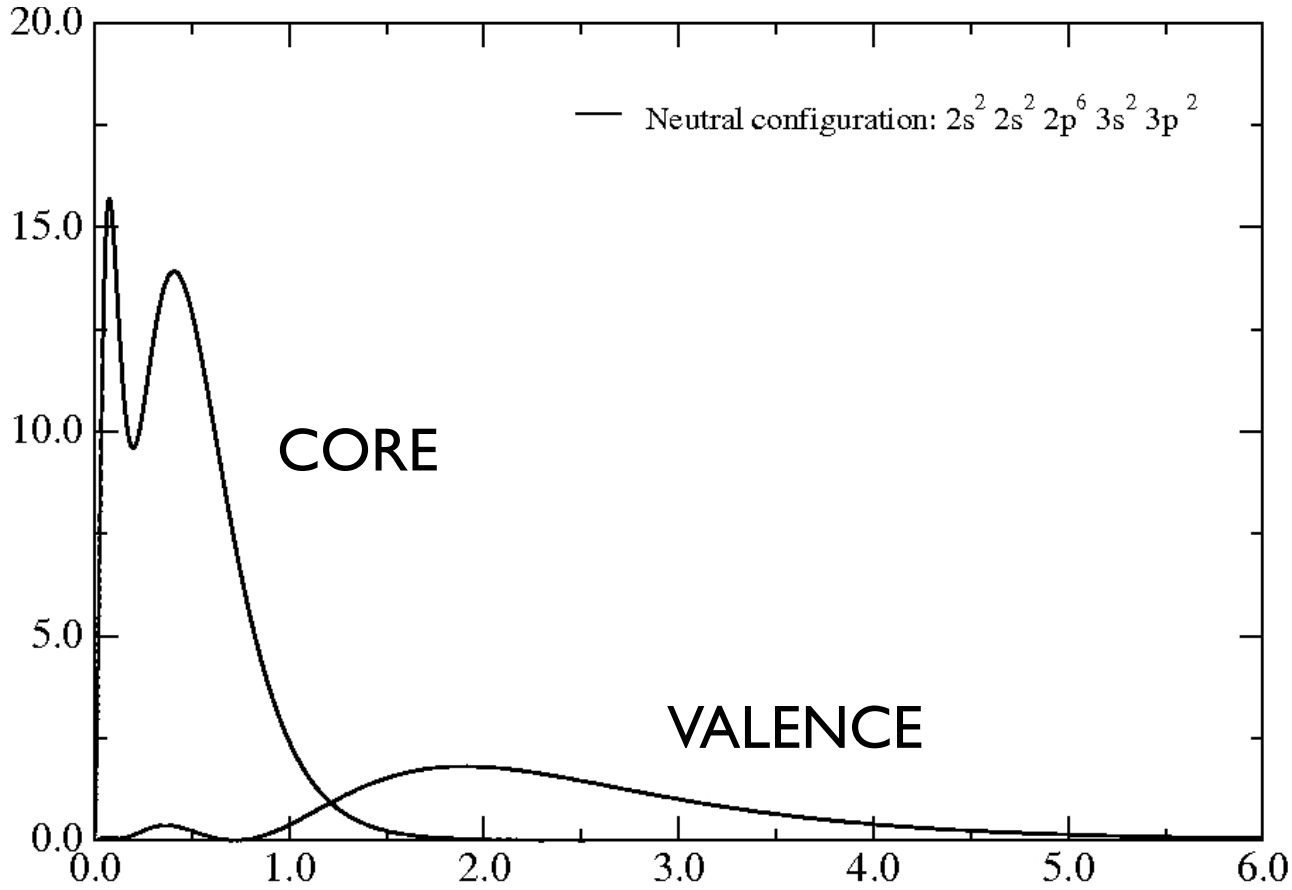
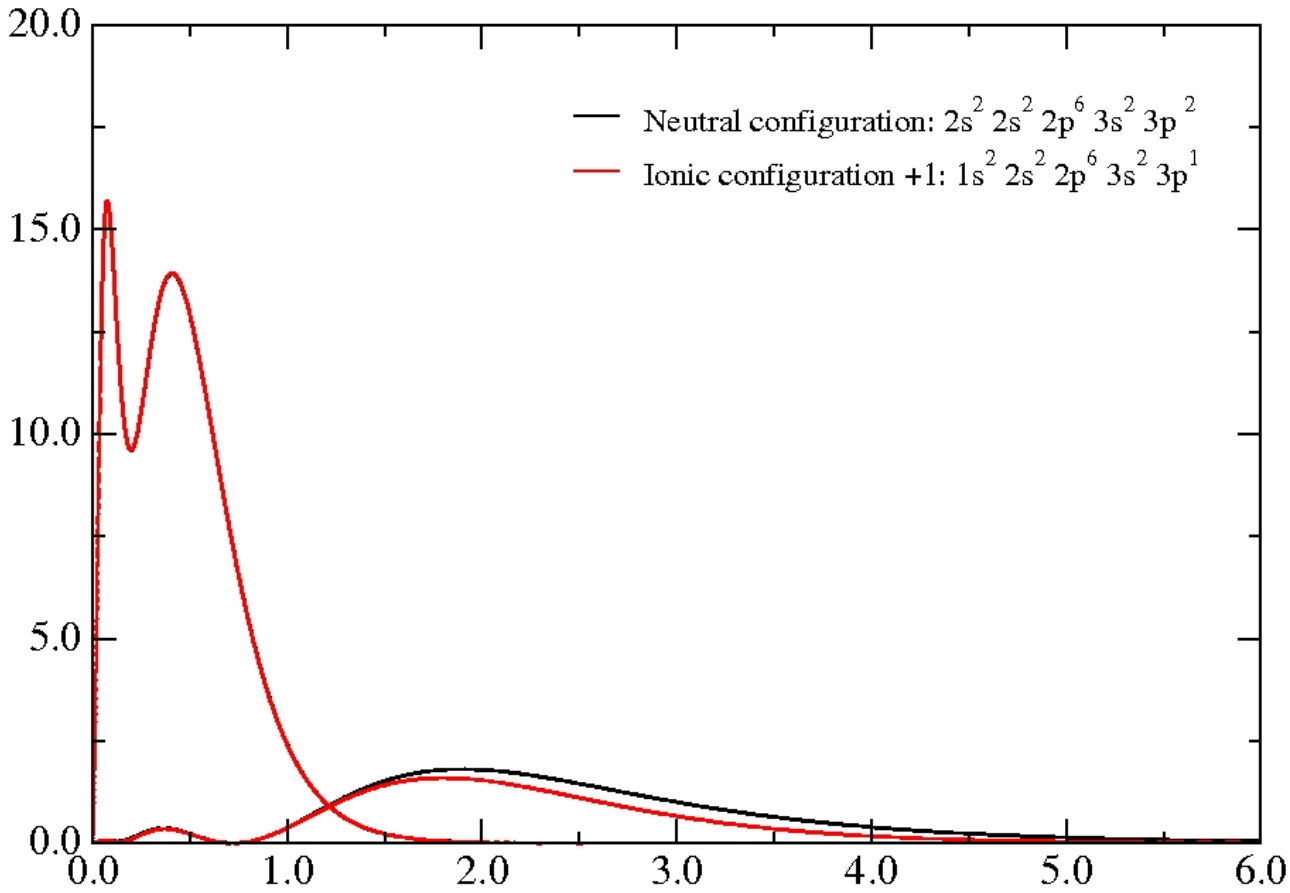
EXCELENCIA SEVERO OCHOA

# Radial profile of charge density for Si atom

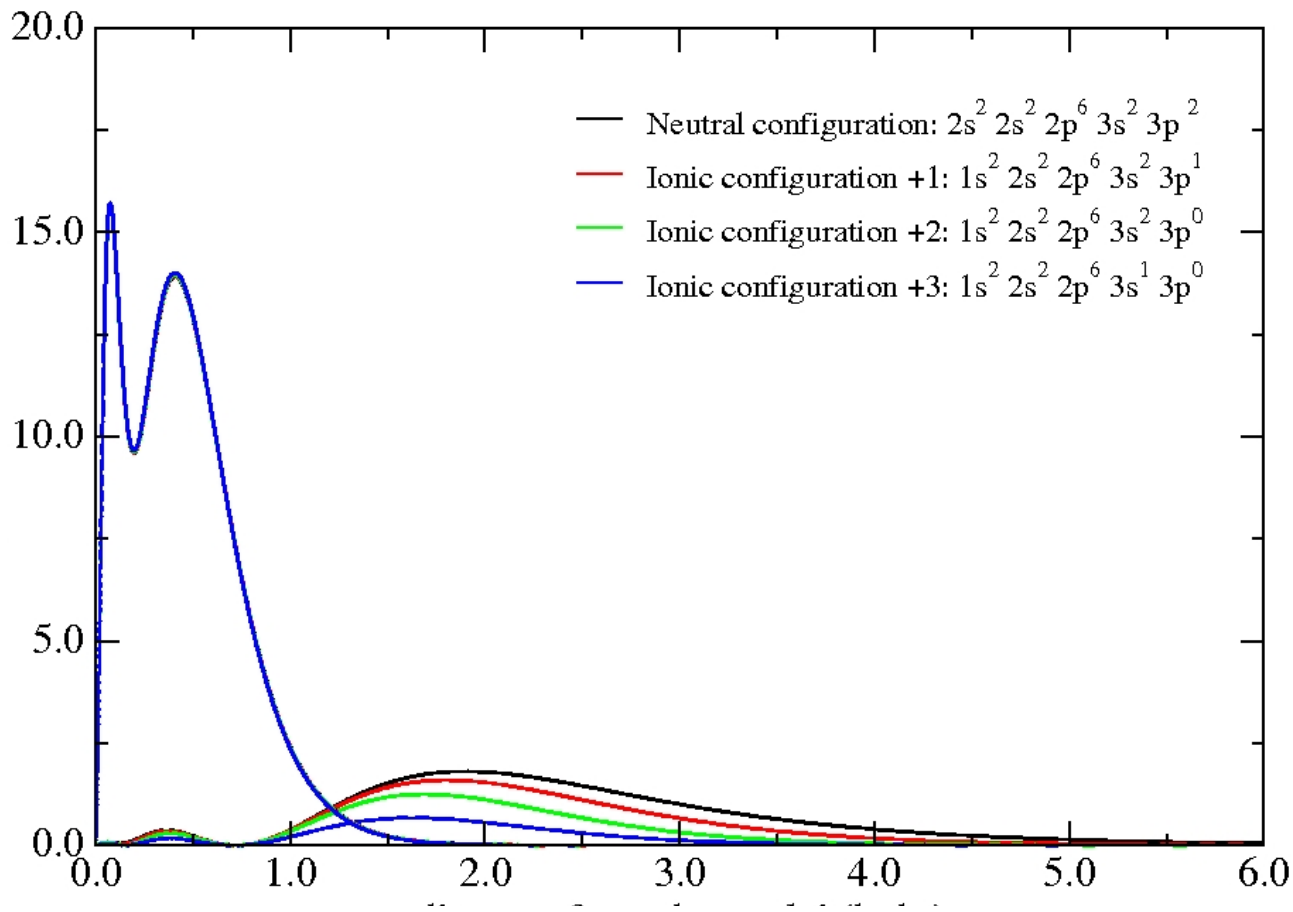
$$1s^2 2s^2 2p^6 3s^2 3p^2$$



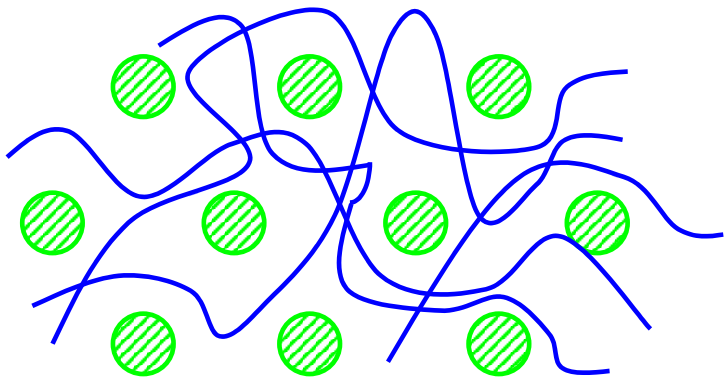
# Radial profile of charge density for Si atom

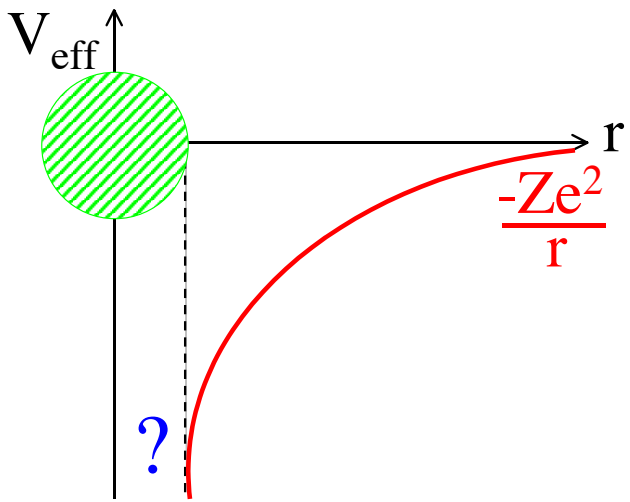


# Radial profile of charge density for Si atom



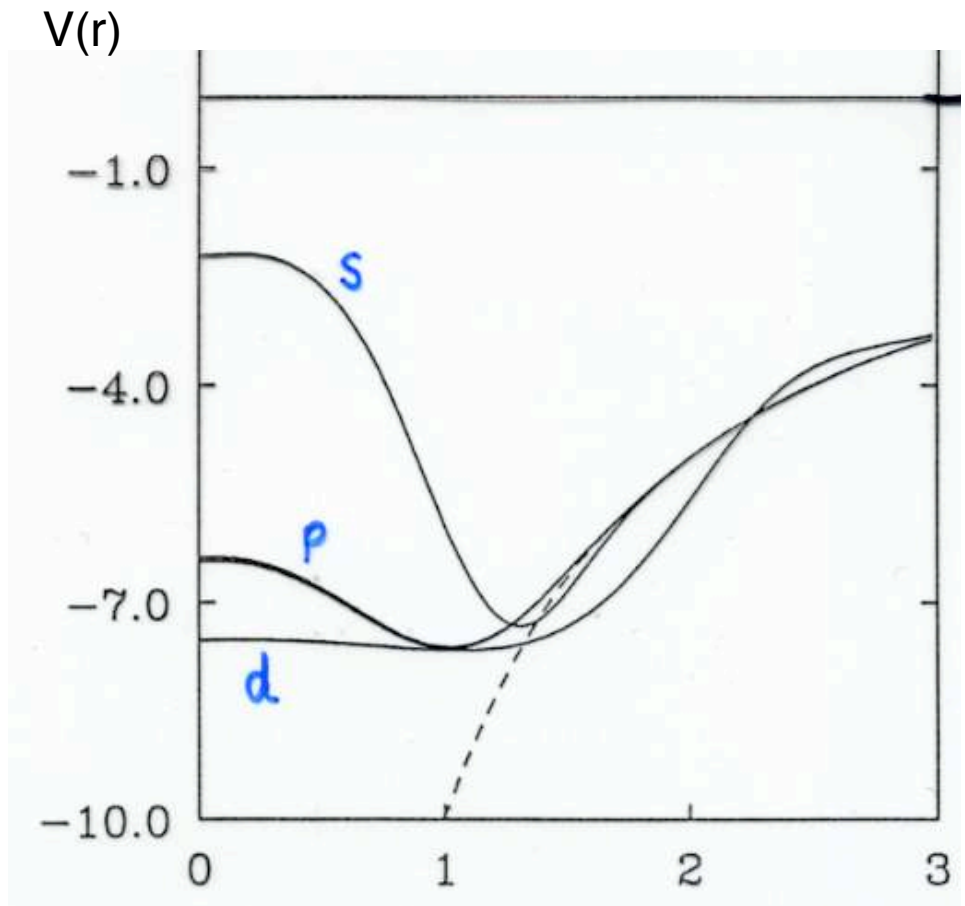
# Internal electrons are inert, and do not participate in the chemical bond



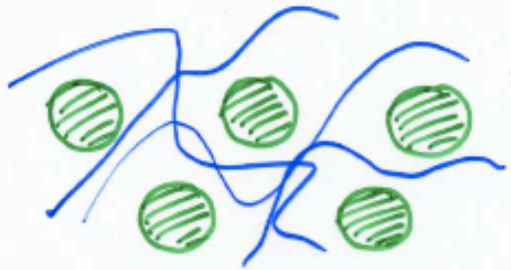



Effective potential for valence electrons

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 $|\Psi_c\rangle$

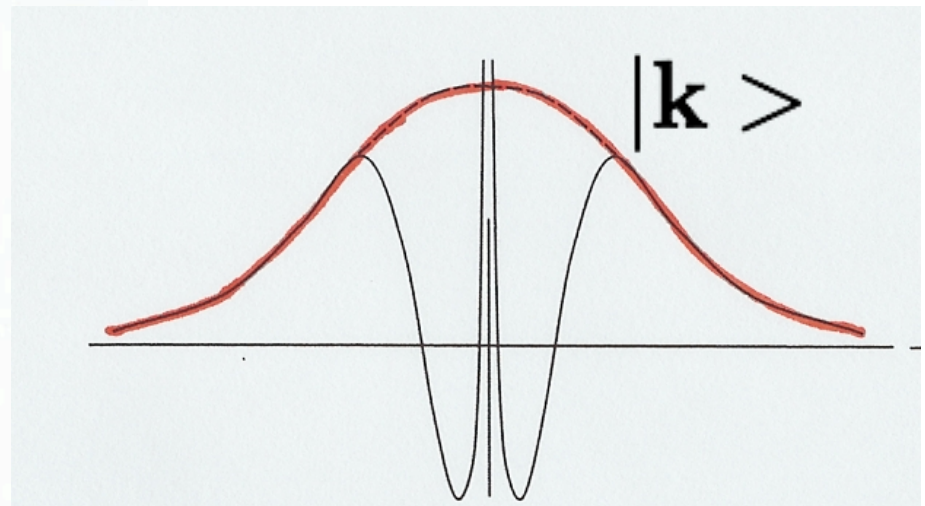
$\hat{H}\,|OPW\rangle = \varepsilon\,|OPW\rangle \Rightarrow$

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

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

is a repulsive potential

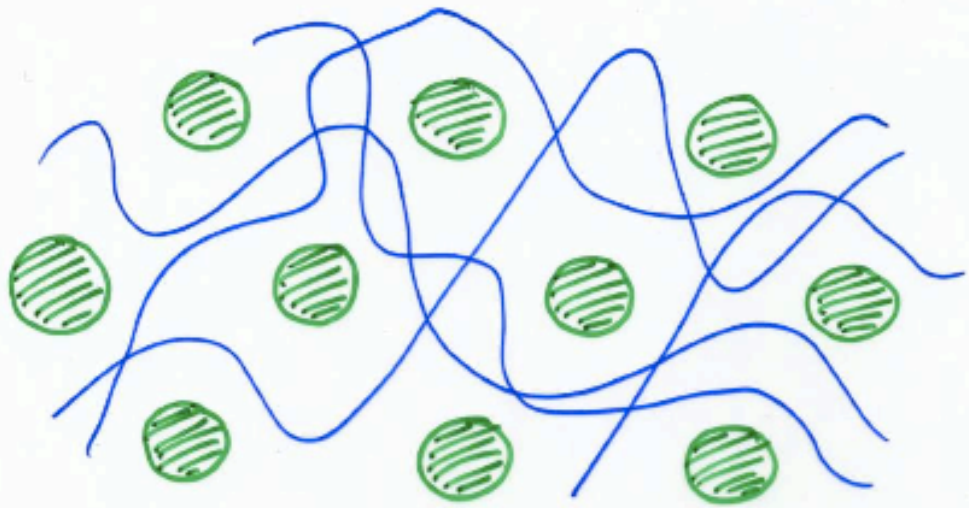
$\hat{H} = \hat{T} + \hat{V} \Rightarrow \hat{V}_{eff} = \hat{V} + \hat{V}_{Rep}$ is a "soft" pseudopotential

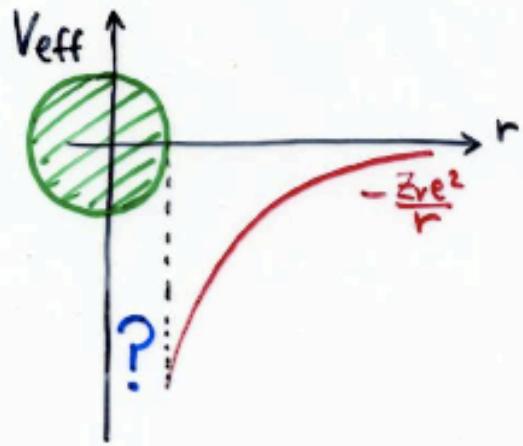



Phillips-Kleinman cancellation theorem (1959)

# Common metal: Na

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



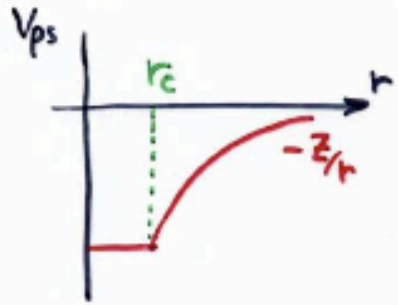



In the core zone, the effective potential will be <u>softer</u> than the coulomb $-\frac{Ze^2}{r}$ pot.

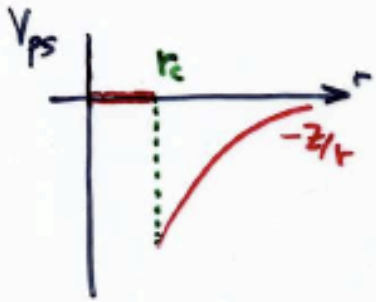
- Pseudopotential (pre) history

- Fermi (1934)

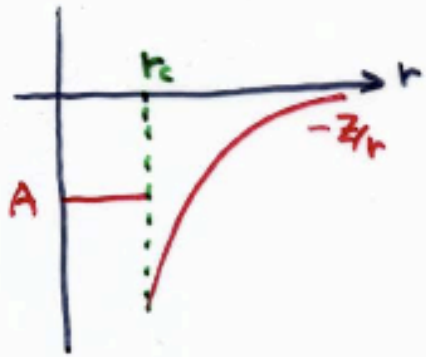
- Simple empirically-adjustable pseudopotentials




$r_c$ adjusted to reproduce the valence eigenvalue



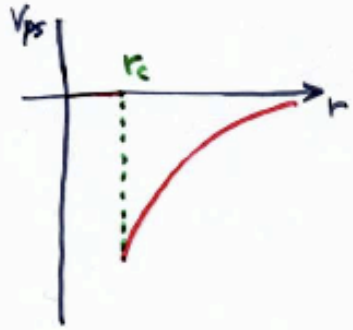

"Empty-core" pseudopotential
Ashcroft (1966)

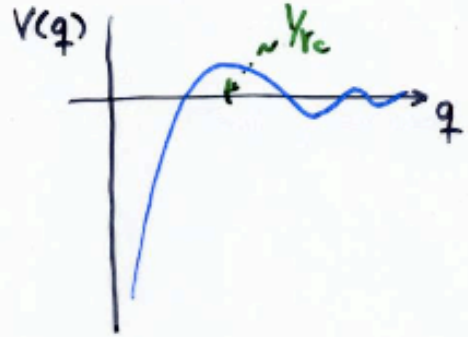



Heine - Abarenkov (~1964)

A = A(ℓ) : angular-momentum-dependent

A = A(E, ℓ) : energy-dependent



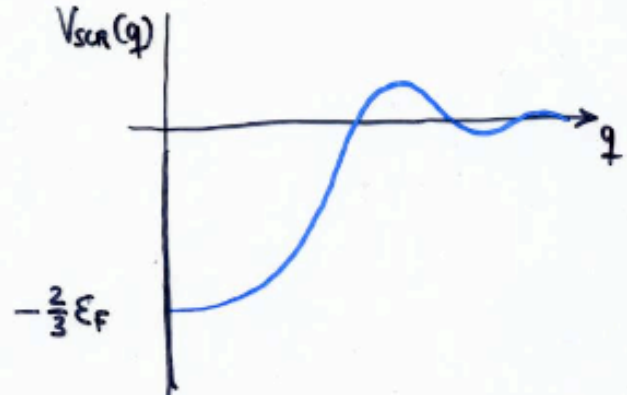




Fourier transform : $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

- Screening

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

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



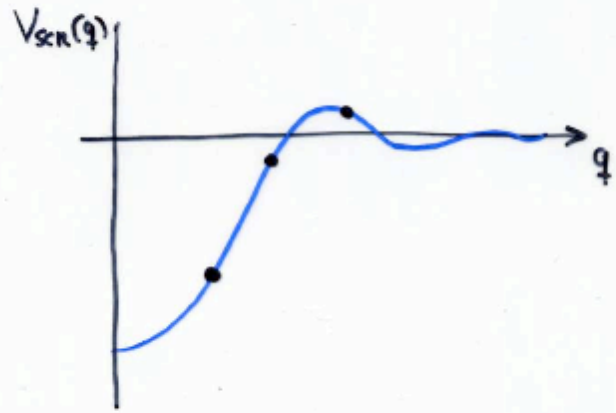
- In a periodic solid :

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

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


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

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



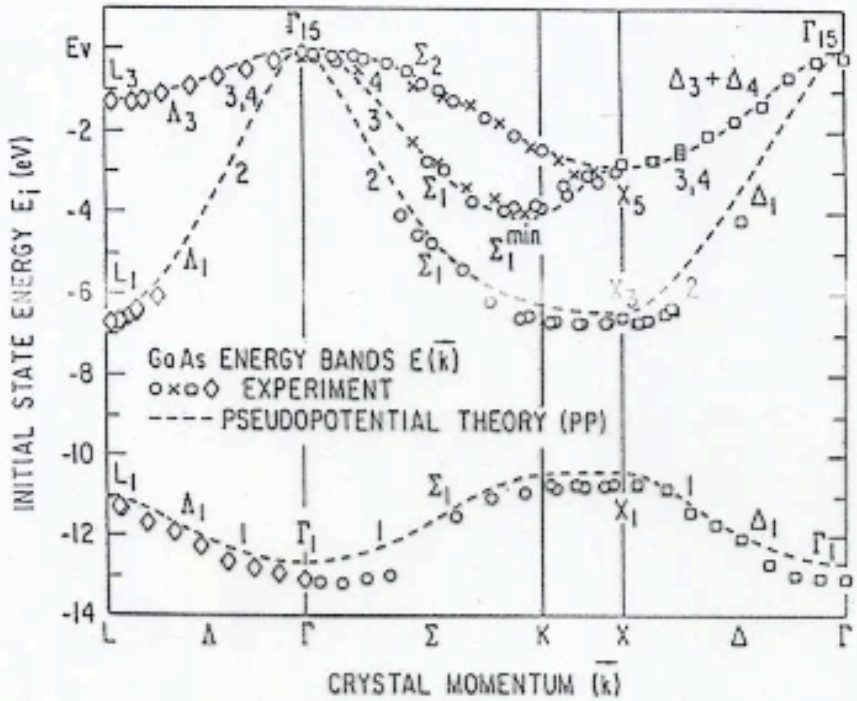

ONLY three parameters are needed for a reasonably good description

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

$V_{eff}(G)$ fitted !

# Empirical Pseudopotential Method (EPM)

(Marvin L. Cohen et al. ~ 1962)




Band structure of GaAs

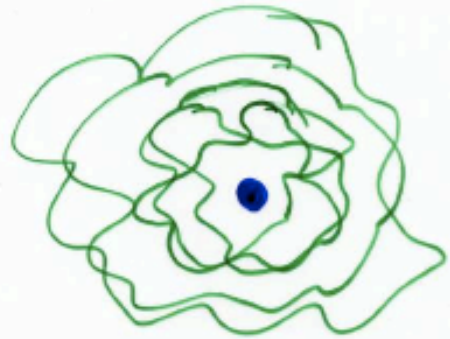
EPM needs a few experimental inputs

(absorption edge, reflectivity features...)

and provides the whole band structure

# The modern era of pseudopotentials

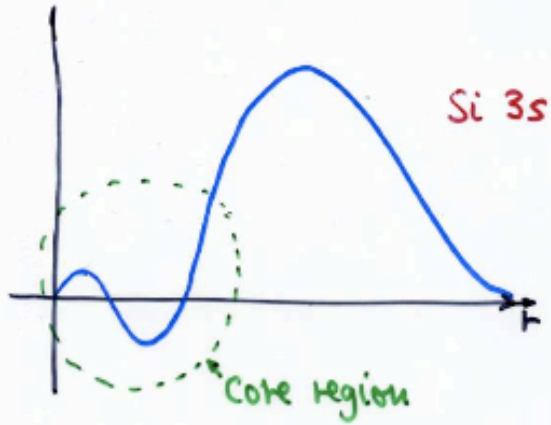
- Atomic calculations using DFT



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

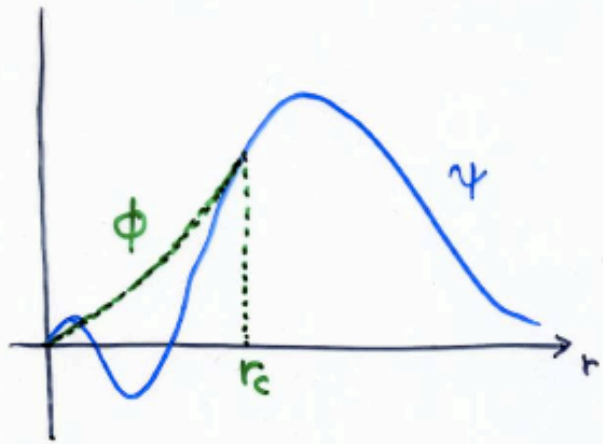
$$V_{nucleus} \rightarrow -\frac{Ze^2}{r}$$

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

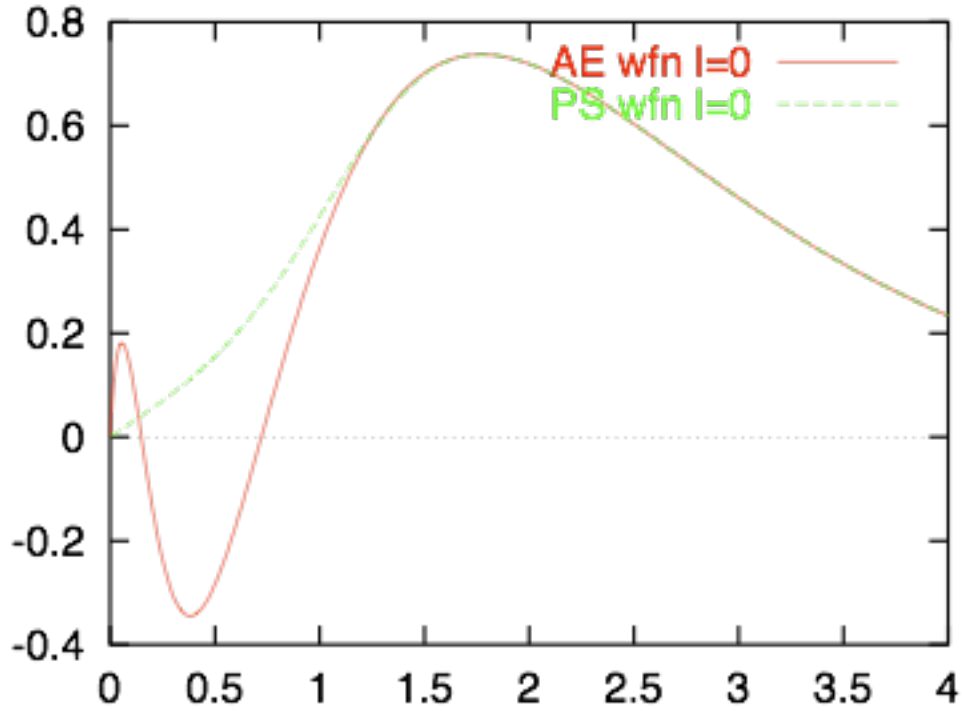


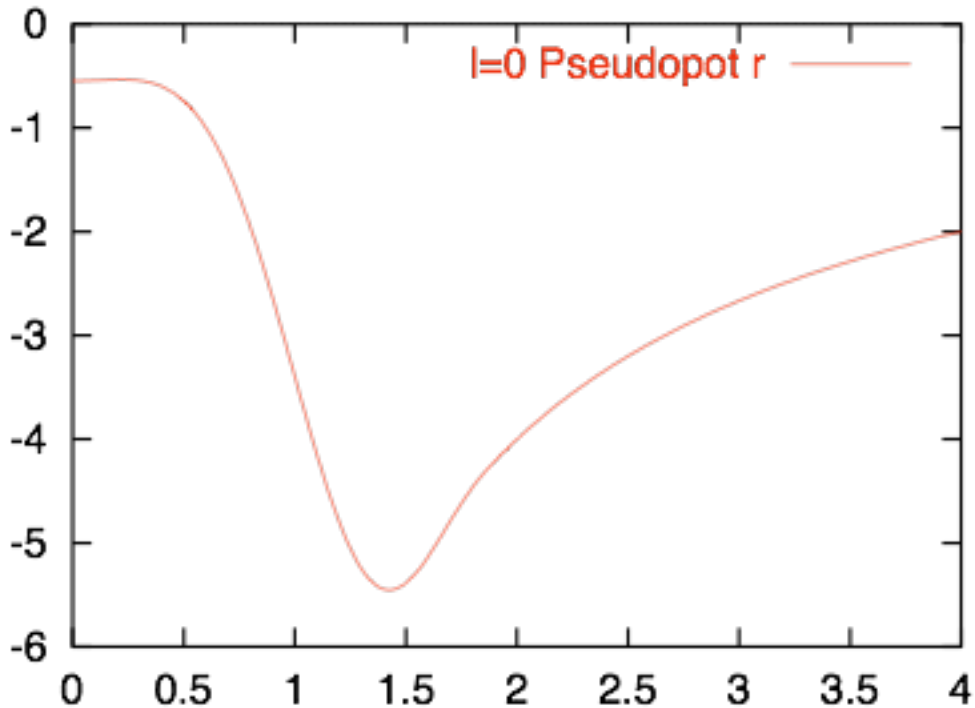

nodes : Imposed by orthogonality to the core states.

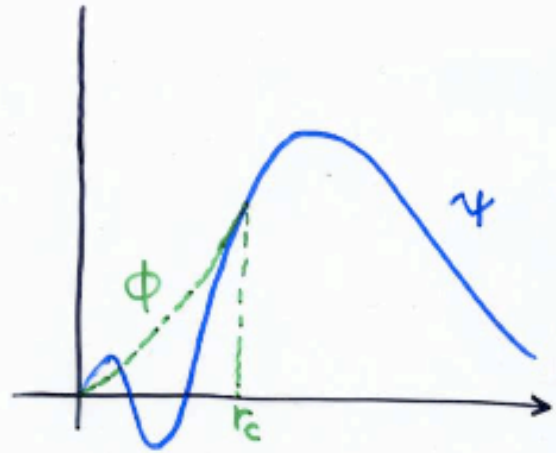
Idea : Eliminate the core electrons by "ironing out" the nodes :




$\phi$: 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

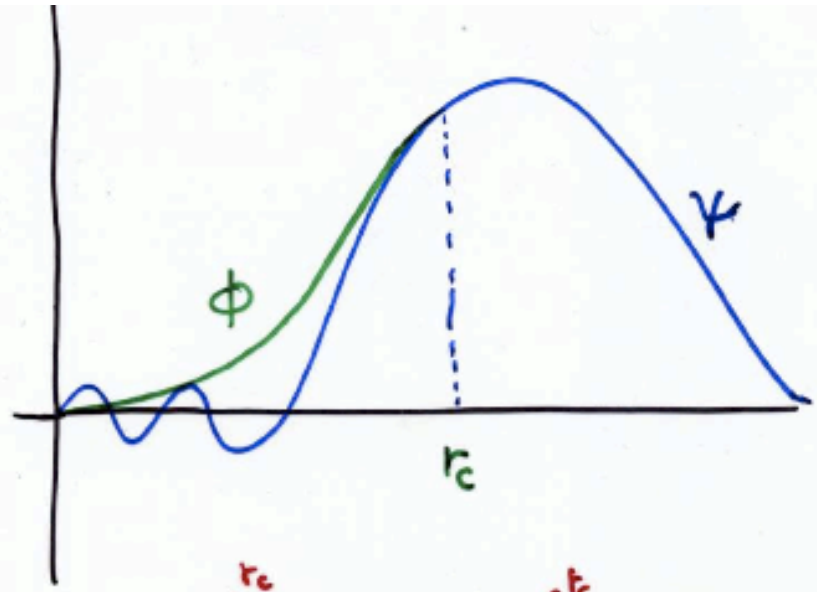



HOW does one get $\phi$ from $\psi$ ?

Essential steps:

- Pick $r_c$ (typically between the last node and the maximum)
- Match $\phi$ and $\psi$ at or near $r_c$.
- Conserve the norm:

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



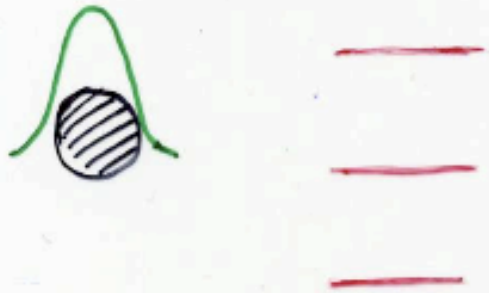

$$\int_0^{r_c} |\phi|^2 r^2 dr = \int_0^{r_c} |\psi|^2 r^2 dr$$

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

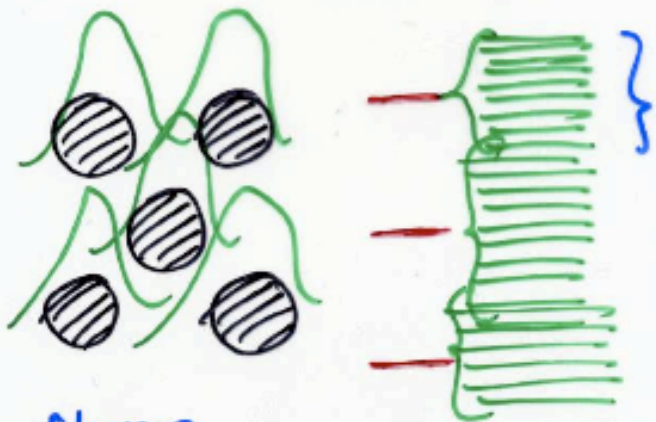


Atomic eigenvalues

$V_{ps}$ "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

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

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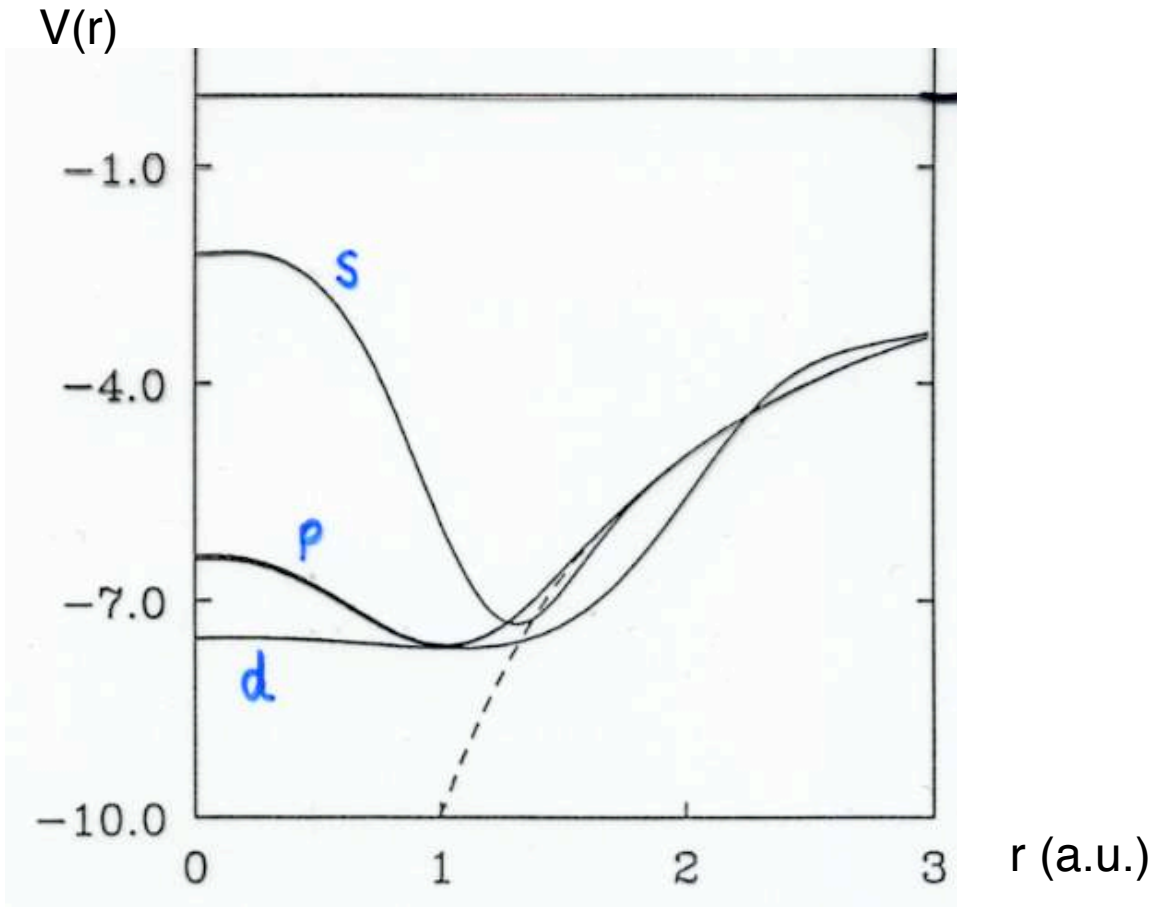
"Bare" or ionic pseudopotential:

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

$V_{xc}^{[n]}$ → 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:

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

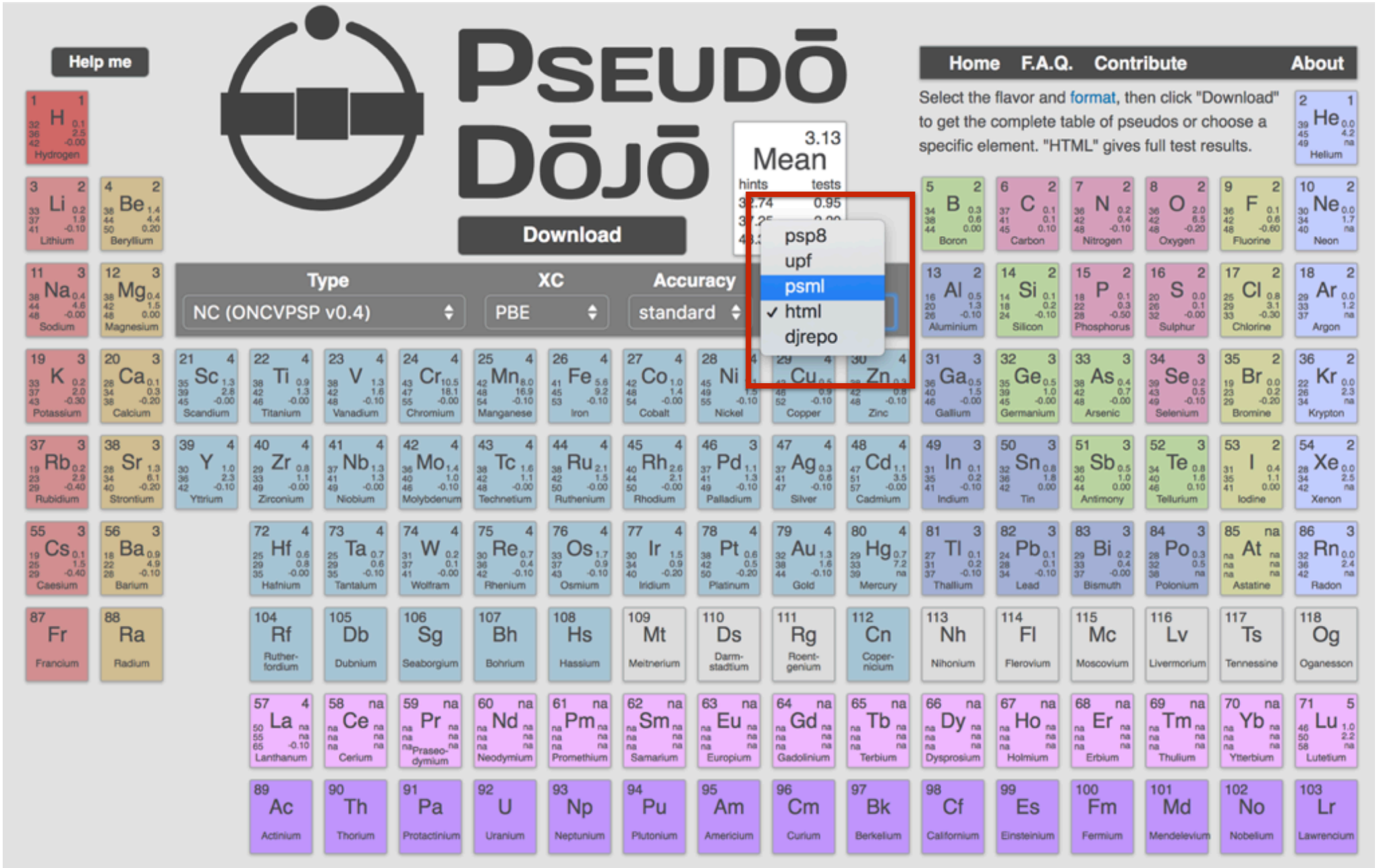
(Fully non-local form)

# (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

# Databases of curated pseudopotentials

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



# More…

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