The pseudopotential concept

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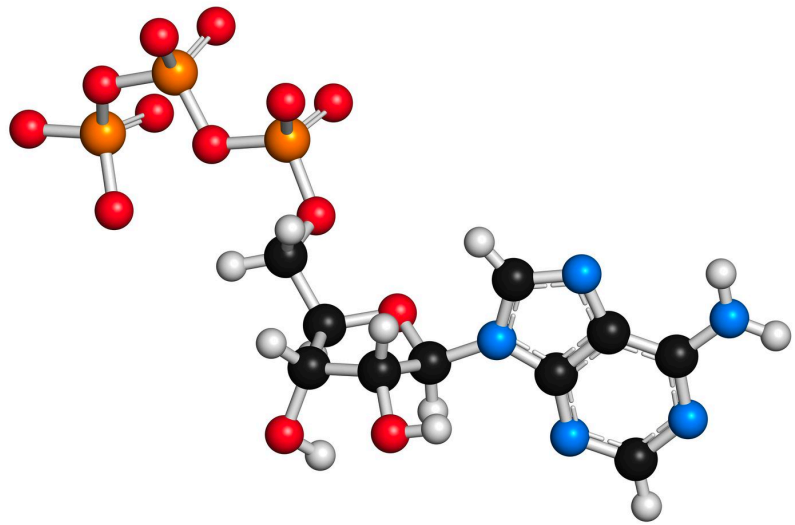
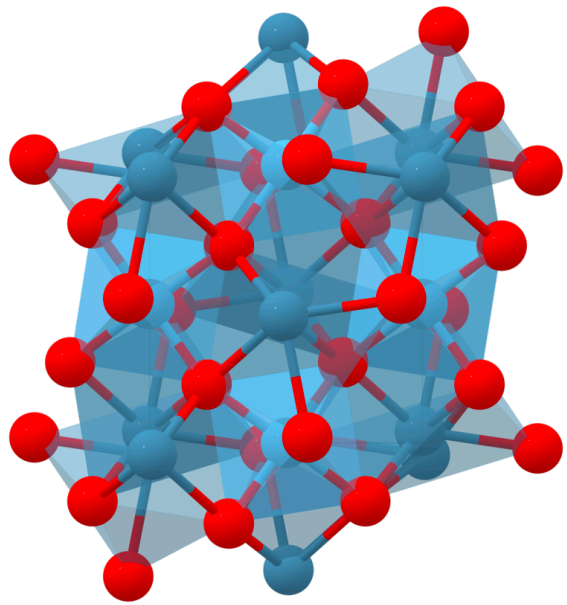
…using the work of many others!

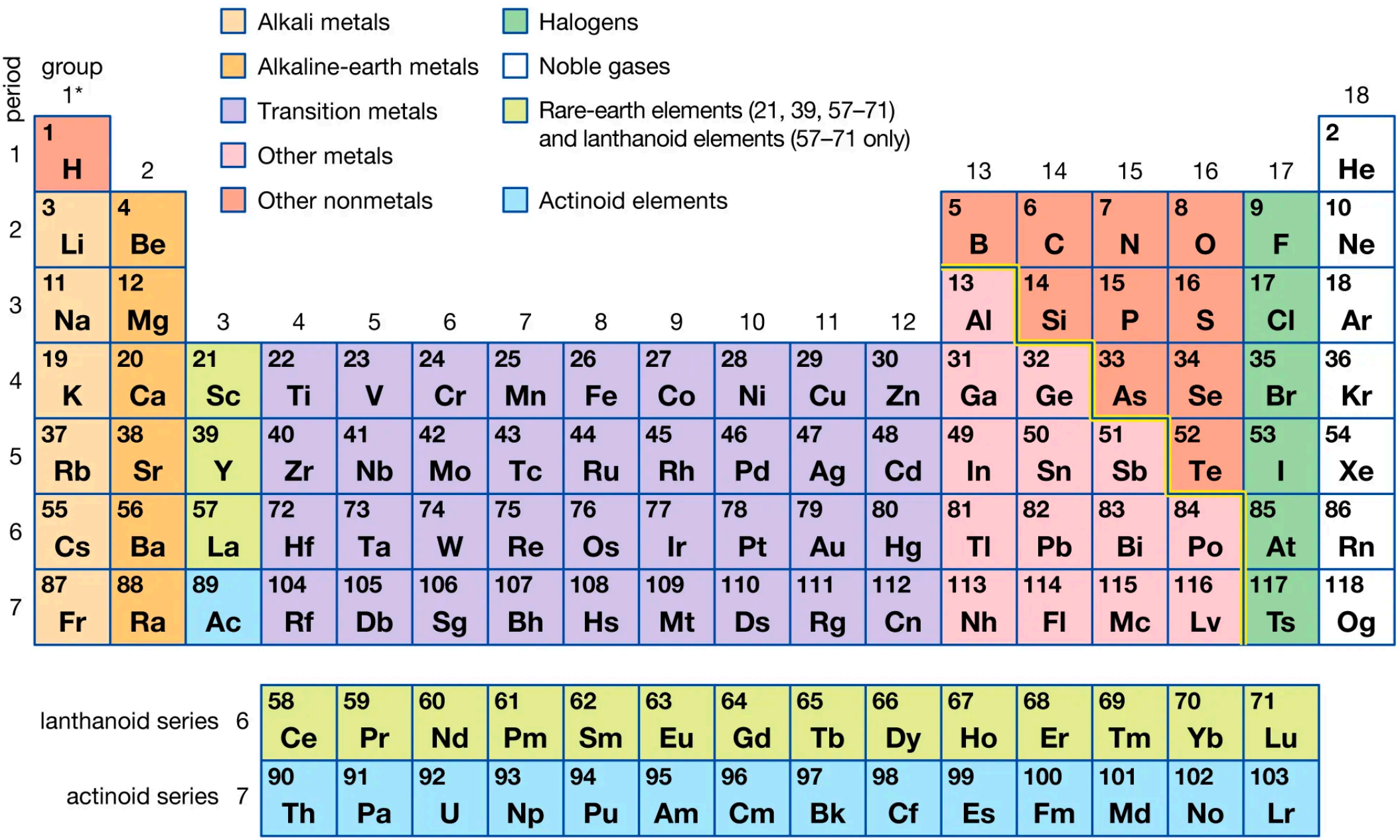
SIESTA school, 11-15 November 2024

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





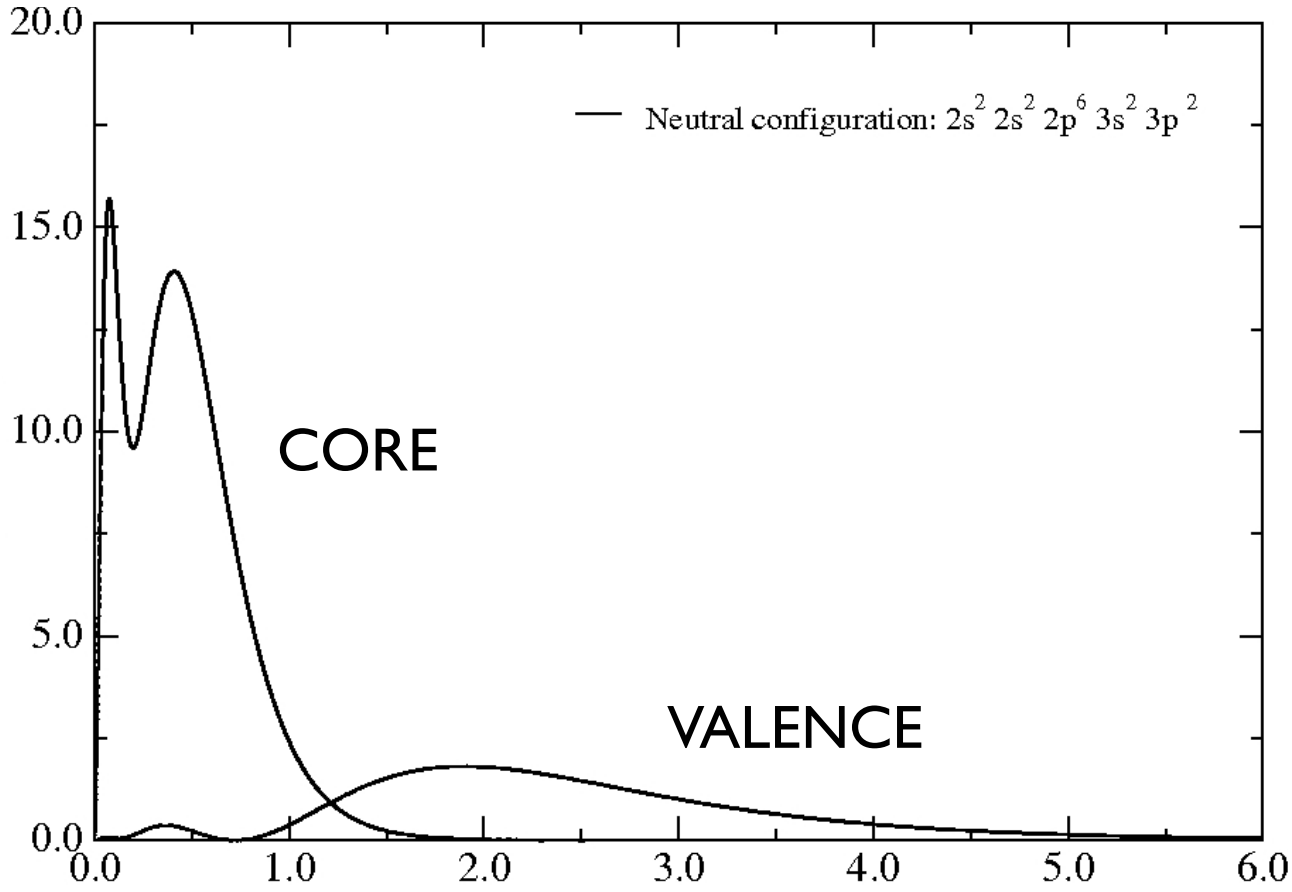
Periodic table of the elements



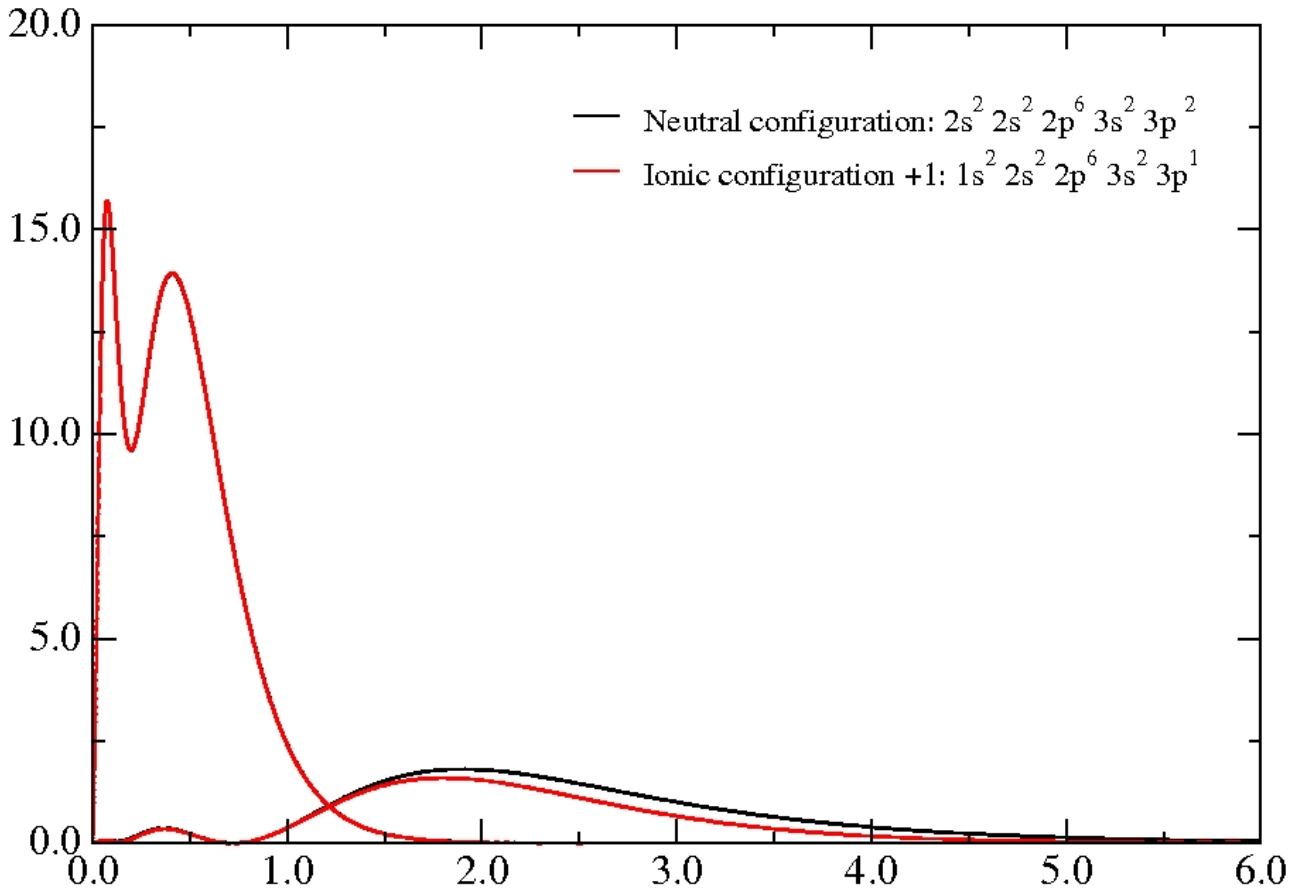
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

Radial profile of charge density for Si atom

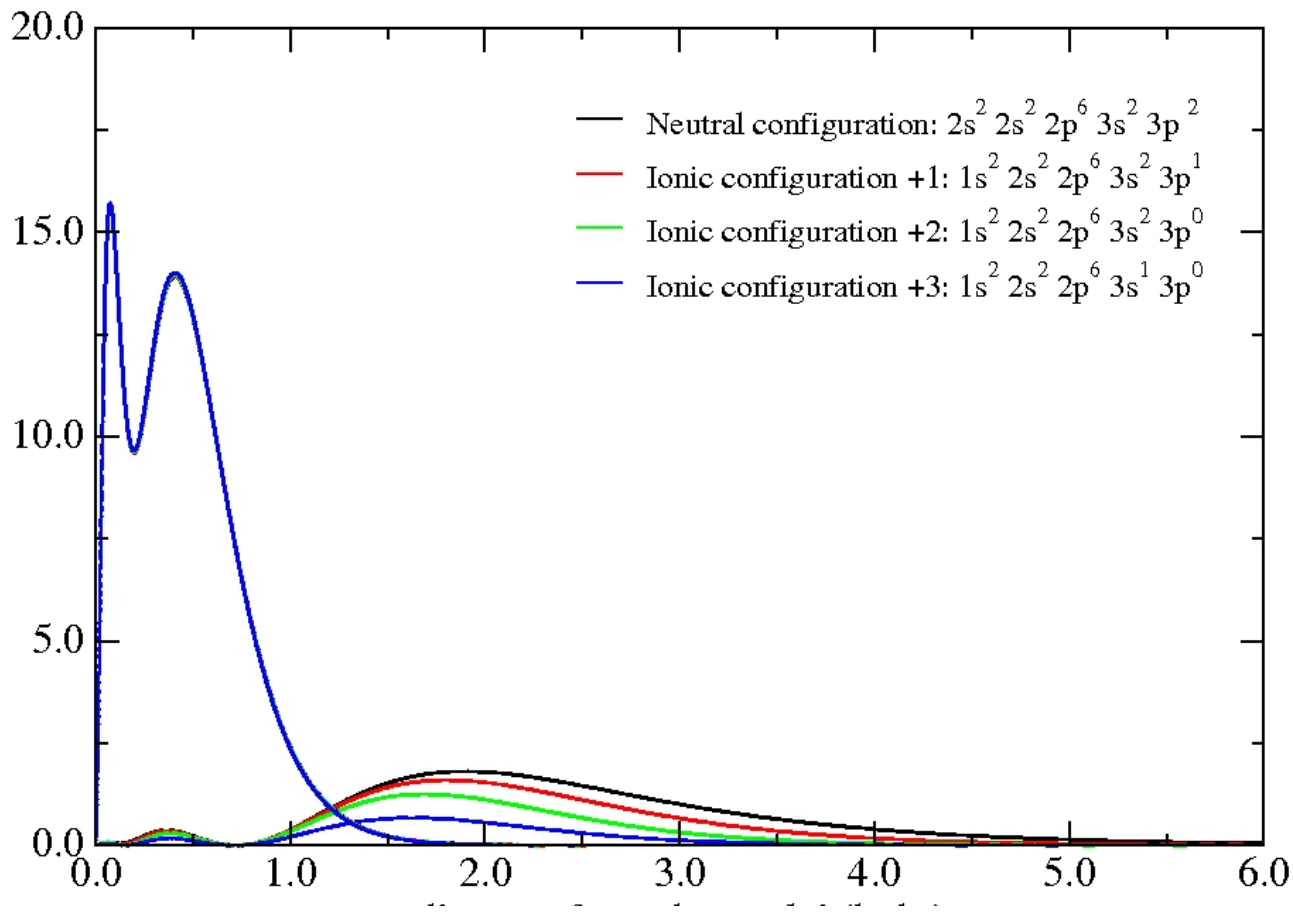
$$1s^2 2s^2 2p^6 3s^2 3p^2$$



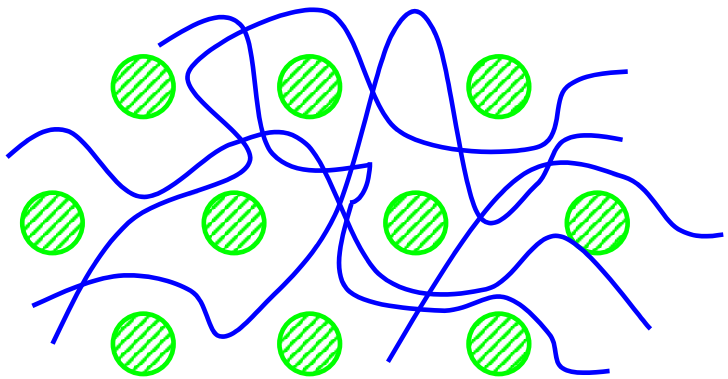
Radial profile of charge density for Si atom

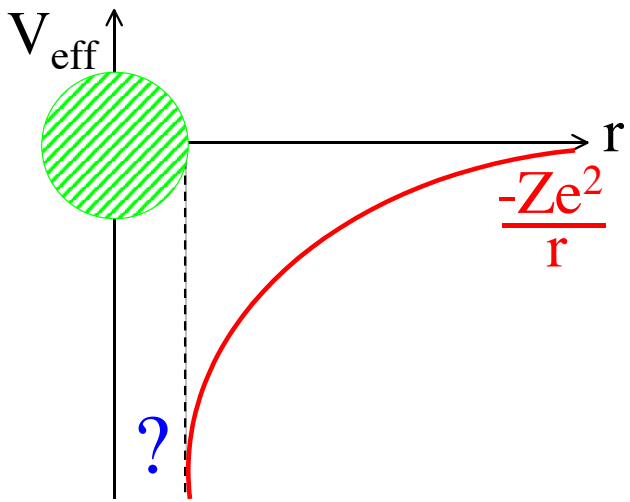


Radial profile of charge density for Si atom



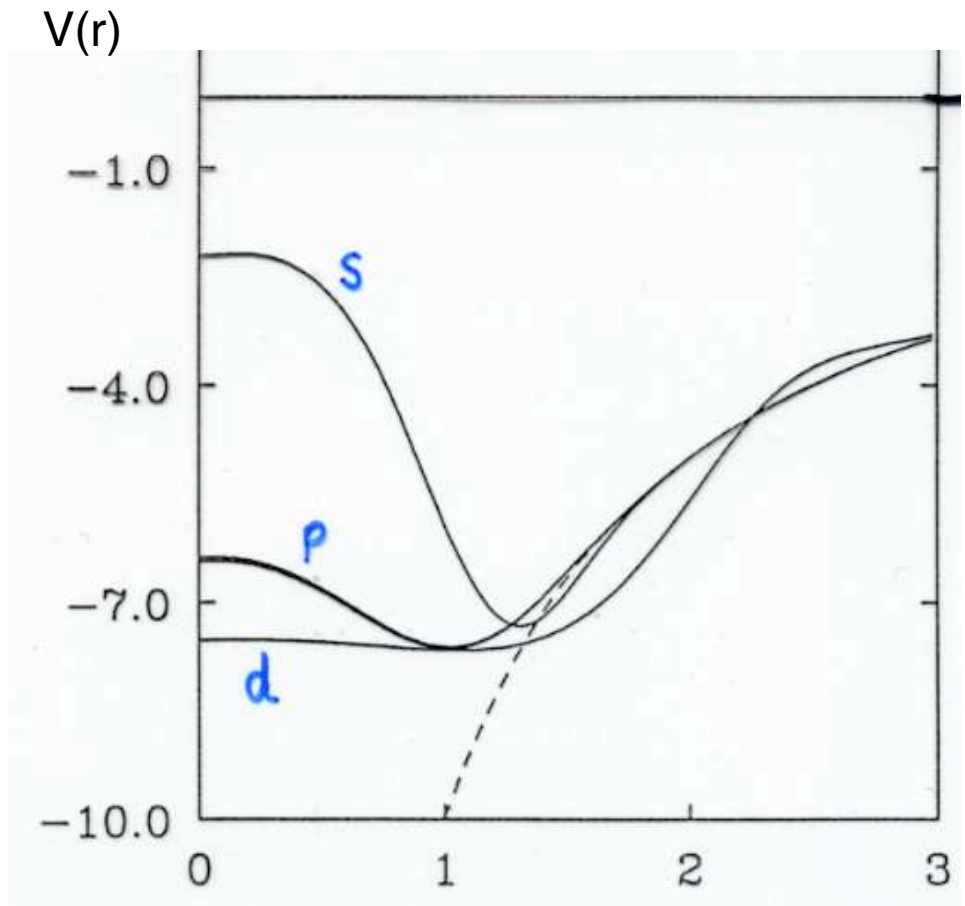
Internal electrons are inert, and do not participate in the chemical bond





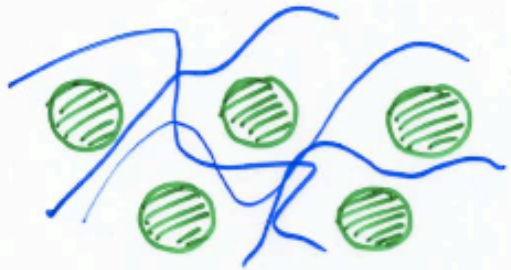
Effective potential for valence electrons

Pseudopotential



A bit of history

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 $|\Psi_c\rangle$

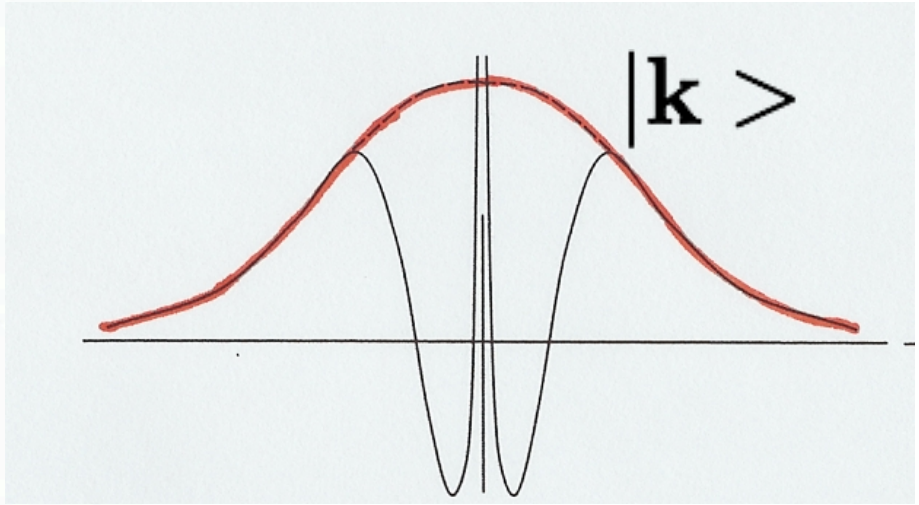
$\hat{H}\,|OPW\rangle = \varepsilon\,|OPW\rangle \Rightarrow$

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

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

is a repulsive potential

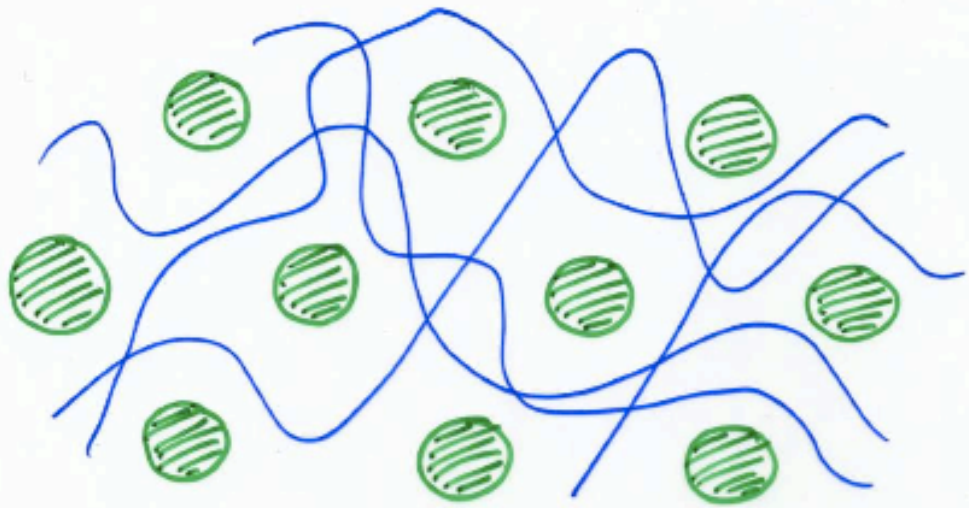
$\hat{H} = \hat{T} + \hat{V} \Rightarrow \hat{V}_{eff} = \hat{V} + \hat{V}_{Rep}$ is a "soft" pseudopotential

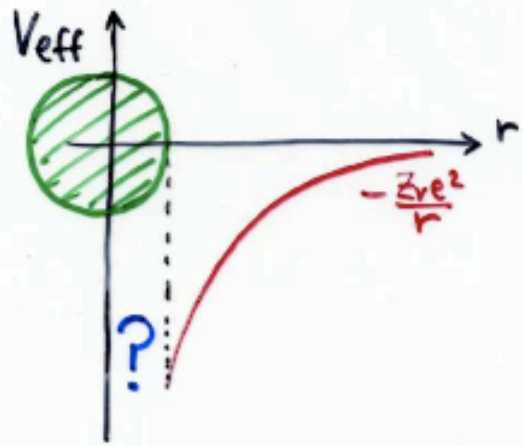


Phillips-Kleinman cancellation theorem (1959)

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.

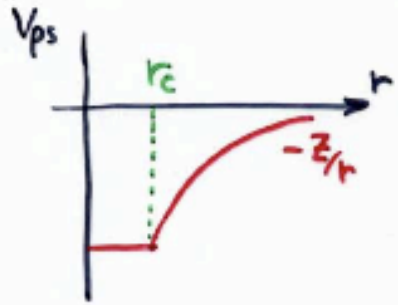
A bit of history…

Empirical pseudopotentials

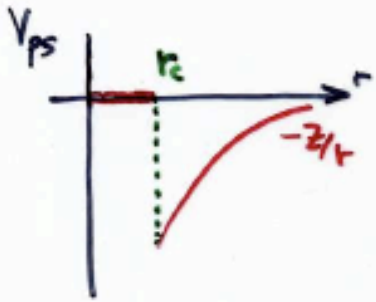
- Pseudopotential (pre) history

- Fermi (1934)

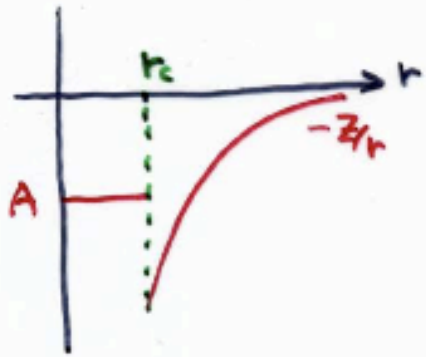
- Simple empirically-adjustable pseudopotentials



r_c adjusted to reproduce the valence eigenvalue



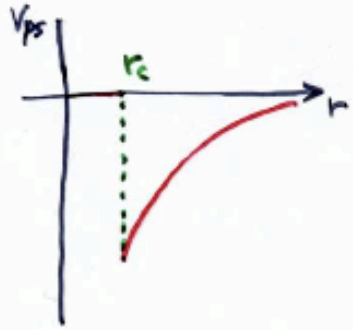
"Empty-core" pseudopotential
Ashcroft (1966)

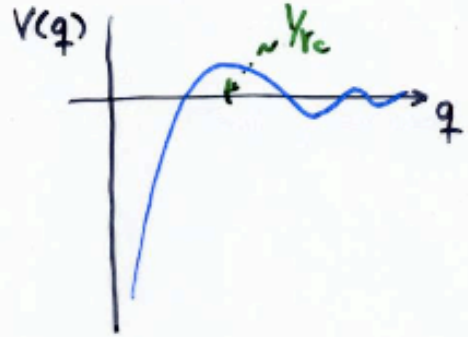


Heine - Abarenkov (~1964)

A = A(ℓ) : angular-momentum-dependent

A = A(E, ℓ) : energy-dependent



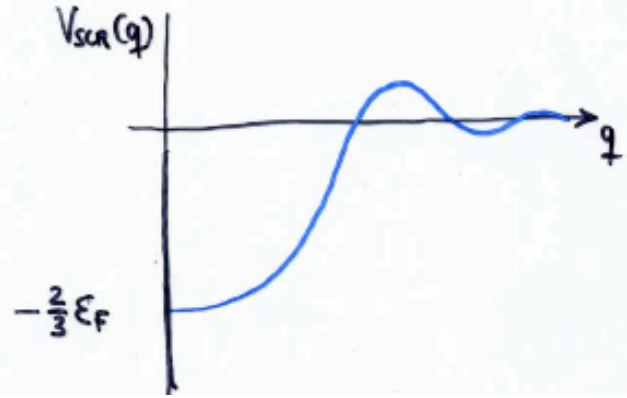


Fourier transform : $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

- Screening

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

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



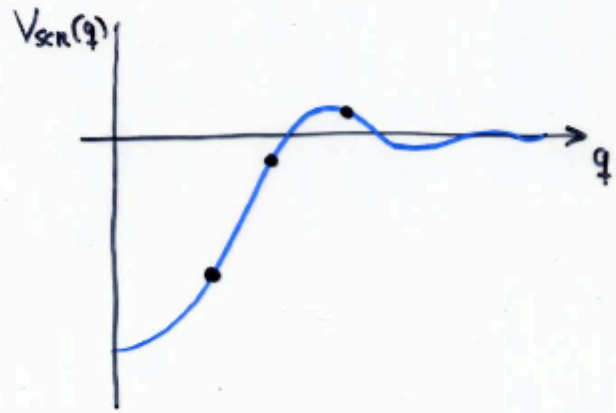
- In a periodic solid :

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

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

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

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



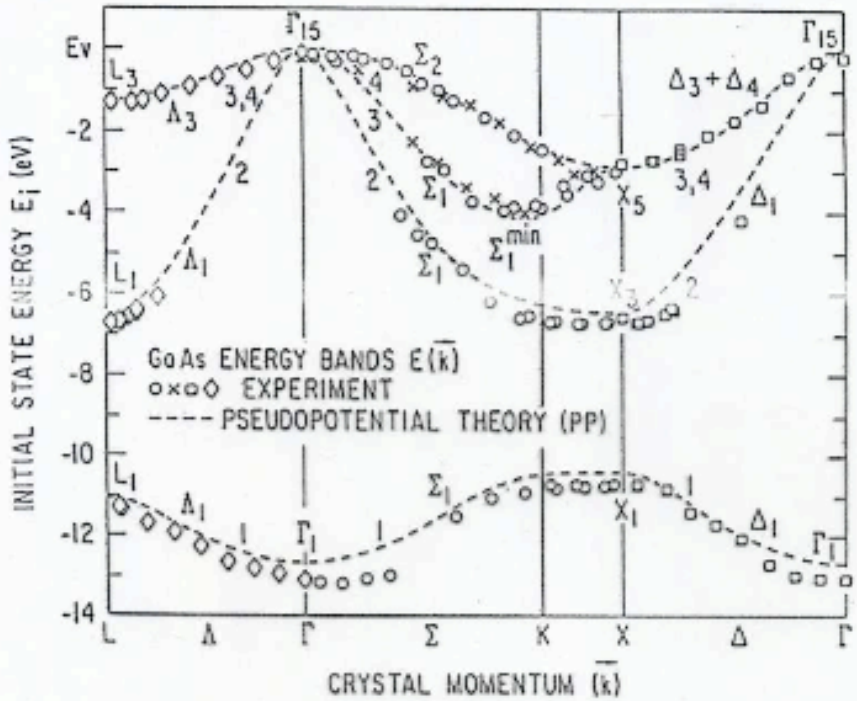
ONLY three parameters are needed for a reasonably good description

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

$V_{eff}(G)$ 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...)

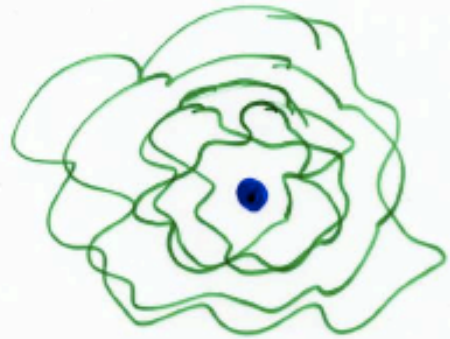
and provides the whole band structure

A bit of history…

The modern era of pseudopotentials

Hamann, Schlüter, Chiang (1979)
Kerker (1980)

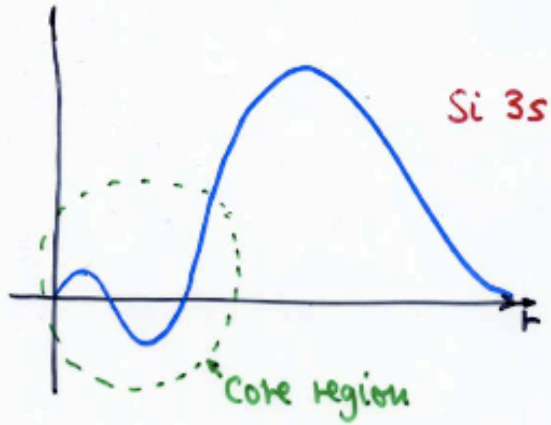
- Atomic calculations using DFT



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

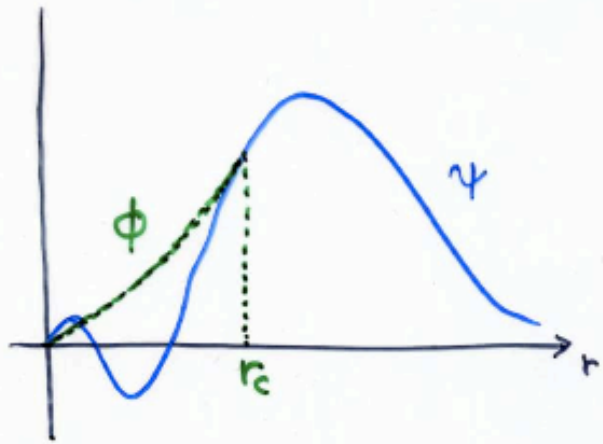
$$V_{nucleus} \rightarrow -\frac{Ze^2}{r}$$

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



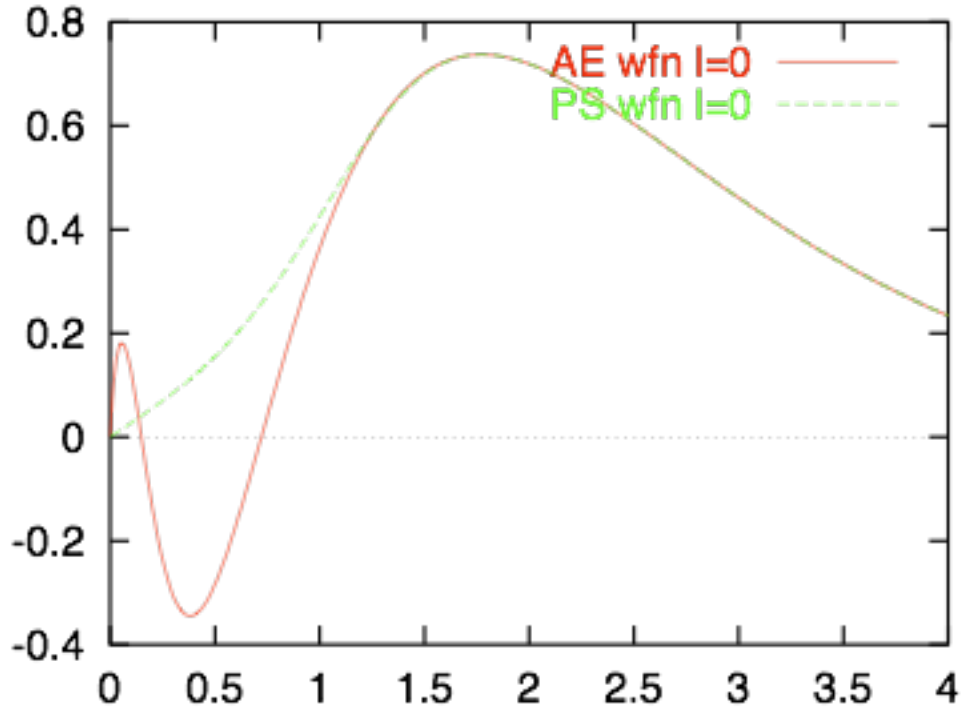
nodes : Imposed by orthogonality to the core states.

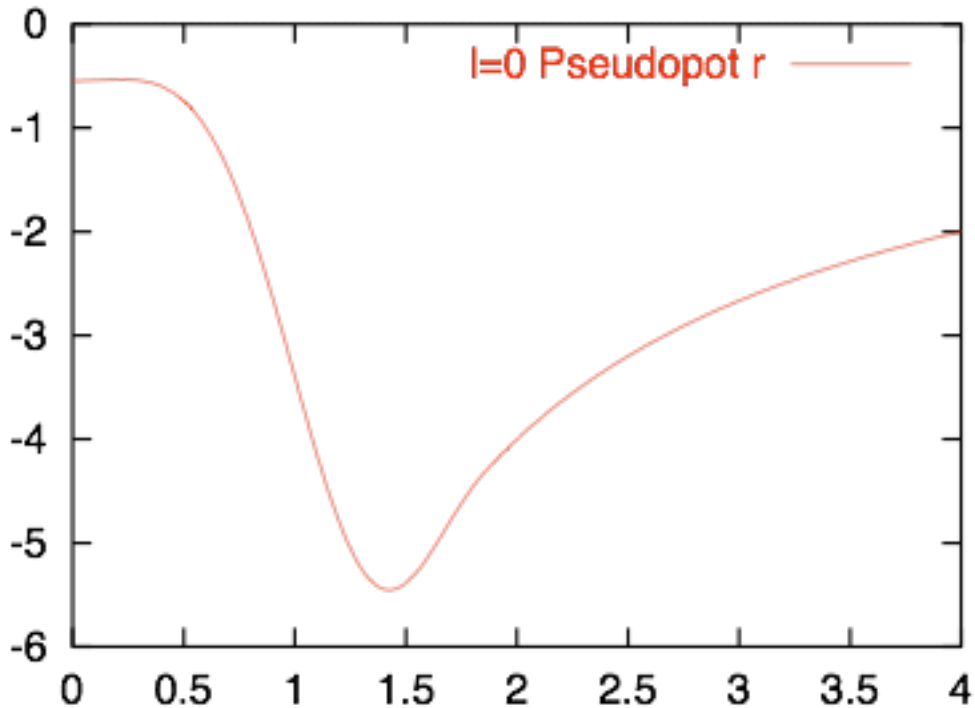
Idea : Eliminate the core electrons by "ironing out" the nodes :

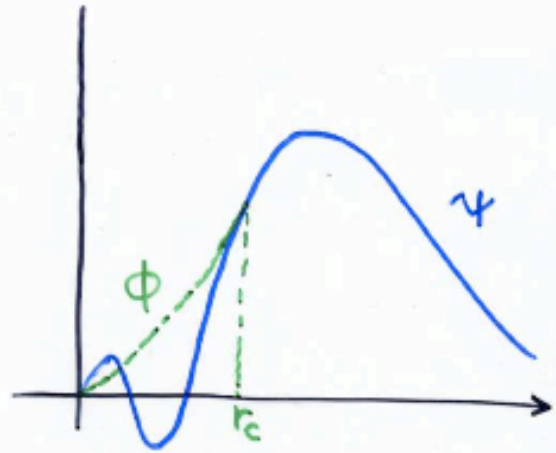


ϕ: Pseudo wavefunction

Hamann, Schluter, Chiang (1979)
Kerker (1980)


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

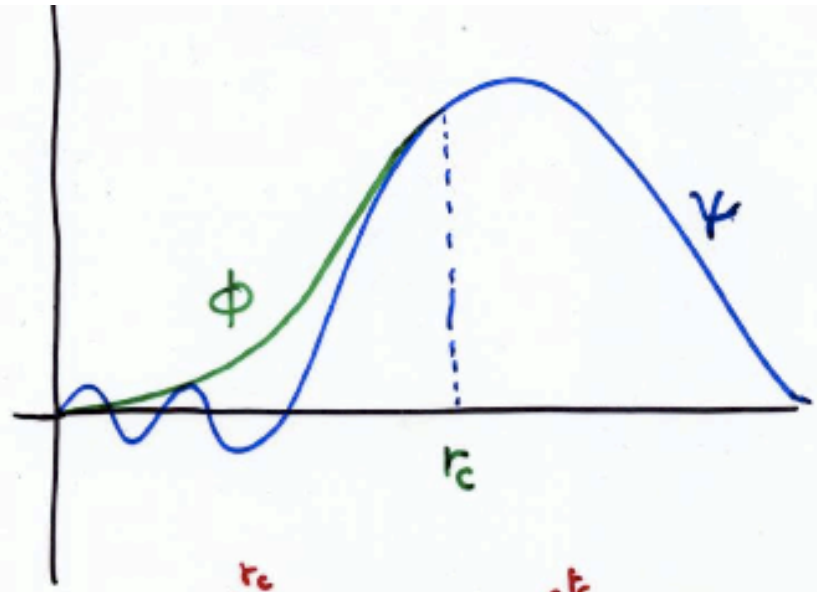


HOW does one get ϕ from ψ ?

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:

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



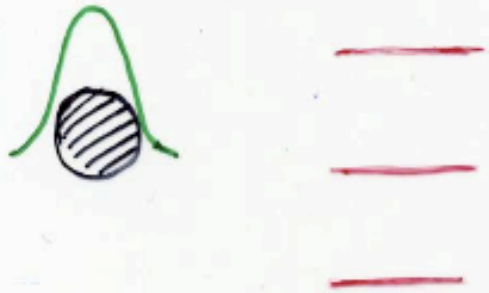
$$\int_0^{r_c} |\phi|^2 r^2 dr = \int_0^{r_c} |\psi|^2 r^2 dr$$

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

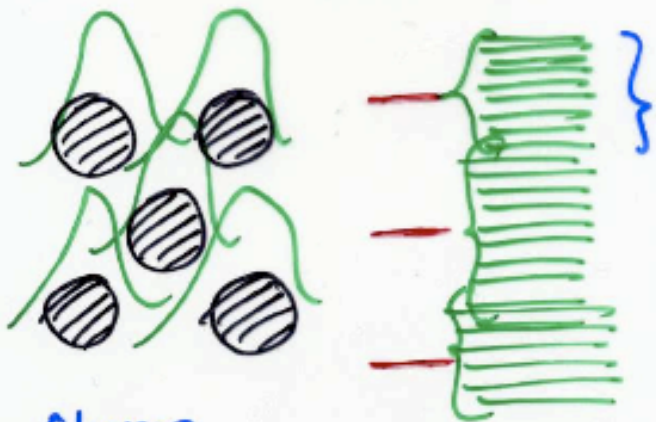


Atomic eigenvalues

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

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

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

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

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

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

"Bare" or ionic pseudopotential:

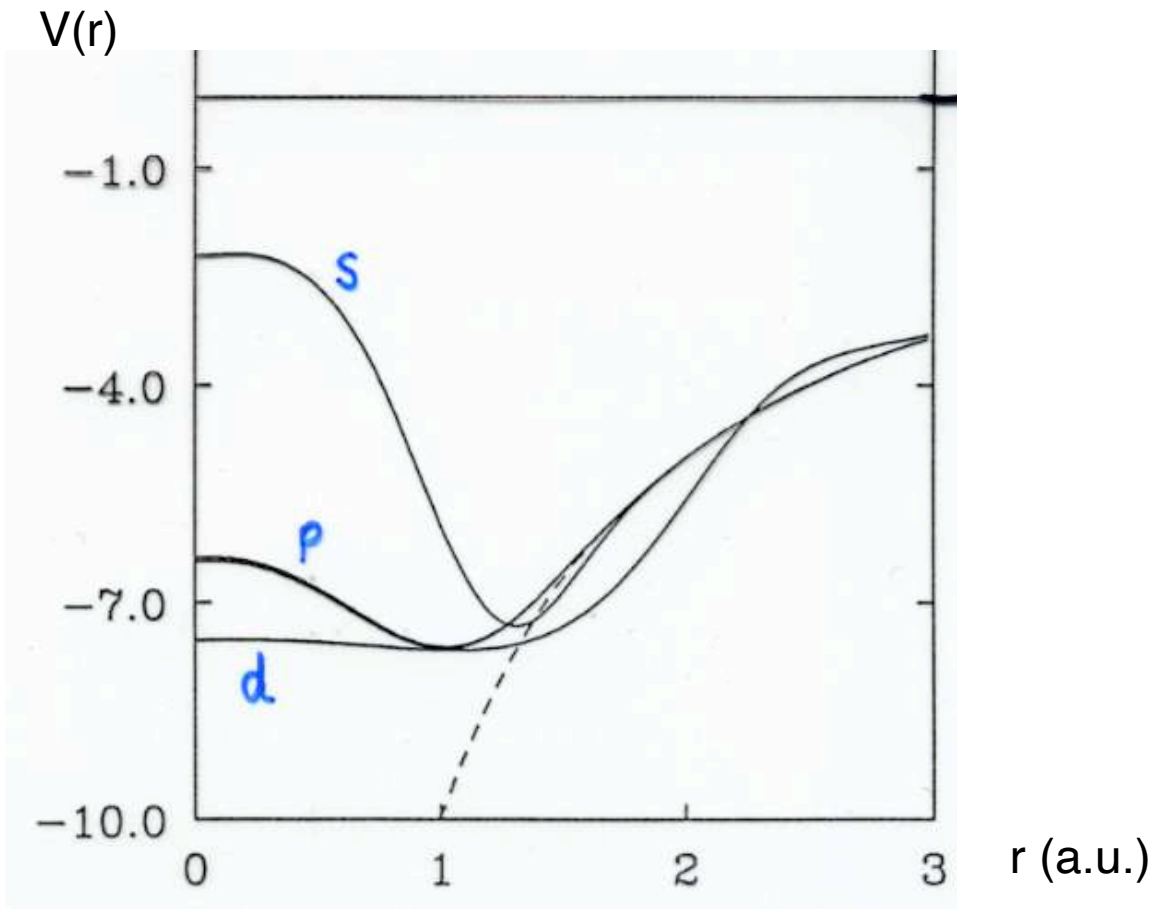
$$V_{ps}(r) = V_{ps}^{[n]} - V_H^{[n]} - V_{xc}^{[n]}$$

non-linear core corrections

n : Valence charge density

Ab-initio pseudopotentials

Essential non-locality



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

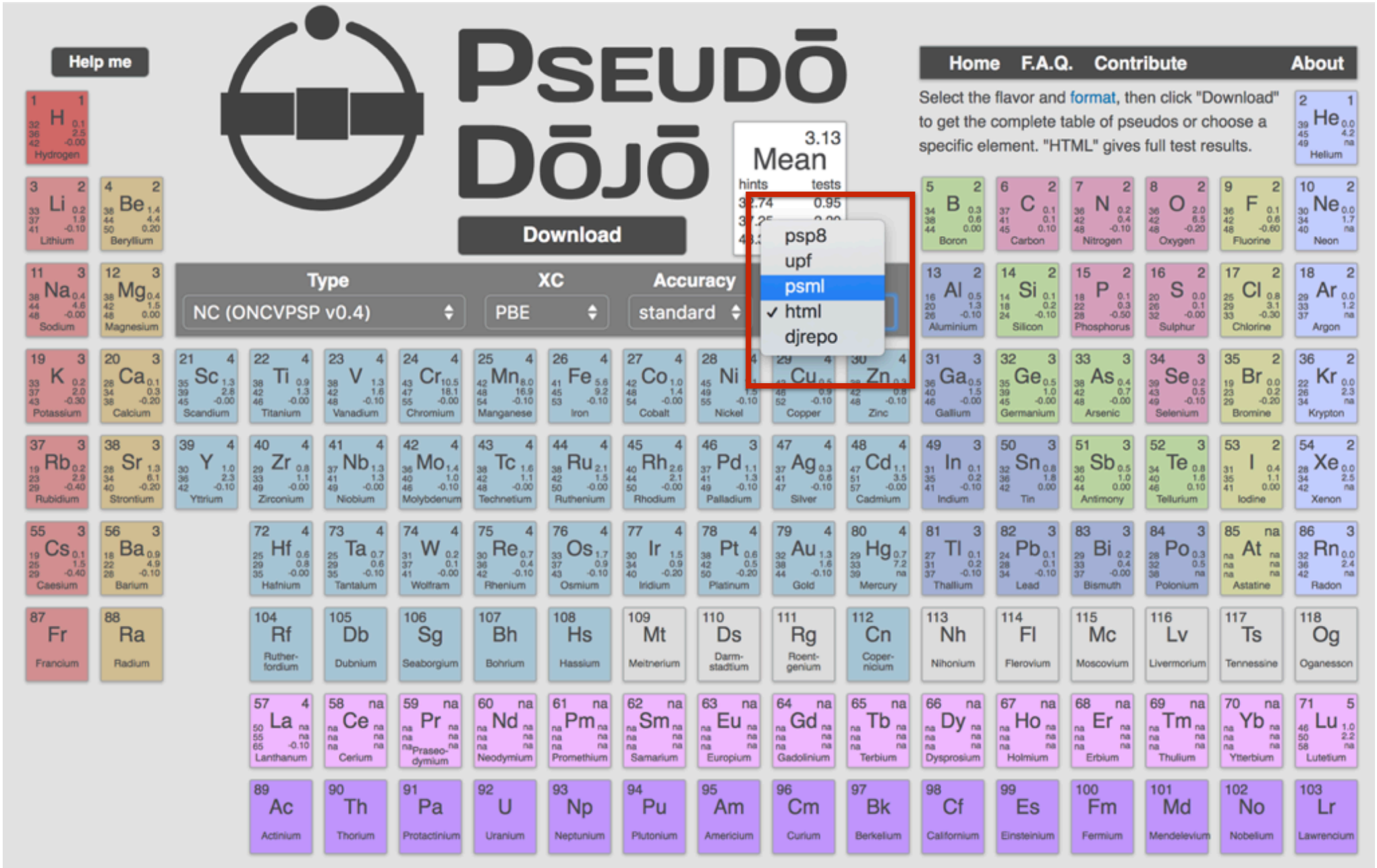
- Refinements of the "node ironing" and inversion procedures. (Many authors)
- Ultrasoft pseudopotentials (Vanderbilt, 1990)
- Norm-conserving schemes using multiple projectors (Hamann, 2013)

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

Norm-conserving pseudopotentials only

- Legacy format: .psf extension
- PSML format: .psml extension (recommended)
  - 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

PS use in Siesta

Norm-conserving pseudopotentials only

- Siesta will:
  - Process the pseudopotential information, generating the Kleinman-Bylander projectors.
  - Generate the appropriate basis set (with almost automatic handling of special features, such as semi-core states)

```
---- Processing specs for species: O
Ground state valence configuration:   2s02  2p04
Reading pseudopotential information in formatted form from: O.psf
```

```
KBgen: Kleinman-Bylander projectors:
  l= 0   rc=  1.293209   el= -1.742414   Ekb=  9.076872   kbcos=  0.325320
  l= 1   rc=  1.284119   el= -0.676589   Ekb= -8.194485   kbcos= -0.396010
  l= 2   rc=  1.433152   el=  0.013307   Ekb= -2.071665   kbcos= -0.003690
  l= 3   rc=  1.540891   el=  0.019584   Ekb= -0.817137   kbcos= -0.000371
```

```
%block PAO.Basis                 # Define Basis set
O                     2              # Species label, number of l-shells
 n=2   0   2                        # n, l, Nzeta
   3.561      2.320
   1.000      1.000
 n=2   1   2 P   1                  # n, l, Nzeta, Polarization, NzetaPol
   4.291      2.782
   1.000      1.000
```

Information on projectors and basis orbitals is stored in O.ion (or O.ion.nc) file

Thanks !