

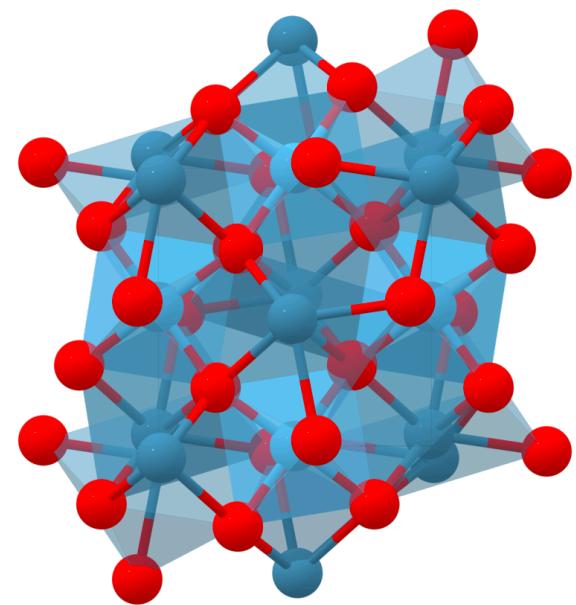
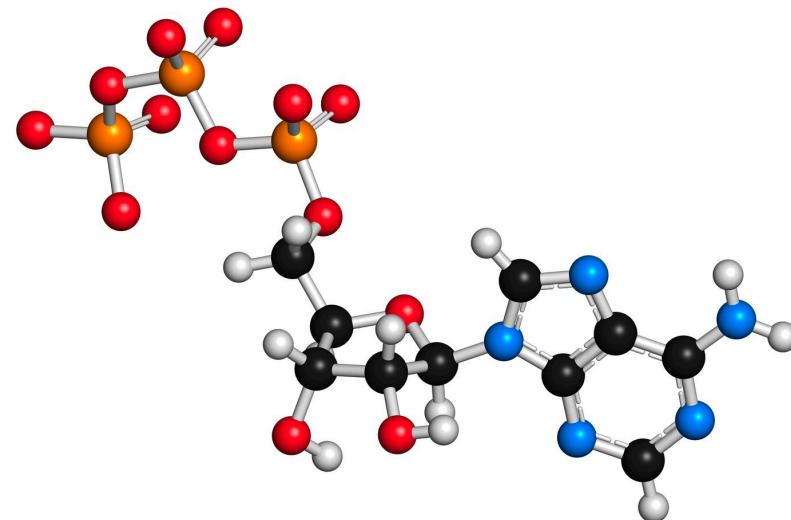
The pseudopotential concept

Alberto García
(ICMAB-CSIC, Barcelona)

...using the work of many others!



EXCELENCIA
SEVERO
OCHOA



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

Periodic table of the elements

period
group

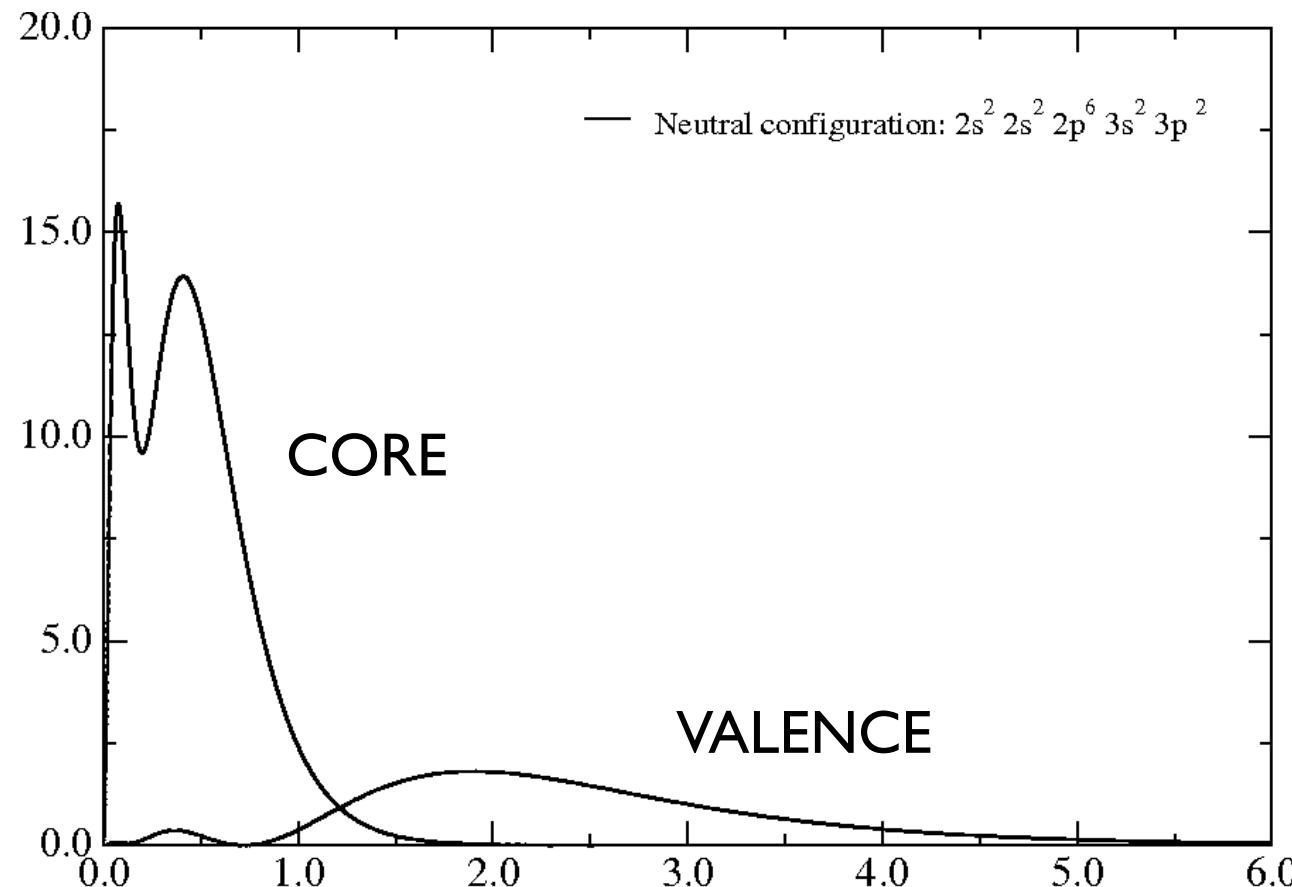
1*	1	H	2																							18			
1	3	Li	4	Be																					2				
2	11	Na	12	Mg	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17										
3	19	K	20	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	31	32	33	34	35						36				
4	37	Rb	38	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe									
5	55	Cs	56	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn									
6	87	Fr	88	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og									
lanthanoid series	6	58	59	60	61	62	63	64	65	66	67	68	69	70	71														
actinoid series	7	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	90	91	92	93	94	95	96	97	98	99	100	101	102	103

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

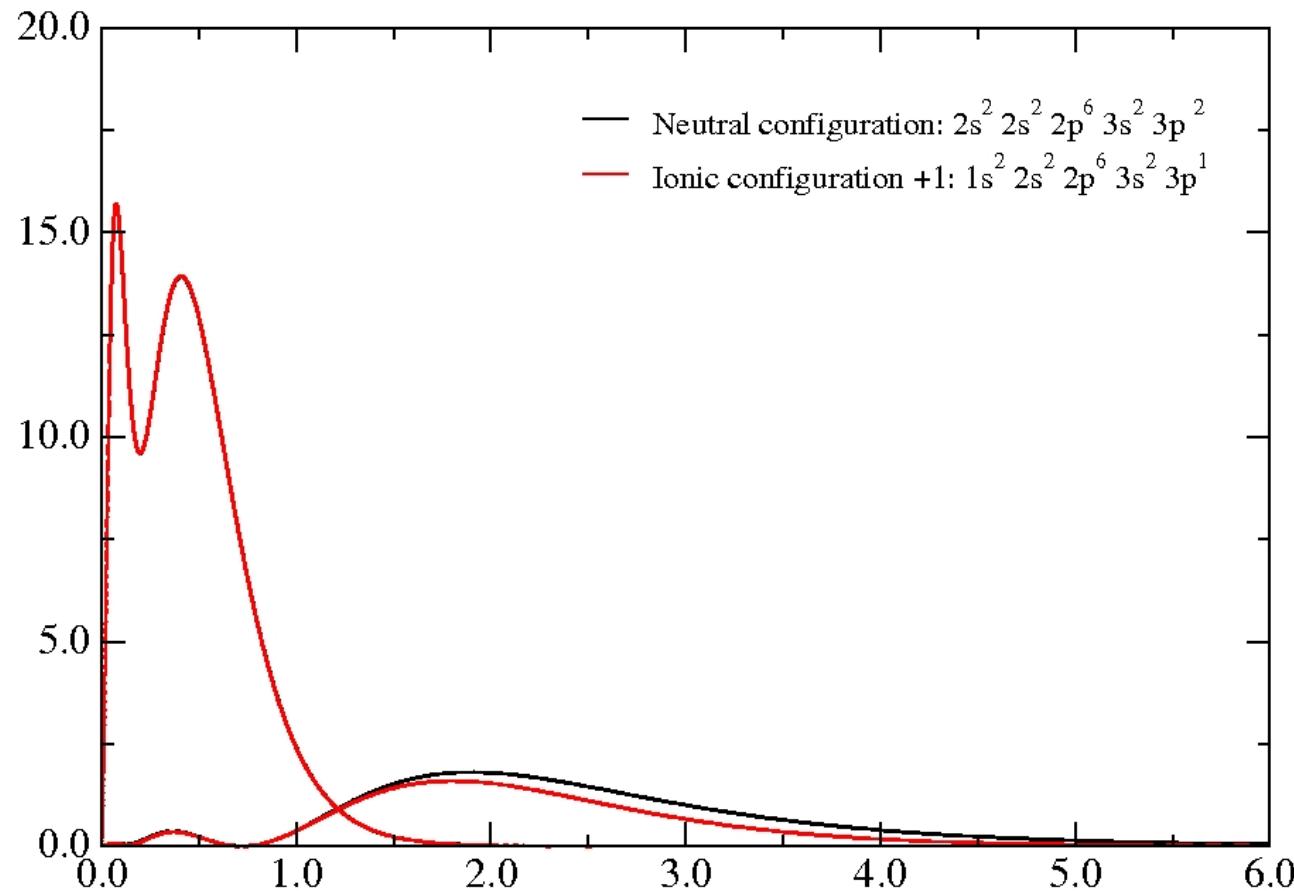
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Radial profile of charge density for Si atom

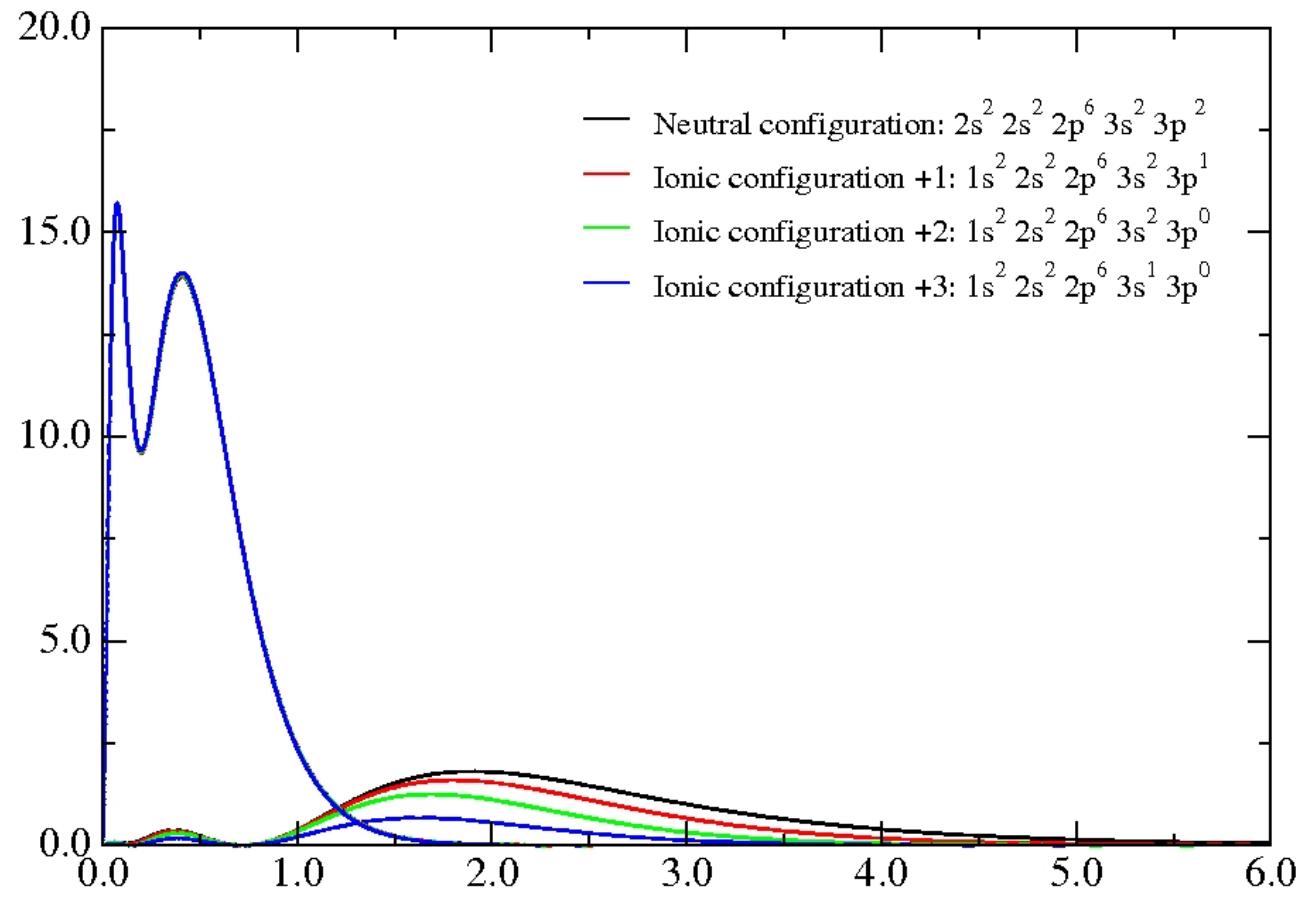
$1s^2 2s^2 2p^6 \color{red}{3s^2 3p^2}$



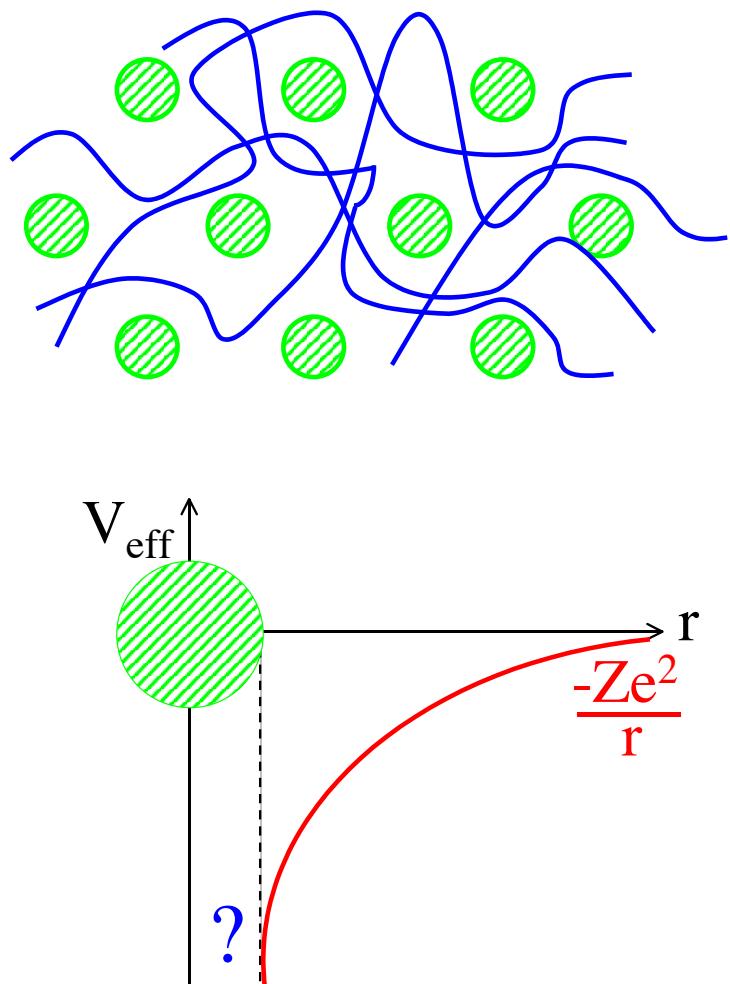
Radial profile of charge density for Si atom



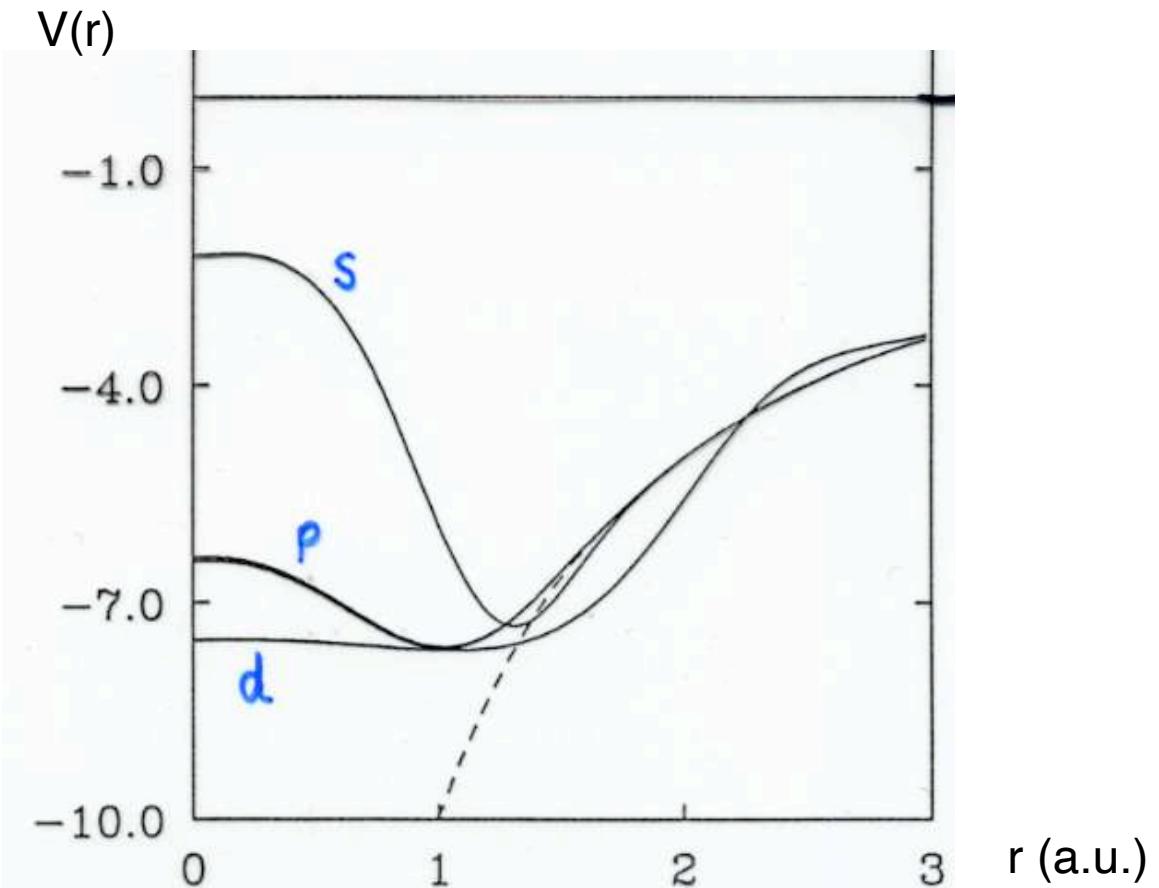
Radial profile of charge density for Si atom



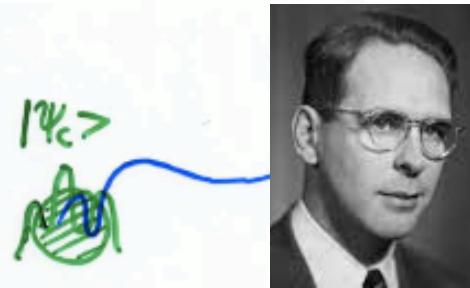
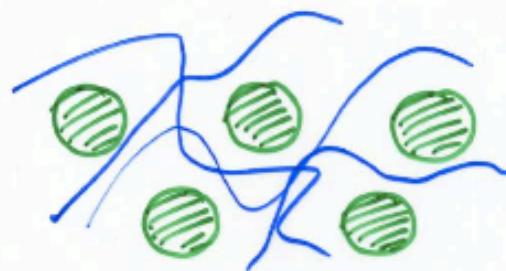
Internal electrons are inert, and do not participate in the chemical bond



Effective potential for valence electrons
Pseudopotential



Orthogonalized plane-wave method (Herring, 1940)



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

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

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

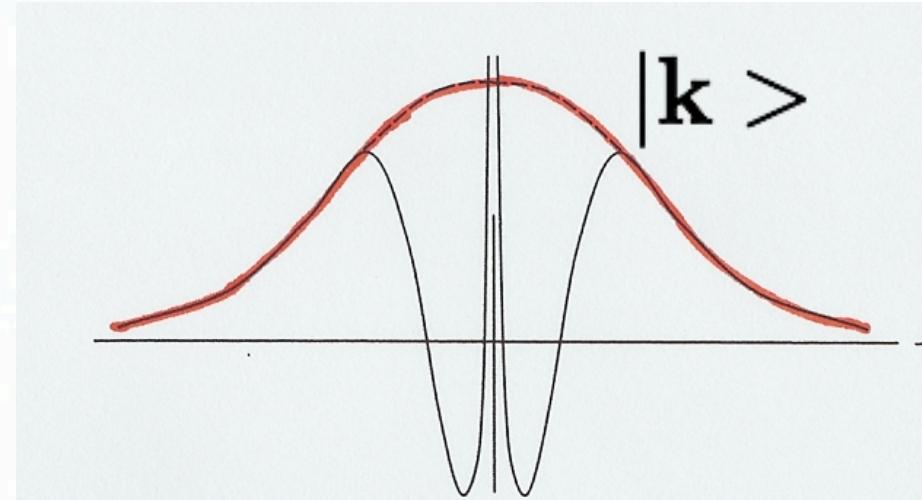
$$\Rightarrow (\hat{H} + \hat{V}_{\text{Rep}}) |\vec{k}\rangle = \varepsilon |\vec{k}\rangle$$

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

is a repulsive potential

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

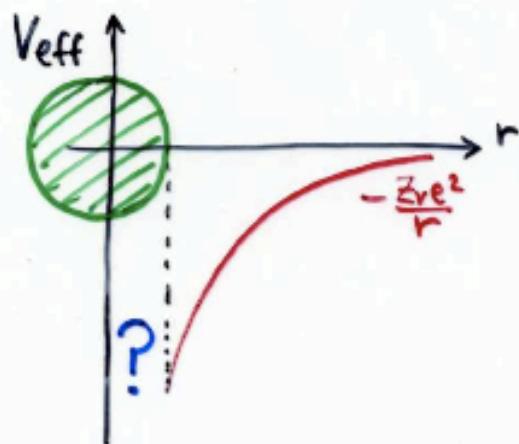
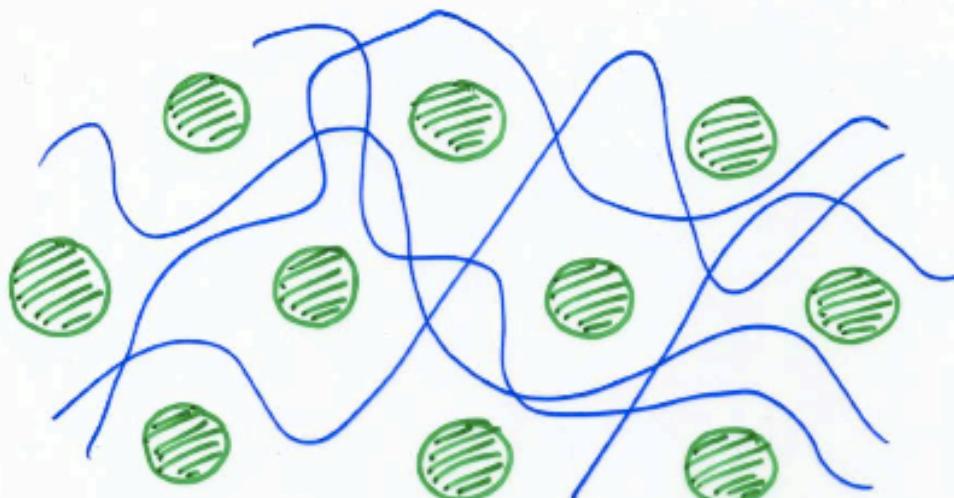
"soft" pseudopotential



Phillips-Kleinman
cancellation theorem
(1959)

Common metal: Na

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



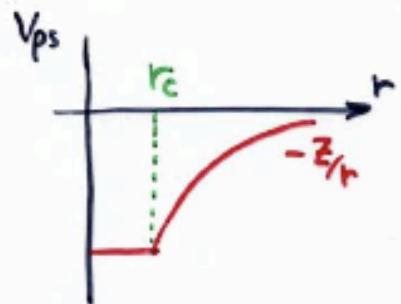
In the core zone, the effective potential will be softer than the coulomb $-\frac{Zre^2}{r}$ pot.

Empirical pseudopotentials

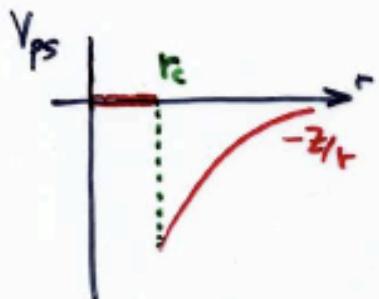
- Pseudopotential (pre) history

 - Fermi (1934)

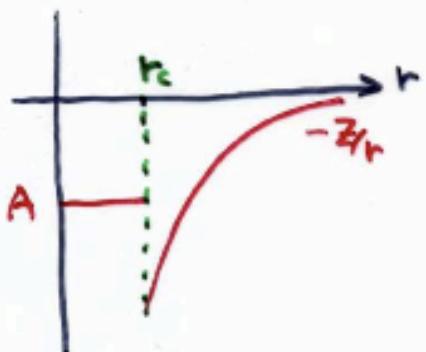
 - Simple empirically-adjustable pseudopotentials



r_c adjusted to reproduce
the valence eigenvalue



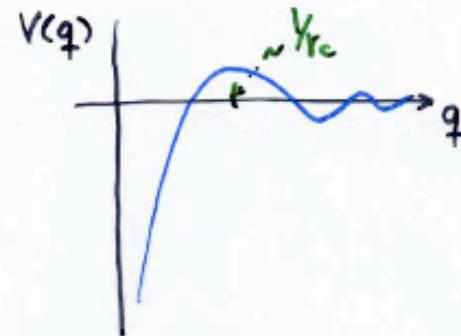
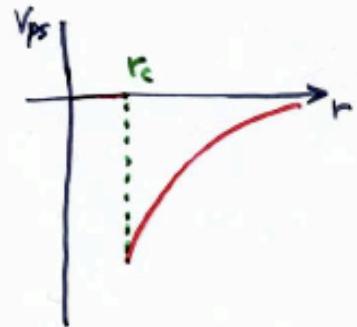
"Empty-core" pseudopotential
Ashcroft (1966)



Heine - Abarenkov (~1964)

$A = A(\ell)$: angular-momentum-
dependent

$A = A(E, \ell)$: energy-dependent



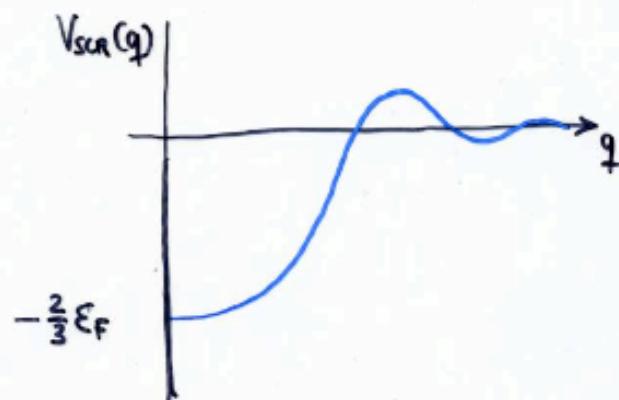
Fourier transform : $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

• Screening

$$\frac{1}{r} \rightarrow \frac{1}{r} e^{-K_{TF} \cdot r}$$

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 :

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

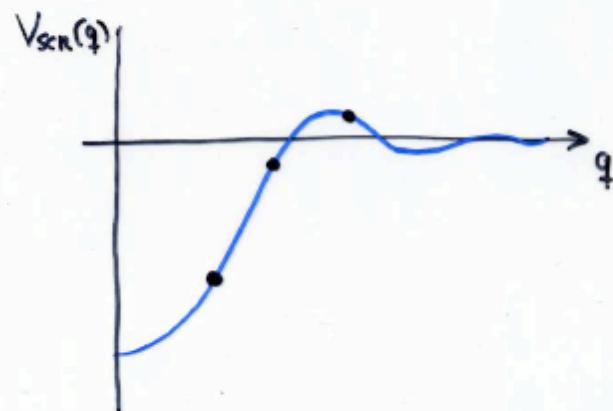
$$S(\vec{G}) = \frac{1}{N_a} \sum_{\vec{e}_i} e^{-i\vec{G} \cdot \vec{e}_i}$$

structure factor



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

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



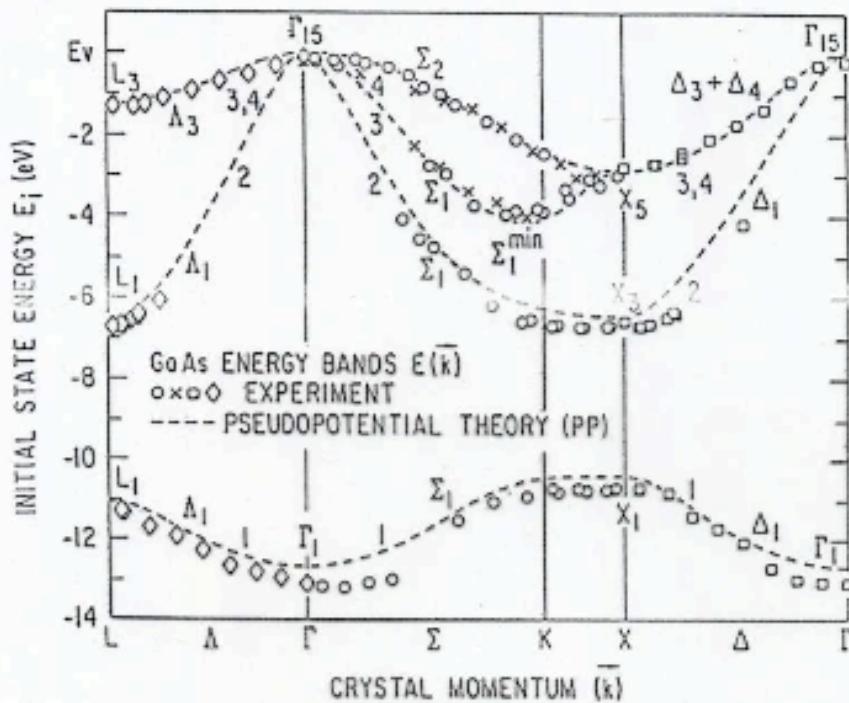
ONLY three parameters are needed for
a reasonably good description

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

$V_{eff}(G)$ fitted !

Empirical Pseudopotential Method (EPM)

(Marvin L. Cohen et al. ~1962)

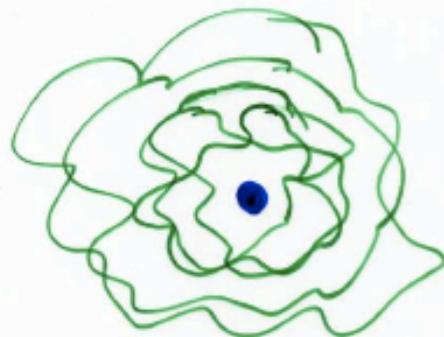


Band structure of GaAs

EPM needs a few experimental inputs
(absorption edge, reflectivity features...)
and provides the whole band structure

The modern era of pseudopotentials

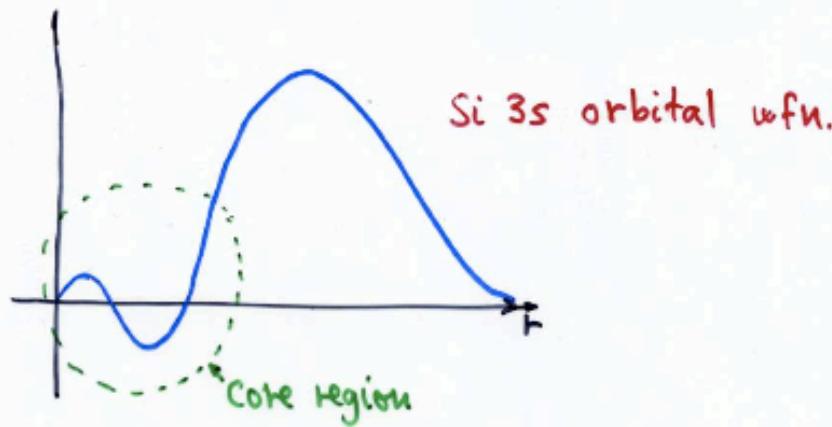
- Atomic calculations using DFT



$$\left\{ -\nabla^2 + V_{\text{nucleus}} + V_H + V_{XC} \right\} \Psi_i = \varepsilon_i \Psi_i$$

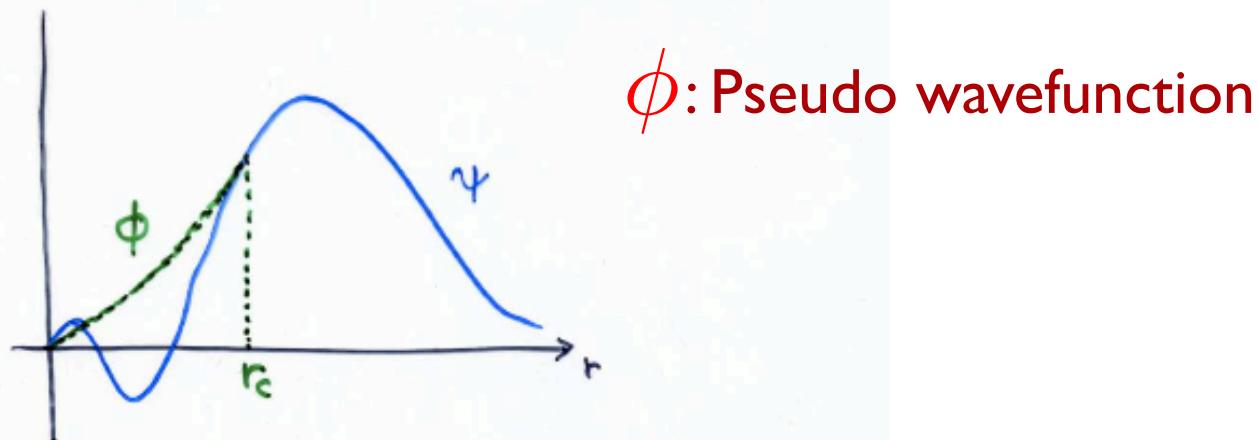
\downarrow
 $- \frac{ze^2}{r}$

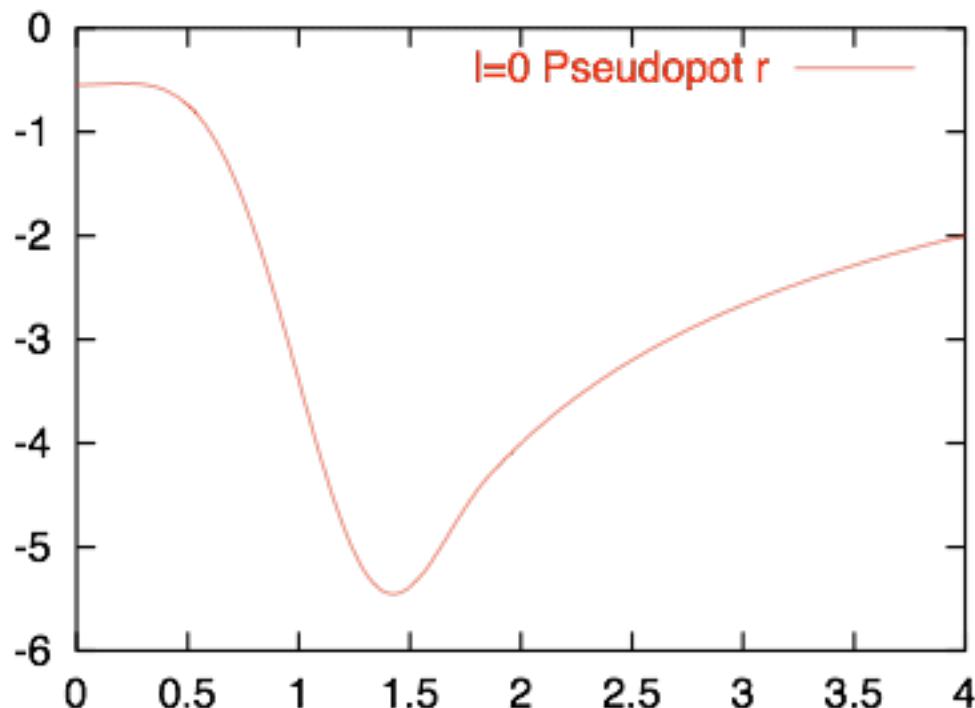
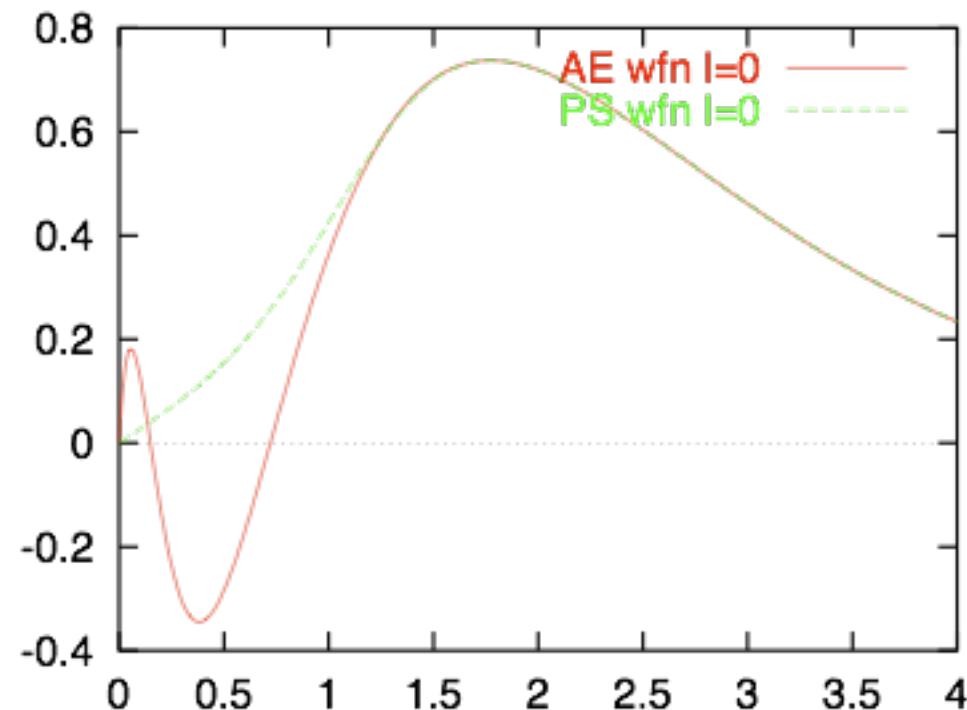
$$n_{el}(\vec{r}) = \sum_i |\Psi_i|^2$$

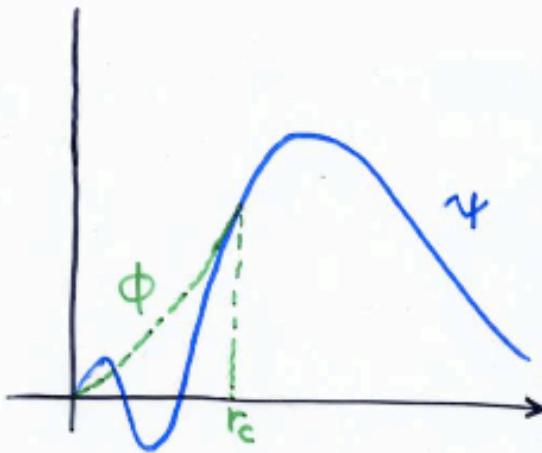


nodes : Imposed by orthogonality
to the core states.

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





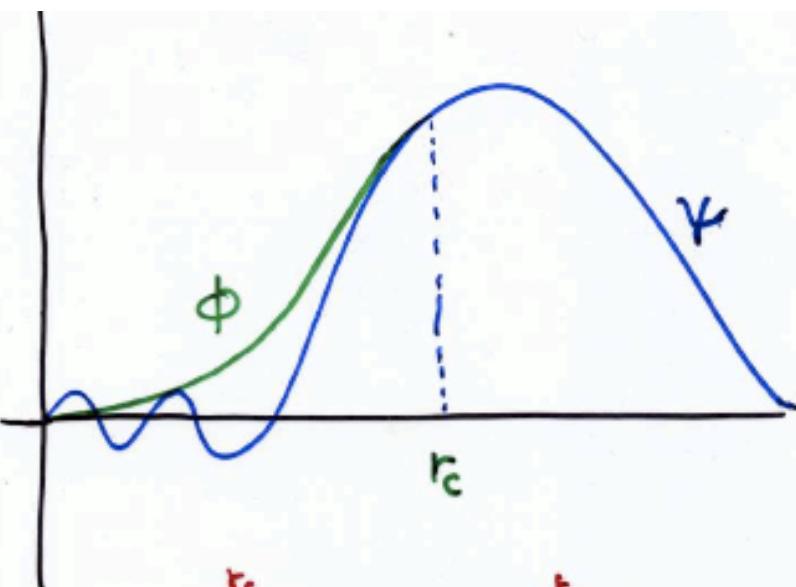


HOW does one get ϕ from ψ ?

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 :

$$\int |\phi|^2 dV = \int |\psi|^2 dV$$



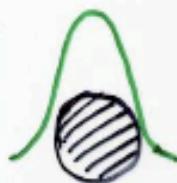
$$\int_0^{r_c} |\phi|^2 r^2 dr = \int_0^{r_c} |\psi|^2 r^2 dr$$

Norm - conservation

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

Preserves scattering properties
(and their first energy derivative)

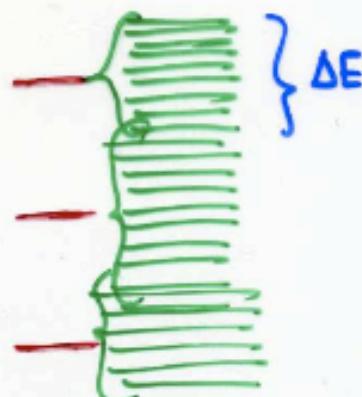
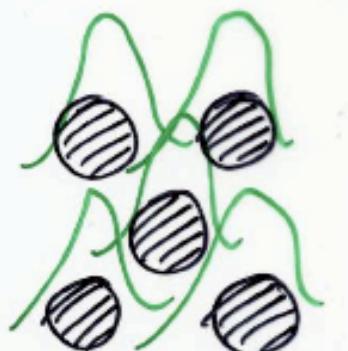
Isolated atom



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

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

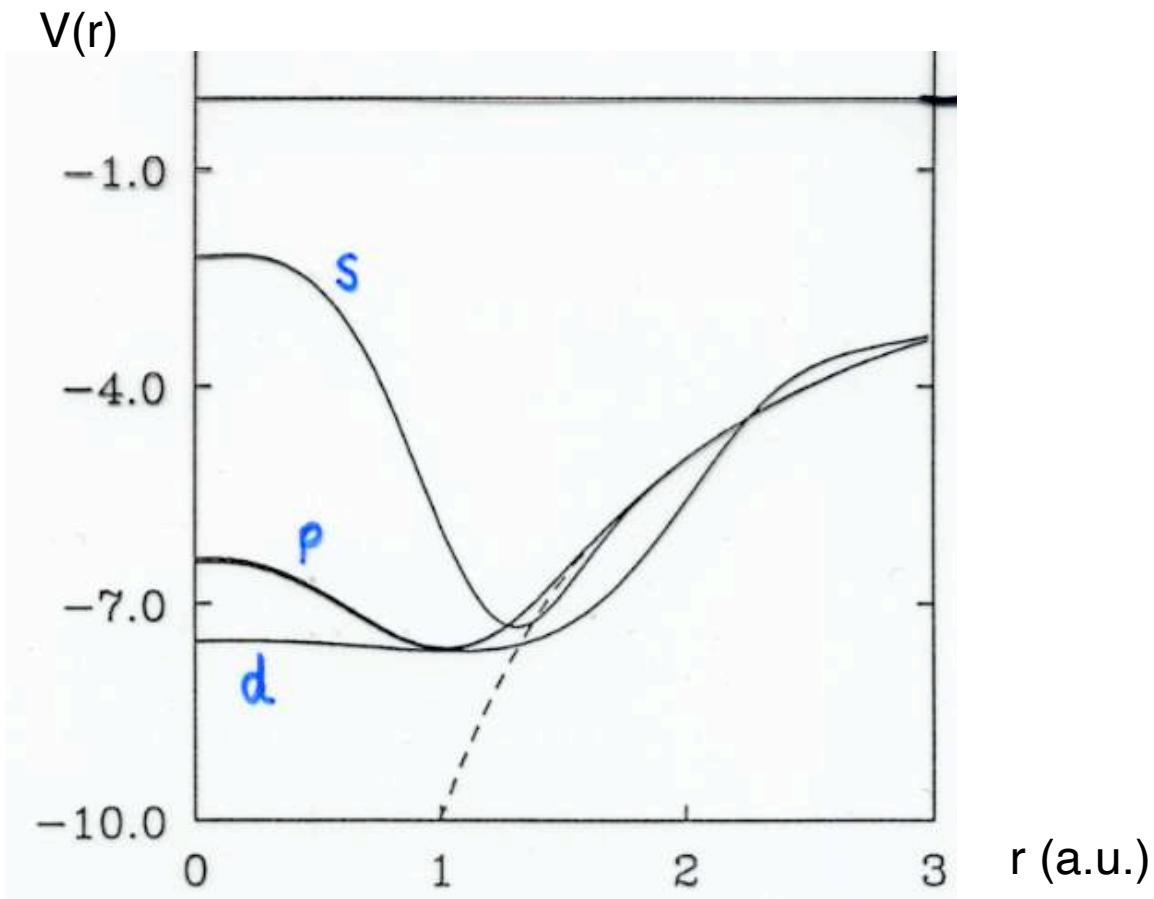
"Bare" or ionic pseudopotential:

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

non-linear
core corrections

n: Valence charge density

Ab-initio pseudopotentials



Semi-local form:

$$\hat{V}_{ps} = \sum_l V_l(r) |l\rangle \langle l|$$

Projector for l

$$= V_{\text{LOCAL}}(r) + \sum_l \Delta V_l(r) |l\rangle \langle l|$$

Short ranged

Kleinman-Bylander form:

$$\hat{V}_{ps} = V_{\text{LOCAL}}(r) + \sum_{em} \frac{|\Delta V_e \phi_{em}\rangle \langle \phi_{em} \Delta V_e|}{\langle \phi_{em} | \Delta V_e | \phi_{em} \rangle}$$

(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/>

[Help me](#)



PSEUDŌ Dōjō

[Download](#)

	Type	XC	Accuracy								
NC (ONCVPSP v0.4)	PBE	standard	<ul style="list-style-type: none"> hints tests 3.74 0.95 3.72 0.99 4.01 0.99 psp8 upf psml ✓ html djrepo 								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Techneium	Ruthenium	Rhodium	Palladium	Silver	Cadmium
Cs	Ba	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Thallium
Caesium	Barium	Hafnium	Tantalum	Wolfram	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Lead
Fr	Ra	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh
Francium	Radium	Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Meltinanium	Darm-stadtimium	Roentgenium	Copernicium	Nihonium
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium
Lu	Yb	Lu	Ytterbium								

Select the flavor and [format](#), then click "Download" to get the complete table of pseudos or choose a specific element. "HTML" gives full test results.

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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>