

The pseudopotential concept

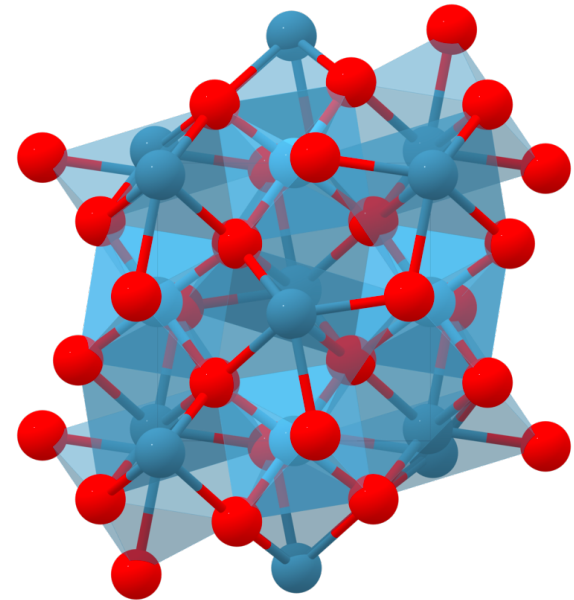
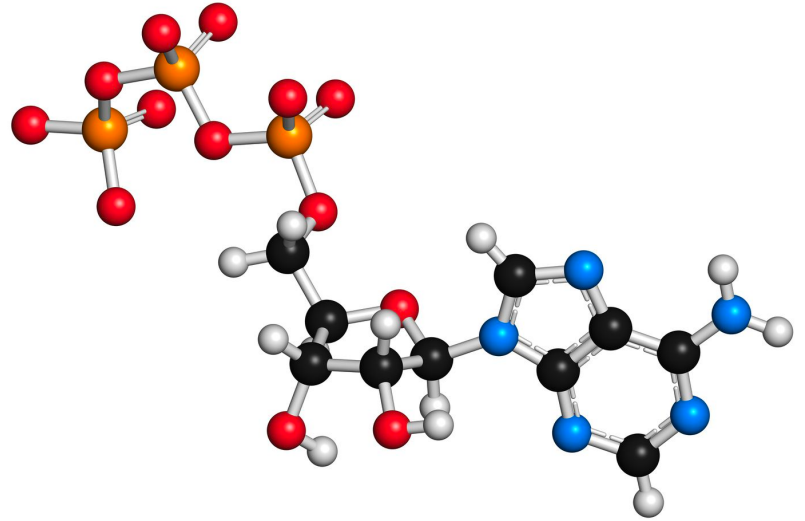
Alberto García
(ICMAB-CSIC, Barcelona)

...using the work of many others!

SIESTA school, 11-15 November 2024



Bonding
(the 'glue' in matter)
is determined
by the **valence** electrons

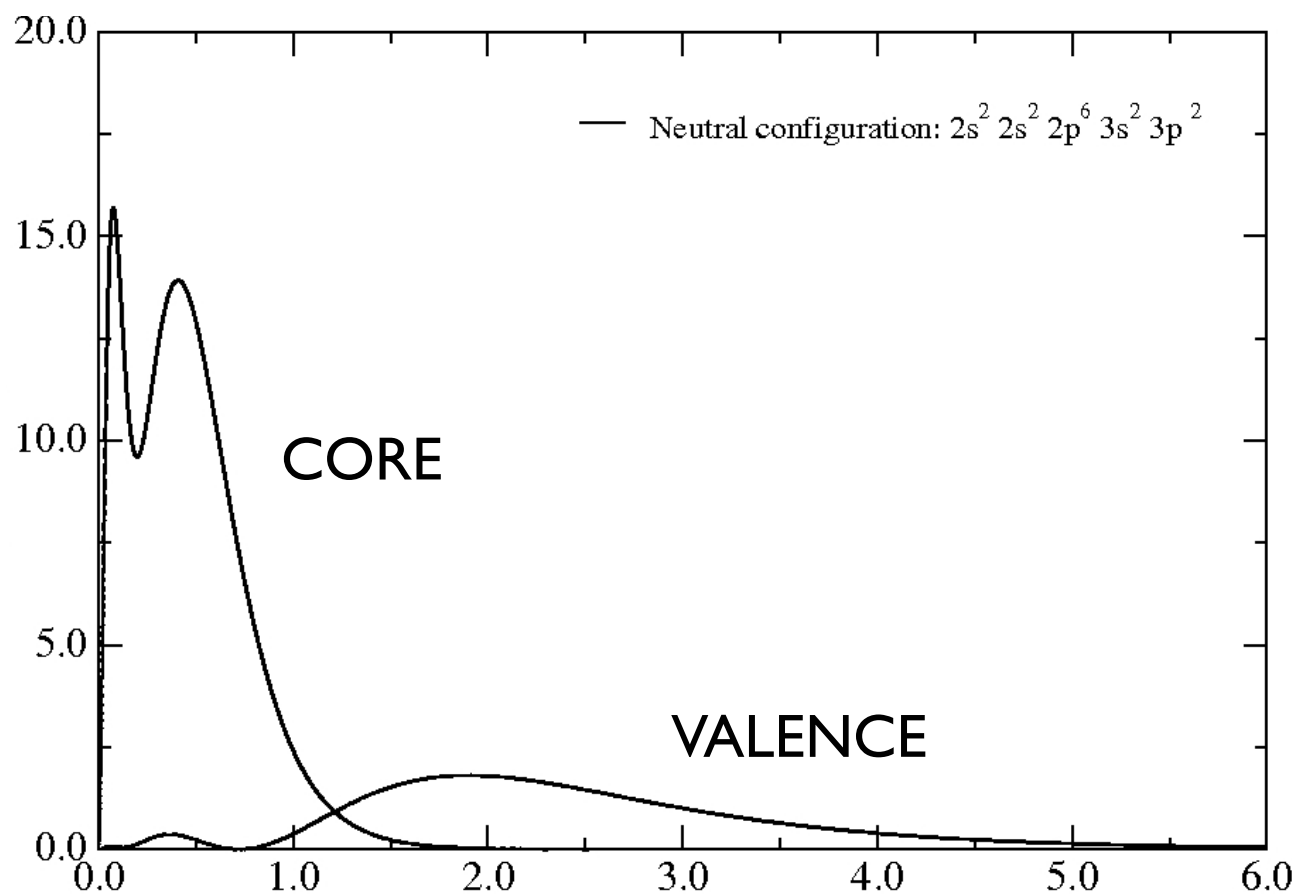
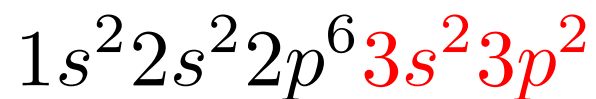


Periodic table of the elements

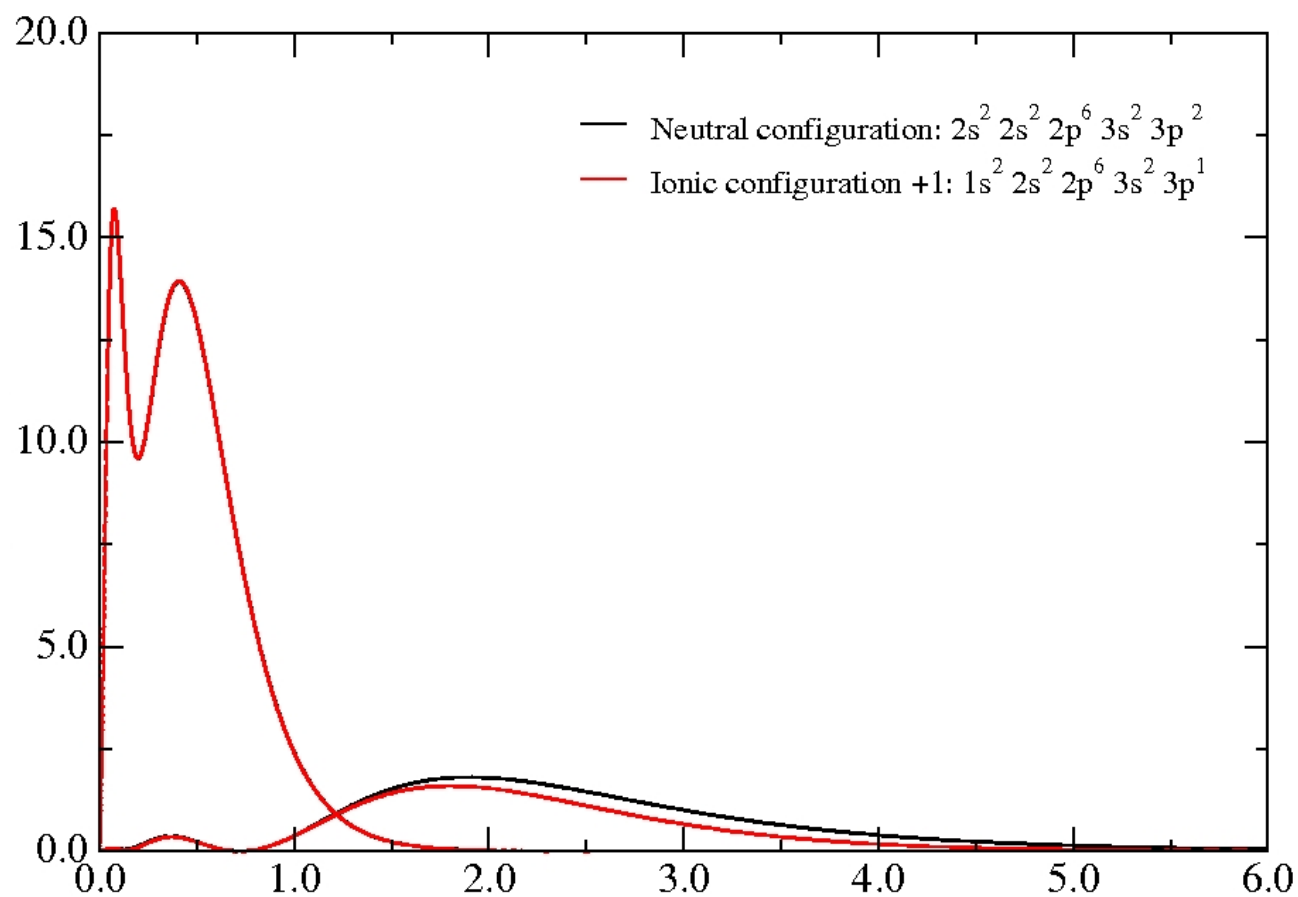
group 1*																		18				
period 1	1																	2				
	H																	He				
2	3	4															5	6	7	8	9	10
	Li	Be															B	C	N	O	F	Ne
3	11	12													13	14	15	16	17	18		
	Na	Mg													Al	Si	P	S	Cl	Ar		
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36				
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54				
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86				
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
7	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118				
	Fr	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							
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							
actinoid series 7		90	91	92	93	94	95	96	97	98	99	100	101	102	103							
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr							

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC). © Encyclopædia Britannica, Inc.

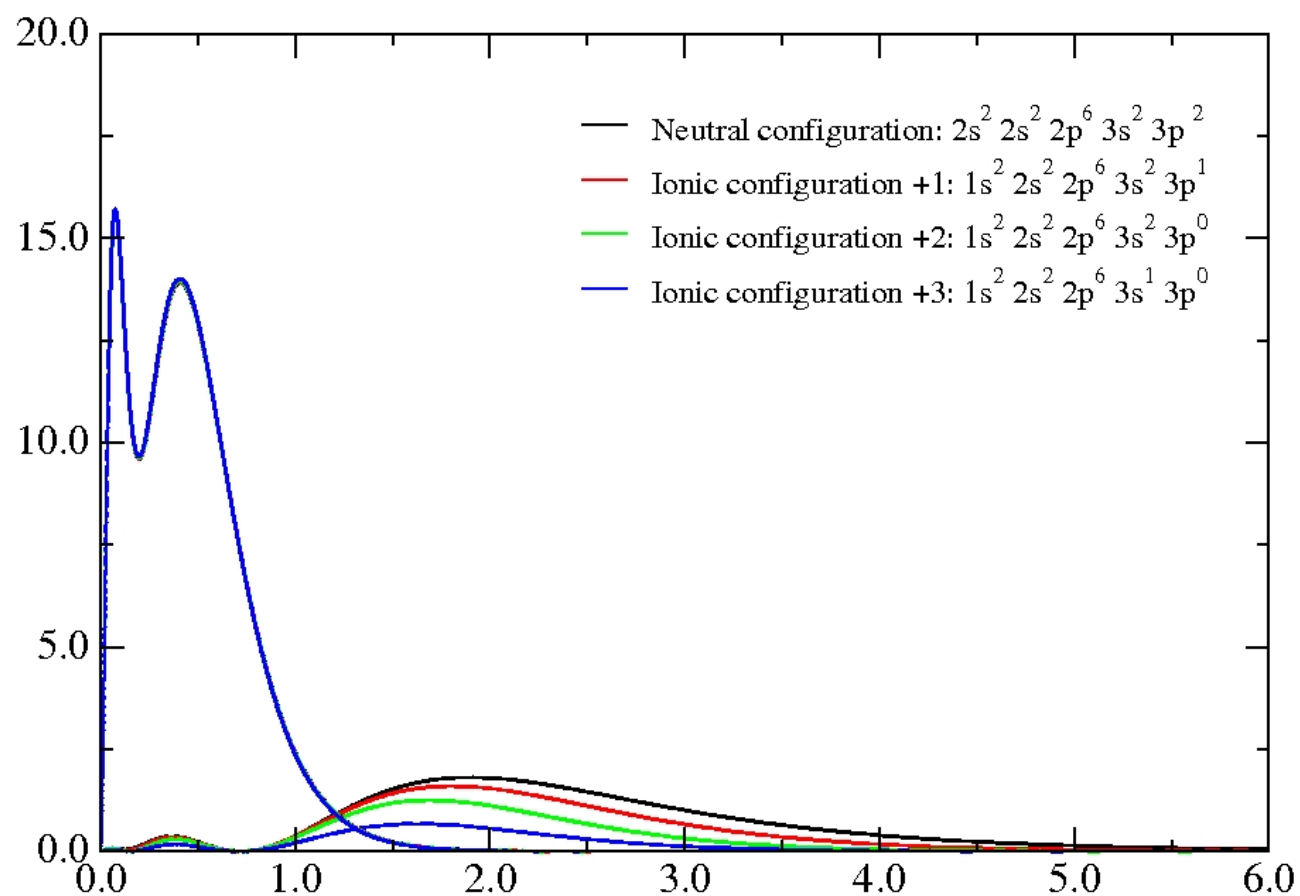
Radial profile of charge density for Si atom



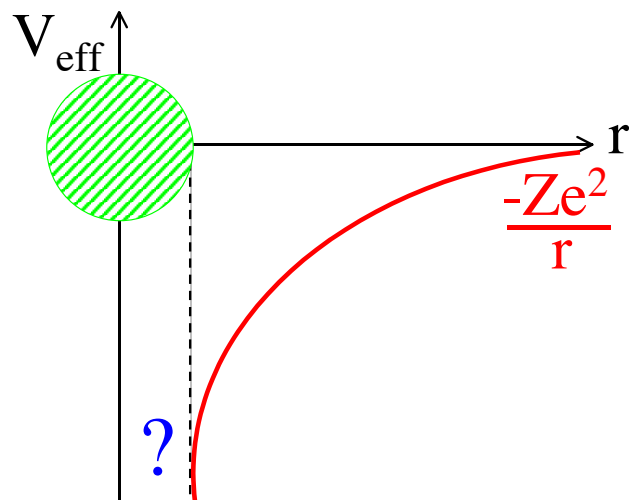
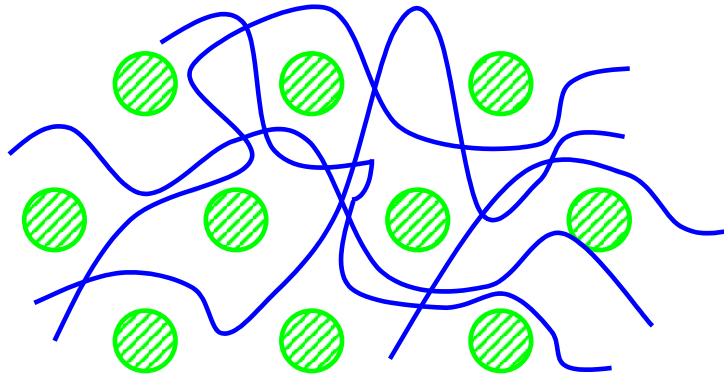
Radial profile of charge density for Si atom



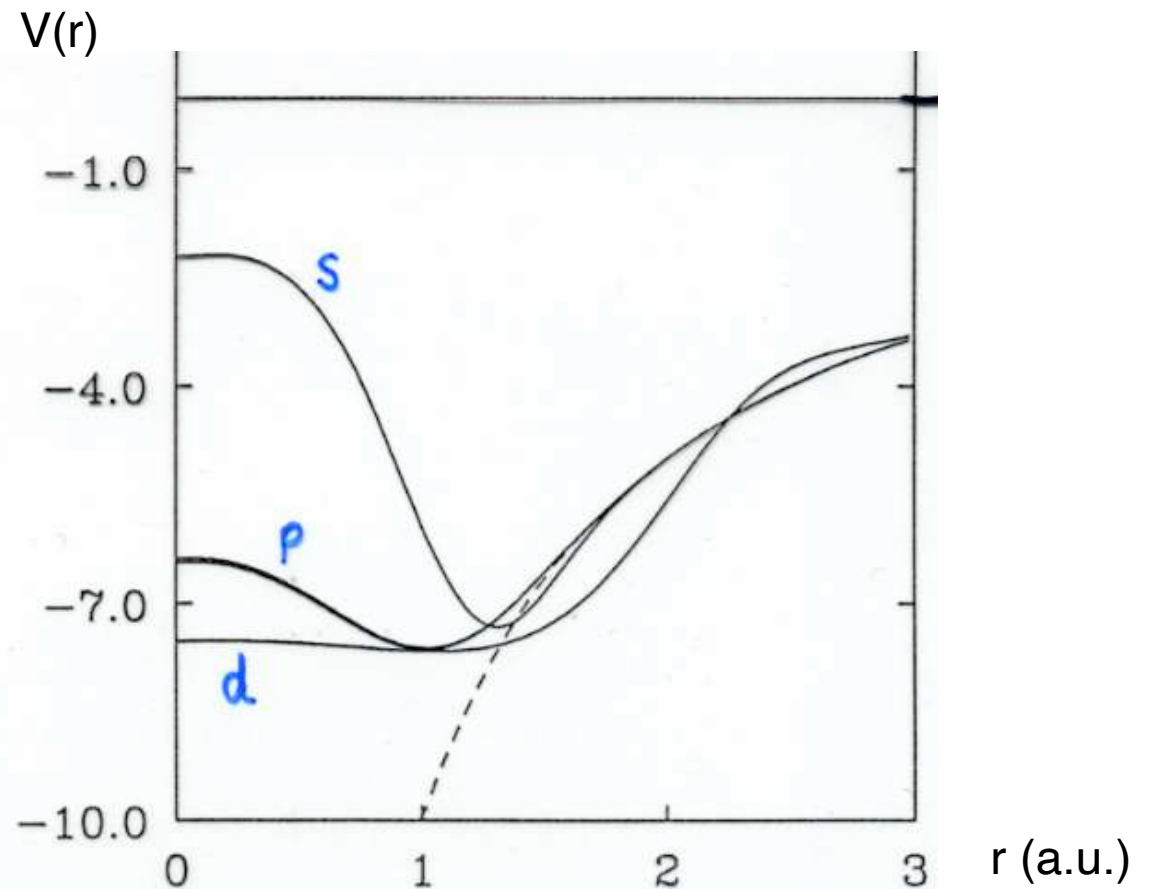
Radial profile of charge density for Si atom



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: $|\vec{k}, \text{opw}\rangle = |\vec{k}\rangle - \sum_c |\psi_c\rangle \langle \psi_c | \vec{k}\rangle$
 orthogonal to the core states $|\psi_c\rangle$

$$\hat{H} |\text{opw}\rangle = \epsilon |\text{opw}\rangle \Rightarrow$$

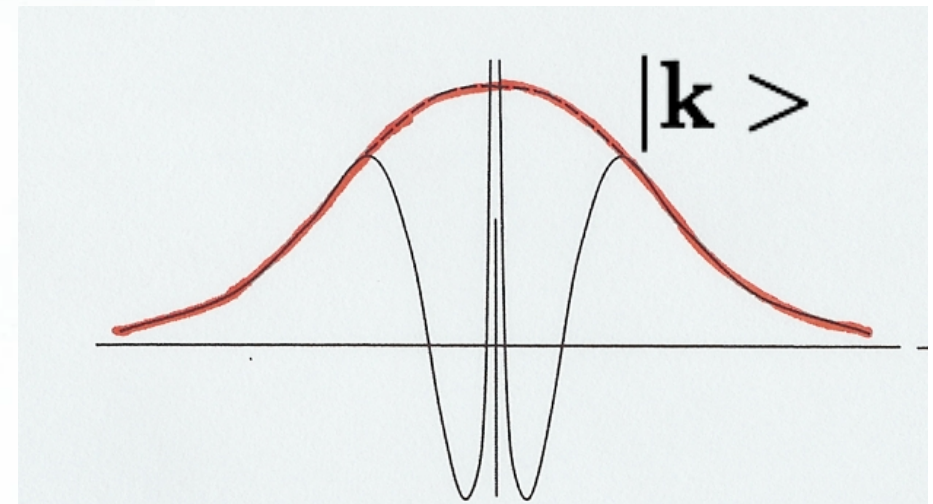
$$\Rightarrow (\hat{H} + \hat{V}_{\text{rep}}) |\vec{k}\rangle = \epsilon |\vec{k}\rangle$$

where: $\hat{V}_{\text{rep}} = \sum_c (\epsilon - \epsilon_c) |\psi_c\rangle \langle \psi_c|$

is a repulsive potential

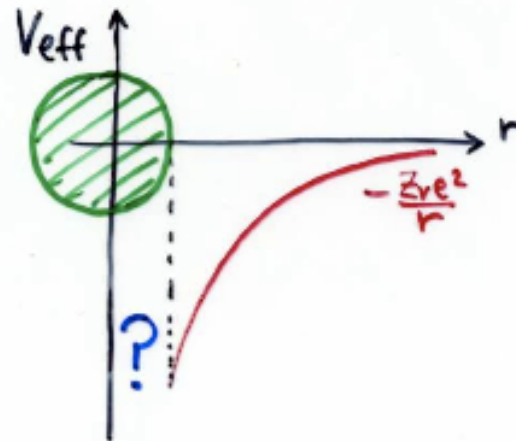
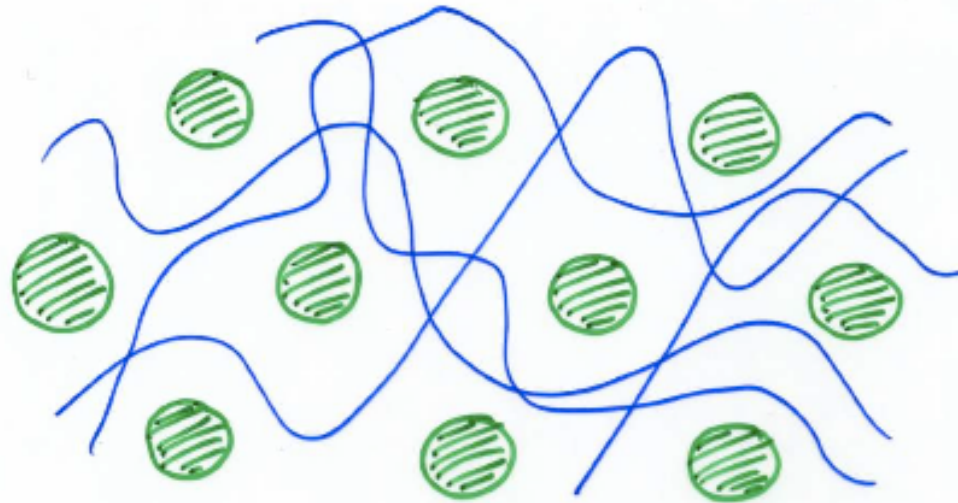
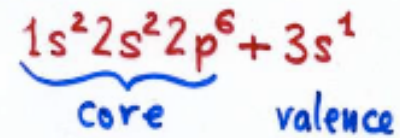
$$\hat{H} = \hat{T} + \hat{V} \Rightarrow \hat{V}_{\text{eff}} = \hat{V} + \hat{V}_{\text{rep}} \text{ is a}$$

"soft" pseudopotential



Phillips-Kleinman
 cancellation theorem
 (1959)

Common metal: Na



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

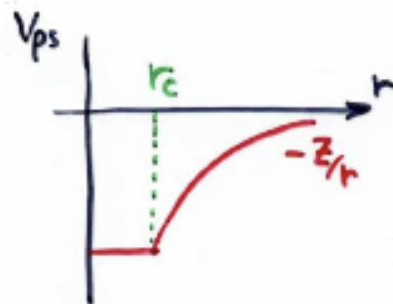
A bit of history...

Empirical pseudopotentials

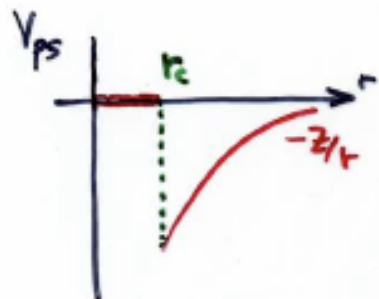
- Pseudopotential (pre) history

- Fermi (1934)

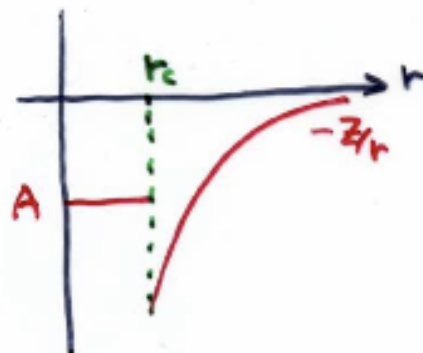
- Simple empirically-adjustable pseudopotentials



r_c adjusted to reproduce the valence eigenvalue



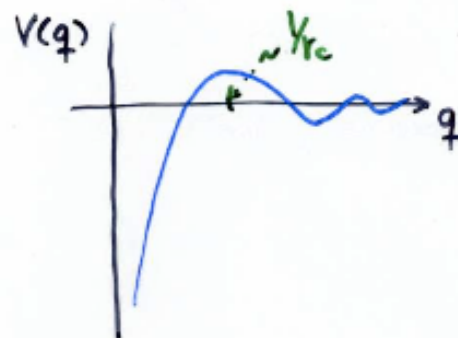
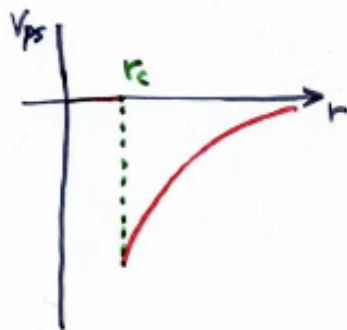
"Empty-core" pseudopotential
Ashcroft (1966)



Heine - Abarankov (~ 1964)

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

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



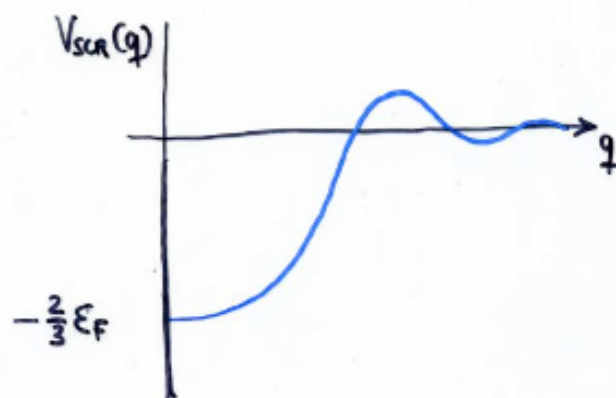
Fourier transform: $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

• 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 :

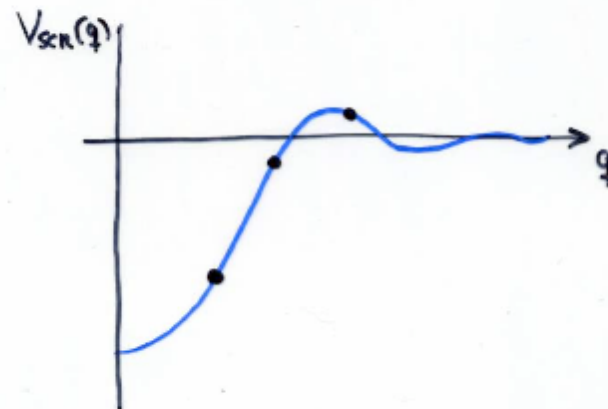
$$V(\vec{G}) = S(\vec{G}) \cdot V(q = |\vec{G}|)$$

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



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

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



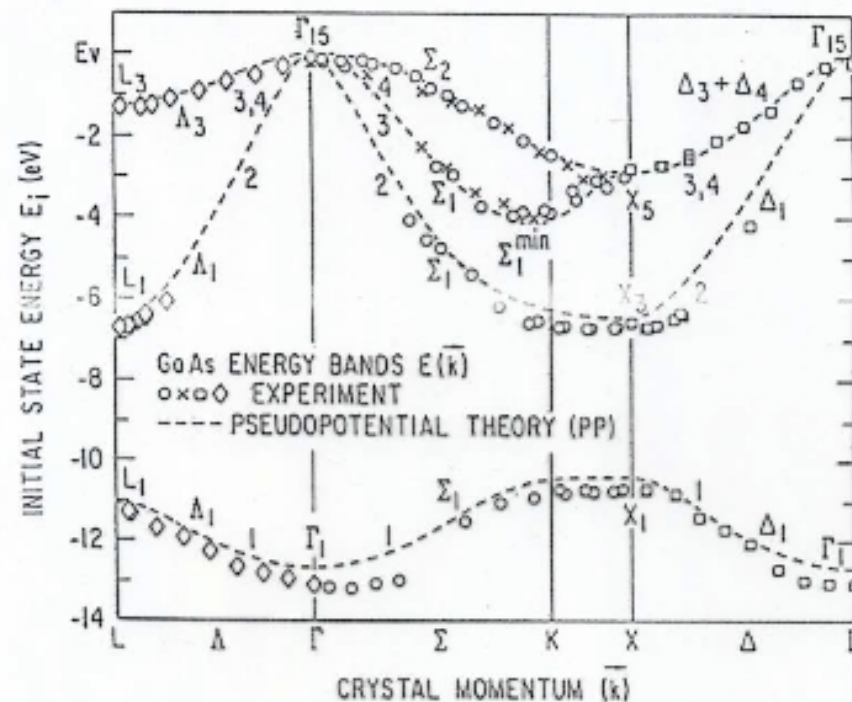
ONLY three parameters are needed for
 a reasonably good description

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

$V_{eff}(G)$ fitted !

Empirical Pseudopotential Method (EPM)

(Marvin L. Cohen et al. ~ 1962)



Band structure of GaAs

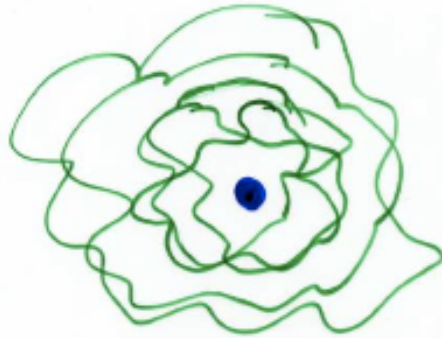
EPM needs a few experimental inputs
(absorption edge, reflectivity features...)
and provides the whole band structure

A bit of history...

The modern era of pseudopotentials

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

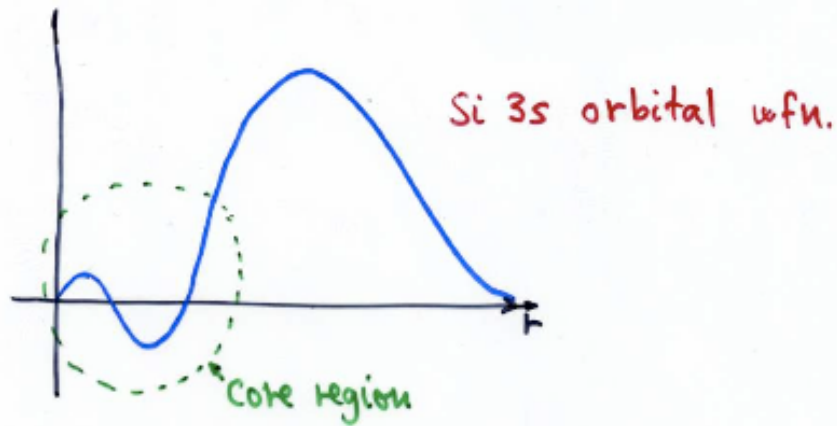
- Atomic calculations using DFT



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

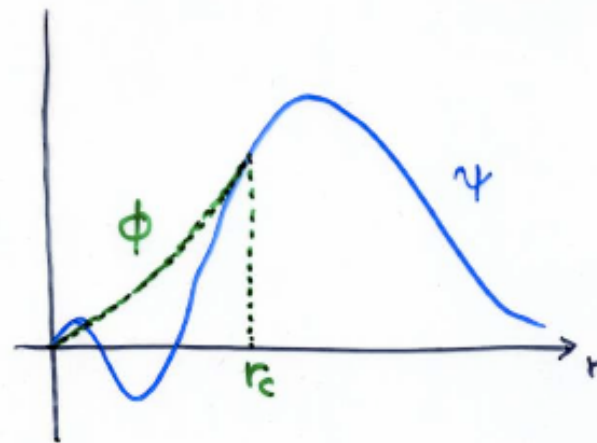
$\downarrow$
 $-\frac{Ze^2}{r}$

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



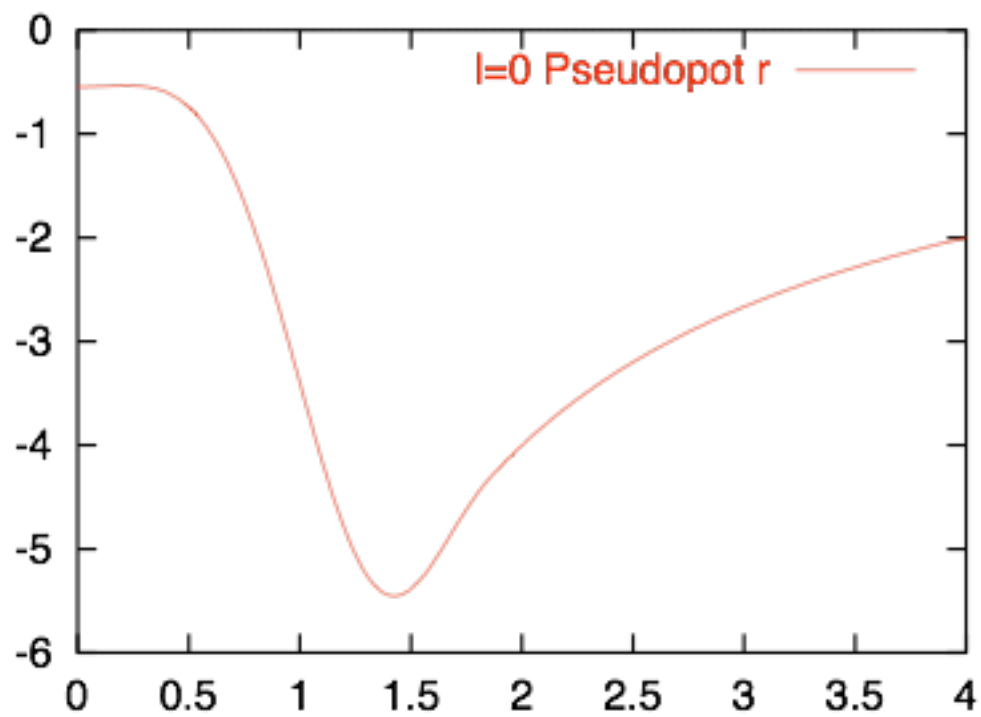
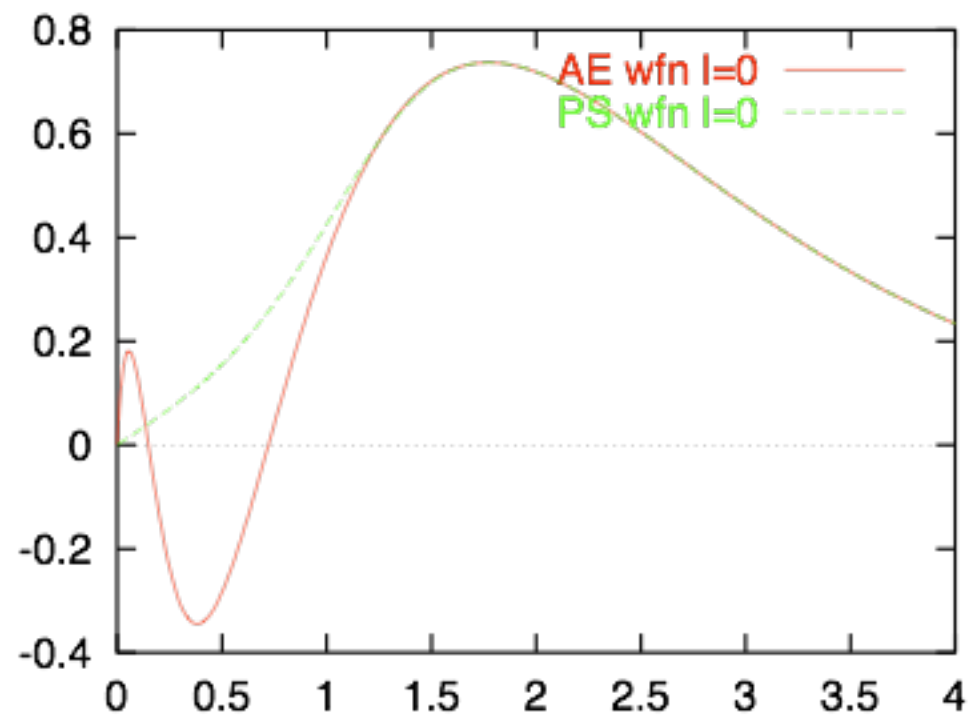
nodes: Imposed by orthogonality to the core states.

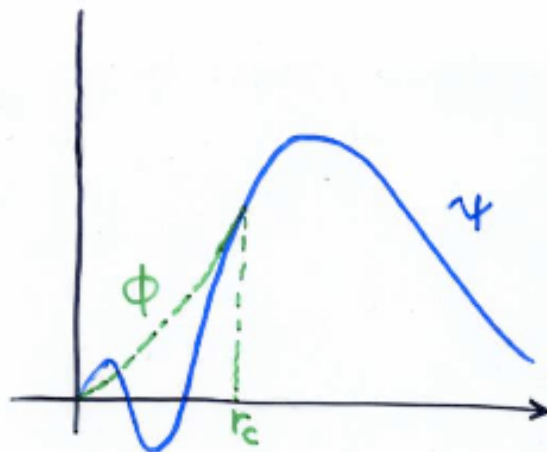
Idea: Eliminate the core electrons by "ironing out" the nodes:



ϕ : Pseudo wavefunction

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





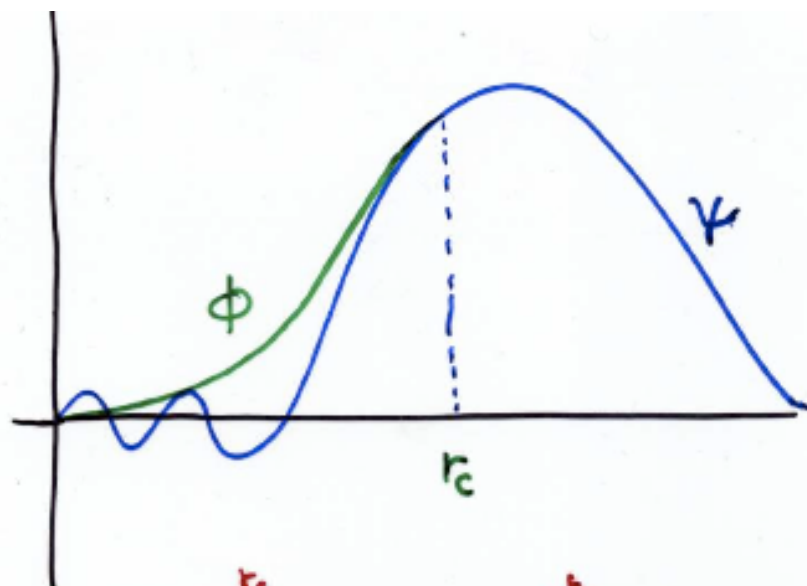
HOW does one get ϕ from ψ ?

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 :

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



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

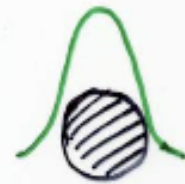
Norm - conservation

- Preserves electrostatic potential outside r_c

$$\frac{d}{dE} \left(\frac{d}{dr} h_m(r\phi) \right) \Big|_R \propto \frac{1}{(r\phi)^2} \int_0^R (r\phi)^2 dr$$

Preserves scattering properties
(and their first energy derivative)

Isolated atom

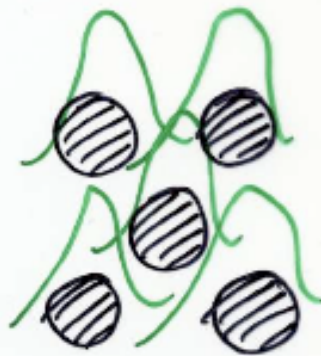


Atomic eigenvalues

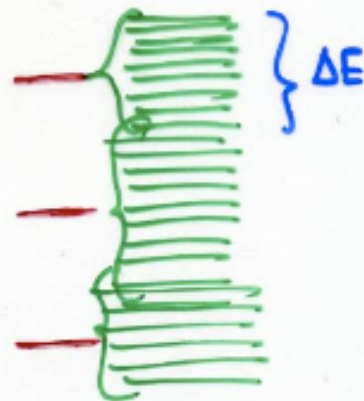
V_{ps} "perfect"

TRANSFERABILITY

Solid



Charge Transfer...



ΔE

Bands

V_{ps} ?

$$\{-\nabla^2 + \hat{V}_{AE}\} \psi = \epsilon \psi$$

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

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

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

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

"Bare" or ionic pseudopotential:

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

n : Valence charge density

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

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

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

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

"Bare" or ionic pseudopotential:

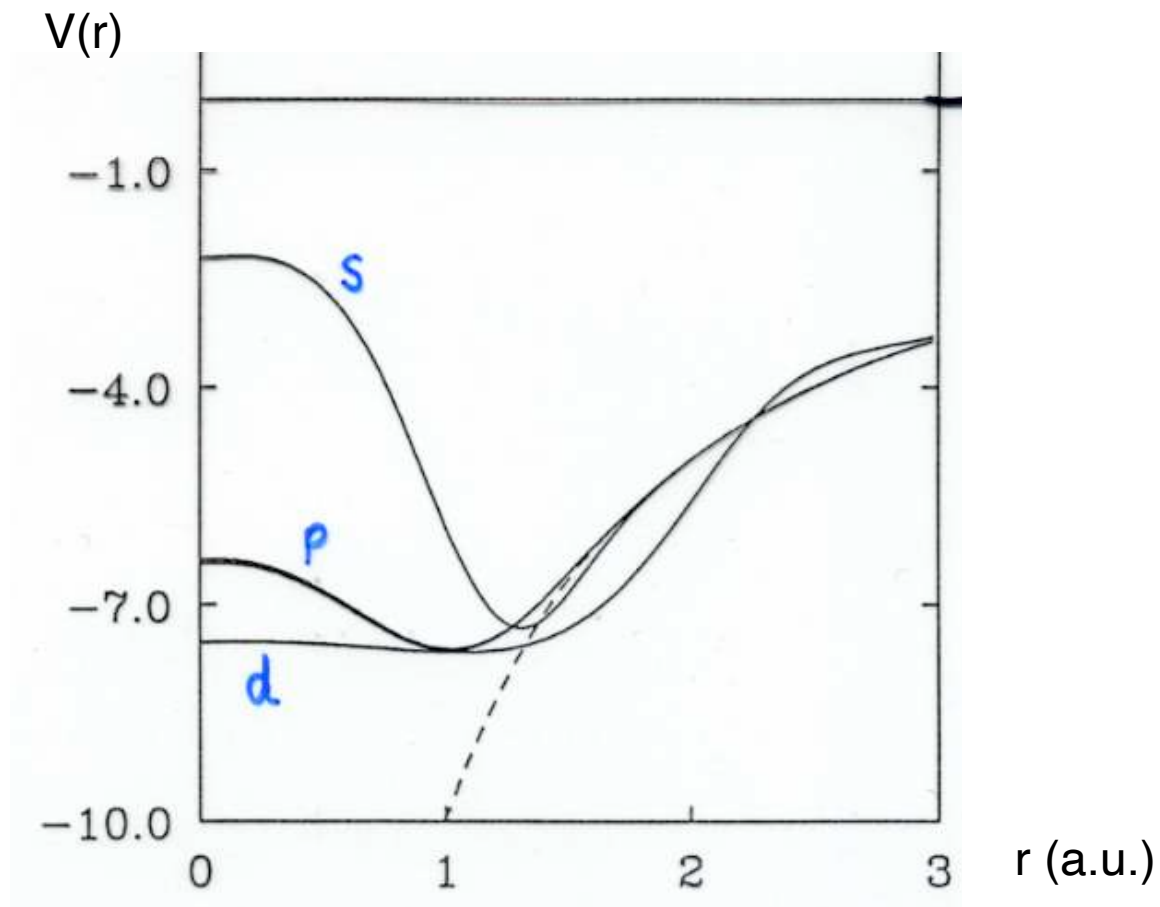
$$V_{ps}(r) = V_{ps}^{[n]} - V_H^{[n]} - V_{xc}^{[n]}$$

non-linear
core corrections

n : Valence charge density

Ab-initio pseudopotentials

Essential non-locality



Semi-local form:

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

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

Kleinman-Bylander form:

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

(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/>

[Help me](#)



PSEUDO DOJO

Download

3.13
Mean

hints tests

32.74 0.95

37.25 0.93

48.1 0.93

psp8

upf

psml

✓ html

djrepo

Type

XC

Accuracy

NC (ONCVSP v0.4)

PBE

standard

Home

F.A.Q.

Contribute

About

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.

1 H 0.1 32 0.1 36 2.5 43 -0.00 Hydrogen	2 He 0.0 39 0.0 45 4.2 49 na Helium
3 Li 0.2 33 0.2 37 1.9 41 -0.10 Lithium	4 Be 1.4 36 1.4 44 4.4 50 0.20 Beryllium
11 Na 0.4 38 0.4 44 4.6 48 -0.00 Sodium	12 Mg 0.4 38 0.4 42 1.5 48 0.00 Magnesium
19 K 0.2 33 0.2 37 2.0 43 -0.30 Potassium	20 Ca 0.1 26 0.1 34 0.3 38 -0.20 Calcium
21 Sc 1.3 35 1.3 39 2.8 45 -0.00 Scandium	22 Ti 0.9 38 0.9 42 1.3 46 -0.10 Titanium
23 V 1.3 38 1.3 42 1.6 46 -0.10 Vanadium	24 Cr 10.5 43 10.5 47 18.1 55 -0.00 Chromium
25 Mn 8.0 42 8.0 46 16.9 54 -0.10 Manganese	26 Fe 5.6 41 5.6 45 9.2 53 -0.10 Iron
27 Co 1.0 42 1.0 46 1.4 54 -0.00 Cobalt	28 Ni 1.0 45 1.0 49 1.4 55 -0.10 Nickel
29 Cu 0.6 43 0.6 47 0.9 52 -0.10 Copper	30 Zn 0.3 46 0.3 50 0.8 58 -0.10 Zinc
31 Ga 0.5 36 0.5 40 1.5 46 -0.00 Gallium	32 Ge 0.5 35 0.5 39 1.0 45 -0.00 Germanium
33 As 0.4 38 0.4 42 0.7 48 -0.00 Arsenic	34 Se 0.2 39 0.2 43 0.5 49 -0.10 Selenium
35 Br 0.0 19 0.0 22 0.2 26 -0.20 Bromine	36 Kr 0.0 22 0.0 26 2.3 34 na Krypton
37 Rb 0.2 19 0.2 23 2.9 29 -0.40 Rubidium	38 Sr 1.3 26 1.3 34 6.1 40 -0.20 Strontium
39 Y 1.0 30 1.0 36 2.3 42 -0.10 Yttrium	40 Zr 0.8 29 0.8 33 1.1 49 -0.00 Zirconium
41 Nb 1.3 37 1.3 41 1.3 49 -0.00 Niobium	42 Mo 1.4 36 1.4 40 1.0 46 -0.10 Molybdenum
43 Tc 1.6 38 1.6 42 1.1 48 -0.00 Technetium	44 Ru 2.1 38 2.1 42 1.5 50 -0.00 Ruthenium
45 Rh 2.6 40 2.6 44 2.1 50 -0.00 Rhodium	46 Pd 1.1 37 1.1 41 1.3 49 -0.10 Palladium
47 Ag 0.3 37 0.3 41 0.6 47 -0.10 Silver	48 Cd 1.1 47 1.1 51 3.5 57 -0.00 Cadmium
49 In 0.1 31 0.1 35 0.2 41 -0.10 Indium	50 Sn 0.8 32 0.8 36 1.8 42 0.00 Tin
51 Sb 0.5 36 0.5 40 1.0 44 0.00 Antimony	52 Te 0.8 34 0.8 40 1.6 46 0.10 Tellurium
53 I 0.4 31 0.4 35 1.1 41 0.00 Iodine	54 Xe 0.0 26 0.0 34 2.5 42 na Xenon
55 Cs 0.1 19 0.1 25 1.5 29 -0.40 Caesium	56 Ba 0.9 16 0.9 22 4.9 28 -0.10 Barium
72 Hf 0.6 25 0.6 29 0.8 35 -0.00 Hafnium	73 Ta 0.7 25 0.7 29 0.6 35 -0.10 Tantalum
74 W 0.2 31 0.2 37 0.1 41 -0.00 Wolfram	75 Re 0.7 30 0.7 36 0.4 42 -0.10 Rhenium
76 Os 1.7 33 1.7 37 0.9 43 -0.10 Osmium	77 Ir 1.5 30 1.5 34 0.9 40 -0.20 Iridium
78 Pt 0.6 38 0.6 42 0.5 50 -0.20 Platinum	79 Au 1.3 32 1.3 36 1.6 44 -0.10 Gold
80 Hg 0.7 29 0.7 33 7.2 39 na Mercury	81 Tl 0.1 27 0.1 31 0.2 37 -0.10 Thallium
82 Pb 0.1 24 0.1 28 0.1 34 -0.10 Lead	83 Bi 0.2 29 0.2 33 0.4 37 -0.00 Bismuth
84 Po 0.3 26 0.3 32 0.5 38 na Polonium	85 At na na na na Astatine
86 Rn 0.0 32 0.0 36 2.4 42 na Radon	
104 Rf na na na na Rutherfordium	105 Db na na na na Dubnium
106 Sg na na na na Seaborgium	107 Bh na na na na Bohrium
108 Hs na na na na Hassium	109 Mt na na na na Meitnerium
110 Ds na na na na Darmstadtium	111 Rg na na na na Roentgenium
112 Cn na na na na Copernicium	113 Nh na na na na Nihonium
114 Fl na na na na Flerovium	115 Mc na na na na Moscovium
116 Lv na na na na Livermorium	117 Ts na na na na Tennessine
118 Og na na na na Oganesson	
57 La na 50 na 55 -0.10 Lanthanum	58 Ce na na na na Cerium
59 Pr na na na na Praseodymium	60 Nd na na na na Neodymium
61 Pm na na na na Promethium	62 Sm na na na na Samarium
63 Eu na na na na Europium	64 Gd na na na na Gadolinium
65 Tb na na na na Terbium	66 Dy na na na na Dysprosium
67 Ho na na na na Holmium	68 Er na na na na Erbium
69 Tm na na na na Thulium	70 Yb na na na na Ytterbium
71 Lu 1.0 46 1.0 50 2.2 58 na Lutetium	
89 Ac na na na na Actinium	90 Th na na na na Thorium
91 Pa na na na na Protactinium	92 U na na na na Uranium
93 Np na na na na Neptunium	94 Pu na na na na Plutonium
95 Am na na na na Americium	96 Cm na na na na Curium
97 Bk na na na na Berkelium	98 Cf na na na na Californium
99 Es na na na na Einsteinium	100 Fm na na na na Fermium
101 Md na na na na Mendelevium	102 No na na na na Nobelium
103 Lr na na na na Lawrencium	

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: 0
Ground state valence configuration: 2s02 2p04
Reading pseudopotential information in formatted form from: 0.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 PA0.Basis		# Define Basis set
0	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 !