

The pseudopotential concept

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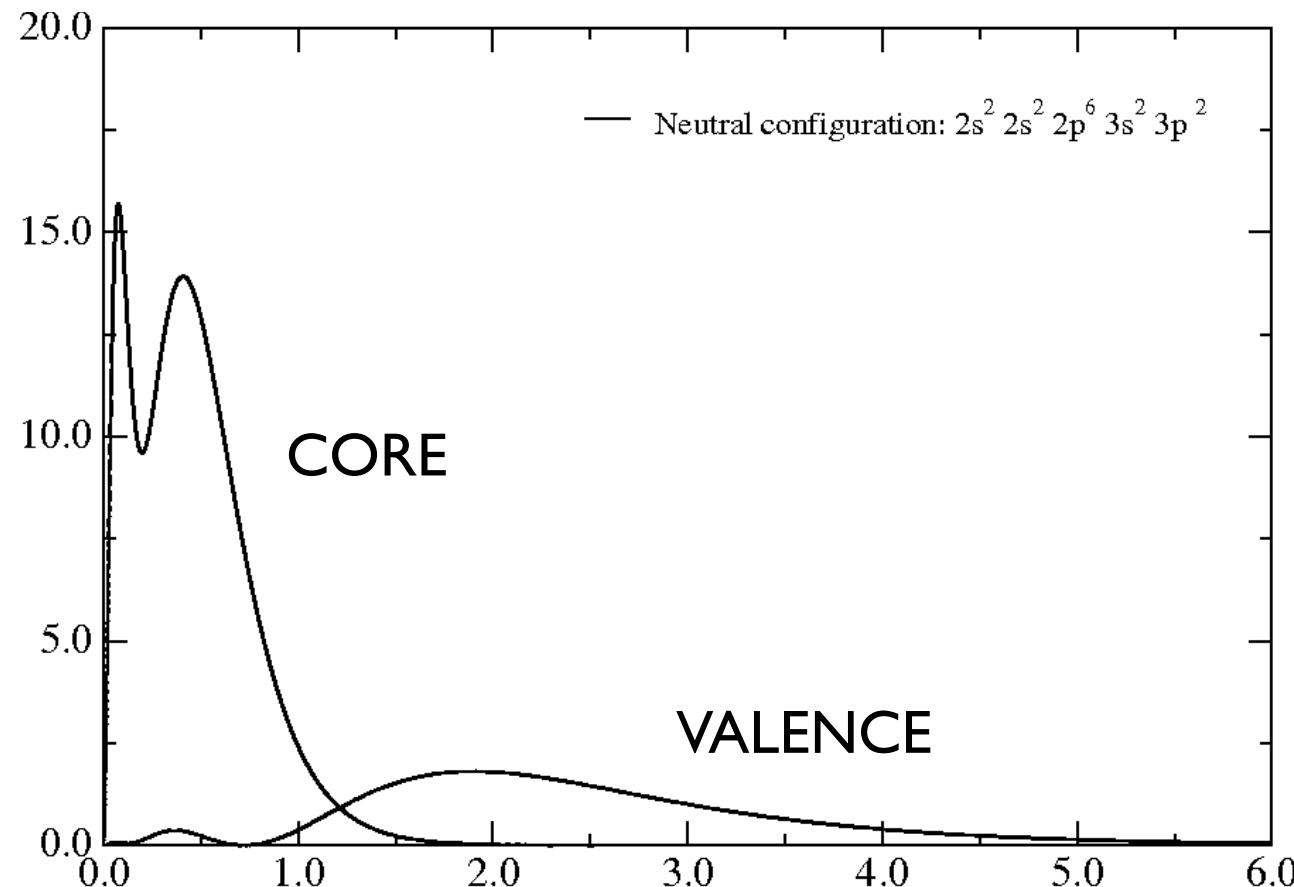
...using the work of many others!



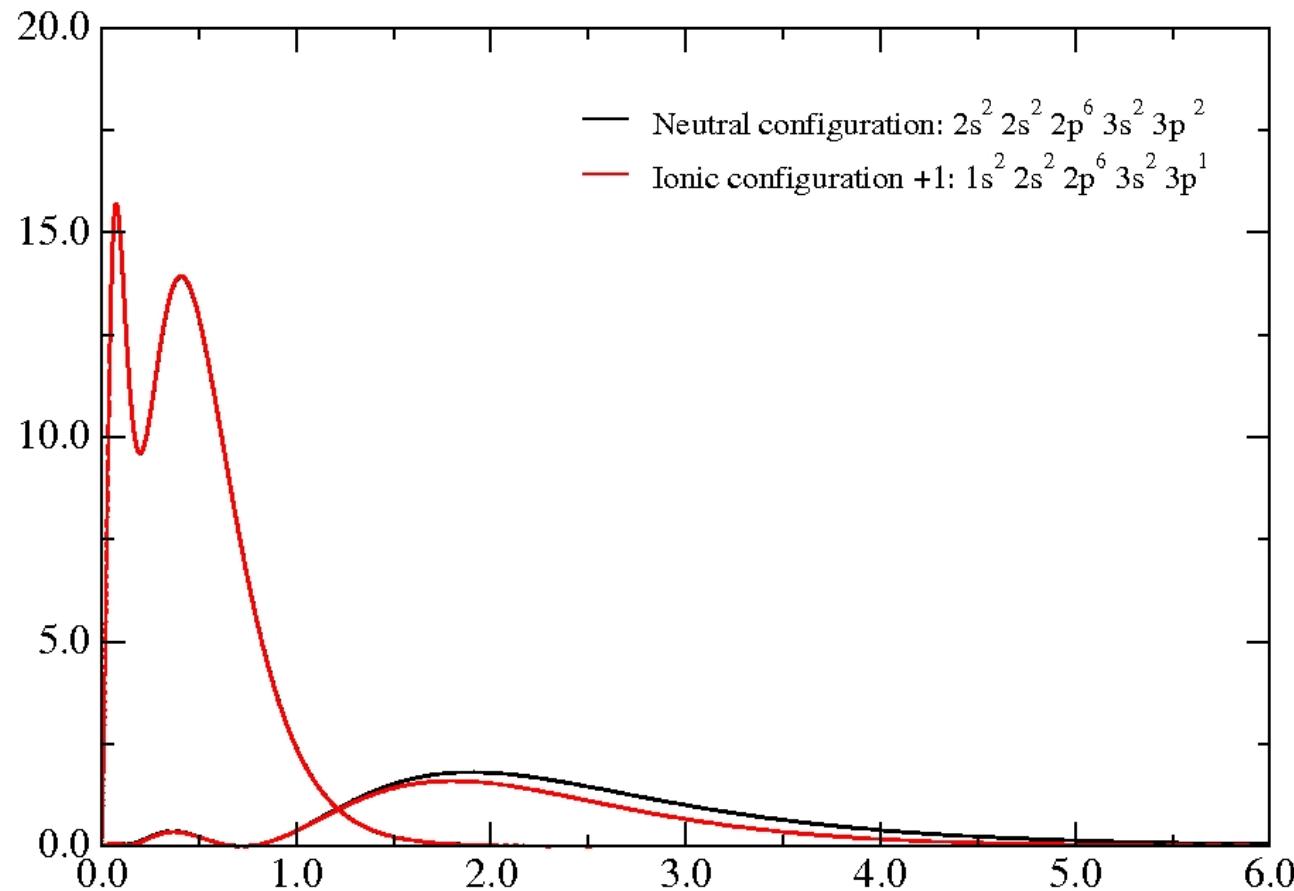
EXCELENCIA
SEVERO
OCHOA

Radial profile of charge density for Si atom

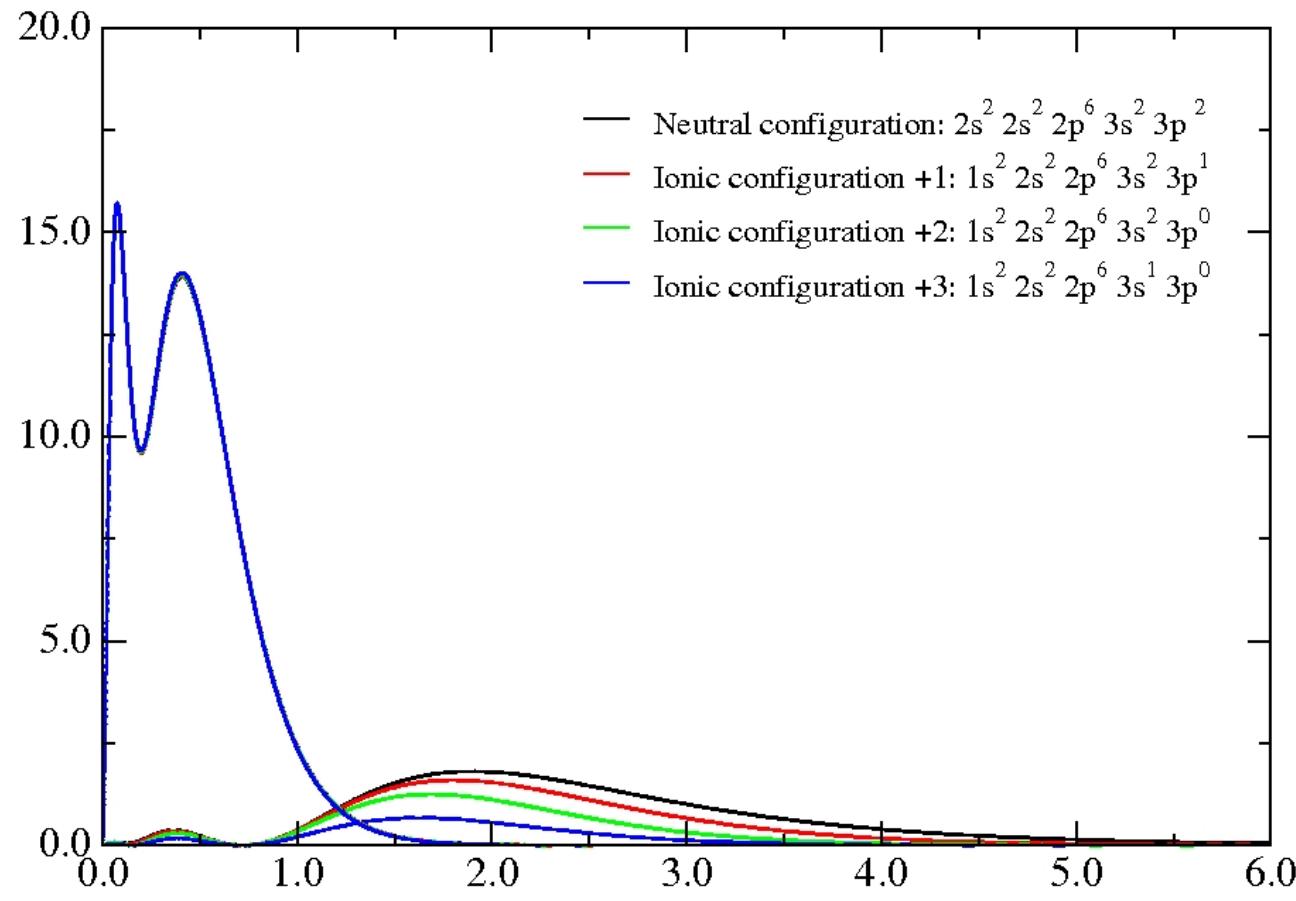
$1s^2 2s^2 2p^6 \color{red}{3s^2 3p^2}$



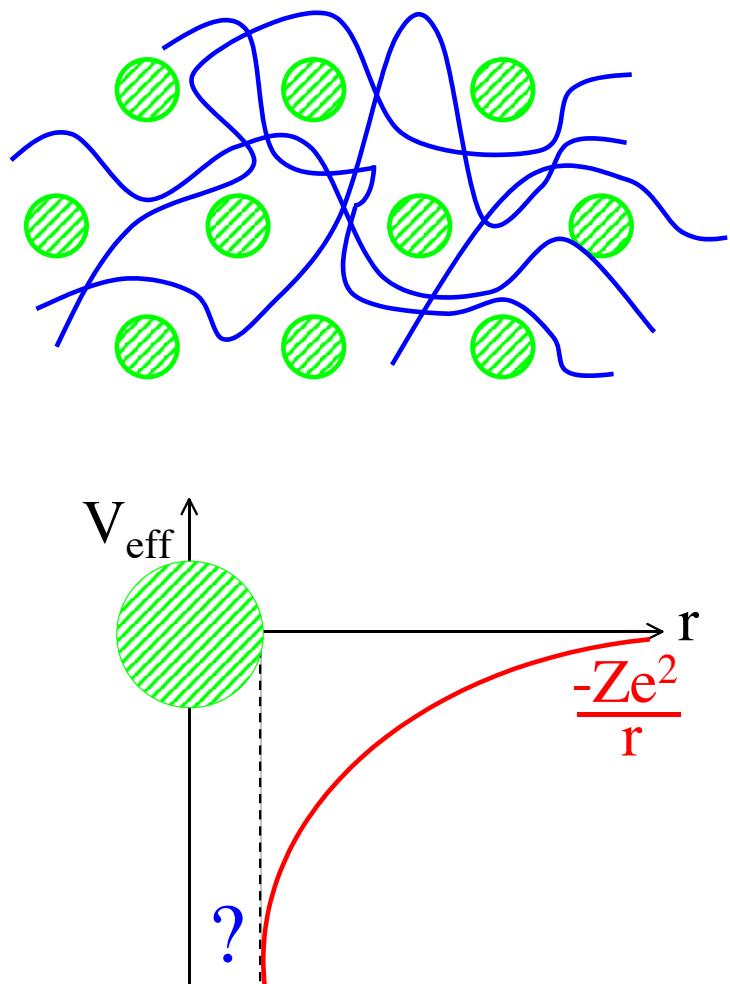
Radial profile of charge density for Si atom



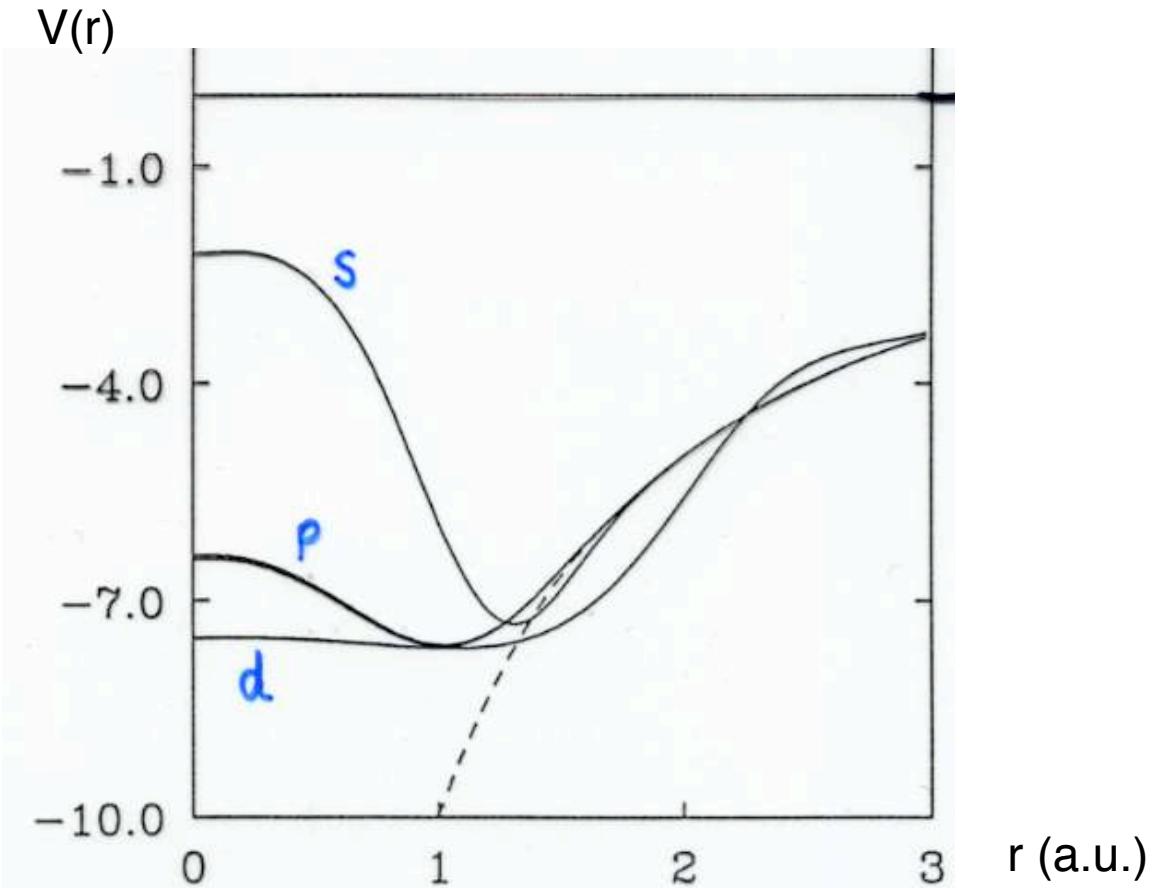
Radial profile of charge density for Si atom



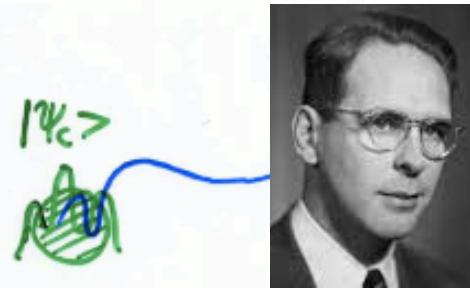
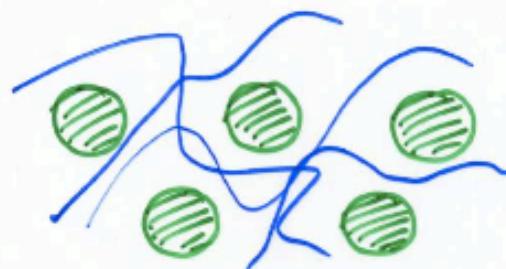
Internal electrons are inert, and do not participate in the chemical bond



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 $|\Psi_c\rangle$

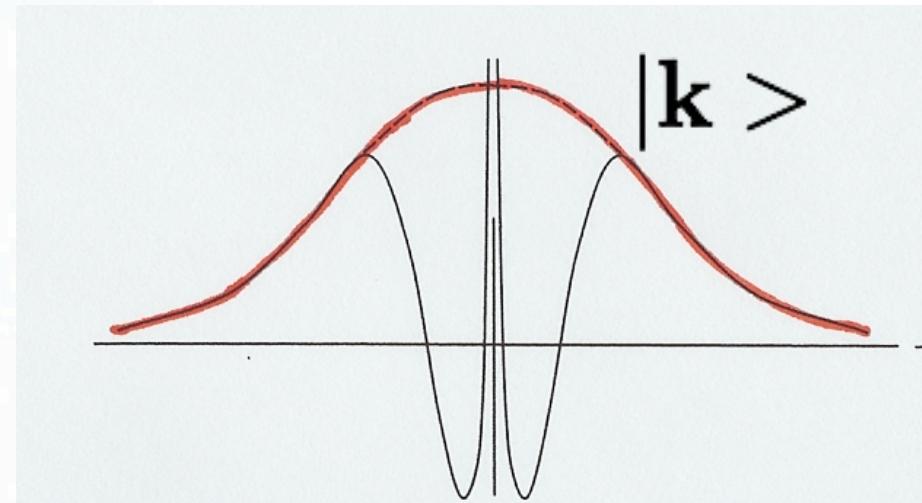
$$\hat{H} |\text{OPW}\rangle = \varepsilon |\text{OPW}\rangle \Rightarrow$$

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

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

is a repulsive potential

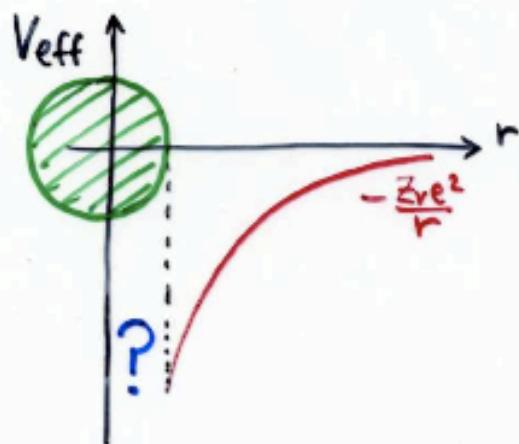
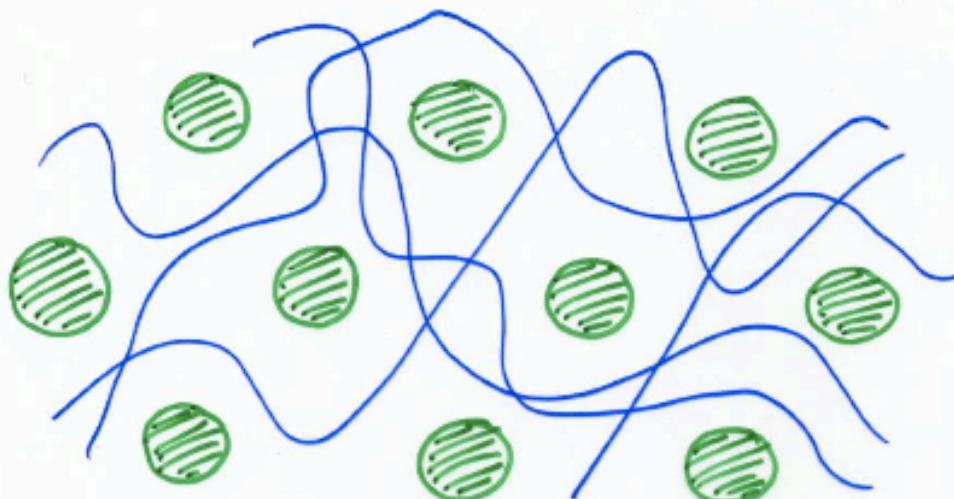
$$\hat{H} = \hat{T} + \hat{V} \Rightarrow \hat{V}_{\text{eff}} = \hat{V} + \hat{V}_{\text{Rep}} \text{ is a "soft" pseudopotential}$$



Phillips-Kleinman
cancellation theorem
(1959)

Common metal: Na

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

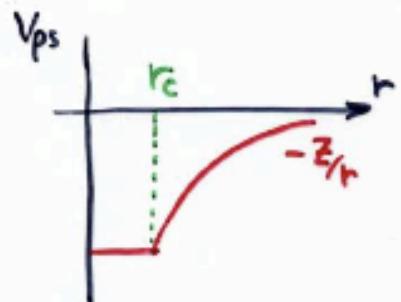


In the core zone, the effective potential will be softer than the coulomb $-\frac{Zre^2}{r}$ pot.

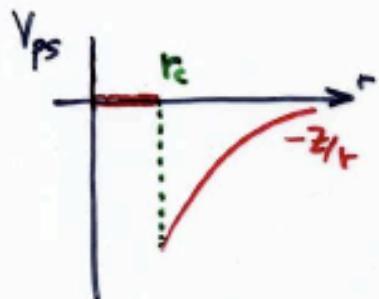
- Pseudopotential (pre) history

 - Fermi (1934)

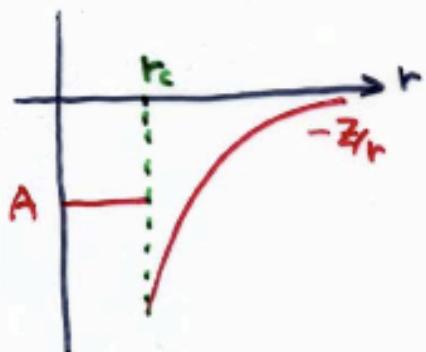
 - Simple empirically-adjustable pseudopotentials



r_c adjusted to reproduce
the valence eigenvalue



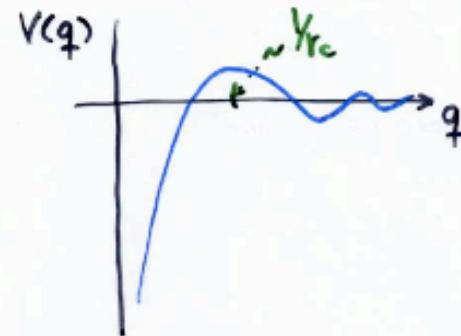
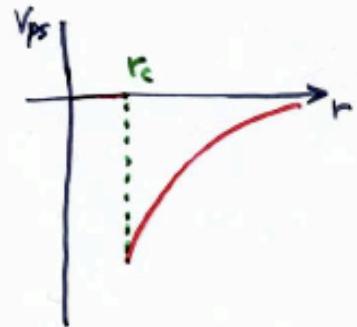
"Empty-core" pseudopotential
Ashcroft (1966)



Heine - Abarenkov (~1964)

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

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



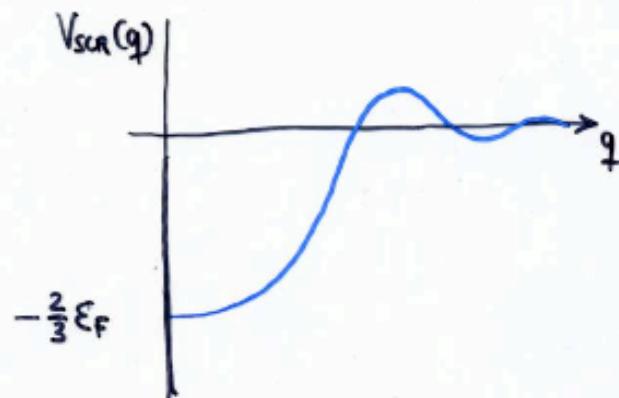
Fourier transform : $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

• 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 :

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

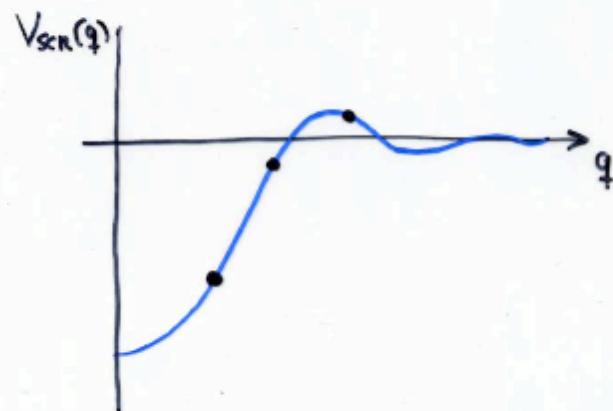
$$S(\vec{G}) = \frac{1}{N_a} \sum_{\vec{e}_i} e^{-i\vec{G} \cdot \vec{e}_i}$$

structure factor



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

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



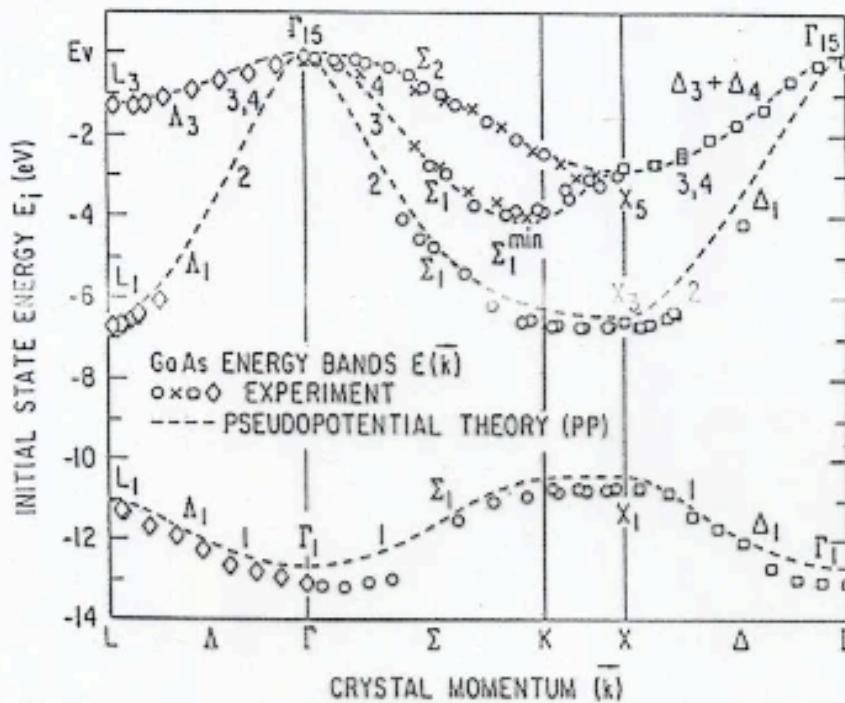
ONLY three parameters are needed for
a reasonably good description

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

$V_{eff}(G)$ fitted !

Empirical Pseudopotential Method (EPM)

(Marvin L. Cohen et al. ~1962)

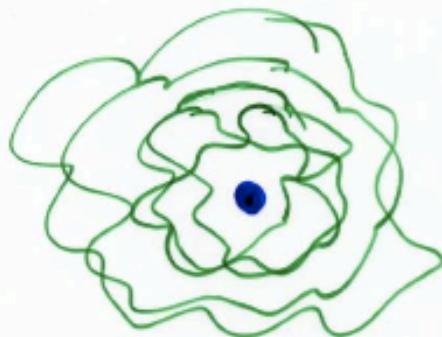


Band structure of GaAs

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

The modern era of pseudopotentials

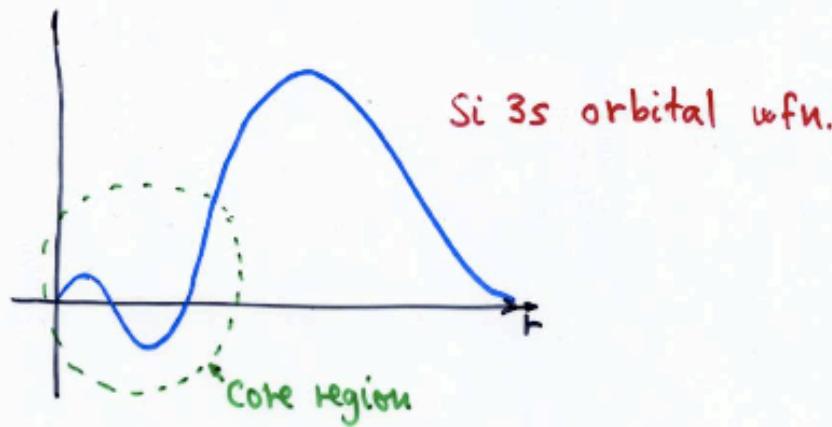
- Atomic calculations using DFT



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

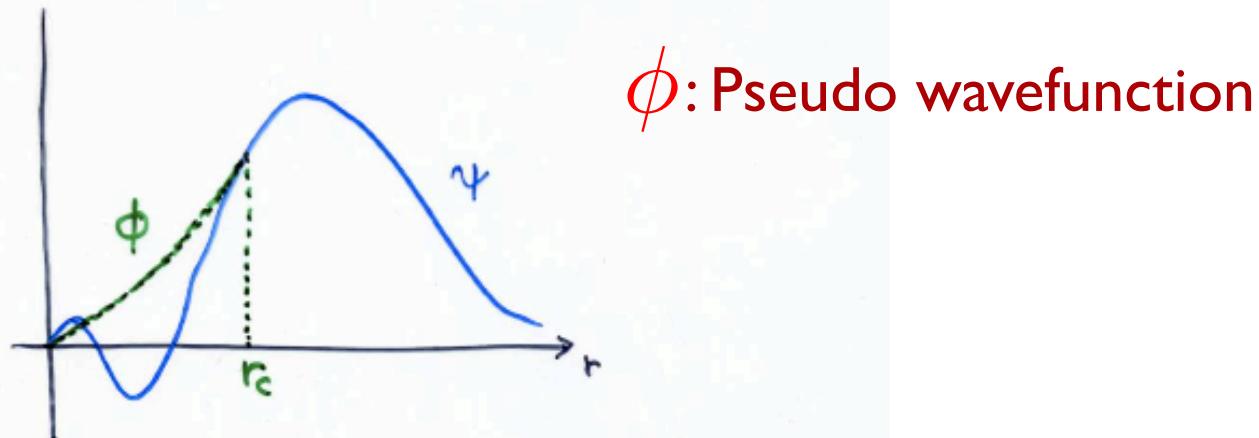
\downarrow
 $- \frac{ze^2}{r}$

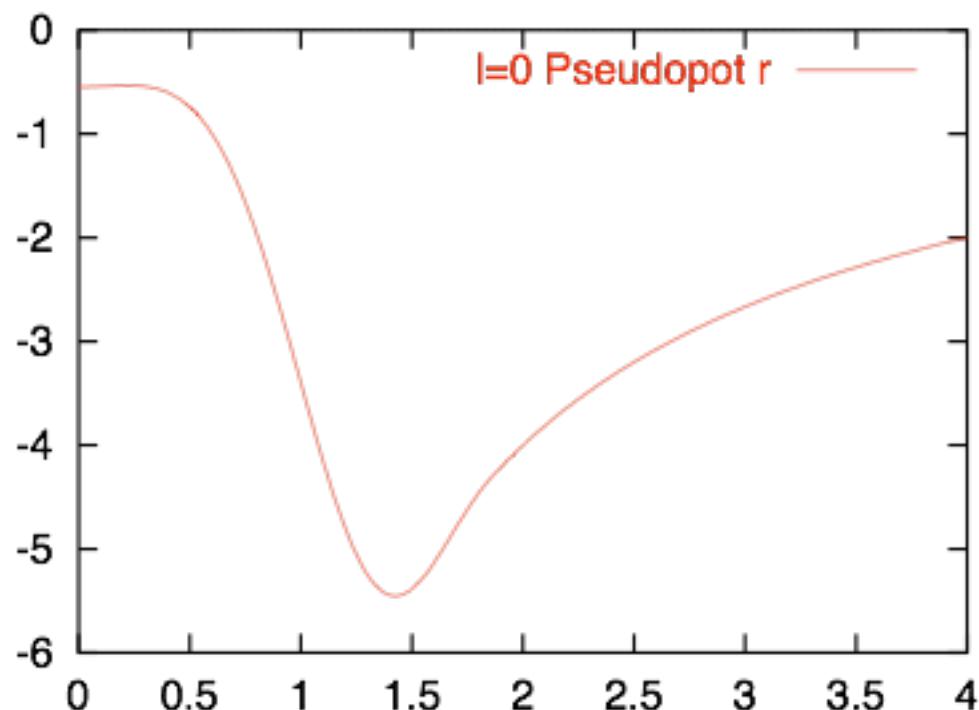
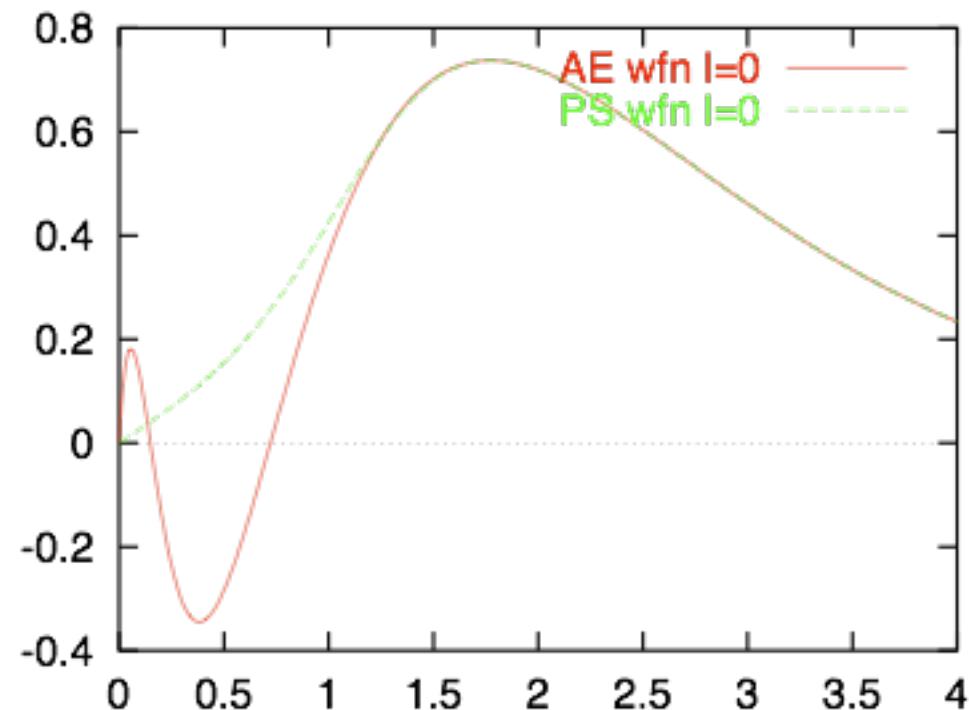
$$n_{el}(\vec{r}) = \sum_i |\Psi_i|^2$$

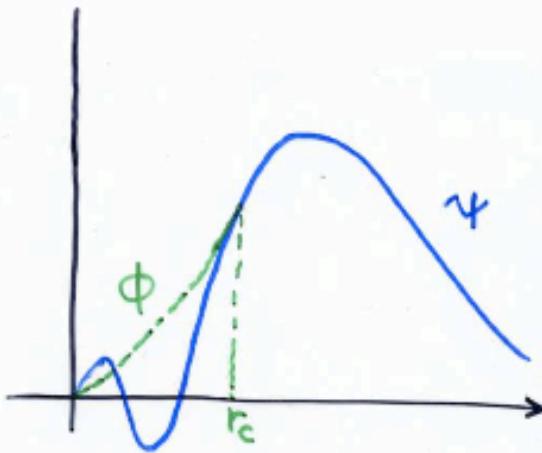


nodes : Imposed by orthogonality
to the core states.

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





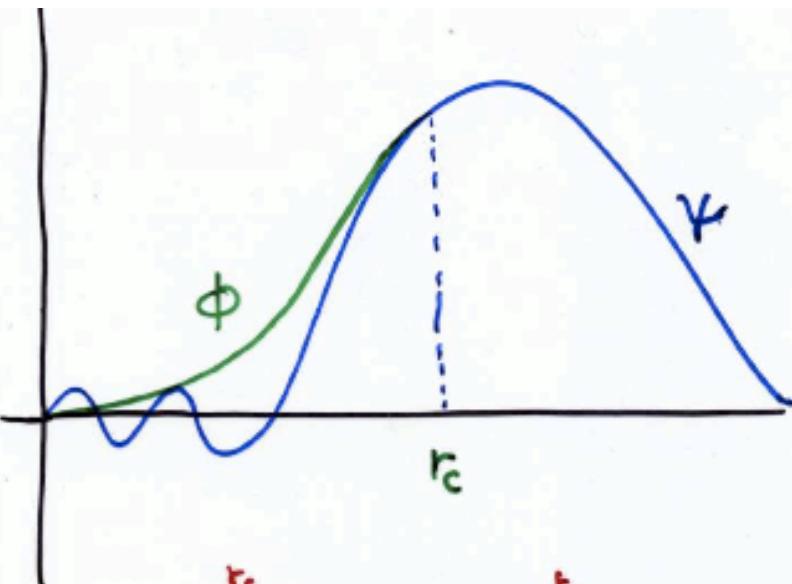


HOW does one get ϕ from Ψ ?

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 :

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



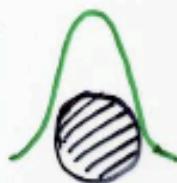
$$\int_0^{r_c} |\phi|^2 r^2 dr = \int_0^{r_c} |\psi|^2 r^2 dr$$

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)

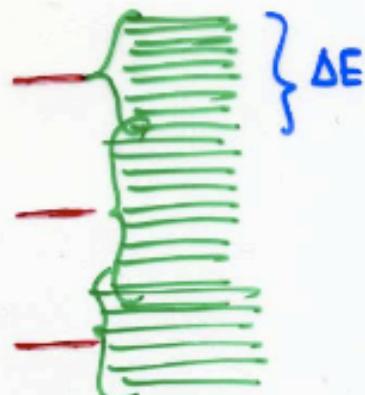
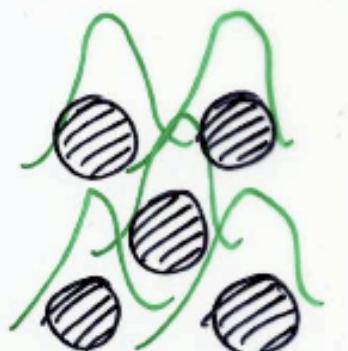
Isolated atom



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

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

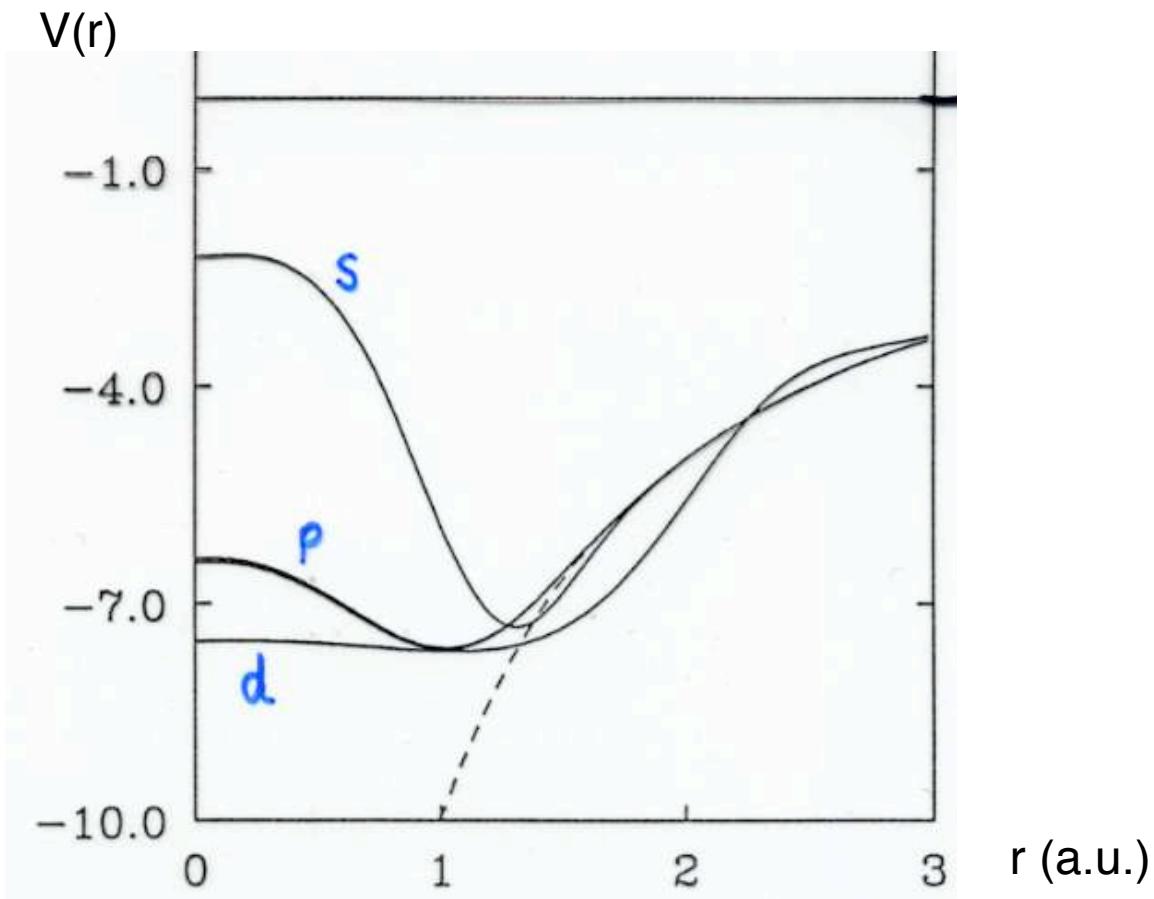
"Bare" or ionic pseudopotential:

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

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

Databases of curated pseudopotentials

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

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PSEUDŌ Dōjō

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	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 <input checked="" type="checkbox"/> html djrepo

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 1	32 He 1
33 Hydrogen 0.1	39 Helium 0.0
36 2.5	45 4.2
42 -0.00	49 na
Lithium	Neon
3 Li 2	2 He 2
33 0.2	39 0.0
37 2.0	45 4.2
41 -0.10	49 na
Beryllium	
4 Be 2	36 Ne 2
38 1.4	37 Oxygen 2.0
44 4.4	42 6.5
50 0.20	48 -0.10
	36 6.5
Sodium	Oxygen
11 Na 3	8 F 2
38 0.4	36 0.1
44 4.6	34 1.7
48 -0.00	40 na
Magnesium	Neon
12 Mg 3	10 Ne 2
38 0.4	30 0.0
42 1.5	34 1.7
46 0.00	40 na
K 3	14 Si 2
19 0.2	16 Al 2
33 0.2	14 0.5
37 0.3	20 1.3
43 -0.30	26 -0.10
Potassium	Aluminium
Ca 3	15 P 2
20 0.1	18 0.1
35 1.3	22 0.3
39 0.3	26 0.1
45 -0.00	28 -0.50
Calcium	Silicon
Sc 4	17 Cl 2
21 0.1	25 0.0
35 1.3	29 3.1
39 0.3	33 -0.30
Titanium	Chlorine
Ti 4	18 Ar 2
22 0.9	29 1.2
38 1.3	37 na
42 0.3	
V 4	
23 0.3	
39 0.3	
46 -0.10	
Vanadium	
Cr 4	13 Cu 2
24 10.5	16 0.5
38 10.5	20 0.0
42 18.1	26 -0.10
47 16.9	28 -0.50
Manganese	Copper
Mn 4	12 Ni 4
25 8.0	14 0.5
38 8.0	18 0.2
42 9.2	22 0.3
47 9.2	26 -0.10
52 0.10	28 -0.50
Iron	Nickel
Fe 4	11 Co 4
26 5.6	15 0.5
38 5.6	19 0.1
41 9.2	23 0.1
45 9.2	27 0.1
50 0.00	29 0.10
Cobalt	Cobalt
Co 4	10 Ni 4
27 5.6	14 0.5
38 5.6	18 0.2
42 9.2	22 0.3
47 9.2	26 -0.10
Zinc	Nickel
Ni 4	9 Cu 4
28 0.5	13 0.5
41 0.5	17 0.1
45 0.5	21 0.1
49 0.5	25 0.10
53 0.10	27 0.10
Copper	Copper
Cu 4	8 Zn 4
29 0.5	12 0.5
42 0.5	16 0.2
46 0.5	20 0.1
50 0.10	24 0.10
Zinc	Zinc
Ga 3	31 Ge 3
32 0.5	35 0.5
38 0.4	40 1.0
42 0.5	45 -0.00
48 0.7	49 -0.10
Gallium	Germanium
Ge 3	33 As 3
34 0.5	38 0.4
38 0.4	43 0.5
42 0.5	47 0.7
46 0.5	49 -0.10
Arsenic	Selenium
As 3	35 Se 3
34 0.4	39 0.5
38 0.4	43 0.5
42 0.5	47 0.7
46 0.5	49 -0.10
Selenium	Bromine
Br 2	36 Kr 2
35 0.0	22 0.0
39 0.0	26 2.3
43 0.0	49 na
Krypton	
Rb 3	37 Rb 3
19 0.2	28 0.2
23 2.9	34 0.2
29 -0.40	40 na
Rubidium	
Sr 3	38 Sr 3
28 0.3	29 1.3
34 0.1	36 6.1
40 -0.20	40 -0.20
Strontium	
Y 4	39 Y 4
38 1.0	30 1.0
42 1.1	36 1.1
46 -0.10	40 -0.10
Zirconium	
Zr 4	40 Nb 4
29 0.8	37 1.3
36 1.1	41 1.3
42 0.8	46 -0.10
Niobium	
Tc 4	41 Mo 4
38 1.6	40 1.4
42 1.1	44 1.0
46 0.00	50 0.00
Molybdenum	
Ru 4	42 Ru 4
38 2.1	40 2.1
42 1.5	44 2.1
46 0.00	50 0.00
Ruthenium	
Rh 4	43 Rh 4
38 2.6	40 2.6
42 2.1	44 2.1
46 0.00	50 0.00
Rhodium	
Pd 3	44 Pd 3
37 1.1	38 1.1
41 0.6	42 0.6
47 0.00	51 0.00
Palladium	
Ag 4	45 Ag 4
37 0.3	38 0.3
41 0.6	42 0.6
47 0.00	51 0.00
Silver	
Cd 4	46 Cd 4
37 1.1	38 1.1
41 0.6	42 0.6
47 0.00	51 0.00
Cadmium	
In 3	47 In 3
31 0.1	32 0.1
35 0.2	36 1.8
41 0.00	40 1.0
Indium	
Sn 3	50 Sn 3
32 0.8	36 0.5
36 1.8	40 1.0
42 0.00	46 0.10
Tin	
Sb 3	51 Sb 3
32 0.5	34 0.8
36 1.0	40 1.1
42 0.00	44 0.00
Antimony	
Te 3	52 Te 3
31 0.4	34 0.8
35 1.1	40 1.0
41 0.00	46 0.10
Tellurium	
I 2	53 I 2
31 0.4	34 0.8
35 2.5	40 1.0
42 0.00	46 0.10
Iodine	
Rb 3	54 Xe 2
28 0.0	22 0.0
34 2.5	26 2.3
42 na	34 na
Xenon	
Fr 3	55 Cs 3
19 0.1	25 0.1
25 1.5	32 0.5
29 -0.40	36 0.5
Caesium	
Ba 3	56 Ba 3
18 0.9	22 4.9
22 4.9	28 -0.10
Barium	
Hf 4	72 Ta 4
25 0.6	25 0.7
29 0.8	29 0.6
35 0.00	35 -0.10
Tantalum	
Ta 4	73 W 4
31 0.2	30 0.2
37 0.1	36 0.4
41 0.00	42 -0.10
Wolfram	
Re 4	74 Re 4
30 0.7	33 1.7
36 0.4	37 0.9
42 0.10	43 -0.10
Rhenium	
Os 4	75 Os 4
33 1.7	30 1.5
36 0.9	34 0.9
42 0.20	44 -0.20
Osmium	
Ir 4	76 Ir 4
30 1.5	33 1.5
34 0.9	38 1.6
40 0.20	44 -0.20
Iridium	
Pt 4	77 Pt 4
38 0.6	32 1.3
42 0.5	36 1.6
46 0.00	44 -0.10
Platinum	
Au 4	78 Au 4
32 1.3	29 0.7
36 1.6	33 7.2
40 0.20	44 na
Gold	
Hg 4	79 Hg 4
29 0.7	27 0.1
33 7.2	31 0.4
37 na	34 0.4
Mercury	
Tl 3	80 Tl 3
27 0.1	24 0.1
31 0.4	28 0.4
37 -0.10	34 -0.10
Thallium	
Pb 3	81 Tl 3
24 0.1	29 0.2
31 0.4	33 0.4
37 -0.10	34 -0.10
Lead	
Bi 3	82 Bi 3
24 0.1	29 0.2
28 0.1	33 0.4
34 -0.10	37 -0.00
Bismuth	
Po 3	83 Po 3
28 0.3	32 0.5
32 0.5	36 0.5
38 na	42 na
Polonium	
At 3	84 At 3
na na	na na
na na	na na
na na	na na
Astatine	
Rn 3	85 Rn 3
na na	na na
na na	na na
na na	na na
Radon	
Rf 3	104 Rf 3
na na	na na
na na	na na
na na	na na
Rutherfordium	
Db 3	105 Db 3
na na	na na
na na	na na
na na	na na
Dubnium	
Sg 3	106 Sg 3
na na	na na
na na	na na
na na	na na
Seaborgium	
Bh 3	107 Bh 3
na na	na na
na na	na na
na na	na na
Bohrium	
Hs 3	108 Hs 3
na na	na na
na na	na na
na na	na na
Hassium	
Mt 3	109 Mt 3
na na	na na
na na	na na
na na	na na
Meitnerium	
Ds 3	110 Ds 3
na na	na na
na na	na na
na na	na na
Darmstadtium	
Rg 3	111 Rg 3
na na	na na
na na	na na
na na	na na
Roentgenium	
Cn 3	112 Cn 3
na na	na na
na na	na na
na na	na na
Nihonium	
Nh 3	113 Nh 3
na na	na na
na na	na na
na na	na na
Flerovium	
Fl 3	114 Fl 3
na na	na na
na na	na na
na na	na na
Moscovium	
Mc 3	115 Mc 3
na na	na na
na na	na na
na na	na na
Livermorium	
Lv 3	116 Lv 3
na na	na na
na na	na na
na na	na na
Tennessee	
Ts 3	117 Ts 3
na na	na na
na na	na na
na na	na na
Oganesson	
Lu 5	118 Og 5
71 Lu 5	72 Yb 5
46 1.0	46 2.2
50 2.2	50 na
58 na	58 na
Lutetium	

More...

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