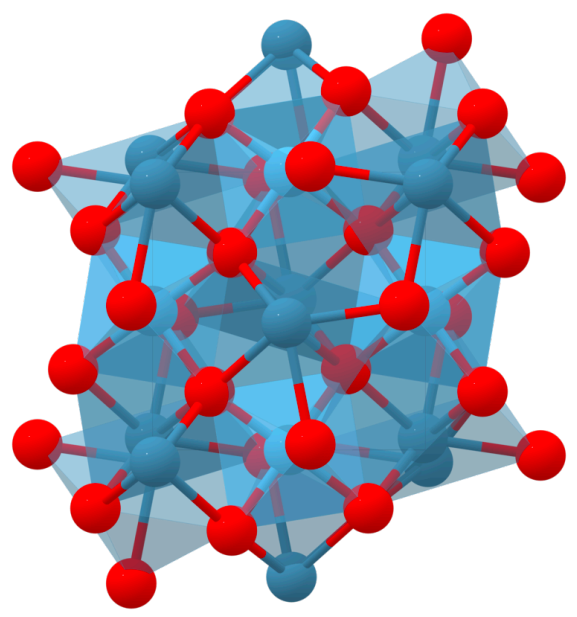
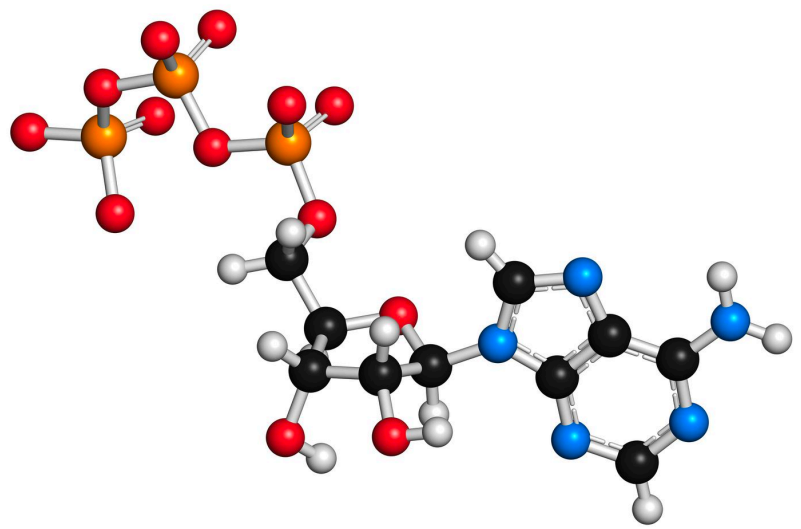


# The pseudopotential concept

Alberto García  
(ICMAB-CSIC, Barcelona)

...using the work of many others!





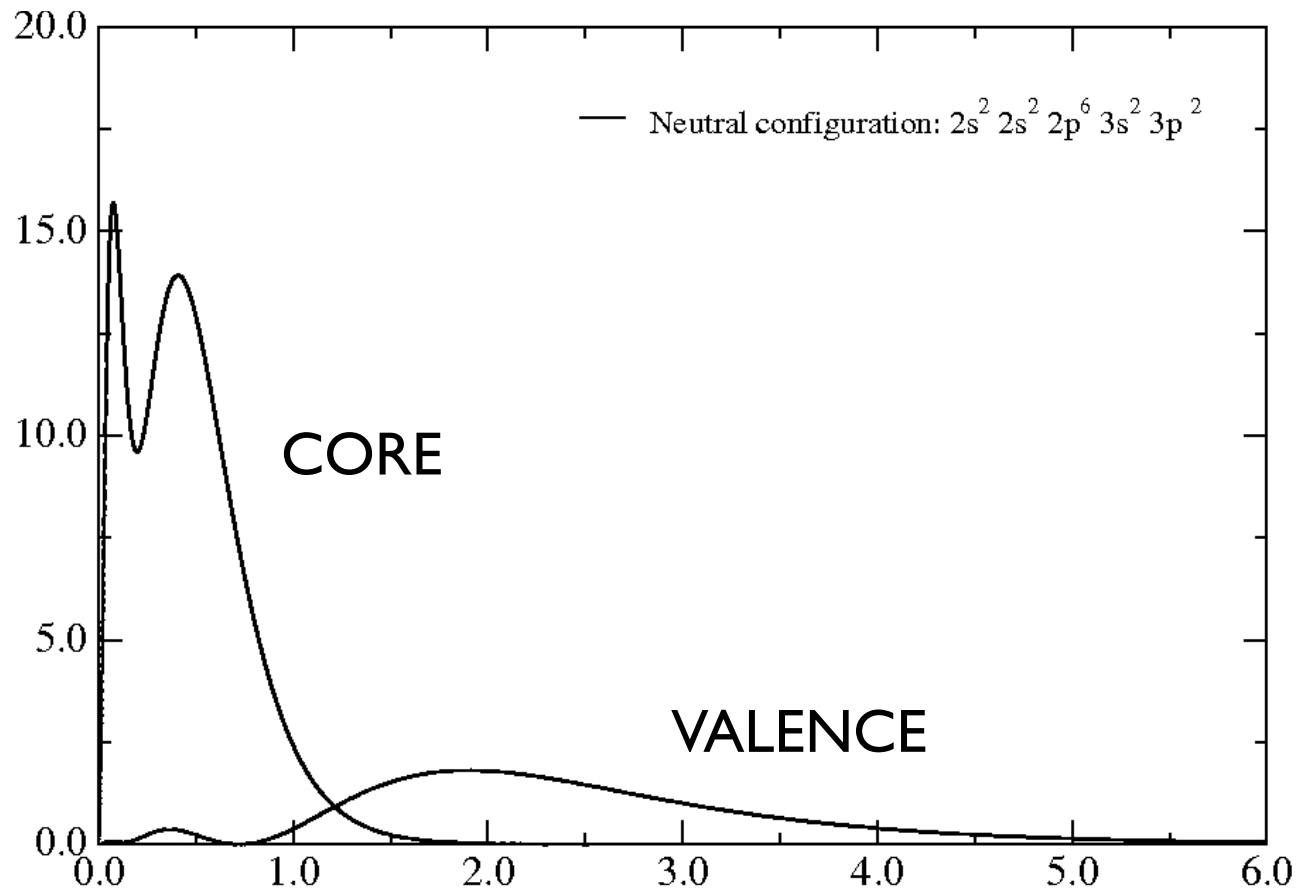
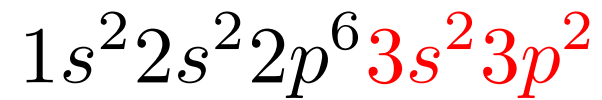
Bonding  
(the 'glue' in matter)  
is determined  
by the **valence** electrons

# Periodic table of the elements

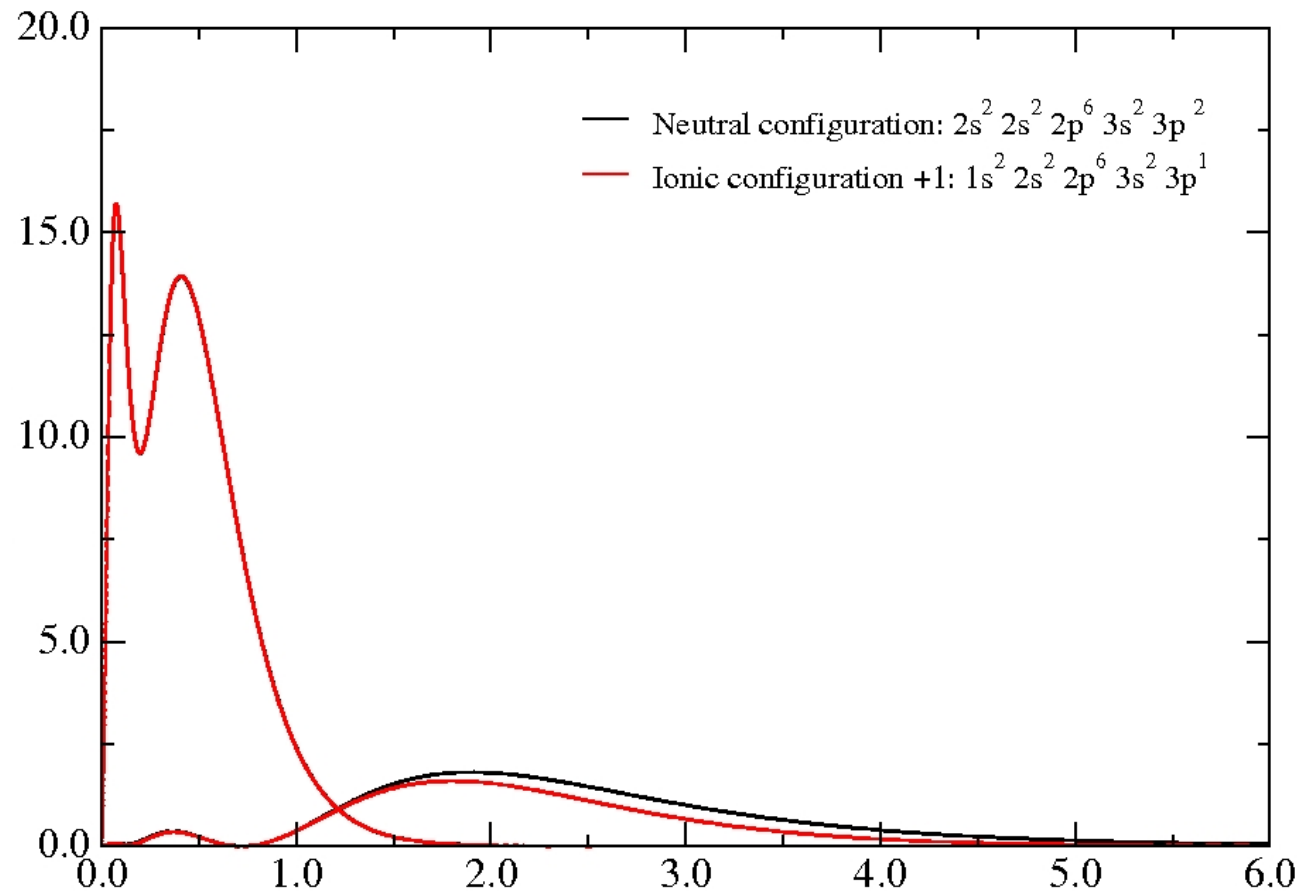
group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	<b>1</b> <b>H</b>																	<b>2</b> <b>He</b>
2	<b>3</b> <b>Li</b>	<b>4</b> <b>Be</b>											<b>5</b> <b>B</b>	<b>6</b> <b>C</b>	<b>7</b> <b>N</b>	<b>8</b> <b>O</b>	<b>9</b> <b>F</b>	<b>10</b> <b>Ne</b>
3	<b>11</b> <b>Na</b>	<b>12</b> <b>Mg</b>											<b>13</b> <b>Al</b>	<b>14</b> <b>Si</b>	<b>15</b> <b>P</b>	<b>16</b> <b>S</b>	<b>17</b> <b>Cl</b>	<b>18</b> <b>Ar</b>
4	<b>19</b> <b>K</b>	<b>20</b> <b>Ca</b>	<b>21</b> <b>Sc</b>	<b>22</b> <b>Ti</b>	<b>23</b> <b>V</b>	<b>24</b> <b>Cr</b>	<b>25</b> <b>Mn</b>	<b>26</b> <b>Fe</b>	<b>27</b> <b>Co</b>	<b>28</b> <b>Ni</b>	<b>29</b> <b>Cu</b>	<b>30</b> <b>Zn</b>	<b>31</b> <b>Ga</b>	<b>32</b> <b>Ge</b>	<b>33</b> <b>As</b>	<b>34</b> <b>Se</b>	<b>35</b> <b>Br</b>	<b>36</b> <b>Kr</b>
5	<b>37</b> <b>Rb</b>	<b>38</b> <b>Sr</b>	<b>39</b> <b>Y</b>	<b>40</b> <b>Zr</b>	<b>41</b> <b>Nb</b>	<b>42</b> <b>Mo</b>	<b>43</b> <b>Tc</b>	<b>44</b> <b>Ru</b>	<b>45</b> <b>Rh</b>	<b>46</b> <b>Pd</b>	<b>47</b> <b>Ag</b>	<b>48</b> <b>Cd</b>	<b>49</b> <b>In</b>	<b>50</b> <b>Sn</b>	<b>51</b> <b>Sb</b>	<b>52</b> <b>Te</b>	<b>53</b> <b>I</b>	<b>54</b> <b>Xe</b>
6	<b>55</b> <b>Cs</b>	<b>56</b> <b>Ba</b>	<b>57</b> <b>La</b>	<b>72</b> <b>Hf</b>	<b>73</b> <b>Ta</b>	<b>74</b> <b>W</b>	<b>75</b> <b>Re</b>	<b>76</b> <b>Os</b>	<b>77</b> <b>Ir</b>	<b>78</b> <b>Pt</b>	<b>79</b> <b>Au</b>	<b>80</b> <b>Hg</b>	<b>81</b> <b>Tl</b>	<b>82</b> <b>Pb</b>	<b>83</b> <b>Bi</b>	<b>84</b> <b>Po</b>	<b>85</b> <b>At</b>	<b>86</b> <b>Rn</b>
7	<b>87</b> <b>Fr</b>	<b>88</b> <b>Ra</b>	<b>89</b> <b>Ac</b>	<b>104</b> <b>Rf</b>	<b>105</b> <b>Db</b>	<b>106</b> <b>Sg</b>	<b>107</b> <b>Bh</b>	<b>108</b> <b>Hs</b>	<b>109</b> <b>Mt</b>	<b>110</b> <b>Ds</b>	<b>111</b> <b>Rg</b>	<b>112</b> <b>Cn</b>	<b>113</b> <b>Nh</b>	<b>114</b> <b>Fl</b>	<b>115</b> <b>Mc</b>	<b>116</b> <b>Lv</b>	<b>117</b> <b>Ts</b>	<b>118</b> <b>Og</b>
lanthanoid series	<b>6</b>	<b>58</b> <b>Ce</b>	<b>59</b> <b>Pr</b>	<b>60</b> <b>Nd</b>	<b>61</b> <b>Pm</b>	<b>62</b> <b>Sm</b>	<b>63</b> <b>Eu</b>	<b>64</b> <b>Gd</b>	<b>65</b> <b>Tb</b>	<b>66</b> <b>Dy</b>	<b>67</b> <b>Ho</b>	<b>68</b> <b>Er</b>	<b>69</b> <b>Tm</b>	<b>70</b> <b>Yb</b>	<b>71</b> <b>Lu</b>			
actinoid series	<b>7</b>	<b>90</b> <b>Th</b>	<b>91</b> <b>Pa</b>	<b>92</b> <b>U</b>	<b>93</b> <b>Np</b>	<b>94</b> <b>Pu</b>	<b>95</b> <b>Am</b>	<b>96</b> <b>Cm</b>	<b>97</b> <b>Bk</b>	<b>98</b> <b>Cf</b>	<b>99</b> <b>Es</b>	<b>100</b> <b>Fm</b>	<b>101</b> <b>Md</b>	<b>102</b> <b>No</b>	<b>103</b> <b>Lr</b>			

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

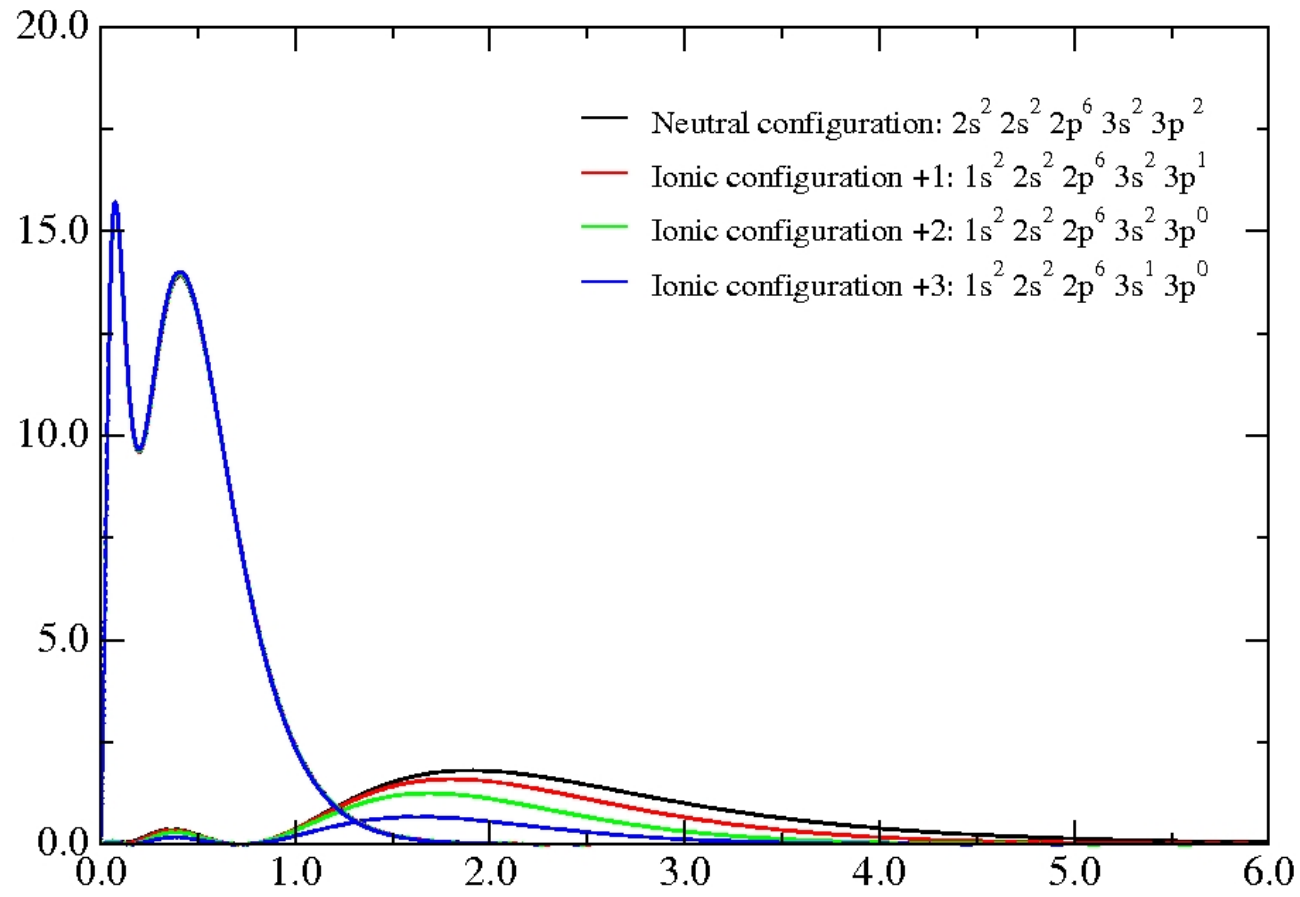
# Radial profile of charge density for Si atom



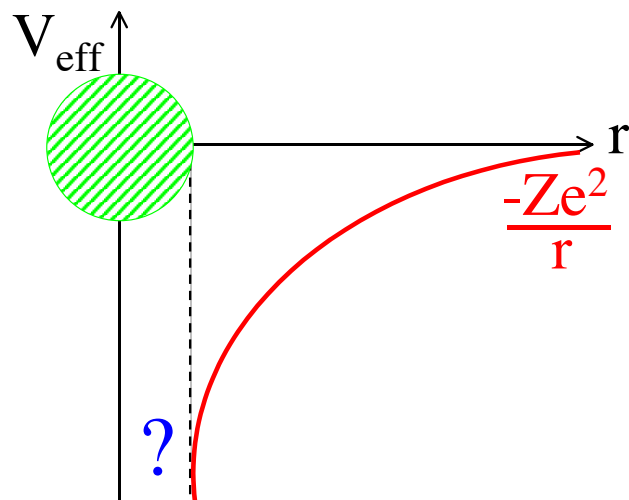
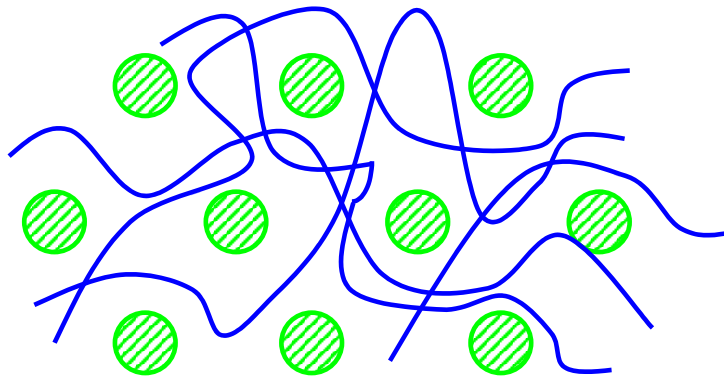
# Radial profile of charge density for Si atom



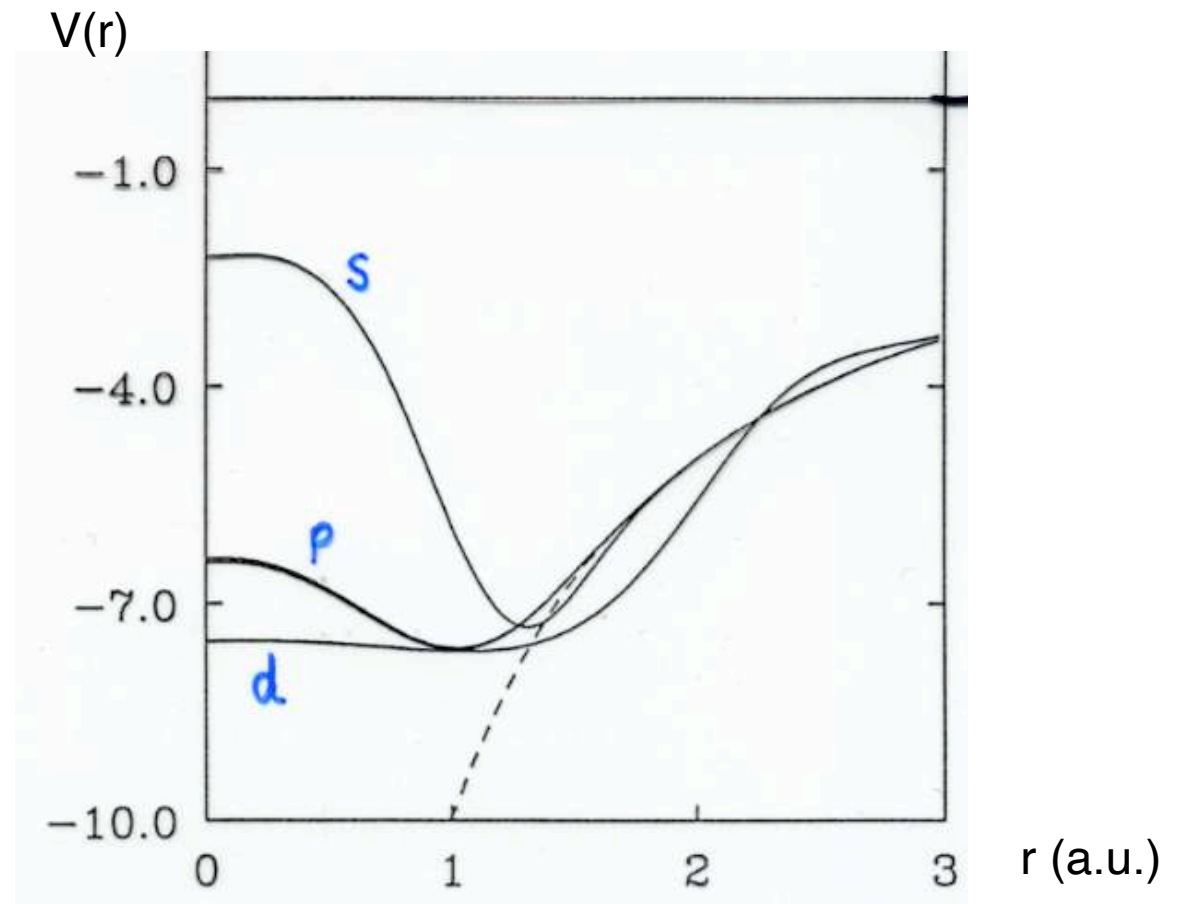
# Radial profile of charge density for Si atom



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



Effective potential for valence electrons  
**Pseudopotential**





# 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  $|\psi_c\rangle$

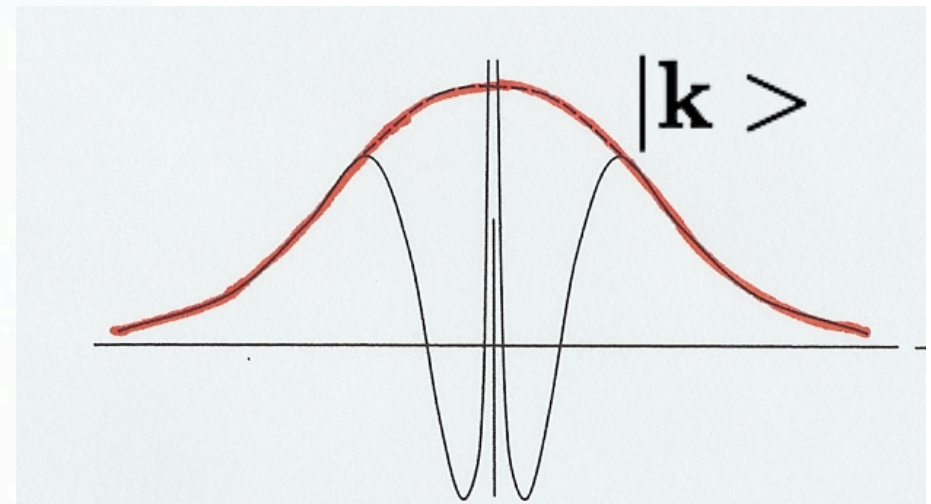
$$\hat{H} |\text{OPW}\rangle = \epsilon |\text{OPW}\rangle \Rightarrow$$

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

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

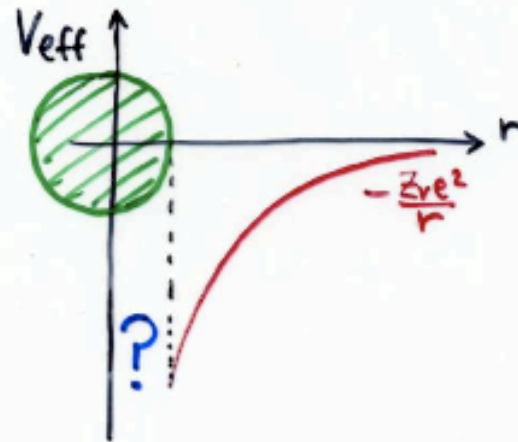
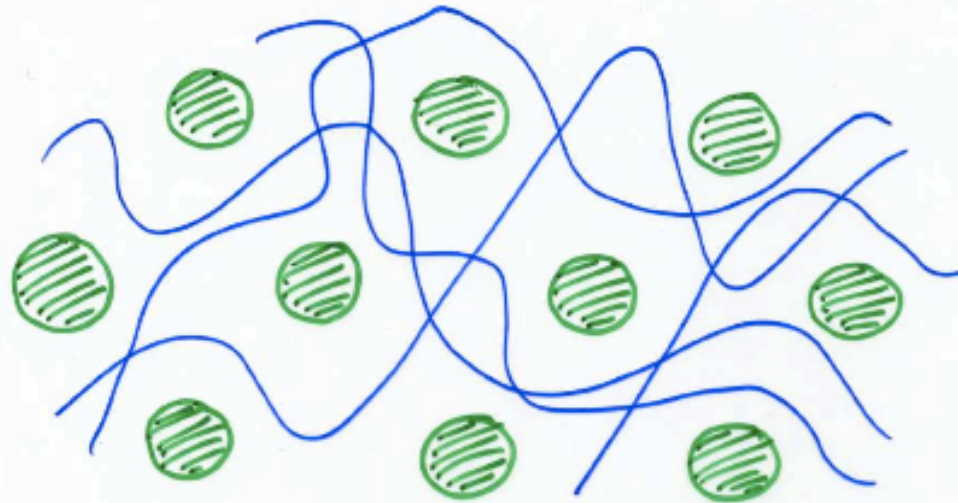
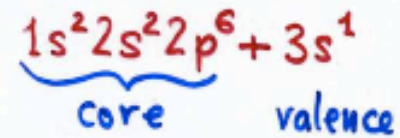
is a repulsive potential

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



Phillips-Kleinman  
 cancellation theorem  
 (1959)

Common metal: Na



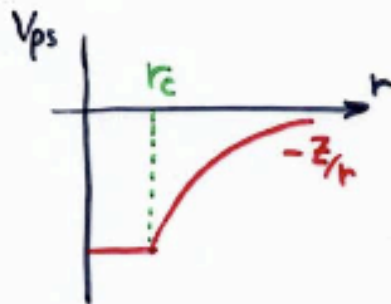
In the core zone, the effective potential will be softer than the coulomb  $-\frac{Ze^2}{r}$  pot.

# Empirical pseudopotentials

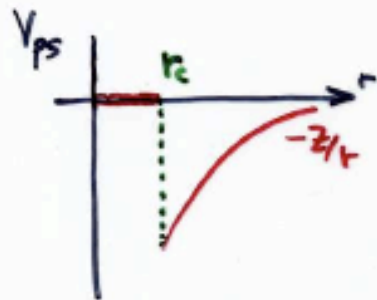
• Pseudopotential (pre) history

- Fermi (1934)

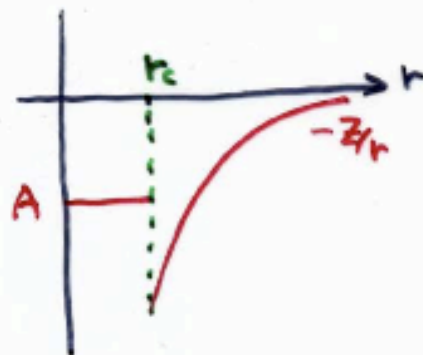
- Simple empirically-adjustable pseudopotentials



$r_c$  adjusted to reproduce the valence eigenvalue



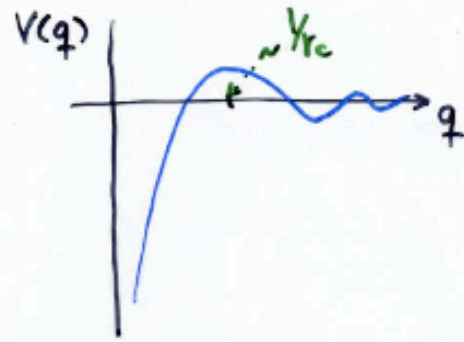
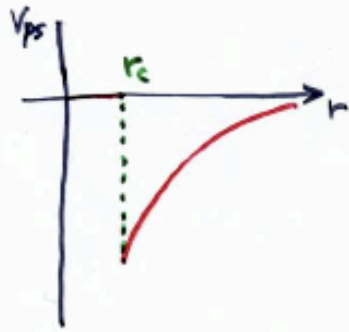
"Empty-core" pseudopotential  
Ashcroft (1966)



Heine - Abarankov (~1964)

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

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



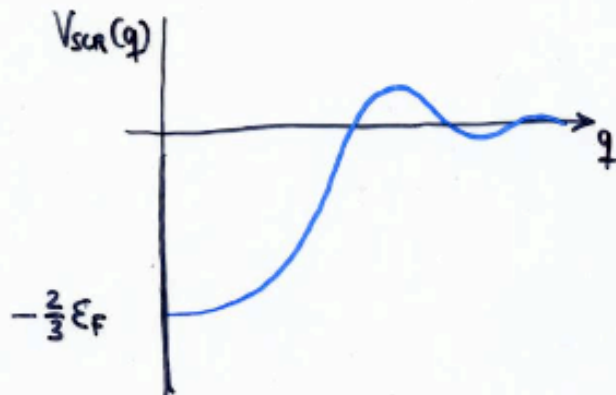
Fourier transform:  $V(q) \sim -\frac{4\pi e^2}{q^2} \cos q \cdot r_c$

• Screening

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

$K_{TF}$ : Thomas-Fermi wave vector

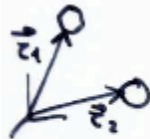
$$V_{scr}(q) = -\frac{4\pi e^2}{q^2 + K_{TF}^2} \cos q \cdot r_c$$



- In a periodic solid :

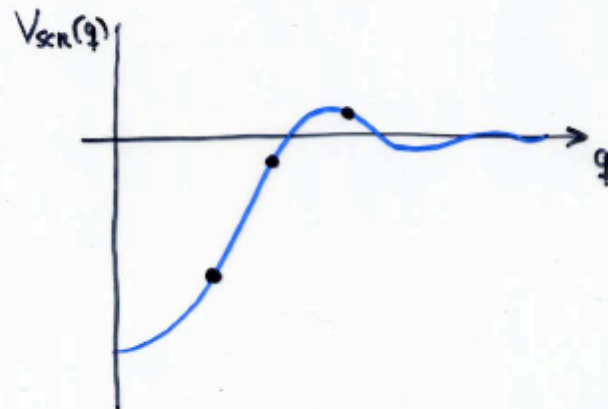
$$V(\vec{G}) = S(\vec{G}) \cdot V(q = |\vec{G}|)$$

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



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

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



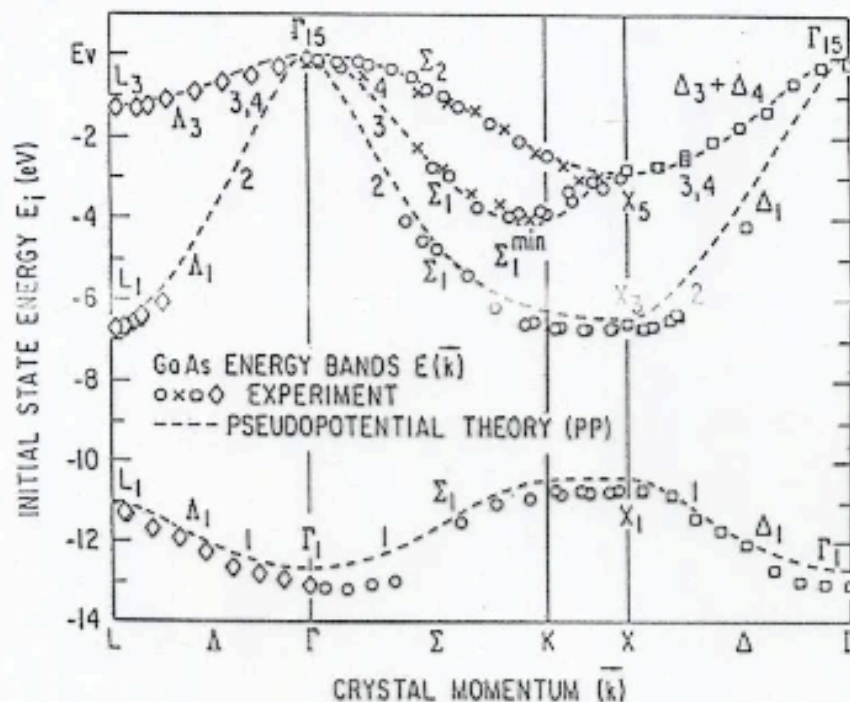
ONLY three parameters are needed for  
 a reasonably good description

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

$V_{\text{eff}}(G)$  fitted!

# Empirical Pseudopotential Method (EPM)

(Marvin L. Cohen et al. ~1962)



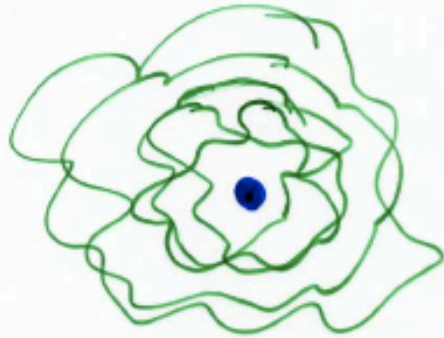
## Band structure of GaAs

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

The modern era  
of pseudopotentials



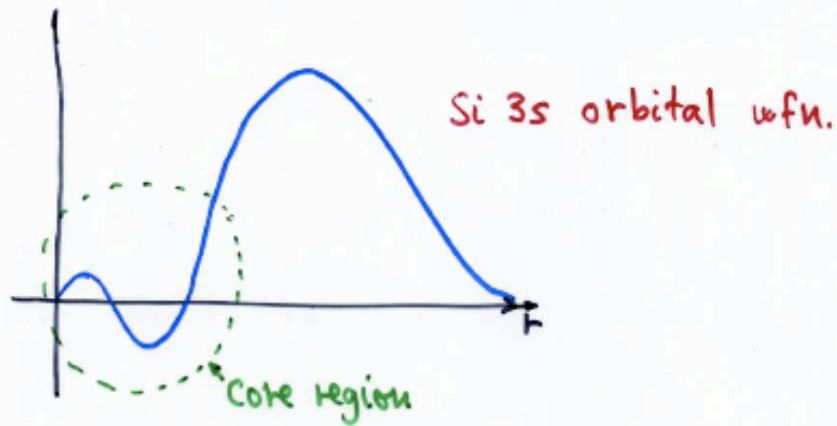
- Atomic calculations using DFT



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

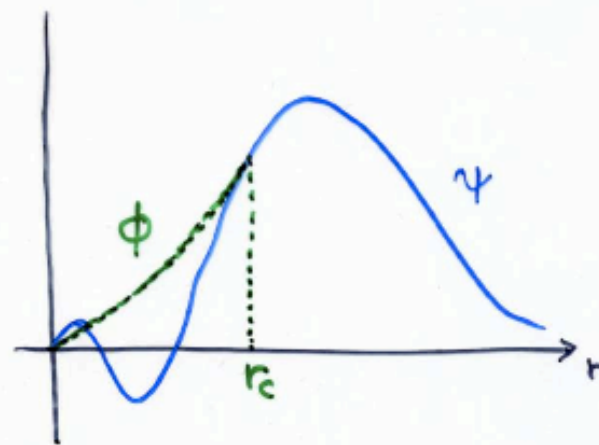
$\downarrow$   
 $-\frac{Ze^2}{r}$

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

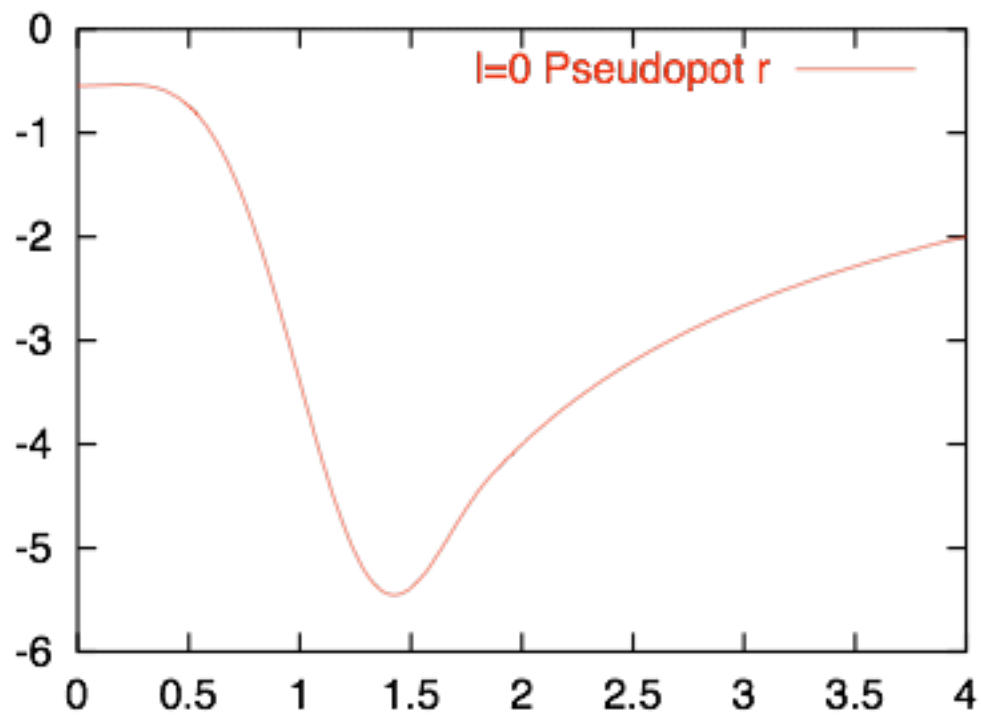
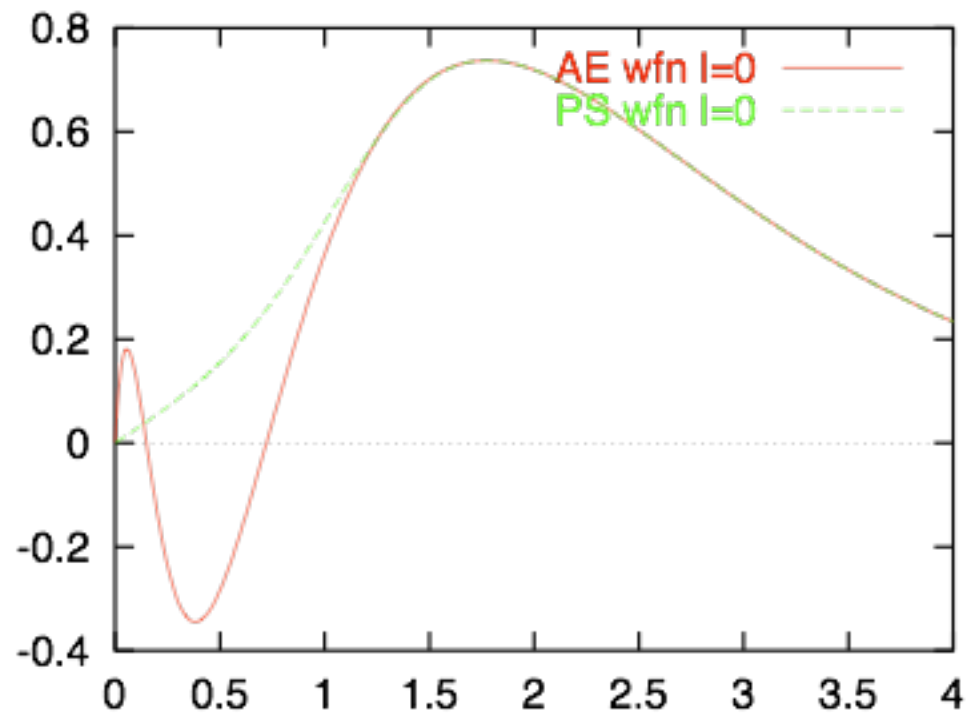


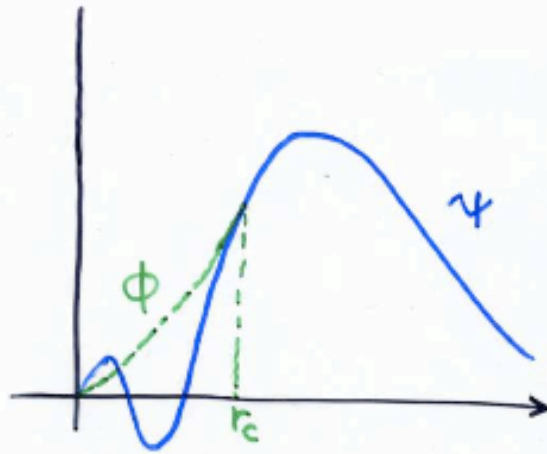
nodes: Imposed by orthogonality to the core states.

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



$\phi$ : Pseudo wavefunction





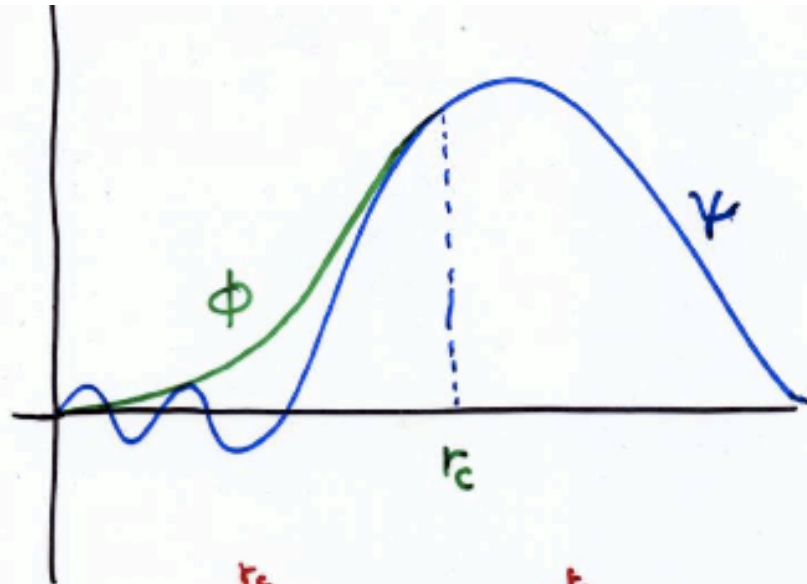
HOW does one get  $\phi$  from  $\psi$  ?

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 :

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



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

Norm - conservation

- Preserves electrostatic potential outside  $r_c$

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

Preserves scattering properties  
(and their first energy derivative)

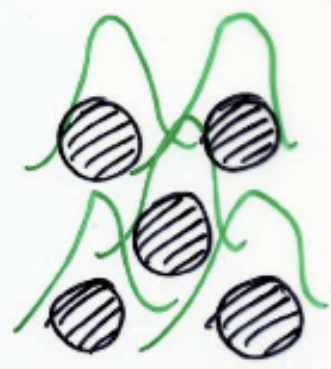
# Isolated atom



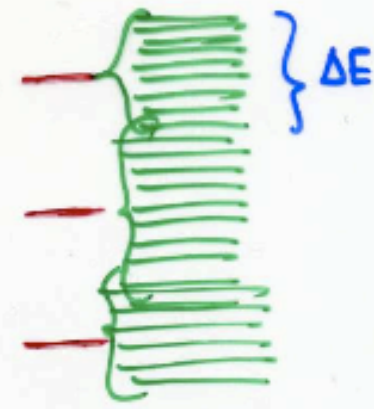
Atomic eigenvalues  
 $V_{ps}$  "perfect"

TRANSFERABILITY

# Solid



Charge Transfer...



$\Delta E$   
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

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

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

---

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

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

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

"Bare" or ionic pseudopotential:

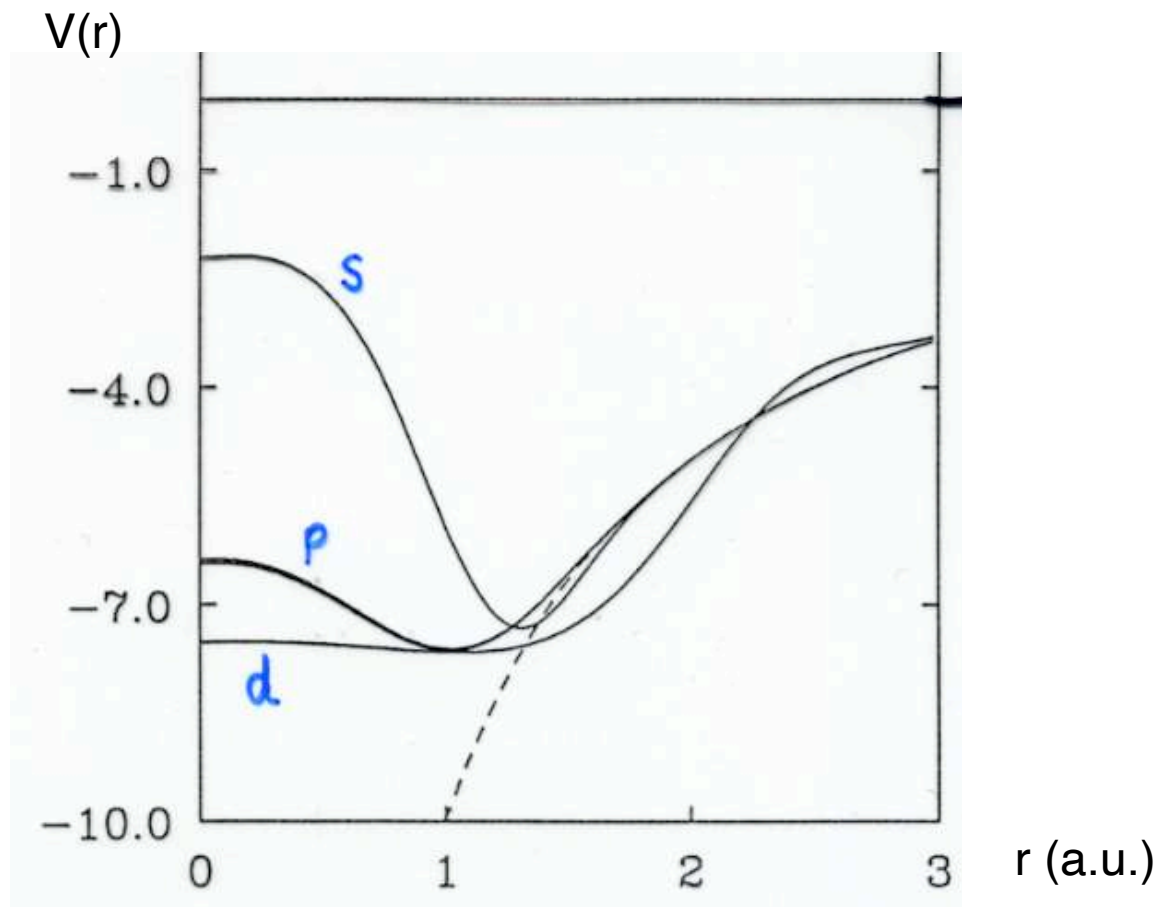
$$V_{ps}(r) = V_{ps}^{[n]} - V_H^{[n]} - V_{xc}^{[n]}$$

non-linear  
core corrections

n: Valence charge density



# Ab-initio pseudopotentials



Semi-local form:

$$\hat{V}_{ps} = \sum_{\ell} V_{\ell}(r) \underbrace{|\ell\rangle\langle\ell|}_{\text{Projector for } \ell}$$

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

Kleinman-Bylander form:

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

(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**

# PSEUDO DOJO

**Download**

Type: **NC (ONCVPSP v0.4)** | XC: **PBE** | Accuracy: **standard**

Mean: 3.13  
hints: 32.74 | tests: 0.95

psp8  
upf  
**psml**  
✓ html  
djrepo

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

# Practical issues in Siesta

# PS use in Siesta

- Legacy format: **.psf** extension
- PSMML 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>