

# **Solid State Theory: Band Structure Methods**

**Lilia Boeri**

**Wed., 12:00-13:30**

**HS P3 (PH02112)**

<http://itp.tugraz.at/LV/boeri/ELE/>

	12/3 Intro	19/3 DFT1	26/3 DFT2	
2/4 DFT3	9/4 DFT4	16/4 BREAK	23/4 BREAK	30/4 BREAK
7/5 DFT5	14/5 P1	21/5 ADV1	28/5 ADV2	
4/6 P2	11/6 ADV3	25/6 P2		

- **DFT1+2: Hohenberg-Kohn Theorem and Kohn and Sham equations.**
- **DFT3+4: Solving K-S in practice; basis functions, augmented methods and psp theory.**
- **DFT5: Practical problems in DFT (k space integration, convergence etc)**
- **P1: EOS and band structure of silicon.**
- **ADV1+2: Linear Response theory (mostly for phonons).**
- **P2: Phonons of silicon**
- **ADV3: Wannier Functions and TB approximation.**
- **P3: Wannier Functions and BOM for silicon.**

# Important Dates:

## **Easter Break:**

First lecture after the break is 7/5 (theory).

## **Exercises:**

First appointment:

- Thursday 15/5 16-18 (the room is free 16-19);
- Friday 6/6 and 26/6 14-16

(but again, the room is free 13-19, so we might find another time).

# Solving Kohn-Sham Equations in Practice (DFT 3-4):

- Charge self-consistency (mixing).
- Atoms: solution of the radial equations.
- Solids: Bloch Theorem.
- Basis functions and secular equations: Kohn-Sham equations for plane waves.
- **Pseudopotential Theory.**
- **PSP theory: Basic Concepts; Empirical Pseudopotentials; Ab-initio pseudopotential, construction (Chiang, Hamann, Schlueter method).**

*For these topics I will follow “A primer in Density Functional Theory” (Springer), chapters 6;*

*Pseudopotential Method, G.B. Bachelet and A. Filippetti (notes).*

# Kohn-Sham equations in plane-wave basis:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\sum_{\mathbf{G}'} \left[ \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + \tilde{v}(\mathbf{G} - \mathbf{G}') \right] c_{n\mathbf{k}}(\mathbf{G}') = \varepsilon_{n\mathbf{k}} c_{n\mathbf{k}}(\mathbf{G})$$

\*

If the total scf potential is periodic, the K-S equations couple only Fourier components  $\mathbf{G}$  which differ by a lattice vector (new proof). If the number of  $\mathbf{G}$  is infinite, **PWs form a complete basis set** (\* is exact.)

If we use only a finite number of plane waves ( $N_{\text{PW}}$ ), the computational time scales like  $(N_{\text{PW}})^3$ .

Typically, the cutoff on the maximum number of plane waves is introduced requiring that:

$$|\mathbf{k}+\mathbf{G}|^2 < E_{\text{cut}}.$$

# Meaning of the cut-off energy:

A cut-off energy (or wave-vector) determines what is the smallest length scale that can be represented by our plane-wave basis:

$$|\mathbf{k} + \mathbf{G}| < G_{cut}$$

$$\lambda_{min} = \frac{2\pi}{G_{cut}}$$

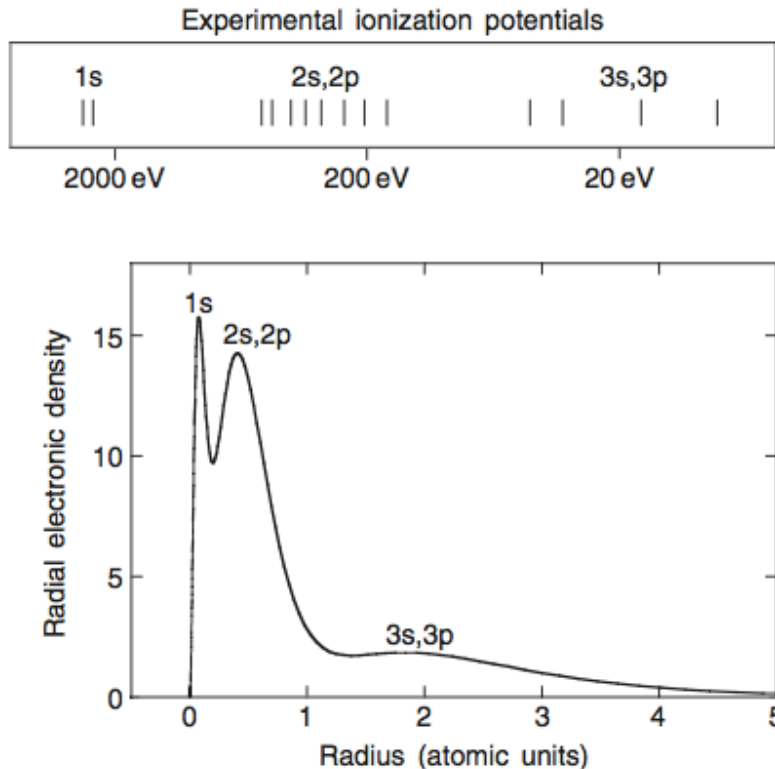
In a true (full) atom, the minimum length scale is set by the *1s* orbital; **pseudopotentials** represent an efficient (physically meaningful) way to derive an effective atomic potential, which requires less plane-wave components to be represented.

**Empirical pseudopotentials** use only a few Fourier components of Eq. (\*) as adjustable parameters to reproduce the electronic structures of given compounds. These are ***ad-hoc*** fit of the electronic structure, and we will not treat them here. “Modern” pseudopotentials derive suitable expressions for the  $v^{ps}(\mathbf{G})$  starting from the atomic problem (**full->pseudo construction**).

# Key Concepts in pseudopotential Theory:

- Core-Valence Separation.
- Orthogonalization and nodes of the atomic wave-functions.
- Pseudopotential Transferability.
- Norm conservation.
- Unscreening.

# Core-Valence Separation:



**Figure 1** Atomic shell structure: the example of silicon ( $Z = 14$ ). Top: the 14 ionization potentials of silicon, in electron volts (note the logarithmic scale). Bottom: radial electronic density as a function of the distance from the nucleus; both in energy (top) and in space (bottom), the core shells (1s,  $n = 1$ , and 2s, 2p,  $n = 2$ ) are well-separated from each other and from the valence 3s, 3p shell ( $n = 3$ ).

Many of the important properties of solids (chemical bonds, electric and thermal properties) are due to **valence electrons** (core electrons play a minor role).

**Valence electrons** (i.e. electrons belonging to the outermost shell of the atom) are well separated in energy and space from core electrons.

**Pseudopotentials replace the true atom with a pseudoatom which contains only valence electrons.**



# Periodic Table

1 <b>H</b> Hydrogen																	2 <b>He</b> Helium
3 <b>Li</b> Lithium	4 <b>Be</b> Beryllium											5 <b>B</b> Boron	6 <b>C</b> Carbon	7 <b>N</b> Nitrogen	8 <b>O</b> Oxygen	9 <b>F</b> Fluorine	10 <b>Ne</b> Neon
11 <b>Na</b> Sodium	12 <b>Mg</b> Magnesium											13 <b>Al</b> Aluminium	14 <b>Si</b> Silicon	15 <b>P</b> Phosphorus	16 <b>S</b> Sulfur	17 <b>Cl</b> Chlorine	18 <b>Ar</b> Argon
19 <b>K</b> Potassium	20 <b>Ca</b> Calcium	21 <b>Sc</b> Scandium	22 <b>Ti</b> Titanium	23 <b>V</b> Vanadium	24 <b>Cr</b> Chromium	25 <b>Mn</b> Manganese	26 <b>Fe</b> Iron	27 <b>Co</b> Cobalt	28 <b>Ni</b> Nickel	29 <b>Cu</b> Copper	30 <b>Zn</b> Zinc	31 <b>Ga</b> Gallium	32 <b>Ge</b> Germanium	33 <b>As</b> Arsenic	34 <b>Se</b> Selenium	35 <b>Br</b> Bromine	36 <b>Kr</b> Krypton
37 <b>Rb</b> Rubidium	38 <b>Sr</b> Strontium	39 <b>Y</b> Yttrium	40 <b>Zr</b> Zirconium	41 <b>Nb</b> Niobium	42 <b>Mo</b> Molybdenum	43 <b>Tc</b> Technetium	44 <b>Ru</b> Ruthenium	45 <b>Rh</b> Rhodium	46 <b>Pd</b> Palladium	47 <b>Ag</b> Silver	48 <b>Cd</b> Cadmium	49 <b>In</b> Indium	50 <b>Sn</b> Tin	51 <b>Sb</b> Antimony	52 <b>Te</b> Tellurium	53 <b>I</b> Iodine	54 <b>Xe</b> Xenon
55 <b>Cs</b> Cesium	56 <b>Ba</b> Barium	* *	72 <b>Hf</b> Hafnium	73 <b>Ta</b> Tantalum	74 <b>W</b> Tungsten	75 <b>Re</b> Rhenium	76 <b>Os</b> Osmium	77 <b>Ir</b> Iridium	78 <b>Pt</b> Platinum	79 <b>Au</b> Gold	80 <b>Hg</b> Mercury	81 <b>Tl</b> Thallium	82 <b>Pb</b> Lead	83 <b>Bi</b> Bismuth	84 <b>Po</b> Polonium	85 <b>At</b> Astatine	86 <b>Rn</b> Radon
87 <b>Fr</b> Francium	88 <b>Ra</b> Radium	** **	104 <b>Rf</b> Rutherfordium	105 <b>Db</b> Dubnium	106 <b>Sg</b> Seaborgium	107 <b>Bh</b> Bohrium	108 <b>Hs</b> Hassium	109 <b>Mt</b> Meitnerium	110 <b>Ds</b> Darmstadtium	111 <b>Rg</b> Roentgenium	112 <b>Cn</b> Copernicium	113 <b>Uut</b> Ununtrium	114 <b>Fl</b> Flerovium	115 <b>Uup</b> Ununpentium	116 <b>Lv</b> Livermorium	117 <b>Uus</b> Ununseptium	118 <b>Uuo</b> Ununoctium
*		57 <b>La</b> Lanthanum	58 <b>Ce</b> Cerium	59 <b>Pr</b> Praseodymium	60 <b>Nd</b> Neodymium	61 <b>Pm</b> Promethium	62 <b>Sm</b> Samarium	63 <b>Eu</b> Europium	64 <b>Gd</b> Gadolinium	65 <b>Tb</b> Terbium	66 <b>Dy</b> Dysprosium	67 <b>Ho</b> Holmium	68 <b>Er</b> Erbium	69 <b>Tm</b> Thulium	70 <b>Yb</b> Ytterbium	71 <b>Lu</b> Lutetium	
**		89 <b>Ac</b> Actinium	90 <b>Th</b> Thorium	91 <b>Pa</b> Protactinium	92 <b>U</b> Uranium	93 <b>Np</b> Neptunium	94 <b>Pu</b> Plutonium	95 <b>Am</b> Americium	96 <b>Cm</b> Curium	97 <b>Bk</b> Berkelium	98 <b>Cf</b> Californium	99 <b>Es</b> Einsteinium	100 <b>Fm</b> Fermium	101 <b>Md</b> Mendelevium	102 <b>No</b> Nobelium	103 <b>Lr</b> Lawrencium	

- Alkali
- Alkaline
- Transition
- Lanthanoid
- Actinoid
- Post-transition
- Metalloid
- Nonmetal
- Halogen
- Noble gas
- Unknown

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# Schroedinger Equation for Atoms:

If the “effective potential” felt by the electrons in an atom has spherical symmetry, the wave-functions factorize into an angular and a radial part:

$$\varphi_i(\mathbf{r}) = Y_{lm}(\vartheta, \varphi) R_{nl}(r)$$

$Y_{lm}$  are the spherical harmonics; the **radial** part obeys the one-dimensional Schroedinger equation:

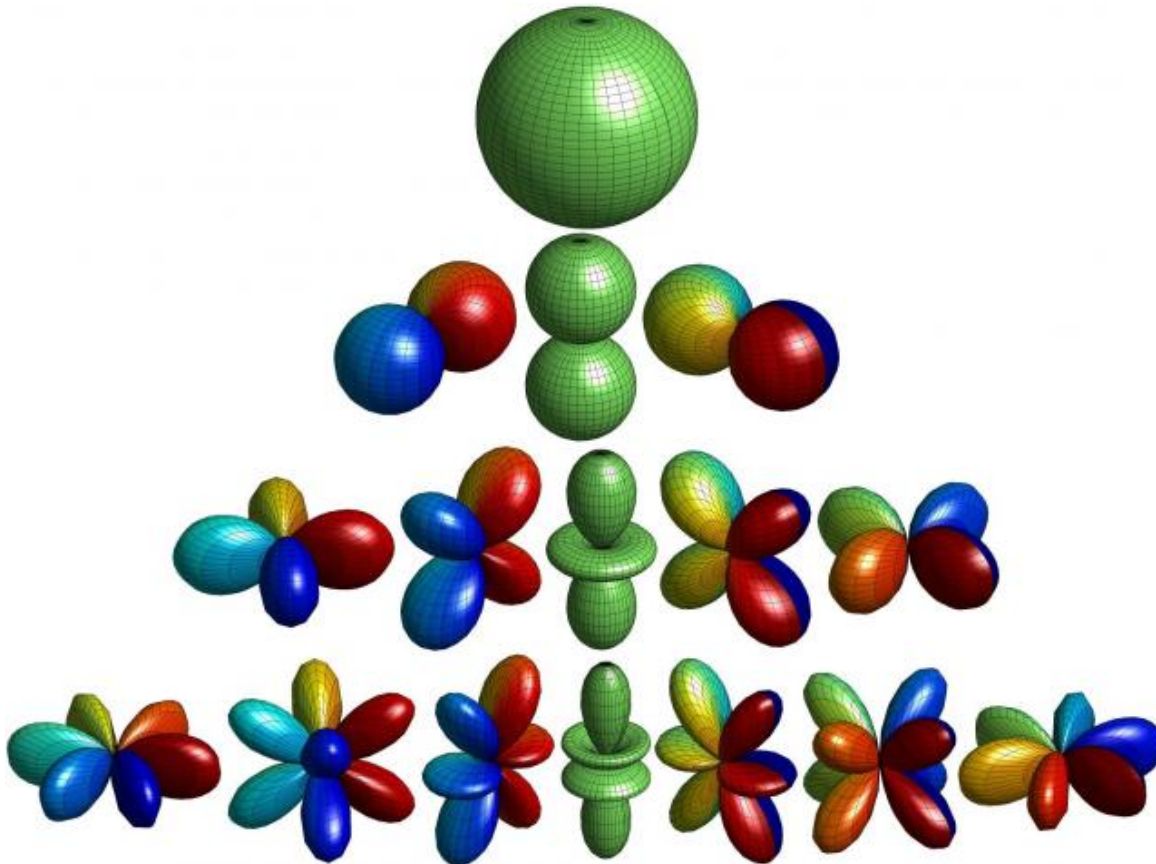
$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} + \frac{l(l+1)}{2r^2} + v_{eff}(r) \right] R_{nl}(r) = \epsilon_{nl} R_{nl}(r)$$

The effective potential is  $-Z/r$  + some effective screening; for example, in DFT,  $V_{eff} = -Z/r + v_H[n] + v_{xc}[n]$ ; the largest contribution to the screening is the **Hartree** term.

Even when screening is included, the solutions of the atomic problem still have a hydrogen-like shell (n,l) structure; the shells are occupied in order of increasing n,l.

# Atoms: spherical harmonics

$$Y_{lm}(\vartheta, \varphi) = \alpha e^{im\varphi} P_l^m(\cos \vartheta)$$



# Atoms: hydrogenoid wavefunctions

First terms (explicit form):

$$R_{10} = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

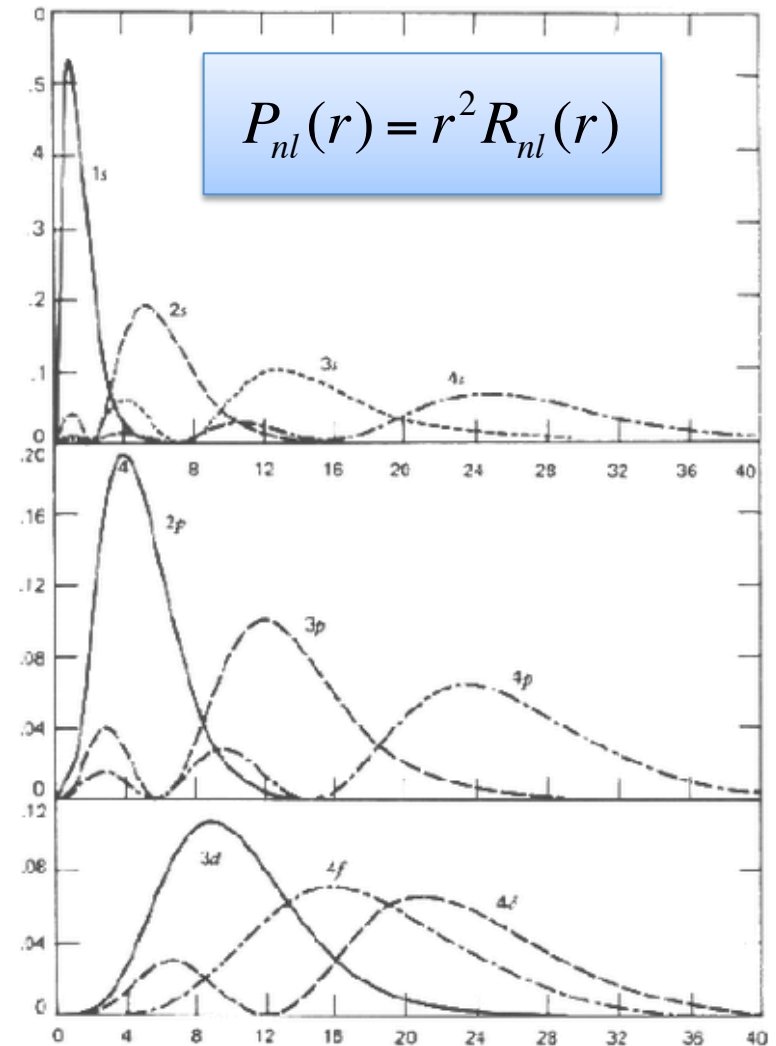
$$R_{20} = 2 \left( \frac{Z}{2a_0} \right)^{3/2} \left( 1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}} \left( \frac{Z}{3a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3} \left( \frac{Z}{3a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) \left( 1 - \frac{Zr}{6a_0} \right) e^{-Zr/3a_0}$$

$$R_{30} = 2 \left( \frac{Z}{3a_0} \right)^{3/2} \left( 1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2} \right) e^{-Zr/3a_0}$$

$$\langle r \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]$$



# Orthogonality Condition and “wiggles”:

The “total” wave-function (radial x angular part) has to be orthogonal, *i.e.*:

$$\int d^3r \varphi_j^*(\mathbf{r}) \varphi_i(\mathbf{r}) = \delta_{ij}$$

$$\varphi_i(\mathbf{r}) = Y_{lm}(\vartheta, \varphi) R_{nl}(r)$$

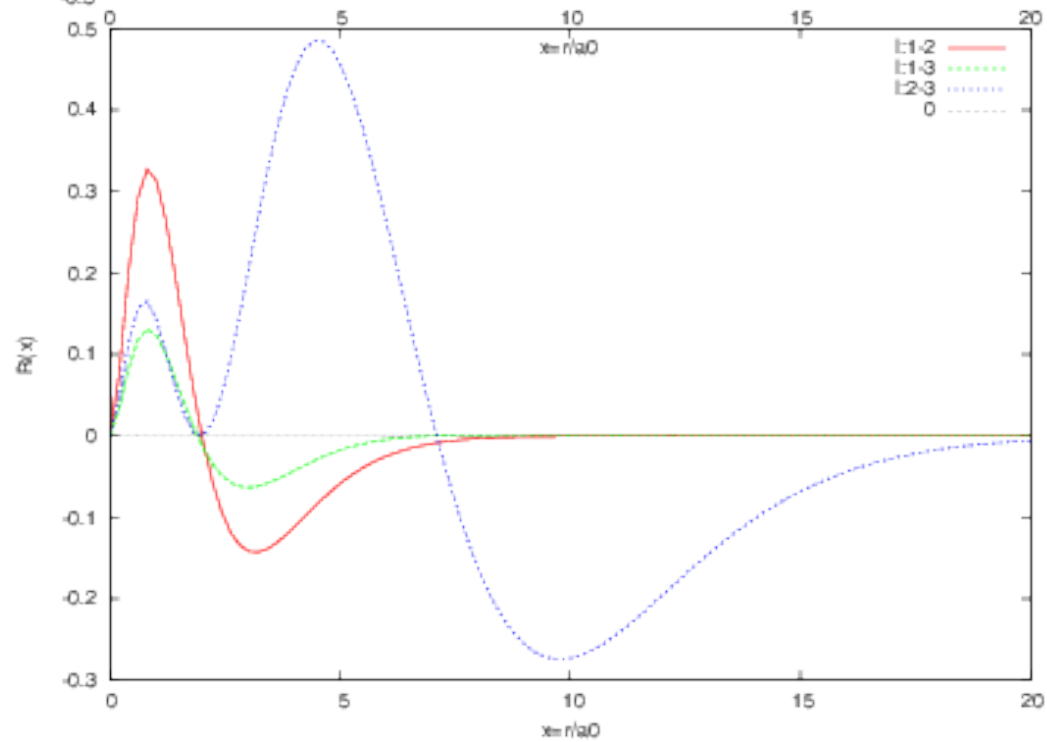
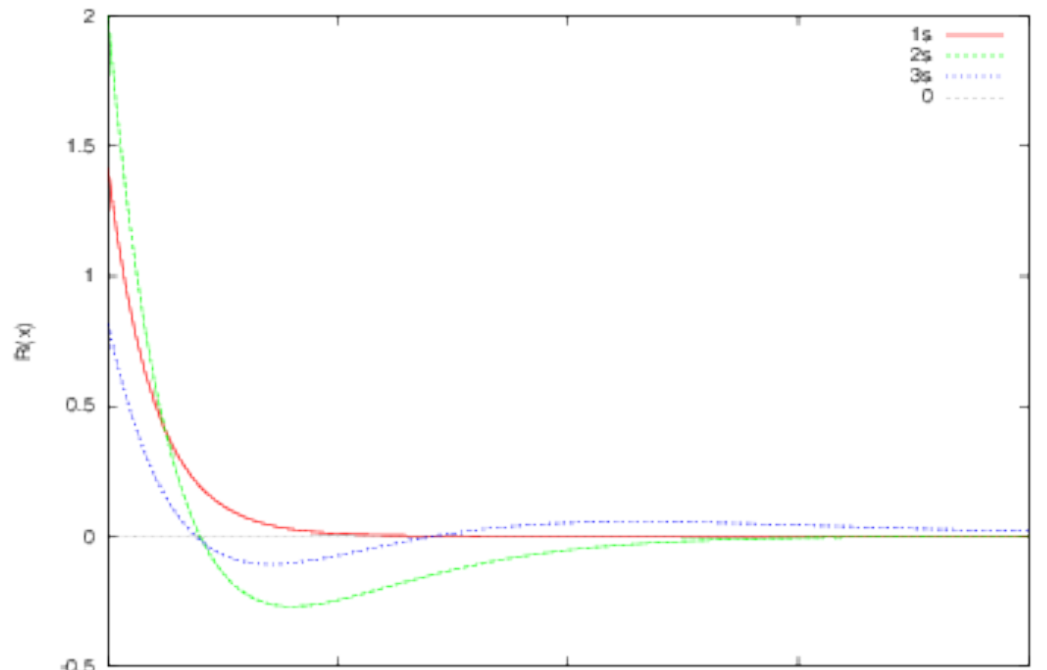
Spherical Harmonics are orthogonal, *i.e.*:

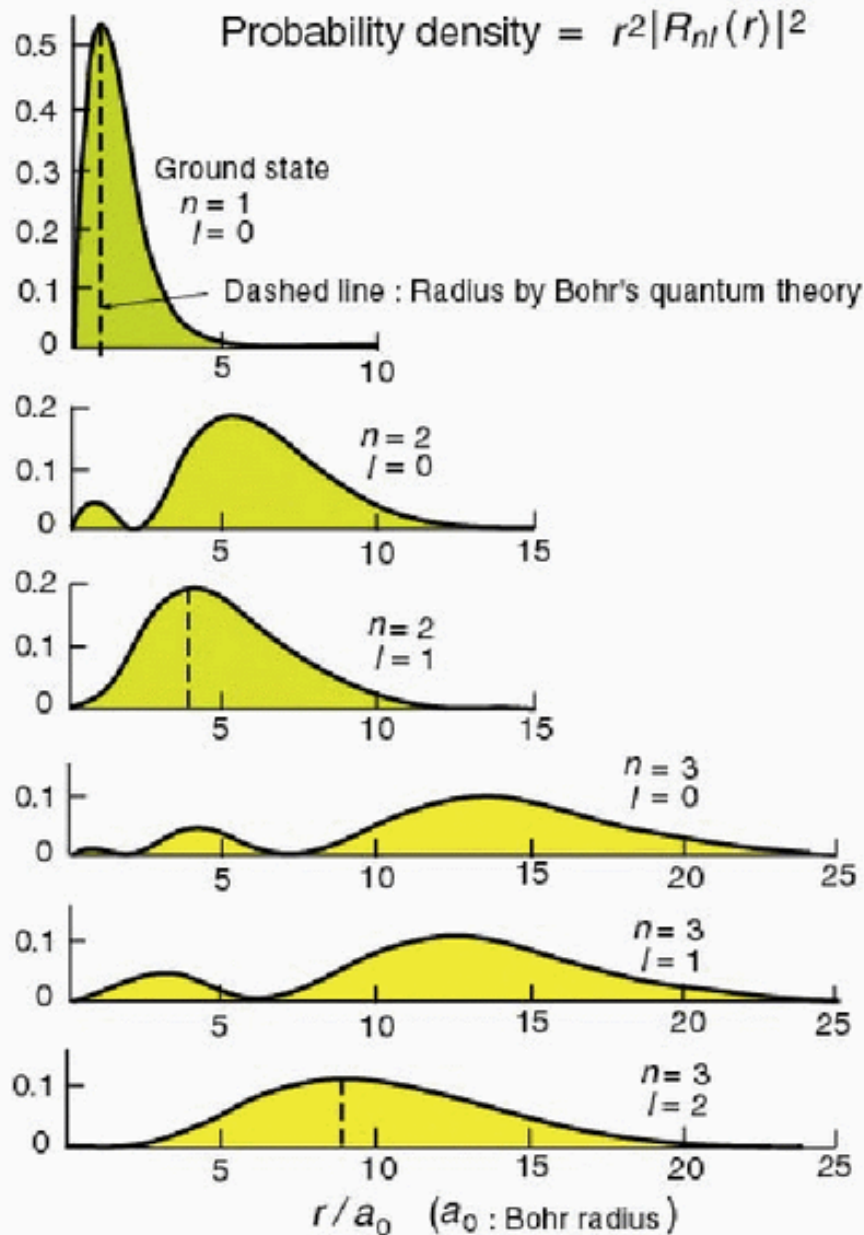
$$\iint \sin \vartheta d\vartheta d\varphi Y_{lm}(\vartheta, \varphi) Y_{l'm'}(\vartheta, \varphi) = \delta_{ll'} \delta_{mm'}$$

So eigenfunctions corresponding to *different l shells (s and p, p and d, s and d, a.s.o. )* are orthogonal to each other ***because their angular part are orthogonal.*** On the other hand, two wavefunctions corresponding to states with the ***same l*** and ***different n*** must have ***orthogonal radial wavefunctions, i.e.***

$$\int r^2 dr R_{nl}(r) R_{n'l}(r) = \delta_{nn'}$$

This introduces orthogonality “wiggles”, *i.e.* small amplitude oscillations on radial wfs with large *n*.



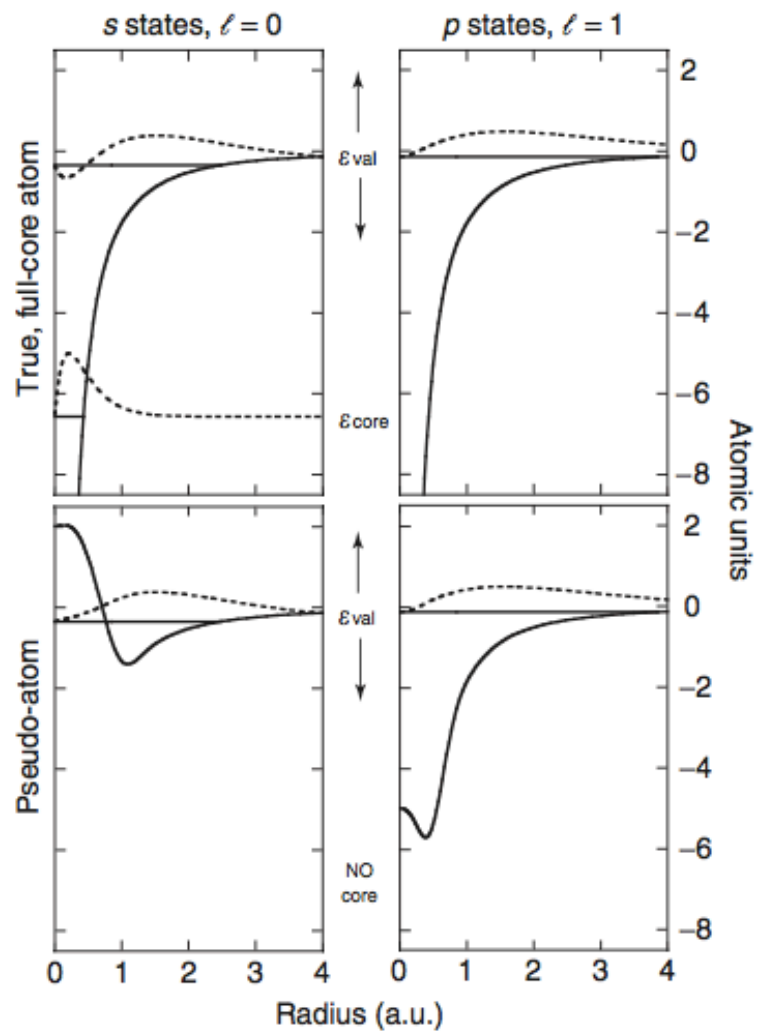


$$\langle r \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]$$

In real (full) atoms, valence wavefunctions have oscillations on length scales which are much smaller than the physically-relevant region.

In pseudo-atoms, these oscillations are cut out...

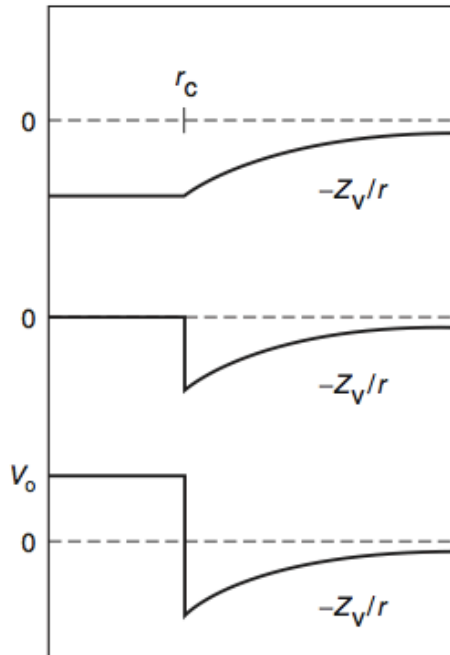
# Full-pseudo problem:



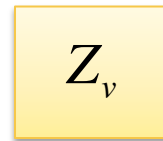


# Model Pseudopotentials:

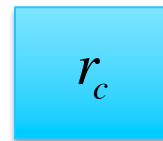
The solid can be approximated as isolated (rigid) pseudo-atoms + valence electrons which re-arrange self-consistently due to different environment (chemical bonds). The tail of the potential of the pseudo-atoms must behave as  $-Z_v/r$ .



A model pseudopotential has two important physical parameters:



Valence charge



Core radius

**Figure 3** Model bare pseudopotentials. Lower panel: two-parameter pseudopotential. Upper and middle panels: one-parameter pseudopotentials, where the only parameter is the core radius  $r_c$ , roughly corresponding to the spatial extent of the outermost core orbitals, or to the outermost radial node of the true valence orbitals (see **Figure 2** and text).

Good agreement for charge density distributions (defects, impurities), bad results for total energy.

# Valence charge



## Periodic Table

1 H Hydrogen																	2 He Helium
3 Li Lithium	4 Be Beryllium											5 B Boron	6 C Carbon	7 N Nitrogen	8 O Oxygen	9 F Fluorine	10 Ne Neon
11 Na Sodium	12 Mg Magnesium											13 Al Aluminium	14 Si Silicon	15 P Phosphorus	16 S Sulfur	17 Cl Chlorine	18 Ar Argon
19 K Potassium	20 Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton
37 Rb Rubidium	38 Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon
55 Cs Cesium	56 Ba Barium	* *	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon
87 Fr Francium	88 Ra Radium	** **	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 Uut Ununtrium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium
		* *	57 La Lanthanum	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium	61 Pm Promethium	62 Sm Samarium	63 Eu Europium	64 Gd Gadolinium	65 Tb Terbium	66 Dy Dysprosium	67 Ho Holmium	68 Er Erbium	69 Tm Thulium	70 Yb Ytterbium	71 Lu 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

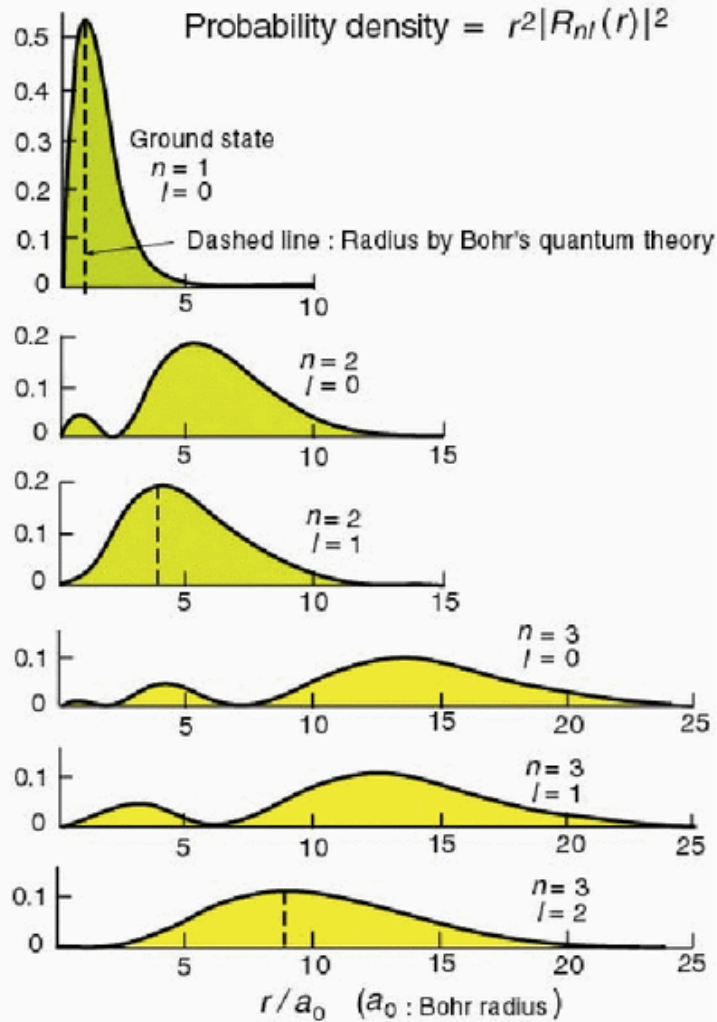
- Alkali
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- Unknown

Core Radius



# Non-local Pseudopotentials:

To reproduce the correct shape of the valence electron wave-function, the pseudo-potential should be  $l$ -dependent.



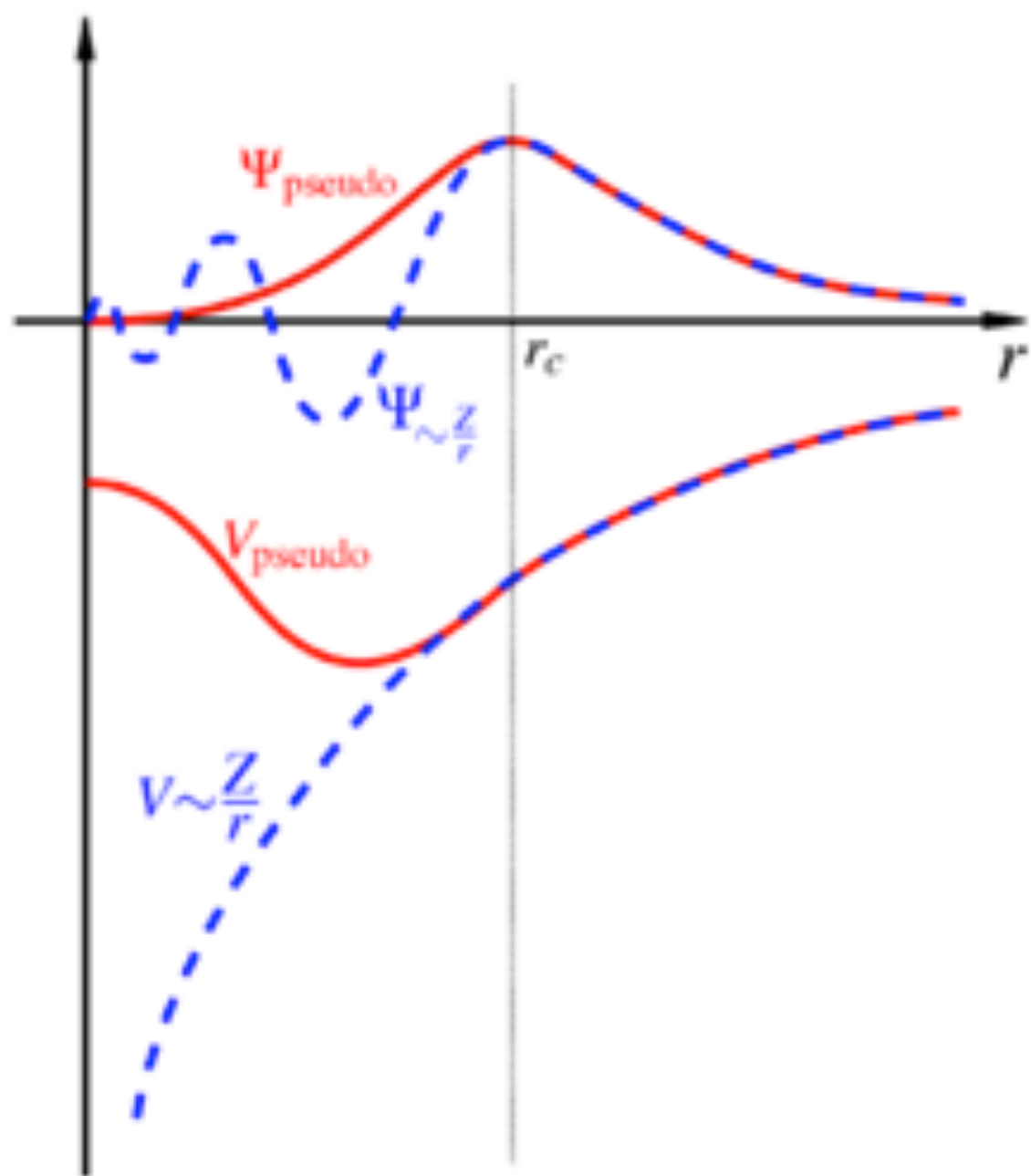
# Ab-initio Pseudopotentials:

**Hamann-Schlüter-Chiang (1979):** A fully *ab-initio* pseudopotential can be constructed, requiring that the solution of the radial Schrödinger equation for the full and the pseudo atoms are the same, above a cut-off radius  $r_c$  :

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + v_{screen}(r) \right] \chi_{nl} = \epsilon_{nl} \chi_{nl}$$

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_l^{ps,screened}(r) \right] \chi_l^{ps} = \epsilon_l \chi_l^{ps}$$

The pseudo wave function is a **smooth** function **without nodes**.



# Transferability:

A pseudopotential is transferable, when it can be used to describe accurately the properties of a system, where the chemical and physical environment is different than the one it was derived for. In 1979 (Hamann, Schlüter, Chiang) it was realized that matching exactly the tails of the wavefunctions ensured optimal transferability. This was guaranteed by the condition of **norm conservation**:

$$\int_0^{r_c} |\chi_l^{ps}(r)|^2 dr = \int_0^{r_c} |\chi_{nl}(r)|^2 dr$$

Which guarantees that the pseudoatom has the correct electrostatic properties (Gauss Theorem) and the right scattering conditions (bonding properties).

# Unscreening:

In the HSC procedure, the pseudopotential is obtained by inverting the Schroedinger equations for the wave functions; however, the potential which is found by the inversion of the Sch's equations is "bare", but screened by its valence electrons. Since the behaviour of the valence electrons depends strongly on the local environment of the (pseudo) atom, the pseudopotential found with this procedure has to be "unscreened", *i.e.*:

$$v_l^{ps,bare}(r) = v_l^{ps,screened}(r) - v_H[n^{ps,v}] - v_{xc}[n^{ps,v}]$$

This "bare" pseudopotential can now be used to solve the K-S equations for the given atom in any chemical environment.

# In summary:

Solve the Schroedinger's equations for a given **atom**  
**and find the full atomic wavefunctions**

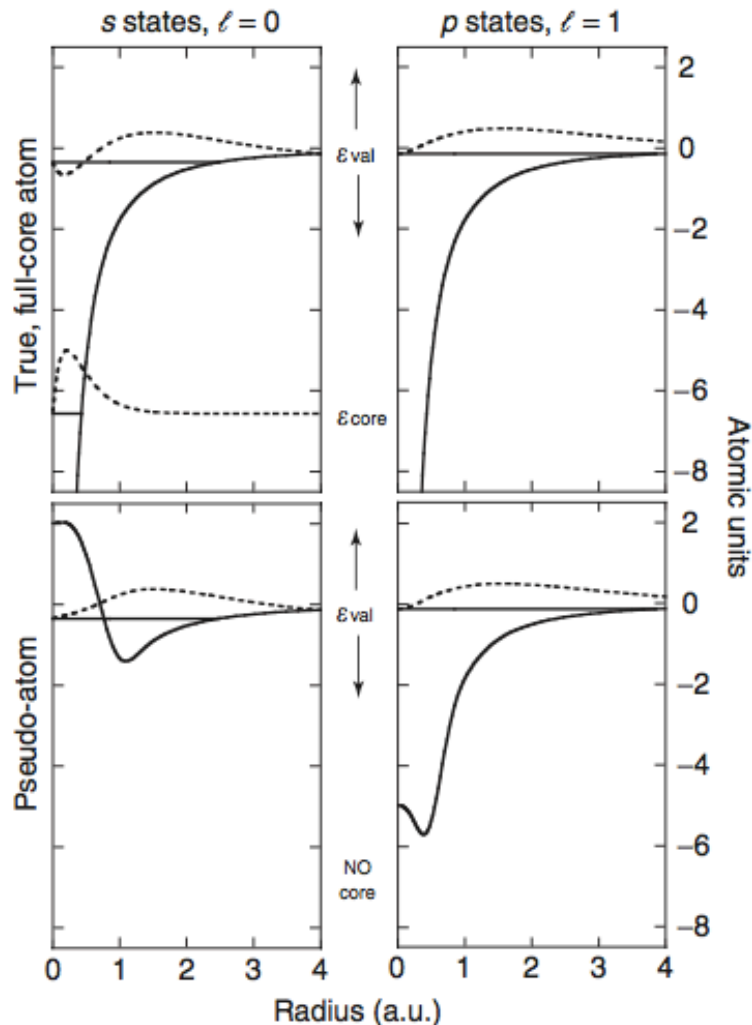
Match the valence wavefunctions of the true atom  
with nodeless, smooth functions above  $r_c$ .

Invert the Schroedinger equations for the  
pseudoatom to find  $v^{ps}$ .

Unscreen the pseudopotential from its  
valence electrons.



# Ab-initio pseudopotentials:



**Figure 2** True vs. pseudo-atom, the example of boron ( $Z = 5$ ). In the true neutral atom (top panels) there are five electrons. Two occupy the tightly bound  $1s$  core orbital  $\psi_{100} = R_{10} Y_{00}$ , another two the shallow  $2s$  valence orbital  $\psi_{200} = R_{20} Y_{00}$  (top left), and the last one the  $2p$  valence orbital (e.g.,  $p_z$ , or  $\psi_{210} = R_{21} Y_{10}$ : top right). Here the radial orbitals  $\chi_{nl} = r R_{nl}$  are dashed lines and their zero is vertically shifted and lined up to the corresponding energy eigenvalue (gray line). The screened nuclear potential (top panels, black solid line) retains much of its original Coulombic shape, and a hydrogen-like shell structure results: the  $1s$  orbital corresponds to a deep eigenvalue ( $\epsilon_{\text{core}}$ , gray thick line) and is localized near the nucleus, while the  $2s$  and  $2p$  valence orbital are “fatter” and correspond to a shallower energy ( $\epsilon_{\text{val}}$ , gray thick line). In a pseudo-atom (bottom panels) the core electrons and the nucleus are simultaneously eliminated and replaced by a pseudopotential (bottom, black solid line); in boron we are thus left with just three electrons, two in the  $s$  (left) and one in the  $p$  (right) pseudo-valence-orbital. These orbitals should ideally have the same energy eigenvalue and wave function amplitude as the true valence orbitals (top, dashes). The amplitude, though, can be the same only outside the core: inside it, the true valence  $2s$  orbital (top left) is radially orthogonal to the core  $1s$  orbital and changes sign (has one radial node), while, by definition, the pseudo-valence-orbital (bottom left) has no underlying core, and is thus nodeless. Similar considerations apply to energy: the pseudopotential (black solid, right) may effectively replace the true potential (left) only within some energy window around the valence eigenvalue  $\epsilon_{\text{val}}$ . But this may be sufficient for an excellent approximation of the atom’s behavior in a molecule or a solid, since bands and bonds spread the valence energies only a few atomic units away from the eigenvalue of isolated atom (see text).

# Literature (psp development):

**PRL**

## [Norm-Conserving Pseudopotentials](#)

D. R. Hamann, M. Schlüter, and C. Chiang

Phys. Rev. Lett. **43**, 1494 – Published 12 November 1979

[Show Abstract +](#)

**PRB**

## [Projector augmented-wave method](#)

P. E. Blöchl

Phys. Rev. B **50**, 17953 – Published 15 December 1994

[Show Abstract +](#)

**PRB**

## [Pseudopotentials that work: From H to Pu](#)

G. B. Bachelet, D. R. Hamann, and M. Schlüter

Phys. Rev. B **26**, 4199 – Published 15 October 1982

[Show Abstract +](#)

**PRB** Rapid Communication

**7,701 citations**

## [Soft self-consistent pseudopotentials in a generalized eigenvalue formalism](#)

David Vanderbilt

Phys. Rev. B **41**, 7892(R) – Published 15 April 1990

[Show Abstract +](#)

**PRB**

## [Efficient pseudopotentials for plane-wave calculations](#)

N. Troullier and José Luriaas Martins

Phys. Rev. B **43**, 1993 – Published 15 January 1991

[Show Abstract +](#)