

# African School on Electronic Structure Methods and Applications

**Theory and practice of pseudopotentials  
Crucial in Plane Wave Methods**

**Lecture by**

**Richard M. Martin**

**Department of Physics and Materials Computation Center  
University of Illinois at Urbana-Champaign  
and**

**Department of Applied Physics, Stanford University**



HOME

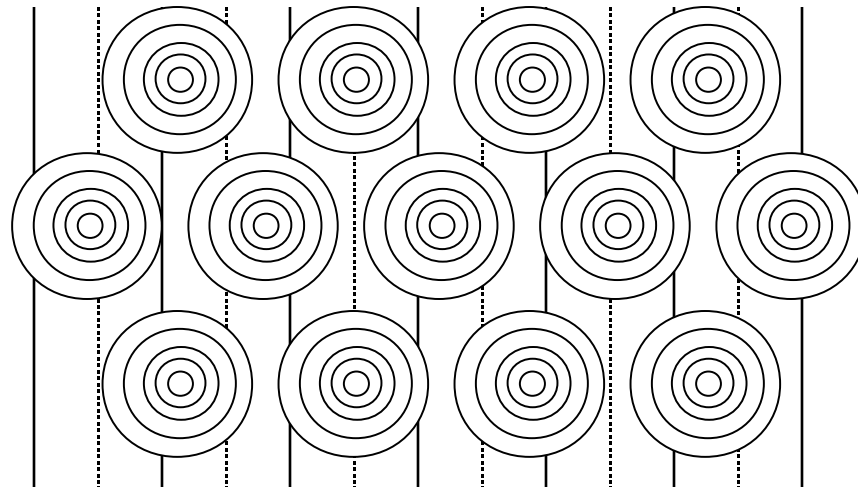
Materials Computation Center



# Calculations on Materials

## Molecules, Clusters, Solids, ....

- **Basic problem** - many electrons in the presence of the nuclei

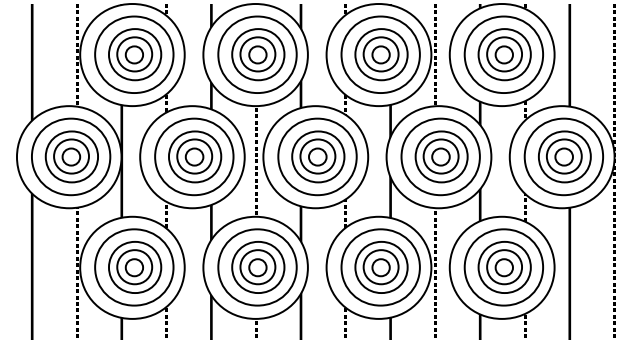


- **Core states** – strongly bound to nuclei – atomic-like
- **Valence states** – change in the material – determine the bonding, electronic and optical properties, magnetism, .....

# The Three Basic Methods for Modern Electronic Structure Calculations

- **Plane waves**

- The simplicity of Fourier Expansions
- The speed of Fast Fourier Transforms
- Requires smooth pseudopotentials



- **Localized orbitals**

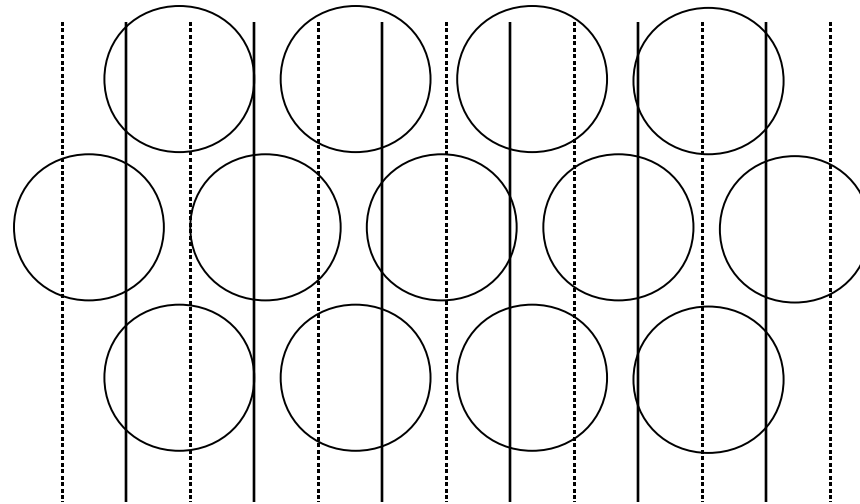
- The intuitive appeal of atomic-like states
- Simplest interpretation in tight-binding form
- Gaussian basis widely used in chemistry
- Numerical orbitals used in SIESTA

- **Augmented methods**

- “Best of both worlds” – also most demanding
- Requires matching inside and outside functions
- Most general form – (L)APW

# Plane Waves

- **A general approach with many advantages**



$$\psi_{i,\mathbf{k}}(\mathbf{r}) \propto \sum_m c_{i,m}(\mathbf{k}) \times \exp(i(\mathbf{k} + \mathbf{G}_m) \cdot \mathbf{r}) \quad (1)$$

- **Kohn-Sham Equations in a crystal**

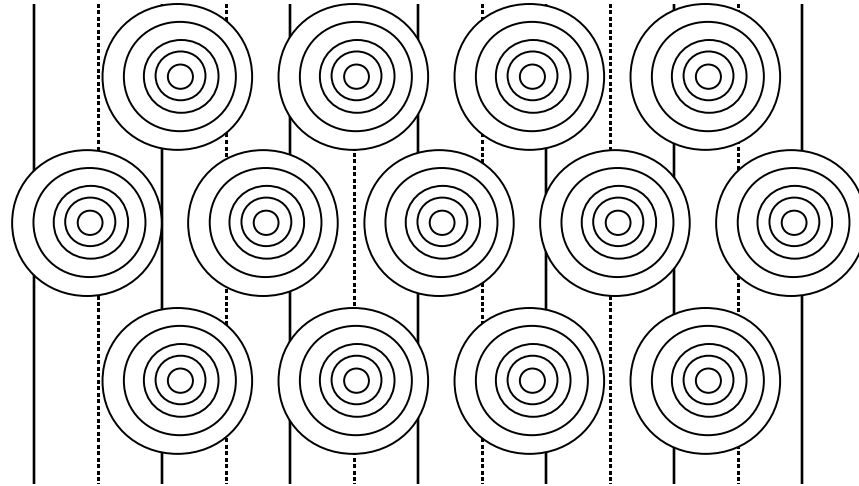
$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k}) \quad (2)$$

$$H_{m,m'}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}). \quad (3)$$

- **The problem is the atoms! High Fourier components!**

# Plane Waves

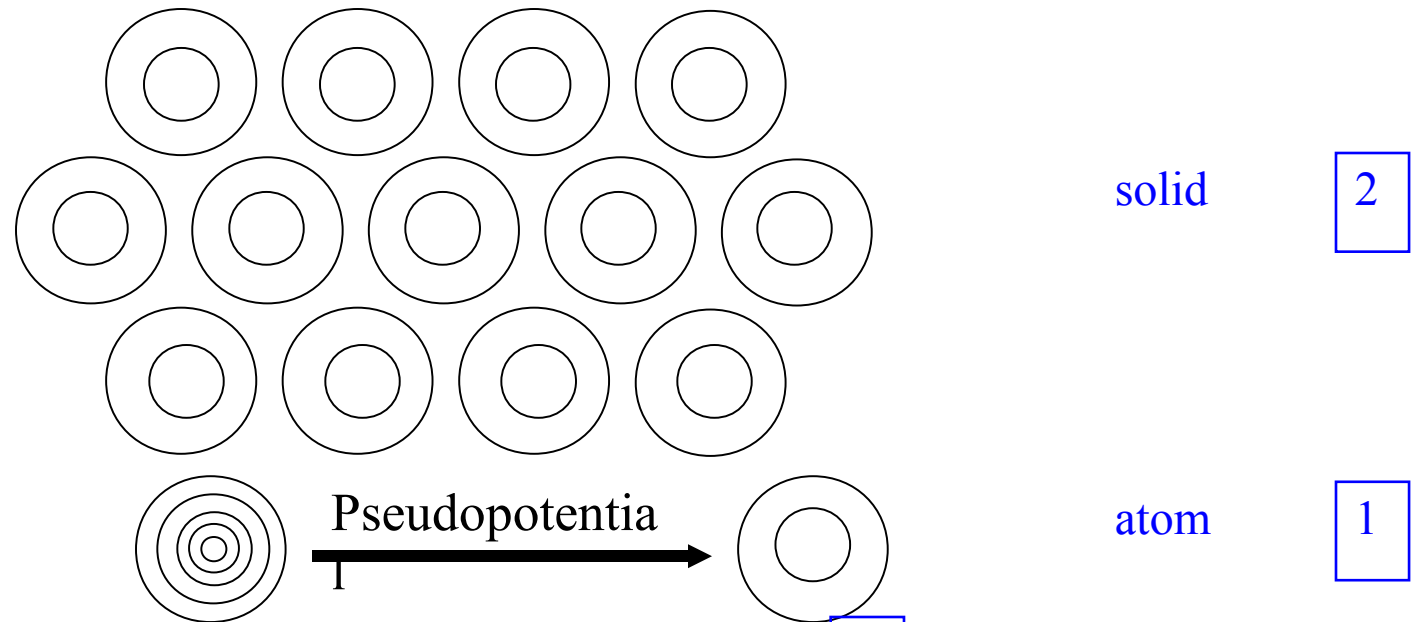
- **(L)APW method**



- **Augmentation:** represent the wave function inside each sphere in spherical harmonics
  - “Best of both worlds”
  - But requires matching inside and outside functions
  - Most general form – can approach arbitrarily precision

# Plane Waves

- **Pseudopotential Method** – replace each potential

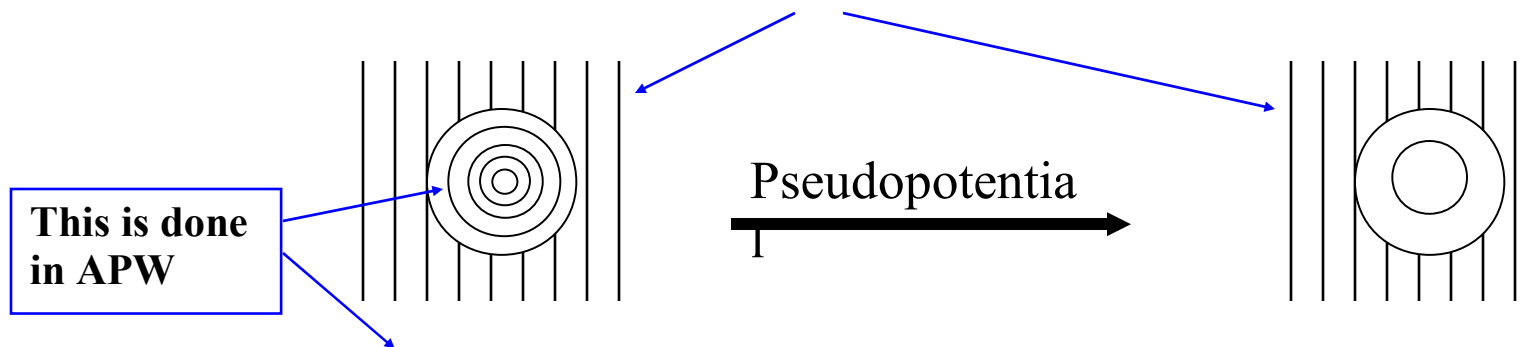


**1** Generate **Pseudopotential** in atom (spherical) – **2** use in solid

- Can be constructed to be **weaker than original atomic potential**
  - Can be chosen to be smooth – not as many Fourier components
  - Solve Kohn-Sham equations in solid directly in Fourier space

# Ideas behind pseudopotentials

- Near the nucleus the wavefunctions vary rapidly, but far from the nucleus (outside some core region of radius  $R_c$ ) the wavefunctions are smooth
- The valence properties of atoms (bonding, valence electron excitations, etc.) are determined primarily by the wavefunctions outside the core.



- What is the effect of the core? It provides a boundary condition on the wavefunctions outside the core region.
- The wavefunctions outside are exactly the same if we invent a pseudopotential that gives the same boundary conditions

# Interaction of a small object with a large heavy object



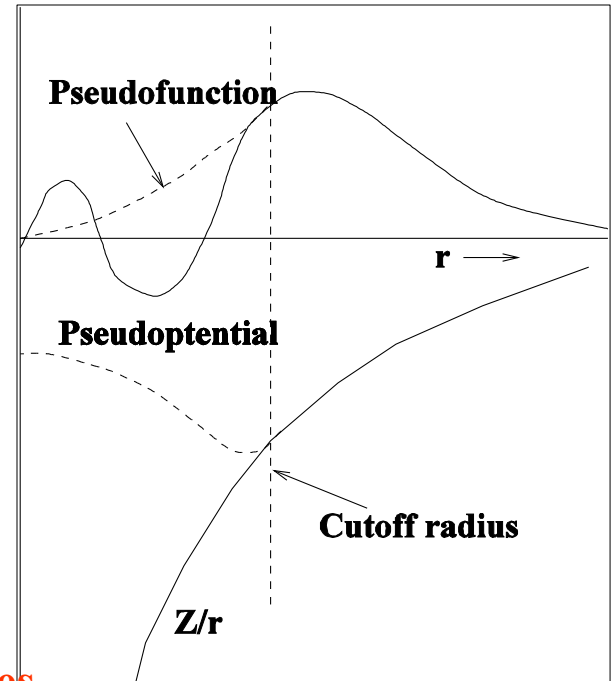
- What is the effect of the core of this truck? It provides a boundary condition on the car outside the core region (the truck).
- If the truck is transporting televisions, can we replace the televisions with carpet (smooth) of the same mass and have the same effect on the car?
- The truck can be replaced by a carefully constructed wall
- In quantum mechanics the car would pass through (and around) the truck emerging with only a phase shift....

# Norm-Conserving Pseudopotentials

- **Norm-Conserving Pseudopotential (NCPP)**
  - Hamann, Schluter, Chaing



- **Generate weak pseudopotential** in atom with same scattering properties for valence states as the strong all-electron potential
- **Conditions**
  - Potential same for  $r > R_c$
  - Pseudofunction “norm-conserving” for  $r < R_c$



- **Standard (already constructed) pseudopotentials and codes to generate new ones are included in PWSCF (also other codes)**

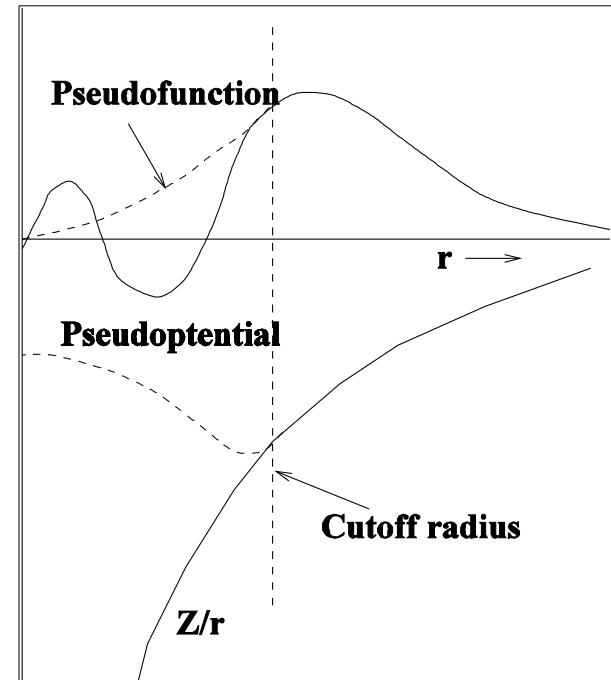
# Norm-Conserving Pseudopotentials

- **Summary of the theory and steps in constructing a NCPP**

- 1. DFT calculations for the all-electron atom – find the valence eigenvalues and eigenfunctions for each angular momentum  $L$
- 2. Construct a pseudofunction that is the same outside  $R_c$  and is continued inside smoothly
- 3. Require “norm conservation” which means the function is normalized. This is satisfied if the integral over the core region is the same as for the original valence function.
- 4. Find the pseudopotential by inverting the Schrodinger equation:

$$V(r) \psi(r) = \epsilon \psi(r) + (\hbar^2/2m) [(2/r) (d\psi/dr) + (d^2\psi/dr^2)]$$

**This must be done separately for each angular momentum  $L$**



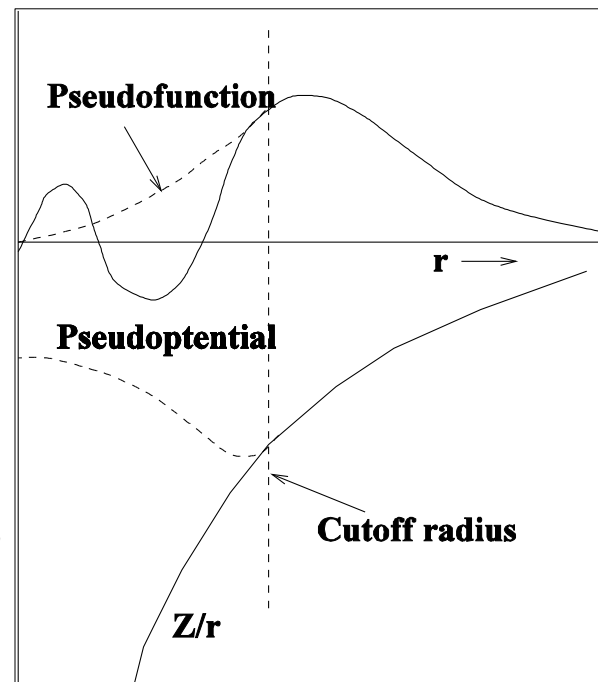
Very nice proof by  
Hamann, Schluter, Chiang

# Norm-Conserving Pseudopotentials

- **Summary of the theory and steps in constructing a NCPP**

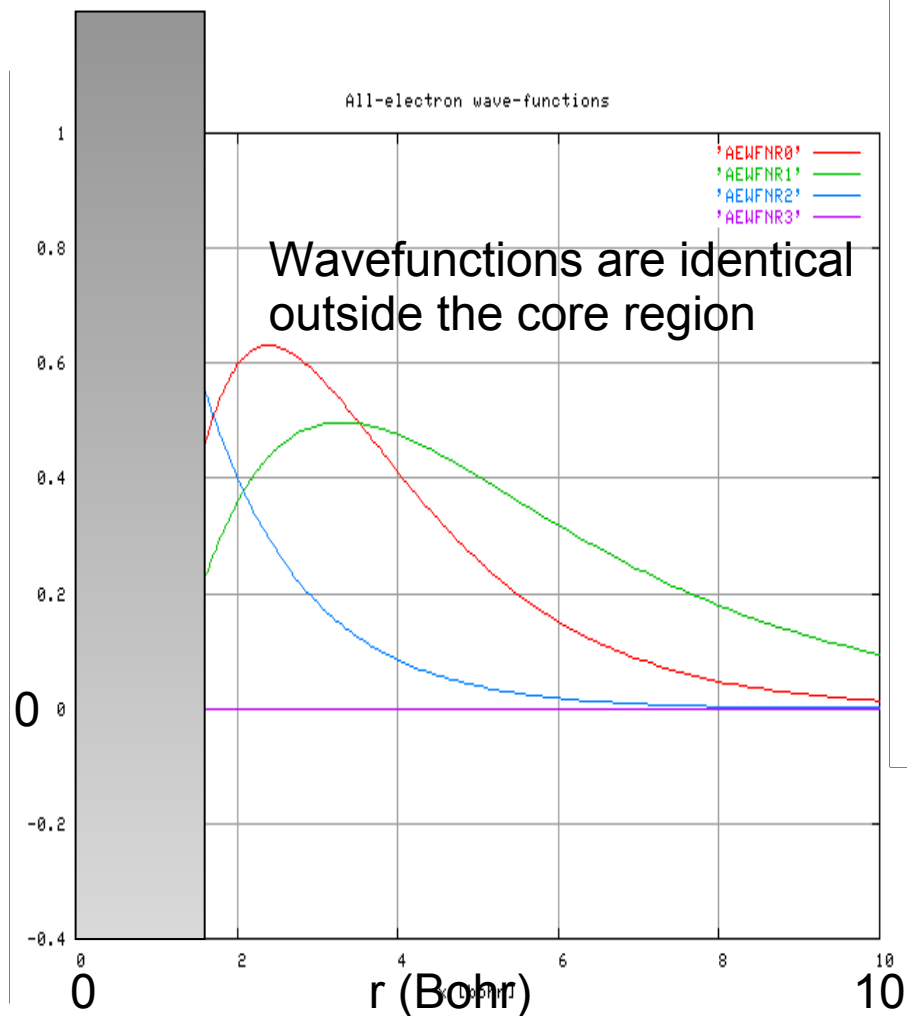
- **Properties of a NCPP**

- The potential is “non-local” – it is not simply a function of position – the potential for each angular momentum is different
- An elegant proof (see section 11.4) shows that if the pseudopotential is norm-conserving, then it also has the property that the logarithmic derivative is not only correct at the given energy  $\epsilon$ , but also correct to linear order for energies  $\epsilon + \Delta\epsilon$
- The last point is the feature that makes the potentials more “transferable” from the atom to the molecule or solid where the energies change.

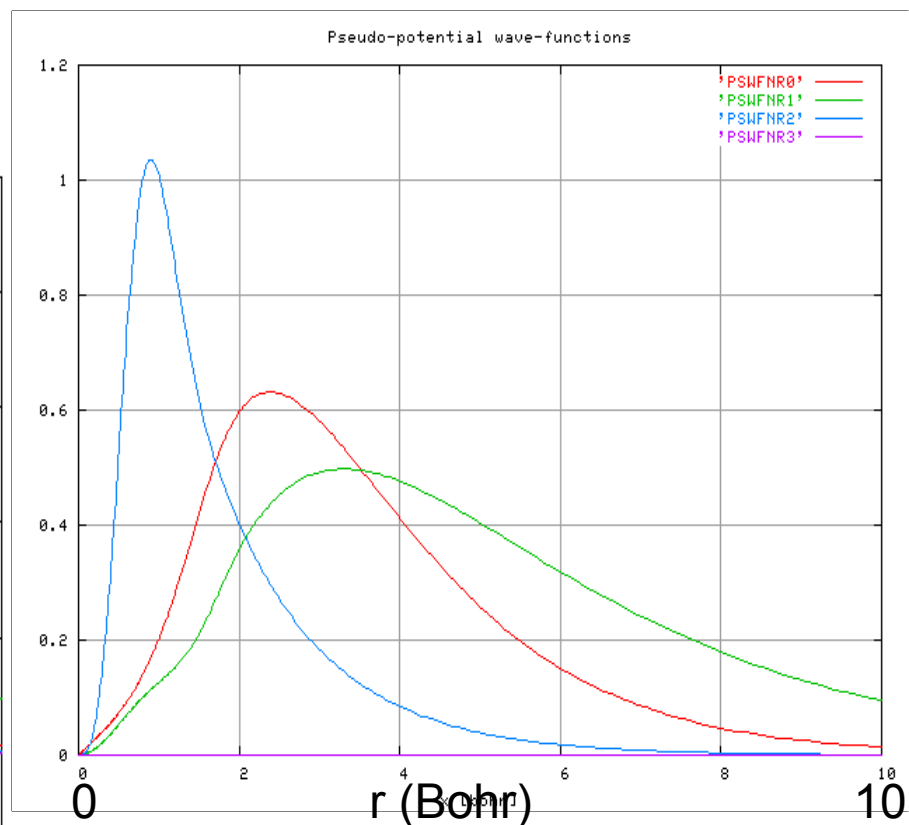


# Example -Fe – s,p,d valence wavefunctions – $r \Psi(r)$

## All electron functions



## Pseudo functions



From <http://www.tddft.org/>

# How good are pseudopotentials?

- **Almost exact for many elements and properties**
  - Example – in carbon, the pseudopotential only replaces the 1s electrons – very good approximation
  - Many tests show that carefully constructed pseudopotentials are very good for most elements
  - See next slide for examples
- **They are not as definitive for transition metal d-states and rare earth f-state which are very localized**
  - Note the d state in Fe is mainly inside the core region  $r < R_c$ , But it is essential for magnetism – an example where the pseudopotential can give errors unless one makes additional requirements

# Comparisons – LAPW – PAW - - Pseudopotentials (VASP code)

Method	C		Si		CaF <sub>2</sub>		bcc Fe		
	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>a</i>	<i>B</i>	<i>m</i>
NCPW <sup>a</sup>	3.54	460	5.39	98	5.21	90	2.75 <sup>c</sup>	226 <sup>c</sup>	
PAW <sup>a</sup>	3.54	460	5.38	98	5.34	100			
PAW <sup>b</sup>	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP <sup>b</sup>	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW <sup>a</sup>	3.54	470	5.41	98	5.33	110	2.72 <sup>d</sup>	245 <sup>d</sup>	2.04 <sup>d</sup>
EXP <sup>a</sup>	3.56	443	5.43	99	5.45	85-90	2.87 <sup>d</sup>	172 <sup>d</sup>	2.12 <sup>d</sup>

- *a* – lattice constant; *B* – bulk modulus; *m* – magnetization
- <sup>a</sup>Holzwarth , *et al.*; <sup>b</sup>Kresse & Joubert; <sup>c</sup>Cho & Scheffler; <sup>d</sup>Stizrude, *et al.*

# How useful are pseudopotentials?

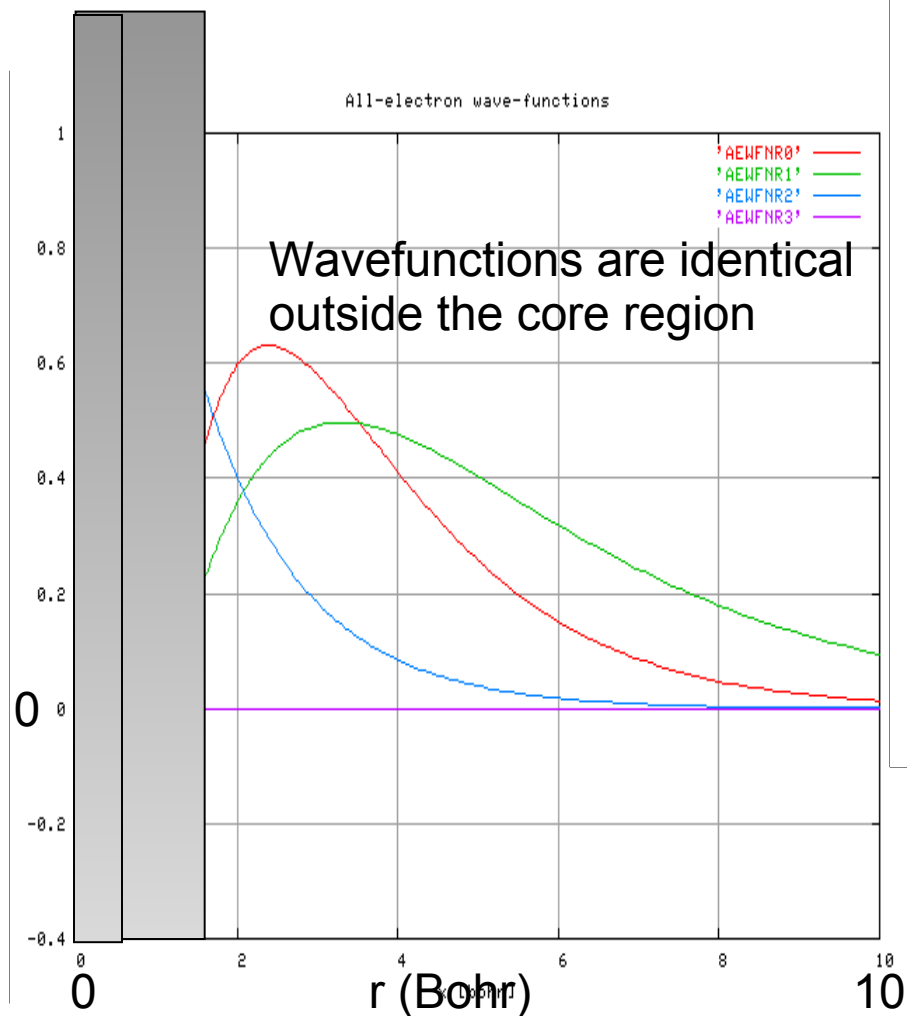
- Pseudopotentials have made possible many of the important advancements of the last years
  - Plane wave methods are useful only with pseudopotentials
  - The generality of plane waves means the same methods are applied to crystals, surfaces, molecules, nanostructures, ....
  - Car-Parrinello simulations have only been done with pseudopotentials because it is so much faster than all-electron methods
  - Greens function methods to calculate phonon frequencies
  - Many other developments
- Continuing developments are overcoming the limitations in accuracy for systems like transition metals, . . .

# Untrasoft pseudopotentials

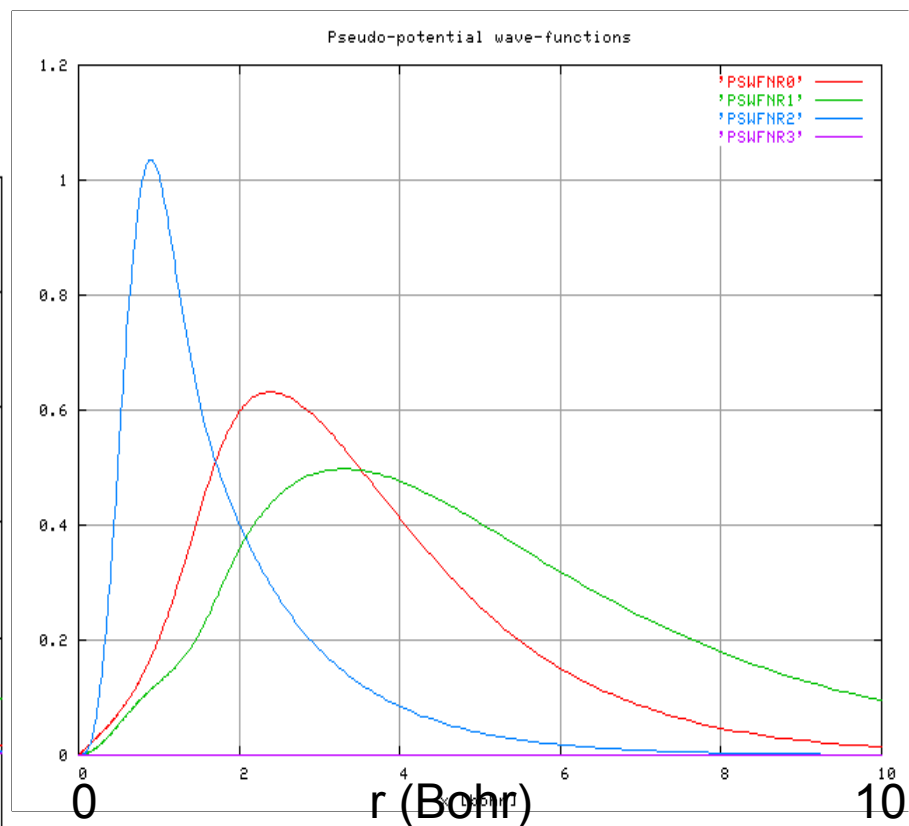
- In order to describe rapidly varying functions accurately the “norm-conserving” pseudopotentials must be rather strong (weaker than the original potential but still requiring many plane waves).
- Example p states of O, 3d states of a transition metal
- Ultrasoft pseudopotentials replace the core with a weak potential plus an added function in the core region.
- Example on next slide
- . .

# Example -Fe – s,p,d valence wavefunctions – $r \Psi(r)$

## All electron functions



## Pseudo functions



From <http://www.tddft.org/>

# Conclusions

- Pseudopotentials are a part of elegant theoretical methods to reformulate a problem in a way that it is easier to solve
- Pseudopotentials greatly simplify electronic calculations by replacing the effects of core electrons with a potential
- Pseudopotentials have made possible many of the important advancements of the last years in electronic structure
- There are well developed theories and practical codes to generate pseudopotentials
- Recent advances make pseudopotentials more powerful – “ultrasoft” potentials, . . .
- **Most important -- understand what you are doing!**
  - Errors if pseudopotentials are used that are not accurate
  - Care to use codes properly