Electronic Structure of Condensed Matter
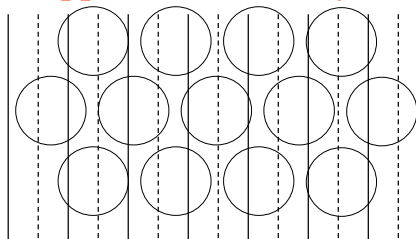## Fudan University - April 2010

Lecture 6, Part 2: Methods Using Plane Waves:
Pseudopotentials, APW, PAW

Instructor: Richard M. Martin
University of Illinois
Stanford University

rmartin@illinois.edu
and
rmartin42@gmail.com

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

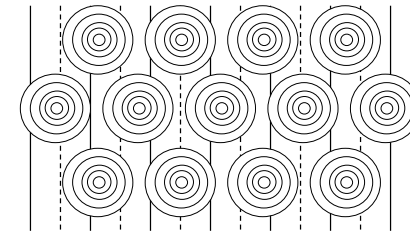$$\sum_{m'} H_{m,m'}(\mathbf{k})c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k})c_{i,m}(\mathbf{k}) \quad (2)$$

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

- The problem is the atoms! High Fourier components!

Why not use plane waves directly?

- 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, …..

# Basic Methods with plane waves

- **Pseudopotentials**
  - Replace cores by smooth pseudopotentials
  - Then use Fourier Expansions directly
  - The speed of Fast Fourier Transforms

- **Augmentation method 1 (APW)**
  - Define spheres around atoms
  - Solve with plane waves outside, spherical harmonics inside
  - Most general form – (L)APW   - linearization very important for simplifying calculations
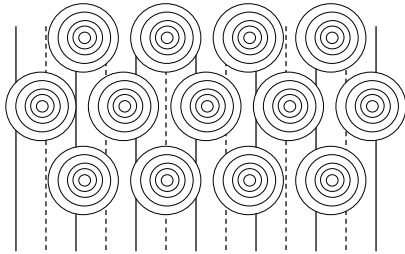- **Augmentation method 2(PAW)**
  - Add core-like functions to plane wanes – do not use spheres
  - Can consider as a combination of the ideas form pseudopotentials and APW
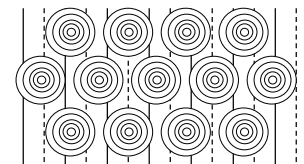
Augmentation -APW

- **(L)APW method**

- Augmentation: represent the wave function inside each sphere in spherical harmonics

 | Difficult – non-linear Made much more useful by linearization |
  | --- |

  - "Best of both worlds" calculate both core and valence states
  - But requires matching inside and outside functions
  - Most general form – can approach arbitrarily precision

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.


This is done in APW
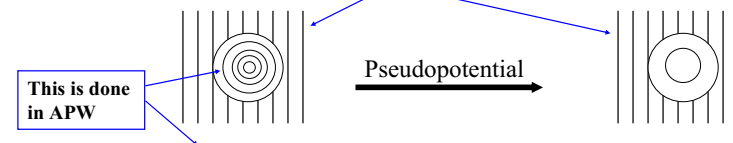
Pseudopotential

- 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

Pseudopotentials

- **Pseudopotential Method** – replace each potential

solid 2

Pseudopotential

atom 1
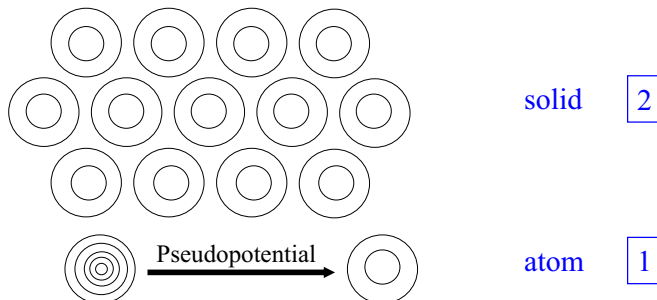
- 1 Generate Pseudopotential in atom (spherical) – 2 use in solid
- Pseudopotential can be constructed to be weak
  - Can be chosen to be smooth
 - Solve Kohn-Sham equations in solid directly in Fourier space

Norm-Conserving Pseudopotentials

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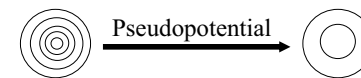
Pseudopotential

- **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 $r < R_c$

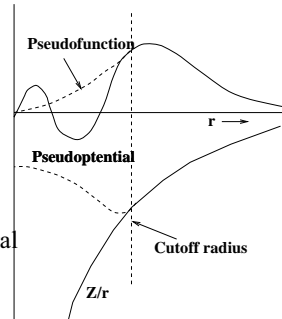- **Codes available for generating potentials**

Pseudofunction

r

Pseudoptential

Cutoff radius

Z/r
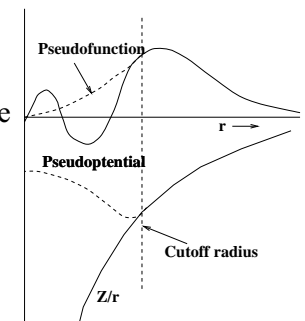
Norm-Conserving Pseudopotentials I

- **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 Rc 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.

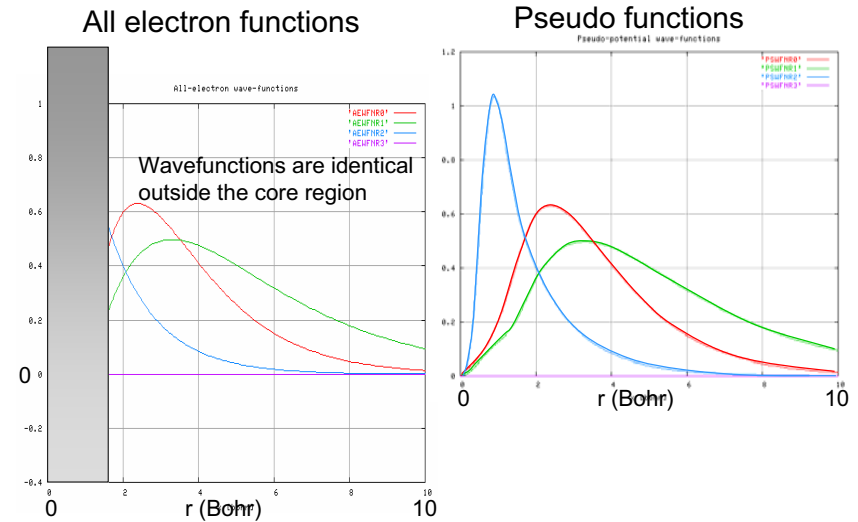- 4. Find the pseudopotential by inverting the Schrodinger equation:
$$V(r) \psi(r) = \varepsilon\psi(r) + (h^2/2m) [(2/r) (d\psi/dr) + (d^2\psi/dr^2)]$$
This must be done separately for each ang. mom. L

Pseudofunction

Pseudoptential

r →

Cutoff radius

Z/r

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Example -Fe – s,p,d valence wavefunctions – r Ψ(r)

All electron functions

Pseudo functions

Wavefunctions are identical outside the core region

0

r (Bohr) 10


From http://www.tddft.org/

Norm-Conserving Pseudopotentials

- **Summary of the properties of 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 ε, but also correct to linear order for energies $\varepsilon + \Delta\varepsilon$

- The last point is the feature that makes the potentials more "transferable" from the atom to the molecule or solid where the energies change.

Pseudofunction

Pseudoptential

r →

Cutoff radius

Z/r
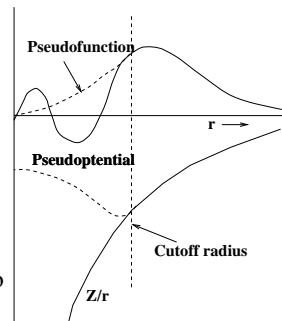
Different for different angular momenta

10

Examples of pseudopotentials

All these pseudopotentials give essentially the same results in a calculation on a solid!
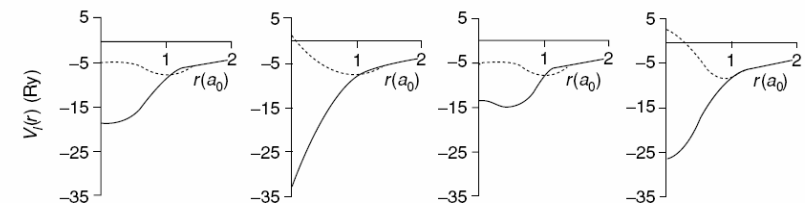

Figure 11.5 in the book

Key points:
 The potentials are "non-local" – different for different angular momenta. A complication but it can be done by projecting plane waves onto spherical harmonics
Many different potentials can give the same wavefunctions outside the core region – and essentially the same results in a solid

Augmentation - PAW

• **PAW – add core functions in core region**
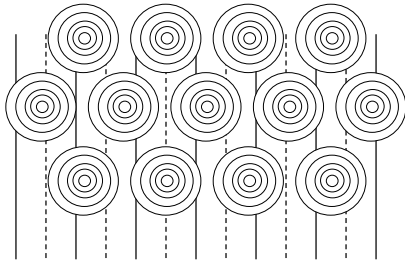
• Planes extend throughout crystal – like pseudopotentials

• Add core functions in core regions – like APW (where the full equations for core and valence states are solved inside sphere

• Great advantage – can use FFTs as in pseudopotentials

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

| Method	C		Si		CaF$_2$		bcc Fe		
	a	B	a	B	a	B	a	B	m
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443	5.43	99	5.45	85-90	2.87[d]	172[d]	2.12[d]

• a – lattice constant;   B – bulk modulus;   m – magnetization

• [a]Holzwarth , *et al.*; [b]Kresse & Joubert; [c]Cho & Scheffler; [d]Stizrude, *et al.*

Summary of Methods to use plane waves

• **Pseudopotentials**
  – Cores are replced by pseudopotentials
  – Calculations are very fast
    Simple algoriths - FFTs
  – This is the reason why this method is the basis for so much work
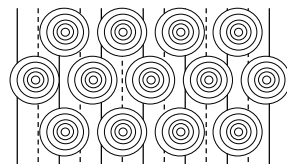
• **Augmentation (APW)**
  – More difficult – solves core and valence problems together
  – Most general form – (L)APW   - best to use for transition metals |where d and f states are localized` but are also valence states

• **Augmentation (PAW)**
  – Can consider as a combination of the ideas form pseudopotentials and APW

Conclusions

• **APW is the most direct, exact method, but it is difficult to use.**

• **Pseudopotentials greatly greatly simply electronic calculations by replacing the effects of core electrons with a potential. They have made possible many of the important advancements of the last years in electronic structure**

• **PAW is in some wayes analogous to a combination of the above**

• **Recent advances (discussed next time) in algorithms have made plane waves + pseudopotentials very efficient and the basis for many other advances.**

• **Most important -- understand what you are doing!**
  – **Errors if pseudopotentials are used that are not accurate**
  – **Care to use codes properly**
  – **Care to test all the convergences**

• **Other developments and applications next time**