Pseudopotentials
Theory and application

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What is a pseudopotential?

The fundamental idea of a "pseudopotential" is the replacement of one problem with another:

- A difficult problem with one that is easier to solve
- And which leads to the same result for certain properties

What is the problem we deal with in electronic structure?

- The potential due to the nuclei is so strong that the lowest energy states are strongly bound near the nucleus
- These ``core states'' are filled and are almost inert. They hardly change when atoms bind together to form a solid
- The higher energy ``valence states" extyend to larger distanced from the nuclei. These are the states the determine the properties of the solid:
  - Binding energy
  - Crystal structure
  - Whether it is a metal or insulator
  - ……….

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  - ……….

# The goal for a pseudopotential in a solid

The goal for a pseudopotential in a solid is to replace the problem with a strong potential with a weaker potential:

- That has the same properties for the valence states
  - The same crystal straure
  - The same band structure for the valance bands
  - ………

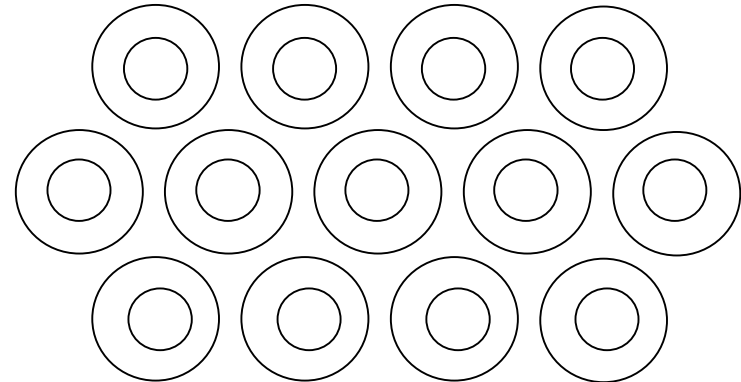We want the same properties without having to deal with the strongly bound core states!

The goal for a pseudopotential in a solid

To replace this problem
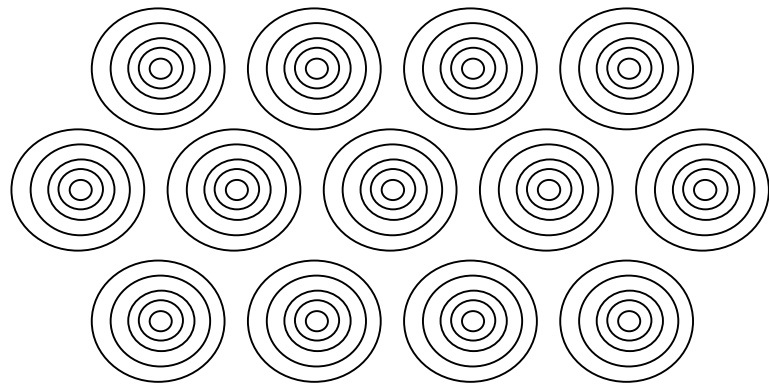
With this problem

Strong potential with core and valence states

Weak potential with no core states and only valence states

Remember Shobhana's analogy

- "Dummy cops" used by many law-enforcement agencies!

Stick a mannequin in uniform by the highway … if it looks like a cop, it works like a cop!

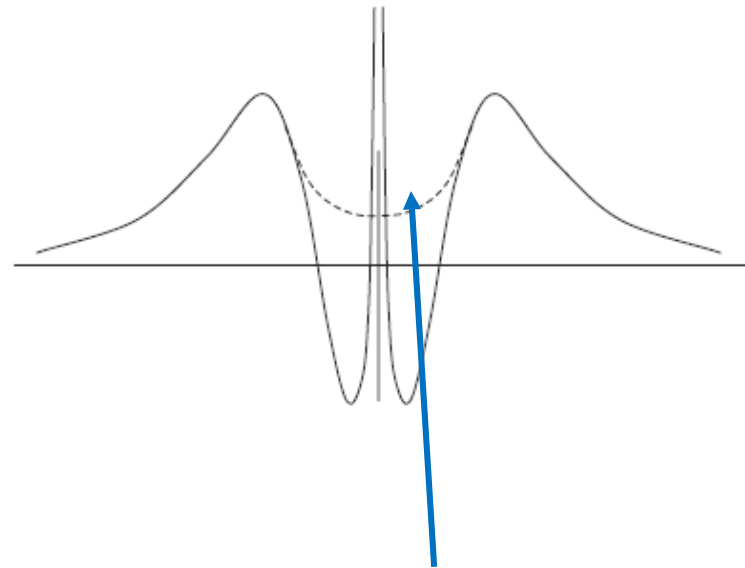Don't care about internal structure as long as it works right!

But cheaper!!

Obviously it can't reproduce all the functions of a real cop, but should be convincing enough to produce desired results….

6
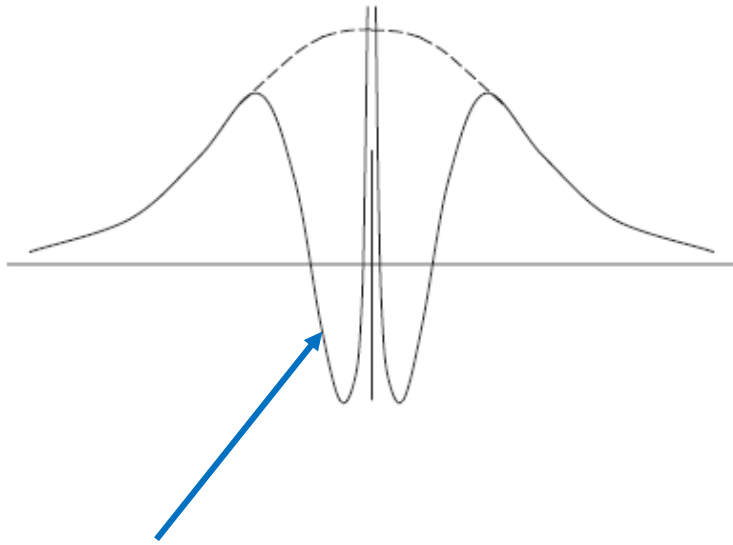
Pseudofunctions

Valence state that is orthogonal to the core states

Smooth pseudopfunction that has the same properties outside the core region

Method that is very useful for valence states in a crystal: Plane Waves

The good thing about PWs
They are general

Not biased to assume some atomic-like form

The bad thing about PWs
They are general

Requires very many PWs to reconstruct the atomic-like aspects of actual wavefunctions

Advantages of PWs
Simple algorithms – fast FFTs
Can be very efficient even for many PWs
So simple and efficient that they have made it possible develop many new methods – MD, response functions, …

Relation to other methods
Many PW methods – APW, PAW, pseudopotential -- can be related by the effect of the core region upon to wavefunctions outside the core (phase shifts)

Plane Waves

- A general approach with many advantages
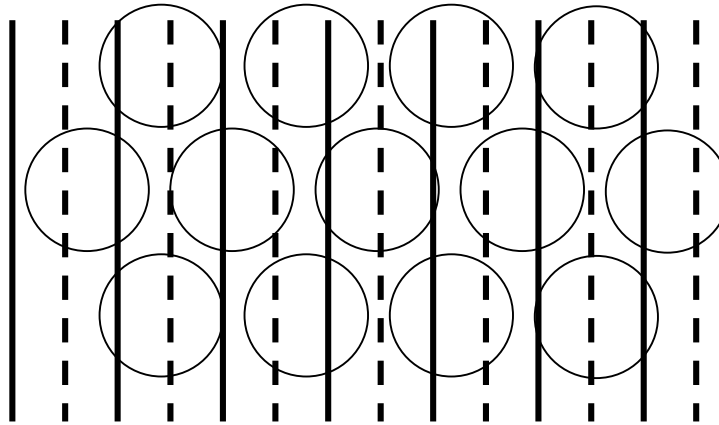
$$\psi_{i,\mathbf{k}}(\mathbf{r}) \propto \sum_m c_{i,m}(\mathbf{k}) \times \exp(i(\mathbf{k} + \mathbf{G}_m) \cdot \mathbf{r}) \quad (1)$$

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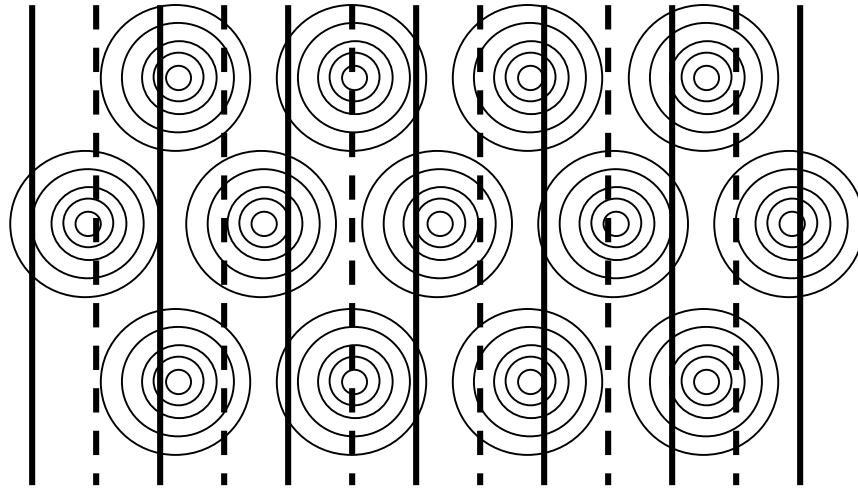
- Core states – strongly bound to nuclei – atomic-like
- Valence states – change in the material – determine the bonding, electronic and optical properties, magnetism, …..

Basic Methods with Plane Waves

- Pseudopotentials (PPs)
  - Replace cores by smooth pseudopotentials
  - Then use Fourier Expansions directly
  - The speed of Fast Fourier Transforms
- Ultrasoft and a type of Augmentation (PAW)
  - Add localized functions around the atoms in addition to the plane waves
  - Can consider as a combination of the ideas form pseudopotentials and APW
- Original Augmentation method (APW)
  - Define spheres around atoms
  - Solve with plane waves outside, spherical harmonics inside
  - Most general form – (L)APW   - linearization very important for simplifying calculations
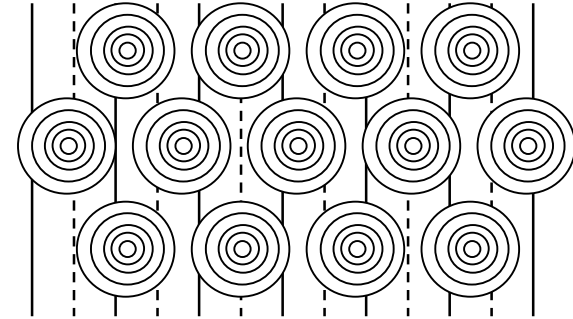
Pseudopotentials

- **Pseudopotential Method** – replace each potential

1 atom
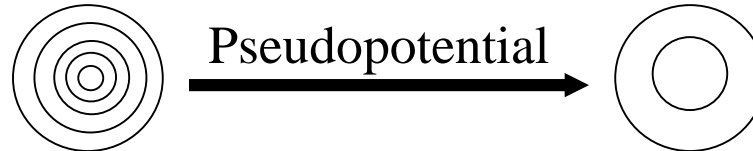
Pseudopotential →
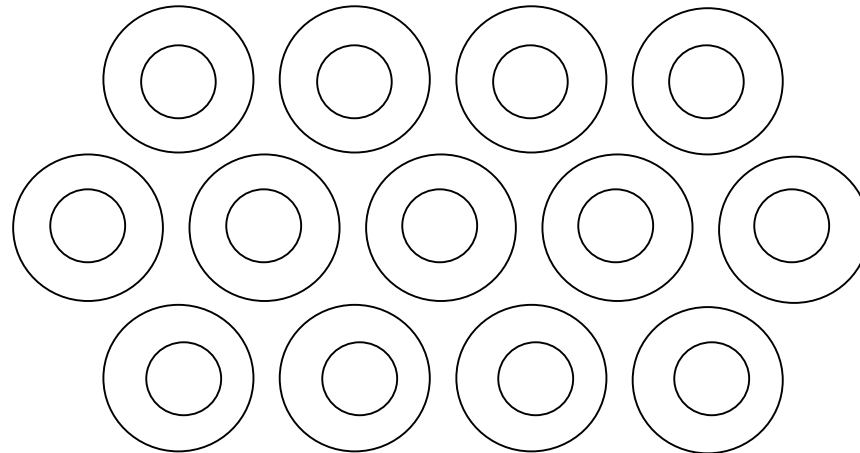
2 solid

- 1 Generate Pseudopotential in atom (spherical)

- 2 Use Pseudopotential in the solid

Norm-Conserving Pseudopotentials

- ## Norm-Conserving Pseudopotential (NCPP)
  - Hamann, Schluter, Chiang (1979)
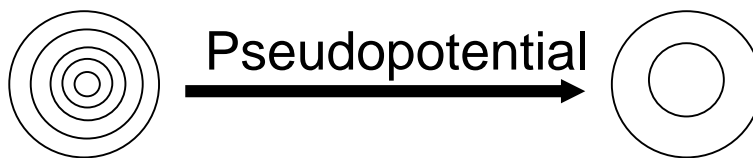
Pseudopotential →

- Generate weak pseudopotential in atom with same properties for valence states as the strong all-electron potential

- Conditions
  - Potential same for $r > R_c$
  - Pseudofunction "norm-conserving" for $r < R_c$

Pseudofunction

Pseudoptential

Cutoff radius

Z/r

r →
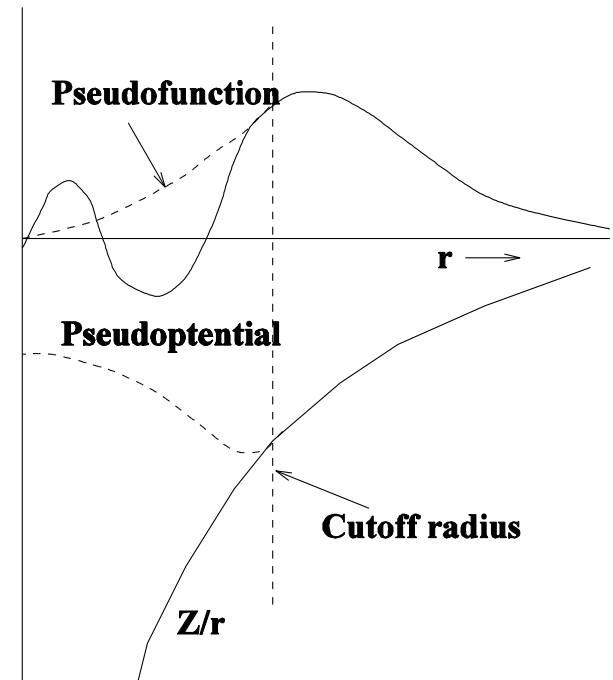
Norm-Conserving Pseudopotentials

- ## 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 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:
$V(r) \, \psi(r) = e\psi(r) + (h^2/2m) \, [(2/r) \, (d\psi/dr) + (d^2\psi/dr^2)]$
Done separately for each ang. mom. L

Pseudofunction

Pseudopotential

Cutoff radius

Z/r

r →
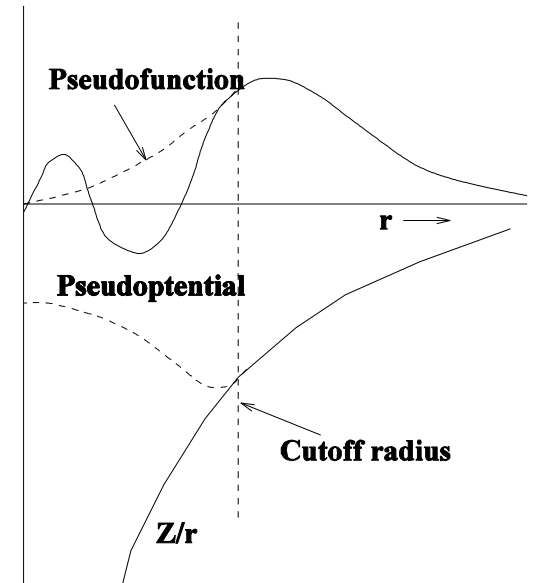
Norm-Conserving Pseudopotentials

- ## 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 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 e, 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

Pseudopotential

r →

Cutoff radius

Z/r
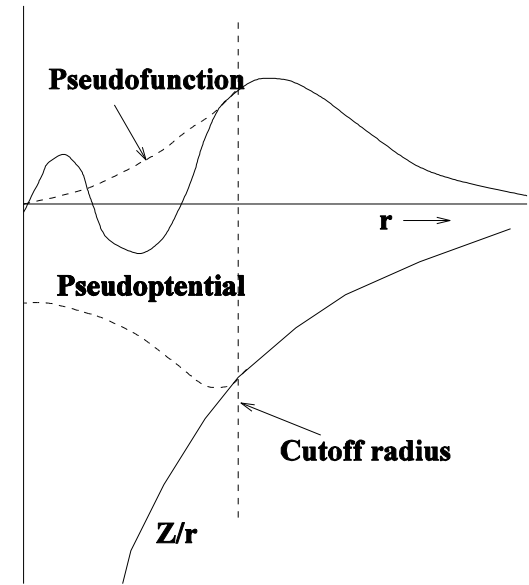
Nonlocal - Different $V_l(r)$ for different angular momenta l

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

All electron functions

All-electron wave-functions

Wavefunctions are identical outside the core region

0

r (Bohr)

0   10

Pseudo functions

Pseudo-potential wave-functions

0

r (Bohr)

0   10

From http://www.tddft.org/
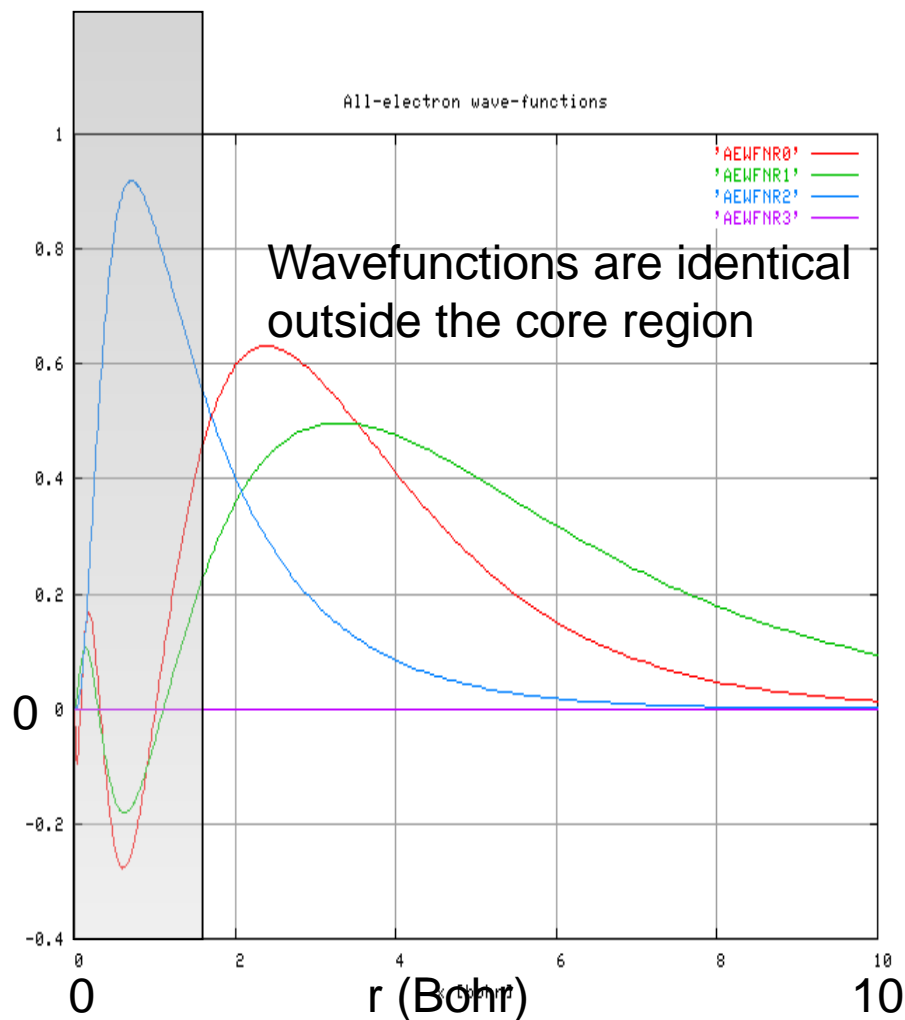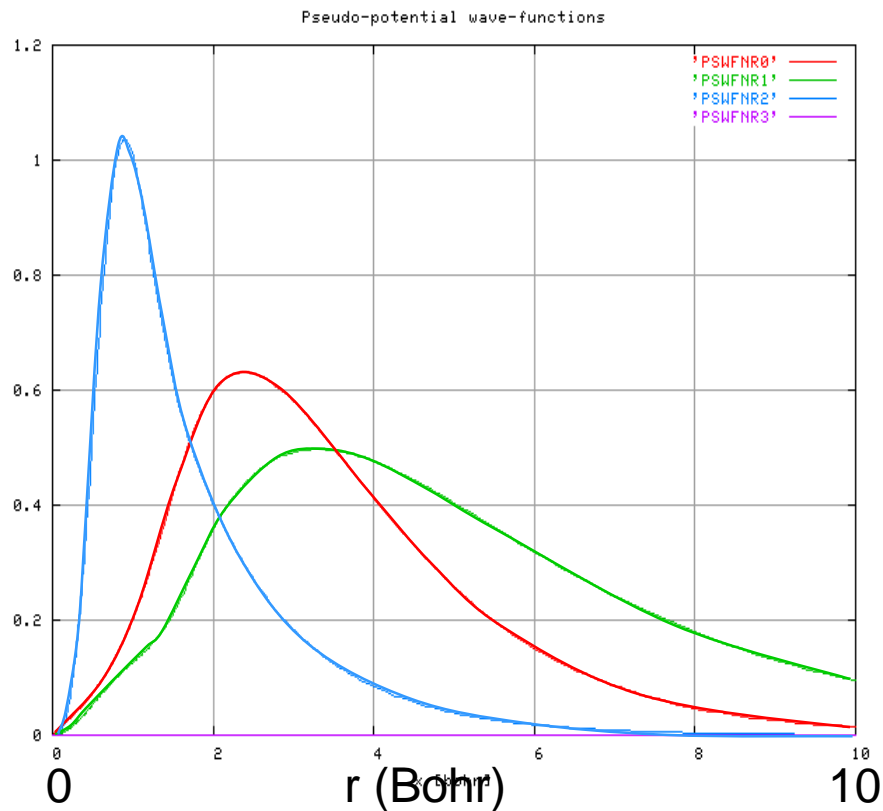
Examples of pseudopotentials

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

s – dotted lines
p - solid lines
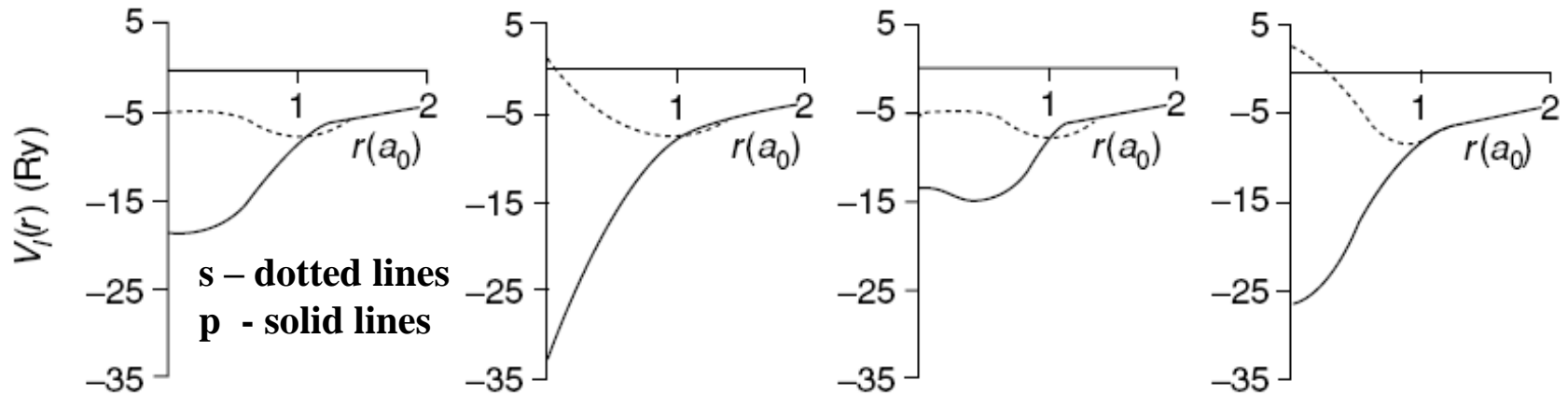
Figure 11.5 in the book

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

Ultrasoft pseudopotentials

- **Forerunner for PAW – next slide**
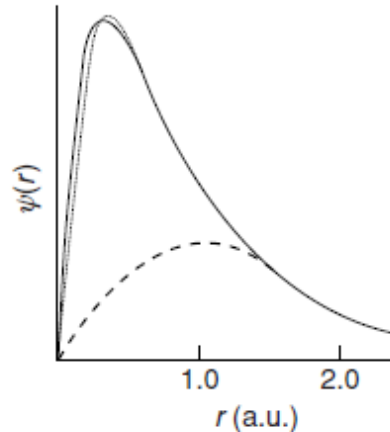
- Smooth functions extend throughout crystal – expressed in plane waves - like norm-conserving pseudopotentials

- Add functions inside the core region to better represent pseudofunctions – Very helpful for O, transition metals, ...

- Equations for smooth functions similar to norm-conserving pseudopotential Eqs. – but generalized eigenvalue problem

- Can use FFTs as in norm-conserving pseudopotentials

Projector Augmented Plane Wave (PAW)

- **PAW – add core functions in core region**

Change this to a state that is not smooth
be has the wiggles of the actual valence state

$\psi(r)$

1.0   2.0

r (a.u.)
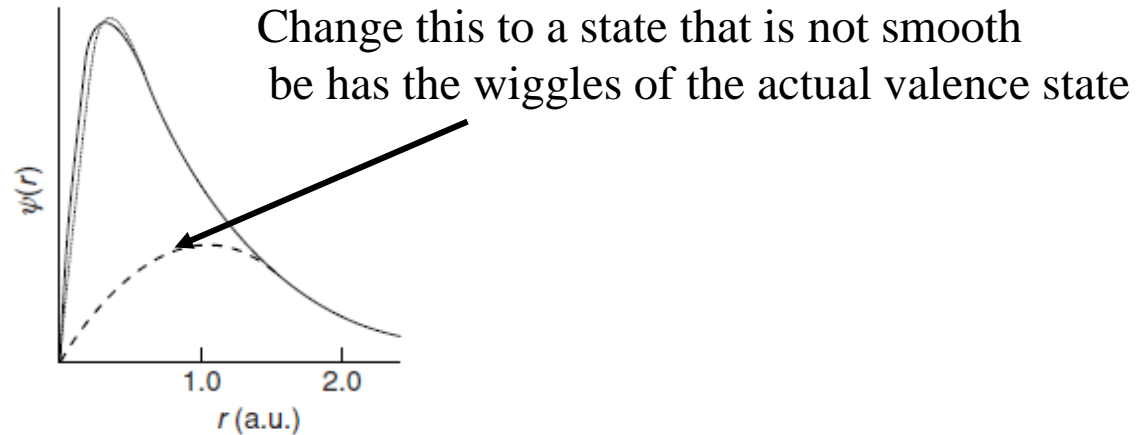
- Smooth functions extend throughout crystal – expressed in plane waves - like ultrasoft pseudopotentials

- Add core functions in core regions – in the simplest form the functions are assumed to be the same as in an atom

- Equations for smooth functions similar to ultrasoft PP Eqs. while having a full atomic like functions inside sphere

- Can use FFTs as in pseudopotentials

Kleinman-Bylander separable potential

- Norm-conserving potentials are:
  - Different radial dependence for each angular momentum -- semilocal

- This can be transformed into a separable operator

$$\hat{V}_{\mathrm{NL}} = V_{\mathrm{local}}(r) + \sum_{lm} \frac{|\psi_{lm}^{\mathrm{PS}}\delta V_l\rangle\langle\delta V_l\psi_{lm}^{\mathrm{PS}}|}{\langle\psi_{lm}^{\mathrm{PS}}|\delta V_l|\psi_{lm}^{\mathrm{PS}}\rangle},$$

Results agree with experiment
(in important classes of materials)

Different methods agree
(when done carefully)

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.*

Comparison of Methods for DFT

DFT METHODS

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,* Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E. Castelli, Stewart J. Clark, Andrea Dal Corso, Stefano de Gironcoli, Thierry Deutsch, John Kay Dewhurst, Igor Di Marco, Claudia Draxl, Marcin Dułak, Olle Eriksson, José A. Flores-Livas, Kevin F. Garrity, Luigi Genovese, Paolo Giannozzi, Matteo Giantomassi, Stefan Goedecker, Xavier Gonze, Oscar Grånäs, E. K. U. Gross, Andris Gulans, François Gygi, D. R. Hamann, Phil J. Hasnip, N. A. W. Holzwarth, Diana Iuşan, Dominik B. Jochym, François Jollet, Daniel Jones, Georg Kresse, Klaus Koepernik, Emine Küçükbenli, Yaroslav O. Kvashnin, Inka L. M. Locht, Sven Lubeck, Martijn Marsman, Nicola Marzari, Ulrike Nitzsche, Lars Nordström, Taisuke Ozaki, Lorenzo Paulatto, Chris J. Pickard, Ward Poelmans, Matt I. J. Probert, Keith Refson, Manuel Richter, Gian-Marco Rignanese, Santanu Saha, Matthias Scheffler, Martin Schlipf, Karlheinz Schwarz, Sangeeta Sharma, Francesca Tavazza, Patrik Thunström, Alexandre Tkatchenko, Marc Torrent, David Vanderbilt, Michiel J. van Setten, Veronique Van Speybroeck, John M. Wills, Jonathan R. Yates, Guo-Xu Zhang, Stefaan Cottenier*

The main conclusion: Methods agree when done carefully

Science   25 march 2018

Comparison of Methods for DFT

Green is good - Red is bad

Science 25 march 2018

Comparison of Methods

The main conclusion:
Modern methods done carefully agree

		average ⟨Δ⟩	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3
USPP	GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0
	GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0
	OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5
	SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3
	Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2
NCPP	FHI98pp/ABINIT	13.3	13.5	13.4	13.4	13.2	13.0	13.2	13.4
	HGH/ABINIT	2.2	2.2	2.2	2.2	2.0	2.3	2.2	2.1
	HGH-NLCC/BigDFT	1.1	1.1	1.1	1.1	1.0	1.2	1.1	1.0
	MBK2013/OpenMX	2.0	2.1	2.1	2.1	1.9	1.8	1.8	2.0
	ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
	ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
	ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

Pseudopotentials

AE comparison table (columns: average ⟨Δ⟩, Elk, exciting, FHI-aims/tier2, FLEUR, FPLO/T+F+s, RSPt, WIEN2k/acc)

	average ⟨Δ⟩	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
AE								
Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW								
GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3

	average	Elk	exciting	FHI-aims/tier2	FLEUR	FPLO/T+F+s	RSPt	WIEN2k/acc
USPP								
GBRV14/CASTEP	1.1	1.1	1.1	1.0	1.0	1.4	1.3	1.0
GBRV14/QE	1.1	1.0	1.0	0.9	1.0	1.4	1.3	1.0
OTFG9/CASTEP	0.7	0.4	0.5	0.5	0.7	1.0	1.0	0.5
SSSP/QE	0.5	0.4	0.3	0.3	0.5	0.9	0.8	0.3
Vdb2/DACAPO	6.3	6.3	6.3	6.3	6.3	6.4	6.5	6.2
NCPP								
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ONCVPSP(PD0.1)/ABINIT	0.7	0.7	0.7	0.7	0.6	1.0	0.8	0.6
ONCVPSP(SG15)1/QE	1.4	1.4	1.3	1.3	1.3	1.6	1.5	1.3
ONCVPSP(SG15)2/CASTEP	1.4	1.4	1.4	1.4	1.3	1.6	1.5	1.4

Comparison of Methods for DFT
One of the examples using QE

Table S41.2. ONCVPSP (SG15) 1/QE calculation settings and results per element. Valence Z_{val}, k-point mesh in the full 1st Brillouin zone of the conventional cell *kpts* and number of irreducible k-points # *k*, equilibrium volume per atom V_0, bulk modulus B_0, pressure derivative of the bulk modulus B_1.

	Z_{val} [–]	kpts [–]	# k [–]	V_0 [Å³/atom]	B_0 [GPa]	B_1 [–]
H	1	28×28×20	6 020	17.356	10.288	2.666
He	2	40×40×22	4 620	17.708	0.882	6.528
Li	3	38×38×38	27 436	20.244	13.846	3.345
Be	4	52×52×28	9 828	7.931	123.706	3.308
B	3	26×26×24	12 324	7.18	235.366	3.428
C	4	48×48×12	10 512	11.586	207.537	3.728
N	5	16×16×16	688	28.773	53.217	3.662
O	6	26×24×24	7 488	18.594	50.245	3.779
F	7	16×28×14	3 136	19.284	33.755	4.001
Ne	8	22×22×22	286	24.259	1.352	7.255
Na	9	32×32×32	16 384	37.113	7.762	3.697
Mg	10	36×36×20	9 900	22.961	36.548	4.05
Al	11	24×24×24	364	16.528	77.801	4.976
Si	4	32×32×32	8 448	20.522	87.495	4.268
Au	19	24×24×24	364	17.982	138.715	6.007
Hg	20	24×24×28	1 092	29.55	7.772	9.92
Tl	13	32×32×18	7 056	31.361	26.88	5.448
Pb	14	20×20×20	220	31.943	40.077	5.575
Bi	15	26×26×8	4 108	36.917	42.82	4.69
Po	N/A	N/A	N/A	N/A	N/A	N/A
Rn	N/A	N/A	N/A	N/A	N/A	N/A

```
name and version of the code: QUANTUM ESPRESSO 5.1 (84)
type of basis set: plane waves
method: norm-conserving pseudopotentials (Schlipf-Gygi ONCVPSP 2015-01-24 (94, 9
```

wave function cutoff	100 Ry
density cutoff	400 Ry

Choice of pseudopotential?

What potential do you really want to use for a particular problem?

The best best potentials with huge numbers of plane waves?

Another choice that is less expensive

Now we arrive at reality!
What is good enough?
How do I verify that it is a good choicd?
……….

Discussion

Following Slides from Shobhana on Pseudopotentials for QE

Pseudopotentials

- HOME
- PROJECT »
- DOWNLOAD
- RESOURCES »
- PSEUDOPOTENTIALS
- CONTACTS
- NEWS & EVENTS »

PSEUDOPOTENTIALS
- More about pseudopotentials
- SSSP on Materials Cloud
- Pseudo DoJo
- SG15 ONCV Potentials
- PSlibrary table
- Original QE PP table
- Hartwigesen-Goedecker-Hutter PP table
- Old FHI PP table

https://www.quantum-espresso.org/pseudopotentials

Pseudopotentials

Quantum Espresso

Pseudopotentials for Quantum Espresso - 2

• Click on element for which pseudopotential wanted.

Pseudopotentials for Quantum-ESPRESSO

O.pbe-rrkjus.UPF

```
Pseudopotential type: ULTRASOFT
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
scalar relativistic

Origin: Original QE PP library
Author: Andrea Dal Corso
Generated by Andrea Dal Corso code (rrkj3)
Uploaded by Layla Martin-Samos
Classification controlled by Paolo Giannozzi
```

O.pbe-van_ak.UPF

```
Pseudopotential type: ULTRASOFT
Method: Vanderbilt ultrasoft
Functional type: Perdew-Burke-Ernzerh
scalar relativistic

Origin: Original QE PP library
Generated by Vanderbilt code version 7.3.4
More Information: O.pbe-van_ak.txt
Uploaded by Layla Martin-Samos
Classification controlled by Paolo Giannozzi
```

Pseudopotential's name gives information about :

- type of exchange-correlation functional
- type of pseudopotential
- e.g.:

O.pbe-rrkjus.UPF   (details)
Perdew-Burke-Ernzerhof (PBE) exch-corr
Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

Element & V_{ext} for Quantum-ESPRESSO

e.g, for calculation on BaTiO$_3$.

```
ATOMIC_SPECIES
Ba 137.327 Ba.pbe-nsp-van.UPF
Ti 47.867 Ti.pbe-sp-van_ak.UPF
O  15.999 O.pbe-van_ak.UPF
```

- **ecutwfc, ecutrho** depend on type of pseudopotentials used (should test).

- When using ultrasoft pseudopotentials, set **ecutrho** = 8-12 × **ecutwfc** !!

Element & V_{ion} for Quantum-ESPRESSO

- Should have same exchange-correlation functional for all pseudopotentials.

input

```
diagonalization = 'cg', mixing_
mixing_beta = 0.7, conv_thr = 1.0
/
ATOMIC_SPECIES
 Fe  55.85 Fe.pz-nd-rrkjus.UPF
 Co  58.93 Co.pbe-nd-rrkjus.UPF
ATOMIC_POSITIONS {crystal}
 Fe 0.00  0.00  0.00
```

oops!

output

```
Max angular momentum in pseudopotentials

from readpp : error #          2
inconsistent DFT read

stopping ..
```

Pseudopotentials

Quantum Espresso

Pseudopotentials

Quantum Espresso