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Pseudopotentials

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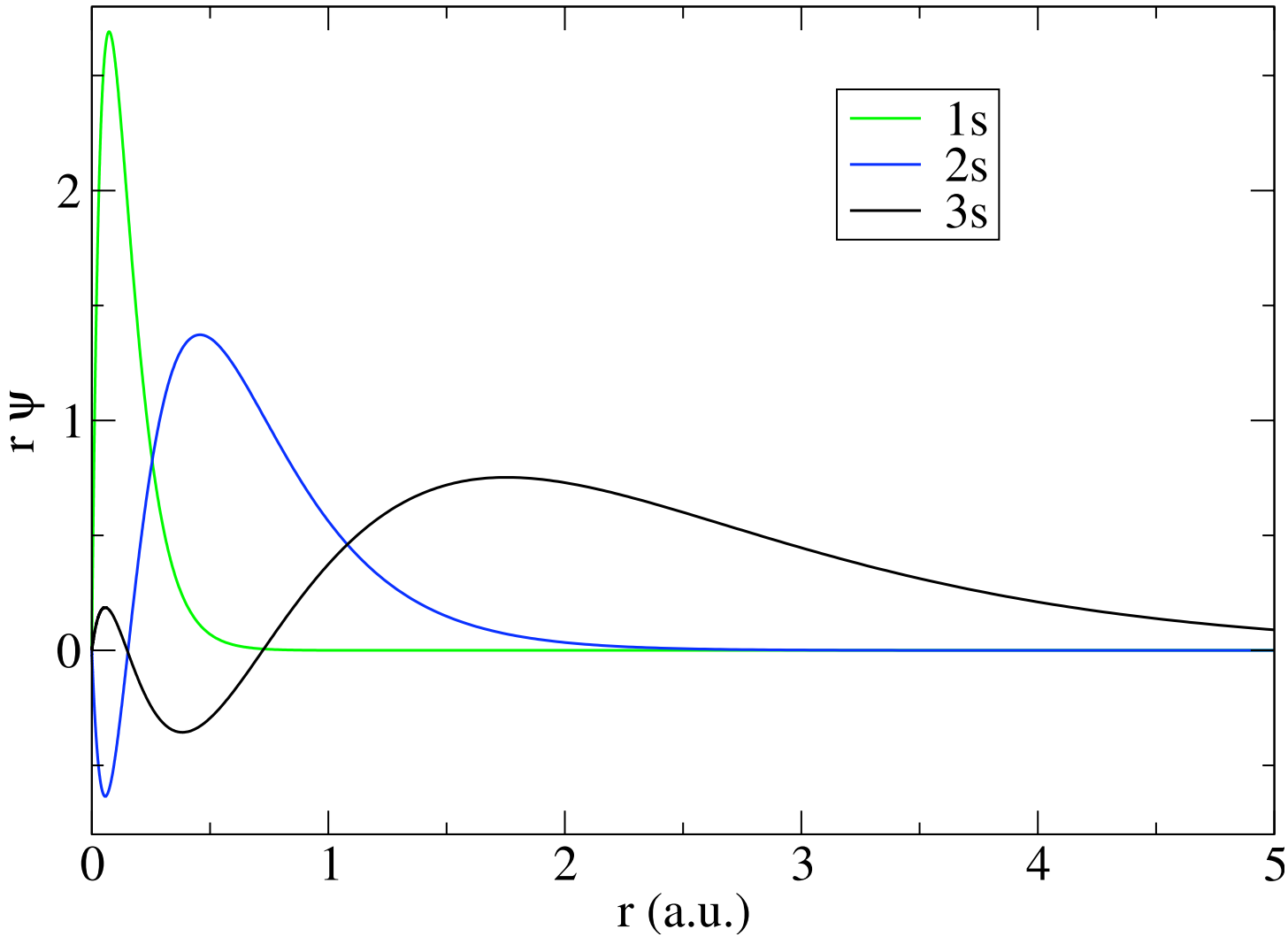
Many slides courtesy of Daniel Jones (University of Oxford)

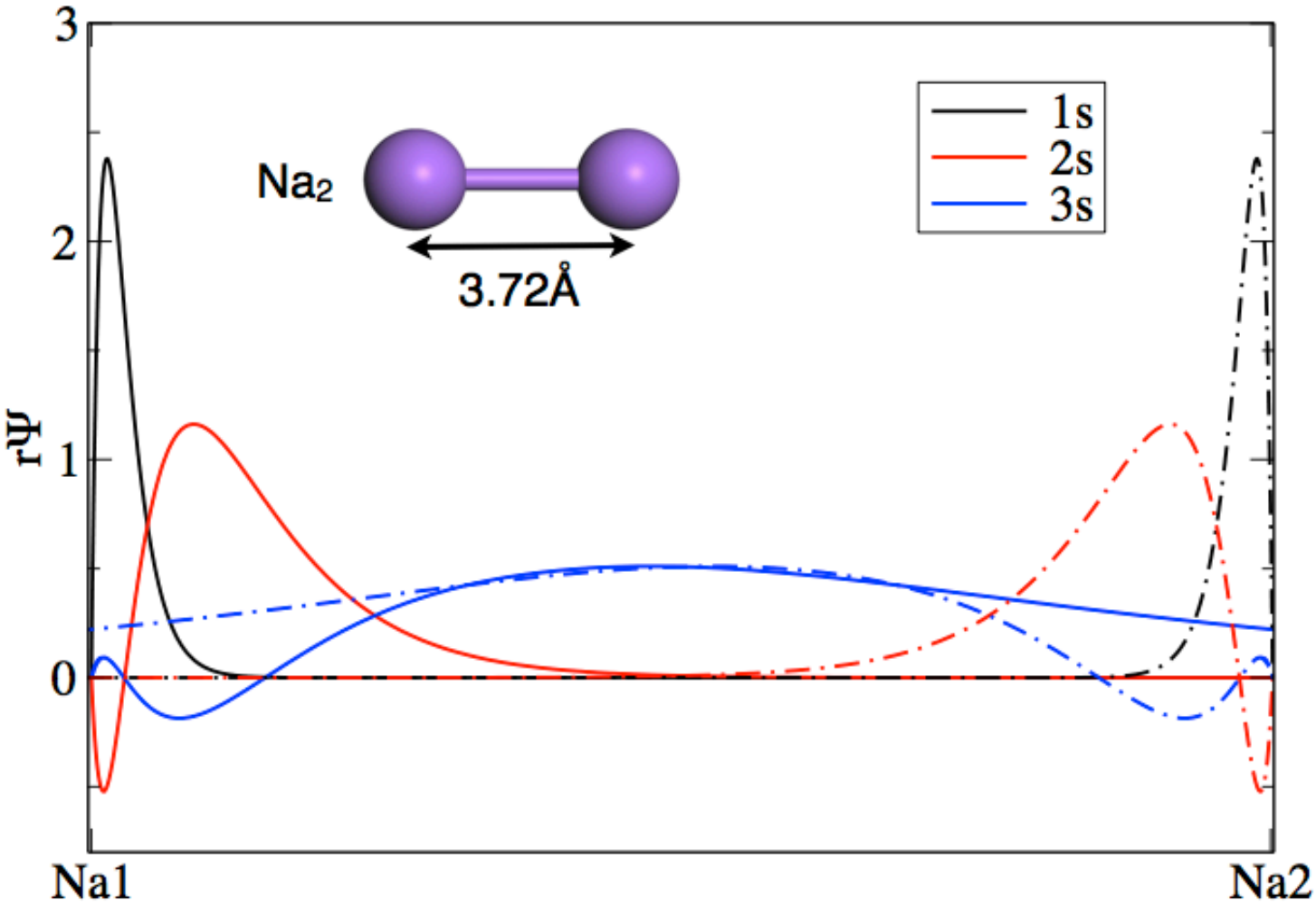
Overview of lecture

- Background
  - What is a pseudopotential and why do we use them?
  - What approximations do we make to use pseudopotentials?
  - Where can you find pseudopotentials to use with CASTEP?
- (Healthy) Fear
  - Poor pseudopotentials can lead to nonsense calculations
  - How to check that the pseudopotentials you are using are good (enough)
- Hope (and confidence)
  - Good pseudopotentials give results that are as good as all electron calculations
  - All approximations made are controllable approximations

Atomic Sodium



Sodium Dimer

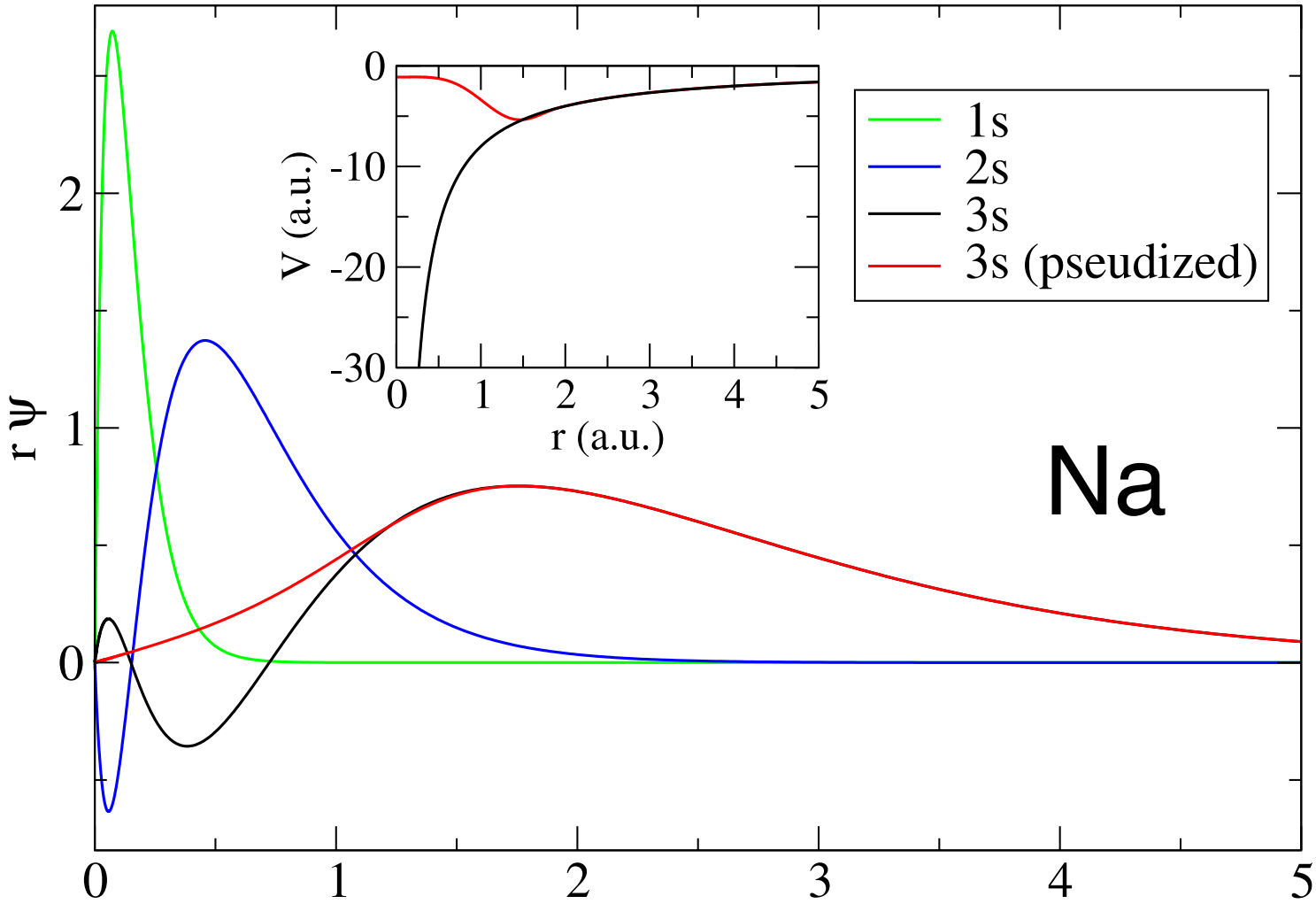


The Pseudopotential Approximation

Core states are tightly bound and have short wavelength oscillations so are prohibitively expensive to model, yet have little direct effect on bonding (i.e. material, chemical and electronic properties). We make 2 approximations…

1. Frozen core
   - Core electrons do not participate in bonding, we freeze them during the calculation.
2. Pseudopotential
   - Valence electrons feel a weaker effective potential in the core region.
   - Pseudowavefunction for valence electrons, which has no nodes.

Sodium Atom



Sodium atom

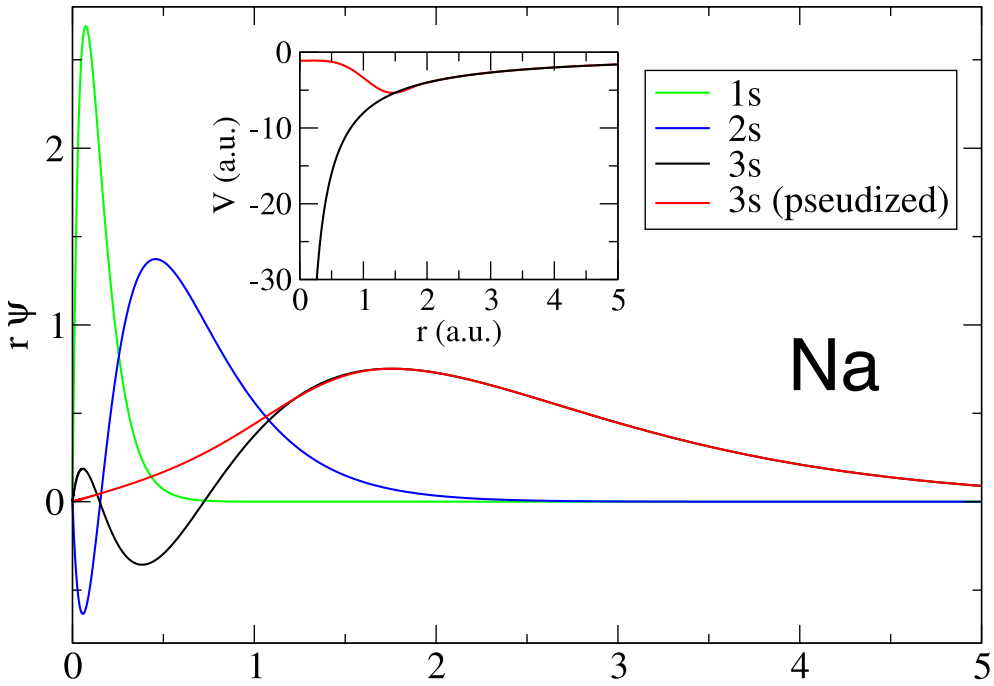
s states of a sodium atom shown.

1s and 2s states are considered core states.

3s all electron wavefunction (black) has short wavelength oscillations in the core region.

3s pseudowavefunction (red) is nodeless, therefore requires a smaller plane wave cutoff to simulate accurately.

Inset is the coulomb potential (black) and the pseudopotential (red). At high distances they are identical, but the potential is much weaker at $r < r_c$



All-electron?

In the literature, calculations which treat all of the electrons as valence electrons are called all-electron (AE) calculations.

The term all-electron can be misleading; in a pseudopotential (PS) calculation ***all electrons are included;*** what is different is that the core electrons' states are "precomputed" and only enter the main calculations via the pseudopotential.

Pseudopotential constraints

We can't just choose any form for the pseudopotential:

- The pseudowavefunction (PS) and the all-electron (AE) wavefunction must be identical outside a cutoff radius (r_c)

$$\phi^{PS}(r > r_c) = \psi^{AE}(r > r_c)$$

- PS and AE eigenvalues must be identical

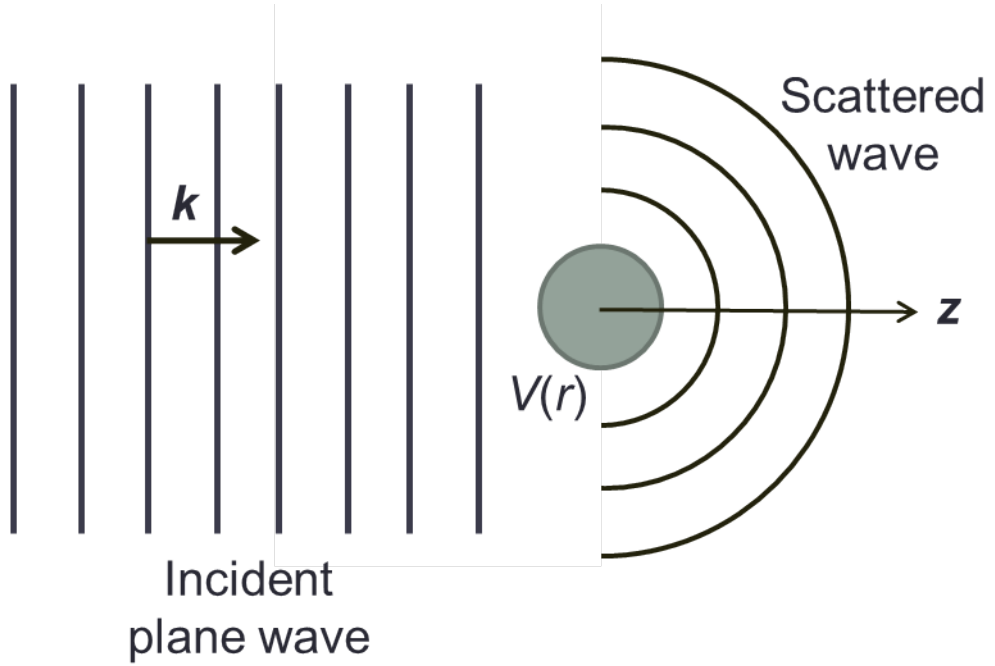
$$\varepsilon_i^{PS} = \varepsilon_i^{AE}$$

- Pseudopotential must reproduce the scattering properties of the original (Coulomb) potential.

Scattering of incident waves

The unbound states associated with a localised potential $V(r)$ describe scattering processes

$$E = \frac{k^2}{2}$$

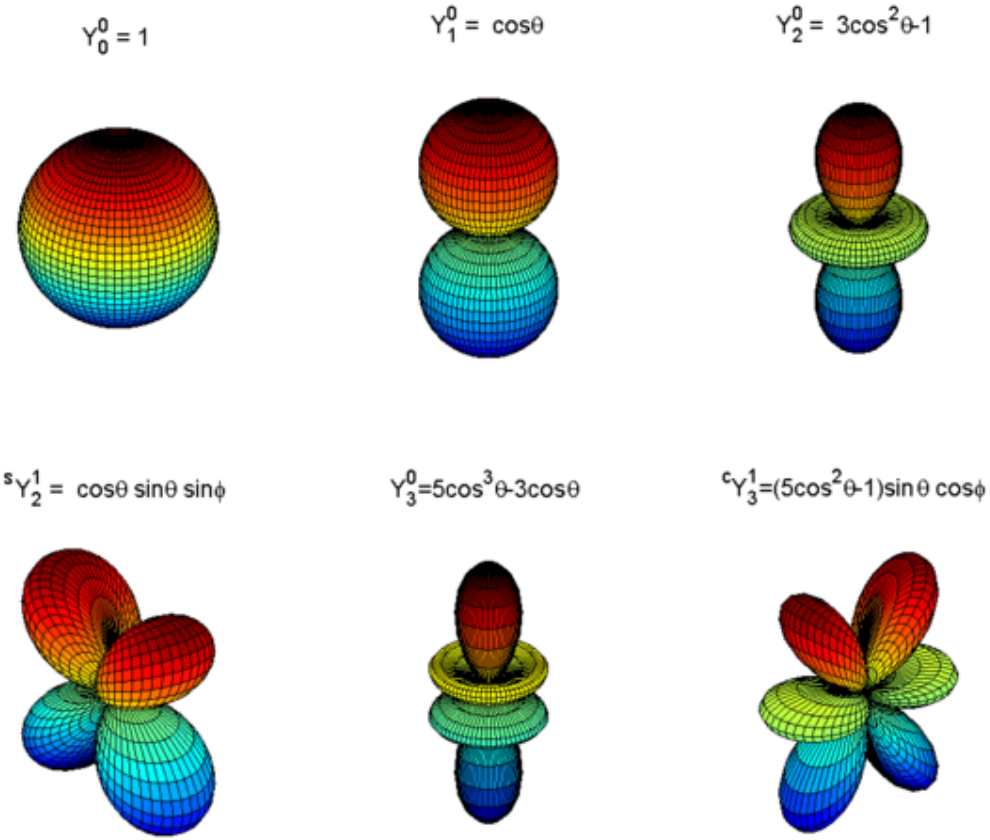


$$e^{ikz} = e^{ikr\cos\theta} = A\sum_l i^l(2l+1)j_l(kr)P_l(\cos\theta)$$

Single plane wave → infinite spherical waves

Spherical harmonics

$Y_{lm}(\theta,\phi)$



Angular dependence is independent of form of V(r)

Eigenfunctions of angular momentum characterised by quantum numbers *l*,*m*

Norm conservation?

- Norm conservation: the total charge of the AE and PS wavefunctions are identical.

$$\int_0^{r_c} \left|\phi^{PS}\right|^2 r^2\, dr = \int_0^{r_c} \left|\psi^{AE}\right|^2 r^2\, dr$$

- Nodeless (2*p*,3*d*,4*f*) wavefunctions are thus necessarily hard.
- Is norm-conservation really necessary?

Ultrasoft Pseudopotentials

- Norm conservation *can be relaxed* (PRB 41,7892(1990)).
- Need to keep track of the missing charge using augmentation charge in the core region.
- Orthonormality of AE wavefunctions becomes S-orthonormality of PS wavefunctions

$$\hat{S} = \hat{1} + \sum_{jk} q_{jk} \left|\beta_j\right\rangle\left\langle\beta_k\right|$$

$$q_{jk} = \left\langle \psi_j^{AE} \middle| \psi_k^{AE} \right\rangle - \left\langle \phi_j^{PS} \middle| \phi_k^{PS} \right\rangle$$

- Called “ultrasoft” pseudopotentials; fewer plane waves req’d.
- USPs generally more transferable – add semi-core states.
- Computationally more difficult, so some functionality cannot use ultrasoft PPs.

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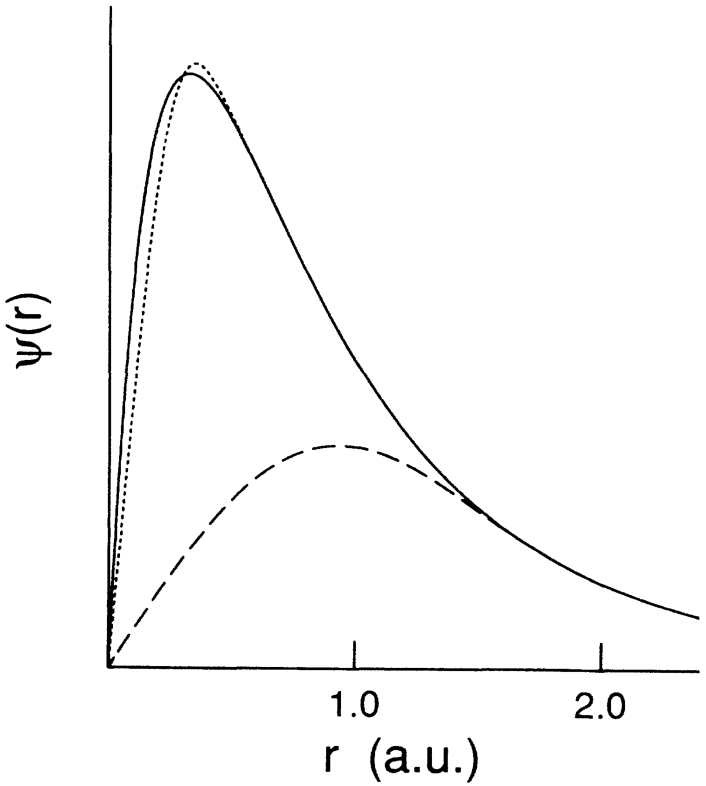
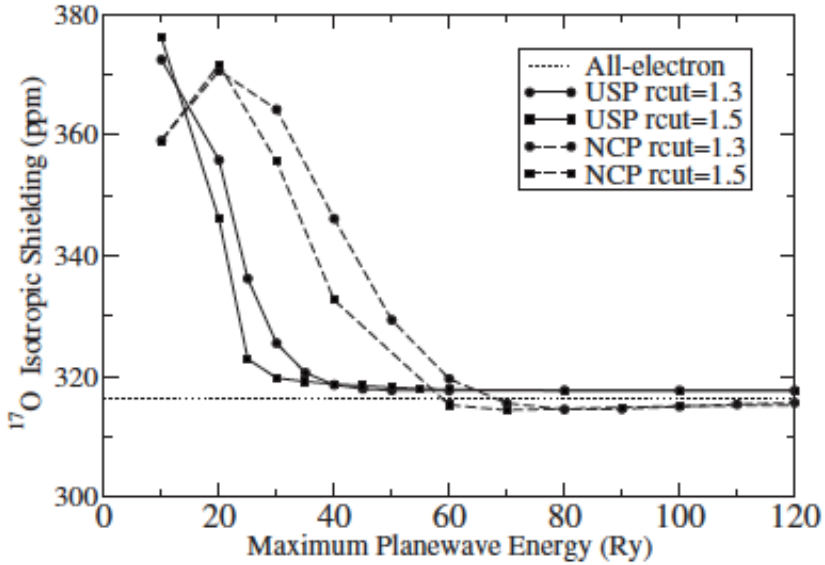
Oxygen and NMR convergence





Oxygen 2p wavefunction, all electron (solid), NC (dotted), ultrasoft (dashed).
From Vanderbilt, PRB **41** (1990), pp 7892

Some properties require NC PPs

The following functionality is not yet implemented for ultrasoft pseudopotentials in CASTEP:

- DFPT Phonons
- DFPT E-field response
- Non-local (‘exact’) exchange
- Spin-orbit coupling – requires fully relativistic PPs.

Recap

- Tightly bound states with short wavelength oscillations require a large plane wave cut off to model – Expensive
- Assume core states do not participate in chemistry
- Replace Coulomb potential with weaker effective pseudopotential
- Pseudowavefunctions are smoother and require fewer plane waves.
- Norm conservation (NC) is not required – relaxing this means valence pseudowavefunctions can be even softer.
- Complexity that arises from losing the orthogonality of the valence states and augmenting the density means that some functionality in CASTEP requires NC PPs.

Computing Materials Properties Using Pseudopotentials

- An appropriate set of core radii are required.
- To accurately recover some materials properties, small core radii are necessary:
  - More states are required to be treated as valence.
  - More plane waves are typically required (pseudopotential is ‘harder’).

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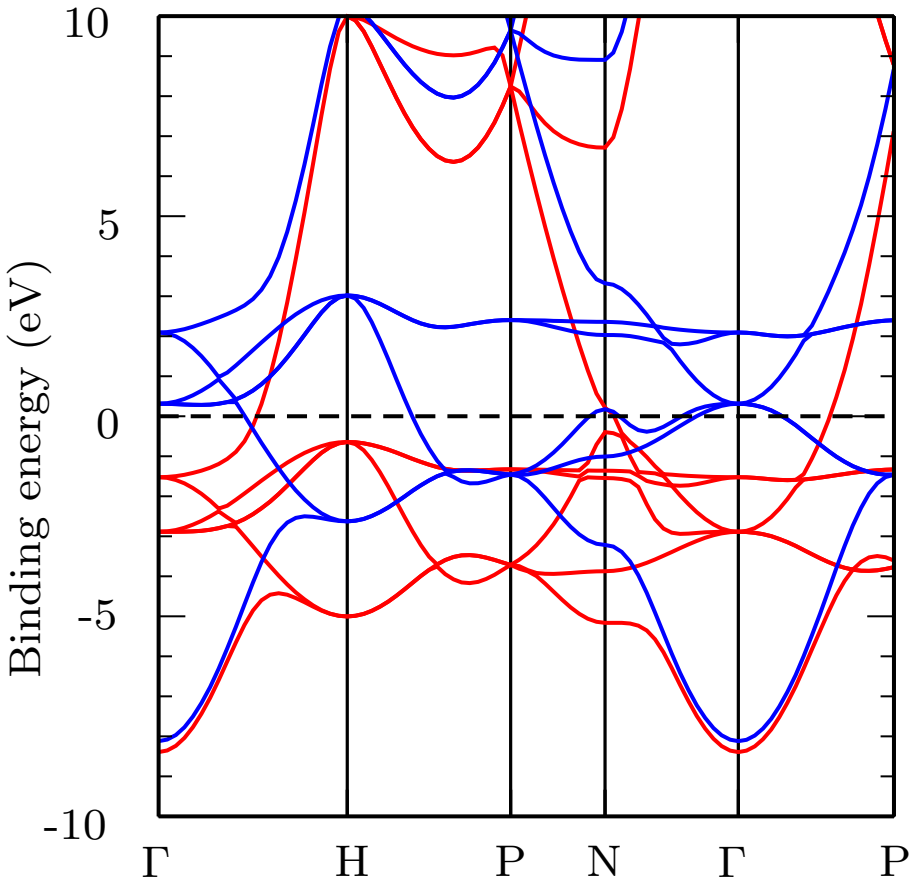
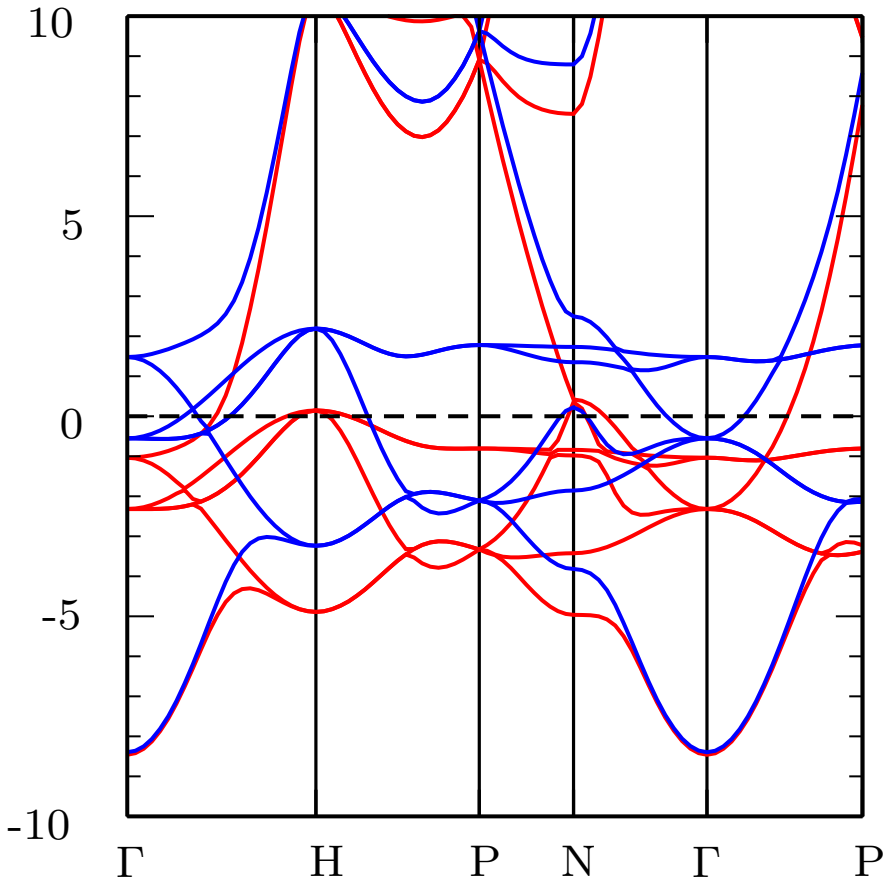
Magnetic moment of Iron



(a) $r_a = 1.5$ a u , $M = 2.59\ \mu_{\mathrm{B}}$



(b) $r_a = 1.0$ a u , $M = 2.19\ \mu_{\mathrm{B}}$

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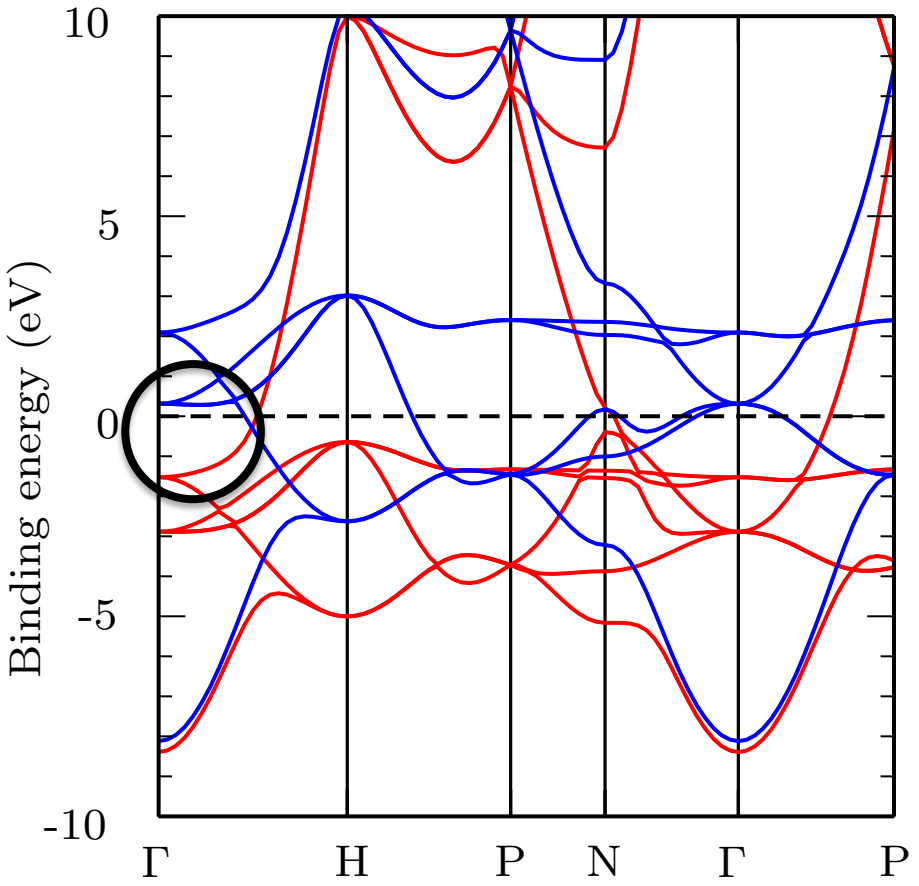
Magnetic moment of Iron



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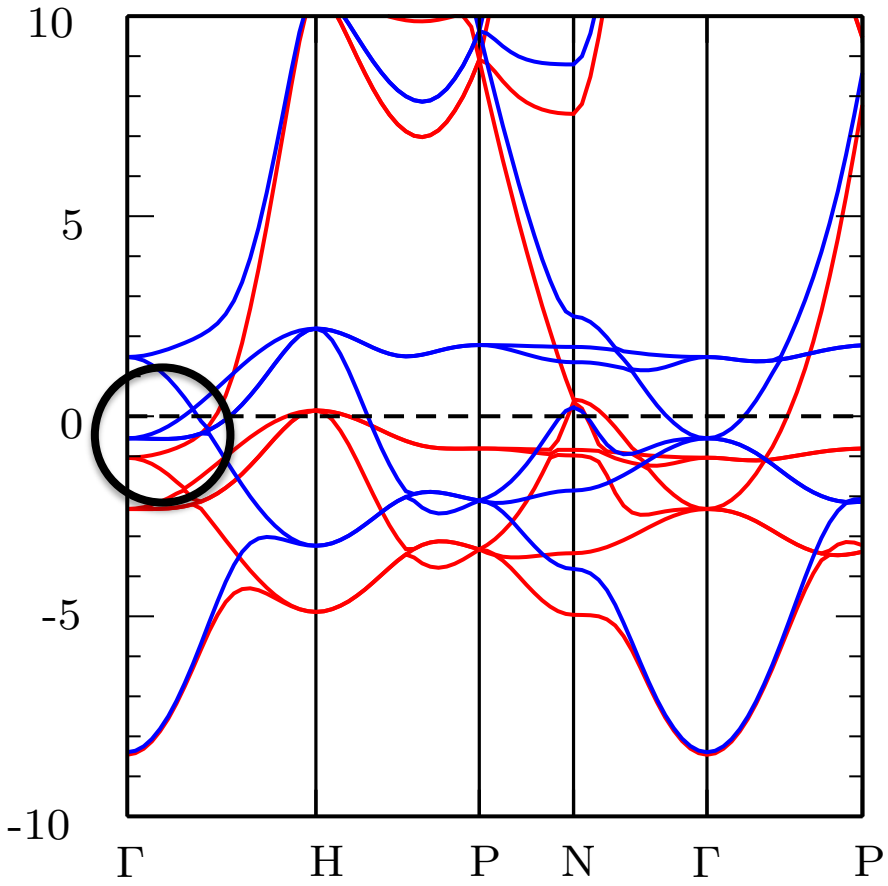

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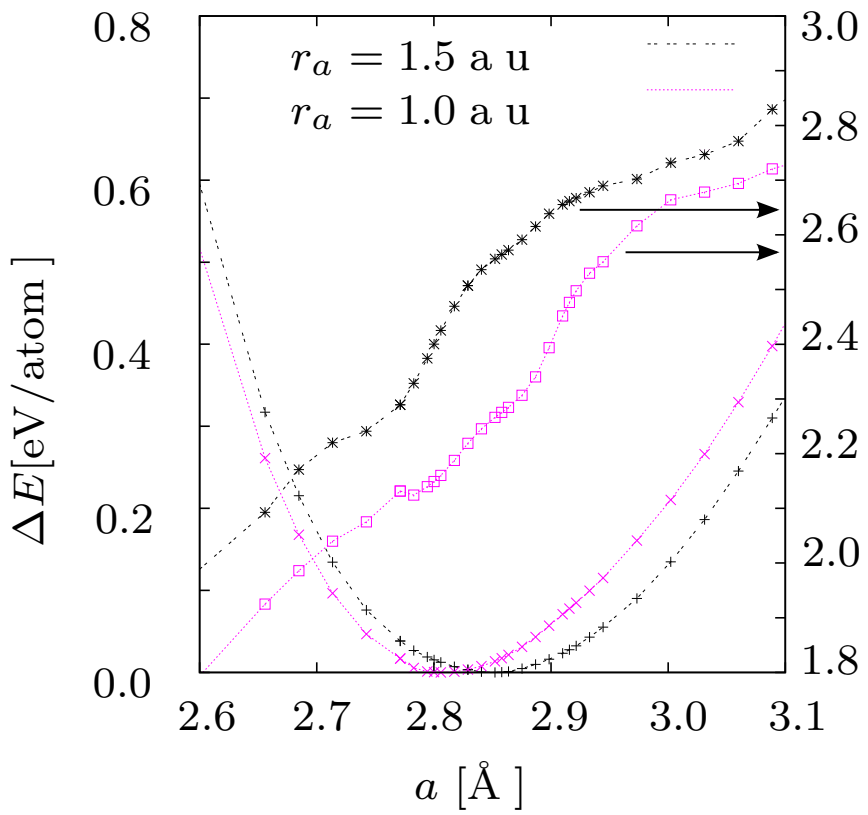
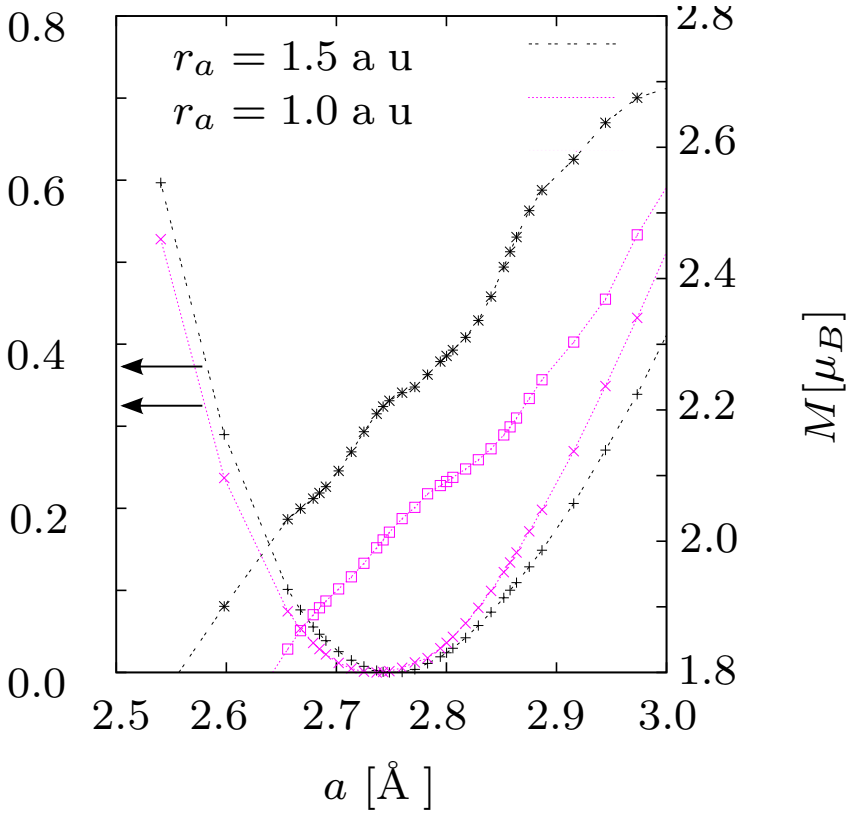
Magnetic Moment of Iron



a) PBE functional



b) LDA functional

Computing Materials Properties Using Pseudopotentials II

- Some materials properties are strongly dependent on core electron density and Kohn-Sham wavefunctions e.g. NMR.
- Computing these properties from PP computations requires the core electron density to be reconstructed.
- In this case a *projector-augmented wave* (PAW) method is used to effectively generate a core electron density from which materials properties can be computed.

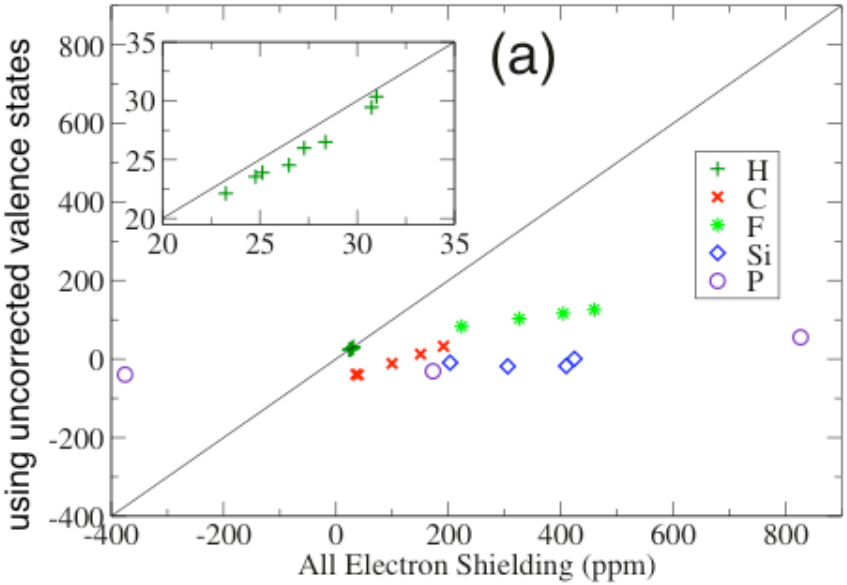
GIPAW

A theory for solid-state NMR

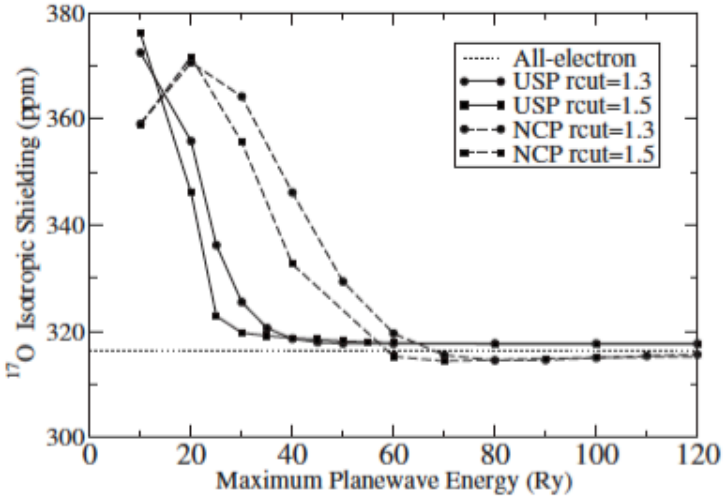
GIPAW vs Gaussian

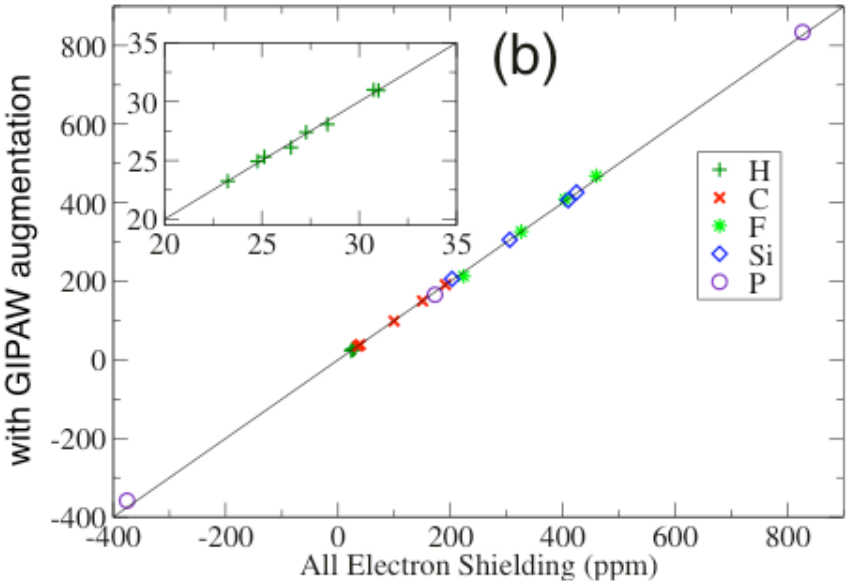
test on small molecules
n.b. v. big Gaussian basis sets

JRY, C. Pickard, F. Mauri PRB 76, 024401 (2007)



Convergence of shielding with #planewaves





Testing Pseudopotentials

1. Atomic Tests

2. Solid State Tests

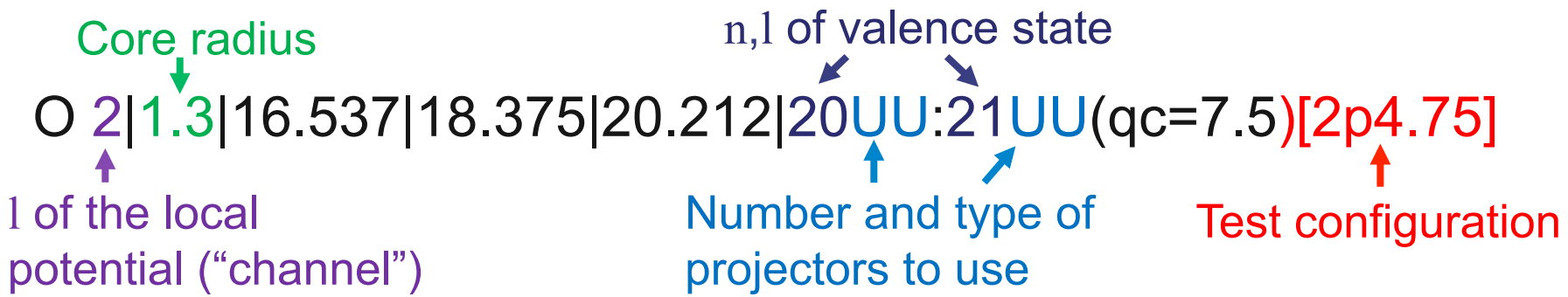
3. ‘Delta Project’

Atomic Tests

- Requires the software used to generate the PP and the input files/ parameters.
- Simple checks that can be performed – check the eigenvalues of AE and PS atom match.
- Check the transferability by testing with a configuration that differs from the reference configuration.

Testing using CASTEP

- CASTEPs PP generator can be used to perform atomic tests for the PP.
- Add [] at the end of the PP string to print files to plot beta projectors, potentials and how the energy varies with plane wave cut off.
- Put an alternative configuration in the [] to test the pseudopotential at that alternative configuration



Solid State Tests

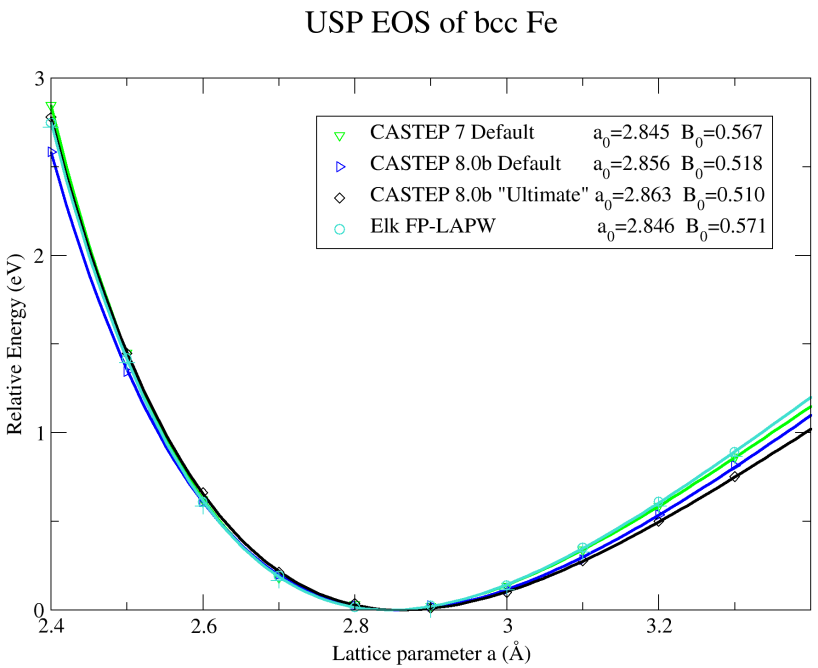
- Lattice parameters (good start, but not sufficient).
- Phonons (good test)
- Birch-Murnaghan plot – compressibility equation of state (good test)
- Stringent (but expensive) test is the cohesive energy of solid.

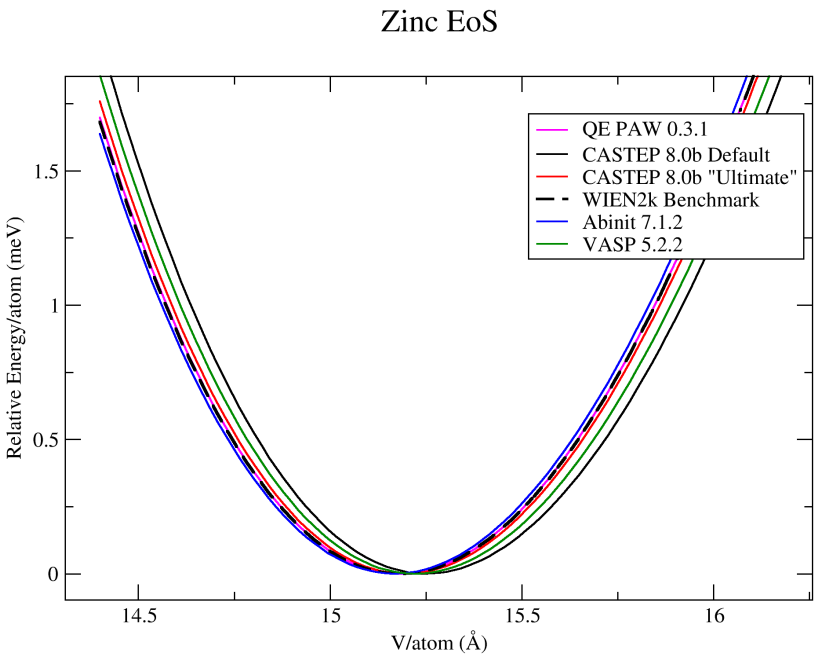
Delta Project

Stefaan Cottenier's Delta Project compares the results of various DFT implementations including the pseudopotentials.

The Delta Project can be found online at:

https://molmod.ugent.be/deltacodesdft





CASTEP PP library results

PP Library	Delta (meV/ Atom)
OTFG.cell	1.47
Library .usp files	7.85
CASTEP 8.0 internal defaults (ongoing)	Currently 0.91

- Comparable with the best libraries in other codes.
- Internal PP generator is typically better than file libraries – though the library error is overstated due to very few very poor pseudopotentials.
- Delta value is a good headline figure, but it hides important detail. Don’t pay too much attention to it.

Need for semi-core states

- Partitioning electrons into core and valence is artificial.
- Small energy separation between core and valence usually means *semi-core* states (e.g. partly-filled 3*d*) must be treated as valence in PP.
- This can cause a problem if only one reference energy is used – easier if more than 1 projector is used for each angular momentum channel.

Recap

- Poor pseudopotentials lead to poor results, but can usually be identified.
- Make sure the tests performed use all electron calculations as a reference, test the pseudopotential, not the XC functional/DFT.
- Atomic tests – check eigenvalues, transferability (different configuration)
- Solid state tests – lattice parameters are a start but insufficient. Phonons are excellent, Birch-Murnaghan compression parameters are very good.
- Remember to check vs**. all-electron results** with the same functional, rather than experiment.

On-the-fly PPs

- CASTEP has a built in pseudopotential generator which can construct ultrasoft or norm-conserving pseudopotentials.
- Each atom has a default which CASTEP will use if you do not specify a pseudopotential.
- The CASTEP 8.0 or 9.0 default strings are the new recommended standard.
- Properties which require information about the core region electrons require OTF pseudopotentials.
  - Magnetic resonance properties
  - Core loss spectroscopy

- For more information about CASTEP's on the fly pseudopotentials, see www.castep.org/CASTEP/Pseudopotentials

Norm Conserving OTF Pseudopotentials

- New for version 9.0 is a library of internal norm conserving pseudopotentials.
- This is **not** automatically used for functionality that requires norm conserving potentials.
- If you need to use NC potentials add the following block to your .cell input file.

```
%block species_pot
      NCP
%end_block species_pot
```

- To just use the Norm Conserving library for a particular atom use, e.g. to use a Norm Conserving PP for carbon.

```
%block species_pot
      C NCP
%end_block species_pot
```

Where to get PPs

Libraries distributed with CASTEP

- Norm-conserving library (1990s) xx_00.recpot

LDA-only. Comprehensive coverage of periodic table (except *f*-block). Moderate accuracy, with some poor, but well documented. Supplied along with commercial and academic CASTEP.

- New norm-conserving library (2010-) xx_OP_00PBE.recpot

LDA and PBE-GGA. Sporadic coverage of elements. Higher accuracy and transferability. Supplied along with commercial and academic CASTEP.

- Rappe and Bennett library http://opium.sourceforge.net.

Norm-conserving with DNL. Good accuracy. Reasonable converage of elements. LDA and PBE-GGA. .recpot version downloadable from http://ccpforge.cse.rl.ac.uk/gf/project/castep/

- Vanderbilt USP library (1995-) xx_00.usp

LDA and PBE-GGA. Comprehensive coverage of periodic table. Mostly reasonable accuracy with occasional exceptions (Fe_00.uspcc). Supplied along with CASTEP (commercial and academic).

Programs to generate PPs

- fhi98pp - http://th.fhi-berlin.mpg.de/th/fhi98md/fhi98PP/
  TM, Hamman
- OPIUM - http://opium.sourceforge.net RRJK, TM, Kerker
- Vanderbilt USP code -
  http://www.physics.rutgers.edu/~dhv/uspp/ USP

- CASTEP - USP, TM

Finding PPs for your calculation

- Use ultrasoft PPs when you can.
- To be confident the pseudopotential is satisfactory you should test the pseudopotential vs. a comparable all-electron calculation.
- If the PP from the CASTEP libraries aren't good enough, post to the CASTEP mailing list. We want the defaults in CASTEP to be good for the vast majority of calculations.

Conclusions

- Pseudopotentials are used in CASTEP to reduce the number of basis functions required.
- Choice of PP is important as a poor PP leads to poor calculation however the defaults and otfg.cell supplied with CASTEP are generally good.
- Using USPs is recommended when applicable to your computation.
- PPs should be tested vs. comparable all electron computations.