Vanderbilt Ultrasoft Pseudopotentials

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Introduction

- General overview of pseudopotentials
- The Vanderbilt Scheme
- Further wrinkles
- Perspectives - relationships
- CASTEP/MSI database

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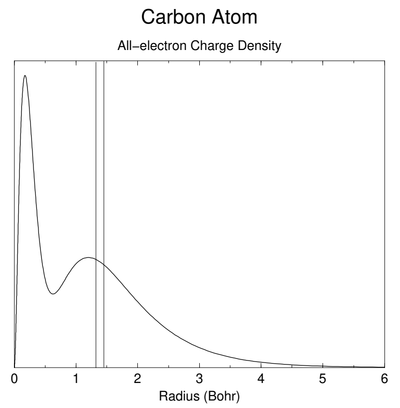
Core and Valence electrons

- Core electrons don't take part in bonding (definition!)



Level	Energy(Ry)	Occupation
1s	-19.90408	2.000
2s	-1.00279	2.000
2p	-0.39838	2.000

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Pseudopotentials

- Too many planewaves needed for core states, and related orthogonality
- Physical properties depend on valence electrons - throw away cores
- Pseudopotential constructed so that
  - Scattering properties preserved
  - Potential and Ψ identical outside core
  - Norm conserved (can be relaxed)
- Transferability . . .
- Local/Non-local and realspace potentials . . .

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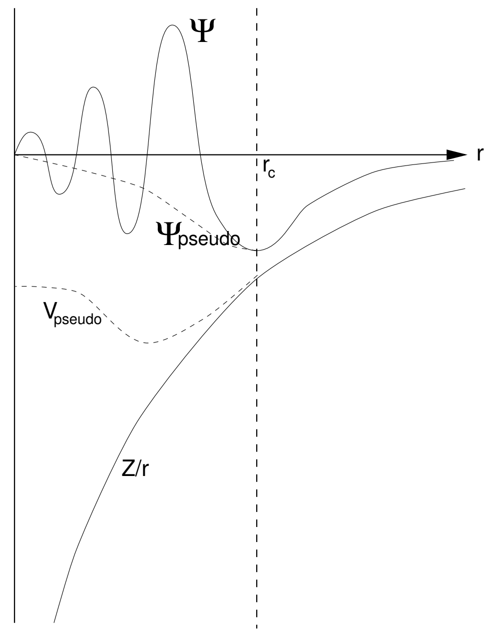
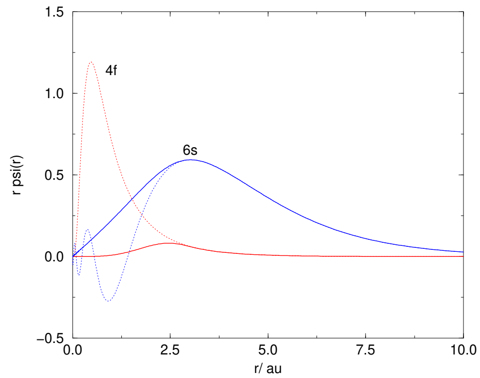


Ultrasoft Pseudopotentials

- Relax norm conservation - soft for 2p,3d,4f
- Augment - to replace lost charge
- Multiple projectors at any energy
- Accurate, soft and transferable



Pseudized and all electron valence states for Lutetium

Pseudopotentials

- General idea
  - lowest calculated electronic states are optimally smooth (wrt a given basis)
  - smoothness obtained by (approximate) freedom to change wavefunctions near the nucleus without changing the chemistry
- Long history in physics — and chemistry
- Empirical
  - fit to optical data for semiconductors
- First principles
  - fit to atomic reference calculations
- Most modern and general used by the physics community — Vanderbilt's Ultrasoft Pseudopotentials

The Kohn-Sham Equations

We start with an expression for the total energy

$$\begin{aligned} E_{tot}[\{\phi_i\},\{\mathbf{R}_I\}] &= \sum_i \langle \phi_i | -\nabla^2 + V_{NL} | \phi_i \rangle \\ &+ \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n] \\ &+ \int d\mathbf{r} V_{loc}^{ion}(\mathbf{r})n(\mathbf{r}) + U(\{\mathbf{R}_I\}) \end{aligned}$$

The non-local potential is given by,

$$V_{NL} = \sum_{nm,I} D^{(0)}_{nm} |\beta^I_n\rangle\langle\beta^I_m|,$$

and the projectors depend on the ionic positions,

$$\beta^I_n = \beta_n(\mathbf{r}-\mathbf{R}_I).$$

The total charge density is written as,

$$n(\mathbf{r}) = \sum_i [|\phi_i(\mathbf{r})|^2 + \sum_{nm,I} Q^I_{nm}(\mathbf{r})\langle\phi_i|\beta^I_n\rangle\langle\beta^I_m|\phi_i\rangle].$$

In this scheme, there is no requirement that the wavefunctions are normalised, and so the orthonormalisation condition is generalised:

$$\langle\phi_i|S(\{\mathbf{R}_I\})|\phi_j\rangle = \delta_{ij},$$

where

$$S = 1 + \sum_{nm,I} q_{nm}|\beta^I_n\rangle\langle\beta^I_m|,$$

and

$$q_{nm} = \int d\mathbf{r} Q_{nm}(\mathbf{r}).$$

The ground-state wavefunctions minimise E_{tot} subject to the ortho-norm condition:

$$\frac{\delta E_{tot}}{\delta\phi^*_i(\mathbf{r})} = \varepsilon_i S\phi_i(\mathbf{r})$$

The $\{\varepsilon_i\}$ are introduced as Lagrange multipliers. However, the augmentation depends on the $\{\phi_i\}$, hence we get some extra terms.

$$\frac{\delta n(\mathbf{r}')}{\delta\phi^*_i(\mathbf{r})} = \phi_i(\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}) + \sum_{nm,I} Q^I_{nm}(\mathbf{r}')\beta^I_n(\mathbf{r})\langle\beta^I_m|\phi_i\rangle$$

As an example, the E_{xc},

$$\begin{aligned}\frac{\delta E_{xc}[n]}{\delta\phi^*_i(\mathbf{r})} &= \int d\mathbf{r}'\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r}')}\frac{\delta n(\mathbf{r}')}{\delta\phi^*_i(\mathbf{r})} \\ &= \mu_{xc}(\mathbf{r})\phi_i(\mathbf{r}) \\ &\quad + \sum_{nm,I}\beta^I_n(\mathbf{r})\langle\beta^I_m|\phi_i\rangle\int d\mathbf{r}'\mu_{xc}(\mathbf{r}')Q^I_{nm}(\mathbf{r}'),\end{aligned}$$

where

$$\mu_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}.$$

Finally we arrive at,

$$H|\phi_i\rangle = \varepsilon_i S|\phi_i\rangle,$$

where

$$H = -\nabla^2 + V_{eff} + \sum_{nm,I} D^I_{nm}|\beta^I_n\rangle\langle\beta^I_m|,$$

and

$$V_{eff}(\mathbf{r}) = \frac{\delta E_{tot}}{\delta n(\mathbf{r})} = V^{ion}_{loc}(\mathbf{r}) + \int d\mathbf{r}'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \mu_{xc}(\mathbf{r}).$$

The terms from the augmented part of the density are grouped with V_{NL}:

$$D^I_{nm} = D^{(0)}_{nm} + \int d\mathbf{r} V_{eff}(\mathbf{r})Q^I_{nm}(\mathbf{r})$$

Generating the pseudopotentials

First, do an all electron atomic calculation — in a chosen reference configuration. The resulting screened potential is V_{AE}. Then solve the Schrödinger equation for a set of chosen ε_n (*not* necessarily eigenvalues).

$$[T + V_{AE}(\mathbf{r})]\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r}),$$

or,

$$(T + V_{AE} - \varepsilon_n)|\psi_n\rangle = 0.$$

Then *pseudise* the wavefunctions to produce a set $\{\phi_n\}$. This means, change the wavefunctions within a given r_{cl} so they are as smooth as possible, subject to smoothly joining $\{\psi_n\}$ at r_{cl}. Also, generate a smooth V_{loc}, matching the V_{AE} beyond r^{loc}_c.

Then form,

$$|\chi_n\rangle = (\varepsilon_n - T - V_{loc})|\phi_n\rangle,$$

$$B_{nm} = \langle\phi_n|\chi_m\rangle,$$

$$Q_{nm}(\mathbf{r}) = \psi_n^*(\mathbf{r})\psi_m(\mathbf{r}) - \phi_n^*(\mathbf{r})\phi_m(\mathbf{r}),$$

and the projectors,

$$|\beta_n\rangle = \sum_m (B^{-1})_{mn}|\chi_m\rangle.$$

$$q_{nm} = \langle\psi_n|\psi_m\rangle_R - \langle\phi_n|\phi_m\rangle_R$$

The $|\phi_n\rangle$ then obey the secular equation,

$$\left(T + V_{loc} + \sum_{nm} D_{nm}|\beta_n\rangle\langle\beta_m|\right)|\phi_i\rangle = \varepsilon_i\left(1 + \sum_{nm} q_{nm}|\beta_n\rangle\langle\beta_m|\right)|\phi_i\rangle,$$

where,

$$D_{nm} = B_{nm} + \varepsilon_m q_{nm}, \;\langle\beta_n|\phi_m\rangle = \delta_{nm}$$

It finally remains to descreen the local potential, and non-local coefficients.

$$V_{loc}^{ion}(\mathbf{r}) = V_{loc}(\mathbf{r}) - \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \mu_{xc}(\mathbf{r})$$

$$D_{nm}^{(0)} = D_{nm} - \int d\mathbf{r} V_{loc}(\mathbf{r}) Q_{nm}(\mathbf{r})$$

Dealing with the augmentation

The following relationship between the cutoff for the charge and wavefunctions doesn't hold.

$$E_c^{dens} = 4E_c^{wf}$$

$$Q_{nm}(\mathbf{r}) = \sum_{LM} c_{LM}^{nm} Y_{LM}(\hat{r}) Q_{nm}^{rad}(r)$$

$$Q_{nm}(\mathbf{r}) = \sum_{LM} c_{LM}^{nm} Y_{LM}(\hat{r}) Q_{nm}^{L}(r)$$

$$\int_0^{r_{in}^L} r^2 dr\; r^L Q_{nm}^L(r) = \int_0^{r_{in}^L} r^2 dr\; r^L Q_{nm}^{rad}(r)$$

… and there is more

- Exchange correlation functionals
  - in principle, different potentials needed for different functionals
  - in practice, we just tend to use LDA potentials in all cases
  - not too bad — due to descreening procedure
- Non-linear core corrections
  - despite being frozen — the core charge has a non-linear effect on the $E_{xc}[n]$
- Double grid techniques
  - efficient treatment of the "hard" charge density
- Real-space projections
  - the projectors, $|\beta\rangle$, are localised
  - if the projection is done in realspace, only over the non-zero region of each projector, N^2 scaling is obtained

- Forces and stresses
  - extra terms due to charge augmentation and $S \neq I$
- Optimisation
  - pseudise using a basis within r_c
  - maximise smoothness, subject to constraints
  - linear problem, Lagrange multipliers

Choices ...

- Core — Valence
- All electron solver
- Exchange-correlation
- Reference energies
- Number of projectors
- Local channel
- Core radii : projector, local and charge
- Pseudisation parameters — optimisation

Perspectives

- Blöchl has introduced the Projector Augmented Wave (PAW) approach to electronic structure calculations
- PAW is an all electron technique, and Blöchl shows the connection between PAW, LAPW, and the various flavours of pseudopotentials schemes
- At the same time he gives a recipe for extracting all electron properties from the pseudo-wavefunctions
- Recently, Kresse has numerically investigated the relationships between PAW and the Vanderbilt scheme

CASTEP/MSI Database

- (Nearly) whole periodic table represented
- All generated with LDA
- Contributions from Ming-Hsien Lee *et al*, Vanderbilt and CJP
- All (I think) potentials have tested on 2 or more compounds
- NLCC potentials available for some elements
- Some more "agressive" potentials also supplied
- Despite testing ...
  - some errors have been found (H_00.usp)
  - the potentials were not intended to be optimal - but hopefully safe
  - serious users should at least test the potentials needed for their project
  - or consider generating potentials themselves

Recommended reading

- David Vanderbilt, Soft self-consistent pseudopotentials in a generalised eigenvalue formalism, PRB 1990 **41** 7892

- Kari Laasonen *et al*, Car-Parinello molecular dynamics with Vanderbilt ultrasoft pseudopotentials, PRB 1993 **47** 10142

- P.E. Blöchl, Projector augmented-wave method, PRB 1994 **50** 17953

- G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, PRB 1999 **59** 1758