Theory of Pseudopotentials

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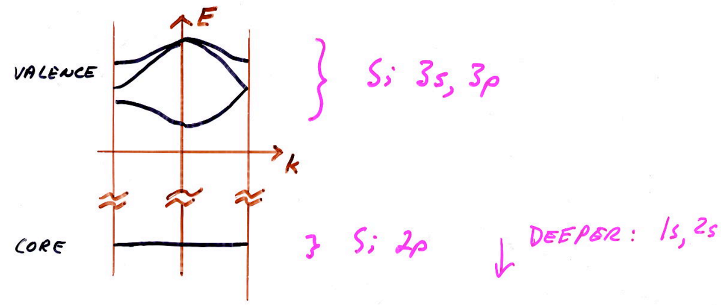
Outline of Talk

- Introduction
  - Motivation
  - Basic Idea
  - History and Terminology
- First-Principles Pseudopotentials
  - Construction
  - Scattering Properties
  - Norm Conservation
  - Transferability Tests
  - Relativistic Case
  - Computational Considerations: Softness
- Ultrasoft Pseudopotentials and PAW
- Resources
  - Reference list
  - Web resources

Motivation

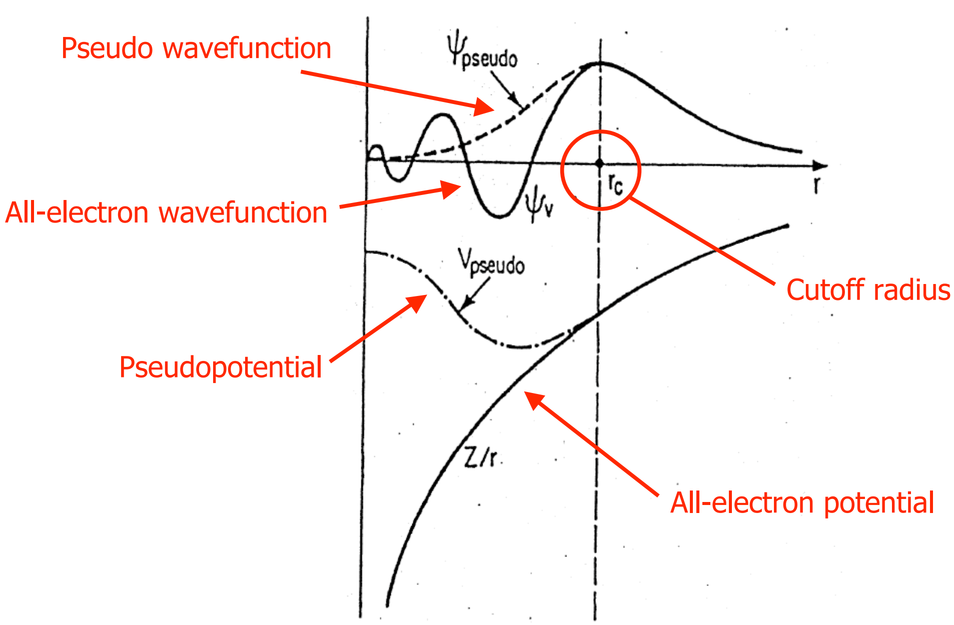
Bandstructure of Si:



If core states are included:

- More bands to solve for
  - But core states are essentially inert!
- Need much larger $N_{\rm PW}$ for each band
  - Because of core wiggles
  - Example: Si $3s$

Basic idea of pseudopotentials



Pseudopotentials: History

Early history of pseudopotentials

- Phillips and Kleinman, 1959
  - Based on OPW formalism
- Empirical pseudopotentials, 1970's
  - For use in non-selfconsistent bandstructure calculations
  - See, e.g., Chelikowsky and Cohen
- Model pseudopotentials, late 1970's
  - For use in DFT calculations
  - Not exact by construction for any property
  - Usually local
- First-principles pseudopotentials, 1979–present
  - Usually semilocal or nonlocal

Pseudopotentials: Terminology

Local PSP

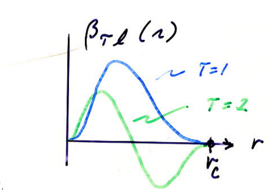
$$\hat{V}_{\rm ps} = V_{\rm ps}(r) \qquad \text{(local in } r,\ \theta,\ \phi)$$

Semilocal PSP

$$\hat{V}_{\rm ps} = \sum_l V_{\rm ps}^{(l)}(r)\,\hat{P}_l \qquad \text{(local in } r\text{, nonlocal in } \theta,\ \phi)$$

Nonlocal separable PSP (e.g., Kleinman-Bylander)

$$\hat{V}_{\rm ps} = V_{\rm ps}^{\rm loc}(r) + \sum_{lm} D_l \,|\,\beta_{lm}\,\rangle\langle\,\beta_{lm}\,|$$



General nonlocal separable PSP

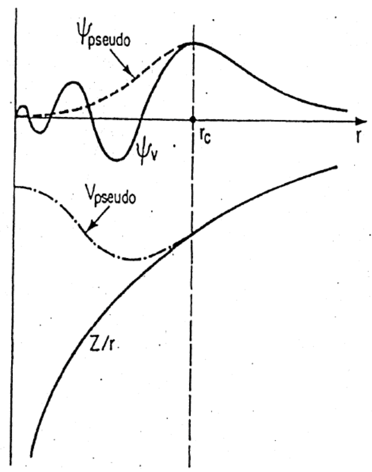
$$\hat{V}_{\rm ps} = V_{\rm ps}^{\rm loc}(r) + \sum_{\tau\tau'}\sum_{lm} D_{\tau\tau' l}\,|\,\beta_{\tau lm}\,\rangle\langle\,\beta_{\tau' l}$$

(Note: All are spherically symmetric.)

Pseudopotentials: Terminology

Local PSP

$$\hat{V}_{\rm ps} = V_{\rm ps}(r) \qquad \text{(local in } r, \theta, \phi\text{)}$$

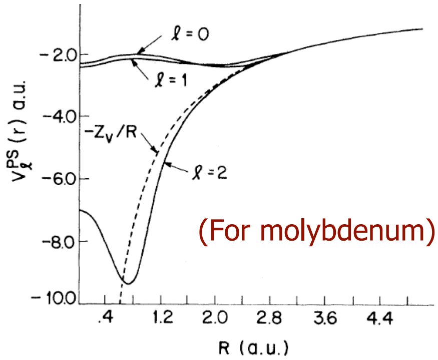


s, *p*, and *d* electrons
all feel the same potential

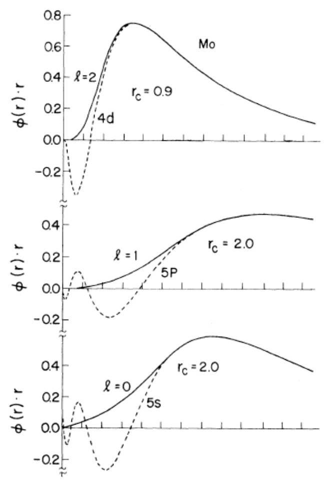
Pseudopotentials: Terminology

Semilocal PSP

$$\hat{V}_{\rm ps} = \sum_l V_{\rm ps}^{(l)}(r)\, \hat{P}_l \qquad \text{(local in } r, \text{ nonlocal in } \theta, \phi\text{)}$$



(For molybdenum)



s, *p*, and *d* electrons
feel different potentials

Pseudopotentials: Terminology

<u>Nonlocal separable PSP</u> (e.g., Kleinman-Bylander)

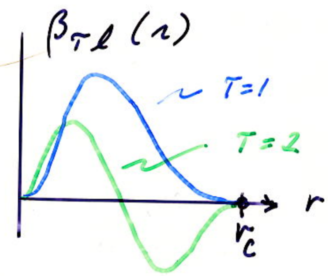
$$\hat{V}_{\rm ps} = V_{\rm ps}^{\rm loc}(r) + \boxed{\sum_{lm} D_l \,|\, \beta_{lm} \,\rangle\langle\, \beta_{lm} \,|}$$

<u>General nonlocal separable PSP</u>

$$\hat{V}_{\rm ps} = V_{\rm ps}^{\rm loc}(r) + \boxed{\sum_{\tau\tau'} \sum_{lm} D_{\tau\tau' l} \,|\, \beta_{\tau lm} \,\rangle\langle\, \beta_{\tau' lm} \,|}$$

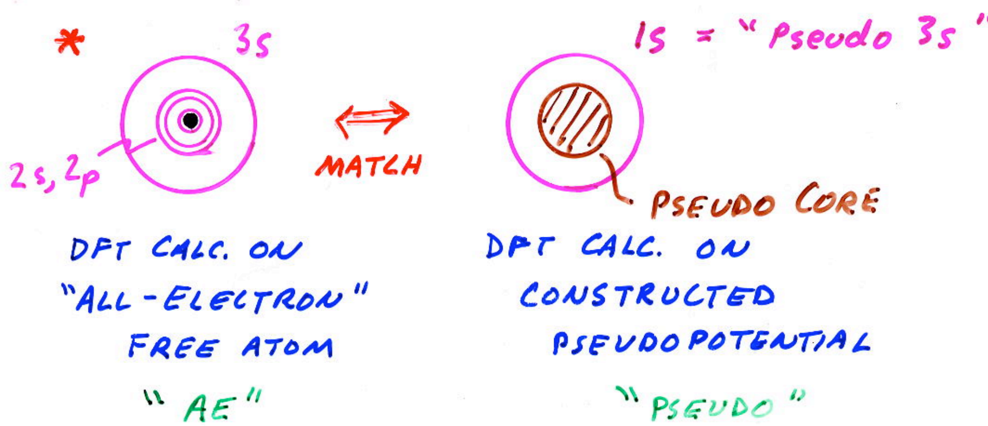
These terms vanish outside r_c

s, *p*, and *d* electrons feel different nonlocal operators



First-principles pseudopotentials

<u>Philosophy:</u>



First-principles pseudopotentials

First-principles pseudopotentials: History

- Zunger & Cohen, Starkloff & Joannoupoulos, Kerker: ∼1978
- Hamann, Schlüter & Chang, 1979
- Separability
  - Kleinman & Bylander, 1982
- Smoothness
  - Vanderbilt, 1985
  - Rappe, Rabe, Kaxiras & Joannopoulos, 1990
  - Troullier & Martins, 1991
- Ultrasoft pseudopotentials
  - Vanderbilt, 1990
- Projector-augmented-wave (PAW) potentials
  - Blöchl, 1994

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First-principles PSP construction

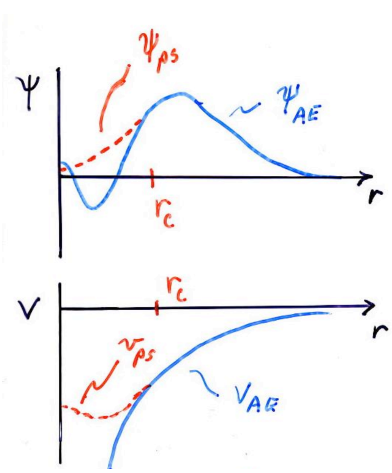
- Use "atomic DFT program"
  - $\psi_{nlm}(\mathbf{r}) = R_{nl}(r)\,Y_{lm}(\theta,\phi)$
  - Works entirely with $R_{nl}(r)$ on radial grid
- Ignore self-consistency for the moment
- Match:

Given:
$$\left[-\frac{1}{2m}\frac{d^2}{dr^2}+\frac{l(l+1)}{2mr^2}+\boxed{V_{\rm ae}(r)}-\epsilon_{nl}\right]\boxed{\psi^{\rm ae}_{nl}(r)}=0$$

Same for $r > r_c$

Invent:
$$\left[-\frac{1}{2m}\frac{d^2}{dr^2}+\frac{l(l+1)}{2mr^2}+\boxed{V_{\rm ps}(r)}-\epsilon_{nl}\right]\boxed{\psi^{\rm ps}_{nl}(r)}=0$$

First-principles PSP construction



Beyond r_c :

$\psi_{AE}(r) \rightarrow \psi_{PS}(r)$

$V_{AE}(r) \rightarrow V_{PS}(r)$

Also

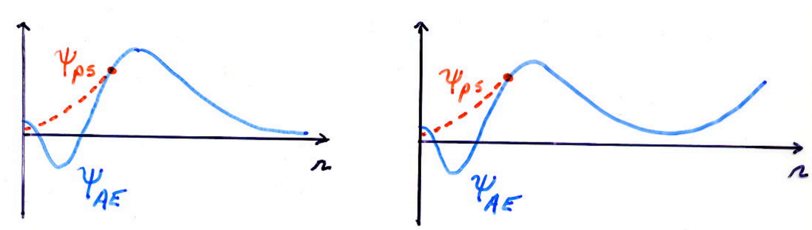
$\varepsilon_{AE} = \varepsilon_{PS}$

First-principles PSP construction

- By construction, $V_{\rm ps}$ has correct ϵ_{nl}.
  - Scattering properties are correct at ϵ_{nl}
- Also want:
  - Norm conservation
  - Scattering properties remain pretty good for nearby ϵ_{nl}
- Surprising result of Hamann, Schlüter & Chang:
  - These two properties come together!
  - Norm-conserving PSPs have good scattering properties!
- Define these concepts:

Scattering properties

- For AE and PS separately:
  - Choose channel l and energy ε
  - Find solution of SE that is regular at the origin at this ε
- Compare beyond r_c
- If match $\Rightarrow$ "good scattering properties"

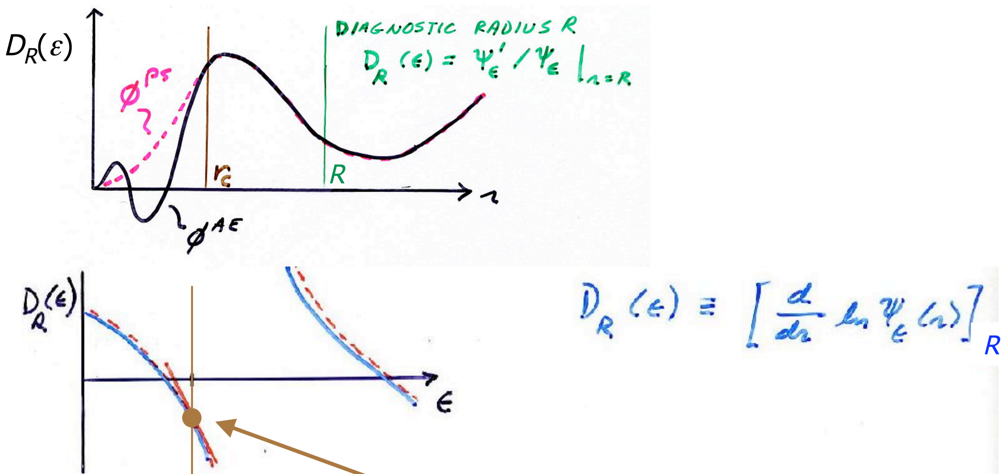


$\varepsilon = \varepsilon_{bound}$ (Used for construction)

$\varepsilon > \varepsilon_{bound}$ (Used for testing)

Scattering properties

Quantify: "Logarithmic derivatives" $D_R(\varepsilon)$

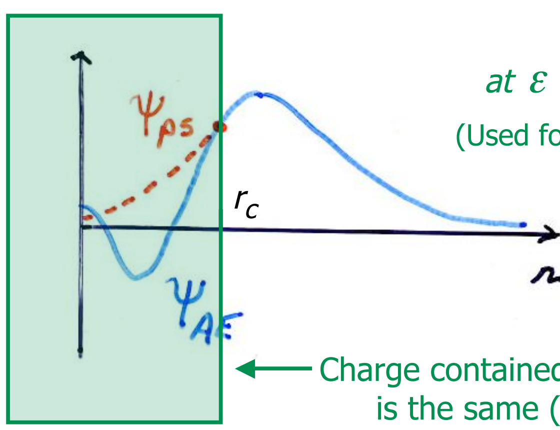


ε_{bound} Correct by construction at ε_{bound}

Norm conservation

- Norm conservation:

$$\int_0^{r_c} r^2 \left|\psi_{nl}^{\mathrm{ps}}(r)\right|^2 dr = \int_0^{r_c} r^2 \left|\psi_{nl}^{\mathrm{ae}}(r)\right|^2 dr$$



at $\varepsilon = \varepsilon_{bound}$

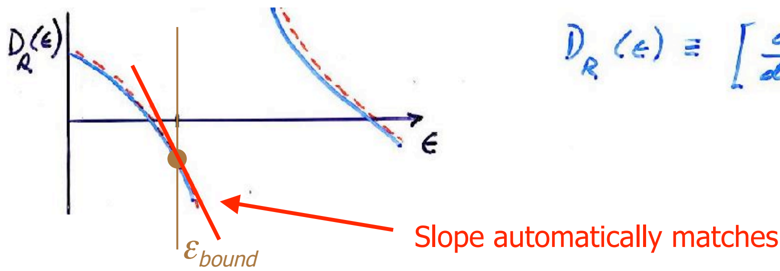
(Used for construction)

Charge contained in this region is the same (AE vs. PS)

Norm conservation ⇔ Scattering properties

Fundamental advance of Hamann, Schlüter and Chang, 1979:

> If norm conservation is imposed, then pseudo $D_R(\varepsilon)$ matches all-electron $D_R(\varepsilon)$ to second order in ($\varepsilon - \varepsilon_{bound}$)



$$D_R(\epsilon) \equiv \left[\frac{d}{dr} \ln \psi_\epsilon(r)\right]_R$$

First-principles PSP construction

Typical construction algorithm for semilocal pseudopotential

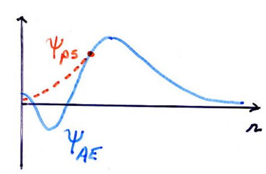
- Pick reference configuration

  E.g., for Si: $[1s^2 2s^2 2p^6] 3s^2 3p^2$

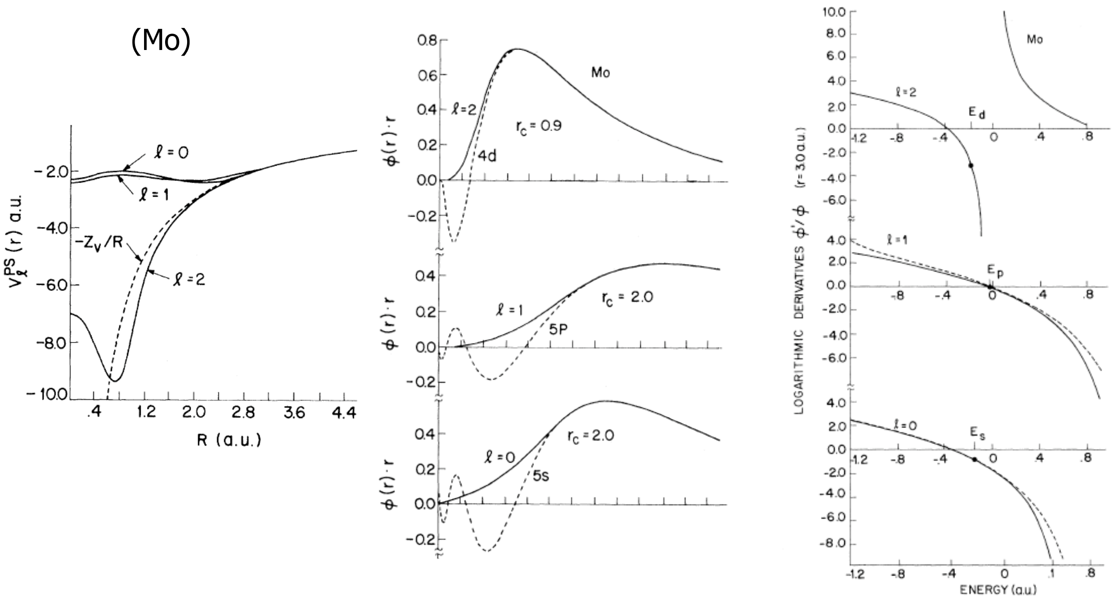
- Solve all-electron problem $\to V^{\rm ae}_{\rm scr}(r)$, $\psi^{\rm ae}_{nl}(r)$

- For each angular momentum channel l:

  1. Construct $\psi_{\rm ae}(r) \to \psi_{\rm ps}(r)$
     - Nodeless
     - Joins smoothly at r_c
     - Obeys norm conservation
  2. Invert Schroedinger equation to get $V^{\rm ps}_{{\rm scr},l}(r)$
  3. Descreen to obtain $V^{\rm ps}_{{\rm ion},l}(r)$
  4. Export $V^{\rm ps}_{{\rm ion},l}(r)$ for tests and applications



Example: Hamann, Schlüter, and Chang (Semilocal PSP), 1979



Charge self-consistency in PSP construction

Unscreening

- Construct $n_{\rm ps}(r) = \sum_l f_l\, |\psi_l^{\rm ps}(r)|^2$

  where f_l is shell occupancy (e.g., 4 for p shell of oxygen)
- Obtain $V_{\rm Hxc}^{\rm ps}(r)$ from $n_{\rm ps}(r)$
- For each l, set $V_{{\rm ion},l}^{\rm ps}(r) = V_{{\rm scr},l}^{\rm ps}(r) - V_{\rm Hxc}^{\rm ps}(r)$

In target calculation

- $V_{\rm ion}(\mathbf{r}) = \sum_I \sum_l V_{{\rm ion},l}^{\rm ps}(\mathbf{r} - \mathbf{R}_I)$
- $V = V_{\rm ion} + V_{\rm Hxc}[n]$ where $n(\mathbf{r}) = \sum_{n\mathbf{k}} f_{n\mathbf{k}}\, |\psi_{n\mathbf{k}}^{\rm ps}(\mathbf{r})|^2$
- Solve Schrödinger equation to obtain new $\psi_{n\mathbf{k}}^{\rm ps}(\mathbf{r})$ and repeat

(This procedure guarantees the desired result if the target is the free atom in its reference configuration.)

Transferability tests

- PSP was generated in "reference configuration", e.g.:
  [core]s^2p^2 for Si
- Now, pick a couple of excited configurations, e.g.:
  [core]sp^3
  [core]s^2p (+1 ion)
- For each excited configuration, compare:
  All-electron calculation
  Pseudopotential calculation using previously generated PSP
- Points of comparison:
  – Total energies
  – Energy eigenvalues
  – Logarithmic derivatives

Transferability tests

Example: HSC pseudopotential for oxygen

State		AE	HSC
s^1p^5	s	-1.7662	-1.7649
	p	-0.6981	-0.6982
	ΔE_{tot}	1.0658	1.0651
s^0p^6	s	-1.7987	-1.7957
	p	-0.7262	-0.7261
	ΔE_{tot}	2.1361	2.1331
s^2p^3	s	-2.8738	-2.8737
	p	-1.7909	-1.7904
	ΔE_{tot}	1.2066	1.2065

Relativisitic pseudopotentials

- Do all-electron calculation on free atom using Dirac equation
- Obtain $\psi_{nlj}(r)$ for $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$
- Invert Schrödinger equation to get $V^{\rm ps}_{lj}(r)$
- For "scalar relativistic" target calc., use j-averaged PSPs:

$$V^{\rm ps}_l(r) = \frac{1}{2l+1}\left[(l+1)\,V^{\rm ps}_{l,l+\frac{1}{2}} + l\,V^{\rm ps}_{l,l-\frac{1}{2}}\right]$$

- For spin-orbit interactions, keep also

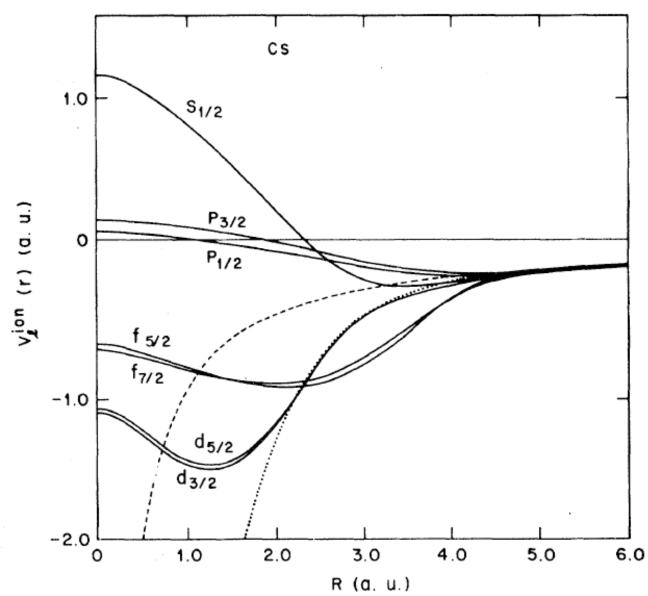
$$V^{\rm so}_l(r) = \frac{1}{2l+1}\left[V^{\rm ps}_{l,l+\frac{1}{2}} - V^{\rm ps}_{l,l-\frac{1}{2}}\right]$$

and use, schematically speaking,

$$\hat{V}_{\rm ps} = \sum_l |\,l\,\rangle\;\left[V^{\rm ps}_l(r) + V^{\rm so}_l(r)\,\mathbf{L}\cdot\mathbf{S}\right]\;\langle\,l\,|$$

Relativisitic pseudopotentials

Bachelet, Hamann & Schluter, PRB 26, 4199 (1982)



Issues of computational expense

- The expense is in the target calculation
  (PSP construction is extremely cheap)
- First consideration:
  - Compatibility with FFT approach to $H\psi$?

$$
\begin{tikzcd}
H\,\psi(G) = KE\,\psi(G) \arrow[d, "\text{FFT}"] & + & (V\psi)(G) \\
\psi(r) \arrow[rr, "\text{Multiply on Real space mesh}"'] & & (V\psi)(r) \arrow[u, "\text{FFT}"']
\end{tikzcd}
$$

Issues of computational expense

Cheap, but poor transferability

Local PSP

$$\hat{V}_{\mathrm{ps}} = V_{\mathrm{ps}}(r) \qquad \text{(local in } r,\ \theta,\ \phi\text{)}$$

Good transferability, but expensive

Semilocal PSP

$$\hat{V}_{\mathrm{ps}} = \sum_l V_{\mathrm{ps}}^{(l)}(r)\,\hat{P}_l \qquad \text{(local in } r\text{, nonlocal in } \theta,\ \phi\text{)}$$

~ All modern calculations done this way with one or two projectors

Nonlocal separable PSP (e.g., Kleinman-Bylander)

$$\hat{V}_{\mathrm{ps}} = V_{\mathrm{ps}}^{\mathrm{loc}}(r) + \sum_{lm} D_l\,|\beta_{lm}\rangle\langle\beta_{lm}|$$

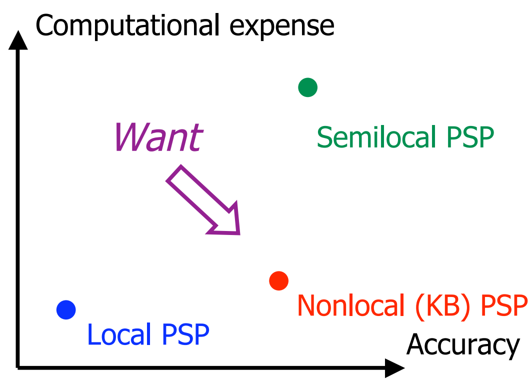
General nonlocal separable PSP

$$\hat{V}_{\mathrm{ps}} = V_{\mathrm{ps}}^{\mathrm{loc}}(r) + \sum_{\tau\tau'}\sum_{lm} D_{\tau\tau' l}\,|\beta_{\tau lm}\rangle\langle\beta_{\tau' lm}|$$

(Note: All are spherically symmetric.)

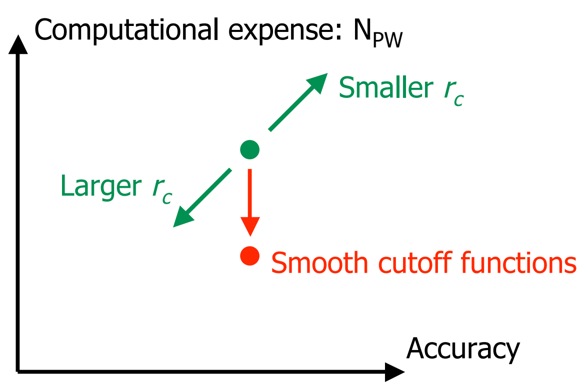
Expense vs. accuracy

Compare different functional forms:



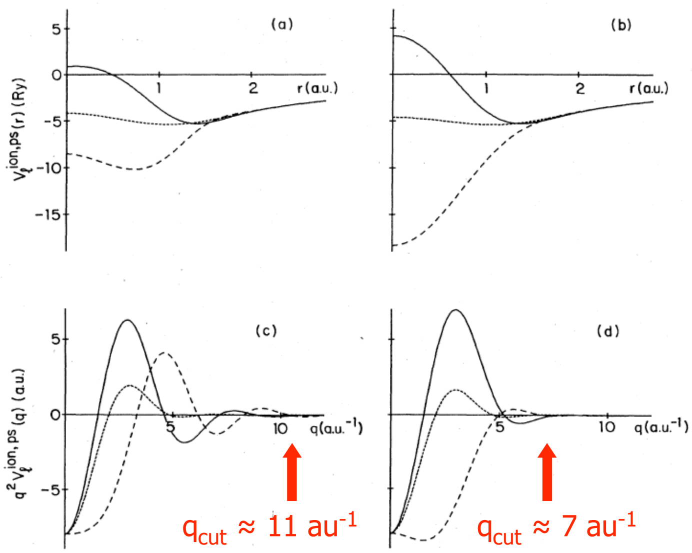
Improved softness

Now assume nonlocal (KB):



Softness and plane-wave convergence

Usual HSC | Vanderbilt, 1985



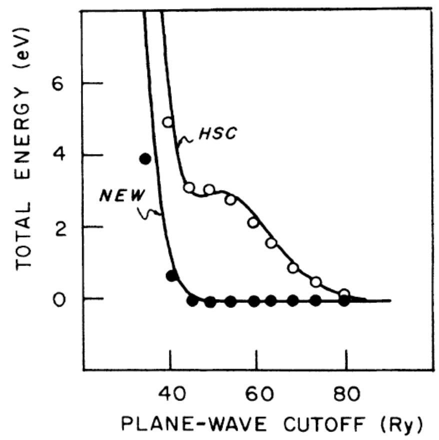
Softness and plane-wave convergence

- Apply maximal smoothness to V_{ps} construction
  - ⇒Vanderbilt, 1985
  - – This was only marginally successful in lowering the cutoff needed for the wavefunction
- Apply maximal smoothness to ψ_{ps} construction
  - ⇒Rappe, Rabe, Kaxiras, Joannopoulos (RRKJ, 1990)
  - ⇒Troullier and Martins (TM, 1991)
  - – Much more successful
  - – These (especially TM) are "standard" kind of potentials in use today

Softness and plane-wave convergence

Plane-wave convergence of energy
for free Cu atom

(RRKJ, 1990)



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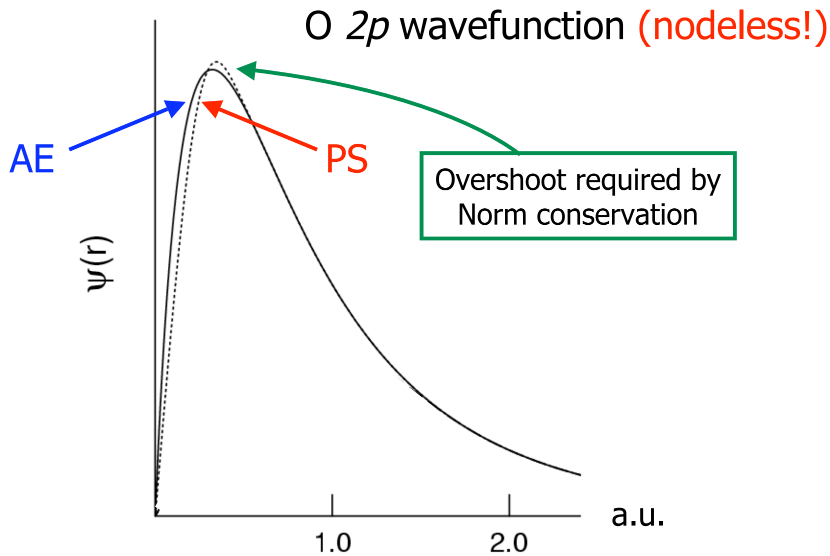
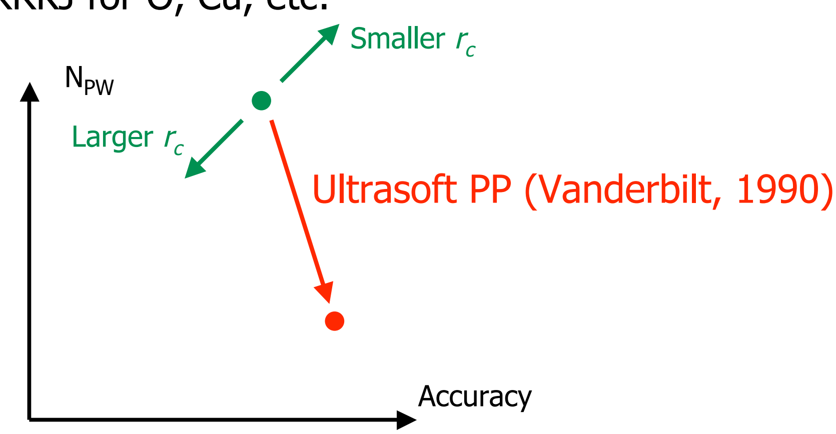
Ultrasoft pseudopotentials

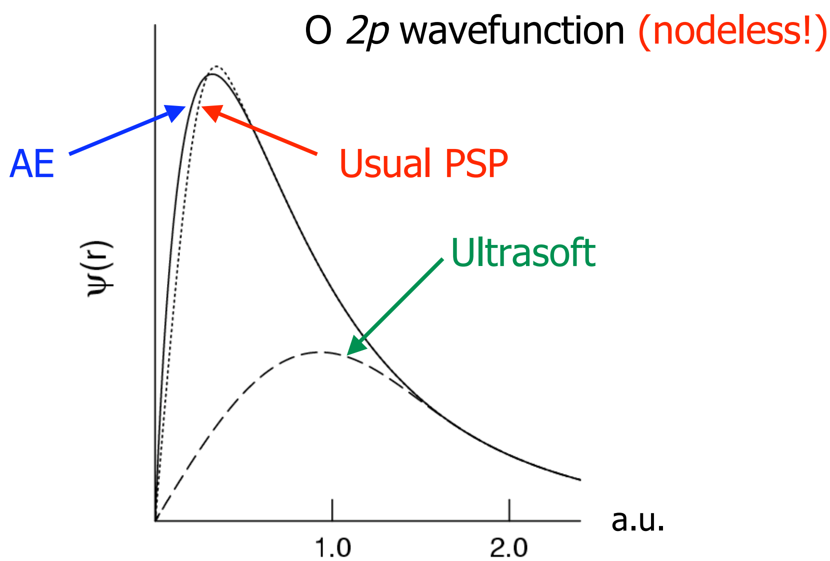


Ultrasoft pseudopotentials

TM or RRKJ for O, Cu, etc:

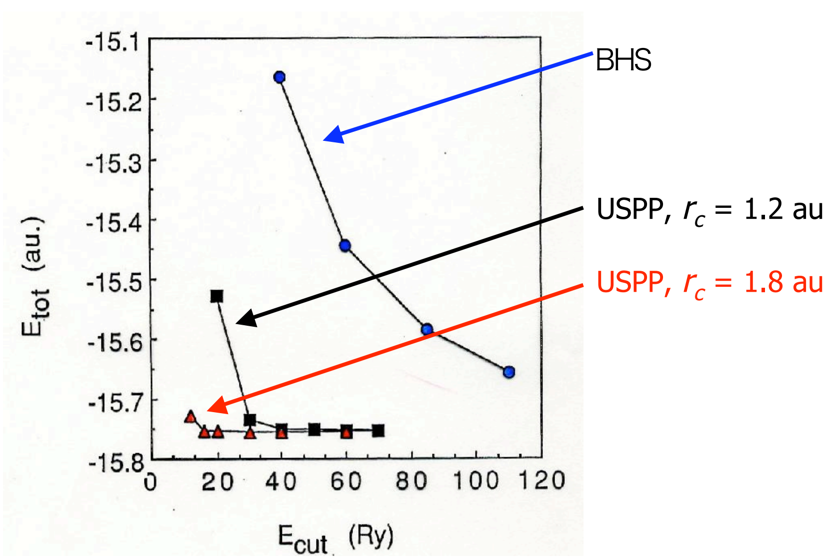


Ultrasoft pseudopotentials



Ultrasoft pseudopotentials

Covergence tests for oxygen



Ultrasoft pseudopotentials: Formalism

(Notation is for a molecule or cluster; α labels eigenstates.)

Minimize

$$E = \sum_\alpha \langle \psi_\alpha | T + \hat{V}^{\rm ps}_{nl} | \psi_\alpha \rangle + \int d^3r\, n(\mathbf{r})\, V^{\rm ps}_{\rm loc}(\mathbf{r}) + E_{\rm Hxc}[n]$$

subject to

$$\langle \psi_\alpha | 1 + \hat{N}^{\rm ps}_{nl} | \psi_\beta \rangle = \delta_{\alpha\beta}$$

where

$$n(\mathbf{r}) = \sum_\alpha \langle \psi_\alpha | \left(| \mathbf{r} \rangle \langle \mathbf{r} | + \hat{K}^{\rm ps}_{nl}(\mathbf{r}) \right) | \psi_\alpha \rangle$$

and for consistency

$$\hat{N}^{\rm ps}_{nl} = \int d^3r\, \hat{K}^{\rm ps}_{nl}(\mathbf{r}) \quad \text{just as} \quad 1 = \int d^3r\, | \mathbf{r} \rangle \langle \mathbf{r} |$$

Euler-Lagrange equation resulting from minimization:

$$(T + V^{\rm ps}_{\rm loc} + \hat{V}^{\rm ps}_{nl}) | \psi_\alpha \rangle = \epsilon_\alpha (1 + \hat{N}^{\rm ps}_{nl}) | \psi_\alpha \rangle$$

Ultrasoft pseudopotentials: Formalism

Usual NCPP:

$$\hat{K}^{\rm ps}_{nl}(\mathbf{r}) = 0$$

$$\hat{N}^{\rm ps}_{nl} = 0 \quad \text{(so that } n(\mathbf{r}) = \textstyle\sum_\alpha |\psi_\alpha(\mathbf{r})|^2 \text{ as usual)}$$

USPP:

$$\hat{K}^{\rm ps}_{nl}(\mathbf{r}) = \sum_{\tau\tau' lm} Q_{\tau\tau' l}(r)\, | \beta_{\tau lm} \rangle \langle \beta_{\tau' lm} |$$

$$\hat{N}^{\rm ps}_{nl} = \sum_{\tau\tau' lm} Q_{\tau\tau' l}\, | \beta_{\tau lm} \rangle \langle \beta_{\tau' lm} |$$

These are known as "charge augmentation terms"

Compare

$$\hat{V}^{\rm ps}_{nl} = \sum_{\tau\tau' lm} D_{\tau\tau' l}\, | \beta_{\tau lm} \rangle \langle \beta_{\tau' lm} |$$

Ultrasoft pseudopotentials: Formalism

USPP are naively not norm-conserving.

$$\langle \psi_\alpha^{\rm ps} | \psi_\alpha^{\rm ps} \rangle \neq \langle \psi_\alpha^{\rm ae} | \psi_\alpha^{\rm ae} \rangle$$

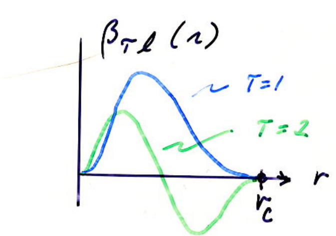
USPP *are* norm-conserving in a generalized sense:

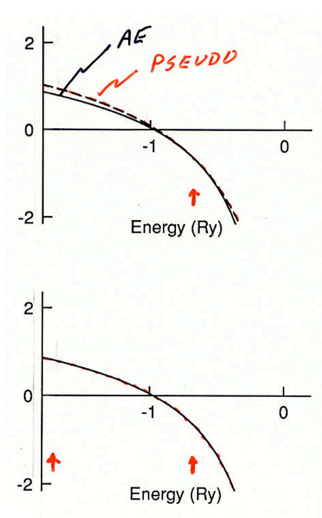
$$\langle \psi_\alpha^{\rm ps} | 1 + \hat{N}_{nl}^{\rm ps} | \psi_\alpha^{\rm ps} \rangle = \langle \psi_\alpha^{\rm ae} | \psi_\alpha^{\rm ae} \rangle$$

This can be shown to imply that scattering properties remain correct to second order in $(\epsilon - \epsilon_{\rm bound})$.

Ultrasoft pseudopotentials: Formalism

Typically, τ=(1,2) in each angular momentum channel:





Terminology and Comparison

- In current usage, PSPs are classified as either
  - NCPP = Norm-conserving pseudopotentials
  - USPP = Ultrasoft pseudopotentials
- However, remember that USPP are norm-conserving in a generalized sense
- Thus, they retain the "good features" of NCPP
  - In fact, their accuracy is usually better than NCPP
- Warning:
  - Extra coding required in solid-state code
  - Not all code packages accept USPP

Ultrasoft Pseudopotentials

Referee B

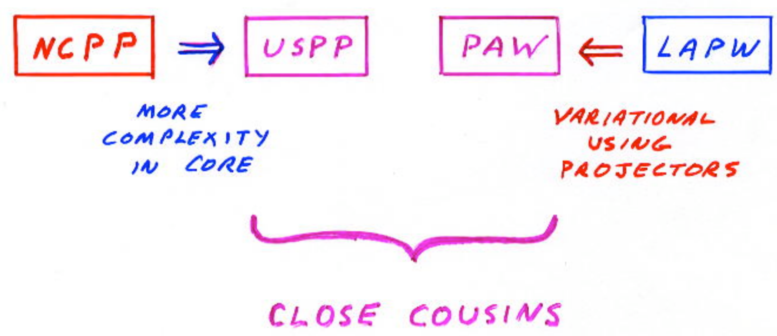
Referee's Report: Manuscript #LJ4237

Title: Soft self-consistent pseudopotentials in ...

USPP and PAW

P.E. Blöchl, “Projector Augmented-Wave Method”
PRB **50**, 17953 (1994)

G. Kresse and D. Joubert, “From USPP to PAW”
PRB **59**, 1758 (1999)



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Resources: References

Articles

D.R. Hamann, M. Schlüter, and C. Chang, Phys. Rev. Lett. **43**, 1494 (1979).

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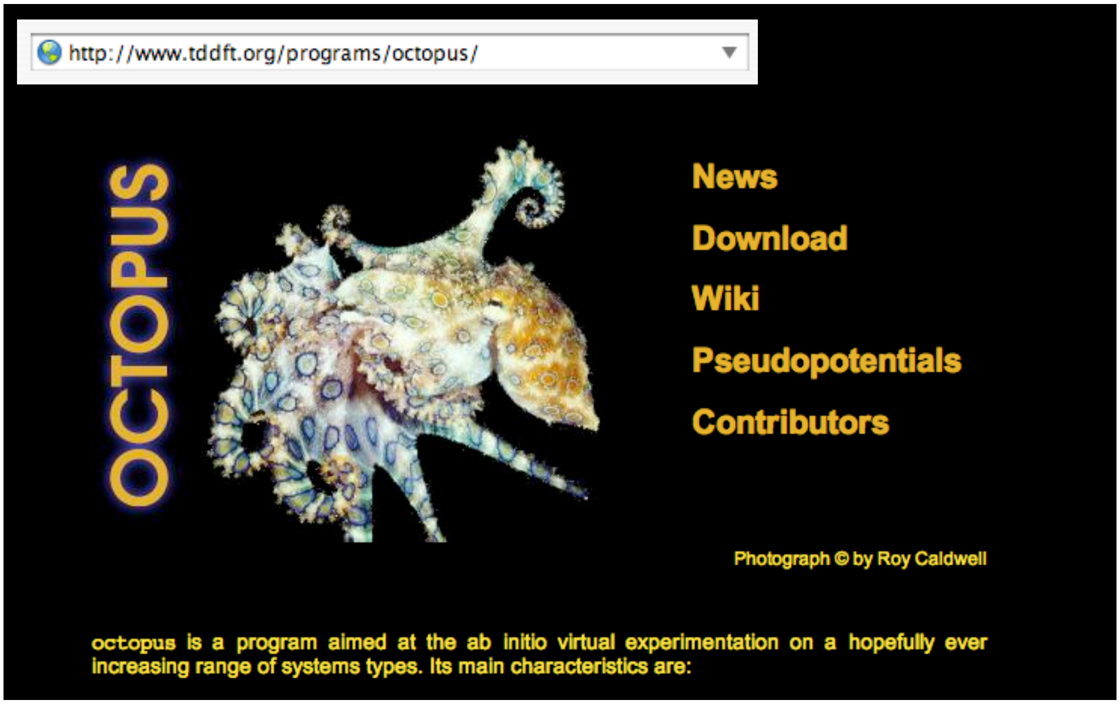
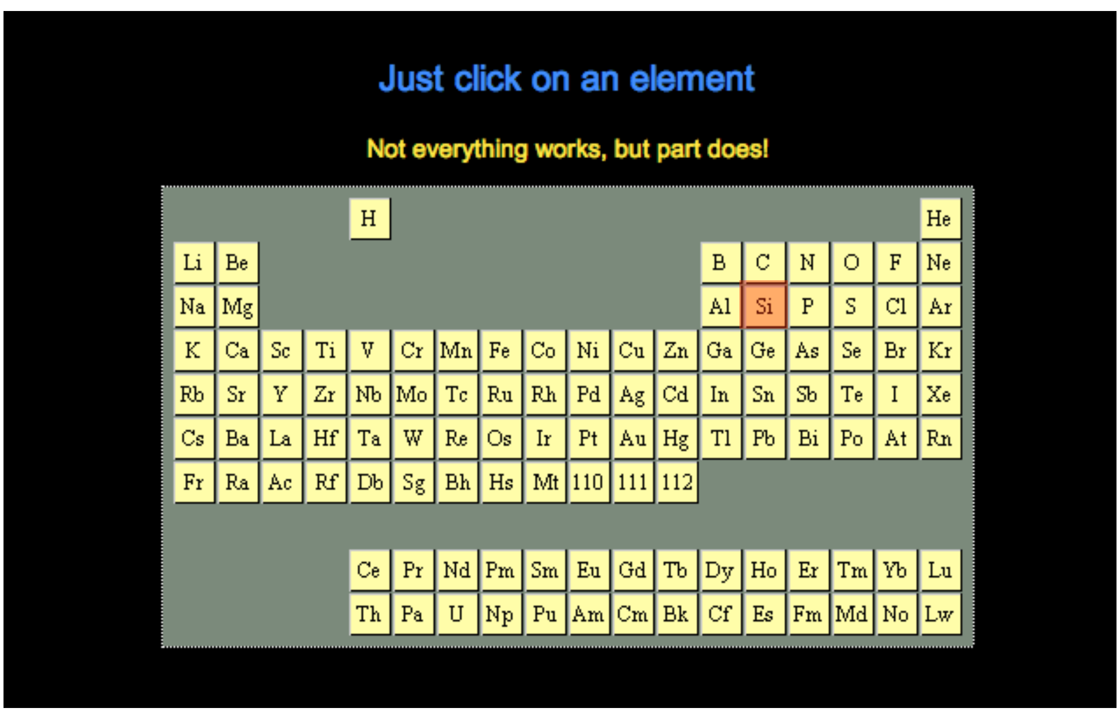
Resources: Web Sites

- Jose Luis Martins site for Troullier-Martins potentials:
  http://bohr.inesc-mn.pt/~jlm/pseudo.html
- "Octopus" web interface for pseudopotential generation
  http://www.tddft.org/programs/octopus/pseudo.php
- Vanderbilt Ultrasoft Pseudopotential site:
  http://www.physics.rutgers.edu/~dhv/uspp

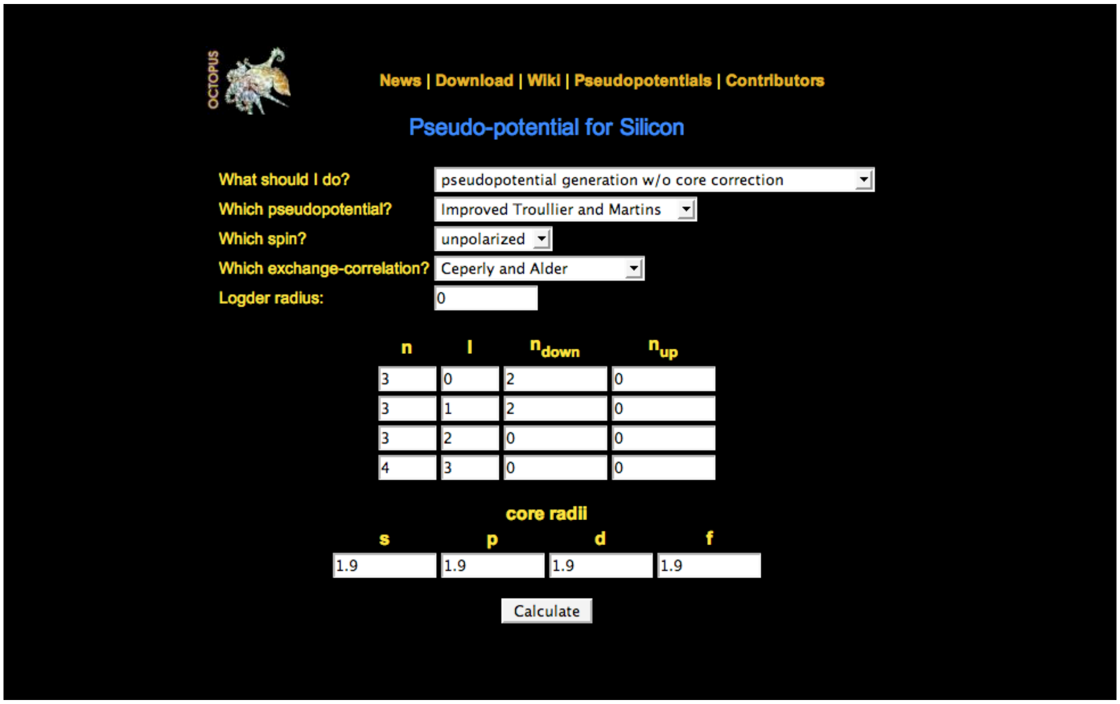
Octopus Web Site



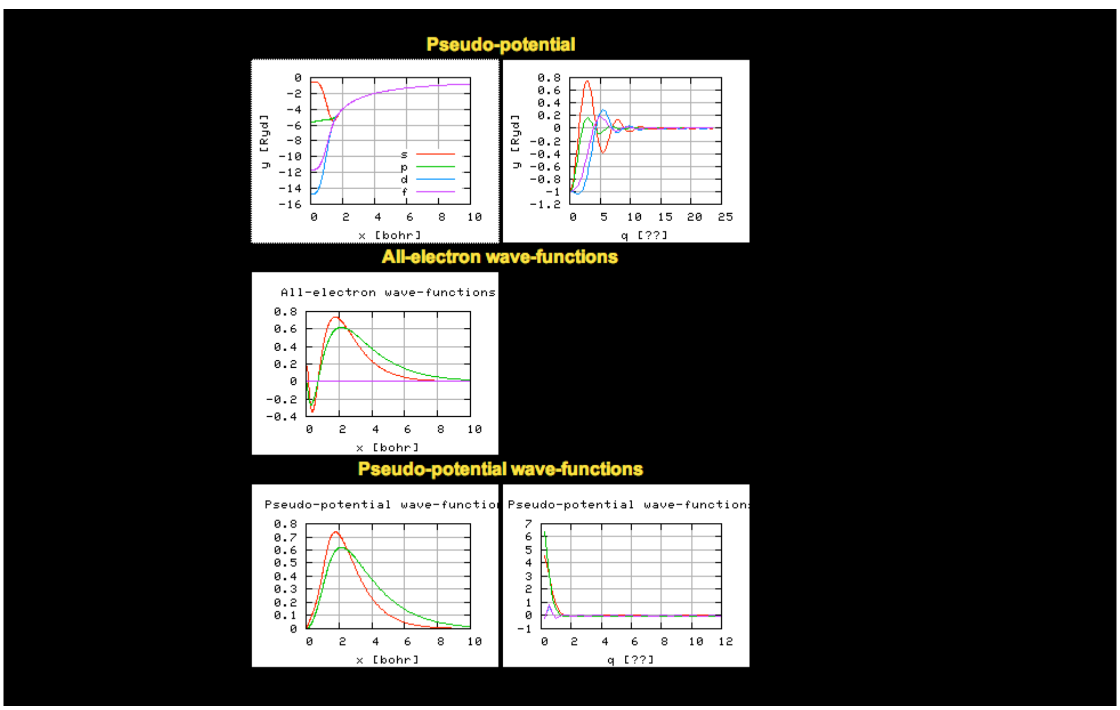
Octopus Web Site



Octopus Web Site



Octopus Web Site



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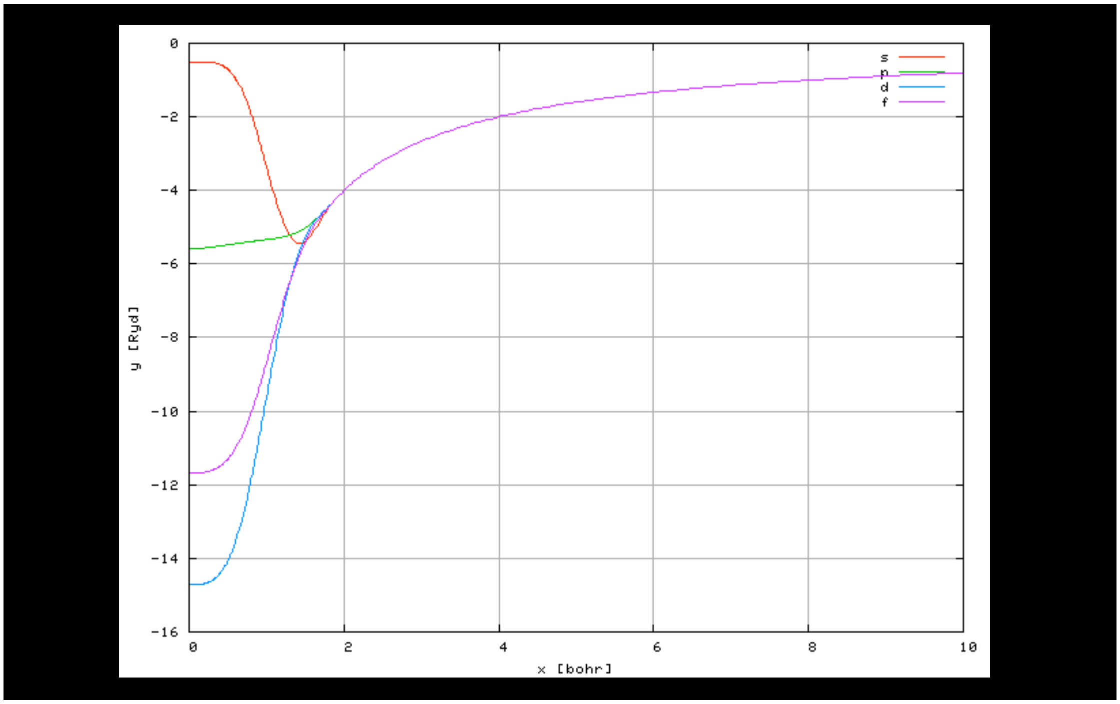
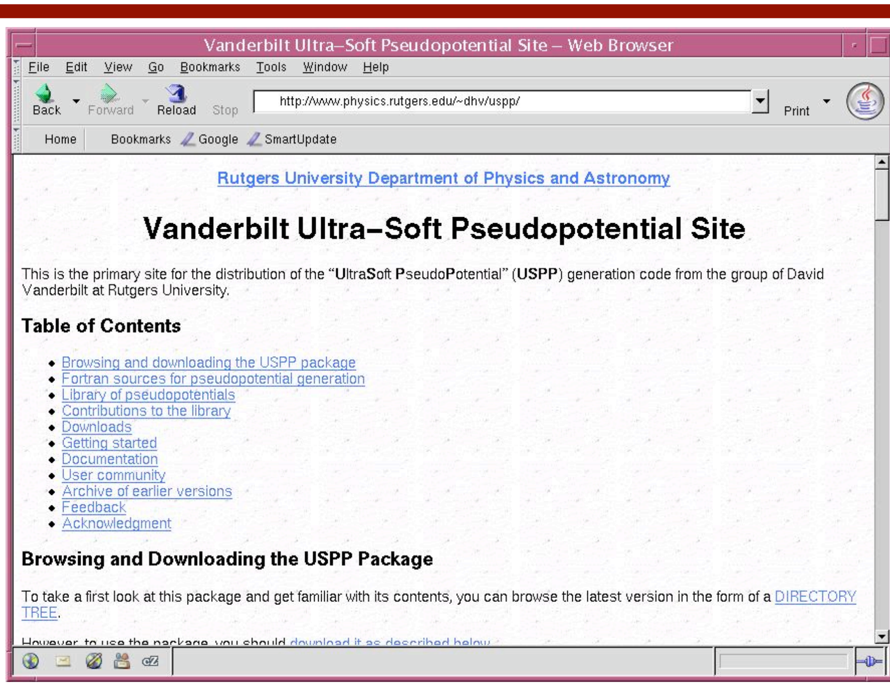
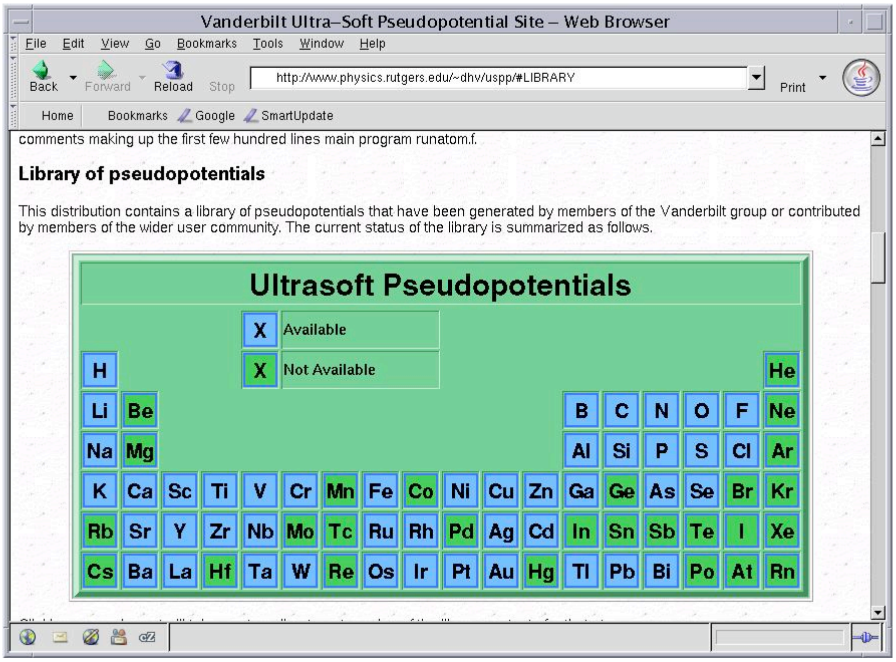


Ultrasoft Pseudopotential Web Site



Ultrasoft Pseudopotential Web Site



Summary

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Talk will be posted on
http://www.physics.rutgers.edu/~dhv