An Introduction to OPIUM

Andrew M. Rappe
Makineni Theoretical Laboratories
Department of Chemistry
University of Pennsylvania

&

Eric J. Walter
Center for Piezoelectrics by Design
Department of Physics
College of William and Mary

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Why Construct a Pseudopotential?

- There are a handful of repositories with prefabbed pseudopotentials:
- Abinit's web site: http://www.abinit.org
- Rappe Group: http://lorax.chem.upenn.edu
- Vanderbilt's library of ultrasoft pseudopotentials:
  http://www.physics.rutgers.edu/~dhv/uspp/uspp-734.html

- But, it is very likely that you may want to make your own:
- All elements may not be available
- Pseudopotential may not give accurate results
- Pseudopotential may be too expensive to use for your problem
- Incorporate new energy functionals

- Having the ability to construct pseudopotential can be an important research tool.

What is a Good Pseudopotential?

- For a pseudopotential to be useful, it must be both **accurate** and **efficient**

accuracy - reproduction of all-electron atomic properties

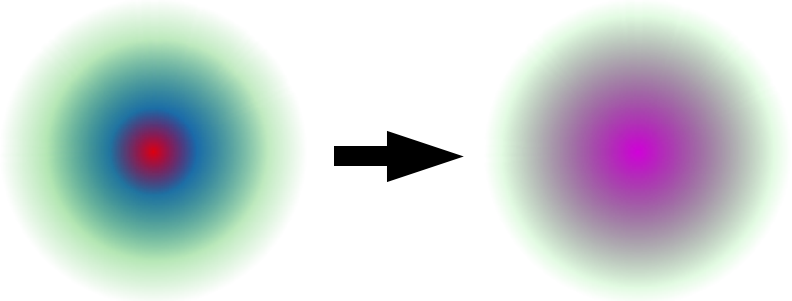
efficiency - cost of using the pseudopotential in solid-state calculations

- Need a self-contained program to construct and test the accuracy and efficiency of pseudopotentials

Open-source **P**seudopotential **I**nterface and **U**nification **M**odule

http://opium.sourceforge.net - OPIUM homepage

The OPIUM Project



Goal: Combine all aspects of PSP generation into one program

- Mutiple generation schemes (Optimized, Troullier-Martins, Kerker)
- Interfaces with multiple solid-state codes (ABINIT, PWSCF, CASTEP, etc.)

- C/Fortran – works on all platforms tried to date:
  LinuxPC, OSX, AlphaLinux, LinuxPPC, SGI/Irix, Sun/Solaris
- Xmgrace plotting interface http://plasma-gate.weizmann.ac.il/Grace/

- Scalar or non-relativistic pseudopotentials
- Partial core-correction
- Gonze *et al.* ghost testing
- Designed non-local procedure

Basic OPIUM Operation

- Main input: **param** file uses **keyblocks** ("Flexilib" - ***G. Theurich***)

```
[Atom]
# example param file
Cu
8
100   2.00   -
200   2.00   -
210   6.00   -
300   2.00   -
310   6.00   -
400   0.75   -
410   0.25   -
320   9.00   -

[XC]
lda

[Pseudo]
3 1.70 1.90 2.00
opt

.
.
.
```

Command syntax:

```
./opium <param> <log> <command 1> [<command 2> ...]
```

```
./opium cu cu.log ae ps nl tc rpt plot vi fhi
```

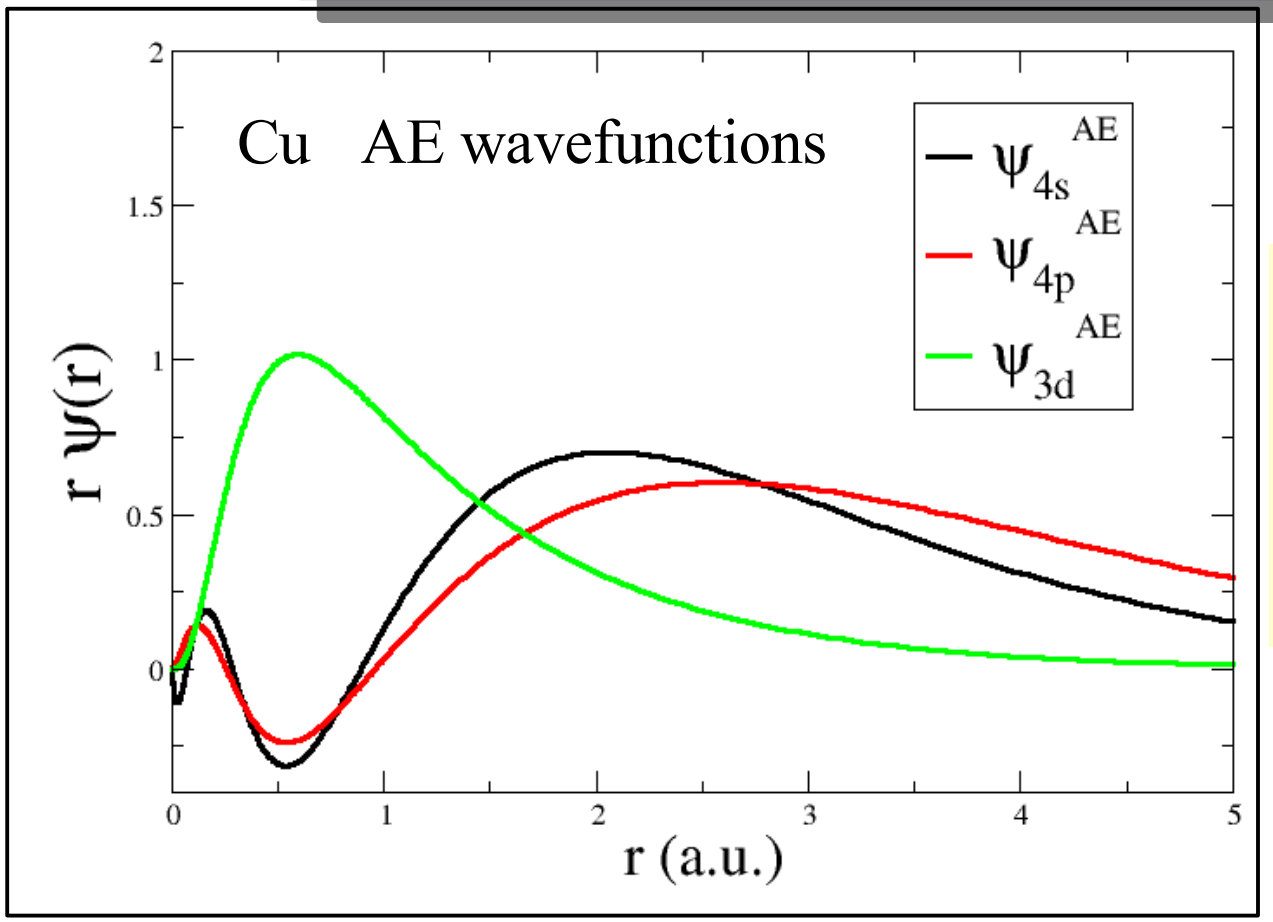
cu – cu.param is the input file (.param is optional)
cu.log – collect output
ae, ps, nl – steps of the PSP calculation
tc – test configurations
rpt – generates "summary of output"
plot – indicates next token is plot type
vi – plot ionic potential
fhi – output in "fhi" psp style

./opium -h - online help

Pseudopotential Construction: AE

$\left\{\phi_l^{\mathrm{AE}}(r)\right\}, \left\{\epsilon_l^{\mathrm{AE}}\right\}$ • Get the all-electron eigenvalues and wavefunctions.

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2Z}{r} + V_{\mathrm{hxc}}[\rho(r)]\right)\phi_l(r) = \epsilon_l \phi_l(r)$$



Command line:

```
./opium cu cu.log ae plot wa
```

wa – AE wavefunction plot

Pseudopotential Construction: PS

- **First step of construction is to design pseudowavefunctions**
- **Choose reference configuration and cutoff radii (r_c)**

5 rules for a good pseudopotential :

D. R. Hamann, M. Schlüter, and C. Chiang,
PRL **43**, 1494 (1979)

1. $\{\epsilon_l^{\rm AE}\}_{\rm ref} = \{\epsilon_l^{\rm PS}\}_{\rm ref}$
2. $\psi_{l,{\rm ref}}^{\rm AE} = \psi_{l,{\rm ref}}^{\rm PS} \qquad r \geq r_c$
3. $N_{l,{\rm ref}}^{\rm AE} = N_{l,{\rm ref}}^{\rm PS}$
4. $D_l^{\rm AE}(\epsilon, r_c) = D_l^{\rm PS}(\epsilon, r_c)$
5. $\dfrac{\partial}{\partial\epsilon} D_l^{\rm AE}(\epsilon, r_c) = \dfrac{\partial}{\partial\epsilon} D_l^{\rm PS}(\epsilon, r_c)$

Norm conservation guarantees

$$N_l = \int_0^{r_c} r^2 \psi_l^2(r) dr$$

$$D_l(\epsilon, r) = r \frac{d}{dr} \ln \psi_l(\epsilon, r)$$

Pseudowavefunctions are nodeless and satisfy (at least) the above criteria

Pseudopotential Construction: PS

Invert the KS equation to find the **screened** semi-local pseudopotential: $V_l^{\rm scr}(r)$

$$V_l^{\rm scr}(r) = \epsilon_l - \frac{l(l+1)}{r^2} + \frac{1}{\phi_l(r)} \frac{d^2\left[\phi_l(r)\right]}{dr^2}$$

Descreen the screened pseudopotential to give the **ionic** pseudopotential:

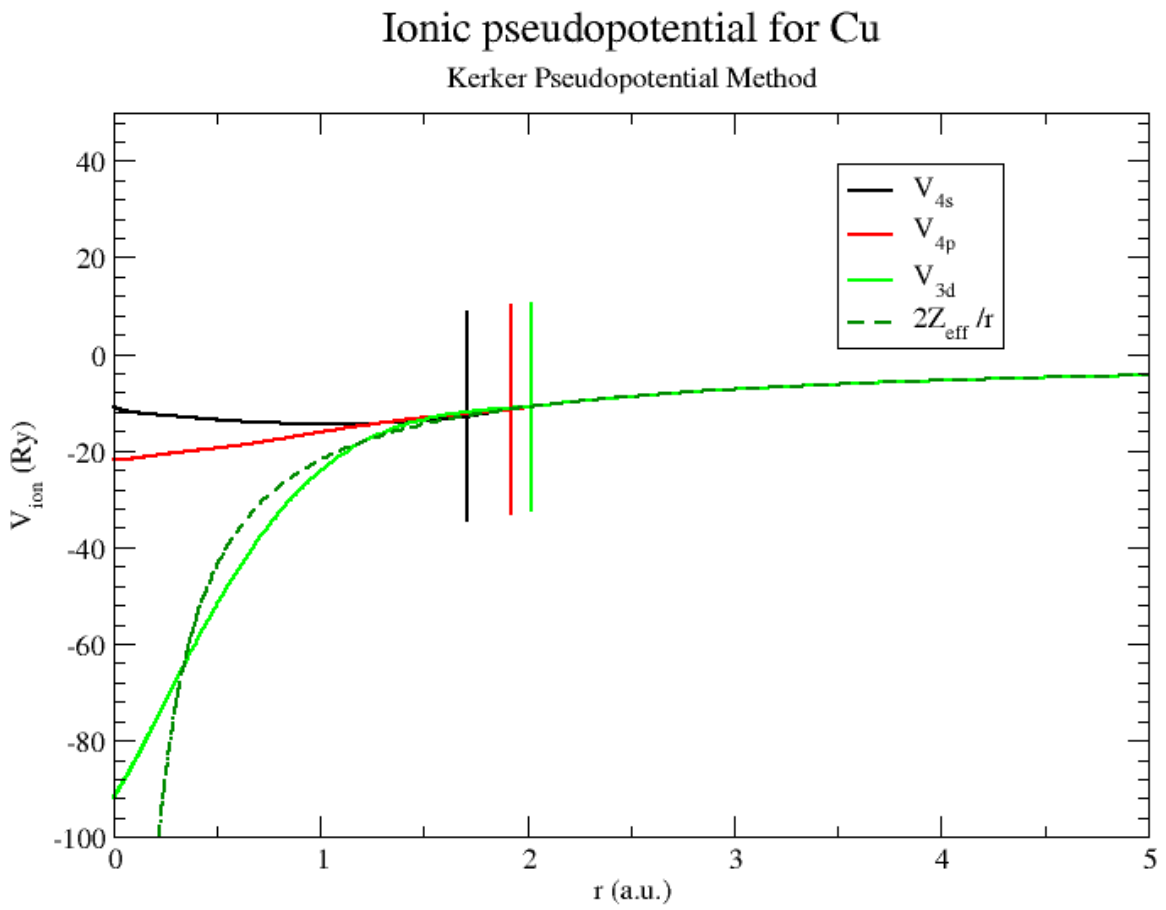
$$V_l^{\rm ps}(r) = V_l^{\rm scr}(r) - V_{\rm hxc}[\rho^{\rm val}(r)]$$

Ghost testing perfomed for all possible choices of **local potential**

Pseudopotential Construction: PS

Command line:

```
./opium cu cu.log ae ps plot vi
```

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400   0.75   -
410   0.25   -
320   9.00   -

[XC]
lda

[Pseudo]
3 1.70 1.90 2.00
kerker

.
.
.
```

Pseudopotential Construction: NL

$$\hat{V}_{NL} = V_{\rm loc}(r) + \sum_l \frac{|\Delta V_l(r)\psi_l^{\rm ref}\rangle\langle\psi_l^{\rm ref}\Delta V_l(r)|}{\langle\psi_l^{\rm ref}|\Delta V_l(r)|\psi_l^{\rm ref}\rangle}$$

Kleinman-Bylander non-local form *PRL* **48**, 1425 (1982).

- More efficient than semi-local in planewave calculations
- Used in ABINIT

$$\Delta V_l(r) = V_l^{\rm ps}(r) - V_{\rm loc}(r)$$ Select local potential

Action of non-local potential on reference:

$$\hat{V}_{NL}|\psi_l^{\rm ref}\rangle = V_{\rm loc}(r)|\psi_l^{\rm ref}\rangle + \sum_l \frac{|\Delta V_l(r)\psi_l^{\rm ref}\rangle\langle\psi_l^{\rm ref}\Delta V_l(r)||\psi_l^{\rm ref}\rangle}{\langle\psi_l^{\rm ref}|\Delta V_l(r)|\psi_l^{\rm ref}\rangle}$$

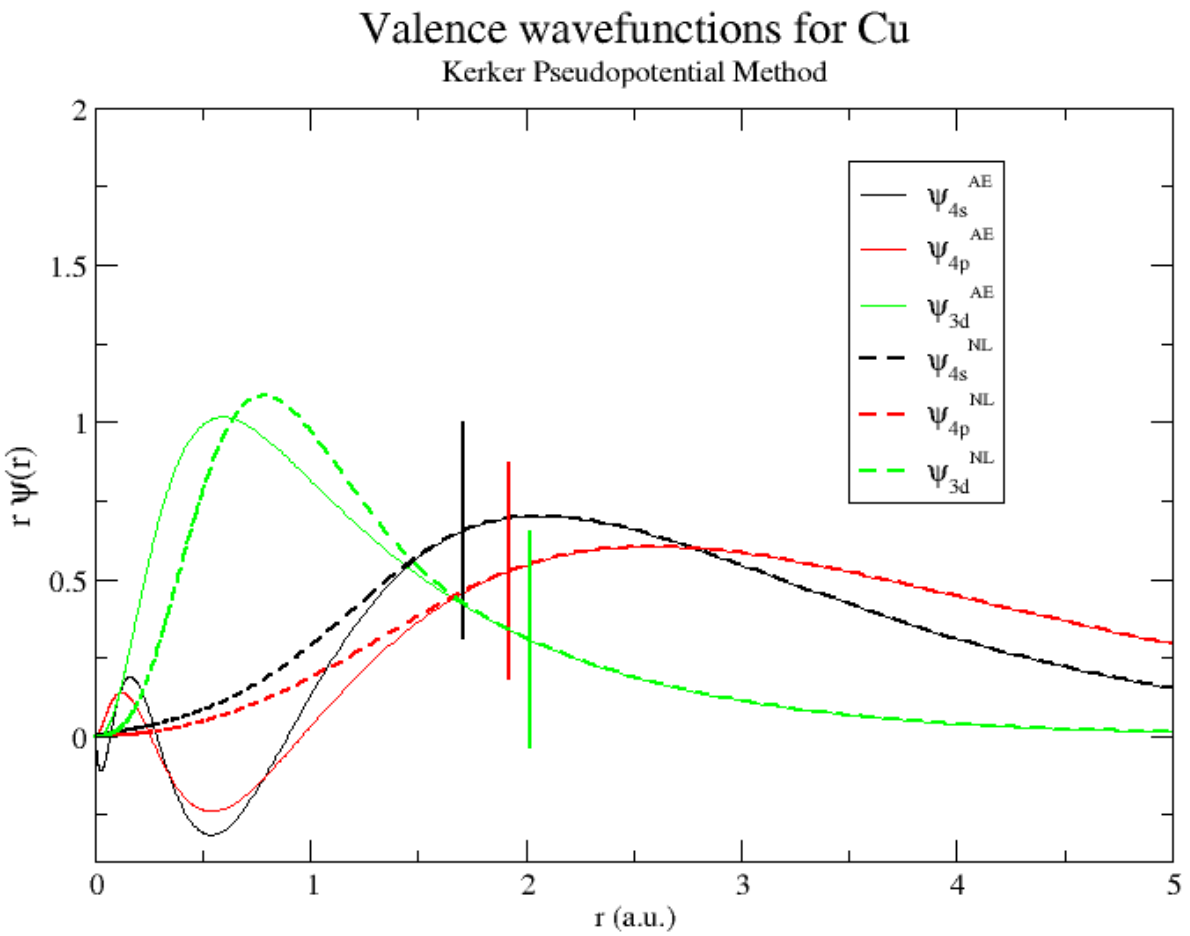
$$\hat{V}_{NL}|\psi_l^{\rm ref}\rangle = \sum_l V_l^{\rm ps}(r)|\psi_l^{\rm ref}\rangle$$

KB form equivalent to semi-local for **reference** configuration

Pseudopotential Construction: NL

Command line:

```
./opium cu cu.log ae ps nl plot wp
```

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# example param file
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200   2.00   -
210   6.00   -
300   2.00   -
310   6.00   -
400   0.75   -
410   0.25   -
320   9.00   -

[XC]
lda

[Pseudo]
3 1.70 1.90 2.00
kerker

[Kbdesign]
s

.
.
.
```

Pseudopotential Construction: TC

Command line:

```
./opium cu cu.log ae ps nl tc
```

- OPIUM allows for a set of test configurations to be defined and tested
- AE and NL solutions are found and compared

```
.
.
.
[XC]
lda

[Pseudo]
3 1.70 1.90 2.00
kerker

[Kbdesign]
s

[Configs]
3
400  0.00  -
410  0.00  -
320 10.00  -

400  0.50  -
410  0.00  -
320  9.50  -

400  1.00  -
410  0.00  -
320  9.00  -
```

Pseudopotential Construction

Command line:

```
./opium cu cu.log ae ps nl tc fhi
```

- Writing out the pseudopotential to a file is **trivial**
- The **fhi** command writes to a format that is compatible with **ABINIT**
- Able to create pseudopotentials for **multiple programs**

FCC Al total energy

	Energy(eV)
ABINIT	-57.935217
PWSCF	-57.934777
BH	-57.934650

Better than 1 meV agreement among multiple solid-state codes

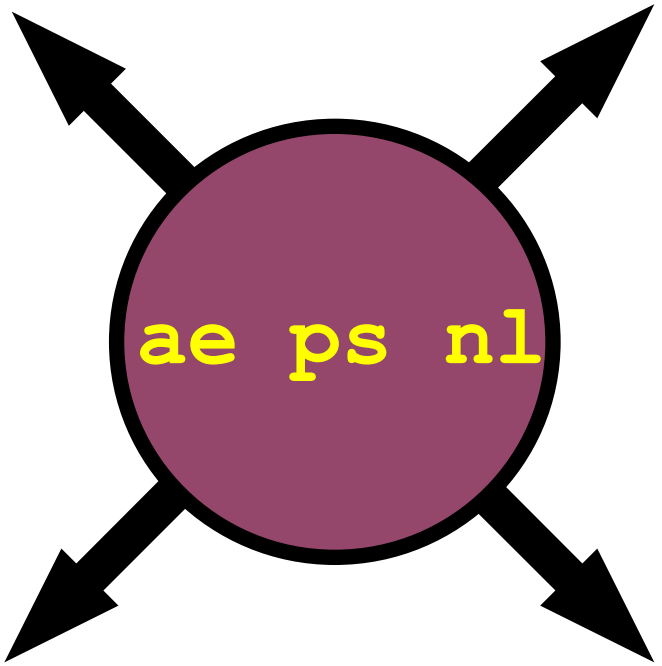
Construction Summary

rpt

Make summary report

tc

Test other configurations



AE wavefunctions **wa**
NL wavefunctions **wp**
Ionic potentials **vi**
Screened potentials **vs**

fhi

Generate pseudopotential

plot

Kinetic energy convergence **ke**
Core, valence, and core-correction **den**
Bessel transform of ionic potential **qp**
Bessel transform of NL wavefunctions **qp**
Logarithmic derivatives **logd**

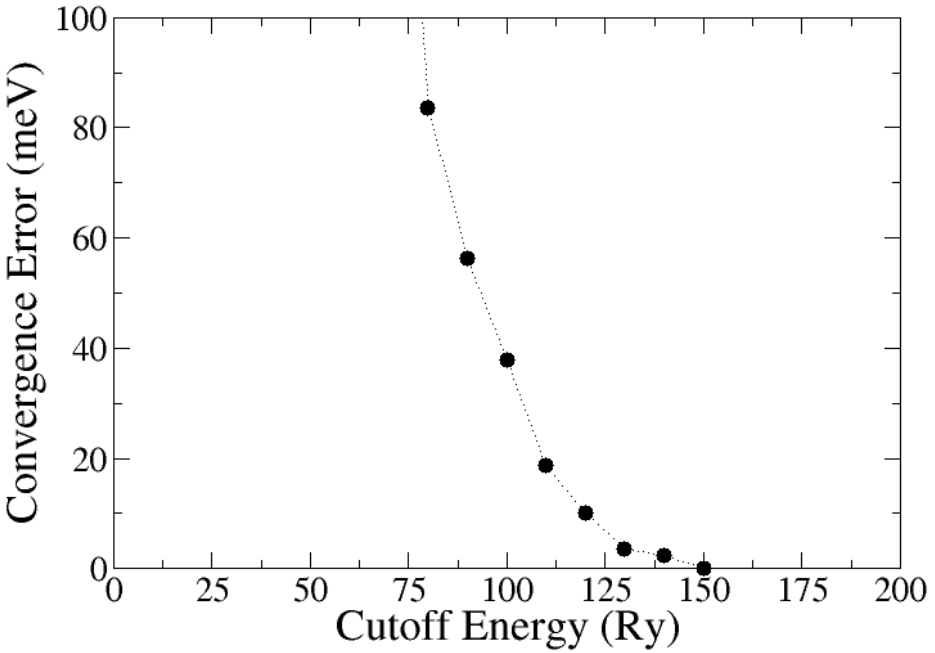
Pseudopotential Convergence

OPIUM will give convergence information

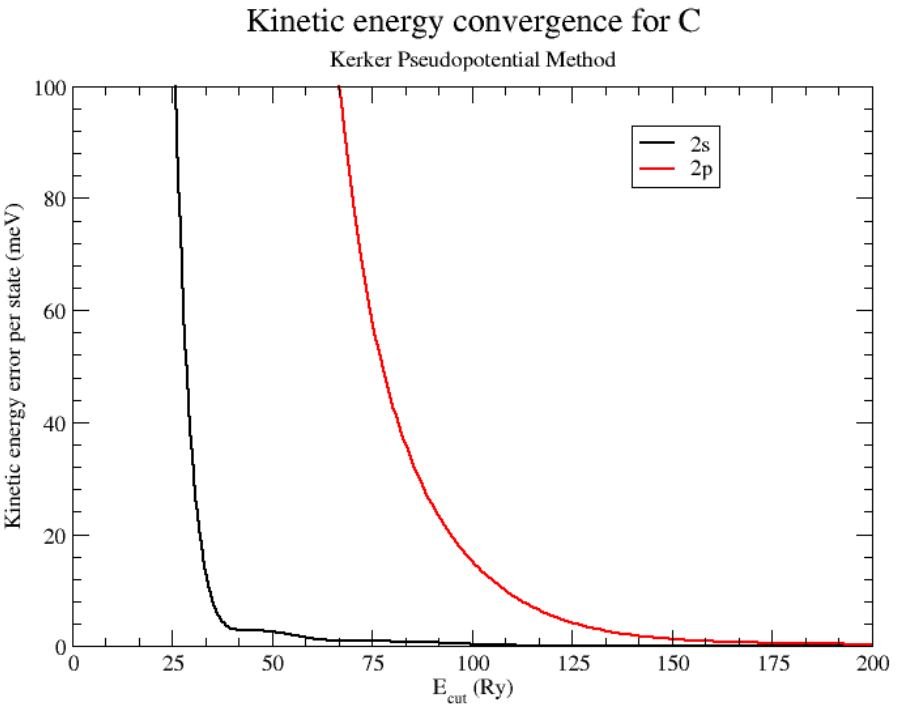
Command line:

```
./opium c c.log plot ke
```

Error in Total Energy vs. PSP Cutoff energy (Ecut)



From ABINIT



From OPIUM

- Want to minimize cutoff energy
- Optimized method delivers highly **efficient** pseudopotentials

Optimized Pseudopotentials

Excellent convergence obtained when high Fourier components of kinetic energy are minimized

$$\psi_l(r) = \begin{cases} \sum_i c_i \, j_l(q_i r) & r < r_c \\ \phi_l(r) & r \geq r_c \end{cases}$$

Pseudowavefunction expanded in series of Bessel functions

$$\Delta \mathrm{E}_l^{\mathrm{conv}}(c_1, c_2, \ldots, q_c) = -\int_0^{\infty} d\vec{r}\psi(\vec{r})\nabla\psi(\vec{r}) - \int_0^{q_c} d\vec{q}q^2|(\psi(q))|^2$$

Converengence error = Total kinetic energy - $q < q_c$ contribution

q_c is selected to yield small convergence error

Rappe *et. al. PRB* **41** 1227 (1990)

Transferability

$$\eta_{ij} = \frac{1}{2}\frac{\partial^2 E[\rho]}{\partial f_i \partial f_j} = \frac{1}{2}\frac{\partial \epsilon_i}{\partial f_j}$$

Chemical hardness

$$\epsilon_i^{\mathrm{ae}} - \epsilon_i^{\mathrm{ps}} \propto \eta_{ij}^{\mathrm{ae}} - \eta_{ij}^{\mathrm{ps}}$$

transferability ⟷ hardness

$$\gamma_{ij} = \frac{1}{2}\frac{\partial \mathrm{N}_i}{\partial f_j}$$

Can define tail norm tensor

$$\mathrm{N}_i^{\mathrm{ae}} - \mathrm{N}_i^{\mathrm{ps}} \propto \gamma_{ij}^{\mathrm{ae}} - \gamma_{ij}^{\mathrm{ps}}$$

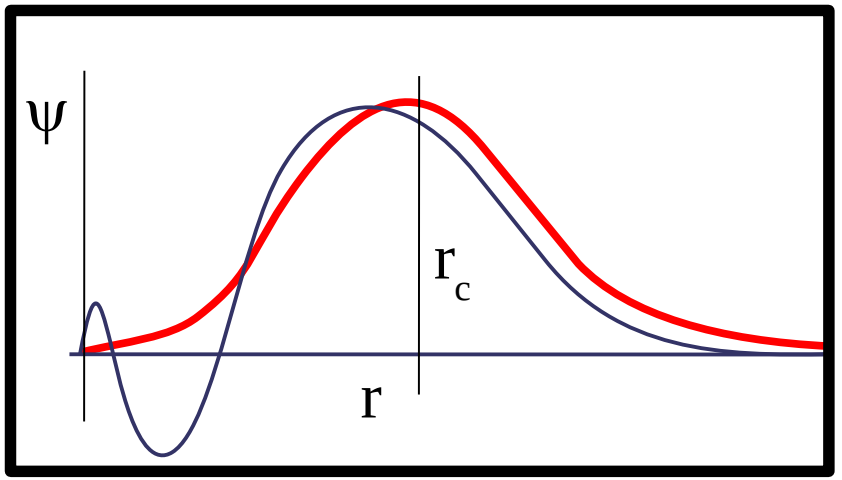
$$\mathrm{N}_l = \int_{r_c}^{\infty} r^2 \psi_l^2(r) dr$$

Tail norm

Improving **eigenvalues** and **tail norms** at **multiple** configurations increases pseudopotential performance

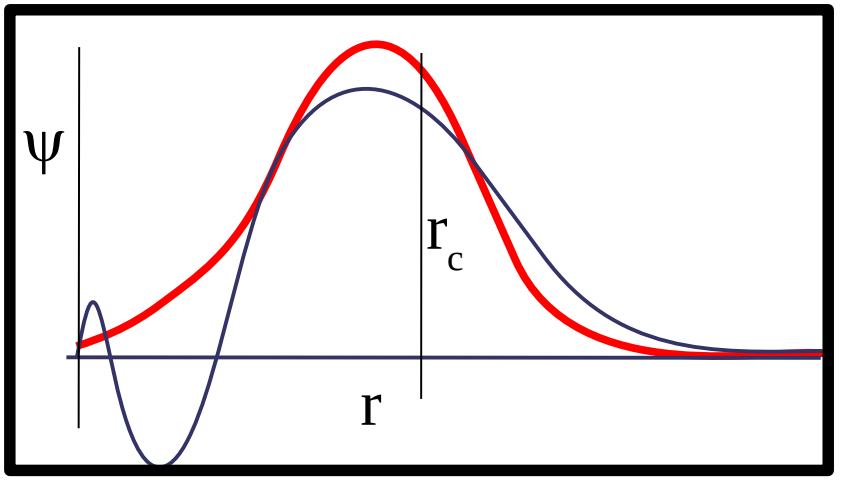
finite changes more informative

Eigenvalues and Tail Norm



$$\epsilon^{ae} = \epsilon^{ps}$$

$$N^{ae} \neq N^{ps}$$



$$\epsilon^{ae} \neq \epsilon^{ps}$$

$$N^{ae} = N^{ps}$$

Must enforce conservation of both!

Designed Non-local

$$\hat{V}_{NL} = V_{\rm loc}(r) + \sum_l \frac{|\Delta V_l(r)\psi_l^{\rm ref}\rangle\langle\psi_l^{\rm ref}\Delta V_l(r)|}{\langle\psi_l^{\rm ref}|\Delta V_l(r)|\psi_l^{\rm ref}\rangle}$$

KB **non-local** form

Add augmentation function, ***A(r)*** ,to local potential:

$$\hat{V}_{NL} = V_{\rm loc}(r) + A(r) + \sum_l \frac{|\left(\Delta V_l(r) - A(r)\right)\psi_l^{\rm ref}\rangle\langle\psi_l^{\rm ref}\left(\Delta V_l(r) - A(r)\right)|}{\langle\psi_l^{\rm ref}|\left(\Delta V_l(r) - A(r)\right)|\psi_l^{\rm ref}\rangle}$$

- Will change transferability for **non-reference states**
- **Does not affect reference state**

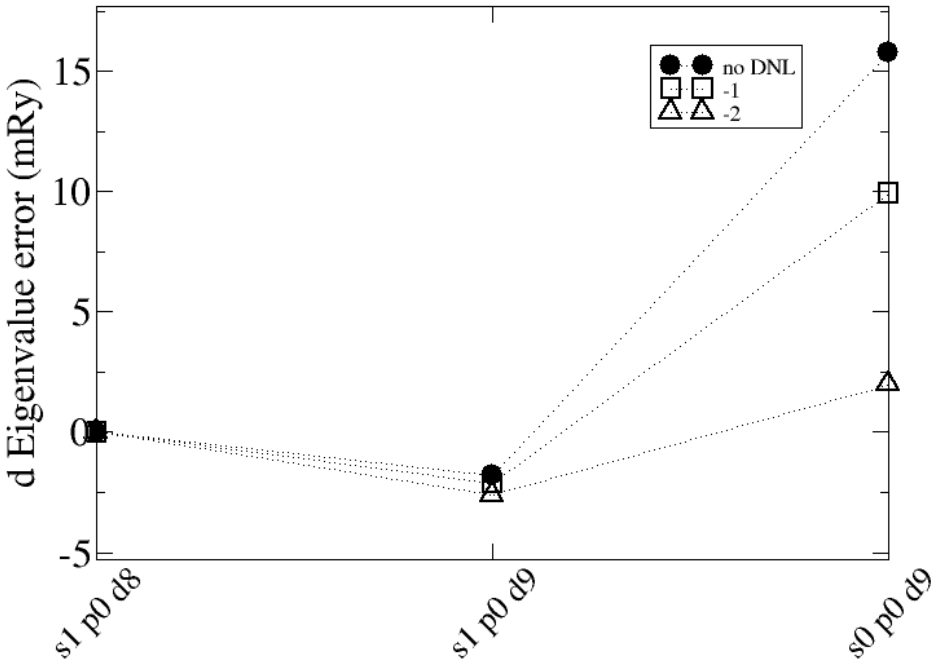
Designed Non-local PSPs
Ramer and Rappe
PRB **59**, 12471 (1999).

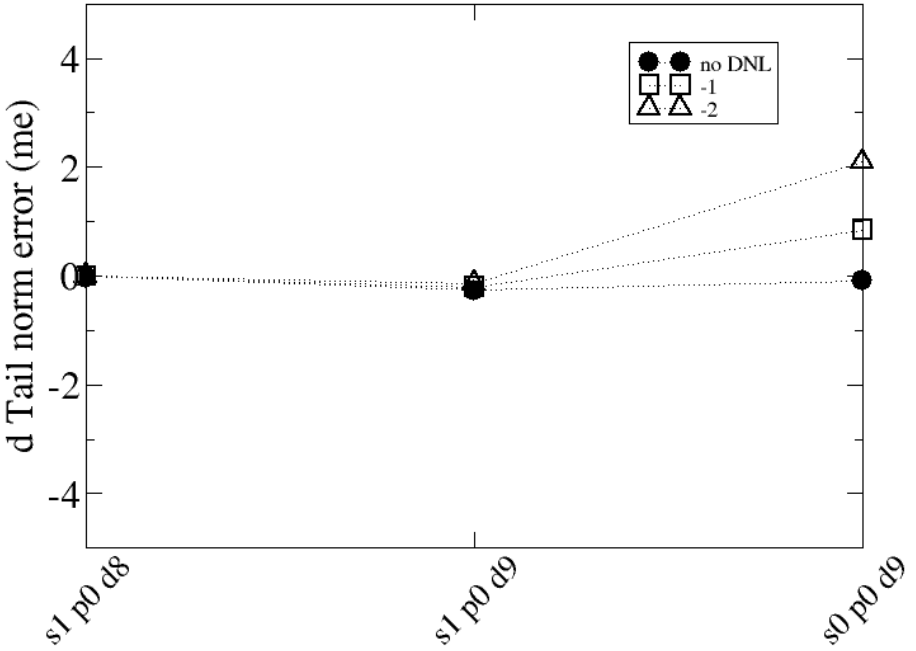
Tunable enhancement of transferability

Designed Non-local in OPIUM

Eigenvalues

Rh *s1p0d8*






```
[KBdesign]
s
0
au 0.0 2.0 -2.0

[Pseudo]
3 2.0 2.0 2.0
opt
```

DNL can greatly enhance transferability

Acknowledgments

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Jessica Pfeffer