Comments on Generating and Testing PAW Datasets*

N. A. W. Holzwarth

Department of Physics, Wake Forest University, Winston-Salem, NC, 27109 USA

Collaborators in France: Marc Torrent, François Jollet, Yann Pouillon

Collaborators in USA: Xiao Xu (WFU Ph. D. 2012, current at Matlab), Nicholas Lepley and Qi Li (WFU graduate students), James Drewery and Cameron Kates (WFU undergraduate students), Alan Wright (Sandia National Laboratory), Alan Tackett, Greg Walker, Rachael Hansel, Ryan Hatcher (Vanderbilt University)

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Discussion points

- Review of basic content of PAW datasets for various codes – abinit, quantum espresso, socorro, (pwpaw), GPAW??
- atompaw 3.0.1.9 ➔4.0.0.0
  - Modular programing structure
  - More robust atomic solver
  - Some new options for pseudo functions
  - Option for systematic exploration of pseudo parameters
  - Hartree-Fock and hybrid functionals
  - Integration with features developed by Marc Torrent, François Jollet, etc

Basic content of PAW datasets

Basic principles of "Projector Augmented Wave" method

*(P. Blöchl, Phys. Rev. B **50**,17953 (1994))*

Provides mapping between full ("all-electron") wavefunctions and pseudo-wavefunctions $\Psi_s \Leftrightarrow \tilde{\Psi}_s$

atom-centered functions:

$$\left|\Psi_s\right\rangle = \left|\tilde{\Psi}_s\right\rangle + \sum_{a,i}\left(\left|\varphi_i^a\left(\mathbf{r}-\mathbf{R}^a\right)\right\rangle - \left|\tilde{\varphi}_i^a\left(\mathbf{r}-\mathbf{R}^a\right)\right\rangle\right)\left\langle p_i^a\middle|\tilde{\Psi}_s\right\rangle$$

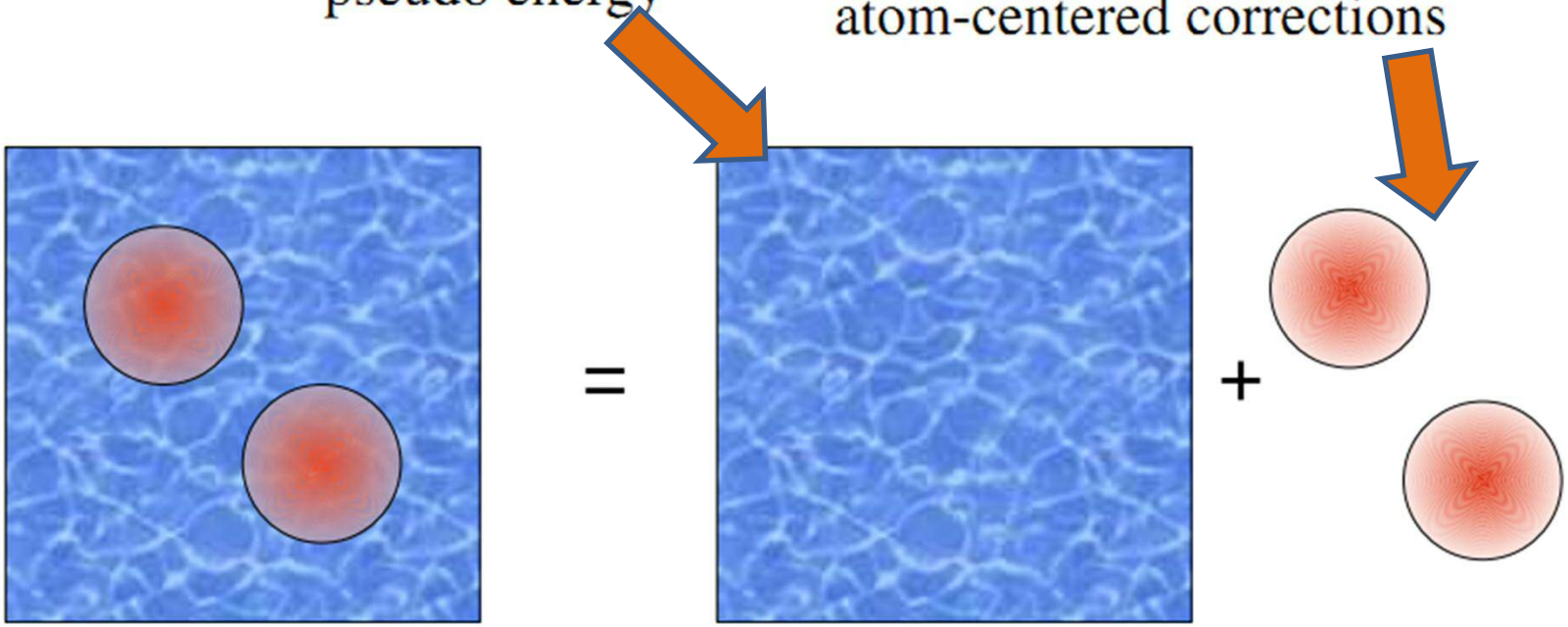
full basis function

pseudo basis function

projector function

PAW evaluations – separated into extended “pseudo” and atom-centered contributions

$$E_{tot}^{\text{vale}} = \underbrace{\widetilde{E}_{tot}}_{\text{pseudo energy}} + \sum_a \underbrace{\left(E_{tot}^a - \widetilde{E}_{tot}^a\right)}_{\text{atom-centered corrections}} .$$



➔compensation charge $\hat{\rho}^a(r)$

➔local pseudopotential $\widetilde{V}^a{}_{loc}(r)$

➔core electron information

http://pwpaw.wfu.edu

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ATOMPAW
INFO
DATASETS
NAWH Web
PHYSICS Web
WFU Web

ATOMPAW

Download source code and example files:

- atompaw-3.0.1.9.tar.gz (3.8mb) Updated version of *atompaw* code (09/20/2012 -- Yann Pouillon updated the autotools for constructing the tar file; 07/16/2012 -- Geoffrey Pourois corrected GIPAW portion of pwscfinterface.f90; 06/26/12 -- NAWH corrected bug in pwscfinterface.f90 on top of previous revisions on 06/13/12 and 04/14/12 by Marc Torrent), and previous changes 10/03/11 by Marc Torrent and Yann Pouillon updating interface for use with LibXc. This version is still compatible with pwscf including recent addition by D. Ceresoli for gipaw calculations. The 3.0+ versions have several features due largely to the magic of Marc Torrent (CEA, France) and Yann Pouillon (ETSF, Spain) including compatability for use with LibXC.
  - The code package now complies with linux installation standards.
  - Using new options in the input file, datasets for use with *abinit* (replacing the need to run the separate atompaw2abinit code) or *pwscf, quantum-espresso* can be generated. (For developing the UPF file for use with *pwscf*, help from Lorenzo Paulatto and Paolo Giannozzi is gratefully acknowledged.)
  - The use of atompaw with LibXC library of exchange-correlation functionals are now possible for generating datasets for *abinit*.
  - Details are given in the user's guide written by Marc Torrent.
  - Some details concerning choices of the shapes of compensation charge densities have been clarified as explained in a recent publication.
  - Simple gnuplot scripts are available to help analyze some of the outputs of the atompaw program.
- pwpaw_2.4.tgz (0.2 mb) Updated 05/12/2010 version of *pwpaw* with very minor changes to accomodate changes to input files generated by new *atompaw* output files; also includes a BSD license file.
- Older versions of atompaw and pwpaw

Some notes on formalism (PDF format):

- Notes on new atompaw implementation.
  Also presented is a discussion of the relationship between pwpaw and abinit implementations of the PAW equations.
- Notes on crystal symmetry
- Notes on generalized coordinates
- Notes on GGA implementation
- Notes on scalar-relativistic implementation

Thanks to Sina Zolghadr (with help from Eric Chapman) for the webpage design.

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http://pwpaw.wfu.edu

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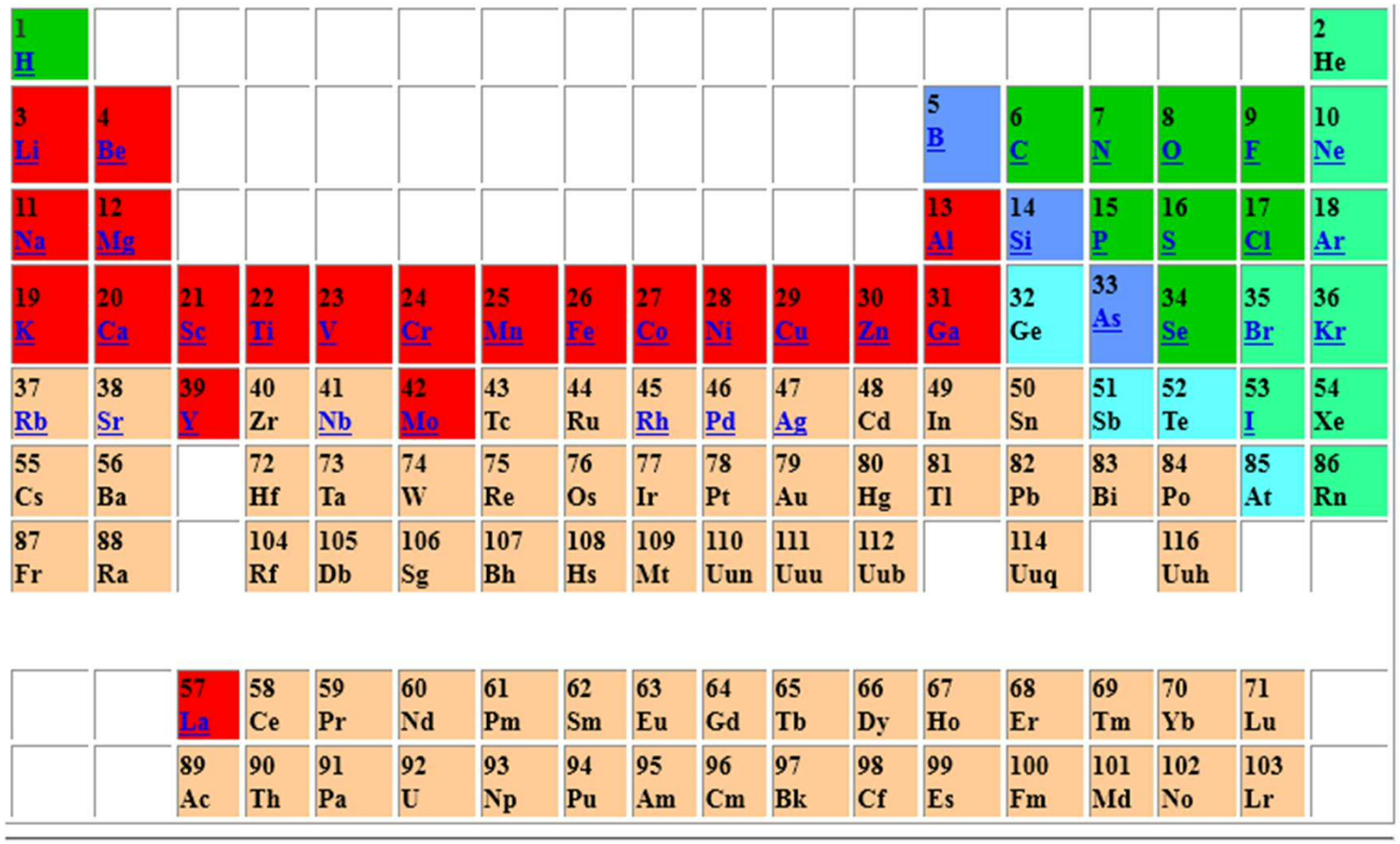
Periodic Table of the Elements for PAW Functions (<2012)



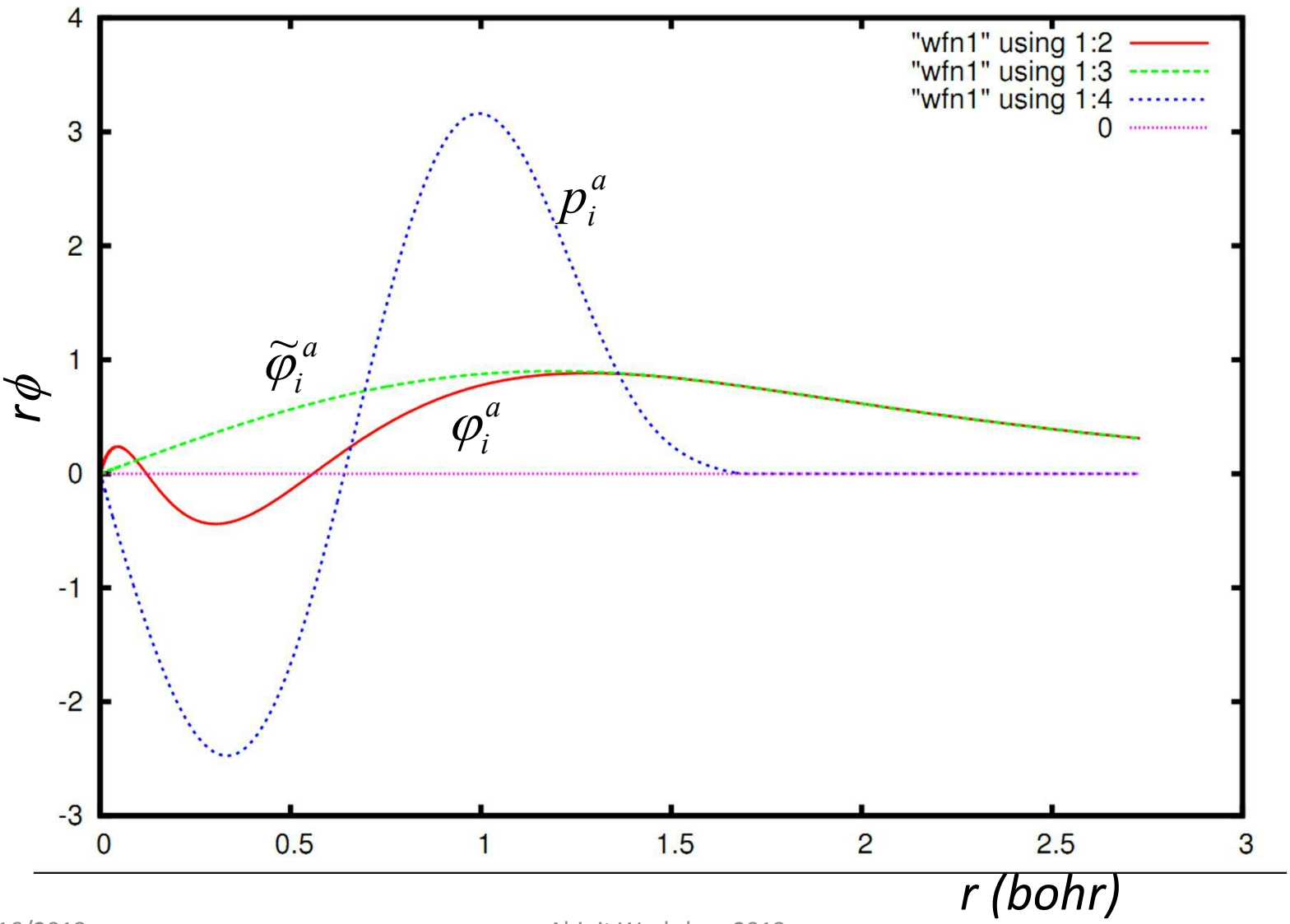
Past students contributing to this effort: John Tumbleston, Nick Dellaripa, David Harris, Xiao Xu, Nicholas Lepley, Sina Zolghadr

How hard could it be to generate efficient and accurate PAW datasets for the entire periodic table??

Unfortunately, I have not yet found the secret recipe…

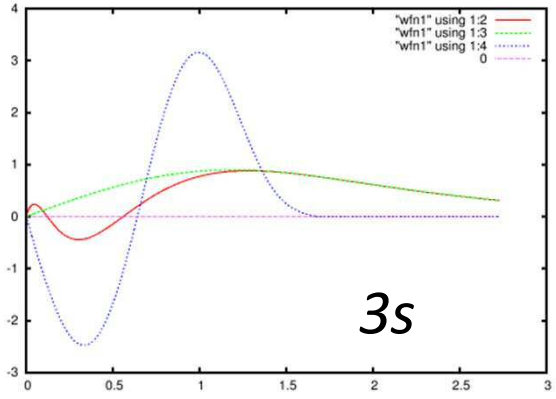
With the help of two undergraduate students – James Drewer and Cameron Kates – we hope to update the PAW datasets on the http://pwpaw.wfu.edu web page including output for use in *abinit*, *quantum espresso*, and *GPAW*??

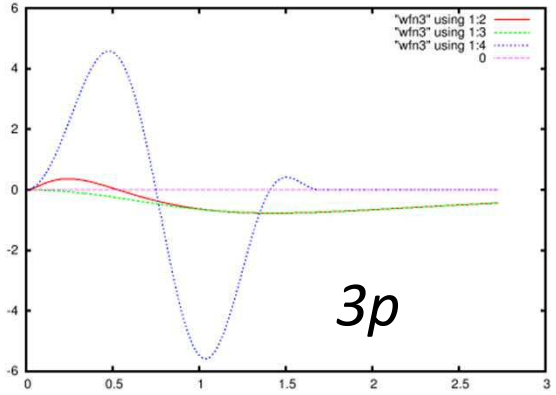
Example functions for Cl ***3s***

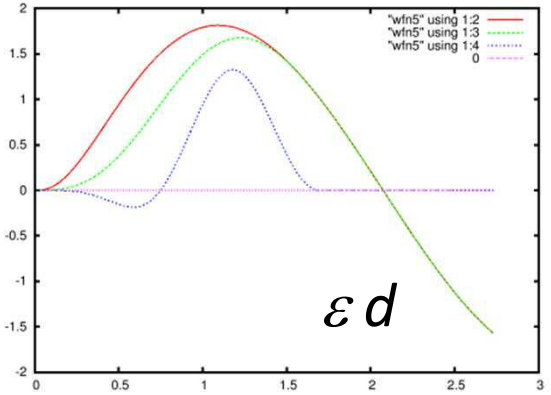


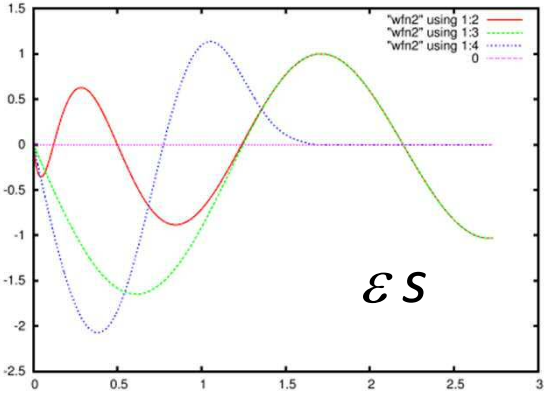
Example functions for Cl

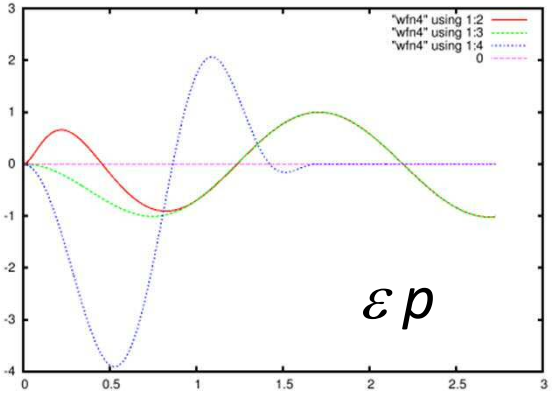
$\ell = 0$ $\ell = 1$ $\ell = 2$

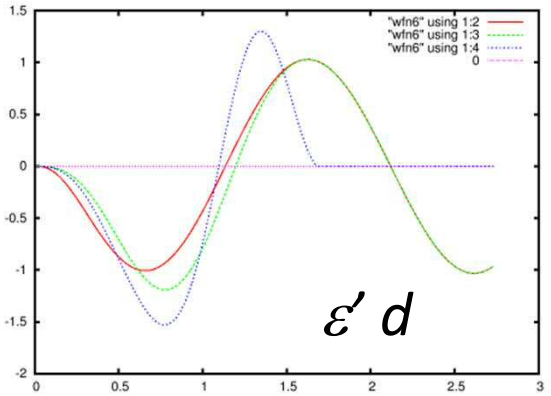












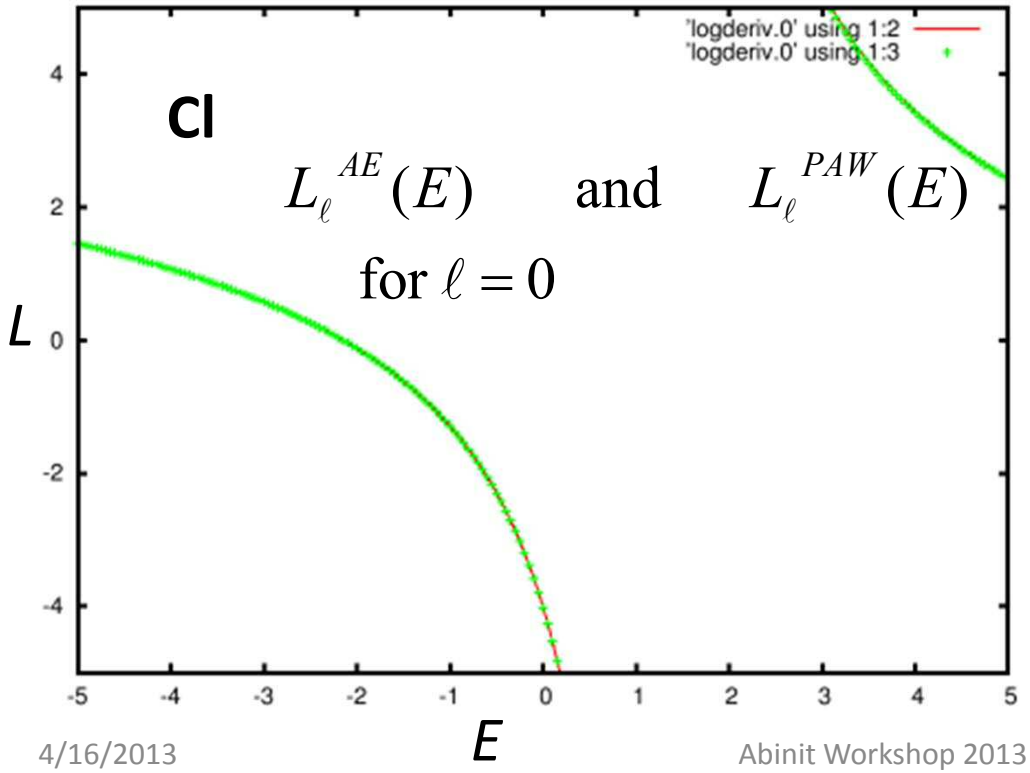
Quality measurements for datasets

- **Logderivatives**
- **Binding energy curves for representative solids**
- **Plane wave convergence properties**

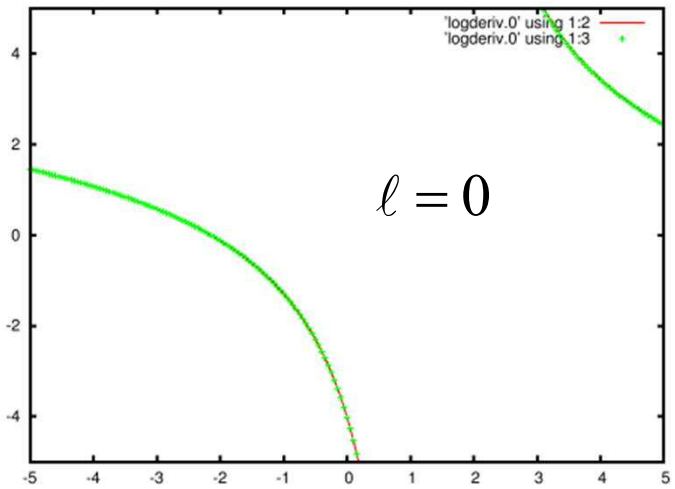
➢ Logderivatives

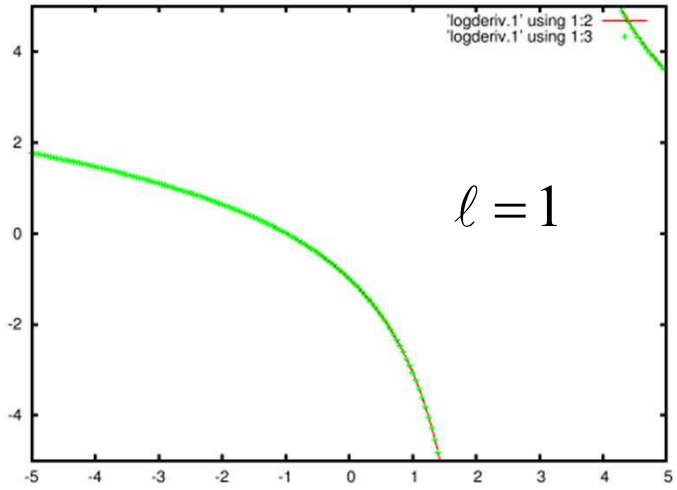
For each ℓ, solve the Schrodinger equation for range of energies E; at a radius r_c compare all electron (AE) and reconstructed PAW wavefunctions :

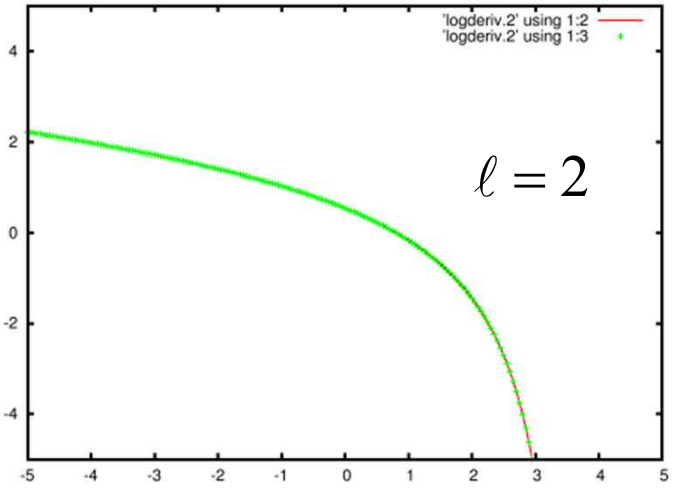
$$L_\ell^{AE}(E) \equiv \left. \frac{d\Psi_{\ell E}^{AE} / dr}{\Psi_{\ell E}^{AE}} \right|_{r_c} \qquad L_\ell^{PAW}(E) \equiv \left. \frac{d\Psi_{\ell E}^{PAW} / dr}{\Psi_{\ell E}^{PAW}} \right|_{r_c}$$

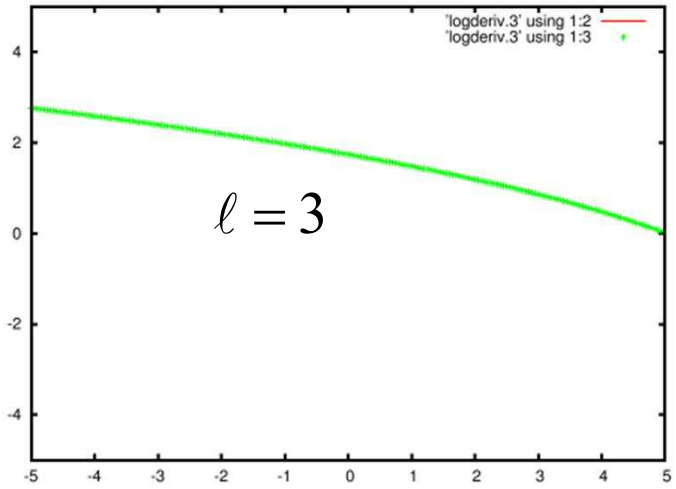


Complete logderivatives for Cl

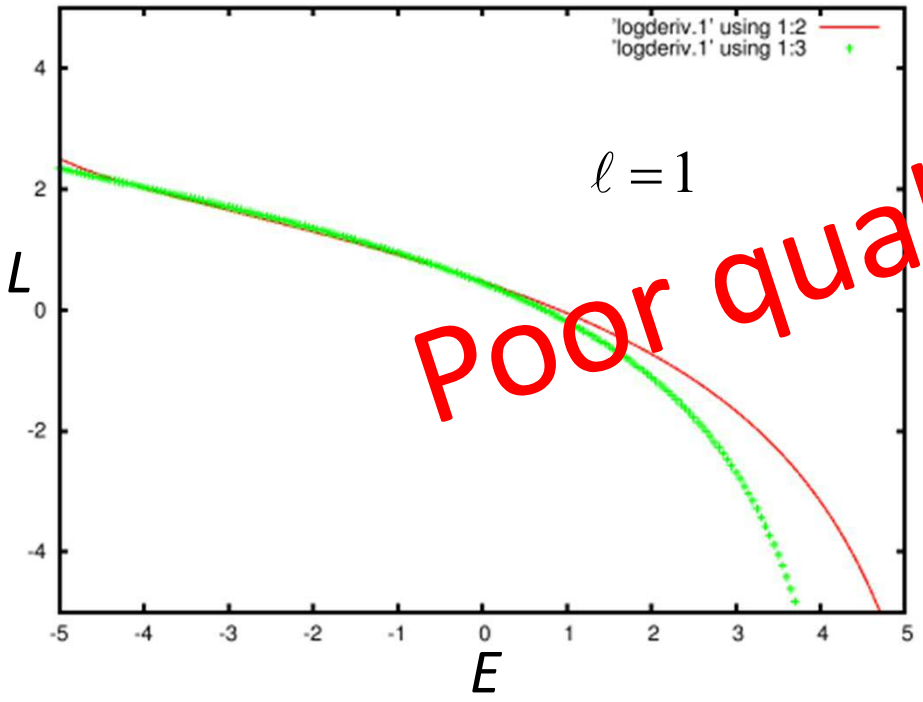


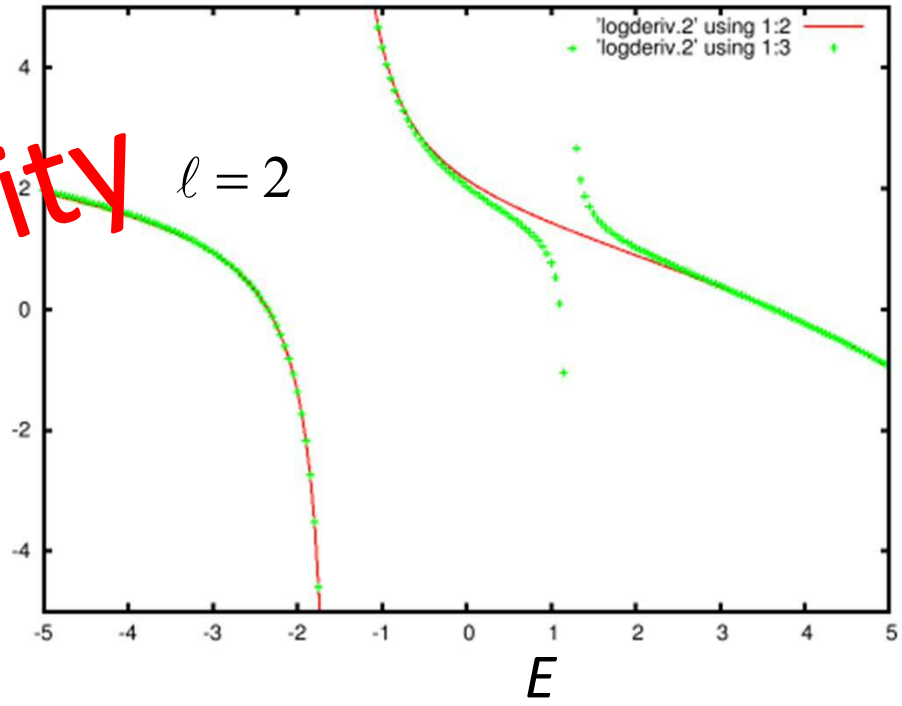






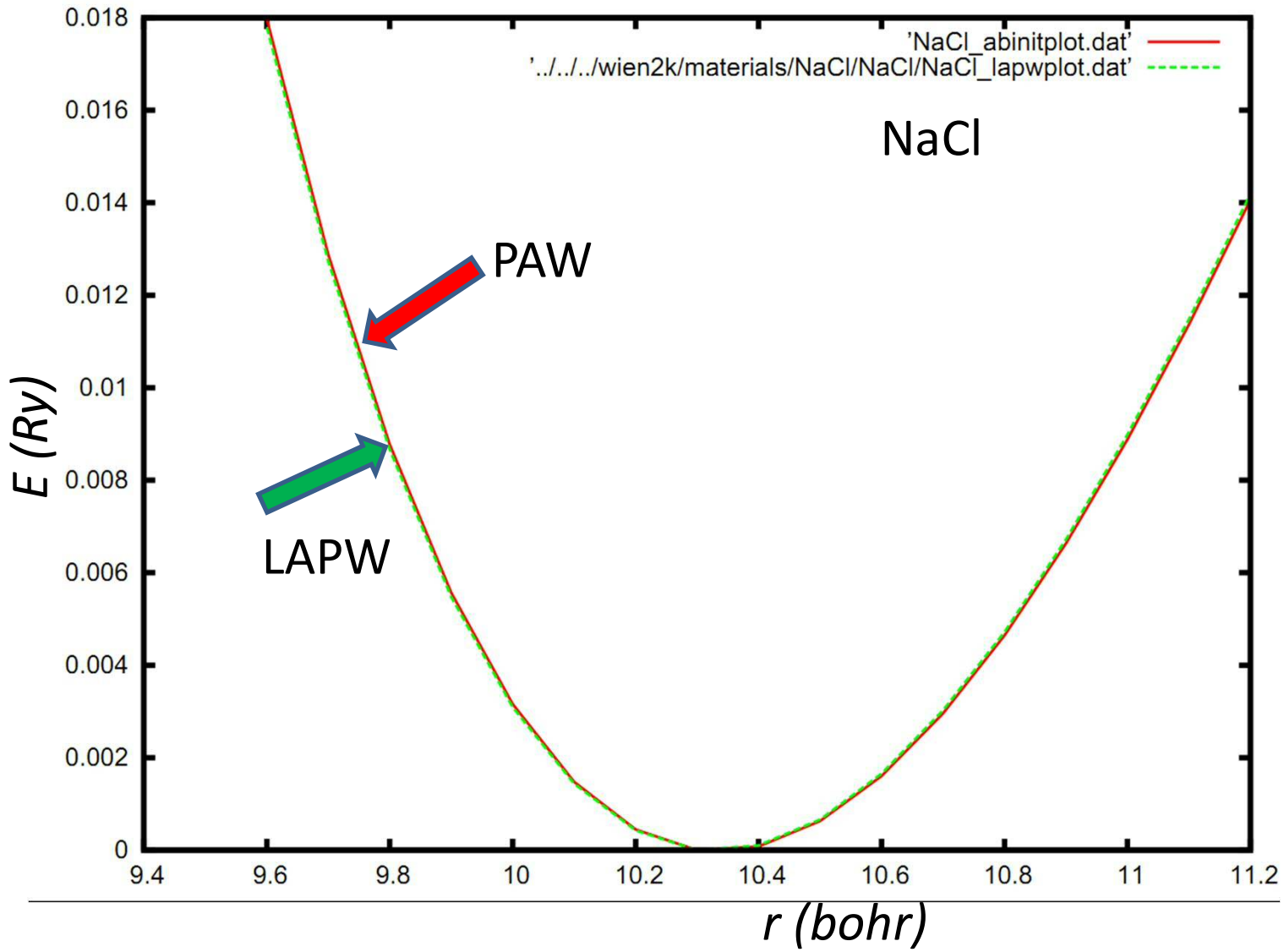
Another example of logderivatives – for Sn



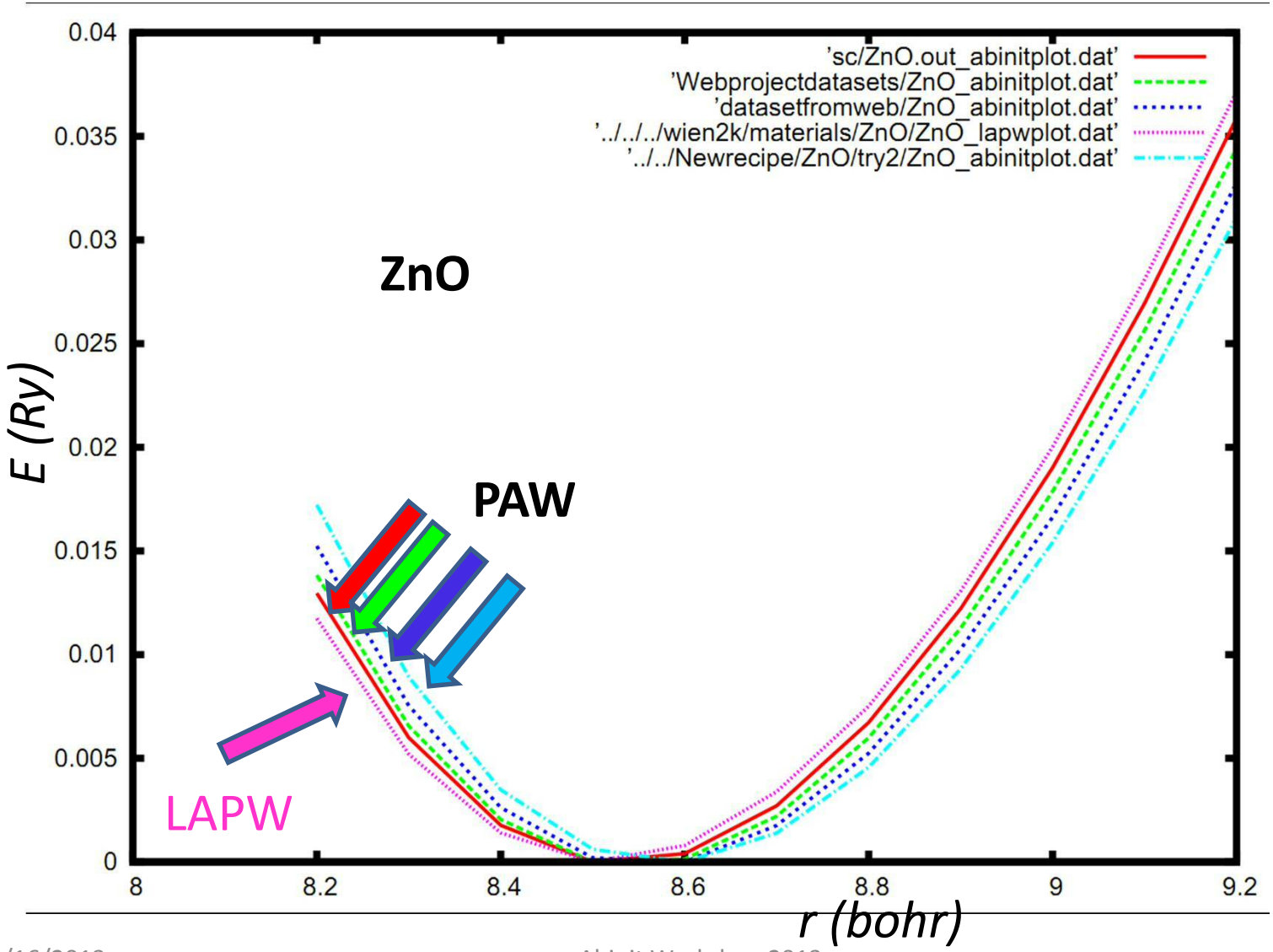


Poor quality

➢ Binding energy curves



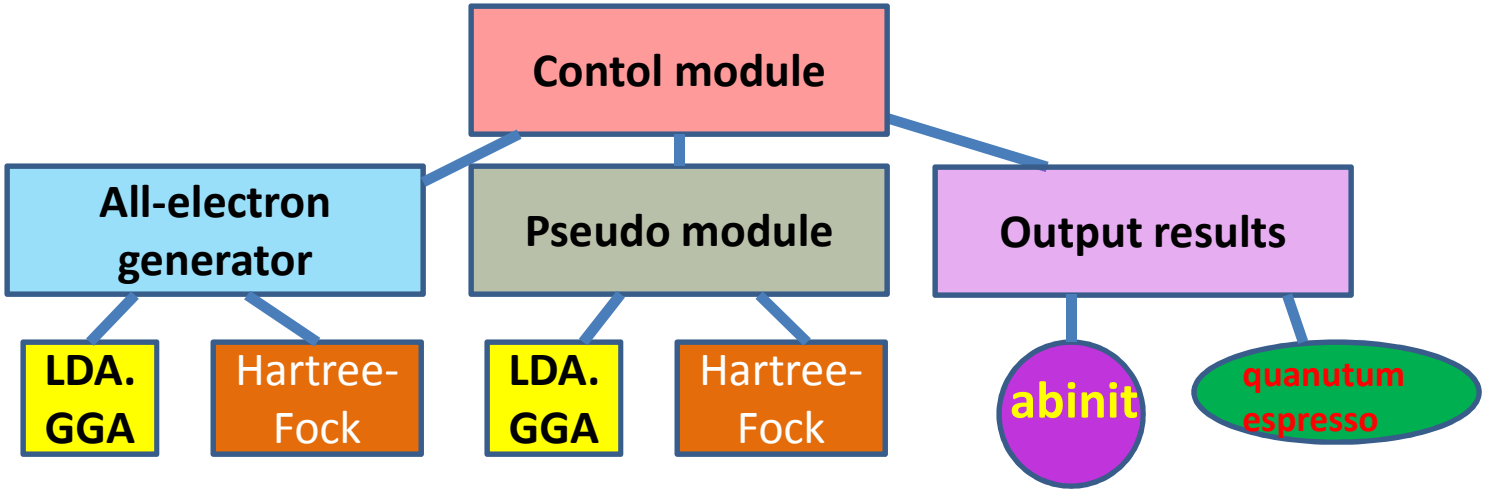
Another example of binding energy curves -- ZnO



Some ideas

- **Modular program structure (from Xiao Xu)**

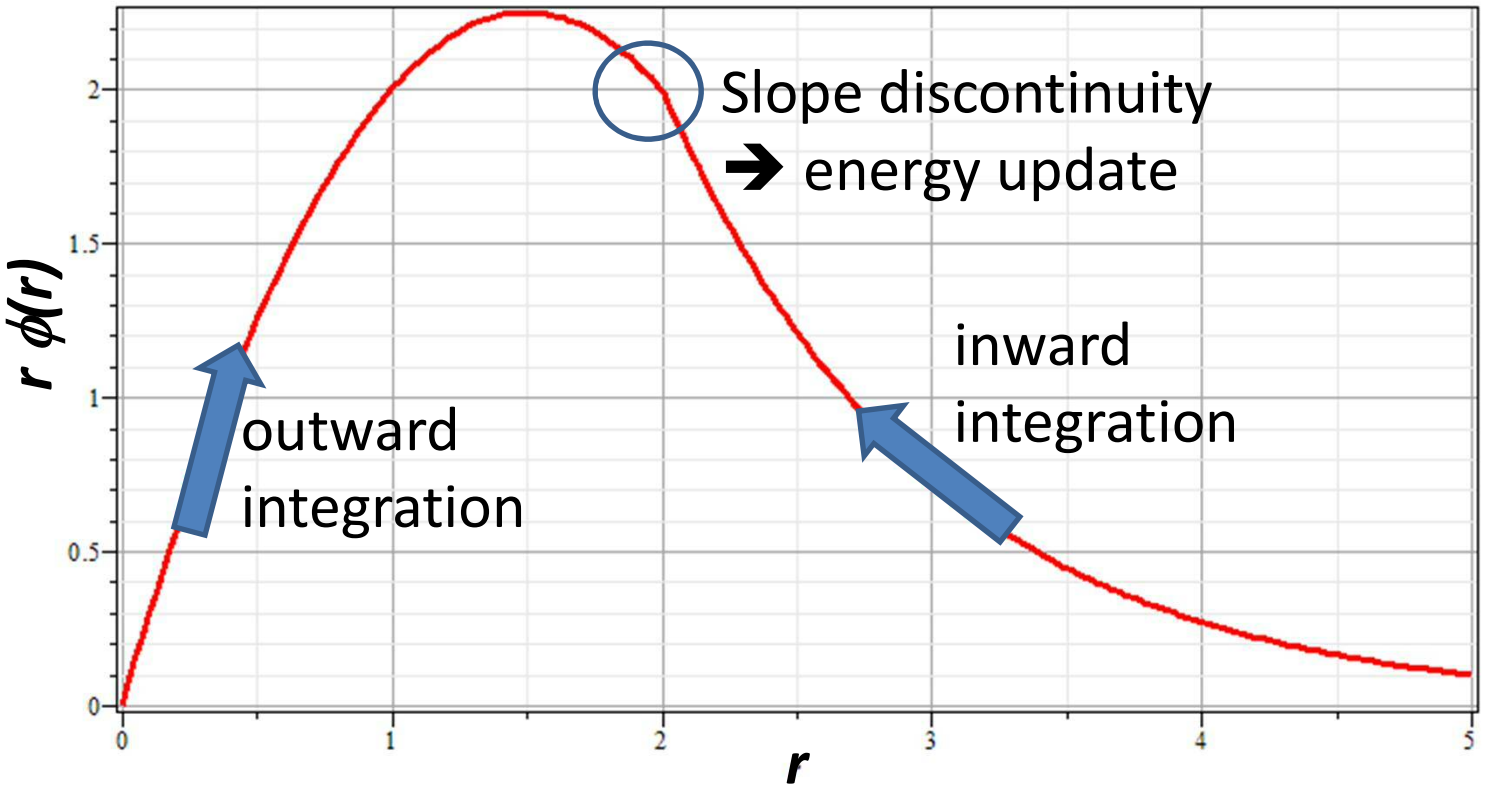
Goal – make it easier to modify the code to implement new ideas and capabilities



Some ideas -- continued

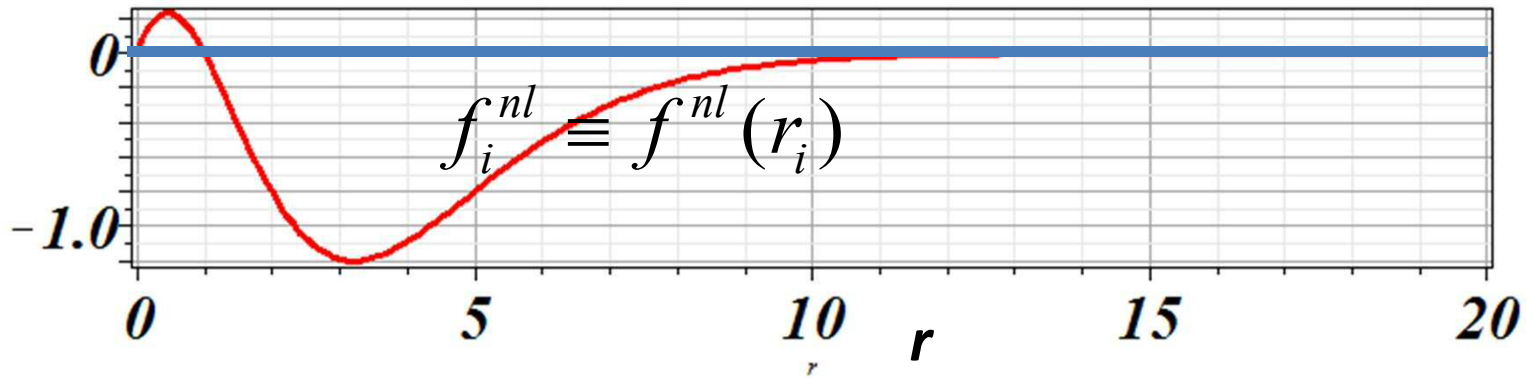
- **More robust all-electron bound state solver**

Traditional solver (from Hartree's text book)



Some ideas -- continued

- **More robust all-electron bound state solver – continued**
  Hartree's method works well for reasonable good guesses of the atomic bound state energies ε_{nl} , but occasionally convergence is difficult.



Basic idea : Use grid discretization $f_i^{nl} \equiv f^{nl}(r_i)$ and boundary values $f_i^{nl} = f_i^{nl} = 0$ as a $(N-1)\times(N-1)$ matrix eigenvalue problem : $Mf^{nl} = \varepsilon_{nl} f^{nl}$ or more generally $Mf^{nl} = \varepsilon_{nl} Sf^{nl}$ where both M and S are determined by the finite difference method (such as Numerov). Eigenvalues ε_{nl} are determined by iterative diagonalization. Once ε_{nl} are determined, need to run Hartree method to get final functions $f^{nl}(r)$.

Some ideas -- continued

- **Some new options for pseudo functions – "MODRRKJ"**
  A new option to control the shape of the pseudo basis functions

$$\text{Vanderbilt}^{*}\ \text{polynomial scheme}: \quad r\tilde{\varphi}^{a}_{n_i\ell_i}(r) = \begin{cases} r^{\ell_i+1}\sum_{s=0}^{S} C_s r^s & \text{for } r \le r_c \\ r\varphi^{a}_{n_i\ell_i}(r) & \text{for } r > r_c \end{cases}$$

$$\text{modRRKJ}^{**}\ \text{scheme}: \quad r\tilde{\varphi}^{a}_{n_i\ell_i}(r) = \begin{cases} r\sum_{s=1}^{S} C_s j_{\ell_i}(k_s r) & \text{for } r \le r_c \\ r\varphi^{a}_{n_i\ell_i}(r) & \text{for } r > r_c \end{cases}$$

*D. Vanderbilt, PRB **41**, 7892 (1990)

A. M. Rappe, K. M. Rabe, E. Kaxiras, J. D. Joannopoulos, PRB **41, 1227 (1990)

Some ideas -- continued

- **"MODRRKJ" -- continued**

$$\text{modRRKJ}^{**}\ \text{scheme}: \quad r\tilde{\varphi}^{a}_{n_i\ell_i}(r) = \begin{cases} r\sum_{s=1}^{S} C_s j_{\ell_i}(k_s r) & \text{for } r \le r_c \\ r\varphi^{a}_{n_i\ell_i}(r) & \text{for } r > r_c \end{cases}$$

The nodes are controlled by the coice of k_s. In practice, we choose 5 values of k_s: $k_s = k_0 + (s-3)\delta k$ for $s = 1,2,...5$ and k_0 is chosen so that $rj_{\ell_i}(k_0 r)$ has the correct number of nodes in the range $0 \le r \le r_c$ and so that

$$\left.\frac{d\left[rj_{\ell_i}(k_0 r)\right]/dr}{rj_{\ell_i}(k_0 r)}\right|_{r_c} = \left.\frac{d\left[r\phi_{n_i\ell_i}(r)\right]/dr}{r\phi_{n_i\ell_i}(r)}\right|_{r_c} \quad ; \quad \delta k r_c \approx \pi/20 \text{ and } C_s \text{ are the non-singular}$$

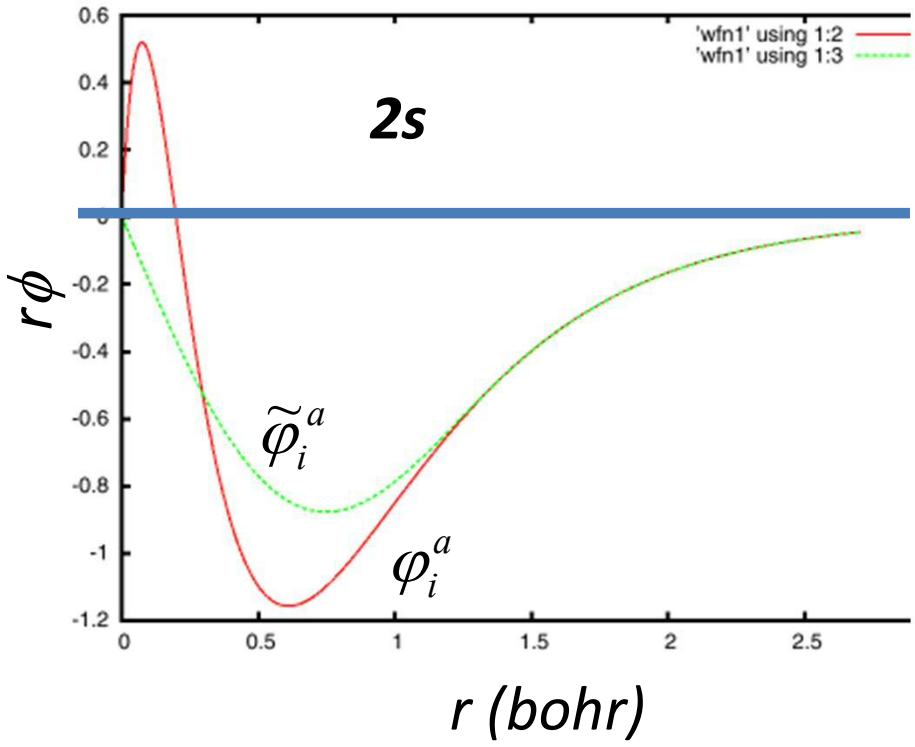
solutions to: $r_q \sum_{s=1}^{S} C_s j_{\ell_i}(k_s r_q) = r_q \varphi^{a}_{n_i\ell_i}(r_q)$ at 5 radii r_q near r_c.

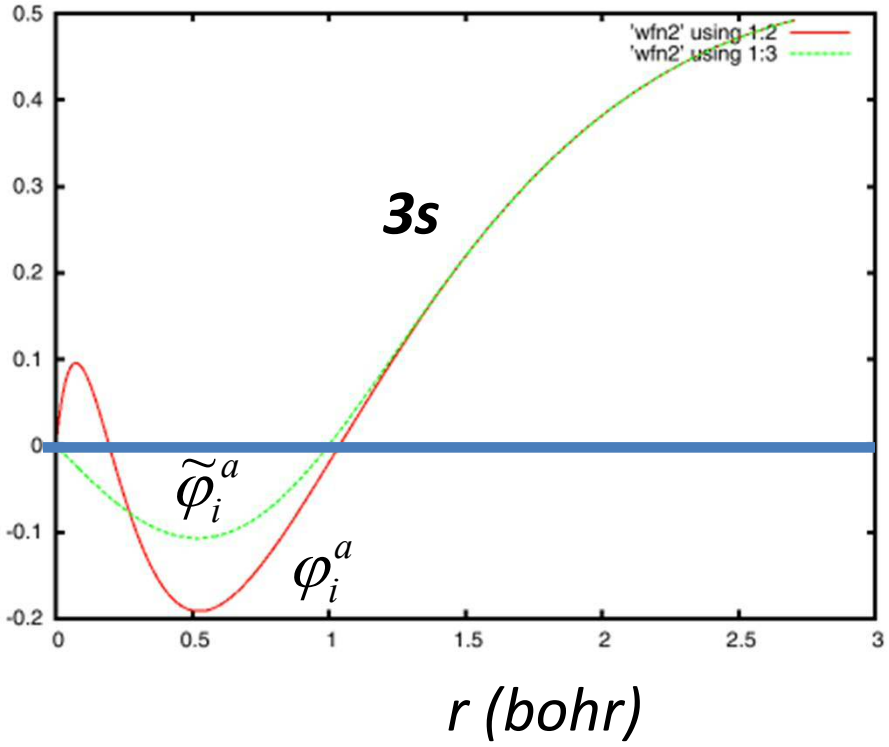
A. M. Rappe, K. M. Rabe, E. Kaxiras, J. D. Joannopoulos, PRB **41, 1227 (1990)

Some ideas -- continued

- **"MODRRKJ" – continued**

  Example for Na:





Some ideas -- continued

- **Options for systematic exploration of pseudo parameters**

Problem: There are many pseudopotential parameters that can be varied in the preparation of PAW datasets .

Machine optimization solution: Developed by Alan Wright (Sandia National Laboratory), Alan Tackett, Greg Walker, and Rachael Hansel (Vanderbilt University). (Manuscript in preparation.)

Some ideas -- continued

- **Options for systematic exploration of pseudo parameters -- continued**

Partial solution implemented into atompaw 4.0.0.0 (with inspiration from Qi Li); for a given all-electron configuration, the new version of the program allows you to run up to 9999 sets of input parameters, keeping track of the best overall success value for each *l* channel.

Some ideas -- continued

- **Options for systematic exploration of pseudo parameters -- continued** -- Example input file for Na

```
Na 11
LDA-PW   loggrid    2001
3 2 0 0 0 0
3 0 1
0 0 0
c
v
v
v
1
1.7   1.5   1.7    1.7
n
y
4.6
n
MODRRKJ VANDERBILTORTHO  Besselshape
2 0   MTROULLIER
1.5
1.7
1.5
1.7
2
default
3
UPFDX  0.0125d0   UPFXMIN   -7.d0     UPFZMESH 11.d0
0
```

Atomic configuration

Pseudo parameters

Output datasets

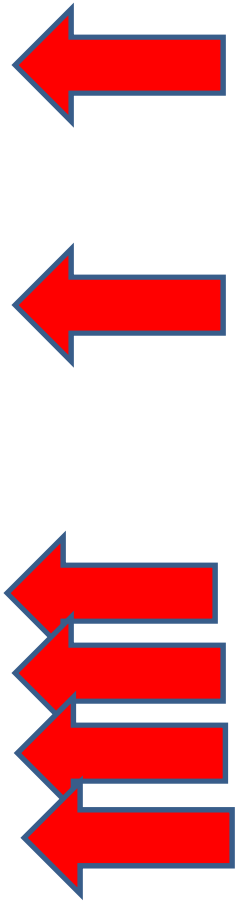
Some ideas -- continued

- **Options for systematic exploration of pseudo parameters -- continued --**

Pseudo parameters for Na

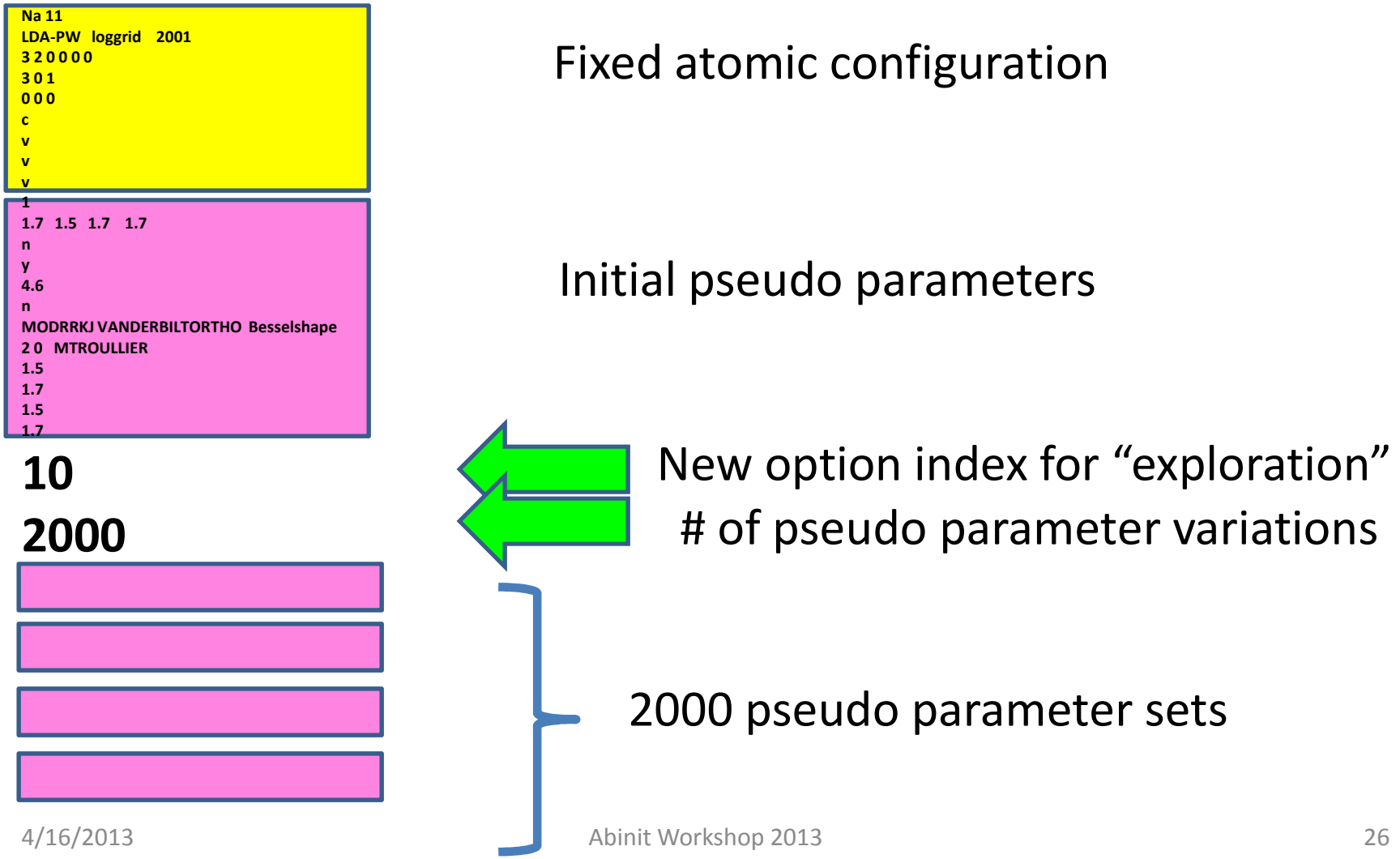
Variable

```
1
1.7  1.5  1.7  1.7
n
y
4.6
n
MODRRKJ VANDERBILTORTHO  Besselshape
2 0   MTROULLIER
1.5
1.7
1.5
1.7
```



Some ideas -- continued

- **Options for systematic exploration of pseudo parameters -- continued** -- Example input file for Na



Some ideas -- continued

- **Options for systematic exploration of pseudo parameters -- continued --**

Merit criterion based on logderivative accuracy

$$L_\ell^{AE}(E) \equiv \left. \frac{d\Psi_{\ell E}^{AE} / dr}{\Psi_{\ell E}^{AE}} \right|_{r_c} \qquad L_\ell^{PAW}(E) \equiv \left. \frac{d\Psi_{\ell E}^{PAW} / dr}{\Psi_{\ell E}^{PAW}} \right|_{r_c}$$

Figure of merit for p^{th} pseudo parameter set for each ℓ :

$$M^{\ell}{}_p = \sum_E \left| \tan\left(L_\ell^{AE}(E)\right) - \tan\left(L_\ell^{PAW}(E)\right) \right|$$

(idea attributed to Alan Tackett)

➔For each *l* channel, choose set with smallest $M^l{}_p$

Summary

- **atompaw 3.0.1.9 ➔4.0.0.0**
  - **Modular programing structure**
    - ***Intended to facilitate future modifications***
  - **More robust atomic solver**
    - ***Should be optimized; adapted to relativistic solver***
  - **Some new options for pseudo functions**
    - **MODRRKJ – *further evaluation needed***
  - **Option for systematic exploration of pseudo parameters**
    - ***Promising??***

Further work needed

- **Hartree-Fock and hybrid functionals**
  - ***Preliminary version developed; not yet compatible with abinit***
- **Integration with features developed by Marc Torrent, François Jollet, etc**

Summary -- continued

Goals for atompaw collaboration

- **To develop a flexible atomic PAW dataset generator for use in materials simulations**
  - **Control the numerical representation and allow for investigation of physical phenomena; in principle, PAW calculations should be competitive with all-electron frozen core calculations (such as LAPW or LMTO)**
  - **Provide outputs for use in several independent codes for solids (pwpaw, socorro, abinit, quantum espresso, perhaps GPAW??)**
  - **While a PAW dataset library is desirable, it will often be important to generate new datasets (for excited states, etc.)**

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Thanks to the abinit community for setting up and sustaining an exemplary collaboration!