Acquisition of Diffusion Data from Ab Initio

Part II: Representation of *ab initio* results in a database

Patrice Turchi (turchi1@llnl.gov)

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Lawrence Livermore
National Laboratory

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Review

From

Yong Du, W. B. Zhang, D. D. Liu, S. L. Cui, D. D. Zhao, L. J. Zhang, and H. H. Xu

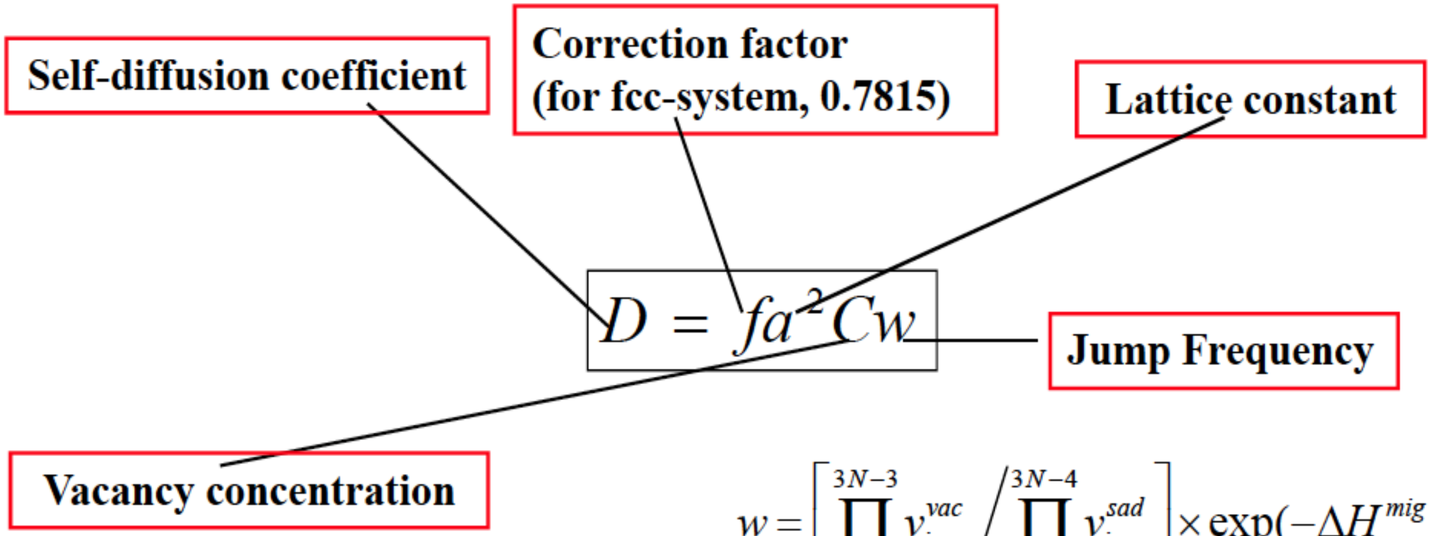
"Atomic Mobility and Diffusivity in Al Alloys"

NIST Diffusion Workshop, March 23-24, 2010

Review (Cont'd)

Self-diffusion: **M.Mantina,Y.Wang, R.Arryave, L.Q.Chen,Z.K.Liu, PRL, 100,215901(2008)**

Self-diffusion coefficient is calculated by the following equation:



Self-diffusion coefficient

Correction factor (for fcc-system, 0.7815)

Lattice constant

$$D = fa^2Cw$$

Jump Frequency

Vacancy concentration

$$C_{eq} = \exp(\frac{\Delta S_f^v}{k_B})\exp(-\frac{\Delta H_f}{k_B T})$$

ΔS^v_f = entropy of vacancy formation

ΔH_f = enthalpy of vacancy formation

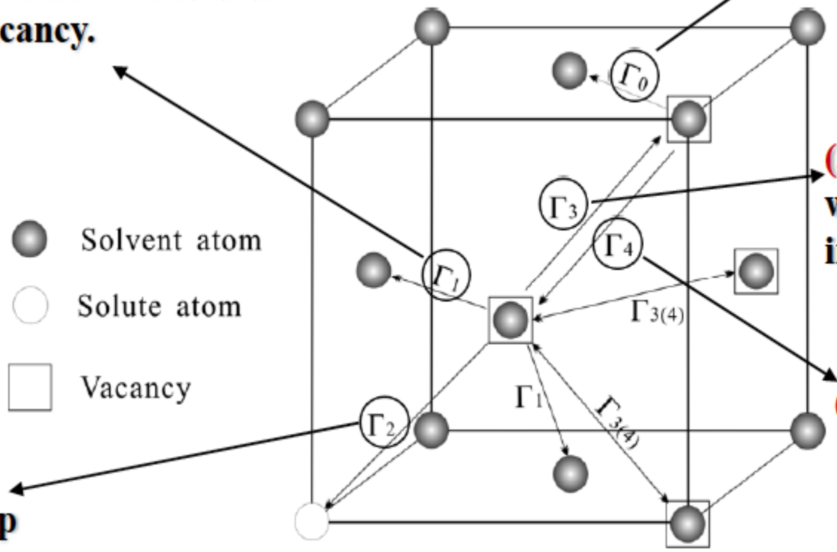
$$w = \left[\prod_{i=1}^{3N-3} \nu_i^{vac} \Big/ \prod_{i=1}^{3N-4} \nu_i^{sad}\right] \times \exp(-\Delta H_v^{mig} / k_B T)$$

ΔH_v^{mig} = vacancy migration enthalpy
(energy barrier to be overcome for an atom to jump into the vacancy)

ν_i^{vac} and ν_i^{sad} = Phonon frequencies in normal and saddle-point configurations

Review (Cont'd)

Impurity-diffusion:



(1) **a host atom (nearest neighbor to an impurity) jump which does not "dissociate" the impurity from the vacancy.**

(5) **host atom jump in the absence of an impurity.**

(3) **a host atom jump which "dissociates" the impurity and vacancy**

(4) **Reverse of jump Γ_3**

(2) **impurity atom jump**

Fig .3. Five frequency model illustration for the case of an fcc system with a dilute impurity concentration. The arrows indicate the direction of the vacancy jump.

A.D. LeClaire and A.B. Lidiard, Phil. Mag., 47, 518 (1970)

Review (Cont’d)

Impurity-diffusion:

f_2= correction factor for impurity diffusion

f_0 =self-diffusion correction factor

According to the five jump frequency model, we have:

$$\frac{D_2}{D_0} = \frac{f_2}{f_0}\frac{w_4}{w_0}\frac{w_1}{w_3}\frac{w_2}{w_1} \Longrightarrow$$

we can obtain:

$$D_2 = f_2 w_2 a^2 \exp\left(-\frac{\Delta G_f^0 - \Delta G_b}{k_B T}\right)$$

Since jump frequency of the solute atom is:

$$w_2 = v^* \exp\left(-\frac{\Delta H_m}{k_B T}\right)$$

Substitute

So we can get the expression for impurity diffusion coefficient:

$$D_2 = f_2 v^* a^2 \exp\left(\frac{\Delta S_f}{k_B}\right)\exp\left(-\frac{\Delta H_m + \Delta H_f - \Delta G_B}{k_B T}\right)$$

***E*nthalpy of vacancy formation**

Solute-vacancy binding energy

Energy barrier for the exchange of the solute impurity with a nearest-neighbor vacancy.

Review (Cont'd)

DFT Method (VASP – Transition State Theory)
First-Principles Calculation of Self-Diffusion Coefficients
M. Mantina, Y. Wang, R. Arroyave, L. Q. Chen, Z. K. Liu, and C. Wolverton
Phys. Rev. Lett. **100**, 215901-1 to 4 (2008).
In fcc Al

Impurity diffusion activation energies in Al from first principles
D. Simonovic and M. H. F. Sluiter
Phys. Rev. B **79**, 054304-1 to 12 (2009)

First principles impurity diffusion coefficients
M. Mantina, Y. Wang, L.Q. Chen, Z.K. Liu, and C. Wolverton
Acta Materialia **57**, 4102-4108 (2009).
Mg, Si, Cu in fcc Al

Vacancy mediated substitutional diffusion in binary crystalline solids
Anton Van der Ven, Hui-Chia Yu, Gerbrand Ceder, and Katsuyo Thornton
Progress in Materials Science 55, 61-105 (2010)

Atomistic modeling of As diffusion in ZnO
B. Puchala and D. Morgan
Phys. Rev. B **85**, 064106-1 to 8 (2012).

Ab initio calculations of rare-earth diffusion in magnesium
Liam Huber, Ilya Elfimov, Jörg Rottler, and Matthias Militzer
Phys. Rev. B **85**, 144301-1 to 7 (2012).
Al, Ca, RE (Gd, Sm, Nd, Pr, Ce, La, Eu) in Mg

Other Methods
Molecular Dynamics
Kinetic Monte Carlo

Representation of *ab initio* results in a database?

Requirement
The information should be self-contained so that over time the results can be reproduced by anyone

So besides the output files that summarize the relevant data, there is a need to provide:

- **the critical input files associated with the *ab initio* code (especially the pseudo-potential file),**
- **a short description (in words) of the major approximations that have been made, and**
- **a "sense" of the accuracy of the results.**

The *ab initio* code should be specified by its version, and the method that has been considered to generate the relevant data

What Are We Talking About?

There is a suite of popular pseudo-potential codes available:

Abinit – www.abinit.org
Pseudo-potentials and plane-wave basis set

CAMPOS – www.fysik.dtu.dk/CAMP/CAMPOS_welcome.html
Pseudo-potentials and plane-wave basis set.

CASTEP – www.tcm.phys.cam.uk/castep
Pseudo-potentials and plane-wave basis set

FHI96MD – www.fhi-berlin.mpg.de/th/fhimd
Pseudo-potentials and plane-wave basis set,
with molecular dynamics capabilities based on the Car-Parrinello technique

PWSCF – www.pwscf.org
Pseudo-potentials and plane-wave basis set.
DFT codes include response function (phonon) features.

Quantum Expresso – www.democritos.it/scientific.php
Pseudo-potentials and LCAO basis set.
Open-source package for research in electronic structure, simulation, and optimization.

SIESTA – www.uam.es/depatamentos/ciencas/fismateriac/siesta
Pseudo-potentials and LCAO basis set

★ **VASP – www.mpi.univie.ac.at/vasp** ★
Pseudo-potentials and plane-wave basis set

ELECTRONIC STRUCTURE METHODS: What are they for?

Ab initio Approaches: “Trends & Understanding” versus “Numbers”

Equilibrium Properties:	Lattice parameter(s) ✡ Structural energy difference
Elastic Properties:	Bulk modulus, elastic constants ✡ Phonon spectrum ✡
Electronic Properties:	Density of states (γ of specific heat) ✡ N.B.: low $n(E_F)$ is not a necessary condition for stability Charge density Spectroscopic data (UPS,XPS,PAS,ARPES,…)
Transport Properties:	Conductivity (DC and AC) Reflectivity
Magnetic Properties:	Magnetic ordering Moments
Defect Properties:	Energetics (defect formation energy, energy barrier, etc.) ✡
Surface Properties:	Structure (reconstruction, chemical order) Energetics
Alloy Properties:	All of the above Formation energy Ordering energy Stacking fault and anti-phase boundary energies

Electronic Structure Methods

Ab initio Approaches:

“Wave” versus “Green Function”
or
“Order” versus “Disorder”

Pseudo-potential-based Methods:

- **VASP** (http://cms.mpi.univie.ac.at/vasp)
  Pseudo-potentials and plane-wave basis set
- **Siesta** (http://www.uam.es/depatamentos/ciencias/fismateriac/siesta)
  Pseudo-potentials and LCAO basis set
- **ABINIT** (http://www.abinit.org)
  Pseudo-potentials and plane-wave basis set

Full-potential Methods:

- **Wien97** (http://www.tuwien.ac.at/theochem/wien97), replaced now by:
- **Wien2k** (http://www.wien2k.at)
  Linear Augmented Plane Wave (LAPW) and local orbital method
- **LmtART** (http://www.mpi-stuttgart.mpg.de/andersen/LMTOMAN/lmtman.pdf)
- **Full-Potential Linear Muffin-Tin Orbital (FP-LMTO)**
- **Full-Potential Linearized-Augmented Plane Wave (FP-LAPW)**

Other Methods:

- **KKR**
- **TB-LMTO-ASA** (http://www.mpi-stuttgart.mpg.de/andersen/LMTODOC/LMTODOC.html)

Electronic Structure Methods (cont’d)

Ab initio Approaches:

“Wave” versus “Green Function”
or
“Order” versus “Disorder”

Methods Limited to Ordered Structures:
(Wave Methods)

- Pseudo-Potential
- LAPW or FP-LAPW
- LMTO or FP-LMTO
- ASW
- FP-LASTO

Methods that can also handle Disordered Structures (via, e.g., the CPA):
(Green’s function Methods)

- KKR
- TB-LMTO

Electronic Structure Methods (cont' d)

Ab initio Approaches:
What does "Accuracy" mean?

Most *ab initio* methods are based on "Density Functional Theory (DFT)"

Approximations:

Exchange and correlation effects

Local Density Approximation (LDA)

- Von Barth & Hedin
- Hedin and Lundqvist
- Wigner
- Vosko
- Ceperley and Alder (Perdew and Zunger)

Beyond LDA

- GGA
- LDA+U
- SIC
- GW
- DMFT

Other Approximations:

Shape of the potential function

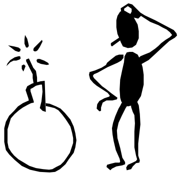
- Muffin-tin
- ASA (Equal versus non-equal sphere radii)
- Full potential

Core versus Valence electrons

Scalar relativistic versus Fully relativistic

Collinear versus Non-collinear magnetism

Born-Oppenheimer approximation



Hence an energy can be obtained within less than 1 J/mol and at the same time be off by several kJ/mol

Electronic Structure Methods (cont’d)

“Accuracy” versus “Precision”
Structural stability of Mo and Ru

Method	$\Delta E_{Mo}^{fcc-bcc}$	$\Delta E_{Ru}^{fcc-bcc}$
LMTO-ASA+CC	+31.42	-39.43
LMTO-ASA	+28.00	-34.00
TB-LMTO (F.R.)	+48.00	-34.40
LAPW (NRL)	+25.64	-44.59
FP-LASTO	+30.10	-35.98
FP-LAPW	+31.52	

Energies in mRy/atom

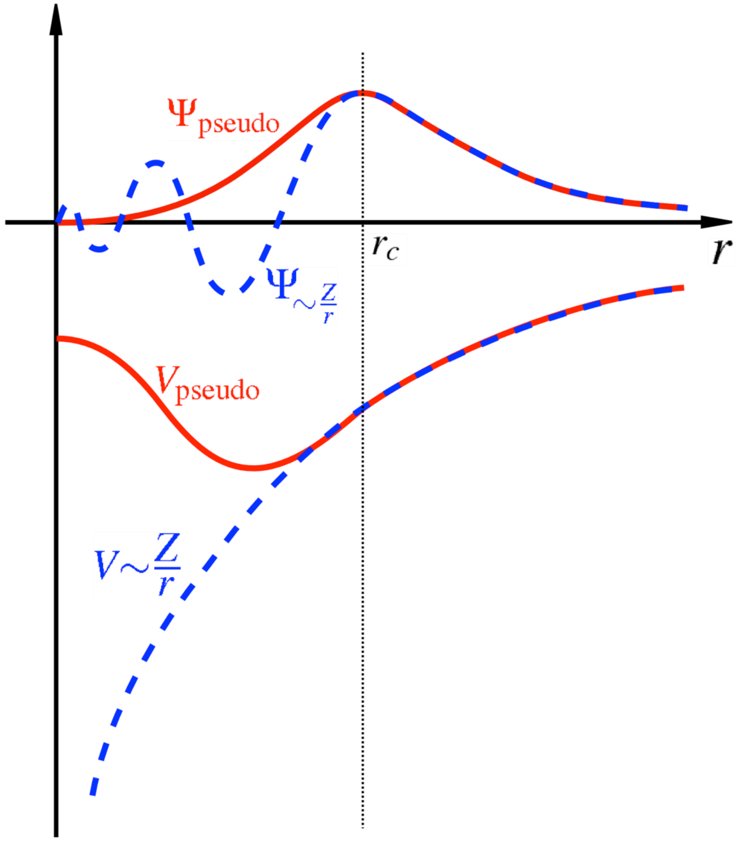
Why Pseudo-potentials?

- Reduction of the basis set size.
- Reduction of the number of electrons.

Critical Approximations:

- One-electron picture
- No significant overlap between core and valence wavefunctions (frozen core)

The only role of the core electrons is to provide an effective external potential (or pseudo-potential) in which the outer electrons move.



SPEED versus ACCURACY and TRANSFERABILITY

Results from a pseudo-potential-based code are as good as the pseudo-potentials are.

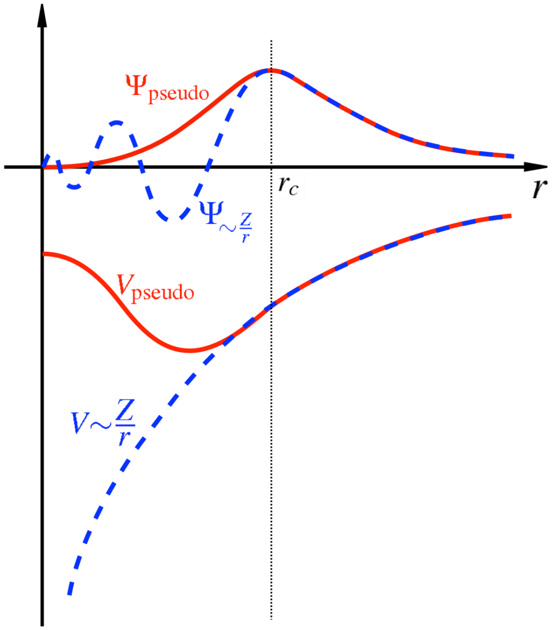
What Are We Talking About?

Norm-conserving pseudo-potentials: outside r_c the norm of each pseudo-wavefunction is identical to its corresponding all-electron wavefunction.

Ultra-soft pseudo-potentials: relax the norm-conserving constraint to reduce the basis set size (other related technique: PAW).

Critical Approximations (true for most DFT-based methods and codes):

- Exchange and correlation potential (LDA, LSDA, GGA, SIC, GWM, DMFT)
- Relativistic effects (scalar relativistic, fully relativistic, spin-orbit coupling)
- In most DFT-based codes, the zero-point motion contribution to the total energy is absent.



Why Construct a Pseudo-potential?

- There is a handful of repositories with prefabbed pseudo-potentials:
- Abinit's web site: http://www.abinit.org
- Rappe Group: http://lorax.chem.upenn.edu
- Vanderbilt's library of ultrasoft pseudo-potentials:
  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
  - Pseudo-potential may not give accurate results
  - Pseudo-potential may be too expensive to use for your problem

- Furthermore, having the ability to construct pseudo-potentials can be an important research tool.

What is a Good Pseudo-potential?

- For a pseudo-potential to be useful, it must be both accurate and efficient

accuracy - reproduction of all-electron atomic properties

efficiency - cost of using the pseudo-potential in solid-state calculations

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

Open-source Pseudo-potential Interface and Unification Module
(J. Bennett & A.M. Rappe)

http://opium.sourceforge.net/index.html

Representation of *ab initio* results in a database?

Requirement
The information should be self-contained so that over time the results can be reproduced

Let us consider VASP as an example
4 main input files:
POSCAR
INCAR
POTCAR
KPOINTS

These are the files that are used to generate the main results

The **INCAR** file is the central input file of VASP. It determines "what to do and how to do it". There is a relatively large number of parameters that may be set by means of tags in the INCAR file. Most of these parameters have convenient defaults, and a user unaware of their meaning should not change any of the default values.

Representation of *ab initio* results in a database?

POSCAR

(Example of Al_2Cu, C16)

```
     5.6377963814923238
     1.0000000000000000     0.0000000000000000     0.0000000000000000
     0.0000000000000000     1.0000000000000000     0.0000000000000000
     0.0000000000000000     0.0000000000000000     1.0000000000000000
Cu  Al
4   8
d
     0.0000000000000000     0.0000000000000000     0.2500000000000000
     0.0000000000000000     0.0000000000000000     0.7500000000000000
     0.5000000000000000     0.5000000000000000     0.7500000000000000
     0.5000000000000000     0.5000000000000000     0.2500000000000000
     0.2500000000000000     0.7500000000000000     0.0000000000000000
     0.7500000000000000     0.2500000000000000     0.0000000000000000
     0.2500000000000000     0.2500000000000000     0.0000000000000000
     0.7500000000000000     0.7500000000000000     0.0000000000000000
     0.7500000000000000     0.2500000000000000     0.5000000000000000
     0.2500000000000000     0.7500000000000000     0.5000000000000000
     0.7500000000000000     0.7500000000000000     0.5000000000000000
     0.2500000000000000     0.2500000000000000     0.5000000000000000
```

Representation of *ab initio* results in a database?

The **INCAR** file is the central input file of VASP. It determines "what to do and how to do it". There is a relatively large number of parameters that may be set by means of tags in the INCAR file. Most of these parameters have convenient defaults, and a user unaware of their meaning should not change any of the default values.

INCAR

```
SYSTEM = for sample bulk (R.S)

  PREC = H     Medium=default, Low, High; affects ENMAX, mesh, pspot
#   NSW    =     3   max number of geometry steps
#   IBRION =      2    ionic relax: 0-MD 1-quasi-New 2-CG
#   ISIF = 2
  LORBIT = 11
  ISMEAR =     -5    -4-tet -1-fermi 1=Methfessel/Paxton 1.order
  SIGMA  =     .13    broadening in eV
  ALGO = FAST
  EDIFF = 1e-5

#   NELM = 60
#   LREAL  =  AUTO   real-space projection
   LREAL=.FALSE.

#   NBANDS =   12    # of bands; default = 1.2 * #elec/2 + 4
#    ISPIN = 2

#     KPAR = 12
#     NCORE = 1

# write WAVECAR
# LWAVE=.FALSE.

IALGO = 48
LPLANE = .TRUE.
LSCALU = .FALSE.
NSIM   = 4
NPAR = 4
```

Representation of *ab initio* results in a database?

The **POTCAR** file contains the pseudo-potential for each atomic species used in the calculation.
If the number of species is larger than one simply concats the POTCAR files of the species.

POTCAR

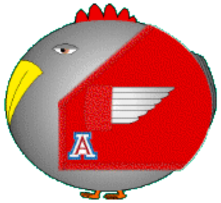
```
PAW_PBE Cu 05Jan2001
 11.0000000000000000
 parameters from PSCTR are:
   VRHFIN =Cu: d10 p1
   LEXCH  = PE
   EATOM  =  1390.9800 eV,  102.2341 Ry

   TITEL  = PAW_PBE Cu 05Jan2001
   LULTRA =        F    use ultrasoft PP ?
   IUNSCR =        1    unscreen: 0-lin 1-nonlin 2-no
   RPACOR =    2.000    partial core radius
   POMASS =   63.546; ZVAL   =   11.000    mass and valenz
   RCORE  =    2.300    outmost cutoff radius
   RWIGS  =    2.480; RWIGS  =    1.312    wigner-seitz radius (au A)
   ENMAX  =  273.214; ENMIN  =  204.910 eV
   RCLOC  =    1.712    cutoff for local pot
   LCOR   =        T    correct aug charges
   LPAW   =        T    paw PP
   EAUG   =  516.456
   DEXC   =    -.008
   RMAX   =    2.789    core radius for proj-oper
   RAUG   =    1.300    factor for augmentation sphere
   RDEP   =    2.302    radius for radial grids
   QCUT   =   -4.481; QGAM   =    8.962    optimization parameters
```

../..

```
Description
   l     E      TYP  RCUT    TYP  RCUT
   2   .000     23  2.300
   2   .000     23  2.300
   0   .000     23  2.300
   0   .000     23  2.300
   1  -.200     23  2.300
   1   .000     23  2.300
   3   .000      7   .000
  Error from kinetic energy argument (eV)
  NDATA  =      100
  STEP   =   20.000   1.050
 109.      107.      107.      105.      104.      103.      101.      100.
 98.3      96.3      95.3      93.2      91.0      88.7      86.3      83.9
 81.3      78.7      76.1      72.1      69.4      66.6      62.5      59.8
 57.0      52.9      48.9      46.3      42.4      38.7      35.1      31.7
 28.5      25.5      22.6      20.0      16.7      14.5      11.9      10.2
 8.20      6.49      5.05      3.87      2.91      2.14      1.55      .993
 .677      .403      .230      .144      .805E-01  .493E-01  .351E-01  .324E-01
 .322E-01  .315E-01  .287E-01  .242E-01  .187E-01  .135E-01  .919E-02  .577E-02
 .414E-02  .333E-02  .317E-02  .315E-02  .295E-02  .256E-02  .195E-02  .137E-02
 .935E-03  .701E-03  .618E-03  .611E-03  .587E-03  .509E-03  .381E-03  .272E-03
 .197E-03  .172E-03  .169E-03  .159E-03  .131E-03  .952E-04  .697E-04  .595E-04
 .584E-04  .539E-04  .420E-04  .308E-04  .246E-04  .238E-04  .221E-04  .174E-04
 .126E-04  .110E-04  .107E-04  .919E-05
END of PSCTR-controll parameters
 local part
 81.2582175088937078
  .11614773E+03  .11612882E+03  .11607207E+03  .11597758E+03  .11584543E+03
  .11567580E+03  .11546888E+03  .11522490E+03  .11494414E+03  .11462690E+03
...........................................................................................
```

Conclusions

- Yes, there are plenty of “good” user friendly pseudo-potential-based codes out there



- The question is: are the pseudo-potentials for a given set of elements designed to tackle a problem never looked at before?
  - Pseudo-potentials must be checked out within a new atomic configuration space against full potential-based electronic structure results (the same way EAM potentials should) to make sure that accuracy is preserved

- There will always be a trade off between speed and accuracy (and therefore transferability)