Acquisition of Diffusion Data from Ab Initio
Part II: Representation of \textit{ab initio} results in a database

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\textit{NIST Diffusion Workshop, May 9-10, 2013, Gaithersburg, MD}
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

Self-diffusion coefficient is calculated by the following equation:

\[
D = f a^2 C_W
\]

**Vacancy concentration**

\[
C_{eq} = \exp\left(\frac{\Delta S^v_f}{k_B}\right) \exp\left(-\frac{\Delta H_f}{k_B T}\right)
\]

\(\Delta S^v_f = \) entropy of vacancy formation

\(\Delta H_f = \) enthalpy of vacancy formation

**Correction factor**

(for fcc-system, 0.7815)

**Lattice constant**

**Jump Frequency**

\[
\omega = \frac{3N-3}{\prod_{i=1}^{3N-4}} v_i^{vac} \times \exp\left(-\frac{\Delta H^\text{mig}_v}{k_B T}\right)
\]

\(\Delta H^\text{mig}_v = \) vacancy migration enthalpy

(energy barrier to be overcome for an atom to jump into the vacancy)

\(v_i^{vac}\) and \(v_i^{sad}\) = Phonon frequencies in normal and saddle-point configurations
Impurity-diffusion:

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

(2) impurity atom jump

(3) a host atom jump which “dissociates” the impurity and vacancy

(4) Reverse of jump $\Gamma_3$

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

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)
Impurity-diffusion:

According to the five jump frequency model, we have:

\[
\frac{D_2}{D_0} = \frac{f_2}{f_0} \frac{w_4}{w_0} \frac{w_1}{w_3} \frac{w_2}{w_1}
\]

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:

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

Enthalpy of vacancy formation

Solute-vacancy binding energy

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

Impurity diffusion activation energies in Al from first principles
D. Simonovic and M. H. F. Sluiter

First principles impurity diffusion coefficients
M. Mantina, Y. Wang, L.Q. Chen, Z.K. Liu, and C. Wolverton
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

Ab initio calculations of rare-earth diffusion in magnesium
Liam Huber, Ilya Elfimov, Jörg Rottler, and Matthias Militzer
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

**SIESTA** – www.uam.es/departamentos/ciencias/fismateriaf/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 (\(\gamma\) 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](http://cms.mpi.univie.ac.at/vasp))
  - Pseudo-potentials and plane-wave basis set
- **Siesta** ([http://www.uam.es/depatamentos/ciencias/fismateriac/siesta](http://www.uam.es/depatamentos/ciencias/fismateriac/siesta))
  - Pseudo-potentials and LCAO basis set
- **ABINIT** ([http://www.abinit.org](http://www.abinit.org))
  - Pseudo-potentials and plane-wave basis set

**Full-potential Methods:**

- **Wien97** ([http://www.tuwien.ac.at/theochem/wien97](http://www.tuwien.ac.at/theochem/wien97)), replaced now by:
  - **Wien2k** ([http://www.wien2k.at](http://www.wien2k.at))
  - Linear Augmented Plane Wave (LAPW) and local orbital method
- **LmtART** ([http://www.mpi-stuttgart.mpg.de/andersen/LMTOMAN/lmtman.pdf](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](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

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta E_{\text{fcc-bcc}}^{\text{Mo}}$</th>
<th>$\Delta E_{\text{fcc-bcc}}^{\text{Ru}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMTO-ASA+CC</td>
<td>+31.42</td>
<td>-39.43</td>
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<tr>
<td>LMTO-ASA</td>
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<td>TB-LMTO (F.R.)</td>
<td>+48.00</td>
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<tr>
<td>LAPW (NRL)</td>
<td>+25.64</td>
<td>-44.59</td>
</tr>
<tr>
<td>FP-LASTO</td>
<td>+30.10</td>
<td>-35.98</td>
</tr>
<tr>
<td>FP-LAPW</td>
<td>+31.52</td>
<td></td>
</tr>
</tbody>
</table>

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)

Representation of \textit{ab initio} results in a database?

\textbf{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:

\begin{itemize}
  \item POSCAR
  \item INCAR
  \item POTCAR
  \item KPOINTS
\end{itemize}

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

The \texttt{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 \texttt{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\textsubscript{2}Cu, 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
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<td>0.5000000000000000</td>
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<td>0.2500000000000000</td>
<td>0.7500000000000000</td>
<td>0.0000000000000000</td>
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</tr>
<tr>
<td>0.7500000000000000</td>
<td>0.2500000000000000</td>
<td>0.0000000000000000</td>
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<td>0.2500000000000000</td>
<td>0.5000000000000000</td>
<td></td>
</tr>
</tbody>
</table>
```
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.

```
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.
LSCALE = .FALSE.
NSIM   = 4
NPAR   = 4
```
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.
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).