« PROJECTOR AUGMENTED-WAVE »
METHOD: GENERATION OF ATOMIC DATASETS

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OUTLINE

The PAW data set

Generation of PAW atomic data

Validation of PAW atomic data
THE PAW DATASET
ATOMIC DATA: WHAT DO WE NEED?

Wavefunction: \[ |\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i \left( |\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle\tilde{p}_i|\tilde{\psi}_n\rangle = \tau |\tilde{\psi}_n\rangle \]

Hamiltonian: \[ \tilde{H}\tilde{\psi}_n = \varepsilon_n S\tilde{\psi}_n \]

\[ S = 1 + \sum_{R,ij} \tilde{p}_i^R \left( \langle \phi_i^R | \phi_j^R \rangle - \langle \tilde{\phi}_i^R | \tilde{\phi}_j^R \rangle \right) \tilde{p}_j^R \]

\[ D_{ij} = \sum_L \int \tilde{v}_{eff}(\mathbf{r}) Q_{ij}^L(\mathbf{r}) d\mathbf{r} \]

\[ + \langle\phi_i| - \frac{\Delta}{2} + v_H [n^1 + n_{Zc}] + v_{xc} [n^1 + n_c] \phi_j \rangle \]

\[ - \langle\tilde{\phi}_i| - \frac{\Delta}{2} + v_H [\tilde{n}^1 + \tilde{n} + \tilde{n}_{Zc}] + v_{xc} [\tilde{n}^1 + \tilde{n} + \tilde{n}_c] \tilde{\phi}_j \rangle - \sum_L \int \tilde{v}_{eff}^1(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r} \]

\[ D_{ij} = D_{ij}^0 + \sum_{kl} \rho_{kl} E_{ijkl} + D_{ij}^{xc} + \sum_L \int \tilde{v}_{eff}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r} \]

Inside circles: atomic data needed
In order to perform a PAW calculation, following atomic data are needed:

For each atomic specie

\[
\{ \phi_i^R \}, \quad \{ \tilde{\phi}_i^R \}, \quad \{ \tilde{p}_i^R \}, \quad V_H [\tilde{n}_{Zc}], \quad n_c, \quad \tilde{n}_c, \quad D_{ij}^0
\]

- All electron partial waves
- Projectors (dual of $\tilde{\phi}_i^R$)
- Pseudized soft partial waves
- Hartree potential due to nuclueus and core electrons (local pot.)
- Core density
- Pseudized core density
- Frozen part of $D_{ij}$ term

Definitions of radial grids are also needed

Constraints:
- Precision of the calculation
- Speed of convergence (number of plane waves)

Have to generate an adapted basis
Generation process

1. Solve "exactly" the atomic problem (for the given LDA/GGA functional)

2. Transform some quantities into smooth ones ("pseudization")

3. Build the partial wave basis and projectors

**ATOMPAAW**

Download source code and example files:

- atompaw-4.0.0.tar.gz (5.4mb) new version, atompaw code with solver and corelpoints bugs corrected, updated version of xml interface (but not completely tested. (01/17/2014).
- atompaw-3.1.0.tar.gz (5.3mb) Updated version of atompaw code (01/03/2014 and 09/18/2013 - Marc Torrent and Francois Jollet introduced improve to the xml and abinit dataset generation routines, 07/09/2013 - Marc Torrent introduced small corrections; 06/22/2013 - Marc Torrent and Francois Jollet added a new option for outputting a file in XML format according to the specifications set up by the GPAW group. The output file format is controled by a menu at the end of the dataset: 2 for standard abinit output, 3 for quantum-espresso (UPF) output, 4 for XML output.) (Older change 09/20/2012 - Yann Pouillon updated the automods for constructing the tar file, 07/16/2012 - Geoffrey Poureis corrected GPAW portion of pwscifinterface file. 06/26/12 - NAHW corrected bug in pwscifinterface 06/38/12 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 gpaw calculations. The 3.0+ versions have several features due largely to the magic of Marc Torrent (CEA, France) and Yann Pouillon (ITISF, Spain) including compatibility for use with LibXC.

- Older versions of atompaw and pwscf can be generated. (For developing the UPF file for use with pwscf, help from Lorenzo Paulatto and Paolo Giannozzi is gratefully acknowledged.)
- 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 analyze some of the outputs of the atompaw program.
- pwscf_2.4.tar.gz (0.2 mb) Updated 09/12/2010 version of pwscf with very minor changes to accomodate changes to input files generated by new atompaw output files; also includes a BSD license file.

Independent of ABINIT (initiated by N. Holzwarth from Wake Forest University)

Automatically download and installed by ABINIT build system

http://pwpaw.wfu.edu

PAW atomic datasets | May 12, 2014 | PAGE 6
GENERATION OF PAW ATOMIC DATA
**Step 1**  
**All electrons atomic calculation** (with ATOMPAW for instance)

- Choose an electronic valence configuration \( O : 1s^22s^22p^4 \)
- Solve atomic Schrödinger equation \( \text{Get } n_c (r), V_{ae}(r) \)
- Choose an energy set \( \{\epsilon_i\} \) an radii \( \{r_i\} \)
- and invert the Schrödinger equation \( \text{Get } \{\phi_i(r)\} \)

\[
[T + V_{AE}(r)]\phi_i = \epsilon_i \phi_i
\]

**Step 2**  
**Pseudo functions**

- Apply a soft pseudization scheme

\[
\widetilde{\phi}_i \quad \text{and} \quad \phi_i \quad \text{join at} \quad r_i \\
\widetilde{n}_c \quad \text{and} \quad n_c \quad \text{join at} \quad r_{core} \\
V_{loc} \quad \text{and} \quad V_{ae} \quad \text{join at} \quad r_{loc}
\]
Step 3  Projectors
✓ Apply a scheme (Vanderbilt or Bloechl) to calculate (optimized) \( \{ \tilde{p}_i(r) \} \)

Step 4  Local potential
✓ Compute \( v_H(\tilde{n}_{Zc}) \) from \( V_{loc} \)

Step 5  Additional data

\[
D_{ij}^0 = \langle \phi_i | -\frac{\Delta}{2} + v_H[n_{Zc}] \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{\Delta}{2} + v_H[\tilde{n}_{Zc}] \tilde{\phi}_j \rangle - \sum_{lm} \int_R v_H[\tilde{n}_{Zc}] \hat{O}_{ij}^{lm} d\mathbf{r}
\]
The PAW calculation must give the same physical results as a reference *all electrons* calculation.

- The logarithmic derivatives of wavefunctions must be equal to the ones of a reference calculation (good diffusion properties):
  \[
  \left[ -\Delta + V_l(r) \right] \phi_i(\varepsilon, r) = \varepsilon \phi_i(\varepsilon, r) \quad \Rightarrow \quad \phi_i^2(\varepsilon, r) \frac{d}{d \varepsilon} \ln \phi_i(\varepsilon, r) = - \int_0^R \phi_i^2(\varepsilon, r) dr
  \]

- The energies of excited configurations must be equal to the *all electron* one.

\[\text{Transferability}\]

AE log derivatives and "base 2" log derivatives are superimposed.
The plane wave basis must be as small as possible

- Radius of augmentation regions (spheres).  
  *Spheres are in principle not allowed to overlap* 
  *In practice a little overlap is allowed*

- Number of partial waves per atom

- Pseudization scheme

- Size of radial grids

- Softness of $V_{loc}$

⚠️ Good atomic data are always a compromise between accuracy and efficiency
Approximations can be controlled

- Frozen-core approximation: adding more semicore states
- Size of PW basis: choosing the radius of spheres, the pseudization scheme
- Size of partial waves basis: adding more basis elements

Efficiency can be controlled

- Plane wave basis:
  Adjusting the radius of spheres, choosing a « soft » pseudization scheme
- Partial waves basis:
  Reducing the number of basis elements by choosing them judiciously
In addition to its proprietary format, ABINIT is able to read atomic datasets in an XML specification shared by several PAW codes.

<?xml version="1.0"?>
<paw_setup version="0.5">
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<atom symbol="O" Z="8.00" valence="2.00"/>
We follow the XML specification for atomic PAW setups (http://wiki.fysik.dtu.dk/gpaw/setups/pawxml.html)
AVAILABLE PAW ATOMIC DATASETS FOR ABINIT

PAW atomic data JTH table

All these PAW datasets of this JTH table have been generated by F. Jollet, M. Tournet and N. Holzwarth with ATOMPAW 9.1.0.2.

They have been validated in ABINIT against all-electron calculations using the data package.

The results are published here.
The Δ-factors (resp. Δt-factors) factors have been calculated for each element.
Curent average values of these indicators:
Δ = 0.4 meV
Δt = 0.9 meV

Right now, only GGA-PBE datasets are provided; LDA datasets coming soon...
All the datasets are in XML format according to specifications making them readable by several codes.

Opening a highlighted element in the periodic table will bring you into a directory corresponding to the selected chemical element.
Browse down the subdirectories and start a download procedure that will transfer a text file containing PAW atomic data.

The PAW atomic data present on this page are provided without any guarantee.
Users must carefully test them adequately before using them in their applications.

Note: The size of the file may vary between 120 KB and 300 KB.

Last modification: September 26, 2013
AVAILABLE PAW ATOMIC DATASETS FOR ABINIT

  *CEA France + Wake-Forest University*

- G-B-R-V table: [http://physics.rutgers.edu/gbrv](http://physics.rutgers.edu/gbrv)
  *Rutgers University*

- ATOMPAW table: [http://pwpaw.wfu.edu](http://pwpaw.wfu.edu)
  *Wake-Forest University*

  *DTU Denmark*

*And more to come…*
VALIDATION OF PAW ATOMIC DATA
THE DELTA FACTOR

« Error estimates for solid-state density-functional theory predictions: an overview by means of the ground-state elemental crystals »,
by K. Lejaeghere, V. Van Speybroeck, G. Van Oost and S. Cottenier


available on arXiv: 1204.2733v3

The Delta parameter:

\[
\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V) \, dV}{\Delta V}} \right\rangle
\]

Tested on 71 elements (from H to Rn)
Atomic datasets validation against all electron calculations

Comparing Solid State DFT Codes, Basis Sets and Potentials

This webpage offers all necessary information to determine the $\Delta$-factor of a solid state DFT code within the PBE formalism. $\Delta$ is defined as the root-mean-square energy difference between the equations of state of a test code and of WIEN2k, averaged over all crystals in a purely elemental benchmark set. This quantity can act as an accuracy-based guideline when selecting a solid state DFT code for a specific task. A README has been provided in the zip file (see below), as well as the required input and script files. In addition, the code comparison database has been implemented in ASE. Further information is available in the paper:


All codes that have been assessed up until now, are mentioned in the following table. Code developers and/or experts are invited to report the $\Delta$-value of their code to us. We will try to keep this list up to date.

**NOTE:** A significant update is expected soon! It will use new WIEN2k reference data and add more functionality.

<table>
<thead>
<tr>
<th>Code</th>
<th>Version/Basis</th>
<th>Potentials</th>
<th>$\Delta$-factor</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>WIEN2k</td>
<td>11.1 LAPW+LO+ao</td>
<td>full potential</td>
<td>0.0 meV/atom</td>
<td>by definition</td>
</tr>
<tr>
<td>Abinit</td>
<td>7.4.1 plane waves</td>
<td>PAW JTH (40 Ha cut-off)</td>
<td>0.5 meV/atom</td>
<td>F. Jolet et al. [3]</td>
</tr>
<tr>
<td>Abinit</td>
<td>7.1.2 plane waves</td>
<td>GPAW PAW 0.9 (40 Ha cut-off)</td>
<td>1.6 meV/atom</td>
<td>F. Jolet et al. [3]</td>
</tr>
<tr>
<td>OpenMX</td>
<td>3.7 pseudo-atomic orbitals</td>
<td>Morrison-Bylander-Kleinman norm-conserving (2013)</td>
<td>1.6 meV/atom</td>
<td>OpenMX [4]</td>
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<tr>
<td>GPAW</td>
<td>0.9.1 plane waves</td>
<td>PAW 0.9</td>
<td>1.7 meV/atom</td>
<td>ASE [2]</td>
</tr>
<tr>
<td>VASP</td>
<td>5.2.2 plane waves</td>
<td>PAW 2011</td>
<td>1.9 meV/atom</td>
<td>K. Lejaeghere et al. [1]</td>
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<tr>
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<td>plane waves</td>
<td>PAW GLLR-V1 (40 Ha cut-off)</td>
<td>2.3 meV/atom</td>
<td>F. Jolet et al. [3]</td>
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<tr>
<td>GPAW</td>
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<td>PAW 0.6</td>
<td>3.3 meV/atom</td>
<td>K. Lejaeghere et al. [1]</td>
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<td>Troullier-Martins norm-conserving (FHl)</td>
<td>2.17 meV/atom</td>
<td>ASE [2]</td>
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</table>
The delta factor

With the delta calculation package (v1.1), CIF files for 71 elements are available.

- 71 input files for ABINIT are generated (python script)
- 6750/N kpoints for a N atoms unit cell
- 7 calculations with volumes from 0.94 $V_0^{\text{ref}}$ to 1.06 $V_0^{\text{ref}}$
- $V_0$, $B_0$, $B'_0$ are deduced from the E(V) curve
- The delta factor is calculated comparing with the Wien2k results
Results in ABINIT

<table>
<thead>
<tr>
<th>Δ (meV)</th>
<th>12 Ha</th>
<th>15 Ha</th>
<th>20 Ha</th>
<th>40 Ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAW 0.9 68 elements</td>
<td>4.845</td>
<td>2.289</td>
<td>1.559</td>
<td>1.552</td>
</tr>
<tr>
<td>GBRV 63 elements</td>
<td>4.486</td>
<td>2.617</td>
<td>2.420</td>
<td>2.345</td>
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<tr>
<td>JTH 71 elements</td>
<td>2.461</td>
<td>0.817</td>
<td>0.363</td>
<td>0.453</td>
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</tbody>
</table>

JTH table : 71 elements

GBRV-v1.01: Δ=1.606 m eV
Results about ABINIT efficiency $\text{ecut}=20$ Ha

GPAW $0.9 \ \Delta = 1.6 \text{ meV}$

GBRV $\Delta = 1.606 \text{ meV}$

JTH $\Delta = 0.4 \text{ meV}$
Comments about the $\Delta$ factor

The $\Delta$ factor is a good tool to benchmark codes and pseudopotentials.

However, it supposes:
- The reference all-electron calculation is well done
- References are calculated for lanthanides and actinides
- Some compounds are added (oxydes, …)
- It is given together with a cut-off energy (for plane waves)

The $\Delta$ factor is very sensitive to the values of $V_0$, $B$ and $B'$ for some elements and not for others.
For instance:
- For Cs: $\Delta V_0 = 0.76\%$ leads to $\Delta_{\text{Cs}} = 0.39$ meV
- For Os: $\Delta V_0 = 0.76\%$ leads to $\Delta_{\text{Os}} = 9.14$ meV

Towards a modified $\Delta$ factor?
The $\Delta_1$ factor

(a) High B element
(b) Low B element

0.57 GPa (Ar) < $B$ < 401 GPa (Os)
7.2 Bohr$^3$(B) < $V$ < 117.7 Bohr$^3$(Cs)

$\Delta_1$ factor → renormalized $\Delta$ factor

$$\Delta_1 = \frac{V_{\text{ref}} B_{\text{ref}}}{V_{AE} B_{AE}} \Delta$$

For all elements:
- $B_{\text{ref}}$ is set to 100 GPa
- $V_{\text{ref}}$ is set to 30 Bohr$^3$

<table>
<thead>
<tr>
<th></th>
<th>12 Ha</th>
<th>15 Ha</th>
<th>20 Ha</th>
<th>40 Ha</th>
</tr>
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<tr>
<td>$\Delta_1$ (meV)</td>
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<tr>
<td>PAW 0.968 elements</td>
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<td>2.828</td>
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<tr>
<td>JTH 71 elements</td>
<td>7.671</td>
<td>2.187</td>
<td>0.888</td>
<td>0.970</td>
</tr>
</tbody>
</table>
The $\Delta_1$ factor

HOW TO GENERATE ATOMIC DATASETS

Follow the tutorial!
Delivered with ABINIT package

ABINIT, lesson PAW2:
Projector augmented-wave technique : the generation of atomic data files

This lesson aims at showing how to compute atomic data files for the projector-augmented-wave method.
You will learn how to generate the atomic data and what the main variables are to govern their softness and transferability.
It is supposed you already know how to use ABINIT in the PAW case.

This lesson should take about 1h30.

Contents of lesson PAW2 :
1. The PAW atomic dataset - introduction
2. Use of the generation code
3. First (and basic) PAW dataset for Niobet
4. Checking the sensitivity of results to some parameters
5. Adjusting partial waves and projectors
6. Examine the logarithmic derivatives
7. Testing efficiency of PAW dataset
8. Calculate physical quantities
9. The Real Space Optimization (RSO) - experienced users

1. The PAW atomic dataset - introduction

The PAW method is based on the definition of atomic spheres (augmentation regions) of radius $r_a$ around the atoms of the system in which a basis of atomic partial waves $\phi_a$ of "pseudized" partial waves $\tilde{\phi}_a$ and of projectors $\tilde{p}_a$ (shells $\tilde{S}_a$) have to be defined.

This set of partial waves and projector functions plus some additional atomic data are stored in a so-called PAW dataset. A PAW dataset has to be generated for each atomic species in order to reproduce atomic behavior as accurate as possible while requiring minimal CPU and memory resources in executing ABINIT for the crystal simulations. These two constraints are conflicting.

The PAW dataset generation is the purpose of this tutorial.
It is done according the following procedure (all parameters that define a PAW dataset are in bold):

1. Choose and define the concerned chemical species (name and atomic number).
2. Solve the atomic all-electrons problem in a given atomic configuration. The atomic problem is solved within the DFT formalism, using an exchange-correlation functional and either a Schrödinger (default) or scalar-relativistic approximation. It is a spherical problem and it is solved on a radial grid. The atomic problem is solved for a given electronic configuration that can be an ionized one.
3. Choose a set of electrons that will be considered as frozen around the nucleus (core electrons). The other electrons are valence ones and will be used in the PAW basis. The core density is then deduced from the core electrons wave functions. A smooth core density equal to the core density outside a given core matching radius is computed.