Plane waves, pseudopotentials and PAW

X. Gonze
Université catholique de Louvain, Louvain-la-neuve, Belgium
Basic equations in DFT

Solve self-consistently the Kohn-Sham equation

\[
\hat{H} \left| \psi_n \right\rangle = \varepsilon_n \left| \psi_n \right\rangle
\]

\[
\rho(\vec{r}) = \sum_n \psi_n^*(\vec{r}) \psi_n(\vec{r})
\]

\[
\hat{H} = \hat{T} + \hat{V} + \hat{V}_{\text{Hxc}}[\rho]
\]

or minimize

\[
E_{el} \{ \psi \} = \sum_n \left\langle \psi_n \left| \hat{T} + \hat{V} \right| \psi_n \right\rangle + E_{\text{Hxc}}[\rho]
\]

with

\[
\hat{V}(\vec{r}) = \sum_{a\kappa} - \frac{Z_\kappa}{|\vec{r} - \vec{R}_\kappa|^a}
\]

How to represent these quantities?
Let’s try plane waves …
Prerequisites of plane waves

Plane waves $e^{i\mathbf{k}\mathbf{r}}$: simple but infinite spatial extent ...

Cannot use a finite set of planewaves for finite systems!
Need periodic boundary conditions.
Primitive vectors $\mathbf{R}_j$, primitive cell volume $\Omega_0$

OK for crystalline solids
But: finite systems, surfaces, defects, polymers, nanosystems ... ?
The supercell technique

Molecule, cluster

Surface: treatment of a slab

Interface

Point defect in a bulk solid

The supercell must be sufficiently big: convergence study
Plane wave basis set: the maths

$$\psi_k(r) = \left( N \Omega_0 \right)^{-1/2} \sum_G u_k(G) e^{i(k+G)r}$$
Periodic system : wavevectors

For a periodic Hamiltonian, wavefunctions characterized by a wavevector \( \mathbf{k} \) (crystal momentum) in Brillouin Zone

**Bloch’s theorem**

\[
\psi_{m,k}(\mathbf{r} + \mathbf{R}_j) = e^{i\mathbf{k} \cdot \mathbf{R}_j} \psi_{m,k}(\mathbf{r})
\]

\[
\psi_{m,k}(\mathbf{r}) = \left( N \Omega_0 \right)^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}} u_{m,k}(\mathbf{r})
\]

\[ u = \text{periodic part of the Bloch wavefunction} \]

**Normalization ?**

**Born-von Karman supercell**

supercell vectors \( N_j \mathbf{R}_j \) with \( N=N_1N_2N_3 \)

\[
\psi_{m,k}(\mathbf{r} + N_j \mathbf{R}_j) = \psi_{m,k}(\mathbf{r})
\]

\[
1 = \frac{1}{\Omega_0} \int_{\Omega_0} u^*_k(\mathbf{r}) u_k(\mathbf{r}) \, d\mathbf{r}
\]
Planewave basis set

Reciprocal lattice: set of $\mathbf{G}$ vectors such that $e^{i \mathbf{G} \mathbf{r}}$ has the periodicity of the real lattice

$$u_k(\mathbf{r}) = \sum_{\mathbf{G}} u_k(\mathbf{G}) e^{i \mathbf{G} \mathbf{r}}$$

$$u_k(\mathbf{G}) = \frac{1}{\Omega_0} \int_{\Omega_0} e^{-i \mathbf{G} \mathbf{r}} u_k(\mathbf{r}) \, d\mathbf{r} \quad \text{(Fourier transform)}$$

Kinetic energy of a plane wave

$$-\frac{\nabla^2}{2} \rightarrow \frac{(\mathbf{k} + \mathbf{G})^2}{2}$$

The coefficients $u_k(\mathbf{G})$ for the lowest eigenvectors decrease fast with the kinetic energy

Selection of plane waves determined by a cut-off energy $E_{\text{cut}}$

$$\frac{(\mathbf{k} + \mathbf{G})^2}{2} < E_{\text{cut}} \quad \text{Plane wave sphere}$$
Plane waves: the density and potential

Fourier transform of a periodic function \( f(\mathbf{r}) \)

\[
f(\mathbf{G}) = \frac{1}{\Omega_{\text{or}}} \int_{\Omega_{\text{or}}} \exp(-i\mathbf{G} \cdot \mathbf{r}) f(\mathbf{r}) \, d\mathbf{r}
\]

\[
f(\mathbf{r}) = \sum_{\tilde{\mathbf{G}}} \exp(i\mathbf{G} \cdot \mathbf{r}) f(\mathbf{G})
\]

Poisson equation \( \Rightarrow n(\mathbf{G}) \) and \( V_{H}(\mathbf{G}) \)

\[
V_{H}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \iff \nabla^2 V_{H}(\mathbf{r}) = -4\pi n(\mathbf{r})
\]

Relation between Fourier coefficients:

\[
G^2 \, V_{H}(\mathbf{G}) = 4\pi n(\mathbf{G})
\]

\[
V_{H}(\mathbf{G}) = \frac{4\pi}{G^2} n(\mathbf{G})
\]

For \( G^2 = 0 \) (\( G=0 \)) divergence of \( V_{H}(\mathbf{G}=0) \)

\[
n(G=0) = \frac{1}{\Omega_{\text{or}}} \int_{\Omega_{\text{or}}} n(\mathbf{r}) \, d\mathbf{r}
\]

Average

Compensation with ionic potential
Representation of the density

Density associated with one eigenfunction:

\[ n_{nk}(r) = u^*_{nk}(r) u_{nk}(r) \]

Computation of \( u^*_{nk}(r) u_{nk}(r) \):

\[
\begin{align*}
&= \left( \sum_{G} u^*_{nk}(G) e^{-iGr} \right) \left( \sum_{G'} u_{nk}(G') e^{-iG'r} \right) \\
&= \sum_{GG'} \left[ u^*_{nk}(G) u_{nk}(G') \right] e^{i(G'-G)r}
\end{align*}
\]

Non-zero coefficients for \( k+G \in \) sphere \( k+G' \in \) sphere

The sphere for \( n(G) \) has a doubled radius

Berlin, August 2, 2017
From real space to reciprocal space

\[ n(\mathbf{r}) = \sum_{\mathbf{G} \in \text{sphere}(2)} n(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \]

Use of the discrete Fourier transform \( \{ \mathbf{r}_i \} \leftrightarrow \{ \mathbf{G} \} \)

Reciprocal lattice

Real lattice: original cell

\[ n(\mathbf{G}) = \frac{1}{N_{r_i} \{ r_i \}} \sum n(\mathbf{r}_i) e^{-i\mathbf{G}\cdot\mathbf{r}_i} \]

Fast Fourier Transform algorithm

FFT grid in real space used to evaluate the XC contribution

\[ E_{el} \{ \psi \} = \sum_{n}^{occ} \langle \psi_n | \hat{T} + \hat{V} | \psi_n \rangle + E_{Hxc}[\rho] \]
Simplicity of PW requires psps

The Fourier transform theory teaches us:
- details in real space are described if their characteristic length is larger than the inverse of the largest wavevector norm (roughly speaking)
- quality of a plane wave basis set can be systematically increased by increasing the cut-off energy

Problem:
huge number of PWs is required to describe localized features (core orbitals, oscillations of other orbitals close to the nucleus)

Pseudopotentials (or, in general, « pseudization ») to eliminate the undesirable small wavelength features (will be the subject of a later section)
Convergence wrt to kinetic energy cutoff

![Graph showing convergence with respect to kinetic energy cutoff]

Total energy (Ha)

Cut-off energy (Ha)

Bulk silicon

Courtesy of F. Bruneval
Number of plane waves

Number of plane waves
= function of the kinetic energy cut-off

… not continuous

Also, a (discontinuous) function of lattice parameter at fixed kinetic energy
Discontinuities in energy and pressure

=> Energy (and pressure) also (discontinuous) functions of lattice parameter at fixed kinetic energy
Removing discontinuities

Kinetic energy

\[ u(G) \neq 0 \quad u(G) = 0 \]

\[ (2E_{\text{cut}})^{1/2} \quad \mid k+G \mid \]

Kinetic energy

\[ u(G) \neq 0 \quad u(G) = 0 \]

\[ (2E_{\text{cut}})^{1/2} \quad \mid k+G \mid \]

\[ (2(E_{\text{cut}} - E_{\text{cut smear}}))^{1/2} \]
Representation : wrap-up

- Choice of a basis (e.g. Plane waves)
- Truncating of the basis -> finite basis

\[
\frac{(k+G)^2}{2} < E_{\text{cut}}
\]

Sphere of plane waves

- Discontinuous increase of the number of plane waves ?
  Smearing of \( u(G) \)
  => Progressive incorporation of new \( G \) vectors

- Representation of the density
  Sphere with a double radius in the reciprocal space

- Going from the real space to reciprocal space
  Discrete Fourier transform
  Grid of points + Fast Fourier Transform \( \{ r_i \} \leftrightarrow \{ G \} \)
Pseudopotentials
Core and valence electrons (I)

Core electrons occupy orbitals that are "the same" in the atomic environment or in the bonding environment

"the same" depends on the accuracy of the calculation!

Separation between core and valence orbitals: the density...

\[
n(r) = \sum_{i}^{N} \psi_i^*(r) \psi_i(r)
\]

\[
= \sum_{i \in \text{core}}^{N_{\text{core}}} \psi_i^*(r) \psi_i(r) + \sum_{i \in \text{val}}^{N_{\text{val}}} \psi_i^*(r) \psi_i(r) = n_{\text{core}}(r) + n_{\text{val}}(r)
\]

« Frozen core » for \( i \in \text{core}: \psi_i = \psi_i^{\text{atom}} \)
Separation between core/valence

Depends on the target accuracy of the calculation!

(remark also valid for pseudopotentials, with similar cores)

For some elements, core/valence partitioning is obvious, for some others, it is not.

F atom: $\left(1s\right)^2 + \left(2s\right)^2 \left(2p\right)^5$

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<td>100</td>
<td>10-100</td>
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<td>Ti atom: $\left(1s\right)^2 \left(2s\right)^2 \left(2p\right)^5 \left(3s\right)^2 \left(3p\right)^6 \left(4s\right)^2 \left(3d\right)^2$ small core</td>
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<tr>
<td></td>
<td>large core</td>
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<tr>
<td>Gd atom: small core with n=1,2,3 shells, might include 4s, 4p, and 4d in the core. 4f partially filled</td>
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</table>
Energy : core and valence

\[
E_{KS} \left[ \{ \psi_i \} \right] = \sum_i \langle \psi_i | - \frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[n]
\]

\[
E_{KS} \left[ \{ \psi_i \} \right] = \sum_{i \in \text{core}}^{N_{\text{core}}} \langle \psi_i | - \frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n_{\text{core}}(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \int \frac{n_{\text{core}}(\mathbf{r}_1)n_{\text{core}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2
\]

\[
+ \sum_{i \in \text{val}}^{N_{\text{val}}} \langle \psi_i | - \frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}}(\mathbf{r}) n_{\text{val}}(\mathbf{r}) \, d\mathbf{r} + \frac{1}{2} \int \frac{n_{\text{val}}(\mathbf{r}_1)n_{\text{val}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2
\]

\[
+ \int \frac{n_{\text{val}}(\mathbf{r}_1)n_{\text{core}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 d\mathbf{r}_2 + E_{xc}[n_{\text{core}} + n_{\text{val}}]
\]
Valence electrons in screened potential

The potential of the nuclei $\kappa$ is screened by the core electrons

$$V_{\text{ion},\kappa}(\mathbf{r}) = -\frac{Z_{\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \int \frac{n_{\text{core},\kappa}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1$$

$$V_{\text{ion},\kappa}(\mathbf{r}) = -\frac{Z_{\text{val},\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \left(-\frac{Z_{\text{core},\kappa}}{|\mathbf{r} - \mathbf{R}_{\kappa}|} + \int \frac{n_{\text{core},\kappa}(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1\right)$$

The total energy becomes

$$E = \left(E_{\text{val}} + \sum\limits_{\kappa} E_{\text{core},\kappa}\right) + \frac{1}{2} \sum\limits_{\kappa \neq \kappa'} \frac{Z_{\text{val},\kappa}Z_{\text{val},\kappa'}}{|\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa'}|}$$

with

$$E_{\text{val,KS}}\left[\{\psi_i\}\right] = \sum\limits_{i \in \text{val}} \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int \left(\sum\limits_{\kappa} V_{\text{ion},\kappa}(\mathbf{r})\right) n_{\text{val}}(\mathbf{r}) d\mathbf{r}$$

$$+ \frac{1}{2} \int \frac{n_{\text{val}}(\mathbf{r}_1)n_{\text{val}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}} \left[n_{\text{core}} + n_{\text{val}}\right]$$

Non-linear XC core correction
Removing core electrons (I)

From the previous construction: valence orbitals must still be orthogonal to core orbitals (\( \Rightarrow \) oscillations, slope at the nucleus ...)

Pseudopotentials try to remove completely the core orbitals from the simulation

Problem with the number of nodes
This is a strong modification of the system ...

Pseudopotentials confine the strong changes within a « cut-off radius »
Removing core electrons (II)

Going from \( \left( -\frac{1}{2} \nabla^2 + v \right) |\psi_i> = \varepsilon_i |\psi_i> \)

To \( \left( -\frac{1}{2} \nabla^2 + v_{ps} \right) |\psi_{ps,i}> = \varepsilon_{ps,i} |\psi_{ps,i}> \)

Possible set of conditions (norm-conserving pseudopotentials)


\( \varepsilon_i = \varepsilon_{ps,i} \)

\( \psi_i(r) = \psi_{ps,i}(r) \) for \( r > r_c \)

\[ \int_{r < r_c} |\psi_i(r)|^2 \, dr = \int_{r < r_c} |\psi_{ps,i}(r)|^2 \, dr \]

For the lowest angular momentum channels (s + p ... d ...f)

Generalisation: ultra-soft pseudopotentials (USPP), projector-augmented plane waves (PAW)
Example of NC pseudopotential

3s Radial wave function of Si

Radial distance [a.u.]

Amplitude

-0.5 0 0.5 1.0

All-electron wave function
Pseudo-wave function

Radial distance [a.u.]

V_{ps}(r) [Ha]

-5 -4 -3 -2 -1 0

s
p
d

$-\frac{Z_{val}}{r}$
Forms of pseudopotentials

Must be a linear, hermitian operator

General form: \[ (\hat{V}_{ps}\psi)(r) = \int V^{\text{kernel}}_{ps}(r,r')\psi(r')dr' \]

\[ V^{\text{kernel}}_{ps}(r,r') = V_{\text{loc}}(r)\delta(r-r') + V_{\text{nloc}}(r,r') \quad \text{includes a "non-local" part} \]

+ Spherically symmetric!

\[ V_{\text{loc}}(r) = V(r) \quad \quad V_{\text{nloc}}(r,r') = \sum_{\ell m} Y^*_{\ell m}(\theta,\varphi)V_{\ell}(r,r')Y_{\ell m}(\theta',\varphi') \]

Semi-local psp \[ V_{\ell}(r,r') = V_{\ell}(r)\delta(r-r') \]


Separable psp \[ V_{\ell}(r,r') = \xi^*_{\ell}(r)f_{\ell}\xi_{\ell}(r') \]

Ultrasoft Pseudopotentials and Projector-Augmented Waves (PAW)
Ultra-soft pseudopotentials: the idea

Problem with NC pseudopotentials: norm conservation limits the softness!

When orbitals without nodes (1s, 2p, 3d, 4f) treated as valence => small characteristic length energy cut-off large.

Idea (Vanderbilt, Phys. Rev. B 41, 7892 (1990))

Suppress norm-conservation condition:
- modify normalization, to keep correct scattering properties
- introduce charge density corrections,

For selected elements, can decrease number of PW/FFT Grid points by a factor of two or three, with even larger speed up.
More difficult to implement than norm-conserving PPs.

Can be obtained as a particular case of PAW construction ...
Projector-Augmented Waves: the idea


The true wave-function and a well-behaving pseudo-wavefunction are linked by a linear transformation

\[ \Psi = T \tilde{\Psi} \]

- Strong oscillations near the nucleus
- True wave function (all electrons)
- No oscillation near the nucleus
- Auxiliary wave function (soft pseudofunction)

More rigorous than USPP
USPP and PAW: common features

Generalized Schrödinger Eq., with overlap operator S.

\[
\left[-\frac{\nabla^2}{2} + v_{ps}\right] \psi_{ps,i} = \varepsilon_i S \psi_{ps,i}
\]

Charge density of each state to be corrected for the missing norm.
Projector-Augmented Waves: the math

True wave-function \( \Psi \)
Well-behaving pseudo-wavefunction \( \tilde{\Psi} \)
Linked by a linear transformation \( \Psi = T\tilde{\Psi} \)

Physical quantities like \( \langle \Psi | A | \Psi \rangle \)
computed in the pseudo representation \( \langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi} \rangle \),

with \( \tilde{A} = T^+ A T \)

Similarly, variational principle for total energy gives

\[
\frac{\partial E[T|\tilde{\Psi}|]}{\partial \langle \tilde{\Psi} |} = \epsilon T^+ T |\tilde{\Psi}| \]

equivalent to Kohn-Sham equation, for pseudowavefunctions.
Search for ground state can also be done in the pseudo space.
Transformation operator

Operator $T$ has to modify the smooth pseudowavefunction in each atomic region, to give it the correct nodal structure.

Identity + sum of atomic contributions

$$\Psi = T \tilde{\Psi}$$
with
$$T = 1 + \sum_R S_R$$
(R=atomic site label)

Choose:

Partial waves $|\phi_i\rangle$ = basis set, solutions of the Schrödinger Eq. for the isolated atoms within some cut-off radius $r_{c,R}$

Pseudo partial waves $|\tilde{\phi}_i\rangle$, identical to the partial waves beyond the cut-off radius, but smoother inside

Define $S$ such as:

$$|\phi_i\rangle = (1 + S_R) |\tilde{\phi}_i\rangle$$
Representation of the wavefunctions

\[ \Psi = T \tilde{\Psi} \]

\[ T = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle \tilde{p}_i | \]

Explicitly,

\[ \Psi = \tilde{\Psi} + \sum_R (|\Psi_R^i\rangle - |\tilde{\Psi}_R^i\rangle) \]

\[ |\Psi_R^i\rangle = \sum_{i \in R} |\phi_i\rangle \langle \tilde{p}_i | \tilde{\Psi} \]

\[ |\tilde{\Psi}_R^i\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi} \]
Wavefunctions, density, energy

$\tilde{\Psi}$ represented by plane waves (might use other representations)

$|\Psi^I_R\rangle$ and $|\tilde{\Psi}^I_R\rangle$ represented on a radial grid, centered on R, times spherical harmonics

Note:

Outside of the spheres,

Inside one sphere,

$\tilde{\Psi} = |\tilde{\Psi}^I_R\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i |\tilde{\Psi}\rangle$

Density:

$\bar{n}(r) = \tilde{n}(r) + \sum_R \left( n^I_R(r) - \tilde{n}^I_R(r) \right)$

Energy:

$E = \tilde{E} + \sum_R \left( E^I_R - \tilde{E}^I_R \right)$
Approximations

(1) Core electrons: usually treated in the frozen-core approximation, and treated on radial grid (spherical harmonics).

(2) Finite PW basis set (same as PPs)

(3) The partial wave expansion is truncated: only one or two partial wave(s), for each atom R, and each l,m channel

$$\sum_{i} |\tilde{\phi}_i \rangle \langle \tilde{p}_i | \neq 1$$

Inside one sphere, $$\tilde{\Psi} = |\tilde{\Psi}_R \rangle = \sum_{i \in R} |\tilde{\phi}_i \rangle \langle \tilde{p}_i | \tilde{\Psi} \rangle$$ is only approximately true!

$\tilde{\Psi}$ contributes inside the atomic spheres, and corrects for the missing terms due to truncation of partial wave expansion.
Advantages of PW+PP or PAW method?

(1) The basis set does not depend on atomic coordinates:
   easy computation of forces as numerically exact derivatives
   of the total energy with respect to atomic coordinates
   (no Pulay forces). Easy structural optimisation, or MD.
   This leads also to Car-Parrinello technique.

(2) Systematic way to complete the basis set

For PW-PP: simple implementation

For PW-PAW: can be a numerically accurate
   implementation of DFT, including properties
   related to cores; usually faster than PW-PP

Disadvantages: cannot lead to Order(N) implementation,
   does not treat efficiently finite systems (vacuum!).
   Higher lying states (very high in energy) cannot be trusted...
Pseudopotential and PAW atomic data availability and reliability
Generators (non-complete list)

Norm-conserving pseudos:
- ONCVPSP (Don Hamann, http://www.mat-simresearch.com/)
- APE (M. Oliveira http://www.tddft.org/programs/APE)
- OPIUM (A. Rappe http://opium.sourceforge.net/)

USPP:
- Vanderbilt USPP generator (http://www.physics.rutgers.edu/~dhv/uspp/)

PAW
- ATOMPAW (N. Holzwarth http://users.wfu.edu/natalie/papers/pwpaw/man.html)
- GPAW generator (https://wiki.fysik.dtu.dk/gpaw/setups/setups.html)
  + converter USPP2PAW (http://www.abinit.org/downloads/PAW2/USPP/uspp.html)
Implementations

Plane Waves need pseudopotentials (or PAW), but pseudopotentials can be used with many basis sets!

Norm-conserving pseudos:
- with planewave basis set: ABINIT, QE, CASTEP ...
- with localized orbitals: SIESTA ...
- with wavelets: BigDFT ...

USPP:
- with planewave basis set: QE, DaCapo, CASTEP ...

PAW:
- with planewave basis set: ABINIT, QE, GPAW, VASP ...

Same pseudopotentials can sometimes be used by different codes.
Pseudopotentials/PAW data

- Example of PAW atomic dataset table: JTH v1.0 \( \Delta = 0.4 \text{ meV} \)
  
  *Jollet, Torrent, Holzwarth, Computer Physics Comm. 185, 1246 (2014)*
  

Also: GPAW table, GBRV v1.0 table, norm-conserving pseudopotential table (e.g. ONCVPSP pseudo generator), or many other pseudos …

[Atomic data available](http://www.abinit.org/downloads/atomic-data-files)

[Atomic data non available](http://www.abinit.org/downloads/atomic-data-files)
Testing pseudopotentials

Precision

Accuracy

PBE (1996)

Experiment

year of publication


PBE lattice parameter of Si [Å]

5.41 5.43 5.45 5.47 5.49 5.51

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Comparing code/pseudopotential

Recently, large effort to improve uncertainty related to psps:
« Delta-factor » collaboration
Lejaeghere ... Cottenier, Science 351, aad3000 (2016)
Specification of 71 elemental solids for different volumes.
# More about pseudopotentials / PAW datasets

<table>
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<th>AE</th>
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*Berlin, August 2, 2017*
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Berlin, August 2, 2017
More about pseudopotentials / PAW datasets

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## Improvement with time

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JTH 1.0 => 0.4 meV
Other comparison with All-Electron data

ONCVPSP PBE table
Summary

- Plane waves basis set
  \[ \psi_k(r) = \left( N \Omega_0 \right)^{-1/2} \sum_G u_k(G) e^{i(k+G)r} \]

- PW need pseudopotentials

- Easy computation of forces
  relaxation of geometry, or molecular dynamics

- PAW (also USPP) : more accurate, faster for cases with 3d and 4f orbitals