Solution of the Kohn-Sham equations

We now have an *ab-initio*, approximate DFT which can be used in practice to compute properties of molecules and condensed systems.

The basic variable: electronic charge density
$$\rho = \sum_{i=1}^{N} |\psi_i(\bar{r})|^2 \quad \text{with} \quad \langle \psi_i | \psi_j \rangle = \delta_{ij}$$

The total energy in terms of the charge density and the single particle orbitals

$$E_{KS} = -\frac{1}{2} \sum_{i=1}^{N} \int \psi_i^*(\bar{r}) \nabla^2 \psi_i(\bar{r}) \, d\bar{r} + \frac{1}{2} \int d\bar{r} \, d\bar{r}' \frac{\rho(\bar{r})\rho(\bar{r}')}{|\bar{r}-\bar{r}'|} + \int d\bar{r} \, \rho(\bar{r}) \, \varepsilon_{xc}(\rho) + \int d\bar{r} \, V_{ext}(\bar{r}) \rho(\bar{r})$$

The Kohn-Sham equations: set of N non linear differential equations for the single particles orbitals; the potential V$_{KS}$ depends *'self-consistently'* upon the charge density

$$\left(-\frac{1}{2} \nabla^2 + V_{KS}[\rho(\bar{r})] \right) \psi_i(\bar{r}) = \varepsilon_i \, \psi_i(\bar{r}) \quad \text{with} \quad V_{KS} = \frac{\delta E_{KS}}{\delta \rho(\bar{r})}$$
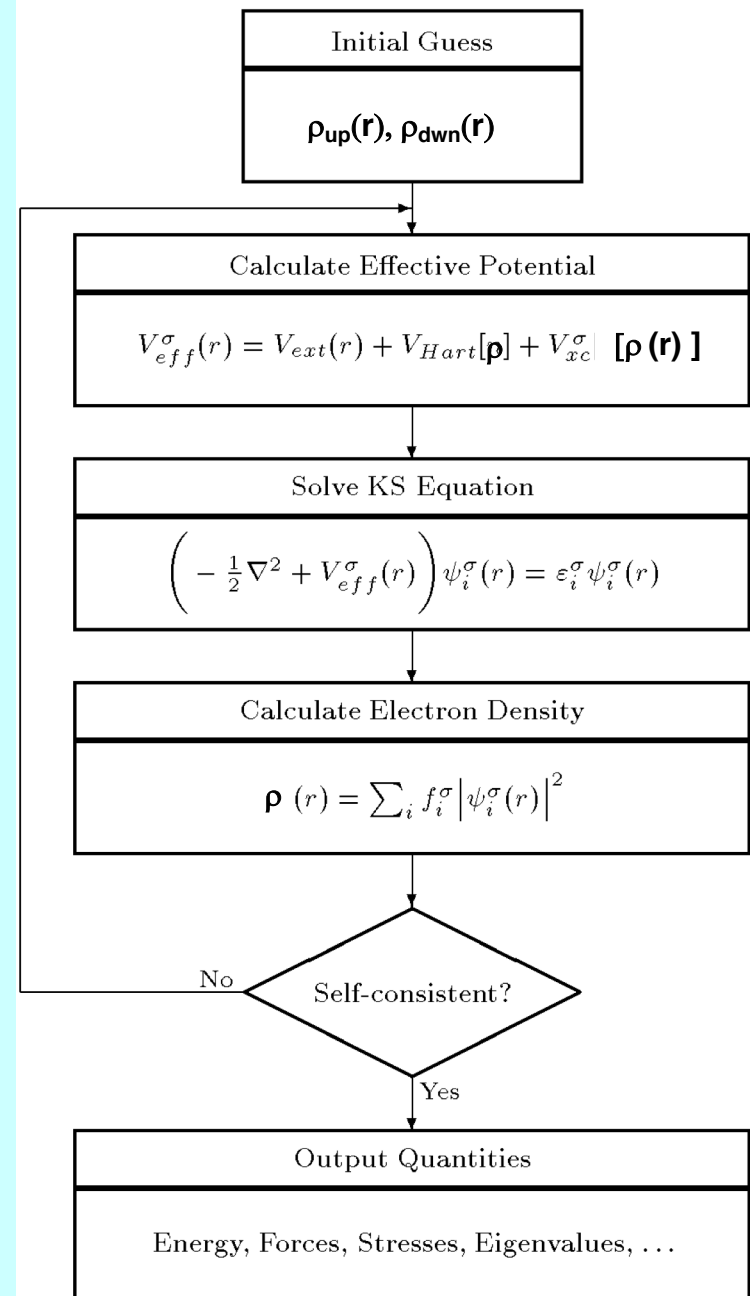
Approximations (e.g. LDA, GGA, etc.) for the exchange correlation energy density

ε_{xc} and $E_{xc}[\rho]$ are in general unknown and one needs to resort to approximations

Solving KS equations

•Choose **approximation for exchange and correlation potential**

•Choose **atomic configuration**, i.e. positions of the nuclei R_I

•Choose:

 •**how to treat atomic cores** (all-electron, frozen core, pseudopotentials)

 •**basis set** to expand single particle orbitals

• Start self-consistent cycle by "**guess**ing" a **set of single particle orbitals** (i.e. the expansion coefficients in terms of a given basis set) and thus an input charge density ρ.

•Solve KS **eigenvalue problem** in an **iterative manner.**

Self-Consistent Kohn-Sham Equations

Initial Guess

$\rho_{up}(r)$, $\rho_{dwn}(r)$

Calculate Effective Potential

$$V_{eff}^{\sigma}(r) = V_{ext}(r) + V_{Hart}[\rho] + V_{xc}^{\sigma} \,[\rho\,(r)\,]$$

Solve KS Equation

$$\left(-\tfrac{1}{2}\nabla^2 + V_{eff}^{\sigma}(r)\right)\psi_i^{\sigma}(r) = \varepsilon_i^{\sigma}\psi_i^{\sigma}(r)$$

Calculate Electron Density

$$\rho\,(r) = \sum_i f_i^{\sigma}\left|\psi_i^{\sigma}(r)\right|^2$$

Self-consistent? No / Yes

Output Quantities

Energy, Forces, Stresses, Eigenvalues, . . .

Compare with solution of Hartree-Fock equations

How do we solve the Hartree-Fock equations, i.e. an eigenvalue problem where the operator depends on the solutions? **Using an self-consistent iterative procedure**

Guess an initial Slater determinant: $\psi \approx \psi^{IN} \equiv |\psi_1^{IN} \cdots \psi_N^{IN}|$

$\downarrow$

Constructs the Coulomb and exchange potentials using the orbitals from the guessed Slater determinant $J[\{\psi_i^{IN}\}] ; K[\{\psi_i^{IN}\}]$

$\downarrow$

Construct the Fock operator and **solve the eigenvalue problem** (e.g. my matrix diagonalization, after expanding the single particle orbitals in a suitable **basis set**, for example a Gaussian basis set):

$$\hat{F}[\{\psi_i^{IN}\}; \bar{r}]\psi_m^{out} = \varepsilon^{out}\psi_m$$

$\downarrow$

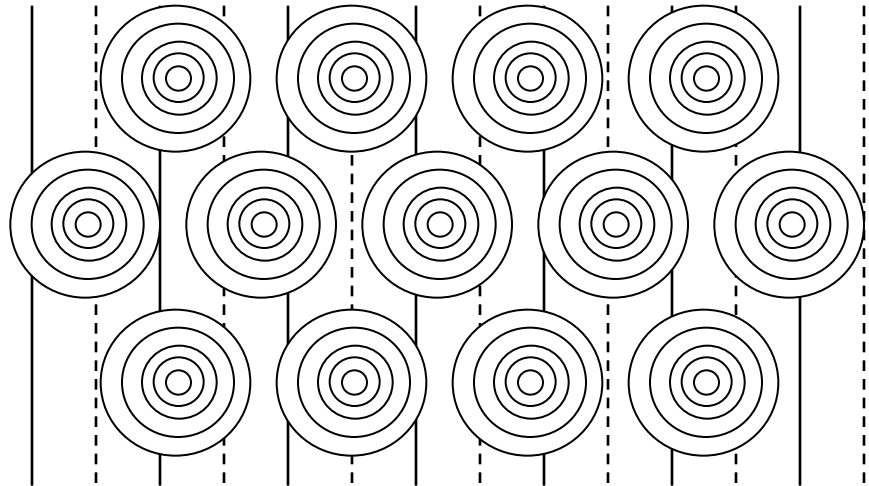$\psi^{IN} \approx \psi^{out}$ $\rightarrow$ (NO) $\rightarrow$ $\psi \approx \alpha\psi^{IN} + \beta\psi^{out}$

$\downarrow$ yes

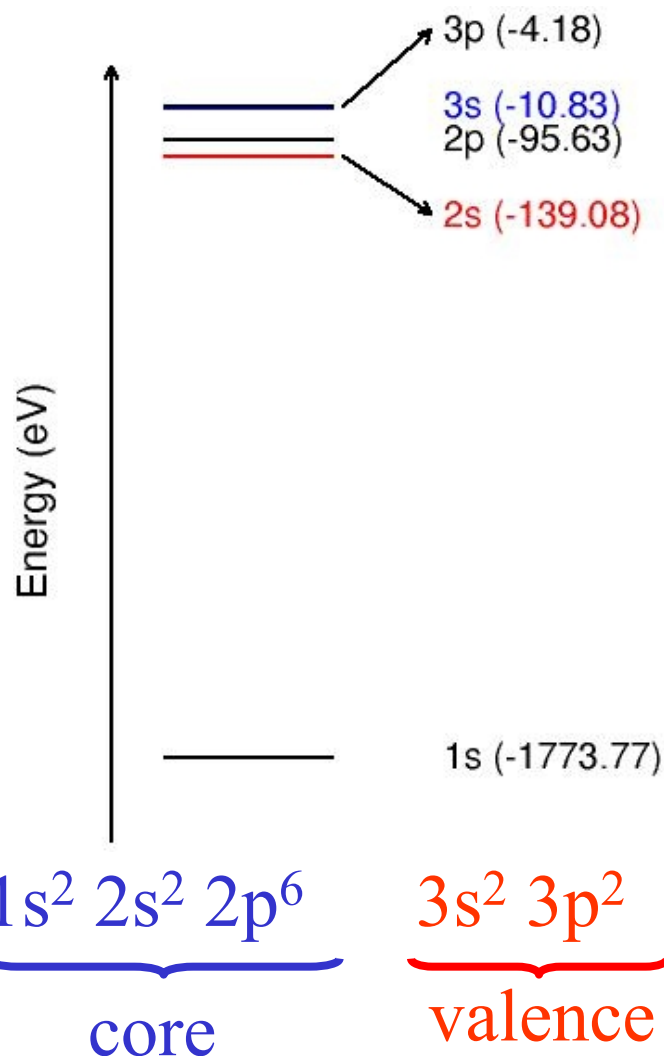Self-consistency attained; Compute total energies and orbital energies

Representation of atomic cores

- **All-electron (AE) methods: all electrons in the system are treated explicitly; some of them may be considered "frozen" in the configuration they have in the atom**

- **Pseudopotential (PP) method: only valence electrons are treated explicitly**

  - **Core states – strongly bound to nuclei – atomic-like**
  - **Valence states (treated explicitly) – they undergo changes when going from an atom to a molecule or a condensed system; the way they change determine the bonding, electronic and optical properties, magnetism, …..**
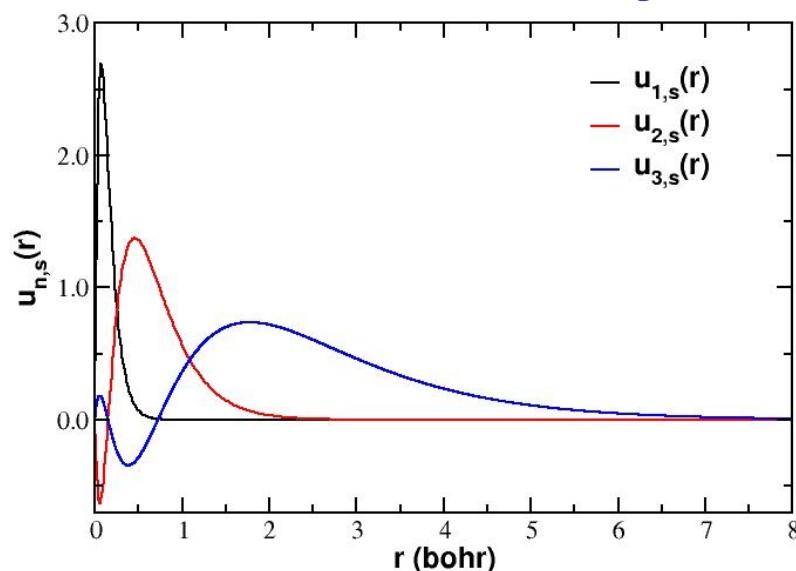
Pseudopotentials and pseudo-wavefunctions (I)

Atomic Si

3p (-4.18)

3s (-10.83)
2p (-95.63)

2s (-139.08)

Energy (eV)

1s (-1773.77)

$\underbrace{1s^2\ 2s^2\ 2p^6}_{\text{core}}$ $\underbrace{3s^2\ 3p^2}_{\text{valence}}$

Core electrons…

highly localized

very low energy compared to valence states

… are chemically inert

— $u_{1,s}(r)$
— $u_{2,s}(r)$
— $u_{3,s}(r)$

$u_{n,s}(r)$

r (bohr)

Valence wave functions must be orthogonal to the core wave functions

Pseudopotentials and pseudo-wavefunctions (II)

- **Idea: construct 'pseudo-atom' which has the valence states of the real atom as its lowest electronic states**

- **Preserves scattering properties and total energy *differences* for the real atom**

- **Removal of orbital nodes makes plane-wave expansion feasible**

- **Possible limitations: Can the pseudo-atom correctly describe the bonding in different environments ?
→ transferability of pseudo-potentials in different chemical environments needs to be checked.**
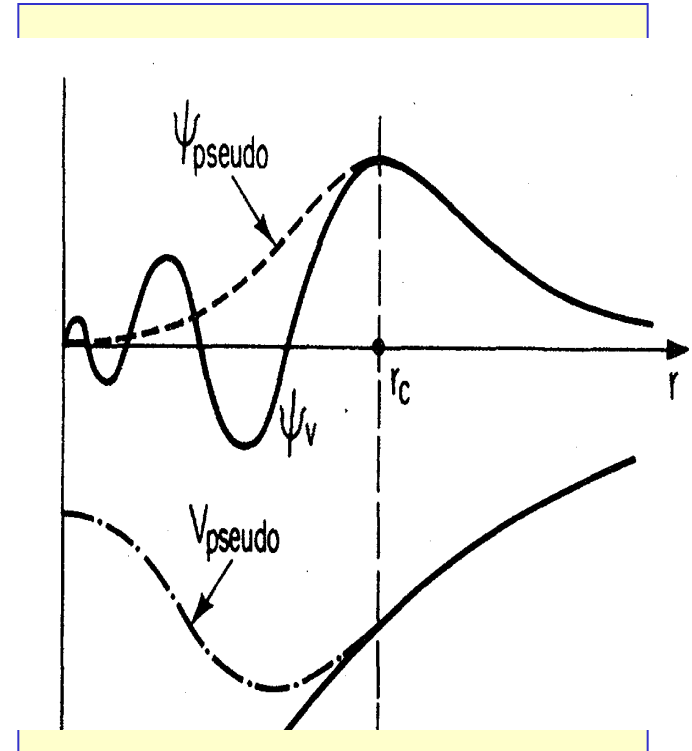
Transferability of pseudopotentials: atoms

• Compute the energy of two different configurations with AE and PP methods for the chosen atom

• Compute the difference in energy using both AE and PP methods

• For the pseudopotential to be transferable: $\Delta E_{AE} = \Delta E_{PP}$

Example of configurations for the SI atom:

→ $3s^2\ 3p^2$ (reference)
→ $3s^2\ 3p^1\ 3d^1$
→ $3s^1\ 3p^3$
→ $3s^1\ 3p^2\ 3d^1$
→ $3s^0\ 3p^3\ 3d^1$

Pseudopotentials and pseudo-wavefunctions (III)

**Comparison between all electron and pseudo-charge density**
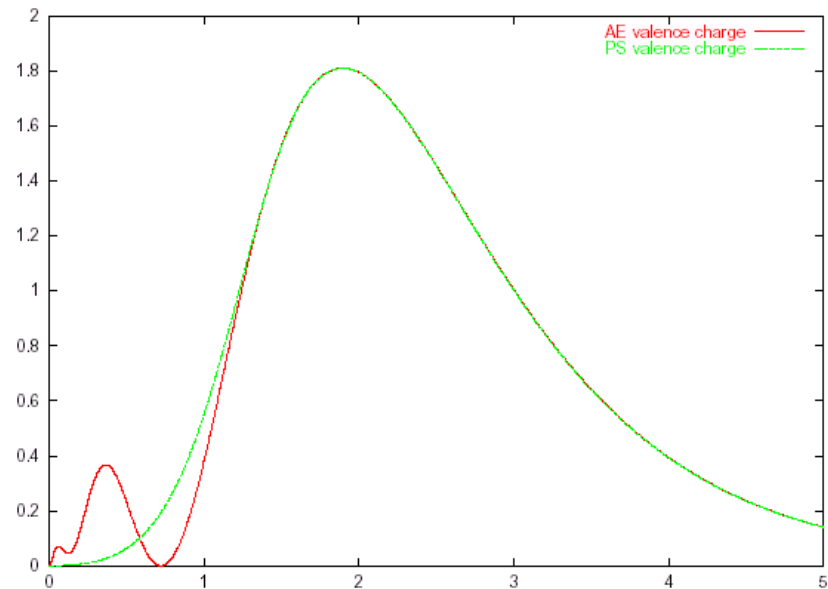
Four choices for single particle orbital representation in modern DFT calculations

- **Plane waves**
  - **The simplicity of Fourier Expansions**
  - **The speed of Fast Fourier Transforms**
  - **Requires smooth pseudopotentials**

- **Localized orbitals**
  - **The intuitive appeal of atomic-like states**
  - **Simplest interpretation in tight-binding form**
  - **Gaussian basis widely used for finite systems (within all quantum in chemistry**

- **Augmented methods**
  - **"Best of both (plane waves and localized orbital) worlds" – also most demanding**
  - **Requires matching technique to match functions inside and outside spheres.**

- **Real Space representation of wavefunctions, charge densities and potentials** (not as popular as the other three methods)
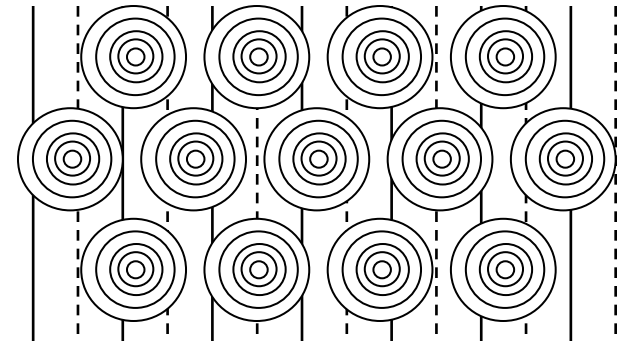
Plane wave basis sets

- The most general and unbiased approach: no dependence on nuclei positions

$$\psi_{i,\mathbf{k}}(\mathbf{r}) \propto \sum_m c_{i,m}(\mathbf{k}) \times \exp(i(\mathbf{k} + \mathbf{G}_m) \cdot \mathbf{r})$$
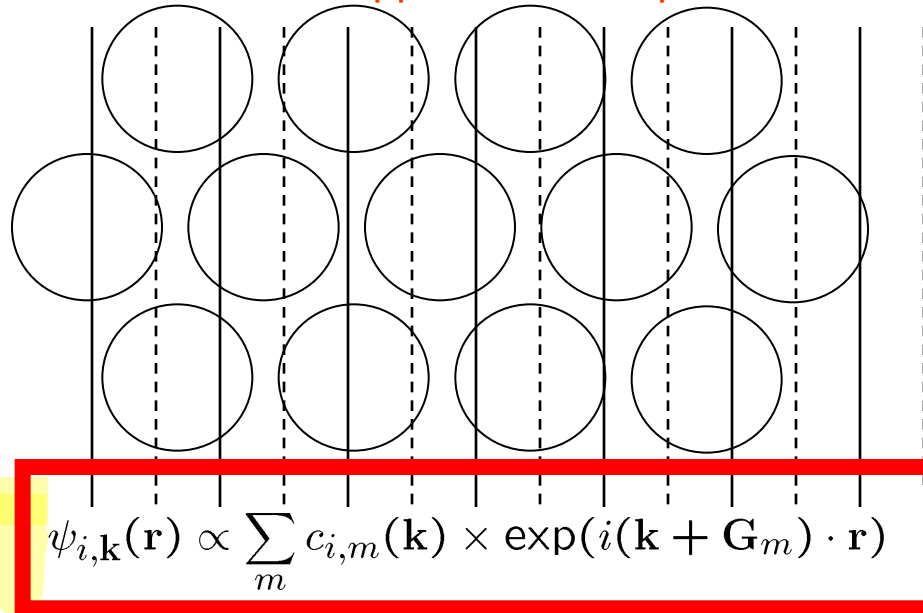
$$\sum_{m'} H_{m,m'}(\mathbf{k}) c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k}) c_{i,m}(\mathbf{k})$$
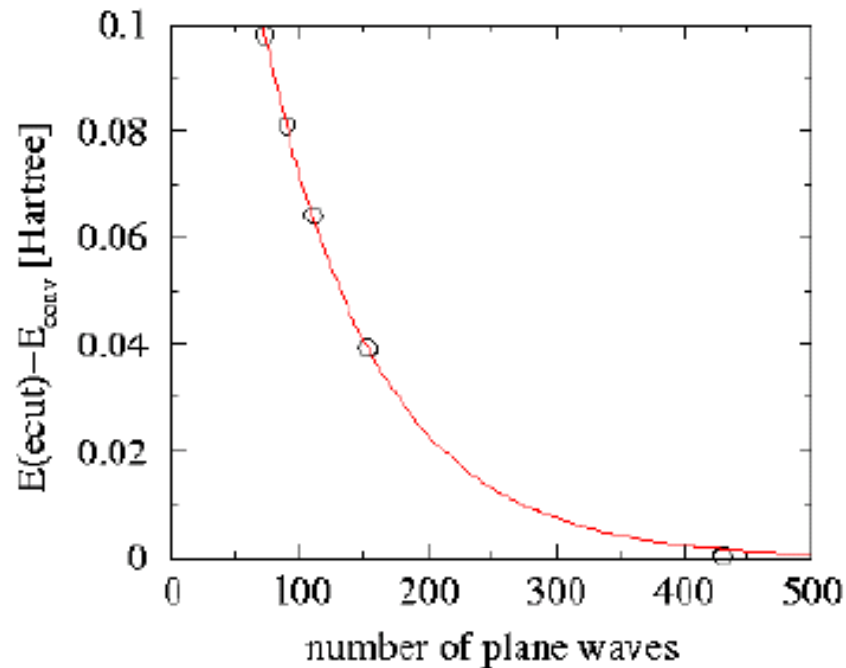
$$H_{m,m'}(\mathbf{k}) = \frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}).$$

- **The problem is the atoms!** High Fourier components. Solution: use pseudopotentials.
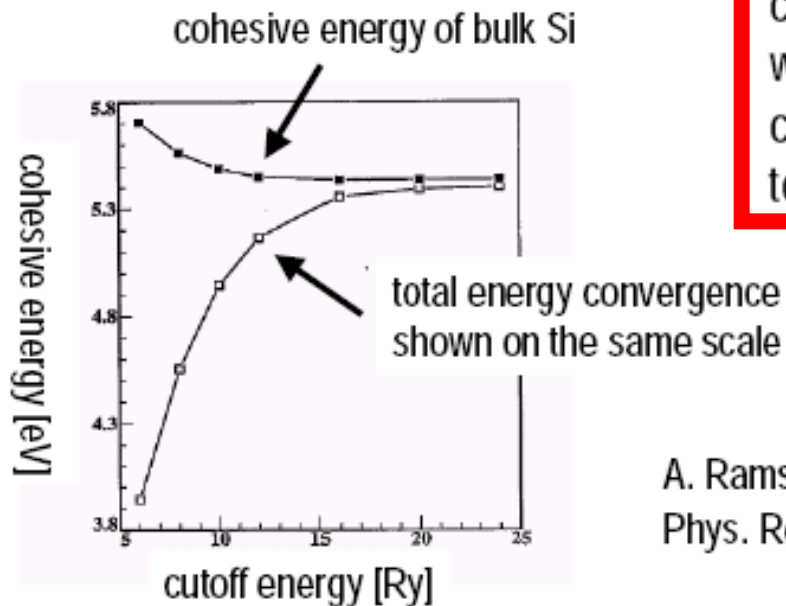
Convergence as a function of # of PWs (or PW energy cutoff)

Example 1:
absolute convergence
for GaAs, LDA, Hamann
pseudopotential,
data points at
E_{cut} = 7, 8, 10, 20 Ry

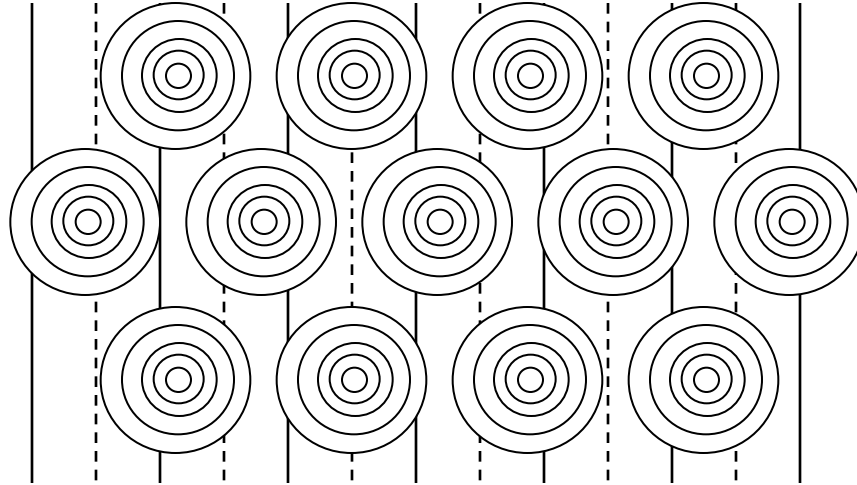# Convergence as a function of # of PWs (or PW energy cutoff)

Example 2: Si

cohesive energy of bulk Si

relative energies converge much faster with the plane wave cutoff than the absolute total energy !

total energy convergence shown on the same scale

A. Ramstad, G. Brocks, and P. J. Kelly, Phys. Rev. B **51**, 14504 (1995).

Augmented plane waves (I)

- (L)APW method

- **Augmentation: represent the wave function inside given spheres centered on atoms in spherical harmonics, and as plane wave outside.**

  - **"Best of both worlds"**

  - **Requires matching inside and outside functions**

  - **Most general form – can approach arbitrarily precision as it does not require the use of pseudopotentials.**

Augmented plane waves (II)

The unit cell is partitioned into:
  atomic spheres
  Interstitial region

unit cell

R_{mt} $r \in I$

PWs | atomic | Plane Waves (PWs)

sphere | I | R_a
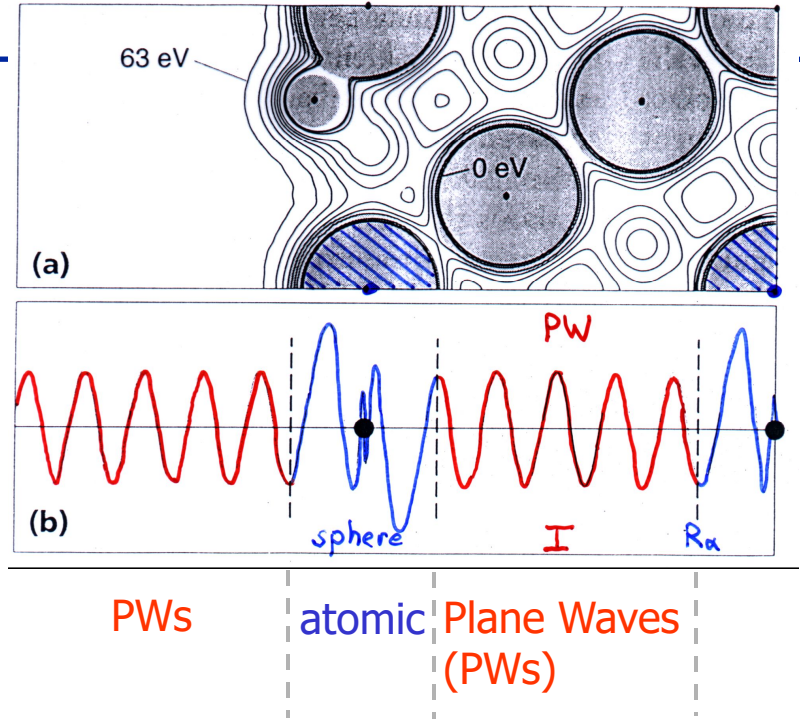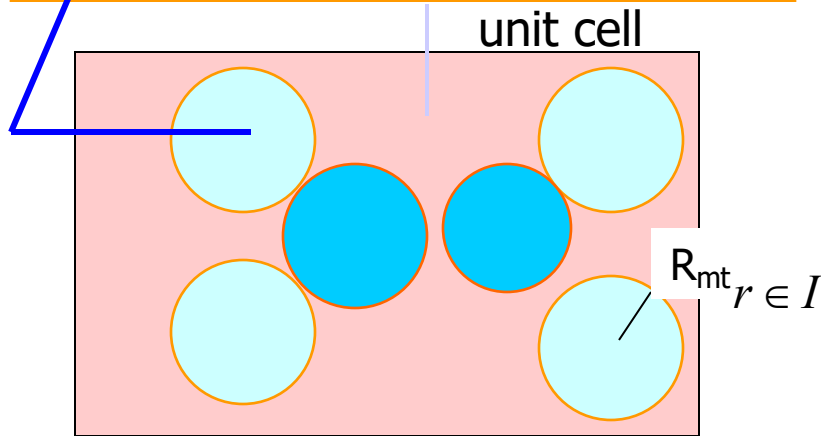
Basis set:

PW: $e^{i(\vec{k}+\vec{K}).\vec{r}}$

Atomic partial waves

$$\sum_{\ell m} A_{\ell m}^{K} u_\ell(r', \varepsilon) Y_{\ell m}(\hat{r}')$$

join

$u_l(r,\varepsilon)$ are the numerical solutions
of the radial Schrödinger equation
in a given spherical potential
for a particular energy ε
$A_{lm}{}^K$ coefficients for matching the PW

Finite-difference representation of KS eigenvalue problem:

$$
-\frac{1}{2h^2}
\begin{bmatrix}
-2 & 1 & 0 & \dots \\
1 & -2 & 1 & \dots \\
0 & 1 & -2 & \dots \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\begin{bmatrix}
\psi(x_1) \\
\cdot \\
\cdot \\
\cdot \\
\cdot \\
\psi(x_N)
\end{bmatrix}
$$

$$
+
\begin{bmatrix}
V(x_1) & 0 & 0 & \dots \\
0 & V(x_2) & 0 & \dots \\
0 & 0 & V(x_3) & \dots \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\begin{bmatrix}
\psi(x_1) \\
\cdot \\
\cdot \\
\cdot \\
\psi(x_N)
\end{bmatrix}
$$

$$
= \lambda
\begin{bmatrix}
\psi(x_1) \\
\cdot \\
\cdot \\
\cdot \\
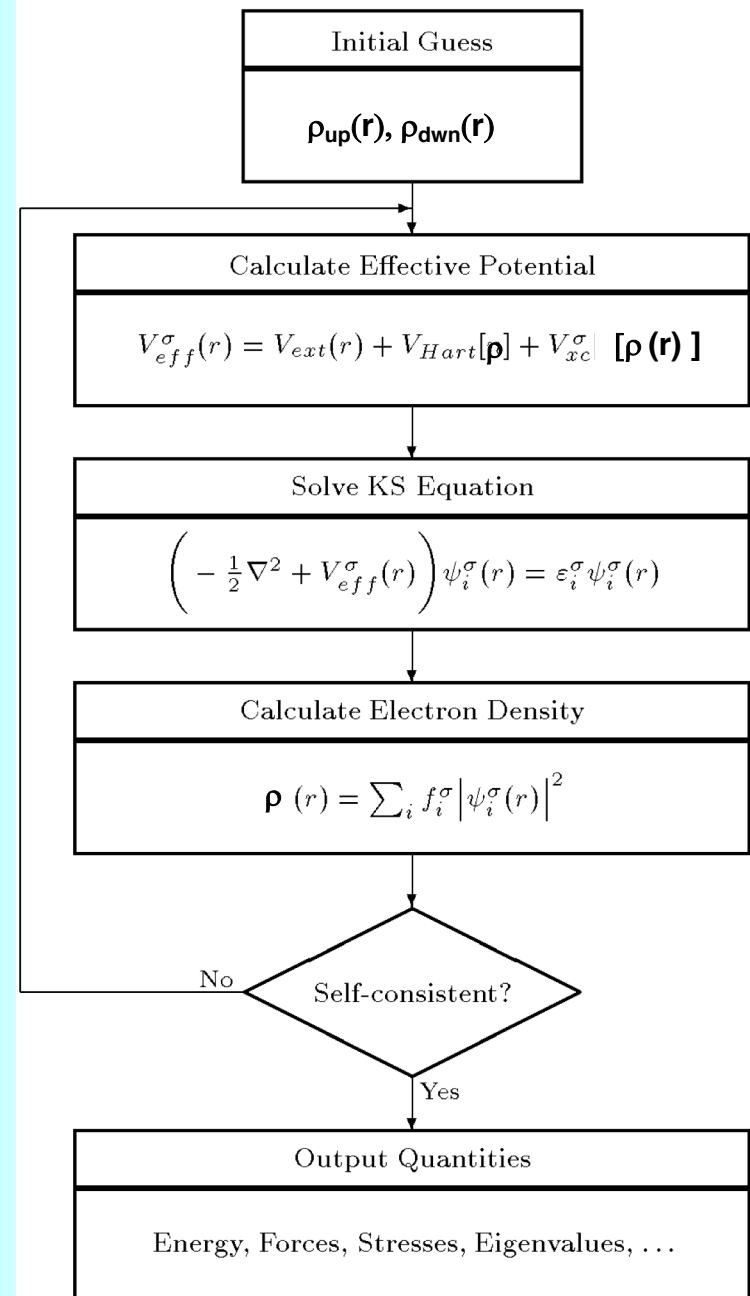\psi(x_N)
\end{bmatrix}.
$$

Example: 2-d 4th order Laplacian
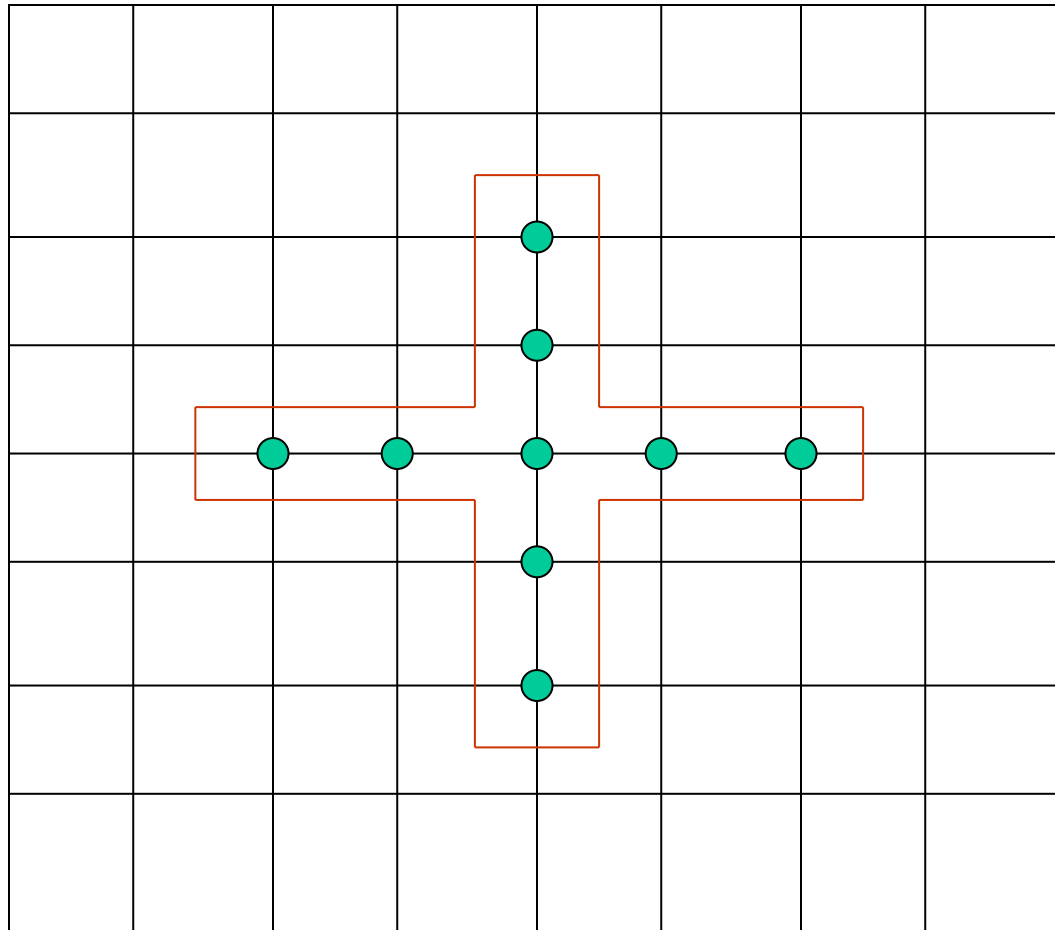
Solving KS equations

- Choose **approximation for exchange and correlation potential**

- Choose **atomic configuration**, i.e. positions of the nuclei $\mathbf{R_I}$

- Choose:

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  - **basis set** to expand single particle orbitals

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- Solve KS **eigenvalue problem** in an **iterative manner.**

Self-Consistent Kohn-Sham Equations

Initial Guess

$\rho_{up}(\mathbf{r}), \rho_{dwn}(\mathbf{r})$

Calculate Effective Potential

$$V_{eff}^{\sigma}(r) = V_{ext}(r) + V_{Hart}[\boldsymbol{\rho}] + V_{xc}^{\sigma}\,[\boldsymbol{\rho}\,(\mathbf{r})\,]$$

Solve KS Equation

$$\left(-\tfrac{1}{2}\nabla^2 + V_{eff}^{\sigma}(r) \right) \psi_i^{\sigma}(r) = \varepsilon_i^{\sigma}\psi_i^{\sigma}(r)$$

Calculate Electron Density

$$\boldsymbol{\rho}\,(r) = \sum_i f_i^{\sigma}\left|\psi_i^{\sigma}(r)\right|^2$$

Self-consistent? — No / Yes

Output Quantities

Energy, Forces, Stresses, Eigenvalues, . . .

Iterative solutions of KS eigenvalue problem

- **Linear mixing (or following the direction of "steepest descent")**

$$\rho_{i+1}^{in} = \alpha \, \rho_i^{out} + (1-\alpha) \, \rho_i^{in} = \rho_i^{in} + \alpha \left(\rho_i^{out} - \rho_i^{in} \right)$$

- **How do we choose α ?**

$$\delta\rho = \rho - \rho_{ks} = \text{deviation from ground state density } \rho_{ks}$$

α **is related to the response function of a system and to a measure of the polarizability. Linear mixing with large a works better for rigid, strongly bound systems; however convergence can be difficult to obtain for "soft" systems such as a metal surface.**

Eigenvalue problem

- **Direct methods:**
  - **Full diagonalization of the Hamiltonian matrix in a chosen basis set:** all **eigenvalues** $\varepsilon_{j,k}$ and **eigenvectors** $\Psi_{j,k}$ are computed
  - **In general, suitable for methods with atom-centered, localized orbitals *only***
  - **Practical up to a Hamiltonian matrix size of ~10,000 basis functions**

- **Variational approaches:**
  - **Diagonalization problem can be presented as a minimization problem for a quadratic form (the total energy)**
  - **Steepest descent and conjugate gradients methods**
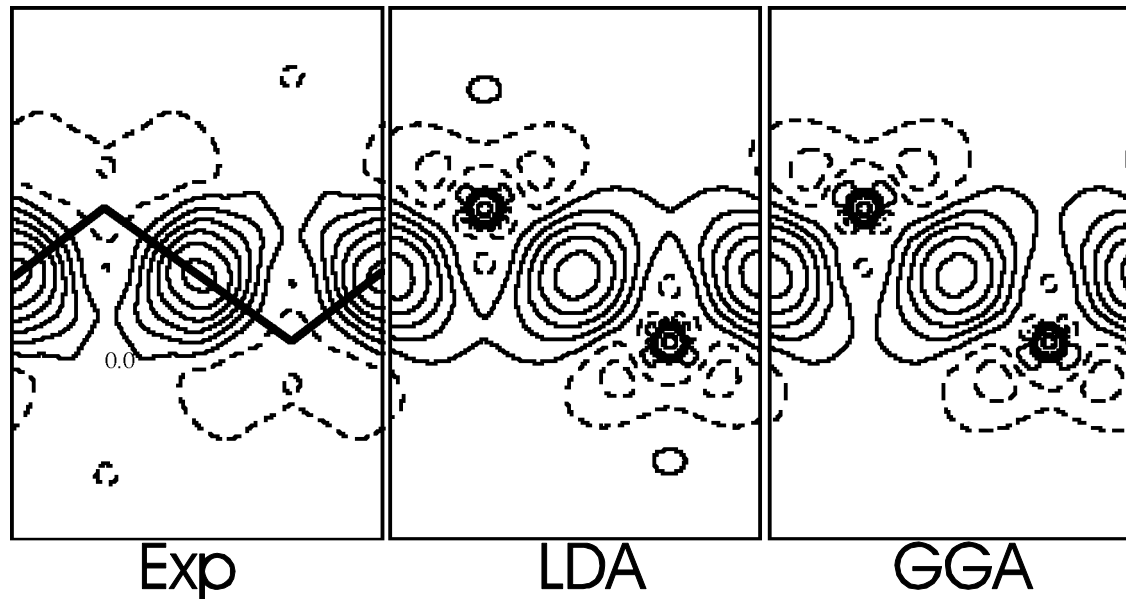
Electron density in solids, e.g. Silicon

From : "Electronic Structure: Basic Theory and Practical Methods", R. M. Martin, Cambridge University Press, 2004 –

τ_2
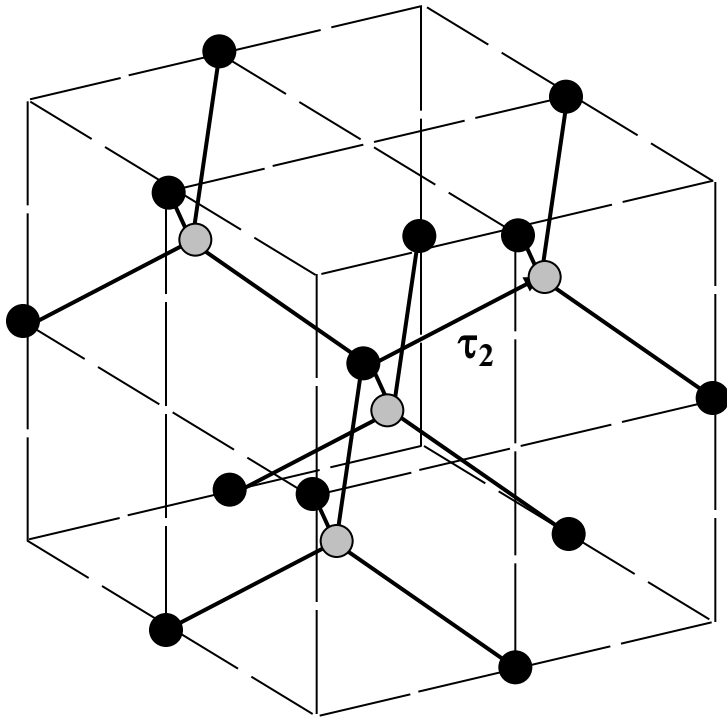
In Si the black and grey atoms are identical
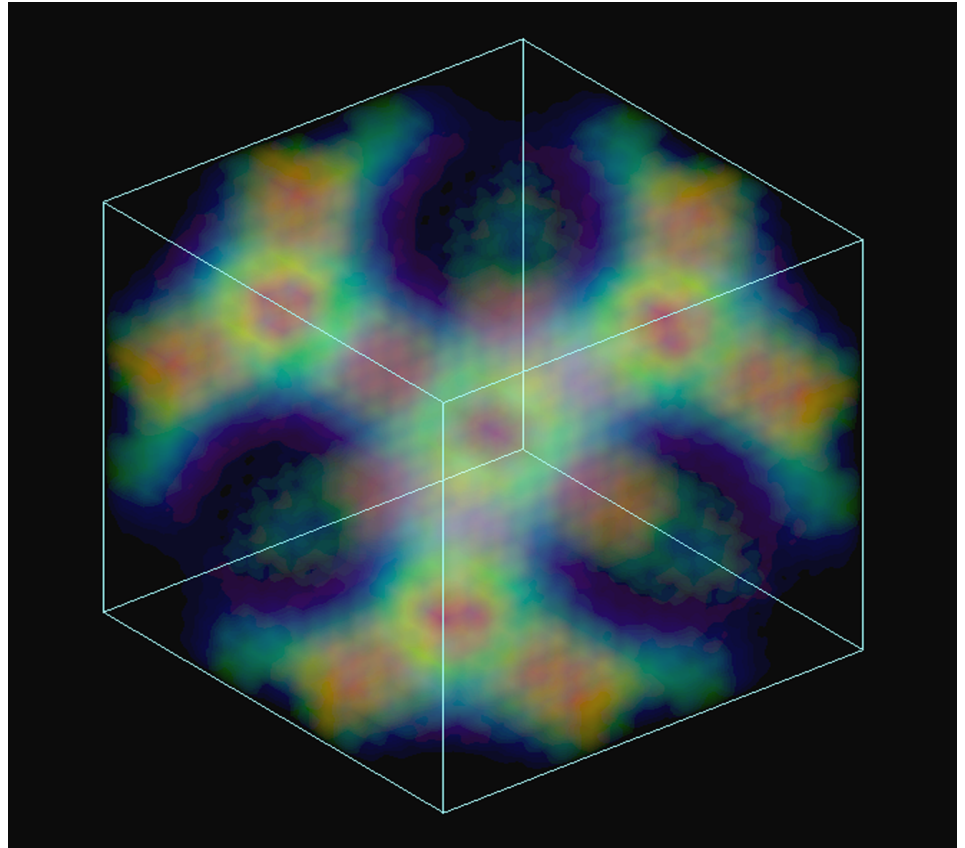
Electron density in Silicon: comparison with experiment

Exp   LDA   GGA

- **Electron density <u>difference</u> from sum of atoms**
  - **Experimental density from electron scattering**
  - **Calculations with two different functionals and LAPW basis**
    - **J. M. Zuo, P. Blaha, and K. Schwarz, J. Phys. Cond. Mat. 9, 7541 (1997).**
  - **Very similar results with pseudopotentials**
    - **O. H. Nielsen and R. M. Martin (1995)**

Comparison of structural parameters obtained using different basis sets.

Method	C		Si		CaF$_2$		bcc Fe		
	a	B	a	B	a	B	a	B	m
NCPP[a]	3.54	460	5.39	98	5.21	90	2.75[c]	226[c]	
PAW[a]	3.54	460	5.38	98	5.34	100			
PAW[b]	3.54	460	5.40	95	5.34	101	2.75	247	2.00
USPP[b]	3.54	461	5.40	95	5.34	101	2.72	237	2.08
LAPW[a]	3.54	470	5.41	98	5.33	110	2.72[d]	245[d]	2.04[d]
EXP[a]	3.56	443	5.43	99	5.45	85-90	2.87[d]	172[d]	2.12[d]

PW

- a – lattice constant;   B – bulk modulus;   m – magnetization

- [a]Holzwarth , *et al.*; [b]Kresse & Joubert; [c]Cho & Scheffler; [d]Stizrude, *et al.*