Localized basis methods

Theory and implementations

- Introduction of OpenMX
- Implementation of OpenMX
  - Total energy
  - Pseudopontials
  - Basis functions
- Δ-gauge
- Practical guide to OpenMX calc.

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The Summer School on DFT: Theories and Practical Aspects, July 2-6, 2018, ISSP

OpenMX **Open source package for Material eXplorer**

- Software package for density functional calculations of molecules and bulks
- Norm-conserving pseudopotentials (PPs)
- Variationally optimized numerical atomic basis functions

Basic functionalities

- SCF calc. by LDA, GGA, DFT+U
- Total energy and forces on atoms
- Band dispersion and density of states
- Geometry optimization by BFGS, RF, EF
- Charge analysis by Mullken, Voronoi, ESP
- Molecular dynamics with NEV and NVT ensembles
- Charge doping
- Fermi surface
- Analysis of charge, spin, potentials by cube files
- Database of optimized PPs and basis funcitons

Extensions

- O(N) and low-order scaling diagonalization
- Non-collinear DFT for non-collinear magnetism
- Spin-orbit coupling included self-consistently
- Electronic transport by non-equilibrium Green function
- Electronic polarization by the Berry phase formalism
- Maximally localized Wannier functions
- Effective screening medium method for biased system
- Reaction path search by the NEB method
- Band unfolding method
- STM image by the Tersoff-Hamann method
- etc.

History of OpenMX

2000 Start of development

2003 Public release (GNU-GPL)

2003 Collaboration:
AIST, NIMS, SNU
KAIST, JAIST,
Kanazawa Univ.
CAS, UAM
NISSAN, Fujitsu Labs.
etc.

2018 18 public releases
Latest version: 3.8

Welcome to OpenMX

Open source package for Material eXplorer

Contents

- What's new
  - OpenMX Hands-On Workshop on 10th Oct. in Kobe
  - Patch (Ver.3.7.8) to OpenMX Ver. 3.7 (17/Feb/2014)
  - Release of OpenFFT Ver. 1.0 (04/Sep/2013)
- What is OpenMX?
- Download
- Manual
- Technical Notes
- Publications
- OpenMX Forum
- Workshop
- Database of VPS and PAO
  - Ver. 2013
- ADPACK
- Miscellaneous informations
- Contributors
- Acknowledgment
- Links

http://www.openmx-square.org

About 500 papers published using OpenMX

Developers of OpenMX

- T. Ozaki (U.Tokyo)
- H. Kino (NIMS)
- J. Yu (SNU)
- M. J. Han (KAIST)
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- T. Ohwaki (Nissan)
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- Y.T. Lee (Univ. of Tokyo)
- Masahiro Fukuda (Univ. of Tokyo)

Materials studied by OpenMX

First characterization of silicene on ZrB_2 in collaboration with experimental groups

A. Fleurence et al., Phys. Rev. Lett. 108, 245501 (2012).

First identification of Jeff=1/2 Mott state of Ir oxides

B.J. Kim et al., Phys. Rev. Lett. 101, 076402 (2008).

Theoretical proposal of topological insulators

C.-H. Kim et al., Phys. Rev. Lett. 108, 106401 (2012).
H. Weng et al., Phy. Rev. X 4, 011002 (2014).

First-principles molecular dynamics simulations for Li ion battery

T. Ohwaki et al., J. Chem. Phys. 136, 134101 (2012).
T. Ohwaki et al., J. Chem. Phys. 140, 244105 (2014).

Magnetic anisotropy energy of magnets

Z. Torbatian et al., Appl. Phys. Lett. 104, 242403 (2014).
I. Kitagawa et al., Phys. Rev. B 81, 214408 (2010).

Electronic transport of graphene nanoribbon on surface oxidized Si

H. Jippo et al., Appl. Phys. Express 7, 025101 (2014).
M. Ohfuchi et al., Appl. Phys. Express 4, 095101 (2011).

Interface structures of carbide precipitate in bcc-Fe

H. Sawada et al., Modelling Simul. Mater. Sci. Eng. 21, 045012 (2013).

Universality of medium range ordered structure in amorphous metal oxides

K. Nishio et al., Phys. Rev. Lett. 340, 155502 (2013).

Materials treated so far

Silicene, graphene
Carbon nanotubes
Transition metal oxides
Topological insulators
Intermetallic compounds
Molecular magnets
Rare earth magnets
Lithium ion related materials
Structural materials
etc.

About 500 published papers

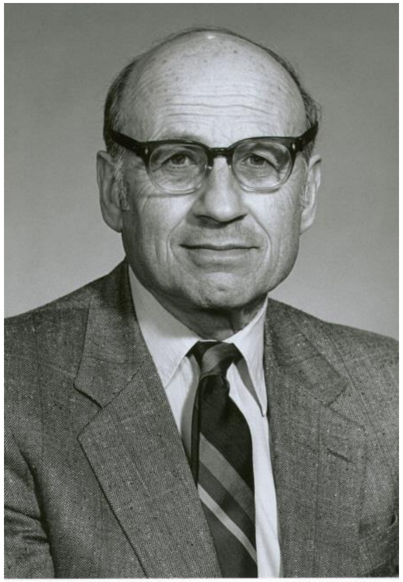
Implementation of OpenMX

- Density functional theory
- Mathematical structure of KS eq.
- LCPAO method
- Total energy
- Pseudopotentials
- Basis functions

Density functional theory

The energy of non-degenerate ground state can be expressed by a functional of electron density. (Hohenberg and Kohn, 1964)

$$E[\rho]=T[\rho]+J[\rho]+\int \rho v_{\mathrm{ext}} d\mathbf{r}+E_{\mathrm{xc}}^{(0)}[\rho]$$



W.Kohn (1923-2016)

The many body problem of the ground state can be reduced to an one-particle problem with an effective potential. (Kohn-Sham, 1965)

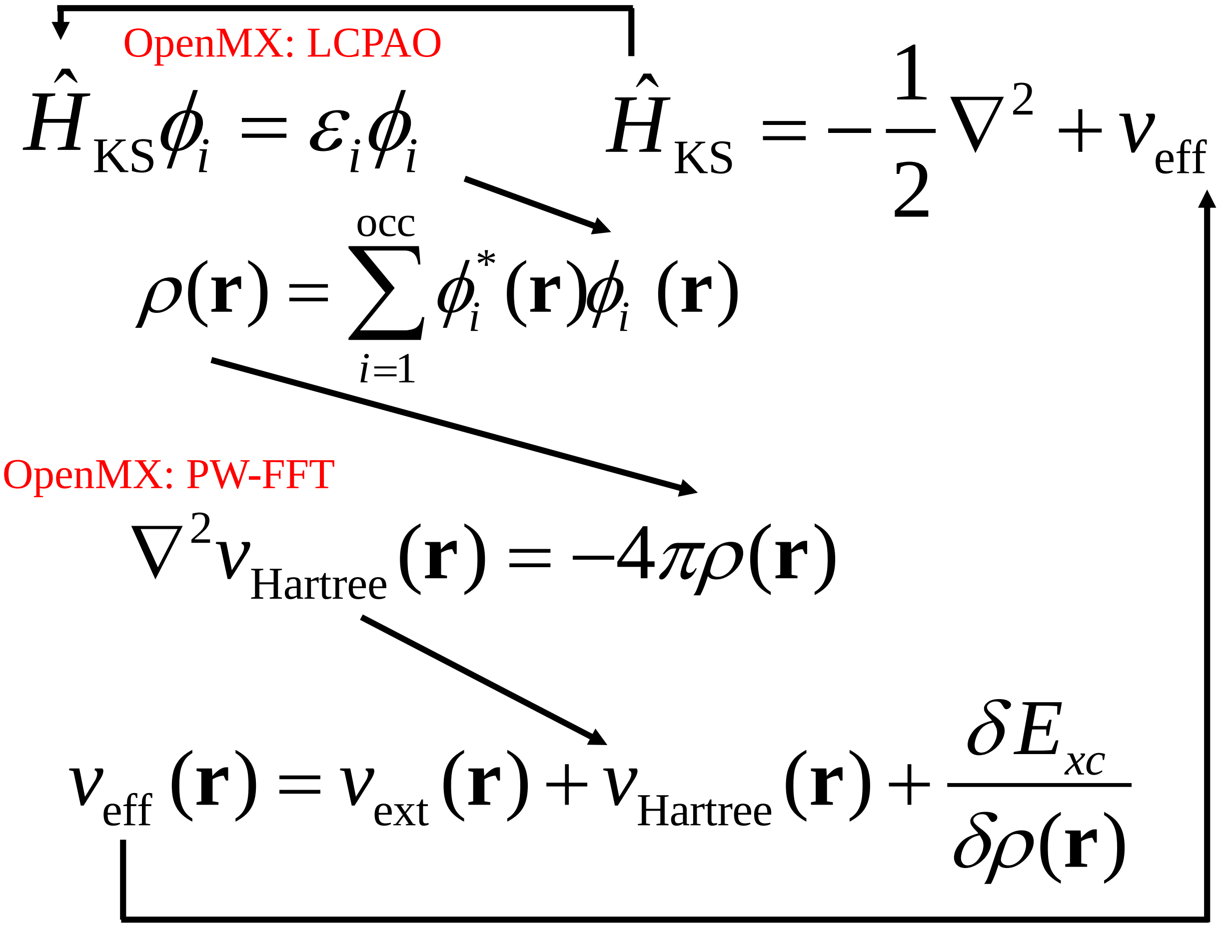
$$\hat{H}_{\mathrm{KS}}\phi_i=\varepsilon_i\phi_i$$

$$\hat{H}_{\mathrm{KS}}=-\frac{1}{2}\nabla^2+v_{\mathrm{eff}}$$

$$v_{\mathrm{eff}}(\mathbf{r})=v_{\mathrm{ext}}(\mathbf{r})+v_{\mathrm{Hartree}}(\mathbf{r})+\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}$$

Mathematical structure of KS eq.

3D coupled non-linear differential equations have to be solved self-consistently.



OpenMX: LCPAO

$$\hat{H}_{\mathrm{KS}}\phi_i = \varepsilon_i \phi_i \qquad \hat{H}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}$$

$$\rho(\mathbf{r}) = \sum_{i=1}^{\mathrm{occ}} \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

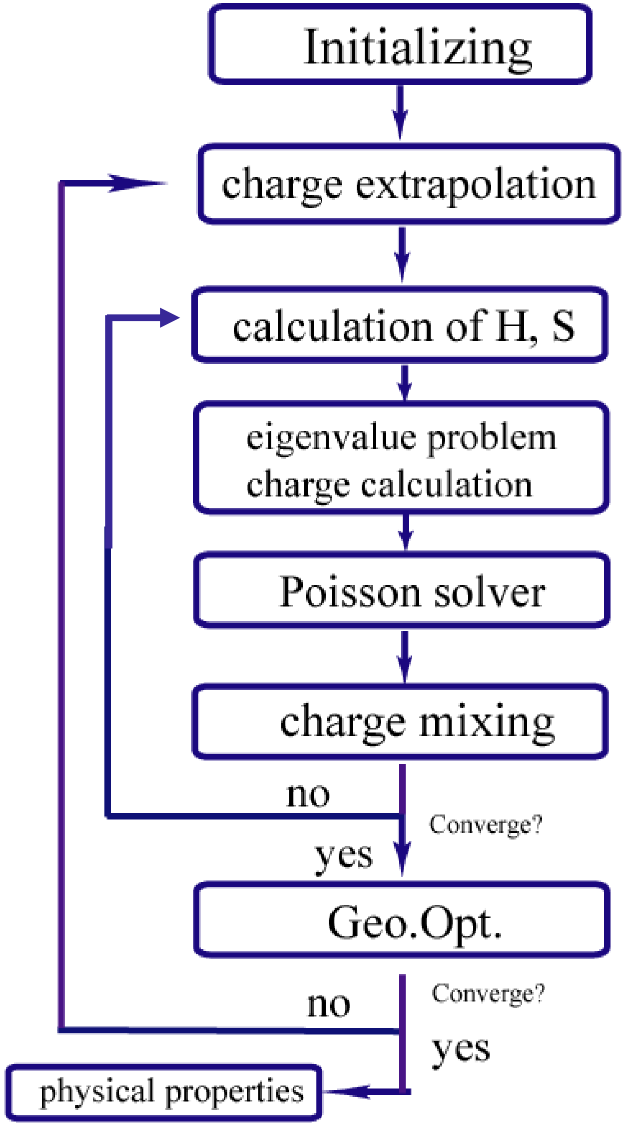
OpenMX: PW-FFT

$$\nabla^2 v_{\mathrm{Hartree}}(\mathbf{r}) = -4\pi\rho(\mathbf{r})$$

$$v_{\mathrm{eff}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}$$

Input charge = Output charge → Self-consistent condition

Flowchart of calculation



The DFT calculations basically consist of two loops. The inner loop is for SCF, and the outer loop is for geometry optimization.

The inner loop may have routines for construction of the KS matrix, eigenvalue problem, solution of Poisson eq., and charge mixing.

After getting a convergent structure, several physical quantities will be calculated.

Classification of the KS solvers

Treatment of core electrons	All electron (AE) method Pseudo-potential (PP) method
Basis functions	Plane wave basis (PW) Mixed basis (MB) Local basis (LB)

	Accuracy	Efficiency
AE+MB: LAPW, LMTO	◎	×
AE+LB: Gaussian	○	○
PP+PW: Plane wave with PP	○	○
PP+LB: OpenMX, SIESTA	△	◎

LCPAO method

(Linear-Combination of Pseudo Atomic Orbital Method)

One-particle KS orbital

$$\psi_{\sigma\mu}^{(\mathbf{k})}(\mathbf{r}) = \frac{1}{\sqrt{N_{\mathrm{c}}}} \sum_{\mathrm{n}}^{N_{\mathrm{c}}} \mathrm{e}^{i\mathbf{R}_{\mathrm{n}} \bullet \mathbf{k}} \sum_{i\alpha} c_{\sigma\mu,i\alpha}^{(\mathbf{k})} \phi_{i\alpha}(\mathbf{r} - \tau_i - \mathbf{R}_{\mathrm{n}})$$

is expressed by a linear combination of atomic like orbitals in the method.

$$\phi(\mathbf{r}) = Y_l^m(\hat{\mathbf{r}}) R(r)$$

Features:

- It is easy to interpret physical and chemical meanings, since the KS orbitals are expressed by the atomic like basis functions.
- It gives rapid convergent results with respect to basis functions due to physical origin. (however, it is not a complete basis set, leading to difficulty in getting full convergence.)
- The memory and computational effort for calculation of matrix elements are O(N).
- It well matches the idea of linear scaling methods.

- Total energy
- Pseudopotentials
- Basis functions

Implementation: Total energy (1)

The total energy is given by the sum of six terms, and a proper integration scheme for each term is applied to accurately evaluate the total energy.

$$E_{\rm tot} = E_{\rm kin} + E_{\rm ec} + E_{\rm ee} + E_{\rm xc} + E_{\rm cc} = E_{\rm kin} + E_{\rm na} + E_{\rm ec}^{\rm (NL)} + E_{\delta {\rm ee}} + E_{\rm xc} + E_{\rm scc}.$$

$$E_{\rm kin} = \sum_{\sigma}\sum_{\rm n}^{N}\sum_{i\alpha,j\beta} \rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_{\rm n})} h_{i\alpha j\beta,{\rm kin}}^{(\mathbf{R}_{\rm n})}$$

Kinetic energy

$$\begin{aligned} E_{\rm ec} &= \boxed{E_{\rm ec}^{\rm (L)}} + E_{\rm ec}^{\rm (NL)}, \\ &= \sum_{\sigma}\sum_{\rm n}^{N}\sum_{i\alpha,j\beta} \rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_{\rm n})} \langle \phi_{i\alpha}(\mathbf{r}-\tau_i)|\sum_{I} V_{{\rm core},I}(\mathbf{r}-\tau_I)|\phi_{j\beta}(\mathbf{r}-\tau_j-\mathbf{R}_{\rm n})\rangle \\ &+ \sum_{\sigma}\sum_{\rm n}^{N}\sum_{i\alpha,j\beta} \rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_{\rm n})} \langle \phi_{i\alpha}(\mathbf{r}-\tau_i)|\sum_{I} V_{{\rm NL},I}(\mathbf{r}-\tau_I)|\phi_{j\beta}(\mathbf{r}-\tau_j-\mathbf{R}_{\rm n})\rangle, \end{aligned}$$

Coulomb energy with external potential

$$\begin{aligned} \boxed{E_{\rm ee}} &= \frac{1}{2}\int dr^3 n(\mathbf{r}) V_{\rm H}(\mathbf{r}), \\ &= \frac{1}{2}\int dr^3 n(\mathbf{r}) \{V_{\rm H}^{\rm (a)}(\mathbf{r}) + \delta V_{\rm H}(\mathbf{r})\} \end{aligned}$$

Hartree energy

$$E_{\rm xc} = \int dr^3 \{n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}) + n_{\rm pcc}(\mathbf{r})\} \epsilon_{\rm xc}(n_{\uparrow} + \frac{1}{2}n_{\rm pcc}, n_{\downarrow} + \frac{1}{2}n_{\rm pcc}),$$

Exchange-correlation energy

$$\boxed{E_{\rm cc}} = \frac{1}{2}\sum_{I,J}\frac{Z_I Z_J}{|\tau_I - \tau_J|}.$$

Core-core Coulomb energy

TO and H. Kino, PRB 72, 045121 (2005).

Implementation: Total energy (2)

The reorganization of Coulomb energies gives three new energy terms.

$$E_{\rm ec}^{(L)} + E_{\rm ee} + E_{\rm cc} = E_{\rm na} + E_{\delta{\rm ee}} + E_{\rm scc},$$

The neutral atom energy

$$\begin{aligned} E_{\rm na} &= \int dr^3 n(\mathbf{r}) \sum_I V_{{\rm na},I}(\mathbf{r}-\tau_I), \\ &= \sum_\sigma \sum_{\rm n}^{N} \sum_{i\alpha,j\beta} \rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_{\rm n})} \sum_I \langle \phi_{i\alpha}(\mathbf{r}-\tau_i) | V_{{\rm na},I}(\mathbf{r}-\tau_I) | \phi_{j\beta}(\mathbf{r}-\tau_j-\mathbf{R}_{\rm n}) \rangle, \end{aligned}$$

Short range and separable to two-center integrals

Difference charge Hartree energy

$$E_{\delta{\rm ee}} = \frac{1}{2}\int dr^3 \delta n(\mathbf{r}) \delta V_{\rm H}(\mathbf{r}),$$

Long range but minor contribution

Screened core-core repulsion energy

$$E_{\rm scc} = \frac{1}{2}\sum_{I,J}\left[\frac{Z_I Z_J}{|\tau_I - \tau_J|} - \int dr^3 n_I^{(\rm a)}(\mathbf{r}) V_{{\rm H},J}^{(\rm a)}(\mathbf{r})\right]$$

Short range and two-center integrals

Difference charge

$$\begin{aligned} \delta n(\mathbf{r}) &= n(\mathbf{r}) - n^{(\rm a)}(\mathbf{r}), \\ &= n(\mathbf{r}) - \sum_i n_i^{(\rm a)}(\mathbf{r}), \end{aligned}$$

Neutral atom potential

$$V_{{\rm na},I}(\mathbf{r}-\tau_I) = V_{{\rm core},I}(\mathbf{r}-\tau_I) + V_{{\rm H},I}^{(\rm a)}(\mathbf{r}-\tau_I).$$

Implementation: Total energy (3)

So, the total energy is given by

$$E_{\mathrm{tot}} = E_{\mathrm{kin}} + E_{\mathrm{na}} + E_{\mathrm{ec}}^{(\mathrm{NL})} + E_{\delta\mathrm{ee}} + E_{\mathrm{xc}} + E_{\mathrm{scc}}.$$

Each term is evaluated by using a different numerical grid with consideration on accuracy and efficiency.

$$\left.\begin{array}{l} E_{\mathrm{kin}} \\ E_{\mathrm{na}} \\ E_{\mathrm{ec}}^{(\mathrm{NL})} \end{array}\right\} \quad \text{Spherical coordinate in momentum space}$$

$$\left.\begin{array}{l} E_{\delta\mathrm{ee}} \\ E_{\mathrm{xc}} \end{array}\right\} \quad \text{Real space regular mesh}$$

$$E_{\mathrm{scc}} \qquad \text{Real space fine mesh}$$

Two center integrals

Fourier-transformation of basis functions

$$
\begin{aligned}
\tilde{\phi}_{i\alpha}(\mathbf{k}) &= \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dr^3 Y_{lm}(\hat{\mathbf{r}}) R_{pl}(r) \left\{ 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-\mathrm{i})^L j_L(kr) Y_{LM}(\hat{\mathbf{k}}) Y^*_{LM}(\hat{\mathbf{r}}) \right\}, \\
&= \left(\frac{1}{\sqrt{2\pi}}\right)^3 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-\mathrm{i})^L Y_{LM}(\hat{\mathbf{k}}) \int dr r^2 R_{pl}(r) j_L(kr) \int d\theta d\phi \sin(\theta) Y_{lm}(\hat{\mathbf{r}}) Y^*_{LM}(\hat{\mathbf{r}}), \\
&= \left[\left(\frac{1}{\sqrt{2\pi}}\right)^3 4\pi (-\mathrm{i})^l \int dr r^2 R_{pl}(r) j_l(kr) \right] Y_{lm}(\hat{\mathbf{k}}), \\
&= \tilde{R}_{pl}(k) Y_{lm}(\hat{\mathbf{k}}),
\end{aligned}
$$

Integrals for angular parts are analytically performed. Thus, we only have to perform one-dimensional integrals along the radial direction.

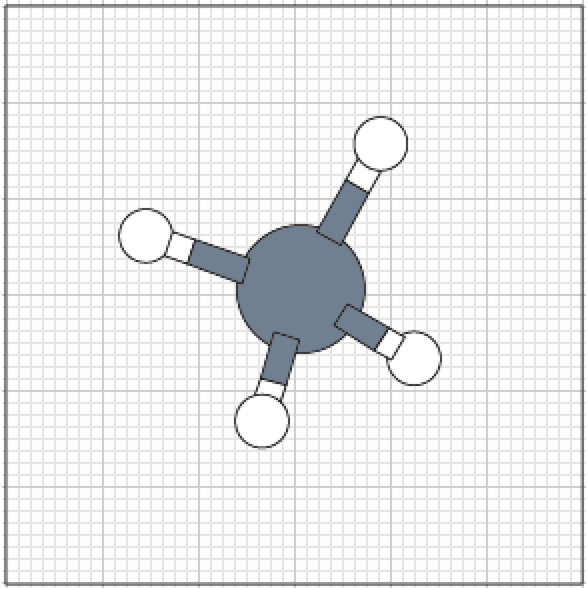
e.g., overlap integral

$$
\begin{aligned}
\langle \phi_{i\alpha}(\mathbf{r}) | \phi_{j\beta}(\mathbf{r}-\tau) \rangle &= \int dr^3 \phi^*_{i\alpha}(\mathbf{r}) \phi_{j\beta}(\mathbf{r}-\tau), \\
&= \int dr^3 \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dk^3 \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dk'^3 \tilde{R}_{p'l'}(k') Y_{l'm'}(\hat{\mathbf{k}}') \mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot(\mathbf{r}-\tau)}, \\
&= \left(\frac{1}{2\pi}\right)^3 \int dk^3 \int dk'^3 \mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\tau} \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k') Y_{l'm'}(\hat{\mathbf{k}}') \int dr^3 \mathrm{e}^{\mathrm{i}(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}, \\
&= \int dk^3 \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\tau} \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k) Y_{l'm'}(\hat{\mathbf{k}}),
\end{aligned}
$$

Cutoff energy for regular mesh

The two energy components **$E_{\delta ee}$ + E_{xc}** are calculated on real space regular mesh. The mesh fineness is determined by plane-wave cutoff energies.

```
scf.energycutoff           150.0          # default=150 (Ry)
```



The cutoff energy can be related to the mesh fineness by the following eqs.

$$E^{(1)}_{\rm cut} = \frac{1}{2}\mathbf{gb}_1 \cdot \mathbf{gb}_1, \quad E^{(2)}_{\rm cut} = \frac{1}{2}\mathbf{gb}_2 \cdot \mathbf{gb}_2, \quad E^{(3)}_{\rm cut} = \frac{1}{2}\mathbf{gb}_3 \cdot \mathbf{gb}_3,$$

$$\mathbf{ga}_1 = \frac{\mathbf{a}_1}{N_1}, \quad \mathbf{ga}_2 = \frac{\mathbf{a}_2}{N_2}, \quad \mathbf{ga}_3 = \frac{\mathbf{a}_3}{N_3},$$

$$\mathbf{gb}_1 = 2\pi\frac{\mathbf{ga}_2 \times \mathbf{ga}_3}{\Delta V}, \quad \mathbf{gb}_2 = 2\pi\frac{\mathbf{ga}_3 \times \mathbf{ga}_1}{\Delta V}, \quad \mathbf{gb}_3 = 2\pi\frac{\mathbf{ga}_1 \times \mathbf{ga}_2}{\Delta V},$$

$$\Delta V = \mathbf{ga}_1 \cdot (\mathbf{ga}_2 \times \mathbf{ga}_3),$$

Forces on atoms

$$\frac{\partial E_{\rm tot}}{\partial \tau_k} = \color{blue}{\boxed{\color{black}{\frac{\partial E_{\rm kin}}{\partial \tau_k}}}} + \color{blue}{\boxed{\color{black}{\frac{\partial E_{\rm na}}{\partial \tau_k}}}} + \color{blue}{\boxed{\color{black}{\frac{\partial E_{\rm ec}^{\rm (NL)}}{\partial \tau_k}}}} + \color{red}{\boxed{\color{black}{\frac{\partial E_{\delta {\rm ee}}}{\partial \tau_k}}}} + \color{red}{\boxed{\color{black}{\frac{\partial E_{\rm xc}}{\partial \tau_k}}}} + \color{blue}{\boxed{\color{black}{\frac{\partial E_{\rm scc}}{\partial \tau_k}}}}.$$

$$\frac{\partial E_{\delta{\rm ee}}}{\partial \tau_k} = \sum_{\bf p} \frac{\partial n({\bf r_p})}{\partial \tau_k}\frac{\partial E_{\delta{\rm ee}}}{\partial n({\bf r_p})} + \sum_{\bf p} \frac{\partial n^{\rm (a)}({\bf r_p})}{\partial \tau_k}\frac{\partial E_{\delta{\rm ee}}}{\partial n^{\rm (a)}({\bf r_p})}.$$

$$\begin{aligned}
\frac{\partial E_{\delta{\rm ee}}}{\partial n({\bf r_q})} &= \frac{1}{2}\Delta V\{\delta V_{\rm H}({\bf r_q}) + \sum_{\bf p}\delta n({\bf r_p})\frac{\partial \delta V_{\rm H}({\bf r_p})}{\partial n({\bf r_q})}\},\\
&= \frac{1}{2}\Delta V\delta V_{\rm H}({\bf r_q}) + \frac{4\pi\Delta V}{2N_1N_2N_3}\sum_{\bf q}\frac{1}{|{\bf q}|^2}\sum_{\bf p}\delta n({\bf r_p}){\rm e}^{i{\bf q}\cdot({\bf r_p}-{\bf r_q})},\\
&= \Delta V\delta V_{\rm H}({\bf r_q}),\\
\frac{\partial E_{\delta{\rm ee}}}{\partial n^{\rm (a)}({\bf r_q})} &= -\frac{1}{2}\Delta V\delta V_{\rm H}({\bf r_q}) + \frac{1}{2}\Delta V\sum_{\bf p}\delta n({\bf r_p})\frac{\partial \delta V_{\rm H}({\bf r_p})}{\partial n^{\rm (a)}({\bf r_q})},\\
&= -\frac{1}{2}\Delta V\delta V_{\rm H}({\bf r_q}) - \frac{1}{2}\Delta V\frac{4\pi}{N_1N_2N_3}\sum_{\bf q}\frac{1}{|{\bf q}|^2}\sum_{\bf p}\delta n({\bf r_p}){\rm e}^{i{\bf q}\cdot({\bf r_p}-{\bf r_q})},\\
&= -\Delta V\delta V_{\rm H}({\bf r_q}).
\end{aligned}$$

🟦 **Easy calc.**

🟥 **See the left**

$$\begin{aligned}
\frac{\partial n({\bf r_p})}{\partial \tau_k} &= \frac{1}{V_{\rm B}}\int_{\rm B} dk^3 \sum_{\sigma}\sum_{\mu}^{\rm occ}\sum_{i\alpha,j\beta}\sum_{\rm n}^{N}{\rm e}^{{\rm i}{\bf R}_{\rm n}\cdot{\bf k}}\left(\frac{\partial c_{\sigma\mu,i\alpha}^{({\bf k})*}}{\partial \tau_k}c_{\sigma\mu,j\beta}^{({\bf k})}\phi_{i\alpha}({\bf r_p})\phi_{j\beta}({\bf r_p}) + c_{\sigma\mu,i\alpha}^{({\bf k})*}\frac{\partial c_{\sigma\mu,j\beta}^{({\bf k})}}{\partial \tau_k}\phi_{i\alpha}({\bf r_p})\phi_{j\beta}({\bf r_p})\right)\\
&+\frac{2}{V_{\rm B}}\int_{\rm B} dk^3 \sum_{\sigma}\sum_{\alpha,j\beta}\sum_{\mu}\sum_{\rm n}^{N}{\rm e}^{{\rm i}{\bf R}_{\rm n}\cdot{\bf k}}c_{\sigma\mu,k\alpha}^{({\bf k})*}c_{\sigma\mu,j\beta}^{({\bf k})}\frac{\partial \phi_{k\alpha}({\bf r_p})}{\partial \tau_k}\phi_{j\beta}({\bf r_p}).
\end{aligned}$$

$$\begin{aligned}
\frac{\partial E_{\rm xc}}{\partial \tau_k} &= \sum_{\sigma}\sum_{\bf p}\frac{\partial n_\sigma({\bf r_p})}{\partial \tau_k}\frac{\partial E_{\rm xc}}{\partial n_\sigma({\bf r_p})} + \sum_{\sigma}\sum_{\bf p}\frac{\partial n_{\rm pcc}({\bf r_p})}{\partial \tau_k}\frac{\partial E_{\rm xc}}{\partial n_{\rm pcc}({\bf r_p})},\\
&= \Delta V\sum_{\sigma}\sum_{\bf p}\frac{\partial n_\sigma({\bf r_p})}{\partial \tau_k}V_{{\rm xc},\sigma}(n({\bf r_p}, n_{\rm pcc}({\bf r_p})) + \frac{\Delta V}{2}\sum_{\sigma}\sum_{\bf p}\frac{\partial n_{\rm pcc}({\bf r_p})}{\partial \tau_k}V_{{\rm xc},\sigma}(n({\bf r_p}), n_{\rm pcc}({\bf r_p})).
\end{aligned}$$

Forces are always analytic at any grid fineness and at zero temperature, even if numerical basis functions and numerical grids.

- Total energy
- Pseudopotentials
- Basis functions

Norm-conserving pseudopotential by MBK

I. Morrion, D.M. Bylander, and L. Kleinman, PRB 47, 6728 (1993).

If $Q_{ij} = 0$, the non-local terms can be transformed to a diagonal form.

$$\begin{aligned} V_{\mathrm{NL}} &= \sum_{i,j} B_{ij} |\beta_i\rangle\langle\beta_j|, \\ &= \sum_i \lambda_i |\alpha_i\rangle\langle\alpha_i| \end{aligned}$$

The form is equivalent to that obtained from the Blochl expansion for TM norm-conserving pseudopotentials. Thus, common routines can be utilized for the MBK and TM pseudopotentials, resulting in easiness of the code development.

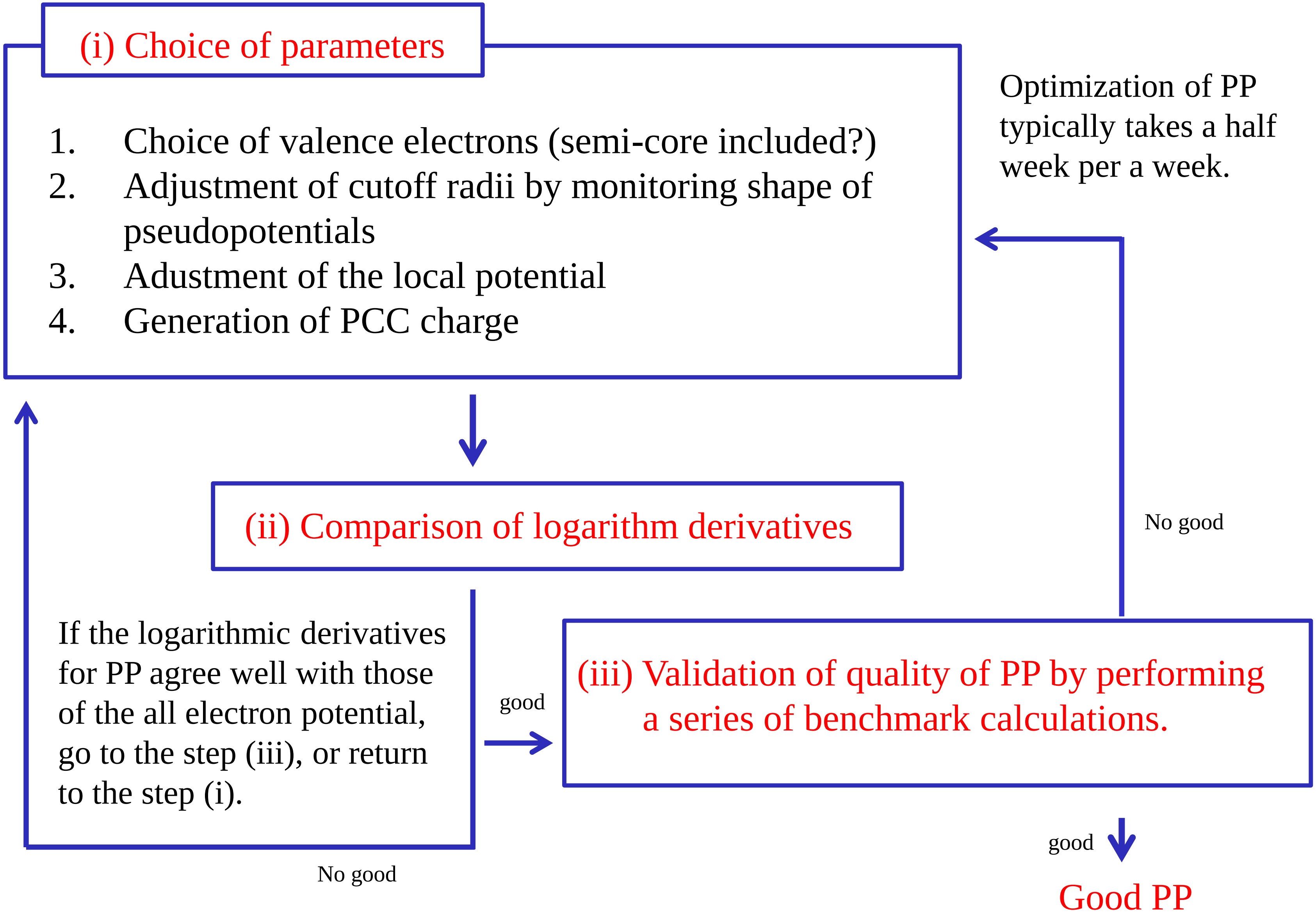
To satisfy $Q_{ij}=0$, pseudofunctions are now given by

$$\phi_i = \phi_{\mathrm{TM},i} + f_i \qquad f_i = \sum_{i=0} c_i \left[r j_l \left(\frac{r}{r_c} u_{li} \right) \right]$$

The coefficients {c} are determined by agreement of derivatives and $Q_{ij}=0$.
Once a set of {c} is determined, χ is given by

$$\chi_i = V_{\mathrm{TM}}^{(i)} \phi_{\mathrm{TM},i} + \varepsilon_i f_i - V_{\mathrm{loc}} \phi_i - \frac{1}{2} \sum_i c_i \left(\frac{u_{li}}{r_c} \right)^2 \left[r j_l \left(\frac{r}{r_c} u_{li} \right) \right]$$

Optimization of pseudopotentials



(i) Choice of parameters

1. Choice of valence electrons (semi-core included?)
2. Adjustment of cutoff radii by monitoring shape of pseudopotentials
3. Adustment of the local potential
4. Generation of PCC charge

Optimization of PP typically takes a half week per a week.

(ii) Comparison of logarithm derivatives

If the logarithmic derivatives for PP agree well with those of the all electron potential, go to the step (iii), or return to the step (i).

(iii) Validation of quality of PP by performing a series of benchmark calculations.

Good PP

- Total energy
- Pseudopotentials
- Basis functions

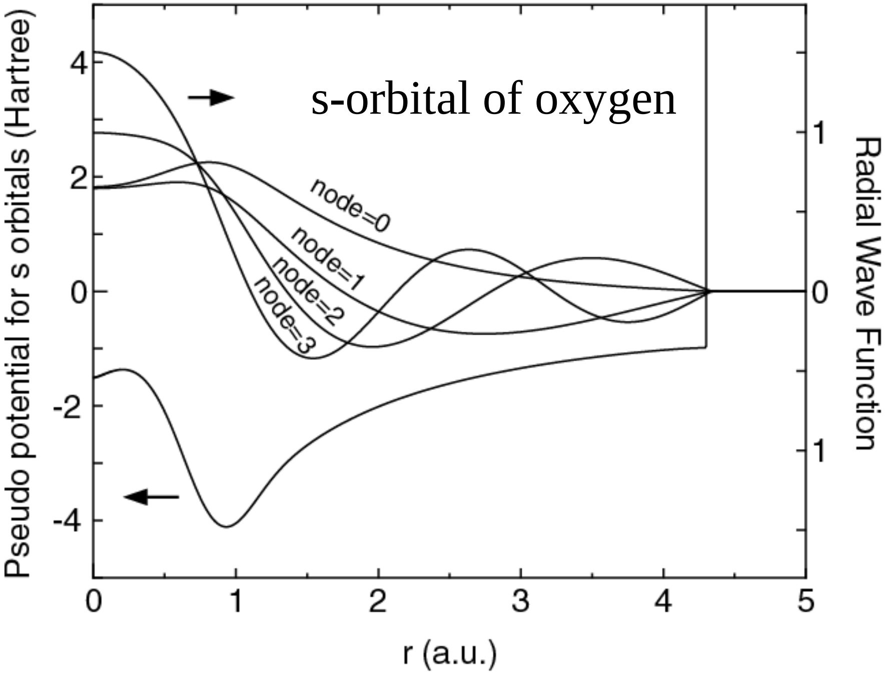
Primitive basis functions

1. Solve an atomic Kohn-Sham eq.
   under a confinement potential:

$$V_{\rm core}(r) = \begin{cases} -\dfrac{Z}{r} & \text{for } r \leq r_1 \\ \displaystyle\sum_{n=0}^{3} b_n r^n & \text{for } r_1 < r \leq r_{\rm c} \\ h & \text{for } r_{\rm c} < r, \end{cases}$$

2. Construct the norm-conserving pseudopotentials.

3. Solve ground and excited states for the the pseudopotential for each L-channel.



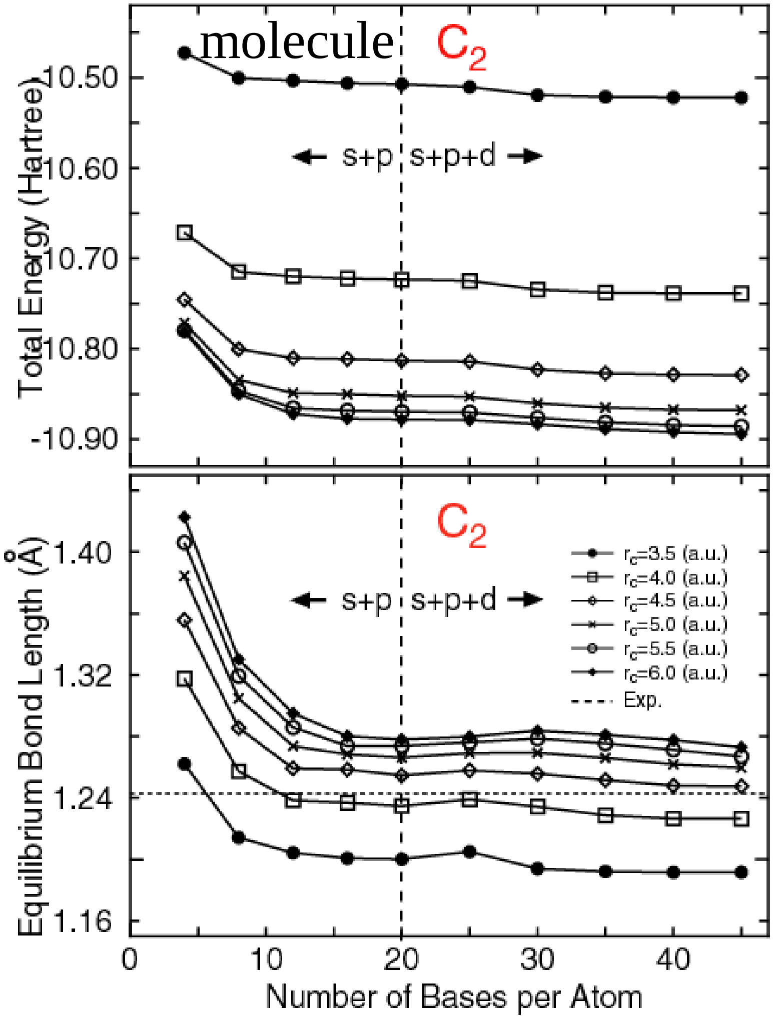
In most cases, the accuracy and efficiency can be controlled by

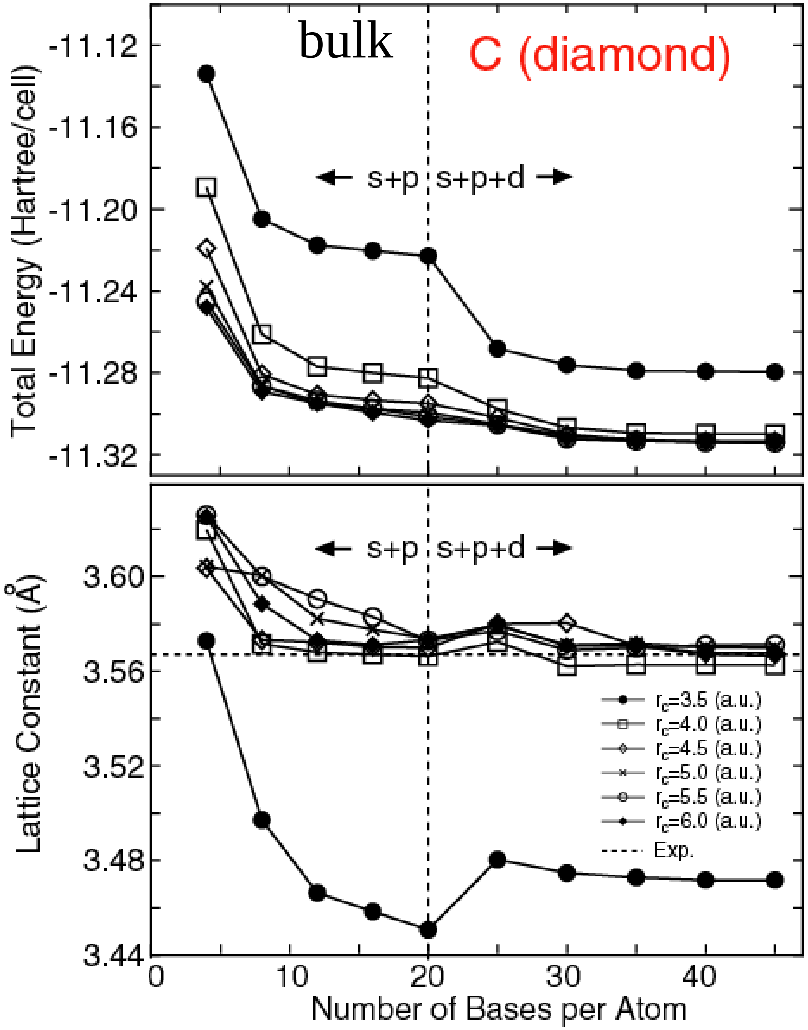
Cutoff radius
Number of orbitals

PRB 67, 155108 (2003)
PRB 69, 195113 (2004)

Convergence with respect to basis functions

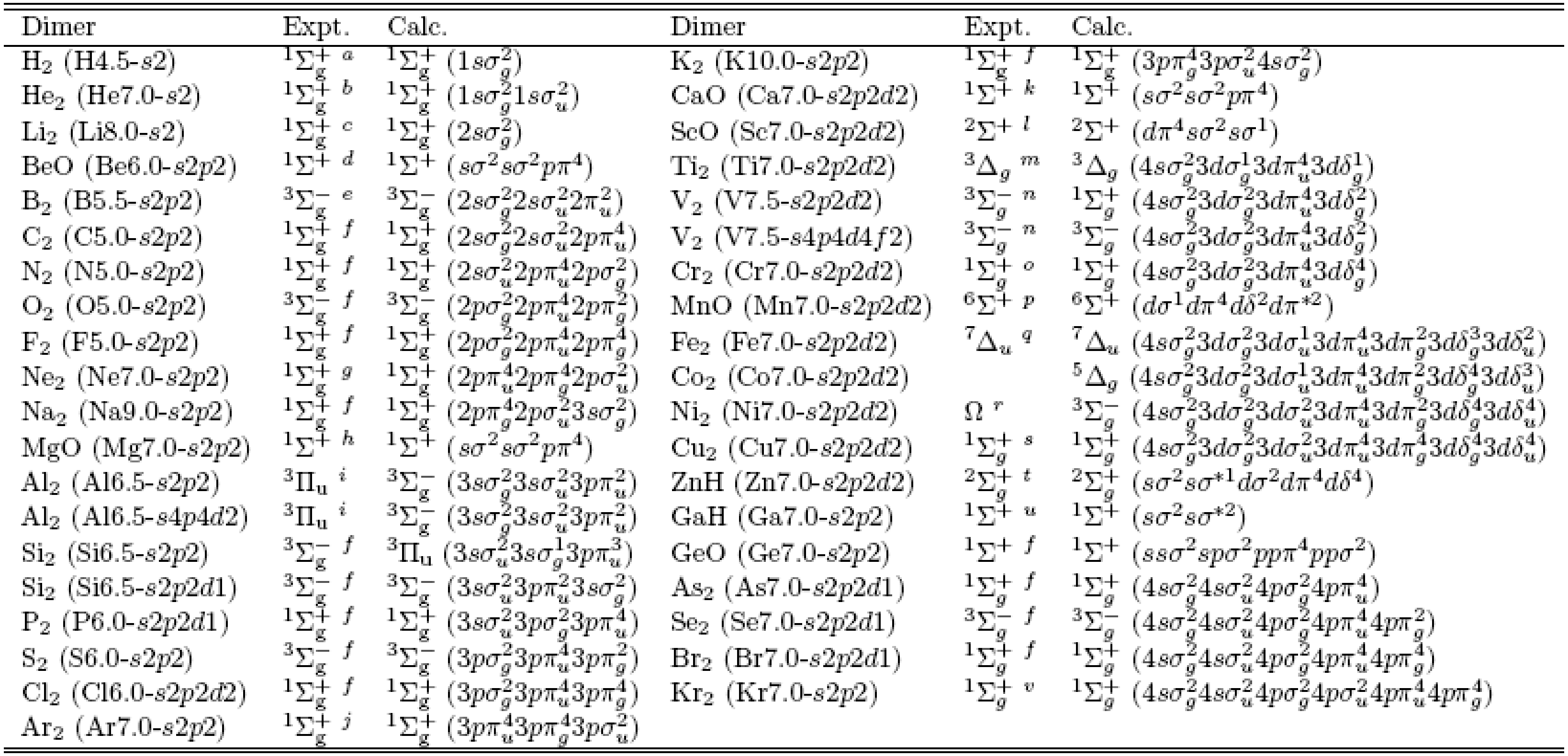
The two parameters can be regarded as variational parameters.





Benchmark of primitive basis functions

Ground state calculations of dimer using primitive basis functions



Dimer	Expt.	Calc.	Dimer	Expt.	Calc.
H_2 (H4.5-$s2$)	$^1\Sigma_g^+$ [a]	$^1\Sigma_g^+$ $(1s\sigma_g^2)$	K_2 (K10.0-$s2p2$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(3p\pi_g^4 3p\sigma_u^2 4s\sigma_g^2)$
He_2 (He7.0-$s2$)	$^1\Sigma_g^+$ [b]	$^1\Sigma_g^+$ $(1s\sigma_g^2 1s\sigma_u^2)$	CaO (Ca7.0-$s2p2d2$)	$^1\Sigma^+$ [k]	$^1\Sigma^+$ $(s\sigma^2 s\sigma^2 p\pi^4)$
Li_2 (Li8.0-$s2$)	$^1\Sigma_g^+$ [c]	$^1\Sigma_g^+$ $(2s\sigma_g^2)$	ScO (Sc7.0-$s2p2d2$)	$^2\Sigma^+$ [l]	$^2\Sigma^+$ $(d\pi^4 s\sigma^2 s\sigma^1)$
BeO (Be6.0-$s2p2$)	$^1\Sigma^+$ [d]	$^1\Sigma^+$ $(s\sigma^2 s\sigma^2 p\pi^4)$	Ti_2 (Ti7.0-$s2p2d2$)	$^3\Delta_g$ [m]	$^3\Delta_g$ $(4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^4 3d\delta_g^1)$
B_2 (B5.5-$s2p2$)	$^3\Sigma_g^-$ [e]	$^3\Sigma_g^-$ $(2s\sigma_g^2 2s\sigma_u^2 2\pi_u^2)$	V_2 (V7.5-$s2p2d2$)	$^3\Sigma_g^-$ [n]	$^1\Sigma_g^+$ $(4s\sigma_g^2 3d\sigma_g^2 3d\pi_u^4 3d\delta_g^2)$
C_2 (C5.0-$s2p2$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(2s\sigma_g^2 2s\sigma_u^2 2p\pi_u^4)$	V_2 (V7.5-$s4p4d4f2$)	$^3\Sigma_g^-$ [n]	$^3\Sigma_g^-$ $(4s\sigma_g^2 3d\sigma_g^2 3d\pi_u^4 3d\delta_g^2)$
N_2 (N5.0-$s2p2$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(2s\sigma_u^2 2p\pi_u^4 2p\sigma_g^2)$	Cr_2 (Cr7.0-$s2p2d2$)	$^1\Sigma_g^+$ [o]	$^1\Sigma_g^+$ $(4s\sigma_g^2 3d\sigma_g^2 3d\pi_u^4 3d\delta_g^4)$
O_2 (O5.0-$s2p2$)	$^3\Sigma_g^-$ [f]	$^3\Sigma_g^-$ $(2p\sigma_g^2 2p\pi_u^4 2p\pi_g^2)$	MnO (Mn7.0-$s2p2d2$)	$^6\Sigma^+$ [p]	$^6\Sigma^+$ $(d\sigma^1 d\pi^4 d\delta^2 d\pi^{*2})$
F_2 (F5.0-$s2p2$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(2p\sigma_g^2 2p\pi_u^4 2p\pi_g^4)$	Fe_2 (Fe7.0-$s2p2d2$)	$^7\Delta_u$ [q]	$^7\Delta_u$ $(4s\sigma_g^2 3d\sigma_g^2 3d\sigma_u^1 3d\pi_u^4 3d\pi_g^2 3d\delta_g^3 3d\delta_u^2)$
Ne_2 (Ne7.0-$s2p2$)	$^1\Sigma_g^+$ [g]	$^1\Sigma_g^+$ $(2p\pi_u^4 2p\pi_g^4 2p\sigma_u^2)$	Co_2 (Co7.0-$s2p2d2$)		$^5\Delta_g$ $(4s\sigma_g^2 3d\sigma_g^2 3d\sigma_u^1 3d\pi_u^4 3d\pi_g^2 3d\delta_g^4 3d\delta_u^3)$
Na_2 (Na9.0-$s2p2$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(2p\pi_g^4 2p\sigma_u^2 3s\sigma_g^2)$	Ni_2 (Ni7.0-$s2p2d2$)	Ω [r]	$^3\Sigma_g^-$ $(4s\sigma_g^2 3d\sigma_g^2 3d\sigma_u^2 3d\pi_u^4 3d\pi_g^2 3d\delta_g^4 3d\delta_u^4)$
MgO (Mg7.0-$s2p2$)	$^1\Sigma^+$ [h]	$^1\Sigma^+$ $(s\sigma^2 s\sigma^2 p\pi^4)$	Cu_2 (Cu7.0-$s2p2d2$)	$^1\Sigma_g^+$ [s]	$^1\Sigma_g^+$ $(4s\sigma_g^2 3d\sigma_g^2 3d\sigma_u^2 3d\pi_u^4 3d\pi_g^4 3d\delta_g^4 3d\delta_u^4)$
Al_2 (Al6.5-$s2p2$)	$^3\Pi_u$ [i]	$^3\Sigma_g^-$ $(3s\sigma_g^2 3s\sigma_u^2 3p\pi_u^2)$	ZnH (Zn7.0-$s2p2d2$)	$^2\Sigma_g^+$ [t]	$^2\Sigma_g^+$ $(s\sigma^2 s\sigma^{*1} d\sigma^2 d\pi^4 d\delta^4)$
Al_2 (Al6.5-$s4p4d2$)	$^3\Pi_u$ [i]	$^3\Sigma_g^-$ $(3s\sigma_g^2 3s\sigma_u^2 3p\pi_u^2)$	GaH (Ga7.0-$s2p2$)	$^1\Sigma^+$ [u]	$^1\Sigma^+$ $(s\sigma^2 s\sigma^{*2})$
Si_2 (Si6.5-$s2p2$)	$^3\Sigma_g^-$ [f]	$^3\Pi_u$ $(3s\sigma_u^2 3s\sigma_g^1 3p\pi_u^3)$	GeO (Ge7.0-$s2p2$)	$^1\Sigma^+$ [f]	$^1\Sigma^+$ $(ss\sigma^2 sp\sigma^2 pp\pi^4 pp\sigma^2)$
Si_2 (Si6.5-$s2p2d1$)	$^3\Sigma_g^-$ [f]	$^3\Sigma_g^-$ $(3s\sigma_u^2 3p\pi_u^2 3s\sigma_g^2)$	As_2 (As7.0-$s2p2d1$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(4s\sigma_g^2 4s\sigma_u^2 4p\sigma_g^2 4p\pi_u^4)$
P_2 (P6.0-$s2p2d1$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(3s\sigma_u^2 3p\sigma_g^2 3p\pi_u^4)$	Se_2 (Se7.0-$s2p2d1$)	$^3\Sigma_g^-$ [f]	$^3\Sigma_g^-$ $(4s\sigma_g^2 4s\sigma_u^2 4p\sigma_g^2 4p\pi_u^4 4p\pi_g^2)$
S_2 (S6.0-$s2p2$)	$^3\Sigma_g^-$ [f]	$^3\Sigma_g^-$ $(3p\sigma_g^2 3p\pi_u^4 3p\pi_g^2)$	Br_2 (Br7.0-$s2p2d1$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(4s\sigma_g^2 4s\sigma_u^2 4p\sigma_g^2 4p\pi_u^4 4p\pi_g^4)$
Cl_2 (Cl6.0-$s2p2d2$)	$^1\Sigma_g^+$ [f]	$^1\Sigma_g^+$ $(3p\sigma_g^2 3p\pi_u^4 3p\pi_g^4)$	Kr_2 (Kr7.0-$s2p2$)	$^1\Sigma_g^+$ [v]	$^1\Sigma_g^+$ $(4s\sigma_g^2 4s\sigma_u^2 4p\sigma_g^2 4p\sigma_u^2 4p\pi_u^4 4p\pi_g^4)$
Ar_2 (Ar7.0-$s2p2$)	$^1\Sigma_g^+$ [j]	$^1\Sigma_g^+$ $(3p\pi_u^4 3p\pi_g^4 3p\sigma_u^2)$			

All the successes and failures by the LDA are reproduced by the modest size of basis functions (DNP in most cases)

Variational optimization of basis functions

One-particle wave functions

$$\psi_\mu(\mathbf{r}) = \sum_{i\alpha} c_{\mu,i\alpha}\phi_{i\alpha}(\mathbf{r}-\mathbf{r}_i)$$

Contracted orbitals

$$\phi_{i\alpha}(\mathbf{r}) = \sum_{q} a_{i\alpha q}\chi_{i\eta}(\mathbf{r})$$

The variation of E with respect to *c* with fixed *a* gives

$$\partial E_{\text{tot}}/\partial c_{\mu,i\alpha} = 0 \quad \rightarrow \quad \sum_{j\beta} \langle \phi_{i\alpha}|\hat{H}|\phi_{j\beta}\rangle c_{\mu,j\beta} = \varepsilon_\mu \sum_{j\beta} \langle \phi_{i\alpha}|\phi_{j\beta}\rangle c_{\mu,j\beta}$$

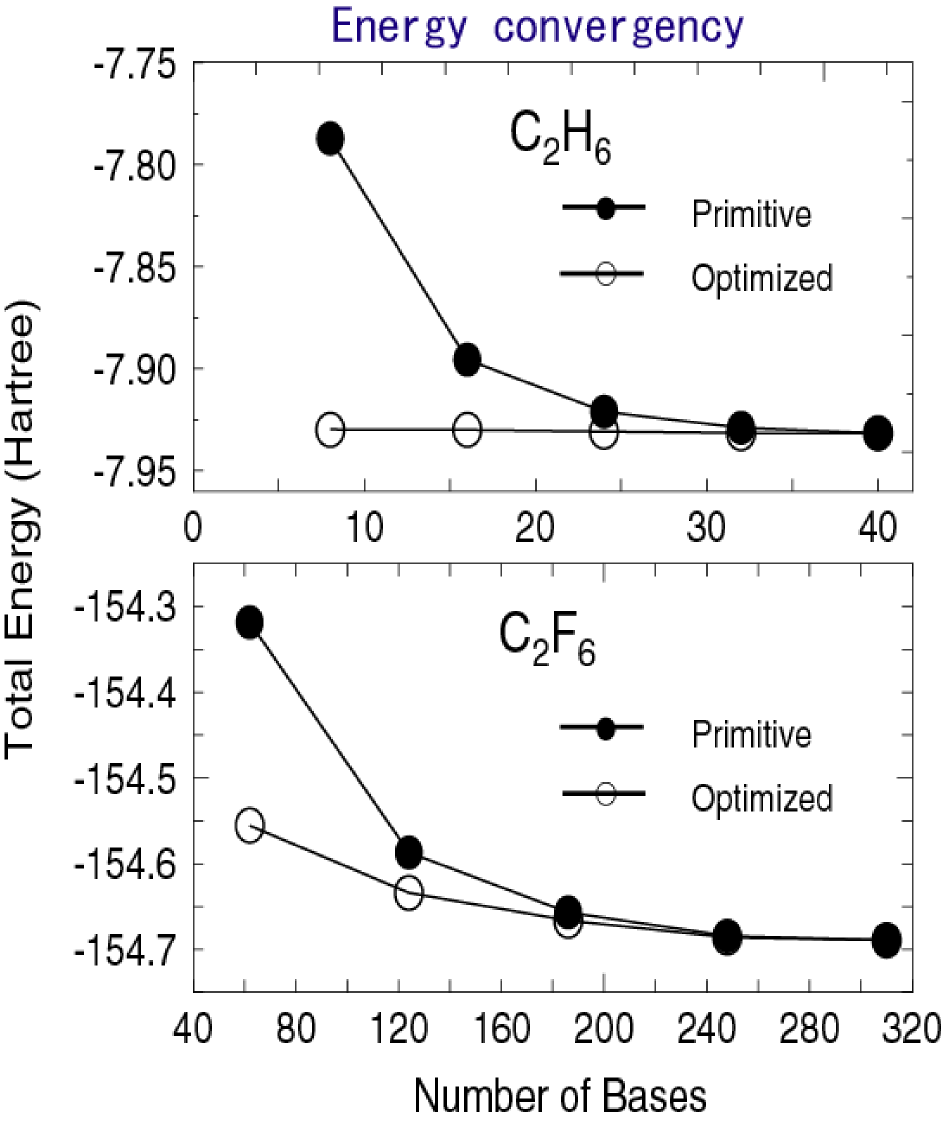
Regarding c as dependent variables on *a* and assuming KS eq. is solved self-consistently with respect to *c*, we have

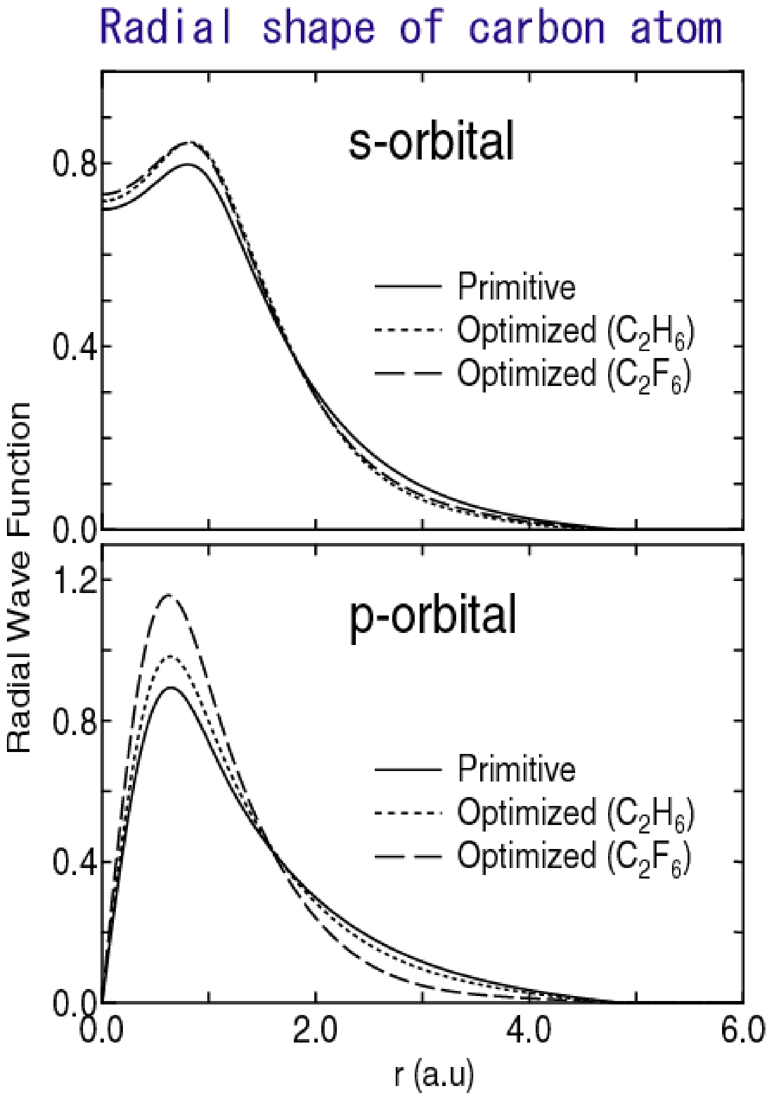
$$\frac{\partial E_{\text{tot}}}{\partial a_{i\alpha q}} = \frac{\delta E_{\text{tot}}}{\delta \rho(\mathbf{r})}\frac{\delta \rho(\mathbf{r})}{\delta a_{i\alpha q}}$$

$$= 2\sum_{j\beta} \left(\Theta_{i\alpha,j\beta}\langle \chi_{i\eta}|\hat{H}|\phi_{j\beta}\rangle - E_{i\alpha,j\beta}\langle \chi_{i\eta}|\phi_{j\beta}\rangle\right)$$

Ozaki, PRB 67, 155108 (2003)

Comparison between primitive and optimized basis functions

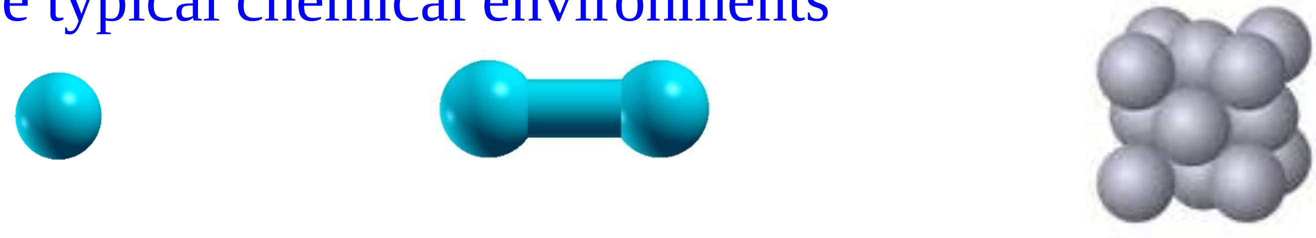

Energy convergency


Radial shape of carbon atom

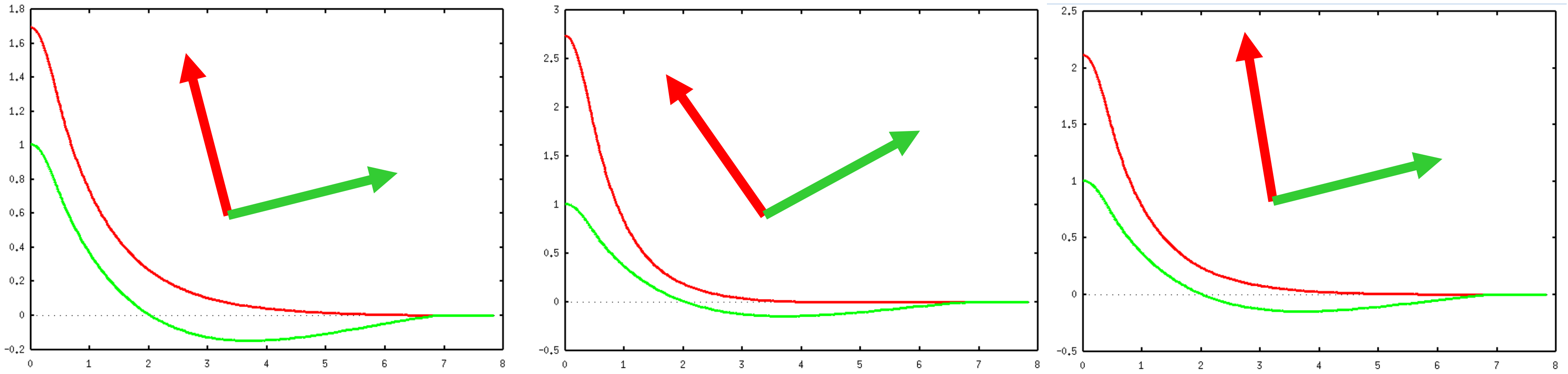
Ozaki, PRB 67, 155108 (2003).

Optimization of basis functions

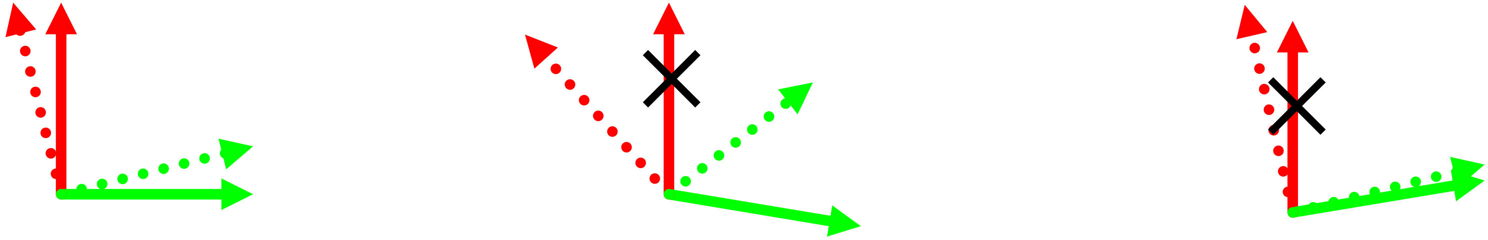
1. Choose typical chemical environments



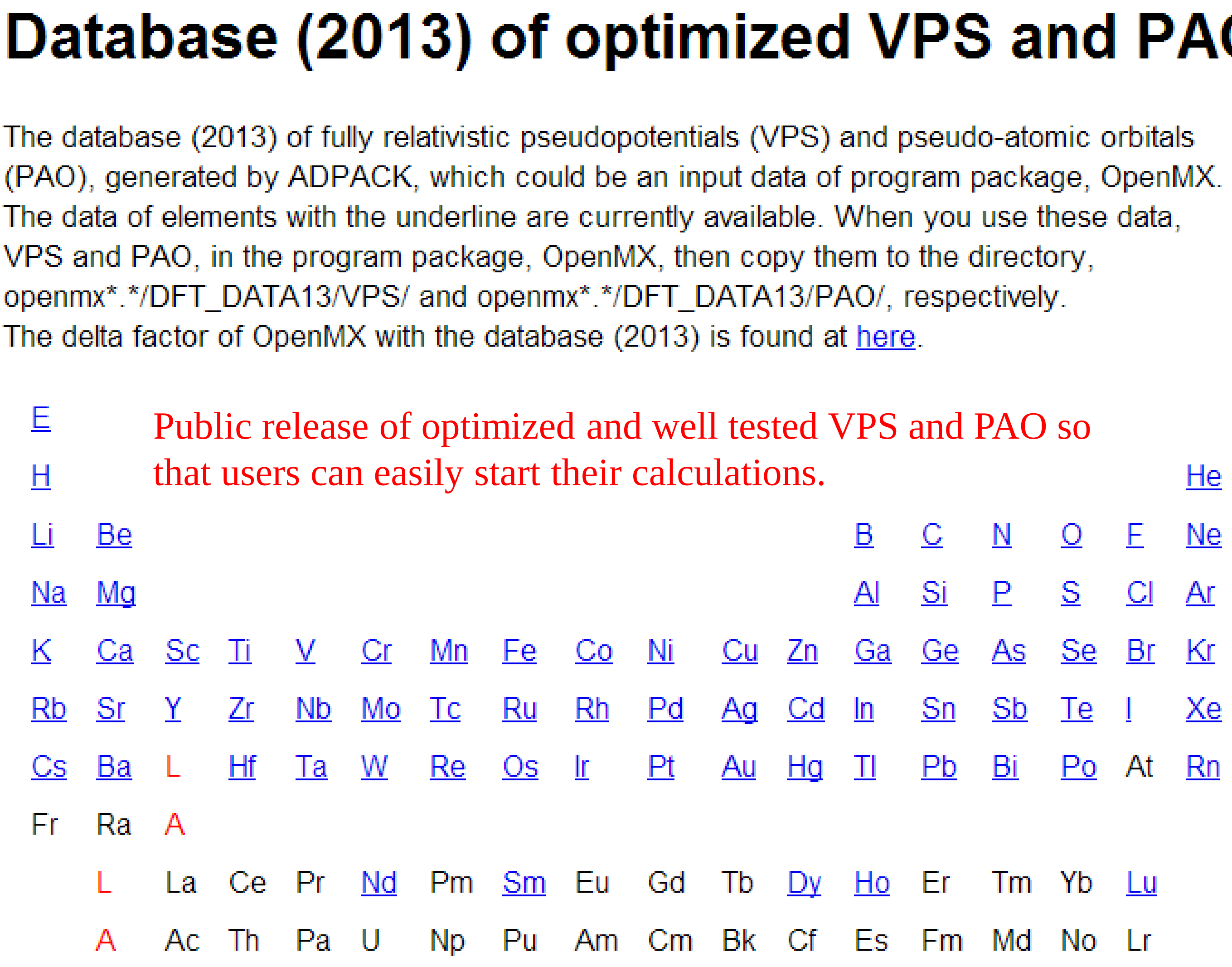
2. Optimize variationally the radial functions



3. Rotate a set of optimized orbitals within the subspace, and discard the redundant funtions



Database of optimized VPS and PAO



Database (2013) of optimized VPS and PAO

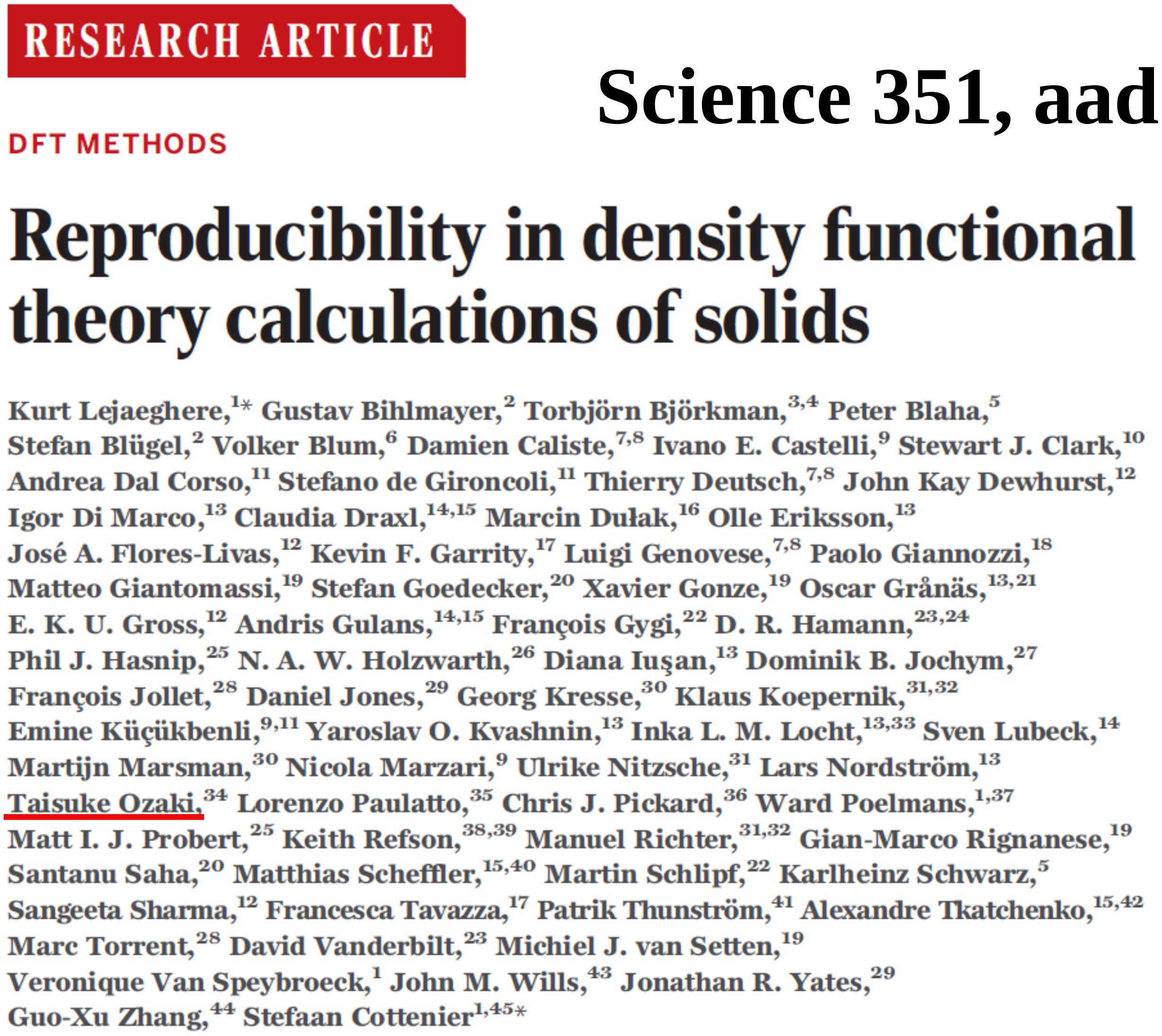
The database (2013) of fully relativistic pseudopotentials (VPS) and pseudo-atomic orbitals (PAO), generated by ADPACK, which could be an input data of program package, OpenMX. The data of elements with the underline are currently available. When you use these data, VPS and PAO, in the program package, OpenMX, then copy them to the directory, openmx*.*/DFT_DATA13/VPS/ and openmx*.*/DFT_DATA13/PAO/, respectively.
The delta factor of OpenMX with the database (2013) is found at here.

E																	
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															
	L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Public release of optimized and well tested VPS and PAO so that users can easily start their calculations.

Reproducibility in DFT calcs

Science 351, aad3000 (2016)



RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

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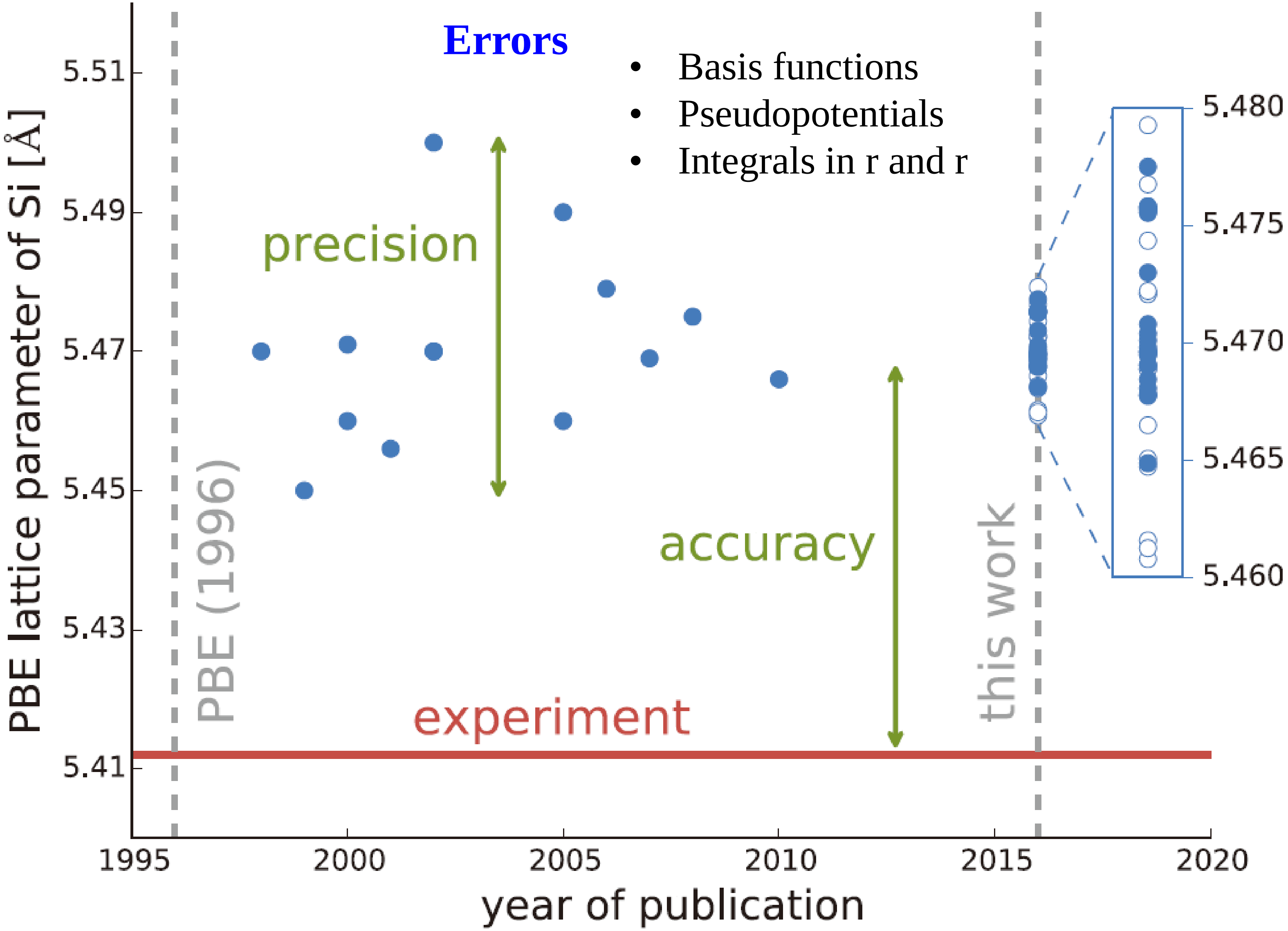
15 codes
69 researchers
71 elemental bulks
GGA-PBE
Scalar relativistic

PBE lattice constant of Si

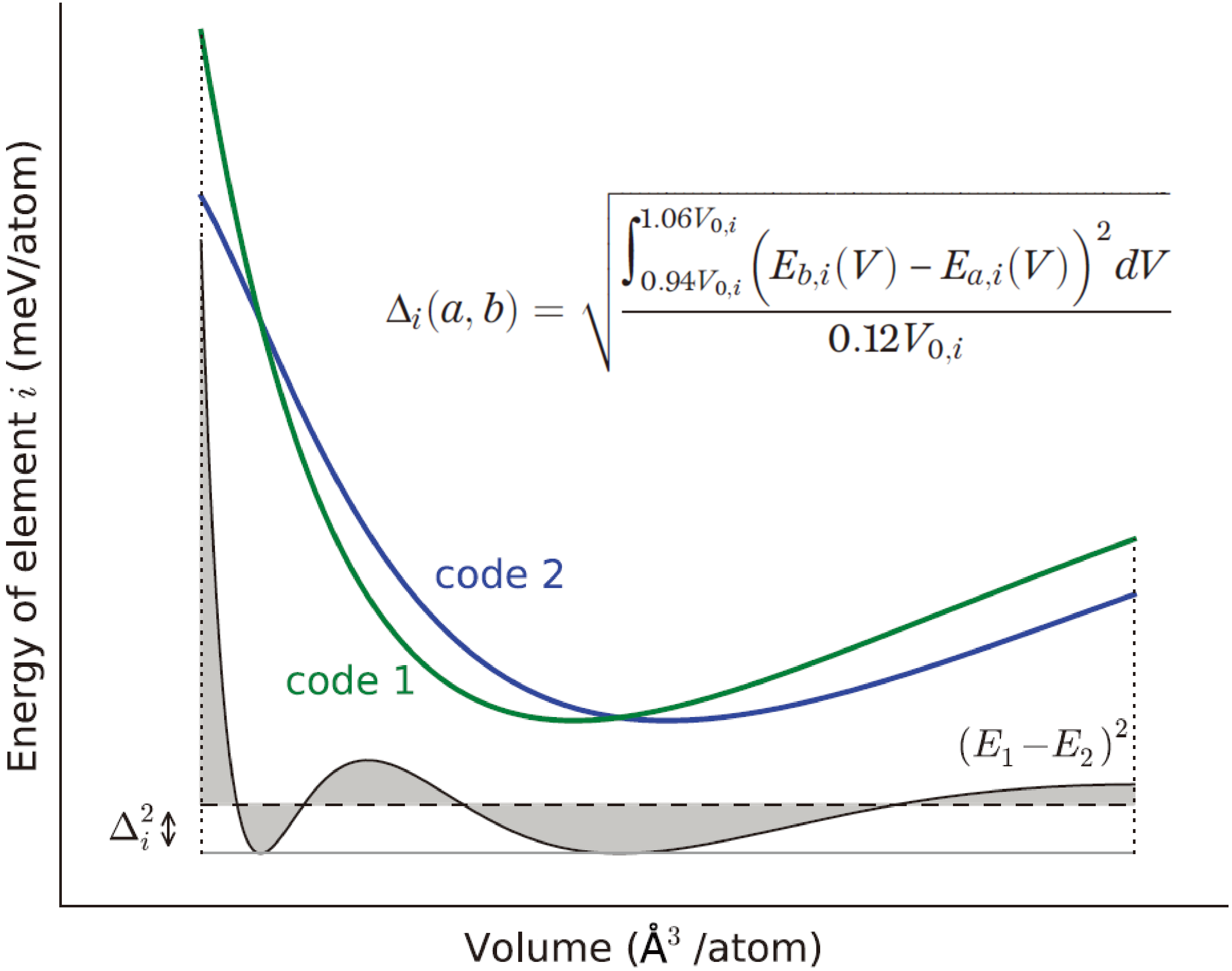
Errors

- Basis functions
- Pseudopotentials
- Integrals in r and r



Δ-gauge

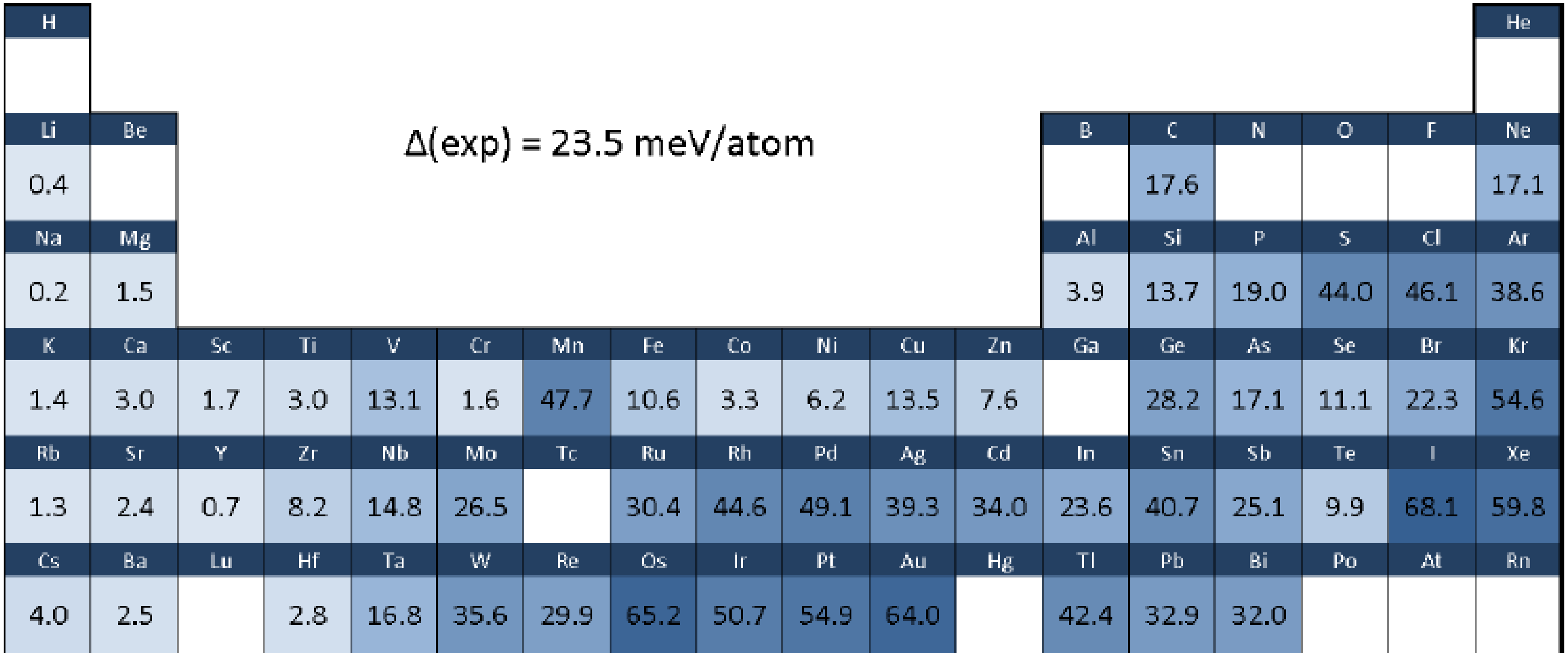
A way of comparing accuracy of codes



$$\Delta_i(a,b) = \sqrt{\frac{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \left(E_{b,i}(V) - E_{a,i}(V)\right)^2 dV}{0.12V_{0,i}}}$$

Evaluation of GGA-PBE By Δ-gauge

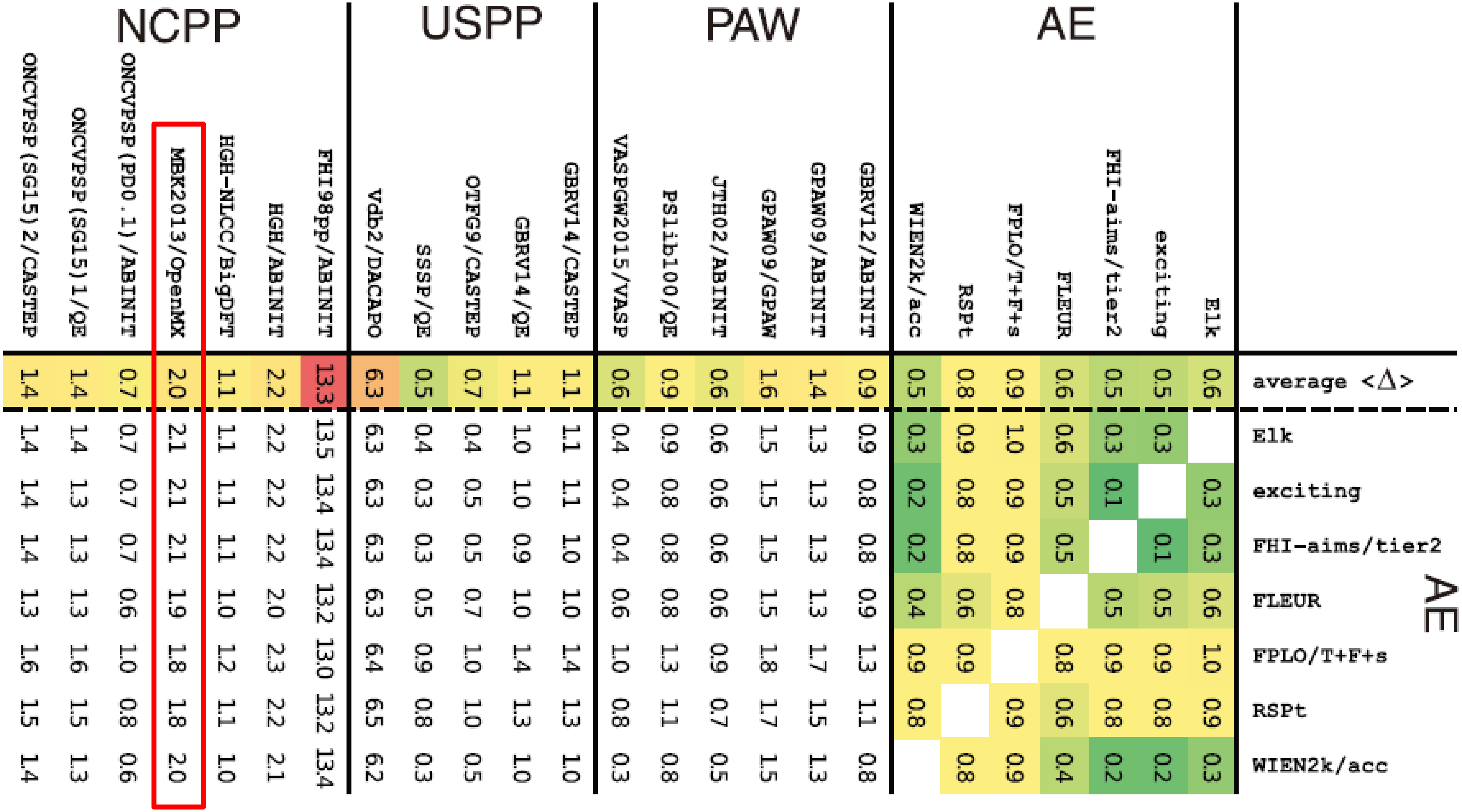
In comparison of GGA-PBE with Expts. of 58 elements, the mean Δ-gauge is 23.5meV/atom.



Δ(exp) = 23.5 meV/atom

H																	He
Li	Be											B	C	N	O	F	Ne
0.4													17.6				17.1
Na	Mg											Al	Si	P	S	Cl	Ar
0.2	1.5											3.9	13.7	19.0	44.0	46.1	38.6
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
1.4	3.0	1.7	3.0	13.1	1.6	47.7	10.6	3.3	6.2	13.5	7.6		28.2	17.1	11.1	22.3	54.6
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
1.3	2.4	0.7	8.2	14.8	26.5		30.4	44.6	49.1	39.3	34.0	23.6	40.7	25.1	9.9	68.1	59.8
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
4.0	2.5		2.8	16.8	35.6	29.9	65.2	50.7	54.9	64.0		42.4	32.9	32.0			

Comparison of codes by Δ-gauge



NCPP							USPP					PAW						AE								
ONCVPSP(SG15)2/CASTEP	ONCVPSP(SG15)1/QE	ONCVPSP(PD0.1)/ABINIT	MBK2013/OpenMX	HGH-NLCC/BigDFT	HGH/ABINIT	FHI98pp/ABINIT	Vdb2/DACAPO	SSSP/QE	OTFG9/CASTEP	GBRV14/QE	GBRV14/CASTEP	VASPGW2015/VASP	PSlib100/QE	JTH02/ABINIT	GPAW09/GPAW	GPAW09/ABINIT	GBRV12/ABINIT	WIEN2k/acc	RSPt	FPLO/T+F+s	FLEUR	FHI-aims/tier2	exciting	Elk		
1.4	1.4	0.7	2.0	1.1	2.2	13.3	6.3	0.5	0.7	1.1	1.1	0.6	0.9	0.6	1.6	1.4	0.9	0.5	0.8	0.9	0.6	0.5	0.5	0.6	average <Δ>	
1.4	1.4	0.7	2.1	1.1	2.2	13.5	6.3	0.4	0.4	1.0	1.1	0.4	0.9	0.6	1.5	1.3	0.9	0.3	0.9	1.0	0.6	0.3	0.3		Elk	AE
1.4	1.3	0.7	2.1	1.1	2.2	13.4	6.3	0.3	0.5	1.0	1.1	0.4	0.8	0.6	1.5	1.3	0.8	0.2	0.8	0.9	0.5	0.1		0.3	exciting	
1.4	1.3	0.7	2.1	1.1	2.2	13.4	6.3	0.3	0.5	0.9	1.0	0.4	0.8	0.6	1.5	1.3	0.8	0.2	0.8	0.9	0.5		0.1	0.3	FHI-aims/tier2	
1.3	1.3	0.6	1.9	1.0	2.0	13.2	6.3	0.5	0.7	1.0	1.0	0.6	0.8	0.6	1.5	1.3	0.9	0.4	0.6	0.8		0.5	0.5	0.6	FLEUR	
1.6	1.6	1.0	1.8	1.2	2.3	13.0	6.4	0.9	1.0	1.4	1.4	1.0	1.3	0.9	1.8	1.7	1.3	0.9	0.9		0.8	0.9	0.9	1.0	FPLO/T+F+s	
1.5	1.5	0.8	1.8	1.1	2.2	13.2	6.5	0.8	1.0	1.3	1.3	0.8	1.1	0.7	1.7	1.5	1.1	0.8		0.9	0.6	0.8	0.8	0.9	RSPt	
1.4	1.3	0.6	2.0	1.0	2.1	13.4	6.2	0.3	0.5	1.0	1.0	0.3	0.8	0.5	1.5	1.3	0.8		0.8	0.9	0.4	0.2	0.2	0.3	WIEN2k/acc	

The mean Δ-gauge of OpenMX is 2.0meV/atom.

Practical guide to OpenMX calculations

- Choice of cutoff energy
- Calculations of energy curves
- SCF calculations
- How to choose basis functions
- Work functions and floating states
- Overcompleteness
- Restarting
- Outputting in a binary mode

Choice of cutoff energy

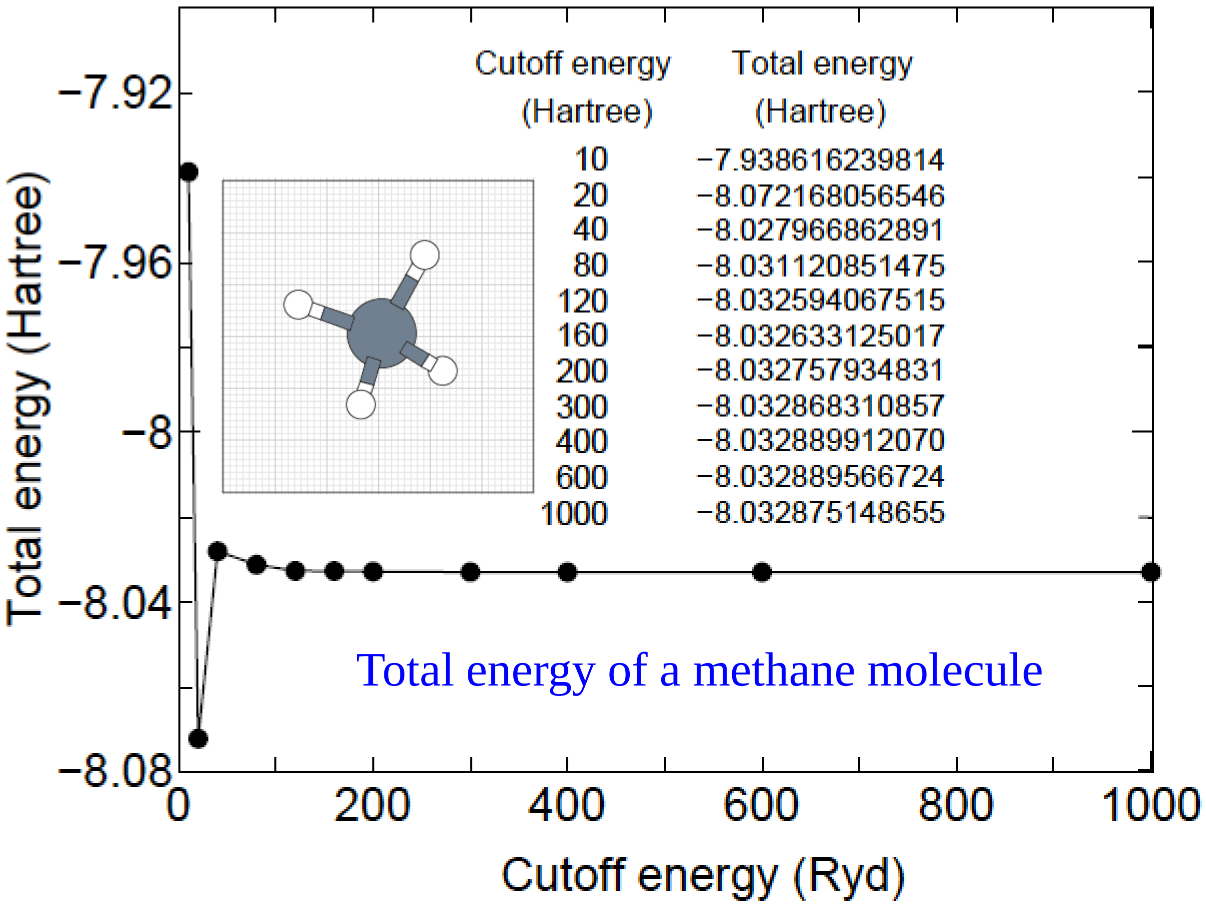
scf.energycutoff 200 # default=150 Ryd

The FFT grid is used to discretize real space and calculate $E_{\delta ee}$, E_{xc}, and can be specified by scf.energycutoff.

In most cases, 200 Ryd is enough to get convergence.

However, large cutoff energy (300-400 Ryd) has be used cases such as use of pseudopotentials with deep semi-core states.

Memory requiment
$O(E^{3/2})$



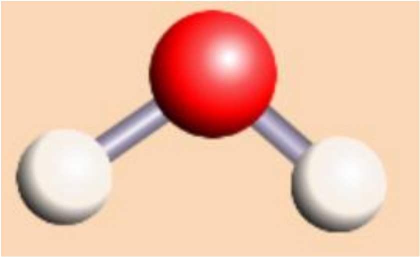
Cutoff energy (Hartree)	Total energy (Hartree)
10	−7.938616239814
20	−8.072168056546
40	−8.027966862891
80	−8.031120851475
120	−8.032594067515
160	−8.032633125017
200	−8.032757934831
300	−8.032868310857
400	−8.032889912070
600	−8.032889566724
1000	−8.032875148655

Total energy of a methane molecule

Choice of cutoff energy

Geometry optimization of H_2O

Dependency of optimized structure of H2O on scf.energycutoff. It turns out that 180Ryd. is enough to reach the convergence.



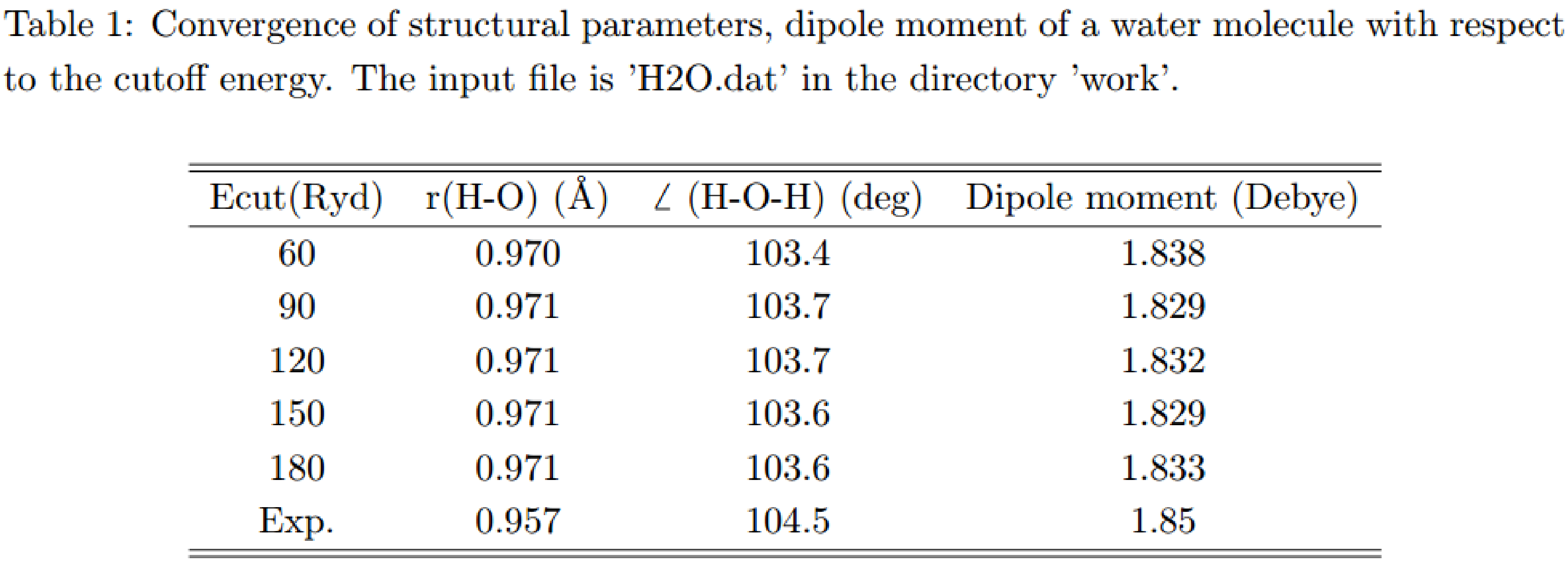


Table 1: Convergence of structural parameters, dipole moment of a water molecule with respect to the cutoff energy. The input file is ’H2O.dat’ in the directory ’work’.

Ecut(Ryd)	r(H-O) (Å)	$\angle$ (H-O-H) (deg)	Dipole moment (Debye)
60	0.970	103.4	1.838
90	0.971	103.7	1.829
120	0.971	103.7	1.832
150	0.971	103.6	1.829
180	0.971	103.6	1.833
Exp.	0.957	104.5	1.85

Volume vs. Energy curves

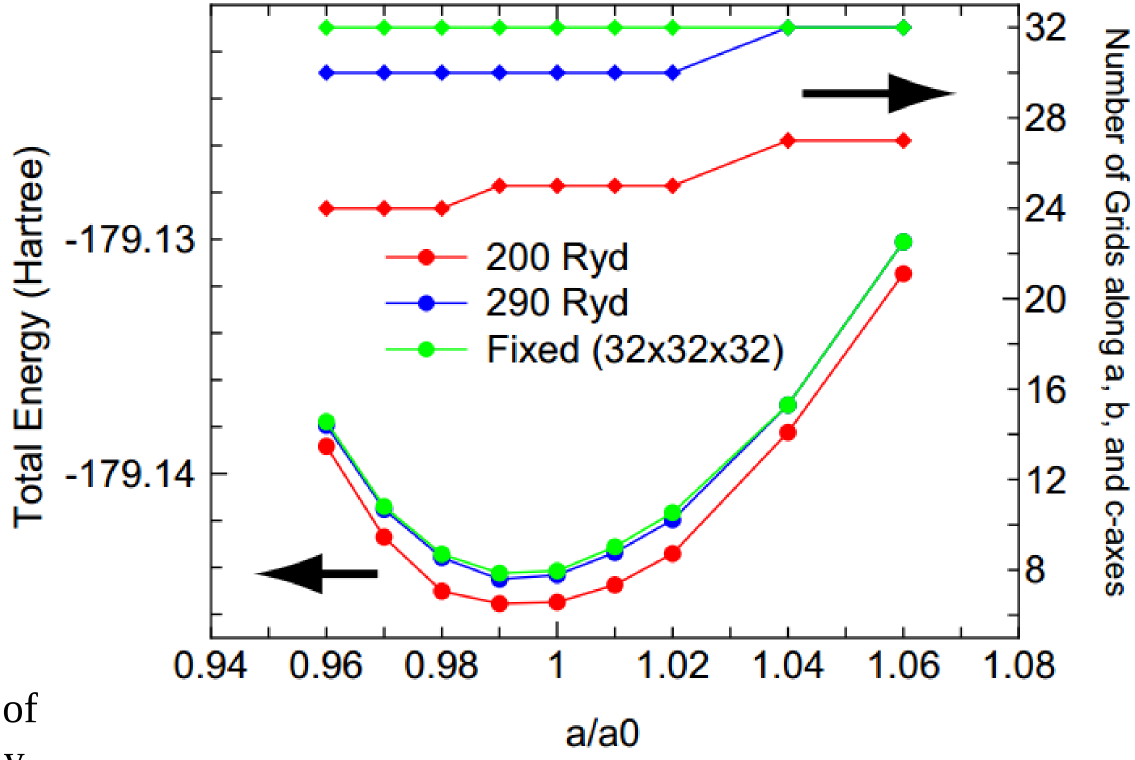
The following keywords are available to calculate energy curves.

```
MD.Type              EvsLC      #
MD.EvsLC.Step          0.4      # default=0.4%
MD.maxIter             32       # default=1
```

When the energy curve for bulk system is calculated as a function of the lattice parameter, a sudden change of the number of real space grids is a serious problem which produces an erratic discontinuity on the energy curve. To avoid this, the number of grids should be fixed by explicitly specifying the following keyword:

```
scf.Ngrid       32 32 32
```

The numbers correspond to the number of grid along a-, b-, and c-axes, respectively. scf.Ngrid is used if both the keywords scf.energycutoff and scf.Ngrid are specified.



```
MD.EvsLC.flag     1  1  0       # along a, b, c-axes
1: varied,  0: fixed
```

Self-consistency: Simple charge mixing

The KS effective is constructed from ρ.
However, ρ is evaluated from eigenfaunctions of KS eq.

$$\hat{H}_{\mathrm{KS}}\phi_i = \varepsilon_i\phi_i \qquad \hat{H}_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}$$

$$v_{\mathrm{eff}} = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{Hartree}}(\mathbf{r}) + \frac{\delta E_{\mathrm{xc}}}{\delta\rho(\mathbf{r})}$$

$$\rho(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r})\phi_i(\mathbf{r})$$

Simple charge mixing method

The next input density is constructed by a simple mixing of input and output densities.

$$\rho_{n+1}^{(\mathrm{in})} = \alpha\rho_n^{(\mathrm{in})} + (1-\alpha)\rho_n^{(\mathrm{out})},$$

It works well for large gap systems and small sized systems.

Self-consistency: RMM-DIIS

Idea:

Minimize the norm of a linear combination of previous residual vectors.

$$\bar{R}_{n+1} = \sum_{m=n-(p-1)}^{n} \alpha_m R_m,$$

$$F = \langle \bar{R}_{n+1} | \bar{R}_{n+1} \rangle - \lambda \left(1 - \sum_m^n a_m \right),$$

$$= \sum_{m,m'} \alpha_m \alpha_{m'} \langle R_m | R_{m'} \rangle - \lambda \left(1 - \sum_m^n a_m \right).$$

$$R_n(\mathbf{q}) \equiv \tilde{n}_n^{(\mathrm{out})}(\mathbf{q}) - \tilde{n}_n^{(\mathrm{in})}(\mathbf{q}),$$

$$\langle R_m | R_{m'} \rangle \equiv \sum_{\mathbf{q}} \frac{R_m^*(\mathbf{q}) R_{m'}(\mathbf{q})}{w(\mathbf{q})},$$

Kerker factor

$$\boxed{w(\mathbf{q}) = \frac{|\mathbf{q}|^2}{|\mathbf{q}|^2 + q_0^2},}$$

Long wave length components corresponding to small |q| are taken into account.

Minimization of F leads to

$$\frac{\partial F}{\partial \alpha_k} = 0$$

$$\frac{\partial F}{\partial \lambda} = 0$$

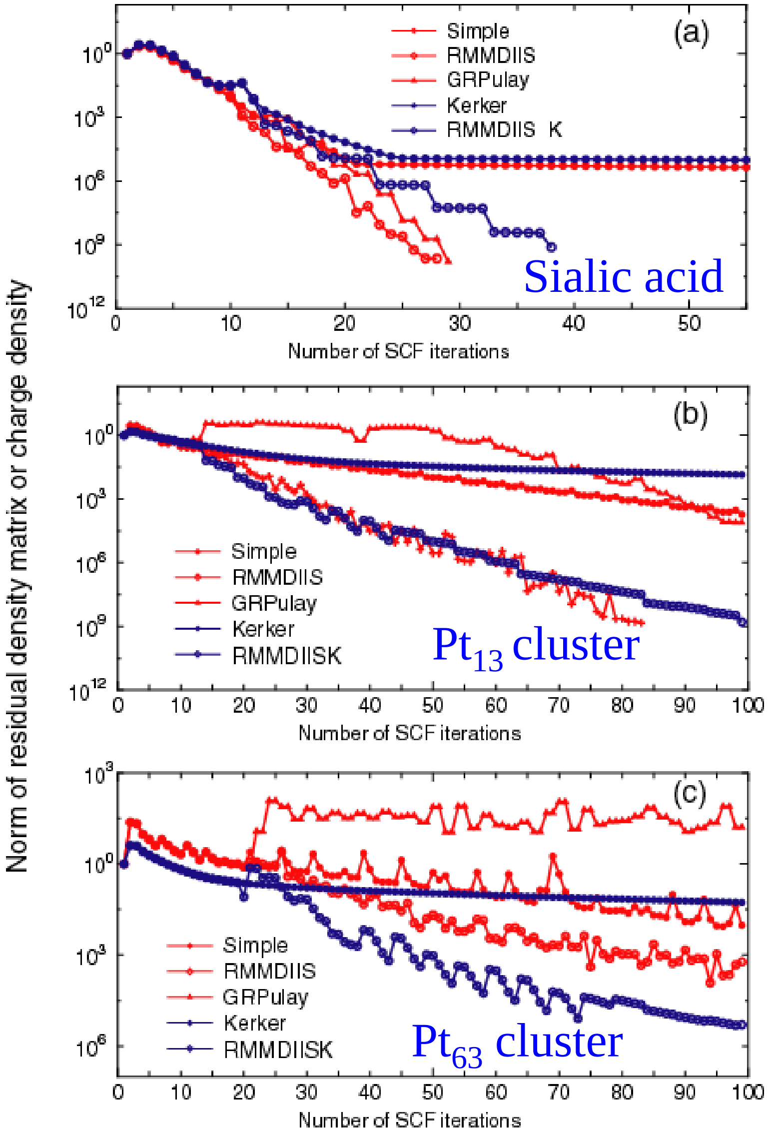
$$\begin{pmatrix} \langle R_{n-(p-1)} | R_{n-(p-1)} \rangle & \cdots & \cdots & 1 \\ \cdots & \cdots & \cdots & 1 \\ \cdots & \cdots & \langle R_n | R_n \rangle & \cdots \\ 1 & 1 & \cdots & 0 \end{pmatrix} \begin{pmatrix} \alpha_{n-(p-1)} \\ \alpha_{n-(p-1)+1} \\ \cdot \\ \frac{1}{2}\lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \cdot \\ 1 \end{pmatrix}.$$

Optimum input density might be given by

$$\boxed{\rho_{n+1}^{(\mathrm{in})} = \sum_{m=n-(p-1)}^{n} \alpha_m \rho_m^{(\mathrm{in})} + \beta \sum_{m=n-(p-1)}^{n} \alpha_m R_m}$$

G.Kresse and J. Furthmeuller,
PRB 54, 11169 (1996).

Mixing methods



Available mixing methods:

Simple mixing (Simple)

Residual minimization method in the direct inversion iterative subspace (RMM-DIIS)

Guaranteed reduction Pulay method (GR-Pulay)

Kerker mixing (Kerker)

RMM-DIIS with Kerker metric (RMM-DIISK)

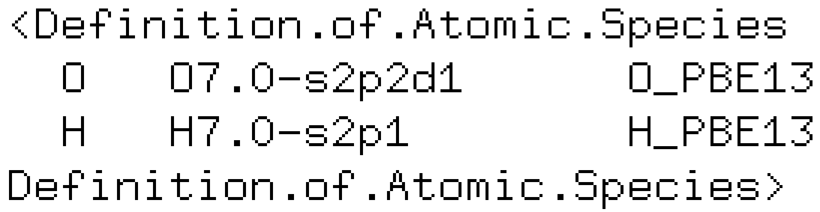
RMM-DIIS for Hamiltonian (RMM-DIISH)

Recommendation:
RMM-DIISK or RMM-DIISH

See also the page 56 in the manual.

Specification of PAO and VPS

PAO and VPS are specified by the following keyword:



```
<Definition.of.Atomic.Species
  O   O7.0-s2p2d1      O_PBE13
  H   H7.0-s2p1        H_PBE13
Definition.of.Atomic.Species>
```

- O7.0 means O7.0.pao.
- -s2p2d1 means 2, 2, and 1 radial functions are allocated to s-, p-, and d-orbitals.
- In this case, for oxygen atom, 2×1+2×3+1×5=13 basis functions are allocated.
- O_PBE13 meand O_PBE13.vps.

The path for O7.0.pao and O_PBE13.vps is specified by

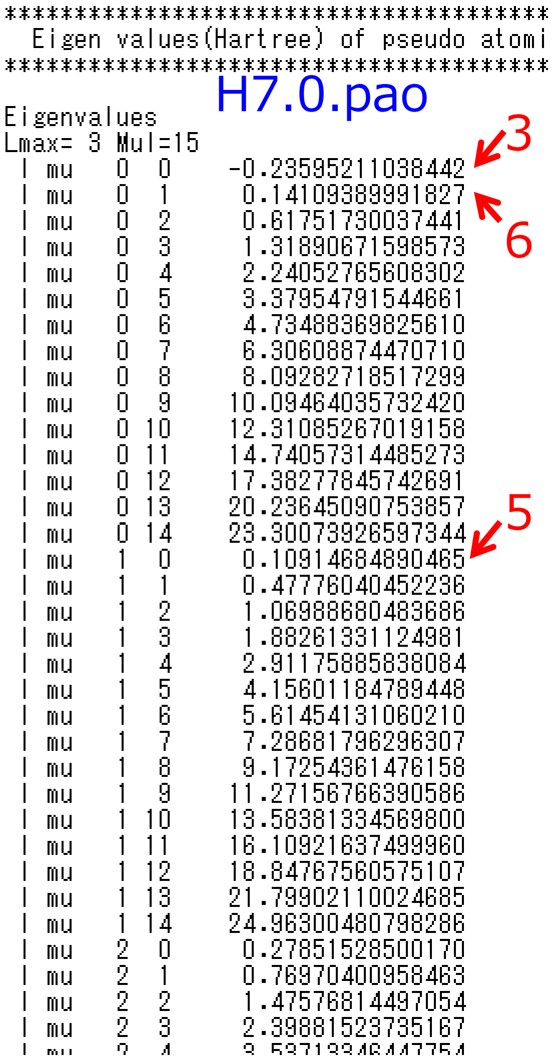
DATA.PATH   /home/soft/openmx3.8/DFT_DATA13

Default value is '../DFT_DATA13'.

How to choose basis functions: H_2O case

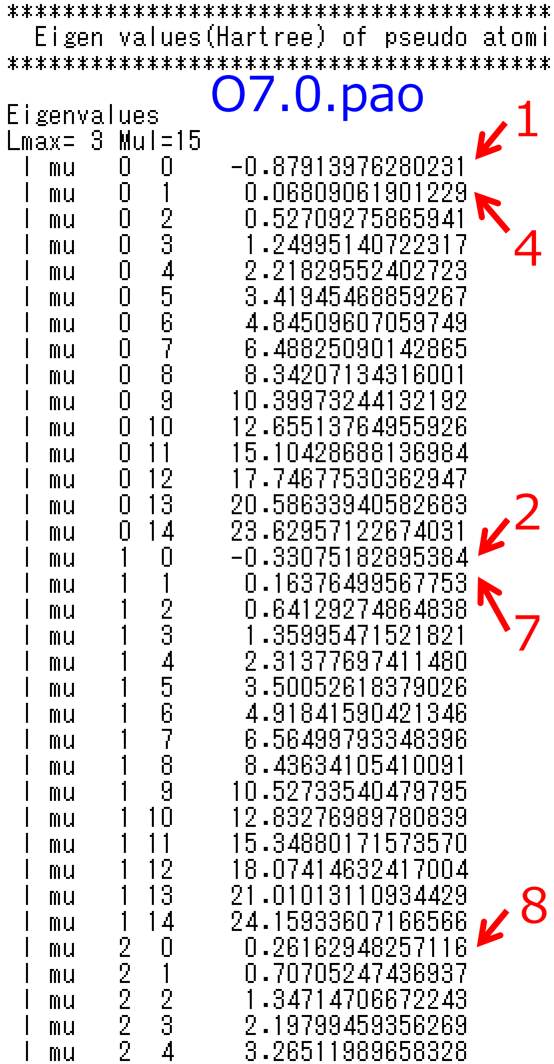
By clicking H7.0.pao and O7.0.pao in the database(2013), you may find the following

http://www.jaist.ac.jp/~t-ozaki/vps_pao2013/H/index.html   http://www.jaist.ac.jp/~t-ozaki/vps_pao2013/O/index.html



```
***************************************************
  Eigen values(Hartree) of pseudo atomic orbitals
***************************************************

Eigenvalues
Lmax= 3 Mul=15
  | mu   0  0    -0.23595211038442
  | mu   0  1     0.14109389991827
  | mu   0  2     0.61751730037441
  | mu   0  3     1.31890671598573
  | mu   0  4     2.24052765608302
  | mu   0  5     3.37954791544661
  | mu   0  6     4.73488369825610
  | mu   0  7     6.30608874470710
  | mu   0  8     8.09282718517299
  | mu   0  9    10.09464035732420
  | mu   0 10    12.31085267019158
  | mu   0 11    14.74057314485273
  | mu   0 12    17.38277845742691
  | mu   0 13    20.23645090753857
  | mu   0 14    23.30073926597344
  | mu   1  0     0.10914684890465
  | mu   1  1     0.47776040452236
  | mu   1  2     1.06988680483686
  | mu   1  3     1.88261331124981
  | mu   1  4     2.91175885838084
  | mu   1  5     4.15601184789448
  | mu   1  6     5.61454131060210
  | mu   1  7     7.28681796296307
  | mu   1  8     9.17254361476158
  | mu   1  9    11.27156766390586
  | mu   1 10    13.58381334569800
  | mu   1 11    16.10921637499960
  | mu   1 12    18.84767560575107
  | mu   1 13    21.79902110024685
  | mu   1 14    24.96300480798286
  | mu   2  0     0.27851528500170
  | mu   2  1     0.76970400958463
  | mu   2  2     1.47576814497054
  | mu   2  3     2.39881523735167
  | mu   2  4     3.53719346447754
```



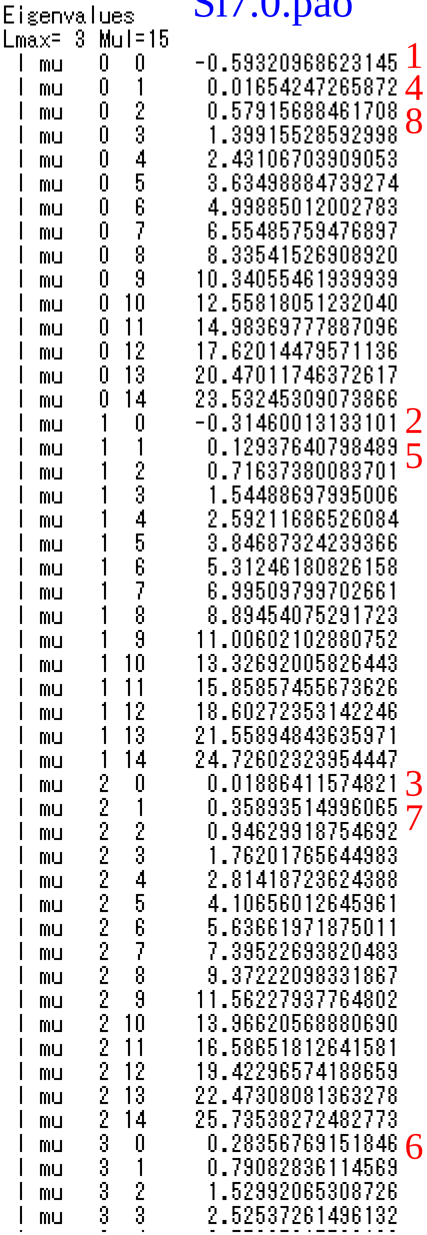
```
***************************************************
  Eigen values(Hartree) of pseudo atomic orbitals
***************************************************

Eigenvalues
Lmax= 3 Mul=15
  | mu   0  0    -0.87913976280231
  | mu   0  1     0.06809061901229
  | mu   0  2     0.52709275865941
  | mu   0  3     1.24995140722317
  | mu   0  4     2.21829552402723
  | mu   0  5     3.41945468859267
  | mu   0  6     4.84509607059749
  | mu   0  7     6.48825090142865
  | mu   0  8     8.34207134316001
  | mu   0  9    10.39973244132192
  | mu   0 10    12.65513764955926
  | mu   0 11    15.10428688136984
  | mu   0 12    17.74677530362947
  | mu   0 13    20.58633940582683
  | mu   0 14    23.62957122674031
  | mu   1  0    -0.33075182895384
  | mu   1  1     0.16376499567753
  | mu   1  2     0.64129274864838
  | mu   1  3     1.35995471521821
  | mu   1  4     2.31377697411480
  | mu   1  5     3.50052618379026
  | mu   1  6     4.91841590421346
  | mu   1  7     6.56499793348396
  | mu   1  8     8.43634105410091
  | mu   1  9    10.52733540479795
  | mu   1 10    12.83276989780839
  | mu   1 11    15.34880171573570
  | mu   1 12    18.07414632417004
  | mu   1 13    21.01013110934429
  | mu   1 14    24.15933607166566
  | mu   2  0     0.26162948257116
  | mu   2  1     0.70705247436937
  | mu   2  2     1.34714706672243
  | mu   2  3     2.19799459356269
  | mu   2  4     3.26511989658328
```

Choosing states with lower eigenvalues leads to H7.0-s2p1 and O7.0-s2p2d1.

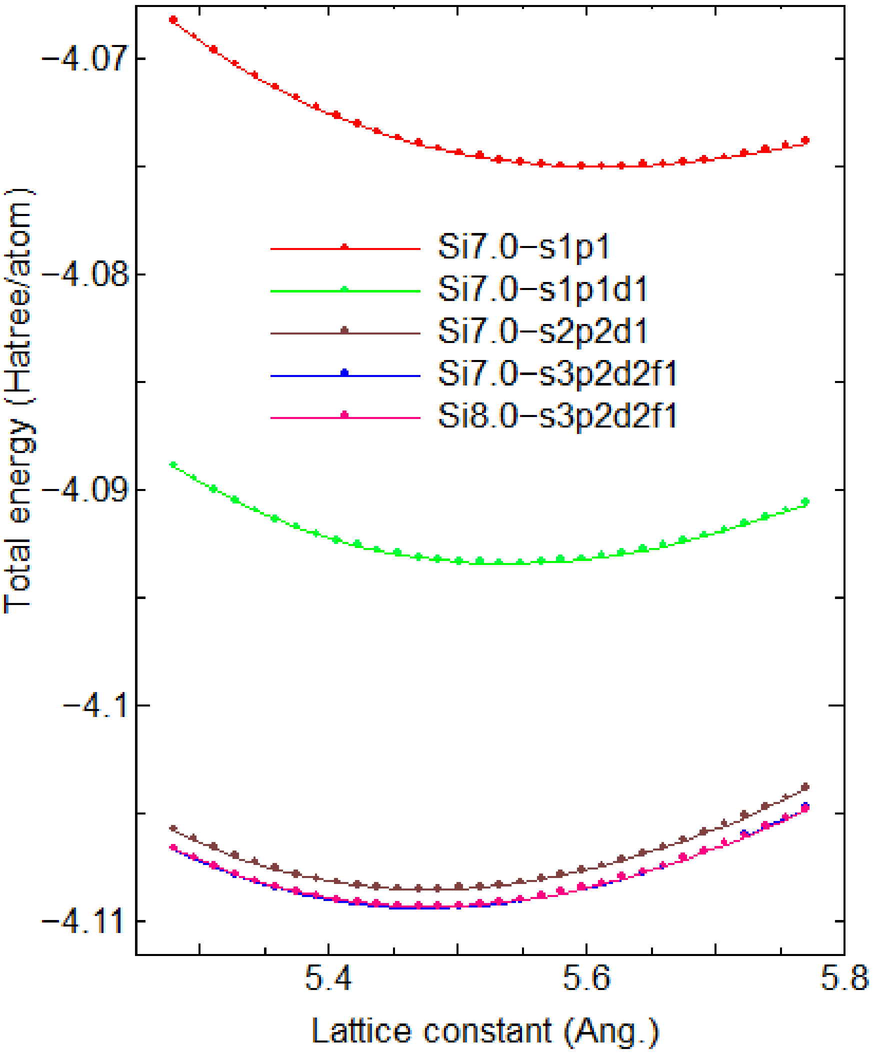
How to choose basis functions: Si case(1)

Si7.0.pao



```
Eigenvalues
Lmax= 3 Mul=15
 | mu    0  0      -0.59320968623145 1
 | mu    0  1       0.01654247265872 4
 | mu    0  2       0.57915688461708 8
 | mu    0  3       1.39915528592998
 | mu    0  4       2.43106703909053
 | mu    0  5       3.63498884739274
 | mu    0  6       4.99885012002783
 | mu    0  7       6.55485759476897
 | mu    0  8       8.33541526908920
 | mu    0  9      10.34055461939939
 | mu    0 10      12.55818051232040
 | mu    0 11      14.98369777887096
 | mu    0 12      17.62014479571136
 | mu    0 13      20.47011746372617
 | mu    0 14      23.53245309073866
 | mu    1  0      -0.31460013133101 2
 | mu    1  1       0.12937640798489 5
 | mu    1  2       0.71637380083701
 | mu    1  3       1.54488697995006
 | mu    1  4       2.59211686526084
 | mu    1  5       3.84687324239366
 | mu    1  6       5.31246180826158
 | mu    1  7       6.99509799702661
 | mu    1  8       8.89454075291723
 | mu    1  9      11.00602102880752
 | mu    1 10      13.32692005826443
 | mu    1 11      15.85857455673626
 | mu    1 12      18.60272353142246
 | mu    1 13      21.55894843635971
 | mu    1 14      24.72602323954447
 | mu    2  0       0.01886411574821 3
 | mu    2  1       0.35893514996065 7
 | mu    2  2       0.94629918754692
 | mu    2  3       1.76201765644983
 | mu    2  4       2.81418723624388
 | mu    2  5       4.10656012645961
 | mu    2  6       5.63661971875011
 | mu    2  7       7.39522693820483
 | mu    2  8       9.37222098331867
 | mu    2  9      11.56227937764802
 | mu    2 10      13.96620568880690
 | mu    2 11      16.58651812641581
 | mu    2 12      19.42296574188659
 | mu    2 13      22.47308081363278
 | mu    2 14      25.73538272482773
 | mu    3  0       0.28356769151846 6
 | mu    3  1       0.79082836114569
 | mu    3  2       1.52992065308726
 | mu    3  3       2.52537261496132
```

Orbitals with lower eigenvalues in Si7.0.pao are taken into account step by step as the quality of basis set is improved.

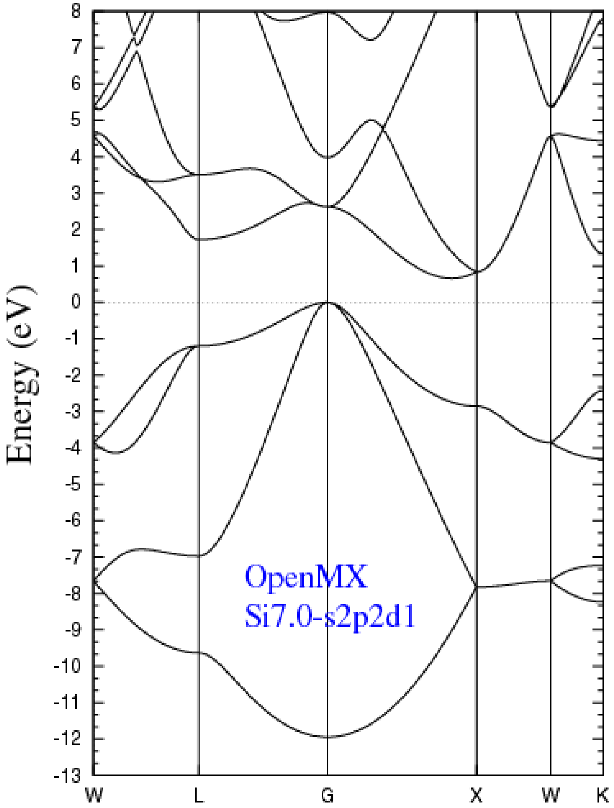


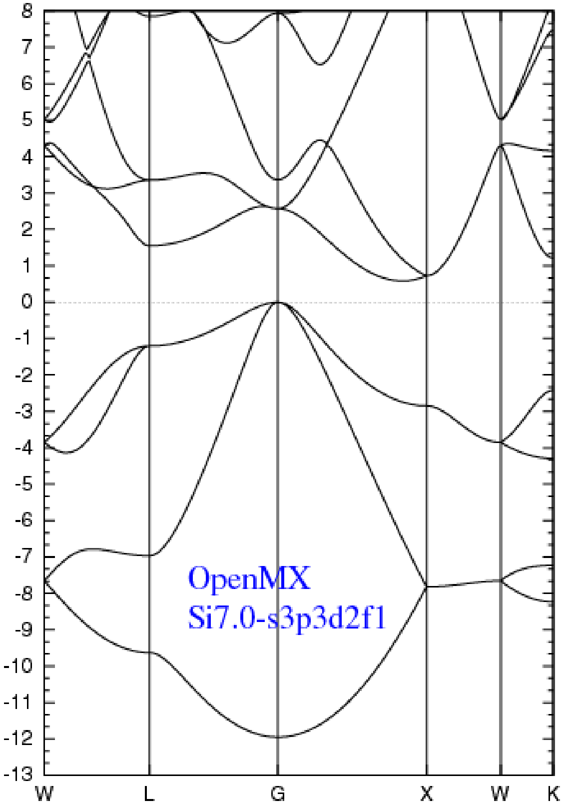
Si7.0-s2p2d1 is enough to discuss structural properties.

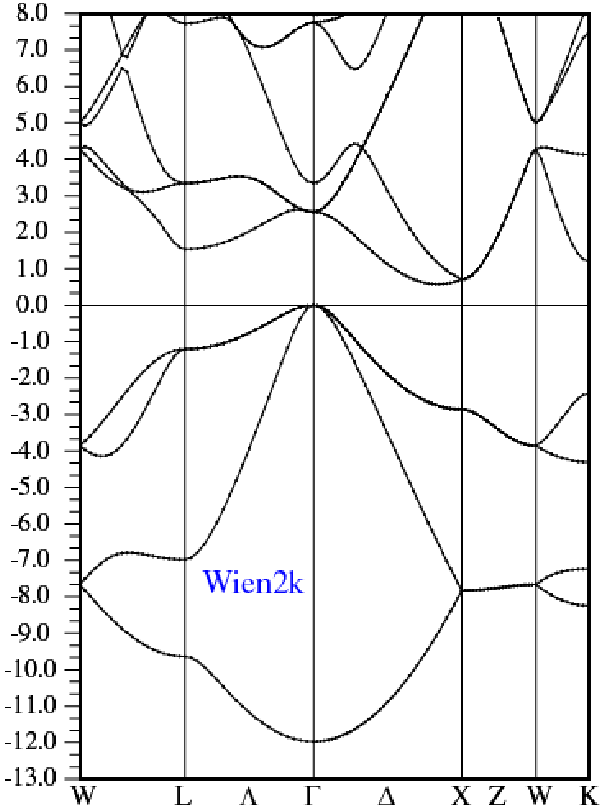
By comparing Si7.0-s3p2d2f1 with Si8.0-s3p2d2f1, it turns out that convergence is achieved at the cutoff of 7.0(a.u.).

How to choose basis functions: Si case(2)

With respect to band structure, one can confirm that Si7.0-s2p2d1 provides a nearly convent result.

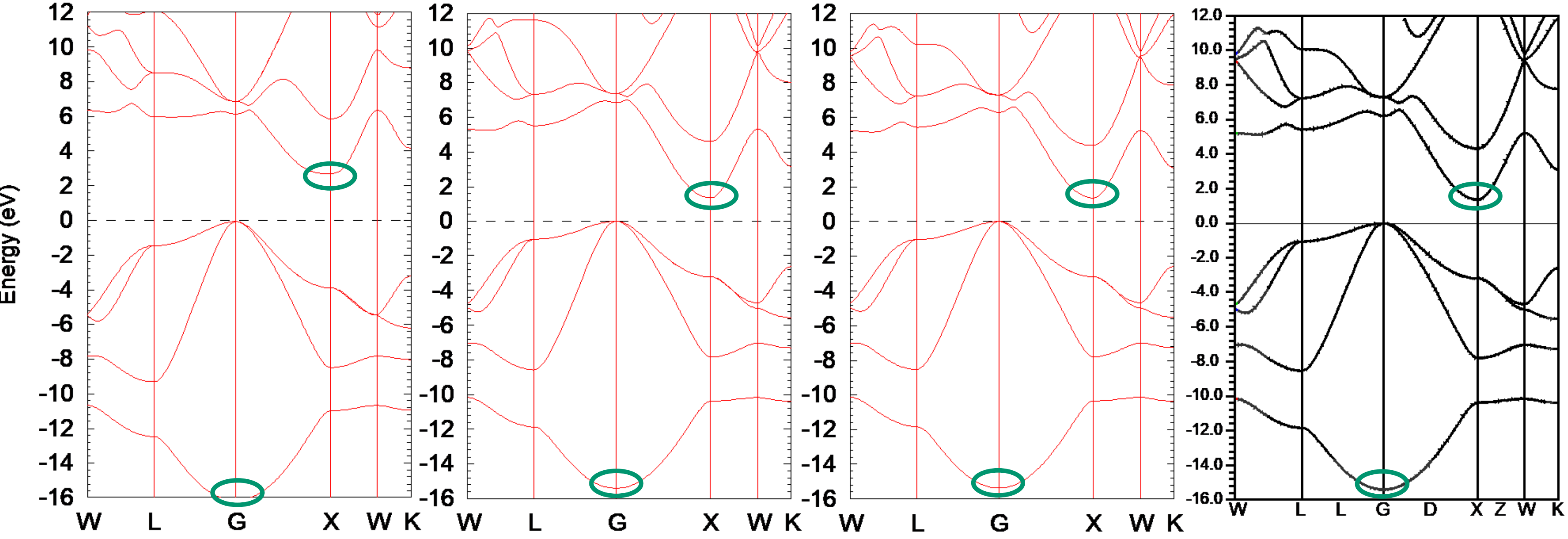






While the convergent result is achieved by use of Si7.0-s3p2d2f1(Si7.0-s3p3d2f1), Si7.0-s2p2d1 is a balanced basis functions compromising accuracy and efficiency to perform a vast range of materials exploration.

Floating states in 3C-SiC



C6.0-s2p2
Si8.0-s2p2

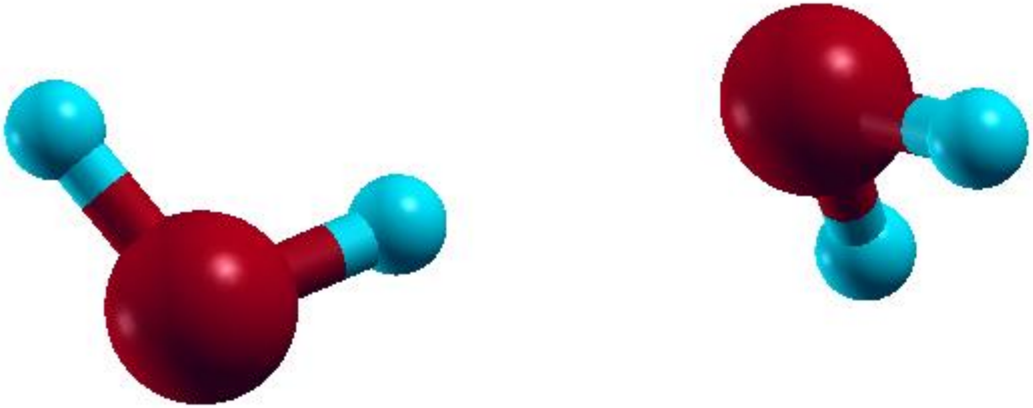
C6.0-s2p2d1
Si8.0-s2p2d1

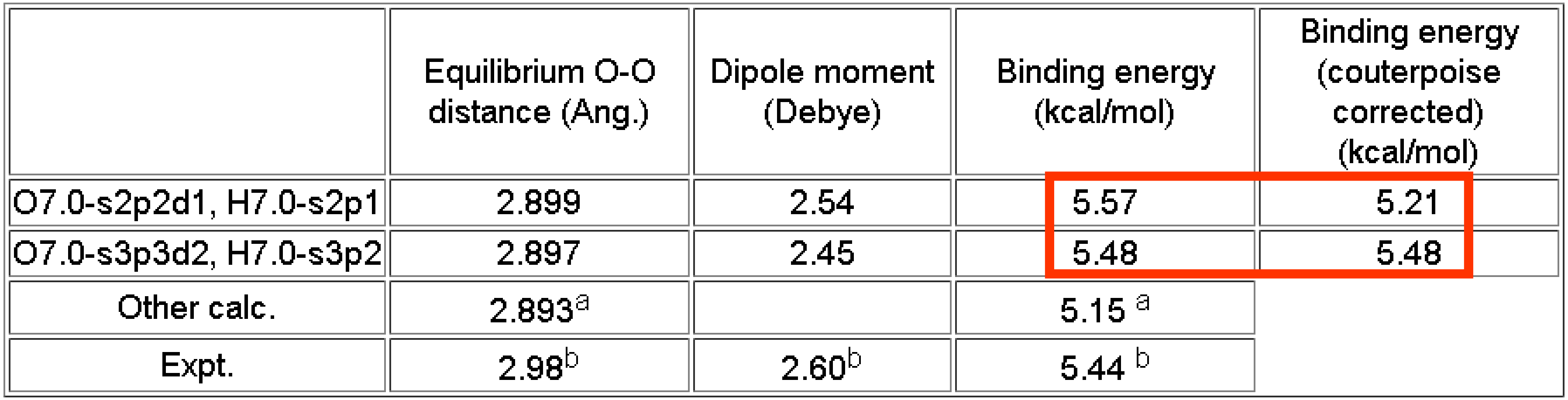
C6.0-s3p3d2f1
Si8.0-s3p3d2f1

Wien2k (FLAPW)

- Inclusion of polarization orbitals is important to reproduce band structures.
- The band structure up to 5 eV is reproduced by s2p2d1.

Basis set superposition Error (BSSE)





	Equilibrium O-O distance (Ang.)	Dipole moment (Debye)	Binding energy (kcal/mol)	Binding energy (couterpoise corrected) (kcal/mol)
O7.0-s2p2d1, H7.0-s2p1	2.899	2.54	5.57	5.21
O7.0-s3p3d2, H7.0-s3p2	2.897	2.45	5.48	5.48
Other calc.	2.893[a]		5.15 [a]	
Expt.	2.98[b]	2.60[b]	5.44 [b]	

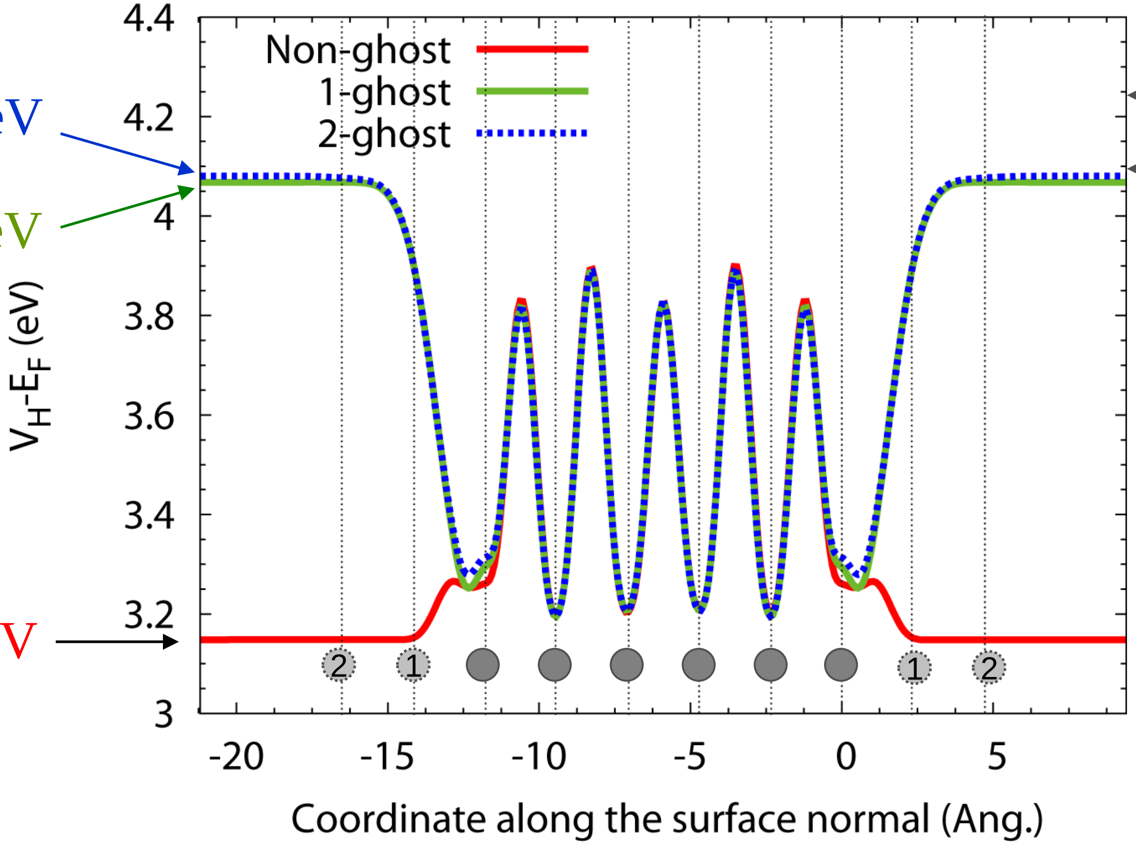
http://www.jaist.ac.jp/~t-ozaki/vps_pao2013/O/index.html

A series of benchmark calculations implies that BSSE is ～0.5 kcal/mol for molecular systems.

Work functions

fcc Al (111) surface

By allocating empty atoms in vacuum near the surface, one can calculate work functions accurately.



4.08 eV

4.07 eV

3.15 eV

Work function

Exp : 4.24 eV

PW : 4.09 eV

Y. Morikawa *et al.*,
PRB **69**, 041403(R)
(2004);
TABLE I.

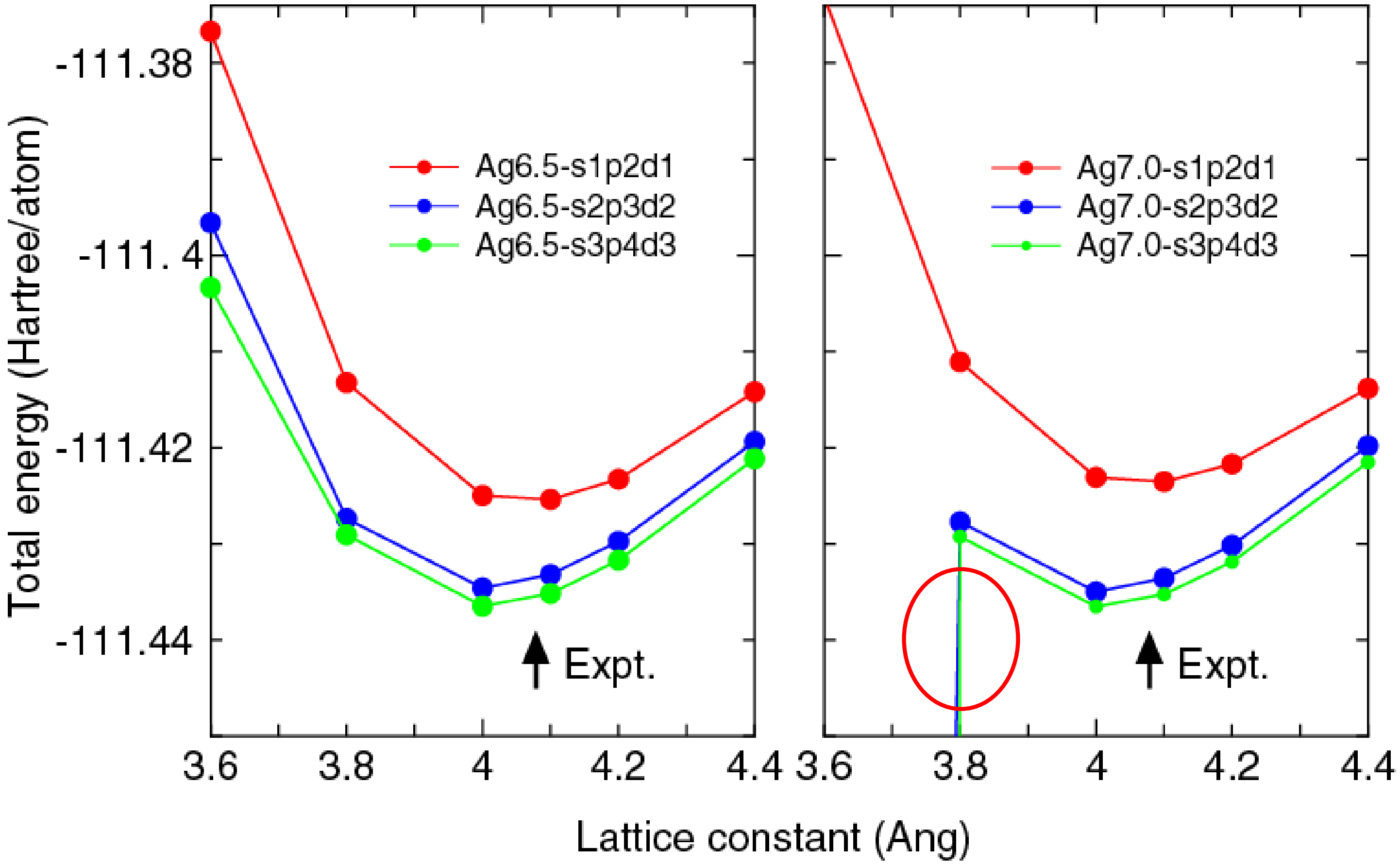
By Jippo and Ohfuti (Fujitsu)

Al(111) fcc 1x1 6L, GGA-PBE, Fix to the equilibrium lattice parameter
Al6.0-s1p2d1, Al_PBE (Database ver. 2006)
E6.0-s1p2d1, E (Database ver. 2006)

See: http://www.openmx-square.org/openmx_man3.8/node32.html
http://www.openmx-square.org/forum/patio.cgi?mode=view&no=2305

Overcompleteness of basis functions

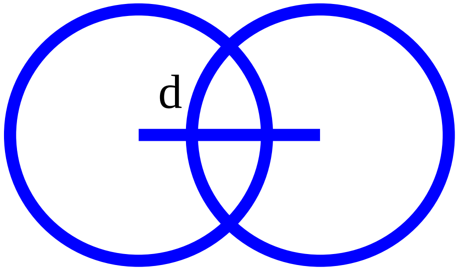
Total energy of fcc-Ag



A numerical instability, called "overcompleteness", tends to appear if a lot of basis functions are used for dense structures such as fcc, hcp, and bcc.

Cause of overcompleteness

Let’s take a H_2 molecule as a simple example, and consider d→0 where d is the interatomic distance.



$$Hc = \varepsilon Sc$$

$$H = \begin{pmatrix} e & h \\ h & e \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}$$

$$S = V \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} V^\dagger = V\lambda V^\dagger$$

$$\boxed{\lambda_1 = 1 - s \qquad v_1 = (1, -1)}$$

$$\lambda_2 = 1 + s \qquad v_2 = (1, 1)$$

$$\begin{aligned} Hc &= \varepsilon Sc \\ Hc &= \varepsilon V\lambda V^\dagger c \\ \lambda^{-1/2}V^\dagger HV\lambda^{-1/2}\lambda^{1/2}V^\dagger c &= \varepsilon\lambda^{1/2}V^\dagger c \end{aligned}$$

$$H' = \lambda^{-1/2}V^\dagger HV\lambda^{-1/2}$$

$$b = V^\dagger c$$

$$H'b = \varepsilon b$$

A round-off error arises when H’ is calculated, and the error is magnified by $1/\sqrt{\lambda_1}$.

Restarting of calculations

- After finishing your first calculation or achieving the self consistency, you may want to continue the calculation or to calculate density of states, band dispersion, molecular orbitals, and etc. using the self consistent charge in order to save the computational time. To do this, a keyword 'scf.restart' is available.

```
scf.restart          on          # on|off,default=off
```

- If the first trial for geometry optimization does not reach a convergent result or molecular a dynamics simulation is terminated due to a wall time, one can restart the geometry optimization using an input file 'System.Name.dat#' which is generated at every step for the restart calculation with the final structure.

See also

http://www.openmx-square.org/openmx_man3.8/node46.html

http://www.openmx-square.org/openmx_man3.8/node54.html

Output of large-sized files in binary mode

Large-scale calculations produce large-sized files in text mode such as cube files. The IO access to output such files can be very time consuming in machines of which IO access is not fast. In such a case, it is better to output those large-sized files in binary mode. The procedure is supported by the following keyword:

```
OutData.bin.flag    on    # default=off, on|off
```

Then, all large-sized files will be output in binary mode. The default is 'off'. The output binary files are converted using a small code 'bin2txt.c' stored in the directory 'source' which can be compiled as

```
gcc bin2txt.c -lm -o bin2txt
```

As a post processing, you will be able to convert as

```
./bin2txt *.bin
```

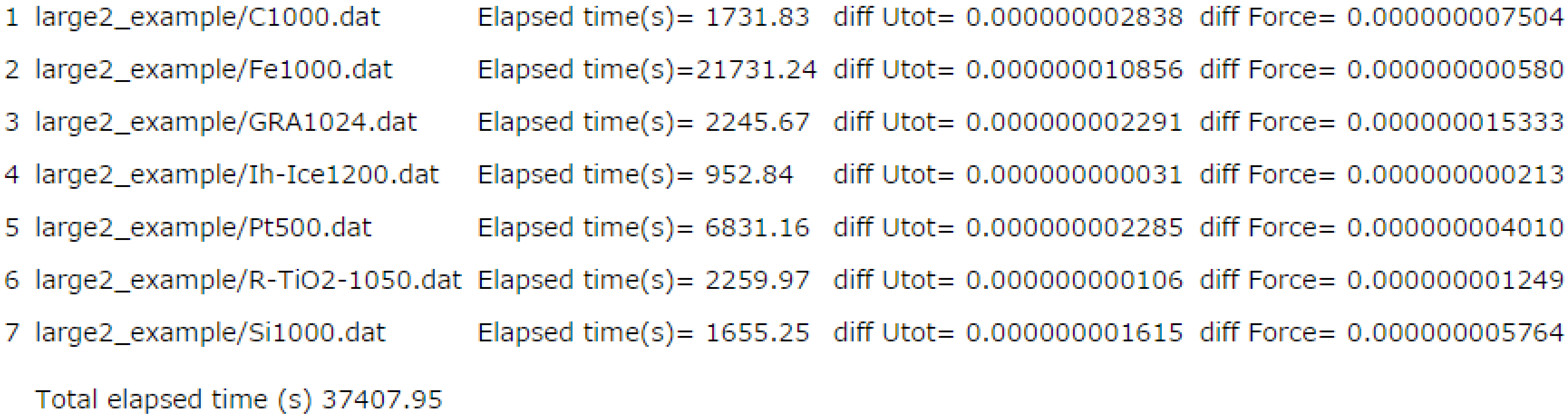
The functionality will be useful for machines of which IO access is not fast.

See also http://www.openmx-square.org/openmx_man3.8/node172.html

Large-scale calculations

The following is a result of 'runtestL2' performed using 264 MPI processes and 2 OpenMP threads on CRAY-XC30.

```
$ mpirun –np 264 openmx -runtestL2 -nt 2
```



```
1  large2_example/C1000.dat         Elapsed time(s)= 1731.83   diff Utot= 0.000000002838  diff Force= 0.000000007504
2  large2_example/Fe1000.dat        Elapsed time(s)=21731.24  diff Utot= 0.000000010856  diff Force= 0.000000000580
3  large2_example/GRA1024.dat       Elapsed time(s)= 2245.67   diff Utot= 0.000000002291  diff Force= 0.000000015333
4  large2_example/Ih-Ice1200.dat    Elapsed time(s)= 952.84    diff Utot= 0.000000000031  diff Force= 0.000000000213
5  large2_example/Pt500.dat         Elapsed time(s)= 6831.16   diff Utot= 0.000000002285  diff Force= 0.000000004010
6  large2_example/R-TiO2-1050.dat Elapsed time(s)= 2259.97   diff Utot= 0.000000000106  diff Force= 0.000000001249
7  large2_example/Si1000.dat        Elapsed time(s)= 1655.25   diff Utot= 0.000000001615  diff Force= 0.000000005764

   Total elapsed time (s) 37407.95
```

The elapsed time implies that geometry optimization for systems consisting of 1000 atoms is possible if several hundreds processor cores are available.

See also
http://www.openmx-square.org/openmx_man3.8/node87.html
http://www.openmx-square.org/openmx_man3.8/node88.html

On the manual

Please download the manual at

http://www.openmx-square.org/openmx_man3.8/openmx3.8.pdf

The manual is self-contained, the most of calculations explained in the manual are traceable by using the input file stored in the directory ‘work’.

Please try to perform those calculations one by one depending on your interests.

Recommended trials

1. Geometry optimization

   Perform a geometry optimization using ‘Methane2.dat’.
   See the page 65 in the manual.

2. Density of states

   Calculate DOS using ‘Cdia.dat’
   See the page 79 in the manual.

All the input files can be found in the directory ‘work’.

3. Wannier functions

   Calculate Wannier functions for Si bulk using ‘work/wf_example/Si.dat’, and perform the band interpolation. See the page 159 in the manual.

4. Reaction barrier by the nudged elastic band (NEB) method

   Calculate a reaction barrier using ‘C2H4_NEB.dat’.
   See the page 182 in the manual.

5. Transmission of a carbon chain

   Calculate an electric transmission of a carbon chain using ‘Lead-Chain.dat’, ‘NEGF-Chain.dat’. See the page 136 in the manual.

6. Spin-orbit coupling

   Calculate a band structure by taking account of SOC using ‘GaAs.dat’.
   See the page 117 in the manual.

Outlook

- A localized basis method, implemented in OpenMX, was discussed with the following focuses:
  - Total energy
  - Pseudopontials
  - Basis functions

- The careful evaluation of the total energy and optimization of PPs and PAOs guarantee accurate and fast DFT calculations in a balanced way.

- The practical guideline may be useful for getting started with OpenMX calculations.