# **Overview of OpenMX**

- Introduction
- Implementation of OpenMX
- Ongoing and planned developments

## Taisuke Ozaki ISSP, Univ. of Tokyo

The 3<sup>rd</sup> OpenMX/QMAS workshop at ISSP, 11<sup>th</sup>-13<sup>th</sup> May 2015

# **About the slides**

# The PDF file can be downloaded from the website for the program of the workshop.

http://www.openmx-square.org/workshop/workshop15/OpenMX-Overview.pdf

# **Purpose of the tutorial**

- First-principles calculations based on the density functional theories (DFT) have been now widely accepted as a useful tool to understand chemical and physical properties of molecules and bulks with reasonable accuracy in relatively small computational cost.
- OpenMX (Open source package for Material eXplorer) is a software package for nano-scale material simulations based on DFT, normconserving pseudopotentials, and pseudo-atomic localized basis functions. The methods and algorithms used in OpenMX and their implementation are carefully designed for the realization of large-scale ab initio electronic structure calculations on parallel computers.
- In the tutorial, we aim to hand on the theoretical background of OpenMX for a wide variety of researchers who pursue deep understanding of materials properties from first-principles.

# **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
- Public release (GNU-GPL) 2003
- 2003 Collaboration: AIST, NIMS, SNU KAIST, JAIST, Kanazawa Univ CAS, UAM NISSAN, Fujitsu Labs. etc.
- 2013 17 public releases Latest version: 3.7

## Workshop

Ver. 2013

- Miscellaneous informations
- Acknowledgment
- Links

http://www.openmx-square.org

About 280 papers published using OpenMX

#### Welcome to OpenMX

#### 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
- Database of VPS and PAO
- ADPACK
- Contributors



# **Developers of OpenMX**

- T. Ozaki (U.Tokyo)
- H. Kino (NIMS)
- J. Yu (SNU)
- M. J. Han (KAIST)
- M. Ohfuti (Fujitsu)
- F. Ishii (Kanazawa Univ.)
- T. Ohwaki (Nissan)
- H. Weng (CAS)
- M. Toyoda (Osaka Univ.)
- H. Kim (SNU)
- P. Pou (UAM)

- T. V. Truong Duy (U.Tokyo)
- C.-C. Lee (JAIST)
- Y. Okuno (Fuji FILM)
- Yang Xiao (NUAA)
- Y. Gohda (TIT)

# **Current status of OpenMX**

- The code with 0.3 million lines is written by a standard C, and partially Fortran90 including 1 makefile, 21 header files, 261 c files, 4 fortran90 files.
- The code is publicly available under GNU-GPL.
- Manual in English and Japanese, and technical notes on implementations in English.
- Database of optimized pseudopotentials and basis functions for 76 elements.
- OpenMP/MPI hybrid parallelization. The parallel efficiency of 68% is achieved using a hundred and thirty thousands cores on K.

## **Publications with OpenMX**



# Materials studied by OpenMX

#### First characterization of silicene on ZrB<sub>2</sub> 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 300 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)

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

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

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W.Kohn (1923-)

$$H_{\rm KS}\phi_i = \varepsilon_i\phi_i$$
$$\hat{H}_{\rm KS} = -\frac{1}{2}\nabla^2 + v_{\rm eff}$$
$$v_{\rm eff} = v_{\rm ext}(\mathbf{r}) + v_{\rm Hartree}(\mathbf{r}) + \frac{\delta E_{\rm x}}{\delta\rho(\mathbf{r})}$$

# Successes and failures of GGA

#### **Successes:**

1. Accuracy:

Atomization energy: Bond length: Bulk modulus: Energy barrier: Mean absolute error 0.3 eV (mostly overbinding) Overestimation of 1 % Underestimation of 5 % Underestimation of 30 %

Accurate description of hydrogen bonding
 Better description of magnetic ground states (e.g., bcc Fe)

#### **Failures:**

Band gap:
 vdW interaction:
 Strongly correlation:

Underestimation of 30~40 % No binding in many cases No orbital polarization of localized d- and f-states

# Mathematical structure of KS eq.

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



Input charge = Output charge  $\rightarrow$  Self-consistent condition

# **Papers on methods in OpenMX**

- 2000 block BOP PRB 59, 16061, PRB 61, 7972
- 2001 ab initio recursion method PRB 64 195126
- 2001 O(N) inversion method by recursion PRB 64, 195110
- 2003 Variational optimized basis functions PRB 67, 155108, PRB 69, 195113, JCP 121, 10879
- 2005 Efficient implementation of LCPAO method PRB 72, 045121
- 2005 O(N) LDA+U method PRB 73, 045110
- 2006 O(N) Krylov subspace method PRB 74, 245101
- 2007 Efficient integration of Green's function PRB 75, 035123
- 2008 Non-collinear DFT with constratints web notes
- 2009 First evaluation of two-electron repulsion integrals JCP 130, 124114
- 2009 First spherical Bessel transform method CPC 181, 277
- 2010 Non- equilibrium Green's function method PRB 81, 035116
- 2011 O(N<sup>2</sup>~) method PRB 82, 075131
- 2011 O(N) nearly exact exchange functional PRA 83, 032515
- 2012 O(N) + ESM method JCP 136, 134101
- 2014 Massively parallelization of OpenMX CPC 185, 777
- 2014 Massively parallelization of 3D-FFT CPC 185, 153
- 2014 Large-scale NBO analysis JCP 140, 244105

## **LCPAO** method

#### (Linear-Combination of Pseudo Atomic Orbital Method)

One-particle KS orbital

$$\psi_{\sigma\mu}^{(\mathbf{k})}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n}^{N} e^{i\mathbf{R}_{n}\cdot\mathbf{k}} \sum_{i\alpha} c_{\sigma\mu,i\alpha}^{(\mathbf{k})} \phi_{i\alpha}(\mathbf{r}-\tau_{i}-\mathbf{R}_{n}),$$

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.

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

 $E_{\rm kin} = \sum_{\sigma} \sum_{n}^{N} \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha j\beta}^{(\rm R_n)} h_{i\alpha j\beta, \rm kin}^{(\rm R_n)}$ . Kinetic energy  $E_{\rm ec} = \underbrace{E_{\rm ec}^{(\rm L)}}_{\sigma} + E_{\rm ec}^{(\rm NL)}, \qquad \text{Coulomb energy with external potential} \\ = \sum_{\sigma} \sum_{n}^{N} \sum_{i\alpha,i\beta} \rho_{\sigma,i\alpha j\beta}^{(\rm R_n)} \langle \phi_{i\alpha}(\mathbf{r} - \tau_i) | \sum_{I} V_{\rm core,I}(\mathbf{r} - \tau_I) | \phi_{j\beta}(\mathbf{r} - \tau_j - \mathbf{R}_n) \rangle$ +  $\sum_{\sigma} \sum_{\mathbf{n}}^{N} \sum_{i\alpha,j\beta} \rho_{\sigma,i\alpha j\beta}^{(\mathbf{R}_{\mathbf{n}})} \langle \phi_{i\alpha}(\mathbf{r}-\tau_{i}) | \sum_{I} V_{\mathrm{NL},I}(\mathbf{r}-\tau_{I}) | \phi_{j\beta}(\mathbf{r}-\tau_{j}-\mathbf{R}_{\mathbf{n}}) \rangle$ ,  $E_{\rm ee} = \frac{1}{2} \int dr^3 n(\mathbf{r}) V_{\rm H}(\mathbf{r}),$  Hartree energy  $= \frac{1}{2} \int dr^3 n(\mathbf{r}) \{ V_{\rm H}^{(\rm a)}(\mathbf{r}) + \delta V_{\rm H}(\mathbf{r}) \},$  $E_{\rm xc} = \int dr^3 \{ n_{\uparrow}({\bf r}) + n_{\downarrow}({\bf r}) + n_{\rm pcc}({\bf r}) \} \epsilon_{\rm xc} (n_{\uparrow} + \frac{1}{2}n_{\rm pcc}, n_{\downarrow} + \frac{1}{2}n_{\rm pcc}), \qquad {\rm Exchange-correlation}$ energy  $E_{\rm cc} = \frac{1}{2} \sum_{I,I} \frac{Z_I Z_J}{|\tau_I - \tau_I|}$ . 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.

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

The neutral atom energy

$$E_{\text{na}} = \int dr^3 n(\mathbf{r}) \sum_{I} V_{\text{na},I}(\mathbf{r} - \tau_{I}), \qquad \begin{array}{l} \text{Short range and separable to two-center integrals} \\ = \sum_{\sigma} \sum_{n}^{N} \sum_{i\alpha,j\beta} \rho_{\sigma,i\alphaj\beta}^{(\mathbf{R}_{n})} \sum_{I} \langle \phi_{i\alpha}(\mathbf{r} - \tau_{i}) | V_{\text{na},I}(\mathbf{r} - \tau_{I}) | \phi_{j\beta}(\mathbf{r} - \tau_{j} - \mathbf{R}_{n}) \rangle, \end{array}$$

Difference charge Hartree energy

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

Long range but minor contribution

#### Screened core-core repulsion energy

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

Difference charge

Neutral atom potential

$$\delta n(\mathbf{r}) = n(\mathbf{r}) - n^{(\mathbf{a})}(\mathbf{r}),$$
  
=  $n(\mathbf{r}) - \sum_{i} n_{i}^{(\mathbf{a})}(\mathbf{r}),$ 

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

# **Implementation: Total energy (3)**

So, the total energy is given by

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

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



# **Two center integrals**

Fourier-transformation of basis functions

 $\tilde{\phi}_{i}$ 

$$\begin{aligned} {}_{\alpha}(\mathbf{k}) &= \left(\frac{1}{\sqrt{2\pi}}\right)^{3} \int dr^{3}\phi_{i\alpha}(\mathbf{r}) \mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{r}} \\ &= \left(\frac{1}{\sqrt{2\pi}}\right)^{3} \int dr^{3}Y_{lm}(\hat{\mathbf{r}})R_{pl}(r) \left\{ 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-\mathbf{i})^{L} j_{L}(kr) Y_{LM}(\hat{\mathbf{k}}) Y_{LM}^{*}(\hat{\mathbf{r}}) \right\}, \\ &= \left(\frac{1}{\sqrt{2\pi}}\right)^{3} 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-\mathbf{i})^{L} Y_{LM}(\hat{\mathbf{k}}) \int drr^{2}R_{pl}(r) j_{L}(kr) \int d\theta d\phi \sin(\theta) Y_{lm}(\hat{\mathbf{r}}) Y_{LM}^{*}(\hat{\mathbf{r}}), \\ &= \left[ \left(\frac{1}{\sqrt{2\pi}}\right)^{3} 4\pi (-\mathbf{i})^{l} \int drr^{2}R_{pl}(r) j_{L}(kr) \right] Y_{lm}(\hat{\mathbf{k}}), \\ &= \tilde{R}_{pl}(k) Y_{lm}(\hat{\mathbf{k}}), \end{aligned}$$
Integrals for angular parts are analytically

 $\begin{array}{lll} \mathbf{e.g., overlap integral} \\ \langle \phi_{i\alpha}(\mathbf{r}) | \phi_{j\beta}(\mathbf{r} - \tau) \rangle &= \int dr^3 \phi_{i\alpha}^*(\mathbf{r}) \phi_{j\beta}(\mathbf{r} - \tau), \end{array} \begin{array}{lll} & \text{performed. Thus, we only have to} \\ & \text{perform one-dimensional integrals along} \\ & \text{the radial direction.} \end{array} \\ &= \int dr^3 \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dk^3 \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{\mathbf{k}}) \mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\mathbf{r}} \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dk'^3 \tilde{R}_{p'l'}(k') Y_{l'm'}(\hat{\mathbf{k}}') \mathrm{e}^{\mathbf{i}\mathbf{k}'\cdot(\mathbf{r}-\tau)}, \\ &= \left(\frac{1}{2\pi}\right)^3 \int dk^3 \int dk'^3 \mathrm{e}^{-\mathbf{i}\mathbf{k}'\cdot\tau} \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k') Y_{l'm'}(\hat{\mathbf{k}}') \int dr^3 \mathrm{e}^{\mathbf{i}(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}, \\ &= \int dk^3 \mathrm{e}^{-\mathbf{i}\mathbf{k}\cdot\tau} \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k) Y_{l'm'}(\hat{\mathbf{k}}), \end{array}$ 

## **Cutoff energy for regular mesh**

The two energy components  $\mathbf{E}_{\delta ee} + \mathbf{E}_{xc}$  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.

$$E_{\text{cut}}^{(1)} = \frac{1}{2}\mathbf{g}\mathbf{b}_1 \cdot \mathbf{g}\mathbf{b}_1, \quad E_{\text{cut}}^{(2)} = \frac{1}{2}\mathbf{g}\mathbf{b}_2 \cdot \mathbf{g}\mathbf{b}_2, \quad E_{\text{cut}}^{(3)} = \frac{1}{2}\mathbf{g}\mathbf{b}_3 \cdot \mathbf{g}\mathbf{b}_3,$$

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

 $\mathbf{g}\mathbf{b}_1 = 2\pi \frac{\mathbf{g}\mathbf{a}_2 \times \mathbf{g}\mathbf{a}_2}{\Delta V}, \quad \mathbf{g}\mathbf{b}_2 = 2\pi \frac{\mathbf{g}\mathbf{a}_3 \times \mathbf{g}\mathbf{a}_1}{\Delta V}, \quad \mathbf{g}\mathbf{b}_2 = 2\pi \frac{\mathbf{g}\mathbf{a}_1 \times \mathbf{g}\mathbf{a}_2}{\Delta V},$ 

 $\Delta V = \mathbf{g}\mathbf{a}_1 \cdot \left(\mathbf{g}\mathbf{a}_2 \times \mathbf{g}\mathbf{a}_3\right),$ 

## Forces



# Total energy Pseudopotentials Basis functions

## Norm-conserving Vanderbilt pseudopotential

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

The following non-local operator proposed by Vanderbilt guarantees that scattering properties are reproduced around multiple reference energies.

D. Vanderbilt, PRB 41, 7892 (1990).

$$V_{\rm NL} = \sum_{i,j} B_{ij} |\beta_i\rangle \langle\beta_j|$$

$$|\chi_i\rangle = V_{\rm NL}^{(i)} |\phi_i\rangle = (\varepsilon_i - T - V_{\rm loc}) |\phi_i\rangle$$
$$B_{ij} = \langle \phi_i |\chi_j\rangle$$
$$|\beta_i\rangle = \sum_j (B^{-1})_{ji} |\chi_j\rangle$$

PP

If the following generalized norm-conserving condition is fulfilled, the matrix B is Hermitian, resulting in that  $V_{NL}$  is also Hermitian.

$$Q_{ij} = \langle \psi_i | \psi_j \rangle_R - \langle \phi_i | \phi_j \rangle_R \qquad \text{If } Q=0, \text{ then } B-B^*=0$$
  
$$B_{ij} - B_{ji}^* = (\varepsilon_i - \varepsilon_j) Q_{ij} \qquad \text{This is the norm-conserving} \\ \text{used in OpenMX}$$

## Non-local potentials by Vanderbilt

Let's operate the non-local potential on a pseudized wave function:

$$\begin{split} \hat{v}^{(\mathrm{NL})} |\phi_{k}^{(\mathrm{PS})}\rangle &= \sum_{ij} |\beta_{i}\rangle B_{ij} \langle \beta_{j} |\phi_{k}^{(\mathrm{PS})}\rangle \\ &= \sum_{ij} |\beta_{i}\rangle B_{ij} \sum_{k'} \left(B^{-1}\right)_{k'j} \langle \chi_{k'} |\phi_{k}^{(\mathrm{PS})}\rangle, \quad \text{Noting the following relations:} \\ &= \sum_{ij} |\beta_{i}\rangle B_{ij} \sum_{k'} \left(B^{-1}\right)_{k'j} B_{kk'}, \\ &= \sum_{ij} |\beta_{i}\rangle B_{ij} \delta_{kj}, \\ &= \sum_{ij} |\beta_{i}\rangle B_{ij} \delta_{kj}, \\ &= \sum_{i} \left(\sum_{j} \left(B^{-1}\right)_{ji} |\chi_{j}\rangle\right) B_{ik}. \\ &= |\chi_{k}\rangle \end{split} \qquad \begin{aligned} &B_{ij} = \langle \phi_{i}^{(\mathrm{PS})} |\chi_{j}\rangle \\ &= B_{ij} \left(B^{-1}\right)_{ji} |\chi_{j}\rangle \\ &= \sum_{i} \left(B^{-1}\right)_{ji} |\chi_{j}\rangle. \end{split}$$

It turns out that the following Schrodinger eq. is hold.

$$\left(-\frac{1}{2}\nabla^2 + v^{(\mathrm{SL})}(r) + \hat{v}^{(\mathrm{NL})}\right) |\phi_i^{(\mathrm{PS})}\rangle = \varepsilon_i |\phi_i^{(\mathrm{PS})}\rangle.$$

## Generalized norm-conserving conditions $Q_{ij}$

In the Vanderbilt pseudopotential, B is given by

$$B_{ij} = \int_0^{r_c} dr P_i^{(PS)}(r) \left( \varepsilon_j + \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} - v^{(SL)}(r) \right) P_j^{(PS)}(r),$$
  

$$B_{ji}^* = \int_0^{r_c} dr P_i^{(PS)}(r) \left( \varepsilon_i + \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} - v^{(SL)}(r) \right) P_j^{(PS)}(r),$$

Thus, we have

$$B_{ij} - B_{ji}^* = (\varepsilon_j - \varepsilon_i) \int_0^{r_c} dr P_i^{(\text{PS})}(r) P_j^{(\text{PS})}(r) + \frac{1}{2} \int_0^{r_c} dr P_i^{(\text{PS})}(r) P_j^{\prime\prime(\text{PS})}(r) - \frac{1}{2} \int_0^{r_c} dr P_i^{\prime\prime(\text{PS})}(r) P_j^{(\text{PS})}(r).$$

By integrating by parts, this can be transformed as

$$B_{ij} - B_{ji}^{*} = (\varepsilon_{j} - \varepsilon_{i}) \langle \phi_{i}^{(\text{PS})} | \phi_{j}^{(\text{PS})} \rangle_{r_{c}} + \frac{1}{2} \left[ P_{i}^{(\text{PS})}(r) P_{j}^{\prime(\text{PS})}(r) \right]_{0}^{r_{c}} - \frac{1}{2} \left[ P_{i}^{\prime(\text{PS})}(r) P_{j}^{(\text{PS})}(r) \right]_{0}^{r_{c}},$$
  
$$= (\varepsilon_{j} - \varepsilon_{i}) \langle \phi_{i}^{(\text{PS})} | \phi_{j}^{(\text{PS})} \rangle_{r_{c}} + \frac{1}{2} P_{i}^{(\text{PS})}(r_{c}) P_{j}^{\prime(\text{PS})}(r_{c}) - \frac{1}{2} P_{i}^{\prime(\text{PS})}(r_{c}) P_{j}^{(\text{PS})}(r_{c}). \quad \cdots \quad (1)$$

As well, the similar calculations can be performed for all electron wave functions.

$$0 = (\varepsilon_j - \varepsilon_i) \langle \phi_i^{(AE)} | \phi_j^{(AE)} \rangle_{r_c} + \frac{1}{2} P_i^{(AE)}(r_c) P_j'^{(AE)}(r_c) - \frac{1}{2} P_i'^{(AE)}(r_c) P_j^{(AE)}(r_c).$$
(2)

By subtracting (2) from (1), we obtain a relation between B and Q.

$$B_{ij} - B_{ji}^* = (\varepsilon_i - \varepsilon_j) \left( \langle \phi_i^{(AE)} | \phi_j^{(AE)} \rangle_{r_c} - \langle \phi_i^{(PS)} | \phi_j^{(PS)} \rangle_{r_c} \right).$$

## Norm-conserving pseudopotential by MBK

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

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

$$V_{\rm NL} = \sum_{i,j} B_{ij} |\beta_i\rangle \langle\beta_j|,$$
$$= \sum_i \lambda_i |\alpha_i\rangle \langle\alpha_i|$$

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

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

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

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

Pseudo-wave funtion and psedopotential of carbon atom

## Red: All electron calculation Blue: Pseudized calculation



# **Optimization of pseudopotentials**



# **Comparison of logarithmic derivatives**

Logarithmic derivatives of s, p, d, f channels for Mn. The deviation between PP and all electron directly affects the band structure.



## **Comparison of band structure for fcc Mn**



# Total energy Pseudopotentials Basis functions

# **Primitive basis functions**

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

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

- 2. Construct the norm-conserving pseudopotentials.
- 3. Solve ground and excited states for the the peudopotential 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**

Dimer	Expt.	Calc.	Dimer	Expt.	Calc.
$H_2$ (H4.5-s2)	${}^{1}\Sigma_{g}^{+a}$	${}^{1}\Sigma_{g}^{+}(1s\sigma_{g}^{2})$	K <sub>2</sub> (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- $s2p2d2$ )	${}^{1}\Sigma^{+}k$	${}^{1}\Sigma^{4}$ $(s\sigma^{2}s\sigma^{2}p\pi^{4})$
Li <sub>2</sub> (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- $s2p2$ )	${}^{1}\Sigma^{\mp} d$	${}^{1}\Sigma^{+} (s\sigma^{2}s\sigma^{2}p\pi^{4})$	Ti <sub>2</sub> (Ti7.0-s2p2d2)	$^{3}\Delta_{g}m$	$^{3}\Delta_{g} (4s\sigma_{q}^{2}3d\sigma_{q}^{1}3d\pi_{u}^{4}3d\delta_{q}^{1})$
$B_2$ (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)	${}^{3}\Sigma_{g}^{-n}$	${}^{1}\Sigma_{q}^{+}$ $(4s\sigma_{q}^{2}3d\sigma_{q}^{2}3d\pi_{u}^{4}3d\delta_{q}^{2})$
$C_2$ (C5.0-s2p2)	${}^{1}\Sigma_{g}^{\downarrow}f$	${}^{1}\Sigma_{g}^{+} (2s\sigma_{g}^{2}2s\sigma_{u}^{2}2p\pi_{u}^{4})$	$V_2$ (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 <sub>2</sub> (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- <i>s</i> 2 <i>p</i> 2 <i>d</i> 2)	${}^{1}\Sigma_{q}^{+} {}^{o}$	${}^{1}\Sigma_{q}^{+}$ $(4s\sigma_{q}^{2}3d\sigma_{q}^{2}3d\pi_{u}^{4}3d\delta_{q}^{4})$
$O_2$ (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- $s2p2$ )	${}^{1}\Sigma_{g}^{\downarrow}f$	${}^{1}\Sigma_{g}^{+} (2p\sigma_{g}^{2}2p\pi_{u}^{4}2p\pi_{g}^{4})$	$Fe_2$ (Fe7.0- $s2p2d2$ )	$^{7}\Delta_{u}^{q}$	$^{7}\Delta_{u} \left(4s\sigma_{g}^{2}3d\sigma_{g}^{2}3d\sigma_{u}^{1}3d\pi_{u}^{4}3d\pi_{g}^{2}3d\delta_{g}^{3}3d\delta_{u}^{2}\right)$
$Ne_2$ (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)		${}^{5}\Delta_{g} (4s\sigma_{q}^{2}3d\sigma_{q}^{2}3d\sigma_{u}^{1}3d\pi_{u}^{4}3d\pi_{q}^{2}3d\delta_{q}^{4}3d\delta_{u}^{3})$
$Na_2$ (Na9.0-s2p2)	${}^{1}\Sigma_{g}^{H}f$	${}^{1}\Sigma_{g}^{+}(2p\pi_{g}^{4}2p\sigma_{u}^{2}3s\sigma_{g}^{2})$	Ni <sub>2</sub> (Ni7.0-s2p2d2)	$\Omega^r$	${}^{3}\Sigma_{q}^{-}(4s\sigma_{q}^{2}3d\sigma_{q}^{2}3d\sigma_{u}^{2}3d\pi_{u}^{4}3d\pi_{q}^{2}3d\delta_{q}^{4}3d\delta_{u}^{4})$
MgO (Mg7.0-s2p2)	${}^{1}\Sigma^{\downarrow h}$	${}^{1}\Sigma^{+} (s\sigma^{2}s\sigma^{2}p\pi^{4})$	$Cu_2$ (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 <sub>2</sub> (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- $s2p2d2$ )	${}^{2}\Sigma_{q}^{+}t$	$^{2}\Sigma_{q}^{+}(s\sigma^{2}s\sigma^{*1}d\sigma^{2}d\pi^{4}d\delta^{4})$
$Al_2$ (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)	${}^{1}\Sigma^{+ u}$	$\Sigma^{+}(s\sigma^2s\sigma^{*2})$
Si <sub>2</sub> (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 <sub>2</sub> (Si6.5-s2p2d1)	${}^{3}\Sigma_{g}^{-}f$	${}^{3}\Sigma_{g}^{-}(3s\sigma_{u}^{2}3p\pi_{u}^{2}3s\sigma_{g}^{2})$	As <sub>2</sub> (As7.0-s2p2d1)	${}^{1}\Sigma_{q}^{+}f$	${}^{1}\Sigma_{q}^{+}$ $(4s\sigma_{q}^{2}4s\sigma_{u}^{2}4p\sigma_{q}^{2}4p\pi_{u}^{4})$
$P_2$ (P6.0-s2p2d1)	${}^{1}\Sigma_{g}^{H}f$	${}^{1}\Sigma_{g}^{+}(3s\sigma_{u}^{2}3p\sigma_{g}^{2}3p\pi_{u}^{4})$	$Se_2$ (Se7.0-s2p2d1)	${}^{3}\Sigma_{q}^{-}f$	${}^{3}\Sigma_{q}^{-}$ $(4s\sigma_{q}^{2}4s\sigma_{u}^{2}4p\sigma_{q}^{2}4p\pi_{u}^{4}4p\pi_{q}^{2})$
S <sub>2</sub> (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 <sub>2</sub> (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)	${}^{1}\Sigma^{+}_{z}j$	${}^{1}\Sigma^{+}(3p\pi^{4}_{3}3p\pi^{4}_{3}3p\sigma^{2}_{2})$		2	

Ground state calculations of dimer using primitive basis functions

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

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

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)

# **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 functions





## **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 <u>here</u>.

E	Public release of optimized and well tested VPS and PAO so																
H		that	user	s ca	n eas	sily s	tart t	heir	calcu	latio	ons.						<u>He</u>
<u>Li</u>	<u>Be</u>											<u>B</u>	<u>C</u>	<u>N</u>	<u>0</u>	E	<u>Ne</u>
<u>Na</u>	Mg											<u>AI</u>	<u>Si</u>	P	<u>s</u>	<u>CI</u>	<u>Ar</u>
<u>K</u>	<u>Ca</u>	<u>Sc</u>	<u>Ti</u>	V	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>Ga</u>	<u>Ge</u>	<u>As</u>	<u>Se</u>	<u>Br</u>	<u>Kr</u>
<u>Rb</u>	<u>Sr</u>	Y	<u>Zr</u>	<u>Nb</u>	<u>Mo</u>	<u>Tc</u>	<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	<u>Ag</u>	<u>Cd</u>	<u>In</u>	<u>Sn</u>	<u>Sb</u>	<u>Te</u>	I	<u>Xe</u>
<u>Cs</u>	<u>Ba</u>	L	<u>Hf</u>	<u>Ta</u>	W	<u>Re</u>	<u>Os</u>	<u>Ir</u>	<u>Pt</u>	<u>Au</u>	<u>Hg</u>	ΤI	<u>Pb</u>	<u>Bi</u>	<u>Po</u>	At	<u>Rn</u>
Fr	Ra	А															
	L	La	Ce	Pr	<u>Nd</u>	Pm	<u>Sm</u>	Eu	Gd	Tb	<u>Dy</u>	<u>Ho</u>	Er	Tm	Yb	<u>Lu</u>	
	А	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

# $\Delta$ -factor

The delta factor is defined as difference of total energy between Wien2k (FLAPW+LO) and a code under testing, which is shown as shaded region in figure below, where the volume is changed by plus and minus 6 % taken from the equilibrium  $V_0$ .



Lejaeghere et al., Critical Reviews in Solid State and Materials Sciences 39, 1-24 (2014).

## Comparison of codes in terms of $\Delta$ -factor

Code	Version	n Basis	Potentials	$\Delta$ -factor	Authors
WIEN2ko	13.1	LAPW/APW+lo	full	0 meV/atom	S. Cottenier
VASP ₽	5.2.12	plane waves	PAW 2012	0.7 meV/atom	K Lejaeghere
VASP ₽	5.2.12	plane waves	PAW 2012 GW-ready	0.8 meV/atom	K Lejaeghere
Abinit 🗗	7.5.3	plane waves	PAW JTH&	1.2 meV/atom	F. Jollet <i>et al.</i> [3]
Abinit 🗗	7.1.2	plane waves	GPAW PAW 0.9 ₪ (40 Ha cut-off)	1.3 meV/atom	F. Jollet <i>et al.</i> [3]
GPAW	0.9.1	plane waves	PAW 0.9 🖉	1.5 meV/atom	ASE [2]
Quantum ESPRESSO	5.0.2	plane waves	PAW 0.3.1 &	1.8 meV/atom	Quantum ESPRESSO [5]
OpenMX교	3.7	pseudo-atomic orbitals	Morrison-Bylander-Kleinman norm-conserving(2013)₪	2.0 meV/atom	OpenMX [4]
VASP ፼	5.2.2	plane waves	PAW 2011	2.1 meV/atom	K Lejaeghere <i>et al.</i> [1]
GPAW	0.8.0	grid-based	PAW <mark>0.6</mark> ₽	3.8 meV/atom	K Lejaeghere <i>et al.</i> [1]
Dacapo 🗗	2.7.16	plane waves	Vanderbilt ultrasoft version 2 🖗	6.2 meV/atom	ASE [2]
Abinit &	5.4.4p	plane waves	Troullier-Martins norm-conserving(FHI®)	14.5 meV/atom	ASE [2]

#### http://molmod.ugent.be/deltacodesdft

## How to choose basis functions: Si case(1)

Si7.0.pao

Eigenvalues	517.0.pa0
Lmax= 3 Mul=15	1
lmu 00	-0.59320968623145
lmu 01	0.016542472658724
lmu 0 2	0.57915688461708 👷
lmu 03	1.39915528592998 🔮
lmu 04	2.43106703909053
lmu 05	3.63498884739274
lmu 06	4.99885012002783
lmu 07	6.55485759476897
lmu 08	8.33541526908920
lmu 0 9	10.34055461939939
lmu 010	12.55818051232040
lmu 011	14.98369777887096
lmu 012	17.62014479571136
lmu 013	20.47011746372617
lmu 014	23.53245309073866
lmu 10	-0.314600131331012
lmu 11	0.12937640798489 🧲
lmu 12	0.71637380083701 🗸
lmu 1 3	1.54488697995006
lmu 14	2.59211686526084
lmu 15	3.84687324239366
lmu 16	5.31246180826158
lmu 17	6.99509799702661
lmu 18	8.89454075291723
lmu 19	11.00602102880752
lmu 110	13.32692005826443
lmu 111	15.85857455673626
lmu 112	18.60272353142246
1 mu 1 13	21.55894843635971
1 mu 1 14	24.72602323954447
Imu 20	0.01886411574821 3
Imu 21	0.358935149960657
Imu 22	0.94629918754692 '
Imu 23	1./6201/65644983
Imu 24	2.81418/23624388
Imu 25	4.10656012645961
1 mu 2 6	5.636619/18/5011
I MUZ /	7.39522693820483
I MU 2 8	9.3/22209833186/
1 mu 2 9	11.5622/93//64802
1 MU 2 10	13.96620568880690
I MU 2 11	16.58651812641581
I MU 2 12	13.422365/4188653
1 MU 2 13	22.4/3080813632/8
1 mu 2 14	25.73538272482773
imu 30	0.28356/69151846
1 MU 3 1	0./9082836114569
imu 32	1.52992065308726
imu 33	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 Si7.0s3p2d2f1 with Si8.0s3p2d2f1, 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.

# **Ongoing and planned developments**

#### • Speeding-up and low computational memory

O(N),  $O(N^3)$ , SCF, geometry optimization

#### Spectral calculations

Phonon dispersion, band unfolding, visible-ultraviolet, IR, Raman, XAS, NMR, ESR

#### • Stress

Stress, local stress, local energy

## Red:OngoingBlack:Planned

#### • Beyond GGA

Hybrid functionals, vdW-DF, mBJ, Machine-learning functionals, GW, RPA

#### • Electronic transport

Gate bias, eigenchannel, real space current, phonon scattering

#### • Molecular dynamics

Constant µ-ESM, Blue moon, Neural network potentials

## New functionalities in the next release

- > Opencore pseudopotentials for rare earth elements
- Band unfolding method
- > Natural atomic and bond orbitals method
- Blue moon ensemble
- > Constant  $\mu$  effective screening medium (ESM) method
- > Total energy decomposition method
- Voronoi volume
- Control of strength of spin-orbit coupling in OpenMX
- Constraint scheme for direction and magnitude of spin
- Crystal field analysis
- > Stress
- Optical conductivity

The release is planned around the end of 2015 or the beginning of 2016.

# Summary

- OpenMX is a program package, supporting DFT within LDA, GGA, and plus U, under GNU-GPL.
- The basic strategy to realize large-scale calculations relies on the use of pseudopotentials (PPs) and localized pseudoatomic orbital (PAO) 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.
- > New functionalities are now under development.