# Localized Basis Method in OpenMX

1. **Introduction**
2. **Implementation**

   ✓ Basis functions
   ✓ Numerical grid
   ✓ Pseudopotentials

3. **Ongoing developments**
4. **Summary**

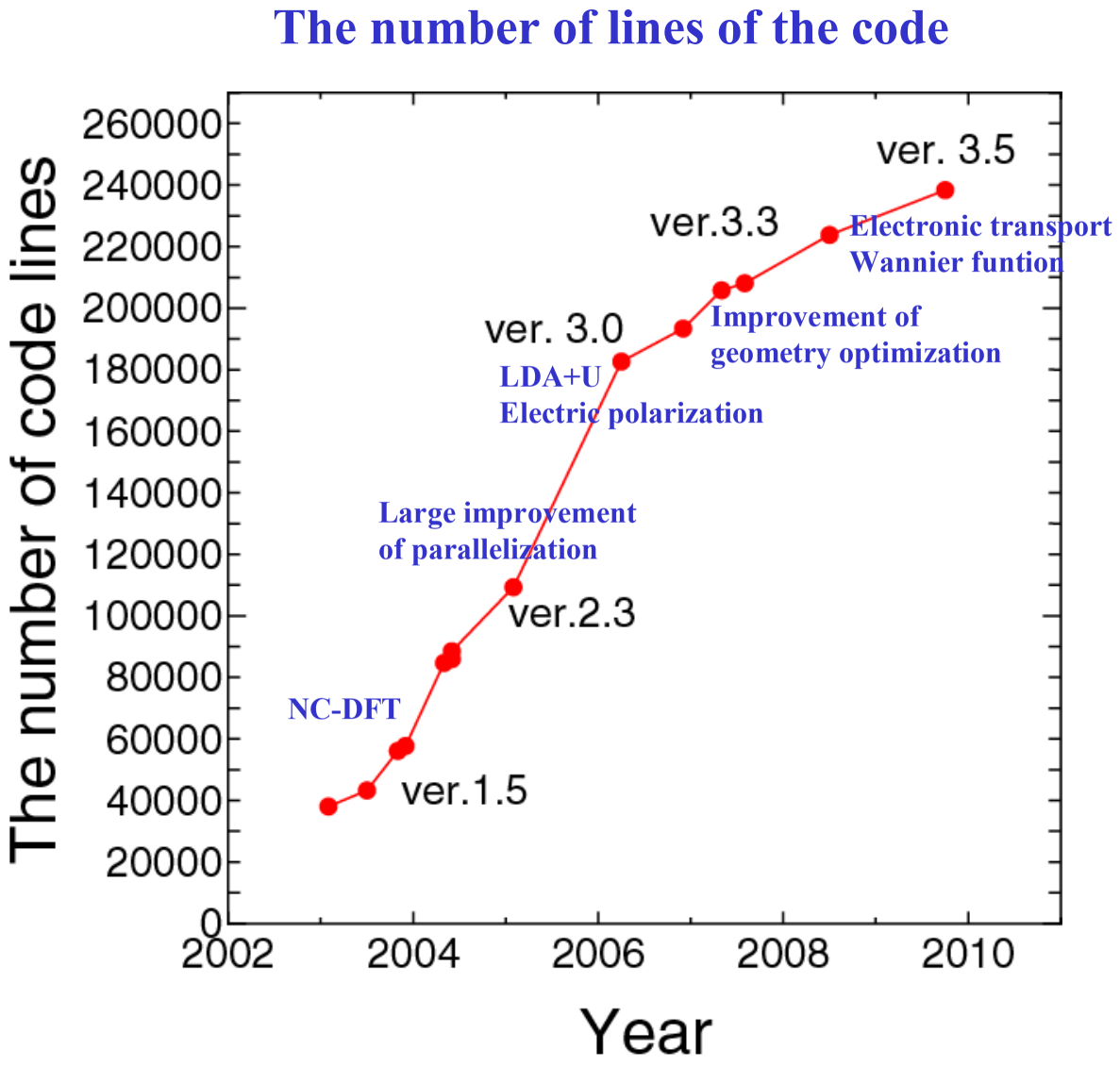
# Short history of OpenMX

The development of the code has been started from the middle of 2000.

The first public release was done at January 2003, and fifteen releases were made until now.

The code has been steadily developed as shown in the figure, and the community itself has been also growing.

About 80 related papers have been published.



# Contributors

- T. Ozaki (JAIST)
- H. Kino (NIMS)
- J. Yu (SNU)
- M. J. Han (Columbia Univ.)
- N. Kobayashi (Tsukuba Univ.)
- M. Ohfuti (Fujitsu)
- F. Ishii (Kanazawa Univ.)
- T. Ohwaki (Nissan)
- H. Weng (JAIST)
- M. Toyoda (JAIST)
- K. Terakura (JAIST)

# OpenMX Open source package for Material eXplorer

## Basic methods:

| | |
|---|---|
| Functional: | LDA, GGA, LDA+U |
| Basis function: | Localized pseudoatomic basis funtions |
| Treatment of core: | Norm-conserving peudopotentials (PP) |
| Poisson solver: | Fast Fourier transform (FFT) |
| Integration method: | Regular mesh + projector expansion method |
| Eigenvalue solver: | Householder+QR methods |
| Geometry opt.: | BFGS and eigenvector following (EF) methods |
| Parallelization: | MPI+OpenMP |

## Extensions:

| | |
|---|---|
| O(N) eigenvalue solver: | Krylov subspace, divide-conqure methods |
| Non-collinear DFT: | Two-component spinor with constrained schemes |
| Relativistic effects: | Fully relativistic PP with spin-orbit coupling |
| Electronic polarization: | Berry phase scheme |
| Electronic transport: | Ballistic transport by NEGF |
| Wannier function (WF): | Maximally localized WF and mapping to a TB model |
| …… | |

# Kohn-Sham (KS) equation

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

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

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

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

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

Input charge = Output charge → Self-consistent condition

# Classification of the KS solvers

**Treatment of core electrons**

All electron (AE) method

Pseudopotential (PP) method

**Basis functions**

Plane wave basis (PW)

Mixed basis (MB)

Localized systematic basis (LSB)

Localized atomic basis (LB)

| | Accuracy | Efficiency |
|---|---|---|
| AE+MB: FLAPW | ◎ | × |
| AE+LB: Gaussian | ○ | ○ |
| PP+PW: Plane wave with PP | ○ | ○ |
| PP+LSB: FEM, FDM, wavelet | ○ | ○ |
| PP+LB: OpenMX, SIESTA | △ | ◎ |

# LCPAO method

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

One-particle KS orbital

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

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.

# Why we employ “PP+LB” scheme?

Many of systems we are interested in include more than 100 atoms. Usually, a lot of systematic calculations for such systems have to be performed in order to comprehensively understand the physics and chemistry of the systems.

Thus, the situation in the actual applications of DFT evidently requires the development of a fast solver of the KS method.

We consider that the “PP+LB” scheme can provide a fast solver for the requirement in a balanced way with respect to accuracy and efficiency.

# How about accuracy?

If we are careful enough so that we can spend some time to tune basis functions and pseudopotentials and validate their quality, then the “PP+LB” method can reproduce results by the AE methods and the “PP+PW” methods with considerable accuracy.

However, the convergence of the localized basis functions is not so systematic like PW. This is a well-known problem and can be disadvantage in “PP+LB”.

The tuning process is troublesome in general especially for beginners. But we think that the tuning process itself is a way to understand specific features of each element and chemical environment in molecules and bulks.

# Accuracy:

## Ground state of molecules

Ground state calculations of dimers

PRB 69, 195113 (2004)

| 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-$s2p2d2$) | $\Omega$ [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).

# Accuracy:

## Equilibrium bond length of molecules

**MAE for expt. 0.067 Å**
**MAE for other calc. 0.033 Å**

PRB 69, 195113 (2004)

| | Expt. | OpenMX | Other calc. |
|---|---|---|---|
| $H_2$ | 0.741 [a] | 0.768 | 0.766 [b] |
| $He_2$ | 2.97 [c] | 2.417 | 2.397 [d] |
| $Li_2$ | 2.673 [a] | 2.748 | 2.699 [b] |
| BeO | 1.331 [a] | 1.339 | 1.319 [e] |
| $B_2$ | 1.590 [a] | 1.603 | |
| $C_2$ | 1.243 [a] | 1.255 | 1.249 [f] |
| $N_2$ | 1.098 [a] | 1.104 | 1.094 [b] |
| $O_2$ | 1.208 [a] | 1.201 | 1.197 [g] |
| $F_2$ | 1.412 [a] | 1.435 | 1.388 [b] |
| $Ne_2$ | 3.09 [c] | 2.692 | 2.641 [d] |
| $Na_2$ | 3.079 [a] | 3.140 | 3.048 [b] |
| MgO | 1.749 [a] | 1.770 | 1.76 [h] |
| $Al_2$ | 2.650 [i] | 2.710 | 2.73 [j] |
| $Si_2$ | 2.246 [a] | 2.281 | 2.280 [k] |
| $P_2$ | 1.893 [a] | 1.926 | 1.877 [b] |
| $S_2$ | 1.889 [a] | 1.936 | 1.942 [l] |
| $Cl_2$ | 1.987 [a] | 1.946 | 1.971 [b] |
| $Ar_2$ | 3.76 [c] | 3.425 | 3.42 [d] |
| $K_2$ | 3.905 [a] | 3.620 | 3.670 [b] |
| CaO | 1.822 [a] | 1.768 | 1.79 [h] |
| ScO | 1.668 [a] | 1.719 | 1.649 [b] |
| $Ti_2$ | 1.942 [m] | 1.957 | - |
| $V_2$ | 1.77 [n] | 1.801 | 1.802 [o] |
| $Cr_2$ | 1.679 [p] | 1.643 | 1.632 [q] |
| MnO | 1.648 [r] | 1.673 | 1.585 [b] |
| $Fe_2$ | 2.02 [s] | 2.076 | 1.963 [t] |
| $Co_2$ | - | 2.033 | 1.93 [u] |
| $Ni_2$ | 2.155 [v] | 2.074 | 2.037 [w] |
| $Cu_2$ | 2.220 [a] | 2.249 | 2.170 [w] |
| ZnH | 1.595 [a] | 1.574 | 1.593 [b] |
| GaH | 1.663 [a] | 1.650 | 1.681 [b] |
| GeO | 1.625 [a] | 1.563 | 1.593 [b] |
| $As_2$ | 2.103 [a] | 2.066 | 2.070 [b] |
| $Se_2$ | 2.166 [a] | 2.150 | 2.164 [b] |
| $Br_2$ | 2.281 [a] | 2.257 | 2.273 [b] |
| $Kr_2$ | 3.951 [c] | 3.705 | 3.715 [d] |

# Accuracy:

## Equilibrium lattice constant and bulk modulus of bulks

| M/MN | Lattice parameter (Å) | Bulk modulus (GPa) |
|---|---|---|
| Al (fcc) | $a_c = 4.05$<br>$a_r = 4.049$ [76] | $B_c = 79.4$<br>$B_r = 75.2$ [77] |
| Cr (bcc) | $a_c = 2.92$<br>$a_r = 2.895$ [76] | $B_c = 156.8$<br>$B_r = 160$ [77] |
| Y (hcp) | $a_c = 3.63$ ($c/a = 1.55$)<br>$a_r = 3.647$ ($c/a = 1.57$) [76] | $B_c = 47.4$<br>$B_r = 41.2$ [77] |
| AlN (fcc) | $a_c = 4.13$<br>$a_r = 4.045$, 4.12 [76], 4.094 [40] | $B_c = 262.2$<br>$B_r = 174$–$329$ [78], 252 [18] |
| AlN (hcp) | $a_c = 3.18$ ($c/a = 1.61$)<br>$a_r = 3.11$ ($c/a = 1.60$) [76], 3.157 [79] | $B_c = 198.1$<br>$B_r = 185$–$208$ [18,61,80] |
| CrN (fcc) (AFM) | $a_c = 4.22$<br>$a_r = 4.148$ [76], 4.162 [81], 4.185 [82], 4.206 [40] | $B_c = 277.7$<br>$B_r = 245$ [18] |
| CrN (hcp) | $a_c = 3.19$ ($c/a = 1.62$)<br>$a_r = 3.111$ ($c/a = 1.64$) [18] | $B_c = 185.6$<br>$B_r = 188$ [18] |
| YN (fcc) | $a_c = 4.99$<br>$a_r = 4.76$–$4.93$ [83], 4.89 [76] | $B_c = 151.4$<br>$B_r = 145$–$187$ [83] |
| YN (hcp) | $a_c = 3.83$ ($c/a = 1.57$)<br>$a_r = 3.67 - 3.78$ ($c/a = 1.58$–$1.62$) [83] | $B_c = 112.6$<br>$B_r = 110$–$139$ [83] |

F. Rovere, D. Music, J.M. Schneider, and P.H. Mayrhofer, Acta Materialia 58, 2708 (2010).

The lattice constants are reproduced within error of 1 % compared to other calculations and experimental results.

The bulk moduli are reproduced within error of 15 % compared to other calculations and experimental results.

# When we go beyond LDA

Although LB is not a systematic basis, it can be a practical platform when we go beyond LDA and GGA, where non-local functionals such as the Hartree-Fock exchange are involved.

In the case, the large number of basis functions in the other methods may cause difficulty in the actual applications.

# Points of concern
# for reliable & efficient calculations

- ✓ Choice of basis functions
- ✓ Numerical grid for $E_{tot}$
- ✓ Quality of pseudopotentials

# Basis functions in OpenMX

## 1) Primitive functions

generated by a confinement scheme

## 2) Optimized functions

by an orbital optimization method

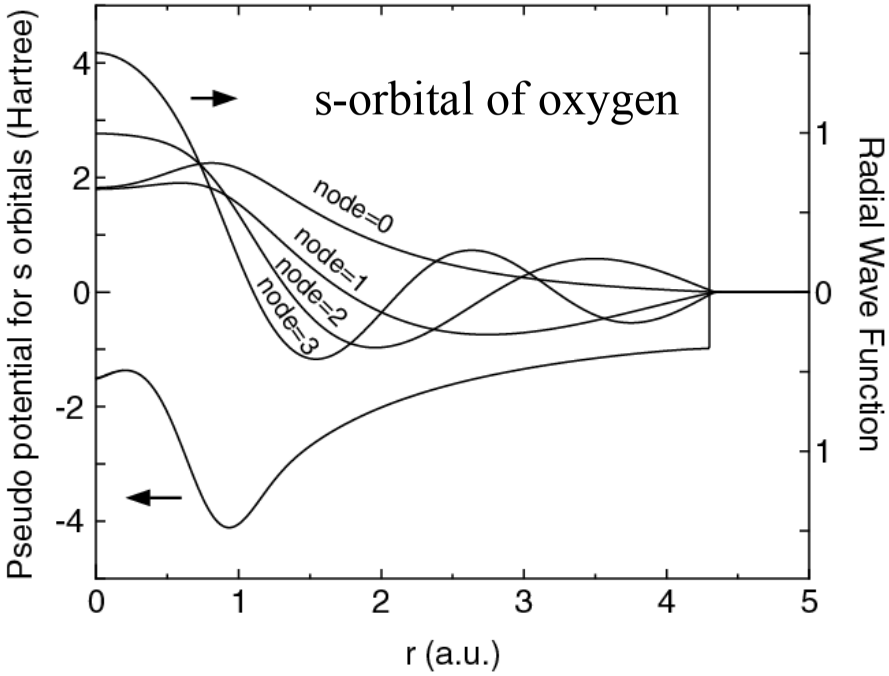
# Primitive basis functions

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

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

2. Construct the norm-conserving pseudopotentials.

3. Solve ground and excited states for the the peudopotentials.



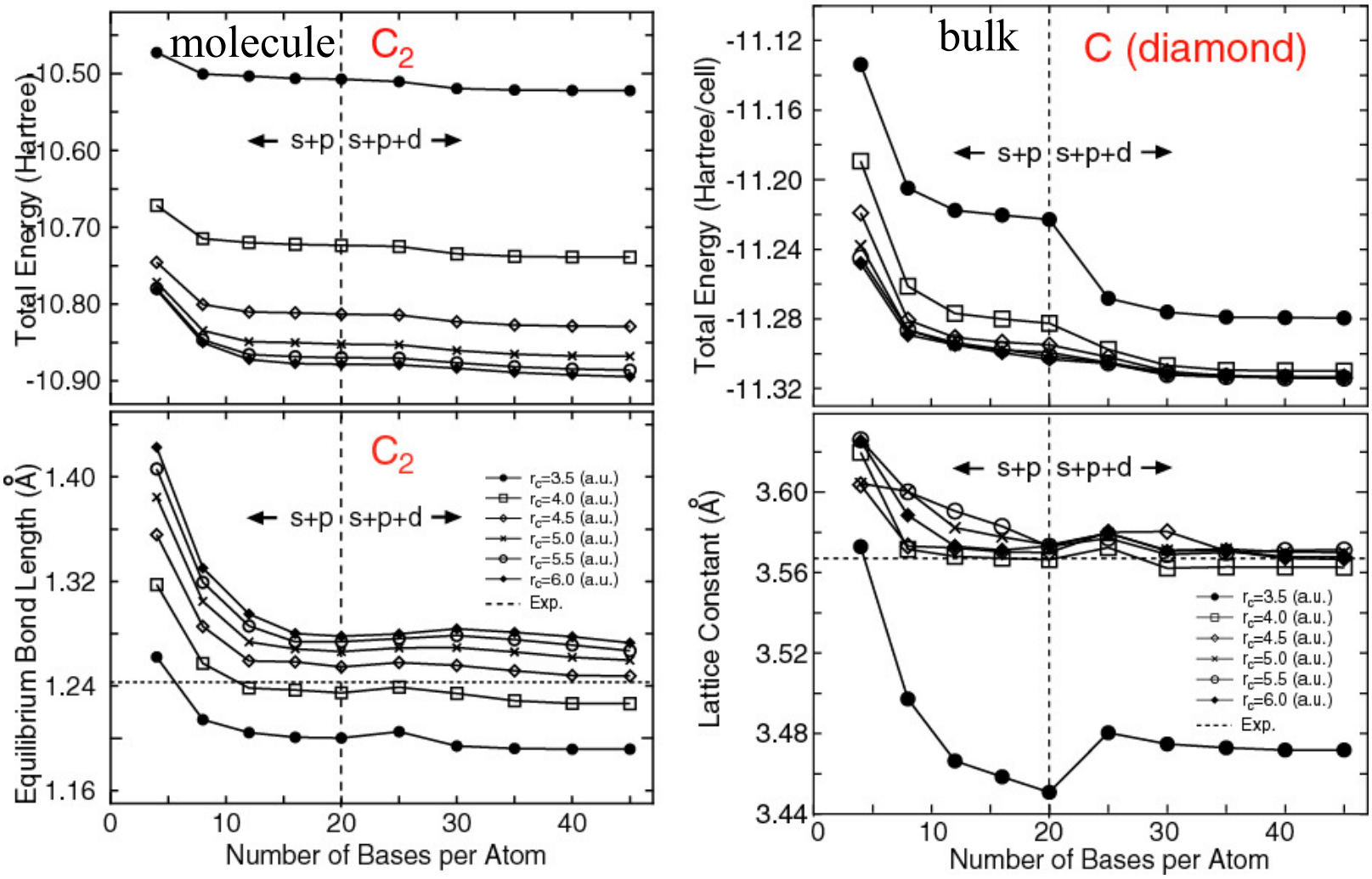

In most cases, the accuracy and efficiency can be controlled by

**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-$s2p2d2$) | $\Omega$ [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)

# Optimization of basis functions

Practically, the accuracy and efficiency can be controlled by

Number of basis functions
Cutoff radius

But, there is another one variational parameter:

Radial shape

If the radial shape can be optimized, it is expected that the high accuracy will be attainable with a small number of basis functions.

# Variational optimization of basis functions No.1

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

$$\frac{\partial E_{\rm tot}}{\partial a} = 0 \qquad \sum_{j\beta}\langle\phi_{i\alpha}|\hat{H}|\phi_{j\beta}\rangle c_{\mu,j\beta} = \varepsilon_\mu \sum_{j\beta}\langle\phi_{i\alpha}|\phi_{j\beta}\rangle c_{\mu,j\beta},$$

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

$$\begin{aligned}
\frac{\partial E_{\rm tot}}{\partial a_{i\alpha q}} &= \frac{\delta E_{\rm tot}}{\delta\rho(\mathbf{r})}\frac{\delta\rho(\mathbf{r})}{\delta a_{i\alpha q}} \\
&= 4\sum_\mu n_\mu \sum_{i\alpha,j\beta} c_{\mu,i\alpha}c_{\mu,j\beta}\langle\frac{\partial\phi_{i\alpha}}{\partial a_{i\alpha q}}|\hat{H}|\phi_{j\beta}\rangle + 4\sum_\mu n_\mu \sum_{i\alpha,j\beta}\frac{\partial c_{\mu,i\alpha}}{\partial a_{i\alpha q}}c_{\mu,j\beta}\langle\phi_{i\alpha}|\hat{H}|\phi_{j\beta}\rangle \\
&= 2\sum_{j\beta}\left(\Theta_{i\alpha,j\beta}\langle\chi_{i\eta}|\hat{H}|\phi_{j\beta}\rangle - E_{i\alpha,j\beta}\langle\chi_{i\eta}|\phi_{j\beta}\rangle\right),
\end{aligned}$$

PRB 67, 155108 (2003)

# Variational optimization of basis functions No.2

The basis functions can be optimized in the same procedure as for the geometry optimization.

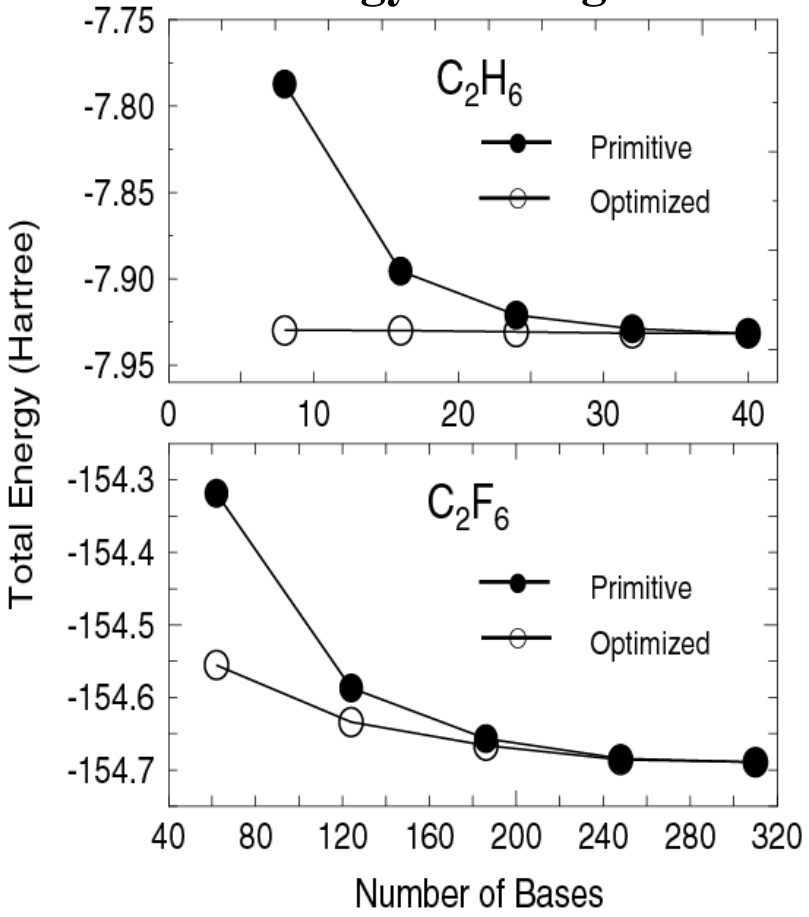
Step 1 Self-consistently solving of Eq. (4),

Step 2 $$a_{i\alpha q}^{(n+1)} = a_{i\alpha q}^{(n)} - \lambda \left( \frac{\partial E_{\mathrm{tot}}}{\partial a_{i\alpha q}} \right)_{a^{(n)}},$$

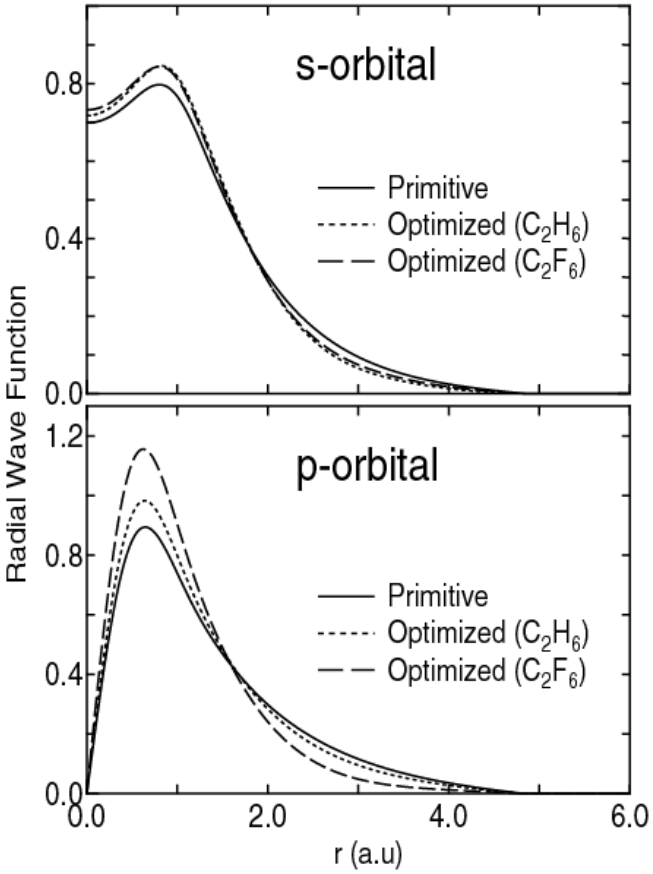
$$n := n + 1,$$

# Primitive vs. Optimized

**Energy convergence**




**Radial shape of carbon atom**




Since the fluorine attracts electrons sitting p-orbitals of carbon, the p-orbital of carbon largely shrinks.

# Points of concern for reliable & efficient calculations

- ✓ Choice of basis functions
- ✓ Numerical grid
- ✓ Quality of pseudopotentials

When you calculate a system consisting of elements A, B, and C, it would be better to start from calculations of elemental systems of A, B and C, which can be easily compared to published results and other codes. These calculations give us a guideline for how large basis functions should be used for these elements. Otherwise, it is difficult to say whether your calculations are reliable or not.

# Possible choice of basis functions

The proper choice of basis functions depends on elements and chemical environment. Although detailed analyses can be found in PRB 69, 195113 (2004) and JCP 121, 10879 (2004), the following can be good starting points.

Examples

| | | | |
|---|---|---|---|
| H4.5-s2 | Li8.0-s2 | Ti5.5-s2p2d1 | Fe5.5-s2p2d1 |
| B4.5-s2p1 | Na9.0-s2 | V5.5-s2p2d1 | Co5.5-s2p2d1 |
| C4.5-s2p1 | K9.0-s2 | Cr5.5-s2p2d1 | Ni5.5-s2p2d1 |
| N4.5-s2p2 | | Mn5.5-s2p2d1 | Cu5.5-s2p2d1 |
| O4.5-s2p2d1 | | | |
| F4.5-s2p2d1 | | | |

Trends:

(1) Elements located in the right side of the periodic table require basis sets with higher angular momentum.

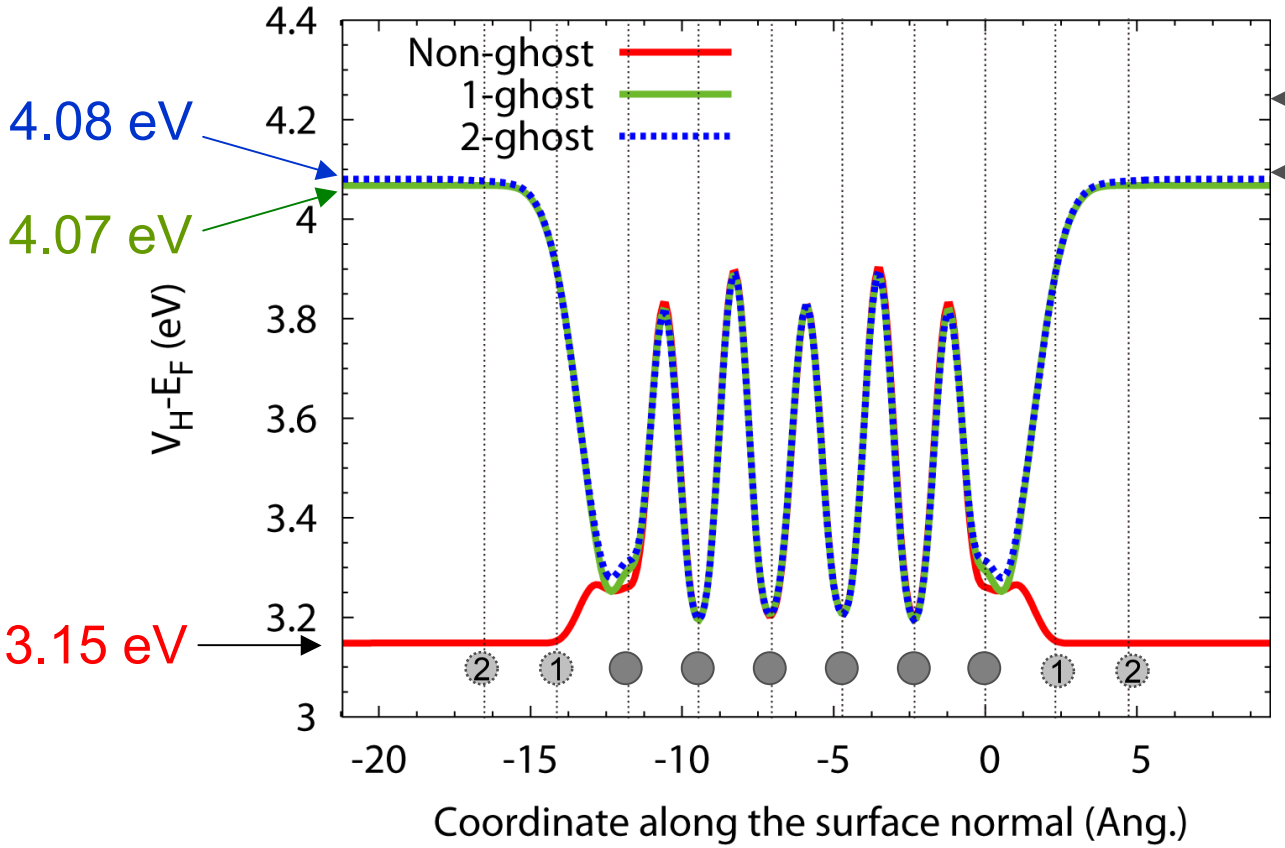
(2) Alkali metals require a long tail of basis functions.

(3) 3d-transition metals are well described by TM5.5-s2p2d1 in their oxide.

# Treatment of surface

## Work function of fcc Al (111) surface

The use of basis functions in the ghost layers is crucial to accurately calculate the work function.




Work function

Exp : 4.24 eV

PW : 4.09 eV

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

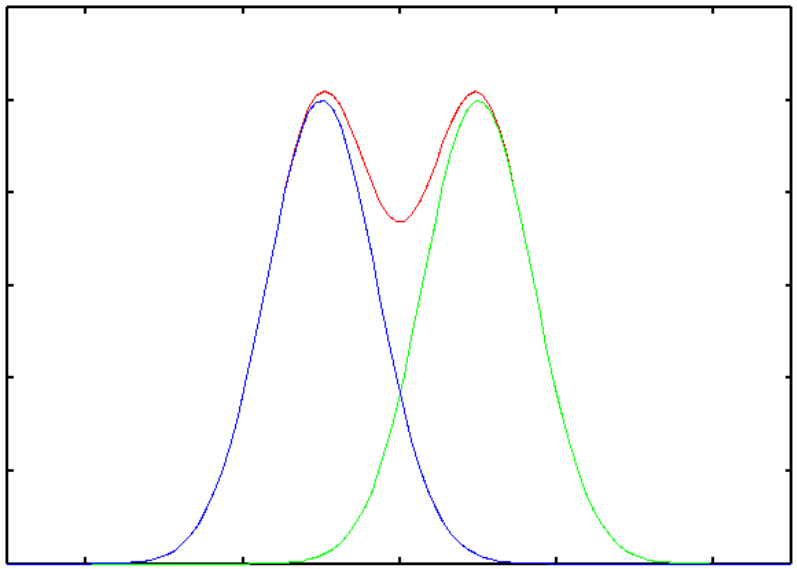
By Jippo and Ohfuti (Fujitsu)

**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)

# Atomization energy:BSSE

## $H_2$ molecule (Expt. 4.5 eV)

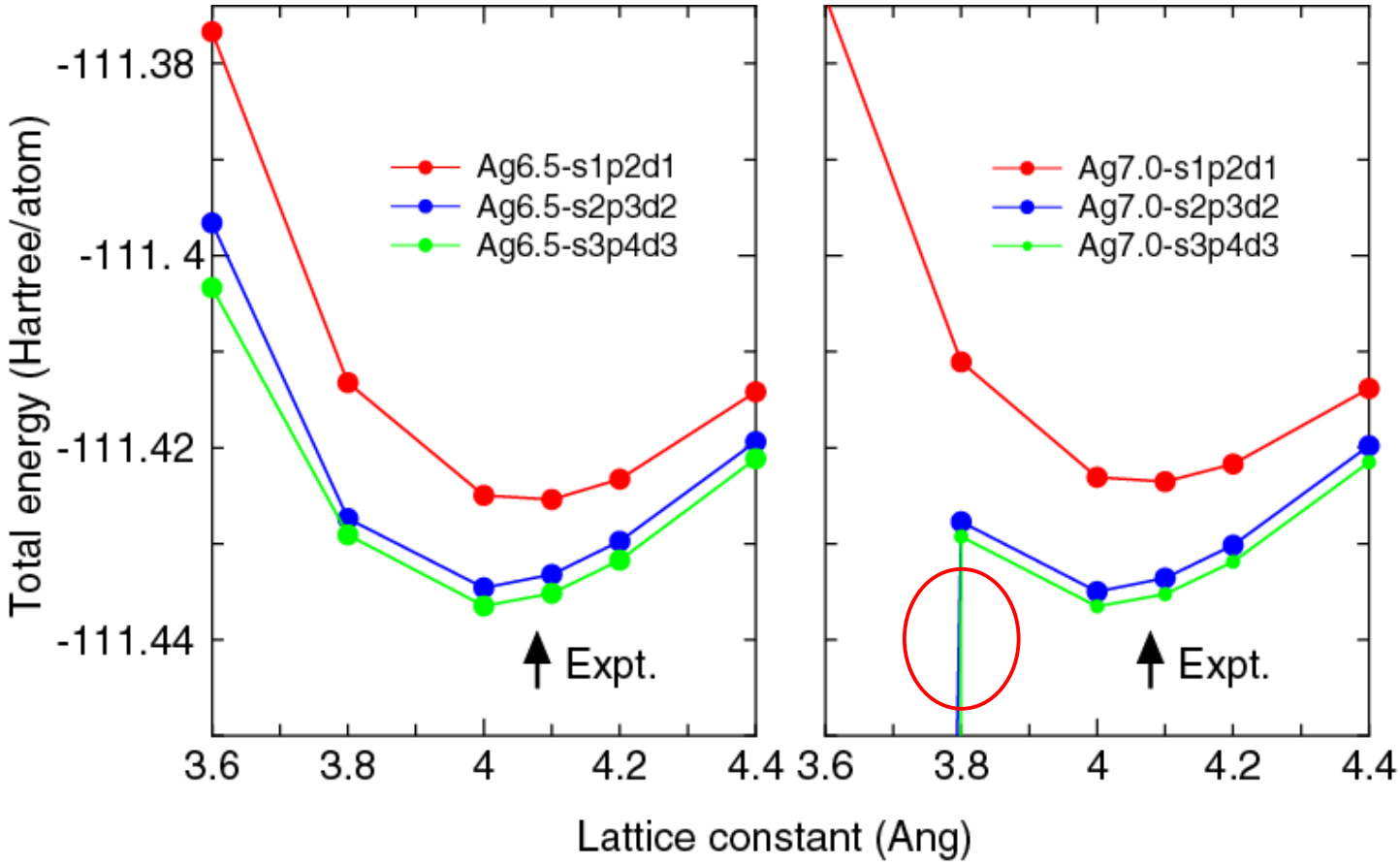
| | H4.0-s1 | H4.0-s2 | H5.5-s4 |
|---|---|---|---|
| Atomization Energy (eV) | 4.89 | 5.35 | 4.88 |
| Corrected by counterpoise method (eV) | 4.68 | 5.18 | 4.85 |
| BSSE (eV) (Basis set superposition error) | 0.21 | 0.17 | 0.03 |



In molecules and bulks, wave functions around certain atom are expressed by basis functions of neighboring atoms. The effect increases the atomization energy. The counterpoise scheme is a prescription.

# Overcompleteness

Total energy curves of fcc-Ag




For dense structures such as fcc, hcp, and bcc, a large basis set tends to cause a numerical instability known as overcompleteness.

# Points of concern
# for reliable & efficient calculations

- ✓ Choice of basis functions
- ✓ Numerical grid for $E_{tot}$
- ✓ Quality of pseudopotentials

# Total energy No.1

**The total energy is given by that of the conventional DFT. The reorganization of the Coulomb energies is a key for the accurate implementation**

$$E_{\rm tot} = E_{\rm kin} + E_{\rm ec} + E_{\rm ee} + E_{\rm xc} + E_{\rm cc}.$$

$$E_{\rm kin} = \sum_{\sigma} \sum_{\rm n}^{N} \sum_{i\alpha,j\beta} \rho^{({\rm R_n})}_{\sigma,i\alpha j\beta} h^{({\rm R_n})}_{i\alpha j\beta,{\rm kin}}.$$

$$E_{\rm ec} = E^{\rm (L)}_{\rm ec} + E^{\rm (NL)}_{\rm ec},$$

$$= \sum_{\sigma} \sum_{\rm n}^{N} \sum_{i\alpha,j\beta} \rho^{({\rm R_n})}_{\sigma,i\alpha j\beta} \langle \phi_{i\alpha}(\mathbf{r}-\tau_i) | \sum_I V_{{\rm core},I}(\mathbf{r}-\tau_I) | \phi_{j\beta}(\mathbf{r}-\tau_j-\mathbf{R}_{\rm n}) \rangle$$

$$+ \sum_{\sigma} \sum_{\rm n}^{N} \sum_{i\alpha,j\beta} \rho^{({\rm R_n})}_{\sigma,i\alpha j\beta} \langle \phi_{i\alpha}(\mathbf{r}-\tau_i) | \sum_I V_{{\rm NL},I}(\mathbf{r}-\tau_I) | \phi_{j\beta}(\mathbf{r}-\tau_j-\mathbf{R}_{\rm n}) \rangle,$$

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

$$= \frac{1}{2} \int dr^3 n(\mathbf{r}) \{ V^{\rm (a)}_{\rm H}(\mathbf{r}) + \delta V_{\rm H}(\mathbf{r}) \},$$

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

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

# Total energy No.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

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

Difference charge Hartree energy

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

Screened core-core repulsion energy

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

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

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

# Total energy No.3

So, the total energy is given by

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

Each term is evaluated by using a different numerical grid.

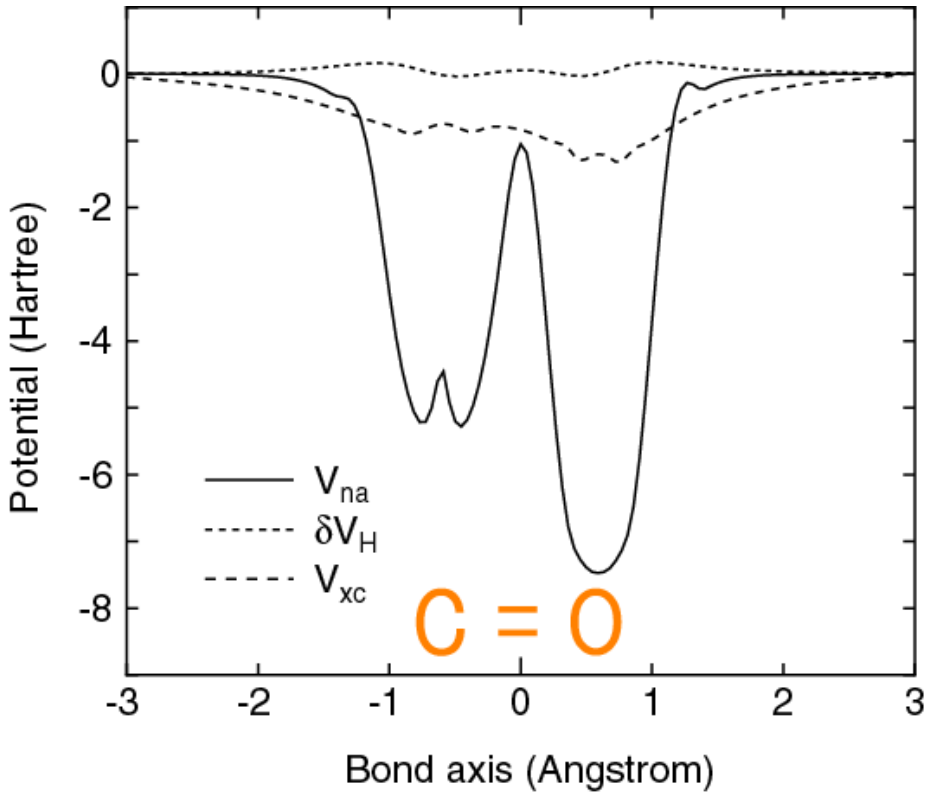
$E_{\rm kin}$
$E_{\rm na}$ } Spherical coordinate in momentum space
$E_{\rm ec}^{\rm (NL)}$

$E_{\delta \rm ee}$
$E_{\rm xc}$ } Real space regular mesh

$E_{\rm scc}$ Real space fine mesh

# Projector expansion of $V_{na}$ No.1

$V_{na}$ tends to be very deep, leading to a serious numerical problem.




$$V_{\rm eff} = \sum_k V_{{\rm NL},k} + \sum_k V_{{\rm na},k} + \delta V_{\rm H} + V_{\rm xc},$$

$V_{na}$ can be expanded by projectors:

$$\hat{V}_{{\rm na},k} = \sum_{lm}^{L_{\rm max}} \sum_{\zeta}^{N_{\rm rad}} |V_{{\rm na},k} \bar{R}_{l\zeta} Y_{lm}\rangle \frac{1}{c_{l\zeta}} \langle Y_{lm} \bar{R}_{l\zeta} V_{{\rm na},k}|,$$

where a set of radial functions $\{R_{l\zeta}\}$ is an orthonormal set defined by a norm $\int r^2 dr R V_{na,k} R'$ for radial functions $R$ and $R'$, and is calculated by the following Gram-Schmidt orthogonalization:

$$\bar{R}_{l\zeta} = R_{l\zeta} - \sum_{\eta}^{\zeta-1} \bar{R}_{l\eta} \frac{1}{c_{l\eta}} \int r^2 dr \bar{R}_{l\eta} V_{{\rm na},k} R_{l\zeta},$$

$$c_{l\zeta} = \int r^2 dr \bar{R}_{l\zeta} V_{{\rm na},k} \bar{R}_{l\zeta}.$$

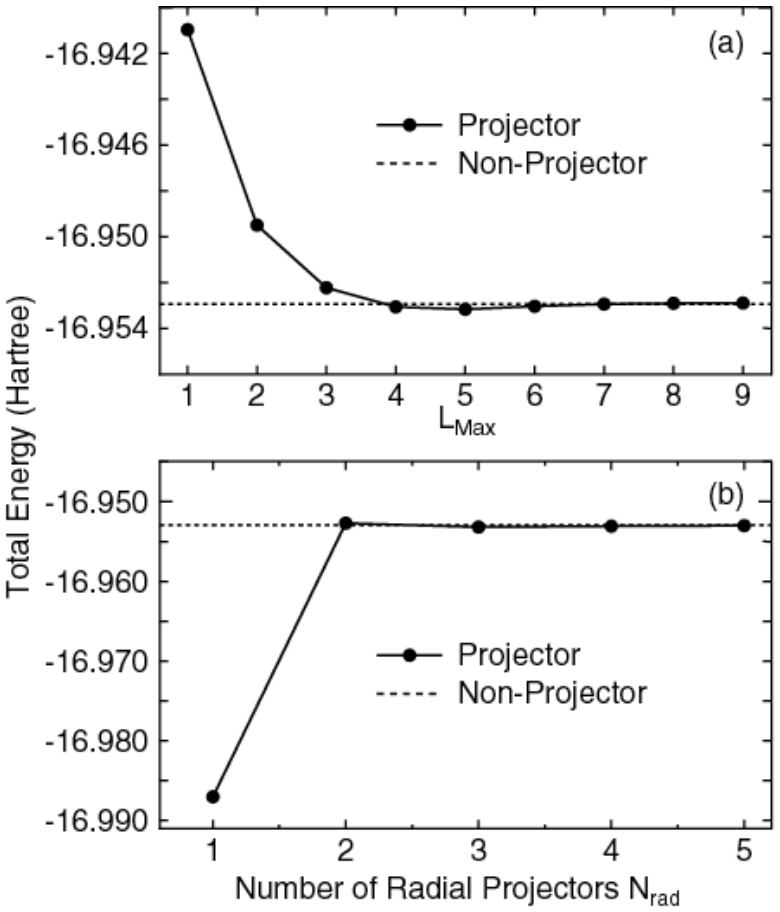
TO and H.Kino, PRB 72, 045121 (2005)

Three center integrals with $V_{na}$ can be transformed to products of two center integrals by the projector expansion method.

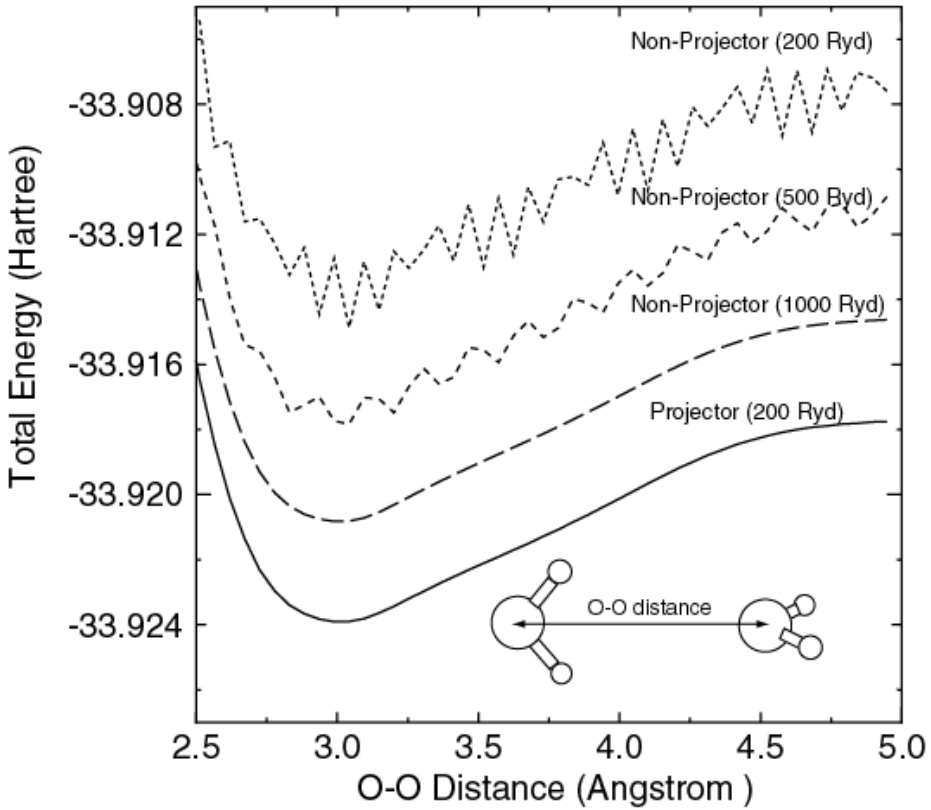
# Projector expansion of $V_{na}$ No.2

Convergence properties

$$\hat{V}_{\mathrm{na},k} = \sum_{lm}^{L_{\max}} \sum_{\zeta}^{N_{\mathrm{rad}}} |V_{\mathrm{na},k}\bar{R}_{l\zeta}Y_{lm}\rangle \frac{1}{c_{l\zeta}} \langle Y_{lm}\bar{R}_{l\zeta}V_{\mathrm{na},k}|,$$




Comparison between non-projector and projector methods



# Two center integrals

## Fourier-transformation of basis functions

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

## e.g., overlap integral

$$
\begin{aligned}
\langle \phi_{i\alpha}(\mathbf{r}) | \phi_{j\beta}(\mathbf{r}-\tau) \rangle &= \int dr^3 \phi^*_{i\alpha}(\mathbf{r}) \phi_{j\beta}(\mathbf{r}-\tau), \\
&= \int dr^3 \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dk^3 \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \left(\frac{1}{\sqrt{2\pi}}\right)^3 \int dk'^3 \tilde{R}_{p'l'}(k') Y_{l'm'}(\hat{\mathbf{k}}') \mathrm{e}^{\mathrm{i}\mathbf{k}'\cdot(\mathbf{r}-\tau)}, \\
&= \left(\frac{1}{2\pi}\right)^3 \int dk^3 \int dk'^3 \mathrm{e}^{-\mathrm{i}\mathbf{k}'\cdot\tau} \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k') Y_{l'm'}(\hat{\mathbf{k}}') \int dr^3 \mathrm{e}^{\mathrm{i}(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}, \\
&= \int dk^3 \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\tau} \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k) Y_{l'm'}(\hat{\mathbf{k}}), \\
&= \int dk^3 \left[ 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-\mathrm{i})^L j_L(kr) Y_{LM}(\hat{\mathbf{k}}) Y^*_{LM}(\hat{\mathbf{r}}) \right] \tilde{R}^*_{pl}(k) Y^*_{lm}(\hat{\mathbf{k}}) \tilde{R}_{p'l'}(k) Y_{l'm'}(\hat{\mathbf{k}}), \\
&= 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-\mathrm{i})^L Y^*_{LM}(\hat{\tau}) C_{l(-m),l'm',LM} \int dk k^2 j_L(k|\tau|) \tilde{R}^*_{pl}(k) \tilde{R}_{p'l'}(k),
\end{aligned}
$$

# Forces

$$\mathbf{F}_i = -\frac{\partial E_{\rm tot}}{\partial \mathbf{R}_i}$$

$$= -\frac{\partial E_{\rm kin}}{\partial \mathbf{R}_i} - \frac{\partial E_{\rm na}}{\partial \mathbf{R}_i} - \frac{\partial E_{\rm scc}}{\partial \mathbf{R}_i} - \frac{\partial E_{\delta\rm ee}}{\partial \mathbf{R}_i} - \frac{\partial E_{\rm xc}}{\partial \mathbf{R}_i} - \frac{\partial E_{\rm cc}}{\partial \mathbf{R}_i}$$

$$\frac{\partial E_{\delta\rm ee}}{\partial \mathbf{R}_k} = \sum_{\rm p} \frac{\partial n(\mathbf{r}_{\rm p})}{\partial \mathbf{R}_k} \frac{\partial E_{\delta\rm ee}}{\partial n(\mathbf{r}_{\rm p})} + \sum_{\rm p} \frac{\partial n^{\rm a}(\mathbf{r}_{\rm p})}{\partial \mathbf{R}_k} \frac{\partial E_{\delta\rm ee}}{\partial n^{\rm a}(\mathbf{r}_{\rm p})}.$$

$$\frac{\partial E_{\delta\rm ee}}{\partial n(\mathbf{r}_{\rm p})} = \frac{1}{2}\Delta V\{\delta V_{\rm H}(\mathbf{r}_{\rm p}) + \sum_{\rm q} \delta n(\mathbf{r}_{\rm q}) \frac{\partial \delta V_{\rm H}(\mathbf{r}_{\rm q})}{\partial n(\mathbf{r}_{\rm p})}\},$$

$$= \frac{1}{2}\Delta V\{\delta V_{\rm H}(\mathbf{r}_{\rm p}) + \frac{4\pi}{N_{\rm rsg}} \sum_{\rm G} \frac{1}{|\mathbf{G}|^2} \sum_{\rm q} \delta n(\mathbf{r}_{\rm q}) e^{i\mathbf{G}\cdot(\mathbf{r}_{\rm q}-\mathbf{r}_{\rm p})}\},$$

$$= \Delta V \delta V_{\rm H}(\mathbf{r}_{\rm p}).$$

$$\frac{\partial E_{\delta\rm ee}}{\partial n^{\rm a}(\mathbf{r}_{\rm p})} = -\frac{1}{2}\Delta V\{\delta V_{\rm H}(\mathbf{r}_{\rm p}) - \sum_{\rm q} \delta n(\mathbf{r}_{\rm q}) \frac{\partial \delta V_{\rm H}(\mathbf{r}_{\rm q})}{\partial n^{\rm a}(\mathbf{r}_{\rm p})}\},$$

$$= -\frac{1}{2}\Delta V\{\delta V_{\rm H}(\mathbf{r}_{\rm p}) + \frac{4\pi}{N_{\rm rsg}} \sum_{\rm G} \frac{1}{|\mathbf{G}|^2} \sum_{\rm q} \delta n(\mathbf{r}_{\rm q}) e^{i\mathbf{G}\cdot(\mathbf{r}_{\rm q}-\mathbf{r}_{\rm p})}\},$$

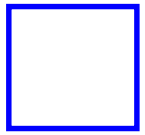
$$= -\Delta V \delta V_{\rm H}(\mathbf{r}_{\rm p}).$$

$$\frac{\partial n(\mathbf{r}_{\rm p})}{\partial \mathbf{R}_k} = \sum_{i\alpha,j\beta} \sum_{\nu} \{\frac{\partial c^*_{i\alpha,\nu}}{\partial \mathbf{R}_k} c_{j\beta,\nu} \chi_{i\alpha}(\mathbf{r}) \chi_{j\beta}(\mathbf{r}) + c^*_{i\alpha,\nu} \frac{\partial c_{j\beta,\nu}}{\partial \mathbf{R}_k} \chi_{i\alpha}(\mathbf{r}_{\rm p}) \chi_{j\beta}(\mathbf{r}_{\rm p})\}$$

$$+2 \sum_{\alpha,j\beta} \rho_{k\alpha,j\beta} \frac{\partial \chi_{k\alpha}(\mathbf{r}_{\rm p})}{\partial \mathbf{R}_k} \chi_{j\beta}(\mathbf{r}_{\rm p}).$$

$$\frac{\partial E_{\rm xc}}{\partial \mathbf{R}_k} = \sum_{\rm p} \frac{\partial n(\mathbf{r}_{\rm p})}{\partial \mathbf{R}_k} \frac{\partial E_{\rm xc}}{\partial n(\mathbf{r}_{\rm p})},$$

$$= \Delta V \sum_{\rm p} \frac{\partial n(\mathbf{r}_{\rm p})}{\partial \mathbf{R}_k} v_{\rm xc}(n(\mathbf{r}_{\rm p})).$$



**Easy calc.**

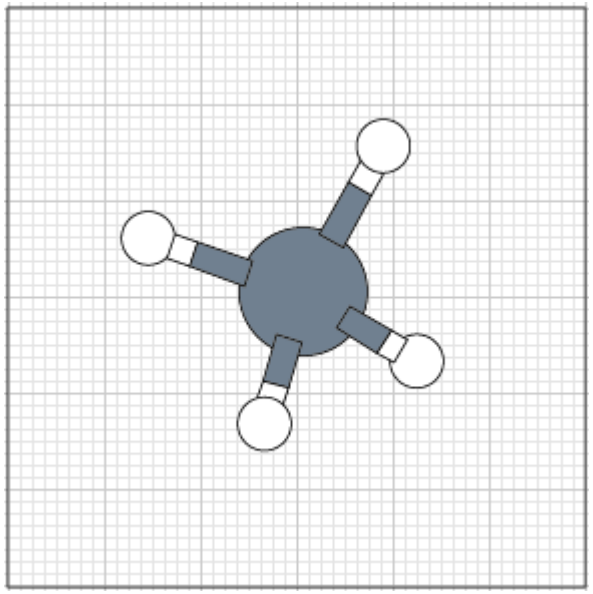
**See the left**

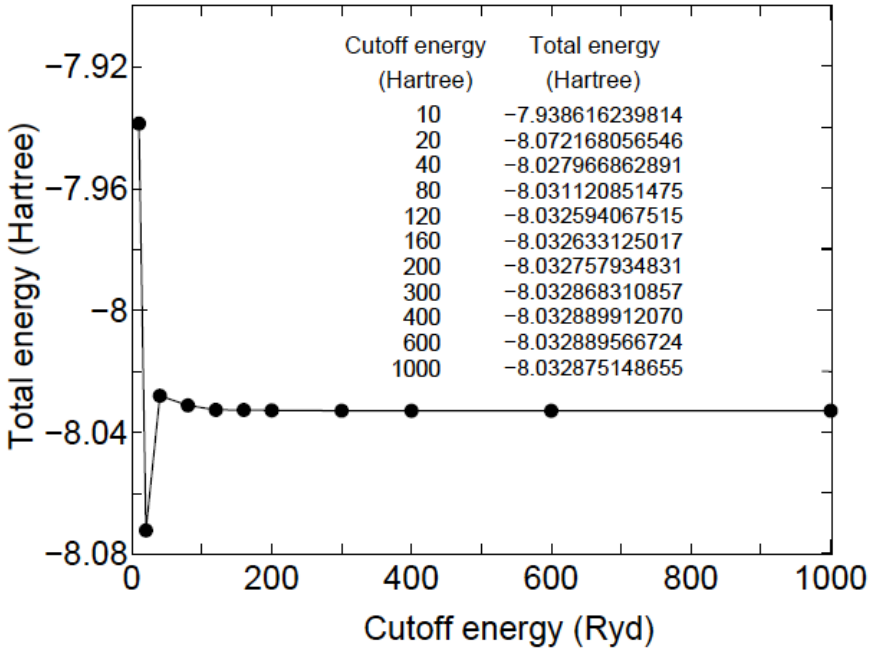
Forces are always analytic at any grid fineness and at zero temperature, even if numerical basis functions and numerical grids.

# Points of concern for reliable & efficient calculations

- ✓ Choice of basis functions
- ✓ Numerical grid
- ✓ Quality of pseudopotentials
- ✓ Charge mixing

The proper choice of the cutoff energy depends on system. 150-250 Ryd is a reasonable choice in most cases.





# Points of concern
# for reliable & efficient calculations

- ✓ Choice of basis functions
- ✓ Numerical grid
- ✓ Quality of pseudopotentials

Even though we get convergent results with respect to basis functions and numerical grid, if our results differ from the other calculated results, then the origin of the discrepancy can be attributed to pseudopotentials we used.

Then, we have to return the optimization of pseudopotentials.

# Relativistic norm-conserving pseudopotential

Radial Dirac eq. for the majority component

$$\left[\frac{1}{2M(r)}\left(\frac{d^2}{dr^2}+\frac{a^2}{2M(r)}\frac{dV}{dr}\frac{d}{dr}+\frac{a^2}{2M(r)}\frac{\kappa}{r}\frac{dV}{dr}-\frac{\kappa(\kappa+1)}{r^2}\right)+\varepsilon_{nlj}-V\right]G_{nlj}=0$$

$$M(r) = 1+\frac{a^2(\varepsilon_{nlj}-V)}{2} \qquad \kappa=l \text{ and } \kappa=-(l+1) \text{ for } j=l-\tfrac{1}{2} \text{ and } j=l+\tfrac{1}{2}$$

For each quantum number j, the Dirac eq. is solved numerically,
and its norm-conserving pseudopotential is constructed by the TM scheme.

**The unified pseudopotential is given by**

$$V_{\rm ps} = \sum_{lm}\left[|\Phi_J^M\rangle V_{\rm ps}^{l+\frac{1}{2}}\langle\Phi_J^M| + |\Phi_{J'}^{M'}\rangle V_{\rm ps}^{l-\frac{1}{2}}\langle\Phi_{J'}^{M'}|\right]$$

with the analytic solution for spherical coordinate:

where for $J=l+\frac{1}{2}$ and $M=m+\frac{1}{2}$

$$|\Phi_J^M\rangle = \left(\frac{l+m+1}{2l+1}\right)^{\frac{1}{2}}|Y_l^m\rangle|\alpha\rangle+\left(\frac{l-m}{2l+1}\right)^{\frac{1}{2}}|Y_l^{m+1}\rangle|\beta\rangle,$$

and for $J'=l-\frac{1}{2}$ and $M'=m-\frac{1}{2}$

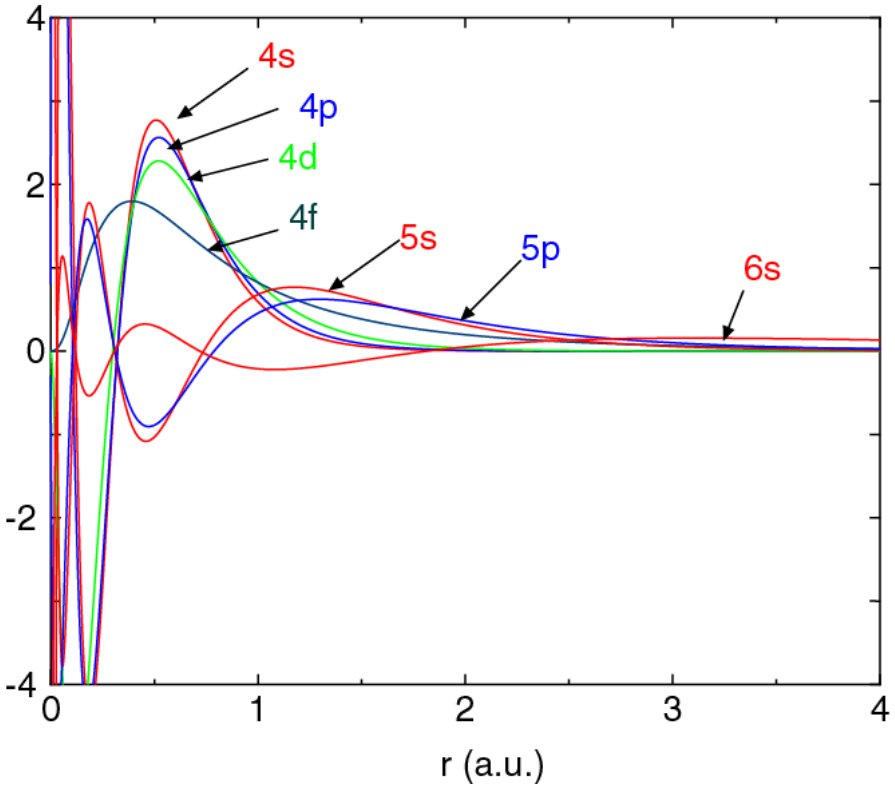
$$|\Phi_{J'}^{M'}\rangle = \left(\frac{l-m+1}{2l+1}\right)^{\frac{1}{2}}|Y_l^{m-1}\rangle|\alpha\rangle-\left(\frac{l+m}{2l+1}\right)^{\frac{1}{2}}|Y_l^{m}\rangle|\beta\rangle.$$

# Relativistic norm-conserving pseudopotential

- All the relativistic effects including the SO coupling are taken into account in the non-collinear calculations.
- In the collinear calculations, the j-dependency is averaged by considering the degeneracy of j, leading to a scalar relativistic pseudopotential.
- The norm-conservation guarantees the correct scattering property around the chosen reference energy for each angular momentum channel.
- The obtained wave function is a pseudo-wave function.
- The non-linearity of exchange-correlation functionals is partially taken into account through the partial core correction.

# Difficult case for the TM pseudopotentials (PP)

All electron wave functions of Pr




Eigenvalues (Hartree)

| | |
|---|---|
| n= 4 l= 0 | -10.5170412883091 |
| n= 4 l= 1 | -7.9076209877241 |
| n= 4 l= 2 | -4.0759804960218 |
| **n= 4 l= 3** | **-0.0525968308191** |
| n= 5 l= 0 | -1.4327844478065 |
| n= 5 l= 1 | -0.8007101193618 |
| n= 6 l= 0 | -0.1346442737184 |

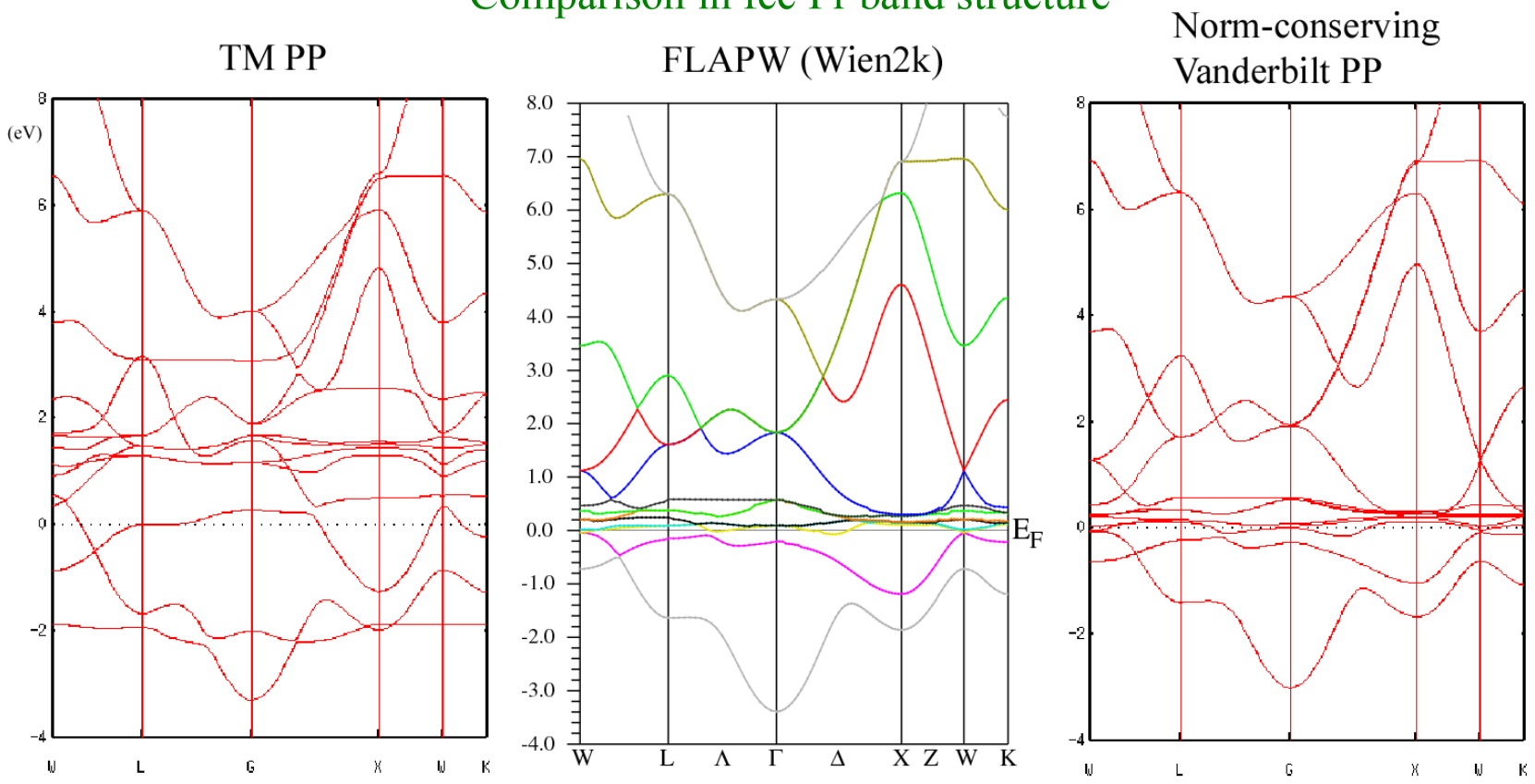
Although the eigenvalue of 4f is close to zero, the peak of the wave function is located in the inner region. This produces a very strong non-linear correlation among 4s, 4p, 4d, 4f, 5s, 5p, and 6s in the exchange-correlation .

Thus, at least it would be better to include 4f, 5s, 5p, and 6s as valence states. However, if the pseudopotential for the s-state is generated for 5s, then the description of the 6s state becomes very poor.

# Norm-conserving Vanderbilt PP

We have been developing a norm-conserving Vanderbilt PP which can employ multiple reference energies for each L-channel. (Morrison et al., PRB 47, 6728 (1993))

Comparison in fcc Pr band structure




The norm-conserving Vanderbilt PP looks very promising.

# Optimization of pseudopotential

- ✓ The number of valence electrons
- ✓ The number of reference energies
- ✓ Choice of cutoff radii
- ✓ Choice of local part
- ✓ Partial core correction (PCC) charge

# Ongoing developments

- $O(N^{2\sim})$ method
- Hybrid functionals
- Effective screening medium (ESM) method
- Several methods using Wannier functions
- Improvement of pseudopotentials
- Improvement of basis functions

# Summary

OpenMX is a state-of-the art software package based on the local PAO basis functions and norm-conserving pseudopotentials.

The method can provide reasonable computational accuracy and effciency in a balanced way for a wide variety of systems including solid state and molecular systems with careful consideration for the basis functions and pseudopotentials. The following items should be taken into account by users.

- ✓ Choice of basis functions
- ✓ Numerical grid
- ✓ Quality of pseudopotentials
- ✓ Charge mixing

To improve the reliability and efficiency, and to add more functionalities, the code is still under development.