Localized basis methods
Theory and implementations

• Introduction of OpenMX
• Implementation of OpenMX
  ➢ Total energy
  ➢ Pseudopentials
  ➢ Basis functions
  ➢ Self-consistency

• $\Delta$-gauge

Taisuke Ozaki (ISSP, Univ. of Tokyo)

The Winter School on DFT: Theories and Practical Aspects, Dec. 19-23, CAS.
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 Mulliken, 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 functions

**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.

2015  18 public releases
       Latest version: 3.8

About 400 papers published using OpenMX

http://www.openmx-square.org
Developers of OpenMX

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

- T. V. Truong Duy (U.Tokyo)
- C.-C. Lee (Univ. of Tokyo)
- Y. Okuno (Fuji FILM)
- Yang Xiao (NUAA)
- F. Ishii (Kanazawa Univ.)
- K. Sawada (RIKEN)
- Y. Kubota (Kanazawa Univ.)
- Y.P. Mizuta (Kanazawa Univ.)
- M. Kawamura (Univ. of Tokyo)
- K. Yoshimi (Univ. of Tokyo)
First characterization of silicene on ZrB$_2$ in collaboration with experimental groups

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

Theoretical proposal of topological insulators

First-principles molecular dynamics simulations for Li ion battery

Electronic transport of graphene nanoribbon on surface oxidized Si

Interface structures of carbide precipitate in bcc-Fe

Universality of medium range ordered structure in amorphous metal oxides

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 400 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)

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

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

\[ \hat{H}_{KS}\phi_i = \varepsilon_i\phi_i \]
\[ \hat{H}_{KS} = -\frac{1}{2}\nabla^2 + v_{\text{eff}} \]
\[ v_{\text{eff}} = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \]
3D coupled non-linear differential equations have to be solved self-consistently.

\[ \hat{H}_{KS} \phi_i = \varepsilon_i \phi_i \]

\[ \hat{H}_{KS} = -\frac{1}{2} \nabla^2 + v_{\text{eff}} \]

\[ \rho(\mathbf{r}) = \sum_{i}^{\text{occ}} \phi_{i}^*(\mathbf{r}) \phi_{i}(\mathbf{r}) \]

\[ \nabla^2 v_{\text{Hartree}}(\mathbf{r}) = -4\pi \rho(\mathbf{r}) \]

\[ v_{\text{eff}} = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \]

Input charge = Output charge → Self-consistent condition
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.
<table>
<thead>
<tr>
<th>Classification of the KS solvers</th>
<th>Treatment of core electrons</th>
<th>Basis functions</th>
<th>PP+PW: Plane wave with PP</th>
<th>PP+LB: OpenMX, SIESTA</th>
<th>AE+MB: LAPW, LMTO</th>
<th>AE+LB: Gaussian</th>
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<tr>
<td>Accuracy</td>
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<td>△</td>
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</table>
One-particle KS orbital

\[ \psi_{\sigma\mu}^{(k)} (\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i \mathbf{R}_n \cdot \mathbf{k}} \sum_{i\alpha} c_{\sigma\mu,i\alpha}^{(k)} \phi_{i\alpha} (\mathbf{r} - \mathbf{R}_n), \]

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
Self-consistency
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.

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

- **Kinetic energy**
  \[ E_{\text{kin}} = \sum_{\sigma} \sum_{n} \sum_{i, j, \alpha, \beta} \rho_{\sigma, i, \alpha}^{(R_n)} \hat{h}_{i, \alpha}^{(R_n)} \hat{h}_{j, \beta, \text{kin}}. \]

- **Coulomb energy with external potential**
  \[ E_{\text{ec}} = E_{\text{ec}}^{(L)} + E_{\text{ec}}^{(\text{NL})}, \]
  \[ E_{\text{ec}} = \sum_{\sigma} \sum_{n} \sum_{i, j, \alpha, \beta} \rho_{\sigma, i, \alpha}^{(R_n)} \phi_{i, \alpha}(r - \tau_i) \left| \sum_{I} V_{\text{core}, I}(r - \tau_I) \phi_{j, \beta}(r - \tau_j - R_n) \right| \]
  \[ + \sum_{\sigma} \sum_{n} \sum_{i, j, \alpha, \beta} \rho_{\sigma, i, \alpha}^{(R_n)} \phi_{i, \alpha}(r - \tau_i) \left| \sum_{I} V_{\text{NL}, I}(r - \tau_I) \phi_{j, \beta}(r - \tau_j - R_n) \right|, \]

- **Hartree energy**
  \[ E_{\text{ee}} = \frac{1}{2} \int dr^3 n(r) V_{H}(r), \]
  \[ E_{\text{ee}} = \frac{1}{2} \int dr^3 n(r) \left\{ V_{H}^{(a)}(r) + \delta V_{H}(r) \right\}, \]

- **Exchange-correlation energy**
  \[ E_{\text{xc}} = \int dr^3 \left\{ n_{\uparrow}(r) + n_{\downarrow}(r) + n_{\text{pcc}}(r) \right\} \epsilon_{\text{xc}}(n_{\uparrow} + \frac{1}{2} n_{\text{pcc}}, n_{\downarrow} + \frac{1}{2} n_{\text{pcc}}), \]

- **Core-core Coulomb energy**
  \[ E_{\text{cc}} = \frac{1}{2} \sum_{I, J} \frac{Z_I Z_J}{|\tau_I - \tau_J|}. \]

TO and H.Kino, PRB 72, 045121 (2005)
The reorganization of Coulomb energies gives three new energy terms.

\[ E_{ec}^{(L)} + E_{ee} + E_{cc} = E_{na} + E_{\delta ee} + E_{sc}, \]

The neutral atom energy

\[ E_{na} = \int dr^3 n(r) \sum_I V_{na,I}(r - \tau_I), \]

\[ = \sum_{\sigma,n} \sum_{i,\alpha,j,\beta} \rho_{\sigma,i,\alpha,j,\beta}^{(R_n)} \sum_I \langle \phi_{i\alpha}(r - \tau_i) | V_{na,I}(r - \tau_I) | \phi_{j\beta}(r - \tau_j - R_n) \rangle, \]

Difference charge Hartree energy

\[ E_{\delta ee} = \frac{1}{2} \int dr^3 \delta n(r) \delta V_H(r), \]

Screened core-core repulsion energy

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

Difference charge

\[ \delta n(r) = n(r) - n^{(a)}(r), \]

\[ = n(r) - \sum_i n_i^{(a)}(r), \]

Neutral atom potential

\[ V_{na,I}(r - \tau_I) = V_{\text{core},I}(r - \tau_I) + V_{H,I}^{(a)}(r - \tau_I). \]
So, the total energy is given by

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

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

$E_{\text{kin}}$

$E_{\text{na}}$

$E_{\text{ec}}^{(\text{NL})}$

$E_{\text{dee}}$

$E_{\text{xc}}$

$E_{\text{scc}}$

\[
\begin{align*}
\{ & E_{\text{kin}} \} \quad \text{Spherical coordinate in momentum space} \\
\{ & E_{\text{na}}, E_{\text{ec}}^{(\text{NL})} \} \quad \text{Spherical coordinate in momentum space} \\
\{ & E_{\text{dee}}, E_{\text{xc}} \} \quad \text{Real space regular mesh} \\
E_{\text{scc}} \quad \text{Real space fine mesh}
\end{align*}
\]
Two center integrals

Fourier-transformation of basis functions

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

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

\[
\langle \phi_{i\alpha}(r) | \phi_{j\beta}(r - \tau) \rangle = \int dr^3 \phi_{i\alpha}^*(r) \phi_{j\beta}(r - \tau), \\
= \int dr^3 \left( \frac{1}{\sqrt{2\pi}} \right)^3 \int dk^3 \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{k}) e^{-ik \cdot r} \left( \frac{1}{\sqrt{2\pi}} \right)^3 \int dk'^3 \tilde{R}_{p'l'}(k') Y_{lm'}(\hat{k'}) e^{ik' \cdot (r - \tau)}, \\
= \left( \frac{1}{2\pi} \right)^3 \int dk^3 \int dk'^3 e^{-ik' \cdot \tau} \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{k}) \tilde{R}_{p'l'}(k') Y_{lm'}(\hat{k'}) \int dr^3 e^{i(k' - k) \cdot r}, \\
= \int dk^3 e^{-i k \cdot \tau} \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{k}) \tilde{R}_{p'l'}(k') Y_{lm'}(\hat{k}),
\]
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.

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

$$E_{\text{cut}}^{(1)} = \frac{1}{2} gb_1 \cdot gb_1, \quad E_{\text{cut}}^{(2)} = \frac{1}{2} gb_2 \cdot gb_2, \quad E_{\text{cut}}^{(3)} = \frac{1}{2} gb_3 \cdot gb_3,$$

$$ga_1 = \frac{a_1}{N_1}, \quad ga_2 = \frac{a_2}{N_2}, \quad ga_3 = \frac{a_3}{N_3},$$

$$gb_1 = 2\pi \frac{ga_2 \times ga_2}{\Delta V}, \quad gb_2 = 2\pi \frac{ga_3 \times ga_1}{\Delta V}, \quad gb_3 = 2\pi \frac{ga_1 \times ga_2}{\Delta V},$$

$$\Delta V = ga_1 \cdot (ga_2 \times ga_3),$$
Forces

\[ F_i = -\frac{\partial E_{\text{tot}}}{\partial R_i} = -\frac{\partial E_{\text{kin}}}{\partial R_i} - \frac{\partial E_{\text{na}}}{\partial R_i} - \frac{\partial E_{\text{scf}}}{\partial R_i} - \frac{\partial E_{\delta\text{e}}}{\partial R_i} - \frac{\partial E_{\text{xc}}}{\partial R_i} - \frac{\partial E_{\text{cc}}}{\partial R_i} \]

\[
\frac{\partial E_{\delta\text{e}}}{\partial R_k} = \sum \frac{\partial n(r_p)}{\partial R_k} \frac{\partial E_{\delta\text{e}}}{\partial n(r_p)} + \sum \frac{\partial n^a(r_p)}{\partial R_k} \frac{\partial E_{\delta\text{e}}}{\partial n^a(r_p)}.
\]

\[
\frac{\partial E_{\delta\text{e}}}{\partial n(r_p)} = \frac{1}{2} \Delta V \{ \delta V_H(r_p) + \sum_q \delta n(r_q) \frac{\partial V_H(r_q)}{\partial n(r_p)} \},
\]

\[
= \frac{1}{2} \Delta V \{ \delta V_H(r_p) + \frac{4\pi}{N_{\text{rg}}} \sum_q \frac{1}{|G|^2} \sum_q \delta n(r_q) e^{iG \cdot (q_r - r_p)} \},
\]

\[
= \Delta V \delta V_H(r_p).
\]

\[
\frac{\partial E_{\delta\text{e}}}{\partial n^a(r_p)} = -\frac{1}{2} \Delta V \{ \delta V_H(r_p) - \sum_q \delta n(r_q) \frac{\partial V_H(r_q)}{\partial n^a(r_p)} \},
\]

\[
= -\frac{1}{2} \Delta V \{ \delta V_H(r_p) + \frac{4\pi}{N_{\text{rg}}} \sum_q \frac{1}{|G|^2} \sum_q \delta n(r_q) e^{iG \cdot (q_r - r_p)} \},
\]

\[
= -\Delta V \delta V_H(r_p).
\]

\[
\frac{\partial n(r_p)}{\partial R_k} = \sum_{ia, j\beta} \sum_{\nu} \frac{\partial c_{ia, j\beta, \nu}}{\partial R_k} c_{ia, j\beta, \nu} \chi_{ia}(r) \chi_{j\beta}(r) + c_{ia, j\beta}^* \frac{\partial c_{ia, j\beta}}{\partial R_k} \chi_{ia}(r_p) \chi_{j\beta}(r_p).
\]

\[
+ 2 \sum_{ia, j\beta} \chi_{ia}(r) \chi_{j\beta}(r_p).
\]

\[
\frac{\partial E_{\text{xc}}}{\partial R_k} = \sum_p \frac{\partial n(r_p)}{\partial R_k} \frac{\partial E_{\text{xc}}}{\partial n(r_p)},
\]

\[
= \Delta V \sum_p \frac{\partial n(r_p)}{\partial R_k} v_{\text{xc}}(n(r_p)).
\]

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

\[ V_{\text{NL}} = \sum_{i,j} B_{ij} |\beta_i\rangle \langle \beta_j| \]

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

\[ |\chi_i\rangle = V_{\text{NL}}^{(i)} |\phi_i\rangle = (\varepsilon_i - T - V_{\text{loc}}) |\phi_i\rangle \]

\[ B_{ij} = \langle \phi_i | \chi_j \rangle \]

\[ |\beta_i\rangle = \sum_j (B^{-1})_{ji} |\chi_j\rangle \]

If \( Q=0 \), then \( B-B^* = 0 \)

If \( Q=0 \), then \( B-B^* = 0 \)

This is the norm-conserving PP used in OpenMX.
If $Q_{ij} = 0$, the non-local terms can be transformed to a diagonal form.

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

\[ = \sum_i \lambda_i |\alpha_i\rangle \langle \alpha_i| \]

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

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

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

\[ \chi_i = V_{TM}^{(i)} \phi_{TM,i} + \varepsilon_i f_i - V_{\text{loc}} \phi_i - \frac{1}{2} \sum_i c_i \left( \frac{u_{li}}{r_c} \right)^2 \left[ r j l \left( \frac{r}{r_c} u_{li} \right) \right] \]
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. Adjustment of the local potential
4. Generation of PCC charge

(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.

Optimization of PP typically takes a half week per a week.
Total energy
Pseudopotentials
Basis functions
Self-consistency
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 pseudopotential for each L-channel.

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

**Cutoff radius**

**Number of orbitals**
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

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<tbody>
<tr>
<td>H₂ (H4.5-s2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>(1σ²)</td>
<td>K₂ (K10.0-s2p2)</td>
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<td>1Σ⁺</td>
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<td>Ti₂ (Ti7.0-s2p2d2)</td>
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<td>3Σ⁻</td>
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<td>1Σ⁺</td>
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<td>3Σ⁺</td>
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<td>1Σ⁺</td>
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<td>3πᵣ</td>
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<td>3πᵣ</td>
<td>(3σ²³σ₂³π₂₂)</td>
<td>GaH (Ga7.0-s2p2d2)</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Si₂ (Si6.5-s2p2)</td>
<td>3π⁺</td>
<td>3π⁺</td>
<td>(3σ₂³σ₂³π₃π₃)</td>
<td>GeO (Ge7.0-s2p2)</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Si₂ (Si6.5-s2p2d1)</td>
<td>3π⁻</td>
<td>3π⁻</td>
<td>(3σ₂³σ₂³π₃π₃)</td>
<td>As₂ (As7.0-s2p2d1)</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>P₂ (P6.0-s2p2d1)</td>
<td>3π⁺</td>
<td>3π⁺</td>
<td>(3σ₂³σ₂³π₃π₃)</td>
<td>Se₂ (Se7.0-s2p2d1)</td>
<td>3Σ⁻</td>
</tr>
<tr>
<td>S₂ (S6.0-s2p2)</td>
<td>3π⁺</td>
<td>3π⁺</td>
<td>(3σ₂³σ₂³π₃π₃)</td>
<td>Br₂ (Br7.0-s2p2d1)</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Cl₂ (Cl6.0-s2p2d2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>(3π₄³σ₂³π₃π₃)</td>
<td>Kr₂ (Kr7.0-s2p2d2)</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Ar₂ (Ar7.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>(3π₄³σ₂³π₃π₃)</td>
<td>(4σ₂³σ₂³π₄π₄)</td>
<td>1Σ⁺</td>
</tr>
</tbody>
</table>

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

\[ \psi_\mu(r) = \sum_{i\alpha} c_{\mu,i\alpha} \phi_{i\alpha}(r - r_i) \]

Contracted orbitals

\[ \phi_{i\alpha}(r) = \sum_q a_{i\alpha q} \chi_{i\eta}(r) \]

The variation of \( E \) with respect to \( c \) with fixed \( a \) gives

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

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

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

\[ = 2 \sum_{j\beta} (\Theta_{i\alpha,j\beta} \langle \chi_{i\eta}\hat{H}\phi_{j\beta} \rangle - E_{i\alpha,j\beta} \langle \chi_{i\eta}\phi_{j\beta} \rangle) \]

Comparison between primitive and optimized basis functions

Energy convergency

C₂H₆

- Primitive
- Optimized

C₂F₆

- Primitive
- Optimized

Radial shape of carbon atom

s-orbital

p-orbital

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 (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.

Public release of optimized and well tested VPS and PAO so that users can easily start their calculations.
Total energy
Pseudopotentials
Basis functions
Self-consistency
Self-consistency: Simple charge mixing

The KS effective is constructed from $\rho$. However, $\rho$ is evaluated from eigenfunctions of KS eq.

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

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

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

Simple charge mixing method

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

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

It works well for large gap systems and small sized systems.
Optimum input density might be given by

\[
\rho_{n+1}^{(\text{in})} = \sum_{m=n-(p-1)}^{n} \alpha_m \rho_m^{(\text{in})} + \beta \sum_{m=n-(p-1)}^{n} \alpha_m R_m
\]

Idea:

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

\[
\begin{align*}
\bar{R}_{n+1} &= \sum_{m=n-(p-1)}^{n} \alpha_m R_m, \\
F &= \langle \bar{R}_{n+1} | \bar{R}_{n+1} \rangle - \lambda \left( 1 - \sum_{m}^{n} a_m \right), \\
&= \sum_{m,m'} \alpha_m \alpha_{m'} \langle R_m | R_{m'} \rangle - \lambda \left( 1 - \sum_{m}^{n} a_m \right).
\end{align*}
\]

Minimization of \( F \) leads to

\[
\begin{align*}
\frac{\partial F}{\partial \alpha_k} &= 0 \\
\frac{\partial F}{\partial \lambda} &= 0
\end{align*}
\]

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

\[
R_n(q) \equiv \tilde{n}_n^{(\text{out})}(q) - \tilde{n}_n^{(\text{in})}(q),
\]

\[
\langle R_m | R_{m'} \rangle = \sum_{q} \frac{R_m^*(q) R_{m'}(q)}{w(q)}
\]

Kerker factor

\[
w(q) = \frac{|q|^2}{|q|^2 + q_0^2},
\]

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

Comparison of various mixing methods

Sialic acid

Pt\textsubscript{13} cluster

Pt\textsubscript{63} cluster

RMM-DIIS shows better performance.
Reproducibility in density functional theory calculations of solids

PBE lattice constant of Si

Errors
- Basis functions
- Pseudopotentials
- Integrals in $r$ and $r'$

Precision

Accuracy

Experiment

This work

Year of publication


PBE lattice parameter of Si [Å]

5.41 5.43 5.45 5.47 5.49 5.51

5.460 5.465 5.470 5.475 5.480
Δ-gauge
A way of comparing accuracy of codes
Evaluation of GGA-PBE By Δ-gauge

In comparison of GGA-PBE with Expts. of 58 elements, the mean Δ-gauge is 23.5 meV/atom.
The mean $\Delta$-gauge of OpenMX is 2.0meV/atom.
Outlook

A localized basis method, implemented in OpenMX, was discussed with the following focuses:

- Total energy
- Pseudopontials
- Basis functions
- Self-consistency

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