Localized basis methods in OpenMX

- Introduction of OpenMX
- Implementation of OpenMX
  - Total energy
  - Pseudopotentials
  - Basis functions
- \(\Delta\)-gauge

Taisuke Ozaki (ISSP, Univ. of Tokyo)
Nov. 23\(^{rd}\), OpenMX hands-on workshop in KAIST
**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

<table>
<thead>
<tr>
<th>Basic functionalities</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF calc. by LDA, GGA, DFT+U</td>
</tr>
<tr>
<td>Total energy and forces on atoms</td>
</tr>
<tr>
<td>Band dispersion and density of states</td>
</tr>
<tr>
<td>Geometry optimization by BFGS, RF, EF</td>
</tr>
<tr>
<td>Charge analysis by Mullken, Voronoi, ESP</td>
</tr>
<tr>
<td>Molecular dynamics with NEV and NVT ensembles</td>
</tr>
<tr>
<td>Charge doping</td>
</tr>
<tr>
<td>Fermi surface</td>
</tr>
<tr>
<td>Analysis of charge, spin, potentials by cube files</td>
</tr>
<tr>
<td>Database of optimized PPs and basis functions</td>
</tr>
</tbody>
</table>

### Extensions

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

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

Magnetic anisotropy energy of magnets

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
e tc.

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)

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

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

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

\[ v_{\text{eff}} = v_{\text{ext}}(r) + v_{\text{Hartree}}(r) + \frac{\delta E_{xc}}{\delta \rho(r)} \]
3D coupled non-linear differential equations have to be solved self-consistently.

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

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

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

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

Input charge = Output charge → Self-consistent condition
One-particle KS orbital

\[ \psi_{\sigma \mu}^{(k)}(r) = \frac{1}{\sqrt{N}} \sum_{n} e^{iR_n \cdot k} \sum_{i\alpha} c_{\sigma \mu, i\alpha}^{(k)} \phi_{i\alpha}(r - \tau_i - R_n), \]

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

\[ \phi(r) = Y_l^m(\hat{r}) R(r) \]

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.

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

\[
E_{\text{kin}} = \sum_{\sigma} \sum_{n} \sum_{i_{\alpha},j_{\beta}} \rho_{\sigma,i_{\alpha}j_{\beta}}^{(R_n)} \hbar_{i_{\alpha}j_{\beta}}^{(R_n)} \text{, } \quad \text{Kinetic energy} 
\]

\[
E_{\text{ec}} = E^{(\text{L})}_{\text{ec}} + E^{(\text{NL})}_{\text{ec}}, \quad \text{Coulomb energy with external potential} 
\]

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

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

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

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

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

The neutral atom energy

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

\[
= \sum_σ \sum_n \sum_{iα,jβ} ρ_σ^{(R_n)} \sum_I ⟨φ_{iα}(r - τ_i)|V_{na,I}(r - τ_I)|φ_{jβ}(r - τ_j - R_n)⟩,
\]

Difference charge Hartree energy

\[ E_{δee} = \frac{1}{2} \int dr^3 δn(r)δV_H(r), \]

Screened core-core repulsion energy

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

Short range and separable to two-center integrals

Long range but minor contribution

Short range and two-center integrals

Difference charge

\[ δn(r) = n(r) - n^{(a)}(r), \]

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

Neutral atom potential

\[ V_{na,I}(r - τ_I) = V_{core,I}(r - τ_I) + V_{H,I}^{(a)}(r - τ_I). \]
Implementation: Total energy (3)

So, the total energy is given by

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

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

\[
\begin{align*}
E_{\text{kin}} \\
E_{\text{na}} \\
E_{\text{ec}}^{(NL)} \\
E_{\delta\text{ee}} \\
E_{\text{xc}} \\
E_{\text{scc}}
\end{align*}
\]

\( \text{Spherical coordinate in momentum space} \)

\( \text{Real space regular mesh} \)

\( \text{Real space fine mesh} \)
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.

e.g., overlap integral

\[ \langle \phi_{i\alpha}(r)|\phi_{j\beta}(r - \tau) \rangle = \int dr^3 \phi_{i\alpha}^*(r) \phi_{j\beta}(r - \tau), \]

\[ = \int dr^3 \left( \frac{1}{\sqrt{2\pi}} \right)^3 \int dk^3 \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{k}) e^{-ik\cdot r} \left( \frac{1}{\sqrt{2\pi}} \right)^3 \int dk'^3 \tilde{R}_{pl'}^*(k') Y_{lm'}(\hat{k'}) e^{ik'\cdot(r - \tau)}, \]

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

\[ = \int dk^3 e^{-ik\cdot\tau} \tilde{R}_{pl}^*(k) Y_{lm}^*(\hat{k}) \tilde{R}_{p'l'}^*(k) Y_{lm'}(\hat{k}), \]
Cutoff energy for regular mesh

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

```
scf.energy cutoff           150.0  # default=150 (Ry)
```

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

\[
E_{\text{cut}}^{(1)} = \frac{1}{2} g_b^1 \cdot g_b^1, \quad E_{\text{cut}}^{(2)} = \frac{1}{2} g_b^2 \cdot g_b^2, \quad E_{\text{cut}}^{(3)} = \frac{1}{2} g_b^3 \cdot g_b^3,
\]

\[
g_a^1 = \frac{a_1}{N_1}, \quad g_a^2 = \frac{a_2}{N_2}, \quad g_a^3 = \frac{a_3}{N_3},
\]

\[
g_b^1 = 2\pi \frac{g_a^2 \times g_a^2}{\Delta V}, \quad g_b^2 = 2\pi \frac{g_a^3 \times g_a^1}{\Delta V}, \quad g_b^2 = 2\pi \frac{g_a^1 \times g_a^2}{\Delta V},
\]

\[
\Delta V = g_a^1 \cdot (g_a^2 \times g_a^3),
\]
Forces

\[ F_i = -\frac{\partial E_{\text{tot}}}{\partial R_i} = -\left( \frac{\partial E_{\text{kin}}}{\partial R_i} + \frac{\partial E_{\text{na}}}{\partial R_i} - \frac{\partial E_{\text{sc}}}{\partial R_i} + \frac{\partial E_{\text{d}}}{\partial R_i} - \frac{\partial E_{\text{xc}}}{\partial R_i} - \frac{\partial E_{\text{cc}}}{\partial R_i} \right) \]

\[
\frac{\partial E_{\text{d}}}{\partial R_k} = \sum_r \frac{\partial n(r_p)}{\partial R_k} \frac{\partial E_{\text{d}}}{\partial R_i} + \sum_r \frac{\partial n^a(r_p)}{\partial R_k} \frac{\partial E_{\text{d}}}{\partial n(r_p)}.
\]

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

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

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

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

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

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

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

\[
+ 2 \sum_{\alpha,\beta} \sum_{\kappa,\lambda} \rho_{\kappa \lambda} \frac{\partial \chi_{\kappa \lambda}(r_p)}{\partial R_k} \chi_{j \beta}(r_p).
\]

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

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

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
Norm-conserving Vanderbilt pseudopotential


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

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

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

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

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

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

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

\[ Q_{ij} = \langle \psi_i | \psi_j \rangle_R - \langle \phi_i | \phi_j \rangle_R \]

\[ B_{ij} - B_{ji}^* = (\varepsilon_i - \varepsilon_j) Q_{ij} \]

This is the norm-conserving PP used in OpenMX.
Non-local potentials by Vanderbilt

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

\[ \hat{v}^{(NL)} | \phi_k^{(PS)} \rangle = \sum_{ij} | \beta_i \rangle B_{ij} \langle \beta_j | \phi_k^{(PS)} \rangle \]

\[ = \sum_{ij} | \beta_i \rangle B_{ij} \sum_{k'} \left( B^{-1} \right)_{k'j} \langle \chi_{k'} | \phi_k^{(PS)} \rangle, \]

\[ = \sum_{ij} | \beta_i \rangle B_{ij} \sum_{k'} B_{k'k} \]

\[ = \sum_{ij} | \beta_i \rangle B_{ij} \delta_{kj}, \]

\[ = \sum_i \left( \sum_j \left( B^{-1} \right)_{ji} | \chi_j \rangle \right) B_{ik}. \]

\[ = | \chi_k \rangle \]

Noting the following relations:

\[ v^{(SL)}(r) = v_L(r) + v_{H}^{(v)}(r) + v_{xc+pcc}^{(v+pcc)}(r). \]

\[ | \chi_i \rangle = \left( \varepsilon_i + \frac{1}{2} \nabla^2 - v^{(SL)}(r) \right) | \phi_i^{(PS)} \rangle, \]

\[ B_{ij} = \langle \phi_i^{(PS)} | \chi_j \rangle \]

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

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

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

$$B_{ij} - B_{ji}^* = (\varepsilon_j - \varepsilon_i) \int_0^{r_c} dr P_i^{(PS)}(r) P_j^{(PS)}(r)$$

$$+ \frac{1}{2} \int_0^{r_c} dr P_i^{(PS)}(r) P_j^{(PS)}(r) - \frac{1}{2} \int_0^{r_c} dr P_i^{(PS)}(r) P_j^{(PS)}(r).$$

By integrating by parts, this can be transformed as

$$B_{ij} - B_{ji}^* = (\varepsilon_j - \varepsilon_i) \langle \phi_i^{(PS)} | \phi_j^{(PS)} \rangle_{rc} + \frac{1}{2} \left[ P_i^{(PS)}(r) P_j^{(PS)}(r) \right]_{0}^{r_c} - \frac{1}{2} \left[ P_i^{(PS)}(r) P_j^{(PS)}(r) \right]_{0}. \tag{1}$$

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

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

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

$$B_{ij} - B_{ji}^* = (\varepsilon_i - \varepsilon_j) \left( \langle \phi_i^{(AE)} | \phi_j^{(AE)} \rangle_{rc} - \langle \phi_i^{(PS)} | \phi_j^{(PS)} \rangle_{rc} \right).$$
If $Q_{ij} = 0$, the non-local terms can be transformed to a diagonal form.

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

$$= \sum_{i} \lambda_i \langle \alpha_i \rangle \langle \alpha_i \rangle$$

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

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

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

$$\chi_i = V_{TM}^{(i)} \phi_{TM,i} + \varepsilon_i f_i - V_{loc} \phi_i - \frac{1}{2} \sum_{i} c_i \left( \frac{u_i}{r_c} \right)^2 \left[ r j_l \left( \frac{r}{r_c u_i} \right) \right]$$
Pseudo-wave function and pseudopotential of carbon atom

Red: All electron calculation
Blue: Pseudized calculation

Pseudopotential for C 2s and $-4/r$

Radial wave function of C 2s

![Graphs showing the pseudopotential and radial wave function of C 2s.](image-url)
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.

Good PP
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

OpenMX Mn6.0-s3p3d3

Wien2k
➤ Total energy
➤ Pseudopotentials
➤ Basis functions
1. Solve an atomic Kohn-Sham eq. under a confinement potential:

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

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**

---

PRB 69, 195113 (2004)
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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<thead>
<tr>
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<tbody>
<tr>
<td>H₂ (H4.5-s2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>K₂ (K10.0-s2p)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>He₂ (He7.0-s2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>CaO (Ca7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Li₂ (Li8.0-s2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>ScO (Sc7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>BeO (Be6.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Ti₂ (Ti7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>B₂ (B5.5-s2p2)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
<td>V₂ (V7.5-s2p2d)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
</tr>
<tr>
<td>C₂ (C5.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>V₂ (V7.5-s4p4d4f)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
</tr>
<tr>
<td>N₂ (N5.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Cr₂ (Cr7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>O₂ (O5.0-s2p2)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
<td>MnO (Mn7.0-s2p2d)</td>
<td>6Σ⁺</td>
<td>6Σ⁺</td>
</tr>
<tr>
<td>F₂ (F5.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Fe₂ (Fe7.0-s2p2d)</td>
<td>7Δₜ</td>
<td>7Δₜ</td>
</tr>
<tr>
<td>Ne₂ (Ne7.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Co₂ (Co7.0-s2p2d)</td>
<td>5Δₙ</td>
<td>5Δₙ</td>
</tr>
<tr>
<td>Na₂ (Na9.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Ni₂ (Ni7.0-s2p2d)</td>
<td>Ω</td>
<td>Ω</td>
</tr>
<tr>
<td>MgO (Mg7.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Cu₂ (Cu7.0-s2p2d)</td>
<td>2Σ⁺</td>
<td>2Σ⁺</td>
</tr>
<tr>
<td>Al₂ (Al16.5-s2p2)</td>
<td>3Πᵢ</td>
<td>3Πᵢ</td>
<td>ZnH (Zn7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Al₂ (Al16.5-s4p4d2)</td>
<td>3Πᵢ</td>
<td>3Πᵢ</td>
<td>GaH (Ga7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Si₂ (Si16.5-s2p2)</td>
<td>3Σ⁻</td>
<td>3Πᵢ</td>
<td>GeO (Ge7.0-s2p2d)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Si₂ (Si16.5-s2p2d1)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
<td>As₂ (As7.0-s2p2d1)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>P₂ (P6.0-s2p2d1)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Se₂ (Se7.0-s2p2d1)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
</tr>
<tr>
<td>S₂ (S6.0-s2p2)</td>
<td>3Σ⁻</td>
<td>3Σ⁻</td>
<td>Br₂ (Br7.0-s2p2d1)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Cl₂ (Cl16.0-s2p2d2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>Kr₂ (Kr7.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
</tr>
<tr>
<td>Ar₂ (Ar7.0-s2p2)</td>
<td>1Σ⁺</td>
<td>1Σ⁺</td>
<td>(3pπ²3pπ²3pσ²)</td>
<td>1Σ⁺</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

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

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

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

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

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

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

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 here.

Public release of optimized and well tested VPS and PAO so that users can easily start their calculations.
Reproducibility in density functional theory calculations of solids

PBE lattice constant of Si

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

Errors

- Precision
- Accuracy

Experiment
**Δ-gauge**

A way of comparing accuracy of codes

\[ \Delta_i(a, b) = \sqrt{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \left( E_{b,i}(V) - E_{a,i}(V) \right)^2 dV / 0.12V_{0,i} } \]
Evaluation of GGA-PBE By Δ-gauge

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

\[
\Delta(\text{exp}) = 23.5 \text{ meV/atom}
\]
The mean $\Delta$-gauge of OpenMX is 2.0meV/atom.
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.

- The $\Delta$-gauge might become a standard measure to check accuracy of newly developed codes and functionals.