Theories of pseudopotentials

1. OPW method
2. PK type pseudopotential
3. Norm-conserving pseudopotential by TM
4. Ultra-soft pseudopotential by Vanderbilt
5. MBK pseudopotential
6. Solving the 1D Dirac eq.
7. What we can do if we generate PPs by ourselves
8. On the vps file

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Intuitive ideas of pseudopotentials

1. Since core electrons is situated at energetically very deeper states, they are inert chemically. In molecules and solids, they do not change so largely.

2. Is there a way of constructing an effective potential consisting of the nucleus potential and Coulomb potential given by the core electrons states calculated in advance ?

3. If the effective potential is much shallower than that of the true nucleus potential, it is expected that the calculation will become quite easier.

Electronic structure of Si bulk
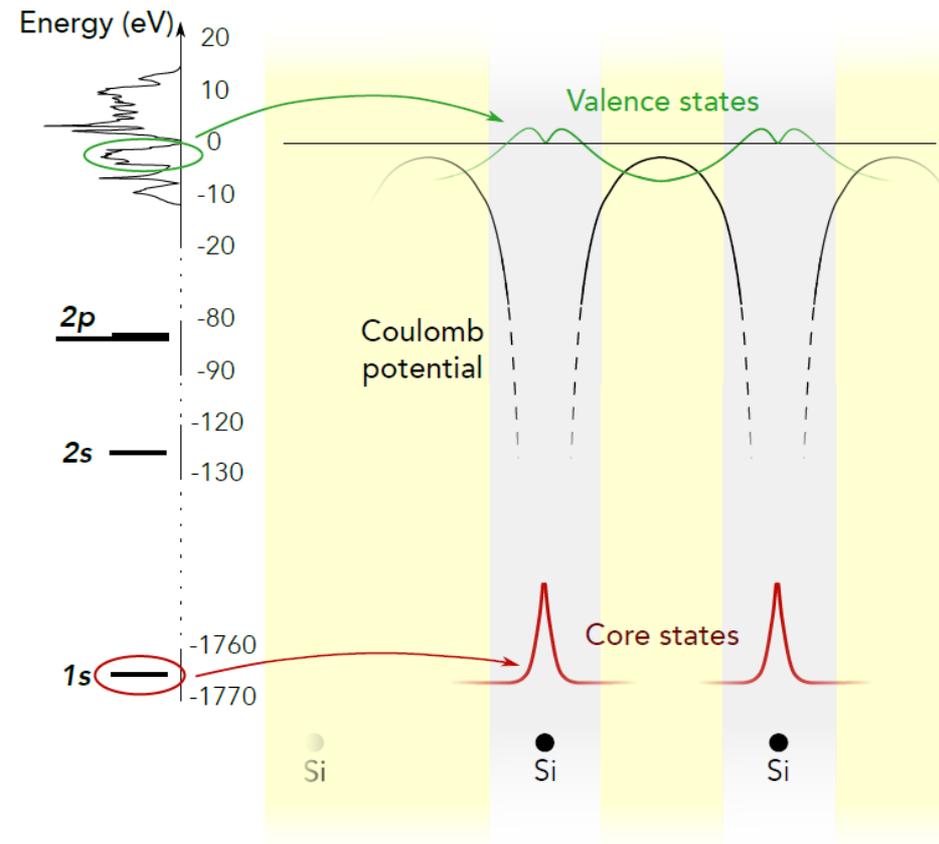
Science **351**, aad3000 (2016).

OPW (Orthogonalized Plane Wave Method) method

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle \quad \text{i=c,v}$$

It is assumed that $|\psi_c\rangle$ has been solved in advance.

$|PW, \mathbf{q}\rangle = \exp(i\mathbf{q}\cdot\mathbf{r})$ is orthogonalized with $|\psi_c\rangle$ by

$$|OPW, \mathbf{q}\rangle = |PW, \mathbf{q}\rangle - \sum_c |\psi_c\rangle\langle\psi_c|PQ, \mathbf{q}\rangle$$

It is easy to verify that

$$
\begin{aligned}
\langle\psi_{c'}|OPW, \mathbf{q}\rangle &= \langle\psi_{c'}|PW, \mathbf{q}\rangle - \sum_c \langle\psi_{c'}|\psi_c\rangle\langle\psi_c|PQ, \mathbf{q}\rangle \\
&= \langle\psi_{c'}|PW, \mathbf{q}\rangle - \langle\psi_{c'}|PW, \mathbf{q}\rangle \\
&= 0
\end{aligned}
$$

By using the OPW as basis set, the number of basis functions can be reduced
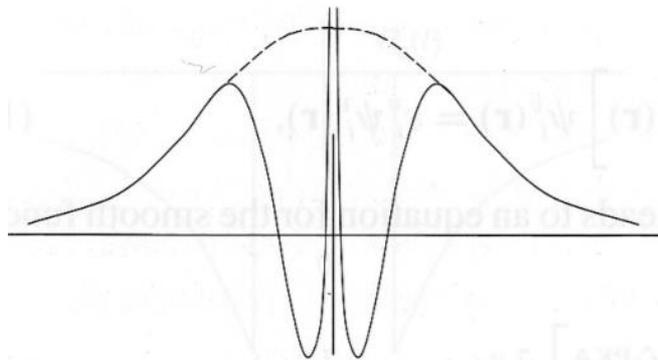
valence electrons oscillate near the vicinity of nucleus because of the orthogonality with core electrons.
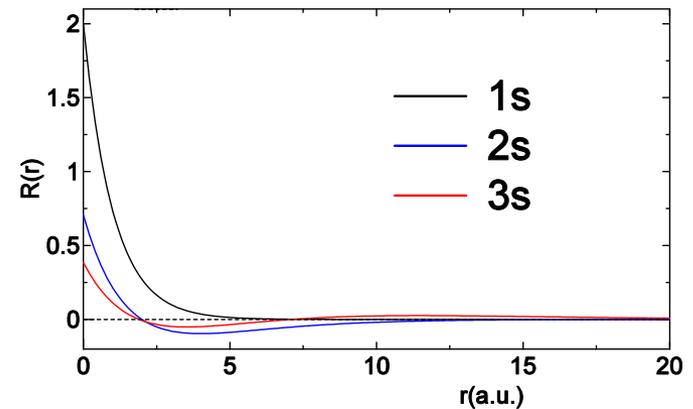
Phillips-Kleinman (PK) method

Smooth part of wave funtion

$$|\phi\rangle = \sum_{\mathbf{G}} C_{\mathbf{G}} |PW, \mathbf{G}\rangle$$

Orthogonalize it with core electrons

$$|\Psi\rangle = |\phi\rangle - \sum |\psi_c\rangle\langle\psi_c|\phi\rangle$$

Let's write Eq. by Φ.

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

L.H.S

$$\hat{H}|\Psi\rangle = \hat{H}|\phi\rangle - \sum_c \hat{H}|\psi_c\rangle\langle\psi_c|\phi\rangle$$
$$\simeq \hat{H}|\phi\rangle - \sum_c E_c|\psi_c\rangle\langle\psi_c|\phi\rangle$$

R.H.S

$$E|\Psi\rangle = E|\phi\rangle - \sum_c E|\psi_c\rangle\langle\psi_c|\phi\rangle$$

One can get by equating L.H.S with R.H.S.

$$\left(\hat{H} + \sum_c (E - E_c)|\psi_c\rangle\langle\psi_c|\right)|\phi\rangle = E|\phi\rangle$$

This gives a new view that Φ feels the following effective potential.

$$v_{\text{eff}} = v + \sum_c \underline{(E - E_c)}|\psi_c\rangle\langle\psi_c|$$

Positive in general

**V$_{\text{eff}}$ is shallower than v.**

Features of V$_{\text{eff}}$

1. Non-local potential

2. Energy dependent

3. For a linear transformation

$$|\phi'\rangle = |\phi\rangle - \sum_c |\psi_c\rangle\langle\psi_c|\phi'\rangle$$

The form of Eq. is invariant.

Scattering by a spherical potential
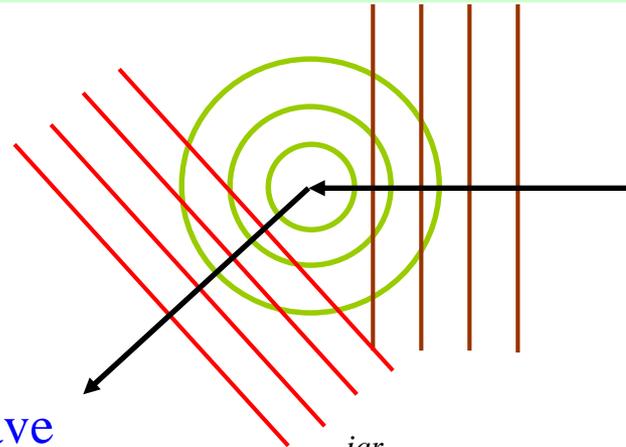
Incident wave

$$e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$\varepsilon = \frac{1}{2}q^2$$

Scattered wave

$$\psi_{\text{sca}}(\varepsilon, r) = e^{i\mathbf{q}\cdot\mathbf{r}} + \frac{e^{iqr}}{qr}\sum_l (2l+1)e^{i\eta_l}\sin\eta_l P_l(\cos\theta)$$

Phase shift η_l

$$\tan\eta_l(\varepsilon, r_0) = \frac{r_0\dfrac{d}{dr}j_l(kr)|_{r_0} - D_l(\varepsilon)j_l(kr_0)}{r_0\dfrac{d}{dr}n_l(kr)|_{r_0} - D_l(\varepsilon)n_l(kr_0)}$$

Logarithmic derivative of ψ

$$D_l(\varepsilon, r) = r\frac{d}{dr}\ln\psi_l(r)$$

$$\frac{\partial}{\partial\varepsilon}D_l(\varepsilon, r)|_{r_0} = -\frac{2}{r_0\psi_l^2(r_0)}\int_0^{r_0}dr\, r^2 |\psi_l(r)|^2$$

If the norm of pseudized wave is conserved within r_0 and the logarithmic derivative coincides with that for the all electron case, the phase shift coincides with the all electron case to first order.

Norm-conserving pseudopotential by Troullier and Matins

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right] u_l(r) = \varepsilon_l u_l(r) \qquad R_l(r) = \frac{u_l(r)}{r}$$

For $u_l(r)$, the following form is used.

$$u_l(r) = \begin{cases} u_l^{(AE)}(r) & r \geq r_{cl} \\ r^{l+1}\exp[p(r)] & r \leq r_{cl} \end{cases} \qquad p(r) = \sum_{i=0}^{6} c_{2i} r^{2i}$$

Putting u_l into radial Schroedinger eq. and solving it with respect to V, we have

$$\begin{aligned} V^{(scr)}(r) &= \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2}\frac{[u_l(r)]''}{u_l(r)} \\ &= \varepsilon_l + \frac{l(l+1)p'(r)}{r} + \frac{1}{2}\left[p''(r) + [p'(r)]^2 \right] \end{aligned}$$

$c_0 \sim c_{12}$ are determined by the following conditions:

- Norm-conserving condition within the cutoff radius
- The second derivatives of $V^{(scr)}$ is zero at r=0
- Equivalence of the derivatives up to 4th orders of u_l at the cutoff radius

Unscreeing and partial core correction (PCC)

Unscreeing

Since V(scr) contains effect of valence electrons, the ionic pseudopotential is constructed by subtracting the effects.

$$V_l^{(\mathrm{ps})}(r) = V_l^{(\mathrm{scr})}(r) - V_{\mathrm{Hartree}}(r) - V_{\mathrm{xc}}[\rho_v(r) + \rho_{\mathrm{pcc}}(r)]$$

PCC

In order take account of the non-linearity of exchange-correlation term, it would be better to include the partial core correction.

Valence and PCC charges of carbon atom

— Valence electron
— Partial core density
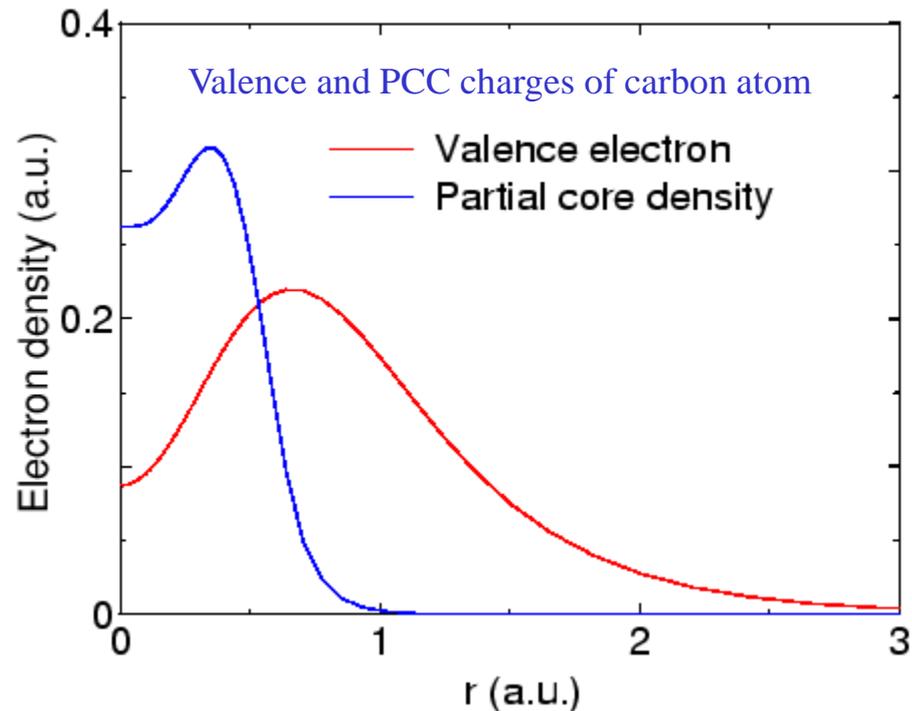
Pseudopotentials by the TM method

Red: All electron calculation
Blue: Pseudopotential

Radial wave function of C 2s
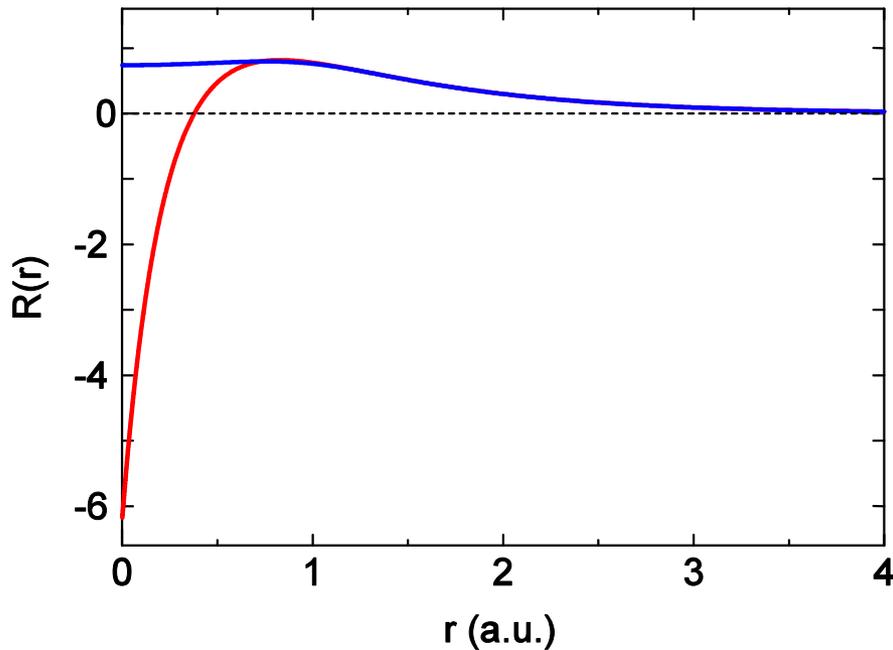
Pseudopotential for C 2s and –4/r
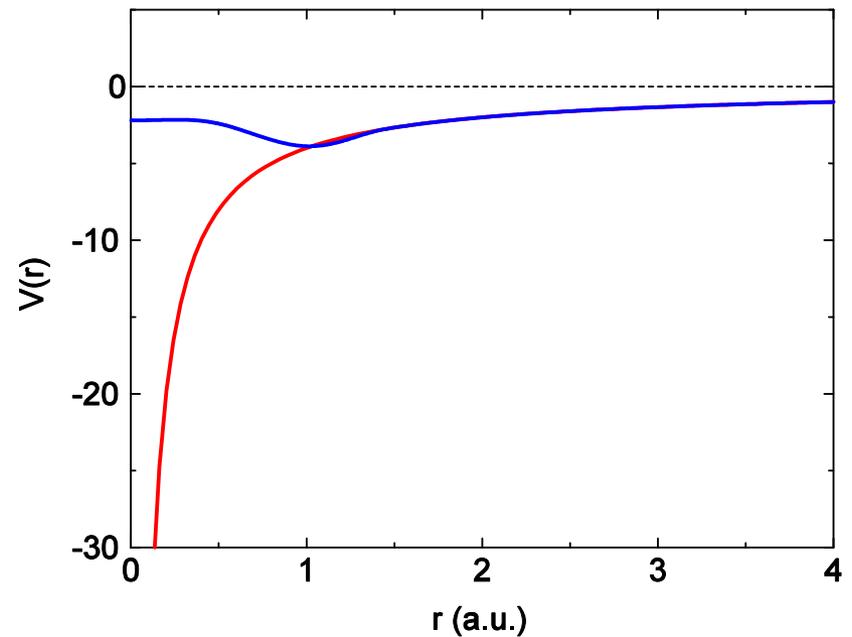
Separable pseudopotentials

Since the pseudopotential depends on the angular momentum l, it is **non-local.**

$$V^{(\mathrm{ps})}(\mathbf{r}) = V_{\mathrm{loc}}(\mathbf{r}, \mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') + V_{\mathrm{NL}}(\mathbf{r}, \mathbf{r}')$$

$$
\begin{aligned}
V_{\mathrm{NL}}(\mathbf{r}, \mathbf{r}') &= \sum_{lm} |Y_l^m(\hat{\mathbf{r}})\rangle \left(V_l^{(\mathrm{ps})}(r) - V_{\mathrm{loc}}(r) \right) \langle Y_l^m(\hat{\mathbf{r}}')| \\
&= \sum_{lm} |Y_l^m(\hat{\mathbf{r}})\rangle V_{\mathrm{NL}}^{(l)}(r) \langle Y_l^m(\hat{\mathbf{r}}')| \\
&= \boxed{\sum_{lm}\sum_{\zeta} |V_{\mathrm{NL}}^{(l)}\bar{R}_{l\zeta}Y_l^m\rangle \frac{1}{c_{l\zeta}} \langle \bar{R}_{l\zeta}Y_l^m V_{\mathrm{NL}}^{(l)}|,}
\end{aligned}
$$

The non-local potential is usually used as a separable form due to the simplicity of calculations.

L Kleinman and D. M. Bylander, PRL **48,** 1425 (1982).

P. E. Blochl, Phys. Rev. B 41, 5414 (1990).

Ultrasoft pseudopotential by Vanderbilt

The phase shift is reproduced around multiple reference energies by the following non-local operator.

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

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

$$B_{ij} = \langle \phi_i | \chi_j \rangle$$

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

If the following generalized norm conserving condition is fulfilled, the matrix B is Hermitian. Thus, in the case the operator V_{NL} is also Hermitian.

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

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

If Q=0, then B-B*=0

How the non-local operator works?

Operation of the non-local operator to pseudized wave function

$$
\begin{aligned}
\hat{v}^{(\mathrm{NL})}|\phi_k^{(\mathrm{PS})}\rangle &= \sum_{ij} |\beta_i\rangle B_{ij} \langle \beta_j | \phi_k^{(\mathrm{PS})}\rangle \\
&= \sum_{ij} |\beta_i\rangle B_{ij} \sum_{k'} \left(B^{-1}\right)_{k'j} \langle \chi_{k'} | \phi_k^{(\mathrm{PS})}\rangle, \\
&= \sum_{ij} |\beta_i\rangle B_{ij} \sum_{k'} \left(B^{-1}\right)_{k'j} B_{kk'}, \\
&= \sum_{ij} |\beta_i\rangle B_{ij} \delta_{kj}, \\
&= \sum_i \left(\sum_j \left(B^{-1}\right)_{ji} |\chi_j\rangle \right) B_{ik}. \\
&= |\chi_k\rangle
\end{aligned}
$$

Note that

$$
\boxed{v^{(\mathrm{SL})}(r) = v_{\mathrm{L}}(r) + v_{\mathrm{H}}^{(\mathrm{v})}(r) + v_{\mathrm{xc}}^{(\mathrm{v+pcc})}(r).}
$$

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

$$
B_{ij} = \langle \phi_i^{(\mathrm{PS})} | \chi_j \rangle
$$

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

It turns out that the following Schroedinger equation is satisfied.

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

The matrix B and the generalized norm conserving condition

The matrix 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

$$B_{ij} - B_{ji}^* = (\varepsilon_j - \varepsilon_i) \langle \phi_i^{(PS)} | \phi_j^{(PS)} \rangle_{r_c} + \frac{1}{2} \left[P_i^{(PS)}(r) P_j'^{(PS)}(r) \right]_0^{r_c} - \frac{1}{2} \left[P_i'^{(PS)}(r) P_j^{(PS)}(r) \right]_0^{r_c},$$

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

By performing the similar calculations, we obtain for the all electron wave functions

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

By subtracting (2) from (1), we have the following relation.

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

Norm-conserving pseudopotential by MBK

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

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

The form is exactly the same as that for the Blochl expansion, resulting in no need for modification of OpenMX.

To satisfy $Q_{ij}=0$, the pseudized wave function is written by

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

The coefficients can be determined by matching up to the third derivatives to those for the all electron, and $Q_{ij}=0$. Once c's are determined, χ is given by

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

The form of MBK pseudopotentials

The pseudopotential is given by the sum of a local term V_{loc} and non-local term V_{NL}.

$$V^{(ps)} = V_{loc}(r) + V_{NL}$$

The local term V_{loc} is independent of the angular channel l. On the other hand, the non-local term V_{NL} is given by projectors

$$V_{NL} = \sum_i \lambda_i \, | \alpha_i \rangle \langle \alpha_i |$$

The projector consists of radial and spherical parts, and depends on species, radial and l-channels.

Relativistic pseudopotentials

By using the eigenfunctions of the spherical operator for the Dirac Eq., one can introduce a relativistic pseudopotential as

$$
\begin{aligned}
V^{(\text{ps})} &= v^{(\text{L})} + \sum_{lm} \left[|\Phi_J^M\rangle v_{l+\frac{1}{2}}^{(\text{NL})} \langle \Phi_J^M| + |\Phi_{J'}^{M'}\rangle v_{l-\frac{1}{2}}^{(\text{NL})} \langle \Phi_{J'}^{M'}| \right] \\
&= v^{(\text{L})} + \hat{v}_{l+\frac{1}{2}}^{(\text{NL})} + \hat{v}_{l-\frac{1}{2}}^{(\text{NL})},
\end{aligned}
$$

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

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

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

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

Optimization of pseudopotentials

(i) Choice of parameters

Optimization of PP typically takes a half week.

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

(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).

good

No good

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

No good

good

Good PP

Comparison of logarithmic derivatives

Logarithmic derivatives of wave functions for s, p, d, and f channels for Mn atom. It is found that the separable MBK is well compared with the all-electron. If there is a deviation in the logarithmic derivatives, the band structure will not be reproduced.
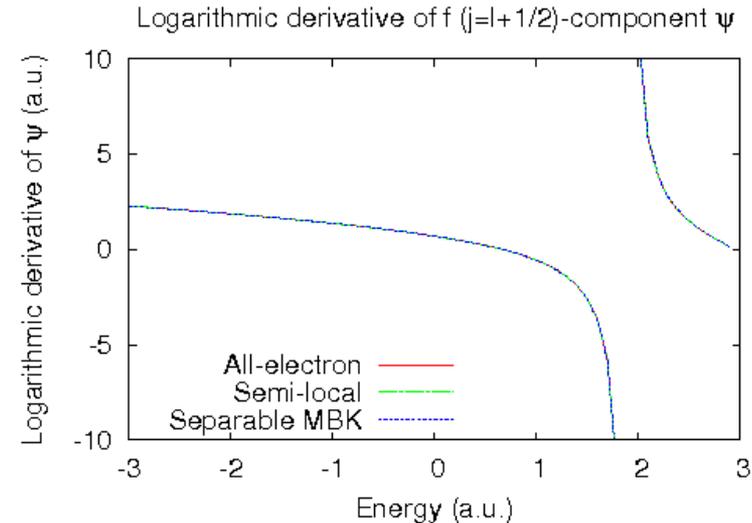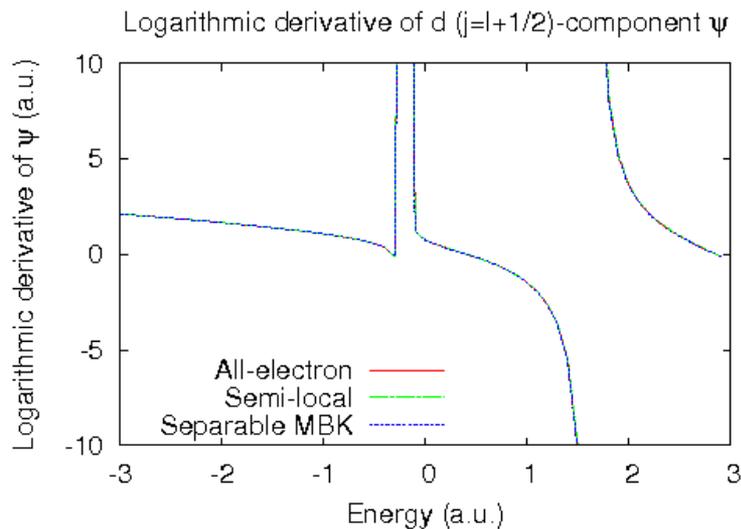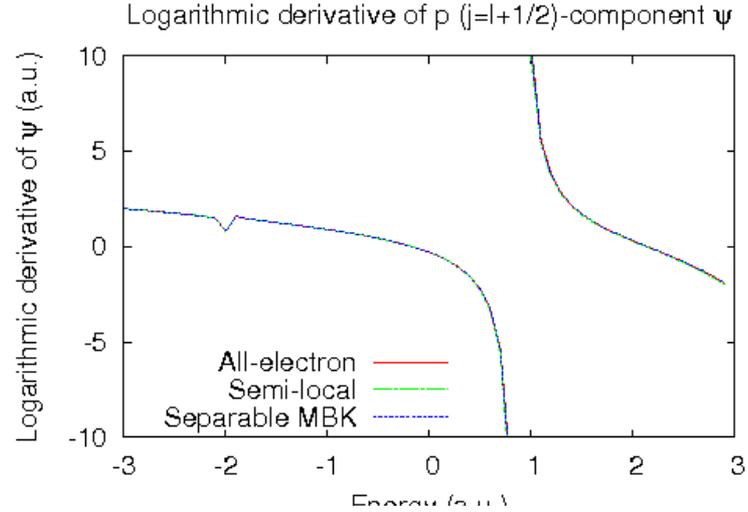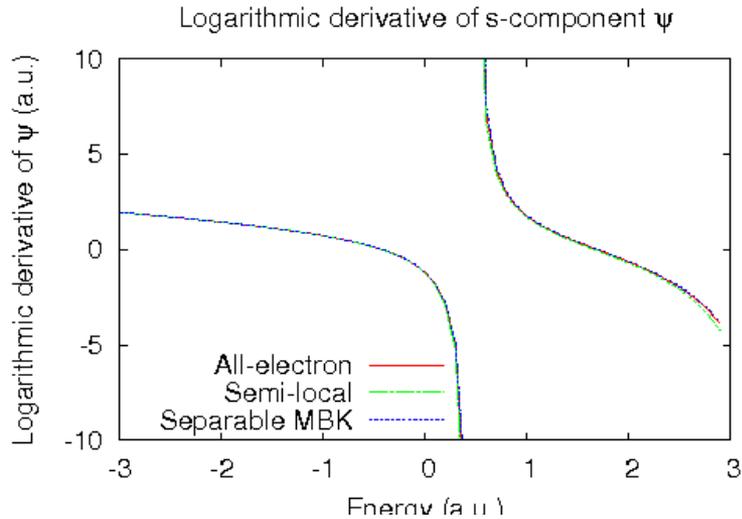
OpenMX vs. Wien2k in fcc Mn
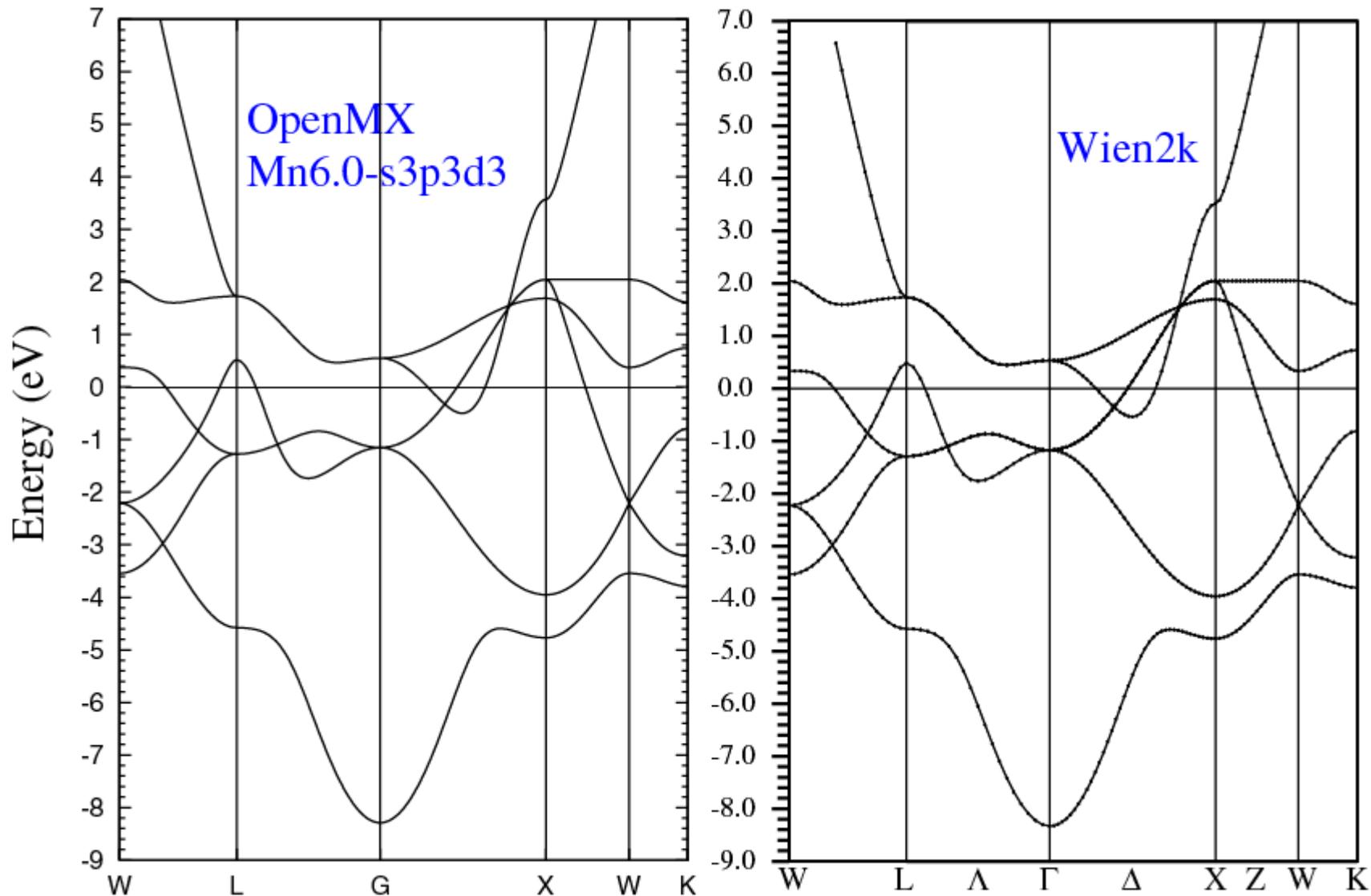
1D-Dirac equation with a spherical potential

1-dimensional radial Dirac equation for the majority component G is given by

$$\left[\frac{1}{2m_{nlj}(r)}\left(\frac{d^2}{dr^2}+\frac{\alpha^2}{2m_{nlj}(r)}\frac{dv_{\mathrm{eff}}}{dr}\frac{d}{dr}+\frac{\alpha^2}{2m_{nlj}(r)}\frac{\kappa}{r}\frac{dv_{\mathrm{eff}}}{dr}-\frac{\kappa(\kappa+1)}{r^2}\right)+\varepsilon_{nlj}-v_{\mathrm{eff}}\right]G_{nlj}=0,$$

The mass term is given by

$$m_{nlj}(r) = 1+\frac{\alpha^2(\varepsilon_{nlj}-v_{\mathrm{eff}})}{2}.$$

Minority component

$$F_{nlj}=\frac{\left(\frac{d}{dr}+\frac{\kappa}{r}\right)G_{nlj}}{\alpha\left[\frac{2}{a^2}+\varepsilon_{nlj}-v_{\mathrm{eff}}(r)\right]F_{nlj}}.$$

By expressing the function G by the following form,

$$G_{nlj}(r) = r^{l+1}L_{nlj}(r).$$

One obtain a set of equations:

$$\frac{dL_{nlj}}{dx} = M_{nlj},$$

$$\frac{dM_{nlj}}{dx} = -(2l+1+\frac{r\alpha^2}{2m_{nlj}}\frac{dv_{\mathrm{eff}}}{dr})M_{nlj}-\frac{r\alpha^2}{2m_{nlj}}\frac{dv_{\mathrm{eff}}}{dr}(l+1+\kappa)L_{nlj}+2m_{nlj}r^2(v_{\mathrm{eff}}-\varepsilon_{nlj})L_{nlj}.$$

The charge density is obtained from

$$\rho(r) = \sum_{n,l,j}q_{nlj}\frac{G_{nlj}(r)^2+F_{nlj}(r)^2}{4\pi r^2},$$

Solving the 1D-Dirac equation

By changing the variable r to x with $r = e^x$, and applying a predictor and corrector method, we can derive the following equations:

$$
\begin{aligned}
L_{i+1}^{(p)} &= 32L_i - 31L_{i-1} - dx(16M_i + 14M_{i-1}) + dx^2(4M_i' - 2M_{i-1}'), \\
M_{i+1}^{(p)} &= -4M_i + 5M_{i-1} + dx(4M_i' + 2M_{i-1}'), \\
M_{i+1}^{(c)} &= M_i + \frac{dx}{12}(8M_i' - M_{i-1}' + 5M_{i+1}'^{(p)}), \\
L_{i+1}^{(c)} &= L_i + \frac{dx}{12}(8M_i - M_{i-1} + 5M_{i+1}^{(c)}).
\end{aligned}
$$

For a given E, the L and M are solved from the origin and distant region, and they are matched at a matching point.
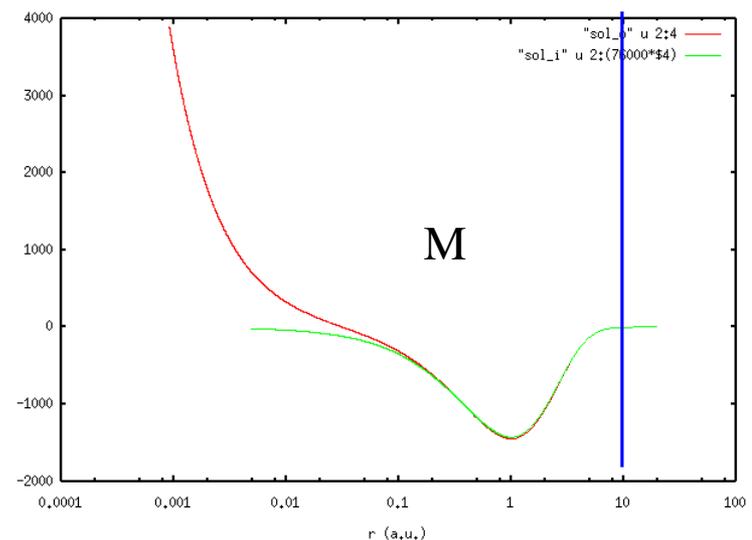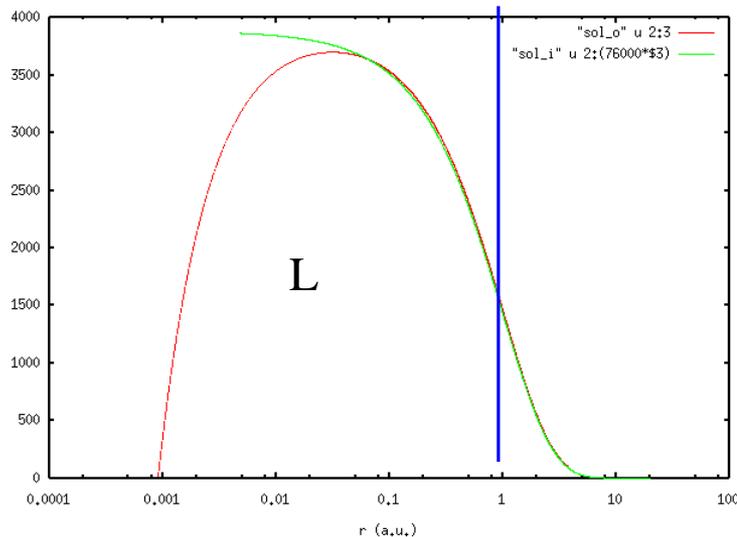
In All_Electron.c, the calculation is performed.

How to find eigenstates #1

If the chosen E is an eigenvalue, the following Eq. is hold:

$$\frac{L_O(r_{\mathrm{MP}})}{L_I(r_{\mathrm{MP}})} = \frac{M_O(r_{\mathrm{MP}})}{M_I(r_{\mathrm{MP}})}$$

r_{MP} is the radius corresponding to the matching point.

So, if ΔD is zero, it turns out that the chosen E is the eigenvalue.

$$\Delta D = M_O(r_{\mathrm{MP}}) - \alpha M_I(r_{\mathrm{MP}}) \qquad \alpha = \frac{L_O(r_{\mathrm{MP}})}{L_I(r_{\mathrm{MP}})}$$

In the right figure ΔD is plotted as a function of E for a hydrogen atom.

Since the analytic solution for a hydrogen atom is known,

$$E = -\frac{1}{2}\frac{Z^2}{n^2}$$

we can confirm that the zeros of ΔD correspond to the analytic eigenvalues/

Ground state
First excited state
Second excited state
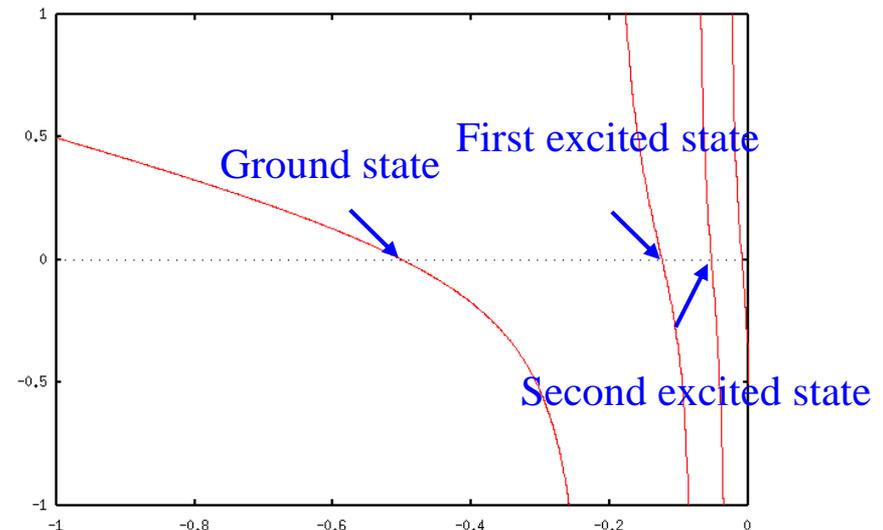
How to find eigenstates #2

The sign of ΔD varies at an eigenvalue.

Algorithm of searching an eigenvalue E

(1) Look for the regime where ΔD changes the sign by scanning energy.
(2) The regime is narrowed by a bisection method.
(3) Once a convergence criterion is fulfilled, an eigenvalue is found

What we can do if we generate PPs by ourselves

It might be true that generating a good PP requires experiences more or less. So, it would be better for beginners to use a well-developed database of PPs. However, if you can generate PPs by yourself, you may be able to explore physics and chemistry by controlling PPs as parameters in a model theory. For example, the following calculations becomes possible.

1. Calculations of core-level binding energies

    In order to calculate core-level binding energies measured by XPS, we need to generate PPs including the targeted core states.

2. Impurity problem using a virtual atom

    PPs having non-integer valence electrons can be used to study effects of dilute impurity.

3. Mixing of PPs for different elements

    It is not easy to identify how the character of elements affects to properties of interest. By using a mixed PPs for different elements, there is a possibility that one finds how the physical property is governed by a specific character of elements.

Calculations of core-level binding energies

It is possible to calculate absolute binding energies of core levels in molecules and solids. To do that we have to generate a proper PP including the targeted state.

It is also important to develop the database of PPs including core states which are well studied in experiments.
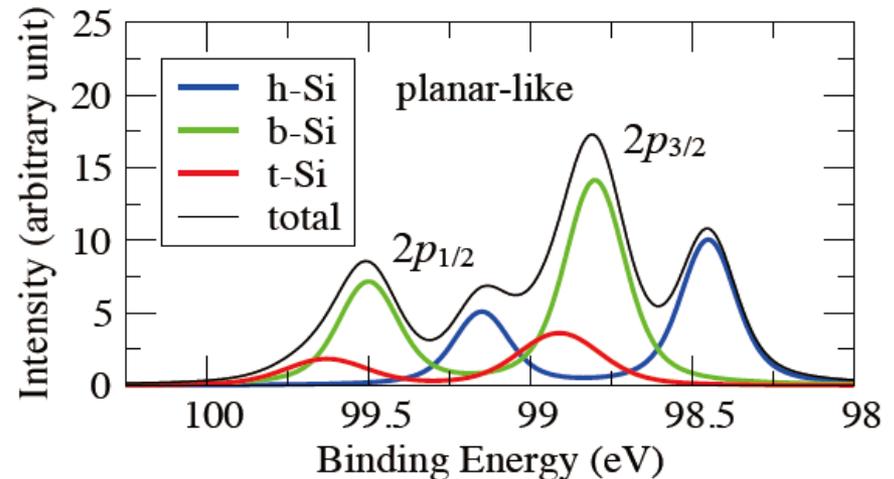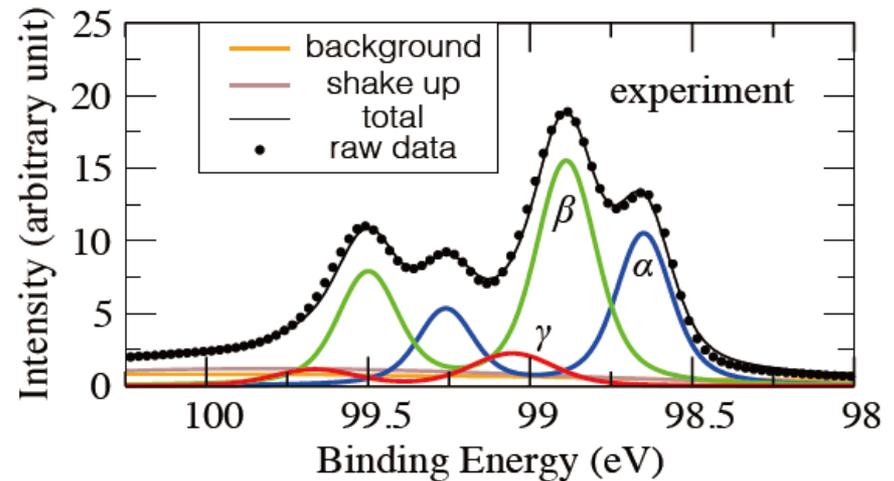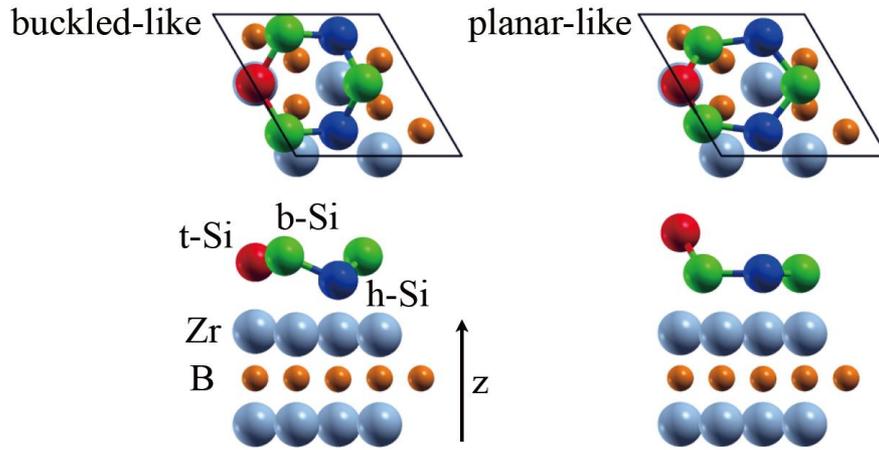
Impurity problem by a virtual atom

One of carbon atoms in the diamond unit cell including 8 carbon atoms is replaced by a virtual atom having 4.2 valence electrons. The calculation corresponds to $C_{7.8}N_{0.2}(=C_{39}N_1)$. Below is the DOS.
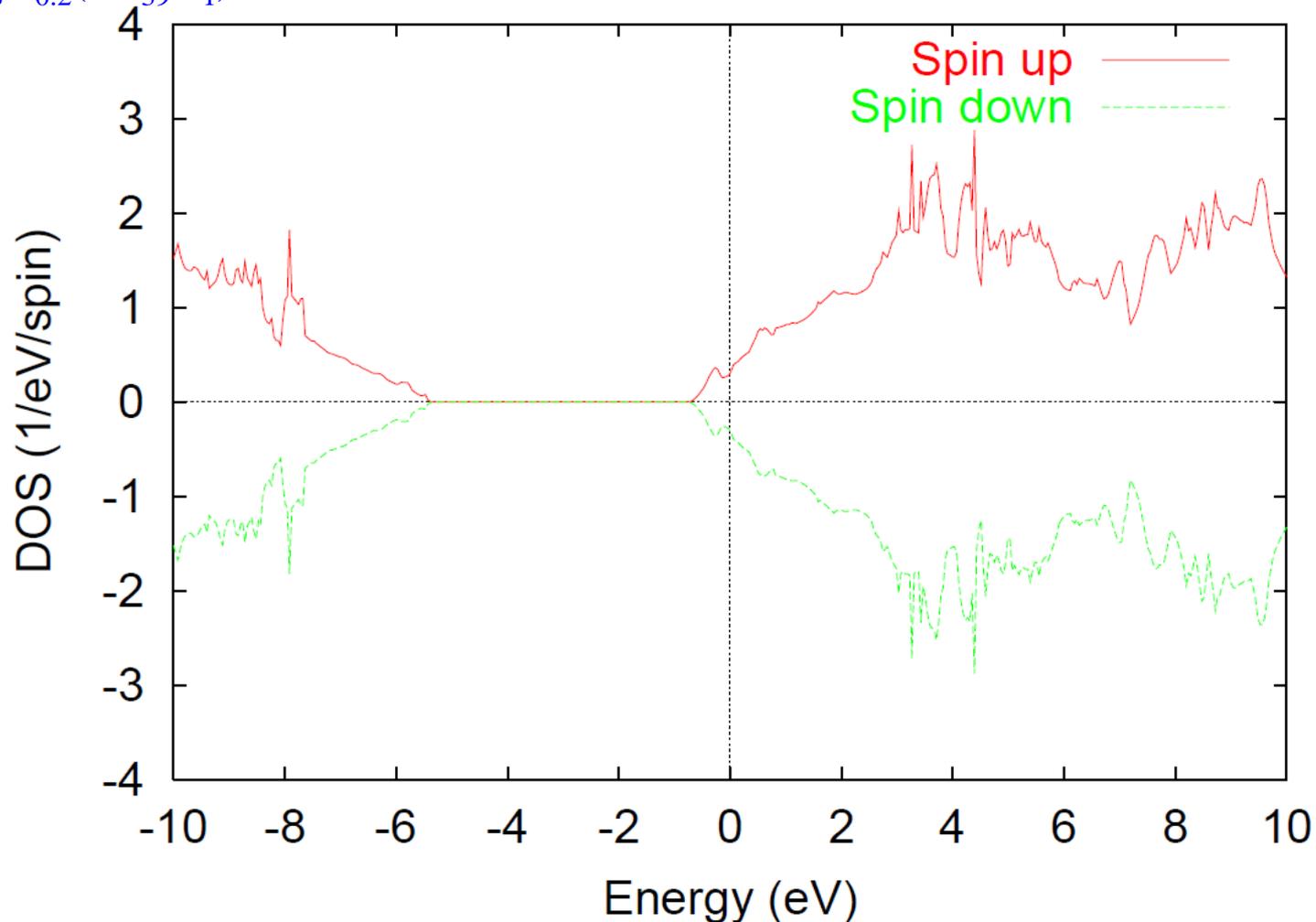
Diamond vs. Graphene
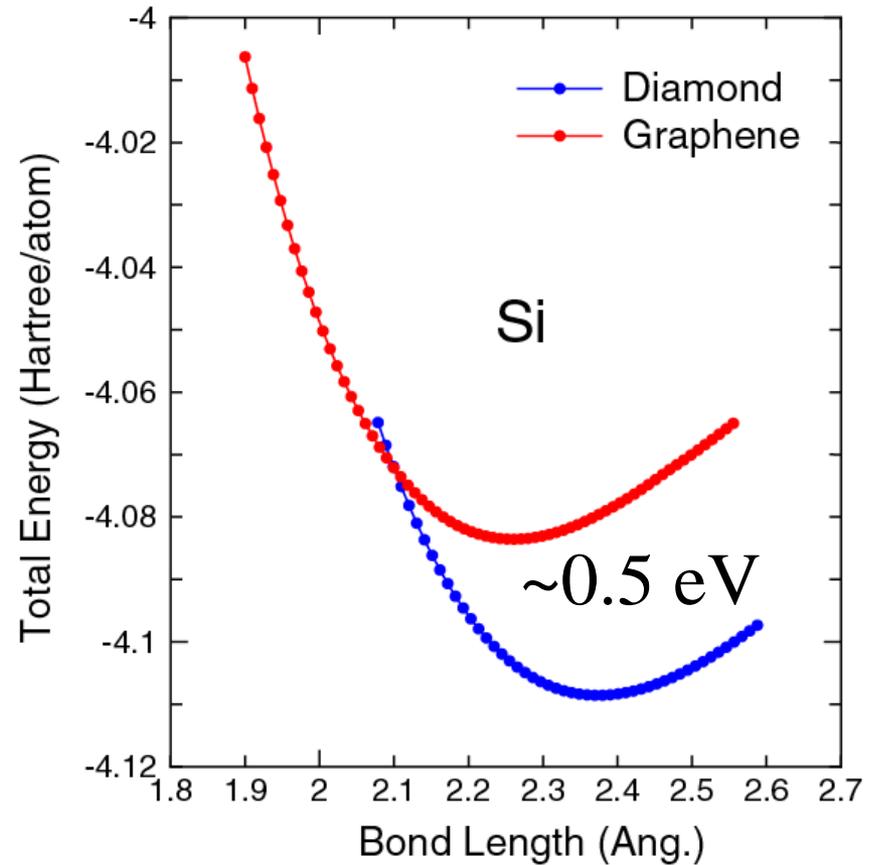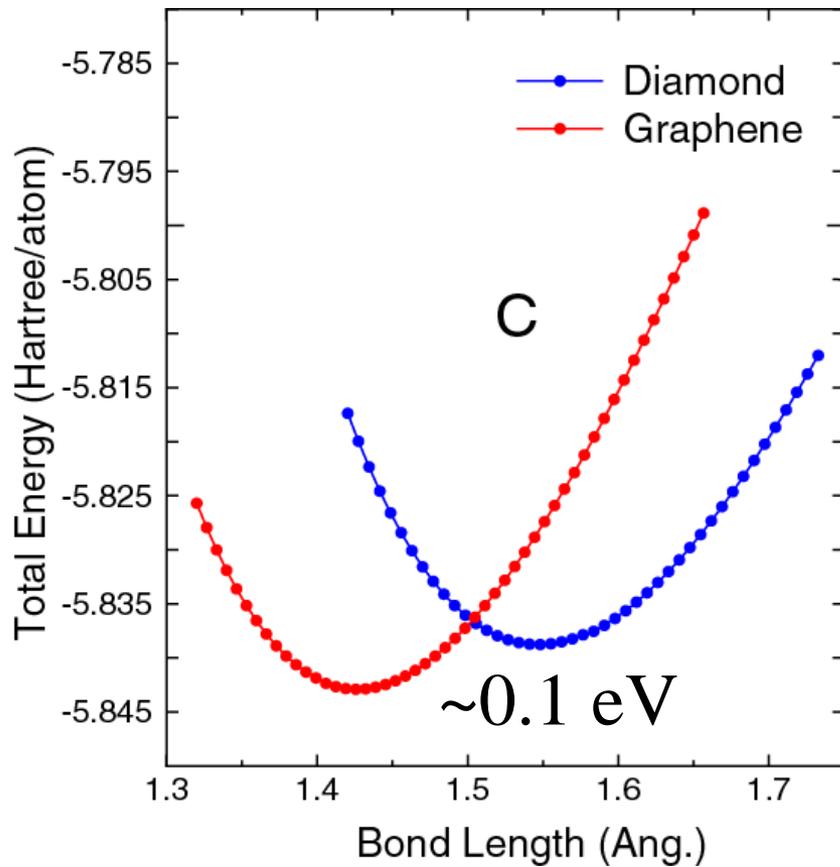
Diamond vs. Graphene from C to Si

Diamond
stabilized

Graphene
stabilized
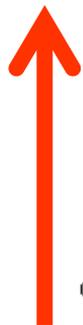
Using a PP for $C_xSi_{(1-x)}$ the energy difference is calculated in the diamond and graphene structures.
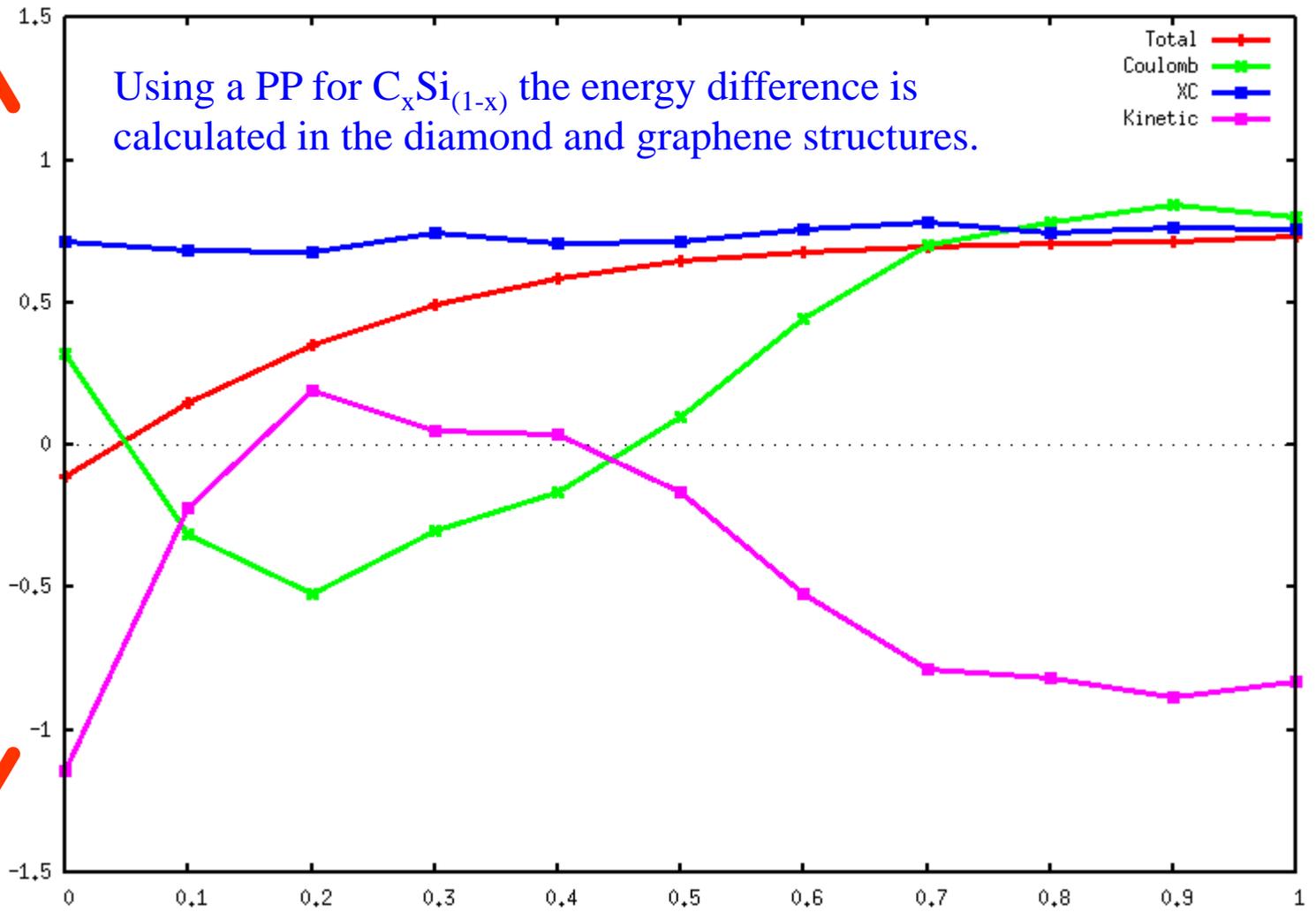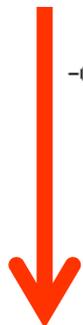
C — The portion of Si in the virtual atom — Si

Pseudopotential generator: ADPACK

Welcome to OpenMX
Open source package for Material eXplorer

Contents

- **What's new**
  - Postdoctoral position opening (Nov. 15, 2016)
  - Patch (Ver. 3.8.1) to OpenMX Ver. 3.8 (Oct. 21, 2016)
  - Winter School in Beijing (Dec. 19-23, 2016)

- **What is OpenMX?**
- **Download**
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- **Manual of Ver. 3.7**
- **Technical Notes**
- **Video Lectures**
- **Publications**
- **OpenMX Forum**
- **OpenMX Viewer**
- **Workshop**
- Database of VPS and PAO
  - **Ver. 2013**
- **ADPACK**
- **Miscellaneous informations**
- **Contributors**
- **Acknowledgment**
- **Opening positions**
- **Links**

The pseudopotential generator for OpenMX is available here.

http://www.openmx-square.org/
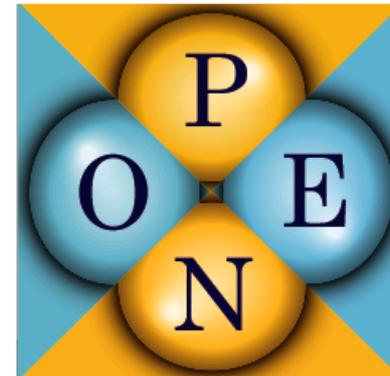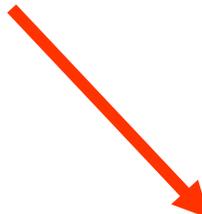
What is ADPACK?

ADPACK (Atomic Density functional program PACKage) is a software to perform density functional calculations for a single atom

The features are listed below:

- All electron calculation by the Schrödinger or Dirac equation
- LDA and GGA treatment to exchange-correlation energy
- Finite element method (FEM) for the Schrödinger equation
- Pseudopotential generation by the TM, BHS, MBK schemes
- Pseudopotential generation for unbound states by Hamann's scheme
- Kleinman and Bylander (KB) separable pseudopotential
- Separable pseudopotential with Blöchl multiple projectors
- Partial core correction to exchange-correlation energy
- Logarithmic derivatives of wave functions
- Detection of ghost states in separable pseudopotentials
- Scalar relativistic treatment
- Fully relativistic treatment with spin-orbit coupling
- Generation of pseudo-atomic orbitals under a confinement potential

The pseudopotentials and pseudo-atomic orbitals can be the input data for OpenMX.

Programs of ADPACK

Programs: 65 C rounties and 5 header files (50,000 lines)

Link: LAPACK and BLAS

Main routine: adpack.c

Input: readfile.c, Inputtool.c

Output: Output.c

All electron calculations: All_Electron.c, Initial_Density.c, Core.c

Numerical solutions for Schroedinger and Dirac eqs.: Hamming_I.c, Hamming_O.c

Density: Density.c, Density_PCC.c, Density_V.c

Exchange-Correlation: XC_CA.c, XC_EX.c, XC_PW91.c, XC_VWN.c, XC_PBE.c

Mixing: Simple_Mixing.c

Pseudopotentials: MBK.c, BHS.c, TM.c

Pseudo-atomic orbitals: Multiple_PAO.c

The global variables are declared in adpack.h.

Database (2013)

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
The data of elements with the underline are currentl
VPS and PAO, in the program package, OpenMX, t
openmx*.*/DFT_DATA13/VPS/ and openmx*.*/DFT_
The delta factor of OpenMX with the database (201

Fully relativistic pseudopotentials

Fully relativistic pseudopotentials generated by the N
(PBE13) which contain a partial core correction an

- ○ **Pt_CA13.vps**
- ○ **Pt_PBE13.vps**

Optimized VPS and PAO
are available, which
includes relativistic effect
with spin-orbit coupling.

E																	
H																	
Li	Be																
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															

L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

http://www.openmx-square.org/

Close look at "vps" files #1

Input file

```
***************************************************
                  Input file
***************************************************

#
# File Name
#

System.CurrrentDir       ./              # default=./
System.Name              Pt_PBE13
Log.print                OFF             # ON|OFF

System.UseRestartfile    yes             # NO|YES, default=NO
System.Restartfile       Pt_PBE13        # default=null

#
# Calculation type
#

eq.type                  dirac           # sch|sdirac|dirac
calc.type                vps             # ALL|VPS|PAO
xc.type                  GGA             # LDA|GGA

#
# Atom
#

AtomSpecies              78
max.occupied.N            6
total.electron           78.0
valence.electron         16.0
<occupied.electrons
  1   2.0
  2   2.0  6.0
  3   2.0  6.0  10.0
  4   2.0  6.0  10.0 14.0
  5   2.0  6.0   9.0  0.0  0.0
  6   1.0  0.0   0.0  0.0  0.0  0.0
occupied.electrons>
```

In the header part, the input file for the ADPACK calculations are shown, which maybe helpful for the next generation of pseudopotentials.

Close look at "vps" files #2

Eigenvalues for all electron calculation

```
**************************************************
Eigenvalues (Hartree) in the all electron calculation
**************************************************
                           j=l+1/2                  j=l-1/2
n=  1  l=  0      -2868.8969439503935      -2868.8969439503935
n=  2  l=  0       -503.1142921617339       -503.1142921617339
n=  2  l=  1       -419.1546670411121       -482.3720670651586
n=  3  l=  0       -118.0771871048129       -118.0771871048129
n=  3  l=  1        -94.8406495857986       -108.7310226714485
n=  3  l=  2        -76.1768324508852        -79.1659107610239
n=  4  l=  0        -25.3345514773071        -25.3345514773071
n=  4  l=  1        -18.0570286040002        -21.3625609002204
n=  4  l=  2        -10.9124371484223        -11.5257406345024
n=  4  l=  3         -2.4568191349790         -2.5821360560534
n=  5  l=  0         -3.6982650446879         -3.6982650446879
n=  5  l=  1         -1.8910921655761         -2.4338351652662
n=  5  l=  2         -0.2019516934267         -0.2496588022815
n=  6  l=  0         -0.2079456213222         -0.2079456213222
```

The eigenvalues with j=l±1/2 for the all electron calculations by the Dirac equation are included, which can be used to estimate the splitting by spin-orbit coupling

Close look at "vps" files #3

Information for pseudopotentials

```
vps.type                  MBK
number.vps                  5
<pseudo.NandL
    0    5    1    1.1000    0.0
    1    5    2    1.7000    0.0
    2    6    0    2.0000    0.0
    3    6    1    2.8000    0.0
    4    7    0    2.9000   -0.1
pseudo.NandL>
```

The specification for the pseudopotentials is made by vps.type, number.vps, and pseudo.NandL.

The project energies λ is shown as follows:

```
<project.energies
  7
  0      1.000000000000000e+00     1.000000000000000e+00
  0      1.000000000000000e+00     1.000000000000000e+00
  1     -1.000000000000000e+00    -1.000000000000000e+00
  1     -1.000000000000000e+00    -1.000000000000000e+00
  2     -1.000000000000000e+00    -1.000000000000000e+00
  2     -1.000000000000000e+00    -1.000000000000000e+00
  2     -1.000000000000000e+00    -1.000000000000000e+00
project.energies>
```

Close look at "vps" files #4

The generated pseudopotentials are output by Pseudo.Potentials

```
<Pseudo.Potentials
-1.000000000000000e+01   4.53999297624849e-05   -1.56274493573701e+01
 1.29016191735297e+00   -3.53576793162279e-04   -2.74501529071506e-04
-2.44604572903325e-08    4.46045901596636e-08    5.09718887954710e-08
-9.97354909819639e+00    4.66168218439265e-05   -1.56274493573701e+01
 1.29016191758754e+00   -3.63054006042743e-04   -2.81859221925009e-04
-2.57892987562848e-08    4.70277839806157e-08    5.37409931750746e-08
-9.94709819639279e+00    4.78663312960476e-05   -1.56274493573701e+01
 1.29016191783448e+00   -3.72785244541990e-04   -2.89414129143262e-04
-2.71903310082123e-08    4.95826204925540e-08    5.66605322202532e-08
-9.92064729458918e+00    4.91493323893655e-05   -1.56274493573701e+01
 1.29016191809451e+00   -3.82773175519879e-04   -2.97171536827178e-04
-2.86674758905822e-08    5.22762513305807e-08    5.97386784609548e-08
-9.89419639278557e+00    5.04667228281981e-05   -1.56274493573701e+01
 1.29016191836861e+00   -3.93037216339845e-04   -3.05136872765505e-04
-3.02248683064018e-08    5.51162166502627e-08    6.29840484088342e-08
-9.86774549098196e+00    5.18194243787784e-05   -1.56274493573701e+01
 1.29016191865760e+00   -4.03572119760603e-04   -3.13315710232509e-04
```

1st column: x

2nd column: $r = \exp(x)$ in a.u.

3rd column: radial part of local pseudopotential

4th and later columns: radial part of non-local pseudopotentials.

Close look at "vps" files #5

Charge density for partial core correction

```
<density.PCC
-1.00000000000000e+01   4.53999297624849e-05   6.84116077628136e-01
-9.97354909819639e+00   4.66168218439265e-05   6.84116077628136e-01
-9.94709819639279e+00   4.78663312960476e-05   6.84116077628136e-01
-9.92064729458918e+00   4.91493323893655e-05   6.84116077628136e-01
-9.89419639278557e+00   5.04667228281981e-05   6.84116077628136e-01
-9.86774549098196e+00   5.18194243787784e-05   6.84116077628136e-01
-9.84129458917836e+00   5.32083835142066e-05   6.84116077628136e-01
-9.81484368737475e+00   5.46345720766889e-05   6.84116077628136e-01
-9.78839278557114e+00   5.60989879575261e-05   6.84116077628136e-01
-9.76194188376754e+00   5.76026557953301e-05   6.84116077628136e-01
-9.73549098196393e+00   5.91466276929535e-05   6.84116077628136e-01
-9.70904008016032e+00   6.07319839536367e-05   6.84116077628136e-01
-9.68258917835671e+00   6.23598338368870e-05   6.84116077628136e-01
-9.65613827655311e+00   6.40313163343160e-05   6.84116077628136e-01
```

1st column: x

2nd column: r=exp(x) in a.u.

3rd column: charge density for PCC

Outlook

■ Although the development of PPs has a long history, and nowadays databases containing high-quality PPs are available. So, it would be better for beginners to use the well-developed database.

■ Nevertheless it is important to understand the theories of PPs since this is a basis of current state-of-the-art technology in first-principles calculations.

■ Actually, OpenMX is based on norm-conserving pseudopotentials developed by Morrison, Bylander, and Kleinman, PRB 47, 6728 (1993).

■ If you can generate PPs by yourself, you may be able to explore physics and chemistry by controlling PPs as parameters in a model theory.