

# Pseudopotentials and primitive basis functions: Ver. 1.0

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In the technical notes, we provide memorandum of methods for generating pseudopotentials and primitive basis functions used in OpenMX. The methods were implemented in ADPACK, and the database (Ver. 2019) of VPSs and PAOs were generated by ADPACK with the methods.

## 1 Derivation of radial equations

### 1.1 Schrödinger equation

Let us start to introduce the Kohn-Sham (KS) equation for a spin-unpolarized atomic system with atomic number of  $Z$  given by

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right\} \phi_{nlm}(\mathbf{r}) = \varepsilon_{nlm} \phi_{nlm}(\mathbf{r}), \quad (1)$$

where  $\phi_{nlm}$  is a KS eigenstate specified by a principal quantum number  $n$ , an azimuthal quantum number  $l$ , and a magnetic quantum number  $m$ , and  $\varepsilon_{nlm}$  is the corresponding eigenenergy. Throughout the derivation we use the atomic unit, i.e.,  $\hbar = 1$ ,  $m_e = 1$ , and  $e^2 = 1$ . The KS effective potential  $v_{\text{eff}}$  is given by

$$v_{\text{eff}}(\mathbf{r}) = -\frac{Z}{|\mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}), \quad (2)$$

where  $\rho$  and  $v_{\text{xc}}$  are the electron density and exchange-correlation potential, respectively. The first term is the Coulombic potential by the atomic nucleus placed at the origin, and the second term is the Hartree potential  $v_{\text{H}}(\mathbf{r})$  produced by the distribution of the electron density. The last term is the exchange-correlation potential, and will be discussed later on. Since pseudopotentials are generated after self-consistently solving the atomic KS equation, we first discuss how the all electron calculation based on the atomic KS equation is performed in ADPACK. It is assumed that the atomic system is spin-unpolarized and the distribution of the electron density is spherical in the all electron calculation even if some of shell specified by  $n$  is partially filled. A way of calculating the spherical electron density will be discussed later on. Under the assumption for the electron density, it would be better to express the Laplacian in polar coordinate  $(r, \theta, \varphi)$  as

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (3)$$

The KS wavefunction  $\phi_{nlm}$  is expressed by

$$\phi_{nlm}(\mathbf{r}) = \frac{P_{nl}(r)}{r} Y_l^m(\theta, \varphi). \quad (4)$$

It is noted that the spherical function  $P$  does not depend on the magnetic quantum number  $m$  due to the assumption of spherical charge density. By putting Eqs. (3) and (4) into Eq. (1) and considering variable separation, we have two independent equations for a radial  $P$  and spherical functions  $Y$  as follows:

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_{\text{eff}}(r) \right] P_{nl}(r) = \varepsilon_{nl} P_{nl}(r), \quad (5)$$

$$\hat{l}^2 Y_l^m(\theta, \varphi) = l(l+1) Y_l^m(\theta, \varphi), \quad (6)$$

where

$$\hat{l}^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}. \quad (7)$$

The spherical function  $Y_l^m$  is an eigenfunction of Eq. (6), and obtained analytically as spherical harmonic function. Thus, we only have to concentrate on how Eq. (5) for the radial function  $P$  can be solved numerically. By assuming that electrons uniformly occupy in states specified by  $(n, l)$  with an occupation number of  $p_{nl}$ , the charge density is calculated by

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{n,l} p_{nl} \sum_m |\phi_{nlm}(\mathbf{r})|^2, \\ &= \sum_{n,l} p_{nl} \left| \frac{P_{nl}(r)}{r} \right|^2 \sum_m |Y_l^m(\theta, \varphi)|^2. \end{aligned} \quad (8)$$

By noting that

$$\sum_{m=-l}^{m=l} |Y_l^m(\theta, \varphi)|^2 = \frac{2l+1}{4\pi}, \quad (9)$$

we have for Eq. (8) the following equation:

$$\rho(r) = \sum_{n,l} q_{nl} \frac{P_{nl}(r)^2}{4\pi r^2} \quad (10)$$

with the definition of  $q_{nl}$ :

$$q_{nl} = p_{nl}(2l+1), \quad (11)$$

where we assumed that  $P$  is a real function. A set of occupation numbers  $\{p\}$  or  $\{q\}$  is chosen so that an electronic configuration of the ground state can be taken into account in principle.

In order to solve Eq. (5) in a numerically stable way, we transform the variable by

$$x = \ln r, \quad (12)$$

and express the radial function  $P$  by

$$P_{nl}(r) = r^{l+1} L_{nl}(r). \quad (13)$$

Then, Eq. (5) is now expressed by two simultaneous differential equations given by

$$\frac{dL_{nl}}{dx} = M_{nl}, \quad (14)$$

$$\frac{dM_{nl}}{dx} = -(2l+1)M_{nl} + 2r^2(v_{\text{eff}} - \varepsilon_{nl})L_{nl}. \quad (15)$$

They are the equations used for self-consistent numerical calculations of the KS method based on the Schrödinger equation in ADPACK.

## 1.2 Dirac equation

Relativistic effects are taken into account by considering the Dirac radial differential equations under a spherical potential:

$$\left[ \frac{d}{dr} + \frac{\kappa}{r} \right] G_{nlj} - \alpha \left[ \frac{2}{\alpha^2} + \varepsilon_{nlj} - v_{\text{eff}}(r) \right] F_{nlj} = 0, \quad (16)$$

$$\left[ \frac{d}{dr} - \frac{\kappa}{r} \right] F_{nlj} + \alpha [\varepsilon_{nlj} - v_{\text{eff}}(r)] G_{nlj} = 0, \quad (17)$$

where  $G$  and  $F$  are the majority and minority components of the radial wave function.  $\alpha \equiv 1/c$  (1/137.036 in a.u.).  $\kappa = l$  and  $\kappa = -(l+1)$  for  $j = l - \frac{1}{2}$  and  $j = l + \frac{1}{2}$ , respectively. Solving Eq. (16) with respect to  $F$ , we have

$$F_{nlj} = \frac{\left( \frac{d}{dr} + \frac{\kappa}{r} \right) G_{nlj}}{\alpha \left[ \frac{2}{\alpha^2} + \varepsilon_{nlj} - v_{\text{eff}}(r) \right] F_{nlj}}. \quad (18)$$

By inserting Eq. (18) and its derivative with respect to  $r$  into Eq. (17), we have the following equation for  $G$ :

$$\left[ \frac{1}{2m_{nlj}(r)} \left( \frac{d^2}{dr^2} + \frac{\alpha^2}{2m_{nlj}(r)} \frac{dv_{\text{eff}}}{dr} \frac{d}{dr} + \frac{\alpha^2}{2m_{nlj}(r)} \frac{\kappa}{r} \frac{dv_{\text{eff}}}{dr} - \frac{\kappa(\kappa+1)}{r^2} \right) + \varepsilon_{nlj} - v_{\text{eff}} \right] G_{nlj} = 0, \quad (19)$$

with

$$m_{nlj}(r) = 1 + \frac{\alpha^2(\varepsilon_{nlj} - v_{\text{eff}})}{2}. \quad (20)$$

As well as the case for the Schrödinger equation, in order to solve Eq. (19) in a numerically stable way, we introduce the variable change given by Eq. (12), and express the majority component of radial function  $P$  by

$$G_{nlj}(r) = r^{l+1} L_{nlj}(r). \quad (21)$$

Then, Eq. (19) is now expressed by two simultaneous differential equations given by

$$\frac{dL_{nlj}}{dx} = M_{nlj}, \quad (22)$$

$$\frac{dM_{nlj}}{dx} = -(2l+1 + \frac{r\alpha^2}{2m_{nlj}} \frac{dv_{\text{eff}}}{dr}) M_{nlj} - \frac{r\alpha^2}{2m_{nlj}} \frac{dv_{\text{eff}}}{dr} (l+1+\kappa) L_{nlj} + 2m_{nlj} r^2 (v_{\text{eff}} - \varepsilon_{nlj}) L_{nlj}. \quad (23)$$

They are the equations used for self-consistent numerical calculations of the KS method based on the Dirac equation in ADPACK. Once the radial function  $L$  is determined through Eqs. (22) and (23), the functions  $G$  and  $F$  can be derived from Eqs. (21) and (18), respectively. Then, the spherical charge density is calculated by

$$\rho(r) = \sum_{n,l,j} q_{nlj} \frac{G_{nlj}(r)^2 + F_{nlj}(r)^2}{4\pi r^2}, \quad (24)$$

where  $q_{nlj}$  is determined by taking account of degeneracy arising from the total angular momentum quantum number  $j$ .

### 1.3 Scalar relativistic Dirac equation

The degeneracies of states specified with  $j = l - \frac{1}{2}$  and  $j = l + \frac{1}{2}$  are  $2l$  and  $2(l + 1)$ , respectively. Here we consider to average the  $\kappa$  dependent terms in Eq. (23). Then,  $\kappa$  can be averaged with the degeneracies as follows:

$$\begin{aligned}\kappa_{\text{av}} &= \frac{2l}{2l + 2(l + 1)} \times \kappa_{j=l-1/2} + \frac{2(l + 1)}{2l + 2(l + 1)} \times \kappa_{j=l+1/2}, \\ &= \frac{2l}{2l + 2(l + 1)} \times l + \frac{2(l + 1)}{2l + 2(l + 1)} \times -(l + 1), \\ &= -1.\end{aligned}\tag{25}$$

By inserting the averaged value  $\kappa_{\text{av}}$  into Eq. (23), we obtain two simultaneous differential equations:

$$\frac{dL_{nl}}{dx} = M_{nl},\tag{26}$$

$$\frac{dM_{nl}}{dx} = -(2l + 1 + \frac{r\alpha^2}{2m_{nl}} \frac{dv_{\text{eff}}}{dr})M_{nl} - \frac{lr\alpha^2}{2m_{nl}} \frac{dv_{\text{eff}}}{dr}L_{nl} + 2m_{nl}r^2(v_{\text{eff}} - \varepsilon_{nl})L_{nl}.\tag{27}$$

They are the equations used for self-consistent numerical calculations of the KS method based on the scalar relativistic Dirac equation in ADPACK.

## 2 Numerical method for solving differential equations

We solve the differential equations, Eqs. (14) and (15), Eqs. (22) and (23), or Eqs. (26) and (27), in a numerical method described below. A uniform grid is introduced over the variable  $x$  defined by Eq. (12). We use  $-4$  and  $10$  for the minimum  $x_{\text{min}}$  and maximum values  $x_{\text{max}}$ , respectively, in atomic unit, but adjust these values within the extent depending on degree of orbital localization of each state. Then, the uniform grid is generated by

$$x_i = x_{\text{xmin}} + i \, dx\tag{28}$$

with

$$dx = \frac{x_{\text{max}} - x_{\text{min}}}{N},\tag{29}$$

where  $i$  runs from  $0$  to  $N - 1$ . In most cases, we use  $N = 12000$ . The simultaneous differential equations with a trial eigenenergy are numerically integrated from both  $x_{\text{min}}$  and  $x_{\text{max}}$ . Then, they are matched at  $x_{\text{mp}}$  which are practically chosen beyond the outer most peak of the radial function. If the trial eigenenergy is a true eigenenergy, the following condition is satisfied:

$$\frac{L^{(\text{min})}(x_{\text{mp}})}{L^{(\text{max})}(x_{\text{mp}})} = \frac{M^{(\text{min})}(x_{\text{mp}})}{M^{(\text{max})}(x_{\text{mp}})},\tag{30}$$

where  $L^{(\text{min})}$  and  $L^{(\text{max})}$  are radial functions which are obtained by solving the equations from  $x_{\text{min}}$  and  $x_{\text{max}}$ , respectively. A true eigenenergy can be found by a bisection method based on Eq. (30).

We now describe a way of solving the differential equations. To simplify notations in the following derivation we define  $L_{nlj}(x_i) \equiv L_i$  and  $M_{nlj}(x_i) \equiv M_i$ . In our implementation, the differential equations are integrated based on the following ideas:

1. **Finding of  $L^{(F)}(x)$**

The function  $F$  around  $x_i$  is fitted to a polynomial function  $L^{(F)}$  defined by

$$L^{(F)}(x) = \sum_{k=0}^5 a_k (x - x_i)^k, \quad (31)$$

where the coefficients  $\{a\}$  are found from  $L_{i-1}$ ,  $L'_{i-1}$ ,  $L''_{i-1}$ ,  $L_i$ ,  $L'_i$ ,  $L''_i$ . It is noted that  $L'$  and  $L''$  are the first and second derivatives with respect to  $x$ , respectively.

2. **Calculation of  $L_{i+1}^{(p)}$**

The predicted value of  $L$  at  $x_{i+1}$ ,  $L_{i+1}^{(p)}$ , is calculated by

$$L_{i+1}^{(p)} = L^{(F)}(x_{i+1}). \quad (32)$$

3. **Finding of  $M^{(F)}(x)$**

The function  $M$  around  $x_i$  is fitted to a polynomial function  $M^{(F)}$  defined by

$$M^{(F)}(x) = \sum_{k=0}^3 b_k (x - x_i)^k, \quad (33)$$

where the coefficients  $\{b\}$  are found from  $M_{i-1}$ ,  $M'_{i-1}$ ,  $M_i$ , and  $M'_i$ .

4. **Calculation of  $M_{i+1}^{(p)}$**

The predicted value of  $M$  at  $x_{i+1}$ ,  $M_{i+1}^{(p)}$ , is calculated by

$$M_{i+1}^{(p)} = M^{(F)}(x_{i+1}). \quad (34)$$

5. **Calculation of  $M'^{(F)}(x)$**

The function  $M'$  around  $x_i$  is fitted to a polynomial function  $M'^{(F)}$  defined by

$$M'^{(F)}(x) = \sum_{k=0}^2 c_k (x - x_i)^k, \quad (35)$$

where the coefficients  $\{c\}$  are found from the right side of Eq. (15), (23), or (27) calculated at three points:  $(x_{i-1}, L_{i-1}, M_{i-1})$ ,  $(x_i, L_i, M_i)$ , and  $(x_{i+1}, L_i^{(p)}, M_i^{(p)})$ .

6. **Calculation of  $M_{i+1}^{(c)}$**

The predicted value of  $M$  at  $x_{i+1}$ ,  $M_{i+1}^{(c)}$ , is found by analytically integrating the following equation:

$$M_{i+1}^{(c)} = M_i + \int_{x_i}^{x_{i+1}} M'^{(F)}(x) dx. \quad (36)$$

7. **Calculation of  $L'^{(F)}(x)$**

The function  $L'$  around  $x_i$  is fitted to a polynomial function  $L'^{(F)}$  defined by

$$L'^{(F)}(x) = \sum_{k=0}^2 d_k (x - x_i)^k, \quad (37)$$

where the coefficients  $\{d\}$  are found from  $M_{i-1}$ ,  $M_i$ , and  $M_{i+1}^{(c)}$ .

## 8. Calculation of $L_{i+1}^{(c)}$

The predicted value of  $L$  at  $x_{i+1}$ ,  $L_{i+1}^{(c)}$ , is found by analytically integrating the following equation:

$$L_{i+1}^{(c)} = L_i + \int_{x_i}^{x_{i+1}} L'^{(F)}(x) dx. \quad (38)$$

The numerical integration of differential equations defined by the procedure is a predictor-corrector method. By analytically performing all the steps in the procedure, we finally obtain the following equations:

$$L_{i+1}^{(p)} = 32L_i - 31L_{i-1} - dx(16M_i + 14M_{i-1}) + dx^2(4M'_i - 2M'_{i-1}), \quad (39)$$

$$M_{i+1}^{(p)} = -4M_i + 5M_{i-1} + dx(4M'_i + 2M'_{i-1}), \quad (40)$$

$$M_{i+1}^{(c)} = M_i + \frac{dx}{12}(8M'_i - M'_{i-1} + 5M'_{i+1}), \quad (41)$$

$$L_{i+1}^{(c)} = L_i + \frac{dx}{12}(8M_i - M_{i-1} + 5M_{i+1}^{(c)}). \quad (42)$$

In order to numerically integrate the differential equations by Eqs. (39)-(42) from  $x_{\text{xmin}}$ , one has to know  $L_0$ ,  $L'_0$ ,  $L''_0$ ,  $L_1$ ,  $L'_1$ , and  $L''_1$ . In ADPACK they are estimated by the Frobenius method as explained below. Following the idea of Frobenius, we expand  $v_{\text{eff}}$  and  $L$  as

$$v_{\text{eff}}(r) = \sum_{\nu=0} A_{\nu} r^{\nu}, \quad (43)$$

$$L(r) = \sum_{\mu=0} B_{\mu} r^{\mu}. \quad (44)$$

By inserting Eqs. (43) and (44) via Eq. (13) into Eq. (5), and comparing the coefficient of each term in the power series of  $r$  piece by piece, one obtain the following equations:

$$B_0 = \text{arbitrary}, \quad (45)$$

$$B_1 = 0, \quad (46)$$

$$B_2 = B_0 \left( \frac{A_0 - \varepsilon}{2l + 3} \right), \quad (47)$$

$$B_3 = B_0 \left( \frac{A_1}{3l + 6} \right), \quad (48)$$

$$B_4 = \frac{A_0 B_2 + A_2 B_0 - \varepsilon B_2}{4l + 10}, \quad (49)$$

where a set of coefficients  $\{A\}$  is obtained by fitting to  $v_{\text{eff}}$ . From Eq. (44), one can estimate  $L_0$ ,  $L'_0$ ,  $L''_0$ ,  $L_1$ ,  $L'_1$ , and  $L''_1$ . A similar estimation can be performed even for the Dirac and the scalar relativistic equations as well. When the differential equations are solved from  $x_{\text{max}}$ , one can estimate  $L_{N-1}$ ,  $L'_{N-1}$ ,  $L''_{N-1}$ ,  $L_{N-2}$ ,  $L'_{N-2}$ , and  $L''_{N-2}$  based on the asymptotic form of radial function. In Eq. (5), we consider  $\frac{l(l+1)}{2r^2}$  and  $v_{\text{eff}}$  negligible at  $x_{\text{max}}$ , and obtain the following equation:

$$-\frac{1}{2} \frac{d^2}{dr^2} P_{nl}(r) = \varepsilon_{nl} P_{nl}(r) \quad (50)$$

of which analytic solution is

$$P_{nl}(r) = \exp(-\sqrt{-2\varepsilon}r). \quad (51)$$

Thus, those values can be easily estimated by the asymptotic form.

### 3 Calculation of Hartree potential

The Hartree potential is calculated by

$$v_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (52)$$

Since the spherical part of the integration is analytically performed by considering contributions from the inside and the outside with respect to position  $\mathbf{r}$ , we only have to perform the radial integration given by

$$v_{\text{H}}(x) = \frac{4\pi}{r} \int_{x_{\min}}^x \rho(x')r'^3 dx' + 4\pi \int_x^{x_{\max}} \rho(x')r'^2 dx'. \quad (53)$$

The integrations are performed by employing a trapezoidal rule in ADPACK.

### 4 Troullier and Martins (TM) pseudopotential

Although we constructed pseudopotentials in the database (Ver. 2019) by the Morrison, Bylander and Kleinman (MBK) pseudopotential method, which will be discussed in the next section, our implementation of the MBK method is based on the Troullier and Martins (TM) method. Thus, we first discuss the TM method in the section. Once the all electron calculation is self-consistently performed, we construct pseudopotentials based on Eq. (5) regardless of equation that we solve for the all electron calculation. This is because pseudopotentials are generally constructed for valence electronic states which are delocalized in space compared to core electrons. Thus, relativistic effects are no longer obvious after achieving the self-consistency in the all electron calculation. In the TM method, a nodeless pseudofunction  $P^{(\text{PS})}$  is defined by

$$P_{nlj}^{(\text{PS})}(r) = \begin{cases} r^{l+1} \exp[p(r)], & \text{for } r \leq r_c \\ P_{nlj}^{(\text{AE})}(r), & \text{for } r_c < r \end{cases} \quad (54)$$

where  $P^{(\text{AE})}$  is the corresponding all electron radial function, and  $r_c$  is a cutoff radius which can be dependent on each state. Also, the function  $p(r)$  is given by

$$p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}. \quad (55)$$

The coefficients  $\{c\}$  are determined by satisfying several conditions explained below. The screened pseudopotential  $v_{nlj}^{(\text{sps})}$  corresponding to  $P_{nlj}^{(\text{PS})}(r)$  is now obtained by solving Eq. (5) with respect to  $v_{nlj}^{(\text{sps})}$  as follows:

$$v_{nlj}^{(\text{sps})}(r) = \varepsilon_{nlj} - \frac{l(l+1)}{2r^2} + \frac{1}{2} \frac{[P_{nlj}^{(\text{PS})}(r)]''}{P_{nlj}^{(\text{PS})}(r)}. \quad (56)$$

Beyond  $r_c$ ,  $v_{nlj}^{(\text{sps})}(r)$  is nothing but the effective potential  $v_{\text{eff}}$  in the all electron calculation. Within  $r_c$ , the pseudopotential  $v_{nlj}^{(\text{sps})}(r)$  is given by

$$v_{nlj}^{(\text{sps})}(r) = \varepsilon_{nlj} + \frac{(l+1)p'(r)}{r} + \frac{1}{2} [p''(r) + [p'(r)]^2]. \quad (57)$$

The polynomial function defined by Eq. (55) is determined by the following conditions:

### 1. Norm-conserving condition

It is imposed that the norm of the pseudofunction is the same as that of the all electron wave function within  $r_c$ .

### 2. Agreement between all electron function and pseudofunction

It is imposed that up to the fourth derivatives of the pseudofunction are the same as those of the all electron wave function.

### 3. Smoothness of $v^{(\text{sps})}$

It is imposed that the second derivative of the screened pseudopotential  $v^{(\text{sps})}$  is zero at the origin.

The first condition leads to the following relation:

$$\ln \left[ \int_0^{r_c} |P_{nlj}^{(AE)}(r)|^2 dr \right] = 2c_0 + \ln \left[ \int_0^{r_c} r^{2(l+1)} \exp[2p(r) - 2c_0] dr \right]. \quad (58)$$

The second condition leads to the following simultaneous linear equation:

$$\begin{pmatrix} 1 & r_c^6 & r_c^8 & r_c^{10} & r_c^{12} \\ 0 & 6r_c^5 & 8r_c^7 & 10r_c^9 & 12r_c^{11} \\ 0 & 30r_c^4 & 56r_c^6 & 90r_c^8 & 132r_c^{10} \\ 0 & 120r_c^3 & 336r_c^5 & 720r_c^7 & 1320r_c^9 \\ 0 & 360r_c^2 & 1680r_c^4 & 5040r_c^6 & 11880r_c^8 \end{pmatrix} \begin{pmatrix} c_0 \\ c_6 \\ c_8 \\ c_{10} \\ c_{12} \end{pmatrix} = \begin{pmatrix} b_0 \\ b_6 \\ b_8 \\ b_{10} \\ b_{12} \end{pmatrix}, \quad (59)$$

where

$$b_0 = A - c_2 r_c^2 - c_4 r_c^4, \quad (60)$$

$$b_6 = B - 2c_2 r_c - 4c_4 r_c^3, \quad (61)$$

$$b_8 = C - 2c_2 - 12c_4 r_c^2, \quad (62)$$

$$b_{10} = D - 24c_4 r_c, \quad (63)$$

$$b_{12} = E - 24c_4 \quad (64)$$

with

$$A = \ln \left[ \frac{P_{nlj}^{(AE)}(r_c)}{r_c^{l+1}} \right], \quad (65)$$

$$B = \frac{P_{nlj}'^{(AE)}(r_c)}{P_{nlj}^{(AE)}(r_c)} - \frac{(l+1)}{r_c}, \quad (66)$$

$$C = 2v_{\text{eff}}(r_c) - 2\varepsilon_{nlj} - 2B \frac{(l+1)}{r_c} - B^2, \quad (67)$$

$$D = 2v_{\text{eff}}'(r_c) + 2B \frac{(l+1)}{r_c^2} - 2C \frac{(l+1)}{r_c} - 2BC, \quad (68)$$

$$E = 2v_{\text{eff}}''(r_c) - 4B \frac{(l+1)}{r_c^3} + 4C \frac{(l+1)}{r_c^2} - 2D \frac{(l+1)}{r_c} - 2C^2 - 2BD. \quad (69)$$

The third condition leads to the following relation:

$$c_2^2 + c_4(2l+5) = 0. \quad (70)$$

In order to satisfy all the conditions above, we vary  $c_2$ , and calculate  $c_4$  using Eq. (70). Then, after calculating  $b_0$ ,  $b_6$ ,  $b_8$ ,  $b_{10}$ , and  $b_{12}$  by using Eqs. (60)-(64), we solve the simultaneous linear equation given by Eq. (59). Finally we validate the norm-conserving condition using Eq. (58). If Eq. (58) is not hold within a criterion with a certain threshold, we update  $c_2$  and repeat the same procedure until the criterion is satisfied. By applying the procedure for a state specified with  $(n, l)$ , a pseudofunction and pseudopotential depending on  $(n, l)$  can be constructed. Then, the bare (unscreened) pseudopotential is obtained by a unscreening process as follows:

$$v_{nlj}^{(\text{ps})}(r) = v_{nlj}^{(\text{sps})}(r) - v_{\text{H}}^{(\text{v})}(r) - v_{\text{xc}}^{(\text{v}+\text{pcc})}(r), \quad (71)$$

where  $v_{\text{H}}^{(\text{v})}$  is the Hartree potential produced by valence charge density  $\rho^{(\text{v})}$  calculated by the pseudofunctions including all the valence electrons chosen for the pseudopotential generation,  $v_{\text{xc}}^{(\text{v}+\text{pcc})}$  is the exchange-correlation potential calculated from the sum of the valence electron density  $\rho^{(\text{v})}$  and a partial core correction (PCC) charge  $\rho^{(\text{pcc})}$ . The addition of  $\rho^{(\text{pcc})}$  to  $\rho^{(\text{v})}$  is made to take account of nonlinearity in the exchange-correlation potential. The PCC charge  $\rho^{(\text{pcc})}$  is calculated by using a polynomial function in ADPACK.

In the TM method a single pseudopotential is constructed for each azimuthal quantum number  $l$  even if multiple states with the same azimuthal quantum number are included in valence electrons. In such a case, the lowest state among valence electrons with the azimuthal quantum number  $l$  is chosen for generating a pseudopotential for the  $l$ -channel. Once  $v_l^{(\text{ps})}$  is generated, a  $l$ -dependent non-local potential  $v_l^{(\text{NL})}$  is constructed as

$$v_{lj}^{(\text{NL})}(r) = v_{nlj}^{(\text{ps})}(r) - v^{(\text{L})}(r), \quad (72)$$

with a local potential  $v^{(\text{L})}(r)$  define by

$$v^{(\text{L})}(r) = \begin{cases} \sum_{k=0}^7 c_k r^k, & \text{for } r \leq r_c^{(\text{L})} \\ -\frac{Z_{\text{v}}}{r}, & \text{for } r_c^{(\text{L})} < r \end{cases} \quad (73)$$

The coefficients  $\{c\}$  in the polynomial function are determined so that the function matches with up to third derivatives of  $-Z_{\text{v}}/r$  at  $r_c^{(\text{L})}$ , becomes  $-\gamma Z_{\text{v}}/r$  at the origin, and also the first, second and third derivatives are zero at the origin, where  $Z_{\text{v}}$  is the number of valence electrons,  $r_c^{(\text{L})}$  is a cutoff radius which is independently chosen from the cutoff radii for the generation of the screened pseudopotentials  $v^{(\text{sps})}$ , and  $\gamma$  is an adjustable parameter which is usually varied between 1.5 and 5. Since  $v_{nlj}^{(\text{ps})}$  approaches to  $-\frac{Z_{\text{v}}}{r}$  as  $r$  increases,  $v_{lj}^{(\text{NL})}$  can be considered to be non-zero only in the vicinity of the atomic nucleus. When those relativistic pseudopotentials are used, they are expanded by projectors as

$$\begin{aligned} V^{(\text{ps})} &= v^{(\text{L})} + \sum_{lm} \left[ |\Phi_J^M\rangle v_{l+\frac{1}{2}}^{(\text{NL})} \langle \Phi_J^M| + |\Phi_{J'}^{M'}\rangle v_{l-\frac{1}{2}}^{(\text{NL})} \langle \Phi_{J'}^{M'}| \right] \\ &= v^{(\text{L})} + \hat{v}_{l+\frac{1}{2}}^{(\text{NL})} + \hat{v}_{l-\frac{1}{2}}^{(\text{NL})}, \end{aligned} \quad (74)$$

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

$$|\Phi_J^M\rangle = \left( \frac{l+m+1}{2l+1} \right)^{\frac{1}{2}} |Y_l^m\rangle |\alpha\rangle + \left( \frac{l-m}{2l+1} \right)^{\frac{1}{2}} |Y_l^{m+1}\rangle |\beta\rangle, \quad (75)$$

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

$$|\Phi_{J'}^{M'}\rangle = \left(\frac{l-m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m-1}\rangle|\alpha\rangle - \left(\frac{l+m}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle|\beta\rangle. \quad (76)$$

The  $\Phi_J^M$  and  $\Phi_{J'}^{M'}$  are constituents of the eigenfunction of the Dirac equation under a spherical potential, and  $|\alpha\rangle$  and  $|\beta\rangle$  are the eigenfunctions in spin space. Since  $-J \leq M \leq J$  and  $-J' \leq M' \leq J'$ , the degeneracies of  $J$  and  $J'$  are  $2(l+1)$  and  $2l$ , respectively. In order to reduce computational complexity in evaluating matrix elements involved, the non-local part in Eq. (76) is transformed to a separable form as described in the technical notes 'Non-Collinear Spin Density Functional'. The final forms of  $\hat{v}_{l+\frac{1}{2}}^{(\text{NL})}$  and  $\hat{v}_{l-\frac{1}{2}}^{(\text{NL})}$  are given by

$$\hat{v}_{l+\frac{1}{2}}^{(\text{NL})} = \sum_{lm} \sum_{\zeta} |v_{l+\frac{1}{2}}^{(\text{NL})} \bar{R}_{J\zeta} \Phi_J^M\rangle \frac{1}{c_{J\zeta}} \langle \bar{R}_{J\zeta} \Phi_J^M v_{l+\frac{1}{2}}^{(\text{NL})} |, \quad (77)$$

$$\hat{v}_{l-\frac{1}{2}}^{(\text{NL})} = \sum_{lm} \sum_{\zeta} |v_{l-\frac{1}{2}}^{(\text{NL})} \bar{R}_{J'\zeta} \Phi_{J'}^{M'}\rangle \frac{1}{c_{J'\zeta}} \langle \bar{R}_{J'\zeta} \Phi_{J'}^{M'} v_{l-\frac{1}{2}}^{(\text{NL})} |. \quad (78)$$

See also the details in the technical notes 'Non-Collinear Spin Density Functional'.

## 5 Morrison, Bylander and Kleinman (MBK) pseudopotential

In this section we explain the Morrison, Bylander and Kleinman (MBK) pseudopotential method which was implemented in ADPACK and used to construct the database (Ver. 2019). It is worth mentioning that The MBK pseudopotential is a norm-conserving one of the Vanderbilt pseudopotential. Thus, let us start to discuss the Vanderbilt pseudopotential method. Assuming that pseudofunctions  $\phi^{(\text{PS})}$  are available for all the valence states of interest, we construct a screened local potential  $v^{(\text{SL})}$  by

$$v^{(\text{SL})}(r) = v_{\text{L}}(r) + v_{\text{H}}^{(\text{v})}(r) + v_{\text{xc}}^{(\text{v+pcc})}(r). \quad (79)$$

Then, a function  $\chi$  is calculated by

$$|\chi_i\rangle = \left(\varepsilon_i + \frac{1}{2}\nabla^2 - v^{(\text{SL})}(r)\right) |\phi_i^{(\text{PS})}\rangle, \quad (80)$$

where  $i$  is a composite index defined by  $i \equiv (nlj)$ , and runs from 1. We now define a non-local potential according to Vanderbilt's idea as

$$\hat{v}^{(\text{NL})} = \sum_{ij} |\beta_i\rangle B_{ij} \langle \beta_j| \quad (81)$$

with definitions:

$$B_{ij} = \langle \phi_i^{(\text{PS})} | \chi_j \rangle \quad (82)$$

and

$$|\beta_i\rangle = \sum_j \left(B^{-1}\right)_{ji} |\chi_j\rangle. \quad (83)$$

By operating  $\hat{v}^{(\text{NL})}$  to  $\phi_k^{(\text{PS})}$ , it turns out that

$$\begin{aligned}
\hat{v}^{(\text{NL})}|\phi_k^{(\text{PS})}\rangle &= \sum_{ij} |\beta_i\rangle B_{ij} \langle\beta_j|\phi_k^{(\text{PS})}\rangle \\
&= \sum_{ij} |\beta_i\rangle B_{ij} \sum_{k'} (B^{-1})_{k'j} \langle\chi_{k'}|\phi_k^{(\text{PS})}\rangle, \\
&= \sum_{ij} |\beta_i\rangle B_{ij} \sum_{k'} (B^{-1})_{k'j} B_{kk'}, \\
&= \sum_{ij} |\beta_i\rangle B_{ij} \delta_{kj}, \\
&= \sum_i \left( \sum_j (B^{-1})_{ji} |\chi_j\rangle \right) B_{ik}. \\
&= |\chi_k\rangle
\end{aligned} \tag{84}$$

Thus, we find that a Schrödinger equation is satisfied as

$$\left( -\frac{1}{2}\nabla^2 + v^{(\text{SL})}(r) + \hat{v}^{(\text{NL})} \right) |\phi_i^{(\text{PS})}\rangle = \varepsilon_i |\phi_i^{(\text{PS})}\rangle. \tag{85}$$

The property of the non-local operator given by Eq. (81) allows us to include multiple reference energies for the construction of pseudopotential of the  $l$ -channel, largely improving transferability of the pseudopotential. Not only eigenenergies, but also non-eigenenergies (even beyond zero energy) can be considered as reference energies by using the Hamman method.

The MBK pseudopotential method is based on the Vanderbilt pseudopotential method, and imposes the Hermiticity property of the matrix  $B$  defined by Eq. (82). The Hermiticity of  $B$  is guaranteed by imposing a generalized norm-conserving condition  $Q_{ij} = 0$ , where  $Q_{ij}$  is defined by

$$Q_{ij} = \langle\phi_i^{(\text{AE})}|\phi_j^{(\text{AE})}\rangle_{r_c} - \langle\phi_i^{(\text{PS})}|\phi_j^{(\text{PS})}\rangle_{r_c}. \tag{86}$$

$\langle\cdot\rangle_{r_c}$  means the intergration inside of the sphere of radius  $r_c$ . We show below the reason why imposing  $Q_{ij} = 0$  guarantees the Hermiticity of  $B$ . By considering radial functions  $P^{(\text{PS})}$ ,  $B_{ij}$  and  $B_{ji}^*$  are calculated, repectively, as

$$B_{ij} = \int_0^{r_c} dr P_i^{(\text{PS})}(r) \left( \varepsilon_j + \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} - v^{(\text{SL})}(r) \right) P_j^{(\text{PS})}(r), \tag{87}$$

$$B_{ji}^* = \int_0^{r_c} dr P_i^{(\text{PS})}(r) \left( \varepsilon_i + \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} - v^{(\text{SL})}(r) \right) P_j^{(\text{PS})}(r), \tag{88}$$

where we assumed that  $P^{(\text{PS})}$  is real. It is noted that in Eq. (87) the operator acts to the right, while in Eq. (88) the operator acts to the left. Then, we find

$$\begin{aligned}
B_{ij} - B_{ji}^* &= (\varepsilon_j - \varepsilon_i) \int_0^{r_c} dr P_i^{(\text{PS})}(r) P_j^{(\text{PS})}(r) \\
&\quad + \frac{1}{2} \int_0^{r_c} dr P_i^{(\text{PS})}(r) P_j''^{(\text{PS})}(r) - \frac{1}{2} \int_0^{r_c} dr P_i''^{(\text{PS})}(r) P_j^{(\text{PS})}(r).
\end{aligned} \tag{89}$$

By performing one integration by parts and considering the asymptotic form of radial functions at the origin, we see

$$\begin{aligned}
B_{ij} - B_{ji}^* &= (\varepsilon_j - \varepsilon_i) \langle\phi_i^{(\text{PS})}|\phi_j^{(\text{PS})}\rangle_{r_c} + \frac{1}{2} \left[ P_i^{(\text{PS})}(r) P_j^{(\text{PS})}(r) \right]_0^{r_c} - \frac{1}{2} \left[ P_i'^{(\text{PS})}(r) P_j^{(\text{PS})}(r) \right]_0^{r_c}, \\
&= (\varepsilon_j - \varepsilon_i) \langle\phi_i^{(\text{PS})}|\phi_j^{(\text{PS})}\rangle_{r_c} + \frac{1}{2} P_i^{(\text{PS})}(r_c) P_j^{(\text{PS})}(r_c) - \frac{1}{2} P_i'^{(\text{PS})}(r_c) P_j^{(\text{PS})}(r_c).
\end{aligned} \tag{90}$$

Similar calculations for the all electron radial functions yield

$$0 = (\varepsilon_j - \varepsilon_i) \langle \phi_i^{(\text{AE})} | \phi_j^{(\text{AE})} \rangle_{r_c} + \frac{1}{2} P_i^{(\text{AE})}(r_c) P_j'^{(\text{AE})}(r_c) - \frac{1}{2} P_i'^{(\text{AE})}(r_c) P_j^{(\text{AE})}(r_c). \quad (91)$$

By subtracting both the terms of Eq. (91) from Eq. (90) and noting that  $P^{(\text{PS})}_s$  are constructed so that the value and the first derivative can match with those of the all electron functions, we obtain

$$B_{ij} - B_{ji}^* = (\varepsilon_i - \varepsilon_j) \left( \langle \phi_i^{(\text{AE})} | \phi_j^{(\text{AE})} \rangle_{r_c} - \langle \phi_i^{(\text{PS})} | \phi_j^{(\text{PS})} \rangle_{r_c} \right). \quad (92)$$

Thus, it is confirmed that B is Hermitian when  $Q_{ij} = 0$ .

We now consider how pseudofunctions can be constructed so that the generalized norm-conserving condition  $Q_{ij} = 0$  can be satisfied, and introduce a form of pseudofunction as

$$P_i^{(\text{PS})}(r) = \begin{cases} P_i^{(\text{TM})}(r) + f_i(r), & \text{for } r \leq r_c^{(L)} \\ P_{nlj}^{(\text{AE})}(r), & \text{for } r_c < r \end{cases} \quad (93)$$

where  $P_i^{(\text{PS})}$  is the pseudofunction generated by the TM method. The function  $f_i$  is a correction term to satisfy  $Q_{ij} = 0$ , and given by

$$f_i(r) = \sum_{k=0}^{N_b-1} c_{ik} [r j_l(q_{lk}r)] = \sum_{k=0}^{N_b-1} c_{ik} g_k(r), \quad (94)$$

where  $j_l$  is the  $l$ th order spherical Bessel function of the first kind, and  $q_{lk}$  is  $u_{lk}/r_c$  with  $u_{lk}$  being the  $k$ th zero point of  $j_l$ . Since at the origin  $g_k$  is expanded as

$$g_k(r) = x^{l+1} \left( \frac{q_{lk}^l \sqrt{\pi}}{2^{l+1} \Gamma[3/2 + l]} + O[r^2] \right), \quad (95)$$

it turns out that the correct asymptotic behavior of the radial function at the origin is maintained.

The coefficients  $\{c\}$  are determined by imposing not only  $Q_{ij} = 0$ , but also the following five conditions for  $f$  at the cutoff radius  $r_c$ .

$$f_i(r_c) = f_i'(r_c) = f_i''(r_c) = f_i'''(r_c) = f_i''''(r_c) = 0. \quad (96)$$

With the conditions, the pseudofunction of Eq. (93) satisfies the same conditions as those for the TM pseudofunction given by Eq. (54). By the definition of  $g$ , we see that  $f_i(r_c) = 0$  is automatically satisfied. In addition, noting that

$$g_k''(r) = 2q_{lk} j_l'(q_{lk}r) + q_{lk}^2 r j_l''(q_{lk}r), \quad (97)$$

and the Helmholtz equation

$$r j_l''(r) = -2j_l'(r) - [r^2 - l(l+1)] j_l(r), \quad (98)$$

we find

$$f_i''(r_c) = 0. \quad (99)$$

Thus, only  $f_i'(r_c) = 0$  and  $f_i'''(r_c) = 0$  need to be satisfied. The evaluation of  $f(r_c)$  is trivial.  $f_i''''(r_c)$

Using Eq. (97) at  $r_c$  and Eq. (98) we obtain

$$g_k'''(r_c) = \frac{u_{li}}{r_c^2} [l(l+1) - u_{li}^2] j_l'(u_{li}). \quad (100)$$

The relation will be used later on.

We now return to the generalizd norm-conserving condition:

$$\langle P_i^{(\text{PS})} | P_j^{(\text{PS})} \rangle_{r_c} = \langle P_i^{(\text{AE})} | P_j^{(\text{AE})} \rangle_{r_c} \quad (101)$$

By inserting the pseudofuntions of Eq. (93) into Eq. (101), we obtain the following equation:

$$\langle P_i^{(\text{PS})} | f_k \rangle_{r_c} = \langle P_i^{(\text{AE})} | P_j^{(\text{AE})} \rangle_{r_c} - \langle P_i^{(\text{PS})} | P_j^{(\text{PS})} \rangle_{r_c} \quad (102)$$

The generalizd norm-conserving condition  $Q_{ij} = 0$  is satisfied by the following steps:

### 1. Generation of norm-conserving pseudofuntions

Norm-conserving pseudofuntions  $\{P^{(\text{TM})}\}$  are generated for all reference energies we choose by the TM method. Thus, all the norm-conserving pseudofuntions are nodeless.

### 2. Calculation of excited states

Excited states  $\{P^{(\text{TME})}\}$  are calculated under the TM pseudopotential being the lowest state among the pseudized states specified with  $j$ , where the excited states correspond to pseudized states except for the lowest state.

### 3. Initial guess of $c$

The coefficients  $\{c\}$  are estimated from the difference  $P^{(\text{TME})} - P^{(\text{TM})}$ .

and a part of the generalizd norm-conserving condition  $Q_{ji} = 0$  for  $j < i$  ( $i, j=1, 2, \dots$ ), the following linear relations can be derived.

$$\begin{pmatrix} c_{i0} \\ c_{i1} \\ c_{i2} \\ \vdots \\ c_{ii} \end{pmatrix} = C^{-1} \quad (103)$$

$$Q_i = \left( \varepsilon_i + \frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} - v^{(\text{SL})}(r) \right) P_i^{(\text{PS})} \quad (104)$$

The further details will be supplemented in near future.

## References

- [1] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).
- [2] I. Morrison, D.M. Bylander, and L. Kleinman, Phys. Rev. B **47**, 6728 (1993).