Numerical Procedures for Generating Ultrasoft Pseudopotentials

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Numerical procedures for generating ultrasoft pseudopotentials are described in detail. Atomic radial pseudo-wave-functions are constructed so as to coincide with radial all-electron wave functions beyond a chosen cutoff radius with continuous derivatives up to the fourth order, which guarantees numerical stability in electronic-structure calculations for materials. We present a method for solving the radial generalized eigenequation with the ultrasoft pseudopotentials, which is required to test their transferability.

§1. Introduction

Ab initio molecular-dynamics (MD) simulations are a powerful approach to investigate the electronic and atomic structures of condensed matters at finite temperature, and have been applied to various kinds of high-temperature materials, such as liquid metals, liquid semiconductors, and superionic conductors. Interatomic forces are computed quantum mechanically[1],[2] in the framework of the density functional theory (DFT)[3],[4] to accurately describe chemical reactions. In this approach, the electronic structure is calculated within the Born-Oppenheimer approximation, which separates ionic and electron degrees-of-freedom, and the electron-ion interaction is calculated using the pseudopotential method.[5],[6]

In the applications of *ab initio* MD simulations, the plane-wave (PW) basis has been used most widely,[7]–[13] because the formulation is simple and the atomic forces are easily calculated. However, implementation of the PW algorithm on parallel computers involves global operations, and hence its scalability becomes problematic on massively parallel computers. To overcome this drawback of the PW algorithm, the real-space (RS) algorithm with a high-order finite difference method to calculate derivatives such as the kinetic-energy operator has been proposed and applied.[14]–[17] In this RS algorithm, all operations are inherently short-ranged, resulting in superior scalability on parallel computers.

In both PW and RS algorithms, the smoothness of the pseudopotentials is crucial in determining the amount of computations. Vanderbilt[18] has proposed a method to construct soft pseudopotentials, so-called ultrasoft pseudopotentials, which reduce computational costs considerably, compared with the usual norm-conserving pseudopotentials.[5] Also, his method allows transferability of the pseudopotentials to be improved systematically, although a generalized eigenvalue problem has to be solved. The ultrasoft pseudopotentials have been applied to first-row and transition-metal systems, which have been hard to be treated by the PW and RS algorithms so far.

In this paper, we describe numerical procedures for generating the ultrasoft pseu-

dopotentials. Kresse and Hafner[19] have proposed an efficient method to generate the ultrasoft pseudopotentials. However, the atomic radial pseudo-wave-functions have continuous derivatives only up to the second order, while they coincide with the radial all-electron wave functions beyond a chosen cutoff radius. The discontinuity of the third derivatives causes numerical instability which is encountered in obtaining the physical quantities associated with the first derivative of the total energy, such as atomic forces and internal stresses. We generalize their method so as to construct the radial pseudo-wave-functions with continuous derivatives up to the fourth order, which guarantees numerical stability. Also, we describe a numerical technique to solve the radial generalized eigenequation with the ultrasoft pseudopotentials in detail. Since the examination of the eigenvalues and eigen functions for various electron configurations, which are different from that used to obtain the pseudopotentials, is necessary to test the transferability of the pseudopotentials, it is important to establish a numerical solver for the radial generalized eigenequation.

§2. Ultrasoft pseudopotentials

2.1. *Input parameters*

For each set of quantum numbers (n, l), where n and l are the principle and the angular momentum quantum numbers, respectively, for electrons in a specified atom, we define four input parameters:
(1) n_l is the number of reference energies to construct pseudopotentials.
(2) ε_{lj} is the jth reference energy $(j = 1, \cdots, n_l)$.
(3) r_{cl} is a cutoff radius for the ultrasoft (US) pseudo-wave-functions $P_{US,lj}(r)$.
(4) r'_{cl} is a cutoff radius for the norm-conserving (NC) pseudo-wave-functions $P_{NC,lj}(r)$. The explicit definitions for $P_{US,lj}(r)$ and $P_{NC,lj}(r)$ are given in the subsections 2.5 and 2.6, respectively. Hereafter the principle quantum number n is omitted for simplicity.

2.2. *Radial all-electron wave functions*

We assume that the all-electron (AE) potential $V_{AE}(r)$, the eigenvalues $\varepsilon_l^{(0)}$, and the radial AE wave functions (eigenfunctions) $P_{AE,l}^{(0)}(r)$ are obtained from self-consistent AE atomic calculations. For each quantum number l and each reference energy ε_{lj}, the radial AE wave function $P_{AE,lj}(r)$ is obtained by solving the following radial Scrödinger equation:

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{AE}(r) \right) P_{AE,lj}(r) = \varepsilon_{lj} \, P_{AE,lj}(r), \tag{2.1}$$

up to $R = \max(r_{cl}, r'_{cl})$ from the origin $(r = 0)$. Note that ε_{lj} is not required to be the eigenvalue $\varepsilon_l^{(0)}$. For heavy atoms, the relativistic effects become important, and one may need to solve the scalar relativistic Scrödinger equation given by

$$\left\{ -\frac{d^2}{dr^2} - \frac{\alpha^2}{M(r)} \frac{dV(r)}{dr} \left(\frac{d}{dr} - \frac{1}{r} \right) \right.$$

$$+ \frac{l(l+1)}{r^2} + M(r)\left(V_{AE}(r) - \varepsilon_{lj} \right) \Big\} P_{AE,lj}(r) = 0, \tag{2.2}$$

where

$$M(r) = 1 + \alpha^2\left(\varepsilon_{lj} - V_{AE}(r) \right), \tag{2.3}$$

with the fine structure constant α related to the speed of light according to $c = 1/\alpha$

Usually, it is enough to set $n_l = 1$ or 2. Although $\varepsilon_{l,j}$ are arbitrary in principle, it is convenient to set $\varepsilon_{l,j=1} = \varepsilon_l^0$ (the eigenvalue). If $n_l = 2$, $\varepsilon_{l,j=2}$ should be different from $\varepsilon_{l,j=1}$ as far as possible.

2.3. *False-position method*

For later use, we describe a method, so-called false-position method, to search solutions $\{x_0\}$ of an equation $f(x) = 0$ for an arbitrary function $f(x)$. We call $\{x_0\}$ zero points of $f(x)$. The procedure consists of the following steps:

1. Find two points x_1 and x_2 that give a relation $f(x_1)f(x_2) < 0$. At least, one zero point x_0 must be between x_1 and x_2. We assume that $f(x)$ is smooth between x_1 and x_2, and that there is only one zero point in this range of x.

2. Calculate $f(x_3)$ with $x_3 = x_1 - \dfrac{f(x_1)}{f(x_2) - f(x_1)}(x_2 - x_1)$.

3. Terminate if $f(x_3) < \epsilon$.

4. If $f(x_1)f(x_3) < 0$ (or > 0), set $x_2 = x_3$ (or $x_1 = x_3$). Return to step 2.

2.4. *Condition for spherical Bessel functions*

Kresse and Hafner[19] have proposed to define the pseudo-wave-functions as a sum of spherical Bessel functions $j_l(q_i r)$, as will be given in Eqs. (2.9) and (2.12). Due to a condition that the logarithmic derivatives of the pseudo-wave-functions should coincide with those of the respective AE wave functions at the cutoff radii, q_i should satisfy the following equation:

$$\frac{r_c}{P_{AE,lj}(r_c)}\left(\frac{d}{dr}P_{AE,lj}(r) \right)_{r=r_c} = 1 + \frac{x}{j_l(x)}\left(\frac{d}{dx}j_l(x) \right), \tag{2.4}$$

where $x = q_i r_c$ ($r_c = r_{cl}$ or r'_{cl}). One has to find the solution x in the range of $x_0^{(i-1)} < x < x_0^{(i)}$, where $x_0^{(i)}$ is the ith zero point of $j_l(x)$. The value of the left hand side of Eq. (2.4) is determined numerically. Since the right hand side is transformed into

$$1 + \frac{x}{j_l(x)}\left(\frac{d}{dx}j_l(x) \right) = 1 + \frac{x}{j_l(x)}\left(-\frac{l+1}{x}j_l(x) + j_{l-1}(x) \right) \tag{2.5}$$

$$= -l + x\frac{j_{l-1}(x)}{j_l(x)}, \tag{2.6}$$

the problem to solve Eq. (2.4) becomes a problem to search the zero point of the following function $f(x)$:

$$f(x) \equiv -l + x\frac{j_{l-1}(x)}{j_l(x)} - \frac{r_c}{P_{\mathrm{AE},lj}(r_c)}\left(\frac{\mathrm{d}}{\mathrm{d}r}P_{\mathrm{AE},lj}(r)\right)_{r=r_c} = 0. \qquad (2.7)$$

The zero point x can be found by the false position method described in the subsection 2.3. Finally, q_i is obtained as

$$q_i = \frac{x}{r_c}. \qquad (2.8)$$

The zero points $x_0^{(i)}$ of $j_l(x)$ are determined analytically or numerically.

2.5. *Ultrasoft pseudo-wave-functions*

The US pseudo-wave-functions $P_{\mathrm{US},lj}(r)$ are defined by the sum of two spherical Bessel functions as

$$P_{\mathrm{US},lj}(r) = \sum_{i=1}^{2} \alpha_i r j_l(q_i r). \qquad (2.9)$$

α_1 and α_2 are determined by the conditions of the continuous first two derivatives of $P_{\mathrm{US},lj}(r)$ at r_{cl}, which are given by

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}P_{\mathrm{AE},lj}(r)\right)_{r=r_{cl}} = \sum_{i=1}^{2} \alpha_i \left[\frac{\mathrm{d}}{\mathrm{d}r}(r j_l(q_i r))\right]_{r=r_{cl}}, \qquad (2.10)$$

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}P_{\mathrm{AE},lj}(r)\right)_{r=r_{cl}} = \sum_{i=1}^{2} \alpha_i \left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r j_l(q_i r))\right]_{r=r_{cl}}. \qquad (2.11)$$

By solving these simultaneous linear equations, α_1 and α_2 are uniquely determined.

2.6. *Norm-conserving pseudo-wave-functions*

The NC pseudo-wave-functions $P_{\mathrm{NC},lj}(r)$ are defined by the sum of three spherical Bessel functions as

$$P_{\mathrm{NC},lj}(r) = \sum_{i=1}^{3} \alpha_i r j_l(q_i r). \qquad (2.12)$$

In addition to the conditions of the continuous first two derivatives of $P_{\mathrm{NC},lj}(r)$ at r'_{cl} given by

$$\left(\frac{\mathrm{d}}{\mathrm{d}r}P_{\mathrm{AE},lj}(r)\right)_{r=r'_{cl}} = \sum_{i=1}^{3} \alpha_i \left[\frac{\mathrm{d}}{\mathrm{d}r}(r j_l(q_i r))\right]_{r=r'_{cl}}, \qquad (2.13)$$

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2}P_{\mathrm{AE},lj}(r)\right)_{r=r'_{cl}} = \sum_{i=1}^{3} \alpha_i \left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r j_l(q_i r))\right]_{r=r'_{cl}}, \qquad (2.14)$$

the condition of the norm conservation has to be satisfied:

$$\int_0^{r'_{cl}} dr |P_{AE,lj}(r)|^2 = \int_0^{r'_{cl}} dr |P_{NC,lj}(r)|^2$$

$$= \sum_{i=1}^{3} \sum_{k=1}^{3} \alpha_i \alpha_k \int_0^{r'_{cl}} dr\, r^2 j_l(q_i r) j_l(q_k r)$$

$$\equiv \sum_{i=1}^{3} \sum_{k=1}^{3} \alpha_i \alpha_k S_l(q_i, q_k; r'_{cl}). \tag{2.15}$$

These three conditions determine the three parameters α_1, α_2, and α_3. In practical procedures, one searches α_3 as a zero point of the following function:

$$f(\alpha_3) \equiv \sum_{i=1}^{3} \sum_{k=1}^{3} \alpha_i \alpha_k S_l(q_i, q_k; r) - \int_0^{r'_{cl}} dr |P_{AE,lj}(r)|^2 = 0, \tag{2.16}$$

where α_1 and α_2 are determined from Eqs. (2.13) and (2.14) for a given α_3.

2.7. *Corrections to continuous derivatives up to forth order*

The US and NC pseudo-wave-functions defined by Eqs. (2.9) and (2.12) have the continuous derivatives only up to the second order, which causes numerical instability in the self-consistent calculations. In this section, we propose a method to construct the pseudo-wave-functions that have the continuous derivatives up to the fouth order, while keeping the numerical efficiency. We add two terms to the original pseudo-wave-functions (Eqs. (2.9) and (2.12)) as

$$P_{PS,lj}(r) = \sum_{i=1}^{n} \alpha_i r j_l(q_i r) + \alpha_{n+1} F_{lj}(r) + \alpha_{n+2} \tilde{F}_{lj}(r), \tag{2.17}$$

where $n = 2$ and 3 for PS=US and PS=NC, respectively. $F_{lj}(r)$ and $\tilde{F}_{lj}(r)$ are given by

$$F_{lj}(r) = \begin{cases} \sin^3(Qr) \exp\left(-\gamma(r_c - r)\right) & \equiv f(r)g(r) & (r \geq \tilde{r}_c) \\ r^{l+1}(c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8) & = \sum_{n=0}^{4} c_{2n} r^{l+1+2n} & (r \leq \tilde{r}_c), \end{cases} \tag{2.18}$$

$$\tilde{F}_{lj}(r) = \begin{cases} \sin^4(Qr) \exp\left(-\gamma(r_c - r)\right) & \equiv \tilde{f}(r)g(r) & (r \geq \tilde{r}_c) \\ r^{l+1}(d_0 + d_2 r^2 + d_4 r^4 + d_6 r^6 + d_8 r^8) & = \sum_{n=0}^{4} d_{2n} r^{l+1+2n} & (r \leq \tilde{r}_c). \end{cases} \tag{2.19}$$

The parameter Q is set to be $Q = \pi/r_c$, which guarantees that the derivatives of $F_{lj}(r)$ and $\tilde{F}_{lj}(r)$ vanish at r_c up to the second and third orders, respectively. γ and $\tilde{r}_c$ are arbitrary parameters. By examining the dependence of the functional form on these parameters, we have found that a smooth function can be obtained by $\gamma = 10.0/r_c$ and $\tilde{r}_c = 0.1 r_c$. The parameters $\{c_{2n}\}$ and $\{d_{2n}\}$, which give $F_{lj}(r)$

and $\tilde{F}_{lj}(r)$, respectively, for $r \leq \tilde{r}_c$, are uniquely determined by the conditions of the continuous derivatives up to the fourth order at $r = \tilde{r}_c$.

At $r = r_c$, the zeroth, first, and second derivatives of $F_{lj}(r)$ and $\tilde{F}_{lj}(r)$ vanish as follows:

$$
\begin{aligned}
F_{lj}(r_c) &= 0, & \tilde{F}_{lj}(r_c) &= 0, \\
\left(\frac{\mathrm{d}F_{lj}(r)}{\mathrm{d}r}\right)_{r=r_c} &= 0, & \left(\frac{\mathrm{d}\tilde{F}_{lj}(r)}{\mathrm{d}r}\right)_{r=r_c} &= 0, \\
\left(\frac{\mathrm{d}^2 F_{lj}(r)}{\mathrm{d}r^2}\right)_{r=r_c} &= 0, & \left(\frac{\mathrm{d}^2 \tilde{F}_{lj}(r)}{\mathrm{d}r^2}\right)_{r=r_c} &= 0.
\end{aligned}
\tag{2.20}
$$

Therefore, the conditions of the first two derivatives for $P_{\mathrm{US},lj}(r)$ (Eqs. (2.10) and (2.11)) and $P_{\mathrm{NC},lj}(r)$ (Eqs. (2.13) and (2.14)) are held, which give α_1 and α_2 in the same way as in the subsections 2.5 and 2.6.

From the third and fourth derivatives of $F_{lj}(r)$ and $\tilde{F}_{lj}(r)$ at $r = r_c$, which are given by

$$
\begin{aligned}
\left(\frac{\mathrm{d}^3 F_{lj}(r)}{\mathrm{d}r^3}\right)_{r=r_c} &= -6Q^3, & \left(\frac{\mathrm{d}^3 \tilde{F}_{lj}(r)}{\mathrm{d}r^3}\right)_{r=r_c} &= 0, \\
\left(\frac{\mathrm{d}^4 F_{lj}(r)}{\mathrm{d}r^4}\right)_{r=r_c} &= -24Q^3\gamma, & \left(\frac{\mathrm{d}^4 \tilde{F}_{lj}(r)}{\mathrm{d}r^4}\right)_{r=r_c} &= 24Q^4,
\end{aligned}
\tag{2.21}
$$

α_{n+1} and α_{n+2} are determined by the conditions of the continuous third and fourth derivatives:

$$
\left(\frac{\mathrm{d}^3}{\mathrm{d}r^3}P_{\mathrm{AE},lj}(r)\right)_{r=r_{cl}} = \sum_{i=1}^n \alpha_i \left[\frac{\mathrm{d}^3}{\mathrm{d}r^3}(rj_l(q_i r))\right]_{r=r_{cl}} - 6Q^3\alpha_{n+1},
\tag{2.22}
$$

$$
\left(\frac{\mathrm{d}^4}{\mathrm{d}r^4}P_{\mathrm{AE},lj}(r)\right)_{r=r_{cl}} = \sum_{i=1}^n \alpha_i \left[\frac{\mathrm{d}^4}{\mathrm{d}r^4}(rj_l(q_i r))\right]_{r=r_{cl}} - 24Q^3\gamma\alpha_{n+1} + 24Q^4\alpha_{n+2}.
\tag{2.23}
$$

The norm-conserving condition for $P_{\mathrm{NC},lj}(r)$ is given by

$$
\begin{aligned}
\int_0^{r'_{cl}} \mathrm{d}r |P_{\mathrm{AE},lj}(r)|^2 &= \int_0^{r'_{cl}} \mathrm{d}r |P_{\mathrm{NC},lj}(r)|^2 \\
&= \int_0^{r'_{cl}} \mathrm{d}r |\sum_{i=1}^3 \alpha_i rj_l(q_i r) + \alpha_4 F_{lj}(r) + \alpha_5 \tilde{F}_{lj}(r)|^2 \\
&\equiv \sum_{i=1}^5 \sum_{k=1}^5 \alpha_i \alpha_k s_{ik}^l(r'_{cl}),
\end{aligned}
\tag{2.24}
$$

where, for $i \leq 3$ and $k \leq 3$,

$$
s_{ik}^l(r'_{cl}) = \int_0^{r'_{cl}} \mathrm{d}r\, r^2 j_l(q_i r) j_l(q_k r),
$$

$$s_{i4}^l(r_{cl}') = \int_0^{r_{cl}'} dr \, r j_l(q_i r) F_{lj}(r),$$

$$s_{i5}^l(r_{cl}') = \int_0^{r_{cl}'} dr \, r j_l(q_i r) \tilde{F}_{lj}(r),$$

$$s_{44}^l(r_{cl}') = \int_0^{r_{cl}'} dr \, F_{lj}(r) F_{lj}(r),$$

$$s_{45}^l(r_{cl}') = \int_0^{r_{cl}'} dr \, F_{lj}(r) \tilde{F}_{lj}(r),$$

$$s_{55}^l(r_{cl}') = \int_0^{r_{cl}'} dr \, \tilde{F}_{lj}(r) \tilde{F}_{lj}(r).$$

Practical procedures are similar to those in the subsection 2.6, i.e., α_3 is determined by the false-position method as a zero point of the following function:

$$f(\alpha_3) \equiv \sum_{i=1}^{5} \sum_{k=1}^{5} \alpha_i \alpha_k s_{ik}^l(r_{cl}') - \int_0^{r_{cl}'} dr |P_{\text{AE},lj}(r)|^2 = 0, \tag{2.25}$$

where α_1 and α_2 are determined from Eqs. (2.13) and (2.14), respectively, and α_4 and α_5 are determined from Eqs. (2.22) and (2.23), respectively, for a given α_3.

2.8. Local pseudopotential $V_{\text{local}}(r)$

We propose the local pseudopotential $V_{\text{local}}(r)$ in the following form

$$V_{\text{local}}(r) = \begin{cases} V_0 \exp(p(r)) & (r \leq r_{\text{local}}) \\ V_{\text{AE}}(r) & (r \geq r_{\text{local}}) \end{cases}, \tag{2.26}$$

where

$$p(r) = \sum_{n=2}^{6} a_{2n} r^{2n}. \tag{2.27}$$

$V_0(< 0)$ gives the value of $V_{\text{local}}(r)$ at $r = 0$. r_{local} is a cutoff radius beyond which $V_{\text{local}}(r)$ coincides with the AE potential $V_{\text{AE}}(r)$. The coefficients $\{a_{2n}\}$ are determined by the conditions of the continuous derivatives at $r = r_{\text{local}}$.

2.9. Ultrasoft pseudopotential operators

In this section, we describe several quantities, which are necessary to characterize the ultrasoft pseudopotentials. These quantities are derived from the USPP and NCPP pseudo-wave-functions and the local potential.

The local functions $\chi_{lj}(r)$ are defined as

$$|\chi_{lj}\rangle = (\varepsilon_{lj} - \hat{T} - V_{\text{local}})|P_{\text{US},lj}\rangle \tag{2.28}$$

$$= \begin{cases} \left(\dfrac{d^2}{dr^2} - \dfrac{l(l+1)}{r^2} + \varepsilon_{lj} - V_{\text{local}}(r) \right) P_{\text{US},lj}(r) & (r \leq r_{cl}) \\ 0 & (r \geq r_{cl}), \end{cases} \tag{2.29}$$

where $\hat{T}$ is the kinetic energy operator.

The basis functions $\beta_{lj}(r)$ are defined as

$$|\beta_{lj}\rangle = \sum_k \left(\boldsymbol{B}_l^{-1}\right)_{kj} |\chi_{lk}\rangle, \tag{2.30}$$

where the elements of the matrix $\boldsymbol{B}$ are given by

$$B_{l,jk} = \langle P_{\text{US},lj}|\chi_{lk}\rangle \tag{2.31}$$

$$= \int_0^{r_{cl}} P_{\text{US},lj}(r)\chi_{lk}(r)\mathrm{d}r. \tag{2.32}$$

The augmentation functions $Q_{l,jk}(r)$ are defined as

$$Q_{l,jk}(r) = P_{\text{NC},lj}(r)P_{\text{NC},lk}(r) - P_{\text{US},lj}(r)P_{\text{US},lk}(r). \tag{2.33}$$

The augmentation charges $q_{l,jk}$ are defined as

$$q_{l,jk} = \langle P_{\text{NC},lj}|P_{\text{NC},lk}\rangle - \langle P_{\text{US},lj}|P_{\text{US},lk}\rangle \tag{2.34}$$

$$= \int_0^{r_{cl}} Q_{l,lj}(r)\mathrm{d}r. \tag{2.35}$$

Finally, the pseudopotential operator $\hat{V}_{\text{NL}}$ and overlap operator $\hat{S}$ are defined, respectively, as

$$\hat{V}_{\text{NL}} = \sum_l \sum_{jk} D_{l,jk}|\beta_{lj}\rangle\langle\beta_{lk}|, \tag{2.36}$$

$$\hat{S} = 1 + \sum_l \sum_{jk} q_{l,jk}|\beta_{lj}\rangle\langle\beta_{lk}|, \tag{2.37}$$

where $D_{l,jk} = B_{l,jk} + \varepsilon_{lk}q_{l,jk}$.

§3. Generalized eigenequation

By the construction, the US pseudo-wave-function $P_{\text{US},lj}(r)$ satisfies the following integro-differential equation:

$$\left(\hat{T} + V_{\text{local}}(r) + \hat{V}_{\text{NL}}\right)P_{\text{US},lj}(r) = \varepsilon_{lj}\hat{S}P_{\text{US},lj}(r). \tag{3.1}$$

For the reference electron configuration used in constructing the pseudopotentials, this generalized eigenequation Eq. (3.1) has the same eigenvalues as the AE eigenvalues $\varepsilon_{lj} = \varepsilon_l^{(0)}$, and the corresponding eigenfunctions coincide with the AE eigenfunctions $P_{\text{AE},l}^{(0)}(r)$ outside the cutoff radius r_{cl}.

The examination of the eigenvalues and eigenfunctions obtained by solving Eq. (3.1) for different electron configurations from the reference configuration is important to test the transferability of the pseudopotentials. By substituting Eqs. (2.36)

and (2.37) for Eq. (3.1), we have

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{\text{local}}(r) + \sum_{jk} D_{l,jk}|\beta_{lj}\rangle\langle\beta_{lk}|\right) P_{\text{US},nl}(r)$$

$$= \varepsilon_{nl}\left(1 + \sum_{jk} q_{l,jk}|\beta_{lj}\rangle\langle\beta_{lk}|\right) P_{\text{US},nl}(r), \tag{3.2}$$

$$-\frac{d^2 P_{\text{US},nl}(r)}{dr^2} + \left(\frac{l(l+1)}{r^2} + V_{\text{local}}(r) - \varepsilon_{nl}\right) P_{\text{US},nl}(r)$$

$$+ \sum_{jk}\left(D_{l,jk} - \varepsilon_{nl}q_{l,jk}\right)|\beta_{lj}\rangle\langle\beta_{lk}|P_{\text{US},nl}\rangle = 0. \tag{3.3}$$

By expressing the bra-ket in the explicit integral notation, Eq. (3.3) becomes

$$-\frac{d^2 P_{\text{US},nl}(r)}{dr^2} + \left(\frac{l(l+1)}{r^2} + V_{\text{local}}(r) - \varepsilon_{nl}\right) P_{\text{US},nl}(r)$$

$$+ \sum_{jk} \beta_{lj}(r)\left(D_{l,jk} - \varepsilon_{nl}q_{l,jk}\right)\int_0^\infty dr'\,\beta_{lk}(r')P_{\text{US},nl}(r') = 0. \tag{3.4}$$

To treat the rapidly oscillating functions near the origin, a log-scale coordinate $x = \ln r$ is used to solve Eq. (3.4). By introducing a function $Y_l(r)$ as

$$P_{\text{US},nl}(r) = r^{1/2}Y_l(r), \tag{3.5}$$

Eq. (3.4) becomes the following integro-differential eigenequation:

$$-\frac{d^2 Y_l(x)}{dx^2} + U_l(x)Y_l(x) + \sum_{jk}\tilde{\beta}_{lj}(x)u_{l,jk}\int_0^\infty dx'\,\tilde{\beta}_{lk}(x')Y_l(x') = 0, \tag{3.6}$$

where

$$U_l(x) = \left(l + \frac{1}{2}\right)^2 + \left(V_{\text{local}}(x) - \varepsilon_{nl}\right)r^2, \tag{3.7}$$

$$u_{l,jk} = D_{l,jk} - \varepsilon_{nl}q_{l,jk}, \tag{3.8}$$

$$\tilde{\beta}_{lj}(x) = r^{3/2}\beta_{lj}(x). \tag{3.9}$$

First, we solve Eq. (3.6) by an outward integration up to the classical turning point x_m from small r near the origin. Using the solution $W_l(x)$ of the following homogeneous differential equation:

$$-\frac{d^2 W_l(x)}{dx^2} + U_l(x)W_l(x) = 0, \tag{3.10}$$

and the solution $w_{lj}(x)$ of the following inhomogeneous equation:

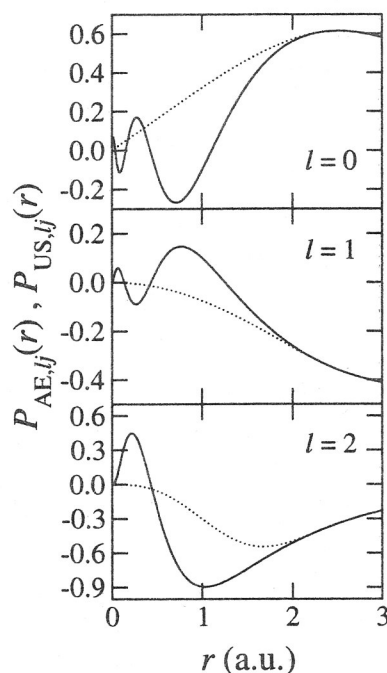$$-\frac{d^2 w_{lj}(x)}{dx^2} + U_l(x)w_{lj}(x) = \tilde{\beta}_{lj}(x), \tag{3.11}$$

Fig. 1. USPP pseudo-wave-functions $P_{\mathrm{US},lj}(r)$ and AE wave functions $P_{\mathrm{AE},lj}(r)$ for $l = 0$ ($5s$), $l = 1$ ($5p$), and $l = 2$ ($4d$) electronic states of Ag. The dotted and solid lines show $P_{\mathrm{US},lj}(r)$ and $P_{\mathrm{AE},lj}(r)$, respectively.

we suppose that the solution $Y_l(x)$ of the integro-differential eigenequation Eq. (3.6) is given by

$$Y_l(x) = b\, W_l(x) + \sum_i a_i\, w_{li}(x), \tag{3.12}$$

where b and $\{a_j\}$ are coefficients to be determined. By substituting Eq. (3.12) for Eq. (3.6), we have

$$\sum_j \tilde{\beta}_{lj}(x)\Big\{ b\sum_k u_{l,jk}\tilde{W}_{lk} + \sum_i (\delta_{ij} + \sum_k u_{l,jk}\tilde{w}_{l,ki})a_i \Big\} = 0, \tag{3.13}$$

where

$$\tilde{W}_{lk} = \int_0^\infty \mathrm{d}x'\, \tilde{\beta}_{lk}(x')W_l(x') = \int_0^\infty \mathrm{d}r'\, r'^{1/2}\beta_{lk}(r')W_l(r'), \tag{3.14}$$

$$\tilde{w}_{l,ki} = \int_0^\infty \mathrm{d}x'\, \tilde{\beta}_{lk}(x')w_{li}(x') = \int_0^\infty \mathrm{d}r'\, r'^{1/2}\beta_{lk}(r')w_{li}(r'). \tag{3.15}$$

Since $\tilde{\beta}_{lj}(x) \neq 0$ and $\{\cdots\} = 0$, the following equation is derived:

$$\sum_i (\delta_{ij} + \sum_k u_{l,jk}\tilde{w}_{l,ki})a_i = -b\sum_k u_{l,jk}\tilde{W}_{lk}. \tag{3.16}$$

From these simultaneous linear equations, the coefficients $\{a_i\}$ are obtained with $b = 1$, which give the solution $Y_l(x)$ through Eq. (3.12).
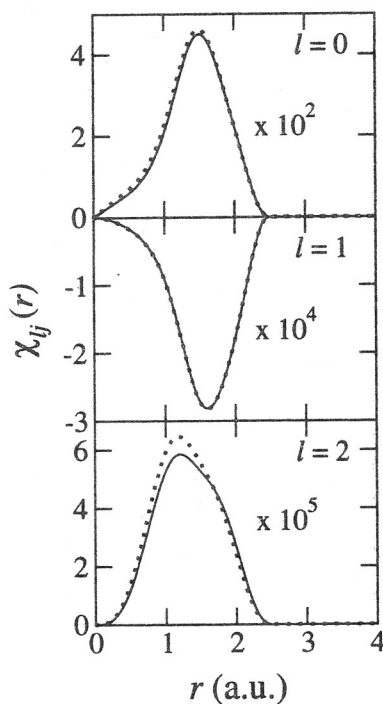
Fig. 2. Local functions $\chi_{lj}(r)$ for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states of Ag.

To obtain the solution $Y_l(x)$ of Eq. (3.6) by an inward integration up to x_m from large $x > x_m$, it is enough to solve the homogeneous equation Eq. (3.10), because $\tilde{\beta}_{lj}(x) = 0$ in this region.

The logarithmic derivative defined as

$$\frac{1}{r} \left\{ \frac{1}{Y_l(x_m)} \left(\frac{dY_l(x)}{dx} \right)_{x=x_m} - \frac{1}{2} \right\} \tag{3.17}$$

is easily obtained by using the relation:

$$\left(\frac{dY_l(x)}{dx} \right)_{x=x_m} = b \, V_l(x_m) + \sum_i a_i \, v_{li}(x_m). \tag{3.18}$$

The eigenvalue is obtained by matching the logarithmic derivatives for the solutions obtained by the outward and inward integrations at the classical turning point x_m.

Finally, the pseudo-wave-function $P_{\mathrm{US},nl}(r)$ is obtained from $Y_l(r)$ using Eq. (3.5), and is normalized as

$$\langle P_{\mathrm{US},nl} | P_{\mathrm{US},nl} \rangle + \sum_{jk} q_{l,jk} \langle P_{\mathrm{US},nl} | \beta_{lj} \rangle \langle \beta_{lk} | P_{\mathrm{US},nl} \rangle = 1. \tag{3.19}$$

§4. Estimation of plane-wave cutoff energies

It is useful to estimate the plane-wave cutoff energies for the pseudo-wave-functions and electron density in the calculations of condensed matters from the
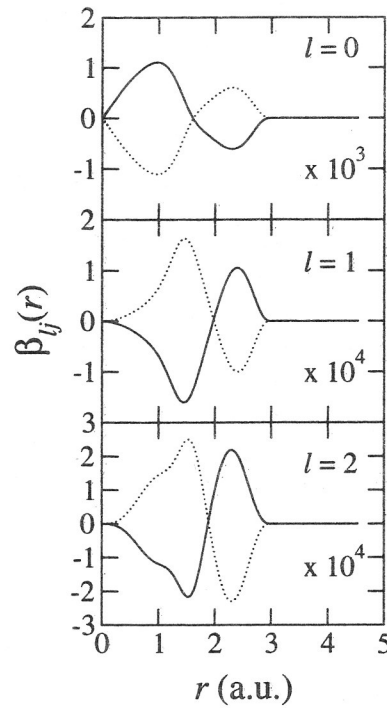
Fig. 3. Basis functions $\beta_{lj}(r)$ for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states of Ag.

atomic quantities. An error in the total energy associated with the cutoff energy E_{cut} for the pseudo-wave-functions is estimated as

$$\Delta E_{kin,l}\left(E_{cut}\right) = \int_{\sqrt{E_{cut}}}^{q_{max}} dq \; |\bar{P}_{US,nl}(q)q|^2, \qquad (4.1)$$

where

$$\bar{P}_{US,nl}(q) = \sqrt{\frac{2}{\pi}} \int_0^\infty dr \; P_{US,nl}(r) \; j_l(qr) \, qr \qquad (4.2)$$

is the Fourier component of $P_{US,nl}(r)$. The cutoff energy E_{cut} has to be selected so as to give a small error $\Delta E_{kin,l}$.

The cutoff energy E_{cut}^{dens} for the electron density is estimated from the Fourier components of the augmentation functions $Q_{l,jk}(r)$:

$$\bar{Q}_{l,jk}^L(q) = (q)^2 \int_0^\infty dr \; Q_{l,jk}(r) \; j_L(qr) \qquad (L = 0, \cdots, 2l). \qquad (4.3)$$

E_{cut}^{dens} has to be large enough to give a small $\bar{Q}_{l,jk}^L(q)$ for $q = \sqrt{E_{cut}^{dens}}$.

The logarithmic derivative of the USPP pseudo-wave-functions is given by

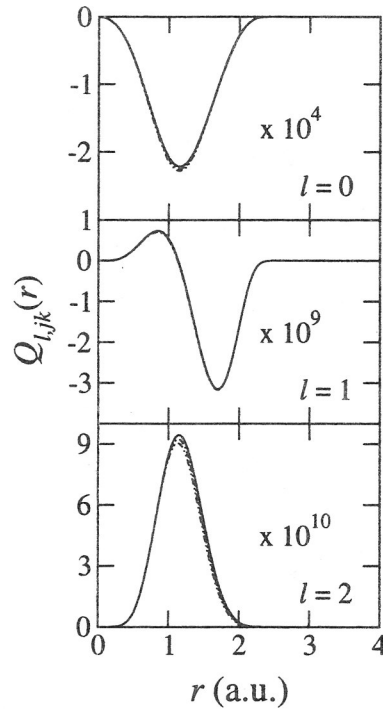$$\zeta_l(\varepsilon, R) = \left(\frac{d}{dr} \ln \frac{P_{US,nl}(r; \varepsilon)}{r}\right)_{r=R}. \qquad (4.4)$$

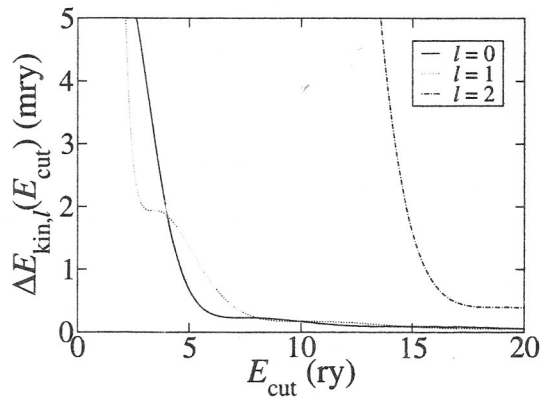Fig. 4. Augmentation functions $Q_{l,jk}(r)$ for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states of Ag.

Fig. 5. Estimation of the error $\Delta E_{\mathrm{kin},l}(E_{\mathrm{cut}})$ for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states of Ag.

The transferability of the pseudopotentials constructed is investigated by the comparison of the energy dependence of $\zeta_l(\varepsilon, R)$ with that of the all-electron $\zeta_{\mathrm{AE},l}(\varepsilon, R)$ for a chosen distance R.
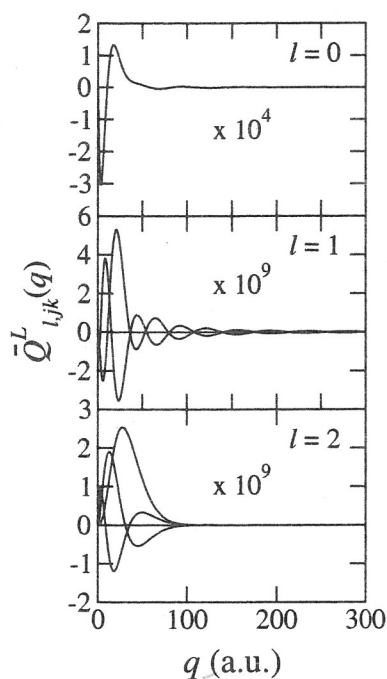
Fig. 6.   Fourier components $\bar{Q}^L_{l,jk}(q)$ of the augmentation functions $Q_{l,jk}(r)$ for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states of Ag.

§5.   Ultrasoft pseudopotentials for Ag

As described in the subsection 2.9, the ultrasoft pseudopotentials consist of the pseudopotential operator $\hat{V}_{NL}$ (Eq. (2.36)) and the overlap operator $\hat{S}$ (Eq. (2.37)). To construct these operators, we have to obtain the AE wave function $P_{AE,lj}(r)$, the USPP pseudo-wave-functions $P_{US,lj}(r)$ (Eq. (2.9)), the NCPP pseudo-wave-functions $P_{NC,lj}(r)$ (Eq. (2.12)), the local functions $\chi_{lj}(r)$ (Eq. (2.28)), the basis functions $\beta_{lj}(r)$ (Eq. (2.30)), and the augmentation functions $Q_{l,jk}(r)$ (Eq. (2.33)). In this section, we calculate these functions for a Ag atom. The ground-state electron configuration is used as the reference electron configuration, and the pseudopotentials are constructed for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states. We use the cutoff lengths of $r_{cl} = 2.53$ and $r'_{cl} = 2.28$ a.u.

Figure 1 shows the USPP pseudo-wave-functions $P_{US,lj}(r)$ and the AE wave functions $P_{AE,lj}(r)$. We see that $P_{US,lj}(r)$ are nodeless, while $P_{AE,lj}(r)$ have oscillating behavior near the origin. Each $P_{US,lj}(r)$ approaches the corresponding $P_{AE,lj}(r)$ smoothly. The NCPP pseudo-wave-functions $P_{NC,lj}(r)$ have similar profiles to those of $P_{US,lj}(r)$. The local functions $\chi_{lj}(r)$ are displayed in Fig. 2. It is seen that $\chi_{lj}(r)$ become zero at r_{cl}, where the first and second derivatives also vanish because $P_{US,lj}(r)$ have the continuous derivatives up to the fourth order. In the method proposed by Kresse and Hafner,[19] the derivative of $P_{US,lj}(r)$ are continuous only up to the second order, and, therefore, $\chi_{lj}(r)$ calculated by Eq. (2.28) vanish with a finite first derivative. The basis functions $\beta_{lj}(r)$ and augmentation functions $Q_{l,jk}(r)$ are
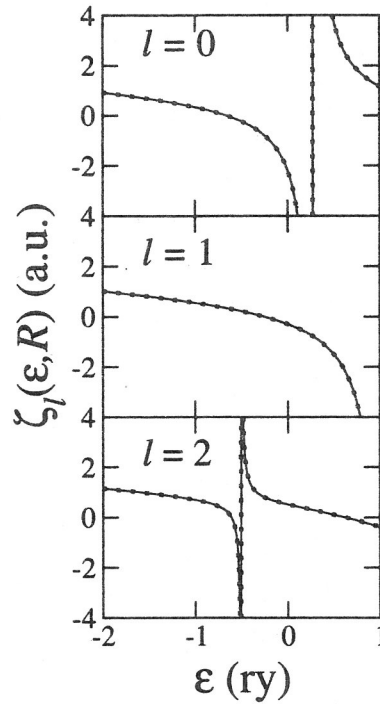
Fig. 7. Comparison of the energy dependence of the logarithmic derivatives $\zeta_l(\varepsilon, R)$ of the pseudo-wave-functions (dotted lines) with that of the all-electron $\zeta_{\mathrm{AE},l}(\varepsilon, R)$ (solid lines) for $l = 0$ (5s), $l = 1$ (5p), and $l = 2$ (4d) electronic states of Ag.

shown in Figs. 3 and 4, respectively. $\beta_{lj}(r)$ and $Q_{l,jk}(r)$ also approach zero smoothly at r_{cl}.

Figure 5 shows the estimation of the error $\Delta E_{\mathrm{kin},l}(E_{\mathrm{cut}})$ (Eq. (4.1)) associated with the plane-wave cutoff energy E_{cut} for the pseudo-wave-functions. We see that the $l = 2$ (4d) electronic state mainly determines the cutoff energy E_{cut}. The required E_{cut} is estimated to be about 16 ry for an error of 1 mry/electron. The cutoff energy $E_{\mathrm{cut}}^{\mathrm{dens}}$ for the electron density is estimated from $\bar{Q}_{l,jk}^{L}(q)$ (Eq. (4.3)), as displayed in Fig. 6. The required $E_{\mathrm{cut}}^{\mathrm{dens}}$ will be about 100 ry.

Figure 7 shows the comparison of the energy dependence of the logarithmic derivatives $\zeta_l(\varepsilon, R)$ of the pseudo-wave-functions with that of the all-electron $\zeta_{\mathrm{AE},l}(\varepsilon, R)$ for $R = 3.5$ a.u. It is seen that $\zeta_l(\varepsilon, R)$ are in good agreement with $\zeta_{\mathrm{AE},l}(\varepsilon, R)$ for a wide range of energy, which means that the pseudopotentials constructed have a high transferability.

References

1) R. Car and M. Parrinello, Phys. Rev. Lett. **55** (1985), 2471.
2) J.-L. Fattebert and F. Gygi, Comput. Phys. Commun. **162** (2004), 24.
3) P. Hohenberg and W. Kohn, Phys. Rev. **136** (1964), B864.
4) W. Kohn and L. J. Sham, Phys. Rev. **140** (1965), A1133.
5) D. R. Hamann, M. Schluter and C. Chiang, Phys. Rev. Lett. **43** (1979), 1494.
6) N. Troullier and J. L. Martins, Phys. Rev. B **43** (1991), 1993.
7) J. Ihm, A. Zunger and M. L. Cohen, J. Phys. C **12** (1979), 4409.

8) W. E. Pickett, Comput. Phys. Rep. **9** (1989), 115.
9) M. P. Teter, M. C. Payne and D. C. Allan, Phys. Rev. B **40** (1989), 12255.
10) M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, Rev. Mod. Phys. **64** (1992), 1045.
11) F. Shimojo, Y. Zempo, K. Hoshino and M. Watabe, Phys. Rev. B **52** (1995), 9320.
12) G. Kresse, J. Furthmuller, Phys. Rev. B **54** (1996), 11169.
13) C. Cavazzoni and G. L. Chiarotti, Comput. Phys. Commun. **123** (1999), 56.
14) J. R. Chelikowsky, N. Troullier and Y. Saad, Phys. Rev. Lett. **72** (1994), 1240.
15) S. Ogut, J. R. Chelikowsky and S. G. Louie, Phys. Rev. Lett. **79** (1997), 1770.
16) F. Ancilotto, P. Blandin and F. Toigo, Phys. Rev. B **59** (1999), 7868.
17) J.-L. Fattebert and J. Bernholc, Phys. Rev. B **63** (2000), 1713.
18) D. Vanderbilt, Phys. Rev. B **41** (1990), 7892.
19) G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6** (1994), 8245.