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Pseudopotential generation*

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Abstract: Different classes of first-principle pseudopotentials are compared and various schemes for pseudopotential generation based on norm conservation are discussed in this paper. BHS (Bachelet, Hamann, and Schlüter)-scheme and V (Vanderbilt)-modifications are used to derive the KB (Kleinman and Bylander)-pseudopotentials and pseudo wave functions of bismuth. Quality test of pseudopotentials shows that no ghost states occur in the logarithmic derivatives of pseudo wave functions of Bismuth. The obtained bond length of bismuth dimer with this type of pseudopotentials is in good agreement with previous accurately calculated *ab initio* quantum chemical result.

Key words: Pseudopotential, Norm conservation
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INTRODUCTION

Since the introduction of the pseudopotential method (Phillips et al., 1959), and the subsequent proof of the Phillips Cancellation Theorem (Anderson, 1963) by Cohen and Heine (1961), this method has become an important tool both for the investigation of electronic band structures of solids and for understanding the behavior of electrons in crystals.

Pseudopotentials may be divided into three classes. One is empirical (Cohen et al., 1966), which can be obtained empirically from crystalline energy levels, and the other two are based on the first-principle.

One of the first-principle pseudopotentials is obtained by adding some core functions ψ_c to the wave function ψ to obtain a smooth pseudo wave function

$$|\psi^{\mathrm{ps}}> = |\psi> + \sum_c \alpha_c |\psi_c>, \quad (1)$$

and in its most general (non-Hermitian) form is (Austin et al., 1962)

$$V_{\mathrm{ps}}^{\mathrm{AHS}} = V + \sum_c |\psi_c> < F_c|, \quad (2)$$

where $F_c(r)$ is an arbitrary function. By substituting Eq.(1) into the Schrödinger equation, the relation

$$\alpha_c = < F_c | \psi^{\mathrm{ps}} > / (E - E_c) \quad (3)$$

is obtained. Zwicker (1975) showed that in general the AHS pseudopotential is nonvariational, i.e., first-order errors in a trial pseudofunction ψ^{ps} cause first-order errors of either sign in the energy E_t. The original Phillips-Kleinman (PK) pseudopotential (Phillips et al., 1959)

$$V_{\mathrm{ps}}^{\mathrm{PK}} = V + \sum_c (E - E_c) | \psi_c > < \psi_c | \quad (4)$$

has a nonunique ψ^{ps} because $\alpha_c^{\mathrm{PK}} = < \psi_c | \psi^{\mathrm{ps}} >$ makes $\psi^{ps'} = \psi^{\mathrm{ps}} + \sum_c \beta_c \psi_c$ a solution of Eq.(1). Zwicker (1975) was able to show that $V_{\mathrm{ps}}^{\mathrm{PK}}$ is variational and when used with a variational ψ_t causes ψ^{ps} to become unique ψ^{ps} which most closely approximates ψ_t. Furthermore, it is obvious from

$$|\psi_t^{\mathrm{PK}}> = |\psi_t> - \sum_c < \psi_c | \psi_t > | \psi_c > \quad (5)$$

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that the trial PK wave function is always orthogonal to the core eigenfunctions. The AHS pseudopotential may also be made variational by making it Hermitian by setting $F_c = A_c \psi_c$， with A_c being a constant. In that case it is easy to see that ψ_t is not orthogonal to ψ_c unless ψ_t has sufficient variational freedom in the core region to make it so. Since the whole purpose of using a pseudopotential is to eliminate the need for core variational freedom in ψ_t， therefore， the PK form is the most efficacious.

However， pseudopotentials in the above class have three shortcomings: （1） For valence functions which are orthogonal to all core functions such as oxygen $2p$ or iron $3d$， $V_{\mathrm{ps}}^{\mathrm{PK}}$ reduces to V; about this nothing can be done. （2） $V_{\mathrm{ps}}^{\mathrm{PK}}$ depends explicitly on the eigenvalue E. This ultimately arises from the nonorthogonality of orthogonalized plane waves and causes no more trouble than the off-diagonal energy dependence of the secular equation obtained from any expansion in nonorthogonal basis functions. （3） Outside the core region the normalized ψ^{ps} is proportional to but not equal to ψ. Thus to perform an accurate self-consistent calculation， one must construct ψ^{ps} using Eq.（1） or Eq.（5） and then renormalize it.

The "model" pseudopotential of Abarenkov and Heine （1965） is based on the idea that the core is a black box from which the valence wave functions emanate with some logarithmic derivative and that any core pseudopotential which yields that logarithmic derivative is a valid first-principle pseudopotential. Thus the model pseudopotential may be written as

$$V_{\mathrm{M}} = \begin{cases} V_{\mathrm{val}}(\boldsymbol{r}) - \sum_{lm} | Y_{lm} > A_l(E) < Y_{lm} | \\ \qquad\qquad\qquad \text{for } \boldsymbol{r} < \boldsymbol{R}_{\mathrm{c}}, \\ - Z/\boldsymbol{r} + V_{\mathrm{val}}(\boldsymbol{r}) \quad \text{for } \boldsymbol{r} > \boldsymbol{R}_c \end{cases} \tag{6}$$

where V_{val} is the coulomb and exchange potential due to the valence electrons， Z is the valence charge， and $A_l(E)$ is a constant （in space） function of E chosen to make the pseudo-function logarithmic derivative equal to that of the true eigenfunction at several atomic eigenvalues. This model pseudopotential contains two defects which in principle are irreparable although in practice are not too serious. One is that E in Eq.（6） is not uniquely determined when V_M is used in energy-band calculations， because the average potential in an infinite crystal is arbitrary. The second problem is the nonequality of the normalized pseudo wave functions and the true wave functions for $\boldsymbol{r} > \boldsymbol{R}_c$.

A giant step forward in model pseudopotentials was taken by Hamann， Schlüter， and Chiang （HSC） （1979） who inverted the Schrödinger equation to obtain a model pseudopotential

$$V_{\mathrm{M}}^{\mathrm{HSC}} = V_{\mathrm{val}}(\boldsymbol{r}) + \sum_{lm} | Y_{lm} > V_l^{\mathrm{HSC}}(\boldsymbol{r}) < Y_{lm} |, \tag{7}$$

where $V_M^{\mathrm{HSC}}(\boldsymbol{r}) \rightarrow - Z/\boldsymbol{r}$ for $\boldsymbol{r} > \boldsymbol{r}_{\mathrm{c}}$（$\boldsymbol{r}_{\mathrm{c}}$ is a core cutoff radius）. The real and pseudo wave functions of $V_{\mathrm{M}}^{\mathrm{HSC}}$ are identical （not merely proportional） for $\boldsymbol{r} > \boldsymbol{r}_c$. Thus the need to calculate the true wave function is minimized. More importantly， it can be proven （Hamann et al.， 1979） that as a consequence of the identity of the functions， the logarithmic derivative and the first energy derivatives of the logarithmic derivatives of the true and pseudo wave functions are identical for $\boldsymbol{r} > \boldsymbol{r}_c$. Hence the energy dependence of $V_{\mathrm{M}}^{\mathrm{HSC}}$ is second order and in most cases may be ignored.

After "unscreening"， the above pseudopotential becomes ionic pseudopotential， and the total ionic pseudopotential then reads

$$\hat{V}_{\mathrm{ion}}^{\mathrm{HSC}} = \sum_{lm} | Y_{lm} > V_{\mathrm{ion}}^{\mathrm{HSC}}(\boldsymbol{r}) < Y_{lm} |, \tag{8}$$

where the l-dependent ionic pseudopotential $V_{\mathrm{ion}}^{\mathrm{HSC}}$ is usually split into a long range l-independent local potential V_{loc} and a short range l-dependent semi-local potential $\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})$，

$$V_l^{\mathrm{HSC}}(\boldsymbol{r}) = V_{\mathrm{loc}}(\boldsymbol{r}) + \Delta V_l^{\mathrm{SL}} l(\boldsymbol{r}), \tag{9}$$

with $V_{\mathrm{loc}}(\boldsymbol{r})$ approaching $- Z/\boldsymbol{r}$ for $\boldsymbol{r} \rightarrow \infty$. Then the total ionic pseudopotential is written as

$$\hat{V}_{\mathrm{ion}}^{\mathrm{HSC}} = V_{\mathrm{loc}}(\boldsymbol{r}) + \sum_{lm} | Y_{lm} > \Delta V_l^{\mathrm{SL}}(\boldsymbol{r}) < Y_{lm} |. \tag{10}$$

However， when attempting to use Eq.（10） for an energy-band calculation in which the basis functions are expanded in plane waves， one is thwarted by the huge number of integrals necessitated by the semi-local （i.e.， nonlocal in angular coordinates but local in radial coordinates) part of the potential. Note that the integral of $|Y_{lm}>\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})<Y_{lm}|$ between a pair of plane waves is

$$\Delta\tilde{V}_l(k+G,k+G')=\frac{1}{\Omega}\sum_m <k+G|Y_{lm}> \Delta V_l^{\mathrm{SL}}(\boldsymbol{r})<Y_{lm}|k+G'>$$
$$=\frac{(4\pi)^2}{\Omega}\sum_m Y_{lm}(k+G)Y_{lm}(k+G')\cdot \int \boldsymbol{r}^2\mathrm{d}\boldsymbol{r}J_l(|k+G|\boldsymbol{r})\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})J_l(|k+G'|\boldsymbol{r}) \tag{11}$$

with Ω the volume of cell. One can find from Eq.(11) that the operation of diagonalization of $\Delta\tilde{V}_l$ scales like N_G^3 with N_G the number of plane waves.

To solve the above problem, Kleinman and Bylander (1982) suggested to use the projector

$$\Delta\hat{V}_l^{\mathrm{KB}}=\sum_{m=-l}^{l}\frac{|\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})\phi_{lm}^0(\boldsymbol{r})><\phi_{lm}^0(\boldsymbol{r})\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})|}{<\phi_{lm}^0(\boldsymbol{r})|\Delta_l^{\mathrm{SL}}(\boldsymbol{r})|\phi_{lm}^0(\boldsymbol{r})|>} \tag{12}$$

instead of function $\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})$, where $\phi_{lm}^0(\boldsymbol{r})=R_l^0(\boldsymbol{r})Y_{lm}(k)$ is the pseudo eigenfunction for which V_l^{SL} is calculated, and

$$\Delta\hat{V}_l^{\mathrm{KB}}|\phi_{l'm}^0>\equiv\delta_{ll'}\Delta V_l^{\mathrm{SL}}|\phi_{lm}^0> \tag{13}$$

Let us to see the integral of $|Y_{lm}>\Delta\hat{V}_l^{\mathrm{KB}}<Y_{lm}|$ between a pair of plane waves,

$$\Delta\tilde{\hat{V}}_l^{\mathrm{KB}}(k+G,k+G')=\frac{(4\pi)^2}{\Omega}\sum_m Y_{lm}(k+G)Y_{lm}(k+G')\cdot\frac{1}{W_l}T_l(|k+G|)T_l(|k+G')|) \tag{14}$$

with

$$W_l=\int\mathrm{d}\boldsymbol{r}\boldsymbol{r}^2R_l^0(\boldsymbol{r})\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})R_l^0(\boldsymbol{r}) \tag{15}$$

and

$$T_l(|k+G|)=\int\mathrm{d}\boldsymbol{r}\boldsymbol{r}^2R_l^0(\boldsymbol{r})\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})J_l(|k+G|\boldsymbol{r}) \tag{16}$$

$\Delta\tilde{\hat{V}}_l^{\mathrm{KB}}(k+G,k+G')$ is separable in $(k+G)$ and $(k+G')$, and the operation of diagonalization of such separable matrices scales like N_G, much less than N_G^3.

Therefore, to save computing time, it is beneficial to use pseudopotential in a fully separable form as proposed by Kleinman and Bylander (1982).

The pseudopotentials and pseudo wave functions should describe the valence region in different chemical environments over the range of valence energies as exactly as possible (transferability) and they should be characterized with a minimum of Fourier components (softness). All pseudopotential generation schemes have to find a compromise between these two properties. For each angular momentum l the pseudopotential approximation is essentially controlled by one parameter, the cut-off radius $\boldsymbol{r}_{cl}$, inside of which the true all electron (ae) wave function is replaced by an approximate one (Bachelet et al., 1982; Vanderbilt, 1985).

Various new schemes were suggested to improve the softness of pseudopotentials (Hamann, 1989). Some new generalizations of KB-scheme had also been proposed (Vanderbilt, 1985; Blöchl, 1990; Saito et al., 1992).

It is important to have well working testing tools to estimate the quality of pseudopotentials before doing expensive electronic structure calculations. Rappe et al. (1990) noticed that the Fourier distribution of the kinetic energy of a pseudo wave function mirrors the convergence of a pseudopotential and that it is essentially independent of the chemical environment. Their suggestion is to take this contribution as a softness criterion to estimate the convergence of the total electronic energy with respect to the size of the plane wave basis.

The necessary cut-off energy E_{cut}(i.e. the size of the plane wave basis set) in a band structure calculation depends on the quantities one wants to calculate. To find the optimal structure minimum of the total energy one only needs moderate accuracy. The main part of the total energy error caused by the finite basis size is the kinetic energy contained in the Fourier coefficients above $q_{\mathrm{cut}}=\sqrt{E_{\mathrm{cut}}}$. This can be easily estimated by the kinetic energy of the electrons in the atomic ground state.

KB-potential may have serious problems with nonphysical ghost states and a careful analysis of this problem is indispensable. This problem arises from the fact that the KB Hamiltonian does not obey the Wronskian theorem（Messiah，1974），which implies that atomic eigenfunctions are energetically ordered such that（for a given quantum number l）the energies increase with the number of nodes. As this theorem is not valid for the KB Hamiltonian，it can have eigenstates with nodes even below the zero-node state. Or，the zero-node state may be followed directly by an $n \geqslant 2$ node state. Both possibilities will usually prevent application of these potentials for a reliable description of chemical binding. Bylander and Kleinman（1990）published some empirical rules to avoid these spurious states. Gonze et al.（1991）and Kresse et al.（1999）gave a detailed analytical recipe to make a ghost state analysis and proposed that the appearance of some rapid deviation of the logarithmic derivative from the all-electron one，results in a spurious bound state（ghost state）. Therefore minimizing the deviation of the logarithmic derivative from the all-electron one can remove the ghost state.

In the following we will discuss various schemes for pseudopotential generation，including the original scheme of Bachelet et al.（BHS-scheme）（1982）optionally with some modifications proposed by Vanderbilt（V-mod.）（1985），and a scheme suggested by Rappe et al.（RRKJ-scheme）（1990）.

PSEUDOPOTENTIAL GENERATION BASED ON NORM CONSERVATION

The starting point of all pseudopotential generation schemes is a self-consistent atomic ae-calculation，and here the scalar relativistic approximation（SRA）is used. For each angular momentum l one replaces the numerically calculated radial ae-wave function $\psi_l^{ae}(\boldsymbol{r}) = \frac{g_l^{ae}}{\boldsymbol{r}} Y_{lm}(\Omega_r)$ by a nodeless ps-wave（pseudo wave）function $\psi_l^{ps}(\boldsymbol{r}) = \frac{g_l^{ps}}{\boldsymbol{r}} Y_{lm}(\Omega_r)$ which is constructed to be norm conserving，continuous at least up to the second derivative and identical with $\psi_l^{ae}(\boldsymbol{r})$ outside a certain cut-off radius $\boldsymbol{r}_{cl}$. With this wave function $g_l^{ps}(\boldsymbol{r})$ the radial Schrödinger equation is inverted to get a screen l-dependent potential. The Hartree and exchange correlation potentials $V_h(n^{ps}(\boldsymbol{r}))$ and $V_{xc}(n^{ps}(\boldsymbol{r}))$ in the LDA with the atomic pseudo charge density $n^{ps}(\boldsymbol{r})$ are subtracted to get an ionic l-dependent ps-potential（pseudopotential）$V_l^{ps}(\boldsymbol{r})$ to be used in LDA calculations.

The various schemes differ only in the construction of the ps-wave（pseudo wave）functions $g_l^{ps}(\boldsymbol{r})$. In one class of schemes（i.e. BHS and V）the functions $g_l^{ps}(\boldsymbol{r})$ are constructed indirectly，using auxiliary potentials $V_{cl}(\boldsymbol{r})$ to cut off the singular Coulomb potentials，while in a second class of schemes（i.e. RRKJ）the direct way，using analytical expressions for $g_l^{ps}(\boldsymbol{r})$，is pursued. The two classes of schemes use different definitions of $\boldsymbol{r}_{cl}$. Smooth cut-off functions $f_c(\frac{\boldsymbol{r}}{\boldsymbol{r}_{cl}})$ are used in the indirect methods to augment the Coulomb singularity and well defined matching radii are used in analytical methods. Comparable ps-potentials are obtained when the matching radius $\boldsymbol{r}_{cl}$ of the analytical methods is about 1.5 times the $\boldsymbol{r}_{cl}$ used in the cut-off functions.

1. BHS-scheme and V-modifications

In a first step the Coulomb singularity of the ae-potential is augmented. This is done with a cut-off function $f_c(x)$ in the BHS case and with a power series ansatz in the case of Vanderbilt's modifications，

$$V_{cl}^{(1)}(\boldsymbol{r}) = \begin{cases} V^{ae}(\boldsymbol{r})\left[1 - f_c\left(\frac{\boldsymbol{r}}{\boldsymbol{r}_{cl}}\right)\right] & \text{(BHS)}, \\ \begin{cases} b_0 + b_2\boldsymbol{r}^2 + b_4\boldsymbol{r}^4 & \boldsymbol{r} < 1.5\boldsymbol{r}_{cl}, \\ V^{ae}(\boldsymbol{r}) & \boldsymbol{r} \geqslant 1.5\boldsymbol{r}_{cl}, \end{cases} & \text{(Vanderbilt)}. \end{cases} \tag{17}$$

In a second step a term $\Delta V_{cl}(\boldsymbol{r}) = c_l f_c(\frac{\boldsymbol{r}}{\boldsymbol{r}_{cl}})$ is added to the potential to yield eigenfunctions $g_l^{(1)}(\boldsymbol{r})$ with the reference ae-eigenvalues e_l^{ae}. This is achieved by determining the potential parameter c_l iteratively. For the reference eigenvalue e_l^{ae} the Schrödinger equation is integrated inwards from infinity（~ 30 $a.u.$）and outwards from the origin to a matching radius typically in the range of the outermost maximum *of* $g_l^{ae}(\boldsymbol{r})$.

The form of the cut-off function is chosen as

$$f_{\mathrm{c}}(x) = \begin{cases} \mathrm{e}^{-x^{\lambda}} & \text{with } \lambda = 3.5 \text{ (BHS)}, \\ 100^{-\frac{\sinh^{\lambda}\left(\frac{bx}{1.5}\right)}{\sinh^{\lambda}(b)}} & \text{with } \lambda = 2.0 \text{ and} \\ & b = 1.0 \text{ (Vanderbilt)}. \end{cases} \tag{18}$$

To establish norm conservation of $g_l^{\mathrm{ps}}(\boldsymbol{r})$ a correction function $\Delta g_l(\boldsymbol{r})$ is added to $g_l^{(1)}(\boldsymbol{r})$ and

$$\Delta g_l(\boldsymbol{r}) = \delta_l \begin{cases} \boldsymbol{r}_{l+1} f_{\mathrm{c}}\left(\dfrac{\boldsymbol{r}}{\boldsymbol{r}_{\mathrm{c}l}}\right) & \text{(BHS)} \\ g_l^{(1)} f_{\mathrm{c}}\left(\dfrac{\boldsymbol{r}}{\boldsymbol{r}_{\mathrm{c}l}}\right) & \text{(Vanderbilt)}. \end{cases} \tag{19}$$

The parameter δ_l is adjusted to establish norm conservation. The choice of $\Delta g_l(\boldsymbol{r})$ is not unique.

2. RRKJ-scheme

Rappe et al. suggested expressing the $g_l^{\mathrm{ps}}(\boldsymbol{r})$ inside the radius $\boldsymbol{r}_{\mathrm{c}l}$ in terms of spherical Bessel functions $J_l(qr)$,

$$g_l^{\mathrm{ps}}(\boldsymbol{r}) = \begin{cases} \sum_{i=1}^{n} \alpha_{il} \boldsymbol{r} J_l(\tilde{q}_{il}\boldsymbol{r}) & \boldsymbol{r} < \boldsymbol{r}_{\mathrm{c}l}, \\ g_l^{\mathrm{ae}}(\boldsymbol{r}) & \boldsymbol{r} \geqslant \boldsymbol{r}_{\mathrm{c}l}, \end{cases} \tag{20}$$

where for each l the $n = 4$ lowest values $\tilde{q}_{\mathrm{c}l}$ are selected which fulfill the following boundary condition,

$$\left. \frac{x \dfrac{\mathrm{d}}{\mathrm{d}x} J_l(x)}{J_l(x)} \right|_{x = \tilde{q}_{cl}} \equiv \left. \frac{\boldsymbol{r} \dfrac{\mathrm{d}}{\mathrm{d}\boldsymbol{r}} g_l^{\mathrm{ae}}(\boldsymbol{r})}{g_l^{\mathrm{ae}}(\boldsymbol{r})} \right|_{r = r_{cl}} - 1. \tag{21}$$

In a second step of the RRKJ-scheme one adds a linear combination of $m = 5$ additional $J_l(qr)$,

$$\Delta g_l^{\mathrm{ps}}(\boldsymbol{r}) = \begin{cases} \sum_{k=1}^{m} \beta_{kl} \boldsymbol{r} J_l(\hat{q}_{kl}\boldsymbol{r}) & \boldsymbol{r} < \boldsymbol{r}_{\mathrm{c}l} \\ 0 & \boldsymbol{r} \geqslant \boldsymbol{r}_{\mathrm{c}l}, \end{cases} \tag{22}$$

where the value $x_{kl} = \hat{q}_{kl}\boldsymbol{r}_{\mathrm{c}l}$ is chosen to make function $J_l(x)$ the kth zero at this point.

This additional step is used to minimize the kinetic energy contributed by the Fourier coefficients of the wave functions $g_l^{\mathrm{ps}}(r)$ above a certain wave vector $\boldsymbol{q}_{\mathrm{c}l}$,

$$E_l^{\mathrm{kin}}(\boldsymbol{q} > \boldsymbol{q}_{\mathrm{c}l}) = \int_{q > q_{cl}} \mathrm{d}\boldsymbol{q}\boldsymbol{q}^2 \mid \psi_{\mathrm{lm}}(\boldsymbol{q})^2. \tag{23}$$

For the ps-potential construction the wave vector $\boldsymbol{q}_{\mathrm{c}l}$ is a free external parameter.

3. KB-pseudopotentials

The l dependent ps-potential $V_l^{\mathrm{ps}}(\boldsymbol{r})$ is usually split into a long range l independent local potential $V_{\mathrm{loc}}(\boldsymbol{r})$ and a short range l-dependent semi local potential $\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})$,

$$V_l^{\mathrm{ps}}(\boldsymbol{r}) = V_{\mathrm{loc}}(\boldsymbol{r}) + \Delta V_l^{\mathrm{SL}}(\boldsymbol{r}). \tag{24}$$

$V_{l_{max}}^{\mathrm{SL}}(\boldsymbol{r})$ is treated as local potential $V_{\mathrm{loc}}(\boldsymbol{r})$. This means that $V_l^{\mathrm{ps}}(\boldsymbol{r}) = V_{\mathrm{loc}}$ for $l \geqslant l_{\max}$. To save time and storage $\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})$ usually is transformed into a fully separable form (KB-potential):

$$\Delta V_l^{\mathrm{SL}}(\boldsymbol{r}) \rightarrow \Delta V_l^{\mathrm{KB}}(\boldsymbol{r}) = \tag{25}$$

$$E_l^{\mathrm{KB}} \sum_{m=-l}^{l} \mid \xi_{lm}^{\mathrm{KB}}(\boldsymbol{r}) > < \xi_{lm}^{\mathrm{KB}}(\boldsymbol{r}) \mid$$

with the projection operator

$$\mid \xi_{lm}^{\mathrm{KB}}(\boldsymbol{r}) > = \frac{\mid \Delta V_l^{\mathrm{SL}} \mid \psi_{lm}^{\mathrm{ps}} >}{\sqrt{< \psi_{lm}^{\mathrm{ps}} \mid \Delta V_l^{\mathrm{SL}} \mid^2 \psi_{lm}^{\mathrm{ps}} >}} \tag{26}$$

and

$$E_l^{\mathrm{KB}} = \frac{< \psi_{lm}^{\mathrm{ps}} \mid \Delta V_l^{\mathrm{SL}} \mid^2 \psi_{lm}^{\mathrm{ps}} >}{< \psi_{lm}^{\mathrm{ps}} \mid \Delta V_l^{\mathrm{SL}} \mid \psi_{lm}^{\mathrm{ps}} >} \tag{27}$$

with

$$\psi_{lm}^{\mathrm{ps}}(\boldsymbol{r}) = \frac{g_l^{\mathrm{ps}}(\boldsymbol{r})}{\boldsymbol{r}} Y_{lm}(\Omega_{\boldsymbol{r}}). \tag{28}$$

The wave functions $g_l^{\mathrm{ps}}(\boldsymbol{r})$ used in the construction of the projector functions $\xi_{lm}^{\mathrm{KB}}(\boldsymbol{r})$ are the ps-wave functions of the atomic reference configuration used in the construction scheme. There is no difference in operating on these wave functions with the separable KB-operator $\Delta V_l^{\mathrm{KB}}(\boldsymbol{r})$ or with the semi local potential $\Delta V_l^{\mathrm{SL}}(\boldsymbol{r})$. Therefore, $\Delta V_l^{\mathrm{KB}}(\boldsymbol{r})$ is a norm conserving ps-potential.

KB-PSEUDOPOTENTIALS AND PSEUDO WAVE FUNCTIONS OF BISMUTH

Here we present results for bismuth (Bi) using BHS-scheme and V-modifications. The pseudo wave functions $g_l^{ps}(r)$ and all-electron functions $g_l^{ae}(r)$ of Bi are shown in Fig. 1.

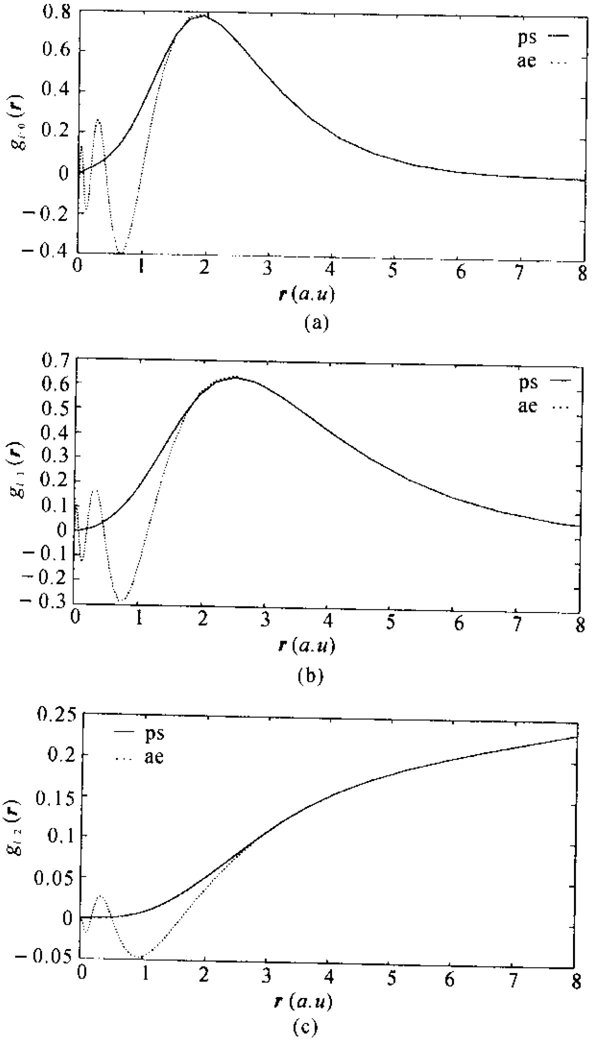

Fig. 1 The ps-wave functions $g_l^{ps}(r)$ and ae-wave functions $g_l^{ae}(r)$ of Bi for $l = 0$, 1, and 2, corresponding to (a), (b), and (c), respectively

One can find, in the Fig. 1 (a-c), that the ae-wave functions with nodes in the core region are replaced by nodeless ps-wave functions, and are identical beyond the core region. Apparently, the ps-wave functions are more smooth than the ae-wave functions in the core region.

The ionic pseudopotentials of Bi for $l = 0$, 1, and 2 are presented in Fig. 2. From Fig. 2 one can find that the Coulomb singularity in the core region disappears in the pseudopotentials. For comparison, the Coulomb potential $-2Z_v/r$, where Z_v is the valence charge, is also presented.

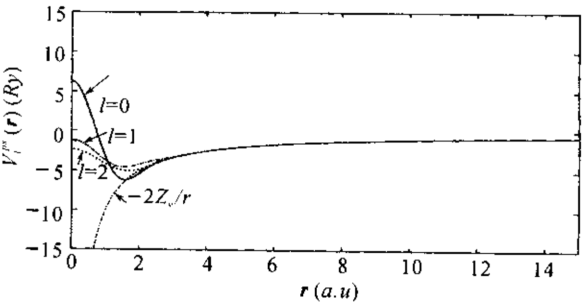

Fig. 2 The pseudopotentials of Bi $V_l^{ps}(r)$ for $l = 0$, 1, and 2, respectively. The local part $V^{loc}(r)$ approaches $-2Z_v/r$ at large r for all l components

The possibility that the above fully nonlocal pseudopotential may give rise to a "ghost" prevents a simple application of the BHS potentials. It is important to ensure in the construction of the potentials that no ghost state occurs in the chemically important energy range around the reference energy E_l. How can one decide if there is a ghost? As discussed above, a careful investigation of the logarithmic derivatives is necessary. A deep-lying ghost state could give rise to a very sharp structure in the logarithmic derivative of wave function $D_l(E)$, which then is likely to be missed. From Fig. 3 (a-c), in which the logarithmic derivatives of pseudo wave functions of Bi are plotted, we find that no ghost states occur.

Furthermore, we carry out first-principle calculations on the relaxation of Bi dimer with this type of pseudopotentials. The obtained bond length of Bi dimer (2.75 Å) is in good agreement with previous accurately calculated *ab initio* quantum chemical value (2.76 Å).

In conclusion, we have discussed different classes of first-principle pseudopotentials and schemes for pseudopotential generation based on norm conservation. Using BHS-scheme and

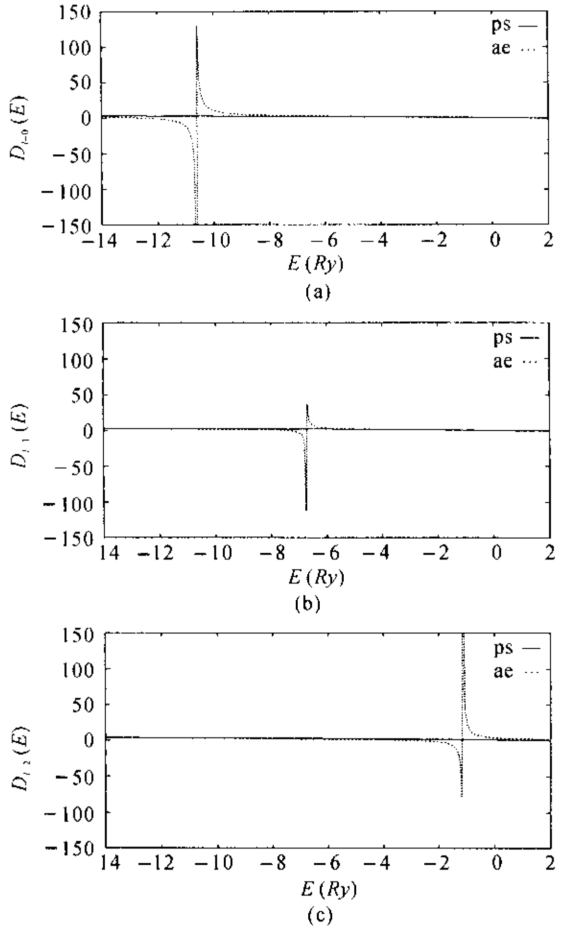

Fig.3 Logarithmic derivatives for *s* (a), *p* (b), and *d* (c) states of the Bi atom. The ghost state does not exist.

V-modifications, we have generated the KB-pseudopotentials and pseudo wave functions of Bismuth. The quality test of pseudopotentials indicated that ghost states do not exist. The obtained bond length of Bismuth dimer with this type of pseudopotentials is in good agreement with previous accurately calculated *ab initio* quantum chemical result.

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