

Optimized Ultrasoft Pseudopotentials

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Optimization of ultrasoft pseudopotentials is discussed from two points, i.e. (1) parametrization and function forms of pseudo-wavefunctions and local part of pseudopotentials, and (2) pseudization of augmentation charge. The cutoff energy for the Fourier components of the non-local part of the ultrasoft pseudopotential should be carefully chosen, because calculated cohesive energy often changes drastically with a change of the cutoff energy for the non-local part. Proposed optimization for the pseudized augmentation charge can efficiently make short wavelength components vanish. Examples of pseudopotentials are shown for a carbon atom. Charge density and cohesive energy are exemplified for diamond.

KEYWORDS: first principle molecular dynamical simulation, ultra-soft pseudopotential, real space method

§1. Introduction

The first principle electronic structure calculation comes into a new era since invention of the first principle pseudopotential method^{1,2)} and the first principle molecular dynamics.³⁾

In the norm-conserving pseudopotential method,¹⁾ a pseudo-wavefunction is determined under conditions that it should be continuously connected with an all-electron wavefunction at some reference energies and that it should have the same value of norm as that of the all-electron wavefunction. These conditions assure the same scattering ability of pseudopotentials as that of all-electron potential. In other words, a pseudo-wavefunction should have the same logarithmic derivative up to the first order energy dependence as those of all-electron wavefunctions. Nevertheless, the norm-conserving pseudopotential method is not suitable to the first row or heavy elements, because the pseudopotential becomes very deep for these elements.

Second type of the first principle pseudopotential method is developed by Vanderbilt, called the ultrasoft pseudopotential,²⁾ which can generally produce a shallow pseudopotential. In this formalism, a pseudo-wavefunction does not give the same value of the norm in order to keep enough freedom for softness of the pseudopotential. Then one should introduce an augmentation charge density to produce the same density as that of the all-electron wavefunction. The ultrasoft pseudopotential is designed for pseudo-wavefunctions so as to have the same logarithmic derivative at the connecting radius and the norm of pseudo-wavefunctions is defined with an overlap operator. Concrete form of an ultrasoft pseudopotential can be determined by setting a large number of parameters and function forms of the local part of pseudopotentials and pseudo-wavefunctions.

The present authors are developing a molecular dynamical method in real space using ultrasoft pseudopotentials with implementing the order-N algorithm.^{4,5)} While developing the calculation algorithm, we noticed

several important points in order to choose parameters and function forms of ultra-soft pseudopotentials.

So far, a choice of parameters of ultrasoft pseudopotentials has been guided only by a principle of widening the energy range of applying the pseudopotential. One might believe that the ultrasoft pseudopotential could be soft *as much as one wants*. However, one should notice that, once one requires excessive softness of local part of pseudopotentials, non-local part of pseudopotentials could not be soft any more. Therefore, a special care should be taken of the non-local part of the ultrasoft pseudopotentials, and it may be very desirable to know how the choice of many parameter values and the function form of local part of the ultrasoft pseudopotential should be related to the softness of the pseudopotential itself. One should also realize that the augmentation charge contains significant contribution of very short wavelength components.⁶⁾ Therefore, it is crucial to pseudize the augmentation charge in an efficient and systematic way so that it does not contain short wavelength components.

In §2, we briefly review the ultrasoft pseudopotential and present the formalism using the projection method. Section 3 is devoted to a discussion of optimal choice of parameters and function forms. In §4, we will emphasize importance of a choice for the cutoff energy for the non-local part of ultrasoft pseudopotentials. Examples of a carbon atom and diamond are also shown and discussed.

§2. Ultrasoft Pseudopotential Scheme

The total energy of valence electrons in the Vanderbilt ultrasoft pseudo-potential method is written (in atomic unit) as^{2,6)}

$$E_{\text{total}}[n, \{\phi_i\}] = \sum_i^{\text{occupied}} 2 \langle \phi_i | -\frac{\nabla^2}{2} + V_{NL} | \phi_i \rangle + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] + \int d\mathbf{r} V_{loc}^{\text{ion}}(\mathbf{r})n(\mathbf{r}) + U[\{\mathbf{R}_I\}]. \quad (2.1)$$

Here, $n(\mathbf{r})$ is the valence electron density, E_{xc} is the exchange-correlation energy functional of the density functional theory, $V_{loc}^{ion}(\mathbf{r})$ and V_{NL} are respectively local and non-local ionic pseudopotentials, $U[\{\mathbf{R}_I\}]$ is the ion-ion interaction energy and $\{\mathbf{R}_I\}$ is a set of ion coordinates. The factor 2 in the first term denotes the spin degeneracy. The orthogonalization of pseudo-wavefunctions $\{\phi_i(\mathbf{r})\}$ will be mentioned later.

The total valence electron charge density $n(\mathbf{r})$ is a sum of charge density related with the occupied states i and is given by

$$n(\mathbf{r}) = 2 \sum_i^{\text{occupied}} n_i(\mathbf{r}),$$

$$n_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2 + \sum_{nn'I} Q_{nn'}^I(\mathbf{r}) \langle \phi_i | \beta_n^I \rangle \langle \beta_{n'}^I | \phi_i \rangle. \quad (2.2)$$

The functions $\beta_n^I(\mathbf{r})$ and the augmentation charge density $Q_{nn'}^I(\mathbf{r})$, specified by an atomic quantum number n or n' , are provided by the ultrasoft pseudopotential method and centered on each ionic position \mathbf{R}_I of an atom I .

The ultrasoft pseudopotential method also provides the local ionic part of the pseudopotential

$$V_{loc}^{ion}(\mathbf{r}) = \sum_I V_{loc}^{ion,I}(\mathbf{r} - \mathbf{R}_I) \quad (2.3)$$

and the non-local part

$$V_{NL} = \sum_{nn'I} D_{nn'}^{I(0)} |\beta_n^I\rangle \langle \beta_{n'}^I| \quad (2.4)$$

in a separable form.

The pseudo-wavefunction $\phi_i(\mathbf{r})$ satisfies an effective Kohn-Sham equation

$$H|\phi_i\rangle = \varepsilon_i S|\phi_i\rangle, \quad (2.5)$$

where the Hamiltonian H and the overlap operator S are

$$H = -\frac{\nabla^2}{2} + V_{loc} + \sum_{nn'I} D_{nn'}^I |\beta_n^I\rangle \langle \beta_{n'}^I|, \quad (2.6)$$

$$S = 1 + \sum_{nn'I} q_{nn'}^I |\beta_n^I\rangle \langle \beta_{n'}^I|, \quad (2.7)$$

and

$$q_{nn'}^I = \int d\mathbf{r} Q_{nn'}^I(\mathbf{r}),$$

$$V_{loc}(\mathbf{r}) = V_{loc}^{ion}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})},$$

$$D_{nn'}^I = D_{nn'}^{I(0)} + \int d\mathbf{r} V_{loc}(\mathbf{r}) Q_{nn'}^I(\mathbf{r}). \quad (2.8)$$

The orthogonalization of $\{\phi_i\}$ is defined by using the overlap operator S as

$$\langle \phi_i | S | \phi_j \rangle = \delta_{ij}. \quad (2.9)$$

With an atomic all-electron Hamiltonian H_{AE} and arbitrarily chosen reference energy ε_n , an atomic all-electron wavefunction $\psi_n(\mathbf{r})$ is defined by

$$H_{AE}\psi_n = \varepsilon_n \psi_n.$$

In the first step of constructing a pseudopotential of an isolated atom I , an atomic pseudo-wavefunction ϕ_n and a local potential V_{loc} are arbitrarily chosen in regions $r < r_{cl}$ (connecting radius for pseudo-wavefunctions depending upon atomic specie and an angular quantum number l) and $r < r_c^{loc}$ (connecting radius for the local potential) around an atom I , respectively. The wavefunction $\phi_n(\mathbf{r})$ coincides with an atomic all-electron wavefunction ψ_n in the region $r > r_{cl}$ and V_{loc} with an all-electron potential V_{AE} in the region $r > r_c^{loc}$. The function $\beta_n(\mathbf{r})$ is determined as

$$|\beta_n\rangle = \sum_{n'} (B^{-1})_{n'n} |\chi_{n'}\rangle, \quad (2.10)$$

where $\chi_n(\mathbf{r})$ is defined by an equation

$$|\chi_n\rangle = \{\varepsilon_n - (-\frac{\nabla^2}{2} + V_{loc})\} |\phi_n\rangle,$$

a matrix $B_{nn'}$ by

$$B_{nn'} = \langle \phi_n | \chi_{n'} \rangle.$$

The function $\beta(\mathbf{r})$ satisfies an orthogonalization relation

$$\langle \phi_n | \beta_{n'} \rangle = \delta_{nn'}. \quad (2.11)$$

It should be noticed that the function χ_n vanishes in a region $r > \text{Max}\{r_{cl}, r_c^{loc}\}$, irrespective to a choice of ε_n and ϕ_n . The augmentation charge $Q_{nn'}(\mathbf{r})$ is defined as

$$Q_{nn'}(\mathbf{r}) = \psi_n^*(\mathbf{r}) \psi_{n'}(\mathbf{r}) - \phi_n^*(\mathbf{r}) \phi_{n'}(\mathbf{r}). \quad (2.12)$$

The coefficient $D_{nn'}$ of the non-local potential part is related with $B_{nn'}$ and $q_{nn'}$ by an equation

$$D_{nn'} = B_{nn'} + \varepsilon_n q_{nn'}. \quad (2.13)$$

Then, in the second step, the local ionic potential V_{loc}^{ion} and the coefficient $D_{nn'}^{(0)}$ are constructed by *descreening* procedure, i.e. subtracting the Hartree and exchange-correlation potentials contributed by valence electron charge as in eq. (2.8).

One can also obtain an equation;

$$\begin{aligned} D_{nm} &= \langle \phi_n | \chi_m \rangle + \varepsilon_m \{ \langle \psi_n | \psi_m \rangle - \langle \phi_n | \phi_m \rangle \} \\ &= \varepsilon_m \langle \psi_n | \psi_m \rangle - \langle \phi_n | T + V_{loc} | \phi_m \rangle \\ &= \langle \psi_n | T + V_{AE} | \psi_m \rangle - \langle \phi_n | T + V_{loc} | \phi_m \rangle. \end{aligned} \quad (2.14)$$

Therefore, once we fix the local potential V_{loc} , essential point is an aspect of counterbalance between the kinetic energy T and the non-local potential D_{nm} . In other words, a very soft pseudo-wavefunction causes a large non-local pseudopotential and, therefore, it is very crucial to choose simple β -functions.

The atomic quantum number n or n' may be denoted by an angular momentum and a magnetic quantum number (l, m) and a reference energy ε_n . The number of reference energies, for each (l, m) , is arbitrary and their values are not necessary to be eigenenergies of an isolated atom. The logarithmic derivative at $r = r_{cl}$ is reproducible in a wider energy range if we choose more reference energies.

The ultrasoft pseudopotential method can be re-

formulated as *the projection method* from a pseudo-wavefunction ϕ_i to an all-electron wavefunction ψ_i by an equation

$$|\psi_i\rangle = |\phi_i\rangle + \sum_n \{|\psi_n\rangle - |\phi_n\rangle\} \langle\beta_n|\phi_i\rangle. \quad (2.15)$$

Actually from eq. (2.15) with a help of eq. (2.11), one can obtain

$$|\psi_i\rangle\langle\psi_j| = |\phi_i\rangle\langle\phi_j| + \sum_{kl} \langle\beta_k|\phi_i\rangle\langle\phi_j|\beta_l\rangle \{|\psi_k\rangle\langle\psi_l| - |\phi_k\rangle\langle\phi_l|\}, \quad (2.16)$$

which is equivalent to eq. (2.2). This result is very important to evaluate physical properties by using pseudo-wavefunctions. The expectation value of an operator A is calculated, by using eq. (2.15), as

$$\langle\psi_i|A|\psi_j\rangle = \langle\phi_i|A|\phi_j\rangle + \sum_{kl} \langle\phi_i|\beta_k\rangle \{ \langle\psi_k|A|\psi_l\rangle - \langle\phi_k|A|\phi_l\rangle \} \langle\beta_l|\phi_j\rangle, \quad (2.17)$$

and this assures an operator equivalence

$$\langle\psi_i|A|\psi_j\rangle = \langle\phi_i|\tilde{A}|\phi_j\rangle \quad (2.18)$$

between A in the Hilbert space of $\{\psi\}$ and \tilde{A} in the Hilbert space of pseudo-wavefunctions $\{\phi\}$;

$$\tilde{A} = A + \sum_{kl} |\beta_k\rangle \{ \langle\psi_k|A|\psi_l\rangle - \langle\phi_k|A|\phi_l\rangle \} \langle\beta_l|. \quad (2.19)$$

§3. Optimal Form of Ultrasoft Pseudopotentials

The Vanderbilt ultrasoft pseudopotential depends upon many parameters, such as matching radii r_c^{loc} for a pseudopotential, matching radii r_{cl} for pseudo-wavefunctions, reference energies ε_n , a concrete form of local part V_{loc}^I , pseudo-wavefunctions ϕ_n^I , and pseudization of augmentation charge Q_{nn}^I . A guiding principle how to determine them has not been outlined.

An ultrasoft pseudopotential could not be soft as much as one wants. An excessively demanded softness of V_{loc}^I and ϕ_n^I can only be allowed at the expenses of a softness of non-local part of pseudopotentials, i.e. spoiling slowly varying behavior of $\beta(\mathbf{r})$ functions.

The effects of functions $\beta(\mathbf{r})$ on a pseudo-wavefunction $\phi(\mathbf{r})$ is expressed by a matrix element $\langle\beta_n^I|\phi\rangle$. Therefore, if a pseudo-wavefunction does not contain short wavelength components, short wavelength components of functions $\beta(\mathbf{r})$ can simply be neglected, though it may not always be possible. In actual cases, the cutoff energy for wavefunctions should be carefully chosen by knowing behavior of functions $\beta(\mathbf{r})$. Choice of the cutoff energy will be discussed in the next section.

In this section, we analyze essential points for a choice of several parameters in ultrasoft pseudopotentials.

3.1 Softness of local part of pseudopotential $V_{loc}(r)$

We use the local part of Troullier-Martins' screened soft pseudopotential $V_{scr,l}^{pp}(r)$ as our local potential.⁷⁾ First, the norm-conserving pseudo-wavefunctions are constructed as

$$R_l^{pp}(r) = \begin{cases} R_l^{AE}(r) & : r > r_c^{loc} \\ r^l \exp(p_l(r)) & : r < r_c^{loc} \end{cases} \quad (3.1)$$

$$p_l(r) = c_0 + c_2 r^2 + \cdots c_{12} r^{12}.$$

Here a polynomial $p_l(r)$ should be determined so that $R_l^{pp}(r)$ and an all-electron wavefunction $R_l^{AE}(r)$ are connected at $r = r_c^{loc}$ continuously up to the forth-order derivatives with conditions of the norm conservation of R_l^{pp} and $d^2 V_{scr,l}^{pp}(r=0)/dr^2 = 0$. It should be noted that odd order coefficients c_{2n+1} are zero. The Kohn-Sham equation is inversely solved and the potential for the angular momentum component l can be determined as

$$V_{scr,l}^{pp}(r) = \begin{cases} V_{AE}(r) & : r > r_c^{loc} \\ \mathcal{E}_l + \frac{l+1}{r} p'_l(r) + \frac{1}{2} \{ p''_l(r) + (p'_l(r))^2 \} & : r < r_c^{loc} \end{cases} \quad (3.2)$$

Here p'_l is the derivative of p_l with respect to r . We can use an appropriate l -component of $V_{scr,l}^{pp}(r)$ as the local pseudopotential $V_{loc}(r)$, which is soft and non singular at $r = 0$. Further constraint to coefficients $c_0 \sim c_{12}$ could be imposed in order to obtain more shallow local part of the pseudopotential.

3.2 Soft pseudo-wavefunctions ϕ_n

In order to have soft pseudo-wavefunctions, we start from similar form of Troullier-Martins' wavefunctions with a small modification; i.e.

$$\tilde{R}_l^{pp}(r) = \begin{cases} R_l^{AE}(r) & : r > r_{cl} \\ r^l \exp(\tilde{p}_l(r)) & : r < r_{cl} \end{cases} \quad (3.3)$$

where

$$\tilde{p}_l(r) = \tilde{c}_0 + \tilde{c}_2 r^2 + \cdots \tilde{c}_{12} r^{12} - \tilde{c} * \{(r/r_{cl})^3 - 1.0\}^4. \quad (3.4)$$

Coefficients $\tilde{c}_2 \sim \tilde{c}_{12}$ are determined after fixing \tilde{c}_0 in the same way as those in the original norm-conserving Troullier-Martins' formalism eq. (3.1), except using a different matching radii $r_{cl} \neq r_c^{loc}$. Coefficients \tilde{c}_0 and \tilde{c} are chosen so as to make a wavefunction soft. The parameter \tilde{c} causes neither change of derivatives at $r = r_{cl}$ nor change of necessary r -dependence near $r = 0$. Despite of these, values near $r \simeq 0$ can be arbitrarily controlled according to a choice of \tilde{c} .

3.3 Optimal pseudization of augmentation charge Q

The augmentation charge can be decomposed as

$$Q_{n_1 l_1 m_1; n_2 l_2 m_2}(\mathbf{r}) = \sum_L A_L^{n_1 l_1 m_1; n_2 l_2 m_2} Y_{L m_2 - m_1}(\hat{\mathbf{r}}) Q^L(r) : 0 < r < r_{cl}$$

$$Q^L(r) = r^L \rho_L(r).$$

The augmentation charge $Q^L(r)$ of angular momentum L contains short wavelength components. We may substitute $Q^L(r)$ by an effective augmentation charge, which does not contain short wavelength components and just gives the same multipole components as those of the original augmentation charge density,⁶⁾ which is called

pseudized augmentation charge and written as $\tilde{Q}^L(r)$.

The most desirable $\tilde{Q}^L(r)$ is the one as smooth as possible and has no components of short wavelengths. In order to have satisfactory $\tilde{Q}^L(r)$, Laasonen *et al.* proposed a condition of minimization of an integral over short wavelength region of the Fourier transformation of $\tilde{Q}^L(r)$.⁶⁾ Here, we will propose another pseudization procedure which can be explicitly written down.

The pseudized augmentation charge $\tilde{Q}^L(r)$ may be expanded into a power series of finite order

$$\begin{aligned}\tilde{Q}^L(r) &= r^L \tilde{\rho}_L(r) = r^L \sum_{k=1}^{k_{\max}} \tilde{d}_k r^{2(k-1)} \quad : 0 < r < r_{cl} \quad (3.6) \\ &= \begin{cases} \tilde{Q}^L(r) \text{ as soft as possible} & : 0 < r < r_{in} \\ \text{original } Q^L(r) & : r_{in} < r < r_{cl} \end{cases} \quad (3.7)\end{aligned}$$

Here r_{in} is chosen inside r_{cl} so that $\tilde{Q}^L(r)$ is smooth without components of short wavelength. We choose $k_{\max} = 12$, which usually can give a set of coefficients \tilde{d}_k for good agreement between a polynomial eq. (3.6) and original Q^L of eq. (3.5) in a range $r_{in} < r < r_{cl}$.

Let us express the Fourier transformed $\tilde{Q}^L(r)$ as

$$\begin{aligned}\tilde{Q}_L(G) &= \int_0^\infty dr r^2 \tilde{Q}^L(r) j_L(Gr) \\ &= \int_0^{r_{cl}} dr r^2 \tilde{Q}^L(r) j_L(Gr) \\ &= a_2 G^{-2} + a_3 G^{-3} + a_4 G^{-4} + a_5 G^{-5} + \dots, \quad (3.8)\end{aligned}$$

where

$$L = 0, 2, \dots : \begin{cases} a_{2n} = \tilde{a}_{2n} \cos r_{cl} G, \\ a_{2n+1} = \tilde{a}_{2n+1} \sin r_{cl} G \end{cases} \quad (3.9)$$

$$L = 1, 3, \dots : \begin{cases} a_{2n} = \tilde{a}_{2n} \sin r_{cl} G, \\ a_{2n+1} = \tilde{a}_{2n+1} \cos r_{cl} G \end{cases} \quad (3.10)$$

The coefficients \tilde{a}_m do not depend on G . The expansion coefficients \tilde{d}_k in eq. (3.6) can be explicitly written down as a function of \tilde{a}_m . If we have non vanishing \tilde{a}_2 , $G^2 \tilde{Q}_L(G)$ is finite at $G \rightarrow \infty$. Vanishing \tilde{a}_m for several lower m are necessary in order to construct pseudized $\tilde{Q}_L(G)$ without short wavelength components and this is especially crucial in the force calculation. We impose the following conditions on the coefficients \tilde{d}_k ;

$$\begin{aligned}(1) \quad & \int_0^{r_{in}} r^{2+L} dr \tilde{Q}^L(r) = \int_0^{r_{in}} r^{2+L} dr Q^L(r) \\ (2) \quad & \tilde{\rho}_L(r_{in}) = \rho_L(r_{in}) \\ (3) \quad & \tilde{\rho}'_L(r_{in}) = \rho'_L(r_{in}) \\ (4) \quad & \tilde{\rho}''_L(r_{in}) = \rho''_L(r_{in}) \\ (5) \quad & \tilde{a}_2 = 0 \\ (6) \quad & \tilde{a}_3 = 0 \\ (7) \quad & \tilde{a}_4 = 0 \\ (8) \quad & \tilde{Q}^L(r_{cl}) = 0 \\ (9) \quad & \int_{r_{in}}^{r_{cl}} dr r^{2+L} \tilde{Q}^L(r) = \int_{r_{in}}^{r_{cl}} dr r^{2+L} Q^L(r)\end{aligned}$$

$$(10) \quad \frac{\partial}{\partial \tilde{a}_{11}} \int_{r_{in}}^{r_{cl}} dr |\tilde{\rho}_L(r) - \rho_L(r)|^2 = 0$$

$$(11) \quad \frac{\partial}{\partial \tilde{a}_{12}} \int_{r_{in}}^{r_{cl}} dr |\tilde{\rho}_L(r) - \rho_L(r)|^2 = 0$$

$$(12) \quad \frac{\partial}{\partial \tilde{a}_{13}} \int_{r_{in}}^{r_{cl}} dr |\tilde{\rho}_L(r) - \rho_L(r)|^2 = 0.$$

The first equation implies a conservation of multipole components of augmentation charge, comparing with the original $Q^L(r)$. Conditions (2) ~ (4) are for continuity of the augmentation charge. Conditions from the 5-th to the 7-th are for softness, i.e. rapidly vanishing $\tilde{Q}_L(G)$ with increasing G . The conditions from the 8-th to the 12-th are for coincidence of $\tilde{Q}^L(r)$ with original $Q^L(r)$ in a region of $r_{in} < r < r_{cl}$ as much as possible. Actually the condition (5) is identical to (8) and we have eleven ($= k_{\max} - 1$) independent conditions. The number of conditions can be increased if necessary.

In many cases of $l_1 = l_2 = L = 0$, we may get $\tilde{d}_1 < 0$. Actually a negative \tilde{d}_1 implies a negative $\tilde{Q}^L(r = 0)$ for $L = 0$ and causes negative augmentation charge density at around $r = 0$. For $l_1 = l_2 = L = 0$, charge density $|\phi_i(\mathbf{r})|^2$ originating from soft pseudo-wavefunctions is too small to compensate the negative (pseudized) augmentation charge density. Therefore, once we have negative \tilde{d}_1 , we should set $\tilde{d}_1 = 0$ and increase k_{\max} by 1 ($k_{\max} = 13$).

3.4 Optimal choice of the number of reference energies

Once we increase a number of reference energies, the energy range becomes wider where a scattering ability of pseudopotential is identical to that of all-electron potential and where logarithmic derivatives of a pseudo-wavefunction is equal to that of corresponding all-electron wavefunction. On the other hand, this makes the form of a non-local part of a pseudopotential very complicated, for example, functions $\beta(\mathbf{r})$ show complicate behavior like oscillation in a narrow range of r . In other words, we may lose the softness of non-local part of ultrasoft pseudopotentials.

It is important to ascertain whether the $\beta(\mathbf{r})$ can be reproduced in the procedure of the Fourier and the inverse Fourier transformations with an actual momentum cutoff. In order to retain the softness of functions $\beta(\mathbf{r})$, we often ought to use single reference energy for one (l, m). Though this choice may restrict applicable energy range of the pseudopotentials, resultant $\beta(\mathbf{r})$ functions and pseudopotentials are always sufficient in our experiences.

3.5 Solving the Kohn-Sham equation

The Kohn-Sham equation, for determining ε and $\phi(\mathbf{r})$,

$$\left(-\frac{\nabla^2}{2} + V_{loc} - \varepsilon\right)|\phi\rangle + \sum_{i,j} |\beta_i\rangle (D_{ij} - \varepsilon q_{ij}) \langle \beta_j | \phi \rangle = 0 \quad (3.11)$$

is not very easy to be solved numerically. Numerical instability originates from the fact, in iterative method, that the inhomogeneous term, the second term, contains

$|\phi\rangle$. In order to avoid this instability, we should decompose the above equation into coupled equations

$$\begin{cases} (-\frac{\nabla^2}{2} + V_{loc} - \varepsilon)|f\rangle = 0 \\ (-\frac{\nabla^2}{2} + V_{loc} - \varepsilon)|g_j\rangle + \sum_i |\beta_i\rangle (D_{ij} - \varepsilon q_{ij}) = 0. \end{cases}$$

The second equation has a definite inhomogeneous term, not in iterative way. Then the wavefunction ϕ can be a linear combination of f and g_j .

§4. Choice of Cutoff Energies for Q and β : Examples of Carbon Atom and Diamond

Here we show an example of the optimized ultrasoft pseudopotential for a carbon atom, and charge density and cohesive energy in diamond. Especially we will discuss effects of the cutoff energies for $Q(\mathbf{r})$ and $\beta(\mathbf{r})$.

4.1 Pseudopotential and pseudo-wavefunctions

We start constructing a pseudopotential of carbon atom with the ground state electron configuration $1s^2 2s^2 2p^2$. The non-local part of $l = 1$ of Troullier-Martins' norm-conserving pseudopotential is used as the local potential V_{loc} . The V_{loc} and descreened V_{loc}^{ion} are shown in Fig. 1. Very flat behavior of pseudopotentials at $r = 0$ is the particular characteristics of Troullier-Martins' form.

We have tried two sets of choice of reference energies and matching radii r_{cl} and r_l^{loc} ;

$$(1) \varepsilon_{2s} = -0.51843 \text{ a.u.}, \quad \varepsilon_{2p} = -0.20833 \text{ a.u.}$$

$$r_{cl} = 1.8 \text{ a.u. (s \& p) (wavefunction)}$$

$$r_c^{loc} = 1.5 \text{ a.u. (s \& p) (pseudopotential)}$$

$$(2) \varepsilon_{2s,a} = -0.51843 \text{ a.u.}, \quad \varepsilon_{2s,b} = -0.20833 \text{ a.u.}$$

$$\varepsilon_{2p,a} = -0.20833 \text{ a.u.}, \quad \varepsilon_{2p,b} = -0.35000 \text{ a.u.}$$

$$r_{cl} = 1.8 \text{ a.u. (s \& p) (wavefunction)}$$

$$r_c^{loc} = 1.5 \text{ a.u. (s \& p) (pseudopotential)}.$$

Corresponding $\beta(\mathbf{r})$ functions are demonstrated in

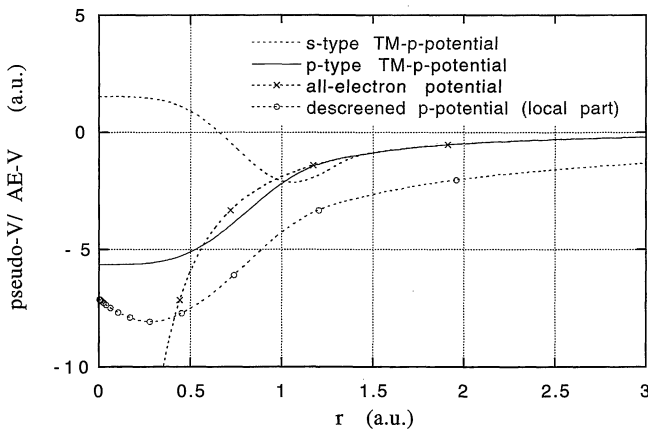


Fig. 1. V_{loc} for each orbital angular momentum component and descreened V_{loc}^{ion} of a carbon atom. The $l = 1$ component of Troullier and Martins' pseudopotential is used as the local part of ultrasoft pseudopotential.

Fig. 2. The reference energies -0.51843 (a.u.) and -0.20833 (a.u.) are the eigenenergies of $2s$ and $2p$ states in an isolated carbon atom. For the choice 1 of the reference energies, both $\beta(\mathbf{r})$ functions of $l = 0$ and 1 have one node. However, for the choice 2, $\beta(\mathbf{r})$ functions of $l = 1$ have two nodes. Furthermore, two choices result in quite different absolute values of the $\beta(\mathbf{r})$ functions. The behavior in the choice 2 may not be reproduced if we use a real space mesh with an interval larger than 0.21 a.u.. In the choice 1, the real space mesh with an interval 0.42 a.u. is enough to reproduce the behavior of functions $\beta(\mathbf{r})$.

4.2 Cutoff energies and mesh intervals

Now we discuss the effects of the cutoff energy, or the corresponding minimum mesh interval in real space. In the standard Car-Parrinello (C-P) method, most calculation is done in k -space. The charge density is evaluated by using wavefunctions in real space, and is transformed into k -space. The Fourier and inverse Fourier transformation should be performed by the First Fourier Transformation (FFT) and, therefore, this is called the dual FFT scheme. Three different cutoff energies (E_c^{wf} , E_c^{soft} and E_c^{hard}) are used in the dual FFT scheme of the ultrasoft pseudopotential method.⁶⁾

Plane wave expansion of pseudo-wavefunctions and Fourier transformed $\beta(\mathbf{r})$ functions are calculated with

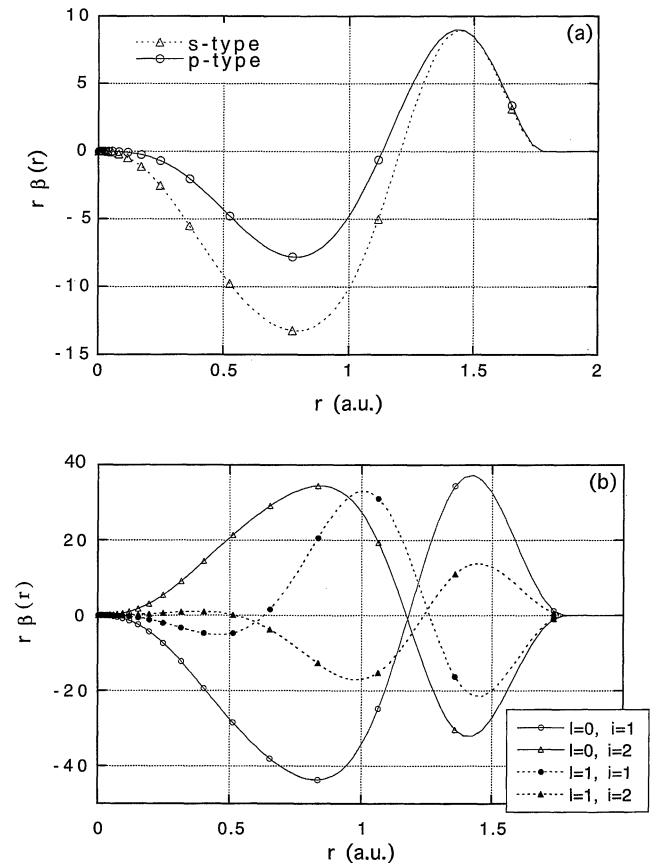


Fig. 2. Functions $\beta(\mathbf{r})$ of carbon for angular momentums $l = 0$ and $l = 1$. (a) Choice 1 (one reference energy for each l); (b) Choice 2 (two reference energies; $i=1,2$), which produces two-nodes $\beta(\mathbf{r})$ functions of $l = 1$.

the cutoff energy $E_c^{wf} = (1/2)(G_c)^2$. The term $\langle \beta | \phi_i \rangle$ is calculated with the cutoff energy E_c^{wf} in the dual FFT scheme.

The soft charge density $2 \sum |\phi(\mathbf{r})|^2$ is calculated in the coarse grid with an interval $h = \pi/(2G_c)$, and the corresponding soft cutoff energy is $E_c^{\text{soft}} = (1/2)(2G_c)^2$.

The pseudized augmentation charge $Q(\mathbf{r})$ and the full pseudo charge density $n(\mathbf{r})$ are calculated in the dense grid with interval $(1/2)h$, corresponding to the hard cutoff energy $E_c^{\text{hard}} = (1/2)(4G_c)^2$.

In the real space scheme, we use the real space grid with the interval h for both $\phi_i(\mathbf{r})$ and $\beta(\mathbf{r})$ and do not use the Fourier expansion with the cutoff energy E_c^{wf} . Though the cutoff energy corresponding to the real space grid interval h is not E_c^{wf} but E_c^{soft} , we refer, both in the dual FFT and the real space schemes, $h = \pi/(2G_c)$ to the real space grid interval and $E_c^{wf} = (1/2)(G_c)^2$ to the cutoff energy.

4.2.1 Cutoff energy for $Q(r)$

The augmentation charge $Q^L(r)$ and pseudized one $\tilde{Q}^L(r)$ with $r_{in} = 0.7 \times r_{cl}$ are shown in Fig. 3, together with their Fourier transformation $Q_L(G)$ and $\tilde{Q}_L(G)$. The result of $\tilde{Q}^{l_1 l_2: L}$ with $l_1 = l_2 = L = 0$ is obtained after setting $k_{\text{max}} = 13$ and $\tilde{d}_1 = 0$. The pseudization of augmentation charge changes the G^2 -dependence very drastically, and the pseudized augmentation charge does not contain components of $G > 10$ (a.u.). In other

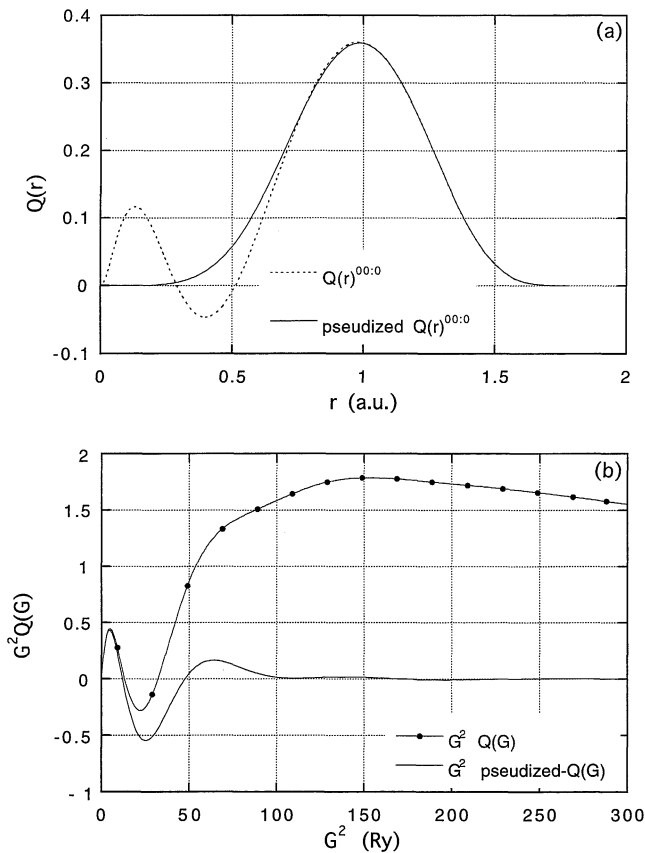


Fig. 3. Augmentation charge and pseudized one (with $r_{in} = 0.7 \times r_{cl}$) of carbon for orbital angular momentum $l = 0$ and $l = 1$ of Choice 1 (one reference energy). (a) Original $Q(r)^L$ and pseudized augmentation charge $\tilde{Q}^L(r)$ for $l_1 = l_2 = L = 0$; (b) Fourier transformed $G^2 Q^L(G)$ and $G^2 \tilde{Q}^L(G)$ for $l_1 = l_2 = L = 0$.

words, the hard cutoff energy E_c^{hard} can be reduced to 100 Ry, owing to the present optimization of augmentation charge.

4.2.2 Cutoff energy for $\beta(\mathbf{r})$

In Fig. 4, we show the inverse Fourier transformed $\beta(\mathbf{r})$ functions with changing the cutoff energy. The $\beta(\mathbf{r})$ function are not directly optimized and, therefore, the identical reproduction cannot be obtained even by a very high cutoff energy. Though it is difficult to point out what characteristics of the inverse Fourier transformed $\beta(\mathbf{r})$ functions are the most crucial, the positions of the peaks and bottoms are certainly very important. In Fig. 4, the cutoff energy 50 Ry can reproduce correct positions of a peak and bottom and, on the other hand, that of 30 Ry could not. Therefore, we can say that the cutoff energy for $\beta(\mathbf{r})$ should be higher than 50 Ry for a carbon atom.

In the dual FFT scheme, the $\beta(\mathbf{r})$ function is Fourier-transformed with the same cutoff energy for pseudo-wavefunctions E_c^{wf} . On the other hand, in the real space scheme, both $\phi(\mathbf{r})$ and $\beta(\mathbf{r})$ are expressed on the real space mesh with an interval $h = \pi/(2G_c)$ and the corresponding cutoff energy is $E_c^{\text{soft}} = 4E_c^{wf}$. This difference of the cutoff energies in two different schemes, the dual FFT and the real space schemes, can be often very serious. Actually, in the above example of a carbon atom, we should choose that $E_c^{wf} > 50\text{Ry}$ for the dual FFT scheme and $E_c^{\text{soft}} > 50\text{Ry}$ for the real space scheme.

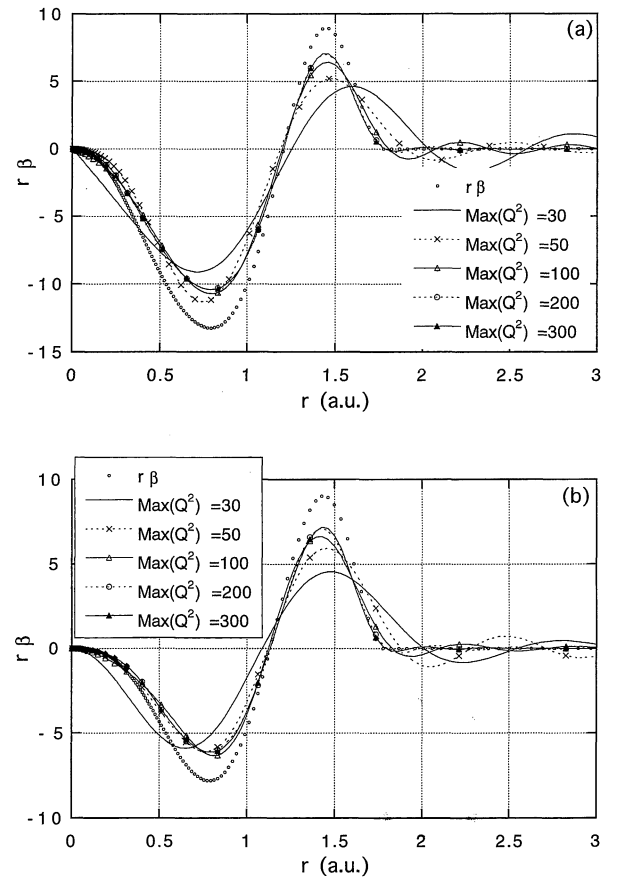


Fig. 4. Inverse Fourier transformation of $\beta(\mathbf{r})$ functions of carbon for orbital angular momentum (a) $l = 0$ and (b) $l = 1$ of Choice 1 (one reference energy) for several cutoff energies. The maximum values of Q^2 are given in the figure in atomic units, which are equal to values of the cutoff energies in Rydberg unit.

Table I. Cohesive energy of diamond per carbon atom for several cutoff energies E_c^{wf} calculated by the dual FFT and the real space schemes together with the conventional LDA (ref. 8).

	$h = 0.42 \text{ a.u.}$ $E_c^{wf} = 15(\text{Ry})$	$h = 0.21 \text{ a.u.}$ $E_c^{wf} = 55(\text{Ry})$
FFT	0.56eV	8.77eV
Real Space	8.48eV	8.65eV
conventional LDA	8.63eV	

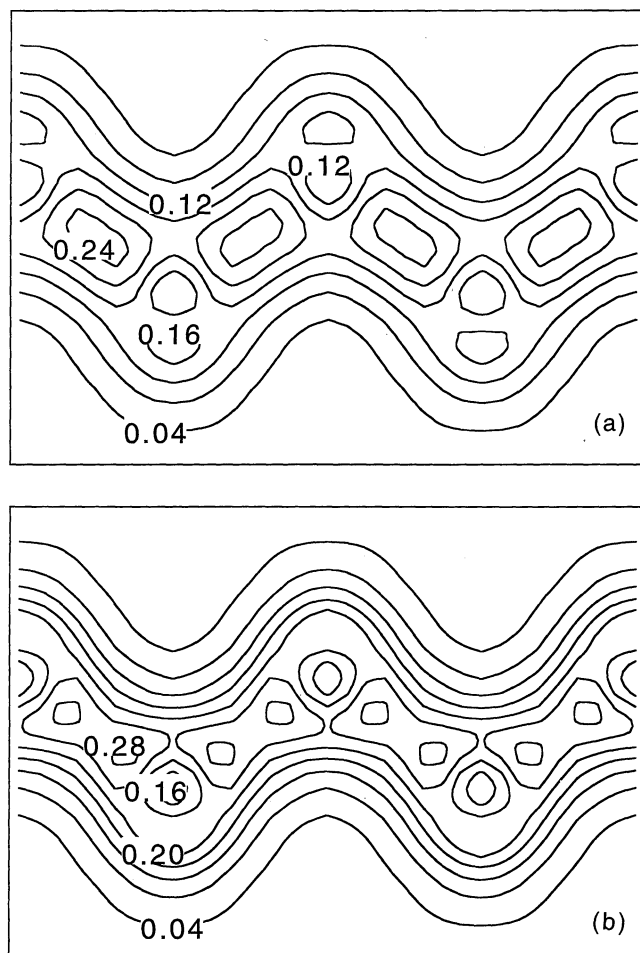


Fig. 5. Charge density of diamond of 8 atoms in a periodic cell on (110) plane with a mesh interval $h = 0.42 \text{ a.u.}$ and a single reference energy for each l orbit. Contours are plotted in every 0.04 a.u. (a) Charge density contributed only by pseudo-wavefunctions $2 \sum |\phi(\mathbf{r})|^2$; (b) Total charge density $n(\mathbf{r})$

4.3 Cohesive energy and charge density of diamond

We use a supercell model of 8 atoms in a unit cell with the periodic boundary condition. The calculated cohesive energy with cutoff energies $E_c^{wf} = 55\text{Ry}$ ($h = 0.21 \text{ a.u.}$) and $E_c^{wf} = 15\text{Ry}$ ($h = 0.42 \text{ a.u.}$) are summarized in Table I, both in the dual FFT and the real space schemes. The cohesive energies per atom can be calculated in the real space scheme as $\Delta E = 8.48 \text{ eV/atom}$ for $h = 0.42 \text{ a.u.}$ and $\Delta E = 8.65 \text{ eV/atom}$ for $h = 0.21 \text{ a.u.}$ These results should be compared with that of the standard LDA calculation $\Delta E = 8.63 \text{ eV/atom}$.⁸⁾

In the dual FFT scheme with $E_c^{wf} = 15\text{Ry}$ or $h = 0.42 \text{ a.u.}$ the cohesive energy is far worse than those by other calculations. As already mentioned, in the dual FFT scheme we should use a cutoff energy $E_c^{wf} > 50\text{Ry}$ to present the $\beta(\mathbf{r})$ and the cutoff energy $E_c^{wf} = 15\text{Ry}$ (or equivalently a mesh interval $2h = 0.84 \text{ a.u.}$) fails to reproduce the spatial behavior of the $\beta(\mathbf{r})$ functions. On the other hand, in the real space scheme, the soft grid mesh of the mesh interval $h = 0.42 \text{ a.u.}$ (or equivalently $E_c^{\text{soft}} = 60\text{Ry}$) can successfully reproduce the spatial behavior of the $\beta(\mathbf{r})$ functions. This is the reason why the dual FFT scheme with $h = 0.42 \text{ a.u.}$ gives a poor result of the cohesive energy, in contrast to a good result by the real space scheme with $h = 0.42 \text{ a.u.}$

Finally we demonstrate the charge density of diamond in Fig. 5, calculated by using a single reference energy and the real space scheme with the real space mesh of $h = 0.42 \text{ a.u.}$ It can be seen that characteristic two peaks of the charge density $n(\mathbf{r})$ appear between bonding carbon atoms,⁹⁾ and are mainly contributed by the augmentation charge.

§5. Summary

We discussed the parametrization of ultrasoft pseudopotentials and proposed the optimal choice of a large number of parameter values and function forms. A change of the $\beta(\mathbf{r})$ functions in accordance to the number of reference energies were demonstrated. The pseudization of augmentation charge was presented in detail and the cutoff energy for $\beta(\mathbf{r})$ was carefully analyzed. An ultrasoft pseudopotential of a carbon atom was exemplified. Spatial behavior of the non-local part was discussed with resultant cohesive energy, calculated by using several different cutoff energies in diamond.

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