

Chapter 1

Foundations of Methodology

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1.1 Real-Space Finite-Difference Method

Today, the performance of computers is highly advanced, and we have reached the conclusion that the use of first-principles calculation is the most appropriate for highly accurate analysis of problems at the atomic or electronic scale. For the current first-principles calculation, high-speed simulation with high accuracy is necessary. Although the conventional methods using basis set such as plane waves or atomic orbitals have achieved some success [see, for example, Car and Parrinello (1985), Szabo and Ostlund (1989), Payne *et al.* (1992), and Jensen (1999)], we should always pay attention to the fact that the boundary condition does not correspond to that of the actual experiments and to whether the basis function used satisfies the required calculation accuracy. On the other hand, with the real-space finite-difference method, since the wave function and potential on real-space grids are directly calculated instead of using basis functions, the above problems are avoided. Furthermore, because it has the following advantages compared with conventional methods, the real-space finite-difference method has recently become the focus of attention.

- (i) Since arbitrary boundary conditions are available, the method can treat a model that corresponds to the actual experiment. In addition, simulation in which an electric and/or magnetic field is applied is possible.
- (ii) In order to improve the calculation accuracy, the grid spacing should be narrowed, the procedure for which is simple and definite.
- (iii) Since most of the values of the Hamiltonian matrix elements are

- zero, one can easily create a calculation program.
- (iv) Since all of the calculations are carried out in ‘real space’, it is easy to incorporate a localized orbital, which is localized in a finite region, required for so-called order- N [$O(N)$] calculation, in which the amount of calculations is proportional to the model size. See, for example, Galli and Parrinello (1992), Aoki (1993), Li *et al.* (1993), Ordejón *et al.* (1993, 1995a, 1995b, 1996), Galli and Mauri (1994), Hierse and Stechel (1994), Nunes and Vanderbilt (1994), Stechel *et al.* (1994), Wang and Zunger (1994), Carlsson (1995), Faulkner *et al.* (1995), Hernández and Gillan (1995), Itoh *et al.* (1995, 1996), Wang *et al.* (1995), Hernández *et al.* (1996), Baer and Head-Gordon (1997), Millam and Scuseria (1997), Yang (1997), Bates *et al.* (1998), Stephan *et al.* (1998), York *et al.* (1998), Abdurixit (1999), Challacombe (1999), Roche (1999), Galli (2000), Hoshi and Fujiwara (2000, 2003), Ozaki *et al.* (2000), Ozaki (2001), Ozaki and Terakura (2001), and Sasaki *et al.* (2004).
 - (v) Since the method does not use fast Fourier transforms, parallel algorithms are easily achieved, enabling high-speed calculation using a massively parallel computer.
 - (vi) It is easy to develop the formalism used to solve the time-dependent Schrödinger equation. See, for example, Nomura *et al.* (1996, 1998, 1999), Sugino and Miyamoto (1999), Bertsch *et al.* (2000), and Watanabe and Tsukada (2000a, 2000b).

In the following sections, fundamental knowledge on the real-space finite-difference method is explained on the basis of the scheme of the density-functional theory. For a review, see Beck (2000). Atomic units $|e| = m = h/2\pi = 1$ are employed throughout this book (unless otherwise specified), where e , m and h are the electron charge, electron mass and Planck’s constant, respectively.

1.2 Density-Functional Theory and Kohn–Sham Equation

We briefly introduce the central equations of the density-functional theory for electronic structure calculations. The most difficult problem in any electronic structure calculation is posed by the need to take account of the effects of electron-electron interaction. Hohenberg and Kohn (1964) provided the underlying theorems showing that for the ground state of the many-electron system, the Thomas–Fermi model [Thomas (1927); Fermi (1927, 1928a, 1928b); March (1975)] can be viewed as an approximation to an exact theory, the density-functional theory. In the theory, the ground-state

energy of the system is the minimum value of the total-energy functional, and the density that yields this minimum value completely determines *all* properties of the system, such as all eigenfunctions and eigenvalues. Later, Kohn and Sham (1965) invented an ingenious approach to obtain the ground-state density by solving a set of accessible one-electron self-consistent eigenvalue equations. For more details on the density-functional theory, see von Barth (1984), Dreizler and da Providencia (1985), Jones and Gunnarsson (1989), Parr and Yang (1989), and Kryachko and Ludena (1990).

The Kohn–Sham total-energy functional is given as

$$\begin{aligned}
 E_{tot} = & 2 \sum_i^M n_i \int_{\Omega} \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r} \\
 & + 2 \sum_s \sum_i^M n_i \int_{\Omega} \psi_i^*(\mathbf{r}) v_{ion}^s(\mathbf{r} - \mathbf{R}^s) \psi_i(\mathbf{r}) d\mathbf{r} + \int_{\Omega} v_f(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \\
 & + \frac{1}{2} \int_{\Omega} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + \int_{\Omega} \varepsilon_{xc}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - \sum_s Z_s v_f(\mathbf{R}^s) + \gamma_E,
 \end{aligned} \tag{1.1}$$

where v_{ion}^s is the ionic pseudopotential describing the interaction between the s -th ion located at position \mathbf{R}^s and electron, v_f is the external-electric-field potential, ε_{xc} is the exchange-correlation potential, γ_E is the Coulomb energy associated with interactions among the nuclei (see Appendix A), Z_s is the valence of the s -th atom, M is the number of total wave functions, and $\rho(\mathbf{r})$ is the electron density distribution,

$$\rho(\mathbf{r}) = 2 \sum_i^M n_i \int_{\Omega} |\psi_i(\mathbf{r})|^2 d\mathbf{r}. \tag{1.2}$$

Here, $\int_{\Omega} f(\mathbf{r}) d\mathbf{r}$ represents the integration of a function $f(\mathbf{r})$ inside the calculation domain Ω . In addition, n_i is the occupation number of each wave function and includes a \mathbf{k} -point weight if there is more than one \mathbf{k} -point for the integration in the Brillouin zone. Although, for simplicity, we here assume that the contributions from up and down spin electrons are the same, the inclusion of the effect of spin polarization is straightforward.

It is necessary to determine the set of wave functions ψ_i that minimize the Kohn–Sham total-energy functional, which is given by the self-consistent solution of the Kohn–Sham equations,

$$\left[-\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \tag{1.3}$$

where

$$v_{eff}(\mathbf{r}) = \sum_s v_{ion}^s(\mathbf{r} - \mathbf{R}^s) + v_f(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}). \quad (1.4)$$

Here, the first, second, third, and fourth terms are the ionic pseudopotential, external-electric-field potential, Hartree potential, and exchange-correlation potential, respectively.

1.3 Finite-Difference Formulas

Differentiation of wave functions and electron density distribution is one of the frequently performed processes in first-principles molecular-dynamics simulations. In the conventional methods using basis functions, the derivative can be obtained by differentiating basis functions. However, the prime concept of the real-space finite-difference method does not include basis functions; thus, the k -th order derivative of a function $f(x)$ at a grid point $x = ih_x$ (i : integer) is approximated by the following finite-difference formulas [Chelikowsky *et al.* (1994a, 1994b, 1996); Jing *et al.* (1994)].

$$\left. \frac{d^{(k)}}{dx^{(k)}} f(x) \right|_{x=ih_x} \approx \sum_{n=-N_f}^{N_f} c_n^{(k)} f(ih_x + nh_x), \quad (1.5)$$

where N_f and h_x represent the parameters determining the order of the finite-difference approximation and the grid spacing, respectively. The larger the N_f , the more accurate the level of finite-difference approximation. Since a computational effort increases in proportion to N_f , a value of 1 – 4 is usually used. The weight in (1.5), $c_n^{(k)}$, is determined using the Taylor expansion. For example, when $N_f = 1$, i.e., in the case of the central finite difference, by expanding $f(ih_x - h_x)$ and $f(ih_x + h_x)$ around ih_x as,

$$f(ih_x - h_x) \approx f(ih_x) - \frac{f'(ih_x)}{1!} h_x + \frac{f''(ih_x)}{2!} h_x^2 + O(h_x^3), \quad (1.6)$$

$$f(ih_x + h_x) \approx f(ih_x) + \frac{f'(ih_x)}{1!} h_x + \frac{f''(ih_x)}{2!} h_x^2 + O(h_x^3), \quad (1.7)$$

and by subtracting (1.6) from (1.7), the first-order derivative

$$f'(ih_x) \approx \frac{-f(ih_x - h_x) + f(ih_x + h_x)}{2h_x}, \quad (1.8)$$

and by adding (1.6) to (1.7), the second-order derivative

$$f''(ih_x) \approx \frac{f(ih_x - h_x) - 2f(ih_x) + f(ih_x + h_x)}{h_x^2} \quad (1.9)$$

are obtained. Hence, from the above equations, in the case of $N_f = 1$, the coefficients for the first-order derivative are found to be $c_{-1}^{(1)} = -1/2h_x$, $c_0^{(1)} = 0$ and $c_1^{(1)} = 1/2h_x$. Those for the second-order derivative are $c_{-1}^{(2)} = c_1^{(2)} = 1/h_x^2$ and $c_0^{(2)} = -2/h_x^2$. Refer to Chelikowsky *et al.* (1994b) for the values of coefficients $c_n^{(k)}$ when $N_f > 1$. For simplicity, hereafter, the case for $N_f = 1$, i.e., the central finite difference, is presented.

1.4 Real-Space Representation of Kohn–Sham Equation

In the real-space finite-difference method, the values of wave functions and the electron density distribution are given only on discrete grid points in real space. Accordingly, the Kohn–Sham Hamiltonian [Kohn and Sham (1965)] acting on a wave function must be given in a form discretized in real space. In this section, the procedure for the discretization of the Kohn–Sham Hamiltonian, according to the finite-difference approximation discussed in the preceding section, is demonstrated. For an example, the case of a one-dimensional model is described.

First, we consider the discretization of the kinetic-energy operator, i.e., the expansion of the Laplacian. When the calculation domain is uniformly divided into N grids and a *nonperiodic* (an isolated) boundary condition is imposed, the kinetic-energy operator is written as

$$-\frac{1}{2}\nabla^2\psi \approx -\frac{1}{2} \begin{pmatrix} c_0 & c_1 & 0 & 0 & \cdots & 0 & 0 \\ c_1 & c_0 & c_1 & 0 & & & 0 \\ 0 & \ddots & \ddots & \ddots & \ddots & & \vdots \\ \vdots & \ddots & c_1 & c_0 & c_1 & \ddots & \vdots \\ \vdots & & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & & 0 & c_1 & c_0 & c_1 \\ 0 & 0 & \cdots & 0 & 0 & c_1 & c_0 \end{pmatrix} \begin{pmatrix} \psi(h_x) \\ \psi(2h_x) \\ \vdots \\ \psi(ih_x) \\ \vdots \\ \psi(Nh_x - h_x) \\ \psi(Nh_x) \end{pmatrix}. \quad (1.10)$$

Here and hereafter, $c_n = c_n^{(2)}$.

In the case of a *periodic* boundary condition,

$$-\frac{1}{2}\nabla^2\psi \approx -\frac{1}{2} \begin{pmatrix} c_0 & c_1 & 0 & 0 & \cdots & 0 & c_1 e^{-ik_x L_x} \\ c_1 & c_0 & c_1 & 0 & & & 0 \\ 0 & \ddots & \ddots & \ddots & \ddots & & \vdots \\ \vdots & \ddots & c_1 & c_0 & c_1 & \ddots & \vdots \\ \vdots & & \ddots & \ddots & \ddots & \ddots & 0 \\ 0 & & & 0 & c_1 & c_0 & c_1 \\ c_1 e^{ik_x L_x} & 0 & \cdots & 0 & 0 & c_1 & c_0 \end{pmatrix} \begin{pmatrix} \psi(h_x) \\ \psi(2h_x) \\ \vdots \\ \psi(ih_x) \\ \vdots \\ \psi(Nh_x - h_x) \\ \psi(Nh_x) \end{pmatrix}, \quad (1.11)$$

where k_x and L_x represent the Bloch wave number and the length of the calculation domain (supercell), respectively.

Next, we discuss the inner product of the potential term in the Kohn-Sham Hamiltonian and the wave function. The potential term consists of the following four terms: ionic pseudopotential v_{ion}^s , external electric field potential v_f , Hartree potential v_H , and exchange-correlation potential v_{xc} . The ionic pseudopotential is divided into local and nonlocal components when the norm-conserving pseudopotential given by Bachelet *et al.* [Hamann *et al.* (1979); Bachelet *et al.* (1982)], or Troullier and Martins (1991) is employed. The norm-conserving pseudopotentials are explained in Section 1.5. When the separable form given by Kleinman and Bylander (1982) is used as a nonlocal component, the inner product between the pseudopotential and wave function is given by

$$v_{ion}^s(ih_x - R_x^s)\psi(ih_x) = v_{loc}^s(ih_x - R_x^s)\psi(ih_x) + \sum_{lm} G_{lm}^s \hat{v}_l^s(ih_x - R_x^s)\psi_{lm}^{ps,s}(ih_x - R_x^s). \quad (1.12)$$

Here,

$$G_{lm}^s = \frac{\sum_{i=1}^N \psi_{lm}^{ps,s*}(ih_x - R_x^s)\hat{v}_l^s(ih_x - R_x^s)\psi(ih_x)h_x}{\langle \psi_{lm}^{ps,s} | \hat{v}_l^s | \psi_{lm}^{ps,s} \rangle}, \quad (1.13)$$

and R_x^s is the position of the nucleus. The first term and the second term on the right-hand side of (1.12) are called the local component and non-local component, respectively. Furthermore, l and m are orbital and azimuthal angular-momentum quantum numbers, respectively, and $\psi_{lm}^{ps,s}$ is the pseudo-wave function used to generate the pseudopotential.

The external electric-field potential which exerts on an electron located at position x is represented by the external electric field $E_f(x)$, i.e.,

$$v_f(x) = \int_{-\infty}^x E_f(x') dx'. \quad (1.14)$$

Eventually, the one-dimensional Kohn–Sham equation discretized in real space is given by

$$\begin{aligned} & -\frac{1}{2} \sum_{n=-N_f}^{N_f} c_n \psi(ih_x + nh_x) \\ & + (\sum_s v_{ion}^s(ih_x - R_x^s) + v_f(ih_x) + v_H(ih_x) + v_{xc}(ih_x)) \psi(ih_x) = \varepsilon \psi(ih_x). \end{aligned} \quad (1.15)$$

The above argument is straightforwardly extended to the case of the three-dimensional Kohn–Sham equation as

$$\begin{aligned} & -\frac{1}{2} \sum_{n=-N_f}^{N_f} [c_{x,n} \psi(ih_x + nh_x, jh_y, kh_z) + c_{y,n} \psi(ih_x, jh_y + nh_y, kh_z) \\ & + c_{z,n} \psi(ih_x, jh_y, kh_z + nh_z)] + v_{eff}(ih_x, jh_y, kh_z) \psi(ih_x, jh_y, kh_z) \\ & = \varepsilon \psi(ih_x, jh_y, kh_z), \end{aligned} \quad (1.16)$$

where

$$\begin{aligned} v_{eff}(ih_x, jh_y, kh_z) = & \sum_s v_{ion}^s(ih_x - R_x^s, jh_y - R_y^s, kh_z - R_z^s) \\ & + v_f(ih_x, jh_y, kh_z) + v_H(ih_x, jh_y, kh_z) \\ & + v_{xc}(ih_x, jh_y, kh_z). \end{aligned} \quad (1.17)$$

1.5 Norm-Conserving Pseudopotentials

The calculations including inner-shell electrons demand a significantly high cutoff energy, i.e., a small grid spacing is required; this prevents us from implementing practical simulations. In addition, in the algorithm used in first-principles calculations, the computational cost is proportional to the square of the number of electrons involved. Thus, it is disadvantageous to include a large number of electrons. Furthermore, in reality, the behavior of inner-shell electrons in molecules and crystals is similar to that of electrons in isolated atoms; valence electrons in atoms constituting a material

determine most of the properties of the material. On the basis of this observation, the pseudopotential method which treats valence electrons alone is commonly used in first-principles calculations [Phillips (1958); Cohen and Heine (1970); Joannopoulos *et al.* (1977); Redondo *et al.* (1977); Starkloff and Joannopoulos (1977); Zunger and Cohen (1979); Hamann *et al.* (1979); Kerker (1980); Bachelet *et al.* (1982); Yin and Cohen (1982); Hamann (1989); Shirley *et al.* (1989); Vanderbilt (1990); Troullier and Martins (1991); Wang and Zunger (1995); Goedecker *et al.* (1996); Wang and Stott (2003)].

The most frequently used pseudopotential in first-principles calculations is the norm-conserving pseudopotential technique developed by Bachelet *et al.* [Hamann *et al.* (1979); Bachelet *et al.* (1982)], as well as the improved version by Troullier and Martins (1991). The pseudo-wave function obtained using these pseudopotentials has the following characteristics (see Fig. 1.1).

- a. There are no nodes in the pseudo-wave function.
- b. The pseudo-wave function agrees with the all-electron wave function outside the inner-shell radius of r_c .
- c. The eigenvalue of the valence electron state using pseudopotentials is in accordance with the eigenvalue calculated including the inner-shell electrons.
- d. The norm $\int_0^{r_c} |u_l^{ps}(r)|^2 dr$ up to the inner-shell radius of r_c of the pseudo-wave function coincides with the norm of the all-electron wave function up to r_c . Here, $u_l(r)$ is equal to $r\varphi_l(r)$, which is obtained by multiplying the radial component $\varphi_l(r)$ of the wave function $\psi_{lm}(\mathbf{r}) = \varphi_l(r)Y_{lm}(\theta, \phi)$ by the distance from the nucleus r . Also, $Y_{lm}(\theta, \phi)$ is a spherical harmonic function.

The following is the outline of the preparation procedure for pseudopotentials.

1. Obtain the one-electron state by solving the Kohn–Sham equation under a spherically symmetric field which includes the inner-shell electrons. Then, the all-electron wave function of valence electrons $u_{lm}^{ae}(r)$ and the potential $V^{ae}(r)$ are obtained.
2. Produce the pseudo-wave function $u_l^{ps}(r)$ which satisfies the conditions **a.** – **d.** above for the valence electron having the angular momentum l .
3. Generate pseudopotential $V_l^{ps}(r)$ by eliminating the Hartree and exchange-correlation potentials of valence electrons from $V^{ae}(r)$.

As shown below, the constructed pseudopotential acts on each angular mo-

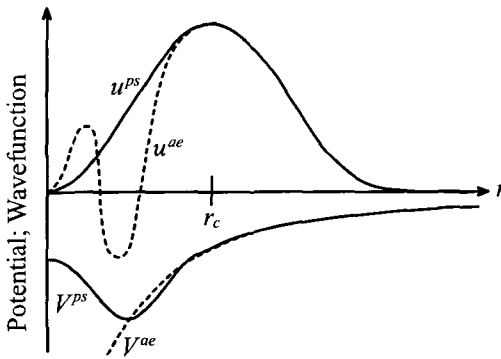


Fig. 1.1 Conceptual diagram of pseudopotential V^{ps} and pseudo-wave function u^{ps} . Here, V^{ae} is the potential obtained by the all-electron calculation; u^{ae} is the all-electron wave function.

mentum l as an operator.

$$V^{ps}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} |Y_{lm}(\theta, \phi)\rangle V_l^{ps}(r) \langle Y_{lm}(\theta, \phi)|. \quad (1.18)$$

Usually, l is cut off at about 2. Furthermore, assuming an appropriate component $v_{loc}(r)$ as a local component and assuming the difference between each component $V_l^{ps}(r)$ and $v_{loc}(r)$,

$$\hat{v}_l(r) = V_l^{ps}(r) - v_{loc}(r), \quad (1.19)$$

to be the nonlocal component, the following form can be used:

$$V^{ps}(\mathbf{r}) = v_{loc}(r) + \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} |Y_{lm}(\theta, \phi)\rangle \hat{v}_l(r) \langle Y_{lm}(\theta, \phi)|. \quad (1.20)$$

In particular, in the pseudopotential given by Bachelet *et al.* [Hamann *et al.* (1979); Bachelet *et al.* (1982)], the local component is given as

$$v_{loc}(r) = -Z \left(\frac{C_1 \operatorname{erf}(\sqrt{\alpha_1} |r|)}{|r|} + \frac{C_2 \operatorname{erf}(\sqrt{\alpha_2} |r|)}{|r|} \right). \quad (1.21)$$

Here, $Z (> 0)$ is the sum of charges of the valence electrons, and $\operatorname{erf}(x)$ is the error function (or probability integral) defined by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \quad (1.22)$$

The form of (1.20) is called the nonseparable form, whereas Kleinman and Bylander (1982) proposed a separable form,

$$V^{ps}(\mathbf{r}) = v_{loc}(\mathbf{r}) + \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{|\psi_{lm}^{ps}(\mathbf{r}, \theta, \phi) \hat{v}_l(\mathbf{r}) \langle \hat{v}_l(\mathbf{r}) \psi_{lm}^{ps}(\mathbf{r}, \theta, \phi) |}{\langle \psi_{lm}^{ps}(\mathbf{r}, \theta, \phi) | \hat{v}_l(\mathbf{r}) | \psi_{lm}^{ps}(\mathbf{r}, \theta, \phi) \rangle}. \quad (1.23)$$

The pseudopotential v_{ion} in (1.12) corresponds to this V^{ps} . It is not an overstatement to say that first-principles calculations have been realized owing to the development of the pseudopotential method. In recent years, softer pseudopotentials [Vanderbilt (1990)] in which the norm-conserving condition is eliminated have been used.

1.6 Hellmann–Feynman Forces Acting on Atoms

The implementation of first-principles molecular-dynamics simulations requires the Hellmann–Feynman forces acting on nuclei, which can be obtained by differentiating the total energy (1.1) with respect to the positions of the nuclei \mathbf{R}^s . Among the components in the total energy, the ionic pseudopotential energy, external electric-field potential energy of nuclei, and Coulomb energy γ_E are functions of the position of the nucleus.

First, the ionic pseudopotential energy E_{ne} is divided into two terms:

$$E_{ne} = E_{loc} + E_{nontocal}, \quad (1.24)$$

and the first term due to the local components per supercell is represented by

$$E_{loc} = 2 \sum_s \sum_i^M n_i \int_{\Omega} \psi_i^*(\mathbf{r}) v_{loc}^s(\mathbf{r} - \mathbf{R}^s) \psi_i(\mathbf{r}) d\mathbf{r}. \quad (1.25)$$

Then, by changing the variable as $\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} - \mathbf{R}^s$ and differentiating E_{loc} with respect to the position of the s -th nucleus \mathbf{R}^s , we have

$$\begin{aligned} -\frac{\partial E_{loc}}{\partial \mathbf{R}^s} &= -2 \sum_i^M n_i \frac{\partial}{\partial \mathbf{R}^s} \int_{\Omega} \psi_i^*(\mathbf{r}' + \mathbf{R}^s) v_{loc}^s(\mathbf{r}') \psi_i(\mathbf{r}' + \mathbf{R}^s) d\mathbf{r}' \\ &= -2 \sum_i^M n_i \left(\int_{\Omega} \frac{\partial \psi_i^*(\mathbf{r}' + \mathbf{R}^s)}{\partial \mathbf{R}^s} v_{loc}^s(\mathbf{r}') \psi_i(\mathbf{r}' + \mathbf{R}^s) d\mathbf{r}' \right. \\ &\quad \left. + \int_{\Omega} \psi_i^*(\mathbf{r}' + \mathbf{R}^s) v_{loc}^s(\mathbf{r}') \frac{\partial \psi_i(\mathbf{r}' + \mathbf{R}^s)}{\partial \mathbf{R}^s} d\mathbf{r}' \right). \end{aligned} \quad (1.26)$$

Thus, with the reversion of the variable \mathbf{r}' to the original form $\mathbf{r} = \mathbf{r}' + \mathbf{R}^s$, (1.26) leads to

$$\begin{aligned} -\frac{\partial E_{loc}}{\partial \mathbf{R}^s} &= -2 \sum_i^M n_i \left(\int_{\Omega} \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mathbf{r}} v_{loc}^s(\mathbf{r} - \mathbf{R}^s) \psi_i(\mathbf{r}) d\mathbf{r} \right. \\ &\quad \left. + \int_{\Omega} \psi_i^*(\mathbf{r}') v_{loc}^s(\mathbf{r} - \mathbf{R}^s) \frac{\partial \psi_i(\mathbf{r})}{\partial \mathbf{r}} d\mathbf{r} \right) \\ &= -4 \sum_i^M n_i \operatorname{Re} \int_{\Omega} \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mathbf{r}} v_{loc}^s(\mathbf{r} - \mathbf{R}^s) \psi_i(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (1.27)$$

Next, using the separable form proposed by Kleinman and Bylander (1982), the second term due to the nonlocal components is given by

$$E_{nonloc} = 2 \sum_s^M \sum_i^M n_i \sum_{lm} \frac{W_{lm}^{s*}(\mathbf{R}^s) W_{lm}^s(\mathbf{R}^s)}{\langle \psi_{lm}^{ps,s} | \hat{v}_l^s | \psi_{lm}^{ps,s} \rangle}, \quad (1.28)$$

where

$$W_{lm}^s(\mathbf{R}^s) = \int_{\Omega} \hat{v}_l^s(\mathbf{r} - \mathbf{R}^s) \psi_{lm}^{ps,s*}(\mathbf{r} - \mathbf{R}^s) \psi_i(\mathbf{r}) d\mathbf{r}, \quad (1.29)$$

for which, along the same line as the derivation of (1.27), we obtain

$$\begin{aligned} -\frac{\partial E_{nonloc}}{\partial \mathbf{R}^s} &= -2 \sum_i^M n_i \sum_{lm} \frac{\partial}{\partial \mathbf{R}^s} \frac{W_{lm}^{s*}(\mathbf{R}^s) W_{lm}^s(\mathbf{R}^s)}{\langle \psi_{lm}^{ps,s} | \hat{v}_l^s | \psi_{lm}^{ps,s} \rangle} \\ &= -4 \sum_i^M n_i \sum_{lm} \frac{1}{\langle \psi_{lm}^{ps,s} | \hat{v}_l^s | \psi_{lm}^{ps,s} \rangle} \\ &\quad \times \operatorname{Re} \int_{\Omega} \hat{v}_l^s(\mathbf{r} - \mathbf{R}^s) \psi_{lm}^{ps,s}(\mathbf{r} - \mathbf{R}^s) \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mathbf{r}} d\mathbf{r} W_{lm}^s(\mathbf{R}^s), \end{aligned} \quad (1.30)$$

where $\hat{v}_l^s(\mathbf{r})$ vanishes on the outside of the inner shell radius r_c of the pseudopotential, and the integration is performed only inside the inner shell radius.

In the real-space finite-difference formalism, the integrations are approximated by the summations on discrete grid points. An efficient technique for these summations is described in Chapter 4.

In addition, the derivative of the external electric field \mathbf{E}_f of the nucleus

is given by

$$-\frac{\partial[-Z_s v_f(\mathbf{R}^s)]}{\partial \mathbf{R}^s} = Z_s \mathbf{E}_f(\mathbf{R}^s). \quad (1.31)$$

Finally, although the derivative of the Coulomb energy among the nuclei is given by $-\partial\gamma_E/\partial\mathbf{R}^s$, the form of γ_E differs depending on the boundary conditions; the differentiation formulas are discussed in Appendix A.