

# Stress formulation in OpenMX

Yoshinori Shiihara\* and Taisuke Ozaki

January 7, 2017

## 1 References

In this formulation, we referred to the following documents:

- [1] OpenMX web site, Technical notes, "Total energy and forces"  
[http://www.openmx-square.org/tech\\_notes/tech1-1\\_2.pdf](http://www.openmx-square.org/tech_notes/tech1-1_2.pdf)
- [2] Stress formulation on LCAO-based DFT by P. J. Feibelman  
P. J. Feibelman, PRB 44, 3916 (1991).
- [3] Stress formulation in SIESTA code  
J. M. Soler, et al., J. Phys.: Condens. Matter, 14, 2745 (2002).
- [4] Stress formulation in plane-wave-based PAW-DFT by M. Kohyama (in Japanese, not published)
- [5] GGA stress formulation in LCAO method by J. M. Solar, et al.  
L. C. Balbas, J. L. Martins, J. M. Soler, PRB 64, 165110 (2001).

## 2 Total energy, wave function, and electron density matrix in LCAO formulation

Denisty functional total energy  $E_{\text{tot}}$  considered in this document is

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{na}} + E_{\text{ec}}^{(\text{NL})} + E_{\delta\text{ee}} + E_{\text{XC}} + E_{\text{SCC}}, \quad (1)$$

that is given as the sum of the kinetic energy  $E_{\text{kin}}$ , the electrostatic energy,  $E_{\text{na}}$ ,  $E_{\delta\text{ee}}$ ,  $E_{\text{SCC}}$ , the exchange-correlation energy  $E_{\text{XC}}$ , and the nonlocal pseudopotential energy  $E_{\text{ec}}^{(\text{NL})}$ . The detail of each energy component will be described in Section 4. The OpenMX is based on the the norm-conserving pseudopotential formulation and its valence and semi-core wave functions are expressed by the Linear Combination of Atomic Orbitals (LCAO) with the expansion coefficients  $c$ :

$$\psi_{\sigma\mu}^{(\mathbf{k})}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n \exp(i\mathbf{R}_n \cdot \mathbf{k}) \sum_{i\alpha} c_{\sigma\mu,i\alpha}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n), \quad (2)$$

where  $\mathbf{R}_n$  is the Bravais lattice vector, and  $\phi$  is a pseudo atomic orbital as the basis function. The indexes  $i$ ,  $\sigma$ ,  $\alpha$  are for site, spin, and atomic orbital, respectively. Then the electron density  $n$  for spin  $\sigma$  is

$$n_{\sigma}(\mathbf{r}) = \sum_n \sum_{i\alpha,j\beta} \rho_{\sigma,i\alpha,j\beta}^{(\mathbf{R}_n)} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n), \quad (3)$$

where the density matrix  $\rho_{\sigma,i\alpha,j\beta}^{(\mathbf{R}_n)}$  is defined as

$$\rho_{\sigma,i\alpha,j\beta}^{(\mathbf{R}_n)} = \frac{1}{V_{\text{B}}} \int_{\text{B}} d\mathbf{k} \sum_{\mu}^{\text{occ}} \exp(i\mathbf{R}_n \cdot \mathbf{k}) c_{\sigma\mu,i\alpha}^* c_{\sigma\mu,j\beta}. \quad (4)$$

The integration is performed over the 1st Brillouin zone whose volume is  $V_{\text{B}}$ . The summation is taken over the occupied states.

---

\*Toyota Technological Institute, 2-12-1 Hisakata, Tenpaku-ku, Nagoya, 468-8511, Japan, email: shiihara@toyota-ti.ac.jp

### 3 Basics for stress formulation

In the stress formulation of the LCAO scheme, the basis function under strain does not change its shape\* but its center moves according to the strain tensor  $\varepsilon$  acting on the supercell:

$$\phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rightarrow \phi_{i\alpha}(\mathbf{r} - (\mathbf{I} + \varepsilon)(\mathbf{t}_i - \mathbf{R}_n)), \quad (5)$$

where  $\mathbf{I}$  is the identical matrix and the cell strain matrix is

$$\varepsilon = \begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{yz} & \varepsilon_{zz} \end{bmatrix}. \quad (6)$$

The cell matrix is supposed to be symmetric. Under the cell strain, an arbitrary position vector in the cell moves as follows:

$$\mathbf{r} \rightarrow (\mathbf{I} + \varepsilon) \cdot \mathbf{r}. \quad (7)$$

An arbitrary position vector in the reciprocal space also moves like

$$\mathbf{k} \rightarrow (\mathbf{I} + \varepsilon)^{-1} \cdot \mathbf{k}. \quad (8)$$

Equations (7) and (8) show that the exponential terms in Eqs (2) and (4) are invariant under strain. Equation (7) also shows that the cell integration under strain is given as

$$\int_{\Omega} \mathbf{dr} \rightarrow \det(\mathbf{I} + \varepsilon) \int_{\Omega} \mathbf{dr} \quad (9)$$

The atomic-scale stress tensor acting on a supercell is defined as the first-order expansion coefficient of the total energy  $E_{\text{tot}}(\varepsilon)$  about a point  $\varepsilon = 0$ :

$$E_{\text{tot}}^{\varepsilon} = E_{\text{tot}} + \sum_{\gamma\eta} A_{\gamma\eta} \varepsilon_{\gamma\eta} + \text{higher order}, \quad (10)$$

and

$$\sigma_{\gamma\eta} = \lim_{\varepsilon \rightarrow 0} \frac{\partial E_{\text{tot}}^{\varepsilon}}{\partial \varepsilon_{\gamma\eta}} = A_{\gamma\eta}. \quad (11)$$

Hereafter an operation like Eq. (11) will be expressed by  $\partial f / \partial \varepsilon_{\gamma\eta}$  ( $f$  is an arbitrary function or functional) and we will call it the strain derivative of  $f$ . According to Eq. (11), it is easily seen that the strain derivative satisfies the product rule:

$$(fg)^{\varepsilon} = \left( f + \sum_{\gamma\eta} F_{\gamma\eta} \varepsilon_{\gamma\eta} + \dots \right) \left( g + \sum_{\gamma\eta} G_{\gamma\eta} \varepsilon_{\gamma\eta} + \dots \right) \quad (12)$$

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} fg = f G_{\gamma\eta} + g F_{\gamma\eta} = f \frac{\partial g}{\partial \varepsilon_{\gamma\eta}} + g \frac{\partial f}{\partial \varepsilon_{\gamma\eta}} \quad (13)$$

In addition, Eq. (7) shows that an arbitrary real-space vector under strain satisfies

$$\frac{\partial l_{\nu}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\nu\eta} l_{\gamma}. \quad (14)$$

This relationship is often utilized to transform the strain derivative to the deviation with respect to the atomic coordinate, corresponding to a force acting on each atom:

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial t^{\eta}}{\partial \varepsilon_{\gamma\eta}} \frac{\partial}{\partial t^{\eta}} = t^{\gamma} \frac{\partial}{\partial t^{\eta}} \quad (15)$$

In the following section, we will derive the strain derivatives for energy components in Eq. (1) using the operation in Eq. (11).

---

\*This is not the case for plane-wave methods.

## 4 Strain derivative of each energy components

### 4.1 Kinetic energy component

The kinetic energy term is

$$E_{\text{kin}} = \sum_{\sigma} \sum_n^N \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right\rangle. \quad (16)$$

Then the strain derivative of the kinetic term is derived as

$$\begin{aligned} \frac{\partial E_{\text{kin}}}{\partial \varepsilon_{\gamma\eta}} &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left( \sum_{\sigma} \sum_n^N \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right\rangle \right) \\ &= \sum_{\sigma} \sum_n^N \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right\rangle \\ &\quad + \sum_{\sigma} \sum_n^N \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right\rangle. \end{aligned} \quad (17)$$

The above expression involves the strain derivative of the electron density matrix. In the following subsections, similar terms to this will be seen in the strain derivative for each energy component. They will be treated at the end of this section and summed up to a term called overlap stress. About the terms in the third line, using the following coordinate transformation  $\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n \rightarrow \mathbf{r}$ , we have

$$\begin{aligned} &\left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right\rangle \\ &\rightarrow \left\langle \phi_{i\alpha}(\mathbf{r}) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} + \mathbf{t}_i - \mathbf{t}_j - \mathbf{R}_n) \right\rangle \\ &= \left\langle \phi_{i\alpha}(\mathbf{r}) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji, n}) \right\rangle, \end{aligned} \quad (18)$$

where only  $\mathbf{t}_{ji, n}$  is affected by the cell strain:

$$\mathbf{t}_{ji, n} \rightarrow (\mathbf{I} + \boldsymbol{\varepsilon}) \cdot \mathbf{t}_{ji, n}. \quad (19)$$

Using the chain rule shown in Eq. (15), we can transform the strain derivative to the derivative with respect to the atomic position:

$$\begin{aligned} &\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \phi_{i\alpha}(\mathbf{r}) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji, n}) \right\rangle \\ &= \left( \frac{\partial}{\partial t_{ji, n}^{\gamma}} \left\langle \phi_{i\alpha}(\mathbf{r}) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji, n}) \right\rangle \right) t_{ji, n}^{\eta}. \end{aligned} \quad (20)$$

After the coordinate transformation,

$$\begin{aligned} &\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \phi_{i\alpha}(\mathbf{r}) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji, n}) \right\rangle \\ &= \left( \frac{\partial}{\partial t_{ji, n}^{\gamma}} \left\langle \phi_{i\alpha}(\mathbf{r}) \left| \hat{T} \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \right\rangle \right) t_{ji, n}^{\eta}. \end{aligned} \quad (21)$$

Inserting Eq. (21) to Eq. (17), we can obtain the strain derivative of the kinetic energy term.

## 4.2 Energy component for $E_{\text{na}}$

$E_{\text{na}}$  is a part of the electrostatic energy:

$$\begin{aligned} E_{\text{na}} &= \int_{\Omega} n(\mathbf{r}) \sum_I V_{\text{na},I}(\mathbf{r} - \mathbf{t}_I) d\mathbf{r} \\ &= \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \sum_I \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I) | V_{\text{na},I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle, \end{aligned} \quad (22)$$

where the potential  $V_{\text{na},I}$  is the sum of the local pseudopotential  $V_{\text{core},I}$  of atom  $I$  and the potential  $V_I^{(a)}(\mathbf{r} - \mathbf{t}_I)$  coming from the atomic electron density  $\rho_I^{(a)}(\mathbf{r} - \mathbf{t}_I)$ . Its strain derivative is

$$\begin{aligned} \frac{\partial E_{\text{na}}}{\partial \varepsilon_{\gamma\eta}} &= \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \sum_I \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I) | V_{\text{na},I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\ &+ \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_I \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I) | V_{\text{na},I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle. \end{aligned} \quad (23)$$

As already explained, the term including the strain derivative of the electron density matrix is included in the overlap stress. The second term in the right hand side of Eq. (23) can be expanded using a projector expansion:

$$\begin{aligned} &\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_I \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I) | V_{\text{na},I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\ &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_I \sum_{lm} \sum_{\zeta}^{L_{\text{max}} N_{\text{rad}}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I) | V_{\text{na},I} \bar{R}_{l\zeta} Y_{lm} \rangle \frac{1}{c_{l\zeta}} \langle V_{\text{na},I} \bar{R}_{l\zeta} Y_{lm} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle. \end{aligned} \quad (24)$$

Contracting the indexes  $(lm\zeta)$  to a single index  $\lambda$  and using  $\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I - \mathbf{R}_n) | V_{\text{na},I} \bar{R}_{l\zeta} Y_{lm} \rangle = S_{i\alpha n, I\lambda}$ , we have

$$\begin{aligned} &\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_I \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_I) | V_{\text{na},I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\ &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_{I\lambda} S_{i\alpha 0, I\lambda} \frac{1}{c_{l\zeta}} S_{j\beta n, I\lambda} \\ &= \sum_{I\lambda} \frac{1}{c_{l\zeta}} \left( \frac{\partial S_{i\alpha 0, I\lambda}}{\partial \varepsilon_{\gamma\eta}} S_{j\beta n, I\lambda} + S_{i\alpha 0, I\lambda} \frac{\partial S_{j\beta n, I\lambda}}{\partial \varepsilon_{\gamma\eta}} \right) \\ &= \sum_{I\lambda} \frac{1}{c_{l\zeta}} \left( \frac{\partial S_{i\alpha 0, I\lambda}}{\partial \tau_{iI}^{\gamma}} \tau_{iI}^{\eta} S_{j\beta n, I\lambda} + S_{i\alpha 0, I\lambda} \frac{\partial S_{j\beta n, I\lambda}}{\partial \tau_{jI, n}^{\gamma}} \tau_{jI, n}^{\eta} \right) \end{aligned} \quad (25)$$

In Eq. (25), we employed the chain rule as in Eq. (20). After some modification,

$$\begin{aligned} &\sum_{I\lambda} \frac{1}{c_{l\zeta}} \left( \frac{\partial S_{i\alpha 0, I\lambda}}{\partial \tau_{iI}^{\gamma}} \tau_{iI}^{\eta} S_{j\beta n, I\lambda} + S_{i\alpha 0, I\lambda} \frac{\partial S_{j\beta n, I\lambda}}{\partial \tau_{jI, n}^{\gamma}} \tau_{jI, n}^{\eta} \right) \\ &= \sum_{I\lambda} \frac{1}{c_{l\zeta}} \left( \frac{\partial S_{i\alpha 0, I\lambda}}{\partial \tau_i^{\gamma}} \tau_{iI}^{\eta} S_{j\beta n, I\lambda} + S_{i\alpha 0, I\lambda} \frac{\partial S_{j\beta n, I\lambda}}{\partial \tau_{j, n}^{\gamma}} \tau_{jI, n}^{\eta} \right). \end{aligned} \quad (26)$$

Inserting Eq. (26) to Eq. (23), we can obtain the strain derivative of  $E_{\text{na}}$ .

### 4.3 Non-local pseudopotential energy component

The nonlocal pseudopotential energy based on the norm-conserving pseudopotential technique is

$$E_{\text{ec}}^{(\text{NL})} = \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \sum_I \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{V}_{\text{NL}, I}(\mathbf{r} - \mathbf{t}_I) \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \right\rangle. \quad (27)$$

The strain derivative of this energy component can be obtained in a similar procedure taken in that of  $E_{\text{na}}$ :

$$\begin{aligned} \frac{\partial E_{\text{ec}}^{(\text{NL})}}{\partial \varepsilon_{\gamma\eta}} &= \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \sum_I \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{V}_{\text{NL}, I}(\mathbf{r} - \mathbf{t}_I) \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \right\rangle \\ &+ \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_I \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{V}_{\text{NL}, I}(\mathbf{r} - \mathbf{t}_I) \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \right\rangle \end{aligned} \quad (28)$$

The Kleinman-Bylander separated form is used to express the second term in the righthand side:

$$\begin{aligned} &\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_I \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left| \hat{V}_{\text{NL}, I}(\mathbf{r} - \mathbf{t}_I) \right| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \right\rangle \\ &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_{I\ell} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \varphi_{I\ell} \rangle v_{\text{KB}, I\ell} \langle \varphi_{I\ell} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \rangle \end{aligned} \quad (29)$$

Since this expression has a similar form to Eq. (24), its strain derivative can be obtained as done in Subsection 4.2. Using  $\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) | \varphi_{I\ell} \rangle = S_{i\alpha, I\ell}$ , we have

$$\begin{aligned} &\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_{I\ell} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \varphi_{I\ell} \rangle v_{\text{KB}, I\ell} \langle \varphi_{I\ell} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \rangle \\ &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_{I\ell} v_{\text{KB}, I\ell} S_{i\alpha 0, I\ell} S_{j\beta n, I\ell} \\ &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_{I\ell} v_{\text{KB}, I\ell} \left( \frac{\partial S_{i\alpha 0, I\ell}}{\partial \varepsilon_{\gamma\eta}} S_{j\beta n, I\ell} + S_{i\alpha 0, I\ell} \frac{\partial S_{j\beta n, I\ell}}{\partial \varepsilon_{\gamma\eta}} \right) \\ &= \sum_{I\ell} v_{\text{KB}, I\ell} \left( \frac{\partial S_{i\alpha 0, I\ell}}{\partial t_{iI}^{\gamma}} t_{iI}^{\eta} S_{j\beta n, I\ell} + S_{i\alpha 0, I\ell} \frac{\partial S_{j\beta n, I\ell}}{\partial t_{jI, n}^{\gamma}} t_{jI, n}^{\eta} \right). \end{aligned} \quad (30)$$

Some simple modification on the derivative with respect to the atomic coordinate leads to

$$\begin{aligned} &\sum_{I\ell} v_{\text{KB}, I\ell} \left( \frac{\partial S_{i\alpha 0, I\ell}}{\partial t_{iI}^{\gamma}} t_{iI}^{\eta} S_{j\beta n, I\ell} + S_{i\alpha 0, I\ell} \frac{\partial S_{j\beta n, I\ell}}{\partial t_{jI, n}^{\gamma}} t_{jI, n}^{\eta} \right) \\ &= \sum_{I\ell} v_{\text{KB}, I\ell} \left( \frac{\partial S_{i\alpha 0, I\ell}}{\partial t_i^{\gamma}} t_{iI}^{\eta} S_{j\beta n, I\ell} + S_{i\alpha 0, I\ell} \frac{\partial S_{j\beta n, I\ell}}{\partial t_{j, n}^{\gamma}} t_{jI, n}^{\eta} \right). \end{aligned} \quad (31)$$

Inserting Eq. (31) to Eq. (28), we can obtain the strain derivative of  $E_{\text{ec}}^{(\text{NL})}$ .

### 4.4 Electrostatic energy component

The electron-electron Coulomb energy is

$$E_{\delta\text{ee}} = \frac{1}{2} \int_{\Omega} \delta n(\mathbf{r}) \delta V_{\text{H}} d\mathbf{r}. \quad (32)$$

This energy component represents the electrostatic interaction between difference charge  $\delta n$  given by

$$\delta n(\mathbf{r}) = n(\mathbf{r}) - \sum_I n_I^{(a)}(\mathbf{r} - \mathbf{t}_I), \quad (33)$$

where  $n_I^{(a)}$  is an atomic charge density evaluated by a confinement atomic calculations associated with the site  $i$ .  $\delta V_H$  is the electrostatic potential coming from  $\delta n$ . Considering Eq. (13), we have the following strain derivative of this electrostatic energy:

$$\frac{\partial E_{\delta ee}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta} \int_{\Omega} \delta n(\mathbf{r}) \delta V_H d\mathbf{r} + \frac{1}{2} \int_{\Omega} \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_H d\mathbf{r} + \frac{1}{2} \int_{\Omega} \delta n(\mathbf{r}) \frac{\partial \delta V_H}{\partial \varepsilon_{\gamma\eta}} d\mathbf{r} \quad (34)$$

Note that the first term of the right-hand side is a strain derivative of the volume term shown in Eq. (9). Here, we expand the second term:

$$\begin{aligned} \frac{1}{2} \int_{\Omega} \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_H d\mathbf{r} &= \frac{1}{2} \int_{\Omega} \delta V_H \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left( n(\mathbf{r}) - \sum_I n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) \right) d\mathbf{r} \\ &= \frac{1}{2} \int_{\Omega} \delta V_H \left( \frac{\partial n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} - \sum_I \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) \right) d\mathbf{r} \\ &= \frac{1}{2} \int_{\Omega} \delta V_H \left( \frac{\partial n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} - \sum_I \nabla_{\gamma} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) (r^{\eta} - t_I^{\eta}) \right) d\mathbf{r}, \end{aligned} \quad (35)$$

where we used the following equation,

$$\partial n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) / \partial \varepsilon_{\gamma\eta} = \nabla_{\gamma} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) (r^{\eta} - t_I^{\eta}). \quad (36)$$

In Eq. (35), we need the strain derivative of the electron density:

$$\begin{aligned} \frac{\partial n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \sum_{\sigma} \sum_n \sum_{\alpha, \beta} \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \\ &= \sum_{\sigma} \sum_n \sum_{\alpha, \beta} \left( \frac{\partial \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right. \\ &\quad \left. + \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i)}{\partial \varepsilon_{\gamma\eta}} \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right. \\ &\quad \left. + \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \frac{\partial \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n)}{\partial \varepsilon_{\gamma\eta}} \right) \end{aligned} \quad (37)$$

The strain derivatives of the PAO are

$$\frac{\partial \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i)}{\partial \varepsilon_{\gamma\eta}} = \nabla_{\gamma} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) (r^{\eta} - t_i^{\eta}), \quad (38)$$

and

$$\frac{\partial \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n)}{\partial \varepsilon_{\gamma\eta}} = \nabla_{\gamma} \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) (r^{\eta} - t_j^{\eta} - R_n^{\eta}). \quad (39)$$

Substituting Eqs. (38) and (39) for Eq. (37), we have

$$\begin{aligned} \frac{\partial n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} &= \sum_{\sigma} \sum_n \sum_{\alpha, \beta} \left( \frac{\partial \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right. \\ &\quad \left. + \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)} \nabla_{\gamma} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) (r^{\eta} - t_i^{\eta}) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right. \\ &\quad \left. + \rho_{\sigma, \alpha, j\beta}^{(\mathbf{R}_n)} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \nabla_{\gamma} \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) (r^{\eta} - t_j^{\eta} - R_n^{\eta}) \right). \end{aligned} \quad (40)$$

Furthermore, substituting Eq. (40) for Eq. (35), the second term in the right-hand side of Eq. (34) turns to be

$$\begin{aligned}
\frac{1}{2} \int_{\Omega} \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_{\text{H}} d\mathbf{r} &= \frac{1}{2} \int_{\Omega} \delta V_{\text{H}} \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \left[ \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \right. \\
&+ \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \{ \nabla_{\gamma} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) (r^{\eta} - t_i^{\eta}) \} \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) \\
&+ \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \left. \left\{ \nabla_{\gamma} \phi_{j\beta}(\mathbf{r} - \mathbf{t}_j - \mathbf{R}_n) (r^{\eta} - t_j^{\eta} - R_n^{\eta}) \right\} \right] d\mathbf{r} \\
&- \frac{1}{2} \int_{\Omega} \delta V_{\text{H}} \left\{ \sum_I \nabla_{\gamma} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) (r^{\eta} - t_I^{\eta}) \right\} d\mathbf{r}.
\end{aligned} \tag{41}$$

We finally consider the third term in the right-hand side Eq. (34), which includes the strain derivative of the Hartree potential. To calculate this term, we employ the Fourier expansion of the Hartree potential:

$$\begin{aligned}
\frac{\partial \delta V_{\text{H}}(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} &= \sum_{\mathbf{G}} \left\{ \frac{4\pi}{|\mathbf{G}|^2} \frac{\partial \delta n(\mathbf{G})}{\partial \varepsilon_{\gamma\eta}} \exp(i\mathbf{G} \cdot \mathbf{r}) + 4\pi \delta n(\mathbf{G}) \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \frac{1}{|\mathbf{G}|^2} \exp(i\mathbf{G} \cdot \mathbf{r}) \right\} \\
&= \int_{\Omega} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \delta n(\mathbf{r}')}{\partial \varepsilon_{\gamma\eta}} d\mathbf{r}' + 8\pi \sum_{\mathbf{G}} \delta n(\mathbf{G}) \frac{G_{\gamma} G_{\eta}}{|\mathbf{G}|^2} \exp(i\mathbf{G} \cdot \mathbf{r}).
\end{aligned} \tag{42}$$

As already mentioned, the exponential term is invariant under strain. To obtain Eq. (42), we used the following expression

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left( \frac{1}{|\mathbf{G}|^2} \right) = \frac{2G_{\gamma} G_{\eta}}{|\mathbf{G}|^4}. \tag{43}$$

Then, the strain derivative of the electrostatic energy is obtained as follows:

$$\begin{aligned}
\frac{\partial E_{\delta\text{ee}}}{\partial \varepsilon_{\gamma\eta}} &= \delta_{\gamma\eta} \int_{\Omega} \delta n(\mathbf{r}) \delta V_{\text{H}} d\mathbf{r} + \frac{1}{2} \int_{\Omega} \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_{\text{H}} d\mathbf{r} \\
&+ \frac{1}{2} \left\{ \int_{\Omega} \delta n(\mathbf{r}) \int_{\Omega} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \delta n(\mathbf{r}')}{\partial \varepsilon_{\gamma\eta}} d\mathbf{r}' + 8\pi \sum_{\mathbf{G}} \delta n(\mathbf{G}) \frac{G_{\gamma} G_{\eta}}{|\mathbf{G}|^2} \exp(i\mathbf{G} \cdot \mathbf{r}) d\mathbf{r} \right\} \\
&= \delta_{\gamma\eta} \int_{\Omega} \delta n(\mathbf{r}) \delta V_{\text{H}} d\mathbf{r} + \int_{\Omega} \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_{\text{H}} d\mathbf{r} \\
&+ 4\pi \int_{\Omega} \delta n(\mathbf{r}) \sum_{\mathbf{G}} \delta n(\mathbf{G}) \frac{G_{\gamma} G_{\eta}}{|\mathbf{G}|^2} \exp(i\mathbf{G} \cdot \mathbf{r}) d\mathbf{r}.
\end{aligned} \tag{44}$$

To obtain the above expression, we used the following relationship:

$$\begin{aligned}
\int_{\Omega} \delta n(\mathbf{r}) \int_{\Omega} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial \delta n(\mathbf{r}')}{\partial \varepsilon_{\gamma\eta}} d\mathbf{r}' d\mathbf{r} &= \int_{\Omega} \frac{\partial \delta n(\mathbf{r}')}{\partial \varepsilon_{\gamma\eta}} \int_{\Omega} \frac{\delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \\
&= \int_{\Omega} \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_{\text{H}} d\mathbf{r}.
\end{aligned} \tag{45}$$

#### 4.5 Exchange correlation energy component

Here we consider the GGA exchange correlation energy given by

$$E_{\text{XC}}^{\text{GGA}} = \int_{\Omega} f_{\text{XC}}(n_{\uparrow}, n_{\downarrow}, n_{\text{pcc}}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \nabla n_{\text{pcc}}) d\mathbf{r}, \tag{46}$$

where  $n_{\text{pcc}}$  is a charge density used for a partial core correction (PCC). Note that the strain derivative of the LDA energy appears as a part of that of GGA, which is

$$\begin{aligned} \frac{\partial E_{\text{XC}}^{\text{GGA}}}{\partial \varepsilon_{\gamma\eta}} &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \int_{\Omega} f_{\text{XC}}(n_{\uparrow}, n_{\downarrow}, n_{\text{pcc}}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \nabla n_{\text{pcc}}) \text{d}\mathbf{r} \\ &= \delta_{\gamma\eta} E_{\text{XC}}^{\text{GGA}} + \int_{\Omega} \left\{ \sum_{\sigma} \left( \frac{\partial f_{\text{XC}}}{\partial n_{\sigma}} \frac{\partial n_{\sigma}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial f_{\text{XC}}}{\partial |\nabla n_{\sigma}|} \frac{\nabla n_{\sigma}}{|\nabla n_{\sigma}|} \cdot \frac{\partial \nabla n_{\sigma}}{\partial \varepsilon_{\gamma\eta}} \right) \right. \\ &\quad \left. + \frac{\partial f_{\text{XC}}}{\partial n_{\text{pcc}}} \frac{\partial n_{\text{pcc}}}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial f_{\text{XC}}}{\partial |\nabla n_{\text{pcc}}|} \frac{\nabla n_{\text{pcc}}}{|\nabla n_{\text{pcc}}|} \cdot \frac{\partial \nabla n_{\text{pcc}}}{\partial \varepsilon_{\gamma\eta}} \right\} \text{d}\mathbf{r}. \end{aligned} \quad (47)$$

The above equation is derived by using the expression,  $\partial |\nabla n| / \partial \nabla n = \nabla n / |\nabla n| \partial n_{\sigma} / \partial \varepsilon_{\gamma\eta}$ . The strain derivative of the LDA energy will be obtained if the terms including the gradient of charges are removed from Eq. (47). The strain derivative of the valence electron density of spin  $\sigma$  has been already shown in Eq. (37). Since  $n_{\text{pcc}}$  is a localized function whose center locates at an atomic core position, the strain derivative of  $n_{\text{pcc}}$  can be calculated as in Eq. (36):

$$\partial n_{\text{pcc}}(\mathbf{r} - \mathbf{t}_I) / \partial \varepsilon_{\gamma\eta} = \nabla_{\gamma} n_{\text{pcc}}(\mathbf{r} - \mathbf{t}_I) (r^{\eta} - t_I^{\eta}) \quad (48)$$

The gradient of  $n_{\sigma}$  in the LCAO formulation is

$$\begin{aligned} \nabla n_{\sigma} &= \nabla \sum_n \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \\ &= \sum_n \sum_{i\alpha, j\beta} \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} (\nabla \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) + \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) \nabla \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n)) \end{aligned} \quad (49)$$

In Eq. (47), the strain derivative of the gradient of electron density,  $\nabla n$ , appears. First we consider the expansion of  $\nabla n$  with respect to strain  $\varepsilon$ ,  $\nabla^{\varepsilon} n^{\varepsilon}$ .<sup>†</sup> The expansion of the gradient operator is

$$\nabla^{\varepsilon} = \begin{bmatrix} \partial x_{\eta} \\ \partial x_{\gamma}^{\varepsilon} \end{bmatrix}. \quad (50)$$

Using  $\begin{bmatrix} \partial x_{\eta} \\ \partial x_{\gamma}^{\varepsilon} \end{bmatrix} = \begin{bmatrix} \partial x_{\gamma}^{\varepsilon} \\ \partial x_{\eta} \end{bmatrix}^{-1}$  and  $\mathbf{r}^{\varepsilon} = [\mathbf{I} + \varepsilon] \cdot \mathbf{r}$ , we have

$$\frac{\partial x_{\gamma}^{\varepsilon}}{\partial x_{\eta}} = \delta_{\gamma\eta} + \varepsilon_{\gamma\eta}. \quad (51)$$

The strain is infinitesimal, hence  $[\delta_{\gamma\eta} + \varepsilon_{\gamma\eta}]^{-1} \rightarrow [\delta_{\gamma\eta} - \varepsilon_{\gamma\eta}]$ . Then, Eq. (50) turns to be

$$\nabla^{\varepsilon} = [\delta_{\gamma\eta} - \varepsilon_{\gamma\eta}] \nabla. \quad (52)$$

Eventually,  $\nabla^{\varepsilon} n^{\varepsilon}$  is obtained as follows:

$$\nabla^{\varepsilon} n^{\varepsilon} = [\delta_{\gamma\eta} - \varepsilon_{\gamma\eta}] \nabla \left( n + \sum_{\gamma\eta} \frac{\partial n}{\partial \varepsilon_{\gamma\eta}} \varepsilon_{\gamma\eta} + \dots \right). \quad (53)$$

The above equation gives the strain derivative of  $\nabla n$ ,

$$\frac{\partial \nabla n}{\partial \varepsilon_{\gamma\eta}} = \nabla \frac{\partial n}{\partial \varepsilon_{\gamma\eta}} + \nabla_{\eta} n \mathbf{e}_{\gamma}, \quad (54)$$

<sup>†</sup>The stress formulation related to this term is different than that actually implemented in the OpenMX code. The formulation used in the OpenMX is described in Appendix A.



where  $\mathbf{e}_\gamma$  indicates the unit vector of  $\gamma$  direction. The above expression is understandable if we consider the following relationship:

$$[\varepsilon_{\gamma\eta}] \nabla n = \begin{pmatrix} \varepsilon_{xx} \nabla_x n & \varepsilon_{xy} \nabla_y n & \varepsilon_{xz} \nabla_z n \\ \varepsilon_{yx} \nabla_x n & \varepsilon_{yy} \nabla_y n & \varepsilon_{yz} \nabla_z n \\ \varepsilon_{zx} \nabla_x n & \varepsilon_{zy} \nabla_y n & \varepsilon_{zz} \nabla_z n \end{pmatrix}. \quad (55)$$

Inserting Eq.(54) to a part of Eq. (49), we have

$$\begin{aligned} \int_{\Omega} \frac{\partial f_{XC}}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \cdot \frac{\partial \nabla n}{\partial \varepsilon_{\gamma\eta}} d\mathbf{r} &= \int_{\Omega} \frac{\partial f_{XC}}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \cdot \left( \nabla \frac{\partial n}{\partial \varepsilon_{\gamma\eta}} + \nabla_\eta n \mathbf{e}_\gamma \right) d\mathbf{r} \\ &= \int_{\Omega} \frac{\partial f_{XC}}{\partial |\nabla n|} \frac{\nabla n}{|\nabla n|} \cdot \nabla \frac{\partial n}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial f_{XC}}{\partial |\nabla n|} \frac{\nabla_\gamma n \nabla_\eta n}{|\nabla n|} d\mathbf{r} \\ &= \int_{\Omega} \frac{\partial f_{XC}}{\partial |\nabla n|} \frac{\nabla^2 n}{|\nabla n|} \frac{\partial n}{\partial \varepsilon_{\gamma\eta}} + \frac{\partial f_{XC}}{\partial |\nabla n|} \frac{\nabla_\gamma n \nabla_\eta n}{|\nabla n|} d\mathbf{r}. \end{aligned} \quad (56)$$

Using Eqs. (40), (48), and (56), the strain derivative of  $E_{XC}^{\text{GGA}}$  shown in Eq. (47) can be calculated.

#### 4.6 Energy component for screened ion-ion potential

The energy coming from screened ion-ion interaction is a part of the electrostatic energy,

$$E_{\text{SCC}} = \sum_{I \neq J} \left[ \frac{1}{2} \frac{Z_I - Z_J}{|\mathbf{t}_I - \mathbf{t}_J|} - \int_{\Omega} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) V_{H,J}^{(a)}(\mathbf{r} - \mathbf{t}_J) d\mathbf{r} \right]. \quad (57)$$

Now we calculate the strain derivative of this energy component,

$$\frac{\partial E_{\text{SCC}}}{\partial \varepsilon_{\gamma\eta}} = \sum_{I \neq J} \left[ \frac{1}{2} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \frac{Z_I - Z_J}{|\mathbf{t}_I - \mathbf{t}_J|} - \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \int_{\Omega} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) V_{H,J}^{(a)}(\mathbf{r} - \mathbf{t}_J) d\mathbf{r} \right]. \quad (58)$$

The first term in the right-hand side is easily obtained using the chain rule, Eq. (14), as follows:

$$\frac{1}{2} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \frac{Z_I - Z_J}{|\mathbf{t}_I - \mathbf{t}_J|} = \frac{1}{2} Z_I Z_J \frac{(t_I^\gamma - t_J^\gamma)(t_I^\eta - t_J^\eta)}{|\mathbf{t}_I - \mathbf{t}_J|^3}. \quad (59)$$

To develop the second term in the right-hand side of Eq. (58), the coordinate transformation is used as in Eq. (18). Then we have

$$\begin{aligned} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \int_{\Omega} n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) V_{H,J}^{(a)}(\mathbf{r} - \mathbf{t}_J) d\mathbf{r} &= \int_{\Omega'} \frac{\partial n_I^{(a)}(\mathbf{r}' - \mathbf{t}_I + \mathbf{t}_J)}{\partial \varepsilon_{\gamma\eta}} V_{H,J}^{(a)}(\mathbf{r}') d\mathbf{r}' \\ &= \int_{\Omega'} \left\{ -\nabla_\gamma n_I^{(a)}(\mathbf{r}' - \mathbf{t}_I + \mathbf{t}_J) (t_I^\eta - t_J^\eta) \right\} V_{H,J}^{(a)}(\mathbf{r}') d\mathbf{r}' \\ &= -(t_I^\eta - t_J^\eta) \int_{\Omega} \nabla_\gamma n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) V_{H,J}^{(a)}(\mathbf{r} - \mathbf{t}_J) d\mathbf{r}'. \end{aligned} \quad (60)$$

Finally we obtain the strain derivative of the energy component as follows:

$$\begin{aligned} \frac{\partial E_{\text{SCC}}}{\partial \varepsilon_{\gamma\eta}} &= \sum_{I \neq J} \left[ \frac{1}{2} Z_I Z_J \frac{(t_I^\gamma - t_J^\gamma)(t_I^\eta - t_J^\eta)}{|\mathbf{t}_I - \mathbf{t}_J|^3} \right. \\ &\quad \left. - (t_I^\eta - t_J^\eta) \int_{\Omega} \nabla_\gamma n_I^{(a)}(\mathbf{r} - \mathbf{t}_I) V_{H,J}^{(a)}(\mathbf{r} - \mathbf{t}_J) d\mathbf{r} \right]. \end{aligned} \quad (61)$$

## 4.7 Overlap component

Summing up the strain derivatives of the density matrix already appeared, we have

$$\begin{aligned}
& \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \hat{T} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\
& + \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | V_{na, I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\
& + \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \hat{V}_{NL, I}(\mathbf{r} - \mathbf{t}_I) | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\
& + \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \delta V_H | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\
& + \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | V_{XC, \sigma} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\
& = \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \hat{H}_{\sigma} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle.
\end{aligned} \tag{62}$$

The density matrix is defined in Eq. (4). Its strain derivative is

$$\begin{aligned}
\frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} &= \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \frac{1}{V_B} \int_B d\mathbf{k} \sum_{\mu}^{\text{occ}} \exp(i\mathbf{R}_n \cdot \mathbf{k}) c_{\sigma\mu, i\alpha}^{(\mathbf{k})*} c_{\sigma\mu, j\beta}^{(\mathbf{k})} \\
&= \frac{1}{V_B} \int_B d\mathbf{k} \sum_{\mu}^{\text{occ}} \exp(i\mathbf{R}_n \cdot \mathbf{k}) \left( \frac{\partial c_{\sigma\mu, i\alpha}^{(\mathbf{k})*}}{\partial \varepsilon_{\gamma\eta}} c_{\sigma\mu, j\beta}^{(\mathbf{k})} + c_{\sigma\mu, i\alpha}^{(\mathbf{k})*} \frac{\partial c_{\sigma\mu, j\beta}^{(\mathbf{k})}}{\partial \varepsilon_{\gamma\eta}} \right).
\end{aligned} \tag{63}$$

To derive this equation, we used the expressions,  $1/V_B \rightarrow 1/\det(\mathbf{I} + \varepsilon)$ ,  $d\mathbf{k} \rightarrow \det(\mathbf{I} - \varepsilon)d\mathbf{k}$ , and  $\mathbf{R}_n \cdot \mathbf{k} \rightarrow \mathbf{R}_n \cdot \mathbf{k}$ . Substituting Eq. (63) for Eq. (62), we obtain

$$\begin{aligned}
& \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} \frac{\partial \rho_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_i) | \hat{H}_{\sigma} | \phi_{j\beta}(\mathbf{r} - \mathbf{t}_i - \mathbf{R}_n) \rangle \\
&= \frac{1}{V_B} \int_B d\mathbf{k} \left\{ \sum_{\sigma} \text{Tr} \left( \Theta \left( E_F - \epsilon_{\sigma}^{(\mathbf{k})} \right) \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger}}{\partial \varepsilon_{\gamma\eta}} \mathbf{H}_{\sigma}^{(\mathbf{k})} \mathbf{c}_{\sigma}^{(\mathbf{k})} \right) + \text{Tr} \left( \Theta \left( E_F - \epsilon_{\sigma}^{(\mathbf{k})} \right) \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger} \mathbf{H}_{\sigma}^{(\mathbf{k})} \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})}}{\partial \varepsilon_{\gamma\eta}} \right) \right\} \\
&= \frac{1}{V_B} \int_B d\mathbf{k} \left\{ \sum_{\sigma} \text{Tr} \left( \Theta \left( E_F - \epsilon_{\sigma}^{(\mathbf{k})} \right) \left( \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger}}{\partial \varepsilon_{\gamma\eta}} \mathbf{S}^{(\mathbf{k})} \mathbf{c}_{\sigma}^{(\mathbf{k})} + \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger} \mathbf{S}^{(\mathbf{k})} \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})}}{\partial \varepsilon_{\gamma\eta}} \right) \varepsilon_{\sigma}^{(\mathbf{k})} \right) \right\}.
\end{aligned} \tag{64}$$

In the above equation,  $\Theta$  is a diagonal matrix consisting of Heaviside step functions, and  $\epsilon_{\sigma}^{(\mathbf{k})}$  indicates the eigenenergy of the wave function. The strain derivative of the orthonormalization condition ( $\mathbf{c}_{\sigma}^{(\mathbf{k})\dagger} \mathbf{S}^{(\mathbf{k})} \mathbf{c}_{\sigma}^{(\mathbf{k})} = \mathbf{I}$ ) is

$$\frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger}}{\partial \varepsilon_{\gamma\eta}} \mathbf{S}^{(\mathbf{k})} \mathbf{c}_{\sigma}^{(\mathbf{k})} + \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger} \mathbf{S}^{(\mathbf{k})} \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})}}{\partial \varepsilon_{\gamma\eta}} = -\mathbf{c}_{\sigma}^{(\mathbf{k})\dagger} \frac{\partial \mathbf{S}^{(\mathbf{k})}}{\partial \varepsilon_{\gamma\eta}} \mathbf{c}_{\sigma}^{(\mathbf{k})}. \tag{65}$$

Inserting Eq. (65) to Eq. (64), we obtain

$$\begin{aligned}
& \frac{1}{V_B} \int_B d\mathbf{k} \left\{ \sum_{\sigma} \text{Tr} \left( \Theta \left( E_F - \varepsilon_{\sigma}^{(\mathbf{k})} \right) \left( \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger}}{\partial \varepsilon_{\gamma\eta}} \mathbf{S}^{(\mathbf{k})} \mathbf{c}_{\sigma}^{(\mathbf{k})} + \mathbf{c}_{\sigma}^{(\mathbf{k})\dagger} \mathbf{S}^{(\mathbf{k})} \frac{\partial \mathbf{c}_{\sigma}^{(\mathbf{k})}}{\partial \varepsilon_{\gamma\eta}} \right) \varepsilon_{\sigma}^{(\mathbf{k})} \right) \right\} \\
&= - \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} E_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial S_{i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial \varepsilon_{\gamma\eta}} \\
&= - \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} E_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial S_{i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial t_{ij, n}^{\gamma}} t_{ij, n}^{\eta} \\
&= - \sum_{\sigma} \sum_n \sum_{i\alpha, j\beta} E_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} \frac{\partial S_{i\alpha, j\beta}^{(\mathbf{R}_n)}}{\partial t_i^{\gamma}} t_{ij, n}^{\eta},
\end{aligned} \tag{66}$$

where

$$E_{\sigma, i\alpha, j\beta}^{(\mathbf{R}_n)} = \frac{1}{V_B} \int_B d\mathbf{k} \sum_{\mu}^{\text{occ}} \exp(i\mathbf{R}_n \cdot \mathbf{k}) \varepsilon_{\sigma}^{(\mathbf{k})} c_{\sigma\mu, i\alpha}^{(\mathbf{k})*} c_{\sigma\mu, j\beta}^{(\mathbf{k})}. \tag{67}$$

This is the overlap stress appearing because of the incompleteness of basis functions.

## A Appendix: OpenMX stress implementation of GGA

This section describes how the strain derivative term related to the gradient of electron density in Eq. (47) is calculated in the OpenMX code. To treat this term accurately, it is necessary to formulate the derivative term according to the discretization manner employed in this software; the GGA exchange-correlation energy functional is integrated by using the trapezoidal rule on a real-space FFT grid:

$$E_{\text{XC}} = \Delta V \sum_{\sigma} \sum_p f_{\text{XC}}(n_p^{\sigma}, |\nabla n_p^{\sigma}|, n_p^{\text{pcc}}), \tag{68}$$

where  $\Delta V$  is the volume per a single grid point. The function or coordinate with the index  $p$  indicates that on the grid point  $p \equiv (i, j, h)$ , *i.e.*,  $n_p^{\sigma} \equiv n^{\sigma}(r_p)$ ,  $\nabla n_p^{\sigma} \equiv \nabla n^{\sigma}(r_p)$ , and  $r_p \equiv (x_i, y_j, z_h)$ . The strain derivative of Eq.(68) is obtained as

$$\frac{\partial E_{\text{XC}}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta} E_{\text{XC}} + \Delta V \sum_{\sigma} \sum_p \frac{\partial f_{\text{XC}}}{\partial n_p^{\sigma}} \frac{\partial n_p^{\sigma}}{\partial \varepsilon_{\gamma\eta}} + \Delta V \sum_{\sigma} \sum_p \frac{\partial f_{\text{XC}}}{\partial |\nabla n_p^{\sigma}|} \frac{\partial |\nabla n_p^{\sigma}|}{\partial \varepsilon_{\gamma\eta}} + [\text{pcc terms}], \tag{69}$$

where [pcc terms] means terms related to the pseudo-core correction.

The problem is how to correctly calculate  $\partial \nabla n_p^{\sigma} / \partial \varepsilon_{\gamma\eta}$  in the third term of the right-hand side of Eq. (69). In the OpenMX, the gradient of a function is calculated by using a finite difference along the lattice vector:  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ . Hence, the finite difference should be transformed into that along the  $xyz$  coordinates to obtain the gradient. First, we consider the total derivative of the density  $\nabla n_p^{\sigma}$ ,

$$dn^{\sigma} = dx \frac{\partial n^{\sigma}}{\partial x} + dy \frac{\partial n^{\sigma}}{\partial y} + dz \frac{\partial n^{\sigma}}{\partial z} \tag{70}$$

Considering a difference in the lattice vector  $\mathbf{a}$ , differences in  $xyz$  directions are

$$dx = \Delta a_x d\lambda, dy = \Delta a_y d\lambda, dz = \Delta a_z d\lambda. \tag{71}$$

where  $\Delta a_x$ ,  $\Delta a_y$ , and  $\Delta a_z$  are determined according to the grid spacing in the axis  $\mathbf{a}$ . Then we can express the finite difference of the density  $n_p^{\sigma}$  along the axis  $\mathbf{a}$  using those along  $xyz$  axes:

$$dn^{\sigma}(\lambda) = \Delta a_x d\lambda \frac{\partial n^{\sigma}}{\partial x} + \Delta a_y d\lambda \frac{\partial n^{\sigma}}{\partial y} + \Delta a_z d\lambda \frac{\partial n^{\sigma}}{\partial z}. \tag{72}$$

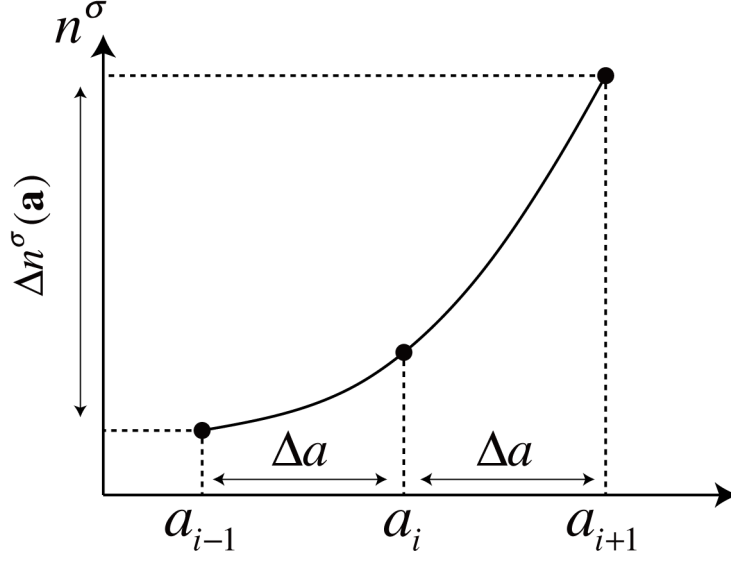


Figure A-1: Finite difference calculation in OpenMX

Generalizing Eq. (72) for the cases of the vectors  $\mathbf{b}$  and  $\mathbf{c}$ , we have

$$\begin{pmatrix} \Delta a_x & \Delta a_y & \Delta a_z \\ \Delta b_x & \Delta b_y & \Delta b_z \\ \Delta c_x & \Delta c_y & \Delta c_z \end{pmatrix} \begin{pmatrix} \frac{\partial n^\sigma}{\partial x} \\ \frac{\partial n^\sigma}{\partial y} \\ \frac{\partial n^\sigma}{\partial z} \end{pmatrix} = \begin{pmatrix} \frac{\partial n^\sigma(a)}{\partial \lambda} \\ \frac{\partial n^\sigma(b)}{\partial \lambda} \\ \frac{\partial n^\sigma(c)}{\partial \lambda} \end{pmatrix}. \quad (73)$$

In the OpenMX, the finite difference is calculated as illustrated in Fig. A-1. Then,

$$2\Delta a_x d\lambda \frac{\partial n^\sigma}{\partial x} + 2\Delta a_y d\lambda \frac{\partial n^\sigma}{\partial y} + 2\Delta a_z d\lambda \frac{\partial n^\sigma}{\partial z} = \Delta n^\sigma(a). \quad (74)$$

Note that, in Eq. (74), the gradients in  $xyz$  directions are the ones at the point  $a_i$  in Fig. A-1. A generalized form of Eq. (74) with  $d\lambda = 1$  is

$$\begin{pmatrix} \Delta a_x & \Delta a_y & \Delta a_z \\ \Delta b_x & \Delta b_y & \Delta b_z \\ \Delta c_x & \Delta c_y & \Delta c_z \end{pmatrix} \begin{pmatrix} \frac{\partial n^\sigma}{\partial x} \\ \frac{\partial n^\sigma}{\partial y} \\ \frac{\partial n^\sigma}{\partial z} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \Delta n^\sigma(a) \\ \Delta n^\sigma(b) \\ \Delta n^\sigma(c) \end{pmatrix}, \quad (75)$$

Using the matrix

$$\mathbf{F} = \begin{pmatrix} \Delta a_x & \Delta a_y & \Delta a_z \\ \Delta b_x & \Delta b_y & \Delta b_z \\ \Delta c_x & \Delta c_y & \Delta c_z \end{pmatrix}, \quad (76)$$

we can rewrite Eq. (75) as

$$\mathbf{F} \nabla n^\sigma = \frac{1}{2} \Delta n^\sigma. \quad (77)$$

This is the relationship between the finite differences along  $xyz$  direction and lattice vectors. Now we consider the strain derivative of Eq. (77):

$$\frac{\partial \mathbf{F}}{\partial \varepsilon_{\gamma\eta}} \nabla n^\sigma + \mathbf{F} \frac{\partial \nabla n^\sigma}{\partial \varepsilon_{\gamma\eta}} = \frac{1}{2} \frac{\partial \Delta n^\sigma}{\partial \varepsilon_{\gamma\eta}}. \quad (78)$$

Then we obtain

$$\frac{\partial \nabla n^\sigma}{\partial \varepsilon_{\gamma\eta}} = \mathbf{G} \frac{1}{2} \frac{\partial \Delta n^\sigma}{\partial \varepsilon_{\gamma\eta}} - \mathbf{G} \frac{\partial \mathbf{F}}{\partial \varepsilon_{\gamma\eta}} \nabla n^\sigma, \quad (79)$$

where  $\mathbf{F}^{-1} = \mathbf{G}$ . Firstly, the second term is considered. The lattice vector  $\mathbf{a}$  under strain becomes

$$\begin{pmatrix} \Delta a_x^\varepsilon \\ \Delta a_y^\varepsilon \\ \Delta a_z^\varepsilon \end{pmatrix} = \begin{pmatrix} 1 + \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & 1 + \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & 1 + \varepsilon_{zz} \end{pmatrix} \begin{pmatrix} \Delta a_x \\ \Delta a_y \\ \Delta a_z \end{pmatrix}. \quad (80)$$

There are similar expressions for the cases of  $\mathbf{b}$  and  $\mathbf{c}$ . Then some examples for the strain derivatives of the matrix  $\mathbf{F}$  can be described as follows:

$$\frac{\partial \mathbf{F}}{\partial \varepsilon_{xx}} = \begin{pmatrix} \Delta a_x & 0 & 0 \\ \Delta b_x & 0 & 0 \\ \Delta c_x & 0 & 0 \end{pmatrix} \quad (81)$$

$$\frac{\partial \mathbf{F}}{\partial \varepsilon_{xy}} = \begin{pmatrix} \Delta a_y & 0 & 0 \\ \Delta b_y & 0 & 0 \\ \Delta c_y & 0 & 0 \end{pmatrix} \quad (82)$$

$$\frac{\partial \mathbf{F}}{\partial \varepsilon_{xz}} = \begin{pmatrix} \Delta a_z & 0 & 0 \\ \Delta b_z & 0 & 0 \\ \Delta c_z & 0 & 0 \end{pmatrix} \quad (83)$$

From the above equations, it is easily seen that  $\partial \mathbf{F} / \partial \varepsilon_{\gamma\eta}$  have

$$\begin{pmatrix} \Delta a_\eta \\ \Delta b_\eta \\ \Delta c_\eta \end{pmatrix} \quad (84)$$

in  $\gamma$  th column and other elements are zero in  $3 \times 3$  matrix. Then, the second term of the right-hand side of Eq. (79) related to  $xy$  strain becomes <sup>‡</sup>

$$\begin{aligned} \mathbf{G} \frac{\partial \mathbf{F}}{\partial \varepsilon_{xy}} \nabla n^\sigma &= \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{11} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix} \begin{pmatrix} a_{12} & 0 & 0 \\ a_{22} & 0 & 0 \\ a_{32} & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial n^\sigma}{\partial x_1} \\ \frac{\partial n^\sigma}{\partial x_2} \\ \frac{\partial n^\sigma}{\partial x_3} \end{pmatrix} \\ &= \begin{pmatrix} \sum_{I=1}^3 G_{1I} a_{I2} & 0 & 0 \\ \sum_{I=1}^3 G_{2I} a_{I2} & 0 & 0 \\ \sum_{I=1}^3 G_{3I} a_{I2} & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial n^\sigma}{\partial x_1} \\ \frac{\partial n^\sigma}{\partial x_2} \\ \frac{\partial n^\sigma}{\partial x_3} \end{pmatrix} \\ &= \begin{pmatrix} \frac{\partial n^\sigma}{\partial x_1} \sum_{I=1}^3 G_{1I} a_{I2} \\ \frac{\partial n^\sigma}{\partial x_2} \sum_{I=1}^3 G_{2I} a_{I2} \\ \frac{\partial n^\sigma}{\partial x_3} \sum_{I=1}^3 G_{3I} a_{I2} \end{pmatrix}. \end{aligned} \quad (85)$$

<sup>‡</sup>Hereafter, the coordinates  $xyz$  are expressed by  $x_1 x_2 x_3$ , and

$$\begin{pmatrix} \Delta a_x & \Delta a_y & \Delta a_z \\ \Delta b_x & \Delta b_y & \Delta b_z \\ \Delta c_x & \Delta c_y & \Delta c_z \end{pmatrix} \rightarrow \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}.$$

Generalizing the result, we have

$$\mathbf{G} \frac{\partial \mathbf{F}}{\partial \varepsilon_{\gamma\eta}} \nabla n^\sigma = \begin{pmatrix} \frac{\partial n^\sigma}{\partial x_\gamma} \sum_{i=1}^3 G_{1i} a_{i\eta} \\ \frac{\partial n^\sigma}{\partial x_\gamma} \sum_{i=1}^3 G_{2i} a_{i\eta} \\ \frac{\partial n^\sigma}{\partial x_\gamma} \sum_{i=1}^3 G_{3i} a_{i\eta} \end{pmatrix}. \quad (86)$$

Since  $\mathbf{G}$  is the inverse matrix of Eq. (76), Eq. (86) becomes

$$\begin{pmatrix} \frac{\partial n^\sigma}{\partial x_\gamma} \sum_{i=1}^3 G_{1i} \delta_{1\eta} \\ \frac{\partial n^\sigma}{\partial x_\gamma} \sum_{i=1}^3 G_{2i} \delta_{2\eta} \\ \frac{\partial n^\sigma}{\partial x_\gamma} \sum_{i=1}^3 G_{3i} \delta_{3\eta} \end{pmatrix}. \quad (87)$$

Returning to Eq. (79), we see that the first term of the right-hand side can be described as follows:

$$\begin{aligned} \frac{1}{2} \mathbf{G} \frac{\partial \Delta n^\sigma}{\partial \varepsilon_{\gamma\eta}} &= \frac{1}{2} \begin{pmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{pmatrix} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \begin{pmatrix} n^\sigma(i+1, j, h) - n^\sigma(i-1, j, h) \\ n^\sigma(i, j+1, h) - n^\sigma(i, j-1, h) \\ n^\sigma(i, j, h+1) - n^\sigma(i, j, h-1) \end{pmatrix} \\ &= \frac{1}{2} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \begin{pmatrix} \sum_{I=1}^3 G_{1I} n_I^\sigma(+) - \sum_{I=1}^3 G_{1I} n_I^\sigma(-) \\ \sum_{I=1}^3 G_{2I} n_I^\sigma(+) - \sum_{I=1}^3 G_{1I} n_I^\sigma(-) \\ \sum_{I=1}^3 G_{3I} n_I^\sigma(+) - \sum_{I=1}^3 G_{1I} n_I^\sigma(-) \end{pmatrix}, \end{aligned} \quad (88)$$

where  $n_I^\sigma(\pm)$  means  $n_{i\pm 1, j, h}^\sigma$  if  $I = 1$ ,  $n_{i, j\pm 1, h}^\sigma$  if  $I = 2$ , and  $n_{i, j, h\pm 1}^\sigma$  if  $I = 3$ . Note that the operator  $\partial/\partial \varepsilon_{\gamma\eta}$  in Eq. (88) only affects to  $n^\sigma$ . Back to Eq. (69), we see that the term related to Eq. (88) becomes

$$\begin{aligned} \Delta V \sum_\sigma \sum_p A_p^\sigma \cdot \left( \frac{1}{2} \mathbf{G} \frac{\partial \Delta n^\sigma}{\partial \varepsilon_{\gamma\eta}} \right) &= \frac{\Delta V}{2} \sum_\sigma \sum_k \sum_{i, j, h} A_{ijh, k}^\sigma \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left( \sum_{I=1}^3 G_{kI} n_I^\sigma(+) - G_{kI} n_I^\sigma(-) \right) \\ &= \frac{\Delta V}{2} \sum_\sigma \sum_k \sum_{i, j, h} A_{ijk}^\sigma G_{kI} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_I^\sigma(+) - \frac{\Delta V}{2} \sum_\sigma \sum_k \sum_{i, j, h} A_{ijk}^\sigma G_{kI} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_I^\sigma(-) \\ &= \frac{\Delta V}{2} \sum_\sigma \sum_k \sum_{i, j, h} \begin{pmatrix} A_{i-1, j, k, h}^\sigma G_{k1} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_{i, j, h}^\sigma - A_{i+1, j, k, h}^\sigma G_{k1} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_{i, j, h}^\sigma \\ A_{i, j-1, k, h}^\sigma G_{k2} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_{i, j, h}^\sigma - A_{i, j+1, k, h}^\sigma G_{k2} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_{i, j, h}^\sigma \\ A_{i, j, k-1, h}^\sigma G_{k3} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_{i, j, h}^\sigma - A_{i, j, k+1, h}^\sigma G_{k3} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_{i, j, h}^\sigma \end{pmatrix} \end{aligned} \quad (89)$$

Considering

$$\frac{1}{2} [\Delta A_k^\sigma(a) G_{k1} + \Delta A_k^\sigma(b) G_{k2} + \Delta A_k^\sigma(c) G_{k3}] = \frac{\partial A_k^\sigma}{\partial x_k}, \quad (90)$$

we have

$$-\Delta V \sum_\sigma \sum_p \nabla \cdot A_p^\sigma \frac{\partial n_p^\sigma}{\partial \varepsilon_{\gamma\eta}}. \quad (91)$$

In Eq. (69), the term related to Eq. (86) becomes

$$\begin{aligned}
& \Delta V \sum_{\sigma} \sum_p A_p^{\sigma} \cdot \left( -\mathbf{G} \frac{\partial \mathbf{F}}{\partial \varepsilon_{\gamma\eta}} \nabla n_p^{\sigma} \right) \\
& = -\Delta V \sum_{\sigma} \sum_p A_p^{\sigma} \left[ A_{p,1}^{\sigma} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} \delta_{1\eta} + A_{p,2}^{\sigma} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} \delta_{2\eta} + A_{p,3}^{\sigma} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} \delta_{3\eta} \right]
\end{aligned} \tag{92}$$

Inserting Eqs. (91) and (92) to Eq. (69), we eventually obtain

$$\begin{aligned}
& \Delta V \sum_{\sigma} \sum_p A_p^{\sigma} \cdot \frac{\partial \nabla n_p^{\sigma}}{\partial \varepsilon_{\gamma\eta}} \\
& = -\Delta V \sum_{\sigma} \sum_p \nabla \cdot A_p^{\sigma} \frac{\partial n_p^{\sigma}}{\partial \varepsilon_{\gamma\eta}} - \sum_{\sigma} \sum_p \frac{\partial n_p^{\sigma}}{\partial \varepsilon_{\gamma\eta}} A_{p,\eta}^{\sigma},
\end{aligned} \tag{93}$$

where  $A_{p,\eta}^{\sigma} = A_{p,1}^{\sigma} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} \delta_{1\eta} + A_{p,2}^{\sigma} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} \delta_{2\eta} + A_{p,3}^{\sigma} \frac{\partial n_p^{\sigma}}{\partial x_{\gamma}} \delta_{3\eta}$ .