Symmetric stress tensor in the local-density-functional framework using a separable nonlocal pseudopotential

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We present the explicit symmetric formulas for the nonlocal pseudopotential contribution to the stress tensor. The symmetric stress tensor can be derived by applying the scaling procedure of wave vector $\mathbf{K}$, which satisfies the symmetry property of $\partial K_\gamma / \partial \varepsilon_{\alpha\beta} = \partial K_\gamma / \partial \varepsilon_{\beta\alpha}$ for the symmetric strain $\varepsilon_{\alpha\beta}$. We note that this scaling procedure gives rise to the same expression for the stress tensor as that derived using a semilocal or a separable nonlocal pseudopotential.

Stress is an important concept in describing the equilibrium state of a system with interacting particles. Based on the local-density-functional approximation (LDA), Nielsen and Martin[1] derived the stress theorem which is related to the virial and force theorems. Using *ab initio* semilocal pseudopotentials, they provided the explicit form for the stress tensor and calculated very accurately the lattice constants, bulk moduli, second-, third-, and fourth-order elastic constants, and the internal-strain parameters for Si, Ge, and GaAs. The stress theorem can also be used to determine the equation of state, which represents the relation of pressure to the density and temperature of the system. Later, Corso and Resta[2] generalized the stress theorem beyond the LDA and found that the exchange-correlation stress becomes anisotropic in the most general case.

Recently, an *ab initio* molecular dynamics algorithm with variable cell shape was proposed,[3,4] in which the stress tensor is an inevitable quantity to achieve the optimization of internal coordinates and to simulate the phase transition of the solid system imposed by external variables such as pressure and temperature. In this approach, the internal stress, thermal stress, and external variables are the driving force for the variation of the cell shape. Because of the computational merits, these kinds of large-scale electronic structure calculations[5] mostly use the separable form of nonlocal pseudopotentials,[6] and the pseudopotential contribution to the force and to the stress tensor was given by Bylander *et al.*[7] However, we find a mistake in the expression of the stress tensor in the literatures and give the symmetric relation of stress to strain in this paper.

In the thermodynamic description of a solid, only the symmetric strain $\varepsilon_{\alpha\beta}$ $(= \varepsilon_{\beta\alpha})$, to the first order, such as linear and/or angular dilations and atomic rearrangements, is relevant, while a pure rigid rotation relevant to the description of the mechanical state gives rise to the antisymmetric strain.[8] Thus, we must consider the symmetric stress tensor which satisfies the relation, $\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$. In the earlier work of Nielsen and Martin,[1] the symmetric stress tensor with six independent elements is derived by

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\alpha\beta}}, \tag{1}$$

where the total energy per unit cell volume Ω is

$$E_{\text{tot}} = \langle H_{\text{int}} + V_{\text{ext}} \rangle = \left\langle \sum_i \frac{p_i^2}{2m_i} + V_{\text{int}} + V_{\text{ext}} \right\rangle. \tag{2}$$

Here i labels the particles, V_{int} and V_{ext} denote interactions between the particles and external potentials, re-
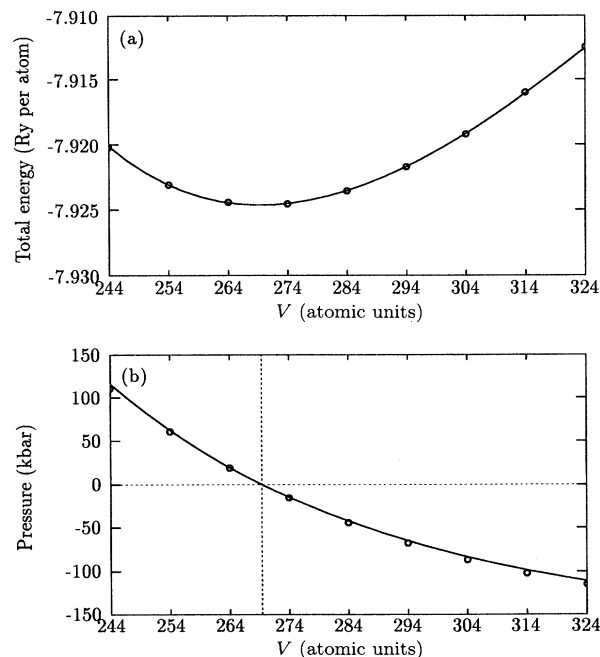

FIG. 1. (a) Calculated total energies (circles) are fitted to the Murnaghan equation (solid line). (b) The equation of state (solid line) derived from the total-energy curve in (a) is compared with that obtained from the directly calculated stress tensor (circles).

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spectively, and angular brakets indicate the expectation value. Under a symmetric strain $\varepsilon_{\alpha\beta}$, to first order, a previous work[1] showed that the wave vector $\mathbf{K}$ ($\equiv \mathbf{k} + \mathbf{G}$), where $\mathbf{k}$ belongs to the first Brillouin zone and $\mathbf{G}$ denotes the reciprocal lattice vectors, is transformed into

$$\frac{\partial K_\gamma}{\partial \varepsilon_{\alpha\beta}} = -\delta_{\alpha\gamma} K_\beta. \tag{3}$$

However, the right hand side of Eq. (3) is not symmetric, in general, for the interchange of α and β, because it may contain superflous pure rotations of strain. Considering only the symmetric part of strain, which meets the symmetric relation $\partial K_\gamma/\partial \varepsilon_{\alpha\beta} = \partial K_\gamma/\partial \varepsilon_{\beta\alpha}$, we find that the correct expression for the scaling of $\mathbf{K}$ is

$$\frac{\partial K_\gamma}{\partial \varepsilon_{\alpha\beta}} = -\frac{1}{2}(\delta_{\alpha\gamma} K_\beta + \delta_{\beta\gamma} K_\alpha)(2 - \delta_{\alpha\beta}). \tag{4}$$

Then, one can show that the two expressions in Eqs. (3) and (4) are equivalent for $\alpha = \beta$ and lead to the same symmetric stress for the semilocal pseudopotential,[1] when the multiplication of $(2 - \delta_{\alpha\beta})\varepsilon_{\alpha\beta}$ in Eq. (4) by Ω is taken as extensive parameters associated with intensive parameters $\sigma_{\alpha\beta}$ such as

$$\sigma_{\alpha\beta} = \frac{1}{\Omega(2 - \delta_{\alpha\beta})} \frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\alpha\beta}}. \tag{5}$$

Here, we note that our definition of the extensive parameters is consistent with the conventional way,[8] while $\Omega\varepsilon_{\alpha\beta}$ was used as an extensive parameter in the work of Nielsen and Martin. Using the scaling procedure of $\mathbf{K}$ in Eq. (4), we can also reformulate the stress tensor[1] in real space,

$$\frac{1}{(2 - \delta_{\alpha\beta})} \frac{\partial \langle H_{\text{int}} \rangle}{\partial \varepsilon_{\alpha\beta}} = -\sum_i \left\langle \Psi \left| \frac{p_{i\alpha} p_{i\beta}}{m_i} - \frac{1}{2}(r_{i\beta} \nabla_{i\alpha} + r_{i\alpha} \nabla_{i\beta}) V_{\text{int}} \right| \Psi \right\rangle. \tag{6}$$

Here, again, Eq. (6) satisfies the symmetric property of the stress tensor.

If V_{int} is represented by two-body central potentials, one can easily show that the stress tensor derived from the scaling procedure in Eq. (3) satisfies the symmetric property.[1] However, for an orientation-dependent potential V_{int}, such as

$$V_{\text{int}} = \sum_{i,j} V_{ij}(\mathbf{A} \cdot \mathbf{r}_{ij}), \tag{7}$$

where $\mathbf{A}$ is a constant vector and $\mathbf{r}_{ij}$ denotes the relative coordinate, Eq. (3) does not provide the symmetric stress because

$$\frac{\partial V_{\text{int}}}{\partial \varepsilon_{\alpha\beta}} \neq \frac{\partial V_{\text{int}}}{\partial \varepsilon_{\beta\alpha}}. \tag{8}$$

In constant pressure molecular dynamics simulations for solid and liquid CF_4, Nosé and Klein[9] employed potentials to describe the pure rotation of the unit cell of a solid, which depend on molecular orientation as well as atomic position.

In the case of the separable form of nonlocal pseudopotentials, Bylander et al.[7] derived the pseudopotential contribution to the atomic forces and to the stress tensor. For a separable nonlocal pseudopotential,[6,7]

$$V_{\text{ps}}(\mathbf{r}) = V_L(r) + \sum_{l,m} |v_l(r) Y_{lm}(\theta_\mathbf{r}, \phi_\mathbf{r})\rangle \langle v_l(r) Y_{lm}(\theta_\mathbf{r}, \phi_\mathbf{r})|, \tag{9}$$

the nonlocal pseudopotential contribution (E_{NL} per unit cell) to the total energy is

$$E_{\text{NL}} = \sum_{n,\mathbf{k},\tau} \sum_{l,m} \left\{ \sum_{\mathbf{G}'} C^*_{n,\mathbf{k}+\mathbf{G}'} v_{\tau l}(k + G') Y_{lm}(\theta_{\mathbf{k}+\mathbf{G}'}, \phi_{\mathbf{k}+\mathbf{G}'}) e^{-i\mathbf{G}' \cdot \boldsymbol{\tau}} \right\}$$

$$\times \left\{ \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} v_{\tau l}(k + G) Y^*_{lm}(\theta_{\mathbf{k}+\mathbf{G}}, \phi_{\mathbf{k}+\mathbf{G}}) e^{i\mathbf{G} \cdot \boldsymbol{\tau}} \right\}, \tag{10}$$

where $C_{n,\mathbf{k}+\mathbf{G}}$ denotes the coefficients in the plane-wave expansion of the wave function $\psi_{n,\mathbf{k}}(\mathbf{r})$ and $Y_{lm}(\theta_{\mathbf{k}+\mathbf{G}}, \phi_{\mathbf{k}+\mathbf{G}})$ is a spherical harmonic of the angle made by the vector $\mathbf{k} + \mathbf{G}$. Here, $v_{\tau l}(k + G)$ is defined as

$$v_{\tau l}(k + G) = \frac{4\pi}{\Omega^{\frac{1}{2}}} \int_0^\infty j_l(|\mathbf{k} + \mathbf{G}|r) v_{\tau l}(r) r^2 dr, \tag{11}$$

where $j_l(|\mathbf{k} + \mathbf{G}|r)$ is the spherical Bessel function, $\boldsymbol{\tau}$ is the vector from the lattice site to the τth atom in the unit cell. The sum on n runs over the occupied states for a given $\mathbf{k}$ point and the $\mathbf{k}$ sum means the average over the Brillouin zone. It is known that the nonlocal pseudopotential contribution in Eq. (10) can be calculated very efficiently because the separable form of potentials allows for the separation of the summations on $\mathbf{G}$ and $\mathbf{G}'$.

The separable nonlocal pseudopotential contribution to the stress tensor consists of the derivatives of $v_{\tau l}(K)$ and $Y_{lm}^*(\theta_{\mathbf{K}}, \phi_{\mathbf{K}})$ with respect to $\varepsilon_{\alpha\beta}$. First, by applying the scaling procedure in Eq. (4), the derivative of $v_{\tau l}(K)$ gives two terms, one of which is different by a constant factor $(2 - \delta_{\alpha\beta})$ from the previous results;[7]

$$-\frac{1}{2}\delta_{\alpha\beta}v_{\tau l}(k + G) + \tilde{v}_{\tau l}(k + G)\frac{(k_\alpha + G_\alpha)(k_\beta + G_\beta)}{|\mathbf{k} + \mathbf{G}|}(2 - \delta_{\alpha\beta}), \tag{12}$$

where $\tilde{v}_{\tau l}(k + G)$ is defined such as

$$\tilde{v}_{\tau l}(k + G) = \frac{4\pi}{\Omega^{\frac{1}{2}}(2l + 1)}\int_0^\infty [(l + 1)j_{l+1}(|\mathbf{k} + \mathbf{G}|\, r) - l j_{l-1}(|\mathbf{k} + \mathbf{G}|\, r)]\, v_{\tau l}(r)r^3 dr. \tag{13}$$

The multiplication of the two terms in Eq. (12) by a spherical harmonic contributes to the stress tensor, however, the spherical harmonic multiplication to the first term is absent in the formulas by Bylander $et\ al.$ Next, the differentiation of $Y_{lm}^*(\theta_{\mathbf{K}}, \phi_{\mathbf{K}})$ with respect to $\varepsilon_{\alpha\beta}$ is

$$\frac{\partial Y_{lm}^*(\theta_{\mathbf{K}}, \phi_{\mathbf{K}})}{\partial \varepsilon_{\alpha\beta}} = -\frac{1}{2}\left(\frac{\partial Y_{lm}^*(\theta_{\mathbf{K}}, \phi_{\mathbf{K}})}{\partial K_\alpha}K_\beta + \frac{\partial Y_{lm}^*(\theta_{\mathbf{K}}, \phi_{\mathbf{K}})}{\partial K_\beta}K_\alpha\right)(2 - \delta_{\alpha\beta}), \tag{14}$$

and this derivative is symmetric for the interchange of α and β. We note that the constant factor $(2 - \delta_{\alpha\beta})$ in Eqs. (12) and (14) does not affect the diagonal part of the stress tensor, compared with the previous calculations.[1] From Eqs. (12) and (14), we finally get the symmetric formulas for the nonlocal pseudopotential contribution to the stress tensor,

$$\frac{1}{(2 - \delta_{\alpha\beta})}\frac{\partial E_{\mathrm{NL}}}{\partial \varepsilon_{\alpha\beta}} = -\sum_{n,k,\tau}\sum_{l,m}\Bigg\{\left[\sum_{\mathbf{G}'}C_{n,\mathbf{k}+\mathbf{G}'}^*v_{\tau l}(k + G')Y_{lm}(\theta_{\mathbf{k}+\mathbf{G}'}, \phi_{\mathbf{k}+\mathbf{G}'})e^{-i\mathbf{G}'\cdot\tau}\right]$$

$$\times \sum_{\mathbf{G}}C_{n,\mathbf{k}+\mathbf{G}}e^{i\mathbf{G}\cdot\tau}\left[\frac{1}{2}v_{\tau l}(k + G)\left((k_\alpha + G_\alpha)\frac{\partial Y_{lm}^*(\theta_{\mathbf{k}+\mathbf{G}}, \phi_{\mathbf{k}+\mathbf{G}})}{\partial(k_\beta + G_\beta)}\right.\right.$$

$$\left.+(k_\beta + G_\beta)\frac{\partial Y_{lm}^*(\theta_{\mathbf{k}+\mathbf{G}}, \phi_{\mathbf{k}+\mathbf{G}})}{\partial(k_\alpha + G_\alpha)}\right)$$

$$+\frac{1}{2}\delta_{\alpha\beta}v_{\tau l}(k + G)Y_{lm}^*(\theta_{\mathbf{k}+\mathbf{G}}, \phi_{\mathbf{k}+\mathbf{G}})$$

$$\left.-\tilde{v}_{\tau l}(k + G)Y_{lm}^*(\theta_{\mathbf{k}+\mathbf{G}}, \phi_{\mathbf{k}+\mathbf{G}})\frac{(k_\alpha + G_\alpha)(k_\beta + G_\beta)}{|\mathbf{k} + \mathbf{G}|}\right] + \mathrm{c.c.}\Bigg\}. \tag{15}$$

Using the addition theorem for spherical harmonics, we note that the symmetric derivatives of the spherical harmonic terms in Eq. (15), $\frac{1}{2}(K_\alpha\frac{\partial Y_{lm}^*}{\partial K_\beta} + K_\beta\frac{\partial Y_{lm}^*}{\partial K_\alpha})$, is equivalent to $K_\alpha\frac{\partial Y_{lm}^*}{\partial K_\beta}$, which was derived from the scaling procedure in Eq. (3).[7]

For numerical tests, we calculate the stress tensor for Si by changing isotropically the crystal volume, and we

TABLE I. The elastic constants c_{ij} (in units of Mbar) and the internal strain parameter ζ are compared with other calculations and experimental data.

	Present calc.	Other calc.	Experiments
c_{11}	1.54	1.59[a]	1.675[b]
c_{12}	0.61	0.61[a]	0.650[b]
c_{44}	0.81	0.85[a]	0.801[b]
ζ	0.64	0.53[a]	0.73[c]

[a]Reference 1.
[b]Reference 14.
[c]Reference 15.

then derive the external pressure (P) for each volume from the relation,

$$P = -(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3. \tag{16}$$

In the calculations, the norm-conserving pseudopotential is generated by the scheme of Troullier and Martins,[10] and it is transformed into the separable form of Kleinman and Bylander,[6] with choosing the $l = 0$ component of the pseudopotential as local. The Wigner interpolation formula[11] for the exchange-correlation potential is employed and the wave function is expanded in a plane-wave basis set with a kinetic energy cutoff of 32 Ry. The summation over the Brillouin zone is performed using 10 special $\mathbf{k}$ points in the irreducible wedge of the Brillouin zone.[12] The energy functional is minimized by the conjugate-gradient method.[7] In Fig. 1, the equation of state derived from the stress tensor is compared with that obtained from the analytical derivative of E_{tot} with respect to volume, $-\partial E_{\mathrm{tot}}/\partial\Omega$. In this case, the calculated total energies for several crystal volumes are fitted to the Murnaghan equation of state.[13] We find good agreements

between the two calculations. The calculated elastic constants (c_{11}, c_{12}, and c_{44}) and internal strain parameter ζ are listed in Table I. The bulk modulus derived from the total energy vs volume curve is found to equal (c_{11} + 2 c_{12})/3, showing internal consistency. Our results for c_{ij} and ζ are in good agreement with previous theoretical calculations based on a semilocal pseudopotential,[1] while both the calculations generally underestimate c_{11} and ζ, compared to experimental data.

In conclusions, we have found the symmetric scaling procedure of wave vectors under a symmetric strain.

With this scaling procedure, we have derived the explicit symmetric formulas for the stress tensor in the momentum space formalism of nonlocal pseudopotentials. From the symmetric scaling relation which eliminates the nonsymmetric strain, we are able to define extensive parameters in the conventional way.

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