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On higher-order quantum stress

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Abstract In this paper, we present a novel theory of the higher-order quantum stress and its formulations in the framework of density functional theory. Specifically, we have systematically derived the third-order quantum stress expression based on the higher-order Cauchy–Born rule in combination with the higher-order strain gradient theory. The higher-order quantum stress formulation provides a theoretical foundation for first-principle calculation of stress couples at atomistic scale, which may help us understand possible quantum strain gradient effects, and related ferroelectric and flexoelectric effects at small scales.

1 Introduction

Stress is a key physical quantity or statistical measurement variable of condensed matters, because it not only manifests the thermodynamics state of the material, but also influences or relates to other physical quantities or state variables of the material, such as temperature, strain, electron density distribution, chemical element concentration, and electric and magnetic polarizations. In continuum mechanics, stress or Cauchy stress is defined as the intensity of the internal force based on a phenomenological physical model and mathematical idealization. Even though the concept of the stress is extensively used in macroscale engineering design, the physical origin of the stress has never been emphasized there. On the other hand, the application of continuum theory-based stress concept to nanoscale engineering design is severely limited, because of the ambiguity in the definition of stress at atomistic scale and nanoscale where is now the frontier of nanoscience and nanotechnology. Hence, understanding the quantum mechanical interpretation of stress or the quantum mechanical origin of the stress will greatly facilitate and promote the growth of nanotechnology.

For crystalline or quasi-crystalline solids at nanoscale or atomic scale, the stress state usually corresponds to nonuniformity or heterogeneity of lattice structure and electronic structure. The term of quantum stress is almost uniquely reserved for those stress states caused by the distortion of electronic structures. Moreover, the development of contemporary material engineering and nanotechnology has lead to a host of applications where we encounter highly localized strain gradient at atomistic scale, such as lattice point defects, atomic interstitial, quantum dots, other related quantum confinements, and ultra thin film. In these cases, both local and nonlocal strain gradient or the gradient of electric polarization will generate a significant amount of stress dipole distribution or couple stress that will significantly alter the material responses and hence change its overall behaviors. The objectives of this work are examining the concept of higher order quantum stress and deriving its formulation.

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In continuum mechanics, strain gradient theory [5] has been developed to understand the plastic deformation in mesoscale or other nonlocal elastic deformation [1]. The general higher-order stress is defined as work conjugate of the corresponding strain gradient. Several specialized versions were investigated to simplify the theory and provide physical interpretation. Among them, couple stress theory that deals with only a subset of strain gradient tensor is popularly used, which follows a theoretical framework of work conjugate between couple stress and deformation curvature. We shall adopt a similar mathematical framework in this work as well.

This paper is organized in six sections. We shall first review the Nielsen-Martin quantum stress theory in Sect. 2. In Sect. 3, we start to introduce the concept and to derive the general expressions of the third-order quantum stress. In Sect. 4, we discuss the density functional theory (DFT)-based higher-order quantum stress, and in Sect. 5, we shall derive the DFT-based couple stress formulation. Finally, in Sect. 6, we conclude the presentation by making a few remarks on the proposed quantum strain gradient theory and the quantum couple stress theory.

2 Review of quantum stress theory

Regarding to its atomistic origin, stress in crystalline solids comes from the two sources: (i) the deformation and vibration of crystal lattice or configuration of atom (nuclei or ion) assembly, and (ii) the deformation or re-configuration of both local and global electronic structure in the material.

With respect to the first source, i.e., the origin of stress is due to the kinetic (vibration) as well as kinematic (geometric and deformable) change of lattice structure of the material, this type of stress is mainly associated with the so-called virial stress,

$$\boldsymbol{\sigma} = \frac{1}{|\Omega|} \sum_{i \in \Omega} \left(-m^{(i)} (\mathbf{v}^{(i)} - \bar{\mathbf{v}}) \otimes (\mathbf{v}^{(k)} - \bar{\mathbf{v}}) + \frac{1}{2} \sum_{j \in \Omega} (\mathbf{x}^{(j)} - \mathbf{x}^{(i)}) \otimes \mathbf{f}^{(ij)} \right) \quad (1)$$

where i and j are indices for atoms inside the unit cell Ω ; $\mathbf{x}^{(i)}$ and $\mathbf{x}^{(j)}$ are the position vectors for the i -th atom and j -th atom; $\mathbf{v}^{(i)}$ and $\mathbf{v}^{(j)}$ are the velocity vectors for the i -th atom and j -th atom, while

$$\bar{\mathbf{v}} = \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i$$

is the average velocity, where N is the total number of atoms inside the unit cell Ω . We further note that in Eq. (1) $m^{(i)}$ is the mass for the i -th atom, and $\mathbf{f}^{(ij)}$ is the interatomic force from the i -th atom to the j -th atom.

There are several different ways to derive and to interpret the virial stress, and the most cited source is the so-called Irving–Kirkwood formalism [14]. The virial stress of an atom or molecule assembly can be calculated in molecular dynamics computations. One may also note that the virial stress depends on three things: (i) vibrational state of an assembly of atoms, (ii) deformation or the strain state of the assembly that displace the atom position, and (iii) defect state of the assembly, e.g., adding or deleting an atom from the assembly by radiation or ion diffusion, which will also induce strain eventually, but that is usually called relaxation strain. Since this is beyond the scope of this work, we refer readers to consult the relevant literature, e.g., [14, 15].

In this paper, we are concerned about another type of stress that is the *quantum stress*. Quantum stress is originally referred to the stress induced from the change of the electronic structure or electron density of the many-body quantum system. The change of the electronic structure may be due to different sources, for example, deformation state may distort electron structure, light scattering or radiation may knock some electrons away from bulk materials, holes/electron diffusion, etc. We refer to the quantum stress due to the change of electron density from non-mechanical sources as either *Quantum Electronic Stress* [13] or *Quantum Radiation Stress* if the change of the electronic structure is due to an optical/electrical source or the source of high-energy particles. In fact, those topics are also active and exciting topics in nanomechanics, but in this paper, we are focusing on strain or mechanical source-induced electronic structure change, and its consequence on high-order stress states.

It may be noted that since we do include the interaction among nuclei in the ground state, some part of the lattice virial stress may also be taken into consideration in the quantum stress formulation as well. On the other hand, the atomistic potential used in virial stress may be calibrated by using first-principle-based quantum

mechanical methods, and thus, it contains some information of electron density change, so does the quantum stress, for instance if we use the embedded atom method (EAM) [3]. However, such inclusion of quantum stress is empirical, and until today, no higher-order virial stress has been derived, which remains to be an open subject in nanomechanics.

In their pioneer work, Nielsen and Martin [8,9] first introduced the concept of quantum stress due to a mechanical source, which reveals the quantum mechanical origin of stress–strain relation, and its dependency on the electronic structure and its deformed configuration. The expression of the quantum stress derived by Nielsen and Martin is

$$\mathbf{T} = - \sum_i \left\langle \Psi \left| \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i} - \nabla V_{\text{int}} \otimes \mathbf{r}_i \right| \Psi \right\rangle \quad (2)$$

where \mathbf{p}_i is the moment vector of the electron, m_i is the mass of the electron, \mathbf{r}_i is the position of the electron, Ψ is the wave function, and V_{int} is the internal potential energy. In the literature of physics, we often write the component form of Eq. (2) as

$$T_{\alpha\beta} = - \sum_i \left\langle \Psi \left| \frac{p_{i\alpha} p_{i\beta}}{m_i} - r_{i\beta} \nabla_{i\alpha} (V_{\text{int}}) \right| \Psi \right\rangle \quad (3)$$

where Ψ is the wave function, $p_{i\alpha}$ is the momentum of particle i , V_{int} denotes the internal potential energy, m_i and $r_{i\beta}$ represent mass and coordinate of i -th particles, and \mathbf{T} is the quantum Cauchy stress of the many-body system.

The quantum stress expressed in Eq. (2) is, however, difficult to evaluate due to the complexity of the wave function of the many-body problem. In computational chemistry or computational materials, density functional theory (DFT) [6,7] is proved to be an efficient approach to obtain the ground-state wave function and electron density with satisfactory accuracy.

The total internal energy E_{int} of a many-body system in the framework of DFT has five parts:

$$E_{\text{int}} = E_{\text{kin}} + E_{\text{ion-electron}} + E_{\text{ion-ion}} + E_{\text{Hartree}} + E_{\text{xc}}, \quad (4)$$

that is: E_{kin} —the kinetic energy, $E_{\text{ion-electron}}$ —the potential energy due to the ion–electron interaction, $E_{\text{ion-ion}}$ —the potential energy due to the ion–ion interaction, E_{Hartree} —the Hartree potential, and E_{xc} —the exchange–correlation potential energy. In general, the exchange–correlation potential energy is unknown; however, it can be estimated under different approximations. In this paper, the so-called local density approximation is adopted.

Hence, the total DFT quantum stress based on the local density approximation (LDA) [12] consists of five parts corresponding to the five parts of internal energy. For reference, we list the five parts of the quantum stress one by one as follows:

1. The kinetic contribution of noninteracting electrons,

$$- \sum_i \frac{1}{m_i} \langle \psi_i | \mathbf{p}_i \otimes \mathbf{p}_i | \psi_i \rangle, \quad (5)$$

where m_i is the mass of the electron, and ψ_i are wave functions of a noninteracting system;

2. The ion–electron stress,

$$- \frac{1}{2} e^2 \sum_I \int n(\mathbf{r}) V'_{\text{ion-e}}(|\mathbf{r} - \mathbf{R}_I|) \frac{(\mathbf{r} - \mathbf{R}_I) \otimes (\mathbf{r} - \mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|} d^3 \mathbf{r}, \quad (6)$$

where $V_{\text{ion-e}}$ is the potential energy between nuclei and electrons, $n(\mathbf{r})$ is the electron density, and e is the charge of the electron;

3. The ion–ion potential stress,

$$- \frac{1}{2} e^2 \sum_{\substack{I,J \\ I \neq J}} Z_I Z_J \frac{(\mathbf{R}_I - \mathbf{R}_J) \otimes (\mathbf{R}_I - \mathbf{R}_J)}{|\mathbf{R}_I - \mathbf{R}_J|^3}, \quad (7)$$

where \mathbf{R}_I and Z_I are the I -th nuclei's position and charge number;

4. The Hartree stress,

$$-\frac{1}{2}e^2 \iint n(\mathbf{r})n(\mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}') \otimes (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}d^3\mathbf{r}', \quad (8)$$

5. The exchange and correlation stress,

$$\delta_{\alpha\beta} \int n(\mathbf{r})[\vartheta_{xc}(n) - \mu_{xc}(n)]d^3\mathbf{r}, \quad (9)$$

where ϑ_{xc} and μ_{xc} represent the exchange-correlation energy density and the exchange-correlation potential, respectively.

The sum of the above five parts of the stress is the total quantum stress based on DFT theory, which provides an average measure of stress for a many-body system in the ground state.

3 Higher-order quantum stress theory

Our objective is to study the higher-order quantum stress caused by electronic structure polarization, distortion, and defect. Therefore, in this paper, we neglect the kinetic energy of the nucleus and the effects of its probability distribution (wave function).

We employ an electronic coordinate transform technique that is a generalization of the coordinate transform adopted by Nielsen and Martin [9]. We scale the electronic coordinates in the ground state by using the following second-order transformation.

$$\mathbf{r}_i \rightarrow \mathbf{F}_i \cdot \mathbf{R}_i + \frac{1}{2}\mathbf{G}_i : \mathbf{R}_i \otimes \mathbf{R}_i = \mathbf{B}_i \cdot \mathbf{R}_i, \quad i = 1, 2, \dots, N_e \quad (10)$$

where N_e is the number of electrons in the system. For simplicity in the rest of the paper, we sometimes drop the index i if no confusion will be caused.

Considering the case of infinitesimal deformation, or the case of small strains, we let

$$\mathbf{F} = \mathbf{1} + \boldsymbol{\varepsilon}$$

be the first-order deformation gradient. By defining the gradient of the strain tensor as

$$\mathbf{G} := \nabla \otimes \boldsymbol{\varepsilon},$$

we can express the second-order Taylor expansion of the deformation gradient as follows:

$$\mathbf{B} = \mathbf{F} + \frac{1}{2}\mathbf{G} \cdot \mathbf{R} = \mathbf{1} + \boldsymbol{\varepsilon} + \frac{1}{2}\nabla \otimes \boldsymbol{\varepsilon} \cdot \mathbf{R}. \quad (11)$$

One can readily show that

$$\mathbf{B}^{-1} = \mathbf{1} - \boldsymbol{\varepsilon} - \frac{1}{2}\nabla \otimes \boldsymbol{\varepsilon} \cdot \mathbf{R} + \mathcal{O}\left(|\boldsymbol{\varepsilon}|^2, |\nabla \otimes \boldsymbol{\varepsilon} \cdot \mathbf{R}|^2\right). \quad (12)$$

For the convenience of subsequent derivation, we denote

$$\mathbf{c} := \mathbf{B}^{-T} \cdot \mathbf{B}^{-1} = \mathbf{1} - 2\boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \cdot \nabla \otimes \boldsymbol{\varepsilon} \cdot \mathbf{R} - \boldsymbol{\varepsilon} \cdot \mathbf{R} + \frac{1}{2}\left(\nabla \otimes \boldsymbol{\varepsilon} \cdot \mathbf{R}\right)^T \cdot \left(\nabla \otimes \boldsymbol{\varepsilon} \cdot \mathbf{R}\right). \quad (13)$$

Now, we consider the total energy of the quantum-mechanical system, i.e., the expectation of the Hamiltonian of a many-body system,

$$E = \left\langle \Psi_\varepsilon \left| H \right| \Psi_\varepsilon \right\rangle, \quad (14)$$

where the many-body Hamiltonian is defined as

$$H = \sum_{i=1}^{N_e} \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{2m_i} + V_{\text{int}}(\{\mathbf{r}_i\}, \{\mathbf{r}_I\}) + V_{\text{ext}}(\{\mathbf{r}_i\}, \{\mathbf{r}_I\})$$

where V_{int} is the internal potential energy, and V_{ext} is the external potential energy. Note that the index $i = 1, 2, \dots, N_e$ indicates the number of electrons, and the index $I = 1, 2, \dots, N_a$ indicates the number of nuclei in the system, and we use symbols

$$\{\mathbf{r}_i\} := \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}\} \text{ and } \{\mathbf{r}_I\} := \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_a}\}$$

to denote their assembly sets.

In Eq. (14), Ψ_ϵ is the scaled wave function, which is defined as

$$\Psi_\epsilon(\mathbf{r}) = \frac{1}{J^{1/2}} \Psi(\mathbf{R}) = \frac{1}{J^{1/2}} \Psi(\mathbf{B}^{-1} \cdot \mathbf{r}) = \frac{1}{J^{1/2}} \Psi((\mathbf{I} + \boldsymbol{\epsilon} + 1/2 \nabla \otimes \boldsymbol{\epsilon} \cdot \mathbf{R})^{-1} \mathbf{r})$$

where $J = \det \mathbf{B}$. The factor $J^{1/2}$ will ensure the probability normalization condition,

$$\int \Psi_\epsilon \Psi_\epsilon^* dV_r = 1,$$

because the volume element in the current configuration dV_r is the product of the Jacobian and the volume element in the referential configuration, i.e., $dV_r = J dV_R$.

Changing the variable $\mathbf{r} \rightarrow \mathbf{R}$, we have

$$\begin{aligned} E &= \langle \Psi_\epsilon \mid H \mid \Psi_\epsilon \rangle \\ &= \int \Psi^*(\mathbf{R}) \left[\sum_i \frac{1}{2m_i} (\mathbf{c} : \mathbf{p}_i \otimes \mathbf{p}_i) + V_{\text{int}}(\mathbf{B} \cdot \mathbf{R}) + V_{\text{ext}}(\mathbf{B} \cdot \mathbf{R}) \right] \Psi(\mathbf{R}) dV_R \end{aligned} \quad (15)$$

where $\Psi^*(\mathbf{R})$ is the complex conjugate wave function.

We first change the dummy variable to conform with the standard notation, i.e., $\mathbf{R}_i \rightarrow \mathbf{r}_i$ and $\mathbf{R}_I \rightarrow \mathbf{r}_I$. By assuming that the many-body system is in equilibrium, the stationary condition of the equilibrium system reads as

$$\frac{\partial E}{\partial \{\mathbf{G}\}} \Big|_{\{\boldsymbol{\epsilon}\}=0, \{G\}=0} = \sum_i \left\langle \Psi \mid -\frac{\mathbf{p}_i \otimes \mathbf{p}_i \otimes \mathbf{r}_i}{m_i} + \frac{1}{2} \nabla_i (V_{\text{int}} + V_{\text{ext}}) \otimes \mathbf{r}_i \otimes \mathbf{r}_i \mid \Psi \right\rangle = 0 \quad (16)$$

where

$$\{\mathbf{G}\} = \{\mathbf{G}_1, \mathbf{G}_2, \dots, \mathbf{G}_{N_e}\}, \quad \text{and} \quad \{\boldsymbol{\epsilon}\} = \{\boldsymbol{\epsilon}_1, \boldsymbol{\epsilon}_2, \dots, \boldsymbol{\epsilon}_{N_e}\}.$$

If one defines the higher-order quantum stress as

$$\mathbf{Q} := -\frac{\partial \langle E_{\text{ext}} \rangle}{\partial \mathbf{G}} = -\frac{1}{2} \sum_i \left\langle \Psi \mid \nabla_i V_{\text{ext}} \otimes \mathbf{r}_i \otimes \mathbf{r}_i \mid \Psi \right\rangle, \quad (17)$$

then, based on Eq. (16), we have the following expression for the quantum stress in terms of electronic kinetic energy, position, and their electrostatic interaction:

$$\mathbf{Q} = \sum_i \left\langle \Psi \mid -\frac{\mathbf{p}_i \otimes \mathbf{p}_i \otimes \mathbf{r}_i}{m_i} + \frac{1}{2} \nabla_i (V_{\text{int}}) \otimes \mathbf{r}_i \otimes \mathbf{r}_i \mid \Psi \right\rangle. \quad (18)$$

The above expression may be interpreted as

$$\mathbf{Q} = \frac{\partial}{\partial \mathbf{G}} \left(\langle E_{\text{int}} \rangle \right), \quad \text{and} \quad E_{\text{int}} = E_{\text{kin}} + V_{\text{int}}.$$

4 Higher-order quantum stress in the Kohn–Sham density functional theory

The higher-order quantum stress formulation derived in Eq. (18) is very difficult to be evaluated, because it needs the complete solution of the many-body Schrödinger equation.

Similar to the quantum stress formulation, a more practical approach is to evaluate the higher-order quantum stress by only considering the contribution from the ground-state wave function, or the electronic density, which can be obtained from the standard DFT calculation.

Again, the total energy of the many-body system based on the density functional theory can be split into five parts,

$$E_{\text{int}} = E_{\text{kin}} + E_{\text{ion-electron}} + E_{\text{ion-ion}} + E_{\text{Hartree}} + E_{\text{xc}}, \quad (19)$$

where

$$E_{\text{kin}} = \sum_i \left\langle \psi_i \left| \frac{p_i^2}{2m_i} \right| \psi_i \right\rangle, \quad (20)$$

$$E_{\text{ion-electron}} = \int n(\mathbf{r}) \sum_i V_{\text{ion-e}}(\mathbf{r} - \mathbf{R}_i) d^3\mathbf{r}, \quad (21)$$

$$E_{\text{ion-ion}} = \frac{1}{2} \sum_{I \neq J} \frac{2Z^2}{|\mathbf{R}_I - \mathbf{R}_J|}, \quad (22)$$

$$E_{\text{Hartree}} = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}', \quad (23)$$

$$E_{\text{xc}} = \int n(\mathbf{r}) \vartheta(n) d^3\mathbf{r}, \quad (24)$$

Define the third-order quantum stress as the work conjugate of \mathbf{G} ,

$$\mathbf{Q} = \frac{\partial E_{\text{int}}}{\partial \mathbf{G}} = \frac{\partial E_{\text{int}}}{\partial \mathbf{r}} \cdot \frac{\partial \mathbf{r}}{\partial \mathbf{G}} + \frac{\partial E_{\text{int}}}{\partial \mathbf{R}} \cdot \frac{\partial \mathbf{R}}{\partial \mathbf{G}}. \quad (25)$$

Thus, by applying the transformation (10) to Eqs. (22)–(20), the second-order quantum stress \mathbf{Q} can be derived from Eq. (25), and for clarity, we write down the contribution of each part:

1. The kinetic contribution:

$$\mathbf{Q}_{\text{kin}} = - \sum_i \left\langle \psi_i \left| \frac{\mathbf{p}_i \otimes \mathbf{p}_i \otimes \mathbf{r}_i}{2m_i} \right| \psi_i \right\rangle; \quad (26)$$

2. The ion–electron part:

$$\mathbf{Q}_{ie} = -\frac{1}{4}e^2 \sum_i \int n(\mathbf{r}) V'_{\text{ion}} \frac{(\mathbf{r} - \mathbf{R}_I) \otimes (\mathbf{r} \otimes \mathbf{r} - \mathbf{R}_I \otimes \mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|} d^3\mathbf{r}; \quad (27)$$

3. The ion–ion part:

$$\mathbf{Q}_{ii} = -\frac{1}{4}e^2 \sum_{\substack{I, J \\ I \neq J}} Z_I Z_J \frac{(\mathbf{R}_I - \mathbf{R}_J) \otimes (\mathbf{R}_I \otimes \mathbf{R}_I - \mathbf{R}_J \otimes \mathbf{R}_J)}{|\mathbf{R}_I - \mathbf{R}_J|^3}; \quad (28)$$

4. The Hartree part:

$$\mathbf{Q}_H = -\frac{1}{4}e^2 \iint n(\mathbf{r})n(\mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}') \otimes (\mathbf{r} \otimes \mathbf{r} - \mathbf{r}' \otimes \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}d^3\mathbf{r}'. \quad (29)$$

It is noted that under the local density approximation [7] the exchange and correlation energy in Eq. (24) is a local function of \mathbf{r} , and it gives rise to an isotropic pressure. Thus, it does not contribute to the higher-order quantum stress, namely $\mathbf{Q}_{\text{xc}} = 0$.

5 Quantum couple stress

In this section, motivated by the continuum coupled stress and flexoelectricity, e.g., [4,5,11] and [2,10], we consider a special class of higher-order quantum stress, i.e., the quantum couple stress. Taking into account the quantum effects, we derive the quantum couple stress by using the gradient of rotation to simplify the general quantum strain gradient theory, and moreover, we give plausible physical interpretation of the quantum couple stress.

We first start from decomposing the general second-order strain into a symmetric part \mathbf{G}^S representing the stretch gradient, and an anti-symmetric part of curvature measure \mathbf{G}^A ,

$$\mathbf{G} = \mathbf{G}^S + \mathbf{G}^A. \quad (30)$$

Similarly, \mathbf{Q} can also be partitioned into a symmetric part and an anti-symmetric part, that is,

$$\mathbf{Q} = \mathbf{Q}^S + \mathbf{Q}^A. \quad (31)$$

According to strain gradient theory [5], \mathbf{Q}^S is orthogonal to \mathbf{G}^A ; thus, the density of the virtual work can be written as

$$\delta w = \boldsymbol{\sigma} : \delta \boldsymbol{\varepsilon} + \mathbf{Q}^S : \delta \mathbf{G}^S + \mathbf{Q}^A : \delta \mathbf{G}^A. \quad (32)$$

In this paper, we mainly focus on the anti-symmetric contribution, which has a clear physical meaning. This term represents the work done by the couple stresses \mathbf{m} acting through the curvature increment $\delta \boldsymbol{\chi}$ [5], that is,

$$\mathbf{Q}^A : \delta \mathbf{G}^A = \mathbf{m} : \delta \boldsymbol{\chi}. \quad (33)$$

Since the curvature is defined as [5]

$$\chi_{ij} = \frac{1}{2} e_{iqr} G_{jqr}^A, \quad (34)$$

we then have the relationship

$$G_{ijk}^A = \frac{2}{3} (e_{ikp} \chi_{pj} + e_{jkp} \chi_{pi}) \quad (35)$$

where e_{ikp} is the permutation symbol.

Hence, the transformation becomes

$$\begin{aligned} r_i &\rightarrow F_{ij} r_j + \frac{1}{2} G_{ijk}^A r_j r_k \\ &= F_{ij} r_j + \frac{1}{3} (e_{ikp} \chi_{pj} + e_{jkp} \chi_{pi}) r_j r_k. \end{aligned} \quad (36)$$

Therefore, the quantum couple stress can be derived as

$$\mathbf{m} = \frac{\partial E_{\text{int}}}{\partial \boldsymbol{\chi}} = \frac{\partial E_{\text{int}}}{\partial \mathbf{r}} \cdot \frac{\partial \mathbf{r}}{\partial \boldsymbol{\chi}} + \frac{\partial E_{\text{int}}}{\partial \mathbf{R}} \cdot \frac{\partial \mathbf{R}}{\partial \boldsymbol{\chi}}. \quad (37)$$

Following a similar procedure as the derivation of general higher-order quantum stress and substituting Eq. (36) into Eqs. (22)–(20), and using Eq. (37), we can then write each part of quantum couple stress as follows:

1. Contribution from kinetic energy:

$$\mathbf{m}_{\text{kin}} = -\frac{4}{3} \sum_i \left\langle \psi_i \left| \frac{(\mathbf{p}_i \times \mathbf{r}_i) \otimes \mathbf{p}_i}{2m_i} \right| \psi_i \right\rangle; \quad (38)$$

2. Contribution from the ion–electron interaction:

$$\mathbf{m}_{ie} = -\frac{1}{6}e^2 \sum_i \int n(\mathbf{r}) V'_{\text{ion-e}}(|\mathbf{r} - \mathbf{R}_I|) \frac{(\mathbf{r} \times \mathbf{R}_I) \otimes (\mathbf{r} - \mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|} d^3\mathbf{r} \quad (39)$$

where $n(\mathbf{r})$ is the electron density, and $V_{\text{ion-e}}$ is the potential energy among nuclei and electrons;

3. Contribution from the ion–ion interaction:

$$\mathbf{m}_{ii} = -\frac{1}{6} \sum_{\substack{I,J \\ I \neq J}} Z_I Z_J \frac{(\mathbf{R}_I \times \mathbf{R}_J) \otimes (\mathbf{R}_I - \mathbf{R}_J)}{|\mathbf{R}_I - \mathbf{R}_J|^3} \quad (40)$$

where Z_I is the charge number of I -th ion (nucleus).

4. Contribution from the electron–electron interaction (the Hartree part):

$$\mathbf{m}_H = -\frac{1}{6} \iint n(\mathbf{r}) n(\mathbf{r}') \frac{(\mathbf{r} \times \mathbf{r}') \otimes (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (41)$$

Again the exchange-correlation part of the potential energy is isotropic in the case of local density approximation (LDA), and hence it does not contribute to the quantum couple stress.

6 Summary

The objective of studying higher-order quantum stress is to explore the atomistic origin of the continuum higher-order stress, so that it can help us design novel materials that exhibit desired higher-order effects, for example, the possible flexoelectric effects in advanced materials. In this paper, we have introduced a theory of the higher-order quantum stress, and we have derived for the first time the analytical expressions of the third-order quantum stresses and their expressions based on the Kohn–Sham density functional theory. In particular, we have derived the analytical expression of the quantum couple stress for anisotropic materials in ground state.

For crystalline, quasi-crystalline solids, or even some polymers, the continuum higher-order stress comes from two sources: (i) the polarized lattice structure or the polarized molecular structures, and (ii) the polarized electronic structures. Most time, these two are related, but they are not the same. The higher-order quantum stress derived in this paper is a second part of the origin of the continuum higher-order stress.

Finally, an important point that we would like to emphasize is even though we might refer to the quantum stress as the physical origin of the continuum stress, or continuum stress is the statistical manifestation of the quantum stress, but the concept of continuum stress can never replace the concept of quantum stress. This is because that at the atomistic scale or even nanoscale the concept of the continuum stress may not be valid anymore, and at small scale, quantum stress is the only meaningful physical quantity for measuring material stress state. Therefore, the formulas and expressions derived in this paper for the higher-order quantum stress provide theoretical foundation for a first-principle study on higher-order stress and their applications.

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