Quantum Notions of Stress

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Abstract: Existing notions of stress in a quantum mechanical framework are reviewed and discussed in a semitutorial manner suitable for a mechanics audience. Notwithstanding early fundamental work in this area since the 1930s, the increasing availability of computational tools to perform *ab initio* quantum mechanical calculations with high accuracy and efficacy has renewed interest in this field especially in the context of computational mechanics and materials science. Although some unresolved issues remain, the subject has evolved considerably in the past two decades with various authors offering their own unique viewpoint. In the present paper, we summarize the debate over the "definition" of stress in a quantum mechanical setting and discuss some controversial issues such as the uniqueness of the stress.

Introduction

The stress field in condensed matter is a distribution of internal tractions to balance the applied external tractions and body forces (Kosevich et al. 1986; Nye 2001; Sommerfeld 1950; Wilson 1957). Under the conditions of a homogeneous stress field within a large macroscopic volume, the stress can be related to internal variables such as density, temperature, and internal energy to complete the equation of state (Wilson 1957). The stress field which develops in response to applied deformation provides an important link between the physical material properties and the underlying microstructure. Deeper physical insights into a broad range of phenomena including surface reconstructions, physics at interfaces in solids, piezoelectricity, chemical reactivity, phase transitions, phonon dispersion, band gap-strain coupling (in semiconductors), defect energetics, phase transformations, strain induced phonon splitting, and many others entail an intimate knowledge of how the material will respond to deformation (Ibach 1997; Needs and Godfrey 1987; Needs et al. 1991; Fiorentini et al. 1993; Bach et al. 1997; Filippetti and Fiorentini 1999; Alerhand et al. 1988; Narasimham and Vanderbilt 1992; Mottet et al. 1992; Meunier et al. 1999; Meade and Vanderbilt 1989; Mavrikakis et al. 1998). A description of the stress involving electronic contributions therefore has to proceed in a quantum mechanical fashion. In this paper, we examine the existing literature that provides a quantum-mechanical footing to the well-known stress tensor of classical elasticity. Hereafter, we will use the terms "quantum stress" or "quantum mechanical stress" to denote the stress in a quantum mechanical framework.

There are several essentially equivalent ways to introduce the concept of stress in continuum mechanics. Consider a region of space Ω occupied by material points, loaded with a body force $\mathbf{b}$. The changes in the stored strain energy must depend upon the displacement vector. The invariance of the elastic energy to rigid translations, i.e., T(3) group and rigid rotations SO(3) group, restrict the elastic energy to be solely a function of the symmetric part of the deformation gradients and (if needed) higher order derivatives of the displacement fields. If further, linearity is assumed, then the elastic energy may be written as

$$W[\mathbf{u}] = \tfrac{1}{2}\langle\boldsymbol{\varepsilon}|\mathbf{C}|\boldsymbol{\varepsilon}\rangle \qquad (1)$$

Here $\boldsymbol{\varepsilon}$=symmetric infinitesimal strain tensor defined as $\boldsymbol{\varepsilon}=\mathrm{sym}(\nabla\mathbf{u})$; $\mathbf{C}$=the fourth-order elasticity tensor that parametrizes the changes in elastic energy due to deformation and must be either obtained from microscopic (i.e., quantum) calculations or empirically. Given the explicit and implicit postulates in Eq. (1), the remainder of classical linear elasticity immediately follows from the standard variational approach for deriving field theoretic equations. Stress in particular, which characterizes the resistance to mechanical deformation, then follows as

$$\boldsymbol{\sigma} = \mathbf{C}|\boldsymbol{\varepsilon}\rangle \qquad (2)$$

Euler-Lagrange equations of the functional in Eq. (1) (or more physically, balance of momentum) yield the connection between stress and body forces:

$$\mathrm{div}\,\boldsymbol{\sigma} + \mathbf{b} = 0 \qquad (3)$$

Investigations into the quantum mechanical definition of stress were well preceded by early fundamental work on the concept of quantum mechanical force (Ehrenfest 1927; Pauli 1958; Hellman 1937; Feynman 1939a,b) and pressure (Born et al. 1926; Finkelstein 1928; Hylleraas 1929; Fock 1930; Slater 1933, 1963, 1967). Ehrenfest's theorem (Ehrenfest 1927), which states that *the net force on a particle is given by the expectation value of the negative of the gradient of the potential*, is such an example. We will discuss Ehrenfest's theorem in more detail shortly. Pauli,

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Hellmann, and Feynman (Pauli 1958; Hellman 1937; Feynman 1939a,b) modified Ehrenfest's theorem to a form appropriate for application to forces between molecules. The consequences of the so-called "Hellmann-Feynman" theorem are significant. Previously, forces within molecules and associated problems involving the estimation of lattice constants, calculations of phase transitions, elastic properties, phonon dispersion, stiffness of valence bonds, and others were addressed invoking the energy formalism in an indirect manner. These usually involve calculations of energy for several neighboring configurations of the molecule; the force is then obtained by determining the slope of the plot of energy versus position. The Hellmann-Feynman theorem offers a direct way to estimate the force for a given configuration, given that only the particular configuration of interest is known. The quantum mechanical virial theorem, which states that *the total pressure in a many-body quantum mechanical system is defined by the kinetic energy and the virial of the potential* (much like its classical counterpart), also attracted attention from authors including Born, Heisenberg, and Jordan, Fock, and several others (Born et al. 1926; Finkelstein 1928; Hylleraas 1929; Fock 1930; Slater 1933, 1963, 1967; Ross 1969). Though several early works of varying levels of sophistication have considered the quantum mechanical stress tensor (Pauli 1958; Feynman 1939a,b; Schrödinger 1927; Martin and Schwinger 1959; Kugler 1967; McLellan 1974, 1984; Folland 1981), we will mostly focus on Nielsen and Martin's (1983, 1985a) work on the quantum mechanical formulation of the stress tensor and subsequent works (Folland 1986; Ziesche and Lehmann 1987; Ziesche et al. 1988; Godfrey 1988; Chetty and Martin 1992; Feibelman 1994; Dal Corso and Resta 1994; Passerone et al. 1999; Filippetti and Fiorentini 2000; Pendas 2002; Rogers and Rappe 2002) that can be considered to be offshoots or extensions of the latter. The analysis of the local behavior of stress, i.e., a field theoretic description of the quantum mechanical stress, has been subject to different interpretations though a general consensus seems to exist amongst various authors as regards the *macroscopic* or the *total* stress tensor. A related problem is the nonuniqueness of the quantum mechanical stress field; indeed this issue exists in classical mechanics too but is addressed by invoking a phenomenological constitutive relation between stress and strain [see Eqs. (1) and (2)]. More recently, Rogers and Rappe (2002) have offered a differential geometric formulation of the stress tensor.

The rest of this paper is organized as follows. In the second section we recapitulate the essentials of quantum dynamics primarily intended for a mechanics audience. The writers assume throughout that the reader has at least a cursory acquaintance with quantum mechanics and the section is simply purported to serve as a rather pedestrian refresher. The Ehrenfest theorem is also discussed in this section. Then we provide, intermixed with a literature review, a discussion on the quantum definition of stress. We conclude with a summary where we also present a personal viewpoint on some future research avenues in this research topic.

Preliminaries

Summary of Quantum Mechanics Essentials

Quantum mechanics is presently the *ab initio physical theory* which describes the motion and interaction of particles at "very small" scales and forms the principal framework for many modern day subfields of physics, chemistry, and materials science. Quantum mechanics, as a theory, has stood the test of time and a

century's worth of experiments has only served the cause that quantum mechanics is indeed the correct theory of matter. Quantum mechanics, however, is known to be in direct conflict with the predictions of general relativity when one applies it to regions in the vicinity of black holes or when one considers the universe as a whole. Unifying quantum mechanics and general relativity is one of the major challenges of today but not of much consequence in the present context. A striking feature of quantum mechanics is that it denies the possibility of simultaneously assigning exact values to both the position and momentum of a particle in clear contrast to the deterministic classical (Newtonian) physics. This is the consequence of the celebrated *Heisenberg's uncertainty principle*. Thus, quantum behavior is inherently probabilistic often accounting for its nonintuitive (from the classical viewpoint) predictions.

The principal postulates of quantum mechanics are the following (Greiner 1994; Griffiths 1994):

1. The state of a particle is characterized by a complex scalar quantity called the *wave function*, often represented as $\Psi(\mathbf{r},t)$. This wave function contains *all* such information about the quantum mechanical system such that, in principle, any measurable quantity (referred to as a *physical observable*) can be extracted from it.

2. The second postulate concerns the probabilistic or statistical interpretation of quantum mechanics. For example, if the wave function is expressed in terms of position then the square of the magnitude of the wave function is the probability density of particle's position.

3. The third postulate states that the result of a measurement on a system yields only those values which are the eigenvalues of the operator corresponding to that observable. The eigenfunctions corresponding to that operator form a complete set. In other words, one can describe any state of the system by a combination of either position eigenfunctions or momentum eigenfunctions or energy eigenfunctions. To relate a quantum mechanical calculation to a measurable/observable, the *expectation value* of the corresponding observable is calculated. The expectation value of an operator is the average of its eigenvalues weighted with the corresponding probabilities. In other words, the expectation value of an operator yields the average of an infinite number of measurements of the observable corresponding to the operator. In particular, the expectation value of an operator $\hat{A}$ is defined as

$$A = \int_V \Psi^* \hat{A} \Psi \, dV \qquad (4)$$

In general the wave function Ψ=complex scalar and Ψ^* denotes the complex conjugate of Ψ. Note that the expectation value given by Eq. (4) itself need not be equal to a single measurement (eigenvalues), e.g., the centroid of a ring (which is empty space) is the average position of all the material points that constitute the ring.

4. The fourth postulate states that the time evolution of the wave function $\Psi(\mathbf{r},t)$ is described by the time-dependent Schrödinger's equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r},t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t) \qquad (5)$$

Schrödinger's equation is frequently written as

$$\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = -\frac{i}{\hbar}\hat{H}\Psi(\mathbf{r},t) \qquad (6)$$

The operator $\hat{H}$=Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad (7)$$

In analogy with classical physics, the first term on the right-hand side of Eq. (7) represents the kinetic energy of the system and thus classical notions such as momentum, energy, and others are represented by operators, e.g., momentum corresponds to $\hat{p}=i\hbar\nabla$. The expectation value of the momentum of a quantum mechanical system simply entails application of Eq. (4).

An alternative but equivalent approach to describing quantum mechanics is due to Heisenberg. Implicit to Schrödinger's scheme is the notion that the state functions evolve with time while the operators, representing the dynamical variables of the system, do not change with time (unless they contain some *specific* time-dependence). In the Heisenberg description, the situation is reversed: whereas the wave functions are time-independent, the dynamical evolution is described by time-dependent operators. An operator $\hat{L}$ in the Schrödinger picture is transformed into the Heisenberg picture to $\hat{L}_H(t)$ by a unitary time-dependent transformation

$$\hat{L}_H(t) = \hat{S}^\dagger(t)\hat{L}\hat{S}(t) \qquad (8)$$

The operator $\hat{S}(t)$ is

$$\hat{S}(t) = \exp\left(-\frac{i}{\hbar}\hat{H}t\right) \qquad (9)$$

Thus, *the dynamical variable, which corresponds to a fixed linear operator in Schrödinger's scheme, is a moving linear operator in Heisenberg's equations of motion.*

The equation of motion then becomes

$$i\hbar\frac{d\hat{L}_H(t)}{dt} = \hat{L}_H(t)\hat{H}_H - \hat{H}_H\hat{L}_H(t) \qquad (10)$$

Eq. (10) can be rewritten as

$$\frac{d\hat{L}_H(t)}{dt} = -\frac{i}{\hbar}[\hat{L}_H(t),\hat{H}_H] \qquad (11)$$

Here the Poisson bracket $[\hat{L}_H(t),\hat{H}_H]$ is defined as

$$[\hat{L}_H(t),\hat{H}_H] = \hat{L}_H(t)\hat{H}_H - \hat{H}_H\hat{L}_H(t) \qquad (12)$$

Ehrenfest's Theorem

Heisenberg's equation of motion for the momentum operator yields

$$\frac{d\hat{p}_i}{dt} = \frac{1}{i\hbar}[\hat{p}_i,\hat{H}] = -\frac{\partial V(\mathbf{x})}{\partial x_i} \qquad (13)$$

Also we have

$$\frac{d\hat{x}_i}{dt} = \frac{1}{i\hbar}[\hat{x}_i,\hat{H}] = \frac{\hat{p}_i}{m} \qquad (14)$$

Applying Heisenberg's equations of motion once again to Eq. (14), we obtain

$$\frac{d^2\hat{x}_i}{dt^2} = \frac{1}{i\hbar}\left[\frac{d\hat{x}_i}{dt},\hat{H}\right] = \frac{1}{i\hbar}\left[\frac{\hat{p}_i}{m},\hat{H}\right] = \frac{1}{m}\frac{d\hat{p}_i}{dt} = -\frac{1}{m}\frac{\partial V(\mathbf{x})}{\partial x_i} \qquad (15)$$

In vectorial form a more elegant form emerges

$$m\frac{d^2\hat{\mathbf{x}}}{dt^2} = \frac{d\hat{\mathbf{p}}}{dt} = -\nabla V(\mathbf{x}) \qquad (16)$$

The resemblance of Eq. (16) to Newton's second law is obvious. Taking expectation values of both sides of Eq. (16) with respect to a Heisenberg state function (which does not move with time) we obtain the so-called Ehrenfest's theorem (Ehrenfest 1927)

$$m\frac{d^2\langle\hat{\mathbf{x}}\rangle}{dt^2} = \frac{d\langle\hat{\mathbf{p}}\rangle}{dt} = -\langle\nabla V(\mathbf{x})\rangle \qquad (17)$$

Strikingly, Eq. (17) has no dependence upon $\hbar$ and appears identical to the equation of motion of a classical particle in a potential field. Thus, Ehrenfest's theorem serves as an important step in bridging classical and quantum mechanics.

Stress in Quantum Mechanics

Stress Theorem: Average Macroscopic Stress

The so-called "stress theorem" (Nielsen and Martin 1983, 1985a) provides the average macroscopic stress for arbitrary systems of interacting particles in the ground state. This average stress is in fact an energy-like quantity which can be obtained by taking a volume integral of the *microscopic* locally varying stress *field*. The generalized quantum-mechanical virial theorem (Fock 1930) appears to motivate the form of the average stress tensor in the stress theorem derived by Nielsen and Martin (NM) (1983b, 1985a). As we shall observe shortly, NM's stress theorem is but a generalization of the quantum mechanical virial theorem.

NM's derivation of the Stress theorem essentially follows the same scaling argument that Fock (1930) proposed in his work on the quantum mechanical virial theorem. Consider the following many-body quantum mechanical Hamiltonian:

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V_{\text{int}} + V_{\text{ext}} \qquad (18)$$

where $\mathbf{p}_i$=momentum of the ith particle (i can represent both nuclei and electrons). Please note that henceforth we will refrain from using the caret to denote operators. For example, the operator $\hat{H}$ will be simply written as H. While in most places the distinction between an operator and the corresponding expectation value can be made based on context, we will explicitly mention the distinction if a potential for confusion exists. The internal part of the potential energy denoted by V_{int} is intrinsic to the system (say Coulombic interaction between particles) while V_{ext} arises due to external influences. Out of the several eigenstates Ψ obtained by solving the Schrödinger's equation, $H\Psi = E\Psi$, the ground state is obtained by determining a minimum of the expectation value of the energy $\langle\Psi|H|\Psi\rangle$, with respect to all the variations of Ψ. All the observables pertain to this ground state.

To introduce the notion of *stress*, the wave function $\Psi(\mathbf{r})$ in its ground state is homogeneously *scaled* by means of the following transformation on each material coordinate

$$\mathbf{r} \to \mathbf{r} + \boldsymbol{\varepsilon}\mathbf{r} \qquad (19)$$

where $\mathbf{r}$ represents the particle coordinate and $\boldsymbol{\varepsilon}$=symmetric strain tensor.

The scaled wave function then assumes the following form

$$\Psi_{\boldsymbol{\varepsilon}}(\mathbf{r}) = \det(\mathbf{I} + \boldsymbol{\varepsilon})^{-1/2}\Psi((\mathbf{I} + \boldsymbol{\varepsilon})^{-1}\mathbf{r}) \qquad (20)$$

Here $\mathbf{I}$=identity tensor. The additional factor of $\det(\mathbf{I} + \boldsymbol{\varepsilon})^{-1/2}$ in Eq. (20) is included to ensure that the new scaled wave function is normalizable. The expectation value of the energy is

$$\langle \Psi_{\varepsilon}|H|\Psi_{\varepsilon}\rangle = \int \Psi^*(\mathbf{r})\left[\frac{\mathbf{p}_i^2 - 2\boldsymbol{\varepsilon}\cdot(\mathbf{p}_i \otimes \mathbf{p}_i) + \boldsymbol{\varepsilon}^2\cdot(\mathbf{p}_i \otimes \mathbf{p}_i)}{2m_i}\right.$$
$$\left. + V_{\mathrm{int}}((1+\boldsymbol{\varepsilon})\mathbf{r}) + V_{\mathrm{ext}}((1+\boldsymbol{\varepsilon})\mathbf{r})\right]\Psi(\mathbf{r})d\mathbf{r} \qquad (21)$$

This energy is required to be stationary with respect to variations of applied strain, i.e.

$$\sum_i \left\langle \Psi\left|\frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i} - \nabla_i(V_{\mathrm{int}} + V_{\mathrm{ext}}) \otimes \mathbf{r}_i\right|\Psi\right\rangle = 0 \qquad (22)$$

Based on Eq. (22), NM (1985a) identify the stress exerted by the external environment as

$$\mathbf{T} = -\sum_i \langle \Psi|\nabla_i(V_{\mathrm{ext}}) \otimes \mathbf{r}_i|\Psi\rangle \qquad (23)$$

The internal stress, which develops in response, is identified as

$$\mathbf{T} = \mathbf{T}_{\mathrm{kin}} + \mathbf{T}_{\mathrm{pot}} \qquad (24)$$

where $\mathbf{T}_{\mathrm{kin}}$ and $\mathbf{T}_{\mathrm{pot}}$=kinetic and potential contributions, respectively, to the total stress. From Eq. (22), their forms can be inferred to be

$$\mathbf{T}_{\mathrm{kin}} = -\sum_i \left\langle \Psi\left|\frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i}\right|\Psi\right\rangle$$
$$\qquad (25)$$
$$\mathbf{T}_{\mathrm{pot}} = \sum_i \langle \Psi|\nabla_i(V_{\mathrm{int}}) \otimes \mathbf{r}_i|\Psi\rangle$$

The averaged internal stress $\mathbf{T}$ in Eq. (25) is the *total macroscopic stress* expressed only in terms of operators intrinsic to the system. Eq. (25) is one form of the *stress theorem*.

When V_{int}=simple pair potential (say, a Coulombic interaction) of the form

$$V_{\mathrm{int}} = \frac{1}{2}\sum_{i,j} V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|), \quad j \neq i \qquad (26)$$

then Eq. (25) becomes

$$\mathbf{T} = -\sum_i \left\langle \Psi\left|\frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i}\right|\Psi\right\rangle$$
$$- \frac{1}{2}\sum_{i,j}\left\langle \Psi\left|\frac{(\mathbf{r}_i - \mathbf{r}_j) \otimes (\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|}V'_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)\right|\Psi\right\rangle \qquad (27)$$

The stress tensor of Eq. (27) is symmetric. The macroscopic "stresses" in Eqs. (23) and (25) have dimensions of energy, thereby if the volume of the system Ω is well defined (for example, a unit cell of a crystal), then it is typical to employ an *average stress density*. The average stress density τ (which has the dimensions of stress or pressure as used in continuum elasticity) is defined by $\tau = \mathbf{T}/\Omega$ to represent the state of stress. The

pressure, P, then is derived straightforwardly by taking the trace of both sides of Eq. (27)

$$3P\Omega = 2\sum_i \frac{\langle \Psi|\mathbf{p}_i^2|\Psi\rangle}{2m_i} - \frac{1}{2}\sum_i \langle \Psi||\mathbf{r}_i - \mathbf{r}_j|V'_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)|\Psi\rangle, \quad (j \neq i)$$
$$\qquad (28)$$

An interesting aspect of Eq. (28) pointed out by NM (1985a) is that if all the interactions obey the power law of the form $V_{ij}(x) \sim x^{-n}$, then the familiar form of the virial theorem $(3P\Omega = 2E_{\mathrm{kin}} + E_{\mathrm{pot}})$ follows

$$3P\Omega = 2\sum_i \frac{\langle \Psi|\mathbf{p}_i^2|\Psi\rangle}{2m_i} - \frac{1}{2}\sum_i \langle \Psi|V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)|\Psi\rangle, \quad (j \neq i)$$
$$\qquad (29)$$

Quantum Mechanical Stress and Force Fields

Thus far we have considered the average "macroscopic" stress (stress theorem) and the average macroscopic force (Ehrenfest/Hellmann-Feynman theorem) acting upon a system of particles. However, these treatments do not bring about the *field nature* of stress and force. In other words, the point-to-point spatial variation of the stress and force fields is (obviously) lost in the process of averaging over a macroscopic volume. If one, however, knows the spatially varying stress field, the ramifications can be important. Spatial variations in the "planar stress" can provide an insight into the forces operating in systems which are not in equilibrium (NM 1985a).Filippetti and Fiorentini (1999, 2000) envision using the microscopic stress as what they refer to as a "stress microscope" to examine the microscopic stress's role in explaining the physics of certain surface and interface phenomena. Ramer et al. (1998) applied the microscopic stress field to study piezoelectric effects in perovskites. While the local force field is uniquely specified in terms of kinetic and potential operators (Pauli 1958), the stress field, on the other hand, can only be specified to an arbitrary gauge term (explained shortly) (Feynman 1939a,b). Traditionally, the stress field $\boldsymbol{\sigma}(\mathbf{r})$ is defined as any two-tensor field whose divergence yields the force field of the system

$$\mathbf{f}(\mathbf{r}) = \mathrm{div}\,\boldsymbol{\sigma}(\mathbf{r}) \qquad (30)$$

To this stress field $\sigma_{ij}(\mathbf{r})$ one can add a term of the form

$$\frac{\partial}{\partial r_k}A_{ijk}(\mathbf{r}) \qquad (31)$$

where $A_{ijk}(\mathbf{r})$=arbitrary tensor field antisymmetric in j and k and recover the same force field of Eq. (30). Thus, the stress field is undetermined to an arbitrary gauge term if one chooses to define it via Eq. (30). In particular, consider the curl of an arbitrary two-tensor $H(\mathbf{r})$

$$(\nabla \times H(\mathbf{r}))_{ij} = \epsilon_{ijk}\frac{\partial H_{kl}(\mathbf{r})}{\partial r_l} \qquad (32)$$

ϵ_{ijk}=well-known Levi-Civita symbol. The term on the right-hand side of Eq. (32) has the same properties as those required of the term in Eq. (31). Thereby we conclude that one can add the curl of an arbitrary dyadic field to the stress field of Eq. (30) and still recover the same force field. This is the gauge-arbitrariness associated with the microscopic stress field.

NM (1985a) approach the microscopic stress tensor (MST) by invoking Heisenberg's equation of motion of the symmetrized momentum density operator. The symmetrized momentum density operator for a particle "i" is defined as

$$\mathbf{P}_i = \frac{1}{2}[\mathbf{p}_i, \delta(\mathbf{r} - \mathbf{r}_i)]_+ \tag{33}$$

The notation $[\;]_+$ denotes the anticommutator operator and $\mathbf{r}$ = spatial coordinate. (Given two operators A and B, the anticommutator operator $[A, B]_+$ is defined as $[A, B]_+ = AB + BA$.) The time derivative of $\mathbf{P}_i(\mathbf{r})$ is identified as the force-density *operator* on particle i and NM (1985a) provide the following equation of motion for it

$$\frac{\partial P_{i\alpha}}{\partial t} = \frac{1}{i\hbar}[P_{i\alpha}, H] = -\frac{1}{4m_i}\left[p_{i\alpha}, \sum_\beta [p_{i\beta}, \nabla_\beta(\delta(\mathbf{r} - \mathbf{r}_i))]_+\right]_+$$
$$- \nabla_{i\alpha}(V_{\text{int}} + V_{\text{ext}})\delta(\mathbf{r} - \mathbf{r}_i) \tag{34}$$

The equation of motion for $\mathbf{P}$, Eq. (34), *is a continuity equation where the momentum flux density operator has the properties of a stress tensor operator.*

The net force acting on particle i is then obtained by integrating Eq. (34) over space. The integrals of derivatives of wave functions, which occur on integrating the kinetic energy term (the first term on the right-hand side, representing the motion of the particles), can be expressed in terms of functions and derivatives of wave functions at infinity, which are zero by definition. Therefore the kinetic energy term, on integration, yields zero for a finite system. On integrating both sides of Eq. (34) all over space, NM (1985a) obtain

$$\frac{\partial \mathbf{p}_i}{\partial t} = \frac{1}{i\hbar}[\mathbf{p}_i, H] = -\nabla_i(V_{\text{int}} + V_{\text{ext}}) \tag{35}$$

On taking expectation values of both sides of Eq. (35) for a stationary system, $\langle \partial \mathbf{p}_i/\partial t \rangle$ becomes zero and yields Ehrenfest's theorem

$$F_i = -\langle \nabla_i V_{\text{int}} \rangle \tag{36}$$

F_i = internal force, which is canceled exactly by the external force and $F_{i,\text{ext}} = -\langle \nabla_i V_{\text{ext}} \rangle$ acting on particle i.

The MST $\boldsymbol{\sigma}(\mathbf{r})$ can now be defined such that its divergence results in the vector force density field. The internal stress field developed due to internal interactions and motion of particles (in response to external forces) then follows

$$\nabla \cdot \boldsymbol{\sigma}(\mathbf{r}) = \left\langle \sum_i \frac{\partial \mathbf{P}_i}{\partial t} + \nabla_i V_{\text{ext}}\delta(\mathbf{r} - \mathbf{r}_i) \right\rangle \tag{37}$$

The stress field given by Eq. (37) can be determined only unto the inclusion of the curl of an arbitrary tensor field. Thus, *the stress field is not uniquely defined.* The *macroscopic* stress tensor is unaltered by the addition of this arbitrary curl tensor as the curl term integrates to zero when Eq. (37) is integrated over all space for finite systems, for periodic systems, and for integrals over infinite planes. NM (1985a) believe that microscopic stress fields in quantum theory are not physical observables, and thus one cannot uniquely specify exact expressions for the dynamical operators which correspond to the microscopic stress $\boldsymbol{\sigma}(\mathbf{r})$. The physically observable macroscopic stresses $\mathbf{T}$, on the other hand, are unaffected by the addition of this arbitrary curl. However, this viewpoint is not shared by all authors and some controversy exists regarding the issue of quantum stress uniqueness. Folland (Folland 1986; NM 1988), for example, claims that since the

MST features in a continuity-like equation for the force-density, MSTs can be viewed as physical observables and thereby should be unique.

If the nonuniqueness or gauge arbitrariness of the MST is accepted then the gauge arbitrariness, in principle, allows one to choose a stress field according to a specific situation/problem (as convenient). Kugler (1967) proposed a form for the microscopic stress tensor satisfying Eq. (37) which applies for arbitrary interactions V_{int}. Kugler's form of stress (added to the kinetic contribution) is given in the following:

$$\sigma_{\alpha\beta}(\mathbf{r}) = -\sum_i \frac{1}{4m_i}\langle[p_{i\alpha}, [p_{i\beta}, \delta(\mathbf{r} - \mathbf{r}_i)]_+]_+\rangle$$
$$+ \sum_i \frac{1}{4\pi}\langle \nabla_{i\alpha}(V_{\text{int}})\nabla_\beta(|\mathbf{r} - \mathbf{r}_i|^{-1})\rangle \tag{38}$$

The first term on the right-hand side representing the kinetic contribution is due to Pauli (1958). This term, being symmetric, does not contribute to the torque density, which is generated by the antisymmetric part of the stress. The kinetic term contains both a gradient term and a curl term; the curl term does not contribute to the force density (being the divergence of the stress tensor). The second term on the right-hand side of Eq. (38), which denotes the potential stress, has no curl term but is asymmetric and therefore may contribute to the torque density.

As also noted by other, Kugler's stress definition contains some objectionable features. Even if the interactions defined by V_{int} are short-ranged, the curl-free nature of the potential term renders the Kugler stress inherently long-range and thus nonlocal. In particular, the long-range character of the Kugler stress derives from the term $\nabla(|\mathbf{r} - \mathbf{r}_i|^{-1}) = (\mathbf{r} - \mathbf{r}_i)/|\mathbf{r} - \mathbf{r}_i|^3$. The Kugler stress corresponding to the interaction between two particles A and B can be visualized as a radial flow of momentum from A to infinity, superimposed on a radial flow from infinity to B. This makes it possible to assign a distribution of sources at infinity which need not bear any relation to the actual physical sources. The issue of the long-range character of the Kugler stress may be partially circumvented by computing stress by summing over pairs of interacting particles thereby resulting in a dipole-like long-range distance dependence of the form $\sim 1/r^3$. Note that this form of stress field is still long-range albeit of a somewhat weaker form than the original form. When the interaction is Coulombic, the Kugler's form of stress results in severe anomalies and a different form of the stress tensor called the Maxwell form (Feynman 1939a,b; Jackson 1999) is employed. The latter is applicable for particles interacting via Coulombic forces. In the static limit (in the absence of magnetic effects), Maxwell's stress field is given as

$$\boldsymbol{\sigma}_M(\mathbf{r}) = -\frac{1}{4\pi}\left\langle \mathbf{E}(\mathbf{r}) \otimes \mathbf{E}(\mathbf{r}) - \frac{1}{2}\mathbf{I}|\mathbf{E}(\mathbf{r})|^2 \right\rangle \tag{39}$$

The operator $\mathbf{E}(\mathbf{r})$ is the electric field due to charges Z_i with positions $\mathbf{r}_i$ according to

$$\mathbf{E}(\mathbf{r}) = \sum_i Z_i \frac{(\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3} \tag{40}$$

Of course one has to add the kinetic contribution [given by the first term on the right-hand side of Eq. (38)] to the stress field of Eq. (39). The Maxwell form of stress is symmetric and is bereft of the long-range character that plagues the Kugler's form. NM (1985a) illuminate this point by considering the example of a hydrogen atom and an ion, H^+ and H. In particular, for the H

atom, the long-range behavior of the Maxwell stress is found to be particularly agreeable in comparison to the Kugler's form. Whereas Kugler's stress decays only as r^{-3} (which is rather unphysical), the Maxwell's stress exhibits an r^{-6} dependence which bears the expected resemblance to the van der Waal forces for neutral atoms. NM also point out an important caveat while employing Kugler's form for the stress field near a surface or an interface. The Kugler stress decays slowly away from the plane of a surface or an interface; since the Kugler's stress is not explicitly given in terms of relative coordinates, it is ill-defined in the limit of an infinite plane. This characteristic nonlocality is a major pitfall while applying the Kugler's form of stress in the vicinity of surfaces and interfaces. Godfrey (1988) has proposed a form of stress which, analogous to the Kugler's form of stress, holds for arbitrary interactions but is devoid of the long-ranged character.

The total force on all the particles in a volume Ω can be expressed as a surface integral of the microscopic stress field over the surface S bounding Ω. Thus from Eq. (30), the total force is

$$F_{\Omega\alpha} = \int_S \sum_\beta \sigma_{\alpha\beta}(\mathbf{r})\hat{n}_\beta dS \qquad (41)$$

where $\mathbf{F}_\Omega$=total force acting on all particles in volume Ω, $\sigma_{\alpha\beta}(\mathbf{r})$ is the microscopic stress field, and $\hat{\mathbf{n}}$ is the normal unit vector at the surface. The kinetic term of Eq. (41) involves only the derivatives of the wave function on the surface and the potential term involves only the evaluation of forces on particles inside the closed surface S, since the integral of $\hat{\mathbf{n}} \cdot \nabla|\mathbf{r}-\mathbf{r}_i|^{-1}/4\pi$ is unity if $\mathbf{r}_i$ is inside the surface, and zero if $\mathbf{r}_i$ is outside. Employing the Kugler's form of stress, the expression for total force from Eq. (41) reads

$$F_{\Omega\alpha} = -\sum_i \frac{1}{4m_i} \int_S \langle[p_{i\alpha},[\mathbf{p}_i \cdot \hat{\mathbf{n}},\delta(\mathbf{r}-\mathbf{r}_i)]_+]_+\rangle dS - \sum_i \langle\nabla_{i\alpha}(V_{\mathrm{int}})\rangle_\Omega$$

$$(42)$$

The subscript Ω on the final term indicates that the summation is restricted to particles inside the volume Ω. The interactions between particles that are entirely inside or entirely outside the surface do not contribute to the total force on particles inside the volume Ω NM (1985a). Therefore the final term of Eq. (42) can be determined simply by considering interactions that cross the boundary S.

Eq. (42) is particularly advantageous when one tries to evaluate the force $F_{\Omega\alpha}$, when the surface is chosen such that it does not pass through any ion core. One just needs to consider the kinetic terms at the boundary, which involve only the valence-electron states. To this one adds the potential terms crossing the boundary. The potential forces from the nuclei can be combined with those from the core electrons in case of spherical ion cores, to result in an electrostatic field of point ions with charge $Z_{\mathrm{ion}}=Z_{\mathrm{nucleus}}-Z_{\mathrm{core}}$. Further, while evaluating the force, one need not consider the complex node structure that the valence electron wave functions possess in the core region, because the crossing potential terms only require the total valence charge in the core region. On the other hand, one needs to take into consideration the core states while evaluating the total force and stress using the volume integrals of Eqs. (25) and (27). Also, when the effect of the core electrons is replaced by a nonlocal pseudopotential, the evaluation of nonlocal terms can be avoided if one computes the forces and stresses using a surface sufficiently far away from the core region where the effect of the nonlocal corrections is negligible.

To introduce an alternate route to the macroscopic stress tensor through the MST, NM (1985a) consider an infinite surface which divides the entire space into two infinite regions. If one of the regions is denoted as Ω then Eq. (42) will yield the net force that the remainder of the space exerts on Ω in the α-direction. In particular, assume an infinite plane P_β, perpendicular to the β-axis and intersecting the β-axis at r_β, as the partitioning surface. Then Eq. (42) provides a "planar stress" $S_{\alpha\beta}(r_\beta)$ which represents the force in the α direction transmitted across P_β

$$S_{\alpha\beta}(r_\beta) = -\sum_i \frac{1}{4m_i}\langle[p_{i\alpha},[p_{i\beta},\delta(\mathbf{r}-\mathbf{r}_{i\beta})]_+]_+\rangle$$

$$-\sum_i \left\langle \nabla_{i\alpha}(V_{\mathrm{int}})\frac{1}{2}\,\mathrm{sgn}(r_\beta - r_{i\beta})\right\rangle \qquad (43)$$

Note that the planar stress is a function of r_β (and not the vector $\mathbf{r}$) and thus is a constant over the surface P_β. The familiar macroscopic stress tensor is obtained by integrating the planar stress $S_{\alpha\beta}(r_\beta)$ with respect to r_β. When the solid is in equilibrium then $\sigma_{\alpha\beta}(\mathbf{r})$ has zero divergence, which renders $S_{\alpha\beta}(r_\beta)$ a constant tensor. An interesting application suggested by NM (1985a) is that if some atoms are not in their equilibrium positions, the variations in the planar stress can provide knowledge of the forces involved.

Density Functional Approach: Kohn-Sham Method

The expressions for the stress tensors in preceding sections appear reasonably facile at a casual glance but in fact conceal a full many-body quantum mechanical problem in the form of correlation functions which appear in the potential contributions. The density functional theory (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965; Sham and Kohn 1966; Jones and Gunnarsson 1989; Bamzai and Deb 1981) originally proposed by Hohenberg and Kohn (1964) provides a viable computational approach to implement the quantum stress formalism. DFT also provides a prescription to map the many-body problem onto a single-body problem [Kohn-Sham approach (Kohn and Sham 1965)]. These simplifications are achieved by touting the single particle density $\rho(\mathbf{r})$ to the status of the crucial observable. This is justified on the basis of the Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) which states that: *for both nondegenerate and degenerate ground states of many-electron systems, the energy is a unique functional of the single particle density*. Given the ground state density, it is possible in principle to calculate the corresponding ground state wave function. The simplification that results is unprecedented: (1) the single particle density is a function of only one (vectorial) variable unlike the wave function which is a function of N variables, N being the number of particles in the system; (2) the single particle density can be related to classical concepts; and (3) the single particle density can be measured directly from experiments. Even for excited states, the single particle density can be exploited to yield extensive information about the state. Within the general umbrella of the DFT concept, variations of different sophistication exist mostly differentiated by how the exchange-correlation functional is handled (to be discussed shortly). Several authors (Nielsen and Martin 1985a; Folland 1986; Ziesche et al. 1988; Godfrey 1988; Filippetti and Fiorentini 2000; Rogers and Rappe 2002) have employed DFT to investigate quantum stresses and have provided expressions for the form of the stress tensor (both macroscopic and microscopic) under its formalism.

The Kohn-Sham method (Kohn and Sham 1965) is one of the most popular approaches to DFT. Under the Kohn-Sham formalism, DFT becomes an effective "single-body" theory. Interestingly, one does not (explicitly) deal with the particle density $\rho(\mathbf{r})$ in the Kohn-Sham approach! Rather, *noninteracting single-particle wave functions* are introduced. Remember that the extraordinary simplification that results from DFT is due to the fact that one need not deal with wave functions any longer. However, the wave functions that feature in the Kohn-Sham approach are special in that they are noninteracting, single-particle wave functions.

Assuming the nuclei positions to be fixed, the total energy E under the Kohn-Sham formalism can be written as

$$E = T_{\mathrm{KS}} + E_{\mathrm{Coulomb}} + E_{\mathrm{XC}} \qquad (44)$$

where T_{KS}=Kohn-Sham kinetic energy of a *noninteracting* electron system (i.e., an electron gas). E_{Coulomb}=classical Coulomb interaction energy, which can be split into ion-ion, ion-electron, and electron-electron (Hartree part), respectively; and E_{XC}=exchange-correlation energy as a functional of the electronic charge density. NM (1985a) prefer to add the Kohn-Sham kinetic energy T_{KS} and the exchange-correlation energy E_{XC} together and write is as a functional $F[\rho]$. This is justified on the basis of the Hohenberg-Kohn theorem (Hohenberg and Kohn 1964).

The energy can now be written as

$$E = E_{\mathrm{ion\text{-}ion}} + E_{\mathrm{ion\text{-}electron}} + E_{\mathrm{Hartree}} + F(\rho) \qquad (45)$$

where $E_{\mathrm{ion\text{-}ion}}$=Coulombic interaction energy between ions.

The electrostatic interaction between ions and electrons is given by $E_{\mathrm{ion\text{-}electron}}$

$$E_{\mathrm{ion\text{-}electron}} = \int \rho(\mathbf{r}) \sum_i V_{\mathrm{ion\text{-}electron}}(\mathbf{r} - \mathbf{R}_i) d^3 r \qquad (46)$$

where $V_{\mathrm{ion\text{-}electron}}(\mathbf{r} - \mathbf{R}_i)$=ion-electron potential and $\rho(\mathbf{r})$=electronic charge density. The Hartree term E_{Hartree}, represents the self-interaction amongst the electrons and is given by

$$E_{\mathrm{Hartree}} = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r \, d^3 r' \qquad (47)$$

The functional $F[\rho]$ is

$$F[\rho] = \sum_i \left\langle \Psi_i \left| \frac{\mathbf{p}_i^2}{2m_i} \right| \Psi_i \right\rangle + E_{\mathrm{XC}}[\rho] \qquad (48)$$

The electronic density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = \sum_i |\Psi_i|^2 \qquad (49)$$

The single-orbital wave functions Ψ_i arise out of the Kohn-Sham scheme. In particular, the many-body electronic system in a potential $v(\mathbf{r})$ is replaced by a noninteracting single-body system in an auxiliary potential say $v_s(\mathbf{r})$; the corresponding Schrödinger's equation is solved to yield the single-particle wave functions Ψ_i. The potential $v_s(\mathbf{r})$ is such that the orbitals Ψ_i reproduce the density $\rho(\mathbf{r})$ of the original system according to Eq. (47).

On a related note, the diverging nature of the terms containing Coulombic interactions in Eq. (45) is taken care of by adding neutralizing background charge densities and treated by means of

the Ewald transformation (Fuchs 1935). The contribution to stress due to Coulombic interactions is most conveniently represented by the Maxwell stress tensor.

Though the decomposition shown in Eq. (45) is formally exact, the exact form of the exchange and correlation functionals $E_{\mathrm{XC}}[\rho]$ is unknown. To overcome this problem, recourse is often sought in some approximations, a common choice of which is the local density approximation (LDA) (Hohenberg and Kohn 1964; Kohn and Sham 1965; Sham and Kohn 1966; Moruzzi et al. 1978; Liberman 1974; Pettifor 1976a,b; Averill and Painter 1981). The LDA poses the following scenario: Each point in a solid is associated with an electron density; an electron at such a point experiences the same force by the surrounding electrons as if the density of the surrounding electrons had the same value throughout the entire space as at the point of the reference electron. [Clearly, any real system has a spatially varying electron density. The gradient expansion approximations and the generalized gradient approximations incorporate gradient corrections in order to include the effect of the spatial variation of the electron density and hence are "usually" more accurate than the LDA (Dreizler and Cross 1990; Parr and Yang 1989; Perdew and Yang 1986; Perdew et al. 1996)]. In LDA, $F[\rho]$ may be written as a functional of the charge density, e.g., under the Thomas-Fermi scheme, and the evaluation of its contribution to the stress tensor can proceed in an analytical fashion (but at the cost of loss of accuracy). However, the usual method is to express $E_{\mathrm{XC}}[\rho]$ in a LDA setting as follows (Moruzzi et al. 1978; Yin and Cohen 1982)

$$E_{\mathrm{XC}}[\rho] = \int \rho(\mathbf{r}) \vartheta_{\mathrm{XC}}(\rho(\mathbf{r})) d^3 r \qquad (50)$$

where $\vartheta_{\mathrm{XC}}(\rho)$=exchange-correlation energy *per electron* in a homogeneous electron gas of density ρ. Such a local approximation is generally good for metals.

The exchange-correlations stress field contribution at $\mathbf{r}$ can be written as

$$\boldsymbol{\sigma}_{\mathrm{XC}}(\mathbf{r}) = [\vartheta_{\mathrm{XC}}(\rho(\mathbf{r})) - \mu_{\mathrm{XC}}(\rho(\mathbf{r}))]\rho(\mathbf{r})\mathbf{I} \qquad (51)$$

where

$$\mu_{\mathrm{XC}}(\rho) = \frac{d(\rho \vartheta_{\mathrm{XC}}(\rho))}{d\rho} \qquad (52)$$

As one can see from Eq. (51), the stress due to exchange-correlation is purely dilatational. Indeed, this happens to be a general property of the local-density approximation.

Thus the total macroscopic stress within a LDA approximation consists of:

1. The kinetic contribution of *noninteracting* electrons of the form

$$-\frac{1}{m_e} \sum_i \langle \Psi_i | \mathbf{p} \otimes \mathbf{p} | \Psi_i \rangle$$

[compare with $\mathbf{T}_{\mathrm{kin}}$ of Eq. (25)].

2. The ion-electron Coulombic stress

$$-\frac{1}{2} e^2 \sum_i \int d^3 r \rho(\mathbf{r}) V'_{\mathrm{ion}}(\mathbf{r} - \mathbf{R}_i) \frac{(\mathbf{r} - \mathbf{R}_i) \otimes (\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|}$$

and the ion-ion Coulombic stress

$$-\frac{1}{2}e^2\sum_{\substack{i,j\\i\neq j}}Z_iZ_j\frac{(\mathbf{R}_i-\mathbf{R}_j)\otimes(\mathbf{R}_i-\mathbf{R}_j)}{|\mathbf{R}_i-\mathbf{R}_j|^3}$$

3. The Hartree stress

$$-\frac{1}{2}e^2\int\int d^3rd^3r'\rho(\mathbf{r})\rho(\mathbf{r}')\frac{(\mathbf{r}-\mathbf{r}')\otimes(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}$$

and

4. The exchange-correlation stress

$$\int d^3r[\vartheta_{XC}(\rho(\mathbf{r}))-\mu_{XC}(\rho(\mathbf{r}))]\rho(\mathbf{r})\mathbf{I}$$

Filippeti and Fiorentini (2000) have exploited NM's expressions for the macroscopic stress in LDA and following Chetty and Martin's formalism for the energy density (Chetty and Martin 1992), have derived expressions for field-like quantities representing the microscopic stress.

The total kinetic stress, which we encountered previously, can be expressed in two equivalent forms:

1. A symmetric form given as follows

$$\mathbf{T}_{KS,kin}=e^2\sum_{\nu k}f_{\nu\mathbf{k}}\omega_{\mathbf{k}}\int d^3r(\nabla\Psi_{\nu\mathbf{k}}^*(\mathbf{r})\otimes\nabla\Psi_{\nu\mathbf{k}}(\mathbf{r}))\quad(53)$$

where $f_{\nu\mathbf{k}}$ and $\omega_{\nu\mathbf{k}}$=occupation numbers and $\mathbf{k}$-point weights, respectively.

2. An asymmetric form as follows

$$\mathbf{T}_{KS,kin}=-e^2\sum_{\nu k}f_{\nu\mathbf{k}}\omega_{\mathbf{k}}\int d^3r\Psi_{\nu\mathbf{k}}^*(\mathbf{r})(\nabla\otimes\nabla\Psi_{\nu\mathbf{k}}(\mathbf{r}))$$

$$(54)$$

The symmetric form given by Eq. (53) is easier to handle as it does not involve second derivatives of the wave functions. Now, one can define a microscopic kinetic stress field as

$$\boldsymbol{\sigma}_{KS,kin}(\mathbf{r})=\frac{e^2}{2}\sum_{\nu k}f_{\nu\mathbf{k}}\omega_{\mathbf{k}}[\nabla\Psi_{\nu\mathbf{k}}^*(\mathbf{r})\otimes\Psi_{\nu\mathbf{k}}(\mathbf{r})+c.c.]\quad(55)$$

The exchange-correlation total stress is given as

$$\mathbf{T}_{XC}(\mathbf{r})=\left(\int d^3r[\vartheta_{XC}(\rho(\mathbf{r}))-\mu_{XC}(\rho(\mathbf{r}))]\mathbf{I}\right)\quad(56)$$

Then, the microscopic stress field corresponding to exchange-correlation is easily identified as

$$\boldsymbol{\sigma}_{XC}(\mathbf{r})=[\vartheta_{XC}(\rho(\mathbf{r}))-\mu_{XC}(\rho(\mathbf{r}))]\mathbf{I}\quad(57)$$

Due to the long-ranged nonlocal nature of Coulombic interactions, it does not seem possible to assign a "stress density" for a particular point, but as mentioned earlier, the form represented by Maxwell's stress tensor is often chosen for convenience. Interestingly, Rogers and Rappe (2002) point out that the energy-momentum tensor for electromagnetism, which corresponds to the Maxwell stress in the nonrelativistic limit and in the absence of magnetic fields, has been mathematically proven to be *unique* in the gravitational literature (Collinson 1969; Lovelock 1974; Kerringhan 1982). Thus, the *Coulombic contribution is without any gauge arbitrariness* and is rigorously equal to the Maxwell stress!

The Maxwell stress density operator $\boldsymbol{\sigma}_M(\mathbf{r})$ is given by Eq. (39). The electric field $\mathbf{E}(\mathbf{r})$ of Eq. (39) is given by

$$\mathbf{E}(\mathbf{r})=-\nabla\int d^3r'\frac{\bar{\rho}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\quad(58)$$

The issue of the divergence of the Coulombic terms is taken care of by introducing the total charge density $\bar{\rho}$ instead of the electronic charge density ρ as follows:

$$\bar{\rho}=\rho_n+\rho\quad(59)$$

The ionic charge density $\rho_n(\mathbf{r})$ is represented by [Filippetti and Fiorentini (2000)] as the sum of ion-centered Gaussians

$$\rho_n(\mathbf{r})=-\sum_j\frac{Z_j}{\pi^{3/2}R_c^3}e^{-|\mathbf{r}-\mathbf{R}_j|^2/R_c^2}\quad(60)$$

where R_c=Gaussian radius and $\mathbf{R}_j$ denotes the position of the nuclei.

Further Ewald-like contribution to the stress tensor arises out of the strain derivative of the ion-charge density

$$\boldsymbol{\sigma}_{Ewald}(\mathbf{r})=-\frac{R_c^2}{2}(\nabla\rho_n(\mathbf{r})\otimes\mathbf{E}(\mathbf{r}))\quad(61)$$

If one considers only Coulombic interactions in the system, Eq. (60) completes the analysis for the stress densities. However, Filippetti and Fiorentini (2000) have considered the plane-wave pseudopotential method where one needs to separately analyze *non-Coulombic* interactions due to the pseudopotential.

The plane-wave pseudopotential method is based on the expansion of the electronic wave functions in terms of a plane-wave basis. The total energy, derived from DFT, is minimized with respect to the coefficients of the plane-wave basis set. Quite a few iterative diagonalization methods exist which can significantly reduce the computational cost of the minimization procedure (Car and Parinello 1985; Payne et al. 1992). As is intuitive, the smoothly varying valence electron wave functions can be expanded in terms of less number of plane waves as against the rapidly varying core-electron wave functions which would necessitate a large number of plane waves. Thus, the effect of the nucleus and the core electrons is replaced by a pseudopotential which is typically derived from a free atom all-electron calculation.

The local pseudopotential contribution to the total stress is given by

$$\mathbf{T}_{e-i}=\int d^3r\rho(\mathbf{r})\sum_j\frac{\partial}{\partial\boldsymbol{\varepsilon}}V_{loc,j}(\mathbf{r}-\mathbf{R}_j)\quad(62)$$

where $V_{loc,j}$=local part of the pseudopotential at atom "j."

This in turn can be written as

$$\mathbf{T}_{e-i}=\sum_j\int d^3r\rho(\mathbf{r})(V'_{loc,j}(\mathbf{r}-\mathbf{R}_j))\frac{(\mathbf{r}-\mathbf{R}_j)\otimes(\mathbf{r}-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{R}_j|}\quad(63)$$

Here

$$V'_{loc,j}(x)=\frac{\partial V_{loc,j}(x)}{\partial x}.$$

From Eq. (62), Filippetti and Fiorentini (2000) define a microscopic stress tensor corresponding to the local pseudopotential as follows:

$$\boldsymbol{\sigma}_{e-i}(\mathbf{r})=\rho(\mathbf{r})\sum_j\frac{\partial[V_{loc,j}(\mathbf{r})+V_{ion\text{-}electron,j}(\mathbf{r})]}{\partial\boldsymbol{\varepsilon}}\quad(64)$$

Filippetti and Fiorentini (2000) mention that the interaction between the electronic and the Gaussian-ion charge densities occurring in Eq. (56) is unphysical and is an artifact resulting from the assumption in Eq. (59) that the ionic charge density is a sum of ion-centered Gaussian. To resolve this issue the contribution from the Gaussian ionic charges has been added in Eq. (63).

The nonlocal pseudopotential contribution to stress is important only in the core region of the atoms (Filippetti and Fiorentini 2000). This can be represented as a superposition of ionic centered contributions as follows:

$$\boldsymbol{\sigma}_{\mathrm{NL}}(\mathbf{r}) = \sum_j \mathbf{P}_j \delta(\mathbf{r} - \mathbf{R}_j) \tag{65}$$

The stress contribution from the jth ionic site $\mathbf{P}_j$ is given by

$$\mathbf{P}_j = \sum_{\nu \mathbf{k}} f_{\nu \mathbf{k}} \omega_{\nu \mathbf{k}} \left\langle \Psi_{\nu \mathbf{k}} \left| \frac{\partial V_{\mathrm{NL},j}}{\partial \boldsymbol{\varepsilon}} \right| \Psi_{\nu \mathbf{k}} \right\rangle \tag{66}$$

where $V_{\mathrm{NL},j}$=nonlocal part of the pseudopotential. Thus under a pseudopotential approximation, the microscopic stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ reads as

$$\boldsymbol{\sigma}(\mathbf{r}) = \boldsymbol{\sigma}_{\mathrm{KS,kin}}(\mathbf{r}) + \boldsymbol{\sigma}_M(\mathbf{r}) + \boldsymbol{\sigma}_{\mathrm{XC}}(\mathbf{r}) + \boldsymbol{\sigma}_{\mathrm{Ewald}}(\mathbf{r}) + \boldsymbol{\sigma}_{e-i}(\mathbf{r}) + \boldsymbol{\sigma}_{\mathrm{NL}}(\mathbf{r}) \tag{67}$$

All the terms (except the exchange-correlation terms) are first evaluated in Fourier space and then transformed back into real space. The computational effort is comparable to that required to calculate the macroscopic stress tensor.

DFT Approach via Reduced Density Matrices

Ziesche et al. (1988) present formulas for the stress tensor of finite clusters as well as infinite crystals using *reduced density matrices* within the many-body Schrödinger equation [as well as the single-particle Kohn-Sham (Kohn and Sham 1965) approach]. Using the one-particle density matrix and the pair distribution matrix, Ziesche et al. (1988) define a local stress tensor with the divergence equal to the forces acting upon the *nuclei*.

Ziesche et al. (1988) introduce the following charge densities and charge density operators. The nuclear density denoted by $\rho_n(\mathbf{r})$ and the nuclear pair distribution $\rho_n(\mathbf{r}_1;\mathbf{r}_2)$ is given by

$$\rho_n(\mathbf{r}) = \sum_i Z_i \delta(\mathbf{r} - \mathbf{R}_i)$$

$$\rho_n(\mathbf{r}_1;\mathbf{r}_2) = \sum_{i \neq j} Z_i Z_j \delta(\mathbf{r}_1 - \mathbf{R}_i) \delta(\mathbf{r}_2 - \mathbf{R}_j) \tag{68}$$

The corresponding electronic density operator $\rho(\mathbf{r})$ and the electronic pair distribution operator $\rho(\mathbf{r}_1;\mathbf{r}_2)$ are given by

$$\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\rho(\mathbf{r}_1;\mathbf{r}_2) = \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \tag{69}$$

Note that the pair distributions do not include the self-interaction terms as $i \neq j$ in Eqs. (68) and (69). Now the potential energy operator V constituting the many-body Hamiltonian can be written as

$$V = E_{\mathrm{ion-ion}} + E_{\mathrm{ion-electron}} + E_{\mathrm{electron-electron}} \tag{70}$$

The individual components are explained in the following.

$E_{\mathrm{ion-ion}}$ represents the nuclear-nuclear interaction potential energy

$$E_{\mathrm{ion-ion}} = \frac{1}{2} e^2 \int \int d^3 r_1 d^3 r_2 \frac{\rho_n(\mathbf{r}_1;\mathbf{r}_2)}{r_{12}} \tag{71}$$

Here $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

$E_{\mathrm{ion-electron}}$ and $E_{\mathrm{electron-electron}}$=nuclear-electron and electron-electron potential energy operators, respectively. It is useful to point out that the XC contribution of the potential energy to the total energy is embedded in the $E_{\mathrm{electron-electron}}$ term. The $E_{\mathrm{electron-electron}}$ term can be split into a Hartree contribution and an XC contribution [see Eq. (45)]

$$E_{\mathrm{ion-electron}} = -\frac{1}{2} e^2 \int \int d^3 r_1 d^3 r_2 \frac{\rho_n(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho_n(\mathbf{r}_2)\rho(\mathbf{r}_1)}{r_{12}}$$

$$E_{\mathrm{electron-electron}} = \frac{1}{2} e^2 \int \int d^3 r_1 d^3 r_2 \frac{\rho(\mathbf{r}_1;\mathbf{r}_2)}{r_{12}} \tag{72}$$

The net potential energy operator V can be written in terms of the total pair distribution operator as

$$V = \frac{1}{2} e^2 \int \int d^3 r_1 d^3 r_2 \frac{\nu(\mathbf{r}_1;\mathbf{r}_2)}{r_{12}} \tag{73}$$

where

$$\nu(\mathbf{r}_1;\mathbf{r}_2) = \rho_n(\mathbf{r}_1;\mathbf{r}_2) - (\rho_n(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)\rho_n(\mathbf{r}_2)) + \rho(\mathbf{r}_1;\mathbf{r}_2)$$

One can similarly think of a net density operator $\nu(\mathbf{r})$ such that

$$\nu(\mathbf{r}) = \rho_n(\mathbf{r}) - \rho(\mathbf{r}) \tag{74}$$

The expectation values of the operators $\rho(\mathbf{r})$ and $\rho(\mathbf{r}_1;\mathbf{r}_2)$ are subject to the following normalization conditions:

$$\int d^3 r \langle \rho(\mathbf{r}) \rangle = N$$

$$\int d^3 r_1 \langle \rho(\mathbf{r};\mathbf{r}_1) \rangle = (N-1) \langle \rho(\mathbf{r}) \rangle \tag{75}$$

The one-particle density matrix $\rho(\mathbf{r},\mathbf{r}')$ is defined as

$$\rho(\mathbf{r},\mathbf{r}') = \frac{1}{(N-1)!} \sum_{\sigma_1,\sigma_2 \ldots,\mathbf{r}_N,\sigma_N} \int d^3 r_2 \ldots$$

$$\times \int d^3 r_N \Psi(\mathbf{r},\sigma_1;\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_N,\sigma_N)$$

$$\times \Psi^*(\mathbf{r}',\sigma_1;\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_N,\sigma_N) \tag{76}$$

The following relation holds

$$\rho(\mathbf{r},\mathbf{r}) = \langle \rho(\mathbf{r}) \rangle \tag{77}$$

The kinetic and potential energies can be written in terms of these density distributions as

$$T = \int d^3 r \frac{\mathbf{p}^2}{2m_e} \langle \rho(\mathbf{r}) \rangle \tag{78}$$

$$V = \frac{1}{2}e^2 \int \int d^3r_1 d^3r_2 \frac{\langle \nu(\mathbf{r}_1;\mathbf{r}_2)\rangle}{r_{12}}$$

The net electrostatic force on all particles at a point $\mathbf{r}$ is given by

$$\mathbf{f}(\mathbf{r}) = \frac{1}{2}e^2 \int \int d^3r_1 d^3r_2 \langle \nu(\mathbf{r}_1;\mathbf{r}_2)\rangle$$
$$\times [\delta(\mathbf{r} - \mathbf{r}_1)\mathbf{E}_2(\mathbf{r}) + \delta(\mathbf{r} - \mathbf{r}_2)\mathbf{E}_1(\mathbf{r})] \qquad (79)$$

Here $\mathbf{E}_i(\mathbf{r})$ is defined as

$$\mathbf{E}_i(\mathbf{r}) = \frac{\mathbf{r} - \mathbf{r}_i}{|\mathbf{r} - \mathbf{r}_i|^3} \qquad (80)$$

Because $\langle \nu(\mathbf{r}_1;\mathbf{r}_2)\rangle$ is symmetric with respect to $\mathbf{r}_1$ and $\mathbf{r}_2$, Eq. (79) reduces to

$$\mathbf{f}(\mathbf{r}) = e^2 \int d^3r_1 \langle \nu(\mathbf{r};\mathbf{r}_1)\rangle \mathbf{E}_1(\mathbf{r}) \qquad (81)$$

The net force density at a point $\mathbf{r}$ given by Eq. (81) can be split into two components, (1) $\mathbf{f}^+(\mathbf{r})$ = force density on the nuclear subsystem and (2) $\mathbf{f}^-(\mathbf{r})$ = force density on the electronic subsystem.

The expressions for $\mathbf{f}^+(\mathbf{r})$ and $\mathbf{f}^-(\mathbf{r})$ are given as

$$\mathbf{f}^+(\mathbf{r}) = e^2 \int d^3r_1 \rho_n(\mathbf{r};\mathbf{r}_1)\mathbf{E}_1(\mathbf{r}) + e\rho_n(\mathbf{r})\mathbf{E}^-(\mathbf{r}) \qquad (82a)$$

$$\mathbf{f}^+(\mathbf{r}) = e^2 \int d^3r_1 \langle \rho(\mathbf{r};\mathbf{r}_1)\rangle \mathbf{E}_1(\mathbf{r}) - e\langle \rho(\mathbf{r})\rangle \mathbf{E}^+(\mathbf{r}) \qquad (82b)$$

The following definitions for $\mathbf{E}^-(\mathbf{r})$ and $\mathbf{E}^+(\mathbf{r})$ hold

$$\mathbf{E}^-(\mathbf{r}) = -e \int d^3r_1 \langle \rho(\mathbf{r}_1)\rangle \mathbf{E}_1(\mathbf{r})$$
$$(83)$$
$$\mathbf{E}^+(\mathbf{r}) = e \int d^3r_1 \rho_n(\mathbf{r})\mathbf{E}_1(\mathbf{r})$$

As the nuclei are viewed as discrete classical particles, $\mathbf{f}^+(\mathbf{r})$ consists of δ functions

$$\mathbf{f}^+(\mathbf{r}) = \sum_i \mathbf{F}_i \delta(\mathbf{r} - \mathbf{R}_i) \qquad (84)$$

where the following definitions hold

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}^-(\mathbf{r}) + \mathbf{E}^+(\mathbf{r}) \qquad (85a)$$

$$\mathbf{F}_i(\mathbf{r}) = Z_i e \left[\mathbf{E}(\mathbf{r}) - Z_i e \frac{\mathbf{r} - \mathbf{R}_i}{|\mathbf{r} - \mathbf{R}_i|^3} \right]_{\mathbf{r} = \mathbf{R}_i} \qquad (85b)$$

Note that in Eq. (85a), the nuclear self-interaction term has been subtracted in order to calculate the force density. From the Hellmann-Feynman theorem the force on the classical nucleus in ground state at $\mathbf{R}_i$ is

$$\frac{-\partial \langle H\rangle}{\partial \mathbf{R}_i} = -\left\langle \frac{\partial H}{\partial \mathbf{R}_i}\right\rangle = -\left\langle \frac{\partial V}{\partial \mathbf{R}_i}\right\rangle = \mathbf{F}_i \qquad (86)$$

Thus $\mathbf{F}_i$ = Hellmann-Feynman force on the classical nucleus at $\mathbf{R}_i$ whereas $\mathbf{f}^+(\mathbf{r})$ = "Hellmann-Feynman force density."

In the ground state, no net force or torque may act on the subsystem of the classical nuclei. This can be mathematically written as

$$\int d^3r \mathbf{f}^+(\mathbf{r}) = 0 \qquad (87a)$$

$$\int d^3r \mathbf{r} \times \mathbf{f}^+(\mathbf{r}) = 0 \qquad (87b)$$

Equation (87b) can also be interpreted as follows: if the dyadic product $\mathbf{r} \otimes \mathbf{f}^+(\mathbf{r})$ has an antisymmetric part then this antisymmetric part must integrate out to zero when the integration is carried over the cluster.

With the preceding formulation, Ziesche et al. (1988) proceed to the local momentum balance in order to introduce the local stress tensor. The kinetic contribution to the stress is evaluated by first introducing the real momentum flux density $\mathbf{\Pi}(\mathbf{r})$ as follows (Pauli 1958; Schrödinger 1927; Ziesche and Lehmann 1987)

$$\mathbf{\Pi}(\mathbf{r}) = \frac{1}{m_e} \frac{(\mathbf{p}'^* + \mathbf{p})}{2} \otimes \frac{(\mathbf{p}'^* + \mathbf{p})}{2} \rho(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \qquad (88)$$

The kinetic contribution $\boldsymbol{\sigma}_{\mathrm{kin}}(\mathbf{r})$ is

$$\boldsymbol{\sigma}_{\mathrm{kin}}(\mathbf{r}) = -\frac{1}{m_e} \frac{(\mathbf{p}'^* + \mathbf{p})}{2} \otimes \frac{(\mathbf{p}'^* + \mathbf{p})}{2} \rho(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \qquad (89)$$

Eq. (89) can also be rewritten as

$$\boldsymbol{\sigma}_{\mathrm{kin}}(\mathbf{r}) = \frac{\hbar^2}{4m_e} (\nabla' - \nabla) \otimes (\nabla' - \nabla) \rho(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \qquad (90)$$

The divergence of $\boldsymbol{\sigma}_{\mathrm{kin}}(\mathbf{r})$ can be shown to be the negative of the electron force density $\mathbf{f}^-(\mathbf{r})$

$$\mathrm{div}\, \boldsymbol{\sigma}_{\mathrm{kin}}(\mathbf{r}) = -\mathbf{f}^-(\mathbf{r}) \qquad (91)$$

For the potential contribution define $\boldsymbol{\eta}_{12}(\mathbf{r})$ such that

$$\boldsymbol{\eta}_{12}(\mathbf{r}) = -\frac{1}{4\pi}[\mathbf{E}_1(\mathbf{r}) \otimes \mathbf{E}_2(\mathbf{r}) + \mathbf{E}_2(\mathbf{r}) \otimes \mathbf{E}_1(\mathbf{r}) - (\mathbf{E}_1(\mathbf{r}) \cdot \mathbf{E}_2(\mathbf{r}))\mathbf{I}]$$
$$(92)$$

$-\boldsymbol{\eta}_{12}(\mathbf{r})$ = Maxwell tensor of two interacting point charges placed at $\mathbf{r}_1$ and $\mathbf{r}_2$ minus the self-interaction terms. The potential stress $\boldsymbol{\sigma}_{\mathrm{pot}}(\mathbf{r})$ is defined as

$$\boldsymbol{\sigma}_{\mathrm{pot}}(\mathbf{r}) = -\frac{1}{2}e^2 \int \int d^3r_1 d^3r_2 \langle \nu(\mathbf{r}_1;\mathbf{r}_2)\rangle \boldsymbol{\eta}_{12}(\mathbf{r}) \qquad (93)$$

The divergence of $-\boldsymbol{\eta}_{12}(\mathbf{r})$ yields

$$\mathrm{div}(-\boldsymbol{\eta}_{12}(\mathbf{r})) = [\delta(\mathbf{r} - \mathbf{r}_1)\mathbf{E}_2(\mathbf{r}) + \delta(\mathbf{r} - \mathbf{r}_2)\mathbf{E}_1(\mathbf{r})] \qquad (94)$$

Using Eqs. (93) and (94) one can obtain

$$\mathrm{div}\, \boldsymbol{\sigma}_{\mathrm{por}}(\mathbf{r}) = -\mathbf{f}(\mathbf{r}) \qquad (95)$$

Adding Eqs. (91) and (95) we have

$$\mathrm{div}\, \boldsymbol{\sigma}(\mathbf{r}) = \mathbf{f}^+(\mathbf{r}) \qquad (96)$$

Ziesche et al. (1988) define $\boldsymbol{\sigma}(\mathbf{r})$ as the local stress tensor

$$\boldsymbol{\sigma}(\mathbf{r}) = \boldsymbol{\sigma}_{\mathrm{pot}}(\mathbf{r}) + \boldsymbol{\sigma}_{\mathrm{kin}}(\mathbf{r}) \qquad (97)$$

As one can see from Eq. (96), the local stress tensor is associated only with the nuclear force density. These forces exactly compensate the forces induced by the external potential; if the external potential is zero then the force density of Eq. (96) is also zero.

Further, multiplying both sides of Eq. (96) dyadically by $\mathbf{r}$ we obtain

$$\boldsymbol{\sigma}(\mathbf{r}) = \nabla(\boldsymbol{\sigma}(\mathbf{r}) \otimes \mathbf{r}) - \mathbf{f}^+(\mathbf{r}) \otimes \mathbf{r} \qquad (98)$$

Now integrating Eq. (98) over a volume Ω results in

$$\int_\Omega d^3r\,\boldsymbol{\sigma}(\mathbf{r}) = \int_S d\mathbf{S}(\boldsymbol{\sigma}(\mathbf{r}) \otimes \mathbf{r}) - \int_\Omega d^3r\,\mathbf{f}^+(\mathbf{r}) \otimes \mathbf{r} \qquad (99)$$

For a finite cluster, if Ω is taken as all of space, then the surface integral vanishes because the stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ falls off rapidly outside the cluster. What follows is the relation for the total stress

$$\mathbf{T}_{\text{kin}} + \mathbf{T}_{\text{pot}} = \sum_i \mathbf{R}_i \otimes \mathbf{F}_i \qquad (100)$$

The tensors $\mathbf{T}_{\text{kin}}$ and $\mathbf{T}_{\text{pot}}$=kinetic and potential contributions to the global stress tensor, respectively

$$\mathbf{T}_{\text{kin}}(\mathbf{r}) = \int d^3r\,\boldsymbol{\sigma}_{\text{kin}}(\mathbf{r}) = - \int d^3r\left(\frac{\mathbf{p} \otimes \mathbf{p}}{m_e}\right)\rho(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}$$

$$\mathbf{T}_{\text{pot}}(\mathbf{r}) = \int d^3r\,\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) = -\frac{e^2}{2} \int\int d^3r_1 d^3r_2 \langle v(\mathbf{r}_1;\mathbf{r}_2)\rangle \frac{\mathbf{r}_{12} \otimes \mathbf{r}_{12}}{r_{12}^3} \qquad (101)$$

From the Hellmann-Feynman theorem of Eq. (86), Eq. (101) can be rewritten as

$$\mathbf{T}_{\text{kin}} + \mathbf{T}_{\text{pot}} = \sum_i \mathbf{R}_i \otimes \frac{\partial}{\partial \mathbf{R}_i} E \qquad (102)$$

In Eq. (102) we have, in effect, recovered the Stress theorem which NM (1985a) obtained via the scaling argument. If $\boldsymbol{\tau}$ is the global stress density and Ω_c is the volume of the cluster then

$$\boldsymbol{\tau}\Omega_c = \sum_i \mathbf{R}_i \otimes \frac{\partial}{\partial \mathbf{R}_i} E \qquad (103)$$

In the thermodynamic limit, when the cluster tends to an infinite crystal ($\Omega_c \to \infty$) then the *total* quantities (which refer to the whole volume for a finite cluster) now refer to a unit cell volume $\Omega_0 = \Omega_c/N_c$, where N_c is the number of unit cells. For example, the kinetic global stress tensor $\mathbf{T}_{\text{kin}}$ and the potential global stress tensor $\mathbf{T}_{\text{pot}}$ have to be divided by N_c, before evaluating the thermodynamic limit as shown in the following

$$\mathbf{T}_{\text{kin}}/N_c = \int_{\Omega_0} d^3r\,\boldsymbol{\sigma}_{\text{kin}}(\mathbf{r}), \quad \mathbf{T}_{\text{pot}}/N_c = \int_{\Omega_0} d^3r\,\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) \qquad (104)$$

The average stress density takes the form

$$\boldsymbol{\tau}\Omega_0 = \sum_i \mathbf{a}_i \otimes \frac{\partial}{\partial \mathbf{a}_i} \varepsilon \qquad (105)$$

where ε=energy per unit cell and $\mathbf{a}_i$ are the lattice vectors.

Using the scheme shown in Eq. (98) and after some further manipulations, Ziesche et al. (1988) arrive at the following expression for the average stress density in the thermodynamic limit

$$\boldsymbol{\tau}\Omega_0 =: - \text{Re} \int_{S_0} \text{sym}(\mathbf{r} \otimes \mathbf{p})\left(\frac{\mathbf{p}'^* + \mathbf{p}}{2m_e}\right)\rho(\mathbf{r},\mathbf{r}')d\mathbf{S}\Bigg|_{\mathbf{r}=\mathbf{r}'}$$

$$- e^2 \int_{\Omega_0} d^3r_1 \int_{\infty-\Omega_0} d^3r_2 \langle v(\mathbf{r}_1;\mathbf{r}_2)\rangle$$

$$\times \frac{1}{2}\left[\text{sym}\left(\mathbf{r}_1 \otimes \frac{\partial}{\partial \mathbf{r}_1} - \mathbf{r}_2 \otimes \frac{\partial}{\partial \mathbf{r}_2}\right)\right]\frac{1}{r_{12}} \qquad (106)$$

The first term on the right-hand side of Eq. (106) corresponds to the momentum flux across S_0, the surface of the unit cell. The second term denotes the Coulombic interactions between particles *inside* the volume of the unit cell Ω_0 and the particles *outside* the unit cell.

Returning to Eq. (97), the kinetic part of the local stress $\boldsymbol{\sigma}_{\text{kin}}(\mathbf{r})$ is associated with the single-particle density while the potential contribution $\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r})$ is associated with the pair distribution densities. The electronic pair distribution can be written in terms a sum of a product of Hartree terms (single-particle densities) and the XC term $\rho_{\text{XC}}(\mathbf{r}_1;\mathbf{r}_2)$ shown in the following

$$\rho(\mathbf{r}_1;\mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho_{\text{XC}}(\mathbf{r}_1;\mathbf{r}_2) \qquad (107)$$

This separation enables $\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r})$ to be separated into single-particle (Hartree) and XC parts.

The Hartree part $\boldsymbol{\sigma}_{\text{Hartree}}(\mathbf{r})$ is given by

$$\boldsymbol{\sigma}_{\text{Hartree}}(\mathbf{r}) = -\left(\boldsymbol{\sigma}_M(\mathbf{r}) - \sum_i \boldsymbol{\sigma}_{M,i}(\mathbf{r})\right) \qquad (108)$$

where $\boldsymbol{\sigma}_M(\mathbf{r})$=Maxwell stress due to total electrostatic field $\mathbf{E}(\mathbf{r})$ from Eq. (85a). $\boldsymbol{\sigma}_{M,i}(\mathbf{r})$=the self-interaction terms

$$\boldsymbol{\sigma}_{M,i}(\mathbf{r}) = \frac{Z_i}{4\pi}\left(\mathbf{E}_i(\mathbf{r}) \otimes \mathbf{E}_i(\mathbf{r}) - \frac{1}{2}\mathbf{E}_i(\mathbf{r})^2\mathbf{I}\right) \qquad (109)$$

The XC contribution to $\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r})$ can be written as

$$\boldsymbol{\sigma}_{\text{pot,XC}}(\mathbf{r}) = -\frac{1}{2}e^2 \int\int d^3r_1 d^3r_2 \langle v(\mathbf{r}_1;\mathbf{r}_2)\rangle \boldsymbol{\eta}_{12}(\mathbf{r}) \qquad (110)$$

Finally, the stress field can be written as

$$\boldsymbol{\sigma}(\mathbf{r}) = \boldsymbol{\sigma}_{\text{kin}}(\mathbf{r}) + \boldsymbol{\sigma}_{\text{Hartree}}(\mathbf{r}) + \boldsymbol{\sigma}_{\text{pot,XC}}(\mathbf{r}) \qquad (111)$$

Amongst the terms which constitute the stress field $\boldsymbol{\sigma}(\mathbf{r})$, the single-particle term $\boldsymbol{\sigma}_{\text{Hartree}}(\mathbf{r})$ admits the simplest evaluation as it involves only the electron density $\rho(\mathbf{r})$ and the nuclear density $\rho_n(\mathbf{r})$. The kinetic term $\boldsymbol{\sigma}_{\text{kin}}(\mathbf{r})$, however, entails the knowledge of the one-particle density matrix $\rho(\mathbf{r},\mathbf{r}')$ which is a many-body term. Prescriptions to calculate the density matrix have been proposed by Hybertsen and Louie (1986, 1987), Godby et al. (1986, 1987), and others (Horsch et al. 1987; Kulikov et al. 1987; Mazin et al. 1984). Experimental determination of $\rho(\mathbf{r},\mathbf{r}')$ is also possible. However, an appropriate discussion of these methods is beyond the scope of this paper. The exchange-correlation term is the most difficult to deal with as not much is known about the density $\rho_{\text{XC}}(\mathbf{r}_1;\mathbf{r}_2)$. Ziesche et al. (1988) have subsequently provided expressions for the stress in a LDA setting for practical considerations.

Nonuniqueness of Quantum Stress Fields

As stated earlier, if we define the stress field via a continuity equation, i.e., as a two-tensor such that its divergence results in the corresponding force field, one can add to the stress tensor the curl of an arbitrary dyadic field and still recover the same force field. Whereas we have seen some authors [like Filippetti and Fiorentini (2000); Ziesche et al. (1988)] provide certain forms for the stress fields, these representations are by no means unique. The results obtained by applying these fields to material systems can be thought of as being representative at best.

While agreeing to the conclusion that invoking the force related definition will always result in a nonunique stress field, Folland (1986, 1988) suggests that any term constituting the expression for the stress field should entail a physical interpretation

and thus only physically motivated terms should be added to the expression of the stress field (as against any arbitrary curl of a two-tensor). In particular, Folland opines that the MST operator should be considered as corresponding to a physical observable (of itself) rather than as a mathematical artifact to aid in calculation of forces, macroscopic stresses, and the like. Folland's biggest motivation for viewing the MST as corresponding to a physical observable seems to be its appearance in a continuity-like equation [Eq. (34)] in complete parallel with the mass-density continuity equation shown in the following

$$\frac{\partial}{\partial t}[m(\mathbf{r})] + \nabla \cdot \mathbf{P}(\mathbf{r}) = 0 \tag{112}$$

Folland further states that a physically motivated expression for the stress field can be additionally constrained by requiring it to be mathematically well-behaved and vanishing at a rate greater than $1/r^2$ for finite systems. The latter constraint ensures that at large distances the stress falls down to zero for a finite system; also with this constraint the integral of the microscopic stress over the volume of the system will remain finite. Perhaps, considering a model with more structure (such as a relativistic model) and approaching the stress field via a route other than the typically employed force or energy formalism may throw more light on this issue.

The nonuniqueness of the stress field can manifest itself both in the potential contribution and the kinetic contribution. Godfrey (1988) has shown that the *kinetic contribution to the stress field is ambiguous only unto a single arbitrary real number.*

The kinetic contribution to the stress is realized by considering the quantum mechanical momentum flux density [see Eqs. (88)–(90)]. The quantum mechanical momentum flux density takes the form (Pauli 1958; Schrödinger 1927)

$$\mathbf{\Pi}(\mathbf{r}) = -\frac{\hbar^2}{4m_e} \lim_{\mathbf{r}' \to \mathbf{r}} (\nabla - \nabla') \otimes (\nabla - \nabla') \Psi^*(\mathbf{r}) \Psi(\mathbf{r}') \tag{113}$$

Note that Eqs. (88)–(90) and Eq. (112) are essentially equivalent. Because, Eq. (112) represents a flux-like quantity, additional terms can be added to it such that its divergence remains unaltered. For example, the following form may also be employed

$$\mathbf{\Pi}(\mathbf{r}) = \frac{\hbar^2}{2m_e} \lim_{\mathbf{r}' \to \mathbf{r}} \left(\text{sym}(\nabla \otimes \nabla') - \frac{1}{2}\mathbf{I}(\nabla + \nabla')^2 \right) \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) \tag{114}$$

However, Godfrey (1988) argues that under the restrictions of $\mathbf{\Pi}(\mathbf{r})$ being a single-particle operator involving only Ψ, Ψ^*, and their derivatives, the most general flux density $\mathbf{G}(\mathbf{r})$ that can be added to $\mathbf{\Pi}(\mathbf{r})$ while retaining its physical significance is given by

$$\mathbf{G}(\mathbf{r}) = \frac{\hbar^2}{m_e} \lim_{\mathbf{r}' \to \mathbf{r}} [A \nabla \otimes \nabla + A^* \nabla' \otimes \nabla' + B \nabla \otimes \nabla' + B^* \nabla' \otimes \nabla$$
$$+ \mathbf{I}(C \nabla \cdot \nabla' + D \nabla^2 + D^* \nabla'^2)] \Psi^*(\mathbf{r}) \Psi(\mathbf{r}') \tag{115}$$

Only one arbitrary constant, say A, remains after applying the condition that $\mathbf{G}(\mathbf{r})$ is divergence-free. Further requiring that $\mathbf{\Pi}(\mathbf{r})$ remain a momentum flux density under the Galilean transformation $\Psi(\mathbf{r}) \to \Psi(\mathbf{r}) \exp(i\mathbf{p} \cdot \mathbf{r}/\hbar)$ results that the constant A be real. This reduces $\mathbf{G}(\mathbf{r})$ to

$$\mathbf{G}(\mathbf{r}) = A\frac{\hbar^2}{m_e}(\nabla \otimes \nabla - \mathbf{I}\nabla^2)\Psi^*(\mathbf{r})\Psi(\mathbf{r}) \tag{116}$$

This particular form of $\mathbf{G}(\mathbf{r})$ is symmetric. Hence, Godfrey

(1988) concludes that *the kinetic stress is arbitrary only unto a single real number A*.

In addition Godfrey (1988) proposes a potential stress-density operator which results in short-ranged *configurational* stresses when the interactions are short-ranged themselves. Remember that there are inherent shortcomings in both Kugler's and the Maxwell forms of stress. Whereas Kugler's form exhibits disagreeable long-range character, the Maxwell form holds only when the interactions are Coulombic. Whereas Godfrey's form for the potential stress holds for arbitrary interactions (like Kugler's form) it is without the inherent long-ranged character of Kugler's form.

The configurational stress is obtained by Godfrey (1988) by applying an *inhomogeneous* scaling of the wave function. In particular, for the case of interaction via pair potentials Godfrey obtains the following form for the configurational stress tensor

$$\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) = -\frac{1}{16\pi} \lim_{\mathbf{r}' \to \mathbf{r}} (\nabla - \nabla') \otimes (\nabla - \nabla')$$
$$\times \sum_{i,j} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_i|} + \frac{1}{|\mathbf{r}' - \mathbf{r}_j|} \right) \times V_{\text{int}}(|\mathbf{r} - \mathbf{r}_i| + |\mathbf{r}' - \mathbf{r}_j|)$$
$$-\frac{1}{2}\mathbf{I}\sum_{i,j} \delta(\mathbf{r} - \mathbf{r}_i) V_{\text{int}}(|\mathbf{r} - \mathbf{r}_i|) \tag{117}$$

For a system of N particles at the origin, the long distance limit becomes

$$\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) = -\frac{N^2}{8\pi} \left[(\nabla \otimes \nabla)\left(\frac{1}{r}\right) V_{\text{int}}(2r) + \frac{\nabla \otimes \nabla(r)}{r} 2V'_{\text{int}}(2r) \right]$$
$$r \to \infty \tag{118}$$

This stress field is clearly short ranged. Another form of the configurational stress operator is

$$\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) = \frac{1}{8\pi} \lim_{\mathbf{r}' \to \mathbf{r}} \left(\text{sym}(\nabla \otimes \nabla') - \frac{1}{2}\mathbf{I}(\nabla + \nabla')^2 \right)$$
$$\times \sum_{i,j} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_i|} + \frac{1}{|\mathbf{r}' - \mathbf{r}|} \right) \times V_{\text{int}}(|\mathbf{r} - \mathbf{r}_i| + |\mathbf{r}' - \mathbf{r}_j|)$$
$$-\frac{1}{2}\mathbf{I}\sum_{i,j} \delta(\mathbf{r} - \mathbf{r}_i) V_{\text{int}}(|\mathbf{r} - \mathbf{r}_j|) \tag{119}$$

The similarity between the forms of momentum flux density operator in Eqs. (112) and (113) and the forms of the potential stress operator in Eqs. (116) and (118) is manifest.

For the special case of Coulombic interactions Eq. (118) reduces to the Maxwell stress

$$\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) = \frac{1}{4\pi} \sum_{i,j} \left(\nabla \frac{1}{|\mathbf{r} - \mathbf{r}_i|} \right) \otimes \left(\nabla \frac{1}{|\mathbf{r} - \mathbf{r}_j|} \right)$$
$$-\frac{1}{2}\mathbf{I}\left(\nabla \frac{1}{|\mathbf{r} - \mathbf{r}_i|} \right) \cdot \left(\nabla \frac{1}{|\mathbf{r} - \mathbf{r}_j|} \right) \tag{120}$$

The diagonal terms on the right-hand side of Eq. (119) are a cause of concern. They diverge as r^{-4} near a particle which may result in their expectation value being infinite in regions of finite particle density. These terms occur as a result of including self-energy in the interaction energy as a part of Godfrey's analysis. They suggest omission of these diagonal terms for the case of Coulombic interactions. This operation does not alter the physical significance of the configurational stress in any way.

The total stress (kinetic plus potential) is then proposed as

$$\boldsymbol{\sigma}_{\text{pot}}(\mathbf{r}) = \boldsymbol{\Pi}(\mathbf{r}) = \lim_{\mathbf{r}' \to \mathbf{r}} \mathbf{L}(\nabla, \nabla') \left[-\frac{\hbar^2}{2m_e} \Psi^*(\mathbf{r})\Psi(\mathbf{r}') \right.$$

$$+ \left\{ \frac{1}{8\pi} \int \int d^3r_1 d^3r_2 \Psi^*(\mathbf{r}_1)\Psi^*(\mathbf{r}_2) \left(\frac{1}{|\mathbf{r}-\mathbf{r}_1|} + \frac{1}{|\mathbf{r}'-\mathbf{r}_2|} \right) \right.$$

$$\left. \left. \times V_{\text{int}}(|\mathbf{r}-\mathbf{r}_1| + |\mathbf{r}'-\mathbf{r}_2|)\Psi(\mathbf{r}_2)\Psi(\mathbf{r}_1) \right\} \right] \qquad (121)$$

The operators Ψ can be normal-ordered to remove the self-interaction stresses mentioned earlier. The operator $\mathbf{L}(\nabla, \nabla')$ can be a linear combination of the following operators in any ratio A: B such that $A + B = 1$

$$\mathbf{L}^1(\nabla, \nabla') = -\text{sym}(\nabla \otimes \nabla') - \tfrac{1}{2}\mathbf{I}(\nabla + \nabla')^2 \qquad (122a)$$

$$\mathbf{L}^2(\nabla, \nabla') = \tfrac{1}{2}(\nabla - \nabla') \otimes (\nabla - \nabla') \qquad (122b)$$

Adapting from Mitsura's (1985, 1987) original work on classical inhomogeneous fluids, Rogers and Rappe (2002) have formulated the quantum stress field within a differential geometric setting. This formulation is established following the well-known relationship between the strain tensor field and the Riemannian metric tensor field. As we shall see presently, using this geometric approach Rogers and Rappe (2002) were able to identify the origin of the nonuniqueness of the stress field to the lack of a unique relationship between the kinetic energy and the metric tensor.

Before broaching the issue of uniqueness as discussed by Rogers and Rappe, the requisite geometrical framework is first constructed. The infinitesimal squared shortest distance between two points on a Riemannian manifold can be written as $ds^2 = g_{ij} dr^i dr^j$, where g_{ij}=metric tensor. When an infinitesimal distortion is applied of the form, $dr'^i = dr^i + du^i$ then the squared distance changes to $ds'^2 = g_{ij} dr'^i dr'^j$. With a new metric g'_{kl}, defined as $g'_{kl} = g_{ij}(\delta_k^i + \partial_k u^i)(\delta_l^i + \partial_l u^j)$, the distance can still be computed in terms of the predistorted positions as $ds'^2 = g'_{ij} dr^i dr^j$.

The strain field is now introduced into the picture as $ds'^2 - ds^2 = 2\varepsilon_{ij} dr^i dr^j$. The new metric g'_{ij} can now related to the strain ε_{ij} and the original metric g_{ij} as

$$g'_{ij} = 2\varepsilon_{ij} + g_{ij} \qquad (123)$$

The stress field σ^{ij} can then be defined via the virtual work relation

$$\delta E = \int \sqrt{g}\,\sigma^{ij} \delta\varepsilon_{ij} d^3r \qquad (124)$$

where $g = \det(\mathbf{g})$. Using Eq. (123), an explicit form of the stress field is

$$\sigma^{ij} = \frac{1}{\sqrt{g}} \frac{\delta E}{\delta\varepsilon_{ij}} = \frac{2}{\sqrt{g}} \frac{\delta E}{\delta g_{ij}} \qquad (125a)$$

$$\sigma_{ij} = -\frac{2}{\sqrt{g}} \frac{\delta E}{\delta g^{ij}} \qquad (125b)$$

Note that in Eq. (124b) g^{ij} is the inverse of g_{ij}.

Metric tensor fields can be classified into two categories: (1) flat metrics, which cause the Riemannian curvature to vanish at each point in space. The simplest example of a flat metric is the familiar Euclidean space R^3; and (2) non-Euclidean metrics, which result in a nonzero curvature.

The Riemannian curvature R_{iklm}=four-tensor which expresses the curvature of a Riemannian manifold as

$$R_{iklm} = \tfrac{1}{2}(\partial_k \partial_l g_{im} + \partial_i \partial_m g_{kl} - \partial_k \partial_m g_{il} - \partial_i \partial_l g_{km})$$

$$+ g_{np}(\Gamma_{kl}^n \Gamma_{im}^p - \Gamma_{km}^n \Gamma_{il}^p) \qquad (126)$$

The Γ_{jk}^i in Eq. (125) are the Christoffel symbols

$$\Gamma_{jk}^i = \tfrac{1}{2}g^{il}(\partial_k g_{lj} + \partial_j g_{lk} - \partial_l g_{jk}) \qquad (127)$$

It trivially follows that the Riemannian curvature tensor for a flat manifold is zero.

Now, the material system under consideration can be considered to be a collection of particles and fields in a *flat* manifold M that can be mapped diffeomorphically to the Euclidean space R^3. Any physical distortion is constrained to keep the particles embedded in the manifold M. Therefore any applied strain should correspond to flat metric tensor fields [via Eq. (122)].

All flat metrics can be expressed as

$$g_{ij} = \delta_{ij} + \partial_i u_j + \partial_j u_i \qquad (128)$$

where u_i=vector field continuous over M. Then the constrained strain results in Eq. (123) being written as

$$\delta E = \int \sqrt{g}\,\sigma^{ij}(\partial_i \delta u_j + \partial_j \delta u_i)d^3r \qquad (129)$$

The flat metric can be chosen to represent Cartesian space in which case $\sqrt{g} = 1$. Then, Eq. (128) becomes

$$\delta E = \int \sigma^{ij}(\partial_i \delta u_j + \partial_j \delta u_i)d^3r \qquad (130a)$$

$$= -\int (\partial_i \sigma^{ij}\delta u_j + \partial_j \sigma^{ij}\delta u_i)d^3r \qquad (130b)$$

Eq. (129b) contains the divergence of the stress field, which we have seen results in the stress field being ambiguous. This problem of nonuniqueness arises because of the introduction of the constraint on the metric in Eq. (127). Thus, as Rogers and Rappe point out, *the first criterion that must hold for the virtual-work relationship given by Eq. (123) to specify a unique stress field is that the metric must be freely varied, without any constraints.* If this criterion holds, then the Riemannian curvature no longer remains zero at all points in the manifold M. This can be physically achieved by introducing "defect" (analogous to gravitational point sources) sources that would then generate a curvature in the background manifold M. Such non-Euclidean metrics occur in continuum theory of solids in the context of dislocations and disclinations. In the presence of such defects, the displacement field $\mathbf{u}$ is no longer smooth and the following relation no longer holds:

$$(\partial_i \partial_j - \partial_j \partial_i)u_k = 0 \qquad (131)$$

The defect density can be represented by a two-tensor $\boldsymbol{\eta}$ which is defined as

$$\boldsymbol{\eta} = \nabla \times (\nabla \times \boldsymbol{\varepsilon}) \qquad (132)$$

where $\boldsymbol{\varepsilon}$=strain field. When $\eta_{ij}=0$, then the strain field obeys the familiar strain-displacement compatibility relationship

$$\boldsymbol{\varepsilon} = \text{sym}(\nabla\mathbf{u}) \qquad (133)$$

The defect density can be related to the Riemannian curvature R_{limj}, through the Ricci curvature $R_{ij}=g^{lm}R_{limj}$ and the scalar curvature $R=g^{ij}R_{ij}$ as follows:

$$\eta_{ij} = R_{ij} - \tfrac{1}{2}g_{ij}R = G_{ij} \qquad (134)$$

G_{ij} is called the Einstein curvature. However, at the quantum level, it is not clear as to what constitutes a defect in an electron gas and offers (perhaps) a tantalizing avenue for future research.

Keeping the first criterion in mind, we now recognize that the quantum mechanical stress is the energetic response of the system to a generalized non-Euclidean metric. Therefore, the quantum mechanical energy also must be unambiguously defined for non-Euclidean metrics. This constitutes Rogers and Rappe's (2002) second criterion for the virtual-work theorem to uniquely specify a stress field. A generalized Hamiltonian can be constrained in several ways so that it bears a unique relationship with the metric tensor. First, the energy can be required to transform as a covariant scalar for all geometries. Second, the generalized Hamiltonian should yield the appropriate flat-space result when evaluated with a Euclidean metric. Third, the Hamiltonian should correspond to a fully renormalizable quantum-mechanical theory. However, as we shall see these constraints do not suffice in order to specify a unique Hamiltonian. The ambiguity manifests itself in the kinetic energy.

The Hamiltonian for an arbitrary non-Euclidean manifold for a spin-zero Ψ can be written in a very general manner as

$$H = \int \sqrt{g}\left(\tfrac{1}{2} g^{ij}\partial_i\Psi^*\partial_j\Psi + \alpha R + \beta R\Psi^*\Psi + \gamma R^{ij}\partial_i\Psi^*\partial_j\Psi \right)d^3r$$

$$(135)$$

α, β, and λ = arbitrary coupling constants to the various curvature terms.

With the Hamiltonian being constrained in the above-mentioned ways, one might consequently expect a reduction in the number of arbitrary coupling constants in Eq. (134). Under the requirement that the Hamiltonian correspond to a fully renormalizable theory, the constant γ has to be set to be zero as it can be shown via a dimensional analysis that the inclusion of the curvature term multiplied to γ results in the theory being non-renormalizable. From Eq. (134) one can observe that since the wave function does not feature at all in the αR term, this term is like a background term which will exist even in the absence of any matter in the system. Consequently, the constant α can be set to zero as well.

However, as Rogers and Rappe concede, no such constraints exist for the value of β. Therefore, the quantum stress field is undetermined to the arbitrary factor of β. Interestingly, similar unresolved issues exist in the gravitational and constrained-dynamics literature.

Rogers and Rappe further extend this formulation to DFT within a LDA approximation. To begin, the total charge density can be written as

$$\nu(\mathbf{r}) = \sum_i \frac{Z_i}{\sqrt{g}}\delta(\mathbf{r} - \mathbf{R}_i) - \rho(\mathbf{r}) \qquad (136)$$

The factor of $1/\sqrt{g}$ in Eq. (136) ensures proper normalization of the delta function. The energy of the system for arbitrary Riemannian spaces is given by

$$E = T_{\mathrm{KS}} + E_{\mathrm{Coulomb}} + E_{\mathrm{XC}} - \sum_t \lambda_t\left(\int \sqrt{g}\Psi_t^*\Psi_t d^3r - 1 \right) \qquad (137)$$

As we have seen before, T_{KS} = single-particle Kohn-Sham kinetic energy

$$T_{\mathrm{KS}} = \int \sqrt{g}\left(\tfrac{1}{2}\sum_t g^{ij}\partial_i\Psi_t^*\partial_j\Psi_t + \beta R\rho(\mathbf{r}) \right)d^3r \qquad (138)$$

where E_{Coulomb} = classical Coulombic interaction energy

$$E_{\mathrm{Coulomb}} = \int \sqrt{g}\left(\rho V - \frac{1}{8\pi}g^{ij}F_iF_j \right)d^3r \qquad (139)$$

Here $\mathbf{F} = -\nabla V$, where V = potential generated by the charge distribution ρ. In LDA, the exchange-correlation energy functional becomes

$$E_{\mathrm{XC}} = \int \sqrt{g}\rho(\mathbf{r})\vartheta_{\mathrm{XC}}(\rho(\mathbf{r}))d^3r \qquad (140)$$

Here ϑ_{XC} = exchange-correlation density encountered before. The last term of Eq. (137) occurs due to orthonormality constraint on the orbitals. The stress field is obtained from Eq. (124) as

$$\sigma_{ij} = -\sum_t \partial_i\Psi_t^*\partial_j\Psi_t + A_{ij} + \frac{1}{4\pi}F_iF_j + g_{ij}\left(\tfrac{1}{2}\sum_t \partial_k\Psi_t^*\partial^k\Psi_t \right.$$

$$\left. -\frac{1}{8\pi}F_kF^k + \rho(\mathbf{r})\vartheta_{\mathrm{XC}}(\rho(\mathbf{r}) - \sum_t \Psi_t^*\Psi_t(\lambda_t + V) \right) \qquad (141)$$

The ambiguity in the kinetic stress is denoted as A_{ij}.

For Euclidean space, i.e., $g_{ij} = \delta_{ij}$, the explicit form of A_{ij} looks like

$$A_{ij} = \beta(\partial_i\partial_j\rho(\mathbf{r}) - \delta_{ij}\partial^k\partial_k\rho(\mathbf{r})) \qquad (142)$$

Note that this form of A_{ij} is similar to the ambiguity identified by Godfrey (1988) in Eq. (115).

The complete stress field in Euclidean space under the LDA approximation can finally be written as

$$\sigma_{ij} = -\sum_t \partial_i\Psi_t^*\partial_j\Psi_t + \beta(\partial_i\partial_j\rho(\mathbf{r}) - \delta_{ij}\partial_k\partial^k\rho(\mathbf{r})) + \frac{1}{4\pi}F_iF_j$$

$$+ \delta_{ij}\left(\tfrac{1}{2}\sum_t \partial_k\Psi_t^*\partial^k\Psi_t - \frac{1}{8\pi}F_kF^k + \tfrac{1}{2}\sum_t \Psi_t^*\partial^k\partial_k\Psi_t + \rho(\mathbf{r}) \right.$$

$$\times \left.\left(\vartheta_{\mathrm{XC}}(\rho(\mathbf{r})) - \frac{\delta E_{\mathrm{XC}}}{\delta\rho(\mathbf{r})} \right) \right) \qquad (143)$$

The Coulombic contribution to the stress field is given by $(1/4\pi)F_iF_j - \delta_{ij}(1/8\pi)F_kF^k$. Note that this exhibits the same form as the Maxwell stress tensor. More important, this form of the potential stress tensor is unique and rigorous proofs to this effect exist in the gravitational and constrained dynamics literature (Rogers and Rappe 2002). *Thus, there is no arbitrariness associated with the potential contribution of stress. Only the kinetic part of stress is ambiguous and can be specified to one arbitrary real constant.* The diagonal terms in the kinetic stress of Eq. (143) (which contribute to the pressure) contain symmetric and anti-symmetric kinetic-energy densities. On varying β through 0 to $-1/4$, the kinetic energy density changes from being completely symmetric to being completely antisymmetric. We have encountered similar forms before in Eqs. (53) and (54).

Summary

In conclusion, we have reviewed and discussed several works and issues pertaining to quantum mechanical notions of stress. Though some early fundamental work on the meaning of force

and pressure was accomplished when quantum mechanics was still a fledgling theory, recent authors have sought to dig deeper into the meaning of the stress tensor at a quantum mechanical scale. This renewed interest is mostly due to increased availability of tools and techniques which facilitate efficient *ab initio* calculations to study various stress-mediated phenomena.

The issue of uniqueness of the locally varying quantum stress field is still open for discussion. Godfrey (1988) and Rogers and Rappe (2002) have nailed the origin of this ambiguity to the kinetic stress tensor. Folland claims that the MSTs are physical observables and hence the expressions for the corresponding operators should be uniquely defined. His claims are largely based on the fact that MSTs feature in continuity-like equations. In particular, Folland (1986, 1988) suggests that only those terms to which a physical meaning can be assigned constitute the stress tensor expression. A further extension of Rogers and Rappe's (2002) geometric formulation looks particularly promising in regards to resolving this issue.

Though we have hardly discussed any work concerning applications of the quantum mechanical stress, we mention that several works have applied this concept to material systems using DFT. Nielsen and Martin (1985b), in particular, applied the pseudopotential method to Si, Ge, and GaAs semiconductors and reported lattice constants, elastic constants, optical Γ phonon frequencies, anharmonic (pressure-dependent) elastic constants, etc. Filippeti and Fiorentini (2000) applied their stress field to study certain interface and surface phenomena; issues which cannot be reconciled solely on using the average stress tensor. Ramer et al. (1998) used a stress field constrained to being a smooth fit to the ionic forces and applied it to the study of perovskites. Rogers and Rappe (2002) used their geometrically formulated DFT stress field to explain the energetics of two phases of solid molecular hydrogen. They report that the ambiguity in the kinetic stress does not affect the qualitative nature of their results. An appropriate form of the stress field can indeed prove to be a powerful tool to understanding and predicting physics of stress-mediated phenomena.

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