

Microscopic stress tensors in quantum systems

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Microscopic stress tensors are derived for the local-density-approximation and Hartree-Fock models for quantum systems. Dynamically derived stress tensors appear as elements of a continuity equation for the force density in direct correspondence to Newton's laws of classical physics. Equilibrium stress tensors S , derived from the dynamics of the model satisfy a simple, microscopic relationship, $\text{div}S=0$, balancing electric field and momentum-flux contributions at each point in a quantum system. Stress tensors are well-behaved, integrable functions of position which tend to zero as r^{-4} at large distances r from finite Coulombic systems. The microscopic stress tensor and pressure are shown to be consistent with macroscopic expressions for these quantities. Comparisons are made of the present work to related work on microscopic stress.

I. INTRODUCTION

This, the first of two papers on the theory of microscopic quantum stress tensors, is concerned with general aspects of the theory. The antecedents for contributions to the theory of stress tensors are long and often illustrious, indicating a continued interest over many years in the theory of stressed systems. Probably, part of the motivation of the earliest work¹⁻⁷ was to establish the close relationship of quantum theories to their classical correspondents and thus give credence to the then dubious quantum theory. The emphasis was on the concept of force and pressure in quantum systems. Force and pressure remain a subject of theoretical interest,⁸⁻¹² but the focus now is on formulations which lend themselves to efficient calculation. Complete stress tensors for quantum systems have been derived in various forms,^{3,4,13-15} but only recently have there been serious attempts to calculate the stress tensor in nontrivial quantum systems.^{14,15} The common feature to Refs. 1-15 is that they treat force, pressure, or stress as a macroscopic average quantity. Please note that the references to the theory of macroscopic forces, pressures, and stresses are intended only to be representative in acknowledging the conceptual foundations to the theory and in no sense are claimed to be exhaustive.

The objective of the present work is to explore further the theory of forces, pressure, and stress at the microscopic level. It is shown that stress tensors derived from the dynamical equations for the quantum system are valid at the microscopic level. The physical systems considered are nonrelativistic models of many-electron systems, including the local density (LDA) and Hartree-Fock (HF) approximations.

At the microscopic, quantum dynamical level, stress tensors S occur in a continuity equation,

$$\mathbf{F}_{\text{net}}(\mathbf{r}) + \text{div}\vec{S}(\mathbf{r}) = \mathbf{0}, \quad (1)$$

relating the net force density F_{net} acting upon a system to the divergence of the stress tensor. The stress tensor itself is expressed

$$\vec{S} = \vec{K} + \vec{M}, \quad (2)$$

where K (kinetic) involves terms which are interpreted as momentum-flux densities in direct correspondence to classical kinetic theory and M (mechanical) involves force fields including the Maxwell stress tensor with obvious classical significance and additive contributions of a purely quantum-mechanical origin.

In a macroscopic sense, stress tensors are ambiguous quantities because the stress tensor defined by Eq. (1) is unaffected by the addition to it of the curl of a dyadic field and because macroscopic quantities based on a volume integral of S will be unaffected by the addition to S of the gradient of a vector field which vanishes on the volume surface or whose contribution to the surface integral over the volume surface vanishes. It is found here that a stress tensor which is derived from the quantum dynamical equations has an essential microscopic significance of itself.

Stress tensors appear physically transparent in that it seems that one should be able to simply write down a stress tensor based on physical arguments and not be concerned with deriving one from basic principles. Such observations tend to give the apparent ambiguities more weight than they really deserve.

Another source of potential confusion in the theory of stress tensors is that numerous "stress tensors" may be defined for a given physical system. For example, each of the terms in the right member of Eq. (2) has a legitimate interpretation as a stress tensor in its own right. In this paper the term "stress tensor" is reserved for tensors which occur in a continuity equation of the form of Eq. (1) where the force density includes all forces acting on the system. When a system is in equilibrium, by definition the net force density at any point in the system is zero and the divergence of the equilibrium stress tensor is zero. Further examples illustrating this point are given in Sec. III.

In the following section Hartree-Fock and local-density-approximation models are briefly summarized and the notation used in describing these models is established.

In Sec. III stress tensors for LDA models are derived from their dynamical equations. The presentation emphasizes the intimate correspondence to classical physics. Microscopic stress tensors have been considered previously using similar techniques.^{16–26} The present formulation is compared and contrasted with related work at the end of Sec. III. Stress tensors for the more involved HF model are derived in Sec. IV by evaluating the HF expectation value of the many-electron stress-tensor operator. In Sec. V macroscopic stress tensors are derived and found to be identical to stress tensors derived from scaling arguments. In the final section the main results are summarized briefly and discussed. In the companion paper²⁷ applications of the theory are made to closed-shell atomic systems. The objective of the applications is to provide explicit examples of the concepts of stress.

II. ONE-ELECTRON APPROXIMATIONS

The currently popular one-electron LDA where the self-interaction energy of an electron is approximated by a local operator is closely associated with the HF approximation. In either model the total energy of the electronic system has the form

$$E_{\text{tot}} = E_k + E_N + E_e + E_x, \quad (3)$$

where

$$E_k = \sum_I (\phi_I, p^2 \phi_I) / 2m \quad (4)$$

is the electronic kinetic energy and the sum in Eq. (4) includes only occupied one-electron states ϕ_I . The term

$$E_N = - \sum_N \int d^3r_1 n(\mathbf{r}_1) Z_N e^2 / r_{1N} \quad (5)$$

is the interaction energy of nuclei of charge number Z_N (or any other charges external to the electronic system) with the electrons of number density

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2. \quad (6)$$

The interaction energy of the electronic system is

$$E_e = \frac{1}{2} \int d^3r_1 \int d^3r_2 n(\mathbf{r}_1) n(\mathbf{r}_2) e^2 / r_{12}. \quad (7)$$

The exchange-correlation energy of the electrons is represented as

$$E_x = \frac{1}{2} \sum_I (\phi_I, U_x \phi_I), \quad (8)$$

where in the HF model,

$$U_x \phi_I(\mathbf{r}_1) = - \sum_J \int d^3r_2 \phi_J(\mathbf{r}_2)^* \phi_I(\mathbf{r}_2) (e^2 / r_{12}) \phi_J(\mathbf{r}_1), \quad (9a)$$

is an integrodifferential operator and in the LDA models is a multiplicative operator,

$$U_x = 2\varepsilon_x(n) \quad (9b)$$

which depends upon the electron number density n .

The dynamical equations for the one-electron models

are found by minimizing the total energy with respect to variations in the one-electron functions constrained to remain normalized to unity and expressed by the eigenvalue equation

$$H\phi_I = e_I \phi_I. \quad (10)$$

The one-electron Hamiltonian operator

$$H = p^2 / 2m + V + V_x \quad (11)$$

includes kinetic and potential-energy terms in direct correspondence to the partition of the total energy, Eq. (3),

$$V = V_N + V_e, \quad (12)$$

where the nuclear-electron potential energy is

$$V_N(\mathbf{r}_1) = \sum_{N'} (-Z_{N'} e^2) / r_{1N'} \quad (13)$$

and the electron-electron potential energy is

$$V_e(\mathbf{r}_1) = \int d^3r_2 e^2 n(\mathbf{r}_2) / r_{12}. \quad (14)$$

The HF exchange-correlation operator is $V_x = U_x$ of Eq. (9a), while for LDA models,

$$V_x = \frac{\partial}{\partial n} [n \varepsilon_x(n)]. \quad (15)$$

In deriving the stress-tensor operators and their expectation values it is assumed that the dynamics of the one-electron system is governed by the appropriate Schrödinger equation

$$H\phi = i\hbar \frac{\partial}{\partial t} \phi. \quad (16)$$

III. LDA STRESS TENSORS

The equation-of-motion (EOM) method is used to derive the stress tensor. In the presentation here one example will be given in detail and after that the results will simply be listed. The detailed example is given to avert any possible misunderstanding about the method and to point out the origin and nature of certain ambiguities which have been associated with microscopic stress tensors.

It is convenient to consider operators in the Heisenberg representation

$$A^H = \exp(iHt/\hbar) A \exp(-iHt/\hbar), \quad (17)$$

where the EOM for a time-independent Schrödinger operator A is expressed

$$i\hbar \frac{\partial}{\partial t} A^H = (AH - HA)^H, \quad (18)$$

and where the convention established in Eq. (17) that Heisenberg operators are distinguished from the corresponding Schrödinger operators by a superscript H is maintained.

Consider the one-electron mass density operator

$$m(\mathbf{r}) = m_0 \delta(\mathbf{r} - \mathbf{r}_1), \quad (19)$$

where m_0 is the electron mass, $\delta(\mathbf{x})$ is the Dirac δ function, and the explicit reference to the position of the electron \mathbf{r}_1 is suppressed in the notation for m . The EOM of m for the LDA is expressed as

$$\frac{\partial}{\partial t} m(\mathbf{r})^H + \text{div} \mathbf{P}(\mathbf{r})^H = 0 \quad (20)$$

in the form of a continuity equation in which the operator corresponding to the mass flux density is found to be

$$\mathbf{P}(\mathbf{r}) = \frac{1}{2} [\mathbf{p}_1 \delta(\mathbf{r} - \mathbf{r}_1) + \delta(\mathbf{r} - \mathbf{r}_1) \mathbf{p}_1], \quad (21)$$

where p_1 is the electron momentum operator. Alternatively, P may be interpreted as the momentum density operator. The EOM for P leads to a continuity equation in which the momentum-flux density operator has the properties of a stress tensor.

In the context of Eq. (20) operator P is unaffected by the addition of the curl of an arbitrary vector field and in this sense is ambiguous. A current proportional to the curl of a magnetization density is expected from classical considerations. However, as the Hamiltonian for the model system does not include spin-dependent contributions, such terms in the momentum density will have no dynamical manifestations. A model including spin-orbit coupling or a Dirac model will produce spin-dependent contributions to the momentum density operator. It is hypothesized here that the microscopic operators found using the EOM technique uniquely represent the dynamics of the model. In particular, it is assumed that the expectation value of $P(\mathbf{r})$ corresponds within the context of the dynamics uniquely to the observable momentum density of the system at position \mathbf{r} .

Another situation which suggests that the microscopic operators can not be defined uniquely is one in which only a macroscopic quantity is observed. For example, suppose the expectation value, $(\phi(\mathbf{r}_1), \mathbf{P}(\mathbf{r})\phi(\mathbf{r}_1))$, of the microscopic momentum density operator above is integrated over a volume V ,

$$\mathbf{P}_{\text{av}} = \int d^3r (\phi, \mathbf{P}(\mathbf{r})\phi). \quad (22)$$

Equation (22) can be reorganized into the form

$$\mathbf{P}_{\text{av}} = \int d^3r (\phi^* \mathbf{p} + \frac{1}{2} i \hbar \text{grad}(|\phi|^2)). \quad (23)$$

If the volume considered is the volume of the system, then the second term in the right member of Eq. (23) must vanish so that the momentum operator is Hermitian. Of course, by definition expectation values are evaluated with respect to the volume of the system. Integrals over the volume of the system allow several equivalent forms of the operators and in this sense the operators are ambiguous. However, if the volume is arbitrary, then no ambiguity of this type occurs.

The same sorts of concerns over uniqueness as described above affect stress tensors. Stress tensors derived from scaling arguments occur as integrals over the volume of the system and it is not possible to infer on this basis alone operators having a unique microscopic significance.

The EOM for the momentum density operator in the LDA is

$$\begin{aligned} \frac{\partial}{\partial t} [\mathbf{P}(\mathbf{r})]^H &= -\text{div}(\vec{\mathbf{K}}_{\text{op}})^H \\ &\quad - \{ \delta(\mathbf{r} - \mathbf{r}_1) \text{grad}[V(\mathbf{r}) + V_x(\mathbf{r})] \}^H, \end{aligned} \quad (24)$$

where the tensor operator with Cartesian coordinates

$i, j = 1, 2, 3$

$$(K_{\text{op}})_{ij} = [p_{ii} P(\mathbf{r})_j + P(\mathbf{r})_j p_{ii}] / 2m \quad (25)$$

corresponds to the momentum-flux density. The second term in the right member of Eq. (24) corresponds to the force density of the entire Coulombic system acting on an electron at the point \mathbf{r} .

At this point it is convenient to consider expectation values of these one-electron operators. Expectation values for the electronic system are defined for operator A by

$$A(\mathbf{r}, t) = \sum_I (\phi_I(\mathbf{r}_1), [A(\mathbf{r})]^H \phi_I(\mathbf{r}_1)), \quad (26)$$

where the sum includes "occupied" electronic states. The expectation values are time independent when the electronic states are eigenstates of the Hamiltonian. For example, the expectation value of the mass density operator is

$$m(\mathbf{r}, t) = m_0 n(\mathbf{r}, t), \quad (27)$$

where n is defined in Eq. (6). Since a primary concern here is with eigenstates, the possible time dependence will be suppressed in the notation but should not be forgotten.

The expectation value of the operator, Eq. (24),

$$\frac{\partial}{\partial t} \mathbf{P}(\mathbf{r}) = -\text{div} \vec{\mathbf{K}}(\mathbf{r}) - n(\mathbf{r}) \text{grad}[V(\mathbf{r}) + V_x(\mathbf{r})], \quad (28a)$$

where the expectation value of K_{op} , Eq. (25), is

$$K_{ij} = \sum_I \{ [\phi_I^* p_i p_j \phi_I + (p_i \phi_I)^* p_j \phi_I] + \text{c.c.} \} / 4m. \quad (28b)$$

Equation (28a) is recognized as a microscopic form of Ehrenfest's theorem. The conventional form of Ehrenfest's theorem¹ is found by integrating Eq. (28a) over the volume of the system. In this case, divergence terms vanish as discussed above. The integral of Eq. (28a) corresponds to the classical relation,

$$\frac{d}{dt} \mathbf{P}_{\text{elec}} = \mathbf{F}_{\text{net}(\text{elec})}. \quad (28c)$$

Even closer correspondences to classical physics may be found. The force density terms corresponding to the interaction between the electrons can be reexpressed as

$$n(\mathbf{r}) \text{grad}[V_e(\mathbf{r}) + V_x(\mathbf{r})] = \text{div}(\vec{\mathbf{M}}_e + \vec{\mathbf{M}}_x), \quad (29)$$

in terms of the (negative) Maxwell stress tensor for the electronic system,

$$\vec{\mathbf{M}}_e(\mathbf{r}) = [\frac{1}{2} \vec{\mathbf{I}} E_e(\mathbf{r})^2 - \mathbf{E}_e(\mathbf{r}) \mathbf{E}_e(\mathbf{r})] / 4\pi, \quad (30)$$

where the electronic contribution to the electric field at point \mathbf{r} is

$$\mathbf{E}_e(\mathbf{r}) = \text{grad}[V_e(\mathbf{r})] / e, \quad (31)$$

where V_e is defined by Eq. (14) and an exchange term (LDA) (Ref. 10)

$$\vec{M}_x = \vec{I}n(\mathbf{r})(V_x - \varepsilon_x). \quad (32)$$

Equation (28a) becomes

$$\frac{\partial}{\partial t} \mathbf{P}(\mathbf{r}) = -\text{div}(\vec{K} + \vec{M}_e + \vec{M}_x) - n(\mathbf{r})\text{grad}[V_N(\mathbf{r})]. \quad (33a)$$

The integral of Eq. (33a) over the volume of the system corresponds to the classical relationship

$$\frac{d}{dt} \mathbf{P}_{\text{elec}} = \mathbf{F}_{\text{ext}}, \quad (33b)$$

where F_{ext} is the resultant “external” force applied to the electron system.

The divergence terms in each of continuity equations, Eqs. (28a) and (33a) correspond to “stress tensors” with obvious physical interpretation. However, as noted above the designation stress tensor will be reserved here for tensors which occur in continuity equations in which the force density of the total system is included.

Let the “system” be extended to include both the electrons and the nuclei. To do this a term must be included in the left member of Eq. (33) corresponding to the reaction force density of the electrons on the nuclei and the interaction of the nuclei with one another,

$$\mathbf{F}_N(\mathbf{r}) = \sum_{N'} \delta(\mathbf{r} - \mathbf{r}_{N'}) Z_{N'} e \left(\mathbf{E}_e(\mathbf{r}) + \sum_{N'' (\neq N')} \mathbf{E}_{N''}(\mathbf{r}) \right), \quad (34)$$

where E_e is defined in Eq. (31) and

$$\mathbf{E}_N(\mathbf{r}_1) = -\text{grad}(Z_N e / r_{1N}) \quad (35)$$

is the electric field from nucleus N at a point r_1 . The force density of Eq. (34) is added to both sides of Eq. (33) and the right member is reorganized into the form

$$\frac{\partial}{\partial t} \mathbf{P}(\mathbf{r}) + \mathbf{F}_N(\mathbf{r}) = -\text{div}[\vec{S}(\mathbf{r})], \quad (36)$$

where the stress tensor for the entire system is

$$\vec{S} = \vec{K} + \vec{M}_{eN} + \vec{M}_x \quad (37)$$

in which

$$\vec{M}_{eN}(\mathbf{r}) = [\frac{1}{2} \vec{I} \mathbf{E}_{eN}(\mathbf{r})^2 - \mathbf{E}_{eN}(\mathbf{r}) \mathbf{E}_{eN}(\mathbf{r})] / 4\pi \quad (38)$$

is the Maxwell stress tensor for the entire system, where

$$\mathbf{E}_{eN}(\mathbf{r}) = \mathbf{E}_e(\mathbf{r}) + \sum_{N'} \mathbf{E}_{N'}(\mathbf{r}) = \text{grad}[V(\mathbf{r})] / e \quad (39)$$

is the total electric field of electrons and nuclei. In evaluating Eq. (38) it is understood that terms involving nuclear self-interactions are to be excluded. [Note that this condition follows from the algebra and the fact that infinite nuclear self-interaction electric fields are excluded in Eq. (34). It is not an imposed condition based on physical reasoning.] This exclusion of nuclear self-interactions has the counterintuitive consequence that the stress field from the electrons is not completely screened by the nuclear fields, even in the case of neutral systems. As a result, the Maxwell stress tensor, Eq. (38), for a finite system behaves asymptotically as the square of the electric field of a point charge r^{-4} . To simply include nuclear

self-interactions results in stress tensors with more physically sensible asymptotic behavior but introduces nonintegrable singularities at the nuclear sites. Explicit examples concerning this point are discussed in the application to atoms.²⁷ For the present purpose it is preferred to treat stress tensors which are well behaved everywhere.

For localized systems of nuclei and electrons the integral of Eq. (36)

$$\mathbf{F}_{\text{net}(\text{total})} = \mathbf{F}_{\text{net}(\text{elec})} + \mathbf{F}_{\text{net}(\text{nuclei})} = 0 \quad (36')$$

is closely associated with the Hellman-Feynman theorem.^{6,7,9} In Eq. (36') the time rate of change of the total electron momentum has been replaced by the net force on the electrons using Eq. (28c). An isolated system does not exert a force on itself. The integral of the divergence terms in Eqs. (28a), (33a), or (36) will be zero because of the charge localization and because the Maxwell stress-tensor term approaches zero as r^{-4} at large distances.

For the entire system to be in equilibrium the net force on each nucleus must be zero and the electronic states must be eigenstates. Hence, the left member of Eq. (36) is identically zero. A direct evaluation confirms that $\text{div}S=0$ if the net force on each nucleus is zero and the electronic states are self-consistent eigenstates.

The stress tensor obtained through the EOM technique, Eq. (37), contains no terms which may be manipulated away at the microscopic level and still satisfy the equilibrium condition $\text{div}S=0$. All terms are needed and are essential. The equilibrium condition is utilized in Sec. V to make the connection between the microscopic theory and time-honored macroscopic results.

The integral over an arbitrary volume of the left member of Eq. (36) is interpreted to be the net force on all charges inside the volume,

$$\mathbf{F}_{\text{net}}(V) = \int_{A(V)} (-d\mathbf{A}) \cdot \vec{S}(\mathbf{r}), \quad (40)$$

where the divergence theorem is used to express the integral of the right member of Eq. (36) as a surface integral. The minus sign is associated with the differential area vector, giving it the appropriate sense of an inward normal.²⁸ Thus, S has the properties of a directed force per unit area or a stress tensor. In equilibrium these contributions to an integral over any closed surface must completely cancel to give zero net force. Adding to S the curl of a dyadic field has no effect in Eq. (40) in equilibrium or otherwise. By Stokes theorem such a contribution to S has zero contribution to Eq. (40) since $A(V)$ is the surface enclosing volume V . A special case is the curl of a dyadic field equal to a constant dyadic. If such a term were added to S , then S must be understood as a “gauge” stress tensor. However, as noted above for localized systems the stress tensor properly tends to zero outside the region of charge localization and the constant dyadic must be zero.

Stress has an immediate observable physical significance. While it has not been established that microscopic stress is directly observable in a general sense, any physically meaningful representation of these quantities should be well-behaved, integrable functions everywhere and van-

ish at large distances from finite systems at a rate greater than r^{-2} . The latter condition assures that a finite system will have zero stress at large distances. It is desirable that stress vanish at a more rapid rate, so that integrals of the microscopic stress over the volume of the system remain finite.

Nielsen and Martin²⁵ (NM) have also considered microscopic stress in quantum systems. NM use the EOM technique to derive microscopic stress tensors. However, the resulting formulations of microscopic stress appear to be very different. This paper is concerned with single-particle models for systems of electrons with fixed nuclei. Since the system and the forces are stipulated, the present approach incorporates the forces directly into the microscopic stress tensor and they physically motivate its form. NM consider a system of particles with general forces. These general forces can then be specialized to the Coulombic case. In order to maintain generality, NM followed Kugler¹⁷ in treating "force" contributions to the microscopic stress tensor $N(14)$. In the case of Coulombic systems, the Kugler treatment of force terms leads to troublesome technical difficulties. NM are aware of these problems and consider them in their appendices. The Kugler approach is also discussed here in the context of a many-electron formulation of microscopic stress tensor operators in the Appendix.

The main difference between the present and NM formulations concerns how the microscopic results are applied.²⁹ NM use their microscopic stress tensor to derive the total force on a finite volume of the system, $N(16)$. When specialized to Coulombic systems in equilibrium, the corresponding result in this paper is obtained by taking the integral over the same volume of Eq. (28a). For this application the Kugler approach leads to the same result. The rest of the NM paper is concerned with obtaining identities for the macroscopic stress. Thus, as far as the microscopic theory is concerned, the only point of contact between NM and the present work is $N(14)$. The reader might be warned not mistake $N(18)$ for a microscopic stress tensor, as I did. This is clearly described by NM as a "planar" stress. The force terms in this tensor are designed to reproduce the macroscopic stress, but they are not consistent with the EOM in the sense that a microscopic stress tensor must be. In particular, the divergence is nonzero. However, NM do use this tensor as a microscopic stress tensor to obtain alternatives to the scaling form of the macroscopic stress and pressure. This point will be reconsidered in the context of the connection between macroscopic and microscopic stress discussed in Sec. V.

The presentation in this paper has emphasized the classical correspondences between quantum and classical dynamics as evidenced at the macroscopic level by Eqs. (28c), (33b), and (36'). These are general results in the sense that there is no requirement that the systems be in equilibrium. A central point of the paper is to observe that the underlying microscopic relationships, Eqs. (28a),

(33a), and (36), are equally valid and general. The special case of equilibrium as defined above implies that the divergence of the microscopic stress tensor for the entire system is zero at each point in the system. As will be seen in Sec. V this equilibrium condition is essential for establishing the relationship between microscopic and macroscopic stress tensors.

IV. THE HARTREE-FOCK STRESS TENSOR

The HF model poses problems when one tries to apply the EOM technique to derive stress tensors in parallel to the derivation of LDA stress tensors. For example, to parallel the LDA derivation of a momentum density operator, Eqs. (20) and (21), is complicated by the failure of the HF exchange operator to commute with the mass density operator. It is possible to "force" the EOM method to produce a momentum density operator corresponding to Eq. (21) following the methods of Refs. 17, 25, etc. However, the present approach parallels the HF approximation to the many-electron energy. The stress tensor is evaluated simply as the HF expectation value of the many-electron stress-tensor operator.

The many-electron dynamics implies a many-electron stress-tensor operator.²⁶ For a finite system of electrons and nuclei the stress-tensor operator has the form of Eq. (2) where the kinetic term

$$K_{\text{op}}(\mathbf{r})_{ij} = \sum_I [p_{Ii} P_I(\mathbf{r})_j + P_I(\mathbf{r})_j p_{Ii}] / 2m \quad (41a)$$

is summed over electrons at positions r_I and where the momentum density operator for electron I is

$$P_I(\mathbf{r})_j = \frac{1}{2} [p_{Ij} \delta(\mathbf{r} - \mathbf{r}_I) + \delta(\mathbf{r} - \mathbf{r}_I) p_{Ij}] . \quad (41b)$$

The Maxwell stress-tensor operator

$$M_{\text{op}}(\mathbf{r}) = \sum_{\substack{I,j \\ I \neq j}} [\frac{1}{2} \vec{\nabla} \mathbf{E}_I(\mathbf{r}) \cdot \mathbf{E}_J(\mathbf{r}) - \mathbf{E}_I(\mathbf{r}) \mathbf{E}_J(\mathbf{r})] / 4\pi \quad (42a)$$

is summed over both electronic and nuclear coordinates and

$$\mathbf{E}_I(\mathbf{r}_1) = -\text{grad}(e_I / r_{1I}) \quad (42b)$$

is the electric field at position r_1 from a particle of charge e_I at position r_I .²⁶

The stress-tensor operator consists of one-electron and pair interaction terms and the evaluation of the HF expectation value proceeds in exact parallel to the evaluation of the HF expectation value for the many-electron Hamiltonian. The form of the result is identical to Eq. (37), except that the exchange contribution to the stress tensor is

$$\vec{M}_x = - \sum_{I,J} \langle \phi_I(1) \phi_J(2) | (\frac{1}{2} \vec{\nabla} \mathbf{E}_1 \cdot \mathbf{E}_2 - \mathbf{E}_1 \mathbf{E}_2) | \phi_I(2) \phi_J(1) \rangle / 4\pi , \quad (43)$$

where the electric field operators for electron, $k = 1$ or 2 , are

$$\mathbf{E}_k(\mathbf{r}) = \text{grad}(e / |\mathbf{r} - \mathbf{r}_k|). \quad (44)$$

The divergence of the HF stress tensor is zero if the resultant force on each nucleus is zero and the electron states are self-consistent eigenstates of the HF one-electron Hamiltonian. Thus, the same conditions for equilibrium are found for the HF and LDA models.

V. MACROSCOPIC STRESS TENSORS

Stress tensors derived via scaling arguments have the form of macroscopic averages. A connection between the microscopic stress tensors considered here and macroscopic average stress tensors can be made for localized systems by considering volumes in Eq. (40) which extend to infinite distances on a hemisphere and are enclosed by a planar surface which slices through the system,

$$\mathbf{F}_{\text{av}} = \int (-dA \hat{\mathbf{n}}) \cdot \vec{\mathbf{S}}. \quad (45a)$$

The result is interpreted as the force exerted on the charge inside the volume by the charge outside the volume. The only contributions to the integral occur on the surface slicing the plane. In equilibrium this force is zero for each such surface. The volume integral,

$$\mathbf{E}_{\text{av}} = \int dx (-dA \hat{\mathbf{n}}) \cdot \vec{\mathbf{S}}(\mathbf{r}) = - \int d^3r \hat{\mathbf{n}} \cdot \vec{\mathbf{S}}(\mathbf{r}), \quad (45b)$$

where dx is a displacement normal to the surface normal to unit vector $\hat{\mathbf{n}}$, has units of energy, and may be viewed as a measure of the potential for the stresses to do work. In equilibrium \mathbf{E}_{av} is identically zero. For approximations to an equilibrium solution \mathbf{E}_{av} is subject to cancellation effects and may be a spurious indication of equilibrium.

Similar arguments may be used for infinite systems with periodic boundary conditions (PBC).²⁶ Then, the integral over the PBC volume V ,

$$\vec{\mathbf{S}}_{\text{av}} V = \int d^3r \vec{\mathbf{S}}(\mathbf{r}), \quad (46)$$

may be interpreted as a macroscopic average stress tensor. Integrals over the system volume allow gradient-type manipulations. These are used to express the macroscopic averages of the terms of the stress tensor as given in Eq. (37) in a more familiar form:

$$K_{ij(\text{av})} = \sum_I \langle \phi_I(r) | p_i p_j | \phi_I \rangle / m, \quad (47)$$

$$\mathbf{M}_{ij(\text{av})} = \int d^3r V (\nabla_i \nabla_j - \frac{1}{2} \delta_{ij} \nabla^2) V / (4\pi e^2), \quad (48)$$

where V is defined by Eqs. (12)–(14) [intranuclear interactions are excluded in the evaluation of Eq. (48)] and in the LDA model

$$\vec{\mathbf{M}}_{x(\text{av})} = \vec{\mathbf{I}} \int d^3r n(\mathbf{r}) (V_x - \epsilon_x). \quad (49)$$

The HF exchange term can be reorganized in the manner of Eq. (48). The result will not be quoted here.

The average trace of S is defined to be the pressure. Thus, the macroscopic average pressure is given by

$$3P_{\text{av}} V = 2E_k + E_{NN} + E_N + E_e + E_{xc}, \quad (50)$$

where E_k , E_N , and E_e are defined in Eqs. (4), (5), and (7). The nuclear interaction energy is

$$E_{NN} = \frac{1}{2} \sum_{\substack{N, N' \\ N \neq N'}} Z_N Z_{N'} e^2 / r_{NN'}. \quad (51)$$

In the LDA the exchange-correlation contribution to the macroscopic pressure is

$$E_{xc}(\text{LDA}) = 3 \int d^3r n(\mathbf{r}) (V_x - \epsilon_x), \quad (52)$$

while in the HF

$$E_{xc}(\text{HF}) = E_x, \quad (53)$$

where E_x is defined by Eqs. (8) and (9a). Of course, Eq. (50) is just a form of the virial theorem and is in complete agreement with results from scaling arguments.⁸

A remarkable formulation of the macroscopic pressure in equilibrium has been noted by Liberman.¹⁰ Liberman showed that the macroscopic pressure can be described by the surface integral of a “virial” of the momentum-flux density. Liberman’s virial,

$$L_i = \sum_j K_{ij} r_j - \hbar^2 \nabla_i h / 4m, \quad (54)$$

is macroscopically equivalent to $\vec{\mathbf{K}} \cdot \mathbf{r}$, where $\vec{\mathbf{K}}$ is defined by Eq. (28b). Consider the integral over the volume of the system of the quantity,

$$\text{div}(\vec{\mathbf{K}} \cdot \mathbf{r}) = (\text{div} \vec{\mathbf{K}}) \cdot \mathbf{r} + \text{Tr}(K). \quad (55a)$$

Using the equilibrium specialization of Eq. (28a) to replace $\text{div} \vec{\mathbf{K}}$ and recognizing the trace of K to be twice the kinetic energy density gives the identity

$$\int d\mathbf{A} \cdot (\vec{\mathbf{K}} \cdot \mathbf{r}) = 2E_k - \int d^3r n \mathbf{r} \cdot \text{grad}(V + V_x). \quad (55b)$$

The manipulations described by Liberman¹⁰ for LDA exchange and the manipulations of Slater⁹ for the r grad operator acting on Coulomb potential energies produces Liberman’s identity

$$\int d\mathbf{A} \cdot (\vec{\mathbf{K}} \cdot \mathbf{r}) = 3P_{\text{av}} V + \sum_N \mathbf{r}_N \cdot \mathbf{f}_N - \int d\mathbf{A} \cdot \vec{\mathbf{M}}_x \cdot \mathbf{r}. \quad (56)$$

In Eq. (56) $\mathbf{f}_N = Z_N e \mathbf{E}_{eN}$ is the total force on nucleus N (excluding self-interactions). In equilibrium the force on each nucleus is zero. The exchange surface virial in the right member of Eq. (56) is identical to the “missing” surface term that prompted Liberman’s paper.¹⁰ In the case of HF exchange no exchange surface term occurs and Liberman’s identity is

$$\int d\mathbf{A} \cdot (\vec{\mathbf{K}} \cdot \mathbf{r}) = 3P_{\text{av}} V. \quad (57)$$

It is shown in the Appendix that Eq. (57) is also valid in the many-electron case. In Eqs. (56) and (57) the quantity $3P_{\text{av}} V$ is defined by Eqs. (50)–(53).

However, it should be noted that Liberman’s identity cannot be simply applied to Coulomb systems infinitely extended with PBC’s. Conventional treatments of the conditional convergence of the Coulomb interactions preclude this facile use of the Slater manipulations. Sham

has previously pointed out the need for corrections to Liberman's identity for systems with PBC's.³⁰ The necessity of such corrections may be seen in the present context as follows. Consider for a PBC system the identity

$$\operatorname{div}(\vec{S} \cdot \mathbf{r}) = (\operatorname{div} \vec{S}) \cdot \mathbf{r} + \operatorname{Tr}(S). \quad (58)$$

In equilibrium $\operatorname{div}(S) = 0$ and the integral over the PBC periodic cell [using Eq. (50)] is

$$3P_{\text{av}}V = \int dA \cdot \vec{S} \cdot \mathbf{r}. \quad (59)$$

A conventional formulation of an infinitely extended Coulomb system will result in microscopic stress tensors in which the kinetic, mechanical, and exchange terms are each periodic. For simplicity suppose that the PBC cell is a cube. Then, using the periodicity, Eq. (59) can be evaluated to be (the r -dependent terms from the opposing sides of the cell cancel)

$$3P_{\text{av}}V = V \sum_i P_{\text{av}}(i), \quad (60a)$$

where

$$P_{\text{av}}(i) = \int dA \hat{\mathbf{x}}_i \cdot \vec{S}(\mathbf{r}) \cdot \hat{\mathbf{x}}_i / A \quad (60b)$$

is the average compressive stress exerted on the PBC cell surface of area A normal to unit vector $\hat{\mathbf{x}}_i$. This result may be generalized to PBC cells of arbitrary geometry.²⁶ Since S includes all contributions to the stress tensor, not just kinetic terms, the "corrections" to Liberman's identity in the case of PBC systems cannot be ignored.

The Nielsen and Martin formulation of macroscopic stress tensors $N(30)$ agrees in every detail with the macroscopic results here. However, their expression for the macroscopic pressure, $N(35)$, is incorrect. This can be proved by following the argument above, Eqs. (58)–(60), but regarding NM's "planar stress," $N(17)$ or $N(18)$, as a genuine microscopic stress tensor. For PBC's the integral of $\operatorname{Tr}(S)$ gives the same macroscopic pressure that is found here, but since the divergence of $N(18)$ is nonzero, in general, there will be a volume integral correction to their expression for the pressure involving this divergence.

VI. CONCLUSIONS

Microscopic stress tensors occur in the context of a continuity equation for the force density of an entire system, Eq. (1). Their occurrence as a divergence has motivated concern about possible additive terms and suggests that they may represent a relative measure of stress or gauge stress. It has been observed above that such additive terms have no relevance in applications in which the stress tensor is used to calculate forces. The stress tensors described here are easily shown²⁷ to be well-behaved, weakly singular (integrable) functions of position which for finite systems approach zero as r^{-4} at large distances from the system. In equilibrium the divergence of the microscopic stress tensor is zero at each point in the system. At the microscopic level no terms may be discarded or manipulated away. However, while such observations may alleviate concerns about possible ambiguities, that does not eliminate them. Rather, one must conclude

that considerations of forces can never resolve such an issue.

Microscopic stress tensors provided detailed information about how the equilibrium momentum and electric field fluxes balance one another, on how the nonequilibrium fluxes do not balance. Each of the contributions to a microscopic stress tensor has an immediate physical interpretation. This suggests that only terms which can be physically motivated should be added. Of course, this can be done. The easiest way to find such contributions is to consider a dynamical model with more structure, such as a relativistic model. However, such considerations exceed the scope of this paper.

One of the original motivations for studying the HF model along with LDA models was the possibility that the study of microscopic stress tensors might lead to an insight about electron correlation. It was not obvious to me that the HF expectation value of the many-electron stress tensor operator would have equilibrium conditions completely parallel to the LDA model as, indeed, was found to be true.

The crucial requirement for a model system to be in equilibrium is self-consistency. By comparing different models one can observe how their differences affect the way in which self-consistency is achieved. This is one of the questions which is pursued through detailed calculations and analysis of atomic models in the companion paper.²⁷

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I thank Richard Martin for "stressing" to me that finite systems and infinitely extended PBC systems are necessarily of different character.

APPENDIX

It is claimed above that the Liberman expression for the macroscopic pressure¹⁰ is a general many-electron result. Liberman does not explicitly make this claim in his paper, but it appears from Eqs. (2) and (3), Ref. 10 that he was fully aware of the generality of his result. A derivation of the many-electron Liberman form is given here using the EOM technique. The derivation provides a convenient context in which to compare the Maxwell and Kugler formulations of mechanical stress. This is done in the concluding paragraphs of the Appendix.

The many-electron momentum density operator,

$$P_{\text{op}}(\mathbf{r})_i = \sum_I P_I(\mathbf{r})_i, \quad (A1)$$

is defined in terms of the momentum density operator, Eq. (41b), for an electron I . The EOM for this operator is

$$\frac{\partial}{\partial t} [P_{\text{op}}(\mathbf{r})]_i^H = \left[-[\operatorname{div} \vec{K}_{\text{op}}(\mathbf{r})]_i + \sum_I \delta(\mathbf{r} - \mathbf{r}_I) [F_I(\mathbf{r})]_i \right]^H, \quad (A2)$$

where the kinetic operator is defined by Eqs. (41) and the force operator for electron I ,

$$F_I(\mathbf{r}) = -\operatorname{grad} V_I(\mathbf{r}), \quad (A3)$$

is expressed in terms of the operator

$$V_I(\mathbf{r}) = \sum_{J(\neq I)} e^2/|\mathbf{r}-\mathbf{r}_J| - \sum_N Z_N e^2/|\mathbf{r}-\mathbf{r}_N| \quad (\text{A4})$$

corresponding to the potential interaction energy of all other electrons and nuclei with electron I . If the operator corresponding to the force density of the electrons and other nuclei on each nucleus is added to both sides of Eq. (A2), then the force terms in the right member may be expressed as the negative divergence of the Maxwell stress tensor operator, Eqs. (42).

A Liberman-type operator is defined,

$$[L_{\text{op}}(\mathbf{r})]_i = \sum_j r_j [K_{\text{op}}(\mathbf{r})]_{ij} \quad (\text{A5})$$

The divergence of L is reexpressed using Eq. (A2) as

$$\text{div}[L_{\text{op}}(\mathbf{r})]^H = \left[-\mathbf{r} \cdot \frac{\partial}{\partial t} \mathbf{P}_{\text{op}}(\mathbf{r}) + 2E_{\text{kin,op}}(\mathbf{r}) + \sum_I \delta(\mathbf{r}-\mathbf{r}_I) \mathbf{r} \cdot \mathbf{F}_I(\mathbf{r}) \right]^H, \quad (\text{A6})$$

where

$$E_{\text{kin,op}}(\mathbf{r}) = \frac{1}{2} \text{Tr}[K_{\text{op}}(\mathbf{r})] \quad (\text{A7})$$

is the kinetic energy density operator. Slater manipulations⁹ cannot be performed on the microscopic force density terms.

Macroscopic observables involve an expectation value of the corresponding microscopic operator and an integral over the volume of the system. The macroscopic equation corresponding to Eq. (A6) is

$$\int d^3r \left[\text{div}[\mathbf{L}(r)] - \mathbf{r} \cdot \frac{\partial}{\partial t} \mathbf{P}(r) \right] = 2E_k + \left\langle \sum_I \mathbf{r}_I \cdot \mathbf{F}_I(\mathbf{r}_I) \right\rangle, \quad (\text{A8})$$

where the expectation values of the Liberman and momentum density operators are

$$\mathbf{L}(\mathbf{r}) = \langle L_{\text{op}}(\mathbf{r})^H \rangle \quad (\text{A9})$$

and

$$\mathbf{P}(\mathbf{r}) = \langle \mathbf{P}_{\text{op}}(\mathbf{r})^H \rangle. \quad (\text{A10})$$

The macroscopic kinetic energy of the electronic system,

$$E_k = \sum_I \langle p_I^2/2m \rangle, \quad (\text{A11})$$

is the total kinetic energy of the system. The Coulomb force terms in Eq. (A8) are amenable to Slater manipulations. For example, the electron-electron interaction term

$$E_e = \sum_{I(\neq J)} \langle \mathbf{r}_I \cdot \text{grad}_I (e^2/r_{IJ}) \rangle \quad (\text{A12a})$$

is easily reexpressed as the electron-electron potential energy

$$E_e = \frac{1}{2} \sum_{I(\neq J)} \langle e^2/r_{IJ} \rangle. \quad (\text{A12b})$$

Similar manipulations on the nuclear terms allow Eq. (A8) to be written as

$$\int d^3r \left[\text{div} \mathbf{L}(r) + \mathbf{r} \cdot \frac{\partial}{\partial t} \mathbf{P}(r) \right] = 2E_k + V_{\text{pot}} - \sum_N \mathbf{r}_N \cdot \mathbf{F}_N, \quad (\text{A13})$$

where the total potential energy

$$V_{\text{pot}} = E_e + E_{eN} + E_{NN} \quad (\text{A14})$$

also includes nuclear interaction energy, Eq. (51), and electron-nuclear interaction energy

$$E_{eN} = - \sum_{I,N} \langle Z_N e^2/r_{IN} \rangle. \quad (\text{A15})$$

The remaining term in Eq. (A13) is a nuclear virial where the force is

$$\mathbf{F}_N = - \text{grad}_N \sum_{N'(\neq N)} Z_N Z_{N'} e^2/r_{NN'} - \sum_I \langle Z_N e^2/r_{IN} \rangle. \quad (\text{A16})$$

In equilibrium the nuclear virial and electrons force terms are zero and the result is a many-electron version of Liberman's form for the macroscopic pressure.

It should be noted that a choice was made in Eq. (A2) in treating the force term. The force term was regarded as a force field evaluated at the position r . Because of the δ -function property the alternative "Kugler" choice¹⁷ of considering the force factor in Eq. (A2) to be evaluated at the electron position appears attractive because then the replacement of the δ function by the Laplacian of the standard Coulomb Green's function, $1/|\mathbf{r}-\mathbf{r}_I|$, immediately leads to a form which can be interpreted as the mechanical contribution to the microscopic stress-tensor operator,

$$M^K(\mathbf{r})_{ji} = \sum_I \text{grad}_j (1/|\mathbf{r}-\mathbf{r}_I|) \text{grad}_i V_I(r_I)/4\pi. \quad (\text{A17})$$

For nonequilibrium situations I argue that to regard this quantity alone as the mechanical stress operator is conceptually incorrect because the stress tensor does not involve the total force on the system. For equilibrium situations this point is moot because the force density on the nucleus which is added above and whose addition makes it possible to express the total force density as the divergence of a stress tensor is zero by definition. For general stress tensors this concern can be resolved by including the Kugler version of the nuclear force terms.

Practically, it is difficult to contemplate making a calculation based on the Kugler form as compared to the Maxwell form. Some terms in the Kugler form have no obvious physical meaning, such as a stress tensor which gives a finite stress asymptotically on a surface subtended by a finite solid angle. Formally, it may be noted that a tensor formed from the difference between the Maxwell and Kugler forms have zero divergence. This suggests that this difference may be represented as the curl of a dyadic field and the forms are in this sense equivalent. However, the weak (r^{-2}) asymptotic behavior of the Kugler form may preclude an actual calculation of this dyadic field using conventional techniques of vector calculus. While these observations express concern about the

Kugler form they do not demonstrate that it is in some sense "wrong."

The strongest argument that I have found against the Kugler form is that its connection with macroscopic quantities is ill-defined. Macroscopic quantities in this appendix and in Sec. V are found by integrating the microscopic quantity over the volume of the system. The comparison is simplest in the case of the macroscopic

pressure. The integral of the trace of the Kugler tensor over the volume of the system is

$$\int d^2r \text{Tr}(M^K) = \int d\mathbf{A} \cdot \text{grad}_I V_I(\mathbf{r}_I) / |\mathbf{r} - \mathbf{r}_I|. \quad (\text{A18})$$

The result is ambiguous, but would appear to be zero for finite systems. The corresponding result for the Maxwell operator is the potential-energy operator for the system.

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