

Quantum-mechanical theory of stress and force

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The stress theorem presented previously by the present authors is derived in detail and is related to the virial and force theorems. Stress fields are considered in two alternative forms, both of which give the same macroscopic stress and forces on nuclei when integrated over appropriate surfaces. A crucial concept is interactions that "cross" surfaces. Explicit forms of the stress field within the local-density approximation are given, together with a generalization of the approximate Liberman form for pressure. Reciprocal-space expressions and *ab initio* calculations are considered in detail in an accompanying paper.

I. INTRODUCTION

The purpose of the work presented here and in related papers^{1,2} is to investigate stress as an intrinsic property of the quantum-mechanical ground state of matter and to carry out *ab initio* calculations of stresses, as well as energy and forces, in solids. The present paper is devoted to the derivation of general expressions for stress and force in quantum-mechanical systems with interacting particles. We consider total forces and stresses, definitions of the microscopic stress field, and the relation of the stress field to the forces acting upon the particles. In the following paper¹ (denoted here as II) are presented reciprocal-space expressions appropriate for a periodic crystal and detailed *ab initio* calculations of the elastic properties of the semiconductors Si, Ge, and GaAs. Portions of this work have been presented previously in a Letter.²

Stress is an important concept in characterizing the states of condensed matter.³⁻⁶ A body is in a state of stress if it is acted upon by external forces or, more generally, if one part of the body exerts forces upon another part.^{3,4} If we consider a volume element within a stressed body, we can distinguish the effects of two types of forces: those acting directly in the interior of the element and those exerted upon the surface of the element by the surrounding material. The latter forces (per unit area) are stresses that are transmitted throughout the interior of the volume. For condensed matter in which the stress is homogeneous in volumes of macroscopic dimensions, the equation of state is the relation between the stress and the internal variables, such as the density and temperature.⁶

A familiar example of condensed matter in the presence of externally applied stress is a homogeneous liquid of constant chemical composition which is under pressure. Since a liquid can flow, there can be no shear stress in its equilibrium state and no net force exerted upon any atom by the external environment. There can be a pressure P (which is a homogeneous, isotropic stress), and the equation of state is the relation of P to the density and tem-

perature. The fundamental expression of this intrinsic relation in terms of the Hamiltonian and the quantum-mechanical wave functions is provided by the virial theorem, which gives an exact expression for P in terms of the expectation values of the operators for kinetic energy and the virial of the interactions between the particles.⁶

Stresses and forces are more complex in solids, which are macroscopic bodies in which the nuclei and electrons form a spatial structure that is stationary over long periods of time. The solid state can be distinguished from the liquid state by the property that the structure is stable under the application of moderate forces and shear stresses, in addition to pressure. Under external influences the solid adjusts to a new distorted structure, which can be defined in terms of a macroscopic strain tensor plus microscopic displacements of atoms.^{3-5,7} In this structure there are internal forces and stresses which balance the external ones. The full set of relations of the applied stresses and forces to the strains and displacements is necessary to specify completely the equation of state of the solid.

We note that it is an excellent approximation in most solids (the Born-Oppenheimer or adiabatic approximation⁷) that the dynamical vibrations of the structures are on such a slow time scale that the electrons follow the ions adiabatically, always being in their ground state for the instantaneous positions of the ions. Thus for most cases the full generalized equation of state of the solid in the electronic ground state, i.e., the microscopic stresses and forces as functions of displacements of the ions discussed here, determine the dynamical vibrations as well as strictly static properties.

In this paper we consider the fundamental expressions for stress and force in a solid that are generalizations of the virial theorem. The derivations follow closely some of the fundamental early papers in quantum mechanics, adapted to be useful for modern computations in solids.

The force theorem was first derived by Ehrenfest,⁸ showing that the net force on a particle is the expectation

value of the negative of the gradient of the potential. This theorem was one of the cornerstones in establishing the correspondence between classical and quantum mechanics. The result was used in the treatises of Pauli⁹ and Hellmann,¹⁰ and the latter reformulated it by a variational argument to give a form convenient for applications to molecules. The same form was later derived independently by Feynman.^{11,12} The force theorem has often been associated with the names of Hellmann and Feynman, but we shall refer to it as the "force theorem" in the following.

Closely related to the force theorem is the quantum-mechanical virial theorem which was first proven by Born, Heisenberg, and Jordan¹³ and later by Finkelstein,¹⁴ Hylleraas,¹⁵ Fock,¹⁶ Pauli,⁹ and Slater.¹⁷ These authors showed that the total pressure in a many-body quantum system is defined by the kinetic energy and the virial of the potential, in exact correspondence with classical mechanics. Although Schrödinger,¹⁸ Pauli,⁹ Feynman,¹² and others^{19–22} have considered the complete stress tensor field in quantum systems, a theorem for stress having the same form as the virial theorem for arbitrary systems of interacting particles has only recently been derived² to our knowledge. A detailed proof is given below using essentially the same scaling argument as given over half a century ago in the elegant paper by Fock.¹⁶ McLellan²² used the equation-of-motion technique⁹ to derive a similar form, and there are also relations to the "hypervirial theorems" discussed by Hirschfelder.²³ It should be noted that the stress theorem gives only the *average* macroscopic stress of the system. Thus inhomogeneous stresses require additional considerations, such as assuming the system to consist of subsystems which are small but macroscopic, so that the stress theorem applies to each subsystem separately. This can then form the starting point for treating the system by the methods of classical elasticity theory.

In addition to total forces and stresses, fields defining the force and stress at each point in space have both formal and practical consequences for the theory of matter. The force field is uniquely defined in terms of kinetic and potential operators as shown by Pauli.⁹ The stress field, however, can be any tensor field which satisfies the condition that its divergence is the vector force field.^{3–5} The nonuniqueness of the stress field has the advantage that different forms can be chosen to be most useful in particular problems. We shall consider the Maxwell stress,^{24,12} which describes matter interacting via Coulomb fields, and the form given by Kugler,²⁰ which applies to arbitrary potentials. We will use the term *microscopic* stress field to denote fields which vary on the scale of atomic dimensions. Since the range of the forces is on the same length scale, it is essential to recognize that the stress at point \mathbf{r} is a nonlocal function of the state of the matter at all points in some vicinity of \mathbf{r} , in contrast to the local stress field used in continuum theories of stress in solids.^{3–5} A consequence of the present investigation is the derivation of quantum-mechanical expressions for forces on particles in terms of surface integrals of the stress tensor. These are different from and complementary to the well-known expressions^{8,10,11} given by the "force

theorem." We shall also derive expressions for the macroscopic stress in terms of surface integrals of the microscopic stress field. These are useful expressions for the stress, complementary to the volume integrals of the stress theorem.

Despite the simplicity of the exact expressions for stress and force, their evaluation is in general very difficult because they involve many-body correlation functions. Calculations for systems of interacting particles are formidable tasks, even in the simplest of cases, and it is important to recast the stress and force theorems within a more tractable framework. One possibility is to use the density-functional theory of Hohenberg, Kohn, and Sham,^{25–27} who proved that the total energy of the system is a unique *functional* of the charge density. This provides alternative exact expressions for stress, with a different form of the virial, in which the expectation values for correlated, interacting particles are replaced by a functional of the charge density. In addition the local-density-functional approximation²⁷ (LDA) provides a practical approximate scheme which has been shown to be remarkably accurate for real solids.^{2,28–31} The LDA formulations for the isotropic pressure has been considered previously by several authors.^{32–38}

The present paper is organized as follows. In Sec. II the stress and force theorems are derived. Section III gives force and stress fields, surface integrals of the stress field, connections of the force and stress theorems, and alternative forms for calculating forces and stresses. Section IV describes the form of the expressions in the density-functional representation for exchange and correlation. Section V gives surface-integral formulas for the macroscopic stress in periodic systems. The appendices describe properties of the stress fields as defined by Kugler and by Maxwell, and give simple examples. The accompanying paper II deals with explicit formulas appropriate for periodic crystals and gives the results of *ab initio* calculations of the elastic properties of the semiconductors silicon, germanium, and gallium arsenide.¹

II. THE STRESS AND FORCE THEOREMS

The total stress of a stationary system can be derived by applying the variational principle together with a scaling of the wave function. The derivation, which has been outlined by the present authors previously,² is essentially the same as that given for the virial theorem in an elegant paper by Fock.¹⁶ We consider a general many-body Hamiltonian of the form

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V_{\text{int}} + V_{\text{ext}}, \quad (1)$$

where \mathbf{p}_i is the momentum of particle i , and V denotes the potential energy which is a function of the positions \mathbf{r}_i of all the particles. Note that i denotes *both* nuclei and electrons. The potential energy is divided into an internal part V_{int} which is intrinsic to the system under consideration, and a part V_{ext} which describes external influences. Here we do not consider velocity-dependent interactions such as magnetic fields, but the results below can be generalized to include such cases. The solutions of the

Schrödinger equation $H\Psi = E\Psi$ define the exact many-body eigenstates Ψ and energies E , and the variational principle requires that the ground state of Eq. (1) is determined by the minimum of $E = \langle \Psi | H | \Psi \rangle$ with respect to all allowed variations in Ψ . In the following, expectation values of operators refer to this ground state, except as noted.

To derive the stress, an infinitesimal homogeneous scaling is applied to the ground state $\Psi(\mathbf{r})$, where \mathbf{r} denotes all particle coordinates. The function $\Psi(\mathbf{r})$ is "stretched"⁹ by

the transformation on each particle coordinate $r_{i\alpha} \rightarrow r_{i\alpha} + \sum_{\beta} \epsilon_{\alpha\beta} r_{i\beta}$, where $\epsilon_{\alpha\beta}$ is a symmetric (i.e., rotation-free) strain tensor.^{3,4} The wave function becomes

$$\Psi_{\epsilon}(\mathbf{r}) = \det(\mathbb{1} + \epsilon)^{-1/2} \Psi((\mathbb{1} + \epsilon)^{-1}\mathbf{r}), \quad (2)$$

where the prefactor preserves the normalization of Ψ_{ϵ} . The expectation value of H with respect to Ψ_{ϵ} involves an integral over all coordinates \mathbf{r} , which by the variable substitution $\mathbf{r} \rightarrow (\mathbb{1} + \epsilon)\mathbf{r}$ becomes

$$\langle \Psi_{\epsilon} | H | \Psi_{\epsilon} \rangle = \int \Psi^*(\mathbf{r}) \left[\sum_i \frac{1}{2m_i} \left[\mathbf{p}_i^2 - 2 \sum_{\alpha, \beta} \epsilon_{\alpha\beta} p_{i\alpha} p_{i\beta} + \sum_{\alpha, \beta, \gamma} \epsilon_{\alpha\beta} \epsilon_{\alpha\gamma} p_{i\beta} p_{i\gamma} \right] + V_{\text{int}}((\mathbb{1} + \epsilon)\mathbf{r}) + V_{\text{ext}}((\mathbb{1} + \epsilon)\mathbf{r}) \right] \Psi(\mathbf{r}) d\mathbf{r}, \quad (3)$$

where Ψ_{ϵ} has been replaced by Ψ using Eq. (2). The variational principle requires that $\langle \Psi_{\epsilon} | H | \Psi_{\epsilon} \rangle$ differ from $\langle \Psi | H | \Psi \rangle$ only to second order in $\epsilon_{\alpha\beta}$, i.e., that the derivative of Eq. (3) with respect to $\epsilon_{\alpha\beta}$ is zero:

$$\frac{\partial \langle \Psi_{\epsilon} | H | \Psi_{\epsilon} \rangle}{\partial \epsilon_{\alpha\beta}} = 0 = \sum_i \left\langle \Psi \left| \frac{p_{i\alpha} p_{i\beta}}{m_i} - r_{i\beta} \nabla_{i\alpha} (V_{\text{int}} + V_{\text{ext}}) \right| \Psi \right\rangle. \quad (4)$$

Equation (4) is the fundamental equation which is used to derive the macroscopic stress and the stress theorem. The term involving V_{ext} in Eq. (4) is the stress $T_{\alpha\beta}$ exerted by the external environment upon the solid, as defined in classical mechanics,^{3,4}

$$T_{\alpha\beta} = - \sum_i \langle \Psi | r_{i\beta} \nabla_{i\alpha} (V_{\text{ext}}) | \Psi \rangle, \quad (5)$$

where the sign convention in Eq. (5) is chosen to be the same as in Refs. 3, 4, and 9. The stress $T_{\alpha\beta}$ is symmetric for a system in equilibrium without any externally applied torques. It follows from Eqs. (4) and (5) that the stress intrinsic to the system is given by

$$T_{\alpha\beta} = - \sum_i \left\langle \Psi \left| \frac{p_{i\alpha} p_{i\beta}}{m_i} - r_{i\beta} \nabla_{i\alpha} (V_{\text{int}}) \right| \Psi \right\rangle. \quad (6)$$

Equation (6) is one form of the stress theorem which expresses the total macroscopic stress in terms only of expectation values of internal operators intrinsic to the system. The present result shows that the total stress is a sum of operators defined for each particle. However, in an interacting system each operator $\nabla_i(V_{\text{int}})$ is a function of the coordinates of other particles, and the expectation value in Eq. (6) involves the position \mathbf{r}_i and the gradients of interactions caused by other particles which are correlated with particle i . Note that Eq. (6) gives the total stress, even for systems subjected to inhomogeneous external stresses. The evaluation of spatially varying stress fields is discussed in Sec. III.

The stress theorem is applicable to general quantum-mechanical systems with interactions which are differentiable functions of the particle coordinates. In particular, the interactions may be functions simultaneously of the coordinates of more than two particles and may be nonlo-

cal, i.e., functions of the coordinate of a given particle at more than one point in space. The latter are important aspects of pseudopotentials³⁹⁻⁴¹ and are explicitly utilized in paper II.

Equation (6) is not in the most desirable form for application to large macroscopic systems because of the presence of the position coordinate \mathbf{r}_i of each particle. In order to define the stress in a way that the limit of large systems is unambiguous, we must express the stress manifestly in terms of relative coordinates of the interacting particles. In the case of particles interacting via two-body central potentials,

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

the stress theorem can be written

$$T_{\alpha\beta} = - \sum_i \left\langle \frac{p_{i\alpha} p_{i\beta}}{m_i} \right\rangle - \frac{1}{2} \sum_{i,j} \left\langle \frac{(\mathbf{r}_i - \mathbf{r}_j)_{\alpha} (\mathbf{r}_i - \mathbf{r}_j)_{\beta}}{|\mathbf{r}_i - \mathbf{r}_j|} V'_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) \right\rangle, \quad (7)$$

where $V'(x) = dV(x)/dx$. Here we have omitted the explicit reference to Ψ . This form is symmetric, i.e., torque free, and is manifestly dependent only upon the relative positions of the particles. In macroscopic systems where the volume Ω is well defined, the average stress density is defined as $\sigma_{\alpha\beta} = T_{\alpha\beta}/\Omega$. In a periodic system Ω may be chosen to be a unit cell, and the stress may be evaluated per unit-cell volume. Of course the stress $T_{\alpha\beta}$ for the given cell in general involves interactions with all other cells through the potential interactions.

The well-known quantum form of the virial theorem^{9,13-17} is a special case of the stress theorem since

the negative trace of $T_{\alpha\beta}$ is by Eq. (6)

$$3P\Omega = 2 \sum_i \frac{\langle \mathbf{p}_i^2 \rangle}{2m_i} - \sum_i \langle \mathbf{r}_i \cdot \nabla_i V_{\text{int}} \rangle \quad (8a)$$

or, from Eq. (7),

$$3P\Omega = 2 \sum_i \frac{\langle \mathbf{p}_i^2 \rangle}{2m_i} - \frac{1}{2} \sum_{i,j} \langle |\mathbf{r}_i - \mathbf{r}_j| V'_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) \rangle, \quad (j \neq i) \quad (8b)$$

where P denotes the pressure. Furthermore, if the interactions all have the same power-law dependence, $V_{ij}(x) \sim x^{-n}$, Eqs. (7) and (8b) show that the virial theorem can be written simply in terms of kinetic and potential energies. For the Coulomb potential, $n=1$, the theorem takes the familiar form¹⁶ $3P\Omega = 2E_{\text{kin}} + E_{\text{pot}}$.

Hellmann¹⁰ and Feynman¹¹ have given a simple derivation of the force theorem based upon the variational principle. The steps are exactly parallel to the derivation of the stress theorem in Eqs. (3)–(5), except that instead of Eq. (2), the ground-state wave function is modified by displacing the coordinate of one particle i by the infinitesimal vector \mathbf{u}_i . The expectation value of the Hamiltonian analogous to Eq. (3) has no change in the kinetic energy and the potential terms are modified simply by the translation of particle i relative to all the other particles. From the derivative of the energy with respect to \mathbf{u}_i one finds the well-known result that the internal force on particle i is

$$\mathbf{F}_i = -\langle \nabla_i V_{\text{int}} \rangle, \quad (9)$$

which is cancelled exactly by the external force $\mathbf{F}_{i,\text{ext}} = -\langle \nabla_i V_{\text{ext}} \rangle$ acting upon particle i . This expression is also completely general and holds for systems with arbitrary many-body interactions.

It is usually most advantageous to carry out the calculations without introducing V_{ext} explicitly, and instead to determine the ground state of $H_{\text{int}} = T_{\text{kin}} + V_{\text{int}}$ in the presence of constraints, such as fixed atomic positions, volume, or strain. For example, it is more pertinent to calculate the pressure in a macroscopic body with fixed volume rather than to construct explicitly a potential at the boundaries to cause the body to be in equilibrium at the desired volume. In this case the ground state Ψ satisfies a restricted variational principle with respect to only those variations in Ψ which obey the given constraints. Using the same reasoning as before, it is straightforward to show that for each constraint, $x = x_0$, there exists a conjugate generalized force $-\partial \langle H \rangle / \partial x$ which is given by $-\langle \partial H / \partial x \rangle$ evaluated at $x = x_0$. This specifies the generalized forces which must be applied for the system to be in equilibrium at these constraints, without explicit introduction of an external potential. This analysis can be applied also to other variations, such as changes in the number of particles and the conjugate chemical potential, but we shall not explore such possibilities here.

III. STRESS AND FORCE FIELDS

In the preceding section we have discussed the *total* stress and force acting upon a particle or a system of par-

ticles. We now turn to microscopic stress and force as fields defined at every point in space. Among the many works describing the construction of these fields in quantum mechanics, the classic papers of Schrödinger,¹⁸ Pauli,⁹ Feynman,¹² Martin and Schwinger,¹⁹ and the more recent work of Kugler²⁰ are particularly pertinent to the present development. The force field may be derived from the quantum-mechanical equations of motion as shown by Pauli.⁹ The stress field, however, is not uniquely defined. It may be chosen to be any tensor field whose divergence is the force field. In this section we present expressions for the stress field, examine the link between the force and stress theorems, derive alternative formulas for stress and forces in terms of the microscopic stress field, and discuss the utility of these formulas for calculations of force and stress in condensed matter.

The fields under consideration can be derived from the equation of motion of the symmetrized momentum density operator for each particle i

$$\mathbf{P}_i(\mathbf{r}) = \frac{1}{2} [\mathbf{p}_i, \delta(\mathbf{r} - \mathbf{r}_i)]_+, \quad (10)$$

where $[\cdot]_+$ denotes the anticommutator and \mathbf{r} the spatial coordinate. The time derivative of $\mathbf{P}_i(\mathbf{r})$ is interpreted as the force-density operator acting on particle i (*not* the force itself), and can be rewritten as^{9,20}

$$\begin{aligned} \frac{\partial P_{i\alpha}(\mathbf{r})}{\partial t} &= \frac{1}{i\hbar} [P_{i\alpha}(\mathbf{r}), H] \\ &= -\frac{1}{4m_i} \left[p_{i\alpha}, \sum_{\beta} [p_{i\beta}, \nabla_{\beta} \delta(\mathbf{r} - \mathbf{r}_i)]_+ \right]_+ \\ &\quad - \nabla_{i\alpha} (V_{\text{int}} + V_{\text{ext}}) \delta(\mathbf{r} - \mathbf{r}_i). \end{aligned} \quad (11)$$

The right-hand side is the particle flux $p_{i\alpha}/m_i$ times a component of the kinetic energy, plus the gradient of the potential-energy operators. The total force on particle i follows by integrating Eq. (11) over all space. The kinetic term yields zero for a finite system,⁹ since the integrals of derivatives of the wave functions can be expressed in terms of the functions and derivatives at infinity. The result is

$$\frac{\partial \mathbf{p}_i}{\partial t} = \frac{1}{i\hbar} [\mathbf{p}_i, H] = -\nabla_i (V_{\text{int}} + V_{\text{ext}}). \quad (12)$$

In a stationary system $\langle \partial \mathbf{p}_i / \partial t \rangle$ is zero, so that the internal force acting on the particle is given by the *force theorem*, $\mathbf{F}_i = -\langle \nabla_i V_{\text{int}} \rangle$. This is exactly the same as Eq. (9), which was derived from the variational property of the ground state.

The *stress density* $\sigma_{\alpha\beta}(\mathbf{r})$ is defined to be a tensor field whose divergence is the vector force density field.^{3-5,9,20} The stress field due to *internal* interactions and motion of particles therefore satisfies

$$\begin{aligned} [\text{div} \sigma(\mathbf{r})]_{\alpha} &= \sum_{\beta} \frac{\partial \sigma_{\alpha\beta}(\mathbf{r})}{\partial r_{\beta}} \\ &= \sum_i \left\langle \frac{\partial P_{i\alpha}(\mathbf{r})}{\partial t} + \nabla_{i\alpha} (V_{\text{ext}}) \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle, \end{aligned} \quad (13)$$

where the last term is added to the force operator in Eq. (11) in order to remove the external part of the stress. The stress field defined by Eq. (13) is only determined up to the addition of the curl of an arbitrary tensor field $\mathbf{A}(\mathbf{r})$, an ambiguity which is also present in classical elasticity theory³⁻⁵ and in the electrodynamic stress-energy-momentum field.^{24,12} Thus stress fields can in general be subjected to gauge transformations and the criteria for selecting a particular gauge may be different for different problems. Notwithstanding this ambiguity, it can be seen that total stresses are unaffected, as physical observables should be. The curl term integrates out to zero for the integral of $\sigma_{\alpha\beta}(\mathbf{r})$ over all space for finite systems, for an integral over a unit cell in a crystal in which $\sigma_{\alpha\beta}(\mathbf{r})$ is a periodic function of \mathbf{r} , and for integrals over infinite planes.

By inspection it is seen that one solution $\sigma_{\alpha\beta}(\mathbf{r})$ satisfying Eqs. (11) and (13) is the form given by Kugler,²⁰

$$\sigma_{\alpha\beta}(\mathbf{r}) = - \sum_i \frac{1}{4m_i} [p_{i\alpha} [p_{i\beta} \delta(\mathbf{r} - \mathbf{r}_i)]_+]_+ - \frac{1}{4\pi} \nabla_{i\alpha} (V_{\text{int}}) \nabla_{i\beta} (|\mathbf{r} - \mathbf{r}_i|^{-1}). \quad (14)$$

The presence of $\nabla |\mathbf{r} - \mathbf{r}_i|^{-1} = (\mathbf{r} - \mathbf{r}_i) / |\mathbf{r} - \mathbf{r}_i|^3$ in the potential term implies long-range character of the stress field Eq. (14). This is a consequence of Kugler's definition and occurs whether or not the interactions are long range. These terms present difficulties analogous to dipole fields in electrostatics, since they have the same form as the electric field of a point charge with magnitude proportional to the force on the particle. A more detailed discussion and examples are presented in the appendixes. Although Eq. (14) is not unique, it is sufficient for demonstrating the properties of the stress field discussed below.

For Coulomb interactions the potential part of the stress can be given conveniently in terms of the Maxwell stress tensor^{24,12} as described in Appendix B. This form expresses the potential stress field at any point \mathbf{r} in terms of the expectation value of bilinear products of the electric field $\mathbf{E}(\mathbf{r})$ at the point \mathbf{r} . This is very useful for many cases, as will be discussed below.

The microscopic stress field can be used to calculate forces in terms of integrals over closed surfaces. Equation (13) shows that the integral over any volume Ω of the force field can by Gauss's theorem be written as the integral of the stress field over the surface S of the volume Ω ,

$$F_{\Omega\alpha} = \int_S \sum_{\beta} \sigma_{\alpha\beta}(\mathbf{r}) \hat{n}_{\beta} dS, \quad (15)$$

where \hat{n} is the unit surface-normal vector, \mathbf{F}_{Ω} is the total force on all particles in the volume Ω , and $\sigma_{\alpha\beta}(\mathbf{r})$ is the stress field given, e.g., by Eq. (14) or an alternative form. In Eq. (15) the kinetic term involves only derivatives of the wave function on the surface and the potential term involves only evaluation of forces on particles inside the closed surface S , since the integral of $\hat{n} \cdot \nabla |\mathbf{r} - \mathbf{r}_i|^{-1} / 4\pi$ is unity if \mathbf{r}_i is inside the surface, and zero if \mathbf{r}_i is outside. Thus Eqs. (14) and (15) lead to the expression for

the force on all particles in the volume Ω

$$F_{\Omega\alpha} = - \sum_i \frac{1}{4m_i} \int_S \langle [p_{i\alpha} [p_i \cdot \hat{n} \delta(\mathbf{r} - \mathbf{r}_i)]_+]_+ \rangle dS - \sum_i \langle \nabla_{i\alpha} (V_{\text{int}}) \rangle_{\Omega}. \quad (16)$$

The final term has a subscript Ω to indicate that the particle coordinate i is restricted to the volume Ω . Furthermore, interactions between particles which are either entirely inside or entirely outside the surface give no contribution to the total force on particles in the volume Ω . Therefore, the final term in Eq. (16) can be determined solely from interactions that cross the boundary. For two-body interactions this is just the total force on particles inside Ω due to interactions with particles outside Ω . Interactions involving simultaneously more than two particles can be treated in a similar way and may contribute if any two of the particles are on opposite sides of the surface S .

At this point it is useful to see that Eq. (16) is a generalization of the well-known "Hellmann-Feynman" form of the force theorem and that it provides alternative ways to calculate the force through different choices of the region Ω . We consider the case described in Sec. II where the nuclei are held fixed and the electrons are in their corresponding ground state. It follows that there is no net force density acting upon the electrons at any point \mathbf{r} . There may, however, be a force acting upon a fixed nucleus due to the internal interactions. The force follows from Eq. (16) if the volume Ω is taken as vanishingly small but enclosing the given nucleus (as illustrated by the volume $\Omega_1 \rightarrow 0$ in Fig. 1). The surface term in Eq. (16) vanishes as $\Omega \rightarrow 0$, and the volume term reduces to the electrostatic force acting upon the nucleus. This result is exactly the force theorem given by Eq. (9). We have thus recovered the famous result that the force on a classical particle can be calculated strictly from the expectation value of the potential force, with no kinetic terms and no terms that explicitly involve the electron-electron interactions.

On the other hand, the same force may be calculated in a different way by choosing a finite volume Ω in Eq. (16) which contains only one fixed nucleus (as illustrated by the volume Ω_2 in Fig. 1). Even though the electrons contribute no net force, the electron kinetic and potential terms in Eq. (16) are separately nonzero, in general. From Eq. (16) the force on the nucleus is given by the electron kinetic term on the surface of Ω , plus all potential terms that cross the surface, i.e., nucleus-nucleus, nucleus-electron, and electron-electron terms.

The form Eq. (16) for the force $F_{\Omega\alpha}$ shows immediately one of the advantages of a surface expression for stress, if the surface is chosen so that it does not pass through the core of any atom. It is necessary to determine the kinetic terms only on the boundary, which involve only the valence-electron states outside the core region. To this are added all potential terms which cross the boundary. For spherical ion cores the potential forces from the nuclei and cores can be combined into the electrostatic field of point ions with the charge $Z_{\text{ion}} = Z_{\text{nucleus}} - Z_{\text{core}}$. Similar-

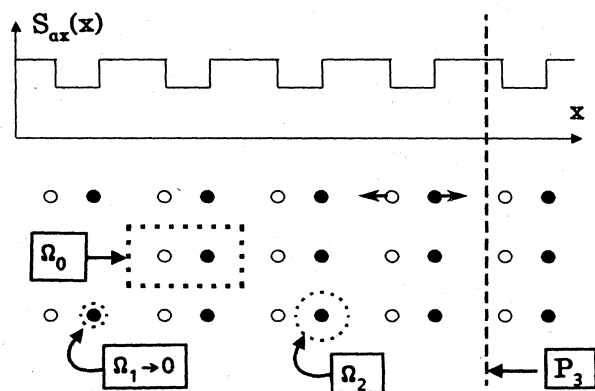


FIG. 1. Schematic illustration of a periodic crystal with unit cell Ω_0 . The symmetry of this crystal is such that forces in the x direction upon the atoms are not zero by symmetry. For fixed positions of the nuclei the forces are nonzero, except for the equilibrium structure where they vanish. The volumes $\Omega_1 \rightarrow 0$ and Ω_2 illustrate two choices for computing the force on an atom from Eq. (16), and the infinite plane P_3 is used for the macroscopic stress as well as forces, as described in the text. The plot of planar stress (top), Eq. (17), has discontinuous jumps at the atomic planes due to forces (arrows on atoms).

ly, the fact that the valence-electron wave functions have complex node structure in the core does not enter the expressions for stress because the surface-crossing potential terms require only the *total* valence charge in the core region. This may be compared to the volume integrals, Eqs. (6) and (7), or the force expression, Eq. (9), which require accurate knowledge of the core states in order to evaluate the sum of large terms which almost cancel one another. Thus the surface expressions for forces can be very useful to avoid such problems, especially for solids with high- Z atoms.

If the effect of the core electrons is replaced by the pseudopotential, then part of the above-mentioned cancellation is done implicitly. One may compute forces and stresses without great difficulty from either the volume integrals (as is done in the following paper II) or the surface expressions. Even in this case, however, the surface expressions have practical and pedagogical value. Since the norm-conserving pseudopotential is nonlocal in the core regions,³⁹⁻⁴¹ the surface expressions can make it possible to calculate force and stresses without explicitly evaluating any nonlocal terms, provided the surface can be chosen sufficiently far from the nucleus where the nonlocal corrections to the potentials vanish.

The so-called "force theorem" derived by Pettifor³⁶ and Andersen³⁷ is closely related to the form Eq. (16) of force

evaluated as a surface integral over a finite volume. This result, derived in detail by Heine,³⁹ considers an infinitesimal displacement of a finite volume in the solid. The first-order change in total energy per unit displacement equals the force. For the ground state it is shown (within density-functional theory) that *rigid displacement* of the potential inside the volume leads to a particularly simple form of the energy change in terms of the change in single-particle eigenvalues plus the Coulomb force crossing the surface of the volume. The force thus calculated is identical to the one expressed by Eq. (16) (or the density-functional form thereof discussed in Sec. IV). Both forms give the force on a single nucleus independent of the actual volume containing the nucleus, and in the limit of vanishing volume both reduce to the "Hellmann-Feynman" form of electrostatic forces. The Pettifor-Andersen form is particularly useful when potentials in, e.g., Wigner-Seitz spheres can be shifted rigidly in a straightforward manner, and when the electrostatic term is negligible or at least simple to calculate.

The microscopic stress field $\sigma_{\alpha\beta}(\mathbf{r})$ can furthermore be used to derive alternative expressions for the macroscopic stress $\sigma_{\alpha\beta}$. To accomplish this, Eq. (16) is considered with an infinite surface that divides space into two infinite regions, one of which is denoted Ω . For example, Fig. 1 shows an infinite surface P_3 bounding the volume Ω_3 to the left of P_3 , say. The integral Eq. (16) is the force $F_{\Omega\alpha}$ which is exerted on Ω_3 by the volume complement to Ω_3 . A convenient choice of surface is the infinite plane P_β perpendicular to the β axis and intersecting the axis at \mathbf{r}_β . Equation (16) gives the force in the α direction transmitted across P_β , which we denote the planar stress $S_{\alpha\beta}(\mathbf{r}_\beta)$:

$$S_{\alpha\beta}(\mathbf{r}_\beta) = - \sum_i \frac{1}{4m_i} \langle [p_{i\alpha}, [p_{i\beta}, \delta(\mathbf{r} - \mathbf{r}_{i\beta})]_+]_+ \rangle - \sum_i \langle \nabla_{i\alpha} (V_{\text{int}})^{\frac{1}{2}} \text{sgn}(\mathbf{r}_\beta - \mathbf{r}_{i\beta}) \rangle. \quad (17)$$

It is straightforward to show that the integral of $S_{\alpha\beta}(\mathbf{r}_\beta)$ with respect to \mathbf{r}_β is exactly the same as the total stress $T_{\alpha\beta}$ given by the stress theorem expression Eq. (6), since the integral of the sgn function gives, after summing over all particles, the factor of $\mathbf{r}_{i\beta}$ in the virial in Eq. (6). For infinite systems we must consider the planar average stress per unit area and the total stress per unit volume.

The potential "crossing" terms pervade the theory of stress and are worthy of special attention. Just as in the preceding section, it is imperative to express the potential terms in Eq. (17) in terms of relative coordinates of interacting particles in order for the expression to be appropriate for the limit of an infinite system. In particular, if V_{int} is assumed to consist of two-body interactions as in Eq. (7), the planar stress can be written

$$S_{\alpha\beta}(\mathbf{r}_\beta) = - \sum_i \frac{1}{4m_i} \langle [p_{i\alpha}, [p_{i\beta}, \delta(\mathbf{r} - \mathbf{r}_{i\beta})]_+]_+ \rangle - \sum_{\substack{i,j \\ (i < j)}} \langle \nabla_{i\alpha} [\phi_{ij}(\mathbf{r}_i - \mathbf{r}_j)]^{\frac{1}{2}} [\text{sgn}(\mathbf{r}_\beta - \mathbf{r}_{i\beta}) - \text{sgn}(\mathbf{r}_\beta - \mathbf{r}_{j\beta})] \rangle. \quad (18)$$

This means that the planar stress consists of contributions only from the momenta of particles crossing the plane and interactions Φ_{ij} between particles on opposite sides of the plane, whereas interactions contained within either half-space give no contribution to the integrated stress on the plane separating the half-spaces. Interactions simultaneously involving more than two particles can be treated in a similar way and contribute if any two of the particles are on opposite sides of the plane.

The interpretation of the stress is straightforward and agrees with the classical definitions.^{3,4} The kinetic term in Eqs. (16)–(18) is the transfer of momenta $p_{i\alpha}$ by the quantum flux $p_{i\beta}/m_i$ crossing the surface S (or the plane P_β). In cases where the interactions are short range it is easy to see that the potential term is well defined and involves only interactions between particles on opposite sides of the surface in a local region near the surface. This is the force transmitted across the surface. In the case of Coulomb fields it is most convenient to use the Maxwell form of stress given in Appendix B. This form is expressed solely in terms of bilinear products of the electric field $\mathbf{E}(\mathbf{r})$ evaluated on the surface. This may be divided into local fields from charges near the surface S , and from long-range fields from net accumulations of charge. The latter are, of course, very nonlocal, and are properly included in the theory of stress by the presence of long-range macroscopic electric fields in the Maxwell stress tensor. We will not consider further this aspect of stress, but assume that all macroscopic fields are zero, and that only the local fields need be considered.

If the solid is in equilibrium, i.e., the force field is everywhere zero, then $\sigma_{\alpha\beta}(\mathbf{r})$ has zero divergence which implies that $S_{\alpha\beta}(r_\beta)$ is a constant tensor. If some atoms are not in their equilibrium position, the variations in the planar stress can provide information on the forces in addition to the macroscopic stress. Consider the crystal shown in Fig. 1, where the symmetry allows equal and opposite forces acting on the two atoms (shown as solid and open circles) in each unit cell. If the force is nonzero, the planar stress $S_{\alpha\beta}(r_\beta)$ has equal and opposite steps as the plane P_β crosses the planes of atoms. In this example, the force on each atom is equal to the jumps in $S_{\alpha\beta}(r_\beta)$, using the divergence of the stress field. The macroscopic stress is furthermore the average of $S_{\alpha\beta}(r_\beta)$ over r_β , with r_β running over a cell in which the sum of total forces on the nuclei is zero, e.g., a unit cell of a crystal. It is clear that evaluation of $S_{\alpha\beta}(r_\beta)$ on a limited set of well-chosen planes (or nonplanar surfaces) can provide expressions for both forces and macroscopic stress.

Correlations among the particles have a definite effect which is explicitly contained in the force expression Eq. (16) and the stress expressions Eqs. (17) and (18). Whenever there is a correlation between particles on opposite sides of the surface, there is a contribution to the force crossing the surface, in addition to the average forces that would exist if the particles were uncorrelated. This effect may be formulated in terms of electrons interacting with their own exchange-correlation holes through Coulomb interactions.⁴² As is clear from the expressions, Eqs. (16)–(18), there is a contribution to the force crossing the surface whenever the exchange-correlation hole intersects

the surface. Since exchange and correlation always work to keep electrons further apart than independent particles would be, these terms in general give a tensile stress, i.e., positive diagonal terms in $\sigma_{\alpha\beta}$. However, for off-diagonal terms in $\sigma_{\alpha\beta}$, the contribution may have either sign.

IV. DENSITY FUNCTIONALS

The preceding sections have derived formal expressions for stress applicable to general many-body systems. Despite the simplicity of the general forms, they contain all the complexity of the full many-body problem^{19,20} in the form of correlation functions which enter the potential terms in the stress. It is very valuable to find alternative forms that are more tractable in practice. One such form is the density-functional approach which provides expressions for the ground-state energy and charge density which are in principle exact.^{25–27} Equally important, there are *local* density functionals which, although not exact, seem to work quite well and form the basis of many modern calculational schemes for real condensed matter.^{1,2,25–44} The expressions given above are not, however, in a form which can take advantage of the simplifications resulting from expressing the energy as a non-linear functional of the electronic density. In this section we will derive forms alternative to the ones derived above.

The basis of the density-functional approach is the proof by Hohenberg and Kohn²⁵ that the ground-state energy of the electron system is a unique functional of the ion-electron potential $\sum_I V_{\text{ion}}(\mathbf{r}-\mathbf{R}_I)$ and the electronic charge density $\rho(\mathbf{r})$. For fixed nuclei the most general density-functional total energy can be written^{26,27,42}

$$E_{\text{tot}} = E_{\text{ion-ion}} + E_{\text{ion-electron}} + E_{\text{Hartree}} + F[\rho], \quad (19)$$

where $E_{\text{ion-ion}}$ is the direct Coulomb interaction energy of the ions, and

$$E_{\text{ion-electron}} = \int \rho(\mathbf{r}) \sum_I V_{\text{ion}}(\mathbf{r}-\mathbf{R}_I) d^3\mathbf{r}, \quad (20)$$

$$E_{\text{Hartree}} = \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}'. \quad (21)$$

Here $F[\rho]$ is a functional describing the kinetic, exchange, and correlation energies of the electrons. Kohn and Sham²⁶ showed that it is advantageous to replace $F[\rho]$ by the kinetic energy of a noninteracting electron system of the same density $\rho(\mathbf{r})$, plus a functional $E_{\text{xc}}[\rho]$ for exchange and correlation

$$F[\rho] = \sum_i \left\langle \Psi_i \left| \frac{\mathbf{p}_i^2}{2m_i} \right| \Psi_i \right\rangle + E_{\text{xc}}[\rho], \quad (22)$$

with the density given by

$$\rho(\mathbf{r}) = \sum_i |\Psi_i|^2. \quad (23)$$

For the case of infinite systems it is necessary to consider the total energy E_{tot} per unit volume. Furthermore, the first three terms of Eq. (19) formally diverge due to the long-range nature of the Coulomb interactions. This is remedied by adding a constant positive neutralizing background density to $\rho(\mathbf{r})$, and adding a similar negative

background to the lattice of ions. In this way the background term is grouped with $E_{\text{ion-ion}}$, which together can be evaluated by the Ewald transformation.⁴⁵ This is referred to as γ_{Ewald} in Ref. 44. Since the first three terms in Eq. (19) result from two-body interactions, their contribution to the total stress or the stress field may be derived from Eq. (7), Eq. (18), or the Maxwell stress equation (B1) for Coulomb interactions. In those equations one must simply take the electrons to be uncorrelated.

If an explicit form for $F[\rho]$ existed, the total stress might be derived directly by differentiating F with respect to the strain $\epsilon_{\alpha\beta}$. Some approximate forms of $F[\rho]$, such as the Thomas-Fermi model, can be differentiated analytically and used in this way. The general form may be recast using Eq. (22) for $F[\rho]$, and expressing $E_{\text{xc}}[\rho]$ in terms of electrons interacting with their surrounding exchange-correlation hole through Coulomb interactions.⁴² Then the contribution of $F[\rho]$ to the stress becomes the strain derivative of $E_{\text{xc}}[\rho]$ plus a kinetic term of the same form as in the equations of Secs. II and III, but for the uncorrelated wave functions Ψ_i . This would be exact if the exact scaling behavior of $E_{\text{xc}}[\rho]$ were known.

Much recent work²⁸⁻³¹ has shown that it is a good approximation to assume that $E_{\text{xc}}[\rho]$ is a local function of the charge density, i.e.,

$$E_{\text{xc}}[\rho] = \int \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r})) d^3\mathbf{r}, \quad (24)$$

where $\rho(\mathbf{r})$ is the charge density and $\epsilon_{\text{xc}}(\rho)$ is the exchange plus correlation energy per electron in a homogeneous electron gas of density ρ . With this local-density approximation (LDA) Kohn and Sham^{25,26} derived from the variational principle the wave functions $\Psi_i(\mathbf{r})$ as eigenstates of an effective self-consistent single-electron Hamiltonian

$$H[\rho]\Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}), \quad (25)$$

with

$$H[\rho] = \frac{\mathbf{p}^2}{2m} + \sum_I V_{\text{ion}}(\mathbf{r} - \mathbf{R}_I) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \mu_{\text{xc}}(\rho(\mathbf{r})), \quad (26)$$

and

$$\mu_{\text{xc}}(\rho) = \frac{d(\rho \epsilon_{\text{xc}}(\rho))}{d\rho}. \quad (27)$$

We note that by Eq. (24) the exchange-correlation energy density is a *local* function of \mathbf{r} , and thus the exchange-correlation term gives rise to an isotropic pressure at each point \mathbf{r} in space, which is equal to the exchange-correlation pressure in a homogeneous electron gas of density $\rho = \rho(\mathbf{r})$. The pressure per electron is in this case just the volume derivative of $\epsilon_{\text{xc}}(\rho)$,

$$\Omega \frac{\partial \epsilon_{\text{xc}}(\rho)}{\partial \Omega} = \epsilon_{\text{xc}}(\rho) - \mu_{\text{xc}}(\rho), \quad (28)$$

and the exchange-correlation stress field at point \mathbf{r} is

$$\sigma_{\alpha\beta}(\mathbf{r}) = \delta_{\alpha\beta} [\epsilon_{\text{xc}}(\rho(\mathbf{r})) - \mu_{\text{xc}}(\rho(\mathbf{r}))] \rho(\mathbf{r}). \quad (29)$$

This purely diagonal term contains only isotropic pressure, and no shearing stresses. This is a general property of all local-density approximations.

The total stress within the LDA thus consists of the following terms: (1) the kinetic stress,

$$-\frac{1}{m_e} \sum_i \langle \Psi_i | p_\alpha p_\beta | \Psi_i \rangle \quad (30a)$$

(note that this kinetic stress of noninteracting electrons enters the LDA expressions although it is not the exact kinetic energy of the interacting system); (2) the ion-electron potential stress,

$$-\frac{1}{2} e^2 \sum_I \int d^3\mathbf{r} \rho(\mathbf{r}) V'_{\text{ion}}(\mathbf{r} - \mathbf{R}_I) \frac{(\mathbf{r} - \mathbf{R}_I)_\alpha (\mathbf{r} - \mathbf{R}_I)_\beta}{|\mathbf{r} - \mathbf{R}_I|}, \quad (30b)$$

where a prime denotes differentiation; (3) the ion-ion potential stress,

$$-\frac{1}{2} e^2 \sum_{\substack{I, J \\ I \neq J}} Z_I Z_J \frac{(\mathbf{R}_I - \mathbf{R}_J)_\alpha (\mathbf{R}_I - \mathbf{R}_J)_\beta}{|\mathbf{R}_I - \mathbf{R}_J|^3}; \quad (30c)$$

(4) the Hartree stress,

$$-\frac{1}{2} e^2 \int \int d^3\mathbf{r} d^3\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \frac{(\mathbf{r} - \mathbf{r}')_\alpha (\mathbf{r} - \mathbf{r}')_\beta}{|\mathbf{r} - \mathbf{r}'|^3}; \quad (30d)$$

and (5) the exchange and correlation stress,

$$\delta_{\alpha\beta} \int d^3\mathbf{r} \rho(\mathbf{r}) [\epsilon_{\text{xc}}(\rho(\mathbf{r})) - \mu_{\text{xc}}(\rho(\mathbf{r}))]. \quad (30e)$$

For infinite systems the stress terms must be evaluated per unit volume and terms (2)–(4) must be grouped and evaluated by the Ewald method as done in paper II.

Stress integrated over surfaces proceeds similarly within the LDA, using the expression Eq. (18) instead of Eq. (7) for volume integrals. The potential-crossing terms are divided into the average uncorrelated terms plus the contribution from the exchange-correlation hole, which is Eq. (29) integrated over the surface. Within the LDA, the latter term involves only the charge density on the surface. For pure Coulomb interactions it may be more convenient to evaluate the Maxwell stress from the electric fields on the surface as described in Appendix B. For nonlocal pseudopotentials the Maxwell stress may be evaluated after the wave function has been projected onto the angular momenta at each atomic site.

In the accompanying paper II we reexpress the present real-space formulas for stress in reciprocal space for calculations on periodic systems using plane-wave basis sets. Expressions for nonlocal pseudopotentials are also presented.

V. PERIODIC SYSTEMS AND SURFACE INTEGRALS

In this section we give explicit formulas for the stress evaluated as an integral over the faces of the unit cell of a period system, and we show that these results generalize the approximate expressions given by Liberman³⁴ for the pressure. We choose the unit cell to be the parallelepiped at the origin spanned by the lattice translation vectors \mathbf{a}_i ,

\mathbf{a}_2 , and \mathbf{a}_3 . One could equally well consider other unit cells, e.g., the Wigner-Seitz polyhedron. The planar stress $S_{\alpha\beta}$, Eq. (17), can be evaluated from integrals over the three inequivalent faces of a single unit cell, owing to the periodicity of the system. We will assume that all forces within the unit cell are zero, so that the planar stress $S_{\alpha\beta}$ is constant everywhere. Nonzero forces have to be dealt with by averaging over planes, as described in Sec. III.

We denote the three parallelogram faces at the origin as A_1 , A_2 , and A_3 normal to the reciprocal-lattice vectors \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 , respectively. $S_{\alpha\beta}$ is expanded in the \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 basis as a sum of stresses on the faces A_j ,

$$S_{\alpha\beta} = \sum_{j=1}^3 a_{j\beta} \sum_{\gamma} S_{\alpha\gamma} b_{j\gamma}. \quad (31)$$

To relate this to the macroscopic stress $\sigma_{\alpha\beta}$ we multiply for each j by the height $1/|\mathbf{b}_j|$ of the parallelepiped with base A_j (since $S_{\alpha\beta}$ is a constant) and divide by the cell volume Ω to obtain

$$\sigma_{\alpha\beta} = \sum_{j=1}^3 a_{j\beta} \sum_{\gamma} \frac{S_{\alpha\gamma}}{|A_j|} b_{j\gamma}, \quad (32)$$

where $|A_j| = |\mathbf{b}_j| \Omega$ denotes the area of A_j . Using Eq. (17) we find the macroscopic stress

$$\sigma_{\alpha\beta} = - \sum_{j=1}^3 a_{j\beta} \sum_i \left[\frac{1}{4m_i} \frac{1}{|A_j|} \int_{A_j} dA_j \langle [p_{i\alpha}, [\mathbf{p}_i \cdot \mathbf{b}_j, \delta(\mathbf{r}_i \cdot \mathbf{b}_j)]_+]_+ \rangle - \frac{1}{N_j |A_j|} \langle \nabla_{i\alpha} (V_{\text{int}})^{\frac{1}{2}} \text{sgn}(-\mathbf{r}_i \cdot \mathbf{b}_j) \rangle \right]. \quad (33)$$

The term $\text{sgn}(-\mathbf{r}_i \cdot \mathbf{b}_j)$ determines whether \mathbf{r}_i is on the positive or negative side of A_j , and the δ -function term restricts the kinetic term to A_j . The first term is the kinetic stress per unit area. The second term is an integral over the infinite plane normal to \mathbf{b}_j of the force crossing that plane, divided by the total area $N_j |A_j|$, which is thus the potential stress per unit area. In the case of Coulomb interactions the potential stress may alternatively be given by integrating the Maxwell stress on the face A_j since this involves only the total electric field on the face. For calculations within the LDA, the local isotropic exchange-correlation stress per unit area

$$\sum_{j=1}^3 \frac{1}{|A_j|} \int_{A_j} dA_j \delta_{\alpha\beta} [\epsilon_{xc}(\rho(\mathbf{r})) - \mu_{xc}(\rho(\mathbf{r}))] \rho(\mathbf{r}) \quad (34)$$

must be added to Eq. (34).

The pressure $P = -\frac{1}{3} \sum_{\alpha} \sigma_{\alpha\alpha}$ has some interest and is given by

$$P = \frac{1}{3} \sum_{j=1}^3 \sum_i \left[\frac{1}{4m_i} \frac{1}{|A_j|} \int_{A_j} dA_j \langle [\mathbf{p}_i \cdot \mathbf{a}_j, [\mathbf{p}_i \cdot \mathbf{b}_j, \delta(\mathbf{r}_i \cdot \mathbf{b}_j)]_+]_+ \rangle + \frac{1}{N_j |A_j|} \langle \mathbf{a}_j \cdot \nabla_i (V_{\text{int}})^{\frac{1}{2}} \text{sgn}(-\mathbf{r}_i \cdot \mathbf{b}_j) \rangle \right]. \quad (35)$$

This result may be compared to the one of Liberman,³⁴ obtained within the LDA for the pressure on a unit cell in a periodic system. Neglecting the simple exchange-correlation term equivalent to Eq. (34), Liberman's expression for occupied one-electron states Ψ_i reads

$$3P\Omega = \frac{\hbar^2}{4m} \sum_i \int_S [(\nabla_i \Psi_i^*)(\mathbf{r}_i \cdot \nabla_i \Psi_i) - \Psi_i^* \nabla_i (\mathbf{r}_i \cdot \nabla_i \Psi_i) + \text{c.c.}] \cdot d\mathbf{S}, \quad (36)$$

where S is the entire surface of the unit cell. We note that opposite faces of S are related by a lattice translation vector, and rewrite Eq. (36) for a parallelepiped unit cell as

$$3P\Omega = \sum_{j=1}^3 \sum_i \frac{\Omega}{4m_i} \frac{1}{|A_j|} \int_{A_j} dA_j [(\mathbf{b}_j \cdot \mathbf{p}_i \Psi_i^*)(\mathbf{a}_j \cdot \mathbf{p}_i \Psi_i) + \Psi_i^* \mathbf{b}_j \cdot \mathbf{p}_i (\mathbf{a}_j \cdot \mathbf{p}_i \Psi_i) + \text{c.c.}], \quad (37)$$

which is the same as the first term in Eq. (35). The remaining potential terms in our expressions Eqs. (33) and (35) involve electron-electron, electron-nucleus, and

nucleus-nucleus interactions crossing the infinite planes containing the faces A_1 , A_2 , and A_3 . Although the potential terms are essential in any complete theory of stress (or pressure) we are not aware of any previous derivation for a quantum-mechanical system. These terms are *not* simply "nuclear virials" as suggested by Liberman,³⁴ because they involve all interactions. The only instances in which these terms are not present are approximations in which the potential term vanishes. This is the case when the unit cells are approximated as nonoverlapping spheres with spherical and overall neutral charge distributions, as was considered by Liberman. Then the electric field due to one sphere is zero everywhere outside the sphere. Clearly there are no potential interactions between different spheres. The Maxwell formulation of the stress shows that this is the only case where the potential terms in the stress vanish, because in general the electric field cannot vanish identically at every point on the boundary of the unit cell.

We propose that Eqs. (33) and (34), or its equivalent with the potential part replaced by the Maxwell stress, is a useful form in which to calculate the stress in a crystal. It is the full generalization of the approximate Liberman form to all components of the stress tensor. The advantages of using a surface formulation rather than a volume integration to avoid the regions of the ion cores were discussed in Sec. III.

VI. CONCLUSIONS

General expressions for the total stress in quantum-mechanical systems of interacting particles have been given in Sec. II, Eqs. (6) and (7). These are termed the "stress theorem" because they are a generalization of the virial theorem involving external pressure. This form is completely general and applies to arbitrary finite and infinite systems with interactions which are differentiable functions of position. The form of the microscopic stress field was considered in Sec. II and it was shown that integrals of stress over surfaces could be used to calculate forces on nuclei as well as the macroscopic stress. The well-known "Hellmann-Feynman" form of the force theorem is a limiting form of our expressions. The definition of the stress field has both pedagogic and practical value. Not only does it give a rigorous nonlocal definition of stress as a force per unit area, but it also provides expressions which can be evaluated entirely outside the central core of any atom. The tightly bound core states enter only in terms of their total charge (or multipole moments) and no details of the wave functions are needed, in contrast to the volume-integral expressions.

The local-density approximation was shown in Sec. IV to contain an exchange-correlation stress which is a simple local pressure with no contribution to the shear stress. This follows simply from the basic local and isotropic approximation. This has led to simple expressions for the total stress, Eq. (30), and to simple stress fields. The complete LDA form of the surface expressions for the total stress were derived in Sec. V and were shown to be a generalization of that given by Liberman for the pressure, and to include terms omitted by him.³⁴ The expressions for the total stress and forces in the LDA are used in paper II for *ab initio* calculations in the crystals Si, Ge, and GaAs.

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APPENDIX A

In this appendix we discuss the properties of the stress field as defined by Kugler²⁰ and given in Eq. (14). The kinetic term is the one derived by Pauli,⁹ and is symmetric in (α, β) so that no torque density is created, since the torque is given by the antisymmetric part of the stress. It contains both a gradient and a curl part, however, of which only the former gives rise to a force density. Other choices can be made for the kinetic term as discussed by Feynman.¹²

The potential stress has zero curl, but is in general non-symmetric so that it may contain a torque density. A physical macroscopic torque exists only if the integrated macroscopic stress tensor is nonsymmetric. The most important feature of Kugler's definition is the long-range character of the potential term. The form in Eq. (14) is mathematically similar to electrostatics owing to the defi-

nition that divergence of stress equals force and the fact that this term is chosen to be curl free. Thus a given force $F(\mathbf{r}_i)$ (the gradient of a potential) applied to a particle with position \mathbf{r}_i gives rise to a $1/r^2$ stress field throughout space

$$\sigma_{\alpha\beta}(\mathbf{r}) = -\frac{1}{4\pi} F(\mathbf{r}_i)_\alpha \frac{(\mathbf{r} - \mathbf{r}_i)_\beta}{|\mathbf{r} - \mathbf{r}_i|^3}. \quad (\text{A1})$$

This stress field is independent of the source or the nature of the interaction field. The most severe problems associated with this long range can be avoided if the interactions are short range and if the stress Eq. (A1) is calculated by summing over pairs of interacting particles. For example, two particles which interact with equal and opposite forces lead to a total stress field with dipole character, i.e., a long-range distance dependence of $\sim 1/r^3$. Note, however, that this still has long-range character and may give undesirable difficulties.

This form of the stress field is different from usual paradigms of stress,³⁻⁵ because the field may extend into regions where there is no matter and where all interaction fields vanish. It also differs from the semimacroscopic forms used in the many-body quantum-mechanical formulation of Martin and Schwinger,¹⁹ who assigned the stress to the spatial point midway between two interacting particles. The resolution of the differences is the inherent ambiguity in stress fields. If Kugler's form [Eqs. (14) or (A1)] is integrated over an infinite plane, the total planar stress vanishes unless the plane passes between two interacting particles. Since it is only the integrated stress that has rigorous physical significance, the Kugler form in fact leads to the same macroscopic stress as the form of Martin and Schwinger.¹⁹

For our purposes, however, we wish to have an exact microscopic form for the stress. Therefore, we have presented the Kugler form for general interactions keeping in mind that the long-range terms must be treated carefully. For the important special case of Coulomb interactions, the Kugler form leads to serious difficulties. Then it is preferable to use the Maxwell form^{24,12} of the stress discussed in Appendix B. Examples of the Kugler and Maxwell stresses are given in Appendix C.

APPENDIX B

In this appendix we comment on the form of the Maxwell stress for particles interacting by Coulomb fields. The fundamental property of this stress originates in the treatment of the electromagnetic field as a real field that can carry energy and momentum. The time-varying fields therefore must be incorporated into the total conservation laws.²⁴ In the static limit, which we are considering here, the Maxwell stress reduces to

$$\sigma_{\alpha\beta}^M(\mathbf{r}) = \frac{1}{4\pi} \langle E_\alpha(\mathbf{r}) E_\beta(\mathbf{r}) - \frac{1}{2} \delta_{\alpha\beta} E^2(\mathbf{r}) \rangle, \quad (\text{B1})$$

where

$$E_\alpha(\mathbf{r}) = \sum_i Z_i \frac{(\mathbf{r} - \mathbf{r}_i)_\alpha}{|\mathbf{r} - \mathbf{r}_i|^3} \quad (\text{B2})$$

is the operator giving the electric field due to particles of

charge Z_i with position operators \mathbf{r}_i . To this must be added the quantum kinetic terms involving the particles [the first term in Eq. (14)]. Except that we are neglecting the quantum fluctuations of the electromagnetic field and the finite propagation speed of light, this form is exact and complete for systems with Coulomb interactions.

There are two advantages of the Maxwell form compared to the Kugler form for the stress. First, it is manifestly symmetric and thus free of torques, unlike the Kugler form. Second, it is well behaved for Coulomb systems, unlike the Kugler form. This means in practice that the electric field in Eq. (B2) can be separated into a macroscopic field plus a microscopic field.⁷ This makes it possible to separate out the macroscopic part which necessarily depends upon the sample shape, surface charge, etc., from the microscopic fields which are intrinsic to the matter. Because we do not consider the macroscopic field here, our results apply only to cases in which the macroscopic field vanishes. This is true for metals in all cases and insulators in cases where either the symmetry or the boundary conditions require $\mathbf{E}_{\text{macroscopic}} = 0$. The form equations (B1) and (B2) for the stress field is very convenient for many problems as discussed in the text and in the examples in Appendix C.

APPENDIX C

Here we discuss illustrative aspects of the Kugler and Maxwell forms of the stress. An example which illustrates the properties of the stress fields in small finite systems is hydrogen in the charge states H^+ and H^0 with the proton considered as a classical particle fixed at the origin. The simplest case is H^+ , where the Maxwell stress field at a radius r has radial component $E^2/6\pi$ and tangential component $-E^2/12\pi$ which both decay as r^{-4} . The Kugler stress, however, is zero because it does not contain the electrostatic field, but only stress due to forces on particles, of which there are none for an isolated proton.

The case of H^0 was considered in depth by Feynman.¹² In the neutral H^0 atom, the Maxwell stress decreases more rapidly outside the atom than the Kugler stress. This is a general property of electrically neutral systems without any permanent dipole or higher-order moments. By Eq. (14) the Kugler potential stress for H^0 in its ground state with the proton fixed at the origin is

$$\sigma_{\alpha\beta}^{\text{pot}}(\mathbf{r}) = -e^2 \int |\Psi_{1s}(\mathbf{r}_e)|^2 \frac{r_{e\alpha}}{|\mathbf{r}_e|^3} \times \left[\frac{(\mathbf{r} - \mathbf{r}_e)_\beta}{|\mathbf{r} - \mathbf{r}_e|^3} - \frac{r_\beta}{r^3} \right] d^3\mathbf{r}_e, \quad (\text{C1})$$

where Ψ_{1s} is the ground state. For large r the limiting behavior of Eq. (C1) is

$$\begin{aligned} \sigma_{\alpha\beta}^{\text{pot}}(\mathbf{r}) &\rightarrow -\frac{4\pi e^2}{r^3} \left[\frac{r_\alpha r_\beta}{r^2} - \frac{1}{3} \right] \int_0^\infty |\Psi_{1s}(\mathbf{r}_e)|^2 r_e dr_e \\ &= \frac{e^2}{a_0} \left[\frac{r}{a_0} \right]^{-3} \left[\frac{r_\alpha r_\beta}{r^2} - \frac{1}{3} \right], \end{aligned} \quad (\text{C2})$$

where a_0 is the Bohr radius. We see the unpleasant feature that the Kugler stress decays only as $1/r^3$ outside the atom. The kinetic term decays exponentially at large r . The important point is that the electron is a quantum particle which is not localized and for which there is a correlation between its force and position vectors. Although the long-range term equation (C2) is divergenceless (and therefore has no physical significance), it is illustrative of terms which appear in the Kugler form for the potential stress, whether or not the interactions are long range. In specific cases such terms can be removed by a gauge transformation, but we are not aware of a general prescription.

In contrast, the Maxwell stress equations (B1) and (B2) for the neutral H^0 atom is given by

$$\sigma_{\alpha\beta}^M(\mathbf{r}) = - \int |\Psi_{1s}(\mathbf{r}_e)|^2 \frac{1}{4\pi} [E_\alpha(\mathbf{r})E_\beta(\mathbf{r}) - \frac{1}{2}\delta_{\alpha\beta}E^2(\mathbf{r})] d^3\mathbf{r}_e \quad (\text{C3})$$

where \mathbf{E} is the electric field

$$E_\alpha(\mathbf{r}) = e \frac{(\mathbf{r} - \mathbf{r}_e)_\alpha}{|\mathbf{r} - \mathbf{r}_e|^3} - e \frac{r_\alpha}{r^3}. \quad (\text{C4})$$

The longest-range terms in Eq. (C3) decrease as r^{-6} . These are due to quantum fluctuations in the electric field around a neutral atom and are the terms that give rise to the van der Waal attraction between two neutral atoms.¹² Thus it is clear in this case that the Maxwell stress decreases more rapidly than the Kugler form and, in addition, the long-range terms have physical significance because they originate in the long-range character of the Coulomb field.

A second example relevant in solids is the stress field near a surface or interface. The important characteristic is that the surface is a distribution of charges restricted in one dimension (z) and extended in two dimensions (x - y). It is straightforward to see from Eq. (14) that the Kugler stress decreases slowly away from the plane of the surface or interface, whether the forces are long or short range. Because the Kugler stress given by Eq. (14) is not explicitly given in terms of relative coordinates, it is not well defined in the limit of an infinite plane. Thus this form is extremely nonlocal and is an example of the dangers of utilizing such expressions. If we use instead the form given in Eq. (18), which is the total stress integrated over a y - z plane, we can get a proper, well-defined result since it is cast in terms of interactions which cross the given y - z plane. If the interactions are of short range, this is acceptable since the forces can extend in the x -direction no further than the range of the interactions. However, for Coulomb fields the contributing interactions are all those between the charges on one side of the y - z plane and the other side of the plane. This is related to the problem of the fringing fields at the edge of a semi-infinite capacitor, and the fields extend to distances much greater than the thickness of the capacitor.

In contrast, the Maxwell stress involves the mean-square electric field which decays rapidly outside a neutral system which is extended in two dimensions. The

fields are analogous to those of a capacitor far from the edges. For a surface with an inhomogeneous charge density on the scale of atomic dimensions a , the average electric fields decay in the z direction as $\sim \exp(-z/a)$ (see Ref. 46). Thus the contributions of the time-average electric fields to the stress is localized to the region near the

surface and is more physically meaningful than the Kugler form. Of course, just as for the H^0 atom, the mean-square fluctuations in the electric field have longer range and have the significant consequence of a van der Waal-type attraction.

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