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First-Principles Calculation of Stress

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A generalization of the virial theorem is presented for all components of the average stress tensor of arbitrary systems of interacting particles. Explicit expressions are given for local-density-functional calculations and the method is tested by *ab initio* pseudopotential calculations on silicon. Accurate determinations are made of lattice constant, bulk moduli, second-, third-, and fourth-order elastic constants, and the internal strain parameter ζ. Agreement with experiment is very good, except for ζ.

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In this Letter we present a general expression for the average stress tensor in an arbitrary system of interacting particles. We term this result the stress theorem, since it is a generalization of the quantum-mechanical virial theorem[1,2] and since it is closely related to the force theorem originally derived by Ehrenfest[3] (now often referred to as the Hellmann-Feynman theorem[4]). This form is used to derive an explicit, practical expression for the stress tensor of a periodic solid within the local-density-functional (LDF) framework. The combined force and stress theorems completely determine the equation of state of the crystal, i.e., external stresses and forces as a function of strains and internal atomic displacements. We apply the expression to silicon, using the *ab initio* pseudopotential method, to derive the equilibrium lattice constant and bulk moduli from calculations of both total energy and pressure. Elastic constants, higher-order elastic constants, the internal strain parameter ζ, and the TO(Γ) phonon frequency are derived by applying anisotropic strains and atomic displacements to the unit cell.

The stress tensor, introduced into quantum mechanics by Schrödinger[5] and Pauli,[6] can be derived in a many-body form with a scaling procedure due to Fock.[2] The total energy is

$$E_{\text{tot}} = \langle H_{\text{int}} + V_{\text{ext}}\rangle = \langle \textstyle\sum_i p_i^2/2m_i + V_{\text{int}} + V_{\text{ext}}\rangle, \quad (1)$$

where i labels the particles, and V_{int} denotes general interactions between the particles; V_{ext}, the external potentials; and angular brackets, the expectation value. Introducing a uniform scaling of the particle coordinates $\vec{r}_i$ by an infinitesimal strain tensor, $r_{i\alpha} \to r_{i\alpha} + \sum_\beta \epsilon_{\alpha\beta} r_{i\beta}$, the desired result follows from the variational property that a "stretching of the ground state"[2] does not change E_{tot} to first order. The stationarity of E_{tot} with respect to $\epsilon_{\alpha\beta}$ leads to the result that the total internal stress tensor $T_{\alpha\beta}$, given by

$$T_{\alpha\beta} = \partial\langle H_{\text{int}}\rangle/\partial\epsilon_{\alpha\beta}$$

$$= -\textstyle\sum_i \langle p_{i\alpha} p_{i\beta}/m_i - r_{i\beta}(\nabla_{r_i} V_{\text{int}})_\alpha\rangle, \quad (2)$$

must be balanced by the stress due to the external potential in order for the system to be in equilibrium. The average stress is denoted by

$\overline{\sigma}_{\alpha\beta} = T_{\alpha\beta}/\Omega$, where Ω is the volume of the system, and the external pressure P is $-\frac{1}{3}\sum_\alpha \overline{\sigma}_{\alpha\alpha}$. Thus Eq. (2) is a generalization of the virial theorem expression for pressure,[1,2] and we refer to it as the "stress theorem." It is closely related to the variational form of the force theorem.[3,4] In periodic solids with n atoms per unit cell, the six stress components and $3n$ forces given by the stress and force theorems are necessary and sufficient to determine all equilibrium conditions.

Evaluation of stress using the LDF proceeds by first carrying out a fully self-consistent calculation of the variational electronic wave functions ψ_i for any chosen structure of the solid. The stress $\overline{\sigma}_{\alpha\beta}$ is an intrinsic property of the solution which, from Eq. (2), can be expressed in reciprocal space (in atomic units) as[7]

$$\begin{aligned}\overline{\sigma}_{\alpha\beta} = &-\sum_{\vec{k},\vec{G},i} |\psi_i(\vec{k}+\vec{G})|^2 (\vec{k}+\vec{G})_\alpha (\vec{k}+\vec{G})_\beta + \tfrac{1}{2}(4\pi)\sum_{\vec{G}\neq 0}[|\rho(\vec{G})|^2/G^2](2G_\alpha G_\beta/G^2 - \delta_{\alpha\beta}) \\ &-\sum_{\vec{G}\neq 0} S(\vec{G})\{[\partial V(|\vec{G}|)/\partial(G^2)]2G_\alpha G_\beta + V(|\vec{G}|)\delta_{\alpha\beta}\}\rho(\vec{G})^* \\ &+\delta_{\alpha\beta}\sum_{\vec{G}}[\epsilon_{xc}(\vec{G}) - \mu_{xc}(\vec{G})]\rho(\vec{G})^* - \delta_{\alpha\beta}\Omega^{-1}\alpha_1 \cdot Z + \Omega^{-1}\partial(\gamma_{\mathrm{Ewald}})/\partial\epsilon_{\alpha\beta}. \qquad (3)\end{aligned}$$

Here ψ_i is the wave function of the ith occupied state, ρ the charge density, S the structure factor, Ω the unit cell volume, V a spherically symmetric local potential, γ_{Ewald} the ion-ion interactions in a constant background, and $\alpha_1 Z$ the average non-Coulombic ion-electron interaction.[8] The expression for nonlocal potentials is straightforward but lengthy, and will be given elsewhere.[7] The LDF contribution to stress is the purely diagonal fourth term in Eq. (3), in accordance with the result of Janak,[9] where ϵ_{xc} and μ_{xc} are the exchange-correlation energy per electron and potential, respectively. Pressures have previously been obtained by use of the virial theorem with the linear-muffin-tin-orbital, atomic-sphere-approximation (LMTO-ASA) method,[10] recasting it as a muffin-tin-sphere surface integral.[11] To our knowledge, these spherical approximations have not permitted the evaluation of anisotropic stresses, and the present work reports the first such calculations.

We have performed calculations of stresses, forces, and total energies for silicon, using the *ab initio* nonlocal pseudopotential method[12] with the Wigner interpolation formula for ϵ_{xc} and μ_{xc}. We have used a large number of plane waves (≈ 540, or kinetic energy up to ≈ 24 Ry) and 10 special $\vec{k}$ points in the irreducible fcc Brillouin zone, except as noted. From the pressure P evaluated using Eq. (3) at *only* two lattice constants near equilibrium, the lattice constant a (where $P=0$) is found by linear interpolation, and the bulk modulus B is $\Omega\Delta P/\Delta\Omega$. The results are given in Table I, where the uncertainty for a is estimated as $<0.2\%$, and $\sim 2\%$ for B. From the pressure at a range of lattice constants (using two special $\vec{k}$ points) fitted to Murnaghan's[13] equation of state, we find the derivative $\partial B/\partial P$ (Table I). The agreement with experiment is very good, $\sim 0.6\%$ for a and $\sim 5\%$ for other quantities. The present results furthermore agree almost exactly with all-electron LMTO-ASA calculations of a and B.[14] In contrast, if one calculates the total energy[8,15-17] it is necessary to include a large range of lattice constants and fit the result by an assumed equation of state in order to deduce the above quantities. This had lead to uncertainties of $\sim 10\%$ in B and a factor of ~ 2 in $\partial B/\partial P$ in the most thorough previous work.[17] Furthermore, we have verified that the lower cutoff (11.5 Ry) used in Ref. 17 leads to additional uncertainties.

The elastic constants c_{11} and c_{12} can be obtained directly from the two independent components σ_{11} and $\sigma_{22} = \sigma_{33}$ of the stress tensor due to a small strain ϵ_{11} (see inset in Fig. 1). There are no internal strains for any magnitude of ϵ_{11}. From Hooke's law for small strains the result is that $c_{11} = \sigma_{11}/\epsilon_{11}$ and $c_{12} = \sigma_{22}/\epsilon_{11}$. We have carried out

TABLE I. Lattice constant a in angstroms, bulk modulus B in megabars, and derivative $\partial B/\partial P$, elastic constants in units of megabars, and internal strain parameter ζ. The TO(Γ) phonon frequency is in terahertz. Experimental values are from Refs. 18 and 23.

	Calculation	Experiment
a	5.400	5.431
B	0.93	0.992
$\partial B/\partial P$	4.2	4.15
c_{11}	1.59	1.675
c_{12}	0.61	0.650
c_{44}	0.85	0.801
c_{111}	−7.5	−8.25(10)
c_{112}	−4.8	−4.51(5)
c_{1111}	≈ 0	...
c_{1112}	32	...
ζ	0.53	0.73(4)
$\omega_{\mathrm{TO}(\Gamma)}$	15.64	15.68(3)

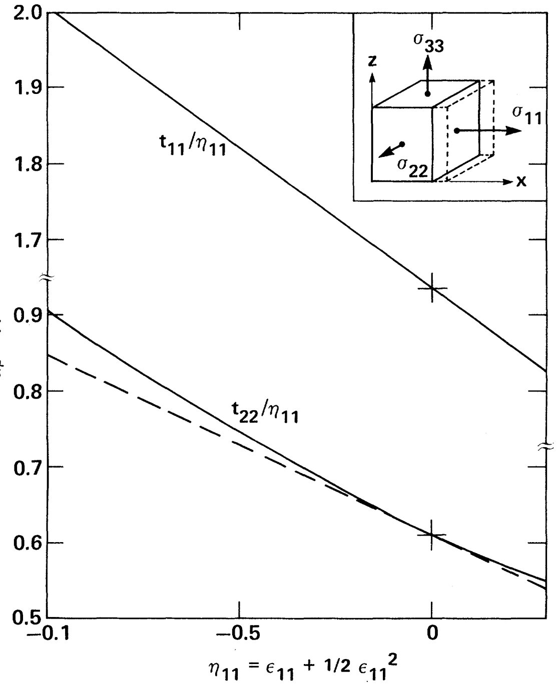

FIG. 1. Stress-strain relation in silicon for large (100) strains. We give the Lagrangian stresses t_{11} and t_{22} in megabars, divided by the uniaxial strain η_{11} (see text). The dashed line represents the linear term in t_{22}/η_{11}.

a calculation for $\epsilon_{11} = -0.004$, with the results given in Table I. The bulk modulus B equals $(c_{11} + 2c_{12})/3$, showing excellent internal consistency. The shear modulus is $\frac{1}{2}(c_{11} - c_{12})$, which previously[15,17] was derived from total energy differences proportional to the square of the strain. The present results are more accurate, and were derived from much smaller strains than were needed in the total energy calculations. Agreement with experimental values[18] is of the order of 5%.

The elastic constant c_{44}, which is obtained from uniaxial compression along the [111] direction, couples to internal strains in the unit cell. We can obtain all harmonic quantities directly from two independent calculations of stresses and forces, a far simpler procedure than other methods.[19-21] A strain $\epsilon_{\alpha\beta} = \frac{1}{2}\epsilon_4(1 - \delta_{\alpha\beta})$ and a relative internal displacement $u(1,1,1)$ gives within the harmonic approximation a force $\pm F(1,1,1)$ on each atom, where

$$F = \Phi(\zeta \tfrac{1}{4} a \epsilon_4 - u) \tag{4}$$

and ζ is the internal strain parameter defined by Kleinman.[22] The force constant Φ equals $\frac{1}{2}M \times \omega^2_{\mathrm{TO}(\Gamma)}$, where M is the atomic mass and $\omega_{\mathrm{TO}(\Gamma)}$ the frequency of the TO(Γ) phonon. The stress is similarly given by $\sigma_{\alpha\beta} = \sigma_4(1 - \delta_{\alpha\beta})$ with

$$\sigma_4 = c_{44}^{(0)}\epsilon_4 - \Omega^{-1}\Phi\zeta \tfrac{1}{4} a u, \tag{5}$$

where $c_{44}^{(0)}$ denotes the elastic constant that would appear in the absence of internal displacements. For a given strain ϵ_4, the internal displacement u is determined by the condition that the force F is zero, and the elastic constant $c_{44} = \sigma_4/\epsilon_4$ is therefore given by $c_{44}^{(0)} - \Omega^{-1}\Phi(\zeta a/4)^2$. On the one hand, calculation of F and σ_4 with $\epsilon_4 = 0$ and a small displacement u gives $\omega_{\mathrm{TO}(\Gamma)}$ from Eq. (4) and ζ from Eq. (5). On the other hand, a small strain ϵ_4 and $u = 0$ yields $c_{44}^{(0)}$, c_{44}, and an independent determination of ζ. The results are given in Table I, with a deviation from experiment of 6% for c_{44} and less than 1% for $\omega_{\mathrm{TO}(\Gamma)}$. The internal strain parameter ζ agrees reasonably with the less accurate calculations in Refs. 19–21, but it is ~27% below the values from independent recent experiments.[23] This is a large discrepancy which we believe is outside the limits of the theoretical uncertainty in view of the accuracy obtained for every other property, including c_{44} and $\omega_{\mathrm{TO}(\Gamma)}$. A possible explanation may be the assumption of overlapping spherical atoms in the analysis of the experimental data, as well as anharmonicity due to finite strains. Resolution of this controversy must await further investigations.

Higher-order elastic constants are found from the stress-strain relation at large strains. We calculated σ_{11} and σ_{22} for ϵ_{11} between -0.1 and $+0.03$ using two special $\vec{k}$ points. Since finite deformations are usually described in terms of Lagrangian stresses $t_{\alpha\beta}$ and strains $\eta_{\alpha\beta}$,[24] the following transformations are applied for an ϵ_{11} strain: $\eta_{11} = \epsilon_{11} + \frac{1}{2}\epsilon_{11}^2$, $t_{11} = \sigma_{11}/(1 + \epsilon_{11})$, $t_{22} = \sigma_{22}(1 + \epsilon_{11})$. In Fig. 1 we display t_{11}/η_{11} and t_{22}/η_{11} as a function of η_{11}, which besides c_{11} and c_{12} yields several third- and fourth-order elastic constants (Table I). The third-order constants are within 10% of experimental values, whereas the fourth-order constants have not been measured. Our results clearly illustrate the value of direct calculations of all stress components for arbitrarily large strains, where the stress-strain relation deviates markedly from the harmonic relations.

In conclusion, we have derived a general expression for the macroscopic stress tensor of a system of interacting particles, termed the stress theorem and closely connected to the virial theorem[1,2] and the force theorem.[3,4] We have applied this formulation to show that simultaneous calculation of stresses, forces, and total energy represents a complete and practical method for studying the structure of periodic solids. The present LDF calculations, using *ab initio* pseudopotentials for silicon, give accurate theoretical values for the lattice constant, elastic constants, internal strain parameter, and nonlinear stress-strain relations. Significant computational savings are obtained with this method compared to direct calculations of total energy differences. Agreement with experiment is very good, with the notable exception of the internal strain parameter ζ.

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