

Geometric formulation of quantum stress fields

Christopher L. Rogers and Andrew M. Rappe

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 4 December 2001; published 18 June 2002)

We present a derivation of the stress field for an interacting quantum system within the framework of local-density-functional theory. The formulation is geometric in nature, and exploits the relationship between the strain tensor field and Riemannian metric tensor field. Within this formulation, we demonstrate that the stress field is unique up to a single ambiguous parameter. The ambiguity is due to the nonunique dependence of the kinetic energy on the metric tensor. To illustrate this formalism, we compute the pressure field for two phases of solid molecular hydrogen. Furthermore, we demonstrate that qualitative results obtained by interpreting the hydrogen pressure field are not influenced by the presence of the kinetic ambiguity.

DOI: 10.1103/PhysRevB.65.224117

PACS number(s): 62.20.-x, 03.65.-w, 02.40.-k, 71.10.-w

I. INTRODUCTION

Stress, or the energetic response to deformation or strain, plays an important role in linking the physical properties of a material (e.g., strength, toughness) with the behavior of its microstructure. In addition, the spatial distribution of stress is an invaluable tool for continuum modeling of the response of materials. The stress concept has been applied at atomistic scales as well. Over the last 15 years, there has been a continuing trend toward understanding various structural and quantum-mechanical phenomena in materials in terms of their response to stress.¹

For example, residual stress at equilibrium has been used to assess the structural stability of systems containing surfaces or strained interfaces. It has been demonstrated that the desire to minimize surface stress can give rise to reconstructions on high-symmetry surfaces,²⁻⁸ and the stability of epitaxially grown bimetallic systems has been attributed to the formation of incommensurate overlayers, defects, and dislocations which minimize the stress near the metal-metal interface.^{9,10} The stress can have significant effects on chemical reactivity as well. It has been shown that small molecule chemisorption energies and reaction barriers on certain strained metal and semiconductor surfaces are quite different from those on the corresponding unstrained surface.^{11,12}

Formally, studies of the above phenomena must include a quantum-mechanical description of the system's electronic degrees of freedom. Therefore, one must consider how a stress is defined quantum mechanically. Methods for calculating the stress in quantum-mechanical systems have been developed since the birth of quantum theory.¹³ However, research in developing a formalism for determining the quantum stress in solid-state systems has recently been revitalized. This is mainly due to ever-increasing opportunities to perform accurate and efficient quantum-mechanical calculations on systems which exhibit stress-mediated phenomena.

The stress is a rank-2 tensor quantity, usually taken to be symmetric and therefore torque free. Two useful representations of the stress tensor are the volume-averaged or total stress T_{ij} , and the spatially varying stress field $\sigma_{ij}(\mathbf{x})$. The two representations are related, since the total stress for a particular region in a system is the stress field integrated over

the volume. Nielsen and Martin developed a formalism for calculating the total quantum stress in periodic systems.¹⁴ They defined the total stress as the variation of the total ground-state energy with respect to a uniform scaling of the entire system. This uniform scaling corresponds to a homogeneous or averaged strain over the entire system. They further demonstrated that the total quantum stress is a unique and well-defined physical quantity. Their formulation has been successfully implemented to study a variety of solid state systems.^{2,3} Other formalisms for determining the total quantum stress have been created as well.^{2,15,16}

Although these formalisms have provided important tools for studying quantum stress, the stress field is a more useful quantity that contains important information regarding the distribution of the stress throughout the system. A knowledge of the spatial dependence of the quantum stress is vital if one wishes to predict the spatial extent of structural modifications or understand phenomena at interfaces in complex heterogeneous systems. However, the quantum stress field can only be specified up to a so-called gauge term. Therefore the quantum stress field is not unique. A traditional way to develop a quantum stress field formalism is to consider the stress field's relationship with the force field. From this perspective, the stress field can be defined as any rank-two tensor field whose divergence is the force field of the system:

$$F^i(\mathbf{x}) = \nabla_j \sigma^{ij}(\mathbf{x}). \quad (1)$$

(Note that the Einstein summation convention for repeated indices is used throughout the paper.) One can add to σ^{ij} a term of the form

$$\frac{\partial}{\partial x^k} A^{ijk}(\mathbf{x}), \quad (2)$$

where A^{ijk} is any tensor field antisymmetric in j and k , and recover the same force field, thereby demonstrating the nonuniqueness of this stress field definition. General formulations for computing stress fields in quantum many-body systems have been derived by Nielsen and Martin, Folland, Ziesche *et al.*, and Godfrey.^{14,17-19} Regardless of issues concerning nonuniqueness, the quantum stress field has been used to investigate material properties. For example, Ramer

et al. developed a method to calculate the resultant stress field from an induced homogeneous strain in order to study piezoelectric effects in perovskites.²⁰ They incorporated the additional constraint that the field must be the smoothest fit to the ionic forces. However, this method cannot be used to calculate the residual stress field at equilibrium, nor can it determine the energy dependence on strains which do not have the periodicity of the unit cell. Filippetti and Fiorentini²¹ developed a formulation of the stress field based on the energy density formalism of Chetty and Martin.²² Since this formulation is based explicitly on the energy density, which cannot be uniquely specified, their stress field is also ambiguous.

In order to ascertain the exact nature of these ambiguities and to determine their effect on using the quantum stress field as an interpretive tool, we have developed a formulation of the quantum stress field based on differential geometry. This approach is similar to Mistura's work in deriving pressure fields for classical inhomogeneous fluids.²³ We first develop the necessary geometric framework and discuss the origin of ambiguities in the stress. We then derive the stress field in the context of the local-density approximation in density-functional theory (LDA-DFT). Finally, we apply our formulation by using the pressure field to explain the energetic ordering between two phases of solid molecular hydrogen.

II. METRIC AND STRAIN FIELDS

The geometric formulation for the stress field is developed from the relationship between a strain tensor field and the Riemannian metric tensor field. This relationship has been derived for flat manifolds²⁴ and for manifolds of arbitrary curvature.²³ The infinitesimal squared distance between two points on a Riemannian manifold can be written as $ds^2 = g_{ij}dx^i dx^j$, where the metric g_{ij} is a rank-2 symmetric tensor field. The system can then be infinitesimally distorted so that the positions of the points change, $dx'^i = dx^i + du^i$, which changes the squared distance to $ds'^2 = g_{ij}dx'^i dx'^j$. However, a coordinate transformation can be made so that the new distance can be computed from the point of view of the predistorted positions: $ds'^2 = g'_{ij}dx^i dx^j$, with the new metric defined as

$$g'_{kl} = g_{ij}(\delta_k^i + \partial_k u^i)(\delta_l^j + \partial_l u^j). \quad (3)$$

The strain field ϵ_{ij} can be related to the difference between distances before and after a distortion has been applied: $ds'^2 - ds^2 = 2\epsilon_{ij}dx^i dx^j$. Therefore, the metric g'_{ij} can be related to the strain

$$g'_{ij} = 2\epsilon_{ij} + g_{ij}. \quad (4)$$

We define the stress field σ^{ij} via the virtual work relation between energy and strain

$$\delta E = \int \sqrt{g} \sigma^{ij} \delta \epsilon_{ij} d^3x, \quad (5)$$

where g is the determinant of g_{ij} . Using Eq. (4), the stress field can be expressed as

$$\begin{aligned} \sigma^{ij} &= \frac{1}{\sqrt{g}} \frac{\delta E}{\delta \epsilon_{ij}} = \frac{2}{\sqrt{g}} \frac{\delta E}{\delta g_{ij}}, \\ \sigma_{ij} &= -\frac{2}{\sqrt{g}} \frac{\delta E}{\delta g^{ij}}, \end{aligned} \quad (6)$$

where g^{ij} is the inverse of the metric. It is this definition which we will use to compute the stress at the quantum length scale, with $E = \langle \Psi | \hat{H} | \Psi \rangle$ defined as the energy of the ground state $|\Psi\rangle$ of a system described by a Hamiltonian operator \hat{H} . This method of deriving the stress field is identical to that used to compute the ‘‘improved’’ energy-momentum tensor in field theories which are coupled to a background gravitational source.²⁵ Specifically, we shall be interested in the value of the stress field evaluated at the Euclidean metric ($g_{ij} = \delta_{ij}$).

III. UNIQUENESS

For the virtual work theorem [and, therefore, Eq. (6)], to specify a unique stress field, two criteria must be obeyed. First the metric must be varied freely, without constraints, when computing the functional derivative. Second the quantum-mechanical total energy must be unambiguously defined for all metrics. Before we can explain the origin and consequences of these criteria, we first must discuss in more detail the relationship between a metric tensor and the geometry of the underlying space containing the physical system. Metric tensor fields, for our purposes, can be classified into two categories: those fields which cause the Riemann curvature tensor to vanish at every point in space (e.g., the Euclidean metric $g_{ij} = \delta_{ij}$), and those fields which give rise to a nonzero Riemann curvature tensor (e.g. the metric for the two-dimensional surface of a sphere). The latter class of metrics will be referred to as non-Euclidean. The Riemann curvature is a rank-4 tensor field defined as

$$\begin{aligned} R_{iklm} &= \frac{1}{2}(\partial_k \partial_l g_{im} + \partial_i \partial_m g_{kl} - \partial_k \partial_m g_{il} - \partial_i \partial_l g_{km}) \\ &+ g_{np}(\Gamma_{kl}^n \Gamma_{im}^p - \Gamma_{km}^n \Gamma_{il}^p), \end{aligned} \quad (7)$$

where the matrices Γ_{kl}^i are the Christoffel symbols

$$\Gamma_{kl}^i = \frac{1}{2} g^{im} (\partial_l g_{mk} + \partial_k g_{ml} - \partial_m g_{kl}). \quad (8)$$

Metrics which give a zero Riemann curvature over the entire manifold are said to be flat. A coordinate transformation can always be performed so that any flat metric will transform into the Euclidean metric over the entire manifold.

We can think of the system as a collection of particles and/or fields embedded in a manifold M diffeomorphic to R^3 . We will refer to M as the background manifold. M is a flat space, and therefore the Euclidean metric can be used to compute distances over the entire manifold. Obviously, any physically possible rearrangement is constrained to keep the particles embedded in M (assuming no gravitational field is present). Therefore the system should only be able to realize

strain configurations which correspond [via the relation in Eq. (4)] to metric tensor fields which do not produce any Riemann curvature, since M is flat. This implies that the virtual work relation in Eq. (5) should be rewritten to reflect this constraint. All flat metrics can be expressed as

$$g_{ij} = \delta_{ij} + \partial_j u_i + \partial_i u_j, \quad (9)$$

where u_i is a vector field continuous over the entire manifold. The constrained virtual work relation is then

$$\delta E = \int \sqrt{g} \sigma^{ij} (\partial_j \delta u_i + \partial_i \delta u_j) d^3 x. \quad (10)$$

Since we are now constrained to a flat space we can choose Cartesian coordinates so that $\sqrt{g} = 1$:

$$\delta E = \int \sigma^{ij} (\partial_j \delta u_i + \partial_i \delta u_j) d^3 x \quad (11)$$

$$= - \int (\partial_j \sigma^{ij} \delta u_i + \partial_i \sigma^{ij} \delta u_j). \quad (12)$$

Note that the divergence of the stress field has appeared in Eq. (12), so this approach cannot be used to uniquely specify the stress field. Therefore, introducing a constraint on variations in the metric has produced an ambiguity in the stress field. This is the origin of the aforementioned first criterion for uniqueness of the stress field. To have a unique stress field, the system must be allowed to realize the energetics of *any* applied strain configuration which can be represented by a continuous symmetric tensor field.

If we hypothesize that stress fields are unique, then we must explain physically how the system can be altered so that the Riemann curvature at some point is nonzero. Even a first-order change away from the Euclidean metric will generate a first-order change in the curvature. One way which such distortions could be realized is by introducing a gravitational “pointlike” source. Then, according to general relativity, the system would be altered by the fact that the source has generated curvature within the background manifold. It is through this thought experiment that the link between the definition of the stress field used in this work and the energy-momentum tensor in the gravitational literature is established. Unfortunately this is not a phenomenon that can be observed by experiment, especially on the quantum scale.

In addition to the gravitational interpretation, we can also consider the meaning of non-Euclidean metrics within the context of the continuum theory of solids. In this theory, the solid within the limit of vanishing lattice parameter can be described by a vector field u_i which indicates the displacement of atomic positions away from some reference (usually taken to be a perfect crystal).²⁶ If the specified atomic configuration contains defects such as disclinations and dislocations, then the displacement field u_i will not be perfectly smooth and therefore will violate the integrability conditions

$$(\partial_i \partial_j - \partial_j \partial_i) u_k = 0. \quad (13)$$

Within linear elasticity theory, the information regarding the disclinations and dislocations can be represented by a symmetric tensor field known as the defect density,²⁷

$$\eta_{ij} = \varepsilon_i^{kl} \varepsilon_j^{mn} \partial_k \partial_m u_{ln}, \quad (14)$$

where ε_{ikl} is the Levi-Civita symbol, and u_{ij} is the continuum strain tensor field. Note that η_{ij} is the double curl of the strain field. If $\eta_{ij} = 0$ over the entire manifold, then the strain field may be written in terms of the gradient of a displacement vector field u_i which obeys the condition in Eq. (13). Specifically,

$$u_{ij} = \frac{1}{2} (\partial_i u_j + \partial_j u_i), \quad (15)$$

This is known as compatibility. If there are no defects present, then the strain field is compatible with a smooth vector displacement field.

The defect density has a rigorous geometric meaning. It can be shown that²⁷

$$\eta_{ij} = R_{ij} - \frac{1}{2} g_{ij} R = G_{ij}. \quad (16)$$

G_{ij} is known as the Einstein curvature tensor, and is related to the Riemann curvature through the Ricci curvature $R_{ij} = g^{lm} R_{limj}$ and the scalar curvature $R = g^{ij} R_{ij}$. Therefore, if a particular strain configuration in a continuum model generates Einstein curvature, it should be interpreted as a mathematical representation of the discontinuity in the displacement of the particles in the system due to defects. The curvature should not be thought of as a physical manipulation of the geometry of the background manifold. However, on the quantum scale, the relationship between the curvature and the compatibility of the strain field requires careful consideration. It is not obvious how to assign physical meaning to, for example, a “defect” that is pointlike in an electron gas.

Since we must consider the energetic response of the system to non-Euclidean metrics, the quantum-mechanical energy must be generalized so that it is unambiguously defined for metrics that generate an arbitrary Riemann curvature. This is the origin of the second criterion for uniqueness of the quantum stress field. If we take the *ab initio* perspective, we can build the generalized Hamiltonian from only a few facts. First it is reasonable to require that the energy transform as a covariant scalar regardless of the geometry. Second, the generalized Hamiltonian must reduce to the known correct flat-space result when evaluated with a metric which generates zero Riemann curvature. Finally, the Hamiltonian must be well behaved in the sense that it corresponds to a quantum field theory that is renormalizable. Unfortunately, these conditions are not strict enough to uniquely specify a single Hamiltonian. There are an infinite number of possible choices, all which satisfy the above three conditions. In particular, the ambiguity manifests itself in the kinetic energy. In Euclidean space, the Hamiltonian for a spin-zero free field $\hat{\psi}$ is

$$\hat{H} = \frac{1}{2} \int \nabla \hat{\psi}^\dagger \cdot \nabla \hat{\psi} d^3 x. \quad (17)$$

To generalize for a manifold of arbitrary curvature, we can write \hat{H} in a covariant form:

$$\hat{H}' = \frac{1}{2} \int \sqrt{g} g^{ij} \partial_i \hat{\psi}^\dagger \partial_j \hat{\psi} d^3x. \quad (18)$$

The operator \hat{H}' satisfies the aforementioned requirements for a generalized Hamiltonian. Note that \hat{H}' could have been constructed by writing \hat{H} in terms of curvilinear coordinates in a flat space. This is known as the principle of least coupling. It is the simplest way to generate operators which are suitably generalized for curved spaces. Also, it is the mathematical formulation of the equivalence principle in general relativity. However, we could postulate another generalized form of \hat{H} ,

$$\begin{aligned} \hat{H}'' = \int \sqrt{g} \left(\frac{1}{2} g^{ij} \partial_i \hat{\psi}^\dagger \partial_j \hat{\psi} + \alpha R + \beta R \hat{\psi}^\dagger \hat{\psi} \right. \\ \left. + \gamma R^{ij} \partial_i \hat{\psi}^\dagger \partial_j \hat{\psi} \right) d^3x, \end{aligned} \quad (19)$$

where α , β , and γ are coupling constants to the various curvature terms. Note that H'' is a scalar and gives the correct Euclidean space Hamiltonian when $g_{ij} = \delta_{ij}$. However, the term multiplied by γ will cause the theory to be nonrenormalizable in a curved space. This can be determined via dimensional analysis. In the units $\hbar = 1$ and $c = 1$ (commonly used in relativistic field theories²⁸) the Hamiltonian must have units of mass, or equivalently $(\text{length})^{-1}$. This implies the integrand, or Hamiltonian density, must have units of $(\text{mass})^4$ since the measure d^3x has units of $(\text{mass})^{-3}$. (The metric is unitless.) The spin-zero field $\hat{\psi}$ has units of $(\text{mass})^1$, which can be deduced from the first term of H'' which contains only gradients. The scalar curvature R has units of $(\text{mass})^2$, since it contains the second derivatives and products of the first derivatives of the metric. Hence we can conclude that α has units of $(\text{mass})^2$, β is dimensionless, and γ has units of $(\text{mass})^{-2}$. If a coupling constant has negative mass dimension, then the theory is nonrenormalizable.²⁹ Therefore, we can set γ equal to zero.

The ambiguity can be further reduced if we physically reason that if no matter is present in the system, then the stress field should be zero everywhere, i.e., the part of H'' multiplied by α is a background term. Furthermore, this term's contribution to the stress field will vanish when the stress field is evaluated at the Euclidean metric. Consequently we may set $\alpha = 0$. However, we currently cannot determine any restrictions on the value of β from first principles. This is the origin of the ambiguity in the dependence of the energy on the metric. Therefore, the quantum stress field will only be unique up to the determination of β . We further note that this problem is well-known in the gravitational and constrained-dynamics literature, and to date remains unresolved.³⁰⁻³²

IV. DFT STRESS FIELD

We now use the geometric approach to derive the quantum stress field of a many-electron system in the presence of a fixed set of classical positive charged ions using local-density functional theory.^{33,34} The ground-state electronic charge density of the system is written as $n(\mathbf{x}) = \sum_\mu \phi_\mu^*(\mathbf{x}) \phi_\mu(\mathbf{x})$, where ϕ_μ are single-particle orthonormal wave functions. For this derivation, we assume orbitals with fixed integer occupation numbers. The extension to metals with Fermi fillings is straightforward, simply necessitating use of the Mermin functional instead of the total energy.³⁵ The total charge density of the system can be written as a sum over all ionic charges and n ,

$$\rho(\mathbf{x}) = \sum_\mu \frac{Z_\mu}{\sqrt{g}} \delta(\mathbf{x} - \mathbf{R}_\mu) - n(\mathbf{x}), \quad (20)$$

where Z_μ is the charge of the μ th ion located at position \mathbf{R}_μ , and the presence of \sqrt{g} insures a proper normalization of the delta function. The energy of the system can be written as the following constrained functional which is appropriately generalized for arbitrary Riemannian spaces:

$$E = E_k + E_{\text{Coulomb}} + E_{\text{xc}} - \sum_\mu \lambda_\mu \left(\int \sqrt{g} \phi_\mu^* \phi_\mu d^3x - 1 \right). \quad (21)$$

Here E_k is the single particle kinetic energy including the aforementioned ambiguity, E_{Coulomb} is the classical Coulomb interaction between the total charge density and itself, and E_{xc} is the exchange-correlation energy of the electrons. The appearance of the last term in Eq. (21) is due to the orthonormality constraint of the orbitals. (We choose a unitary transformation on $\{\phi_\mu\}$ which enforces orthogonality.) One can express E as an integral over an energy density.^{22,36} For convenience, we express the energy terms in Eq. (21) as

$$\begin{aligned} E_k &= \int \sqrt{g} \left(\frac{1}{2} \sum_\mu g^{ij} \partial_i \phi_\mu^* \partial_j \phi_\mu + \beta R n \right) d^3x, \\ E_{\text{Coulomb}} &= \int \sqrt{g} \left(\rho V - \frac{1}{8\pi} g^{ij} \mathcal{F}_i \mathcal{F}_j \right) d^3x, \\ E_{\text{xc}} &= \int \sqrt{g} n \varepsilon_{\text{LDA}}(n) d^3x, \end{aligned} \quad (22)$$

where $\mathcal{F}_i = -\partial_i V$ is the electric field due to the Coulomb potential V generated by ρ , $\varepsilon_{\text{LDA}}(n)$ is the LDA exchange-correlation energy density, and R is the scalar curvature. To obtain the electronic ground-state energy, we require $\delta E / \delta \phi_\mu^* = 0$ with the additional constraints of a fixed metric ($\delta g_{ij} = 0$) and a fixed ionic charge density ($\delta \rho = -\delta n$). This implies that the orbitals must obey the Euler-Lagrange equations

$$\begin{aligned} -\frac{1}{2\sqrt{g}} \partial_i (\sqrt{g} g^{ij} \partial_j \phi_\mu) + \beta R \phi_\mu + \frac{\delta E_{\text{Coulomb}}}{\delta n} \phi_\mu + \frac{\delta E_{\text{xc}}}{\delta n} \phi_\mu \\ = \lambda_\mu \phi_\mu, \end{aligned} \quad (23)$$

which can be considered the Kohn-Sham equations for a general Riemannian manifold. Also, a least-action principle for E_{Coulomb} requires that ρ and V obey the Poisson equation

$$\frac{1}{\sqrt{g}} \partial_i (\sqrt{g} g^{ij} \partial_j V) = -4\pi\rho. \quad (24)$$

We now vary the total energy with respect to the metric. It can be proven that we do not need to consider variations in the electronic wavefunctions, charge density, and potentials, since all such variations would vanish due to Eqs. (23) and (24). This is the same principle used in the derivation of the Hellmann-Feynman force theorem and the energy-momentum tensor (the variation of the action with respect to metric) in general relativity.^{25,37,38} Performing the variation of the total energy with respect to the metric gives the stress field in local density functional theory as

$$\begin{aligned} \sigma_{ij} = & - \sum_{\mu} \partial_i \phi_{\mu}^* \partial_j \phi_{\mu} + A_{ij} + \frac{1}{4\pi} \mathcal{F}_i \mathcal{F}_j \\ & + g_{ij} \left(\frac{1}{2} \sum_{\mu} \partial_k \phi_{\mu}^* \partial^k \phi_{\mu} - \frac{1}{8\pi} \mathcal{F}_k \mathcal{F}^k + n \varepsilon_{\text{LDA}}(n) \right. \\ & \left. - \sum_{\mu} \phi_{\mu}^* \phi_{\mu} [\lambda_{\mu} + V] \right), \end{aligned} \quad (25)$$

where we have used the relation $\partial \sqrt{g} / \partial g^{ij} = -\frac{1}{2} \sqrt{g} g_{ij}$. For the moment, we simply denote the contribution of the kinetic ambiguity to the stress field as A_{ij} . Using Eq. (23), we can rewrite Eq. (25) as

$$\begin{aligned} \sigma_{ij} = & - \sum_{\mu} \partial_i \phi_{\mu}^* \partial_j \phi_{\mu} + A_{ij} + \frac{1}{4\pi} \mathcal{F}_i \mathcal{F}_j \\ & + g_{ij} \left[\frac{1}{2} \sum_{\mu} \partial_k \phi_{\mu}^* \partial^k \phi_{\mu} + \frac{1}{2\sqrt{g}} \sum_{\mu} \phi_{\mu}^* \partial_k (\sqrt{g} g^{kk} \partial_k \phi_{\mu}) \right. \\ & \left. - \beta R n - \frac{1}{8\pi} \mathcal{F}_k \mathcal{F}^k + n \left(\varepsilon_{\text{LDA}}(n) - \frac{\delta E_{\text{xc}}}{\delta n} \right) \right]. \end{aligned} \quad (26)$$

Equation (26) is most useful when evaluated at the Euclidean metric. $\{\phi_{\mu}\}$ are then solutions to the standard Kohn-Sham equations. From here on we will refer to σ_{ij} with an implied evaluation at the Euclidean metric.

At this point we briefly describe how to obtain the explicit form of A_{ij} in Euclidean space. We need to evaluate

$$A_{ij}(\mathbf{y}) = - \frac{2\beta}{\sqrt{g(\mathbf{y})}} \int n(\mathbf{x}) \frac{\delta [\sqrt{g(\mathbf{x})} R(\mathbf{x})]}{\delta g^{ij}(\mathbf{y})} d^3x. \quad (27)$$

(Variations in n are zero due to the aforementioned use of the variational principle.) Keeping in mind we are only interested in the result evaluated for $g_{ij} = \delta_{ij}$, and $R_{ij} = 0$, the only nonzero term is

$$A_{rs}(\mathbf{y}) = - \frac{2\beta}{\sqrt{g(\mathbf{y})}} \int \sqrt{g(\mathbf{x})} n(\mathbf{x}) g^{ik}(\mathbf{x}) \frac{\delta R_{ik}(\mathbf{x})}{\delta g^{rs}(\mathbf{y})} d^3x. \quad (28)$$

After substantial manipulation and an integration by parts, we obtain

$$\begin{aligned} A_{rs}(\mathbf{y}) = & \frac{2\beta}{\sqrt{g(\mathbf{y})}} \int \sqrt{g(\mathbf{x})} \partial_l n(\mathbf{x}) \\ & \times \left(g^{ik}(\mathbf{x}) \frac{\delta \Gamma_{ik}^l(\mathbf{x})}{\delta g^{rs}(\mathbf{y})} - g^{il}(\mathbf{x}) \frac{\delta \Gamma_{ik}^k(\mathbf{x})}{\delta g^{rs}(\mathbf{y})} \right) d^3x, \end{aligned} \quad (29)$$

plus additional terms which are zero when $g_{ij} = \delta_{ij}$. An explicit computation of the functional derivatives gives the final result for Euclidean space:

$$A_{ij} = \beta (\partial_i \partial_j n - \delta_{ij} \partial^k \partial_k n). \quad (30)$$

Therefore, the complete stress field evaluated at $g_{ij} = \delta_{ij}$ is

$$\begin{aligned} \sigma_{ij} = & - \sum_{\mu} \partial_i \phi_{\mu}^* \partial_j \phi_{\mu} + \beta (\partial_i \partial_j n - \delta_{ij} \partial^k \partial_k n) + \frac{1}{4\pi} \mathcal{F}_i \mathcal{F}_j \\ & + \delta_{ij} \left(\frac{1}{2} \sum_{\mu} \partial^k \phi_{\mu}^* \partial_k \phi_{\mu} + \frac{1}{2} \sum_{\mu} \phi_{\mu}^* \partial^k \partial_k \phi_{\mu} \right. \\ & \left. - \frac{1}{8\pi} \mathcal{F}^k \mathcal{F}_k + n \left(\varepsilon_{\text{LDA}}(n) - \frac{\delta E_{\text{xc}}}{\delta n} \right) \right). \end{aligned} \quad (31)$$

It is important to note several key features of the form of σ_{ij} . First the ambiguity in the kinetic stress is identical to that identified by Godfrey via a different formalism.¹⁹ Also, the kinetic stress contains diagonal terms which are similar to the symmetric and antisymmetric kinetic-energy densities. The contribution of the exchange-correlation energy to the stress field is only in the diagonal (pressurelike) terms, which is the proper behavior for local density functionals¹⁴ and is identical to the exchange-correlation stress derived in Ref. 21.

The Coulombic contribution to σ_{ij} is equivalent to the classical Maxwell stress field. This Coulombic term can be obtained by Filippetti and Fiorentini's formalism if one chooses the so-called Maxwell gauge.²¹ We emphasize that it has been mathematically proven in the gravitational literature that the usual energy-momentum tensor for electromagnetism is unique.³⁹⁻⁴¹ Since this energy-momentum tensor is equivalent to the Maxwell stress in the non-relativistic limit and the absence of magnetic fields, the classical Coulombic interaction in the stress field is rigorously free of ambiguities.

By integrating the stress field over all space, note that we can obtain the total stress T_{ij} ,

$$T_{ij} = \int \left\{ - \sum_{\mu} \partial_i \phi_{\mu}^* \partial_j \phi_{\mu} + \frac{1}{4\pi} \mathcal{F}_i \mathcal{F}_j - \delta_{ij} \frac{1}{8\pi} \mathcal{F}_k \mathcal{F}^k + \delta_{ij} n \left(\varepsilon_{\text{LDA}}(n) - \frac{\delta E_{\text{xc}}}{\delta n} \right) \right\} d^3x, \quad (32)$$

which is identical to the expression derived by Nielsen and Martin.¹⁴

It is also instructive to consider the form of the pressure field P defined as one-third the trace of the stress field. Using our formulation for σ_{ij} we obtain

$$P = \frac{1}{3} \left(\frac{1}{2} \sum_{\mu} \partial^k \phi_{\mu}^* \partial_k \phi_{\mu} - 2\beta \partial^k \partial_k n - \frac{1}{8\pi} \mathcal{F}^k \mathcal{F}_k \right) + \frac{1}{2} \sum_{\mu} \phi_{\mu}^* \partial^k \partial_k \phi_{\mu} + n \left(\varepsilon_{\text{LDA}}(n) - \frac{\delta E_{\text{xc}}}{\delta n} \right). \quad (33)$$

Note the pressure field contains the Maxwell energy density and a combination of the symmetric and antisymmetric kinetic energy densities. The contribution of the LDA exchange-correlation pressure is consistent with the unambiguous exchange-correlation energy density derived by Burke *et al.*⁴²

Also present is the undetermined contribution of the Laplacian of the charge density. We should consider whether this kinetic ambiguity impairs us from using the the pressure field to obtain interesting qualitative information from total-energy calculations. We would therefore need to determine a meaningful range for the parameter β . Note that this term is responsible for introducing ambiguity in the kinetic-energy density. Changing β from 0 to $-1/4$ transforms the kinetic-energy density from a symmetric form to an antisymmetric form:

$$\begin{aligned} & \frac{1}{2} \sum_{\mu} \partial^k \phi_{\mu}^* \partial_k \phi_{\mu} - \frac{1}{4} \partial^k \partial_k n \\ &= -\frac{1}{4} \sum_{\mu} (\phi_{\mu}^* \partial^k \partial_k \phi_{\mu} + \phi_{\mu} \partial^k \partial_k \phi_{\mu}^*). \end{aligned} \quad (34)$$

The symmetric and antisymmetric forms have been considered to be physically meaningful expressions for the kinetic-energy density, and they have been studied extensively in previous work.^{21,22} Clearly other valid forms of the kinetic-energy density exist. If the parameter β were to influence physically meaningful results obtained from the energy density or stress field, we would expect to see some effect as the kinetic-energy density is changed from symmetric to antisymmetric form. Therefore, the range which we consider here is $-1/4 \leq \beta \leq 0$.

V. APPLICATION: SOLID HYDROGEN

In order to demonstrate the utility of our stress field formalism, within DFT we compute the pressure field for two phases of solid molecular hydrogen under external hydrostatic pressure of 50 GPa.⁴³ Both structures consist of stacked two-dimensional triangular lattices of hydrogen mol-

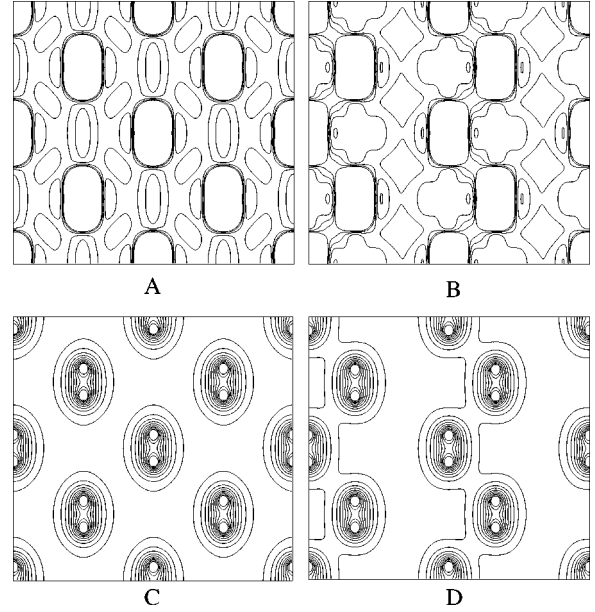


FIG. 1. Contour plots of the pressure field with $\beta=0$ and the charge density within DFT for the $Cmca$ structure [panels (A) and (C)] and for the m -hcp structure [panels (B) and (D)] of solid hydrogen. The vertical axis is the stacking direction for the layers, and the horizontal axis is the direction along which alternating layers are shifted. The plots are 6.794 Å high and 7.206 Å wide. Ten contours are shown, over a range of 0–3 eV/Å³ for the pressure fields, and from 0–2.5 e/Å³ for the charge densities.

ecules, with the molecular axis parallel to the stacking direction and a repeat unit of two layers. The m -hcp structure has alternating layers shifted so that each hydrogen molecule is directly above triangular hollow sites in the neighboring layers. The second structure (belonging to the $Cmca$ space group) has a different shift, so that each molecule lies directly above midpoints between nearest-neighbor pairs of molecules in adjacent layers.⁴⁴ The energetics and electronic properties of both structures have been studied extensively from first principles.^{45,46}

Examination of the pressure field permits us to rationalize the energy ordering of these structures. The m -hcp structure is energetically favored by 60 meV/molecule. Figure 1(A) shows a contour plot of the pressure field for the $Cmca$ structure. Here we have set the constant β equal to zero. The pressure is tensile (greater than zero) through the interstitial region, indicating that contraction is locally favorable. The tensile pressure is greatest in the volume directly above and below each molecule, averaging 3 eV/Å³. This implies that the system would energetically favor increased intermolecular coordination. In Fig. 1(B) we show a similar plot for the m -hcp structure. Again the pressure within the interstitial region is tensile. However, the pressure field has significantly rearranged, and the pressures in the regions above and below molecules have been reduced to approximately 2.25 eV/Å³. It is also clear from the charge density plots [Figs. 1(C) and 1(D)] that the reduction in pressure is correlated with an increase in bonding between molecules and increased charge delocalization. The pressure fields within the molecules are compressive, and they are several orders of magnitude larger

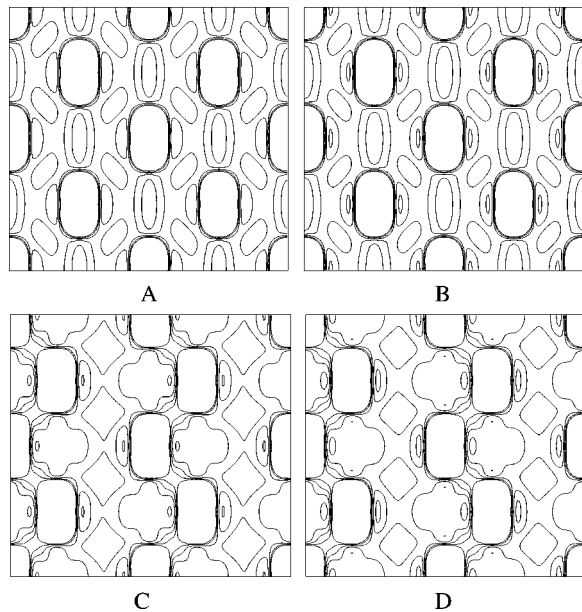


FIG. 2. Contour plots of the pressure field in solid hydrogen for the *Cmca* and *m-hcp* structures with $\beta=0$ [panels (A) and (C)], and $\beta=-1/4$ [panels (B) and (D)]. The vertical axis is the stacking direction for the layers, and the horizontal axis is the direction along which alternating layers are shifted. The plots are 6.794 \AA high and 7.206 \AA wide. Ten contours are shown, over a range of $0-3 \text{ eV/\AA}^3$.

than the interstitial features. However, because these large fields are very similar in both structural phases (and the free molecule), they are not important for understanding the relative phase stability. Thus, changes in the pressure stress field highlight regions and charge-density features that contribute to favorable energetic changes.⁴⁷

Figure 2 contrasts the pressure fields for $\beta=0$ and $\beta=-1/4$. Note that there is no qualitative change in the pressure field within the interstitial regions since the charge density in this area is quite smooth and hence the value of its Laplacian is small (averaging 0.05 eV/\AA^3). Therefore our above analysis holds regardless of our choice of β .

VI. CONCLUSION

We have developed a formulation of the quantum stress field using differential geometry. We identify the stress tensor field as a variation of the total ground-state quantum-mechanical energy with respect to the metric tensor field. Within this formulation we have uniquely specified the stress field up to a single ambiguity. The origin of the ambiguity lies in the inability to uniquely describe the dependence of the kinetic energy on the metric tensor.

We have successfully extended this formulation to local density functional theory. Terms identical to the Maxwell stress can be found within the LDA-DFT stress field. We note that within the gravitational literature, it is well known that the Maxwell stress is unique. We describe the similarities between the pressure field obtained by our method and the various terms found in the total energy density. We then show that the pressure field contains an ambiguity in the form of the Laplacian of the charge density multiplied by a constant β . Through the relationship between terms in the pressure field and the kinetic-energy density we offer a realistic range of choices for the value of β .

To demonstrate the usefulness of the stress field as a qualitative tool in combination with total-energy calculations, we used the pressure field to rationalize the energetics of two phases of solid molecular hydrogen. We finally show that our conclusions remain invariant with respect to realistic choices of β .

The authors wish to acknowledge V. Balasubramanian, J. Bassani, K. Burke, R. P. Kauffman, R. M. Martin, P. Nelson, and D. Vanderbilt for their comments and valuable suggestions regarding this work, and E. J. Walter for his assistance with the numerical calculations. This work was supported by NSF Grant No. DMR 97-02514 and the Air Force Office of Scientific Research, Air Force Materiel Command, USAF, under Grant No. F49620-00-1-0170. A.M.R. would like to thank the Camille and Henry Dreyfus Foundation for support. Computational support was provided by the National Center for Supercomputing Applications and NAVOCEANO MSRC.

- ¹H. Ibach, *Surf. Sci. Rep.* **29**, 193 (1997).
- ²R. J. Needs and M. J. Godfrey, *Phys. Scr.* **T19**, 391 (1987).
- ³R. J. Needs, M. J. Godfrey, and M. Mansfield, *Surf. Sci.* **242**, 215 (1991).
- ⁴V. Fiorentini, M. Methfessel, and M. Scheffler, *Phys. Rev. Lett.* **71**, 1051 (1993).
- ⁵C. E. Bach, M. Giesen, and H. Ibach, *Phys. Rev. Lett.* **78**, 4225 (1997).
- ⁶A. Filippetti and V. Fiorentini, *Phys. Rev. B* **60**, 14 366 (1999).
- ⁷O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, *Phys. Rev. Lett.* **61**, 1973 (1988).
- ⁸S. Narasimhan and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 1564 (1992).
- ⁹C. Mottet, G. Tréglia, and B. Legrand, *Phys. Rev. B* **46**, 16 018 (1992).
- ¹⁰I. Meunier, G. Tréglia, J.-M. Gay, and B. Aufray, *Phys. Rev. B* **59**, 10 910 (1999).
- ¹¹R. D. Meade and D. Vanderbilt, *Phys. Rev. Lett.* **63**, 1404 (1989).
- ¹²M. Mavrikakis, B. Hammer, and J. K. Nørskov, *Phys. Rev. Lett.* **81**, 2819 (1998).
- ¹³E. Schrödinger, *Ann. Phys. (Leipzig)* **82**, 265 (1927).
- ¹⁴O. H. Nielsen and R. M. Martin, *Phys. Rev. B* **32**, 3780 (1985).
- ¹⁵D. Passerone, E. Tosatti, G. L. Chiarotti, and F. Ercolessi, *Phys. Rev. B* **59**, 7687 (1999).
- ¹⁶A. Dal Corso and R. Resta, *Phys. Rev. B* **50**, 4327 (1994).
- ¹⁷N. O. Folland, *Phys. Rev. B* **34**, 8296 (1986).
- ¹⁸P. Ziesche, J. Gräfenstein, and O. H. Nielsen, *Phys. Rev. B* **37**, 8167 (1988).
- ¹⁹M. J. Godfrey, *Phys. Rev. B* **37**, 10 176 (1988).
- ²⁰N. J. Ramer, E. J. Mele, and A. M. Rappe, *Ferroelectrics* **206-207**, 31 (1998).
- ²¹A. Filippetti and V. Fiorentini, *Phys. Rev. B* **61**, 8433 (2000).
- ²²N. Chetty and R. M. Martin, *Phys. Rev. B* **45**, 6074 (1992).

- ²³L. Mistura, J. Chem. Phys. **83**, 3633 (1985); Int. J. Thermophys. **8**, 397 (1987).
- ²⁴Y. C. Fung, *Foundations of Solid Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1965), pp. 90–92.
- ²⁵L. D. Landau and E. M. Lifshitz, *The Classical Theory of Fields*, 4th ed. (Pergamon, Oxford, 1975), pp. 270–273.
- ²⁶L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 3rd ed. (Butterworth-Heinemann, Oxford, 1986), pp. 1–3.
- ²⁷H. Kleinert, *Gauge Fields in Condensed Matter* (World Scientific, Singapore, 1989), pp. 1357–1363.
- ²⁸Choosing c dimensionless is equivalent to measuring distance and time with the same units, giving energy and mass the same units. Making \hbar dimensionless gives energy (and mass) the units of inverse time (or inverse length).
- ²⁹In a perturbative expansion for the energy, the Feynman diagrams involve integrals over all momentum (or mass). A dimensional analysis implies that the dependence of the coupling constant on mass is inversely related to that of the integrand as a whole. Therefore, if the coupling constant depends inversely on the mass, the integrand will contain positive powers of the mass, and higher perturbative orders will diverge increasingly rapidly. This leads to new divergences at each order and a nonrenormalizable theory. Since each divergent term needs to be absorbed into an experimentally measured quantity, nonrenormalizable theories have limited predictive power and are not accepted as valid models of nature. See M.E. Peskin and D.V. Schroeder, *An Introduction to Quantum Field Theory* (Perseus, Reading, PA, 1995), pp. 315–322.
- ³⁰N. D. Birrell and P. C. W. Davies, *Quantum Fields in Curved Space* (Cambridge University Press, New York, 1982), Chap. 2.
- ³¹A. Saa, Class. Quantum Grav. **14**, 385 (1997).
- ³²D. Baleanu and Y. Güler, J. Phys. A **34**, 73 (2001).
- ³³P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ³⁴W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ³⁵N. D. Mermin, Phys. Rev. **137**, A1441 (1965).
- ³⁶M. Cohen, D. Frydel, K. Burke, and E. Engel, J. Chem. Phys. **113**, 2990 (2000).
- ³⁷H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937), pp. 61 and 285.
- ³⁸R. P. Feynman, thesis, Massachusetts Institute of Technology, 1939 (unpublished); Phys. Rev. **56**, 340 (1939).
- ³⁹C. D. Collinson, Proc. Cambridge Philos. Soc. **66**, 437 (1969).
- ⁴⁰D. Lovelock, Int. J. Theor. Phys. **10**, 59 (1974).
- ⁴¹D. B. Kerrighan, J. Math. Phys. **23**, 1979 (1982).
- ⁴²K. Burke, F. Cruz, and K. Lam, J. Chem. Phys. **109**, 8161 (1998).
- ⁴³All calculations were performed using the LDA functional of Perdew and Zunger [J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981)], a plane-wave basis set with a cutoff of 300 Ry, and a 512 k -point sampling of the Brillouin zone. Details regarding efficient implementation of the stress field into plane-wave calculations will be presented elsewhere.
- ⁴⁴K. Nagao, T. Takezawa, and H. Nagara, Phys. Rev. B **59**, 13 741 (1999).
- ⁴⁵E. Kaxiras, J. Broughton, and R. J. Hemley, Phys. Rev. Lett. **67**, 1138 (1991).
- ⁴⁶B. Edwards, N. W. Ashcroft, and T. Lenosky, Europhys. Lett. **34**, 519 (1996).
- ⁴⁷Calculations for both structures were performed in an orthorhombic unit cell with parameters $a=2.08$, b , and c with $b/a=\sqrt{3}$ and $c/a=\sqrt{8/3}$. All atomic forces were relaxed to <5 meV/Å.