Geometric Formulation of Unique 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, PA 19104-6323.

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Abstract

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. The resultant expression obtained for the stress field is gauge-invariant with respect to choice of energy density, and therefore provides a unique, well-defined quantity. To illustrate this formalism, we compute the pressure field for two phases of solid molecular hydrogen.

03.65.-w, 62.20.-x, 02.40.-k, 71.10.-w
The 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 fifteen 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, the 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 strained semiconductor surfaces are quite different from those on the 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 itself [13]. However, research in developing formalisms 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-two 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, \( T_{\alpha\beta} \), and the spatially varying stress field \( \sigma_{\alpha\beta}(x) \). 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 define 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 demonstrate 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, certain definitions of the quantum stress field suggest that it can only be specified up to a gauge. (This ambiguity manifests itself in classical atomistic models as well.) It has therefore been asserted that the quantum stress field is not a well-defined physical quantity, even though physical intuition may suggest otherwise. 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:

$$F^\alpha = \nabla_\beta \sigma^{\alpha\beta}.$$  \hspace{1cm} (1)

(Note that the Einstein summation convention for repeated indices is used throughout the Letter.) One can add to $\sigma^{\alpha\beta}$ a gauge of the form

$$\frac{\partial}{\partial x^\gamma} A^{\alpha\beta\gamma}(x),$$  \hspace{1cm} (2)

where $A^{\alpha\beta\gamma}$ is any tensor field antisymmetric in $\beta$ and $\gamma$, and recover the same force field, thereby demonstrating the non-uniqueness of this stress field definition. General formulations for computing non-gauge-invariant stress fields in quantum many-body systems
have been derived by Nielsen and Martin, Folland, Ziesche and co-workers, and Godfrey  
[14,17–19]. There have been several attempts to overcome this problem of non-uniqueness.  
For example, the stress field formalism of Chen and co-workers has been applied to num-
ernous solid state systems to determine the local pressure around a region [20]. However, their  
method assumes that the potential is pair-wise only. Several \textit{ab-initio} quantum stress field  
formulations have been developed, as well. Ramer and co-workers developed a method to  
calculate the resultant stress field from an induced homogeneous strain [21]. They incorpo-
rate the additional constraint that the field must be the smoothest fit to the ionic forces.  
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 Fiorentini developed a formulation of the stress field based on the energy  
density formalism of Chetty and Martin [22,23]. Since this formulation is based explicitly on  
the energy density, which is not gauge-invariant, the resultant stress field is not unique. Mis-
tura succeeded in developing a general gauge-invariant formalism for pressure tensor fields  
of inhomogeneous fluids within classical statistical models using a Riemannian geometric  
approach [24].

This Letter extends Mistura’s work, developing a Riemannian geometric formalism for  
computing gauge-invariant stress fields in quantum systems within the local density approx-
imation (LDA) of density functional theory (DFT). We show that the response of the total  
ground-state energy of a quantum system to a local spatially varying strain is a unique and  
physically meaningful field quantity which can be determined at every point in the system.

Using a procedure well known in continuum theory (see for example Ref. [25]), one  
can formally relate a Riemannian metric tensor field \( g_{\alpha\beta}(x) \) with the strain field  
\( \epsilon_{\alpha\beta}(x) \):  
\[
g_{\alpha\beta} = \delta_{\alpha\beta} + 2\epsilon_{\alpha\beta}, \quad \text{with} \quad \epsilon_{\alpha\beta} = \frac{1}{2} (\delta_{\alpha\gamma} \partial_\beta u^\gamma + \delta_{\gamma\beta} \partial_\alpha u^\gamma + \delta_{\gamma\kappa} \partial_\alpha u^\gamma \partial_\beta u^\kappa),
\]

where \( \partial_\alpha = \partial/\partial x^\alpha \) [26]. Here the strain field is defined in terms of a vector displacement field  
\( u^\alpha \) which maps coordinates \( x^\alpha \) in the non-deformed system, to the coordinates \( x'^\alpha = x^\alpha + u^\alpha \)
in the deformed system.

The stress field \( \sigma^{\alpha\beta}(x) \) and strain field obey a virtual work theorem expressing the energy response to variations in the strain:

\[
\delta E = \int \sqrt{g} \sigma^{\alpha\beta} \delta \epsilon_{\alpha\beta} d^3x, \tag{4}
\]

where \( g(x) \) is the determinant of \( g_{\alpha\beta}(x) \). It can be shown that the stress field is related to the functional derivative of the energy with respect to the metric field \([24]\):

\[
\sigma^{\alpha\beta} = \frac{1}{\sqrt{g}} \frac{\delta E}{\delta g_{\alpha\beta}} = 2 \sqrt{g} \frac{\delta E}{\delta g_{\alpha\beta}}, \tag{5}
\]

\[
\sigma_{\alpha\beta} = -\frac{2}{\sqrt{g}} \frac{\delta E}{\delta g^{\alpha\beta}}.
\]

We now 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 \([27,28]\). The ground state electronic charge density of the system is written as \( n(x) = \sum_{i} \phi_i^*(x) \phi_i(x) \), where \( \phi_i \) are single-particle orthonormal wavefunctions. 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 \([29]\). The total charge density of the system can be written as a sum over all ionic charges and \( n \):

\[
\rho(x) = \sum_{i} \frac{Z_i}{\sqrt{g}} \delta(x - R_i) - n(x), \tag{6}
\]

where \( Z_i \) is the charge of the \( i \)-th ion located at position \( R_i \), and the presence of \( \sqrt{g} \) insures proper normalization of the delta function. The energy of the system can be written as the following constrained functional:

\[
E = E_k + E_{\text{Coulomb}} + E_{\text{xc}} - \sum_{i} \lambda_i \left( \int \sqrt{g} \phi_i^* \phi_i d^3x - 1 \right). \tag{7}
\]

Here \( E_k \) is the single particle kinetic energy, \( E_{\text{Coulomb}} \) is the classical Coulomb interaction between the total charge density and itself, and \( E_{\text{xc}} \) is the exchange-correlation energy of the electrons. The appearance of the last term in Eq. 7 is due to the orthonormality constraint
of the orbitals. (We choose a unitary transformation on \{\phi_i\} which enforces orthogonality.)

One can express \(E\) as an integral over an energy density \([23]\). The choice of energy density
gauge will not affect the derived stress field, since all our results depend only on the total
energy \(E\). For convenience, we express the energy terms in Eq. \(\text{7}\) as the following:

\[
E_k = \frac{1}{2} \int \sqrt{g} \sum_i g^{\alpha\beta} \partial_\alpha \phi_i^* \partial_\beta \phi_i d^3x
\]

\[
E_{\text{Coulomb}} = \int \sqrt{g} \left( \rho V - \frac{1}{8\pi} g^{\alpha\beta} F_\alpha F_\beta \right) d^3x
\]

\[
E_{\text{xc}} = \int \sqrt{g} n \varepsilon_{\text{LDA}}(n) d^3x,
\]

(8)

where \(F_\alpha = -\partial_\alpha V\) is the electric field due to the Coulomb potential \(V\) generated by \(\rho\), and
\(\varepsilon_{\text{LDA}}(n)\) is the LDA exchange-correlation energy density. To obtain the electronic ground-
state energy, we require \(\delta E/\delta \phi_i = 0\) with the additional constraints of a fixed metric \((\delta g_{\alpha\beta} = 0)\)
and a fixed ionic charge density \((\delta \rho = -\delta n)\). This implies that the orbitals must obey
the Euler-Lagrange equations

\[-\frac{1}{2\sqrt{g}} \partial_\alpha \left( \sqrt{g} g^{\alpha\beta} \partial_\beta \phi_i \right) + \frac{\delta E_{\text{Coulomb}}}{\delta n} \phi_i + \frac{\delta E_{\text{xc}}}{\delta n} \phi_i = \lambda_i \phi_i,\]

(9)

which can be considered the Kohn-Sham equations in curvilinear coordinates. Also, a least-
action principle for \(E_{\text{Coulomb}}\) requires that \(\rho\) and \(V\) obey the Poisson equation:

\[-\frac{1}{\sqrt{g}} \partial_\alpha \left( \sqrt{g} g^{\alpha\beta} \partial_\beta V \right) = -4\pi \rho.\]

(10)

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 Eq. \(\text{8}\) and Eq. \(\text{10}\). 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 \([30-32]\). If a
different electromagnetic gauge is chosen, variations with respect to the potential \(V\) would
have to be computed explicitly; this change has no impact on the stress field in Eq. \(\text{11}\).
Performing the variation of the total energy with respect to the metric gives the stress field
in local density functional theory as:
\[
\sigma_{\alpha\beta} = -\sum_i \partial_\alpha \phi_i^* \partial_\beta \phi_i + \frac{1}{4\pi} F_\alpha F_\beta + g_{\alpha\beta} \left( \frac{1}{2} \sum_i \partial_\gamma \phi_i^* \partial^\gamma \phi_i \right. \\
-\frac{1}{8\pi} F_\gamma F^\gamma + n\varepsilon_{\text{LDA}}(n) - \sum_i \phi_i^* \phi_i [\lambda_i + V],
\]  

(11)

where we have used the relation \( \partial \sqrt{g} / \partial g^\alpha = -\frac{1}{2} \sqrt{g} g^\alpha \). Using Eq. 9, we can rewrite Eq. 11 as

\[
\sigma_{\alpha\beta} = -\sum_i \partial_\alpha \phi_i^* \partial_\beta \phi_i + \frac{1}{4\pi} F_\alpha F_\beta + g_{\alpha\beta} \left( \frac{1}{2} \sum_i \partial_\gamma \phi_i^* \partial^\gamma \phi_i \right. \\
+ \frac{1}{2\sqrt{g}} \sum_i \phi_i^* \partial_\kappa (\sqrt{g} g^{\kappa\gamma} \partial_\gamma \phi_i) - \frac{1}{8\pi} F_\gamma F^\gamma + n \left( \varepsilon_{\text{LDA}}(n) - \frac{\delta E_{\text{xc}}}{\delta n} \right) \right) .
\]  

(12)

When Eq. 12 is evaluated at the Euclidean metric \( (g_{\alpha\beta} = \delta_{\alpha\beta}) \), it gives the stress field at zero applied strain, and the \( \{\phi_i\} \) are then solutions to the standard Kohn-Sham equations. From here on, we will refer to \( \sigma_{\alpha\beta} \) with an implied evaluation at the Euclidean metric.

It is important to note several key features of the form of \( \sigma_{\alpha\beta} \). First, the Coulombic contribution to the quantum stress field is equivalent to the classical Maxwell stress field. This Coulombic term can be obtained by Filippetti and Fiorentini’s formalism in Ref. [22] if one chooses the Maxwell gauge. Also, the contribution of the exchange-correlation energy to our stress field is only in the diagonal (pressure-like) terms, which is the proper behavior for local density functionals [14] and is identical to the exchange-correlation stress derived in Ref. [22]. However, the kinetic contribution to Eq. 12 is unique to our derivation. Our stress field contains diagonal terms which are similar to the symmetric and antisymmetric kinetic energy densities. By integrating the stress field over all space, we can obtain the total stress \( T_{\alpha\beta} \):

\[
T_{\alpha\beta} = \int \left\{ -\sum_i \partial_\alpha \phi_i^* \partial_\beta \phi_i + \frac{1}{4\pi} F_\alpha F_\beta - \delta_{\alpha\beta} \frac{1}{8\pi} F_\gamma F^\gamma \right. \\
+ \delta_{\alpha\beta} n \left( \varepsilon_{\text{LDA}}(n) - \frac{\delta E_{\text{xc}}}{\delta n} \right) \right\} d^3x,
\]  

(13)

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

In order to demonstrate the utility of our stress field formalism, we compute within DFT the pressure field, \( \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \), for two phases of solid molecular hydrogen under external hydrostatic pressure of 50 GPa. [33]. Both structures consist of stacked two-dimensional
triangular lattices of hydrogen molecules, 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 \[34\]. The energetics and electronic properties of both structures have been studied extensively from first principles \[35,36\].

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 1A shows a contour plot of the pressure field for the \( Cmca \) structure. The pressure is tensile (greater than zero) through the interstitial region, indicating that contraction is locally favorable. The pressure is greatest in the volume directly above and below each molecule, averaging \( 3 \) eV/Å\(^3\). This implies that the system would energetically favor increased intermolecular coordination. In Figure 1B 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/Å\(^3\). It is also clear from the charge density plots (Figure 1C and 1D) 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 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 relative phase stability. Thus, changes in the pressure stress field highlight regions and charge density features that contribute to favorable energetic changes.

We have developed a formulation for unambiguously determining the stress field in an interacting quantum system described by local density functional theory. The resultant expression for the stress field is gauge-invariant with respect to choice of energy density and can be obtained via a method analogous to the computation of Hellmann-Feynman forces.
Our application of this formalism to solid molecular hydrogen demonstrates that a stress field analysis can associate energetics with particular microscopic structural features of a material. This stress field formulation has the potential to become an invaluable aid to the understanding of structural phenomena in complex solid-state systems.

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FIG. 1. Contour plots of the pressure field and charge density within DFT for the \textit{Cmca} structure (panels A and C) and for the \textit{m-hcp} structure (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/Å$^3$ for the pressure fields, and from 0–2.5 e/Å$^3$ for the charge densities.
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