Evaluation of Exchange-Correlation Energy, Potential, and Stress

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We describe a method for calculating the exchange and correlation (XC) contributions to the total energy, effective potential, and stress tensor in the generalized gradient approximation. We avoid using the analytical expressions for the functional derivatives of \( E_{xc}(\rho) \), which depend on discontinuous second-order derivatives of the electron density \( \rho \). Instead, we first approximate \( E_{xc} \) by its integral in a real space grid, and then we evaluate its partial derivatives with respect to the density at the grid points. This ensures the exact consistency between the calculated total energy, potential, and stress, and it avoids the need of second-order derivatives. We show a few applications of the method, which requires only the value of the (spin) electron density in a grid (possibly nonuniform) and returns a conventional (local) XC potential.

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I. INTRODUCTION

The generalized gradient approximation (GGA) to density functional theory (DFT) has been growing in acceptance in recent years, due to the development of improved functionals and to the realization of its higher accuracy, for many systems and properties, than that of the local density approximation (LDA). Some continuity problems of earlier functionals have been solved in more recent ones. Still, a basic problem is that, while \( E_{GGA}^{\alpha}(\rho) \) depends only on the local value of \( \rho(r) \) and \( |\nabla \rho(r)| \), its functional derivative depends also on \( \nabla |\nabla \rho(r)| \), which is discontinuous where \( \nabla \rho(r) = 0 \). This implies that, to avoid aliasing effects, very fine integration grids are required to evaluate the XC potential \( v_{xc}(r) \) and its matrix elements. A different problem occurs with grid-oriented implementations of DFT, in which the electron density is known only at the grid points, while its gradients must be evaluated using finite differences. In this case, an inconsistency between the energy \( E_{xc} \) and the potential \( v_{xc} \) may occur because different formulas need to be used for the higher-order derivatives of the density. Hamann proposed an elegant solution to these problems by defining a nonlocal potential, which operates on the gradient of the electron wave functions. Although in principle this does not pose any special difficulty, it requires a specific, unconventional implementation, which may be difficult to adapt to existing DFT codes. White and Bird found another solution, by defining \( E_{xc}^{GGA} \) as an integral in a real space grid (what is always done in practice), and \( v_{xc}(r_i) \) as its partial derivative (as opposed to functional derivative) with respect to the density \( \rho_i \) at the grid points \( r_i \). They applied this method to a plane wave basis set and a uniform integration grid, finding the gradients with fast Fourier transforms (FFTs). Here we generalize their method to arbitrary bases and nonuniform grids, and we calculate the density gradient using finite differences. The method produces a standard, local potential, which is exactly consistent with the definition of \( E_{xc} \), in the sense that \( v_{xc} \) is the correct potential in the Schrödinger equation that results from the variational minimization of the total energy. In addition, we show how to evaluate the XC contribution to the stress tensor in crystals, following the same ideas. The trivial particular case of the LDA is also discussed.

II. EXCHANGE-CORRELATION ENERGY AND POTENTIAL

The LDA and GGA approximations to \( E_{xc} \) have the general forms

\[
E_{xc}^{LDA}[\rho] = \int f_{LDA}(\rho(r)) \, dr,
\]

\[
E_{xc}^{GGA}[\rho] = \int f_{GGA}(\rho(r), g(r)) \, dr, \tag{1}
\]

where \( f = \rho \) \( \epsilon_{xc} \) is the local XC energy density, and \( \epsilon_{xc} \) is the XC energy per electron. We use the notation \( g(r) \equiv \nabla \rho(r) \), \( g_x(r) \equiv \nabla_x \rho(r) \), and \( g(r) \equiv |\nabla \rho(r)| \). The argument \( g(r) \) in Eq.1, rather than \( g(r) \), indicates that, in principle, \( f_{GGA} \) might depend on the relative orientation of the gradients of the two spin components of the density. However, for notational simplicity we will omit the spin index and the sum over it, since their inclusion is trivial. In the limit of slowly varying electron density, we must recover the LDA result, that is \( f_{GGA}(\rho, 0) = f_{LDA}(\rho) \).
In the LDA the XC potential has a simple expression,
\[ v_{\text{xc}}^{\text{LDA}} = \frac{df_{\text{LDA}}}{d\rho} = \epsilon_{\text{xc}}^{\text{LDA}} + \rho \frac{d\epsilon_{\text{xc}}^{\text{LDA}}}{d\rho}, \]
whereas in the GGA it is considerably more complicated
\[ v_{\text{xc}}^{\text{GGA}} = \frac{\partial f_{\text{GGA}}}{\partial \rho} - \nabla \cdot \frac{\partial f_{\text{GGA}}}{\partial g} \]
\[ = \epsilon_{\text{xc}}^{\text{GGA}} + \rho \frac{\partial \epsilon_{\text{xc}}^{\text{GGA}}}{\partial \rho} - g \frac{\partial \epsilon_{\text{xc}}^{\text{GGA}}}{\partial g} - \rho \frac{\partial^2 \epsilon_{\text{xc}}^{\text{GGA}}}{\partial g \partial \rho} \]
\[ - \frac{\rho}{g} \frac{\partial^2 \epsilon_{\text{xc}}^{\text{GGA}}}{\partial g \partial \rho} \nabla^2 g + \frac{\rho}{g^2} \frac{\partial \epsilon_{\text{xc}}^{\text{GGA}}}{\partial g} g \nabla g \]
\[ - \frac{\rho}{g} \frac{\partial^2 \epsilon_{\text{xc}}^{\text{GGA}}}{\partial g \partial \rho} g \nabla g, \]
(2)
as it depends on the first and second gradients of the electron density. Since \( \nabla \rho \) has cusps at extrema of \( \rho \), \( \nabla g \) is discontinuous at these points, what causes problems for its numerical representation. Furthermore, some parameterizations of \( \epsilon_{\text{xc}}^{\text{GGA}} \) which apparently join seamlessly different density regimes, may have higher derivatives which do not behave well in those transition regions.

In what follows, we will omit the label GGA, except to underline a distinction with LDA. In a practical calculation, the XC energy is calculated through a numerical integration. From a set of \( M \) mesh points \( r_i \) and weights \( w_i \), we approximate
\[ E_{\text{xc}} \simeq \sum_{i=1}^{M} w_i f(\rho(r_i), g(r_i)). \]
The weights may be, for example 4\( \pi r_i^2 \Delta r \) in a uniform radial grid, or the Jacobian of the local metric tensor in an adaptive-coordinate grid (see below). In addition, we must specify precisely the meaning of \( g(r_i) \). If a well defined basis set is used, the electron density and its gradient can be calculated exactly at any point in space, from the electron wave functions and their gradients. In practice, this may add an appreciable overhead in terms of computer time and memory. Alternatively, we can use the values of the density at the grid points to calculate its gradient, using either FFTs or finite differences. As the gradient is a linear operator, we can write in general
\[ g_{\alpha}(r_i) \simeq g_{\alpha} = \sum_{j=1}^{M} A_{ij}^\alpha \rho_j, \]
(3)
and \( \partial g_{\alpha}/\partial \rho_j = A_{ij}^\alpha \). \( \{i,j\} \) are combined indexes \( i \equiv \{i_1, i_2, i_3\} \) that label grid points, \( \alpha \) labels the three cartesian coordinates, \( \rho_i \equiv \rho(r_i) \), and the coefficients \( A_{ij}^\alpha \) depend on the mesh and the chosen numerical derivative formula, but not on \( \rho_i \). There are many choices for the coefficients \( A_{ij}^\alpha \), depending on the integration mesh and interpolation method, since the numerical derivative can be defined as the derivative of the interpolation function.

The particular case described by White and Bird uses a uniform mesh and a Fourier-series interpolation. It was developed for plane-wave calculations, and FFTs were used to evaluate Eq. (3). Our method can be generalized to nonuniform grids. In the implementation that we will describe later, we use a local Lagrange interpolation, for which the matrix \( A_{ij}^\alpha \) is sparse.

Notice that in Eq. (3) we are defining \( g; \) as the numerical derivative of \( \rho \) on the mesh (therefore being a function of the values \{\( \rho_j \}\}), while we reserve the notation \( g(r_i) \) for the exact gradient of \( \rho \) at \( r_i \) (in case it is known). It may be argued that the use of \( g \), instead of \( g(r_i) \) represents an additional approximation. However, in practice \( g \) is frequently a better approximation than \( g(r_i) \) to the average value of \( g(r) \) within the spatial “pixel” which corresponds to the integration point \( r_i \). Both values agree for a Fourier interpolation, provided that the plane wave cutoff of the grid is twice as large as that of the wave functions. And of course they must also agree, for any interpolation scheme, in the limit of an infinitely fine grid.

Thus, following White and Bird, we define
\[ \tilde{E}_{\text{xc}}(\{\rho_i\}) \equiv \sum_{i=1}^{M} w_i f(\rho_i, g_i(\{\rho_j\})) \simeq E_{\text{xc}}, \]
(4)
and
\[ \tilde{v}_{\text{xc}}^i = \frac{1}{w_i} \frac{\partial \tilde{E}_{\text{xc}}(\{\rho_i\})}{\partial \rho_i} \]
\[ = \frac{\partial f}{\partial \rho_i} + \sum_{j=1}^{M} \sum_{\alpha=1}^{3} \frac{w_j}{w_i} \frac{\partial f_j}{\partial g_{j\alpha}} \frac{\partial g_{j\alpha}}{\partial \rho_i}. \]
(5)

It is important to emphasize that Eqs. (2) and (5) are asymptotically equivalent in the limit of an infinitely fine grid, but different in practice (in particular, Eq. (5) has no explicit dependence on the second derivatives of \( \rho \)). In fact, it is easy to see that Eq. (5), and not Eq. (2), is the “correct” definition of \( v_{\text{xc}} \), if the functional form \( \{\{\}\} \) is actually used in the variational energy minimization, \( \partial E/\partial \psi^* = H \psi \), because, from Eq. (3),
\[ \frac{\partial \tilde{E}_{\text{xc}}}{\partial \psi_i^*} = \frac{\partial \tilde{E}_{\text{xc}}}{\partial \psi_i} \frac{\partial \psi_i}{\partial \psi_i^*} = w_i \tilde{v}_{\text{xc}}^i \psi_i. \]

In the LDA, \( f_i \) does not depend on \( g_i \), and only the first term in Eq. (5) remains, giving the trivial result
\[ \tilde{v}_{\text{xc}}^i_{\text{LDA}} = \frac{df_i^{\text{LDA}}}{d\rho_i}. \]

There remains the problem of determining the coefficients \( A_{ij}^\alpha \) and the weights \( w_i \) in Eqs. (3) and (5). To this purpose, it is convenient to introduce grid variables \( \{s_\mu; \mu = 1,2,3\} \), which are in principle continuous. In practice, however, the density \( \rho(s) \) and the cartesian coordinates \( r(s) \) of the grid points are evaluated only at integer values of \( s_\mu \). For a regular grid,
By comparison with (4), we conclude that

$$w_i = \frac{s_i}{N_i},$$

where $a_{\mu \nu}$ is the 9th cartesian coordinate of the $\mu$th lattice unit vector, and $N_i$ is the number of grid divisions along that vector. For nonuniform grids, $w_i(s)$ are general functions and it is convenient to introduce the jacobian of the transformation $s \rightarrow r$. The XC energy can then be expressed as

$$E_{xc} = \int f(\rho(s), g(s)) \left| \frac{\partial r}{\partial s} \right| ds$$

or

$$\tilde{E}_{xc} = \sum_{i=1}^{M} f(\rho_i, g_i) \left| D_i \right|$$

where we have used that $\Delta s_i = 1$ by definition of $s_i$. $\left| D_i \right|$ is the determinant at point $i$ of the matrix of partial derivatives

$$D_{\nu \mu}(s) = \frac{\partial r_{\mu}}{\partial s_{\nu}}.$$  

By comparison with (4), we conclude that $w_i = \left| D_i \right|$. Since the grid variables $s_i$ are by definition “orthogonal” and the functions $r_{\mu}$ and $\rho$ are evaluated at regular unit intervals of $s_i$, their derivatives $\partial / \partial s_i$ can be calculated straightforwardly:

$$B_{\mu j}^i = \left( \frac{\partial r_{\mu}}{\partial s_j} \right)_i = \sum_{j=1}^{M} B_{\mu j}^i r_{j \alpha}$$  

(6)

$$\left( \frac{\partial \rho}{\partial s_j} \right)_i = \sum_{j=1}^{M} B_{\mu j}^i \rho_j$$

where the coefficients $B_{\mu j}^i$ depend only on the relative values of $i$ and $j$, and are independent of the grid coordinates $r(s)$:

$$B_{\mu j}^i = \begin{cases} L_k^{(n)} & \text{if } j_\mu = i_\mu + k; j_{\nu} = i_{\nu}, \nu \neq \mu \\ -L_k^{(n)} & \text{if } j_\mu = i_\mu - k; j_{\nu} = i_{\nu}, \nu \neq \mu \\ 0 & \text{otherwise} \end{cases}$$

where the coefficients $L_k^{(n)}$ may be derived from a $(2n+1)$-point Lagrange polynomial interpolation formula.

We can now calculate $g_i$ as

$$g_{i \alpha} = \sum_{\mu=1}^{3} \left( \frac{\partial \rho}{\partial s_\mu} \right)_i \left( \frac{\partial s_\mu}{\partial r_{\alpha}} \right)_i = \sum_{\mu=1}^{3} \sum_{j=1}^{M} (D_{\mu j}^{-1})_{\alpha \mu} B_{\mu j}^i \rho_j$$

and by identifying coefficients with Eq. (3)

$$A_{\alpha j}^i = \frac{\partial g_{j \alpha}}{\partial \rho_i} = \sum_{\mu=1}^{3} (D_{\mu j}^{-1})_{\alpha \mu} B_{\mu j}^i.$$  

(7)

Thus, the calculation of the XC potential from the density on the grid involves the following steps, for every point $j$: 1) find the $3 \times 3$ matrix $D_j$, using Eq. (6); its determinant $w_j$, and its inverse $D_j^{-1}$, storing $w_j$ for later use; 2) find $A_{\alpha j}^i$ from Eq. (3) and $g_i$ from Eq. (3); 3) calculate $f(\rho_j, g_j)$ and its derivatives with respect to $\rho_j$ and $g_{j \alpha}$; 4) add the first term in Eq. (3) (multiplied by $w_j$) to $\tilde{v}_{\alpha}^{xc}$ and the second term (except the denominator $w_j$) to $\tilde{v}_{i}^{xc}$ for every neighbor point $i$ involved in the calculation of $g_j$; 5) when the previous loop is finished, run again over all grid points $i$, dividing $\tilde{v}_{i}^{xc}$ by $w_i$. In the case of a uniform grid, the matrix $D_i$ does not depend on $i$. Thus, $w_i$ and $D_i^{-1}$ can be evaluated once and for all, saving steps 1 and 5, as well as the temporary array required to store $w_i$.

**III. EXCHANGE-CORRELATION CONTRIBUTION TO THE STRESS TENSOR**

We consider now the stress tensor

$$\sigma_{\alpha \beta}^{xc} = \frac{\partial \tilde{E}_{xc}}{\partial \epsilon_{\alpha \beta}}$$

where $\epsilon_{\alpha \beta}$ is the strain tensor, giving the deformation of all points in space (including atomic and grid coordinates):

$$r_{\alpha} \rightarrow \sum_{\beta=1}^{3} (\delta_{\alpha \beta} + \epsilon_{\alpha \beta}) r_{\beta}.$$  

(8)

More generally, we consider the derivative of $\tilde{E}_{xc}$ with respect to a parameter $\lambda$ that affects the position of the grid points. This may be $\epsilon_{\alpha \beta}$ or one of the atomic positions, in case of a nonuniform grid which depends on them. It is therefore convenient to recognize explicitly that, when the system is modified, $\tilde{E}_{xc}$ depends on the grid point coordinates in addition to the densities at the grid points, i.e. $\tilde{E}_{xc}(\{r_i\}, \{\rho_j\})$. Thus,

$$\frac{\partial \tilde{E}_{xc}}{\partial \lambda} = \sum_{i=1}^{M} \left( \frac{\partial \tilde{E}_{xc}}{\partial \rho_i} \frac{\partial \rho_i}{\partial \lambda} + \sum_{\alpha=1}^{3} \frac{\partial \tilde{E}_{xc}}{\partial r_{i \alpha}} \frac{\partial r_{i \alpha}}{\partial \lambda} \right)$$

where $\partial \tilde{E}_{xc}/\partial \rho_i = \tilde{v}_{i}^{xc}$ and

$$\frac{\partial \tilde{E}_{xc}}{\partial r_{i \alpha}} = \sum_{j=1}^{M} \left( \frac{\partial D_j}{\partial r_{i \alpha}} f_j + |D_j| \sum_{\beta=1}^{3} \frac{\partial f_j}{\partial g_{j \beta}} \frac{\partial g_{j \beta}}{\partial r_{i \alpha}} \right)$$

$$\frac{\partial g_{j \beta}}{\partial r_{i \alpha}} = \sum_{\mu=1}^{3} \left( \frac{\partial \rho}{\partial s_\mu} \right)_j \frac{\partial r_{i \alpha}}{\partial r_{i \alpha}} (D_{\mu j}^{-1})_{\beta \mu}$$

Now, using Eq. (3) we find

$$\frac{\partial r_{i \alpha}}{\partial \epsilon_{\alpha \beta}} = \delta_{\alpha \beta} r_{i \beta},$$  

(9)
and taking into account the general properties of a determinant, as well as the fact that \( (DD^{-1} = I) \Rightarrow (\delta D = -D^{-1}\delta DD^{-1}) \), we finally find

\[
\frac{\partial E_{xc}}{\partial c_{\alpha\beta}} = \delta_{\alpha\beta} E_{xc} + \sum_{i=1}^{M} w_i \bar{v}_{ir} \frac{\partial \rho_i}{\partial c_{\alpha\beta}} - \sum_{i=1}^{M} w_i \frac{\partial f_i}{\partial g_{i\beta}} \gamma_{i\alpha} \tag{10}
\]

In the limit of an infinitely fine grid, we have

\[
\frac{\partial E_{xc}}{\partial c_{\alpha\beta}} = \delta_{\alpha\beta} E_{xc} + \int v_{xc}(\mathbf{r}) \frac{\partial \rho(\mathbf{r})}{\partial c_{\alpha\beta}} d\mathbf{r} - \int \frac{\partial f(\rho(\mathbf{r}), \mathbf{g}(\mathbf{r}))}{\partial g_{\beta}(\mathbf{r})} g_{\alpha}(\mathbf{r}) d\mathbf{r}. \tag{11}
\]

The presence of \( \partial \rho/\partial c_{\alpha\beta} \) in Eqs. (10) and (11) requires to clarify what is kept constant when taking the derivatives. We will argue that the “correct” definition (or at least the most useful one) requires to keep constant the variational coefficients \( c_{\alpha\beta} \) of the expansion of the electron wave functions \( \psi_n(\mathbf{r}) \) in terms of the \( N \) basis functions \( \phi_n(\mathbf{r}) \):

\[
\psi_n(\mathbf{r}) = \sum_{\alpha=1}^{N} c_{\alpha n} \phi_\alpha(\mathbf{r}) \tag{12}
\]

Since \( \sigma_{\alpha\beta} \) is generally evaluated at the electronic ground state, the Hellman-Feynman theorem ensures that the change of \( c_{\alpha n} \) will not affect the total energy to first order. Of course, the Hellman-Feynman theorem does not apply to \( E_{xc} \) alone, but in practice we are interested in adding \( \sigma_{\alpha\beta} \) to other contributions of \( \sigma_{\alpha\beta} \), in order to calculate the total stress tensor. And even in the Car-Parrinello method, in which forces and stresses are evaluated out of the ground state, the appropriate definition of these magnitudes involves the derivatives of the total energy at constant \( c_{\alpha n} \).

There are two reasons why \( \rho_\alpha \) depends on \( c_{\alpha\beta} \): the change of the basis functions \( \phi_n(\mathbf{r}) \) at the displaced grid points, and the change of the wave function coefficients \( c_{\alpha n} \) required to maintain the orthonormality constraints \( \langle \psi_m | \psi_n \rangle = \delta_{mn} \). With a plane wave basis set, or with a grid-oriented scheme, in which the wave functions are defined directly at the grid points, and with no explicit grid dependence, the orthonormality constraints are not affected by the deformation of the unit cell, provided that the wave functions and the density are simply scaled by a factor \( (\Omega_0/\Omega)^{1/2} \) and \( \Omega_0/\Omega \), respectively, where \( \Omega_0 \) and \( \Omega \) are the unit cell volumes before and after the deformation. It is easy to verify that \( \partial \Omega / \partial c_{\alpha\beta} = \Omega \delta_{\alpha\beta} \) and therefore

\[
\frac{\partial \rho(\mathbf{r})}{\partial c_{\alpha\beta}} = -\delta_{\alpha\beta} \rho(\mathbf{r}) \tag{13}
\]

Substitution of (13) into (11) leads to

\[
\frac{\partial E_{xc}}{\partial c_{\alpha\beta}} = \delta_{\alpha\beta} \int (\epsilon_{xc}(\mathbf{r}) - v_{xc}(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r} - \int \frac{\partial f(\rho(\mathbf{r}), \mathbf{g}(\mathbf{r}))}{\partial g_{\beta}(\mathbf{r})} g_{\alpha}(\mathbf{r}) d\mathbf{r},
\]

which coincides with Eq. (24) of Dal Corso and Resta.

In the case of an atomic basis set, it is convenient to define the density matrix

\[
\rho_{ab} = \sum_{n=1}^{N} q_n c_{an}^* c_{nb}
\]

with \( q_n \) the occupation of state \( \psi_n \). Then

\[
\frac{\partial \rho(\mathbf{r})}{\partial \lambda} = \sum_{a,b=1}^{N} \left( \frac{\partial \rho_{ab}}{\partial \lambda} \phi_a(\mathbf{r}) \phi_b(\mathbf{r}) \right.
\]

\[
+ 2 \rho_{ab}(\mathbf{r}) \sum_{\alpha=1}^{3} \nabla_\alpha \phi_b(\mathbf{r}) \frac{\partial (r_\alpha - R_{\alpha a})}{\partial \lambda} \right)
\]

where we are assuming real basis orbitals for simplicity. \( \mathbf{R}_\alpha \) is the origin (atomic position) of orbital \( \phi_\alpha \), and the last term in Eq. (14) accounts for the change in the relative position \( \mathbf{r} - \mathbf{R}_\beta \) when we deform the lattice or change the grid point positions (we assume a constant shape of \( \phi_\beta \)). \( \partial \rho_{ab} / \partial \lambda \) is the change in the density matrix required to maintain the orthonormality constraints:

\[
\frac{\partial \rho_{ab}}{\partial \lambda} = -\sum_{c=1}^{N} \rho_{ac} \frac{\partial S_{cb}}{\partial \lambda} = -\sum_{c=1}^{N} \rho_{ac} \sum_{\alpha=1}^{3} \frac{\partial S_{cb}}{\partial \lambda} \frac{\partial r_{\alpha b}}{\partial \lambda} \tag{15}
\]

where \( S_{ab} \equiv \langle \phi_a | \phi_b \rangle \), and \( \mathbf{r}_\alpha \equiv \mathbf{R}_\beta - \mathbf{R}_\alpha \). By combining Eqs. (1), (13), and (15) we obtain

\[
\int v_{xc}(\mathbf{r}) \frac{\partial \rho(\mathbf{r})}{\partial c_{\alpha\beta}} d\mathbf{r} = -\sum_{a,b,c=1}^{N} \rho_{ac} \frac{\partial S_{cb}}{\partial \lambda} \nabla_\beta \phi_a(\mathbf{r}) v_{xc}(\mathbf{r}) \phi_b(\mathbf{r})
\]

\[
+ 2 \sum_{a,b=1}^{N} \rho_{ab} \langle \phi_a | v_{xc}(\mathbf{r}) (r_\beta - R_{\beta b}) \nabla_\alpha | \phi_b \rangle.
\]

The same expression is valid if the integral is replaced by the grid sum \( \sum_i w_i \bar{v}_{xc}(\partial \rho_i / \partial c_{\alpha\beta}) \), except that then the matrix elements must also be calculated on the grid, i.e.

\[
\langle \phi_a | v_{xc} | \phi_b \rangle = \sum_{i=1}^{M} w_i \bar{v}_{xc} \phi_{ai} \phi_{bi}
\]

Similar terms appear in other contributions to the stress tensor. Thus, in the derivation of the Hartree energy, there is an identical term, except for the substitution of \( v_{xc} \) by the Hartree potential \( \nu_H \). Then the total contribution to the stress tensor that arises from the change in the density has the form

\[
\int \frac{\delta E}{\delta \rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial c_{\alpha\beta}} d\mathbf{r} = -\sum_{a,b=1}^{N} E_{ab} \frac{\partial S_{ab}}{\partial \rho_{ab}} r_{\beta b}
\]

\[
+ 2 \sum_{a,b=1}^{N} \rho_{ab} \langle \phi_a | v(\mathbf{r}) (r_\beta - R_{\beta b}) \nabla_\alpha | \phi_b \rangle \tag{16}
\]
where \( v(\mathbf{r}) \) is the total effective potential, and \( E_{ab} \) are energy-density matrix elements,

\[
E_{ab} = \sum_{c=1}^{N} \rho_{ac} H_{cb} = \sum_{n=1}^{N} q_n \epsilon_n c_{an}^* c_{nb}, \tag{17}
\]

with \( H_{ab} = \langle \phi_a | H | \phi_b \rangle, \) \( H \) the total one-electron hamiltonian and \( \epsilon_n \) its \( n \)th eigenvalue. Notice, however, that the derivation of Eqs. (16) and (17) does not assume that the matrix elements \( S_{ab} \) and \( H_{ab} \) or their derivatives are calculated on the grid. In fact, in our atomic-basis DFT implementation, two-center matrix elements like \( S_{ab} \) or \( \langle \phi_a | - \nabla^2 | \phi_b \rangle \), are calculated using reciprocal-space convolution techniques.\[1\]

### IV. ACCURACY TESTS

We have implemented the method described above as an independent package, which we are using with several electronic structure programs, including an atomic pseudopotential generator, the localized-basis program Siesta\[4\] and a pseudopotential wave-packet.

We have implemented two different LDA parameterizations, PZ-LDA\[5\] and PW92-LDA, of Ceperley and Adler electron gas energies\[6\] for \( f_{\text{LDA}} \) and two different GGA recipes, PW91-GGA\[7\] and PBE-GGA\[8\] for \( f_{\text{GGA}} \). They were all implemented in their spin-dependent formulations. As the calculation of \( f \) and its derivatives are kept as separate procedures it is easy to add new parameterizations. As only first derivatives of \( f \) are needed in our method to calculate stresses and potentials, we do not have to calculate second derivatives as in the traditional method. Since GGA functional forms tend to be complicated, this is convenient.

In the atomic pseudopotential generation program the electron density is assumed to have spherical symmetry. The radial mesh points are derived from a monotonous function \( r(s) \). The gradient of the density is calculated analogously to the three-dimensional case:

\[
g_i = \left( \frac{d}{ds} \right)^{-1}_i \left( \frac{d\rho}{ds} \right)_i,
\]

\[
(\frac{d}{ds})_i = \sum_{k=1}^{n} L_k^{(n)} (r_{i+k} - r_{i-k}),
\]

\[
(\frac{d\rho}{ds})_i = \sum_{k=1}^{n} L_k^{(n)} (\rho_{i+k} - \rho_{i-k}).
\]

To illustrate the method we have chosen three simple situations. Fig. 1 shows the \( s \)-pseudopotential for Si, with the Troullier-Martins recipe\[9\] and a core radius of two bohr, calculated with the PBE-GGA and PW91-GGA functionals using both our method (Eq. (16)) and the usual method (Eq. (15)), with the standard radial grid used by the pseudopotential generation program. The curves for the two computational methods agree within 1 \( \times 10^{-4} \) Ry and are indistinguishable in the scale of the figure. The PW91-GGA pseudopotential has some wiggles that are due to the term proportional to \( \exp(-100s^2) \) where \( s = \nabla \rho/(2k_F\rho) \), \( k_F = (3\pi^2\rho)^{1/3} \), in the parameterization of the GGA exchange. Those wiggles occur near the extrema of the valence electron density, and they are not present in the PBE-GGA pseudopotential, which uses a different parameterization of the GGA exchange. By construction the screened pseudopotential is smooth, without wiggles, so the appearance of those wiggles is due to the unscreening of the pseudopotential. To see any difference between the usual and present methods, we must use very coarse radial meshes. This is shown in Fig. 2, where we compare the XC potential for a model density \( \rho(\mathbf{r}) = (\sin r/r)^2 \). The PZ-LDA (dotted thin line), PW91-GGA (solid thick line), and PBE-GGA (dashed line), were first calculated on a fine radial mesh. Again there is no difference between the old and new methods on the scale of fig. 2 for the fine mesh. However, recalculating the PW91-GGA exchange and correlation potential on a much coarser mesh with the new method (squares) one starts to see small differences in the potential values in the regions where the PW91 parameterization has wiggles. The eleven point Lagrange formula for coarse sampling spans to a region of 2 bohr, almost half of the horizontal range of Fig. 2. It misses the small wiggles around \( r = 3\pi/2 \) where \( \nabla \rho = 0 \) and \( \rho \neq 0 \), but it finds wiggles at \( r = \pi \) where both \( \nabla \rho = 0 \) and \( \rho = 0 \).

Our last example uses the pseudo-charge density of diamond. A well converged plane wave expansion of the density is used to calculate \( \rho_i \) for different \( N \times N \times N \) grids. Fig. 3 shows that the calculated XC energy is...
FIG. 2. XC potential for a spherical electron density with the form \( \rho(r) = \left( \sin \frac{r}{r} \right)^2 \). The dashed line is the CA-LDA, the dotted line is the PBE-GGA and the solid line is the PW91-GGA, all accurately calculated on a fine grid with a step of 0.02 bohr. The squares show that the PW91-GGA, calculated with the new method on a coarse grid (step = 0.2 bohr) have small deviations with respect to the fine grid. However, in fact these deviations tend to smooth out the large pathological wiggles developed by the PW91-GGA functional in regions of zero density or zero density gradient. This makes the present method very well behaved even with very coarse grids.

very stable with respect to grid size: even a \( 8 \times 8 \times 8 \) grid gives a value accurate within \( 10^{-3} \) Hartree. The XC component of the stress also converges very fast, and the method is very stable. In practice, the PW cutoffs required for a good convergence of the total energy impose larger grids than those needed to converge \( E_{xc} \) with our method. Thus, the standard grids used in typical PW calculations are more than sufficient for \( E_{xc} \).

V. CONCLUSIONS

We have derived formulas for the GGA-XC energy, potential, and stress, as a function of the electron density given in a spatial mesh of points, which may be unevenly distributed. Density gradients need not be provided, since they are calculated numerically using the density at the grid points, what leads to well behaved formulas. The use of a unique definition of the gradients ensures an exact consistency between the calculated values for the energy, potential, and stress, including all corrections for basis set incompleteness and changing grid points. As the number of grid points increases, we recover the exact results obtained using the virial theorem.

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1 D. C. Langreth and M. J. Mehl, Phys. Rev. B 28, 1809 (1983). A. D. Becke, Phys. Rev. A, 38, 3098 (1988).
2 P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
3 W. Kohn and L. J. Sham, Phys. Rev. 136, A1133 (1965).
4 J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992). J. P. Perdew in Electronic Structure of Solids 91, p. 11, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
5 C. Filippi, C. J. Umrigar and M. Taut, J. Chem. Phys. 100, 1290 (1994). C. Filippi, X. Gonze and C. J. Umrigar in Recent Developments and Applications of Modern Density Functional Theory, p. 295, edited by J. M. Seminario (Elsevier, 1996).
6 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996). We are not considering a new generation of GGA functionals including a dependence with the laplacian of the electron density. Nevertheless, the main approach in this paper is even more useful for that type of functionals. See, i.e., A. Russo, A. A. Pople and M. A. Ratner, Phys. Rev. B 59, 15625 (1999); ibid 62, 2232 (2000).
7 J. R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. 72, 1240 (1994); J. R. Chelikowsky, N. Troullier, K. Wu, and Y. Saad, Phys. Rev. B 50, 11355 (1994).
8 D. R. Hamann, Phys. Rev. B 54, 1568 (1996).
9 N. A. Modine, G. Zumbach, and E. Kaxiras, Phys. Rev. B 55, 10289 (1997).
For convenience, we will place indexes and labels indiscriminately as sub or superscripts, without meaning a tensorial notation nor implicit summations. Indexes $i, j$ are used for the $M$ mesh points, $\alpha, \beta, \gamma$ for the three cartesian coordinates, $\mu, \nu$ for the three lattice or mesh coordinates, $a, b, c$ for the $N$ basis functions, and $n, m$ for the $N$ hamiltonian eigenstates.

As the energy of a crystal does not depend on its orientation in space, only the length of the lattice vectors and the angles between them are important. In other words, the metric tensor $G_{\mu\nu} = a_{\mu} \cdot a_{\nu}$ contains all the relevant information. This allows an equivalent formulation, in which the contravariant components of the stress tensor can be defined as $\tau^{\mu\nu} = 2 \partial E / \partial G_{\mu\nu}$ and its cartesian components are then $\sigma_{\alpha\beta} = \sum_{\mu\nu} \tau^{\mu\nu} a_{\mu\alpha} a_{\nu\beta}$. For details, see I. Souza and J. L. Martins, Phys. Rev. B 55, 8733 (1997).

Handbook of Mathematical Tables, Ed. by M. Abramowitz and I. A. Stegun (Dover, New York, 1965).