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Abstract
It is shown that using a generalized gradient approximation (GGA) functional
describing exchange and correlation (xc) effects in electronic structure
calculations implies additional xc terms in the virial theorem and the pressure
tensor. These new expressions generalize the forms well known in the local
density approximation and are useful for checking the numerical precision of
self-consistent field calculations for atoms and solids, and for accurate pressure
computations in heavy elements. Numerical examples are given.

1. Introduction

The Kohn–Sham formulation of density functional theory [1] for the study of electronic systems
has known recently new developments with the use of better approximations of the exchange
and correlation (xc) energy functional [2]. In particular, the generalized gradient approximation
(GGA) [3–5] has been shown to be powerful in the case of systems having large gradients of the
electron charge density. It can even be successfully applied to localized systems such as atoms
and molecules. From a practical point of view, analytical expressions for this xc functional
have been proposed, from which the xc potential is easily derived.

The implementation of GGA potentials in electronic structure routines, instead of
traditional LDA ones, has several consequences on the formulation of the virial theorem,
that have not been underlined up to now, at least to our knowledge. The aim of this paper
is to discuss this point. In section 2, we derive the virial theorem in the case of GGA by
expressing the total electronic pressure in terms of energy integrals; second, we generalize
an expression known as the 'pressure tensor formula' (spherical symmetry) involving only
quantities calculated on the surface of the atomic cell. Therefore, two forms are obtained for
the pressure: their numerical consistence, and their comparison with the pressure obtained
by numerical differentiation of the total energy with respect to volume, is a very powerful
test of the accuracy of the electronic structure calculations. In section 3, we consider the
implementation of the GGA in a standard APW muffin-tin bandstructure code, and show that
an additional surface term must be introduced in the APW matrix elements in order to deal
with the variational principle. The pressure formula is also adapted to this case. Examples of
numerical results are given in section 4.

2. GGA and the virial theorem

2.1. The pressure from the virial theorem

Let us consider an atom in a spherical box of volume Ω. It is well known that the total pressure can be written as [6]

$$3P\Omega = 2K + U + W_{xc} \tag{1}$$

where K is the total kinetic energy and U is the total potential energy including the interaction of the electrons with the nucleus and the Hartree electron–electron interaction. The last term is the xc contribution. Equation (1) is the most general form of the virial theorem.

In the local density approximation (LDA), restricted for simplicity to the unpolarized case, W_{xc} is [6]

$$W_{xc}^{LDA} = -3E_{xc}^{LDA} + 3 \int_{\Omega} \frac{\mathrm{d}e_{xc}^{LDA}(n)}{\mathrm{d}n} n \, \mathrm{d}^3r \tag{2}$$

with $n(r)$ the electron charge density. The total xc energy is

$$E_{xc}^{LDA} = \int_{\Omega} e_{xc}^{LDA}(n) \, \mathrm{d}^3r \tag{3a}$$

and the xc potential

$$V_{xc}^{LDA} = \frac{\mathrm{d}e_{xc}^{LDA}(n)}{\mathrm{d}n}. \tag{3b}$$

Now, in the case of the GGA, the xc energy depends also on the charge density gradient. Following Perdew [3–5], we introduce the two variables:

$$s = \frac{|\nabla n|}{2k_F n} = \frac{|\nabla n|}{\lambda_s n^{4/3}} \tag{4a}$$

where k_F is the Fermi momentum ($\lambda_s = 2(3\pi^2)^{1/3}$), and

$$t = \frac{|\nabla n|}{2k_{TF} n} = \frac{|\nabla n|}{\lambda_t n^{7/6}} \tag{4b}$$

where k_{TF} is the Thomas–Fermi screening constant ($\lambda_t^2 = 8\lambda_s/\pi$). The variable s is adapted to the description of the gradient effects in the exchange energy while t is relevant to the correlation energy. Therefore, the xc GGA energy functional can be written as

$$E_{xc}^{GGA} = \int_{\Omega} e_{xc}^{GGA}(n, s, t) \, \mathrm{d}^3r. \tag{5}$$

To establish the virial theorem, one has to take the derivative of the total energy with respect to the volume Ω. The way to do it is to make a change of space coordinate and of charge density function: $r = Sx$, $n(r) = f(x)/S^3$, where S is the atomic sphere radius. Doing so, the xc energy becomes

$$E_{xc}^{GGA} = S^3 \int_0^1 e_{xc}\left(\frac{f}{S^3}, \frac{|\nabla f|}{\lambda_s f^{4/3}}, \frac{|\nabla f|}{\lambda_t f^{7/6}} S^{-1/2} \right) 4\pi x^2 \, \mathrm{d}x. \tag{6}$$

Because the total energy is stationary with respect to the charge density variations δf at constant volume, the change in the total energy when the volume changes comes from the variation δS of the explicit variable S only. Thus we find

$$W_{xc}^{GGA} = -3E_{xc}^{GGA} + 3 \int_{\Omega} \frac{\partial e_{xc}^{GGA}(n, s, t)}{\partial n} n \, \mathrm{d}^3r + \frac{1}{2} \int_{\Omega} \frac{\partial e_{xc}^{GGA}(n, s, t)}{\partial t} t \, \mathrm{d}^3r. \tag{7}$$

It should be noticed that there is no contribution from the derivative with respect to s because the variable s has no explicit dependence on S. Equation (7) is the generalization of equation (2) to the GGA case. The total pressure is obtained by inserting equation (7) into equation (1).

2.2. The GGA xc potential

Before deriving another expression for the electronic pressure, we need to go into some details of the GGA xc potential. Starting from equation (5) and performing a variation $\delta n(r)$ of the density $n(r)$, we obtain

$$\delta E_{xc}^{GGA} = \int_{\Omega} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial n} \delta n \, \mathrm{d}^3 r + \int_{\Omega} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial (s^2)} \left(\frac{2 \nabla n \cdot \nabla \delta n}{\lambda_s^2 n^{8/3}} - \frac{8}{3} \frac{|\nabla n|^2}{\lambda_s^2 n^{11/3}} \delta n \right) \mathrm{d}^3 r$$

$$+ \int_{\Omega} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial (t^2)} \left(\frac{2 \nabla n \cdot \nabla \delta n}{\lambda_t^2 n^{7/3}} - \frac{7}{3} \frac{|\nabla n|^2}{\lambda_t^2 n^{10/3}} \delta n \right) \mathrm{d}^3 r. \tag{8a}$$

The integrals containing a product of gradients can be integrated by parts in order to factorize $\delta n(r)$, and, after some transformations, equation (8a) takes the form

$$\delta E_{xc}^{GGA} = \int_{\Omega} V_{xc}^{GGA} \delta n \, \mathrm{d}^3 r + \text{surface integrals.} \tag{8b}$$

The xc potential is

$$V_{xc}^{GGA} = \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial n} - \nabla \left(\frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial s} \frac{\nabla n}{|\nabla n|} \frac{1}{\lambda_s n^{4/3}} \right) - \frac{4}{3} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial s} \frac{s}{n}$$

$$- \nabla \left(\frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial t} \frac{\nabla n}{|\nabla n|} \frac{1}{\lambda_t n^{7/6}} \right) - \frac{7}{6} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial t} \frac{t}{n}. \tag{9}$$

The stationarity of the total energy requires us to get rid of the surface integrals. This can be achieved by imposing boundary conditions such that

$$\int_{\Sigma} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial (s^2)} \frac{\delta n}{\lambda_s^2 n^{8/3}} \nabla n \, \mathrm{d}\Sigma + \int_{\Sigma} \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial (t^2)} \frac{\delta n}{\lambda_t^2 n^{7/3}} \nabla n \, \mathrm{d}\Sigma = 0 \tag{10a}$$

for any δn on the surface Σ. When the system is confined in a spherical box (finite or infinite), such a condition is fulfilled by imposing

$$|\nabla n|_{\Sigma} = 0. \tag{10b}$$

If cancellation of these integrals cannot be obtained through the boundary conditions, the surface terms must be accounted for in the solution of the variational problem. Special cases occurring in band structure methods where it is not possible to impose boundary conditions on the 'muffin-tin' spheres will be discussed in section 3. The pressure given by equations (1) and (7) is identical to the negative of the derivative of the total energy with respect to volume only if this total energy resulting from the DFT calculation with the GGA potential of equation (9) is stationary with respect to any first order variation $\delta n(r)$.

It is also worth noting that the GGA xc potential is singular at the origin. Equation (9) contains Laplacian terms which dominate the behaviour for $r \to 0$ such that the potential behaves as

$$V_{xc}^{GGA} \to -\frac{z}{r} \tag{11a}$$

$$z = 4 \left(\frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial (s^2)} \frac{1}{\lambda_s^2 n^{8/3}} + \frac{\partial e_{xc}^{GGA}(n,s,t)}{\partial (t^2)} \frac{1}{\lambda_t^2 n^{7/3}} \right) \frac{\mathrm{d}n}{\mathrm{d}r} \bigg|_{r=0}. \tag{11b}$$

This singularity modifies the effective nuclear charge which fixes the expansion of the wave functions at small r. The expansion of a radial part of angular momentum l is

$$\phi_l(r) = A r^l \left(1 - \frac{Z^*}{l+1} r + \cdots \right). \tag{11c}$$

Our experience is that the use of the effective charge $Z^* = Z + z$ is necessary in the wave-function initialization if accurate calculations are desired, at least in light materials. Typical values of z for atoms are 0.039 for H and Be and 0.041 for Al. For solids under normal conditions, we have found lower values: 0.018 in H, 0.028 in Be and 0.033 in Al.

2.3. A second expression for the pressure: the 'pressure tensor' formula

In the LDA case, it is well known that the pressure of equations (1) and (2) can be transformed to [7–9]

$$P = P_K + [nV_{xc}^{LDA} - e_{xc}^{LDA}]_{r=S} \tag{12a}$$

$$P_K = \frac{1}{8\pi} \sum_{k,l} |\phi_{k,l}(S)|^2 \left[\frac{(D_{k,l} - l)(D_{k,l} + l + 1)}{S^2} + 2(\varepsilon_{k,l} - V(S)) \right] \tag{12b}$$

where $V(r)$ is the total effective potential. $\phi_{k,l}$ is the radial part of an occupied electronic state of angular momentum l satisfying

$$\frac{d^2(r\phi_{k,l})}{dr^2} + \left(2(\varepsilon_{k,l} - V) - \frac{l(l+1)}{r^2} \right) r\phi_{k,l} = 0 \tag{12c}$$

and $D_{k,l}$ its logarithmic derivative on the boundary

$$D_{k,l} = S \frac{1}{\phi_{k,l}(S)} \frac{d\phi_{k,l}}{dr} \bigg|_{r=S}. \tag{12d}$$

The electron charge density on the surface is given by

$$n(S) = \sum_{k,l} \frac{|\phi_{k,l}(S)|^2}{4\pi}. \tag{12e}$$

A summary of the method used to derive these formulae is given in appendix A. Equation (12b) may also be obtained by working out the general form of the pressure tensor and keeping its radial component only.

In the GGA case, we have used the same kind of technique to derive the following pressure formula:

$$P = P_K + [nV_{xc}^{GGA} - e_{xc}^{GGA}]_{r=S} + \left[\frac{\partial e_{xc}^{GGA}}{\partial s} \left(\frac{3\xi}{S\lambda_s n^{1/3}} + s \right) + \frac{\partial e_{xc}^{GGA}}{\partial t} \left(\frac{3\xi}{S\lambda_t n^{1/6}} + t \right) \right]_{r=S} \tag{13}$$

where the arguments of e_{xc}^{GGA} are omitted for simplicity. ξ takes the value +1 when the density gradient is positive and -1 when negative. The main lines of the derivation of this formula may be found in appendix A.

The interest of this pressure tensor formula is that it allows us, as does its LDA counterpart, to get rid of the very important numerical cancellations between kinetic and Coulomb energies occurring in the virial pressure formula.

Thus, the calculation of the pressure in an electronic system where xc effects are described by the GGA can, as in the LDA case, can be done following three routes.

(i) Simple application of the definition $P = -dE/d\Omega$ either by a finite difference technique or by differentiation of an analytical fit of the energy. The numerical cost of this method can be high, because several energies are needed to calculate the pressure for a single volume. The accuracy on pressure may be poor if too many digits are lost in the differences.

(ii) Use of the virial theorem, equation (1): a single calculation gives the total energy and the pressure at the same time. But here again, large numerical cancellations do occur (between the various terms in the r.h.s. of equation (1)), and the remaining number of significant digits in the pressure is small.

(iii) Use of the pressure tensor formula. As in (ii), the pressure is obtained in the same calculation as the total energy for the volume of interest, and the advantage is that all the cancellations between large kinetic and potential terms have been removed analytically when transforming equation (1) to equation (3). Therefore, this formula, which handles only small quantities, is potentially the most accurate.

3. GGA in the APW band structure method

3.1. GGA and the variational principle

When the GGA is used for band structure calculations, several cases must be considered. If the band structure method uses a set of basis functions which are continuous and have continuous derivatives everywhere in the Wigner–Seitz (WS) cell, then the stationarity conditions in equation (10a) are satisfied because

$$\int_{\Sigma} \nabla n \, \mathrm{d}\Sigma = 0$$

on the WS cell surface results immediately from the Bloch condition imposed on electron states.

However, there are also methods using basis functions with discontinuous derivatives inside the WS cell. This is the case of the augmented plane wave (APW) method, where the basis functions are numerical solutions of the wave equation in a spherical potential inside the 'muffin-tin' (MT) spheres continuous with plane waves outside these spheres. The derivatives are discontinuous on the MT sphere surfaces [10]. In the APW method, the eigenfunction for a state k is expanded as

$$\Phi_k = \sum_j A_{k,j} \Omega^{-1/2} \exp(\mathrm{i}(k + K_j) \cdot r) \tag{14}$$

outside the MT sphere. Ω is the volume of the WS cell and K_j a reciprocal lattice vector. The correct way to deal with the surface integrals in the l.h.s. of equation (10a) is to include them in the variational principle. On the boundary of the MT sphere, the relevant quantity is

$$\sum_{i,j} A_{k,i}^* \delta A_{k,j} M_{ij} \tag{15a}$$

$$M_{ij} = \left(\frac{\partial e_{xc}^{GGA}(n, s, t)}{\partial s} \frac{\xi}{\lambda_s n^{4/3}} + \frac{\partial e_{xc}^{GGA}(n, s, t)}{\partial t} \frac{\xi}{\lambda_t n^{7/6}} \right)_{r=S} \frac{4\pi S^2}{\Omega} j_0(|K_i - K_j|S) \tag{15b}$$

in which S is the MT radius and j_0 the spherical Bessel function. The additional matrix elements M_{ij} are included in the APW determinant in order to insure the stationarity of the total energy.

3.2. Pressure in the APW case

Calculating the pressure with the virial theorem in the APW method, even in the LDA, deserves special attention. The derivative discontinuity is also reflected in the APW matrix elements through a surface contribution to the kinetic energy. The total kinetic energy is divided into three contributions from inside the MT, from the MT surface and from the interstitial region [10]

$$K = K_{in} + K_S + K_{out}. \tag{16}$$

K_{in} is the standard form of the kinetic energy, expressed in terms of the product of the wave functions and their Laplacian. The expression of the two other contributions is given in appendix B. K_{in} can be transformed to give a pressure contribution $P_{K,in}$ similar to that appearing in equation (12b). Finally, the total APW pressure takes the form

$$3P\Omega = 3(P_{K,in} + P_{out})\Omega + 2K_S + 4\pi S^3 \left[nV_{xc}^{GGA} - e_{xc}^{GGA} \right.$$
$$\left. + \frac{\partial e_{xc}^{GGA}}{\partial s} \left(\frac{3\xi}{S\lambda_s n^{1/3}} + s \right) + \frac{\partial e_{xc}^{GGA}}{\partial t} \left(\frac{3\xi}{S\lambda_t n^{1/6}} + t \right) \right]_{r=S}. \tag{17}$$

Details of this formula can be found in appendix B. Deep core states do not contribute to the pressure in equation (17). However, weakly bound core levels may bring some contribution. In such cases, their treatment must be considered with care: when calculated with a single atomic-like wave function, the boundary condition, which must be compatible with the total energy stationarity, may influence the value of the pressure. The treatment of these core states as energy bands might in that case be preferable.

4. Numerical applications

4.1. GGA functional

To illustrate the pressure calculations according to the formulae presented in the preceeding sections, we use parametrized forms of the GGA functional proposed in the literature by Perdew et al [3–5]. Their general form is (paramagnetic case)

$$e_{xc}^{GGA}(n, s, t) = e_x^{GGA}(n, s) + e_c^{GGA}(n, t) \tag{18a}$$

$$e_x^{GGA}(n, s) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{4/3} F(s) \tag{18b}$$

$$e_c^{GGA}(n, t) = e_c^{LDA}(n) + nH(n, t) \tag{18c}$$

$$H(n, t) = \gamma \ln \left(1 + \frac{\beta}{\gamma} t^2 \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \tag{18d}$$

$$A = \frac{\beta}{\gamma} \left[\exp \left(-\frac{1}{\gamma} \frac{e_c^{LDA}}{n} \right) - 1 \right]^{-1}. \tag{18e}$$

These functionals differ in the form of $F(s)$, the approximation chosen for the LDA part in equations (18c, e) and the coefficients β and γ in equations (18d, e).

For the exchange part, several forms are available. One of them is [3]

$$F(s) = \left(1 + a\frac{s^2}{m} + bs^4 + cs^6 \right)^m \tag{18f}$$

with the coefficients $a = 0.0864$, $b = 14$, $c = 0.2$, $m = 1/15$. A more recent one is, with $\kappa = 0.804$ and $\mu = 0.235$ [5],

$$F(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa}. \tag{18g}$$

Our purpose is not to establish which one of these forms is the most accurate in the case of atoms or solids. We only want to illustrate the consequences of using the GGA for calculating the pressure in such systems. So we keep in our computations the particular forms implemented in our codes, which are different for historical reasons. For the LDA part of the correlation $e_c^{LDA}(n)$, we have used the Hedin–Lundqvist form [11] in atoms. For solids, we have used the Ceperley–Alder results in either the Perdew–Zunger or Perdew–Wang representations [12, 13].

Table 1. GGA calculations for free atoms. K is the kinetic energy, U the total Coulomb energy, E_{xc}^{GGA} the xc energy, E the total energy, δ_n and δ_t the xc terms defined in equations (19b, c) and X the virial, which should be zero. All energies are in Ryd. In Be, Al and Ge, the bottom line is from [14].

K	$-U$	$-E_{xc}^{GGA}$	$-E$	$-\delta_n$	δ_t	virial X
Hydrogen						
0.907 1107	1.319 1672	0.523 8450	0.935 9016	0.696 083	0.043 312	−0.000 0042
Beryllium						
29.118 22	52.939 85	5.467 54	29.289 15	7.266 58	0.200 99	−0.000 013
		5.622	29.346			
Aluminium						
484.0656	931.7334	37.2862	484.9540	49.5555	0.8201	−0.000 030
		42.524	484.996			
Germanium						
4151.321 5	8147.372 0	158.174 8	4154.2253	210.295 6	2.1844	0.000 70
		162.008	4155.236			

For the gradient correlation part in equations (18d, e), the value of β is 0.066 725, but two values of γ have been proposed: 0.024 735 [4] and 0.031 0906 [5]. In the following applications, we will indicate in each case the form used.

The analytic form of the correlation potential is given in [4]. Let us just mention that a contribution is missing from equation (33) of this reference. A term

$$-nt\frac{\partial^2 H(n,t)}{\partial n \partial t}$$

involving the cross derivative of $H(n,t)$ with respect to n and t should be added.

4.2. Test for free atoms

For free atoms, the pressure vanishes, so that the virial theorem, equations (1) and (7), gives

$$X = 2K + U - 3E_{xc}^{GGA} + 3\delta_n + \tfrac{1}{2}\delta_t = 0 \tag{19a}$$

$$\delta_n = \int_\infty \frac{\partial e_{xc}^{GGA}}{\partial n} n \, \mathrm{d}^3 r \tag{19b}$$

$$\delta_t = \int_\infty \frac{\partial e_{xc}^{GGA}}{\partial t} t \, \mathrm{d}^3 r. \tag{19c}$$

We have performed calculations for several atoms. The radial mesh of points is exponential: $r_{n+1} = r_n \exp(h)$ with $r_1 = 0.003/Z$ and $h = 0.03$. The boundary condition is that of exponential decay for all the eigenstates at $S \to \infty$:

$$\frac{1}{S\phi(S)}\frac{\mathrm{d}(r\phi)}{\mathrm{d}r}\bigg|_{r=S} = -\sqrt{-2\varepsilon} \tag{20a}$$

which implies for the total charge density at infinity

$$\frac{|\nabla n|}{n} = -2\sqrt{-2\varepsilon_m} \tag{20b}$$

where ε_m is the eigenvalue of the highest occupied state. Numerical results, obtained with the exchange functional of [3], the GGA correlation of [4] and the $e_c^{LDA}(n)$ of Hedin and Lundqvist, are shown in table 1. In Be, Al and Ge, comparison is made with atomic calculations reported by Juan and Kaxiras [14], where the GGA form of [4] is used.

Table 2. Comparison of the pressures calculated using the virial theorem (equations (1) and (7)) and by numerical differentiation of the total energy. Energy units are Ryd.

Boundary cond.	S (au)	$-E$	$3P\Omega$ (virial)	$3P\Omega$ (differ.)
$\left.\dfrac{\mathrm{d}\phi}{\mathrm{d}r}\right|_{r=S} = 0$	2.50	1.321 691	$-0.977\,975$	$-0.977\,976$
$\phi(S) = 0$	3.00	0.747 663	0.790 468	0.790 468

We suspect a misprint in the Al exchange energy in table I of [14], because the value is the same as that reported for Si and very different from ours.

Our results show that the numerical accuracy of the calculations is such that X, which should be zero, vanishes with a precision of 10^{-5} to 10^{-7} relative to the total energy. The differences between the total energy results of Juan and Kaxiras and ours may probably be attributed to the different exchange $F(s)$ and different LDA part of correlation used in the calculations.

4.3. Test for an H atom confined in a spherical box of finite size

Now we want to check that equations (1) and (7) in the GGA are consistent with the pressure obtained by numerical derivation of the total energy with respect to volume. We have calculated an H atom in a spherical box of radius S with two boundary conditions compatible with a vanishing gradient of the density, which are either the wave function or its derivative vanishes for $r = S$. The numerical derivative of the total energy is computed using a four point formula with values of the box radius spaced by $\Delta S = 0.05$ au. The functional is the same as in section 4.2. The results are shown in table 2.

It is to be noticed that, in this calculation, the additional terms in the second pressure formula (tensor formula, equation (13)), due to the use of the GGA, vanish because $s = t = 0$ with the first boundary condition, and s and t are infinite with the second boundary condition. In both cases, the two derivatives of e_{xc} with respect to s and t vanish on the sphere, so that the tensor pressure formula is formally identical to its LDA counterpart. This will not happen in APW–MT calculations, as will be seen in the next subsection.

4.4. APW muffin-tin calculations

The GGA is expected to improve the calculation of the equation of state of solids. A large number of results have been published, often comparing the equilibrium parameter and bulk modulus obtained in LDA and GGA. We will refer to some of them for comparison with our results. Here we present total energy and pressure APW calculations performed in the MT approximation. In this case, the GGA is used inside the MT sphere where the charge density can have rather large gradients, even in simple systems. The gradient correction has no effect outside the spheres where the electron density is assumed to be constant. Because the APW basis functions have discontinuous derivatives on the MT sphere, as already mentioned in section 3, attention must be paid to the implementation of the GGA. We will first report calculations for metallic hydrogen and then results for the equilibrium volume and bulk modulus of hexagonal close packed beryllium, face-centred cubic aluminium and body-centred cubic rubidium.

4.4.1. Hydrogen. Hypothetic metallic hydrogen in the bcc phase has been calculated using the APW–MT method to show that, in a light solid, the numerical calculations allow us to

Table 3. Comparison of the pressures calculated in bcc hydrogen by the virial theorem formula, the tensor formula, equation (B6), or by numerical differentiation of the total energy.

Atomic volume (au)	P (virial) (kbar)	P (tensor) (kbar)	P (differ.) (kbar)	$-E$ (Ryd)
22.00	−83.47	−83.75		1.073 7488
20.18	−3.77	−4.09		1.074 3201
20.00	5.76	5.34	5.60	1.074 3189
19.82	15.40	15.07		1.074 3064
18.00	142.1	141.8		1.073 3803

Table 4. Electronic pressure calculated in the GGA for Be near equilibrium using the three possible forms of the pressure. The total energy is also shown.

Density (g cm^{-3})	P (virial) (kbar)	P (tensor) (kbar)	P (differ.) (kbar)	Energy per atom (Ryd)
1.9727	56.52	55.62	56.41	−29.5274

obtain a good agreement between the various expressions of the pressure, even if four digits are lost in comparing the total energies, as can be seen in table 3.

The agreement between the different forms of the pressure is better than half a kbar.

4.4.2. Beryllium. The calculations have been done with 768 k-points in the entire Brillouin zone. It appeared that the treatment of the core 1s state had some consequence on the accuracy of the results, so that we chose to treat this state as an energy band, on the same footing as the valence states. The experimental ratio $c/a = 1.5677$ has been used.

We consider first a volume, of the order of the equilibrium volume, and compare the electronic pressures calculated with the GGA xc [5] using the three possible methods: (a) from the virial theorem, equations (1) and (7); (b) from the pressure tensor, that is local quantities on the MT sphere, Equation (B6); (c) from the total energy and numerical differences. The results are shown in table 4.

We see that the agreement between the various calculations is good, but slightly less than in hydrogen when comparing the virial and tensor forms. The loss of accuracy is due to accumulation of numerical errors for a larger number of electronic states. Nevertheless the differences remain negligible compared to the zero point pressure (about 38 kbar). This is because the model deals exactly with the required variational properties. Such an agreement would not have been obtained with atomic-like core states satisfying boundary conditions not suitably chosen (see below the Al case). In the light of these results we think that we can have good confidence in our pressure calculations. The possibility of using calculation (b), which avoids cancellation of large numbers, is an advantage which becomes more and more useful in materials of increasing atomic number.

It is interesting to compare the GGA results [5, 13] with those of the LDA [15] and with experiment [18]. Table 5 shows the theoretical total pressure in both approximations. An approximate zero-point vibration contribution has been added to the electronic pressure; it is calculated with a Debye temperature $\theta_D = 1440$ K [16] and a Grüneisen parameter $\gamma = 1.18$ [17]. The equilibrium volume and bulk modulus have been deduced from these values and are given in table 6.

The GGA gives a significantly better equilibrium density than the LDA, but both xc approximations lead to similar bulk modulus in rather good agreement with experiment.

Table 5. Comparison of electronic and total pressures in Be, in the GGA and LDA calculations.

Density (g cm^{-3})	P_e (GGA) (kbar)	P_t (GGA) (kbar)	P_e (LDA) (kbar)	P_t (LDA) (kbar)
1.7355	−90.7	−62.2		
1.8296	−38.0	−6.0		
1.8980			−50.6	−15.9
1.9348	30.0	66.2	−28.3	7.9
1.9727	56.5	94.3	−3.9	33.9
2.0120	85.1	124.5	22.5	61.9

Table 6. Equilibrium density in g cm^{-3} (upper row) and bulk modulus in GPa (lower row), as obtained in GGA and LDA for hcp Be, compared to the experimental values [18].

GGA	LDA	Experiment
1.8383	1.9226	1.8404
126.2	124.3	115.5

Table 7. Influence of the additional xc term in the virial theorem (equation (7)), in the case of Al near equilibrium.

Lattice a (au)	P_e (kbar)	$P_e\Omega$ (Ryd)	$\delta_t/6$ (Ryd)
7.4827	+5.30	+0.003 78	−0.131 30
7.5064	−1.98	−0.001 42	−0.131 35
7.5300	−8.17	−0.005 93	−0.131 36
7.5536	−14.6	−0.010 70	−0.131 40
7.5770	−20.7	−0.015 30	−0.131 44

4.4.3. Aluminium. Several comparisons between GGA and LDA results for aluminium have been published in the past years [14, 19, 20]. We will not make these comparisons again here, but present GGA calculations, performed with the functional of [5], to show the importance of the new energy contribution appearing in the virial expression of the GGA pressure. The calculations are performed with 2048 k-points in the entire Brillouin zone, and the core states are calculated with atomic-like wave functions having, for the angular momentum l, a logarithmic derivative $(1/\phi(S))(\mathrm{d}\phi/\mathrm{d}r)|_{r=S} = -(l+1)/S$ on the MT sphere.

In table 7 we compare the new term in W_{xc}^{GGA}, equation (7):

$$\delta_t = \int_\Omega \frac{\partial e_{xc}^{GGA}(n, s, t)}{\partial t} t \, \mathrm{d}^3 r$$

(involving the derivative of the GGA xc energy with respect to the variable t), to the quantity $P_e\Omega$.

These results prove that the new pressure term produces a nearly constant pressure shift because its variations are small compared to those of the whole pressure, but its neglect would significantly alter the equilibrium volume.

Without including any zero-point vibration correction, the calculated equilibrium lattice parameter is $a_0 = 7.501$ au (3.969 Å) and the bulk modulus is $B_0 = 70.4$ GPa. The most recent similar calculations by Khein *et al* using an all-electron linearized APW method with the Perdew–Wang GGA xc give respectively $a_0 = 7.74$ au and $B_0 = 72.6$ GPa [19]. On including zero-point corrections with a Debye temperature $\theta_D = 428$ K and a Grüneisen parameter

$\gamma = 2.19$, the present calculated values become $a_0 = 7.534$ au and $B_0 = 77.9$ GPa. With respect to experiment [21], a_0 is 1% too small and B_0 is 1% too large.

To end this comparison, let us emphasize again that the treatment of the core states may have non-negligible consequences on the determination of the calculated equilibrium properties of solids. In the calculations just above, the boundary condition imposed on the atomic-like core states (a condition which determines the centre of gravity of the canonical energy bands of the LMTO method [22]) is compatible with the required variational properties of the total energy. If these boundary conditions are replaced by the condition of exponential decay *at finite S* of the form given in equation (20), which does not imply the stationarity of the total energy when the core wave functions vary, then the agreement between the various forms of the pressure may be lost, and the value of the pressure deduced from the virial theorem may change a lot. In the case of Al, the values given above change from $a_0 = 7.534$ to 7.711 au, and from $B_0 = 77.9$ to 74.1 GPa. Even more important changes (+10% to -15% with respect to experiment in B_0) following the treatment of the core states have been reported elsewhere [20]. The problem of the core states has been addressed in tungsten [23], where it is more serious, the highest core state energy being -3.70 Ryd instead of -6.23 Ryd in Al. For Rb (see below), the 4p level is so high (-1.62 Ryd) that the $n = 4$ shell must be treated as an energy band.

4.4.4. Rubidium. In light materials, the three possible calculations of the pressure agree rather well. But in heavier materials, the number of significant digits needed in the energy to see a given variation δE increases. As an example, we see in table 8 that eight digits must be stabilized in rubidium to obtain two digits in energy differences and in the pressures P(differ.) calculated from a fit of these energies. Obtaining a third significant digit on this pressure would require an improvement of one order of magnitude of the accuracy on energy, demanding more iterations in the self-consistent process, more points in the r-grid, more points in the Brillouin zone, ... The pressure calculated from the virial theorem, P(virial), also suffers a loss of accuracy because of the very important numerical cancellations among the various energy contributions occurring in the pressure of equation (1). The consequence of these accuracy issues is that the two pressures begin to show important differences. The situation is not the same with the pressure from the tensor formula, P(tensor), calculated with a much better precision because it is free of numerical cancellations. All the digits shown for P(tensor) are expected to be correct and this pressure is certainly the most reliable one. It can be noticed that P(differ.) is in much closer agreement with P(tensor), a result which was not obvious. We believe that the reason is that the errors in the stabilized total energies are quite systematic when the volume changes, so that they cancel in the difference. Such a cancellation does not happen in the virial calculation. In addition, the virial is not a variational quantity as is the energy, so it is much more sensitive to small errors in the density.

We have calculated the equilibrium lattice parameter and bulk modulus of Rb. The results in table 8 have been fitted for the energy to $E = E_0 + Aa + B/a + C/a^2$ and for the pressure to $P = -2(A - B/a^2 - 2C/a^3)/(3a^2)$. The results are given in table 9.

In these equilibrium properties, ionic zero point motion has been taken into account using the Debye model with a temperature $\theta_D = 56$ K and a Grüneisen coefficient $\gamma = 1.67$ [17]. The experimental values are $a_0 = 10.56$ au [24] and $B_0 = 30.6$ kbar [25].

In conclusion to this discussion, we think that using the tensor formula is the best way to calculate the pressure in all-electron calculations for heavy materials. The calculation by numerical differences leads to the correct order of magnitude, but cannot give the same accuracy at the same cost of computing time.

Table 8. Total energy and electronic pressure calculated in the GGA for bcc Rb near equilibrium. The 4s and 4p levels are treated as energy bands.

Lattice a (au)	P (virial) (kbar)	P (tensor) (kbar)	P (differ.) (kbar)	Energy per atom (Ryd)
9.86	19	12.85	12	−5879.4630
10.24	12	6.19	6.3	−5879.4666
10.62	6.8	1.74	2.1	−5879.4682
11.00	3.4	−1.19	−1.2	−5879.4683
11.38	1.1	−3.10	−3.8	−5879.4672

Table 9. Equilibrium properties calculated in the GGA for bcc Rb.

	From P (virial)	From P (tensor)	From E
Equilib. lattice a_0 (au)	11.6	10.83	10.9
Bulk modulus (kbar)	16	27.78	28

5. Conclusion

We have shown how the use of a GGA xc functional modifies the expression of the virial theorem in electronic systems, either infinite or finite in size. Terms associated with the new variables depending on the electron charge density gradient (which are absent from the LDA counterparts) must also be taken into account in the pressure tensor formula. Only when these correct expressions are used can the three possible expressions of the pressure give identical results. We have illustrated these points by numerical calculations for free atoms, atoms confined in a spherical box and atoms in solids as calculated with the APW method. The comparison of the pressures obtained in these three different ways gives confidence in the calculational accuracy and provides a powerful check that the total energy is really stationary with respect to variations of the charge density. In all-electron calculations for heavy elements, the use of the tensor formula is, in our opinion, the most accurate way to compute the pressure near equilibrium.

Appendix A. Derivation of the general pressure formulae

We consider an electronic system in the presence of a nucleus and having for simplicity spherical symmetry. It can be, for example, a 'compressed atom' localized within a sphere with appropriate boundary conditions. The extension of the formula to the case of an atom in the MT sphere of the APW method is given in appendix B.

We start from equations (1) and (2) and show how to derive equations ($12a, b$). The intermediate quantity to work with is

$$L_{k,l} = \int_0^S r^3 \phi_{k,l}^2 \frac{dV}{dr} dr. \tag{A1}$$

By several integrations by parts, and using the fact that $\phi_{k,l}$ is a solution of the radial Schrödinger equation (equation ($12c$)), $L_{k,l}$ can be written

$$L_{k,l} = 2K_{k,l} - \frac{1}{2} S^3 |\phi_{k,l}(S)|^2 \left[\frac{(D_{k,l} - l)(D_{k,l} + l + 1)}{S^2} + 2(\varepsilon_{k,l} - V(S)) \right] \tag{A2}$$

where $K_{k,l}$ is the kinetic energy of state k, l. $D_{k,l}$ is defined in equation ($12d$). Summation

over all the occupied states k, l gives, with P_K given in equation (12b),

$$\sum_{k,l} L_{k,l} = 2K - 4\pi S^3 P_K. \tag{A3}$$

Replacing in equation (A1) the potential with

$$V = -\frac{Z}{r} + V_e + V_{xc} \tag{A4}$$

where V_e is the potential created by the electron charge distribution $n(r)$, another form of equation (A3) can be obtained:

$$\sum_{k,l} L_{k,l} = -U + 4\pi S^3 n(S) V_{xc}(S) - \int_0^S V_{xc} \frac{d(r^3 n)}{dr} 4\pi \, dr. \tag{A5}$$

Identifying equations (A3) and (A5), we find that

$$2K + U = 3\Omega[P_K + n(S) V_{xc}(S)] - \int_0^S V_{xc} \frac{d(r^3 n)}{dr} 4\pi \, dr. \tag{A6}$$

This expression is valid in both the LDA and GGA cases. Now, we consider separately these two cases in order to transform the last term in equation (A6).

A.1. LDA

In this approximation:

$$V_{xc}^{LDA} \frac{dn}{dr} = \frac{de_{xc}^{LDA}(n)}{dr} \tag{A7}$$

so that the integration of the last term is straightforward and equations (12a, b) are obtained.

A.2. GGA

The complex structure of the xc potential makes the last term in equation (A6) more difficult to work out. Starting from equation (9), the terms containing gradients can be transformed. Let us look for example at the first one:

$$\nabla \left(\frac{\partial e_{xc}^{GGA}}{\partial s} \frac{\nabla n}{|\nabla n|} \frac{1}{\lambda_s n^{4/3}} \right) = -\frac{4}{3} \frac{\partial e_{xc}^{GGA}}{\partial s} \frac{|\nabla n|}{\lambda_s n^{7/3}} + \frac{1}{\lambda_s n^{4/3}} \nabla \left(\frac{\partial e_{xc}^{GGA}}{\partial s} \frac{r}{r} \zeta(r) \right) \tag{A8}$$

where $\zeta(r)$ is a constant piecewise function, the magnitude of which is unity with the sign of the charge density derivative. At points of discontinuity of ξ, $\nabla \zeta$ is a delta-function, but is multiplied in equation (A8) by a factor which vanishes because $s = 0$, so that $\partial e_{xc}^{GGA}/\partial s = 0$ when $|\nabla n| = 0$. Finally,

$$\nabla \left(\frac{\partial e_{xc}^{GGA}}{\partial s} \frac{\nabla n}{|\nabla n|} \frac{1}{\lambda_s n^{4/3}} \right) = -\frac{4}{3} \frac{\partial e_{xc}^{GGA}}{\partial s} \frac{s}{n} + \zeta(r) \frac{1}{\lambda_s n^{4/3}} r^{-2} \frac{d}{dr} \left(r^2 \frac{\partial e_{xc}^{GGA}}{\partial s} \right). \tag{A9}$$

With the same transformation of the term involving the derivative with respect to t, the potential becomes

$$V_{xc}^{GGA} = \frac{\partial e_{xc}^{GGA}}{\partial n} - \zeta(r) \frac{1}{\lambda_s n^{4/3}} r^{-2} \frac{d}{dr} \left(r^2 \frac{\partial e_{xc}^{GGA}}{\partial s} \right) - \zeta(r) \frac{1}{\lambda_t n^{7/6}} r^{-2} \frac{d}{dr} \left(r^2 \frac{\partial e_{xc}^{GGA}}{\partial t} \right). \tag{A10}$$

On inserting equation (A10) into equation (9), the last term in equation (A6) can be integrated by parts to give

$$\int_0^S V_{xc}^{GGA} \frac{d(r^3 n)}{dr} 4\pi \, dr = 3 \int_0^S \frac{\partial e_{xc}^{GGA}}{\partial n} n \, dr + \frac{1}{2} \int_0^S \frac{\partial e_{xc}^{GGA}}{\partial t} t \, dr + \int_0^S \frac{de_{xc}^{GGA}}{dr} 4\pi r^3 \, dr$$

$$-3\Omega \left[\frac{\partial e_{xc}^{GGA}}{\partial s} \left(\frac{3\zeta}{S \lambda_s n^{1/3}} + s \right) + \frac{\partial e_{xc}^{GGA}}{\partial t} \left(\frac{3\zeta}{S \lambda_t n^{1/6}} + t \right) \right]_{r=S}. \tag{A11}$$

This relation, together with equations (1) and (7), leads to the GGA pressure in equation (13).

Appendix B. Application to the APW method

The MT surface contribution to the kinetic energy is [10]

$$K_S = \sum_k \frac{4\pi S^2}{\Omega} \sum_l B_{k,l}^2 \frac{1}{\phi_{k,l}(S)} \frac{\mathrm{d}\phi_{k,l}(r)}{\mathrm{d}r}\bigg|_{r=S} \tag{B1}$$

where the $B_{k,l}$ are the coefficients of the expansion of the spherically averaged charge density of state k in terms of the radial parts inside the MT:

$$B_{k,l}^2 = (2l+1) \sum_{i,j} A_{k,l}^* A_{k,j} j_l(k_i S) j_l(k_j S) P_l(\hat{k}_i \cdot \hat{k}_j) \tag{B2}$$

with $j_l(x)$ the spherical Bessel function, P_l the Legendre polynomial of order l and $k_i = |k + K_i|$. Here, Ω is the total volume of the WS cell, not to be confused with the volume $4\pi S^3/3$ of the MT sphere.

The contribution P_{out} of the interstitial region of volume $\Delta\Omega$ to the pressure is

$$3P_{out}\Omega = 2K_{out} + \frac{1}{2} Q_{out} V_{out} - 3\left(e_{xc}^{LDA}(n_{out}) - n_{out}\frac{\mathrm{d}e_{xc}^{LDA}(n_{out})}{\mathrm{d}n}\right)\Delta\Omega \tag{B3}$$

$$K_{out} = \sum_k \sum_{i,j} A_{k,i}^* A_{k,j} (k_i \cdot k_j)\left[\delta_{ij} - \frac{4\pi S^3}{\Omega}\frac{j_1(|K_j - K_i|S)}{|K_j - K_i|S}\right] \tag{B4}$$

where Q_{out} is the total electron charge in the intersticial region, $n_{out} = Q_{out}/\Delta\Omega$ and V_{out} is the total Coulomb potential outside the spheres if the origin of energies is such that this Coulomb potential, as defined inside the MT spheres, takes the value $-Q_{out}/S$ for $r = S$.

The contribution of inside the MT sphere can be transformed from the integral virial form to an expression in terms of local quantities on the sphere. If the derivation of appendix A is resumed in the APW case, one obtains

$$3P_{K,in}\Omega = \frac{1}{2}S^3 \sum_{k,l} B_{k,l}^2 |\phi_{k,l}(S)|^2\left[\frac{(D_{k,l} - l)(D_{k,l} + l + 1)}{S^2} + 2(\varepsilon_{k,l} - V(S))\right]. \tag{B5}$$

Finally, when using the GGA in the APW scheme, the pressure tensor formula is

$$3P\Omega = 3(P_{K,in} + P_{out})\Omega + 2K_S + 4\pi S^3\left[nV_{xc}^{GGA} - e_{sc}^{GGA} + \frac{\partial e_{xc}^{GGA}}{\partial s}\left(\frac{3\xi}{S\lambda_s n^{1/3}} + s\right)\right.$$
$$\left. + \frac{\partial e_{xc}^{GGA}}{\partial t}\left(\frac{3\xi}{S\lambda_t n^{1/6}} + t\right)\right]_{r=S}. \tag{B6}$$

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