A density gradient-less variable in exchange-correlation functionals for detecting inhomogeneities in the electron density

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A new type of approximation for the exchange and correlation functional in density functional theory is proposed. This approximation depends on a variable, \( u \), that is able to detect inhomogeneities in the electron density \( \rho \) without using derivatives of \( \rho \). Instead, \( u \) depends on the orbital energies which can also be used to measure how a system differs from the homogeneous electron gas. Starting from the functional of Perdew, Burke, and Ernzerhof (PBE) [Phys. Rev. Lett. 77, 3865 (1996)], a functional depending on \( u \) is constructed. Tests on the lattice constant, bulk modulus, and cohesive energy of solids show that this new \( u \)-dependent PBE-like functional is on average as accurate as the original PBE or its solid-state version PBESol. Since \( u \) carries more nonlocality than the reduced density gradient \( s \) used in functionals of the generalized gradient approximation (GGA) like PBE and \( \alpha \) used in meta-GGAs, it will be certainly useful for the future development of more accurate exchange-correlation functionals.

The Kohn-Sham (KS) version [1] of density functional theory (DFT) [2] is the most widely used quantum mechanical method to calculate the geometry and electronic structure of molecules, surfaces, and solids [3, 4]. The success of KS-DFT is due to its ratio cost/accuracy which is quite low compared to other methods, in particular when the exchange-correlation (xc) functional \( E_{xc} \) is approximated at the semilocal level. This allows systems having up to several thousands of atoms to be treated rather routinely. The semilocal functionals \( E_{xc} \) belong to the first three rungs of Jacob’s ladder [5] and the corresponding xc-energy density \( \varepsilon_{xc} \), which is defined as follows:

\[
E_{xc} = \int \varepsilon_{xc}(\mathbf{r}) d^3r
\]  

depends locally on properties of the system. More specifically, in the local density approximation (LDA, 1st rung of Jacob’s ladder) [6], \( \varepsilon_{xc} \) is a function of the electron density \( \rho = \sum_{i=1}^{N} |\psi_i|^2 \), where the summation is over the \( N \) occupied orbitals \( \psi_i \). In the generalized gradient approximation (GGA, 2nd rung of Jacob’s ladder) [6–10], \( \varepsilon_{xc} \) depends on \( \rho \) and its first derivative \( \nabla \rho \). In the meta-GGA (3rd rung of Jacob’s ladder) [8–10], \( \varepsilon_{xc} \) depends on \( \rho \) and \( \nabla \rho \), but also on \( \nabla^2 \rho \) and/or the positive-definite noninteracting kinetic-energy density \( \tau = (1/2) \sum_{i=1}^{N} \nabla \psi_i^* \cdot \nabla \psi_i \).

It is clear that using more and more ingredients (\( \rho, \nabla \rho, \tau, \) etc.) for the construction of a xc functional should increase the overall accuracy, and numerous studies have shown that it is indeed the case (see, e.g., Refs. [10–12] for recent works). For instance, the recently developed meta-GGA SCAN (strongly constrained and appropriately normed) [13] has shown to be quite broadly accurate for properties depending on the total energy [14, 15], although some problems remain [16, 17].

In this work, we propose a new type of approximation for \( \varepsilon_{xc} \) in Eq. (1), which depends on

\[
u(r) = B \sum_{i=1}^{N} \sqrt{\varepsilon_H - \varepsilon_i} \frac{|\psi_i(r)|^2}{\rho^{3/2}(r)},
\]  

where \( \varepsilon_i \) are the energies of the orbitals (\( i = H \) is the highest occupied one) and \( B = 16\sqrt{2\pi}/(3\pi^2)^{4/3} \). The particularity of Eq. (2) is to be \( \varepsilon_i \)-dependent and, to our knowledge, the only existing xc-energy functionals that depend on the orbital energies \( \varepsilon_i \) are those derived from \textit{ab initio} methods, e.g., perturbation theory or the random phase approximation [18, 19]. Actually, \( u \) can be expressed as \( u = u_{GLLB}/u_{X_{RESP}} \), where \( u_{GLLB} \) is the approximation to the response term of the exchange potential proposed by Gritsenko et al. (GLLB) [20] and \( u_{X_{RESP}} = k_F/(2\pi) \), where \( k_F = (3\pi^2\rho)^{1/3} \), is the exact homogeneous electron gas (HEG) limit of \( u_{X_{RESP}} \). Since \( u_{GLLB}/u_{X_{RESP}} \rightarrow u_{X_{RESP}} \) in the HEG-limit (see Ref. [20]), \( u = 1 \) for the HEG and any departure from this value indicates that somewhere in the system the electron density \( \rho \) is not constant.

Two interesting features of Eq. (2) should be mentioned: (a) it can detect inhomogeneities in \( \rho \) without explicitly using the derivatives of \( \rho \) and (b) it does not make the calculation of \( \varepsilon_{xc} \) more expensive than for semilocal methods. Thus, \( u \) could be considered as an alternative or a complement to functions which depend explicitly on derivatives of \( \rho \), e.g., the reduced density gradient

\[
s(r) = \frac{|\nabla \rho(r)|}{2\rho(k_F r)},
\]  

which is used in GGA functionals [21, 22], or \( \tau \)-dependent functions like

\[
\alpha(r) = \frac{\tau(r) - \tau^W(r)}{\tau^{TF}(r)},
\]  

where \( \tau^W = |\nabla \rho|^2/(8\rho) \) and \( \tau^{TF} = (3/10)(3\pi^2)^{2/3}/\rho^{5/3} \) are the von Weizsäcker [23] and Thomas-Fermi kinetic-
energy density \[24, 25\], that is widely used in meta-GGA functionals \[26, 28\].

In the aim of showing the usefulness of \(u\) as a variable in xc-energy functionals and thus its potential interest for improving further the accuracy of computationally cheap DFT methods, we construct an xc-energy density \(\varepsilon_{xc}\) that depends on \(u\). In particular, we want to show that the accuracy obtained with a \(u\)-dependent functional which does not depend on derivatives of \(\rho\) [i.e., \(\varepsilon_{xc} = \varepsilon_{xc}(\rho, u)\)] can be similar to the accuracy of GGA functionals \([\varepsilon_{xc} = \varepsilon_{xc}(\rho, \nabla \rho)\)]. For this we will consider the functional of Perdew, Burke, and Ernzerhof (PBE) \[26\], which is one of the standard GGA functionals, and replace its \(\nabla \rho\)-dependency by a \(u\)-dependency. The analytical form of the PBE functional \(E_{xc}^{PBE} = E_{xc}^{PBE} + E_{xc}^{PBE}\) is now reviewed in detail.

The non-spin-polarized version of the exchange component of PBE (the spin-polarized version is trivially calculated \[29\]) is given by

\[
E_{xc}^{PBE} = \int \varepsilon_{xc}^{LDA}(r_s)E_{xc}^{PBE}(s)d^3r, \tag{5}
\]

where \(\varepsilon_{xc}^{LDA} = -(9/(16\pi))(9/(4\pi^2))^{1/3}r_s^{-4} [r_s = (3/(4\pi\rho))^{1/3}\) is the Wigner-Seitz radius\] is the exchange energy density of the HEG and

\[
E_{xc}^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa^2}}, \tag{6}
\]

is the beyond-LDA enhancement factor, where \(\mu \simeq 0.21951\) and \(\kappa = 0.804\). PBE correlation is given by

\[
E_c^{PBE} = \int \left[\varepsilon_{c}^{LDA}(r_s, \zeta) + H_{xc}^{PBE}(r_s, \zeta, t)\right]d^3r, \tag{7}
\]

where \(\varepsilon_{c}^{LDA}\) is the correlation energy of the HEG \([\zeta = (\rho_i - \rho_s)/\rho\) is the relative spin polarization\], whose exact analytical form as a function of \(\rho\) is unknown, but can be approximated by a fit of very accurate Monte-Carlo data of the HEG \[30, 31\]. The beyond-LDA term in Eq. (7) is given by

\[
H_{xc}^{PBE}(r_s, \zeta, t) = \gamma \phi^3 \ln \left(1 + \frac{\beta t^2}{1 + At^2} \right), \tag{8}
\]

where

\[
t(r) = \left(\frac{3\pi^2}{16}\right)^{1/3} s(r) \sqrt{r_s(r)\phi(r)}, \tag{9}
\]

with \(\phi = \left[(1 + \zeta^3)^{1/3} + (1 - \zeta^2)^{1/3}\right]/2, \ beta = 3\mu/\pi^2 \simeq 0.066725, \ gamma = (1 - \ln 2)/\pi^2, \) and \(A = (\beta/\gamma) \left[\exp(-\varepsilon_{xc}^{LDA}/(\gamma \phi^3)) - 1\right]^{-1}\).

Our construction of \(\varepsilon_{xc}(\rho, u)\) consists of simply replacing \(s\) by \(u - 1\) in Eq. (6) for exchange and in Eq. (8) (via \(t\)) for correlation. This choice is dictated by the requirement that a functional should recover LDA for the HEG, i.e., when \(s = t = 0\) for a GGA or \(u = 1\) for our new approximation. Nevertheless, an important point to note is that, while \(s = t = 0\) if \(\nabla \rho = 0\) (since by definition \(s\) and \(t\) depend locally on \(\nabla \rho\)), this may not be the case for \(u - 1\), since \(u\) depends on \(\epsilon_i\) which in turn depend nonlocally (via the KS equations) on \(\rho, \nabla \rho\), etc [see Eq. (10)]. Thus, it is only for the HEG (i.e., \(\nabla \rho = 0 \forall \rho\)) that one can be sure that \(u = 1\). On the other hand, thanks to this nonlocality, \(u\) should convey more or different informations than \(s\) and \(t\). In this respect, we recall that from the KS equations, the orbital energies can be expressed as

\[
\epsilon_i = -\frac{1}{2} \int \psi_i^*(r)\nabla^2 \psi_i(r)d^3r + \int \left(\psi_{ext}(r) + \psi_{H}(r) + \psi_{xc}(r)\right)|\psi_i(r)|^2d^3r, \tag{10}
\]

where \(\psi_{ext}(r)\) is the external potential due to the nuclei, \(\psi_{H}(r) = \int \rho(r')/|r - r'|d^3r'\) is the Hartree potential, and \(\psi_{xc}(r)\) is the xc potential. Thus, from Eq. (10) we can see that the expression for \(\epsilon_i\) involves nonlocal quantities as \(\psi_{H}\) (see Ref. \[32\] for a \(\psi_{H}\)-dependent exchange functional). Of course, the fact that \(s\) and \(u - 1\) are not equal also means that the results obtained after the replacement \(s \rightarrow u - 1\) will differ from the original ones. In the following, PBE\(u\) refers to the PBE functional with \(s\) substituted by \(u - 1\). As technical detail, we mention that depending on the analytical form of the original GGA, negative values of \(u - 1\) may lead to singularities. However, this is not the case with PBE since only \(s^2\) and \(t^2\) occur in Eqs. (6) and (8).

In order to know to which extent the gradient-less parameter \(u\) can replace \(s\) in a GGA functional or, more generally, can be useful for the future development of xc functionals, the accuracy of PBE\(u\) will be compared to the accuracy of LDA and GGA functionals. A natural choice for a GGA is PBE [Eqs. (5)–(8)], however a certain number of variants of PBE which differ in the value of the parameters \(\mu, \kappa,\) and \(\beta\) in Eqs. (6) and (8) exist (see, e.g., Refs. \[33, 34\]). Among these PBE variants, PBEsol \[34\] for which \(\mu = 10/81 \simeq 0.12346\) and \(\beta = 0.046 (\kappa = 0.804\) as in PBE), is also chosen for the comparison with PBE\(u\).

The xc functionals will be compared for their accuracy on the equilibrium lattice constant \(a_0\), bulk modulus \(B_0\), and cohesive energy \(E_{coh}\) of solids. The test set is the one that we used in our previous work \[12\] and consists of 44 cubic solids of various types (semiconductors,ionic insulators, and metals). The results are shown in Tables S1-S3 and Figs. S1-S6 of Ref. \[39\], while Table I shows the mean error (ME), mean absolute error (MAE), mean relative error (MRE), and mean absolute relative error (MARE) with respect to experiment. All results were obtained non-self-consistently by using the PBE orbitals and density.

It is well known that LDA strongly underestimates (overestimates) the lattice constant (cohesive energy),
TABLE I. The ME, MAE, MRE, and MARE with respect to experiment [37, 38] on the testing set of 44 solids for the lattice constant $a_0$, bulk modulus $B_0$, and cohesive energy $E_{\text{coh}}$. The units of the ME and MAE are Å, GPa, and eV/atom for $a_0$, $B_0$, and $E_{\text{coh}}$, respectively, and % for the MRE and MARE. All results were obtained non-self-consistently using PBE orbitals/density.

| Functional          | $a_0$ ME | $a_0$ MAE | $a_0$ MRE | $a_0$ MARE | $B_0$ ME | $B_0$ MAE | $B_0$ MRE | $B_0$ MARE | $E_{\text{coh}}$ ME | $E_{\text{coh}}$ MAE | $E_{\text{coh}}$ MRE | $E_{\text{coh}}$ MARE |
|---------------------|----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|----------------------|----------------------|------------------------|------------------------|
| LDA                 | -0.071   | 0.071     | -1.5      | 1.5       | 10.1     | 11.6      | 8.1       | 9.5       | 0.78                 | 0.78                 | 17.5                   | 17.5                   |
| PBE                 | 0.056    | 0.061     | 1.1       | 1.2       | -11.1    | 12.2      | -9.7      | 10.9      | -0.12               | 0.18                 | -3.7                   | 4.8                    |
| PBEsol              | 0.005    | 0.030     | -0.1      | 0.6       | 0.8      | 7.8       | 1.3       | 6.9       | 0.30                 | 0.32                 | 6.4                    | 7.0                    |
| PBEu(PBE)           | 0.018    | 0.048     | 0.3       | 1.1       | 2.3      | 10.3      | 4.1       | 11.4      | -0.47               | 0.65                 | -9.3                   | 13.2                   |
| PBEu(PBEsol)        | -0.036   | 0.040     | -0.8      | 0.9       | 7.8      | 11.7      | 2.1       | 8.7       | 0.11                | 0.45                 | 3.3                    | 9.3                    |
| PBEu(0.10,0.02)     | -0.024   | 0.030     | -0.6      | 0.7       | 4.5      | 8.5       | 0.5       | 7.8       | 0.06                | 0.35                 | 1.3                    | 7.1                    |

FIG. 1. Relative error (in %) with respect to experiment [37, 38] in the calculated lattice constant (left panel) and cohesive energy (right panel) for 44 solids.

and from Fig. S1 we can see that it is the case for all solids. The MAE obtained with LDA amount to 0.071 Å and 0.78 eV/atom for $a_0$ and $E_{\text{coh}}$, respectively, and are the largest among all tested functionals. The bulk modulus is overestimated for the vast majority of solids and the MAE is 11.6 GPa. On average, PBE is only slightly more accurate than LDA for the lattice constant (MAE = 0.061 Å), while the reverse is observed for the bulk modulus (MAE = 12.2 GPa). From Fig. S2 and the ME, we can see that the tendency of PBE is to overestimate $a_0$ (and therefore to underestimate $B_0$). For the cohesive energy, PBE is much more accurate than LDA since the MAE is four times smaller (0.18 eV/atom). PBEsol, which was proposed as a more accurate GGA for the lattice constant of solids [34], leads to MAE for $a_0$ (0.030 Å) and $B_0$ (6.9 GPa) that are clearly smaller than for PBE. However, PBEsol is less accurate than PBE for $E_{\text{coh}}$ (MAE = 0.32 eV/atom).

Turning now to the PBEu functional, Table I shows the results obtained with three variants of PBEu, which differ in the values of the parameters $\mu$ and $\beta$ in Eqs. (6) and (8), respectively ($\kappa = 0.804$ for all functionals). In PBEu(PBE) and PBEu(PBEsol), the PBE and PBEsol parameters mentioned above are used, while PBEu(0.10,0.02) is a new reparametrization with $\mu = 0.10$ and $\beta = 0.02$. For the lattice constant, PBEu(PBE) and PBEu(PBEsol) lead to values of 0.048 and 0.040 Å for the MAE, such that their overall accuracy is somewhere in between PBE and PBEsol. The MAE for the bulk modulus obtained with these two functionals (10.3 and 11.7 GPa) are quite similar to the values obtained with LDA and PBE, but larger than for PBEsol. With MAE of 0.65 and 0.45 eV/atom for the cohesive energy, PBEu(PBE) and PBEu(PBEsol) are superior to LDA, but clearly inferior to PBE which is the most accurate functional tested in this work for $E_{\text{coh}}$. Thus, by considering overall the MAE (or the MARE) for the three properties, PBEu(PBE) and PBEu(PBEsol), which are constructed by just replacing $s$ by $u - 1$, improve over LDA quite the same way as PBE and PBEsol do.

However, the results with PBEu can be improved by tuning the parameters $\mu$ and $\beta$. By varying these two parameters independently an interesting combination, $\mu = 0.10$ and $\beta = 0.02$, leads to results which are improved for the three properties. From Table I we can see that the MAE is 0.030 Å, 8.5 GPa, and 0.35 eV/atom for $a_0$, $B_0$, and $E_{\text{coh}}$, respectively. Thus, the accuracy achieved by PBEu(0.10,0.02) is overall very similar to PBEsol accuracy.
Looking in more detail at the results, Fig. 1 shows graphically the results for the lattice constant and cohesive energy obtained with LDA, the two GGA, and PBEu(0.10,0.02). Several observations can be made. Starting with the sp-semiconductors (i.e., from C to InSb), we can see that the values of \( a_0 \) obtained with LDA, which are quite accurate (the errors are similar to PBEsol and much smaller than PBE), are followed closely by PBEu(0.10,0.02) results. However, PBEu(0.10,0.02) improves significantly over LDA for the cohesive energy of the sp-semiconductors and shows similar accuracy as PBE. Concerning the ionic solids (i.e., from LiH to MgO) the errors for \( a_0 \) are overall the smallest with PBEu(0.10,0.02), while for \( E_{\text{coh}} \) the PBEu(0.10,0.02) errors are on average of similar magnitude as with PBE, but with opposite sign. For Al and the alkali and alkaline earth metals, the magnitude of the errors with PBEu(0.10,0.02) and PBEsol are rather similar for both \( a_0 \) and \( E_{\text{coh}} \). The most visible exceptions are Na and Ba for \( a_0 \). The PBEu(0.10,0.02) lattice constants for the transition metals lie in between the LDA and PBEsol results. PBE is the most accurate method for the 3d metals, while PBEsol is recommended for the 5d metals. Regarding the cohesive energy of the transition metals, PBE is the most accurate method, while PBEsol is overall somewhat less accurate and systematically overestimates the values. However, for the cohesive energy PBEu(0.10,0.02) leads for a few cases to large deviations from experiment. For V, Cu, Nb, Mo, and Ta, \( E_{\text{coh}} \) is clearly underestimated, while large overestimations sim-
Figure 2 shows plots of $s$, $u$, and $u - 1$ for a few selected solids. We can see that the positions of the peaks in $s$ and $u$ coincide remarkably well despite $s$ depends on $\nabla \rho$, while $u$ does not. The similar features seen in $s$ and $u$ explain why substituting $s$ by $u - 1$ in a GGA leads to a density gradient-less functional that can also be much more accurate than LDA. Nevertheless, $s$ and $u - 1$ are not the same and differences can be observed. In particular, the difference $s - u$ is not a constant shift, which is more clearly visible in the case of LiH [Fig. 2(b)]. Also, in Si [Fig. 2(a)] $s$ and $u$ show opposite curvatures at $d \sim 2.3$ Å and $u - 1$ is clearly larger than $s$ in the interstitial region. Actually, such differences between $s$ and $u$ indicate that $u$ should be considered as a complementary variable to $s$ and $\alpha$ in the construction of xc-energy density $\varepsilon_{xc}$. The peaks of $\alpha$ are at slightly different positions, which are shifted far away from the nucleus compared to $s$ and $u - 1$.

In summary, we have shown that $u$, as defined by Eq. (2), can be used as a variable in xc functionals to improve the results over the LDA functional. Taking PBE as an example, we have shown that the accuracy of the $u$-dependent functional PBE$_u$ can be made as accurate as the standard GGAs like PBE or PBEsol which depend on $s$. What is remarkable is that $u$ does not depend explicitly on any derivative of the electron density $\rho$, but is able to detect inhomogeneities in $\rho$ pretty much the same way as $s$ does. Furthermore, since $u$ is a more non-local quantity than $s$, it should carry more information and therefore be an useful complement to $s$ and $\alpha$ for the future development of more accurate xc functionals. To finish we would like to mention two points. The first one concerns the dependency of $u$ on $\epsilon_B$ that may lead to a simple way of calculating the derivative discontinuity (relevant for the band gap) with the total energy [40] in the same spirit as it is done with the GLLB potential [41]. The second point concerns the functional derivative of $u$-dependent functionals that is needed for self-consistent calculations. Using chain rule, either $\delta \epsilon_f/\delta \rho$ (in the KS scheme) or $\delta \epsilon_f/\delta \psi^*_i$ (in the generalized KS scheme [42]) would be needed. From Eq. (10), we can see that the calculation of the formers is nontrivial, while the latter seems more amenable and should in our opinion be possible.

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