

Density-gradient-free variable in exchange-correlation functionals for detecting inhomogeneities in the electron density

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An alternative 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 ρ without using derivatives of ρ . 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 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 α used in meta-GGAs, it will be certainly useful for the future development of more accurate exchange-correlation functionals.

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Kohn-Sham density functional theory (KS-DFT) [1,2] is the most 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, particularly when the exchange-correlation (xc) functional E_{xc} is of semilocal type. This allows us to treat up to several thousands of atoms routinely. The semilocal functionals E_{xc} belong to the first three rungs of Jacob's ladder [5] and the xc-energy density ε_{xc} , defined as

$$E_{xc} = \int \varepsilon_{xc}(\mathbf{r}) d^3r, \quad (1)$$

depends locally on properties of the system. In the local density approximation (LDA, first rung of Jacob's ladder) [2], ε_{xc} is a function of the electron density $\rho = \sum_{i=1}^N |\psi_i|^2$, while in the generalized gradient approximation (GGA, second rung of Jacob's ladder) [6,7], ε_{xc} depends on ρ and its first derivative $\nabla\rho$. In meta-GGA (third rung of Jacob's ladder) [8–10], ε_{xc} depends additionally on $\nabla^2\rho$ and/or the 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 (ρ , $\nabla\rho$, τ , etc.) for the construction of an xc functional should increase the overall accuracy, and studies have shown that it is the case (see, e.g., Refs. [10–12] for recent works). For instance, the recent 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 Rapid Communication, we propose an alternative type of approximation for ε_{xc} in Eq. (1), which depends on

$$u(\mathbf{r}) = B \sum_{i=1}^N \sqrt{\epsilon_H - \epsilon_i} \frac{|\psi_i(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})}, \quad (2)$$

where ϵ_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 ϵ_i dependent and, to our knowledge, the only existing xc-energy functionals that depend on the orbital energies ϵ_i are those derived from *ab initio* methods, e.g., perturbation theory or the random phase approximation [18,19]. Actually, u can be expressed as $u = v_{x,\text{resp}}^{\text{GLLB}}/v_{x,\text{resp}}^{\text{HEG}}$, where $v_{x,\text{resp}}^{\text{GLLB}}$ is the approximation to the response term of the exchange potential proposed by Gritsenko *et al.* (GLLB) [20] and $v_{x,\text{resp}}^{\text{HEG}} = k_F/(2\pi)$, where $k_F = (3\pi^2\rho)^{1/3}$, is the exact homogeneous electron gas (HEG) limit of $v_{x,\text{resp}}$. Since $v_{x,\text{resp}}^{\text{GLLB}} \rightarrow v_{x,\text{resp}}^{\text{HEG}}$ 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 density ρ is not constant.

Two interesting features of Eq. (2) should be mentioned: (a) It can detect inhomogeneities in ρ without explicitly using the derivatives of ρ and (b) it does not make the calculation of ε_{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 ρ , e.g., the reduced density gradient

$$s(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{2\rho(\mathbf{r})k_F(\mathbf{r})}, \quad (3)$$

in GGA functionals [21,22], or τ -dependent functions like

$$\alpha(\mathbf{r}) = \frac{\tau(\mathbf{r}) - \tau^{\text{W}}(\mathbf{r})}{\tau^{\text{TF}}(\mathbf{r})}, \quad (4)$$

where $\tau^{\text{W}} = |\nabla\rho|^2/(8\rho)$ and $\tau^{\text{TF}} = (3/10)(3\pi^2)^{2/3}\rho^{5/3}$ are the von Weizsäcker [23] and Thomas-Fermi kinetic-energy density [24,25], that is used in meta-GGAs [26–28]. Note that, similarly as α , $u = 0$ for one- and spin-compensated two-electron systems, such that u can also be used to eliminate the self-interaction error.

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_{coh} . The units of the ME and MAE are Å, GPa, and eV/atom for a_0 , B_0 , and E_{coh} , respectively, and % for the MRE and MARE. All results were obtained non-self-consistently using PBE orbitals/density.

Functional	a_0				B_0				E_{coh}			
	ME	MAE	MRE	MARE	ME	MAE	MRE	MARE	ME	MAE	MRE	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

In the aim of showing the usefulness of u as a variable in xc-energy functionals and its potential interest for improving further the accuracy of fast DFT methods, we construct an xc-energy density ε_{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 ρ [i.e., $\varepsilon_{\text{xc}} = \varepsilon_{\text{xc}}(\rho, u)$] can be similar to the accuracy of GGA functionals [$\varepsilon_{\text{xc}} = \varepsilon_{\text{xc}}(\rho, \nabla\rho)$]. For this we will consider the functional of Perdew, Burke, and Ernzerhof (PBE) [7], 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 $E_{\text{xc}}^{\text{PBE}} = E_{\text{x}}^{\text{PBE}} + E_{\text{c}}^{\text{PBE}}$ 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

$$E_{\text{x}}^{\text{PBE}} = \int \varepsilon_{\text{x}}^{\text{LDA}}(r_s) F_{\text{x}}^{\text{PBE}}(s) d^3r, \quad (5)$$

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

$$F_{\text{x}}^{\text{PBE}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu}{\kappa} s^2} \quad (6)$$

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

$$E_{\text{c}}^{\text{PBE}} = \int [\varepsilon_{\text{c}}^{\text{LDA}}(r_s, \zeta) + H^{\text{PBE}}(r_s, \zeta, t)] d^3r, \quad (7)$$

where $\varepsilon_{\text{c}}^{\text{LDA}}$ is the correlation energy of the HEG [$\zeta = (\rho_{\uparrow} - \rho_{\downarrow})/\rho$ is the relative spin polarization], whose exact analytical form as a function of ρ 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

$$H^{\text{PBE}}(r_s, \zeta, t) = \gamma \phi^3 \ln \left(1 + \frac{\beta}{\gamma} t^2 \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right), \quad (8)$$

where

$$t(\mathbf{r}) = \left(\frac{3\pi^2}{16} \right)^{1/3} \frac{s(\mathbf{r})}{\sqrt{r_s(\mathbf{r})} \phi(\mathbf{r})} \quad (9)$$

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

Our construction of $\varepsilon_{\text{xc}}(\rho, u)$ consists of simply replacing s by $u - 1$ in Eq. (6) for exchange and in Eq. (9) 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 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 ϵ_i which in turn depend *nonlocally* (via the KS equations) on ρ , $\nabla\rho$, etc. [see Eq. (10)]. Thus, it is only for the HEG (i.e., $\nabla\rho = 0 \forall \mathbf{r}$) that one can be sure that $u = 1$. On the other hand, thanks to this nonlocality, u should convey more or different information than s and t . In this respect, we recall that from the KS

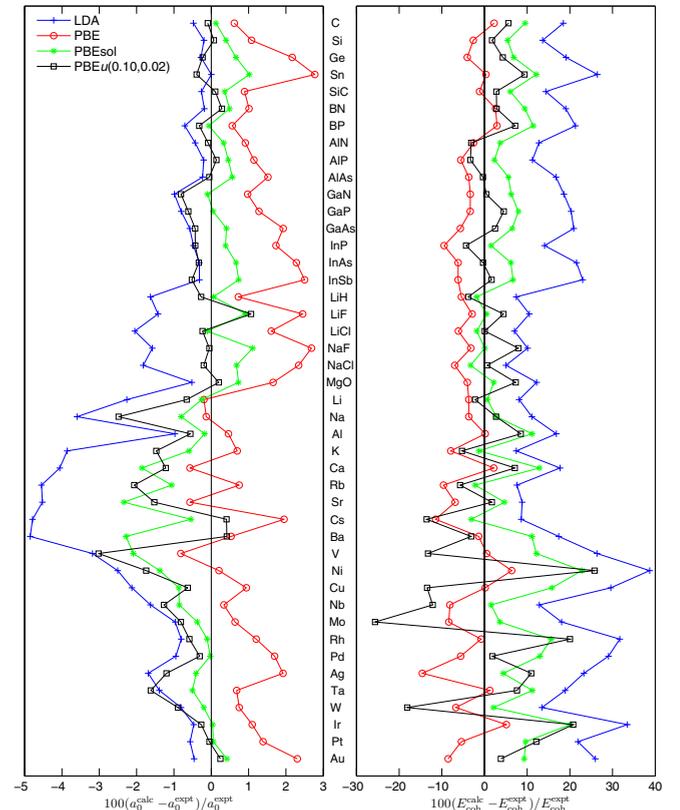


FIG. 1. Relative error (in %) with respect to experiment [37,38] in the calculated lattice constant (left panel) and cohesive energy (right panel) for 44 solids.

equations, the orbital energies can be expressed as

$$\epsilon_i = -\frac{1}{2} \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d^3 r + \int (v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})) |\psi_i(\mathbf{r})|^2 d^3 r, \quad (10)$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential due to the nuclei, $v_{\text{H}}(\mathbf{r}) = \int \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3 r'$ is the Hartree potential, and $v_{\text{xc}}(\mathbf{r})$ is the xc potential. Thus, from Eq. (10) we can see that the expression for ϵ_i involves nonlocal quantities as v_{H} (see Ref. [32] for a v_{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 a technical detail, we mention that depending on the analytical form of the original GGA, negative values of $u - 1$ may lead to problems. 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-free 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)–(9)], however a certain number of variants of PBE which differ in the value of the parameters μ , κ , and β in Eqs. (6) and (8) exist (see, e.g., Refs. [33–36]). 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 (sp semiconductors, ionic insulators, and metals). The calculations were done with the WIEN2k code [39], which is based on the LAPW method [40]. The results are shown in Tables S1–S3 and Figs. S1–S6 of Ref. [41], 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 density ρ

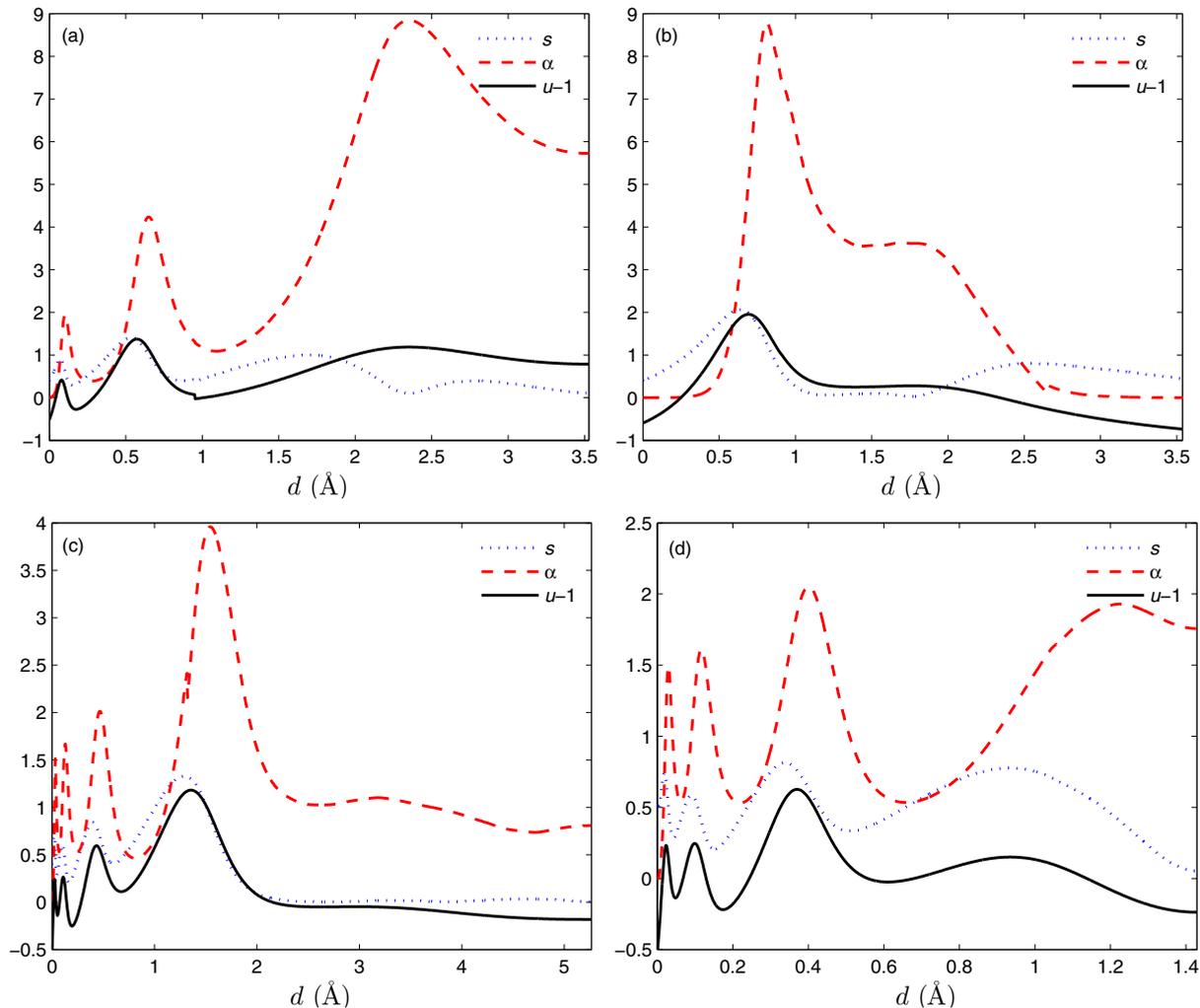


FIG. 2. s [Eq. (3)], α [Eq. (4)], and $u - 1$ [Eq. (2)] in (a) Si from the atom at $(1/8, 1/8, 1/8)$ to $(1/2, 1/2, 1/2)$, (b) LiH from the Li atom at $(0,0,0)$ to the H atom at $(1/2, 1/2, 1/2)$, (c) Sr from the atom at $(0,0,0)$ to $(1/2, 1/2, 1/2)$, and (d) Nb from the atom at $(0,0,0)$ to $(1/4, 1/4, 1/4)$.

and orbitals ψ_i (and ϵ_i) generated by a PBE calculation. We checked that using the density, etc. from LDA leads to negligible changes in the results.

It is known that LDA strongly underestimates (overestimates) the lattice constant (cohesive energy), 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_{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 (7.8 GPa) that are clearly smaller than for PBE. However, PBEsol is less accurate than PBE for E_{coh} (MAE = 0.32 eV/atom).

Turning to the PBE u functional, Table I shows the results obtained with three variants of PBE u , which differ in the values of μ and β in Eqs. (6) and (8), respectively ($\kappa = 0.804$ for all functionals). In PBE u (PBE) and PBE u (PBEsol), the PBE and PBEsol parameters mentioned above are used, while PBE u (0.10,0.02) is a reparametrization with $\mu = 0.10$ and $\beta = 0.02$. For a_0 , PBE u (PBE) and PBE u (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 B_0 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 E_{coh} , PBE u (PBE) and PBE u (PBEsol) are superior to LDA, but clearly inferior to PBE which is the most accurate functional tested in this work for E_{coh} . Thus, by considering overall the MA(R)E for the three properties, PBE u (PBE) and PBE u (PBEsol), which are constructed by just replacing s by $u - 1$, improve over LDA the same way as PBE and PBEsol do.

However, the results with PBE u can be improved by tuning μ and β and a combination, $\mu = 0.10$ and $\beta = 0.02$, leads to errors which are reduced. 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_{coh} , respectively. Thus, the accuracy achieved by PBE u (0.10,0.02) is overall similar to PBEsol accuracy.

Looking in more detail at the results, Fig. 1 shows the results for the lattice constant and cohesive energy. 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 PBE u (0.10,0.02) results. However, PBE u (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 PBE u (0.10,0.02), while for E_{coh} the PBE u (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 PBE u (0.10,0.02) and PBEsol are rather similar for both a_0 and E_{coh} . The most visible exceptions are Na and Ba for a_0 . The PBE u (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 PBE u (0.10,0.02) leads for a few cases to large deviations from experiment. For V, Cu, Nb, Mo, and W, E_{coh} is clearly underestimated, while large overestimations similar to PBEsol are obtained for Ni, Rh, and Ir.

Figure 2 shows plots of s , α , and $u - 1$ for selected solids. We can see that the positions of the peaks in s and u coincide well despite s depends on $\nabla\rho$, while u does not. These similar features explain why substituting s by $u - 1$ in a GGA leads to a functional that can also be much more accurate than LDA. Nevertheless, differences between s and $u - 1$ can also be observed. For instance, $s - u$ is not constant, which is more clearly visible in 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. Actually, such differences indicate that u should be considered as a complementary variable to s and α for functionals development. The peaks of α are at slightly different positions, which are shifted far away from the nucleus compared to s and $u - 1$. However, far from nuclei, where the density tail is, s and $u - 1$ differ drastically. Figure 3 shows their majority-spin component in an isolated Na atom, where we can see that starting from $d \sim 1.5$ Å, s increases (with $\lim_{d \rightarrow \infty} s = \infty$), while u goes to zero.

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

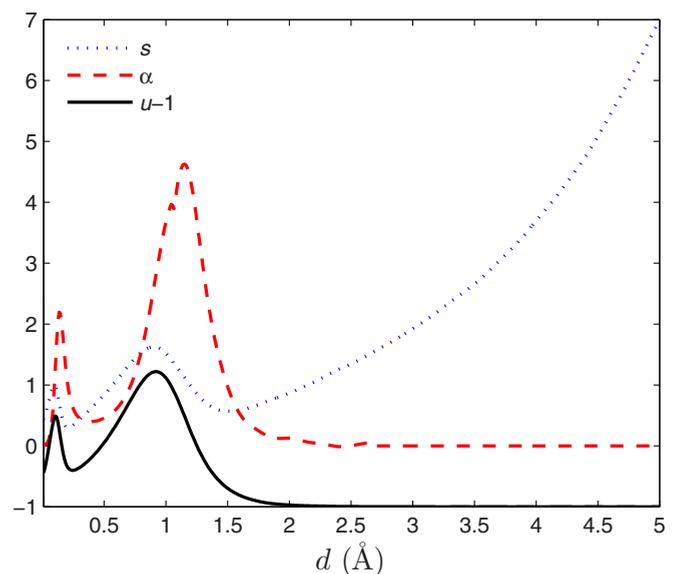


FIG. 3. Majority-spin component of s [Eq. (3)], α [Eq. (4)], and $u - 1$ [Eq. (2)] in an isolated Na atom.

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 density ρ but is able to detect inhomogeneities in ρ pretty much the same way as s does. Furthermore, since u is a more nonlocal quantity than s , it should carry more information and therefore be a useful complement to s and α for the future development of more accurate xc functionals. To finish we mention that the ϵ_{H} dependency may lead to a simple way of calculating the derivative discontinuity (relevant for the band gap) with the total energy [42] in the same spirit as done with the GLLB

potential [43]. Concerning the functional derivative, the use of the chain rule, either $\delta\epsilon_j/\delta\rho$ (in the KS scheme [18]) or $\delta\epsilon_j/\delta\psi_i^*$ (in the generalized KS scheme [44]), would be needed. Either way, its calculation is less straightforward than for semilocal functionals and should require the calculation of the response function. However, how complicated to implement or expensive such a method would be is at present unclear.

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