PHYSICAL REVIEW B **78**, 197101 (2008)

Comment on “More accurate generalized gradient approximation for solids”

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(Received 1 February 2008; revised manuscript received 14 May 2008; published 19 November 2008)

We point out an issue in the derivation of a nonempirical parameter in the Wu-Cohen exchange functional. With the value of the parameter that yields the correct fourth-order gradient expansion of the functional, the performance of the Wu-Cohen exchange functional is worse than the Perdew-Burke-Ernzerhof functional.

DOI: 10.1103/PhysRevB.78.197101 PACS number(s): 71.15.Mb, 71.45.Gm, 77.80.−e

In a recent article,[1] Wu and Cohen developed a generalized gradient approximation (GGA) to the density functional that gives remarkably good performance for lattice constants and bulk moduli for 18 tested solids. Contrary to appearances, the Wu and Cohen (WC) derivation does not yield a functional that recovers the fourth-order gradient expansion. The parameter c was chosen to make the *leading term* in Perdew-Burke-Ernzerhof (PBE) recover the fourth-order expansion, ignoring the higher-order corrections. If, instead, c is chosen to make the final functional recover the fourth-order expansion, the improved performance is lost. We will show the derivation in this comment to clarify this issue.

The spin-scaling relation[2] for exchange energy allows us to just consider the exchange functional for a spin-unpolarized system. In the GGA framework, the exchange energy density per particle can be written as

$$\varepsilon_x(n,s) = \varepsilon_x^{\mathrm{LDA}}(n)F_x(s), \tag{1}$$

where n is the electron density $(n=n_\uparrow+n_\downarrow)$, $s=|\nabla n|/[2(3\pi^2)^{1/3}n^{4/3}]$ is the dimensionless reduced gradient, $\varepsilon_x^{\mathrm{LDA}}(n)$ is the exchange energy density per particle for a uniform electron gas [therefore it is local-density approximation (LDA) for exchange], and $F_x(s)$ is the exchange enhancement factor. For a slowly varying density, F_x has the fourth-order gradient expansion determined by Svendesen and von Barth[3]

$$F_x^{\mathrm{SvB}} = 1 + (10/81)p + (146/2025)q^2 - (73/405)qp + Dp^2 + O(\nabla^6), \tag{2}$$

where $p=s^2$, $q=|\nabla^2 n|/[4(3\pi^2)^{2/3}n^{5/3}]$ is the reduced Laplacian, and D is a coefficient. By using $D=0$ (the best numerical estimate for this coefficient[4]) and $q\approx 2/3p$ [note that this approximation is based on a misinterpretation of Eq. (7) of Ref. 5], Eq. (2) reduces to

$$F_x^{\mathrm{SvB}} = 1 + (10/81)p + [(146/2025)((2/3))^2 - (73/405)(2/3)]p^2 + O(p^3). \tag{3}$$

Since $p^2=s^4$, the p^2 term is the fourth-order term in s. The coefficient of p^2 in Eq. (3) is the target of the construction of the WC exchange functional because the Wu-Cohen paper says “the parameter c is set to recover the fourth-order parameters in Eq. (5) for small s.” Their Eq. (5) is our Eq. (2).

In general one does not use truncated density-gradient expansions (DGEs) such as Eq. (2) directly because higher-order terms are sometimes important in the range of s values that play a significant role in real systems. Furthermore, the truncated expansions do not satisfy certain global constraints on the accurate density functional. Instead one chooses a more general global approximation for F_X and determines its parameters in other ways;[6] this is the essence of a GGA. The WC exchange functional is based on the PBE exchange functional. The PBE (Ref. 7) enhancement factor for exchange is

$$F_x^{\mathrm{PBE}} = 1 + \kappa\left(1 - \frac{1}{1+\dfrac{x}{\kappa}}\right), \tag{4}$$

where $x=\mu s^2=\mu p$. The parameter μ is set to be 0.219 51 in F_x^{PBE}; this value is derived by recovering the LDA linear response, i.e., the second-order exchange gradient correction cancels the second-order correlation gradient correction as $s\to 0$. Note that this choice of μ in PBE exchange violates the second-order term in the DGE of Eq. (2), and μ should be set to $10/81$ to recover the second-order DGE, as done in PBEsol by Perdew *et al.*[8] recently. The parameter κ is set to be 0.804 in F_x^{PBE}, which is determined by ensuring satisfaction of the Lieb-Oxford bound.[9]

Wu and Cohen use the same functional form [our Eq. (4)] and parameters (μ and κ) as in PBE exchange but a complicated ansatz for x:

$$x^{\mathrm{WC}} = (10/81)s^2 + [\mu - (10/81)]s^2\exp(-s^2) + \ln(1+cs^4). \tag{5}$$

They determine the value of c by trying to recover the coefficient of p^2 in Eq. (3). To accomplish this, Wu and Cohen set the parameter c in Eq. (5) to be

$$\begin{aligned} c^{\mathrm{WC}} &= [(146/2025)((2/3))^2 - (73/405)(2/3)] + [\mu - (10/81)] \\ &= 0.007\,932\,5. \end{aligned} \tag{6}$$

However, Eq. (6) does not recover the fourth-order term in the density functional. A Taylor expansion of x^{WC} gives

$$x^{\mathrm{WC}} \approx \mu p + [(146/2025)((2/3))^2 - (73/405)(2/3)]p^2 + O(p^3). \tag{7}$$

Substituting x^{WC} in Eq. (4) to obtain F_x^{WC} and making a Taylor expansion of F_x^{WC} gives

$$F_x^{\mathrm{WC}} = 1 + \mu p + [(146/2025)((2/3))^2 - (73/405)(2/3) - (\mu^2/\kappa)]p^2 + O(p^3). \tag{8}$$

Equation (8) clearly shows that the WC exchange functional

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does not recover the DGE value of the coefficient of p^2 in Eq. (3). The correct value of c to recover the fourth-order expansion in Eq. (3) is

$$\begin{aligned} c' &= [(146/2025)((2/3))^2 - (73/405)(2/3)] \\ &\quad + [\mu - (10/81)] + (\mu^2/\kappa) \\ &= 0.067\,864. \end{aligned} \tag{9}$$

We calculated the lattice constants for three solids, namely, K, NaCl, and Si, with the value of c' given in Eq. (9) by using a locally modified GAUSSIAN03 code[10] with the Gaussian basis sets used in a previous study of Staroverov *et al.*[11] and with 1000 **k** points for Si and NaCl and 12 000 **k** points for K. The results are listed in Table I, along with the results for PBE and the original WC functional from Ref. 1. Table I shows that the original WC exchange functional has much better performance for lattice constants than using the value of c in Eq. (9), although the value of c^{WC} does not yield the functional correct through fourth order. Table I also shows that with $c=c'$ the value of c that makes the resulting functional obey the stated condition; the Wu-Cohen functional performs worse than the original PBE functional. We conclude that enforcing the correct fourth-order term in the DGE does not lead to improved results for real systems. The success of the original WC functional is therefore judged to be empirical or fortuitous.

TABLE I. Calculated and experimental equilibrium lattice constants a_0 (in Å) of three solids.

	PBE[a]	$c^{\mathrm{WC}}=0.007\,932\,5$ [a]	$c'=0.067\,864$	Expt.[b]
K	5.295	5.246	5.403	5.212
NaCl	5.700	5.622	5.768	5.580
Si	5.475	5.433	5.504	5.423

[a] The data for PBE and c^{WC} are from Ref. 1.

[b] From Ref. 11, with estimates of the zero-point anharmonic expansion removed to yield classical equilibrium value.

This work was supported in part by the Office of Naval Research.

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