Reply to "Comment on 'More accurate generalized gradient approximation for solids'"

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In a recent paper [Z. Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006)], we proposed an exchange functional model that better describes crystal structures than that of the Perdew-Burke-Ernzerhof ansatz. In this reply we address the issue raised by Zhao and Truhlar in their comment by emphasizing the rationale of the model.

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Our functional[1] was designed to be an improvement over Perdew-Burke-Ernzerhof (PBE) for solids, by modifying its large reduced gradient (s) behavior. It does not recover the fourth-order gradient expansion for exchange, nor was it intended to. Zhao and Truhlar[2] are correct in this, but have misunderstood our model. We didn't derive the parameter c by enforcing the correct fourth-order terms in $F_X(s)$ for $s \to 0$, as they claim; instead, we adopted parameter c so that the core part of the PBE-style[3] ansatz, x, has the same fourth-order term as that in $F_X^{\mathrm{SvB}}(s)$ by Svendsen and von Barth.[4] However, in the original paper[1] we didn't point this out explicitly, causing the misunderstanding. The failure when this condition is enforced is not surprising, and does not imply that the original model's success is fortuitous.

Our approach is consistent with the generalized gradient approximation (GGA) formalism; even enforcing the exact fourth-order term does not always lead to worse performance. Inspired by our ansatz, Madsen[5] recently constructed a F_X which satisfies this condition when its parameter $\alpha = 0.52$. This latter functional also generally predicts better lattice constants of solids than the PBE.

The rationale of our exchange functional is to construct an exchange enhancement factor F_X based on the gradient expansion of a real-space cutoff of the exchange hole with a *diffuse* tail,[6] in contrast to a *sharp* cutoff used in the PW91 modeling[7] (PBE is a simple numerical fit to PW91 for $s \lesssim 3.0$). In solids, the diffuse cutoff of the exchange hole is often more realistic than the sharp one. As seen in the inset of Fig. 1 in our paper, for $s \lesssim 1.0$, $F_X^{\mathrm{sharp}}(s) \simeq F_X^{\mathrm{diffuse}}(s)$; for $s \gtrsim 1.0$, $F_X^{\mathrm{sharp}}(s) > F_X^{\mathrm{diffuse}}(s)$.

Inspired by the format of the diffuse cutoff factor $[1+(u/u_0)^2]\exp[-(u/u_0)^2]$ proposed in Ref. 6 and using the PBE ansatz,

$$F_X = 1 + \kappa - \kappa/(1 + x/\kappa), \tag{1}$$

we constructed our x functional

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

As emphasized in our paper, we retained the second-order parameter μ [instead of $\frac{10}{81}$ in $F_X^{\mathrm{SvB}}(s)$] for small s, but made the difference, $\mu - \frac{10}{81}s^2$, damping exponentially with increasing s. This results in a smaller F_X than F_X^{PBE} for $s \gtrsim 1.0$. The parameter c is determined by forcing x (not F_X) to have the same fourth-order term of F_X^{VsB}. In the PBE ansatz, the Taylor expansion is

$$F_X^{\mathrm{PBE}} = 1 + x + O(x^2). \tag{3}$$

Zhang and Truhlar are correct that the fourth-order term in F_X^{WC} is not the same as that in F_X^{VsB} because x^2 also has a fourth-order term, $\frac{\mu^2}{\kappa}s^4$, which is the same as that in the original F_X^{PBE}. In our construction of x for small s, we simply added the fourth-order term in F_X^{SvB} to x of PBE (which is μs^2) because we mostly focused on correcting F_X in the $s \gtrsim 1.0$ range, where the fourth- and higher-order terms in x dominate the behavior of F_X^{WC}. For small s, our functional essentially reduces to F_X^{PBE}. As seen in Fig. 1 of our original paper, F_X^{WC} nearly overlaps with that of the Tao-Perdew-Staroverov-Scuseria meta-GGA[8] for slowly varying densities. The success of our functional cannot be regarded as fortuitous.

More recently, Madsen[5] derived the second- and fourth-order Taylor expansion of F_X^{WC}, implicitly indicating that the fourth-order term of F_X^{WC} is not the same as that of F_X^{SvB}. This

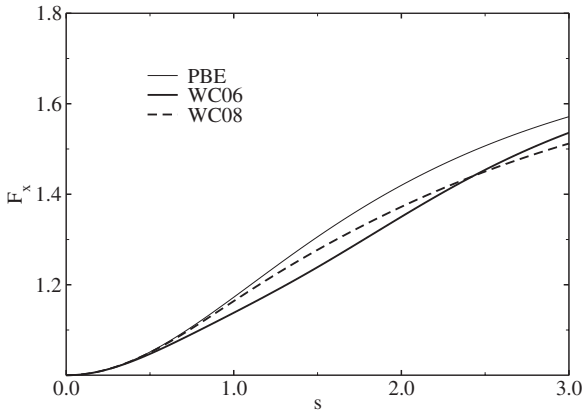

FIG. 1. Exchange enhancement factors F_X as functions of the reduced gradient s.

functional also predicts better lattice constants of solids than the PBE.

We can propose a slightly different functional (WC08) to enforce the exact fourth-order term:

$$x = (10/81)s^2 + [\mu - (10/81)]s^2 \exp(-s^2) + c_2 \ln(1 + s^4), \quad (4)$$

where $c_2 = 0.067864$. As shown in Fig. 1, F_X^{WC08} is between F_X^{PBE} and the original F_X^{WC} (F_X^{WC06}) for $s < 2.4$; for larger s, $F_X^{\mathrm{WC08}} < F_X^{\mathrm{WC06}}$. Although WC08 performs a little worse than WC06 for solid lattice constants, it is better than the PBE.

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