PHYSICAL REVIEW B **75**, 195108 (2007)

Functional form of the generalized gradient approximation for exchange: The PBEα functional

Georg K. H. Madsen*
Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

(Received 18 August 2006; revised manuscript received 14 November 2006; published 9 May 2007)

A functional form for the exchange enhancement in the generalized gradient approximation within density-functional theory is given. It satisfies the constraints used to construct the Perdew-Burke-Ernzerhof (PBE) functional but can be systematically varied using one parameter called α. This gives the possibility to estimate the reliability of a computational result or to fit the parameter for a certain problem. Compared to other semiempirical functionals, the present has the advantage of using only one physically transparent parameter and the fitted functional will obey the same exact conditions as PBE functional. One functional is constructed by fixing α using the exchange enhancement for the slowly varying electron gas. This functional is free of empirical parameters and gives good results for densely packed solids. The simple form of the exchange enhancement means that oscillating terms in the exchange potential are avoided.

DOI: 10.1103/PhysRevB.75.195108 PACS number(s): 71.15.Mb, 61.50.Ah

I. INTRODUCTION

Density-functional theory (DFT) has made it possible to calculate ground-state properties of even very large systems efficiently and accurately. As the exact functional is unknown, practical applications of DFT require an approximate exchange-correlation energy, $E_{xc}[n]$.[1] Of these, the local-spin-density approximation[1–3] (LDA) has been successful despite its simplicity. The generalized gradient approximations (GGAs) are an attempt to improve on the LDA. It is possible to construct a GGA free of empirical parameters, known as the Perdew-Burke-Ernzerhof (PBE)-GGA, by demanding that the GGA obey certain fundamental constraints.[4] Numerical tests have shown that the PBE-GGA gives total-energy-dependent properties in good agreement with experiment.[5,6] Consequently, the PBE-GGA functional has been extremely influential, both for performing actual calculations and as a basis for functionals involving higher derivatives and exact exchange.[7]

As both the density and the gradient can only be constant in the homogeneous electron-gas limit, there can be no unique GGA (Ref. 8) and the constraints of the PBE-GGA are not sufficient to uniquely define the functional. The PBE functional form was based on a numerical GGA,[9,10] where a model of the exchange correlation hole was constructed to satisfy known exact hole constraints. The constraints were satisfied using a sharp real-space cutoff and a damping function and different choices would lead to different functionals.[10] This was recently demonstrated by Wu and Cohen (WC),[11] who used the gradient expansion for slowly varying densities[12] to construct a GGA with a functional form corresponding to a diffuse cutoff.[11] The WC-GGA damps the gradient enhancement, which results in improved equilibrium volumes for densely packed solids, but poorer exchange energies of atoms compared to the PBE.[11] Another modification of the PBE, the RPBE,[13] chooses a functional form with a larger gradient enhancement, which generally leads to very good atomic exchange energies but poor equilibrium volumes of solids.[5] The PBE, RPBE, and WC functionals differ only in the functional form of the exchange energy enhancement and all satisfy the same conditions as the PBE.

A different approach has been to construct GGAs as parametrized fits (see Kurth *et al.*[5] for an overview). These semiempirical functionals are often precise for a certain set of compounds, but the parameters are rarely physically transparent, and it is consequently not clear when they could fail. Furthermore, they generally violate the known exact conditions satisfied by the PBE-GGA. This paper introduces a functional form that brings the WC, PBE, and RPBE exchange functionals onto a common ground and allows semiempirical functionals to be constructed. The shape of the functional is controlled by one physically transparent parameter and in the construction of the functional, it is ensured that the exact conditions of PBE are not violated.

II. BACKGROUND

A. Exchange enhancement

The GGAs write the exchange energy density per particle as

$$\epsilon_x(n,s) = \epsilon_x(n)F_x(s) \tag{1}$$

where $\epsilon_x(n)$ is the LDA exchange energy density per particle. F_x is the enhancement factor due to density gradients and is dependent on the reduced density gradient, $s=\frac{|\nabla n(\mathbf{r})|}{2(3\pi^2)^{1/3}n(\mathbf{r})^{4/3}}$. The PBE enhancement factor is given as

$$F_x^{PBE}(x) = 1 + \kappa\left(1 - \frac{1}{1 + x/\kappa}\right), \tag{2}$$

where $x=\mu p$ and $p=s^2$. The parameters of Eq. (2), $\mu=0.2195$ and $\kappa=0.804$, are determined to ensure that the exchange gradient correction cancels that for PBE correlation as $s\rightarrow 0$ and to ensure that the local Lieb-Oxford bound is obeyed.[4] The RPBE functional differs in the functional form

$$F_x^{RPBE}(x) = 1 + \kappa(1 - e^{-x/\kappa}), \tag{3}$$

while the WC functional retains the functional form of PBE but introduces a complicated $x^{WC}=10/81p+(\mu-10/81)pe^{-p}+\ln(1+cp^2)$.[11]

Obviously, the WC, PBE, and PRBE functionals satisfy the local Lieb-Oxford bound. By Taylor expanding F_x for

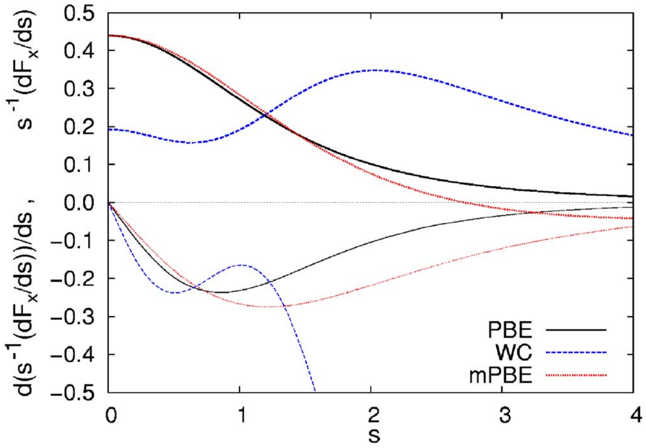

FIG. 1. (Color online) Derivatives of the exchange enhancement that enter the exchange potential [Eq. (7)]. Lines for PBE, WC, and mPBE F_x are shown. The thick lines are for the $s^{-1}\frac{dF_x}{ds}$ term and the thin lines for the $\frac{d}{ds}\left(s^{-1}\frac{dF_x}{ds}\right)$ term.

$p \rightarrow 0$, it is clear that all three exchange functionals have the correct first-order expansion, $F_x = 1 + \mu p + O(p^2)$, and thus obey the cancellation condition,

$$F_x^{PBE} = 1 + \mu p - \frac{\mu^2}{\kappa} p^2 + O(p^3), \tag{4}$$

$$F_x^{RPBE} = 1 + \mu p - \frac{1}{2}\frac{\mu^2}{\kappa} p^2 + O(p^3), \tag{5}$$

$$F_x^{WC} = 1 + \mu p - \left(\frac{\mu^2}{\kappa} + \mu - 10/81 - c\right) p^2 + O(p^3). \tag{6}$$

The exchange-correlation potential is an important quantity in judging the quality of a functional.[14] According to Perdew and Wang,[9] a GGA exchange potential can be calculated as

$$v_x = \frac{dE_x}{dn} = \epsilon_x\left[\frac{4}{3}F_x - q\left(s^{-1}\frac{dF_x}{ds}\right) - \left(u - \frac{4}{3}s^3\right)\frac{d}{ds}\left(s^{-1}\frac{dF_x}{ds}\right)\right], \tag{7}$$

where $u = (2k_F)^{-3} n^{-2} \nabla n \cdot \nabla |\nabla n|$. The potential thus depends on both the first and second derivatives of the enhancement form. In Fig. 1, the terms $s^{-1}\frac{dF_x}{ds}$ and $\frac{d}{ds}\left(s^{-1}\frac{dF_x}{ds}\right)$ from PBE and WC are shown. It can be seen that the WC terms, due to the complicated form of x_2, have an oscillating behavior.

An attempt at systematically varying the PBE functional, called the mPBE, has also been made by expanding the enhancement functional.[15] The mPBE could only ensure the local Lieb-Oxford through a fitting constraint. Furthermore, Fig. 1 shows how the F_x^{mPBE} potential terms change sign and converge very slowly to zero. The slow convergence is potentially problematic as this term is multiplied by an s^3 term, which diverges for large s. Though GGAs, in general, do not have the correct $1/r$ asymptotic decay, the mPBE does not correct this problem and the effect is an artifact of the construction of the functional form. Varying the κ parameter has also been attempted[16,17] but these functionals can violate the local Lieb-Oxford bound.

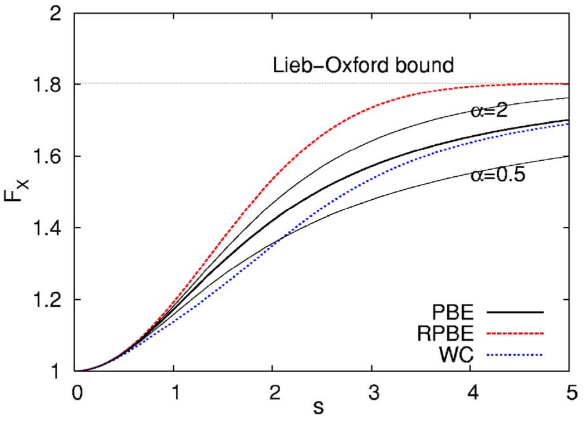

FIG. 2. (Color online) Exchange enhancements F_x due to density gradients. The PBE, RPBE, and WC functionals are shown with thick lines. Two PBEα functionals are shown with thin lines and marked with the α used.

III. THE PBEα

The exchange enhancement, named PBEα, presented here has the form

$$F_x^{PBE\alpha} = 1 + \kappa\left\{1 - \frac{1}{[1 + x_1/(\kappa\alpha)]^{\alpha}}\right\}, \tag{8}$$

where α is a parameter. The Taylor expansion

$$F_x^{PBE\alpha} = 1 + \mu p - \frac{\alpha + 1}{2\alpha}\frac{\mu^2}{\kappa} p^2 + O(p^3) \tag{9}$$

shows that PBEα satisfies the cancellation condition for all α. The PBE and RPBE are then special cases of PBEα=1 and PBE$\alpha \rightarrow \infty$, respectively.

The inspiration for the WC functional[11] was the F_x expansion of the slowly varying density,[12]

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

where $D \approx 0$ and $q = \frac{\nabla^2 n}{4k_F^2 n} = \frac{\nabla^2 n}{4(3\pi^2)^{2/3} n^{5/3}}$. The Laplacian terms were avoided by introducing the approximation: $q \approx 2/3p$. Introducing this approximation into Eq. (10), one obtains $F_x^{SvB} \approx 1 + 10/81p - 0.0881p^2$. From Eq. (9), it is seen that if one sets $\alpha = 0.52$ in the PBEα functional, the same second-order term is obtained. The $\alpha = 0.52$ form will be tested and compared to the WC form in the following. Furthermore, it will be shown how the PBEα form can be used to estimate the reliability of a computational result. The PBEα functional is shown for two different α in Fig. 2.

IV. DISCUSSION

In the following, the influence of the parameter α will be discussed. All calculations have been performed using the

TABLE I. Atomic exchange energies in Ha. The X-OEP marks the optimized effective potential values taken from Kurth *et al.* (Ref. 5) MARE is the mean absolute relative error in %.

	X-OEP	WC	$\alpha=0.52$	$\alpha=1$	$\alpha=2$	$\alpha=5$	$\alpha=20$	RPBE
He	−1.0258	−0.9805	−0.9916	−1.0051	−1.0145	−1.0212	−1.0249	−1.0262
Ne	−12.1050	−11.8676	−11.9597	−12.0275	−12.0716	−12.1015	−12.1176	−12.1231
Ar	−30.1747	−29.6846	−29.8646	−29.9814	−30.0551	−30.1039	−30.1299	−30.1388
Kr	−93.8330	−92.8559	−93.1862	−93.3769	−93.4925	−93.5671	−93.6060	−93.6193
Xe	−179.0635	−177.5052	−177.9762	−178.2368	−178.3923	−178.4914	−178.5428	−178.5602
MARE		1.98	1.37	0.85	0.50	0.26	0.18	0.16

WIEN2K code.[18] The basis sets and k meshes have been converged and equations of states (EOSs) have been found by fitting the stabilized jellium EOS (Ref. 19) to the calculated total energies.

A. Limits of α

The good performance of the RPBE for atoms and WC for densely packed solids can give the impression that these functionals form the upper and lower bounds of the gradient enhancement. The RPBE performs extremely well for the exchange energy of atoms which would indicate that there is no upper limit for α. This is shown in Table I where mean absolute relative error (MARE) decreases with α.

If exponentially decaying densities in atoms constitute one extreme, the other extreme is the slowly varying density. In Tables II and III, the equilibrium volumes and bulk moduli of 18 solids[6,11,20] calculated with the PBEα=0.52 functional are given and compared to the results of the LDA, PBE, RPBE, and WC functionals. It can be seen that the PBEα=0.52 functional gives results that are similar to the WC functional, being slightly worse on the equilibrium volumes and slightly better on the bulk moduli. The performance of PBEα=0.52 thus confirms the importance of the expansion in Eq. (10) for densely packed solids.

B. Influence of α

The influence of the parameter α can be illustrated by comparing the body-centered-cubic (bcc) phase of Fe with the hexagonal close packed (hcp) phase. The example is well studied and it is known that LDA wrongly predicts the nonmagnetic fcc phase to be stable at zero pressure.[21] EOS parameters have been calculated for bcc and hcp iron using LDA and PBEα for three choices of α (Table IV). Using the EOS parameters, bcc-hcp phase transition pressures of 14.0, 16.4, and 18.3 GPa are predicted for PBEα=0.8, α=1.0, and α=1.2, respectively, in reasonable agreement with a recent experimental study which fixed the transition pressure between 14 and 16 GPa.[22]

The iron example shows how the α parameter can be interpreted. A small α favors the close-packed structure (in the extreme case of the LDA the HCP structure is predicted to be stable at ambient pressure), while a large α favors an open structure. This also illustrates the dangers of fitting α for a certain problem. If one uses a data set of densely packed structures and obtains a small α, the results can be biased towards the densely packed structures. If one uses a data set of open structures (or in the extreme: atoms) and obtains a large α, the results can be biased toward the open structures. Often, it is probably better to use the well-tested PBEα=1.0 functional. However, varying α will provide information on how sensitive the results obtained are to variations of the functional. Such a philosophy was also recently proposed in a statistical study of the exchange enhancement.[23] The PBEα functional is probably better suited for this approach than the form actually used, which was similar to the mPBE.[15,23]

TABLE II. Volume of the primitive unit cell (in a_0^3). MRE is mean relative error. STD is the standard deviation of the relative error. MARE as in Table I. All errors are in %.

Solid	V_0^{expt}	V_0^{LDA}	V_0^{PBE}	V_0^{RPBE}	V_0^{WC}	$V_0^{PBE\alpha=0.52}$
Li	141.83	128.32	136.68	142.10	138.37	134.13
Na	255.48	224.17	249.50	266.49	249.48	241.37
K	481.31	432.57	501.21	545.80	497.04	479.00
Al	110.59	106.66	111.37	113.50	109.66	110.16
C	76.57	74.50	77.03	78.13	75.89	76.36
Si	270.11	266.22	274.41	281.58	270.79	273.59
SiC	139.64	136.93	141.88	144.06	139.56	140.58
Ge	304.61	300.20	322.97	332.33	309.20	316.80
GaAs	303.96	297.43	320.53	330.42	306.63	314.20
NaCl	295.48	275.22	312.64	337.12	300.86	300.10
NaF	165.18	153.52	175.11	188.37	169.36	168.36
LiCl	224.58	207.45	231.84	247.88	220.74	223.53
LiF	108.79	100.70	113.23	120.31	108.72	109.41
MgO	125.62	121.69	130.35	134.72	126.71	127.93
Cu	78.91	73.56	80.58	83.44	76.74	78.80
Rh	92.43	89.95	95.29	96.94	92.45	94.11
Pd	98.62	95.82	103.19	105.93	99.05	101.43
Ag	113.66	107.88	119.31	124.57	112.49	116.19
MRE		−5.26	2.88	7.32	−0.03	0.52
STD		3.30	2.76	4.22	1.70	2.56
MARE		5.26	3.54	7.32	1.32	1.93

TABLE III. Bulk moduli B_0 (in GPa). MRE, STD, and MARE as in Table II.

Solid	B_0^{expt}	B_0^{LDA}	B_0^{PBE}	B_0^{RPBE}	B_0^{WC}	$B_0^{PBE\alpha=0.52}$
Li	13.0	15.06	14.01	13.51	13.39	14.40
Na	7.5	9.19	7.71	6.97	7.48	8.15
K	3.7	4.49	3.62	3.35	3.42	3.82
Al	79.4	82.68	76.49	74.43	79.08	77.90
C	443	467.35	432.44	417.49	449.20	441.77
Si	99.2	95.13	87.78	83.95	92.74	90.07
SiC	225	228.70	211.76	204.53	220.72	216.42
Ge	75.8	72.40	59.42	54.07	67.62	62.89
GaAs	75.6	74.50	60.93	55.44	69.42	64.71
NaCl	26.6	32.76	24.32	20.56	24.88	26.77
NaF	51.4	63.65	46.73	40.14	47.08	51.12
LiCl	35.4	42.04	31.81	26.22	35.46	35.20
LiF	69.8	90.66	71.73	65.07	74.12	76.50
MgO	165	173.41	147.76	135.70	156.54	154.80
Cu	142	193.22	143.93	125.90	170.78	156.13
Rh	269	320.43	263.74	245.63	295.16	276.47
Pd	195	241.40	180.36	159.76	214.94	194.81
Ag	109	146.51	96.64	76.98	126.06	109.79
MRE		15.27	−6.17	−14.84	0.61	−0.43
STD		13.04	7.61	9.52	8.82	7.81
MARE		16.39	7.81	15.27	6.80	5.57

TABLE IV. Equation of state parameters for bcc and hcp iron.

		$E_0-E_0^{bcc}$ (mRy/atom)	V_0 (a_0^3/atom)	B_0 (GPa)	B_0'
BCC	LDA	0.00	70.19	250.69	4.97
	PBEα=0.8	0.00	76.18	190.69	5.29
	PBEα=1.0	0.00	76.45	188.11	5.32
	PBEα=1.2	0.00	77.03	182.34	5.33
HCP	LDA	−9.76	64.80	337.72	4.30
	PBEα=0.8	6.15	68.81	288.06	4.52
	PBEα=1.0	7.25	69.10	285.63	4.53
	PBEα=1.2	8.10	69.30	282.70	4.54

V. CONCLUSION

A functional form for GGAs, which can be systematically varied by the parameter α, has been proposed. One can thereby combine the virtues of semiempirical GGAs, high precision for a specific set of compounds, with the virtues of PBE, obeying the same exact constraints as the PBE. Compared to other semiempirical functionals, it is an advantage that only one parameter is used. The parameter has clear interpretation, which can be used to check whether results are biased toward densely packed or open systems. One further advantage of the PBEα is that the simple construction of the functional form leads to a smooth exchange potential.

The limited amount of information in the gradient of the density makes it impossible to make a GGA functional that works equally well for all cases. On higher rungs of the DFT ladder,[7] such as the meta-GGAs, this could be possible. The extra information has been included by making the x dependent on more variables[20] or by improving the exchange hole model.[24] A different route could be to make α be determined by the density and not be the same everywhere in space. One could, e.g., use that for an exponentially decreasing density $q/p=1$ to identify regions where α should be large. Another idea which does not involve higher derivatives was put forward by Wu and Cohen,[11] who suggested making the exchange enhancement dependent directly on the density $[F_x(n,s)]$.

A subroutine implementing the PBEα can be found on Ref. 25.

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*Electronic address: georg@chem.au.dk

[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[3] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[5] S. Kurth, J. P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).

[6] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B **69**, 075102 (2004).

[7] J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, J. Chem. Phys. **123**, 62201 (2005).

[8] J. P. Perdew, M. Ernzerhof, A. Zupan, and K. Burke, J. Chem. Phys. **108**, 1522 (1998).

[9] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, R8800 (1986).

[10] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1996).

[11] Z. Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006).

[12] P. S. Svendsen and U. von Barth, Phys. Rev. B **54**, 17402 (1996).

[13] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).

[14] K. Burke, F. G. Cruz, and K.-C. Lam, J. Chem. Phys. **109**, 8161 (1998).

[15] C. Adamo and V. Barone, J. Chem. Phys. **116**, 5933 (2002).

[16] Y. Zhang and W. Yang, Phys. Rev. Lett. **80**, 890 (1998).

[17] E. L. Peltzer y Blancá, C. O. Rodríguez, J. Shitu, and D. L. Novikov, J. Phys.: Condens. Matter **13**, 9463 (2001).

[18] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, Austria, 2001).

[19] A. B. Alchagirov, J. P. Perdew, J. C. Boettger, R. C. Albers, and C. Fiolhais, Phys. Rev. B **63**, 224115 (2001).

[20] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).

[21] L. Stixrude, R. E. Cohen, and D. J. Singh, Phys. Rev. B **50**, 6442 (1994).

[22] F. Baudelet, S. Pascarelli, O. Mathon, J. P. Itié, A. Polian, M. d'Astuto, and J. C. Chervin, J. Phys.: Condens. Matter **17**, 957 (2005).

[23] J. J. Mortensen, K. Kaasbjerg, S. L. Frederiksen, J. K. Nørskov, J. P. Sethna, and K. W. Jacobsen, Phys. Rev. Lett. **95**, 216401 (2005).

[24] M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **111**, 911 (1999).

[25] http://www.chem-au.dk/~webuorg/georg