

## Comment on "Generalized Gradient Approximation Made Simple"

In their recent Letter, Perdew, Burke, and Ernzerhof (PBE) [1] present a simplified version of the generalized-gradient approximation exchange-correlation functional,

TABLE I. Atomic total energies of atoms and atomization energies of molecules. Self-consistent Kohn-Sham density functional calculations using our DFT program [5] are performed for these molecules at experimental geometries and atoms. "Nonspherical corrections" [6] have been made for all atoms except H, Li, He, and Ne. The exact nonrelativistic atomic total energies are taken from Ref. [7]. The experimental geometries and atomization energies of molecules (with zero point energies removed) are the same as in Ref. [1]

Atom	Atomic total energies (hartree)		Exact
	PBE	revPBE	
He	-2.893	-2.908	-2.904
Li	-7.462	-7.487	-7.478
Be	-14.631	-14.666	-14.667
B	-24.613	-24.656	-24.654
C	-37.798	-37.847	-37.845
N	-54.536	-54.591	-54.589
O	-75.013	-75.075	-75.067
F	-99.675	-99.740	-99.734
Ne	-128.866	-128.936	-128.939
Mean abs. error	0.043	0.004	...

Molecule	Molecule atomization energies (kcal/mol)		Expt.
	PBE	revPBE	
H2	104.5	105.3	109.2
LiH	53.5	53.1	57.8
CH4	419.2	410.9	419.3
NH3	301.0	293.4	297.4
OH	109.5	106.3	106.4
H2O	233.8	227.2	232.2
HF	141.7	137.8	140.8
Li2	19.7	19.0	24.4
LiF	139.5	134.3	138.9
Be2	9.5	7.5	2.6
C2H2	412.9	400.1	405.4
C2H4	570.2	555.0	562.6
HCN	324.5	313.5	311.9
CO	267.6	258.1	259.3
N2	241.2	231.8	228.6
NO	169.7	160.5	152.9
O2	141.7	132.6	120.5
F2	51.9	45.0	38.5
P2	117.2	111.0	117.3
Cl2	63.1	59.0	58.0
CO2	414.0	396.3	389.0
SO	133.2	124.9	125.2
CN	195.8	187.2	179.1
Mean abs. error	8.1	4.9	...
Maximum abs. error	25.0	12.1	...

which improves six shortcomings over the previous Perdew-Wang 1991 (PW91) functional. The authors claim that all parameters (other than those in local spin density) in PBE are fundamental constants; however, there remains a flexibility in the value of  $\kappa$  in the exchange functional which has the form originally proposed by Becke with empirical coefficients ( $\kappa = 0.967, \mu = 0.235$ ) [2]. In [1],  $\kappa$  is fixed by the *local* Lieb-Oxford bound [ $\epsilon_x(\mathbf{r}) \geq -1.68\rho^{4/3}(\mathbf{r})$  for all  $\mathbf{r}$ ], which is a sufficient but not necessary criterion to satisfy the *integrated* Lieb-Oxford bound [3]. We point out that instead of the value of 0.804 in Ref. [1], choosing a new value of 1.245 for  $\kappa$  can improve significantly over the original PBE [1] in both atomic total energies and molecule atomization energies. Here, we obtain this new value of  $\kappa$  by fitting exchange-only total atomic energies (from He to Ar) to exact exchange-only results from the optimized exchange potential method [4]. This revised version is labeled as "revPBE" in Table I.

The revPBE improves PBE's atomic total energies by a factor of 10. For molecular atomization energies, revPBE reduces the maximum absolute error of PBE from 25.0 to 12.1 kcal/mol, and reduces the mean absolute error from 8.1 to 4.9 kcal/mol. These results are encouraging.

For spin-nonpolarized densities, the revPBE still respects the *local* Lieb-Oxford bound. For spin-polarized densities, it is not the case. Instead, it obeys a weaker local bound which is obtained from scaling the spin-unpolarized bound. However, for all spin-polarized systems listed in Table I, revPBE results are well within the *integrated* Lieb-Oxford bound: Numerical results indicate that the values of the Lieb-Oxford bound are almost twice the exchange energies from revPBE. We can expect this observation to hold for most real systems including atoms, molecules, and solids.

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Received 2 June 1997 [S0031-9007(97)05082-5]  
PACS numbers: 71.15.Mb, 71.45.Gm

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