

Construction of an optimal GGA functional for molecules and solids

Philipp Haas, Fabien Tran, Peter Blaha, and Karlheinz Schwarz

Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

(Received 12 April 2011; published 19 May 2011)

The specialized exchange-correlation functionals of Wu and Cohen [*Phys. Rev. B* **73**, 235116 (2006)] (WC) and Hammer *et al.* [*Phys. Rev. B* **59**, 7413 (1999)] [revised Perdew, Burke, and Ernzerhof (RPBE)] yield good results for either the lattice constants of solids or the atomization energies of molecules, respectively, but are rather poor for the opposite quantity. By combining the WC and RPBE functionals, we construct a functional that performs equally well for both molecules and solids. Our proposed functional, which is still in the form of the simple generalized gradient approximation, can thus be applied efficiently to systems that involve both finite and infinite systems, a case that is crucial, for example, in heterogeneous catalysis studies. Therefore, the chemisorption of CO on transition-metal surfaces was considered, and it is shown that our functional gives improved results.

DOI: [10.1103/PhysRevB.83.205117](https://doi.org/10.1103/PhysRevB.83.205117)

PACS number(s): 31.15.E-, 71.15.Mb

I. INTRODUCTION

Density functional theory^{1,2} is the most widely used quantum mechanical method for the calculation of the structural and electronic properties of finite and infinite systems. Density functional theory allows calculations on very large systems (containing up to several thousand atoms), which is clearly not possible with *ab initio* post Hartree-Fock methods. However, it is necessary to choose an approximate functional to represent the exchange-correlation energy since the exact functional is unknown. For solids, the local density approximation (LDA)² and the generalized gradient approximation (GGA) are the most often used functionals. The GGA developed by Perdew, Burke, and Ernzerhof (PBE)³ is considered to be the standard one for solids. Recently, several new GGA functionals were proposed,^{4–8} which (on average) improve, with respect to LDA and PBE, the results for the lattice constants and bulk moduli of solids (see also Refs. 8–12 for extensive tests). Unfortunately, the improvement of the structural properties is accompanied by a worsening of the thermochemical properties, e.g., the cohesive energy of solids or the atomization energies of molecules (see, e.g., Refs. 7 and 8).

The accuracy that can be reached with GGA functionals is limited¹³ due to their rather simple mathematical form (dependence on the electron density ρ and its derivative $\nabla\rho$). Currently, it is fashionable to work on higher rungs of Perdew's "Jacob's ladder."¹⁴ These include meta-GGAs (which additionally depend on the kinetic energy density),¹⁵ hybrid functionals¹⁶ (which mix a certain amount of exact exchange with a GGA), or even more evolved schemes like the correlation corrections within the random-phase approximation^{17,18} or Møller-Plesset perturbation theory.¹⁹ For molecules, hybrid functionals are now the standard choice in calculations, but for periodic solids they are still quite expensive, and their accuracy for metallic and itinerant magnetic systems is low.²⁰ On the other hand, meta-GGA functionals¹⁵ are very promising for both geometries of solids and atomization energies of molecules, but a self-consistent implementation of meta-GGA functionals is not as straightforward as for GGA, which means that forces, which are necessary for geometry optimization, are not easily available. Therefore, it is very important for practical applications of broad interest to find the best approximation

of the second rung of the Jacob's ladder and to design a GGA functional that performs as well as possible for solids *and* molecules.

Concerning the lattice constants of solids and atomization energies of molecules (the two representative properties considered in this work), the trends observed with LDA and GGA are the following: LDA clearly underestimates the lattice constants and overestimates the atomization energies. The PBE functional overestimates lattice constants (almost as much as LDA underestimates them), but the atomization energies are significantly less overestimated than in LDA. The new GGAs [e.g., Wu and Cohen (WC)⁵ and PBE for solids (PBEsol)⁶], yielding more accurate lattice constants, have an exchange enhancement factor $F_x(s)$ (see Sec. II for definition) that increases more slowly with the reduced density gradient s than PBE and thus is closer to LDA. Unfortunately, these "soft" GGAs overestimate the atomization energies much more than PBE. GGAs leading to more accurate atomization energies are "stronger" than PBE [their enhancement factor $F_x(s)$ rises more rapidly than PBE], for example, revised PBE (RPBE).²¹ However, the "strong" GGAs largely overestimate lattice constants (see, e.g., Ref. 22). Therefore, the PBE functional is considered to be the best compromise for these two properties.

An attempt to construct a GGA that improves both quantities was already made by Ruzsinszky *et al.*,²³ who constructed the second regularized gradient expansion (RGE2) functional, whose enhancement factor is larger than that of PBEsol for $s > 1$. It slightly improves the atomization energies over PBEsol, but at the same time, the results for the structural properties are less accurate. Overall, this functional does worse than PBE for atomization energies and is only marginally better than PBE for lattice constants.

In this work we will demonstrate that after a careful analysis one can design a GGA functional that outperforms PBE for both geometry of solids and atomization energy of molecules and reaches an accuracy comparable to the recently proposed meta-GGA functional of Perdew *et al.*¹⁵ We also applied it to the famous problem of CO chemisorption on transition-metal surfaces,²⁴ where, so far, all tested GGAs fail badly either for the adsorption energy or for the surface energy and calculations based on the random-phase approximation (RPA)²⁴ or a meta-GGA functional²⁵ could only recently break this trend.

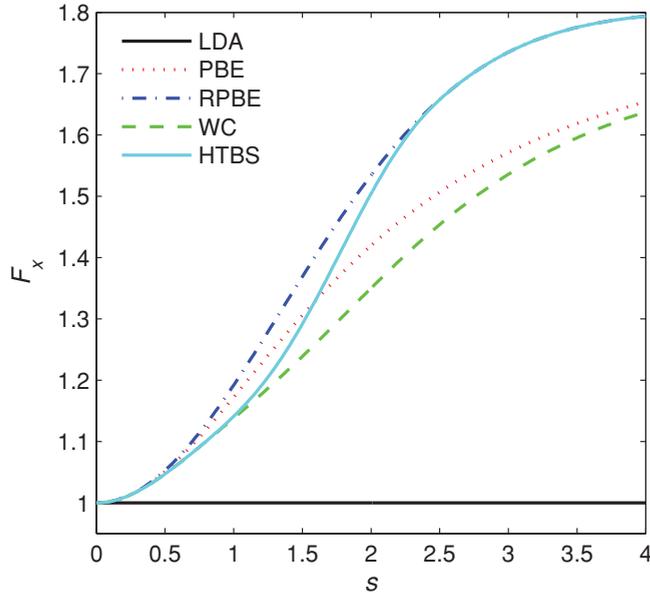


FIG. 1. (Color online) The s dependency of F_x for LDA and various GGAs.

II. THEORY

We propose an exchange functional following a similar strategy to that, e.g., in Ref. 4, which is based on the mixing of two known functionals, namely, the RPBE²¹ and the WC⁵ functionals, which are among the most accurate GGAs for the atomization energies of molecules and lattice constants of solids,^{9,11} respectively. These two functionals have the same correlation functional (the one from PBE) and differ only in the exchange energy (which is one order of magnitude larger than the correlation energy), which simplifies the analysis. A GGA exchange functional can be characterized in terms of its enhancement factor $F_x(s)$, where $s = |\nabla\rho|/[2(3\pi^2)^{1/3}\rho^{4/3}]$ is the reduced density gradient. The corresponding energy is defined as

$$E_x^{\text{GGA}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\mathbf{r}) F_x[s(\mathbf{r})] d^3r. \quad (1)$$

Figure 1 shows the RPBE and WC enhancement factors as well as the LDA and PBE ones.

Now, we construct the following enhancement factor F_x^{HTBS} , which starts like WC for small s and recovers RPBE at large s :

$$F_x^{\text{HTBS}}(s) = \begin{cases} F_x^{\text{WC}}(s), & s \leq s_1, \\ F_x^G(s), & s_1 < s \leq s_2, \\ F_x^{\text{RPBE}}(s), & s > s_2, \end{cases} \quad (2)$$

where, in a spirit similar to Ref. 4 (see also Swart *et al.*²⁶),

$$F_x^G(s) = G(s)F_x^{\text{RPBE}}(s) + [1 - G(s)]F_x^{\text{WC}}(s), \quad (3)$$

with the following spline function:

$$G(s) = \sum_{i=1}^6 c_i(s_1, s_2) s^{i-1}, \quad (4)$$

whose coefficients $c_i(s_1, s_2)$ are determined such that F_x^{HTBS} and the derivatives dF_x^{HTBS}/ds and $d^2F_x^{\text{HTBS}}/ds^2$ are continuous at s_1 and s_2 . Figure 1 shows F_x^{HTBS} with $s_1 = 0.6$ and $s_2 = 2.6$. When s_1 and s_2 tend to zero, RPBE results are recovered, while for large s_1 , the WC results are obtained. Here we search for values of s_1 and s_2 such that both the atomization energies and lattice constants are *optimal*.

For this purpose, we considered for the lattice constants the large test set of 60 solids that we used previously in Refs. 8 and 11, while for the atomization energies, the AE20 test set proposed by Kurth *et al.*²⁷ was chosen. The calculations for solids were performed with the WIEN2K code,²⁸ which solves the Kohn-Sham equations using the full-potential (linearized) augmented plane-wave and local orbitals method.^{29,30} The atomization energies of molecules were calculated using the DEMON code,³¹ which uses Gaussian basis sets.

III. RESULTS AND DISCUSSION

The calculations on the molecules and solids using the enhancement factor F_x^{HTBS} [Eq. (2)] for exchange and PBE for correlation have been done for s_1 ranging from 0 to 4.5 and different values of $\Delta s = s_2 - s_1$ ranging from 0.2 to 2. For small Δs values the rapidly increasing enhancement factor leads to irregularities that are gone with $\Delta s = 2$, a value we fix.

Figure 2 shows the (often sigmoid) evolution of the relative error of the atomization energies for several molecules of the AE20 test set as a function of s_1 . For $s_1 < 0.4$ the deviations from the RPBE results are small, while in the region $0.5 < s_1 < 1.8$ the errors often increase much more and a transition from the good RPBE to the poor WC results is observed. For even larger s_1 , only a small increase is observed, and for $s_1 > 4$ the results remain essentially unchanged.

The opposite trend is observed in Fig. 3 for the relative error of the lattice constants of solids. We see that for low s_1 we obtain large errors (up to 5.5% for NaCl) and a poor

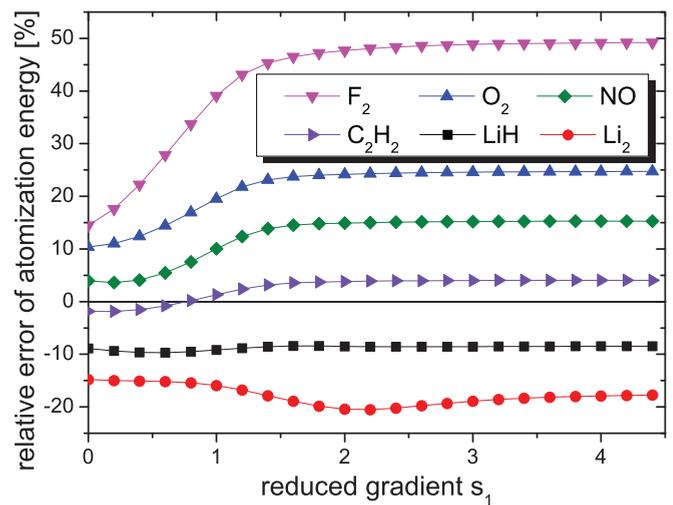


FIG. 2. (Color online) The relative error of atomization energies for a few selected molecules of the AE20 test set²⁷ versus s_1 (with $\Delta s = 2$).

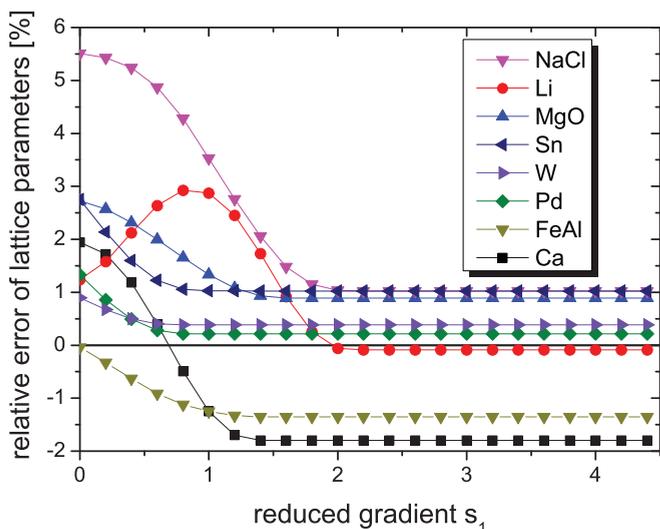


FIG. 3. (Color online) The relative error of lattice constants for a few selected compounds of the 60-solids test set vs s_1 (with $\Delta s = 2$).

“RPBE-like” behavior. In general, increasing s_1 reduces the errors significantly, and the good “WC-like” behavior is obtained at $s_1 = 2$. This is to be expected since the largest value of s in strongly bound solids is about 2 for Li (and slightly smaller for other alkali solids), as was shown previously.³² Furthermore, it was demonstrated that these large values of s occur in the core-valence separation region, which is the “important region” that determines the lattice constant of close-packed solids. For more open structures like Si, there is a second important region, namely, the large interstitial space where the tails of the valence wave functions dominate, but in this region s also remains below 1.5. The analysis given above explains why any further increase of s_1 does not change the results. When we further analyze all 60 solids, we find that when we exclude all compounds that contain group Ia elements, only $s_1 < 1$ has an effect on the results. Furthermore, small s_1 values may even reduce the errors in some cases (see, for example, Ca in Fig. 3).

From these results we can see that acceptable s_1 values for solids are at least larger than 0.5–2.0, while for molecules s_1 should be below 0.5–1.0. In order to make these statements quantitative we show in Fig. 4 the dependence of the mean absolute relative error (MARE) of our functional for molecules and solids versus s_1 . For the lattice constants (solid and dotted lines, left axis) the MARE decreases with increasing s_1 , whereas it increases for the atomization energies (dashed curve, right axis). A balanced compromise is reached for $s_1 = 0.6$ (indicated by the dashed-dotted vertical line). For the solids we show two curves, namely, the MARE for the complete test set of 60 solids (dotted curve) and the one in which we omitted all solids (eight cases) containing group Ia elements (solid line). In particular, for the latter our new HTBS functional achieves an outstanding performance for both, molecules and solids (indicated by the squares), reaching the good quality of the highly specialized WC (stars) and RPBE (triangles) functionals where they work best. WC and RPBE are the two extreme cases: none of them is able to describe both quantities, atomization energies for molecules

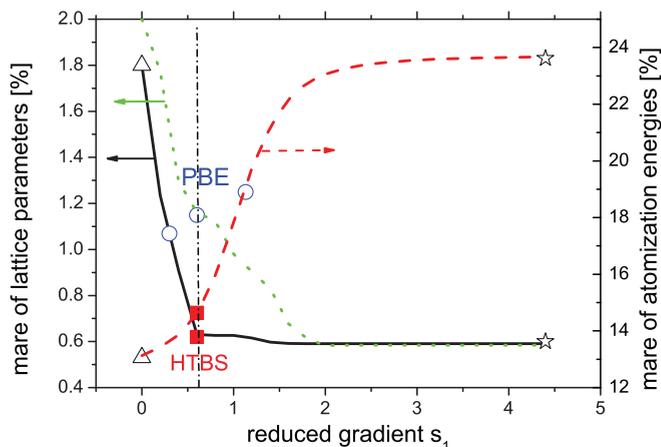


FIG. 4. (Color online) The MARE of atomization energies for the AE20 test set (dashed line, right axis) and the MARE of lattice constants (left axis: solid line, 52 solids without solids containing group Ia elements; dotted line, full 60-solids test set) vs s_1 (with $\Delta s = 2$). The symbols indicate the errors of specific functionals: triangles, RPBE; stars, WC; circles, PBE; and squares, HTBS.

and lattice constants for solids, with an acceptable accuracy, although they are, by far, the best functionals for one of the two properties. Obviously, PBE (its MARE is shown by circles) is some compromise with intermediate errors for the two quantities. However, since the errors are quite large, one could also phrase it that PBE is “equally bad” for both quantities and our HTBS functional performs much better.

The performance of the tested functionals for the atomization energy of the 20 molecules and lattice constant and bulk modulus of the 60 solids are shown in Tables I and II, respectively. The relative errors of the lattice constants are shown in Fig. 5, where for each functional the solids have been ordered such that the relative error goes in the direction of the positive values from bottom to top (in Fig. S1 of the supplementary material³³ the ordering is the same for each functional). The values of the lattice constants and bulk moduli can be found in Table SI of the supplementary material.³³ For the atomization energy of molecules all errors for the HTBS functional are significantly smaller than for PBE and come close to RPBE. As expected, the GGAs for solids namely, WC,⁵ AM05 (Armiento and Mattsson⁴), and PBEsol,⁶ show very poor performance for molecules. In order to check that our conclusions for the atomization energy do not depend on the testing set we also considered the test set of six molecules (called AE6) proposed by Lynch and Truhlar,³⁴ which was shown to be a representative set of much larger test sets of molecules. The results, shown in Table III, confirm our statement that the HTBS functional performs as well as the RPBE functional. Since the lattice constants and bulk moduli of solids containing group Ia elements are not well described by the HTBS functional (see above) and such cases are quite overrepresented in the full data set, we present the statistics for solids with (60 solids) and without group Ia elements (52 solids). Even for the full test set we note that our functional is as good as PBE, and when we neglect cases with group Ia elements, a similar performance as with the WC functional can be achieved.

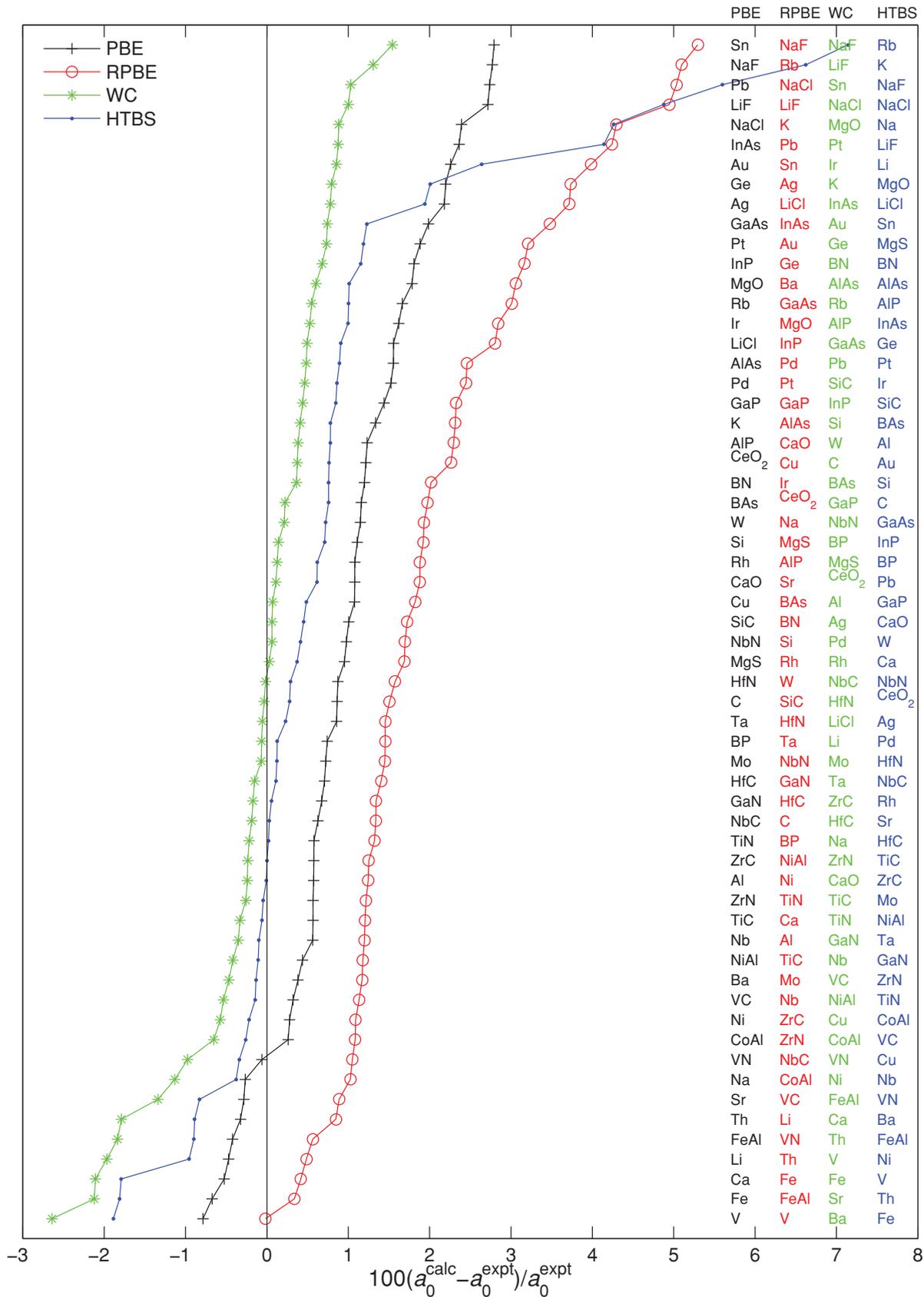


FIG. 5. (Color online) Relative error (in %) in the calculated lattice constants a_0 with respect to the experimental values (see Table SI of the supplementary material³³). For each functional, the solids have been ordered such that the relative error goes in the direction of the positive values from bottom to top. Thus, in one row there might be different solids for each functional. The orderings are shown on the right.

TABLE I. Atomization energy (in kcal/mol) for the molecules of the AE20 test set. ME is the mean error (in kcal/mol), MAE is the mean absolute error (in kcal/mol), MRE is the mean relative error (in %), and MARE is the mean absolute relative error (in %).

Molecule	RPBE	PBE	WC	AM05	PBEsol	HTBS	Expt.
H ₂	105.6	104.7	104.0	111.2	106.6	105.1	109.5
LiH	53.5	53.6	52.9	56.7	54.8	52.2	57.8
OH	107.0	110.6	112.7	116.5	115.1	108.0	106.4
H ₂ O	228.2	235.8	241.5	251.3	246.7	232.6	232.2
HF	138.5	143.1	147.2	153.8	150.2	142.6	140.8
Li ₂	20.9	20.6	20.2	20.2	21.2	20.7	24.4
LiF	133.5	139.2	142.4	144.1	143.7	134.6	138.9
Be ₂	8.5	10.4	11.3	10.0	11.7	8.8	3.0
CO	257.4	268.3	274.9	279.4	278.9	260.4	259.3
N ₂	231.3	241.7	244.4	245.1	248.4	225.8	228.5
O ₂	132.4	142.8	150.3	156.5	154.9	137.8	120.5
F ₂	43.4	51.2	57.5	62.3	60.5	49.2	38.5
P ₂	112.9	120.0	125.8	127.6	127.9	117.5	117.3
NO	161.1	171.3	176.3	179.0	180.4	161.0	152.9
NH ₃	294.4	302.9	307.2	317.1	313.9	294.9	297.4
Cl ₂	58.3	64.4	69.9	71.7	72.0	64.2	58.0
C ₂ H ₂	399.3	413.8	421.9	430.7	429.0	401.7	405.4
C ₂ H ₄	554.4	571.3	581.6	596.2	592.1	559.2	562.6
CH ₄	410.9	420.0	425.9	439.6	434.0	414.1	419.3
HCN	312.7	325.2	330.7	335.2	336.1	311.3	311.9
ME	-1.0	6.3	10.7	16.0	14.7	0.9	
MAE	4.5	7.6	12.2	16.5	15.6	4.5	
MRE	8.5	16.1	20.6	21.8	23.6	10.8	
MARE	12.8	18.9	23.7	23.7	25.7	14.5	

As a real challenging test of our new functional, we present in Fig. 6 the results of the chemisorption energies E_{ads} of CO on Rh and Pt(111) surfaces vs the corresponding surface energies E_{σ} for several functionals. As demonstrated

TABLE II. Summary of the performance of functionals for the lattice constant and bulk modulus of solids for two different test sets: (a) with group Ia elements and (b) without them. See Table I for the definitions of ME, MAE, MRE, and MARE. The values of the lattice constants and bulk moduli can be found in Table SI of the supplementary material.³³

	PBE		WC		HTBS	
	(a)	(b)	(a)	(b)	(a)	(b)
Lattice constant						
ME (Å)	0.049	0.045	-0.001	-0.005	0.041	0.012
MAE (Å)	0.054	0.050	0.029	0.028	0.054	0.028
MRE (%)	1.02	0.95	-0.06	-0.16	0.80	0.21
MARE (%)	1.15	1.07	0.64	0.63	1.16	0.62
Bulk modulus						
ME (GPa)	-2.2	-2.3	11.4	13.3	7.2	9.3
MAE (GPa)	12.8	14.4	14.8	16.9	14.7	15.9
MRE (%)	-3.4	-3.2	4.9	6.3	-0.5	3.0
MARE (%)	9.5	9.8	9.1	9.6	12.0	10.3

TABLE III. Atomization energy (in kcal/mol) for the molecules of the AE6 test set. See Table I for the definition of ME, MAE, MRE, and MARE.

Molecule	RPBE	PBE	WC	AM05	PBEsol	HTBS	Expt.
SiH ₄	308.3	313.0	316.9	329.7	323.4	312.1	322.4
SiO	186.1	195.6	202.1	205.1	204.6	190.5	192.1
S ₂	107.7	114.7	121.1	122.8	123.2	114.4	101.7
C ₃ H ₄	694.8	720.0	735.4	751.1	748.3	701.5	704.8
C ₂ H ₂ O ₂	633.0	663.3	682.9	697.0	695.5	643.9	633.4
C ₄ H ₈	1128.1	1168.5	1195.8	1224.1	1218.9	1144.7	1149.0
ME	-7.5	12.0	25.1	37.7	35.1	0.6	
MAE	9.6	15.1	27.0	37.7	35.1	7.1	
MRE	-0.8	3.4	6.5	8.8	8.3	1.6	
MARE	2.8	4.4	7.0	8.8	8.3	3.2	

recently²⁴ and also verified by our calculations, common GGA results fall on a straight line. “Weaker” GGAs describe well E_{σ} , while “stronger” GGAs yield good E_{ads} , a situation similar to atomization energies vs lattice constants. Clearly, our HTBS functional breaks this trend. It retains the rather good E_{σ} from WC but improves significantly on E_{ads} to yield results at least as good as PBE. Of course, the RPA results,²⁴ which require two orders of magnitude more computational effort (and are still non-self-consistent and for nonrelaxed geometries), are still more accurate than HTBS. In a recent study, Sun *et al.*²⁵ have shown that the meta-GGA revised Tao-Perdew-Staroverov-Scuseria (revTPSS)¹⁵ leads to results for E_{σ} that are similar to LDA [which is the best semi(local) functional for this quantity] and to results for E_{ads} that are close to PBE. Similarly to HTBS, revTPSS (which additionally depends on the kinetic-energy density) represents overall an improvement over common semilocal functionals.

In summary, a systematic analysis allowed us in the present work to develop a GGA functional that competes in accuracy with the best specialized GGAs for molecules and solids. This gain in accuracy comes at the acceptable price of the functional overestimating lattice constants of solids containing alkali

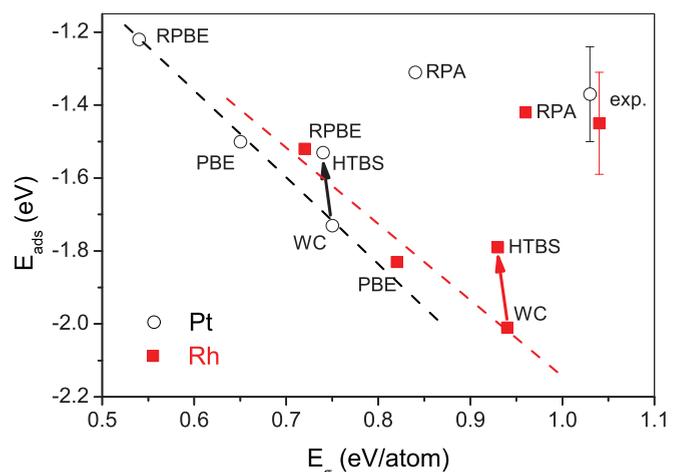


FIG. 6. (Color online) The chemisorption energy E_{ads} of CO on Rh and Pt(111) (for a 2×2 surface cell) vs the surface energy E_{σ} for several GGA functionals. The RPA and experimental data are taken from Ref. 24.

atoms. We proved that this new GGA functional performs very well for molecules and solids and is therefore very promising for calculations on very large systems involving both finite and infinite systems (e.g., heterogeneous catalysis).

ACKNOWLEDGMENTS

This work was supported by projects P20271-N17 and SFB-F41 (ViCoM) of the Austrian Science Fund.

-
- ¹P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
²W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
³J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996); **78**, 1396 (1997); Y. Zhang and W. Yang, *ibid.* **80**, 890 (1998); J. P. Perdew, K. Burke, and M. Ernzerhof, *ibid.* **80**, 891 (1998).
⁴R. Armiento and A. E. Mattsson, *Phys. Rev. B* **72**, 085108 (2005).
⁵Z. Wu and R. E. Cohen, *Phys. Rev. B* **73**, 235116 (2006); Y. Zhao and D. G. Truhlar, *ibid.* **78**, 197101 (2008); Z. Wu and R. E. Cohen, *ibid.* **78**, 197102 (2008).
⁶J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008); **102**, 039902(E) (2009); A. E. Mattsson, R. Armiento, and T. R. Mattsson, *ibid.* **101**, 239701 (2008); J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *ibid.* **101**, 239702 (2008).
⁷Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* **128**, 184109 (2008).
⁸P. Haas, F. Tran, P. Blaha, L. S. Pedroza, A. J. R. da Silva, M. M. Odashima, and K. Capelle, *Phys. Rev. B* **81**, 125136 (2010).
⁹F. Tran, R. Laskowski, P. Blaha, and K. Schwarz, *Phys. Rev. B* **75**, 115131 (2007).
¹⁰A. E. Mattsson, R. Armiento, J. Paier, G. Kresse, J. M. Wills, and T. R. Mattsson, *J. Chem. Phys.* **128**, 084714 (2008).
¹¹P. Haas, F. Tran, and P. Blaha, *Phys. Rev. B* **79**, 085104 (2009); **79**, 209902(E) (2009).
¹²G. I. Csonka, J. P. Perdew, A. Ruzsinszky, P. H. T. Philipsen, S. Lebègue, J. Paier, O. A. Vydrov, and J. G. Ángyán, *Phys. Rev. B* **79**, 155107 (2009).
¹³A. D. Becke, *J. Comput. Chem.* **20**, 63 (1999).
¹⁴J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, *J. Chem. Phys.* **123**, 062201 (2005).
¹⁵J. P. Perdew, A. Ruzsinszky, G. I. Csonka, L. A. Constantin, and J. Sun, *Phys. Rev. Lett.* **103**, 026403 (2009).
¹⁶A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
¹⁷J. Harl and G. Kresse, *Phys. Rev. Lett.* **103**, 056401 (2009).
¹⁸X. Ren, P. Rinke, and M. Scheffler, *Phys. Rev. B* **80**, 045402 (2009).
¹⁹M. Marsman, A. Grüneis, J. Paier, and G. Kresse, *J. Chem. Phys.* **130**, 184103 (2009).
²⁰J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Ángyán, *J. Chem. Phys.* **124**, 154709 (2006); **125**, 249901 (2006).
²¹B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
²²G. K. H. Madsen, *Phys. Rev. B* **75**, 195108 (2007).
²³A. Ruzsinszky, G. I. Csonka, and G. E. Scuseria, *J. Chem. Theory Comput.* **5**, 763 (2009).
²⁴L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, *Nat. Mater.* **9**, 741 (2010).
²⁵J. Sun, M. Marsman, A. Ruzsinszky, G. Kresse, and J. P. Perdew, *Phys. Rev. B* **83**, 121410(R) (2011).
²⁶M. Swart, M. Solá, and F. M. Bickelhaupt, *J. Chem. Phys.* **131**, 094103 (2009).
²⁷S. Kurth, J. Perdew, and P. Blaha, *Int. J. Quantum Chem.* **75**, 889 (1999).
²⁸P. 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, Vienna, 2001.
²⁹D. J. Singh and L. Nordström, *Planewaves, Pseudopotentials and the LAPW Method*, 2nd ed. (Springer, New York, 2006).
³⁰G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, *Phys. Rev. B* **64**, 195134 (2001).
³¹M. E. Casida, C. Daul, A. Goursot, A. Koester, L. G. M. Pettersson, E. Proynov, A. St-Amant, D. R. Salahub, S. Chrétien, H. Duarte, N. Godbout, J. Guan, C. Jamorski, M. Leboeuf, V. Malkin, O. Malkina, M. Nyberg, L. Pedocchi, F. Sim, and A. Vela, DEMON-KS Version 3.5, deMon Software, Montreal (Canada), 1998.
³²P. Haas, F. Tran, P. Blaha, K. Schwarz, and R. Laskowski, *Phys. Rev. B* **80**, 195109 (2009).
³³See supplemental material at [<http://link.aps.org/supplemental/10.1103/PhysRevB.83.205117>] for values of the lattice constants and bulk moduli.
³⁴B. J. Lynch and D. G. Truhlar, *J. Phys. Chem. A* **107**, 8996 (2003); **108**, 1460 (2004).