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Assessing the Perdew-Burke-Ernzerhof exchange-correlation density functional revised for metallic bulk and surface systems

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We test the accuracy of the revised Perdew-Burke-Ernzerhof exchange-correlation density functional (PBEsol) for metallic bulk and surface systems. It is shown that, on average, PBEsol yields equilibrium volumes and bulk moduli in close agreement with the former generalized gradient approximation (PBE) and two gradient level functionals derived from model system approach (LAG and AM05). On the other hand, for close-packed metal surfaces, PBEsol has the same performance as AM05, giving significantly larger surface energies than PBE and LAG.

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Today, density functional theory[1] has become a state-of-the-art approach in the *ab initio* description of condensed matter. Its success, to a large extent, may be attributed to the unanticipated high performance of the local density approximation (LDA) defined as the zeroth order term of the density gradient expansion.[2] Attempts to go beyond LDA have led to the elaboration of the gradient corrected functionals. The pioneering work by Langreth and Mehl[3] was followed by a large number of different approximations.[4–16] For computational solid state physics, the first real breakthrough was the stabilization of the diverging term from the second order gradient expansion within the so-called generalized gradient approximation (GGA).[4,5] With this early approach, one could recover, e.g., the correct ground state of Fe at ambient condition. Later incarnations[6,7,13] refined the GGA with the main goal of designing a universal functional for atoms and molecules as well as bulk and surface systems. During the last decades, among these GGA functionals, the most successful version has been the PBE functional proposed by Perdew, Burke, and Ernzerhof.[7]

An alternative approach for incorporating effects due to inhomogeneous electron density was put forward by Kohn and Mattsson.[17] In particular, they presented a description for the electronic edge within the linear potential or Airy gas approximation. The proposed model was first elaborated by Vitos *et al.*[14,18] by introducing the so-called local airy gas (LAG) approximation and later further developed by Armiento and Mattsson[15] within the subsystem functional (SSF) approach.[19] Functionals from this family, by construction, include important surface effects and, therefore, are expected to perform well for systems with electronic surface. In addition, these functionals turned out to be superior, on average, compared to the common GGA approaches also in bulk systems.[14,15,20,21]

Most recently, Perdew *et al.*[16] have introduced a new gradient level functional by revising the PBE functional[7] for solids and their surfaces. Keeping the exact mathematical constrains of PBE, the authors lifted the orthodox bias toward the atomic energies by restoring the first-principles gradient expansion for exchange and readjusting the correlation term using the jellium surface exchange-correlation energies obtained at meta-GGA level.[22] We note that such readjustment of the (LDA level) correlation energy has originally been proposed by Armiento and Mattsson[15] in their SSF approach. The new GGA functional, referred to as PBEsol,[16] has been designed to yield improved equilibrium properties of densely-packed solids and, most importantly, to remedy the deficiencies of the GGA functionals for surfaces.[23–25]

The aim of this work is to establish the accuracy of the PBEsol exchange-correlation functional in the case of bulk metals and transition metal surfaces. We have selected 10 simple metals and 19 transition metals for testing the equation of state and the 4d transition series plus Rb and Sr for testing the surface energy. For all metals, the experimental low-temperature crystallographic phase has been considered.[26] In these tests, we compare the performance of the PBEsol functional with those obtained in LDA, PBE, LAG, and AM05 approximations. For LDA, we use the Perdew and Wang[27] parametrization of the quantum Monte Carlo data by Ceperley and Alder.[28] The LAG functional[14] is based on the exchange energy obtained within the Airy gas approximation[17] and the LDA correlation energy.[27] The AM05 approximation, proposed by Armiento and Mattsson,[15] goes beyond the LAG approach by taking into account non-LDA correlation effects using the jellium surface model. Hence, the main difference between LAG and AM05, both of them belonging to the SSF class of functionals, is the surfacelike correlation term included in the latter functional. Extensive tests on the LAG and AM05 approximations for bulk metals can be found in Refs. 14, 15, 20, and 21.

The present calculations were performed using the exact muffin-tin orbitals (EMTO) method.[20,29–31] The EMTO method is a screened Korringa-Kohn-Rostoker method that uses optimized overlapping muffin-tin potential spheres to represent the one-electron potential. The total energy was computed at the full charge density level,[32] which has proved to have the accuracy of full potential techniques.[33] The

Kohn-Sham equations were solved within the scalar-relativistic and soft-core approximations. Green's function was calculated for 16 complex energy points distributed exponentially on a semicircular contour including the valence states. We employed the double Taylor expansion approach[34] to get accurate slope matrix for each energy point. The EMTO basis set included *s*, *p*, *d*, and *f* states. In bulk calculations, we used 280, 240, and 320 inequivalent $\vec{k}$ points in the irreducible wedge of the body centered cubic (bcc), face centered cubic (fcc), and hexagonal close-packed (hcp) Brillouin zones, respectively. The equilibrium volumes and bulk moduli were extracted from the equation of state (EOS) described by a Morse function,[35] fitted to the total energies calculated for five different volumes around the equilibrium.

All self-consistent calculations were carried out within LDA and the gradient terms were included in the total energy within the perturbative approach.[33] To assess the accuracy of this approach, we carried out additional fully self-consistent PBE calculations for bulk bcc Fe and W and for fcc Cu and Rh. We find that the average error introduced by the perturbative treatment of the PBE gradient correction is ~ 0.07 Bohr $\times 10^{-2}$ in the equilibrium atomic radius and ~ 4 GPa in the bulk modulus. These errors are below the numerical accuracy of our calculations.

It has been shown[24] that the surface energy anisotropy shows negligible dependence on the exchange-correlation approximation. Hence, in the present work, we focus only on the close-packed surfaces of 4*d* transition metals. The bcc (011), fcc (111), and hcp (0001) surfaces were modeled using slabs consisting of eight atomic layers parallel to the surface plane. The slabs were separated by vacuum layers, having width equivalent with four atomic layers. The irreducible part of the two-dimensional bcc (011) surface Brillouin zone was sampled by 120 $\vec{k}$ points, whereas, for both fcc (111) and hcp (0001) surfaces, we used 240 $\vec{k}$ points. The surface energy was calculated from the slab energy and the corresponding bulk energy as described, e.g., in Ref. 36.

First, we address the accuracy of the present total energy method by comparing the EMTO results for the equilibrium lattice constant of a few selected metals with those reported in Ref. 16. The latter results were generated by the Gaussian code (GC).[37] The errors from Table I represent the differences between the theoretical results and the experimental data corrected for the zero-point expansion.[37] We find that, on average, the errors obtained using the two methods are close to each other and follow the same trend when going from LDA to PBE and from PBE to PBEsol. The deviation between the EMTO and the GC errors is somewhat larger for the simple metals, which may be attributed to the fact that these solids have very shallow energy minimum (small bulk modulus) and thus require a higher accuracy for the EOS fitting. The overall good agreement between the two sets of errors qualify for using the EMTO approach to shed light on the performance of the PBEsol functional in the case of metallic systems.

Next, we discuss the present results obtained for the equation of state. In Table II, we list the EMTO equilibrium atomic radii (w) and bulk moduli (B) for monovalent *sp* metals (Li, Na, K, Rb, and Cs), cubic divalent *sp* metals (Ca, Sr, and Ba), and for Al and Pb. Tables III and V show results for the cubic 3*d* and 5*d* metals, respectively, whereas in Table IV, we give results for the entire 4*d* series. The mean absolute errors (mae) for w and B calculated in LDA, PBE, PBEsol, LAG, and AM05 approximations are shown at the bottom of the tables.

TABLE I. Comparison between the errors in the equilibrium lattice constants for a few selected metals calculated using the present approach (EMTO) and those reported in Ref. 16 (in parentheses). The mean errors (upper panel) and mean absolute errors (lower panel) are shown for LDA, PBE, and PBEsol functionals (in units of Bohr $\times 10^{-2}$).

	LDA	PBE	PBEsol
		Mean error	
Li, Na, K, Al	−21.4	3.6	−2.1
	(−17.0)	(5.5)	(−0.6)
Cu, Rh, Pd, Ag	−7.8	12.9	−0.2
	(−7.6)	(12.1)	(0.0)
		Mean absolute error	
Li, Na, K, Al	21.4	5.7	2.6
	(17.0)	(6.4)	(4.3)
Cu, Rh, Pd, Ag	7.8	12.9	2.1
	(7.6)	(12.1)	(3.6)

As expected, for all metals, the LDA underestimation of the equilibrium volume is reduced by the gradient corrected functionals. This is especially pronounced in the case of simple metals and 3*d* transition metals. When comparing the performances of the four gradient level approximations, we find similar errors for the simple metals and 4*d* transition metals. PBE yields far the best volumes for the 3*d* metals, whereas, the volumes of the 5*d* metals are best described by AM05 followed by PBEsol. For simple metals, we have the following sequence: $w(\mathrm{LDA}) < w(\mathrm{PBEsol}) < w(\mathrm{LAG}) \lesssim w(\mathrm{AM05})$ (except Al and Pb) and $w(\mathrm{AM05}) \lesssim w(\mathrm{PBE})$ (except Li). For all transition metals and also for Al and Pb, we have: $w(\mathrm{LDA}) < w(\mathrm{PBEsol}) \approx w(\mathrm{AM05}) \lesssim w(\mathrm{LAG}) < w(\mathrm{PBE})$. Surprisingly, for most of the metals, the PBEsol atomic radii are only slightly smaller than those obtained within the LAG approximation: the average difference being ~ 0.0018 Bohr for the simple metals and ~ 0.0012 Bohr for the transition metals. For comparison, the corresponding differences between the PBEsol and PBE radii are ~ 0.0076 and ~ 0.0028 Bohr. This finding indicates that the surfacelike correlation effects (present in PBEsol and AM05 but neglected in LAG) play minor role in the bulk equilibrium properties of metals.

The sensitivity of the bulk modulus to the exchange-correlation approximation is similar to that of the atomic radius. PBE gives the smallest mae(B) for the simple and 3*d* metals, while the 4*d* and 5*d* metals have the lowest mae(B) for LAG and PBEsol, respectively. Except a few simple metals, we find $B(\mathrm{LDA}) > B(\mathrm{PBEsol}) \approx B(\mathrm{AM05}) > B(\mathrm{LAG}) > B(\mathrm{PBE})$. The large PBE errors in B for the late 5*d* metals are greatly reduced by the PBEsol and AM05 approximations. Unfortunately, both the atomic radii and bulk moduli

TABLE II. Theoretical (EMTO) and experimental (Ref. 26) equilibrium atomic radii (*w* in Bohr) and bulk moduli (*B* in GPa) for cubic *s* and *p* metals. The theoretical values are shown for the LDA, PBE, PBEsol, LAG, and AM05 functionals. The unit for the mae is Bohr$\times 10^{-2}$ for *w* and GPa for *B*. The lowest mae's are shown in boldface.

		LDA	PBE	PBEsol	LAG	AM05	Expt.
Li	*w*	3.13	3.20	3.20	3.21	3.22	3.237
fcc	*B*	14.0	13.7	13.8	13.5	13.5	12.6
Na	*w*	3.77	3.91	3.89	3.92	3.92	3.928
bcc	*B*	8.56	7.88	7.82	7.54	7.73	7.34
K	*w*	4.69	4.92	4.86	4.92	4.92	4.871
bcc	*B*	3.94	4.06	3.94	3.88	3.97	3.70
Rb	*w*	5.00	5.27	5.18	5.26	5.27	5.200
bcc	*B*	3.21	3.34	3.22	3.19	3.28	2.92
Cs	*w*	5.36	5.73	5.60	5.72	5.74	5.622
bcc	*B*	2.08	2.32	2.15	2.16	2.24	2.10
Ca	*w*	3.95	4.09	4.04	4.06	4.07	4.109
fcc	*B*	17.9	16.8	17.1	16.5	17.0	18.4
Sr	*w*	4.30	4.45	4.38	4.41	4.42	4.470
fcc	*B*	14.0	13.2	13.5	13.1	13.3	12.4
Ba	*w*	4.38	4.67	4.52	4.59	4.61	4.659
bcc	*B*	8.29	7.76	7.72	7.57	7.49	9.30
Al	*w*	2.95	2.99	2.97	2.98	2.96	2.991
fcc	*B*	81.2	75.7	80.1	76.5	84.8	72.8
Pb	*w*	3.60	3.71	3.64	3.67	3.64	3.656
bcc	*B*	59.4	41.2	53.0	46.5	50.1	41.7
mae	*w*	16.13	**3.87**	4.63	4.45	4.47	
	B	3.24	**1.01**	2.49	1.44	2.66	

of magnetic 3*d* metals are very poorly described by the present approximations.

In order to be able to judge the relative merits of the four gradient level functionals for bulk systems, we consider the mean absolute errors for all 29 metals from Tables II–V. We find that the total mae's for *w* are 8.69, 3.32, 3.41, 3.27, and 3.22 Bohr$\times 10^{-2}$ in LDA, PBE, PBEsol, LAG, and AM05, respectively. The same figures for *B* are 23.12, 14.34, 15.03, 12.90, and 15.03 GPa. Thus, AM05 yields marginally better *w* and LAG yields marginally better *B* compared to the other gradient approximations. However, this comparison is meaningful only within the error bar associated with the particular

TABLE III. Theoretical (EMTO) and experimental (Ref. 26) equilibrium atomic radii (*w* in Bohr) and bulk moduli (*B* in GPa) for cubic 3*d* metals. For notations, see caption for Table II.

		LDA	PBE	PBEsol	LAG	AM05	Expt.
V	*w*	2.72	2.79	2.75	2.76	2.75	2.813
Bcc	*B*	199	176	188	183	187	155
Cr	*w*	2.60	2.65	2.62	2.62	2.62	2.684
Bcc	*B*	285	259	274	268	273	160
Fe	*w*	2.56	2.64	2.60	2.60	2.60	2.667
Bcc	*B*	245	191	220	213	223	163
Ni	*w*	2.53	2.61	2.56	2.57	2.56	2.602
Fcc	*B*	243	198	223	214	222	179
Cu	*w*	2.60	2.69	2.64	2.65	2.64	2.669
Fcc	*B*	182	142	165	155	163	133
mae	*w*	8.50	**2.26**	5.30	4.70	5.30	
	B	72.80	**35.20**	56.00	48.60	55.6	

TABLE IV. Theoretical (EMTO) and experimental (Ref. 26) equilibrium atomic radii (*w* in Bohr) and bulk moduli (*B* in GPa) for 4*d* metals. For notations, see caption for Table II.

		LDA	PBE	PBEsol	LAG	AM05	Expt.
Y	*w*	3.65	3.77	3.71	3.72	3.72	3.760
hcp	*B*	40.7	36.5	38.2	37.1	37.5	41.0
Zr	*w*	3.28	3.36	3.31	3.32	3.32	3.347
hcp	*B*	98.5	89.9	93.0	92.2	93.1	94.9
Nb	*w*	3.01	3.08	3.04	3.05	3.04	3.071
bcc	*B*	171	146	160	154	162	169
Mo	*w*	2.90	2.94	2.91	2.92	2.91	2.928
bcc	*B*	272	247	263	256	263	261
Tc	*w*	2.82	2.86	2.83	2.84	2.83	2.847
hcp	*B*	323	286	310	301	312	297
Ru	*w*	2.77	2.82	2.79	2.80	2.78	2.796
hcp	*B*	353	305	336	325	339	303
Rh	*w*	2.78	2.84	2.80	2.81	2.80	2.803
fcc	*B*	304	251	285	272	286	282
Pd	*w*	2.85	2.92	2.87	2.89	2.87	2.840
fcc	*B*	229	166	205	191	204	189
Ag	*w*	2.97	3.07	3.00	3.03	3.01	3.018
fcc	*B*	137	89.6	117	106	110	98.8
mae	*w*	4.44	2.78	2.33	**1.96**	2.11	
	B	21.46	13.63	10.99	**7.98**	10.6	

computational method. Using the GC and EMTO mae's from Table I and assuming a hypothetical fcc structure for all metals from this table, for the average mae in *w*, we obtain 3.5 Bohr × 10^{-2} for GC and 3.4 Bohr × 10^{-2} for EMTO. The deviation between the two average mae's sets the error of the EMTO equilibrium radii to ±0.1 Bohr × 10^{-2}. For the error of the EMTO bulk moduli, we use ±2 GPa, which is the error associated with the present perturbative treatment of the gradient terms. Taking into account these error bars, we conclude that for bulk metals, the PBEsol functional has the accuracy of the PBE, LAG, and AM05 functionals.

Before turning to metal surfaces, we wish to comment on the present and previous verdicts on the accuracy of PBEsol for bulk metals. While Ref. 16 indicates that PBEsol is ~2.4 times (~3.9 times according to the present results in Table I) as good as PBE in predicting lattice constants for Li, Na, K, Al, Cu, Rh, Pd, and Ag, our results from Tables II–V show that for the 29 bulk metals considered, PBEsol yields an average error (3.41 Bohr × 10^{-2}) in close agreement with PBE (3.32 Bohr × 10^{-2}). This unflattering verdict on PBEsol

TABLE V. Theoretical (EMTO) and experimental (Ref. 26) equilibrium atomic radii (*w* in Bohr) and bulk moduli (*B* in GPa) for cubic 5*d* metals. For notations, see caption for Table II.

		LDA	PBE	PBEsol	LAG	AM05	Expt.
Ta	*w*	3.03	3.10	3.06	3.07	3.06	3.073
bcc	*B*	194	180	188	183	188	191
W	*w*	2.92	2.97	2.94	2.95	2.94	2.937
bcc	*B*	308	294	305	298	307	308
Ir	*w*	2.83	2.87	2.84	2.85	2.84	2.835
fcc	*B*	392	340	376	362	382	358
Pt	*w*	2.89	2.95	2.91	2.92	2.90	2.897
fcc	*B*	299	243	281	265	283	277
Au	*w*	3.00	3.08	3.03	3.05	3.02	3.013
fcc	*B*	188	136	170	155	168	166
mae	*w*	1.70	4.30	1.02	1.82	**0.62**	
	B	16.20	21.40	**6.40**	9.00	7.20	

TABLE VI. Theoretical surface energies (in J/m^2) for the close-packed surfaces of 4*d* transition metals. Results are shown for the LDA, PBE, PBEsol, LAG, and AM05 functionals. For comparison, the results for Rb and Sr are also included.

	Surface	LDA	PBE	PBEsol	LAG	AM05
Rb	bcc (110)	0.12	0.09	0.11	0.08	0.09
Sr	fcc (111)	0.55	0.44	0.50	0.44	0.47
Y	hcp (0001)	1.38	1.18	1.31	1.18	1.30
Zr	hcp (0001)	2.15	1.90	2.08	1.89	2.04
Nb	bcc (110)	2.66	2.32	2.58	2.30	2.55
Mo	bcc (110)	3.69	3.23	3.59	3.24	3.58
Tc	hcp (0001)	3.86	3.25	3.70	3.35	3.74
Ru	hcp (0001)	4.18	3.47	3.99	3.62	3.98
Rh	fcc (111)	3.34	2.63	3.14	2.80	3.11
Pd	fcc (111)	2.29	1.65	2.08	1.80	2.02
Ag	fcc (111)	1.40	0.89	1.23	1.13	1.13

is mainly due to its low performance for 3*d* metals (see Table III). For these solids, due to the more localized nature of the *d* electrons, a more atomiclike functional is needed to reproduce the experimental EOS. Thus, by lifting the bias toward the atomic energies in PBEsol, one arrives to a gradient level approximation which is less accurate for the 3*d* series than PBE.

In the following, we discuss the surface energy (γ) calculated for the close-packed surfaces of 4*d* transition metals. The EMTO surface energies γ_{xc} (*xc* stands for LDA, PBE, PBEsol, LAG or AM05) are listed in Table VI. To illustrate the effect of different gradient corrections, in Fig. 1, we show the surface energy differences $\Delta\gamma_{xc} \equiv (\gamma_{xc} - \gamma_{\mathrm{LDA}})$. For completeness, the differences between the experimental[38,39] and LDA surface energies have also been included in the figure.

Today, the most comprehensive experimental surface energy data is the one derived from the surface tension measurement in the liquid phase and extrapolated to zero temperature.[38,39] Using these experimental data, for the mean absolute values of the relative errors, we get 18.7% for LDA, 11.2% for PBE, 12.9% for PBEsol, 10.7% for LAG, and 14.1% for AM05. This would place the LAG approximation on the top followed by the PBE, PBEsol, AM05, and LDA. However, the accuracy of the experimental surface energies at low temperature is not known, and therefore, a direct comparison of the absolute values of γ_{xc} to the experimental data is not suitable for establishing the performance of different functionals for metal surfaces. Because of that, in the following, we investigate the effect of gradient corrections relative to LDA.

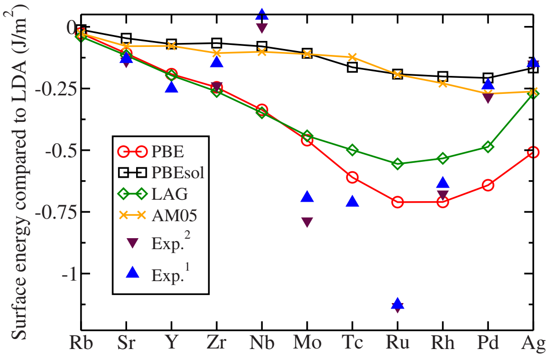

FIG. 1. (Color online) The effect of PBE (red circles), PBEsol (black squares), LAG (green diamonds), and AM05 (yellow crosses) gradient corrections on the LDA surface energies for Rb, Sr, and 4*d* transition metals (in J/m^2). For comparison, the differences between the experimental surface energies (blue triangle up: Expt. 1 of Ref. 38; maroon triangle down: Expt. 2 of Ref. 39) and LDA values are also shown.

From Table VI and Fig. 1, we see that the gradient correction always decreases the surface energy. Except Rb, the theoretical surface energies follow the trend $\gamma_{\mathrm{LDA}} > \gamma_{\mathrm{PBEsol}} \approx \gamma_{\mathrm{AM05}} > \gamma_{\mathrm{LAG}} \gtrsim \gamma_{\mathrm{PBE}}$. It is clear that PBE has large negative effect on the surface energies: its relative effect $\delta_{\mathrm{PBE}} \equiv |\Delta\gamma_{\mathrm{PBE}}|/\gamma_{\mathrm{PBE}}$ is ranging between ~12% (Zr and Mo) and ~38% (Ag). The effect of LAG is somewhat smaller in late 4*d* metals compared to that of PBE. The situation is very different for the PBEsol and AM05 functionals. First, these two approximations lead to a rather uniform change relative to the LDA surface energies. Second, δ_{PBEsol} and δ_{AM05} remain below ~8% for most metals, except Rb, Pd, and Ag, where the PBEsol (AM05) gradient effect reaches ~12% (~20%) of the LDA surface energy. We point out that the large $(\gamma_{\mathrm{AM05}} - \gamma_{\mathrm{LAG}})$ values calculated for Nb, Mo, Tc, Ru, and Rh are due to the surfacelike correlation effects neglected in the LAG approach. While such effects are small for bulk simple metals (Table II) and almost negligible in bulk transition metals (Tables III–V), they can be as large as ~0.4 J/m^2 (or ~10% of the LDA surface energy), obtained for the hcp (0001) surface of Tc.

We recall that the surface energy of jellium surfaces has been found to be more accurately described in LDA than in GGA.[23] Furthermore, it has recently been shown that LDA yields surface energies of ceramics in better agreement with the broken bond model than GGA.[25] This is surprising, especially taking into account that the broken bond model is based on the cohesive energy, which can be calculated accurately within GGA. On this ground, one tends to assume that the LDA surface energies are closer to the true surface energies than the PBE ones. Considering the relatively small effect of the PBEsol and AM05 approximations over the LDA surface energies (Fig. 1), it is likely that these two functionals perform better for metallic surfaces compared to PBE and LAG.

We conclude that for metallic bulk and surface systems, the newly developed PBEsol approximation, belonging to the GGA family of exchange-correlation functionals, has the accuracy of the AM05 functional derived from model subsystem (SSF) approach. Based on the assumption that the true surface energy of transition metals is close to the LDA surface energy, we suggest that these two functionals are superior compared to former gradient level approximations.

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