

Calculation of the lattice constant of solids with semilocal functionals

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The exchange-correlation functionals of the generalized gradient approximation (GGA) are still the most used for the calculations of the geometry and electronic structure of solids. The PBE functional [J. P. Perdew *et al.*, *Phys. Rev. Lett.* **77**, 3865 (1996)], the most common of them, provides excellent results in many cases. However, very recently other GGA functionals have been proposed and compete in accuracy with the PBE functional, in particular for the structure of solids. We have tested these GGA functionals, as well as the local-density approximation (LDA) and TPSS (meta-GGA approximation) functionals, on a large set of solids using an accurate implementation of the Kohn-Sham equations, namely, the full-potential linearized augmented plane-wave and local orbitals method. Often these recently proposed GGA functionals lead to improvement over LDA and PBE, but unfortunately none of them can be considered as good for all investigated solids.

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I. INTRODUCTION AND BACKGROUND

The Kohn-Sham (KS) version of density-functional theory (DFT) (Refs. 1 and 2) is the most used quantum mechanical method for the calculation of the geometrical and electronic properties of molecules, surfaces, and solids.^{3,4} Calculations on very large systems (up to several thousands of atoms) are possible, since DFT has a relatively low cost/accuracy ratio which is due to the mapping of a system of interacting electrons to a system of fictitious noninteracting electrons with same electron density. The price to pay for this computational efficiency is the need to choose an approximate functional to represent the exchange-correlation energy, since the exact functional is unknown (at least not in a form which can be used for practical calculations).⁵ Therefore, the accuracy of the results of a *good* calculation (i.e., use of a software with an accurate implementation of the KS equations, good convergence parameters, etc.) relies only on the chosen exchange-correlation functional.⁶

For molecules, the hybrid functionals (mixing of Hartree-Fock and semilocal exchange) are very popular [e.g., B3LYP (Refs. 7 and 8)], since they very often lead to very good results for the geometrical and thermochemical properties. Unfortunately, the use of Hartree-Fock exchange for very large molecules and solids is computationally very expensive and can lead to severe problems when applied to metallic systems (e.g., opening of a band gap or overestimation of the exchange splitting^{9,10}). Therefore, the functionals of the local-density approximation (LDA) (Refs. 11 and 12) and generalized gradient approximation (GGA) (Refs. 13 and 14) still constitute the standard choice for calculations on periodic solids. PW91 (Ref. 13) is the first GGA functional that has been used extensively for solids. Later, it was replaced by the functional of Perdew, Burke, and Ernzerhof (PBE),¹⁴ which has been the standard functional for solid-state calculations until now. In most cases, the PW91 and PBE functionals lead to quasi-identical results, but PBE has a simpler analytical form. However, the last few years have seen a regain of interest for the development of GGA functionals for solids.^{15–19} These functionals were designed to yield accurate lattice constants and bulk moduli, and all of them have

shown to be better than the PBE functional for many (but not all) compounds. Nevertheless, we note that for some of these new GGA functionals a general improvement of the structural properties is accompanied by a worsening of the thermochemical properties, e.g., the cohesive energy (see, e.g., Ref. 19). More generally, due to their rather simple mathematical form (dependence on the electron density ρ and its derivative $\nabla\rho$), the accuracy that can be reached with GGA functionals is limited.²⁰ Therefore more advanced (and sometimes more expensive) functionals, e.g., the meta-GGA (Ref. 21) and hybrid⁷ functionals, have been proposed.

In this work we present the results of GGA calculations for the lattice constant and bulk modulus of solids. We considered five GGA functionals^{14–16,18,19} as well as the LDA (Refs. 11 and 12) and TPSS (Tao *et al.*²²) functionals. The latter one goes beyond the GGA by considering also the kinetic-energy density as a variable in order to have more flexibility, and hence belongs to the so-called meta-GGA class of functionals (third rung of Jacob's ladder²³). The performance of the LDA and PBE functionals for finite and infinite systems are well documented in the literature (see, e.g., Refs. 24 and 25), therefore we will now briefly describe only the other functionals we considered in this work.

The functional of Wu and Cohen (WC) (Ref. 16) is based on the PBE functional, but with an exchange part which was modified such that the function $x(s)$ [Eq. (6) of Ref. 16] recovers the fourth-order parameters of the gradient expansion of the exchange energy in the limit of a slowly varying electron density²⁶ [i.e., when $s \rightarrow 0$, where $s = |\nabla\rho|/[2(3\pi^2)^{1/3}\rho^{4/3}]$ is the reduced density gradient]. This functional has been shown to be more accurate than PBE for the lattice constant of solids.^{16,17,25,27} The PBEsol functional (Ref. 18) retains the same analytical form as the PBE functional, but two parameters were modified in order to satisfy other conditions. The value of μ (the parameter in the exchange part which determines the behavior of the functional for $s \rightarrow 0$) was set to $\mu = \mu_{\text{GE}} = 10/81$ in order to recover the second-order gradient expansion of the exchange energy, and a parameter in the correlation part was chosen to yield good surface exchange-correlation energy for the jellium model. PBEsol was shown to improve over PBE for various types of solids^{18,27} including 4d- and 5d-transition metals.^{28,29} Zhao

and Truhlar¹⁹ proposed the second-order GGA (SOGGA) functional which consists of an exchange enhancement factor whose analytical form is an average of the PBE and RPBE (Ref. 30) enhancement factors. The parameter μ is set to $\mu = \mu_{\text{GE}}$ and κ (a parameter in the exchange part which controls the behavior at $s \rightarrow \infty$) is set to 0.552 in order to satisfy a tighter Lieb-Oxford bound.^{31,32} SOGGA, used in combination with the PBE correlation functional, yields very accurate lattice constants of solids.¹⁹ AM05 (Ref. 15) was developed by combining functionals from different model systems. For bulklike regions (small values of s) LDA is used, while for surfacelike regions (large values of s) the local Airy approximation (LAA) functional³³ is used. Recently, Mattsson *et al.*³⁴ showed that the performance of AM05 for lattice constants is superior to PBE, and in Ref. 28, it is reported that AM05 is more accurate than PBE and PBEsol for heavy transition-metal elements. The meta-GGA functional TPSS,²² whose mathematical form is based on the PBE functional, has been tested on atoms,^{35,36} molecules,^{35,37–39} (including van der Waals³⁸ and hydrogen-bonded complexes³⁷) and solids,^{22,40–42} and it has been shown that it yields (very) good performances for many types of systems, and thus is a general purpose functional. We note that we used the PBE orbitals and electron density for the evaluation of the TPSS total energy, since there is no TPSS potential implemented into the WIEN2K code.⁴³

II. RESULTS AND DISCUSSION

The performances of the LDA, GGA (PBE, AM05, WC, PBEsol, and SOGGA), and TPSS functionals for the lattice constants and bulk moduli were assessed on a set of 60 cubic solids (see Table I). Graphite and the rare-gas solids Ne and Ar were also chosen since these are systems where the weak interactions play an important role for the structure determination. We note that our testing set of solids (a slightly reduced version of the one used in our previous study²⁵) is much larger than the ones which were considered in other similar previous studies.^{18,19,28,34,40} In particular, we should mention that only in Ref. 28 the 3d-transition metals V, Fe, and Ni were considered, for which the PBE functional is by far still the best functional (see below). The calculations were done with the WIEN2K code⁴³ which solves the KS equations using the full-potential (linearized) augmented plane-wave and local orbitals [FP-(L)APW+lo] method.^{44–46} The FP-(L)APW+lo method is one of the most accurate methods to solve the KS equations and represents a good choice when testing exchange-correlation functionals. When good convergence parameters are used, the error in a calculated ground-state property is solely due to the approximate functional. The calculations have been converged with respect to the number of \mathbf{k} points for the integrations in the Brillouin zone (for most calculations a $21 \times 21 \times 21$ grid was used) and the value of $R_{\text{MT}}^{\text{min}} K_{\text{max}}$ (between 8 and 10) which determines the size of the basis set. The spin-orbit coupling was taken into account for the solids containing Ba, Ce, Hf, Ta, W, Ir, Pt, Au, Pb, and Th atoms.

The experimental lattice constants were corrected for the zero-point anharmonic expansion (ZPAE). Following the

procedure explained in Refs. 47 and 40, the following expression:

$$\frac{\Delta V_0^{\text{expt}}}{V_0^{\text{expt}}} = \frac{9}{16} (B_1 - 1) \frac{k_B \Theta_D}{B_0 v_{0,\text{at}}^{\text{expt}}} \quad (1)$$

was used to calculate the correction ΔV_0^{expt} to the experimental volume V_0^{expt} (the ZPAE-corrected experimental volume is $V_0^{\text{expt}} - \Delta V_0^{\text{expt}}$). In Eq. (1), $v_{0,\text{at}}^{\text{expt}}$ is the experimental volume per atom, B_1 is the derivative of the bulk modulus B_0 with respect to the pressure, and Θ_D is the Debye temperature. As in Ref. 40, we used the experimental values for B_0 and Θ_D , and the TPSS values for B_1 . We mention that the ZPAE-corrected experimental lattice constants of C (diamond phase), Si, Ge, and the compounds shown in Ref. 40 (and used in Refs. 18 and 19) are not correct, since the ZPAE corrections were calculated using the primitive unit cell instead of $v_{0,\text{at}}^{\text{expt}}$ in the right-hand side of Eq. (1). This error led to experimental lattice constants which were 0.005–0.02 Å too large.

For the analysis of the results, the following statistical quantities will be used: the mean error (me), the mean absolute error (mae), the mean relative error (mre, in percent), and the mean absolute relative error (mare, in percent). We mention that the AM05 results obtained for the spin-polarized systems (Fe and Ni) were obtained with the PBE electron density since the AM05 potential is not available in the spin-polarized form (only the energy is at the present time available⁴⁸). The ZPAE-corrected experimental lattice constants were considered for the discussion of the results.

For the solids (listed below) whose experimental lattice constant were measured or extrapolated (using the linear thermal expansion coefficient α) at a temperature below room temperature, the temperature (in K) is indicated in parenthesis. The references from which the experimental values of a_0 (and eventually α), B_0 , and Θ_D were taken are also given: Li (0),^{40,49} Na (0),^{40,49} K (0),^{40,49} Rb (5),^{49,50} Ca (0),⁵¹ Sr (0),⁵¹ Ba (0),⁵¹ V (235),^{49,52} Nb (0),^{49,53} Ta (0),^{49,53,54} Mo (0),^{49,53} W (0),^{49,53,54} Fe (0),^{49,53} Rh (0),^{40,49} Ir (100),^{49,53} Ni (0),^{49,53} Pd (0),^{40,49} Pt (0),^{49,53,54} Cu (0),^{40,49} Ag (0),^{40,49} Au (0),^{49,53,54} Al (0),^{40,49} C (0),^{40,49} Si (0),^{40,49} Ge (0),^{40,49} Sn (20),⁵⁵ Pb (0),^{49,53} Th (75),^{49,53} LiF (0),^{40,53} LiCl (0),^{40,53} NaF (0),^{40,53} NaCl (0),^{40,53} MgO (0),^{40,53} MgS,^{56–58} CaO (17.9),^{55,59} TiC,^{60,61} TiN,^{61,62} ZrC,^{61,62} ZrN,^{61–63} HfC,^{61,62} HfN,^{61–63} VC,^{61,62} VN,^{61,64} NbC,^{61,62} NbN,^{61,63,64} FeAl,^{65–67} CoAl,^{68,69} NiAl,^{69,70} BN (0),^{55,71} BP,⁵⁵ BAs (0),⁵⁵ AlP (0),^{55,71} AlAs (0),⁵⁵ GaN,^{55,72} GaP (0),⁵⁵ GaAs (0),^{40,55} InP (0),⁵⁵ InAs (0),⁵⁵ SiC (0),⁴⁰ and CeO₂ (100).^{73–75}

In Table I we present the calculated equilibrium lattice constants a_0 and in Fig. 1 the corresponding relative errors for the considered elements (discussed in Sec. II A) and compounds (discussed in Sec. II B). Concerning the bulk moduli B_0 , only the statistical quantities are shown (Table II).

A. Elemental solids

For the elements of group IA (Li, Na, K, and Rb), LDA gives much too small a_0 with large relative errors between –2.5 and –4%. For K and Rb, the functionals PBE, AM05,

TABLE I. Equilibrium lattice constant a_0 (in Å) of 60 solids. The Strukturbericht symbols (in parenthesis) are used for the structure: A1=fcc, A2=bcc, A4=diamond, B1=rock-salt, B2=cesium-chloride, B3=zinc-blende, and C1=fluorite. Spin-orbit coupling was taken into account for the solids containing Ba, Ce, Hf, Ta, W, Ir, Pt, Au, Pb, and Th atoms. The “good” (absolute relative error less than 0.5%) theoretical values are in bold and the “bad” (absolute relative error larger than 2%) values are underlined. The experimental values in parenthesis are the non-ZPAE-corrected values. The statistical quantities in parenthesis were calculated using the non-ZPAE-corrected experimental lattice constants. See the text for the definition of the statistical quantities me , mae , mre , and $mare$.

Solid	LDA	SOGGA	PBEsol	WC	AM05	TPSS	PBE	Expt.
Li (A2)	<u>3.363</u>	3.435	3.433	3.449	3.456	3.455	3.435	3.451(3.477)
Na (A2)	<u>4.047</u>	4.175	4.170	4.199	4.209	4.237	4.196	4.209(4.225)
K (A2)	<u>5.045</u>	5.231	5.213	5.256	5.293	<u>5.352</u>	5.282	5.212(5.225)
Rb (A2)	<u>5.374</u>	5.605	5.579	5.609	<u>5.692</u>	<u>5.749</u>	5.670	5.577(5.585)
Ca (A1)	<u>5.333</u>	5.469	5.456	5.458	5.491	5.533	5.530	5.556(5.565)
Sr (A1)	<u>5.786</u>	5.930	<u>5.917</u>	<u>5.914</u>	5.975	6.018	6.027	6.040(6.048)
Ba (A2)	<u>4.754</u>	<u>4.881</u>	<u>4.881</u>	<u>4.870</u>	4.963	4.991	5.030	5.002(5.007)
V (A2)	<u>2.932</u>	<u>2.959</u>	<u>2.963</u>	2.965	<u>2.961</u>	2.979	3.001	3.024(3.028)
Nb (A2)	3.250	3.268	3.274	3.280	3.271	3.297	3.312	3.294(3.296)
Ta (A2)	3.257	3.280	3.285	3.290	3.281	3.300	3.323	3.299(3.301)
Mo (A2)	3.116	3.126	3.133	3.139	3.128	3.151	3.164	3.141(3.144)
W (A2)	3.143	3.155	3.162	3.167	3.156	3.173	3.191	3.160(3.162)
Fe (A2)	<u>2.754</u>	<u>2.783</u>	<u>2.790</u>	<u>2.793</u>	<u>2.787</u>	2.804	2.833	2.853(2.861)
Rh (A1)	3.759	3.772	3.785	3.795	3.777	3.807	3.834	3.793(3.798)
Ir (A1)	3.828	3.834	3.847	3.857	3.837	3.867	3.887	3.831(3.835)
Ni (A1)	<u>3.423</u>	3.453	3.463	3.468	3.461	3.478	3.518	3.508(3.516)
Pd (A1)	3.848	3.867	3.882	3.892	3.878	3.909	3.948	3.876(3.881)
Pt (A1)	3.909	3.917	3.932	3.944	3.923	3.958	3.985	3.913(3.916)
Cu (A1)	<u>3.522</u>	3.557	3.570	3.573	3.568	3.585	3.632	3.596(3.603)
Ag (A1)	4.007	4.038	4.058	4.065	4.059	4.093	<u>4.152</u>	4.062(4.069)
Au (A1)	4.047	4.061	4.081	4.092	4.074	4.115	<u>4.154</u>	4.062(4.065)
Al (A1)	3.983	4.008	4.018	4.023	4.008	4.015	4.041	4.019(4.032)
C (A4)	3.536	3.552	3.557	3.558	3.553	3.573	3.575	3.544(3.567)
Si (A4)	5.407	5.425	5.438	5.437	5.439	5.466	5.475	5.415(5.430)
Ge (A4)	5.632	5.662	5.684	5.686	5.688	5.734	<u>5.769</u>	5.639(5.652)
Sn (A4)	6.481	6.521	6.547	6.548	6.566	<u>6.621</u>	<u>6.661</u>	6.474(6.482)
Pb (A1)	4.874	4.899	4.931	4.936	4.945	4.997	<u>5.048</u>	4.912(4.916)
Th (A1)	<u>4.920</u>	<u>4.928</u>	<u>4.959</u>	4.977	<u>4.954</u>	5.032	5.056	5.071(5.074)
LiF (B1)	3.919	4.008	4.013	4.017	<u>4.046</u>	<u>4.047</u>	<u>4.071</u>	3.960(4.010)
LiCl (B1)	4.986	5.062	5.081	5.087	5.142	5.151	5.167	5.072(5.106)
NaF (B1)	4.507	4.637	4.635	4.652	<u>4.682</u>	<u>4.702</u>	<u>4.709</u>	4.576(4.609)
NaCl (B1)	5.484	5.608	5.619	5.637	<u>5.696</u>	<u>5.715</u>	<u>5.714</u>	5.565(5.595)
MgO (B1)	4.169	4.217	4.222	4.223	4.228	4.244	4.261	4.186(4.207)
MgS (B1)	5.139	5.174	5.190	5.195	5.197	5.237	5.238	5.182(5.202)
CaO (B1)	4.719	4.771	4.778	4.777	4.790	4.819	4.841	4.787(4.803)
TiC (B1)	4.266	4.294	4.302	4.303	4.297	4.336	4.339	4.317(4.330)
TiN (B1)	4.178	4.202	4.210	4.214	4.206	4.241	4.254	4.228(4.239)
ZrC (B1)	4.647	4.664	4.675	4.680	4.670	4.711	4.715	4.688(4.696)
ZrN (B1)	4.532	4.549	4.560	4.565	4.555	4.590	4.602	4.574(4.585)
HfC (B1)	4.578	4.602	4.613	4.618	4.606	4.646	4.660	4.627(4.638)
HfN (B1)	4.482	4.506	4.515	4.520	4.510	4.543	4.560	4.512(4.520)
VC (B1)	4.095	4.114	4.123	4.129	4.116	4.151	4.162	4.148(4.160)
VN (B1)	4.050	4.071	4.081	4.087	4.075	4.112	4.125	4.126(4.141)
NbC (B1)	4.432	4.446	4.457	4.462	4.448	4.487	4.491	4.462(4.470)

TABLE I. (Continued.)

Solid	LDA	SOGGA	PBEsol	WC	AM05	TPSS	PBE	Expt.
NbN (B1)	4.361	4.374	4.385	4.392	4.378	4.419	4.426	4.383(4.392)
FeAl (B2)	<u>2.812</u>	2.837	2.840	2.843	2.839	2.850	2.869	2.882(2.889)
CoAl (B2)	<u>2.795</u>	2.820	2.824	2.826	2.822	2.833	2.853	2.855(2.861)
NiAl (B2)	2.834	2.859	2.864	2.866	2.862	2.873	2.894	2.882(2.887)
BN (B3)	3.585	3.605	3.610	3.610	3.607	3.628	3.629	3.585(3.607)
BP (B3)	4.496	4.514	4.525	4.526	4.522	4.553	4.553	4.520(4.538)
BAs (B3)	4.740	4.761	4.775	4.778	4.772	4.808	4.816	4.760(4.777)
AlP (B3)	5.440	5.464	5.476	5.474	5.479	5.504	5.513	5.445(5.460)
AlAs (B3)	5.636	5.668	5.681	5.680	5.687	5.713	5.734	5.646(5.658)
GaN (B3)	4.463	4.492	4.502	4.504	4.501	4.536	4.551	4.520(4.531)
GaP (B3)	5.401	5.429	5.447	5.448	5.451	5.498	5.514	5.435(5.448)
GaAs (B3)	5.616	5.650	5.670	5.672	5.678	5.724	<u>5.757</u>	5.637(5.648)
InP (B3)	5.839	5.869	5.890	5.890	5.898	5.958	5.968	5.856(5.866)
InAs (B3)	6.038	6.076	6.098	6.100	6.111	<u>6.167</u>	<u>6.195</u>	6.044(6.054)
SiC (B3)	4.333	4.354	4.360	4.360	4.357	4.371	4.384	4.340(4.358)
CeO ₂ (C1)	5.371	5.396	5.410	5.415	5.414	5.454	5.475	5.393(5.401)
me (Å)	-0.058	-0.014	-0.005	0.001	0.005	0.036	0.051	
	(-0.070)	(-0.026)	(-0.017)	(-0.011)	(-0.007)	(0.024)	(0.039)	
mae (Å)	0.058	0.029	0.029	0.031	0.035	0.047	0.055	
	(0.070)	(0.032)	(0.029)	(0.029)	(0.033)	(0.039)	(0.047)	
mre (%)	-1.32	-0.37	-0.17	-0.03	0.01	0.70	1.05	
	(-1.59)	(-0.65)	(-0.44)	(-0.30)	(-0.26)	(0.42)	(0.78)	
mare (%)	1.32	0.68	0.67	0.68	0.77	0.99	1.18	
	(1.59)	(0.75)	(0.67)	(0.65)	(0.76)	(0.83)	(0.99)	

and TPSS (in this order) severely overestimate a_0 , while overall the WC, PBEsol, and SOGGA functionals perform quite well for the alkali metals.

For the group IIA elements Ca, Sr, and Ba, LDA underestimates a_0 again severely by more than -4% (the largest relative error for LDA among all investigated solids is for Ba). PBE and TPSS are the most efficient functionals to correct this underestimation, while the other GGA functionals still give too small lattice constants with errors up to -2.5% . WC, PBEsol, and SOGGA functionals yield very similar lattice constants for these alkaline-earth metals, while AM05 is a bit closer to PBE (and experiment). Note that for groups IA and IIA the LDA absolute relative error does not decrease when the nuclear charge Z increases as it is observed for the other families of solids studied in this work (see below).

For Al, TPSS and all GGA functionals except PBE yield very accurate lattice constants, while LDA and PBE relative errors are larger (-0.8% and 0.5% , respectively). For the elements of group IVA which crystallize in the diamond structure (C, Si, Ge, and Sn), a clear trend with Z can be observed. With increasing Z the relative error changes from slight underestimation (LDA) or slight overestimation (GGA) of a_0 to nearly perfect agreement with experiment (LDA) or strong overestimation of a_0 (TPSS and PBE). The relative error of PBE for Sn ($\sim 3\%$) is one of the largest PBE errors among all investigated solids. Clearly, LDA and

SOGGA are the best functionals for these solids. For Pb, all functionals except PBE and TPSS yield absolute relative errors smaller than 1% .

For the transition-metal elements all functionals show a pronounced and very similar trend within the $3d$, $4d$, and $5d$ series and from left to right in the Periodic Table: the relative error goes in the direction of the positive values. LDA severely underestimates the equilibrium lattice parameters of the $3d$ elements (up to -3.5%), is still too small for the $4d$ elements, but very close to experiment for the $5d$ elements (in particular for those on the right side of the Periodic Table, Ir, Pt, and Au). On the other hand PBE is by far the best functional for the $3d$ elements (except Cu), but overestimates a_0 for the $4d$ elements and in particular the $5d$ elements by up to 2.5% . The new functionals SOGGA, AM05, PBEsol, and WC, as well as TPSS (in that order) yield a_0 within the LDA/PBE bounds and are fairly close together. They lead to modest errors for all elements except V and Fe.

Concerning the actinide Th, all tested functionals show an underestimation of the lattice constant (from $\sim -3\%$ to $\sim -0.5\%$) and the new GGA functionals have for Th one of their largest relative errors among the investigated solids.

B. Compounds

For the series of IA-VIIA compounds AB , where $A=\text{Li}$ or Na and $B=\text{F}$ or Cl , we can see that LDA systematically

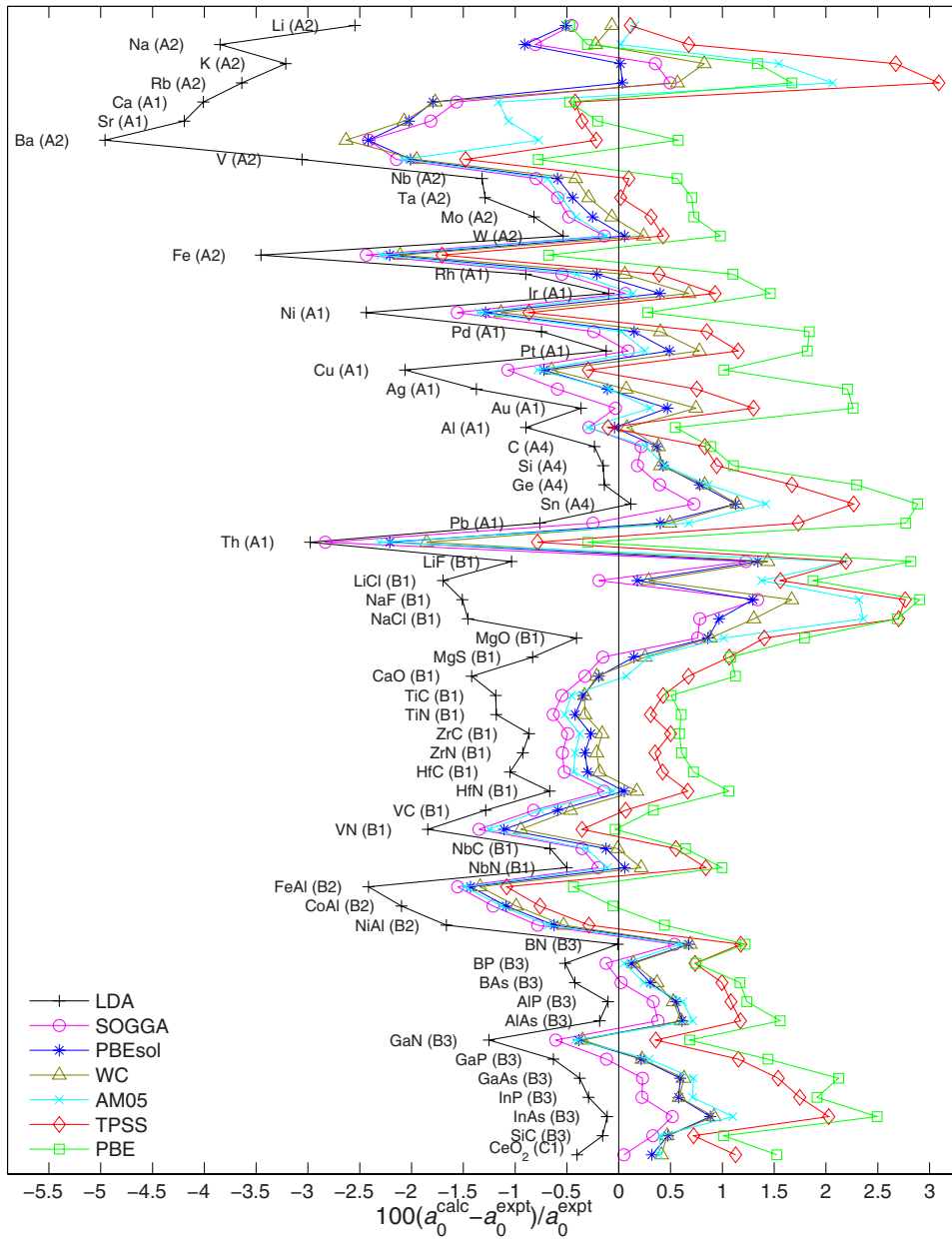


FIG. 1. (Color online) Relative error (in percent) in the calculated lattice constants with respect to the ZPAE-corrected experimental values (see Table I).

underestimates (more than -1%) the lattice constants, while AM05, TPSS, and PBE functionals (in that order) clearly overestimate a_0 by 1% – 3% . Note that for LiF and LiCl the AM05 functional yields results which are very close to the TPSS results. For the IIA-VIA compounds the WC, PBEsol, and SOGGA functionals are on average rather good, while LDA clearly underestimates a_0 and PBE and TPSS clearly overestimate a_0 .

Turning now to the transition-metal monocarbides and mononitrides, we observe that the new functionals underestimate the lattice constants (slightly for HfN and NbN). As usual, LDA underestimates a_0 even more, while PBE and TPSS overestimate a_0 for all these solids except VN.

The results obtained for FeAl, CoAl, and NiAl (cesium-chloride structure) are quite clear: PBE yields lattice constants which are closest to the experimental values, while all

TABLE II. The statistical quantities (see text for their definitions) on the bulk modulus B_0 for the 60 solids listed in Table I.

	LDA	SOGGA	PBEsol	WC	AM05	TPSS	PBE
me (GPa)	24.0	16.6	12.6	11.4	11.9	5.5	-2.2
mae (GPa)	24.8	18.8	15.8	14.8	16.7	13.7	12.8
mre (%)	15.4	8.3	6.0	4.9	3.9	0.6	-3.4
mare (%)	16.3	10.8	9.3	9.1	10.6	9.9	9.5

other functionals (including TPSS) underestimate the lattice constant of these three compounds significantly. For LDA the errors are substantial.

From Fig. 1 we can see that for all IIIA–VA compounds (zinc-blende structure) the trends are very similar as for the elements of group IVA. LDA underestimates a_0 slightly (less than -1%), while PBE and TPSS overestimate a_0 significantly (up to $\sim 2\%$). The new functionals (SOGGA in particular) perform quite reasonably, but none of them can break the trend that a_0 for compounds with lighter/heavier elements is usually under/overestimated. The SOGGA functional yields slightly smaller a_0 than PBEsol, AM05, and WC which give almost identical results. GaN seems to be quite exceptional, as for this case LDA underestimates a_0 significantly while TPSS (and PBE) are as accurate as the new functionals. Concerning the last two compounds in Table I (SiC and CeO₂), the LDA and SOGGA functionals are quite good, while the others overestimate a_0 .

C. General trends

The statistical data for the lattice constant a_0 and the bulk modulus B_0 for the solids considered in Secs. II A and II B are given in Table I (bottom) and Table II, respectively. Clearly the errors for the lattice parameters using PBEsol, WC, AM05, and SOGGA have been significantly reduced. Note that WC and AM05 functionals lead to very small me and mre. However, it should be noted that the relative performances of the functionals depend obviously on the solids included in the testing set, in particular if the testing set is small. The functional which has, for instance, the lowest mae for a particular testing set, may not be the best for another testing set.

For the bulk modulus we can see that the ordering of the functionals (from the largest underestimation to the largest overestimation) is more or less reversed compared to the values for the lattice constant. There is an exception for the me, since it is smaller for WC than for AM05. The mean (relative) errors me and mre are smallest for TPSS and PBE, while for the mean absolute (relative) errors mae and mare, PBEsol, WC, TPSS, and PBE are better than the other functionals.

In Fig. 2 we show the relative errors in a_0 , ordered such that the relative error goes in the direction of positive values from bottom to top (i.e., in one row there might be different compounds for each functional). The general tendency, namely, that LDA underestimates a_0 and PBE and TPSS overestimate it, while the new functionals are much better balanced, is clearly visible. However, from Fig. 2 it is also evident that the slope of the curves, which indicates the trends across the Periodic Table is rather similar for all functionals. The spread between the largest underestimation and overestimation is the smallest for PBE (3.7%) and PBEsol (3.8%), but largest for LDA (5.1%). For the other functionals the spread is in the range 4.2%–4.8%, but we can see that these new GGA functionals yield smaller shifts with respect to LDA, and thus they lead to lattice constants which are on average closer to experiment. However, none of these “weaker” GGAs can cure the unfortunate trends within the

Periodic Table like larger lattice parameters from left to right or within the $3d$, $4d$, and $5d$ series. An “irregular” behavior can be seen for the alkali metals, where WC and AM05 functionals may give larger a_0 than PBE. Unfortunately, for AM05 this leads to even larger errors for K and Rb.

Concerning the comparison of our calculated values [obtained with the FP-(L)APW+lo basis set] with others published in the literature, we have observed that the agreement depends on the used basis set. For many solids the results obtained with Gaussian basis sets^{19,40} can differ from our results by 0.01–0.02 Å, however, for a given compound, the difference varies very little from one functional to another. The comparison with the results obtained with the exact muffin-tin orbital method (EMTO) (Ref. 28) has revealed a few large discrepancies. For instance, we obtained 5.692 Å for Rb with AM05 functional, while the result of Ropo *et al.*²⁸ is 5.664 Å. Also, our LDA results for Sr and Ba differ by 0.04 and 0.05 Å from the EMTO results, respectively, but we have to recall that we used spin-orbit coupling for Ba. Much better agreement is obtained when comparison is done with the results of Mattsson *et al.*³⁴ who performed the calculations with two different types of basis functions (the full-potential linear muffin-tin orbital and projected augmented wave methods). In most cases the disagreement appears only at the third digit after the decimal point.

D. Graphite and the rare gases Ne and Ar

Table III and Fig. 3 show the results obtained for graphite and the rare-gas solids Ne and Ar, as well as the experimental values (Refs. 76–79). For graphite, the in-plane lattice constant a was kept fixed at the experimental value of 2.464 Å during the calculations. It is already known (see Ref. 80 for a collection of previous LDA and GGA results for graphite) that LDA gives excellent results for the lattice constant c_0 (6.7 Å for LDA vs 6.71 Å for experiment), while the PW91 (Ref. 80) and PBE ($c_0=8.8$ Å) functionals severely overestimate c_0 . The good performance of LDA for systems where weak interactions (e.g., London dispersion forces) play an important role is rather exceptional, since most of the time LDA strongly underestimates the bond lengths and lattice constants of such systems (e.g., rare-gas dimers⁸¹). Nevertheless, previously we showed that LDA is also accurate for the layered systems h-BN and MoSe₂ whose interlayer interactions are rather weak.²⁵ But, we should not forget that the London dispersion forces are not taken into account in semilocal functionals, thus good results obtained for such weakly bound systems are mostly fortuitous. From Fig. 3 we can see that the total-energy curves calculated with PBEsol and SOGGA functionals are quasi-identical (minima at $c_0=7.3$ Å), while the flat minimum of WC is at $c_0=9.6$ Å (larger than PBE) and AM05 and TPSS fail by showing no minimum (at least not before $c=15$ Å). Analyzing the total-energy curves with a bit more details reveals that for small c there are hardly any differences between PBEsol, SOGGA, and WC, but as c increases (the reduced density gradient s also increases) the WC results differ more and more from the two other GGAs to finally become very similar to the PBE results. We mention that the

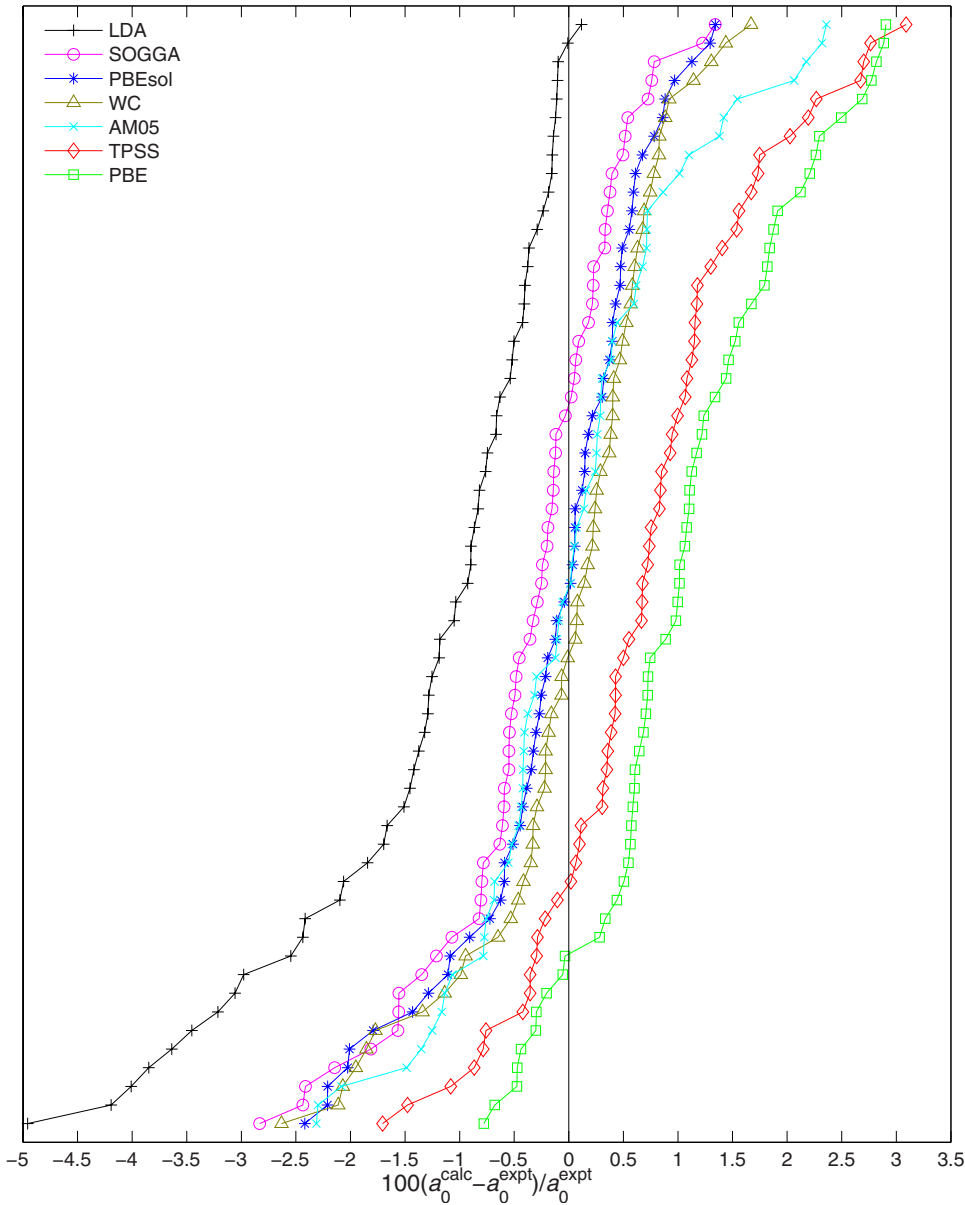


FIG. 2. (Color online) Relative error (in percent) in the calculated lattice constants with respect to the ZPAE-corrected experimental values (see Table I). For each functional, the solids have been ordered such that the relative error goes in the direction of the positive values from bottom to top.

results obtained by Zhao and Truhlar¹⁹ for graphite (using Gaussian basis functions) differ considerably from ours. The most obvious differences appear for PBE (7.290 Å from Ref. 19 vs 8.8 Å in the present work) and TPSS (7.266 Å from Ref. 19 vs an apparently nonbonded system in the present work), but since our LDA and PBE results agree well with other LDA and PBE results found in the literature^{80,82–84} we expect the discrepancies to be due to the limited Gaussian basis set.

In Table III are also shown the results for Ne and Ar. As already well known, we can see that LDA severely underestimates the lattice constants of rare-gas solids (see, e.g., Ref. 25). Among the GGA functionals, SOGGA is the most accurate for both Ne and Ar. PBE and PBEsol lattice constants (slightly larger than with SOGGA) are rather similar, while WC and TPSS results (which show a clear overestimation of a_0) are the same. Similarly as for graphite, the AM05 functional shows no minimum in the studied range of lattice constants.

Overall, SOGGA is the functional which yields the smallest lattice constants among all tested GGAs, and therefore yields the *least bad* results for graphite, Ne, and Ar. The SOGGA results could be anticipated by looking at its enhancement factor (see Ref. 19) which is the closest to LDA for large values of the reduced density gradient s . It has been pointed out that the long-range behavior of the enhancement factor of a functional (the exchange part in particular) is important for the determination of the structural and energetic properties of such systems.^{85,86} The bad results for AM05 are also not surprising since the enhancement factor diverges for $s \rightarrow \infty$, a behavior which leads to very large or no minimum in the total-energy curve for such weakly bound systems.^{85,86} The TPSS results obtained for graphite are more difficult to explain, since, in addition to the s dependence, this functional depends also on the kinetic-energy density.

The observed trends for the bulk modulus B_0 of the rare gases are as we expected from the results for the lattice constant. For Ne, there is a strong overestimation by LDA, a

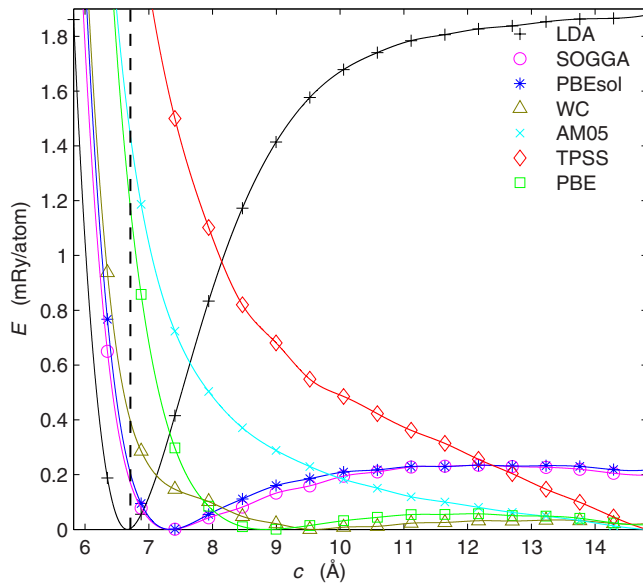


FIG. 3. (Color online) Total energy of graphite vs the lattice constant c (the interlayer distance is $c/2$). The in-plane lattice constant a was kept fixed at the experimental value (2.464 Å) for all values of c . The minima for the AM05 and TPSS functionals are either much larger than 15 Å or absent. The vertical dashed line represents the experimental lattice constant ($c_0=6.71$ Å).

much better agreement with SOGGA, PBEsol, and PBE, and a clear underestimation with WC and TPSS. For Ar, LDA strongly overestimates B_0 , while all other functionals underestimate B_0 .

III. SUMMARY

We have tested some of the recently proposed GGA functionals (AM05, WC, PBEsol, and SOGGA) and have come to the conclusion that they generally improve the geometry predictions compared to LDA. Often they also lead to improvement over PBE (which has a tendency to overestimate the lattice constants). PBE remains the best GGA functional, e.g., for the alkaline-earth metals Ca, Sr, and Ba (for which TPSS is also very good) and most of the solids containing 3d-transition elements. LDA yields very good results for the 5d-transition metals Ir, Pt, and Au. For the large testing set of solids we have considered, the statistics (excluding graphite

TABLE III. Equilibrium lattice constant (in Å, a_0 for Ne and Ar, and c_0 for graphite). The Strukturbericht symbols are indicated in parenthesis.

Method	Graphite (A9)	Ne (A1)	Ar (A1)
LDA	6.7	3.9	4.9
SOGGA	7.3	4.5	5.8
PBEsol	7.3	4.7	5.9
PBE	8.8	4.6	6.0
WC	9.6	4.9	6.4
TPSS	>15	4.9	6.4
AM05	>15	>5.5	>6.7
Expt.	6.71 ^a	4.47 ^b	5.31 ^b

^aReference 76.

^bReferences 77–79.

and the rare-gas solids) show that the new GGA functionals lead to the smallest mean (absolute) errors. Also, the AM05 and WC functionals lead to signed mean relative errors close to zero, showing their well-balanced characters among the solids. The ordering of the functionals from the one which underestimates the most the lattice constants to the one which overestimates the most is LDA, SOGGA, PBEsol, WC, AM05, TPSS, and PBE. PBEsol, WC, and AM05 lead most of the time to similar results (Mattsson *et al.* have also pointed out the similarity between AM05 and PBEsol results¹⁸). TPSS, which is considered as the completion of the third rung of Jacob's ladder of first-principles functionals²³ improves only slightly over PBE; however, we should remember that these two functionals are *equally good* for both finite and infinite systems, while for the thermochemistry of molecules, PBEsol and SOGGA perform very poorly¹⁹ and WC slightly deteriorates the PBE results.²⁵ Unfortunately, there is no functional which is sufficiently accurate for all investigated solids, but the results presented in this paper may serve as guidelines when one wants to select a functional which should give accurate structural parameters for a particular solid.

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