Systematic investigation of a family of gradient-dependent functionals for solids

Philipp Haas, Fabien Tran, and Peter Blaha
Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

Luana S. Pedroza
Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, São Paulo 05315-970, SP, Brazil

Antonio J. R. da Silva
Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, São Paulo 05315-970, SP, Brazil and Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil

Mariana M. Odashima
Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos 13560-970, SP, Brazil

Klaus Capelle
Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC), Santo André 09210-170, SP, Brazil
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Eleven density functionals are compared with regard to their performance for the lattice constants of solids. We consider standard functionals, such as the local-density approximation and the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA), as well as variations of PBE GGA, such as PBEsol and similar functionals, PBE-type functionals employing a tighter Lieb-Oxford bound, and combinations thereof. On a test set of 60 solids, we perform a system-by-system analysis for selected functionals and a full statistical analysis for all of them. The impact of restoring the gradient expansion and of tightening the Lieb-Oxford bound is discussed, and confronted with previous results obtained from other codes, functionals or test sets. No functional is uniformly good for all investigated systems, but surprisingly, and pleasingly, the simplest possible modifications to PBE turn out to have the most beneficial effect on its performance. The atomization energy of molecules was also considered and on a testing set of six molecules, we found that the PBE functional is clearly the best, the others leading to strong overbinding.

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I. INTRODUCTION

Modern electronic structure theory[1,2] relies to a very large extent on density-functional theory (DFT).[3–5] The utility of DFT, in turn, depends crucially on the availability of approximations to the exchange-correlation (*xc*) functional that are sufficiently reliable and sufficiently simple to implement.[1–6]

As a consequence, a large number of approximate *xc* functionals have been developed. Only a few of these, however, have found widespread application, and essentially just two of them account for the large majority of applications of DFT in solid-state physics: the local-density approximation (LDA) and the Perdew-Burke-Ernzerhof (PBE) form of the generalized-gradient approximation (GGA).[7]

Among the main problems of these functionals is that lattice constants are systematically and consistently underestimated by LDA and overestimated by PBE. LDA lattice constants are typically about 1%–5% too short, while PBE lattice constants are too long by almost the same margin. Many other quantities, such as the unit-cell geometry and volume, the cohesive energy, bulk modulus, compressibility, phonon frequencies, sound velocity, elastic constants, Debye temperature, the pressure-dependence of all these quantities, surface reconstruction energies, the possibility of structural phase transitions, etc., depend crucially on the lattice constant. Therefore, the difficulty of LDA and PBE in predicting quantitatively reliable lattice constants is a crucial problem standing in the way of further applications of DFT to solids.

Until quite recently, no generally applicable solution to this problem was in sight, and the very voluminous literature on better *xc* functionals (e.g., the hybrid functionals) largely focused on finite systems (see Refs. 8 and 9 for recent reviews). For solids, however, these functionals do not perform that well in every situation and/or lead to very expensive calculations. For instance, the very popular hybrid functional B3LYP (Refs. 10 and 11) is rather hard to implement for solids, in particular for metals, and the effort does not seem to pay off, as resulting lattice constants overestimate experimental values by about as much as PBE.[12] Similarly, semiempirical[13] and nonempirical[14] meta-GGA functionals (slightly more expensive than GGAs) produce little[14,15] or no[13] improvement for lattice constants. Although many other functionals have been tried over the years, LDA and PBE remained, until very recently, the *de facto* standard DFT approach for the determination of structural properties of solids and nanostructures.

Recently, however, the field of functional construction for solids has gained new impetus through the development of AM05,[16–18] a radically new type of density functional based on the subsystem approach and the Airy gas, and the Wu-Cohen (WC) GGA,[19,20] which employs a simple but efficient modification of the PBE exchange enhancement factor that makes it more reliable for solid-state properties. An even

simpler modification of PBE is PBEsol,[21] which differs from original PBE only in the values of two parameters.

These developments have rekindled the interest in the development of better density functionals for solids. Several such recently developed functionals, AM05, WC, PBEsol, and the second-order GGA (SOGGA) of Zhao and Truhlar[22] have been systematically tested and compared to LDA, PBE, and the meta-GGA TPSS (Tao *et al.*, Ref. 14) in a previous publication by three of us (P.H., F.T., and P.B.).[15] A large test set (60 solids) and a very accurate all-electron implementation of the Kohn-Sham (KS) equations (the WIEN2K code)[23] allowed a detailed investigation of the performance of each of these functionals. Overall, no clear winner has emerged from the comparison, but the new GGA functionals improve over LDA and PBE for many solids and give smaller mean errors. In Ref. 24, we reported a detailed analysis of the functionals, which shed light on some of the trends observed in the lattice constants.

In an independent work, three of us (L.S.P., A.J.R.d.S., and K.C.) noted that the step that led from PBE to PBEsol is not unique, and allows several variations.[25] In fact, PBE and PBEsol turned out to be just two particular members of a family of functionals each of which takes its parameters, β and μ, from a different constraint. The resulting two-parameter family of functionals, collectively denoted PBE(β,μ), has been tested for atoms, molecules and solids in Ref. 25. The calculations for solids performed in that work employed pseudopotentials, which is the standard approach for very large systems with many inequivalent sites, but introduces an additional source of errors and complicates an unbiased assessment of the performance of each functional.

In still other work, two of us (M.M.O. and K.C.) initiated an investigation of the Lieb-Oxford (LO) bound,[26,27] a fundamental property of the quantum mechanics of Coulomb-interacting systems according to which the exact *xc* energy is bounded from below by a simple local density functional that is proportional to the LDA for exchange. An estimate of the proportionality factor, λ, is a parameter in several modern density functionals, among them SOGGA, TPSS, WC, as well as PBE, PBEsol and all other members of the PBE(β,μ) family. Numerical and analytical investigations[27–30] strongly suggest that the value adopted in standard density functionals $\lambda_{\mathrm{LO}}=2.273$ is too large and should be replaced by $\lambda_{\mathrm{EL}}=1.9555$. Of the functionals listed above only SOGGA makes use of this tighter bound. Consequences of a tighter LO bound in PBE calculations for molecular systems have been explored in Ref. 29, but that work did not consider solids and did not include variations in β and μ. We also mention the work of Peltzer y Blancá *et al.*[31] who concluded that reducing the value of λ in PBE leads to better results for the equilibrium volume of 4*d* and 5*d* transition metals as also shown in the present work.

In the present paper we now bring all these developments together. We propose and study the three-parameter family of density functionals PBE(β,μ,λ), explore all meaningful nonempirical combinations of these parameters that are available, implement the resulting ten functionals in the WIEN2K all-electron code,[23] and test them on the large set of 60 solids from Ref. 15. In addition we implemented these functionals in the DEMON code[32] and tested atomization energies on a small but representative set of six molecules.[33]

This paper is organized as follows. In Sec. II, we describe the PBE(β,μ,λ) family of functionals, indicating the possible values and sources of each of its three parameters. Section III is devoted to a system-by-system comparison of three members of the family that differ in just one constraint from original PBE. In Sec. IV, we then present results from a statistical analysis of the full set of ten PBE-type functionals and LDA, for all 60 solids. This section also contains a comparison of our results with those from several other published tests of similar functionals, among them various using different codes and different test sets. Section V analyses our results separately for elements and compounds (metallic transition metal compounds, semiconductors and insulators) and Sec. VI reports the performance of the PBE(β,μ,λ) functionals for atomization energies of small molecules. Finally, Sec. VII contains our conclusions.

II. PBE(β,μ,λ) FAMILY OF FUNCTIONALS

The structure of PBE is explained in the original reference (Ref. 7), and more details are given in the review literature.[34] In the interest of conciseness, we thus refrain from repeating the explicit expression of this widely used functional and directly focus on its parameters and their possible modifications.

PBE contains nonempirical parameters, whose numerical values are obtained by requiring that the functional obeys known universal constraints. Two of them, κ and μ, appear in the exchange functional, E_x, and one, β, appears in the correlation functional, E_c.

In the original construction of PBE,[7] the parameter β is chosen such that in the high-density limit E_c^{PBE} recovers the second-order gradient expansion of the correlation energy of spatially weakly varying systems. The requirement that the combined *xc* functional reproduces the LDA jellium response function (which is accurate) implies

$$\mu = \frac{\pi^2}{3}\beta, \tag{1}$$

which fixes μ. The third parameter, κ, was determined such that E_x^{PBE} alone obeys the Lieb-Oxford lower bound[26] on the *xc* energy. This implies

$$\kappa = \frac{\lambda}{2^{1/3}} - 1 = 0.804, \tag{2}$$

where $\lambda_{\mathrm{LO}}=2.273$ is an estimate of the Lieb-Oxford constant λ obtained in Ref. 26.

This particular choice of constraints proved to be enormously successful, and PBE is one of the most widely used density functionals across physics and chemistry. Nevertheless, the choice is clearly not unique, and has recently been reconsidered along two independent lines. To discuss these, we introduce the notation PBE(β,μ,λ), where the parameters can be replaced either by their numerical values or by symbols indicating the source of these values. Hence, original PBE becomes PBE(G_c,J_r,LO) indicating that β comes from the gradient expansion of E_c, μ from the jellium re-

TABLE I. Parameters of the eleven functionals under investigation in this work, and a statistical summary [Eqs. (3)–(7)] of their performance for lattice constants of 60 solids. Lattice constants differing by less than ≈0.005 Å and mares differing by less than ≈0.05% should be considered equivalent. The lattice constants are given in Table SI of the supplementary material (Ref. 42).

Functional	β	μ	λ [e]	me (Å)	mae (Å)	mre (%)	mare (%)	spread (%)
LDA				−0.060	0.060	−1.37	1.37	4.95
PBE(G_c,J_r,LO) [a]	0.067	0.21951	2.273	0.049	0.053	1.02	1.14	3.68
PBE(J_s,G_x,LO) [b]	0.046	0.12346	2.273	−0.007	0.028	−0.21	0.64	3.71
PBE(J_s,J_r,LO) [c]	0.046	0.15133	2.273	0.014	0.033	0.25	0.72	3.41
PBE(G_c,G_x,LO) [c]	0.067	0.12346	2.273	−0.012	0.029	−0.31	0.67	4.30
PBE(J_r,G_x,LO) [c]	0.038	0.12346	2.273	−0.002	0.030	−0.09	0.67	3.56
PBE(G_c,J_r,EL) [d]	0.067	0.21951	1.9555	0.014	0.037	0.28	0.80	3.73
PBE(J_s,G_x,EL)	0.046	0.12346	1.9555	−0.023	0.033	−0.55	0.76	4.00
PBE(J_s,J_r,EL)	0.046	0.15133	1.9555	−0.008	0.032	−0.20	0.71	3.87
PBE(G_c,G_x,EL)	0.067	0.12346	1.9555	−0.028	0.034	−0.67	0.78	3.75
PBE(J_r,G_x,EL)	0.038	0.12346	1.9555	−0.018	0.034	−0.44	0.75	4.08

[a]This is PBE (Reference 7).
[b]This is PBEsol (Reference 21).
[c]These are the three functionals proposed in Reference 25.
[d]This is the functional of Reference 29.
[e]λ=2.273 and 1.9555 correspond to κ=0.804 and 0.552, respectively [see Eq. (2)].

sponse function, while for λ the original Lieb-Oxford estimate is adopted.

The first line of thought originates with the PBEsol functional, designed specifically to improve on PBE for solids.[21] To construct PBEsol it was argued that for solids the gradient expansion of the exchange functional is expected to be more important than that of the correlation functional. Consequently μ, which appears in the exchange energy, is chosen in PBEsol such as to reproduce the second-order gradient expansion of E_x. The parameter β, appearing in the correlation energy, is determined in PBEsol by requiring that jellium surface energies are accurately reproduced. In our notation, PBEsol becomes PBE(J_s,G_x,LO). PBEsol has been extensively tested[15,21,35–37] and the results have vindicated the revised choice of constraints, as PBEsol indeed provides significant improvement on PBE for solids (at the expense of worsening the results for smaller molecular systems).

Inspired by the PBEsol work, three of the present authors explored some other possible choices of constraints for obtaining β and μ.[25] In one of these, PBE(G_c,G_x,LO), β and μ are both determined from gradient expansions, thus guaranteeing that this expansion is recovered, to the extent possible within the functional form of PBE, for both exchange *and* correlation. In another, PBE(J_s,J_r,LO), β and μ are both determined from jellium: μ from the jellium response function, as in PBE, and β from the jellium surface energy, as in PBEsol. Finally, PBE(J_r,G_x,LO) takes β from the jellium response function and μ from the gradient expansion of E_x. The corresponding values of the parameters in each member of the PBE(β,μ,LO) family are recorded in Table I. Additional information is given in Table I of Ref. 25.

A priori one might expect that functionals such as PBE(G_c,G_x,LO) and PBE(J_s,J_r,LO) that take β and μ from the same type of source, have the potential to benefit from error cancellation between the exchange and the correlation functional to a larger extent than functionals such as PBE and PBEsol that take them from different types of source. Also, one might anticipate that PBE(J_s,J_r,LO) should be rather good for simple metals, as its takes both of its parameters from jellium, the paradigmatic model of such metals. These expectations were put to the test in Ref. 25, for atoms, molecules, and solids. For each class of systems, a different ranking of functionals was found. Here we only record that for solids, where the calculations were done with the SIESTA code,[38] original PBE performed worst of all. As expected, PBEsol provided significant improvement on PBE, but in spite of its name and the rationale behind its construction, it did not consistently provide the best performance for solids. Rather, best lattice constants were obtained from PBE(G_c,G_x,LO). It was not clear, however, to which extent this conclusion was affected by the pseudopotential approximation and the special basis functions employed in the SIESTA code.

In a second, independent, line of thought, the role of the Lieb-Oxford bound in functional construction has recently been reconsidered. Initial numerical and analytical evidence[27–29] suggested that the Lieb-Oxford estimate λ_{LO} =2.273 could be tightened to a value close to $\lambda \approx 2$. Later, general arguments were given[30] that for three-dimensional systems this value should actually be λ_{EL}=1.9555, where the subscript EL indicates that this is the exact value in the low-density limit of the electron liquid. This reduced value of λ implies a corresponding reduction of κ to 0.552. In our present notation, the resulting functional is denoted PBE(G_c,J_r,EL), and differs from original PBE only in the value of λ (or, equivalently, κ). This functional has been

tested for a variety of molecular systems[29] and it was found that PBE is rather insensitive to changes in λ for covalently and ionically bound small molecules, a reduced, and thus, in principle, better, value of λ producing slightly worsened energies and slightly improved bond lengths.

In the present work, we now tie up various open ends from these previous investigations, by implementing all ten functionals that can be obtained from the above-described combinations of β, μ, and λ, i.e., the complete family PBE(β,μ,λ), in the all-electron code WIEN2K,[23] and testing them systematically for a large set of 60 solids, comprising metals, semiconductors and insulators.[15] The PBE(β,μ,λ) functionals were also tested on a set of six molecules for the atomization energy. This test set (called AE6) was proposed by Lynch and Truhlar[33] as a representative set of a much larger set of molecules. The molecules in the AE6 set are SiH_4, SiO, S_2, C_3H_4, $C_2H_2O_2$, and C_4H_8.

The calculations on solids were performed with the WIEN2K code[23] which solves the KS equations using the full-potential (linearized) augmented plane-wave and local orbitals [FP-(L)APW+lo] method.[39] Because the FP-(L)APW+lo method is one of the most accurate methods to solve the KS equations it represents a good choice for testing *xc* functionals. The error in a calculated ground-state property is solely due to the approximate functional if good convergence parameters have been used. All calculations have been converged with respect to the number of **k** points and the size of the basis set. Spin-orbit coupling for solids containing Ba, Ce, Hf, Ta, W, Ir, Pt, Au, Pb, and Th atoms has been taken into account. The experimental lattice constants are taken from Ref. 15 and are corrected for zero-point anharmonic expansion. The calculations on molecules were done with the DEMON code[32] which uses Gaussian basis sets. The very large uncontracted basis sets developed by Partridge[40,41] were used.

The statistical quantities that will be used for the analysis are displayed below, where p_i^{calc} and p_i^{exp} are the calculated and experimental values of the considered property (either the lattice constant or the atomization energy) of the *i*th solid or molecule of the testing set: mean error (in Å or in kcal/mol),

$$\mathrm{me} = \frac{1}{n}\sum_{i=1}^{n}(p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}}), \tag{3}$$

the mean absolute error (in Å or in kcal/mol),

$$\mathrm{mae} = \frac{1}{n}\sum_{i=1}^{n}|p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}}|, \tag{4}$$

the mean relative error (in %),

$$\mathrm{mre} = \frac{1}{n}\sum_{i=1}^{n}100\frac{p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}}}{p_i^{\mathrm{exp}}}, \tag{5}$$

and the mean absolute relative error (in %),

$$\mathrm{mare} = \frac{1}{n}\sum_{i=1}^{n}100\left|\frac{p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}}}{p_i^{\mathrm{exp}}}\right|. \tag{6}$$

The spread (in %), defined as

$$\mathrm{spread} = \max\left(100\frac{p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}}}{p_i^{\mathrm{exp}}}\right) - \min\left(100\frac{p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}}}{p_i^{\mathrm{exp}}}\right) \tag{7}$$

will also be discussed. The smaller the spread, the more predictable a functional behaves. A large spread, by contrast, indicates a more erratic behavior. In situations where a single bad value can be problematic, it may be wiser to choose a functional with a small spread than one with a low mean error, as the latter may still be way off in isolated cases.

III. ANALYSIS OF SINGLE-CONSTRAINT CHANGES WITH RESPECT TO PBE

The calculated lattice constants for all functionals considered in this work are given in Table SI of the supplementary material.[42] Graphical representations of these results are also given in Figs. S1, S2, and S3.

In a first step, we focus our analysis on a subset of functionals that differ from original PBE in the choice of just one constraint. Specifically, these functionals are PBE(J_s,J_r,LO), differing in the constraint for determining β, PBE(G_c,G_x,LO), differing in the constraint chosen for μ, and PBE(G_c,J_r,EL), differing in the choice of λ. Initial focus on just these functionals is useful because it allows to separately assess the influence of each change relative to PBE.

Figures 1 and 2 show the signed relative errors for all 60 solids, for the three functionals just described as well as for original PBE and LDA. While original PBE has the same (modest) performance for elemental solids as for compounds, all other functionals work better for compounds. The difference is particularly pronounced for LDA and PBE(G_c,J_r,EL), which perform significantly better for compounds than for elemental solids. In both classes, however, PBE(G_c,G_x,LO) achieves the lowest mare among this subset of functionals.

Figures 1 and 2 also show very clearly the known trend of LDA to underestimate the lattice constants (negative relative errors) and of PBE to overestimate the lattice constants (positive relative errors). The most interesting fact, which is not at all obvious from the way the various functionals were constructed, is that *all changes* in *parameters relative to PBE produce significantly better lattice constants.* (This remains true even if all the other possible combinations are included.) Since the nature and source of each modified parameter are completely different in each of the three cases, this seems to indicate that the original PBE choice was rather unfortunate for lattice constants, as reasonable changes to any of its parameters end up improving the results.

Comparing the absolute size of the change resulting from each modified parameter, we immediately conclude from Figs. 1 and 2 that PBE is most sensitive to changes in μ and least sensitive to changes in λ.[43] The relative impact of β and

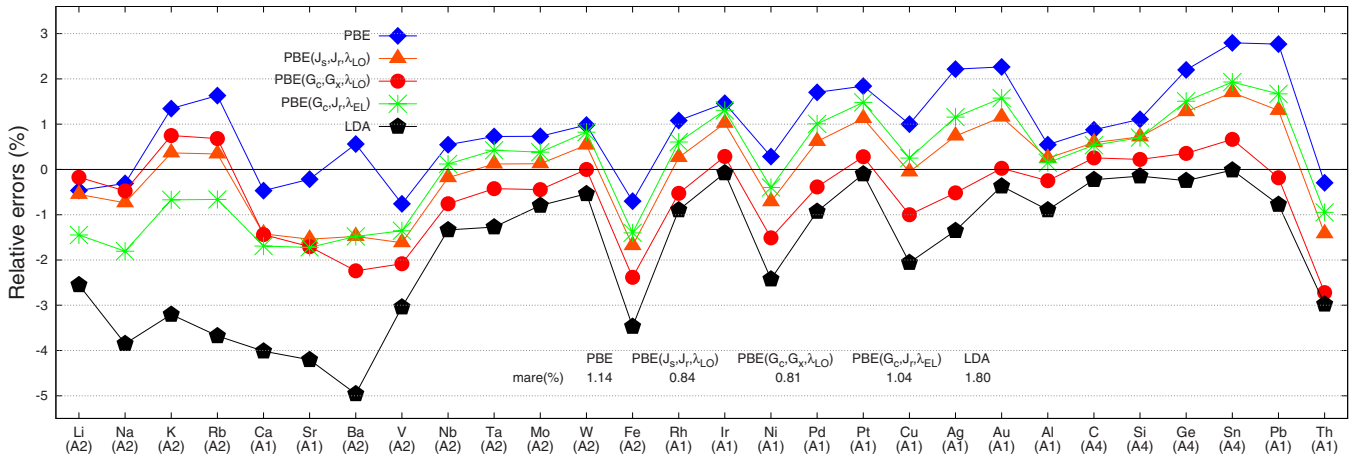

FIG. 1. (Color online) Relative error in the lattice constants of 28 elemental solids, obtained from LDA, original PBE =PBE(G_c,J_r,LO) and three versions of PBE that differ from it in just one constraint each, as described in the main text. Inset: mean absolute relative error (mare) of the five functionals in the figure on this set of elemental solids. The Strukturbericht symbols (in parenthesis) are used for the structure: A1=fcc, A2=bcc, and A4=diamond.

μ is quite reasonable, because β appears in the correlation energy and μ in the exchange energy. Since the exchange energy in ordinary solids is larger than the correlation energy the result should indeed depend more sensitively on changes in that quantity.

Regarding changes only in λ, we see that a change from the Lieb-Oxford value to the electron-gas value has, for most solids, the smallest effect on PBE of the three tested parameter changes. This is consistent with what was previously observed for molecules.[29] The exception is for the alkali metals, where this change has the biggest effect. The reasons for this behavior becomes clear from the analysis given by Haas *et al.* (Ref. 24). In this paper an "important region" was defined which is to a large extent responsible for the changes in lattice parameters of different functionals. For closed packed solids (like elements in the fcc or bcc structure) this region is the separation between the outermost core ("semicore") and the valence states and for the alkali metals the reduced density gradient $s=|\nabla\rho|/(2(3\pi^2)^{1/3}\rho^{4/3})$ in this "important region" is much larger (even above $s=2$ for Li) than for other elements (e.g., in bcc V, $s_{\max}=0.9$). Obviously, a change in λ modifies the enhancement factor $F_{xc}(r_s,s)$ much more for large s, while a change in μ influences $F_{xc}(r_s,s)$ predominantly in the low s region.

IV. FULL STATISTICS FOR ALL TEN PBE(β,μ,λ) FUNCTIONALS

In this section, we present a statistical analysis of all ten functionals of the PBE(β,μ,λ) family, as well as of LDA. We do not include numerical data on other GGA-type functionals, such as SOGGA (Ref. 22) and WC (Ref. 19) and neither on alternative functionals such as AM05[16] and TPSS meta-GGA,[14] as these were already investigated on the same test set in Ref. 15, and on a smaller set (using different codes and basis sets) in Refs. 18, 35, and 36. However, in our

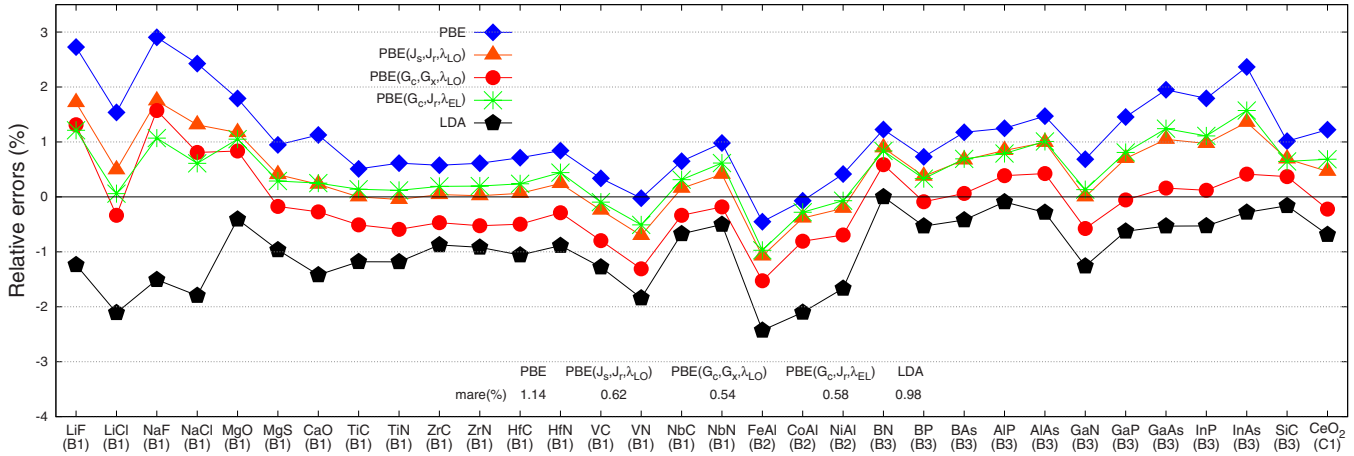

FIG. 2. (Color online) Relative error in the lattice constants of 32 compound solids, obtained from LDA, original PBE =PBE(G_c,J_r,LO) and three versions of PBE that differ from it in just one constraint each, as described in the main text. Inset: mean absolute relative error (mare) of the five functionals in the figure on this set of compound solids. The Strukturbericht symbols (in parenthesis) are used for the structure: B1=rock-salt, B2=cesium-chloride, B3=zinc-blende, and C1=fluorite.

discussion of global trends we compare with results and conclusions from those references. We do not consider earlier variations of PBE, such as revPBE (proposed in the Comment of Zhang and Yang)[7] and RPBE (Ref. 44), which were not designed for solids and tend to worsen PBE for extended systems (see, e.g., Ref. 45 for RPBE).

The choice of the best performing functional for lattice constants depends on the measure of error selected to judge the performance of the functionals. In terms of the mean error, PBE(J_r,G_x,LO) achieves a spectacularly low error of −0.002 Å, followed by PBEsol and PBE(J_s,J_r,EL). These same three functionals also achieve the best mean relative errors. However, such low errors can in part be due to the result of error cancellation in taking the averages. The mean absolute error, which is not influenced by error cancellation, favors PBEsol, closely followed by PBE(G_c,G_x,LO) and PBE(J_r,G_x,LO). The same three functionals also achieve the lowest mean absolute relative error.

In view of the very small differences in the mares of some of the functionals, one must ask how significant these differences are, considering both, the numerical accuracy of the theoretical results and the accuracy of the experimental data, where not for all cases high quality low-temperature lattice parameters and good zero-point energy corrections are available. In fact, changes in mare of 0.05% are about the limit of theoretical accuracy, i.e., we expect to have an absolute precision of about 0.005 Å. Therefore, we consider PBEsol, PBE(J_r,G_x,LO) and PBE(G_c,G_x,LO) to perform equally well in terms of the mare.

Three of the four functionals with good mre or mare take the original λ_{LO} and μ from the gradient expansion for exchange (G_x), but differ in the parameter of the correlation functional, β. As the numbers show, the value of β turns out to be almost irrelevant, while the value of μ appears to be responsible for the improved behavior. The gradient expansion for exchange is thus seen to be the key ingredient in functionals that deliver good lattice constants. When μ is taken a bit larger (e.g., J_r), both β and λ must be set to small values ($\beta=J_s$ and $\lambda=\lambda_{EL}$) to obtain a similar performance [PBE(J_s,J_r,EL)]. This observation, in retrospect, vindicates the PBEsol approach[21] and attests to the solidity of the basic insight presented there regarding the relevance of the gradient expansion of the exchange energy for solids.

In terms of the spread [Eq. (7)], the best performer is PBE(J_s,J_r,LO), followed by PBE(J_r,G_x,LO). Unfortunately, the best performers with regard to mean errors and with regard to the spread are not always the same. In particular PBE(G_c,G_x,LO) has a rather large spread, but PBE(J_r,G_x,LO) appears to be a reasonable compromise, doing well according to all three criteria.

Next, we compare our present conclusions to several different sets of earlier calculations, testing specific members of the full family, employing other test sets, or other implementations and basis functions.

In Ref. 25, three of us tested the five functionals PBE(β,μ,LO) on a set of 13 solids. These functionals were implemented in the SIESTA code.[38] This code, by design, aims at the electronic structure of very large systems, where all-electron calculations, even with simple functionals, would be prohibitively expensive. To this end, it makes use of specially designed localized numerical basis functions, and pseudopotentials. As a consequence, it does not attain the same high accuracy as all-electron codes, such as WIEN2K,[23] and the absolute size of the errors is larger for SIESTA than for WIEN2K.

Nevertheless, the resulting error statistics is rather similar (although not identical). In particular, both the SIESTA and the WIEN2K calculations identify original PBE and PBE(J_s,J_r,LO) as the worst performers for lattice constants of all PBE(β,μ,LO) functionals, and PBEsol, PBE(J_r,G_x,LO), and PBE(G_c,G_x,LO) tied as the best. Among these best performing functionals, SIESTA and WIEN2K produce a different ranking, with SIESTA preferring PBE(G_c,G_x,LO), which according to WIEN2K is beaten by a small margin by PBEsol and PBE(J_r,G_x,LO).

Interestingly, all-electron calculations for solids performed with the GAUSSIAN code[46] also indicate that PBE(G_c,G_x,LO) produces better lattice constants than PBEsol (see Table SIV in the supplementary material of Ref. 21.) which is in line with the SIESTA results. However since neither pseudopotentials (SIESTA) nor Gaussian basis functions are as accurate for solids as all-electron FP-(L)APW+lo calculations, and since all differences are rather small, we still regard these functionals as essentially tied.

In Ref. 29, two of us with Trickey tested the functional PBE(G_c,J_r,EL), which differs from original PBE only in the reduction of λ, corresponding to a tighter (and thus presumably better) Lieb-Oxford bound. The calculations were done for a set of small molecules. The reduction of λ was found to slightly improve interatomic distances. In parallel, from Siesta pseudopotential calculations[47] for the 13 solids of Ref. 25 we found that the same improvement occurs also for the other members of the PBE(β,μ,λ) family, all of which produce better lattice constants when a tighter Lieb-Oxford bound is enforced. By contrast, in the WIEN2K calculations only the badly performing functionals [original PBE and PBE(J_s,J_r,LO)] benefit from a reduced value of λ, while the mare of the other three functionals grows if λ is reduced. Consistently with what was speculated in Ref. 29, this indicates that the algebraic form of PBE is too restricted to systematically benefit from a tighter bound.

In Ref. 15, three of us employed the same set of 60 solids to assess the performance of the AM05, WC, PBEsol, SOGGA, and the meta-GGA TPSS functionals compared to the older LDA and PBE. From this comparison PBEsol emerged as the functional with the lowest mare over all 60 solids, tied with the WC, closely followed by SOGGA and AM05, and more distantly by TPSS, PBE, and LDA, in this order. WC, SOGGA, and AM05 turn out to have mares in the same range as the members of the PBE(β,μ,λ) family (including PBEsol) although they differ from the original PBE by more than just the values of parameters.

The hybrid functional B3LYP,[10,11] which is very popular in quantum chemistry, was shown[12] to overestimate lattice constants by at least as much as PBE, and is thus not competitive with any of the functionals under study here.

Interestingly, SOGGA turns out to be a very good functional making use of the tighter Lieb-Oxford bound, using λ_{EL} instead of λ_{LO}. SOGGA achieves a lower mare (0.68%) than any of the five functionals PBE(β,μ,EL), whose mare

ranges from 0.71 to 0.80%, but unfortunately its mre is twice as large as that of PBE(J_s,J_r,EL). This indicates, one more time, that the functional form of PBE must be changed to fully benefit from a tighter Lieb-Oxford bound, and hints that the form of SOGGA may be a suitable starting point for this purpose.

V. ANALYSIS FOR CLASSES OF SYSTEMS

The above discussion was based on the statistical data of the full set of 60 solids. However, it can also be interesting to analyze the results for a particular class of solids, therefore, below we discuss the performance of all 11 functionals separately for certain classes of solids, for which Table SI and Fig. S1 of the supplementary material[42] are useful.

A. Elemental solids

Let us start out the discussion with the alkali metals. For a given β and μ, the reduction of λ from LO to EL leads to significantly smaller lattice constants a_0. As mentioned before, this effect is particularly strong for the alkali metals and thus all PBE(β,μ,λ) functionals with a tighter Lieb-Oxford bound underestimate the lattice constant. Actually, from Fig. 1 and S1, we can see that for the alkali metals (and also the alkali-earth metals and the compounds with these elements) the difference between the PBE($\lambda=\lambda_{LO}$) and PBE($\lambda=2^{1/3}$) (which reduces to LDA) relative errors is large, an effect that is (at least partially) due to the large values of s (which make λ important) in the region of separation between semicore and valence electrons.[24] By comparing the results with fixed $\mu=G_x$ and a variation of β [PBE(J_s,G_x,LO/EL) with PBE(G_c,G_x,LO/EL) and PBE(J_r,G_x,LO/EL)] we note that an increase of β from J_s to G_c increases the lattice constant more than a reduction of J_r decreases it. J_r worsens the underestimation of a_0 from PBE(J_s,G_x,LO/EL) while G_c reduces it. This trend, namely, that a_0[PBE(G_c,G_x,LO/EL)] $>a_0$[PBE(J_s,G_x,LO/EL)]$>a_0$[PBE(J_r,G_x,LO/EL)] can also be observed for most group IIA elements, but in all other cases the trend is inverted. On the other hand, when μ is taken as J_r [and therefore depends on β, see Eq. (1)], an increase of $\beta=J_s$ to $\beta=G_c$ [comparing PBE(J_s,J_r,LO/EL) with PBE(G_c,J_r,LO/EL)] leads to increased lattice parameters for all classes of compounds, not just the group IA and IIA elements. This effect is most pronounced in K and Rb and reduces the large overestimation of PBE(G_c,J_r,LO) for these two compounds. Usually, a reduction of $\mu=J_r$ to $\mu=G_x$ (at any β and λ) [PBE(G_c,J_r,LO/EL) and PBE(G_c,G_x,LO/EL)] leads to much smaller lattice constants, but for group IA elements this general trend is not true for Li (and in very few cases for Na and K). In general, for group IA elements PBE(J_s,G_x,LO) is the most accurate PBE(β,μ,λ) functional followed by PBE(G_c,G_x,LO).

For the elements of group IIA the original PBE [PBE(G_c,J_r,LO)] gives already quite satisfactory results and thus all modifications of the PBE(β,μ,λ) functionals lead to strong underestimations of the lattice constants. Tightening the Lieb-Oxford bound increases the absolute relative error by about 1.5%. Reduction of μ has an even larger negative effect. Changing β (at fixed $\mu=G_x$) has a fairly small effect (in particular for Ba) and a nonuniform trend.

The lattice parameters of group IVA elements are very well described by standard LDA (only for Pb there is a significant underestimation), while the original PBE functional yields a_0 almost 3% too large for Sn and Pb. In addition, PBE shows a strong tendency for larger overestimation of a_0 for heavier elements. Since LDA is so good, only the "weakest" GGAs, i.e., where the exchange parameter μ is small (G_x), can compete with LDA. When in addition, also the reduced λ_{EL} is used and/or $\beta=G_c$ is kept large, functionals like PBE(G_c,G_x,EL), PBE(J_s,G_x,EL), or PBE(G_c,G_x,LO) (in that order) perform very well.

The trend for the 3*d* transition metals (TM) is very similar to that for the group IIA elements. Since already original PBE is rather accurate for the 3*d* TM (except for Cu), no overall improvement can be expected when one (or several) of the parameters is reduced. A tighter Lieb-Oxford bound [PBE(G_c,J_r,EL)] improves the situation for Cu, but worsens all other cases. A reduction of μ has an even larger negative effect, but PBE(J_s,J_r,LO) is the best modified $\lambda=\lambda_{LO}$ functional. None of the modifications seems to be able to break the trend that lattice parameters of early 3*d* TM are even more underestimated than of late ones.

The lattice constants of the 4*d* transition metals are overestimated by original PBE (the overestimation increases for later TM) and slightly underestimated by PBEsol (getting more accurate with increasing nuclear charge). Using a tighter Lieb-Oxford bound (λ_{EL}) therefore improves PBE (worsens PBEsol), but this modification alone is not enough. An additional reduction of β from G_c to J_s [PBE(J_s,J_r,EL), which also reduces the effective μ] leads to pretty accurate results, while the β reduction alone [PBE(J_s,J_r,LO)] is not sufficient. Similar good results can also be reached when both μ and β are reduced to G_x and J_r, respectively [PBE(J_r,G_x,LO)]. Most interestingly, these two modifications can also significantly reduce the trend toward larger lattice parameters for later TM and are thus an improvement for *all* 4*d* elements. Any further combination with reduced β, μ, and λ underestimates the lattice parameters.

For the 5*d* TM, original PBE overestimates a_0 and for the latest 5*d* element (Au), the error reaches more than 2%. The best functional for the 5*d* elements is PBE(G_c,G_x,LO), where only the exchange factor μ is strongly reduced, but β (and λ) are kept at the large values. As for the 4*d* series, the trend toward larger lattice parameters for late TM elements is more or less completely broken. Similar, but slightly overestimated a_0 can be obtained when both, β and λ are also reduced [PBE(J_s,G_x,EL)]. Reduction of λ alone or intermediate values for μ still overestimate the lattice parameters.

For the heaviest element of our testing set, the 5*f* element Th, the original PBE gives the best result (still underestimating a_0 slightly), while, e.g., PBEsol leads to a more than 2% too small lattice parameter.

B. Compounds

Most prior discussed trends (Sec. V A) can to some extent also be observed for compounds. Sometimes the combined

TABLE II. Parameters of the eleven functionals under investigation in this work, and a statistical summary [Eqs. (3)–(6)] of their performance for the atomization energy of the set AE6 of six molecules (Ref. 33). The atomization energies are given in Table SII of the supplementary material (Ref. 42).

Functional	β	μ	λ [e]	me (kcal/mol)	mae (kcal/mol)	mre (%)	mare (%)
LDA				76.3	76.3	16.9	16.9
PBE(G_c,J_r,LO) [a]	0.067	0.21951	2.273	12.0	15.1	3.4	4.4
PBE(J_s,G_x,LO) [b]	0.046	0.12346	2.273	35.1	35.1	8.3	8.3
PBE(J_s,J_r,LO) [c]	0.046	0.15133	2.273	28.5	28.7	6.9	6.9
PBE(G_c,G_x,LO) [c]	0.067	0.12346	2.273	31.0	32.7	7.6	8.2
PBE(J_r,G_x,LO) [c]	0.038	0.12346	2.273	36.4	36.4	8.5	8.5
PBE(G_c,J_r,EL) [d]	0.067	0.21951	1.9555	26.6	28.5	6.5	7.1
PBE(J_s,G_x,EL)	0.046	0.12346	1.9555	43.5	43.5	10.1	10.1
PBE(J_s,J_r,EL)	0.046	0.15133	1.9555	38.9	38.9	9.1	9.1
PBE(G_c,G_x,EL)	0.067	0.12346	1.9555	39.4	40.4	9.4	9.7
PBE(J_r,G_x,EL)	0.038	0.12346	1.9555	44.8	44.8	10.3	10.3

[a]This is PBE (Reference 7).
[b]This is PBEsol (Reference 21).
[c]These are the three functionals proposed in Reference 25.
[d]This is the functional of Reference 29.
[e]λ=2.273 and 1.9555 correspond to κ=0.804 and 0.552, respectively [see Eq. (2)].

effect of two elements may lead to some kind of cancellation, or in other cases, one element may dominate the effect. We will discuss below the effects starting with the very ionic group IA–VIIA, IIA–VIA, and IIIA–VA compounds, respectively, and TM-compounds.

For the ionic compounds it is obvious that the anion (the tails of the valence p electron density) plays the major role in determining the lattice parameter. This was shown in Ref. 24, but is also obvious by comparing the lattice parameters for e.g., metallic Li and LiF. Using PBE there is a small underestimation of a_0 for Li, but the lattice parameter of LiF is too large by almost 3%. In addition, the anion changes dramatically the results: For fluorides a large overestimation is obtained for all PBE(β,μ,λ) functionals, while for chlorides (and even more for bromides, not included here) this behavior is corrected or some underestimation can be found. The change to a tighter Lieb-Oxford bound has a rather strong effect (often stronger than a reduction of μ) and reduces most errors of the IA–VIIA compounds. While nearly all PBE(β,μ,LO) functionals overestimate the lattice constants, a tighter Lieb-Oxford bound may lead to small underestimations for some chlorides. Nevertheless PBE(J_r,G_x,EL) is the best performing PBE(β,μ,λ) functional for this class of compounds.

For the IIA–VIA compounds, standard PBE overestimates the lattice constants. A reduction from β=G_c to β=J_s at μ=J_r [comparing PBE with PBE(J_s,J_r,LO/EL)] improves PBE significantly, because the change of β reduces the effective μ and therefore PBE(J_s,J_r,LO) becomes the most accurate functional for this group of compounds. The reduction from μ=J_r to μ=G_x at β=G_c [e.g., from PBE to PBE(G_c,G_x,LO)] also lowers the lattice constants significantly leading to quite well performing functionals with λ_{LO}, but with λ_{EL} the correction overshoots and leads to some underestimation for MgS and CaO. For a fixed μ the variation of β hardly modifies the results. Only MgO [which is overestimated by all PBE(β,μ,λ) functionals] benefits from a tighter Lieb-Oxford bound in all cases.

All semiconducting IIIA–VA compounds have significantly too large lattice parameters with PBE. A tighter Lieb-Oxford bound is advantageous, but the effect alone is too small and a strong reduction of μ (to G_x) is essential. For μ=G_x the parameter for correlation has a fairly large effect (in particular for the heavier elements) and with β=G_c the PBE(G_c,G_x,LO) functional is very accurate for all semiconductors.

The metallic transition metal compounds (mainly carbides and nitrides, but also three intermetallic compounds) are fairly well described by standard PBE and the slight overestimation of lattice constants can be reduced by weak modifications. The best functionals are obtained either by switching λ to the tighter EL limit [PBE(G_c,J_r,EL)], or by a modest reduction of β [PBE(J_s,J_r,LO)] (probably because this reduces also the effective μ for μ=J_s). A stronger reduction of μ or a combination of μ and λ reductions leads to too small lattice parameters.

VI. ATOMIZATION ENERGY OF MOLECULES

In this section, we present the performance of the PBE(β,μ,λ) functionals on the atomization energies of molecules using the representative AE6 test set.[33] Table SII of the supplementary material[42] gives the calculated values and Table II gives a summary of the corresponding statistical errors. The me and mae (mre and mare) quantities are very similar since all functionals (maybe except original PBE) always overestimate the atomization energy. We can see that PBE(G_c,J_r,LO) (original PBE) is the best and

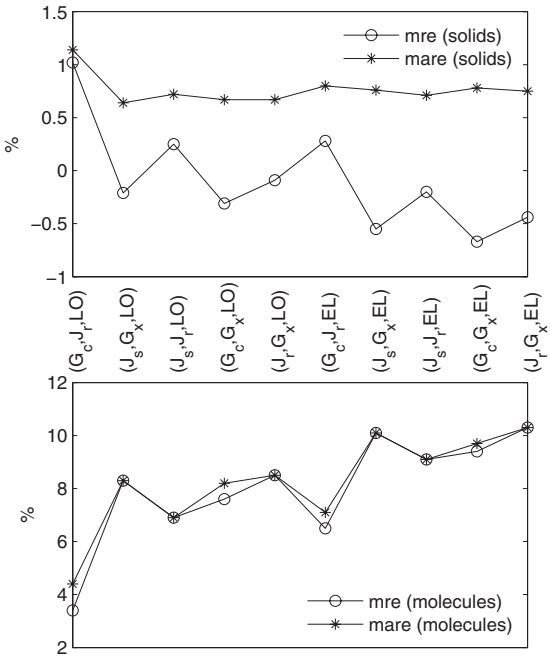

FIG. 3. Mean relative error and mean absolute relative error in the lattice constants (upper panel) and atomization energies (lower panel) of the PBE(β,μ,λ) functionals.

PBE(J_r,G_x,EL) is the worst functional of the PBE(β,μ,λ) family for the atomization energy of molecules. Switching λ to a tighter bound ($\lambda=\lambda_{EL}$) has a rather strong degrading effect, probably because the atomization energies depend a lot on regions in space with large effective density gradient s. In Fig. 3, we compare the mre and mare for solids (lattice constants) and molecules (atomization energies) versus the PBE(β,μ,λ) functionals. As expected the mre behavior of solids is opposite to that of the molecules. Functionals leading to larger lattice constants (larger overestimation) lead to smaller atomization energies (smaller overestimation) and no functional of the current PBE(β,μ,λ) family can describe both quantities in a satisfying way.

VII. CONCLUSIONS

From all of the above we conclude that to obtain precise lattice constants of solids it is not necessary (and in some cases even detrimental) to switch from the PBE family of functionals (differing from original PBE only through the choice of parameters) to functionals that also differ in the form of the exchange enhancement factor (SOGGA and WC) or that employ different design principles (AM05) or further ingredients (meta-GGA TPSS). These more complex functionals have many merits and interesting features, but apparently these features are not required to produce very accurate lattice constants.

In fact, even the simplest possible modification of original PBE, the change in one single parameter (taking μ from the gradient expansion for exchange instead of from the jellium response function) already produces a functional whose lattice constants are, to within the error bars of the WIEN2K code, as good or better than those of any of the other tested functionals: PBE(G_c,G_x,LO). (As pointed out above, SIESTA and GAUSSIAN calculations sustain this claim.)

A change in two parameters relative to PBE produces PBE(J_r,G_x,LO) and PBEsol=PBE(J_s,G_x,LO), the former having the same mare but a lower spread, relative to PBE(G_c,G_x,LO); and the latter a still slightly lower mare (although the improvement is smaller than our estimated error bar) at the expense of a slightly larger spread. Any of these three functionals can be recommended as a useful and reliable GGA for lattice constants of solids, requiring only minimal changes to existing implementations of PBE and attaining much higher accuracy than PBE and LDA, and also than many more complex functionals.

On the other hand, any modification of the original PBE functional which improves lattice parameters of solids, increases significantly the error in the atomization energy of molecules. The overestimation of this quantity by PBE of mae=15.1 kcal/mol becomes 2–3 times larger with the modified functionals and we must conclude that (at least) GGAs of PBE-form cannot describe well lattice parameters of solids and atomization energies of molecules simultaneously (see also Refs. 22 and 48).

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