Optimized Exchange and Correlation Semilocal Functional for the Calculation of Energies of Formation

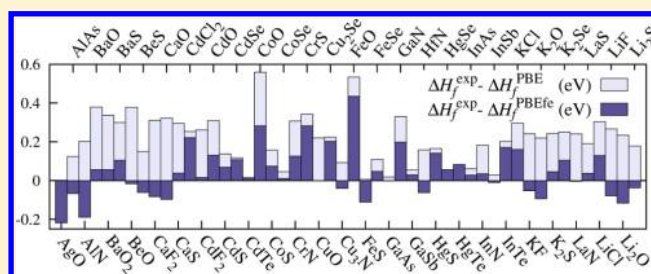Rafael Sarmiento-Pérez,[†,‡] Silvana Botti,*[,‡,†] and Miguel A. L. Marques*[,∥,†]

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S *Supporting Information*

ABSTRACT: We present a semiempirical exchange-correlation functional for density functional theory tailored to calculate energies of formation of solids. It has the same form of a Perdew–Burke–Ernzerhof functional, but three parameters have been fitted to reproduce experimental energies of formation of a representative set of binaries. The quality of the obtained functional has then been assessed for a control set of binary and ternary compounds. Our functional succeeds in reducing the error of the Perdew–Burke–Ernzerhof generalized gradient approximation for energies of formation by a factor of 2. Furthermore, this result is achieved preserving the quality of the optimized geometry.

1. INTRODUCTION

One of the great promises of density functional theory (DFT) was to provide relatively accurate calculations with only a modest computational effort. In many respects this promise has been fulfilled, and DFT is now used routinely and successfully by numerous groups around the world to study a variety of problems in fields ranging from biochemistry to solid-state physics.

In this Article we are concerned with one specific problem, the calculation of energies of formation of solids. This is one of the simplest quantities one can obtain from a DFT calculation, and it is intimately related to the thermodynamic stability of the solid. If the energy of formation is negative, the energy of the solid is lower than the energy of the elementary phases of its constituents, and the solid will not decompose (in the thermodynamic sense) to elementary substances. A closely related concept is the distance to the convex hull of stability. To calculate it, we have to compare the energy of the solid against the energy of all (thermodynamically) stable phases it can hypothetically decompose to. This should include all possible elementary, binary, and ternary, etc. phases that can be constructed with the chemical elements that compose the solid. If the energy difference is positive, then our solid will eventually decompose. Otherwise, the solid is stable. The convex hull of stability is defined as the hypersurface in composition space that passes through all compounds that are thermodynamically stable.

The importance of the distance to the hull cannot be overemphasized, and it is now at the heart of many large-scale projects that try to design new (stable) materials with tailored properties for technological applications. A few recent, high-profile examples can be found, e.g., in refs 1–3 We note that in several cases these predictions have already been confirmed

experimentally.[3] All of these projects use DFT as a workhorse theory, and they mostly rely on the Perdew–Burke–Ernzerhof approximation (PBE)[4] to the exchange-correlation functional (often adding a Hubbard U to treat strongly correlated materials). The choice is easily justifiable as DFT is the only framework able to handle the large number of calculations required by these projects with a reasonable compromise between accuracy and computational effort, and the PBE functional has grown over the past years as the standard semilocal approximation for solid-state systems.

Energies of formation calculated with DFT often benefit from error cancellations when subtracting from the energy of the compound the energy of the elementary substances. This occurs in a larger extent when considering energy differences between similar systems, for example metallic alloys and their (metallic) components.[5] Unfortunately, the same error cancellation does not happen, for example, when the solid decomposes to metals and semiconductors. In fact, it is well-known that the PBE, as well as many other local or semilocal exchange-correlation functionals, yields an average error for the energies of formation substantially larger than the so-called chemical accuracy (around 1 kcal/mol ≈ 43 meV). This means that these functionals cannot in principle be used to consistently and quantitatively predict reaction barriers, the stability of phases, and so on.

There were a few efforts in the community to improve on this situation. A possibility to decrease the error is to change the level of theory. One can, for example, use an empirical Hubbard

U value in order to decrease the error of the energies of formation of compounds containing d or f elements. For example, Wang et al.[2] computed the formation of transition metal oxides with the GGA and GGA+*U* methods, providing Hubbard *U* values for several transition metals that give the best oxidation energies. Jain et al.[6] proposed a way to mix PBE and PBE+*U* total energies to obtain more accurate energies of formation. Their methodology is based on the idea of decomposing the reaction as a set of subreactions that are either well-described with PBE alone or well-described with PBE+*U* alone, or for which there is experimental data available. The subreactions introduce intermediate phases, whose energy is computed with either PBE or PBE+*U*. For a set of 49 ternary oxides, this approach is able to reduce the mean absolute relative error in the calculated formation enthalpies from approximately 7.7–21% in PBE+*U* to under 2%. Note, however, that the *U* required to improve on thermodynamic properties is, in general, quite different from the one required to obtain good electronic properties.

It is in principle also possible to use more precise hybrid functionals, such as the Heyd–Scuseria–Ernzerhof approximation.[7−9] Unfortunately, the substantial increase of computational effort rules out, for the time being, the use of these (or more elaborate) theories for high-throughput investigations.[10]

In a completely different approach, Stevanović et al.[5] fitted the reference atomic chemical potentials used to compute the energies of formation in order to reduce the error in the computed PBE+*U* values. Their method, which they named fitted elementary-phase reference energies (FERE), is very simple to use, does not increase the computational effort of PBE+*U*, and yields an excellent 54 meV/atom error in the calculated energies of formation for a set of 252 solids (the pure PBE calculation yields an error of 250 meV/atom for the same set). This is probably the best method available for the calculation of energies of formation, but unfortunately it has a few shortcomings when used to obtain the distance to the convex hull of stability. To understand these shortcomings, we should remember that to calculate the distance to the convex hull, we need to consider all possible decomposition channels. It turns out that depending on the channel, FERE can give very different errors. Three cases arise: (i) The decomposition is to elementary phases. Then the distance to the hull is simply related to the energy of formation, and FERE yields excellent results. (ii) The solid decomposes into one (or more) elementary phases and one (or more) binary or higher compounds. In this case FERE just corrects the elementary phases, and the error can be substantially higher than for the normal PBE+*U*. This can be easily seen in, e.g., binary phase diagrams as FERE can (incorrectly) stabilize (or destabilize) certain phases. (iii) The decomposition is into binaries or higher phases, and FERE simply yields the same error as the underlying PBE+*U* theory.

Another problem of FERE is, in our opinion, the sheer amount of parameters involved in this method: even ignoring the empirical values of *U* for all transition metals, FERE requires one empirical parameter per element.

If one wishes to remain in a semilocal (and efficient) description of the exchange-correlation functional, one can opt to use semiempirical density functionals. This is an approach often used in quantum chemistry, where there is a long tradition of fitting the exchange-correlation functional to reproduce certain properties of molecules (see, e.g., the popular HCTH[11] or the Minnesota functionals[12,13]). In fact, in some of these functionals, one of the properties fitted (among several others) is actually the cohesive energy of a few selected sp materials.[12,13]

However, because these functionals are designed to be quite general and applicable in many different situations, it cannot be expected that they decrease substantially the error in the energies of formation.

In this Article we push this approach further and propose a semiempirical parametrization of the PBE exchange-correlation functional, which is designed to obtain good energies of formation and distances to the convex hull.

2. FITTING OF THE EXCHANGE-CORRELATION FUNCTIONAL

Our functional is based on the PBE approximation for several reasons: (i) the PBE is already reasonably precise for the calculation of energies of formation; (ii) it is the de facto standard semilocal approximation for solids and is already implemented in virtually all solid-state DFT codes; (iii) it is relatively simple, and it involves few parameters. The original PBE depends on four parameters, usually labeled μ (that fixes the slow varying limit of the exchange), κ (that is used to force the exchange to fulfill locally the Lieb–Oxford bound), β (that determines the slow varying limit of correlation), and γ (that assures that the gradient contribution to the correlation cancels the logarithmic singularity of the correlation energy of the uniform electron gas in the high-density and rapid variation limits).

Although the original derivation of the PBE used solid theoretical arguments to fix these four parameters, still there seems to be a considerable amount of other (reasonably well) justified choices. The form of the exchange part was originally proposed by Becke[14] with the empirical coefficients $\mu = 0.235$ and $\kappa = 0.967$. In ref 4 the value of κ was fitted to exact-exchange energies obtained using the optimized exchange potential method. The resulting revised PBE (revPBE) functional[4] improves PBE atomic total energies by a factor of 10. In the PBEsol functional[15] the gradient expansion of the exchange is restored to describe better real solids, where the density is often slowly varying over space. The β parameter is chosen to fit the TPSS[16] results for large neutral jellium clusters. To construct the extended PBE functional (xPBE),[17] the four parameters are fitted to the Hartree–Fock limit energies and the exact atomic energies for atoms from H to Ar, and to the binding energies, and bond distance of Ne_2. Pedroza et al.[18] also investigated several possible combinations of theoretically justifiable parameters to obtain a family of PBE functionals. There exist other variants of the PBE functional,[19−24] but a complete review goes beyond the scope of this Article.

We emphasize that there are other sources of errors involved when it comes to predicting a thermodynamical quantity, even at zero temperature, namely, originating from the zero-point energy of the phonons. However, and as in the vast majority of cases, the error due to phonons is considerably smaller than the error due to the exchange-correlation approximation; we will ignore it in the following.

To fit our functional, we used an optimization set of 94 compounds (see Table 1 in the Supporting Information) for which the energy of formation was experimentally known. This set was chosen to ensure its chemical diversity. It is a subset of the 252 binary compounds used in ref 5 comprising 47 different elements and including 44 compounds containing transition metals, 38 compounds containing alkali and alkaline-earth metals, plus 12 compounds of the groups 13 and 14. The crystal structures were obtained from the Materials Project Database.[25] The ground-state structures of the elementary substances were obtained from ref 26 or the Materials Project Database.[25]

Table 1. Parameters μ, κ, β, and γ for Some Functionals in the PBE Family

|	PBE	PBEsol	xPBE	revPBE	B86	PBEfe
μ	0.21951	0.123457	0.23214	0.21951	0.23511	0.346
κ	0.804	0.804	0.91954	1.245	0.9672	0.437
β	0.066725	0.046	0.089809	0.066725		0.043
γ	0.031090	0.031090	0.011279	0.031090		0.031090
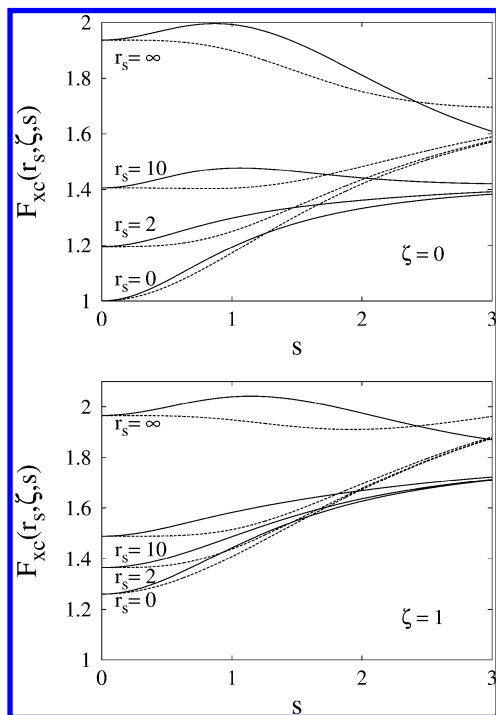
Figure 1. Enhancement factors for the spin-unpolarized ($\zeta = 0$) and the ferromagnetic spin-arrangement ($\zeta = 1$) cases. Solid curves represent the PBEfe functional, and the dashed ones represent the PBE functional.

As the objective function, we used the mean absolute deviation (MAD) with respect to the experimental energies of formation. To minimize the objective function with respect to the parameters μ, κ, β, and γ, we used the downhill simplex method by Nelder and Mead.[27] More than one minimization was performed starting from different initial parameters in order to check the convergence of the method.

All calculations were performed within the projector augmented wave method as implemented in the vasp computer code. The plane wave cutoff was set to a value 30% higher that the one suggested by the pseudopotentials, and numerical convergence to less than 2 meV/atom was ensured by dense k-point meshes. For each functional the structures were relaxed until the forces were smaller than 0.005 eV/Å and the stresses were lower than 1 kB. We note that all total energies used to compute formation energies correspond to theoretical, relaxed structures. It is true that, for the set of materials used here, we could have used the experimental structures. However, the main objective of our functional is to help in the quest to find new materials, for which, necessarily, the experimental structures are not available.

The calculations involving transition metals were performed spin polarized, with a ferromagnetic alignment as initial spin configuration, except for NiO, CoO, CuO, and FeO where we started from an antiferromagnetic alignment. Stevanović et al.[5] found that the energy differences associated with different magnetic configurations are typically of the order of 0.01−0.02 eV/atom and do not contribute appreciably to the relatively large ab initio
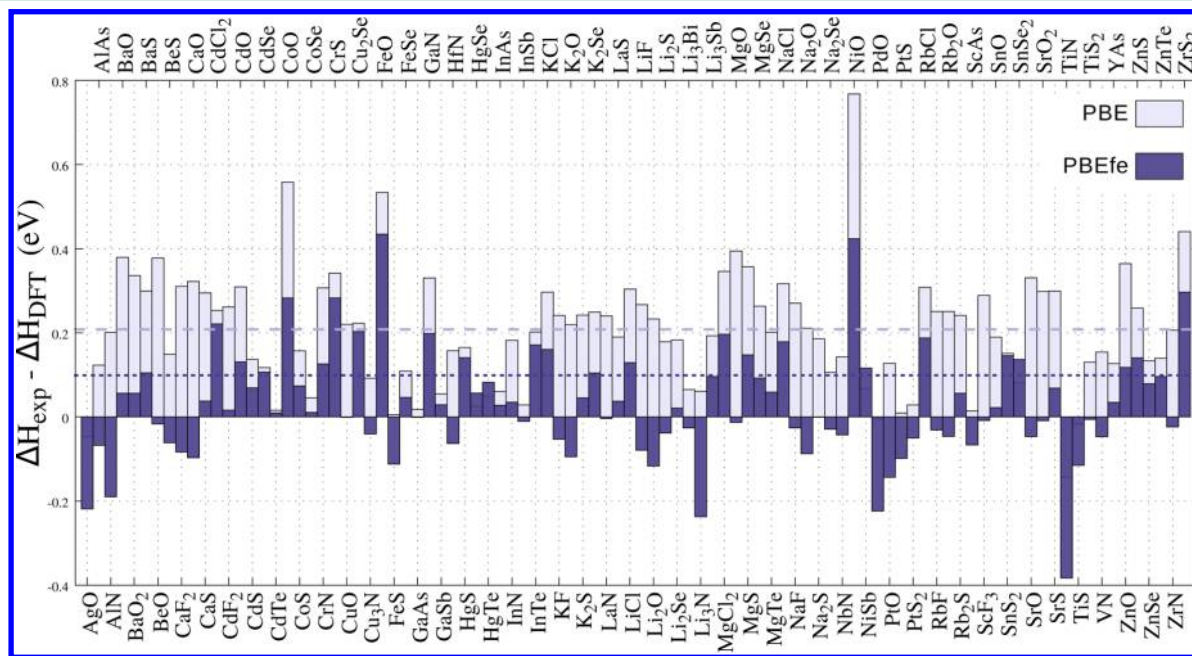
Figure 2. Errors of the calculated energies of formation with the PBE and the PBEfe functionals. The light-blue long-dashed line represents the MAD of the PBE, and the dark-blue short-dotted line represents the MAD of PBEfe.

errors. Relativistic corrections were only taken into account in the pseudopotentials, and the spin−orbit interaction was neglected.

Table 2. Mean Absolute Error, and Maximum Absolute Error for Our Optimization Set for the Different Functionals Studied Here

	MAD (eV/atom)	MAX (eV/atom)
PBE	0.208	0.768
PBEsol	0.193	0.664
xPBE	0.225	0.631
revPBE	0.262	0.701
LDA	0.152	0.672
PBEfe	0.099	0.435
PBEfe+U	0.078	0.336

3. RESULTS

Figure 1 of the Supporting Information shows a typical minimization run starting from the standard PBE parameters. For our training set the PBE yields a MAD of 0.208 eV/atom. The minimum found, after around 35 steps, was 0.097 eV/atom. This corresponds to the parameters $\mu \simeq 0.346$, $\kappa \simeq 0.437$, $\beta \simeq 0.043$, and $\gamma \simeq 0.034$. Repeating the calculations with these values for μ, α, and β but using γ_{PBE} instead does not change significantly the MAD (0.099 eV/atom). Therefore, we decided to keep the value of γ_{PBE} for our optimized functional, which we name PBE for formation energies (PBEfe) (see Table 1). [Our functional PBEfe was implemented in the library of exchange-correlation functionals libxc[28] and is therefore freely available.] We note that we also performed a minimization varying only
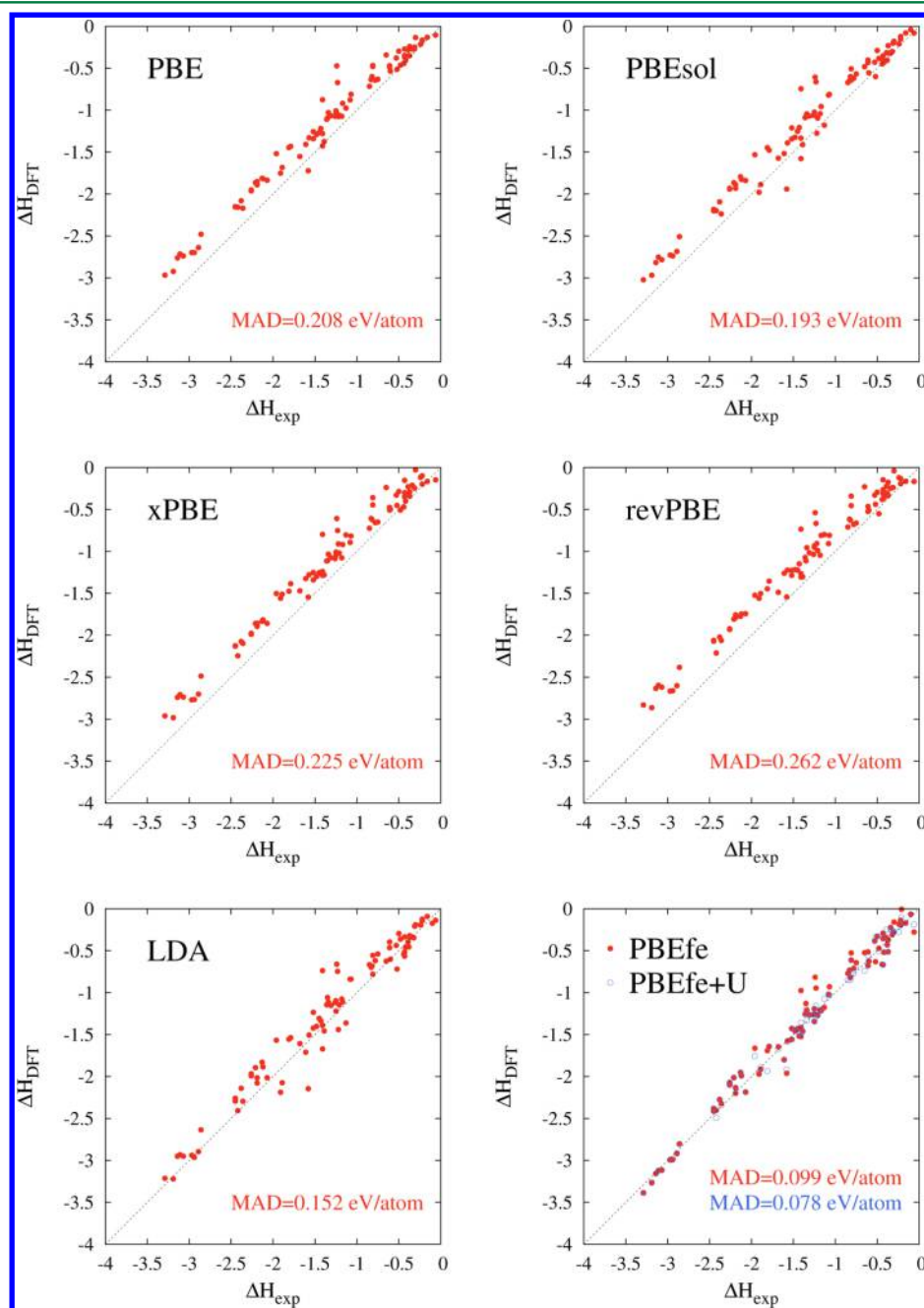
Figure 3. Calculated versus experimental energies of formation of compounds in the optimization set for different exchange-correlation functionals. The corresponding MAD is indicated in the graphs.
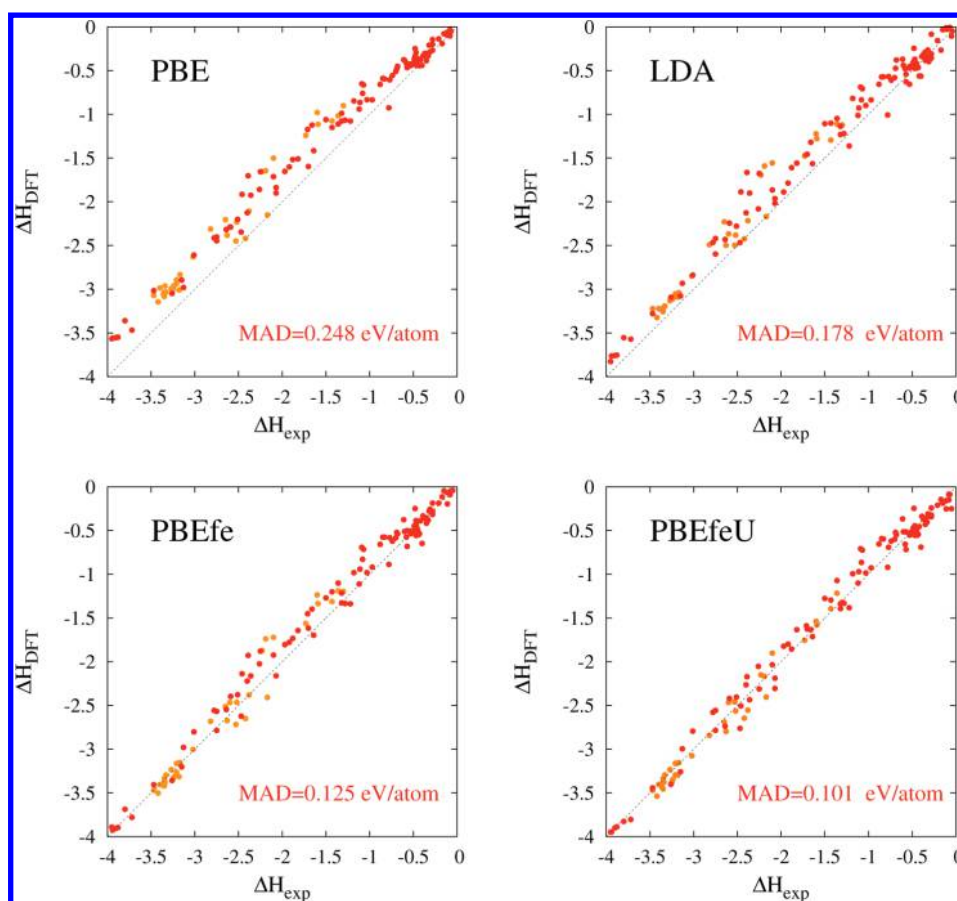
Figure 4. Calculated versus experimental energies of formation for the control set. Orange dots correspond to ternary compounds. The corresponding MAD are indicated in the graphs.

the two parameters of the exchange functional (i.e., keeping the PBE correlation functional). In this case the lowest MAD found was 0.155 eV/atom for $\mu = 0.255$ and $\kappa = 0.395$, indicating the importance of the error cancellation between the exchange and correlation.

It is interesting to compare the values of the parameters of our semiempirical functional to the other members of the PBE family (see Table 1). For the exchange we see that μ is approximately 1.5 times μ_{PBE} (maybe surprisingly, in the opposite direction as PBEsol) and κ_{PBE} is 0.6 times κ_{PBE} (enforcing a stronger Lieb–Oxford bound[29]). On the other hand, β is considerably smaller than β_{PBE}. Of course, it is dangerous to attach any deep theoretical meaning to these numbers as they are fully empirical and because both terms were optimized together, blurring the distinction between exchange and correlation.

Figure 1 shows the PBE and PBEfe enhancement factor $F_{xc}(r_s, \zeta, s)$, defined in a similar way to eq 8 of ref 17, where r_s is the local Seitz radius, ζ is the relative spin polarization, and s is a dimensionless density gradient. In the range of interest for real systems, $0 \leq s \leq 3$ and $0 \leq r_s \leq 10$, the PBEfe enhancement factor varies less than the enhancement factor of the PBE. The simultaneous increasing of μ and decreasing of κ makes the nonlocality of PBEfe, i.e., the dependence with s, larger than in PBE for $s \sim 1$ and $1 \leq r_s \leq 10$, while as s increases, it becomes smaller. Decreasing β, and increasing μ, destroys the cancellation between the exchange and correlation terms for the small s limit ($s \rightarrow 0$). This makes the concave bump of F_{xc} more pronounced while $F_{xc}(r_s, \zeta, s \sim 0)$ remains as in PBE and $F_{xc}(r_s, \zeta, s \sim 3)$ varies slightly. If β were decreased

according to the relation $\mu = \pi^2 \beta / 3$, F_{xc} would become convex as r_s increases. This is because the density for which the exchange stops being dominant would be smaller, reducing the gradient correction for r_s lower than 10.

The individual errors for the different materials can be read from Figure 2. As it is well-known,[30] PBE results lead in the large majority of cases to an underestimation of the energies of formation (i.e., PBE values are less negative than experimental ones). The errors are to some extent systematic, with a few outliers that correspond to highly correlated Mott insulators (such as NiO and CoO) that are incorrectly described by semilocal approximations. In our functional PBEfe the errors are distributed around the experimental values (for 38 compounds the formation energy is overestimated, and for 54 it is underestimated). A summary can be found in Table 2

Figure 3 shows a comparison between the calculated and experimental energies of formation of the 92 compounds with PBE, PBEsol, xPBE, revPBE, LDA, and PBEfe. The functionals xPBE and revPBE give the largest error, increasing the MAD up to 21% with respect to the PBE. The energies obtained with the PBEsol functional are slightly better than the ones that PBE yields. LDA energies are considerably better[30] (MAD of 0.152 eV/atom), and the values do not have such a large systematic error as PBE or PBEsol. Finally, PBEfe results show a much smaller dispersion.

In order to verify the dependence of these errors on the choice of the optimization set, we calculated the error of the PBEfe functional in a control set containing a further 104 binary compounds (including 52 transition metal compounds and 52

alkali, alkaline-earth, or groups 13 and 14 compounds, summarized in Table 2 in the Supporting Information) and 33 ternary compounds (including one transition metal sulfide, seven oxides without transition metals, and 26 oxides with one or two transition metals). The results can be seen in Figure 4 in comparison with PBE and LDA. The conclusions are essentially the same as those for the optimization set, i.e., the PBEfe MAD is substantially smaller than for the PBE (a 50% decrease for this set and a 59% if a Hubbard U is used for transition metals).

The PBEfe functional is worse than PBE for only 36 out of the 197 compounds in the two compound sets, and the increase of the error is generally small (less 0.1 eV/atom for 31 of them, and less than 0.3 eV/atom for the remaining five). Moreover, we also see a reduction in the larger errors. From this analysis, it is clear that computing energies of formation with this new functional will not only give more accurate results but also, in the cases in which the functional fails, the error will likely lie in the same range that is expected if the PBE is used.

We believe that these results validate the use of our proposed PBEfe functional for the calculation of formation energies of general solids. Moreover, as the approximation is performed at the level of the functional, it will correct consistently all energies involved in the calculation of the distance to the convex hull of stability (in contrast with FERE).

Table 3. Values of the Hubbard U (eV) for the Transition Metals Obtained To Give the Lowest Energies of Formation with the PBEfe Functional

Sc	3.0	La	0.5	Pd	0.0
Ni	3.0	Nb	0.0	Ti	2.7
Zn	5.3	V	6.0	Y	3.0
Co	1.3	Cd	3.3	Cr	1.0
Pt	0.0	Zr	3.0	Hg	5.7
Ag	6.0	Fe	2.0	Cu	3.0

We now turn to transition metal compounds that often have localized states hard to describe with semilocal functionals. It is clear that these contribute substantially to the total error of the functional. For example, the PBEfe error of the transition metal compounds is 0.120 eV/atom, while the remaining s and p compounds give an error of 0.077 eV/atom. To address that problem, we performed calculations by applying a Hubbard U term to the d-orbitals of the transition metals. To obtain the values of U, we used the following procedure: (i) For each compound we found the value of U for which PBEfe+U gave the lowest error. (ii) We averaged the best values of U for all compounds containing the element. Note that we do not intend to find universal U values but just to compensate for the difference of errors between the mentioned subsets. Table 3 shows the values of U for each transition metal. The PBEfe+U calculation gives formation energies closer to the experiment (see Figure 3), with a MAD of 0.078 eV/atom.

We also tried to minimize directly the parameters of the PBE by using from the start a Hubbard U set to the same values as in ref 5. However, the minimization scheme did not yield a substantial improvement over our PBEfe functional described earlier.

We have stressed before that the PBEfe is designed exclusively to obtain energies of formation or distances to the convex hull. It is however interesting to study what happens for other quantities that are also important for high-throughput investigations. One of these is the geometry. It is well-known that the standard LDA underestimates lattice constants, while the PBE usually overestimates them (see Figure 5). PBEfe, on the other hand, does not show any clear systematic error, as 47% of the lattice parameters computed with PBEfe are smaller than the experimental ones, while 53% are larger. If we calculate the MAD for the a and b parameters, we find 0.051 Å for PBEfe, to be compared with 0.049 Å for the PBE and 0.080 Å for the LDA. For the c parameter we find 0.068 Å for PBEfe, 0.150 Å
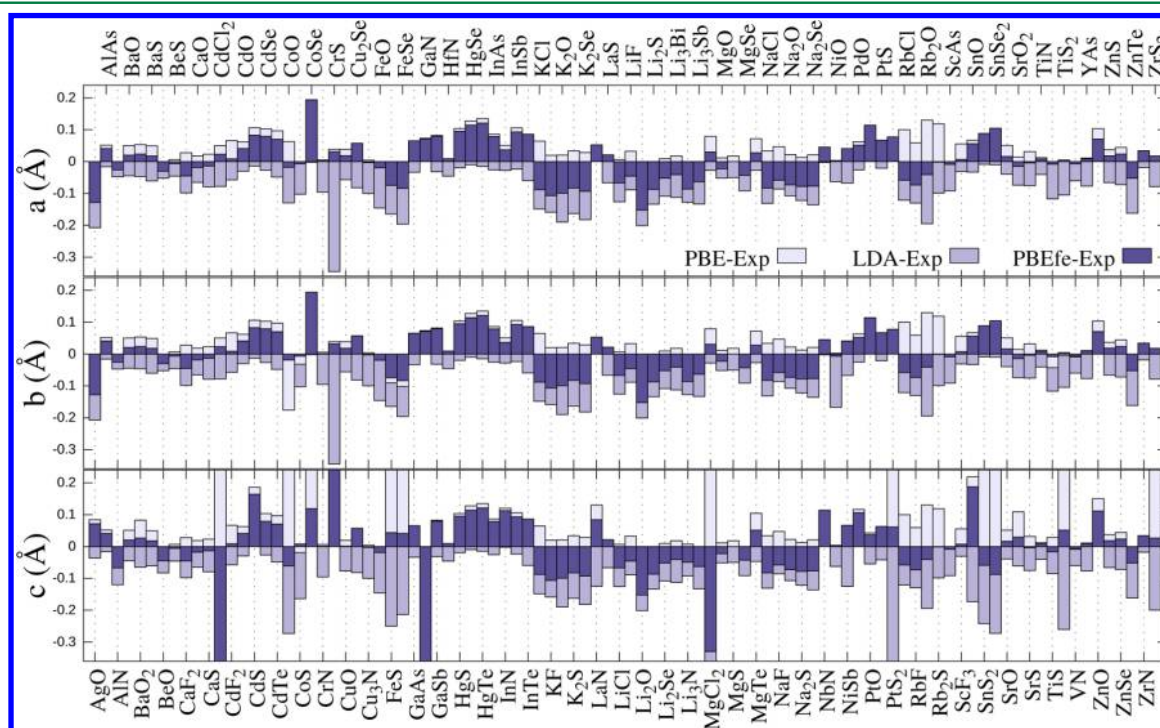
Figure 5. Differences of the experimental and calculated lattice constants for PBE, PBEfe, and LDA functionals.

for PBE, and 0.119 Å for the LDA. We can therefore conclude that PBEfe is at least as good as PBE for the geometries of solids, and often better when it comes to layered systems.

4. CONCLUSIONS

In conclusion, we presented a new semiempirical functional capable of reducing by 40−50% the error in the calculation of formation energies. This is achieved by refitting only *three parameters* of the PBE exchange-correlation functional to experimental formation energies. This means that this functional can be trivially implemented in any code that already has the PBE functional, with no additional computational costs. It can also be easily coupled to postprocessing techniques to reduce the error in the formation energies such as FERE. Furthermore, the theoretical lattice constants are at least as good as the ones calculated with PBE. For these reasons we think that our PBEfe functional is an excellent choice to search for new materials either with use of structural prediction or in high-throughput investigations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables with both calculated and experimentally reported formation energies and lattice constants of all compound in the optimization and control sets and a figure of the minimization of MAD starting from the PBE values of the parameters. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00529.

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Notes
The authors declare no competing financial interest.

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