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Heats of formation of solids with error estimation: The mBEEF functional with and without fitted reference energies

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The need for prediction of accurate electronic binding energies has led to the development of different schemes for combining density functional calculations, typically at the level of the generalized gradient approximation (GGA), with experimental information. We analyze one such scheme by Stevanović *et al.* [Phys. Rev. B **85**, 115104 (2012)] for predictions of compound enthalpies of formation using fitted elemental-phase reference energies. We show that different versions of GGA with or without +U and a meta-GGA (TPSS) lead to comparable accuracy after fitting the reference energies. Our results also show that the recently developed mBEEF, a Bayesian error estimation functional, gives comparable accuracy with the other functionals even without the fitting. The mBEEF functional furthermore supplies an ensemble estimate of the prediction errors in reasonable agreement with the actual errors. We also show that using the fitting scheme on the mBEEF ensemble leads to improved accuracy including realistic error estimation.

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I. INTRODUCTION

In the past two decades, Kohn-Sham density functional theory (KS-DFT) based electronic structure calculations [1,2] have greatly enhanced our understanding of the properties of materials. The drastic reduction in the number of degrees of freedom in the electronic structure problem within the KS-DFT framework makes it an efficient tool for quantum mechanical description of materials. The key ingredient in the KS-DFT is an energy functional which depends on the ground-state electronic density and the accuracy of calculations depends on the quality of the approximations applied to the functional. Efficient and realistic description of materials requires calculations which are not too computationally expensive and reasonably accurate. In the generalized gradient approximation framework (GGA) the PBE functional [3] has been widely used and has a reasonable trade-off between accuracy and efficiency. Despite being remarkably successful in the past, it has its limitations as well. For example, the heats of formation predicted by the PBE functional deviate from experiments by ~ 0.25 eV/atom [4] which makes it difficult to predict the stabilities of compounds in many cases. It severely plagues the process of searching for new materials for different applications where stability of the compounds is one of the main criteria [5–7].

Recently, Stevanović *et al.* proposed a scheme known as fitted elemental reference phase energies (FERE) to improve the prediction of the heats of formation of semiconductors [4,8]. Their scheme is based on the idea of using the reference phase energies as parameters and calculating these parameters by minimizing the root mean square (rms) error between the calculated and experimental heats of formation. The scheme uses a mixture of the PBE and PBE with Hubbard- U correction (PBE+ U) for the calculation of the heats of formation. The proposed scheme shows clear improvement when comparing with the experimental heats of formation of solids. In the present work, we carry out similar analysis with a class of GGA

functionals, namely, the PBE without Hubbard- U corrections, PBE with U corrections, and RPBE [9]. We furthermore exploit the possibilities at the meta-GGA level by including the TPSS functional [10–14] as a representative together with a recently developed meta-GGA functional mBEEF [15], a Bayesian error estimation functional. One of the advantages of the mBEEF functional over the other functionals is that it supplies an error estimate which tells how reliable a particular calculated energy difference is. The details of the mBEEF functional and its comparison to other GGAs and meta-GGA functionals in terms of exchange enhancement factors can be found in Ref. [15]. Calculating the heats of formation on a test set of 24 compounds which have not been used in the the data set for fitting, we show that the mBEEF functional without any fitting is nearly as accurate as the fitted GGA functionals and the fitted TPSS functional and includes a realistic error prediction with a small overestimation. Applying the FERE scheme to the mBEEF ensemble leads to an improved prediction quality and a corresponding reduction of the predicted error bars. Quantitatively, the rms errors in the training data set with the PBE, RPBE, PBE+ U , TPSS, and mBEEF functionals reduce from 0.22, 0.28, 0.21, 0.21, and 0.14 eV per atom to 0.09, 0.09, 0.08, 0.10, and 0.07 eV per atom.

II. COMPUTATIONAL METHODOLOGY

All the calculations in the current work use the GPAW code [16] with the projector augmented wave (PAW) [17] description of the atoms. We consider the PBE [3], RPBE [9], PBE+ U [18], TPSS [10], and mBEEF [15] exchange-correlation functionals. For the PBE+ U calculations, as suggested by Stevanović *et al.*, we use the value of $U = 3.0$ eV for all the transition elements except Ag and Cu for which we use a U value of 5.0 eV. In the calculations involving magnetism, the spin configurations have been taken from the lowest energy structure reported in the experiments. For example, the Fe reference state which has the bcc structure has been treated ferromagnetically whereas the iron oxide has been treated

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antiferromagnetically as reported in the experiments. We use a real-space description of the wave functions with a grid spacing of 0.18 Å. A Fermi temperature of 0.05 eV for the solid phases is used to enhance convergence. Brillouin zone sampling is done with a k -point mesh of $33a_x^{-1} \times 33a_y^{-1} \times 33a_z^{-1}$ with the Monkhorst-Pack [19] sampling scheme. Forces are minimized down to 0.05 eV/Å for all the relaxations. Uncertainties in the heats of formations with the mBEEF functionals are explicitly calculated using the ensemble of functionals proposed in Ref. [20]. All the experimental heats of formation have been taken from Refs. [4,21].

III. RESULTS AND DISCUSSIONS

A. Heats of formation with the DFT

The standard heat of formation of a solid calculated with DFT is

$$\Delta H^{\text{DFT}}(A_{p1}B_{p2}\dots) = E(A_{p1}B_{p2}\dots) - \sum p_i \mu_i^0, \quad (1)$$

where $E(A_{p1}B_{p2}\dots)$ indicates the total energy of $A_{p1}B_{p2}\dots$ calculated with DFT and the μ_i^0 denotes the chemical potentials of the elements under standard conditions calculated with DFT. The entropic and zero-point energy corrections have been ignored in the above expression. The calculation of the heats of formation using the above expression with the PBE, RPBE, TPSS, and PBE+U functionals provide a single number as the best estimate of the heat of formation. In comparison, the mBEEF functional provides both a best estimate but also via the ensemble of functionals an estimation of the error bar on the calculated heat of formation. The functionals in the mBEEF ensemble differ from each other by the values of the parameters defining the functional [15].

The calculated heats of formation versus the experimental heats of formation (eV/per atom) of a set of 257 binary compounds with the PBE, RPBE, PBE+U, TPSS, and mBEEF functionals are shown in Fig. 1, panels (a), (c), (e), (g), and (i). The set of compounds we use has about 80% overlap with the set of 252 compounds used by Stevanović *et al.* [4] and the full list of compounds is given in Table I along with the heats of formation calculated with the mBEEF and the mBEEF with fitting of reference energies. The difference between our data set and the one of Stevanović *et al.* gives rise to somewhat different results in detail but the trends remain the same. In the figure MAE and σ denote the mean absolute error and standard deviation with respect to the experimental heats of formation. The observed trend in Figs. 1(a) and 1(c) is a similar behavior for the PBE and RPBE functionals with underbinding in most of the cases with a very few overbinding cases. This behavior in the GGA functionals arises due to the overbinding of the reference phases and the underbinding in the multinary compounds leading to an incomplete cancellation of the errors [22]. In Fig. 1(e) the direction of the deviation in the PBE+U heats of formation is not very systematic, i.e., underbinding in some cases and overbinding in others. This behavior has also been observed in Ref. [23]. The predictions do not significantly improve with the TPSS functional as shown in Fig. 1(g). The MAE and rms in the TPSS predictions turn out to be similar to the GGA functionals. An important factor in the calculated errors is the dissimilar nature of the reactants and the products. Reactions in which both sides have similar compounds are

FIG. 1. (Color online) (a), (c), (e), (g), and (i) show the heats of formation calculated with the PBE, RPBE, PBE+U, TPSS, and mBEEF functionals, respectively, versus the experimental heats of formation. (b), (d), (f), (h), and (j) show the heats of formation calculated with PBE, RPBE, PBE+U, TPSS, and mBEEF functionals, respectively, versus the experimental heats of formation after correcting the reference phase energies using the experimental heats of formation as the training set. MAE and σ in (a)–(j) indicate the mean absolute error and standard deviation of the calculated heats of formation with respect to the experimental heats of formation.

TABLE I. The heats of formation of the solids used in the training set calculated with the mBEEF (ΔH_{mBEEF}) and mBEEF with the FERE ($\Delta H_{\text{mBEEF}}^{\text{FERE}}$). The experimental values (ΔH_{Expt}) are also given for comparison. All the energies are in eV/atom.

Compound	ΔH_{Expt}	ΔH_{mBEEF}	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$	Compound	ΔH_{Expt}	ΔH_{mBEEF}	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$
Ag ₂ Se	-0.15	0.02 ± 0.12	-0.07 ± 0.09	AgCl	-0.66	-0.56 ± 0.24	-0.58 ± 0.09
AgI	-0.32	-0.32 ± 0.13	-0.39 ± 0.08	Ag ₂ O	-0.11	-0.07 ± 0.20	-0.14 ± 0.03
Ag ₂ O ₂	-0.06	-0.07 ± 0.19	-0.13 ± 0.04	AlCl ₃	-1.82	-1.74 ± 0.19	-1.80 ± 0.05
AlF ₃	-3.90	-3.93 ± 0.27	-3.85 ± 0.06	Al ₂ O ₃	-3.47	-3.24 ± 0.24	-3.41 ± 0.07
AlN	-1.65	-1.55 ± 0.23	-1.72 ± 0.04	AlAs	-0.61	-0.66 ± 0.14	-0.64 ± 0.05
AlP	-0.85	-0.76 ± 0.15	-0.87 ± 0.06	Al ₂ Se ₃	-1.18	-0.93 ± 0.12	-1.13 ± 0.04
AsI ₃	-0.15	-0.18 ± 0.03	-0.12 ± 0.04	AuBr	-0.07	-0.11 ± 0.11	-0.06 ± 0.03
AuCl	-0.18	-0.27 ± 0.17	-0.12 ± 0.04	AuI	-0.00	-0.08 ± 0.11	0.03 ± 0.04
Au ₂ O ₃	-0.01	-0.11 ± 0.19	-0.02 ± 0.05	AuCl ₃	-0.17	-0.39 ± 0.20	-0.29 ± 0.05
AuF ₃	-0.94	-1.24 ± 0.23	-1.01 ± 0.09	BN	-1.32	-1.38 ± 0.14	-1.34 ± 0.04
B ₂ O ₃	-2.64	-2.60 ± 0.16	-2.61 ± 0.05	BaF ₂	-4.17	-4.40 ± 0.28	-4.25 ± 0.04
BaO ₂	-2.19	-2.19 ± 0.23	-2.22 ± 0.05	BaS	-2.38	-2.39 ± 0.17	-2.44 ± 0.04
BaCl ₂	-2.95	-2.96 ± 0.23	-2.94 ± 0.04	BaO	-2.86	-2.75 ± 0.22	-2.77 ± 0.04
BaBr ₂	-2.62	-2.48 ± 0.13	-2.59 ± 0.03	BaI ₂	-2.10	-2.02 ± 0.11	-2.07 ± 0.04
BeO	-3.14	-2.95 ± 0.23	-3.03 ± 0.05	BeS	-1.21	-1.18 ± 0.16	-1.28 ± 0.04
BeI ₂	-0.67	-0.64 ± 0.06	-0.72 ± 0.06	BiBr ₃	-0.72	-0.71 ± 0.08	-0.81 ± 0.05
Bi ₂ O ₃	-1.19	-1.17 ± 0.15	-1.16 ± 0.07	Bi ₂ S ₃	-0.30	-0.29 ± 0.09	-0.31 ± 0.07
CaF ₂	-4.21	-4.56 ± 0.29	-4.39 ± 0.07	CaI ₂	-1.84	-1.82 ± 0.10	-1.84 ± 0.05
CaO	-3.29	-3.25 ± 0.25	-3.23 ± 0.04	CaS	-2.45	-2.43 ± 0.19	-2.43 ± 0.04
CaBr ₂	-2.36	-2.26 ± 0.10	-2.34 ± 0.03	CaCl ₂	-2.75	-2.78 ± 0.22	-2.72 ± 0.05
CaC ₂	-0.21	-0.13 ± 0.12	-0.21 ± 0.04	CdS	-0.78	-0.77 ± 0.13	-0.80 ± 0.05
CdF ₂	-2.42	-2.76 ± 0.29	-2.60 ± 0.08	CdO	-1.34	-1.20 ± 0.20	-1.20 ± 0.10
CdSe	-0.75	-0.71 ± 0.10	-0.74 ± 0.05	CdTe	-0.48	-0.61 ± 0.10	-0.51 ± 0.04
CdI ₂	-0.70	-0.63 ± 0.07	-0.66 ± 0.05	CoS	-0.43	-0.28 ± 0.17	-0.31 ± 0.08
CoSe	-0.32	-0.27 ± 0.19	-0.31 ± 0.03	Co ₃ O ₄	-1.32	-1.50 ± 0.38	-1.51 ± 0.14
Co ₃ S ₄	-0.53	-0.45 ± 0.16	-0.49 ± 0.07	CrS	-0.81	-0.83 ± 0.16	-0.77 ± 0.12
CrF ₃	-3.00	-3.26 ± 0.34	-3.04 ± 0.09	CrO ₂	-2.07	-2.06 ± 0.28	-2.02 ± 0.06
Cr ₂ O ₃	-2.36	-2.52 ± 0.33	-2.46 ± 0.07	CrF ₄	-2.58	-2.72 ± 0.25	-2.50 ± 0.11
CsBr	-2.10	-1.99 ± 0.10	-2.10 ± 0.03	CsCl	-2.30	-2.25 ± 0.18	-2.27 ± 0.01
CsF	-2.87	-2.98 ± 0.22	-2.90 ± 0.04	Cu ₃ N	0.18	0.34 ± 0.14	0.12 ± 0.03
CuO	-0.82	-0.58 ± 0.21	-0.76 ± 0.04	Cu ₂ O	-0.58	-0.36 ± 0.20	-0.58 ± 0.05
CuF ₂	-1.88	-1.85 ± 0.29	-1.80 ± 0.13	Cu ₂ Sb	-0.04	0.02 ± 0.05	-0.07 ± 0.04
CuI	-0.35	-0.15 ± 0.10	-0.33 ± 0.04	Cu ₂ Se	-0.21	0.10 ± 0.10	-0.13 ± 0.03
Cu ₃ P	-0.17	0.01 ± 0.05	-0.18 ± 0.09	CuS	-0.28	-0.17 ± 0.16	-0.37 ± 0.05
Fe ₂ O ₃	-1.71	-1.69 ± 0.26	-1.89 ± 0.11	FeS	-0.52	-0.35 ± 0.12	-0.61 ± 0.04
FeF ₂	-2.46	-2.27 ± 0.31	-2.27 ± 0.10	FeO	-1.41	-1.15 ± 0.19	-1.39 ± 0.08
FeSe	-0.39	-0.04 ± 0.11	-0.30 ± 0.13	GaN	-0.81	-0.48 ± 0.17	-0.72 ± 0.06
GaP	-0.47	-0.44 ± 0.08	-0.63 ± 0.05	GaAs	-0.39	-0.42 ± 0.08	-0.47 ± 0.02
GaSb	-0.22	-0.20 ± 0.06	-0.29 ± 0.03	GaCl ₃	-1.36	-1.25 ± 0.20	-1.34 ± 0.09
GaF ₃	-3.01	-2.96 ± 0.24	-2.92 ± 0.03	Ga ₂ O ₃	-2.26	-1.99 ± 0.19	-2.21 ± 0.03
Ga ₂ S ₃	-1.07	-0.70 ± 0.11	-0.95 ± 0.04	Ga ₂ Se ₃	-0.85	-0.59 ± 0.08	-0.85 ± 0.03
GaSe	-0.83	-0.61 ± 0.06	-0.91 ± 0.03	GaS	-1.09	-0.68 ± 0.08	-0.98 ± 0.04
GeTe	-0.10	-0.04 ± 0.06	-0.17 ± 0.04	GeS	-0.39	-0.20 ± 0.08	-0.46 ± 0.03
Ge ₃ O ₆	-1.90	-1.78 ± 0.16	-1.95 ± 0.07	GeSe	-0.48	-0.11 ± 0.07	-0.38 ± 0.04
Ge ₄ O ₈	-2.00	-1.71 ± 0.15	-1.88 ± 0.08	HfN	-1.91	-1.74 ± 0.14	-1.94 ± 0.06
HfCl ₄	-2.05	-2.07 ± 0.22	-2.11 ± 0.06	HfO ₂	-3.95	-3.71 ± 0.23	-3.88 ± 0.05
HfF ₄	-4.00	-4.07 ± 0.26	-3.98 ± 0.04	HgSe	-0.24	-0.26 ± 0.11	-0.31 ± 0.02
HgTe	-0.22	-0.32 ± 0.13	-0.23 ± 0.02	HgS	-0.30	-0.21 ± 0.13	-0.26 ± 0.03
HgO	-0.47	-0.36 ± 0.14	-0.38 ± 0.05	HgI ₂	-0.36	-0.37 ± 0.07	-0.41 ± 0.02
HgCl ₂	-0.77	-0.82 ± 0.21	-0.79 ± 0.07	InN	-0.10	0.00 ± 0.15	-0.12 ± 0.03
InP	-0.46	-0.34 ± 0.08	-0.41 ± 0.04	InTe	-0.50	-0.32 ± 0.04	-0.37 ± 0.06
InAs	-0.31	-0.39 ± 0.08	-0.31 ± 0.03	InS	-0.70	-0.61 ± 0.13	-0.78 ± 0.02
InSb	-0.16	-0.27 ± 0.07	-0.24 ± 0.03	IrO ₂	-0.95	-0.79 ± 0.18	-0.92 ± 0.03
IrCl ₃	-0.64	-0.59 ± 0.17	-0.64 ± 0.03	IrS ₂	-0.48	-0.36 ± 0.14	-0.52 ± 0.03
K ₂ O	-1.25	-1.22 ± 0.21	-1.28 ± 0.05	K ₂ S	-1.31	-1.24 ± 0.16	-1.31 ± 0.04
K ₂ Se	-1.36	-1.24 ± 0.14	-1.31 ± 0.05	KF	-2.94	-3.19 ± 0.24	-3.11 ± 0.06
KCl	-2.26	-2.25 ± 0.17	-2.26 ± 0.02	K ₂ O ₂	-1.28	-1.23 ± 0.22	-1.28 ± 0.06

TABLE I. (*Continued.*)

Compound	ΔH_{Expt}	ΔH_{mBEEF}	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$	Compound	ΔH_{Expt}	ΔH_{mBEEF}	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$
K ₃ As	-0.48	-0.40 ± 0.11	-0.35 ± 0.06	K ₂ S ₂	-1.12	-1.11 ± 0.14	-1.18 ± 0.03
LaS	-2.36	-2.14 ± 0.16	-2.40 ± 0.07	LaN	-1.57	-1.32 ± 0.18	-1.53 ± 0.07
LaI ₃	-1.73	-1.61 ± 0.09	-1.76 ± 0.03	LaCl ₃	-2.78	-2.67 ± 0.23	-2.75 ± 0.06
Li ₂ O	-2.07	-2.00 ± 0.26	-2.07 ± 0.10	Li ₂ S	-1.52	-1.51 ± 0.15	-1.59 ± 0.03
Li ₂ Se	-1.45	-1.37 ± 0.11	-1.46 ± 0.04	Li ₃ N	-0.43	-0.45 ± 0.24	-0.50 ± 0.10
Li ₃ Sb	-0.83	-0.67 ± 0.07	-0.65 ± 0.09	LiF	-3.19	-3.37 ± 0.23	-3.30 ± 0.07
Li ₃ Bi	-0.60	-0.57 ± 0.05	-0.61 ± 0.09	LiCl	-2.12	-2.03 ± 0.17	-2.05 ± 0.11
Li ₂ O ₂	-1.64	-1.58 ± 0.21	-1.64 ± 0.06	MgTe	-1.08	-1.05 ± 0.09	-1.06 ± 0.04
MgS	-1.79	-1.60 ± 0.15	-1.74 ± 0.06	MgSe	-1.52	-1.41 ± 0.12	-1.56 ± 0.05
MgO	-3.11	-3.14 ± 0.20	-3.26 ± 0.06	Mg ₃ Bi ₂	-0.32	-0.23 ± 0.07	-0.32 ± 0.05
MgF ₂	-3.88	-3.79 ± 0.25	-3.71 ± 0.05	MnS	-1.11	-1.08 ± 0.23	-1.03 ± 0.06
MnO ₂	-1.80	-1.99 ± 0.28	-1.96 ± 0.09	Mn ₃ O ₄	-2.05	-2.13 ± 0.28	-2.07 ± 0.01
Mn ₂ O ₃	-1.99	-1.99 ± 0.27	-1.94 ± 0.02	MoS ₂	-0.81	-0.83 ± 0.08	-0.86 ± 0.03
MoO ₂	-2.03	-1.95 ± 0.18	-1.96 ± 0.04	MoO ₃	-1.93	-1.93 ± 0.18	-1.95 ± 0.05
NaF	-2.97	-3.04 ± 0.21	-2.93 ± 0.05	Na ₂ O	-1.43	-1.49 ± 0.18	-1.51 ± 0.10
Na ₂ S	-1.26	-1.24 ± 0.12	-1.28 ± 0.03	Na ₂ Se	-1.18	-1.19 ± 0.12	-1.23 ± 0.04
Na ₂ C ₂	0.06	0.12 ± 0.09	0.04 ± 0.03	NaCl	-2.13	-2.09 ± 0.17	-2.07 ± 0.06
Na ₂ S ₂	-1.03	-0.97 ± 0.12	-1.02 ± 0.04	Na ₂ Se ₂	-0.97	-0.95 ± 0.13	-1.00 ± 0.06
Na ₃ Bi	-0.46	-0.40 ± 0.07	-0.39 ± 0.06	Na ₂ O ₂	-1.32	-1.26 ± 0.18	-1.29 ± 0.08
NbN	-1.22	-1.15 ± 0.13	-1.13 ± 0.04	NbO	-2.10	-2.06 ± 0.14	-2.07 ± 0.03
Nb ₂ O ₅	-2.81	-2.85 ± 0.21	-2.87 ± 0.04	NbF ₅	-3.13	-3.52 ± 0.23	-3.33 ± 0.13
NbO ₂	-2.75	-2.76 ± 0.23	-2.77 ± 0.05	NbCl ₅	-1.38	-1.46 ± 0.22	-1.42 ± 0.05
NiS	-0.43	-0.17 ± 0.12	-0.35 ± 0.04	NiSb	-0.34	-0.36 ± 0.07	-0.33 ± 0.06
NiTe	-0.28	-0.23 ± 0.06	-0.28 ± 0.03	NiSe	-0.31	-0.14 ± 0.09	-0.32 ± 0.03
Ni ₃ S ₂	-0.42	-0.28 ± 0.13	-0.48 ± 0.03	OsO ₄	-0.82	-1.12 ± 0.19	-0.83 ± 0.01
PI ₃	-0.16	-0.05 ± 0.06	-0.06 ± 0.05	PCl ₃	-0.83	-0.83 ± 0.21	-0.76 ± 0.09
PBr ₅	-0.47	-0.31 ± 0.04	-0.42 ± 0.05	PCl ₅	-0.77	-0.74 ± 0.19	-0.68 ± 0.06
PbO	-1.13	-1.08 ± 0.16	-1.08 ± 0.04	PbS	-0.52	-0.52 ± 0.14	-0.53 ± 0.06
PbF ₂	-2.29	-2.60 ± 0.25	-2.43 ± 0.04	PbO ₂	-0.96	-0.87 ± 0.18	-0.88 ± 0.05
PbCl ₂	-1.24	-1.29 ± 0.19	-1.24 ± 0.06	PbBr ₂	-0.96	-0.88 ± 0.09	-0.97 ± 0.03
PdO	-0.44	-0.56 ± 0.27	-0.52 ± 0.09	Pd ₄ S	-0.14	-0.14 ± 0.09	-0.07 ± 0.09
PdS	-0.39	-0.41 ± 0.19	-0.40 ± 0.07	PdS ₂	-0.28	-0.31 ± 0.14	-0.33 ± 0.05
PtS	-0.42	-0.43 ± 0.18	-0.51 ± 0.03	PtS ₂	-0.38	-0.36 ± 0.12	-0.44 ± 0.06
Pt ₂ O ₂	-0.37	-0.19 ± 0.22	-0.24 ± 0.06	PtO ₂	-0.57	-0.53 ± 0.20	-0.58 ± 0.04
RbF	-2.89	-2.95 ± 0.22	-2.87 ± 0.04	RbI	-1.73	-1.71 ± 0.09	-1.77 ± 0.05
Rb ₂ O	-1.17	-1.04 ± 0.21	-1.10 ± 0.05	Rb ₂ S	-1.25	-1.16 ± 0.15	-1.23 ± 0.04
Rb ₂ O ₂	-1.22	-1.28 ± 0.20	-1.33 ± 0.05	RbCl	-2.26	-2.23 ± 0.17	-2.24 ± 0.02
ReO ₃	-1.58	-1.63 ± 0.17	-1.69 ± 0.06	ReO ₂	-1.54	-1.40 ± 0.17	-1.46 ± 0.05
RhO ₂	-0.85	-0.87 ± 0.23	-0.87 ± 0.04	RhCl ₃	-0.77	-0.87 ± 0.21	-0.81 ± 0.03
Rh ₂ S ₃	-0.54	-0.53 ± 0.18	-0.55 ± 0.04	Rh ₂ O ₃	-0.84	-0.80 ± 0.28	-0.79 ± 0.05
RuO ₂	-1.05	-1.11 ± 0.22	-0.99 ± 0.06	RuBr ₃	-0.36	-0.34 ± 0.08	-0.35 ± 0.04
RuCl ₃	-0.53	-0.74 ± 0.20	-0.60 ± 0.04	RuO ₄	-0.50	-0.58 ± 0.19	-0.53 ± 0.19
SbF ₃	-2.37	-2.49 ± 0.23	-2.24 ± 0.07	Sb ₂ O ₅	-1.44	-1.50 ± 0.19	-1.43 ± 0.06
ScAs	-1.39	-1.53 ± 0.06	-1.45 ± 0.03	ScF ₃	-4.22	-4.22 ± 0.25	-4.11 ± 0.06
ScCl ₃	-2.40	-2.37 ± 0.21	-2.39 ± 0.05	SiC	-0.34	-0.25 ± 0.09	-0.32 ± 0.07
SiO ₂	-3.13	-3.06 ± 0.17	-3.09 ± 0.06	SiS ₂	-0.88	-0.78 ± 0.06	-0.83 ± 0.06
SiSe ₂	-0.61	-0.50 ± 0.06	-0.55 ± 0.06	Si ₃ N ₄	-1.10	-1.17 ± 0.14	-1.15 ± 0.09
SnO	-1.48	-1.20 ± 0.14	-1.42 ± 0.04	SnS ₂	-0.53	-0.37 ± 0.09	-0.56 ± 0.03
SnSe ₂	-0.43	-0.28 ± 0.06	-0.48 ± 0.03	SnO ₂	-1.97	-1.73 ± 0.21	-1.89 ± 0.05
SnS	-0.57	-0.34 ± 0.11	-0.58 ± 0.03	SnSe	-0.47	-0.27 ± 0.10	-0.52 ± 0.04
SrO ₂	-2.19	-2.32 ± 0.23	-2.31 ± 0.06	SrO	-3.07	-3.08 ± 0.24	-3.05 ± 0.04
SrS	-2.45	-2.44 ± 0.19	-2.44 ± 0.04	SrCl ₂	-2.86	-2.88 ± 0.23	-2.81 ± 0.05
SrBr ₂	-2.48	-2.38 ± 0.11	-2.45 ± 0.03	SrI ₂	-1.93	-1.92 ± 0.10	-1.93 ± 0.02
TaN	-1.30	-1.14 ± 0.13	-1.25 ± 0.05	TaSi ₂	-0.47	-0.36 ± 0.17	-0.43 ± 0.07
Ta ₂ O ₅	-3.03	-2.99 ± 0.23	-3.09 ± 0.06	TaF ₅	-3.29	-3.56 ± 0.23	-3.41 ± 0.10
TaCl ₅	-1.48	-1.51 ± 0.21	-1.51 ± 0.06	TiS	-1.41	-1.44 ± 0.10	-1.37 ± 0.06
TiS ₂	-1.41	-1.41 ± 0.12	-1.38 ± 0.04	TiN	-1.58	-1.88 ± 0.12	-1.75 ± 0.03
Ti ₂ O ₃	-3.15	-3.14 ± 0.19	-3.07 ± 0.03	TiAs	-0.78	-1.02 ± 0.05	-0.69 ± 0.03

TABLE I. (Continued.)

Compound	ΔH_{Expt}	ΔH_{mBEEF}	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$	Compound	ΔH_{Expt}	ΔH_{mBEEF}	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$
TiO ₂	-3.26	-3.37 ± 0.21	-3.32 ± 0.05	TiI	-0.64	-0.70 ± 0.10	-0.67 ± 0.04
TiBr	-0.90	-0.95 ± 0.11	-0.97 ± 0.05	TiCl	-1.06	-1.16 ± 0.20	-1.08 ± 0.07
Tl ₂ O	-0.62	-0.68 ± 0.15	-0.61 ± 0.08	TiF	-1.68	-1.80 ± 0.21	-1.62 ± 0.03
Tl ₂ S	-0.34	-0.37 ± 0.12	-0.32 ± 0.05	VN	-1.13	-0.99 ± 0.13	-1.00 ± 0.08
V ₂ O ₃	-2.53	-2.58 ± 0.29	-2.62 ± 0.11	V ₂ O ₅	-2.29	-2.31 ± 0.20	-2.35 ± 0.06
VO ₂	-2.47	-2.48 ± 0.23	-2.52 ± 0.04	WBr ₆	-0.52	-0.41 ± 0.07	-0.51 ± 0.03
WO ₃	-2.04	-2.08 ± 0.19	-2.05 ± 0.02	YAs	-1.68	-1.75 ± 0.08	-1.68 ± 0.02
YCl ₃	-2.59	-2.63 ± 0.22	-2.67 ± 0.05	YF ₃	-4.45	-4.45 ± 0.27	-4.36 ± 0.04
ZnO	-1.81	-1.57 ± 0.21	-1.75 ± 0.04	ZnSe	-0.85	-0.76 ± 0.12	-0.97 ± 0.02
ZnTe	-0.61	-0.56 ± 0.08	-0.64 ± 0.01	ZnS	-1.07	-0.89 ± 0.14	-1.10 ± 0.03
ZnCl ₂	-1.43	-1.36 ± 0.19	-1.44 ± 0.05	ZnF ₂	-2.64	-2.50 ± 0.25	-2.46 ± 0.05
ZrO ₂	-3.80	-3.75 ± 0.23	-3.79 ± 0.05	ZrCl ₄	-2.03	-2.11 ± 0.22	-2.08 ± 0.03
ZrSi	-0.80	-0.93 ± 0.11	-0.94 ± 0.05	ZrN	-1.89	-1.84 ± 0.13	-1.85 ± 0.06
ZrS ₂	-1.96	-1.73 ± 0.14	-1.79 ± 0.06				

shown to give smaller errors when compared to experiments [22]. Figure 1(i) shows the calculated heats of formation with the mBEEF functional with calculated error bars indicated with green bars. The calculated values are significantly closer to the experimental values compared to the values obtained from the PBE, RPBE, PBE+U, and TPSS functionals. As can be seen from the figure the experimental values are within the error bars predicted by the mBEEF functional.

The mBEEF functional thus seems to be more accurate than both the GGA functionals and the TPSS which is also a meta-GGA functional. However, it should also be noted that in the construction of the mBEEF functional considerable optimization to experimental databases was performed. In the following we investigate how the scheme suggested by Stevanović *et al.* [4] helps in improving the predictions for the different functionals.

B. Heats of formation with the FERE

In the previous section we noticed that the limited predictability of the TPSS and the GGA functionals mainly arises from the different nature of the bonding in the multinary phases and the reference phases. The FERE scheme [4] circumvents this problem by adding corrections to the reference phase energies. The heats of formation calculated with the FERE can be written as

$$\begin{aligned} \Delta H^{\text{FERE}}(A_{p1}B_{p2}\dots) \\ = E(A_{p1}B_{p2}\dots) - \sum p_i(\mu_i^0 + \delta\mu_i^0), \end{aligned} \quad (2)$$

where the $\delta\mu_i^0$'s are the corrections added to the reference phase energies to improve the heats of formation. The values of the $\delta\mu_i^0$'s can be calculated by a linear regression fit by minimizing the root mean square (rms) error between the calculated (ΔH^{DFT}) and the experimental (ΔH^{Expt}) heats of formation. The size of the training set has to be sufficiently large to avoid any overfitting and the quality of the fit must be validated on a test set. The linear regression requires that the number of parameters in the linear model which need to be fitted to the observations be smaller than the number of data points; i.e., the system of the equations has to be overdetermined. We calculate 62 parameters which correspond to the

corrections to the reference phase energies of 62 elements by using a training set of 257 compounds with the experimental heats of formation available. The parameters can be calculated using singular value decomposition (SVD) [24] by minimizing the rms error $|\Delta H_{\text{Expt}} - \Delta H_{\text{DFT}}|^2$. The calculated reference energies are tabulated in the Supplemental Material [25].

Figure 1, panels (b), (d), (f), (h), and (j), shows the heats of formation calculated after adding the corrections to the reference phase energies. The comparison with panels (a), (c), (e), (g), and (i) of the figure clearly shows that the MAE and σ are significantly reduced after applying the corrections to the reference phase energies. Interestingly, all the GGA functionals give similar heats of formation after employing the corrections even though they differ before applying the corrections. The TPSS functional does not perform any better than the GGA functionals after applying the corrections.

As noted the performance of mBEEF before fitting is somewhat better than the GGAs and the TPSS functional and in fact, as we shall see later, it is comparable to the fitted GGAs and the TPSS on a test set. However, for comparison we also apply the FERE fitting procedure to the mBEEF functional and this does naturally lead to an improvement on the training set. As mentioned before, we furthermore employ the fitting procedure on all the functionals in the mBEEF ensemble anticipating a reduction of the error and the fluctuations within the ensemble. This is indeed the case. In Fig. 1(j) we can see that the uncertainties are significantly reduced as compared to Fig. 1(i). The reduction in the size of the uncertainties is in agreement with the fact that the fitted mBEEF predictions are more accurate.

C. Analysis of outliers

The appearance of outliers with and without the fitting for the PBE, RPBE, and PBE+U functionals may occur for two reasons: (1) error in the experimental data, and (2) some systems are poorly described with the given functional. The compounds having the deviation of the calculated heat of formation (δH) from the experimental value by twice of the standard deviation (2σ) are shown in Table II. The table clearly shows that all the functionals except for PBE and RPBE

TABLE II. Outliers in the calculations without using the FERE scheme. The compounds exhibiting deviations of the calculated heats of formation from the experimental values by more than 2σ have been identified as outliers. The values of σ for the different functionals are shown in Fig. 1. δH denotes the difference between calculated and experimental heats of formation.

PBE	δH_{PBE}	RPBE	δH_{RPBE}	PBE+U	$\delta H_{\text{PBE+U}}$	TPSS	δH_{TPSS}	mBEEF	δH_{mBEEF}
Al ₂ O ₃	0.48	Al ₂ O ₃	0.69	Al ₂ O ₃	0.48	AlP	0.45	AuF ₃	-0.30
BaS	-0.52	FeF ₂	0.61	BaS	-0.52	BaI ₂	-0.48	CaF ₂	-0.35
BaO	-0.47	FeO	0.60	BaO	-0.47	BiBr ₃	-0.51	CdF ₂	-0.34
FeF ₂	0.61	GaN	0.57	CrS	-0.82	CaS	0.48	Cu ₂ Se	0.31
FeO	0.49	HfO ₂	0.65	CrF ₃	-0.47	FeF ₂	0.57	FeSe	0.35
GaS	0.451	NiF ₂	0.66	Cr ₂ O ₃	-0.75	GaP	0.43	GaN	0.33
LaN	0.46			GaN	0.42	Ga ₂ S ₃	0.44	Ga ₂ S ₃	0.37
MnS	0.60			Ga ₂ S ₃	0.44	NiF ₂	0.57	GaS	0.41
NiF ₂	0.85			GaS	0.45	PbBr ₂	-0.45	GeSe	0.37
				Ge ₄ O ₈	0.42	SrBr ₂	-0.49	Ge ₄ O ₈	0.29
				MnS	-0.48	SrI ₂	-0.55	NbF ₅	-0.38
				Mn ₃ O ₄	-0.42	ZnS	0.43	OsO ₄	-0.30
				V ₂ O ₃	-0.42	ZrS ₂	0.47	PbF ₂	-0.31
								SnO ₂	0.28
								TiN	-0.30

have none or very few common outliers. For example, the predictions for barium-containing compounds is a little worse only in the PBE, PBE+U, and the TPSS whereas the outliers containing chromium are present in the PBE+U functional only. On the other hand, even if the gallium is present in all the functionals it is not the same compound which is an outlier.

Additionally, the outliers present in the mBEEF calculations do not deviate from the experimental value by more than 0.41 eV per atom whereas the outliers present in the GGA functionals and the TPSS have deviations as high as 0.85 and 0.57 eV per atom, respectively. The deviations shown for the mBEEF functional are relative to a common rms error $\sigma = 0.14$ eV and not based on the ensemble estimated errors. The large variation in outliers with functional seems to indicate that the appearance of outliers is as might be expected not due to experimental errors but rather due to limitations of the different functionals.

Table III shows the outliers after the fitting has been applied. We see that the outliers are to a large extent different from the ones before the fitting and again they also vary considerably for the different functionals. This means that we cannot identify particular issues with specific systems. The PBE and RPBE functionals continue to have significant overlap of outliers after the fitting.

D. Statistical analysis of the mBEEF predictions

The error bars predicted by the mBEEF ensemble are in reasonable agreement with the actual errors as can be seen from Fig. 1(i). In order to study the quality of the error bar prediction in more detail we show in Fig. 2(a) a histogram of the actual error, i.e., the deviation between the mBEEF prediction and the experimental value ($\Delta H_{\text{mBEEF}} - \Delta H_{\text{Expt}}$) divided by the predicted error bar (σ_{BEE}). The histogram is a

TABLE III. Outliers in the calculations using the FERE scheme. The compounds exhibiting deviations of the calculated heats of formation from the experimental values by more than 2σ have been identified as outliers. The values of σ for the different functionals are shown in Fig. 1. δH denotes the difference between calculated and experimental heats of formation.

PBE	$\delta H_{\text{PBE}}^{\text{FERE}}$	RPBE	$\delta H_{\text{RPBE}}^{\text{FERE}}$	PBE+U	$\delta H_{\text{PBE+U}}^{\text{FERE}}$	TPSS	$\delta H_{\text{TPSS}}^{\text{FERE}}$	mBEEF	$\delta H_{\text{mBEEF}}^{\text{FERE}}$
CuF ₂	0.22	CuF ₂	0.23	CoS	0.20	BaCl ₂	0.24	CaF ₂	-0.18
FeF ₂	0.33	FeF ₂	0.27	Co ₃ O ₄	-0.23	CaS	0.21	CdF ₂	-0.18
FeSe	-0.19	MnO ₂	-0.21	CrO ₂	0.17	CsF	-0.23	Co ₃ O ₄	-0.19
MnO ₂	-0.25	NbF ₅	-0.32	Fe ₂ O ₃	-0.17	FeF ₂	0.29	Fe ₂ O ₃	-0.17
NbF ₅	-0.29	Ni ₃ S ₂	-0.18	GaF ₃	0.16	KCl	0.32	FeF ₂	0.19
Ni ₃ S ₂	-0.21	NiF ₂	0.38	GeO ₂	0.20	NbF ₅	-0.26	GaP	-0.16
NiF ₂	0.65	PbF ₂	-0.18	MgF ₂	0.19	NiF ₂	0.37	KF	-0.17
RuO ₄	-0.19	RuO ₄	-0.33	NbF ₅	-0.23	RbI	0.25	Li ₃ Sb	0.18
TaF ₅	-0.22	TaF ₅	-0.24	SnO ₂	0.17	SrS	0.25	MgO	-0.15
ZrSi	-0.24	ZrSi	-0.26	TaF ₅	-0.18	SrI ₂	-0.24	MgF ₂	0.17
ZrS ₂	0.26	ZrS ₂	0.24	TiN	-0.19	TiI	0.26	MnO ₂	-0.16
				VN	0.26	ZrSi	-0.24	NbF ₅	-0.20
				V ₂ O ₃	-0.36	ZrS ₂	0.35	TiN	-0.17
				ZnF ₂	0.19			ZnF ₂	0.18
				ZrS ₂	0.16			ZrS ₂	0.16

FIG. 2. (Color online) (a) Shows the probability distribution of the calculated error $(\Delta H_{\text{mBEEF}} - \Delta H_{\text{Expt}})$ in the heat of formation divided by the estimated error (σ_{BEE}) from the ensemble of functionals. (b) Shows the probability distribution of the calculated error $(\Delta H_{\text{mBEEF}}^{\text{FERE}} - \Delta H_{\text{Expt}})$ in the heat of formation divided by the estimated error $(\sigma_{\text{BEE}}^{\text{FERE}})$ from the ensemble of functionals after correcting the reference phase energies. The ensemble energies have also been recalculated employing the fitting eventually giving the new error estimates $\sigma_{\text{BEE}}^{\text{FERE}}$. The green plots in (a) and (b) show the Gaussian distributions with zero mean and unit standard deviation.

running average calculated as [24]

$$P\left(\frac{1}{2}[x_i + x_{i+J}]\right) \approx \frac{J}{N(x_{i+J} - x_i)}, \quad (3)$$

with x_i being the ratio between actual error and predicted error, and the parameter $J = 20$. For a perfect statistical error prediction one could expect that the distribution would be Gaussian with a width of 1, which is also shown in the figure for comparison. The large peak in the histogram around zero shows that there is some tendency for the error prediction to be on the large side, but the overall agreement is quite good.

If the FERE fitting procedure is applied to the mBEEF ensemble the ratios of real to predicted errors result in the histogram shown in Fig. 2(b). Both the real $(\Delta H_{\text{mBEEF}}^{\text{FERE}} - \Delta H_{\text{Expt}})$ and the predicted errors $(\sigma_{\text{BEE}}^{\text{FERE}})$ are now smaller but the relative distribution remains fairly close to a Gaussian of unit width. However, now a tail in the histogram appears

indicating that for some systems the predicted error can be 3 or 4 times smaller than the actual error. This is a fairly common feature of the ensemble approach [26].

E. Cross validation

In any regression process it is necessary to validate the quality of the regression over a set of test data which is not the part of the training data set. Overfitting, i.e., more parameters in the model than required to model the data, will lead to poor prediction of the test data set. One of the most important features that a fitting scheme should possess is the predictability on a completely new data set. One might expect good predictions on a data set which is similar in nature to the training data set. For example, in our case, we expect a good predictability for the binary compounds since we use only binary compounds in the training data set. The fitting procedure provides corrections for the reference energies of the elements which are independent of the chemical environments of the atoms. Therefore, we can expect that if the environments change considerably, which can for example be the case for ternary or quaternary compounds, the improvement will be less pronounced.

Hence, in the test we not only include the binary compounds but the ternary compounds as well. We compose a set of 24 binary and ternary compounds where the experimental heats of formation are available and which are not present in the training data. We summarize the results in Table IV. As for the training set the MAE and σ in general show a significant decrease with the fitted reference energies indicating that we do not overfit. However, the improvement is somewhat less than for the training set which is also what could be expected. Also for the test set we see that the three functionals PBE, RPBE, and PBE+U reach the same level of accuracy after fitting although PBE+U is considerably better before fitting. The performance of the TPSS functional does not seem to be any better than any of the GGA functionals. In fact the rms error for TPSS is only slightly reduced after fitting, while the MAE is reduced more. This behavior can be traced to a single system (Cs_2S), which is clearly poorly corrected by the fitting scheme. We have not been able to identify why this is the case. It can be noted that Cs was not included in the database considered by Stevanović *et al.* [4].

The most interesting feature is that the mBEEF functional already before fitting is of the same quality as the other functionals after fitting. Furthermore, the improvement of the mBEEF results using the fitting is only moderate. This means that moving to mBEEF the fitting procedure can be completely avoided at only a moderate cost in computational time (less than a factor of 2) compared to the GGAs.

In compounds such as SrSe and Mn_2SiO_4 the predictions with mBEEF remain the same after the fitting procedure; however, the estimated error is significantly reduced leading to large real error relative to the predicted uncertainty. It should be noted that it is an inherent limitation in the ensemble error estimation that fluctuations in the predictions can only result from fluctuations within the defined model space (i.e., meta-GGA in this case). If errors appear which cannot be described by such fluctuations an underestimation of the error may result.

TABLE IV. Heats of formation of the solid compounds calculated with the different functionals with and without employing the fitting procedure. The set below was not used in the training set for fitting the reference phase energies. All the energies are in eV/atom.

Compound	ΔH_{Expt}	ΔH_{PBE}	ΔH_{RPBE}	$\Delta H_{\text{PBE+U}}$	ΔH_{TPSS}	ΔH_{mBEEF}	$\Delta H_{\text{PBE}}^{\text{FERE}}$	$\Delta H_{\text{RPBE}}^{\text{FERE}}$	$\Delta H_{\text{PBE+U}}^{\text{FERE}}$	$\Delta H_{\text{TPSS}}^{\text{FERE}}$	$\Delta H_{\text{mBEEF}}^{\text{FERE}}$
AgNO ₃	-0.26	-0.40	-0.31	-0.53	-0.47	-0.60 ± 0.22	-0.58	-0.67	-0.68	-0.45	-0.63 ± 0.16
AlPO ₄	-2.99	-2.71	-2.58	-2.71	-2.86	-2.97 ± 0.19	-2.95	-2.97	-2.94	-3.02	-3.03 ± 0.07
BeSO ₄	-2.16	-1.99	-1.83	-1.99	-2.09	-2.19 ± 0.16	-2.22	-2.23	-2.21	-2.19	-2.25 ± 0.11
BiOCl	-1.27	-1.26	-1.11	-1.26	-1.62	-1.26 ± 0.16	-1.25	-1.20	-1.23	-1.32	-1.23 ± 0.09
CdSO ₄	-1.61	-1.42	-1.27	-1.42	-1.53	-1.59 ± 0.17	-1.61	-1.62	-1.60	-1.60	-1.63 ± 0.12
CuCl ₂	-0.76	-0.51	-0.32	-0.70	-0.80	-0.74 ± 0.21	-0.75	-0.60	-0.84	-0.79	-0.81 ± 0.07
TiBr ₃	-1.42	-1.24	-1.23	-1.52	-1.71	-1.37 ± 0.08	-1.38	-1.39	-1.61	-1.38	-1.43 ± 0.05
NaClO ₄	-0.66	-0.54	-0.41	-0.54	-0.67	-0.63 ± 0.15	-0.76	-0.77	-0.73	-0.68	-0.65 ± 0.16
CaSO ₄	-2.48	-2.24	-2.06	-2.24	-2.37	-2.40 ± 0.17	-2.41	-2.41	-2.41	-2.46	-2.43 ± 0.12
Cs ₂ S	-1.24	-1.01	-0.92	-1.01	-1.47	-1.16 ± 0.18	-1.27	-1.24	-1.33	-1.97	-1.23 ± 0.06
CuWO ₄	-1.91	-1.59	-1.41	-1.76	-1.72	-1.68 ± 0.21	-1.62	-1.60	-1.75	-1.65	-1.71 ± 0.07
PbF ₄	-1.95	-2.13	-2.05	-2.13	-2.26	-2.32 ± 0.23	-2.19	-2.19	-2.11	-2.24	-2.13 ± 0.08
MgSO ₄	-2.22	-1.97	-1.79	-1.97	-2.09	-2.16 ± 0.16	-2.22	-2.21	-2.21	-2.20	-2.24 ± 0.10
SrSe	-2.00	-2.04	-1.98	-2.04	-2.76	-2.29 ± 0.16	-2.25	-2.26	-2.29	-2.66	-2.29 ± 0.05
NiSO ₄	-1.51	-1.11	-0.96	-1.35	-1.23	-1.42 ± 0.23	-1.35	-1.36	-1.54	-1.33	-1.50 ± 0.11
FeWO ₄	-1.99	-1.73	-1.58	-2.01	-1.87	-1.84 ± 0.21	-1.81	-1.81	-1.94	-1.86	-1.89 ± 0.06
GeP	-0.11	+0.04	+0.09	+0.04	-0.19	+0.14 ± 0.08	-0.01	+0.03	-0.05	-0.28	-0.02 ± 0.07
VOCl	-2.10	-1.79	-1.68	-2.45	-2.07	-2.11 ± 0.24	-1.97	-1.98	-2.41	-2.05	-2.12 ± 0.07
LiBO ₂	-2.67	-2.42	-2.30	-2.42	-2.57	-2.58 ± 0.17	-2.61	-2.61	-2.58	-2.64	-2.61 ± 0.05
NaBrO ₃	-0.69	-0.52	-0.41	-0.52	-0.71	-0.60 ± 0.13	-0.74	-0.76	-0.72	-0.69	-0.66 ± 0.11
CoSO ₄	-1.53	-1.09	-0.95	-1.43	-1.24	-1.40 ± 0.23	-1.30	-1.34	-1.56	-1.31	-1.43 ± 0.11
PbSeO ₄	-1.05	-0.94	-0.81	-0.94	-1.13	-1.04 ± 0.16	-1.07	-1.09	-1.06	-1.07	-1.08 ± 0.09
Mn ₂ SiO ₄	-2.56	-1.83	-1.77	-2.58	-2.01	-2.29 ± 0.23	-2.17	-2.19	-2.38	-2.10	-2.25 ± 0.08
ZnSO ₄	-1.70	-1.37	-1.20	-1.37	-1.47	-1.53 ± 0.16	-1.61	-1.61	-1.61	-1.60	-1.62 ± 0.11
MAE		0.24	0.35	0.16	0.20	0.12	0.12	0.13	0.11	0.15	0.09
σ		0.28	0.39	0.19	0.26	0.16	0.16	0.17	0.15	0.25	0.14

IV. CONCLUSION

The need for accurate predictions of material stabilities has led to the development of schemes combining DFT total energy calculations with experimental information. We have analyzed one such scheme for calculation of heats of formation which fit the reference energies for elemental systems. The scheme was developed with the PBE+U functional, but we show that comparable predictive power is obtained using other GGAs such as PBE or RPBE or the meta-GGA TPSS. We have furthermore seen that the mBEEF functional, which is a meta-GGA and which has been extensively optimized to a variety of experimental data, leads to much improved estimation of heats of formation even without applying the fitting procedure. The mBEEF functional furthermore includes realistic ensemble estimates of the calculated formation energies. Applying the fitting scheme to mBEEF leads to a further reduction of the error and narrows the ensemble error estimation accordingly.

The FERE scheme clearly has its limitations. The correction of only the binding energies of the reference systems makes most sense if the character of the bonding differs significantly between the material at hand and the reference systems. This is for example the case for a metal oxide, in which the bonding may be quite different from the one in an oxygen molecule and in the pure metal. However, oxygen can enter in many different ways in different materials and only improving on the molecular energy cannot be a solution to improved heats of formation in the long run. Moving to more accurate functionals is therefore a must, and the current work shows that applying a meta-GGA such as mBEEF already provides a significant improvement in the prediction of solid heats of formation.

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- [1] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [2] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [3] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [4] V. Stevanovic, S. Lany, X. Zhang, and A. Zunger, *Phys. Rev. B* **85**, 115104 (2012).

- [5] I. E. Castelli, T. Olsen, S. Datta, D. D. Landis, S. Dahl, K. S. Thygesen, and K. W. Jacobsen, *Energy Environ. Sci.* **5**, 5814 (2012).
- [6] A. Jain, G. Hautier, C. J. Moore, S. P. Ong, C. C. Fischer, T. Mueller, K. A. Persson, and G. Ceder, *Comput. Mater. Sci.* **50**, 2295 (2011).

- [7] X. Zhang, V. Stevanović, M. d’Avezac, S. Lany, and A. Zunger, *Phys. Rev. B* **86**, 014109 (2012).
- [8] S. Lany, *Phys. Rev. B* **78**, 245207 (2008).
- [9] B. Hammer, L. B. Hansen, and J. K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).
- [10] J. M. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).
- [11] R. Peverati and D. G. Truhlar, *Philos. Trans. R. Soc. A* **372**, 2011 (2014).
- [12] L. A. Constantin, E. Fabiano, and F. Della Sala, *Chem. Theory Comput.* **9**, 2256 (2013).
- [13] J. Sun, J. P. Perdew, and A. Ruzsinszky, *Proc. Natl. Acad. Sci. USA* **112**, 685 (2015).
- [14] F. Della Sala, E. Fabiano, and L. A. Constantin, *Phys. Rev. B* **91**, 035126 (2015).
- [15] J. Wellendorff, K. T. Lundgaard, K. W. Jacobsen, and T. Bligaard, *J. Chem. Phys.* **140**, 144107 (2014).
- [16] J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsarlis, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen, and K. W. Jacobsen, *J. Phys.: Condens. Matter* **22**, 253202 (2010).
- [17] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [18] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- [19] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [20] J. Wellendorff, K. T. Lundgaard, A. Møgelhøj, V. Petzold, D. D. Landis, J. K. Nørskov, T. Bligaard, and K. W. Jacobsen, *Phys. Rev. B* **85**, 235149 (2012).
- [21] Standard thermodynamic properties of chemical substances, http://www.update.uu.se/~jolkkonen/pdf/CRC_TD.pdf.
- [22] M. Fuchs, J. L. F. Da Silva, C. Stampfl, J. Neugebauer, and M. Scheffler, *Phys. Rev. B* **65**, 245212 (2002).
- [23] G. Hautier, S. P. Ong, A. Jain, C. J. Moore, and G. Ceder, *Phys. Rev. B* **85**, 155208 (2012).
- [24] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in C* (Cambridge University Press, Cambridge, 1988).
- [25] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.91.235201> for the reference energies calculated with different functionals with and without the fitting.
- [26] S. L. Frederiksen, K. W. Jacobsen, K. S. Brown, and J. P. Sethna, *Phys. Rev. Lett.* **93**, 165501 (2004).