

Correcting density functional theory for accurate predictions of compound enthalpies of formation: Fitted elemental-phase reference energies

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Despite the great success that theoretical approaches based on density functional theory have in describing properties of solid compounds, accurate predictions of the enthalpies of formation (ΔH_f) of insulating and semiconducting solids still remain a challenge. This is mainly due to incomplete error cancellation when computing the total energy differences between the compound total energy and the total energies of its elemental constituents. In this paper we present an approach based on GGA + U calculations, including the spin-orbit coupling, which involves fitted elemental-phase reference energies (FERE) and which significantly improves the error cancellation resulting in accurate values for the compound enthalpies of formation. We use an extensive set of 252 binary compounds with measured ΔH_f values (pnictides, chalcogenides, and halides) to obtain FERE energies and show that after the fitting, the 252 enthalpies of formation are reproduced with the mean absolute error MAE = 0.054 eV/atom instead of MAE \approx 0.250 eV/

used for accurate predictions of the ΔH_f values of binary,



III. COMPUTATIONAL APPROACH

The standard scheme, frequently used in DFT calculations has been employed also in this work. The PBE exchange-correlation functional

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TABLE II. (Continued.)

Compound	ΔH_f^{FERE}	ΔH_f^{exp}	Compound	ΔH_f^{FERE}	ΔH_f^{exp}	Compound	ΔH_f^{FERE}	ΔH_f^{exp}	Compound	ΔH_f^{FERE}	ΔH_f^{exp}
PdS ₂	-0.32	-0.28	Rh ₂ S ₃	-0.48	-0.54	Sr ₂ Bi	-1.00	-1.08	YCl ₃	-2.65	-2.59
Pd ₄ S	-0.07	-0.14	ScAs	-1.39	-1.39	Sr ₂ Sb	-1.15	-1.11	YF ₃	-4.45	-4.45
PtO	-0.37	-0.37	ScCl ₃	-2.44	-2.40	TaN	-1.25	-1.30	Y ₂ O ₃	-3.92	-3.95
PtO ₂	-0.57	-0.57	ScF ₃	-4.26	-4.22	TaS ₂	-1.29	-1.22	ZnCl ₂	-1.43	-1.43
PtS	-0.41	-0.42	Sc ₂ O ₃	-3.88	-3.94	TiAs	-0.70	-0.78	ZnF ₂	-2.57	-2.64
PtS ₂	-0.34	-0.38	SiO ₂	-3.06	-3.13	TiCl ₄	-1.78	-1.70	ZnO	-1.78	-1.81
Pt ₃ O ₄	-0.45	-0.40	SiS ₂	-0.91	-0.88	TiN	-1.58	-1.58	ZnP ₂	-0.23	-0.21
RbCl	-2.20	-2.26	SiSe ₂	-0.55	-0.61	TiO ₂	-3.24	-3.26	ZnS	-1.09	-1.07
RbF	-2.90	-2.89	Si ₃ N ₄	-1.18	-1.10	TiS	-1.46	-1.41	ZnSb	-0.15	-0.08
RbSb	-0.49	-0.52	SnO	-1.51	-1.48	TiS ₂	-1.44	-1.41	ZnSe	-0.89	-0.85
RbSb ₂	-0.25	-0.35	SnO₂	-1.86	-1.97	Ti ₂ O ₃	-3.14	-3.15	ZnTe	-0.62	-0.61
Rb ₂ O	-1.17	-1.17	SnS	-0.61	-0.57	VF₄	-3.03	-2.91	Zn ₃ As ₂	-0.21	-0.28
Rb ₂ O ₂	-1.24	-1.22	SnS ₂	-0.53	-0.53	VN	-0.93	-1.13	Zn ₃ N ₂	-0.07	-0.05
Rb ₂ S	-1.24	-1.25	SnSe	-0.52	-0.47	VO	-2.24	-2.24	Zn ₃ P ₂	-0.35	-0.33
Rb ₃ Sb	-0.54	-0.45	SnSe ₂	-0.37	-0.43	VO ₂	-2.55	-2.47	ZrN	-1.91	-1.89
RhCl ₃	-0.83	-0.78	SrO	-3.11	-3.07	V₂O₃	-2.67	-2.53	ZrO ₂	-3.81	-3.80
RhO ₂	-0.84	-0.85	SrO ₂	-2.19	-2.19	V ₂ O ₅	-2.28	-2.29	ZrS ₂	-1.93	-1.96
Rh ₂ O ₃	-0.87	-0.84	SrS	-2.47	-2.45	YAs	-1.67	-1.68	Mn ₃ O ₄	-2.08	-2.05

per formula unit amounts to ~ 15 kJ/mol. Table II lists the FERE enthalpies of formation for our set of binary compounds together with the experimental values. There is a relatively small fraction of binary compounds belonging to the fitting set, 20 out of 252 (shown in bold), for which the remaining FERE error exceeds two times the MAE value. These errors

semiconducting and insulating compounds, not only to oxides or other chalcogenides separately, but to oxides, other chalcogenides, pnictides, and halides at the same time. Of course, the fixed U values (3 and 5 eV), in conjunction with fitted $\{\epsilon_{\text{FERE}}\}$, are good for thermochemistry, and are not meant for band-gap predictions.

The fact that this “thermochemical” U to a good approximation “does not recognize” differences in the types of chemical compounds and in chemical identities of elements deserves a closer look into the foundations of GGA and GGA + U , which is beyond the scope of this paper. However, it would be very interesting to analyze our findings in terms of results of more accurate theoretical approaches such as quantum Monte Carlo for example.

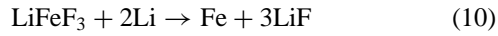
B. Finite temperature effects

Equations (3)–(5) are formulated in the $T \rightarrow 0$ limit. However, for the experimental enthalpies of formation [see Eq. (3)], we use values, compiled in Refs. 10,11, that correspond to *standard* conditions, meaning $T = 298$ K and $p = 1$ atm. Therefore ΔH

TABLE III. Results of our analysis of the influence of spin-orbit coupling on the compound enthalpies of formation. Values (in eV) of the two terms appearing on the right-hand side of Eq. (7), the explicitly calculated SO contribution to the compound total energy ΔE

TABLE IV. Comparison (validation) of ΔH_f values (in eV/atom) from experiment (see Refs. 10 and 11) and computed using the FERE method for 55 ternary compounds. Conversion factor to kJ/mol is $\sim 96.5 \times N$, where N stands for the number of atoms per compound formula unit. For CaSiO_3

which corresponds to fixed $U = 3$ eV for all transition metals appearing in Eq. (9). The same accuracy can be achieved by using the element dependent U values³¹ together with pure GGA value for (Li) as shown in Ref. 4. On the other hand, the following Li intercalation reaction requires a special treatment as noted in Ref. 7:



for which measured electrochemical voltage, half of the enthalpy of the reaction, amounts to 2.5 V. The difficulty here is that there are two pure elemental phases appearing in the reaction Li and Fe. Namely, the pure GGA voltage is calculated to be 2.91 V²⁹ whereas the GGA + U predicts 3.46 V,

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