

Halocarbon Thermochemistry: A Challenge for Density Functional Theory

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 (Received 27 November 2025; revised 5 February 2026; accepted 2 March 2026; published 9 April 2026)

Halocarbons have a vast array of industrial applications and non-negligible environmental impact. Their structures, properties, and thermochemistry are often modeled with the use of density functional theory (DFT) calculations. Here we analyze the DFT-calculated gas-phase formation enthalpies of 56 halocarbons containing various amounts of F, Cl, Br, and I using a group-additivity approach and seven exchange-correlation functionals (Perdew-Burke-Ernzerhof, Perdew-Wang 91, revised Perdew-Burke-Ernzerhof, Bayesian error estimation functional with van der Waals corrections, Tao-Perdew-Staroverov-Scuseria, Becke 3-parameter Lee-Yang-Parr, and Heyd-Scuseria-Ernzerhof 2006). Carbon—halogen bonds are found to introduce significant errors in the formation enthalpies, which are proportional to the electronegativity of the elements. We devised two correction methods based on the number and type of functional groups in each molecule in the reactants and products of the formation reactions. Both methods lower the mean absolute errors from approximately 0.35 eV to approximately 0.05 eV. Finally, the corrections were tested in an independent set of more than 150 reactions, and high accuracy was found without relying on error cancellation.

DOI: [10.1103/xg4n-6mfg](https://doi.org/10.1103/xg4n-6mfg)

I. INTRODUCTION

Halocarbons are chemical compounds with at least one carbon—halogen (C—X) bond. They have attracted considerable attention due to their diverse applications and concerning effects on the environment and human health [1,2]. They are important intermediates in the synthesis of pharmaceuticals [3], refrigerants [4], solvents [5], high-performance polymers [6], and agrochemicals [7]. A significant number of these substances are powerful greenhouse gases and have been directly linked to the depletion of the ozone layer and climate change [8]. Their high stability and distinct reactivity render them crucial species in

diverse domains, ranging from catalytic processes [9–11] to halide-assisted electrocatalysis [12–14].

The remarkable thermodynamic stability of carbon—halogen bonds follows the electronegativity trend C—F > C—Cl > C—Br > C—I and poses significant challenges for degradation [15]. For instance, chlorofluorocarbons and hydrofluorocarbons, initially well regarded for their advantageous thermodynamic and physicochemical properties in refrigeration systems, were later scrutinized in view of their long atmospheric lifetimes and high global warming potential (GWP) [16]. Consequently, catalysis has become central not only to their synthesis but also to their conversion and removal, with supported metal catalysts enabling hydro-dehalogenation and selective decomposition of persistent halocarbons [17]. There is a pressing need for efficient catalytic methods capable of removing halocarbons from the atmosphere, water, and soil [18]. For instance, a shift toward the synthesis of next-generation refrigerants such as hydrofluoroolefins has been driven by the need for low-GWP alternatives that still meet current stringent thermodynamic and operational

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criteria [19]. Experimental analyses of halogen effects on catalytic reactions are often obscured by the brief lifetimes of adsorbed intermediates and the intertwined thermodynamic, kinetic, and transport complexities [20]. Recent reports highlight the importance of halogen anion effects on some electrocatalytic reactions, but their generality is unknown and their operating principle remains a matter of debate [21,22]. In addition, ethylene chlorohydrin ($\text{OHCH}_2\text{CH}_2\text{Cl}$) is an intermediate in the catalytic and electrocatalytic production of oxirane [23]. Consequently, reliable modeling of carbon–halogen bonds and in particular of halocarbons is crucial for both environmental chemistry and energy-related (electro)catalysis.

Furthermore, the modeling of chemical and catalytic reactions through computational methods has experienced significant growth in recent decades, especially with the advent of density functional theory (DFT) codes [24–26]. DFT is one of the cornerstones of computational chemistry because of its balance between accuracy and cost, and is widely used to predict bulk and surface thermochemical properties [27–31]. However, DFT exchange–correlation functionals often suffer from systematic errors when applied to the gas-phase energetics of halogens [32] and halocarbon species [33,34]. Visible discrepancies between experimental results and calculations can significantly affect downstream predictions of redox potentials, reaction free energies, phase diagrams, and adsorption energies in computational chemistry [32]. The propagation of these errors [35] through thermodynamic and kinetic models undermines their predictive capabilities [36,37].

While error cancellation may lower total reaction errors, it is unreliable for two reasons: First, error cancellation is not consistently observed for all types of chemical reactions [35] and typically breaks down when the chemical species differ significantly [29,38]. Second, error cancellation guarantees that an overall reaction energy is well described but the separate species involved are still not well described. This is problematic in catalysis, where thermochemical errors may exist in the reactants and products but also in the reaction intermediates. In other words, even if an overall reaction is well described by virtue of error cancellation, the adsorption energies of reactants and the desorption energies of the products may still be flawed [39–41].

Efforts to correct systematic DFT errors without relying on error cancellation have yielded promising strategies [42–45]. Functional group–based correction schemes have been successfully used for carbon-based and nitrogen-containing molecules [38,42,43,46]. For compounds containing only halogen atoms, a recent approach used a linear correction model based on the electronegativity of the species [32]. This model enables swift corrections that reduce mean absolute errors (MAEs) to the scale of chemical accuracy (1 kcal/mol) across multiple functionals.

These corrections mitigate the negative effects of DFT errors in the prediction of reaction energies, equilibrium potentials, and (surface) Pourbaix diagrams without relying on error cancellation [32,47].

Here we extend the scope of DFT gas-phase corrections by focusing on a broad set of halocarbons, combining established thermochemical benchmarks with a correction protocol. We systematically evaluate gas-phase errors across representative generalized gradient approximation (GGA), meta-GGA, and hybrid functionals, and illustrate the effectiveness of intuitive electronegativity-based corrections in halocarbon thermochemistry. Besides, we rationalize the trends in simple terms. Our findings contribute to improving the reliability of DFT in environmental and catalysis modeling where halocarbon species are involved.

II. METHODS

A. DFT calculations

Initially, we selected a benchmark set of 55 halocarbon compounds. These contain one to five halogen atoms and one to eight carbon atoms in the structure, as shown in Table S1 in Supplemental Material [48] (which includes citations of Refs. [49–54]). Experimental formation energies were taken from Refs. [55–57].

DFT calculations were performed with the Vienna Ab initio Simulation Package code [58] with the Perdew–Burke–Ernzerhof (PBE) [59], Perdew–Wang 1991 (PW91) [60], Revised Perdew–Burke–Ernzerhof (RPBE) [61], Bayesian Error Estimation Functional with van der Waals correlation (BEEF–vdW) [62], Tao–Perdew–Staroverov–Scuseria (TPSS) [63], Becke 3-parameter, Lee–Yang–Parr (B3LYP) [64], and Heyd–Scuseria–Ernzerhof 2006 [65] functionals. Ion–electron interactions were described by means of the projector augmented-wave method [66]. A plane-wave cutoff of 450 eV was used for structure optimizations, which was selected on the basis of the convergence test in Fig. S8 in Supplemental Material [48]. It was considered that the electronic loops converged when the energies of consecutive steps differed by less than 10^{-6} eV. The geometry optimizations using the conjugate gradient algorithm stopped when the maximum force between atoms was below 0.01 eV/Å. Only the Γ point of the Brillouin zone was sampled. Periodic boundary conditions with boxes of $15 \times 15 \times 15 \text{ Å}^3$ were used to represent the gas-phase molecules, with use of Gaussian smearing and $k_B T = 0.001$ eV. Zero-point energy ($E_{i,\text{ZPE}}$) corrections were assessed by means of DFT-based vibrational-frequency analyses under the harmonic oscillator approximation. The ZPEs of gas-phase species do not change importantly across GGA, meta-GGA, and hybrid functionals [47], and the PBE functional has been shown to provide remarkably accurate ZPEs [35]. Thus, we safely assume that the largest part of the errors is not due to the ZPEs. Besides, the experimental ZPEs are not available for

all species in this study; thus, for consistency all of them were assessed with the use of DFT.

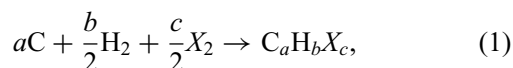
Graphite was simulated as a single graphene layer in view of the small, van der Waals-driven interlayer cohesive energy between graphene layers [38,43,67–72] (0.031–0.064 eV/atom). The calculations for graphene were also performed with the aforementioned plane-wave cutoff and energy and force convergence criteria. The cell contained two C atoms and 15 Å of vacuum between periodically repeated images in the direction perpendicular to the layer, and the k -point sampling was $4 \times 4 \times 1$. The total energy difference with respect to a grid of $8 \times 8 \times 1$ was found in all cases to be below 0.02 eV.

B. Errors in the formation energies

To assess the enthalpy of a given reaction, one needs to choose a reference state and calculate the enthalpies of all reactants and products with respect to it. Formation reactions are a common reference for calculating enthalpy changes using Hess's law. A formation reaction is one in which the target compound is formed from its elemental constituents in their standard state, typically reported at 25 °C (298.15 K) and 1 bar. The enthalpy change associated with the formation of 1 mol of the substance in that reaction is the standard enthalpy of formation of the substance (hereafter $\Delta_f H$) [73].

Since the standard state of Br₂ and I₂ corresponds to the liquid phase, the formation energies of those species were corrected by subtraction of the experimental enthalpies of vaporization (0.32 eV for Br₂ and 0.65 eV for I₂) from the calculated DFT energies.

Since we are interested in estimating DFT errors for reactions involving halocarbons, we used the formation reactions for alkyl fluorides, chlorides, bromides, and iodides. The formation reaction for a generic halocarbon C_aH_bX_c is as follows:



where X is a halogen atom (F, Cl, Br, or I), and a , b , and c are stoichiometric coefficients. To calculate the enthalpy change of a reaction with DFT (ΔH_{DFT}), one first needs to calculate the enthalpy of each species (H^0) participating in the reaction. The enthalpy of the reaction in Eq. (1) calculated on the basis of DFT energies is as follows:

$$\Delta_f H_{C_aH_bX_c}^0 = H_{C_aH_bX_c}^0 - aH_C^0 - \frac{b}{2}H_{H_2}^0 - \frac{c}{2}H_{X_2}^0. \quad (2)$$

The enthalpy of a substance i can be approximated from its DFT energy ($E_{i,\text{DFT}}$) and ZPE ($E_{i,\text{ZPE}}$), as shown in Eq. (3):

$$H_{i,\text{DFT}}^0 = E_{i,\text{DFT}} + E_{i,\text{ZPE}}. \quad (3)$$

The thermal contributions of the enthalpy from 0 to 298.15 K were not included in Eq. (3) because our

calibration targets the electronic and zero-point energy component of the enthalpy and uses error-balanced reactions, where thermal increments largely cancel out between reactants and products [32,44,74]. Adding rigid-rotor-harmonic-oscillator thermal integrals may introduce model-dependent noise (low-frequency mode artifacts) without significantly altering the systematic DFT bias we correct.

Furthermore, the DFT error in species i is defined with respect to experiments as $\varepsilon_i = H_{i,\text{DFT}}^0 - H_{i,\text{expt}}^0 = \Delta H_{i,\text{DFT}}^0 - \Delta H_{i,\text{expt}}^0$, provided that the reference states for the products and reactants in the formation of species i are identical. Hence, the total error ε_T of the generic halocarbons is expressed as follows:

$$\varepsilon_{T,C_aH_bX_c} = \Delta_f H_{C_aH_bX_c,\text{DFT}}^0 - \Delta_f H_{C_aH_bX_c,\text{expt}}^0. \quad (4)$$

The total error in species i can be decomposed with use of a group-additivity scheme [38,43]. In this way, the total error ε_i is the sum of the separate contributions of the functional groups, bonds, or atoms present in the structure [26,32,35, 38,43]. If we have N functional groups and each of them contributes an error ε_j to the total error, we have

$$\varepsilon_i = \sum_{j=1}^N n_j \varepsilon_j, \quad (5)$$

where n_j is the number of functional groups of type j . In this order of ideas, halocarbons contain errors from their CH_y groups and their CX bonds: $\varepsilon_{C_aH_bX_c} = a\varepsilon_{\text{CH}_y} + c\varepsilon_{\text{CX}}$, where ε_{CX} is the error associated with the carbon–halogen bonds and $\varepsilon_{\text{CH}_y}$ is the error of each hydrocarbon unit ($y = 0, 1, 2, 3, 4$). Hence, the total error in $\Delta_f H_{C_aH_bX_c}^0$ can be calculated as

$$\varepsilon_{T,C_aH_bX_c} = (a\varepsilon_{\text{CH}_y} + c\varepsilon_{\text{CX}}) - \left(a\varepsilon_C + \frac{b}{2}\varepsilon_{H_2} + \frac{c}{2}\varepsilon_{X_2} \right), \quad (6)$$

where ε_C , ε_{H_2} , and ε_{X_2} are the errors in graphite, molecular hydrogen, and the diatomic halogen molecules, respectively.

Molecular hydrogen is often well described by DFT [43,75], as it is a simple molecule without unpaired electrons and a single σ bond, and functionals are often built such that they describe it fairly well [75]. In turn, graphite is a solid composed of graphene layers with delocalized electrons, which are generally well described by common DFT functionals. Hence, $\varepsilon_C \approx 0$ and $\varepsilon_{H_2} \approx 0$. Because C does not appear in the verification set, whether or not its error is nil is a good assumption, it does not influence the error difference between two given compounds.

$\varepsilon_{\text{CH}_y}$ is devised to differentiate among primary, secondary, tertiary, and quaternary carbon atoms, which

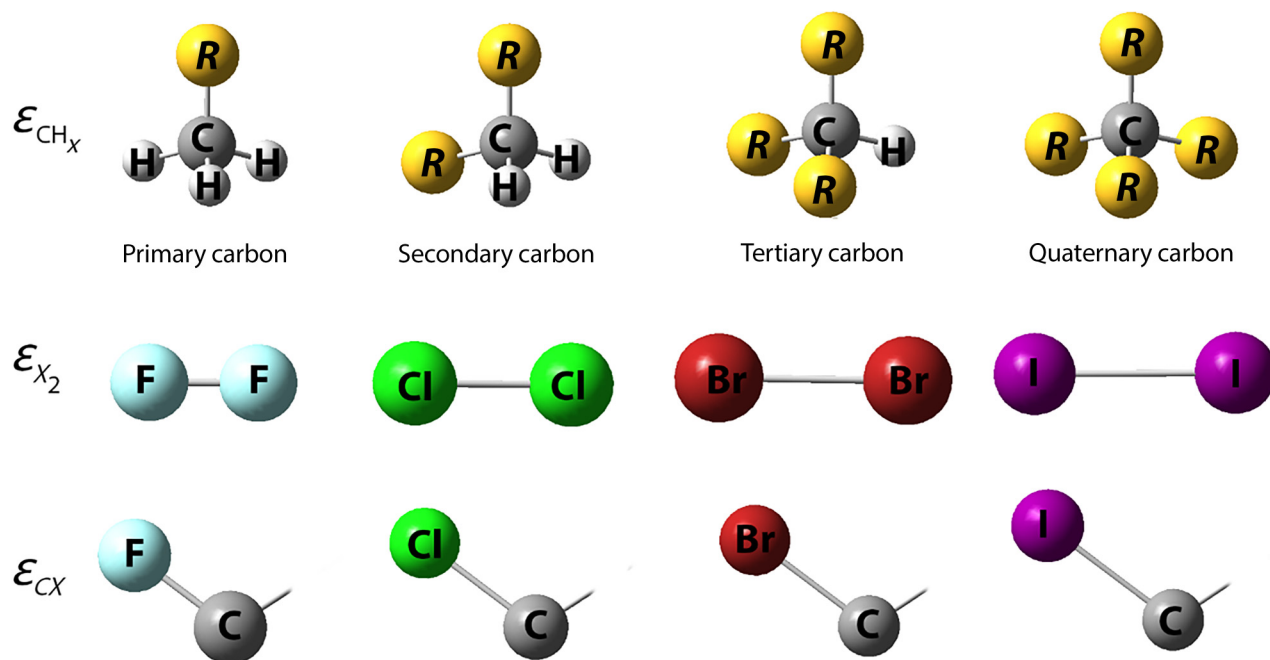


FIG. 1. Functional groups considered in this work and their respective errors. CH_x groups represent different carbon environments: CH_3 (primary carbon atoms), CH_2 (secondary C atoms), CH (tertiary C atoms), and C (quaternary C atoms). The diatomic molecules X_2 are the reference states of halogens and have a DFT error denoted as ε_{X_2} . The CX group represents carbon–halogen bonds and its DFT error is ε_{CX} . Color code: C, gray; H, white; F, teal; Cl, green; Br, red; I, purple. A full list of the compounds is given in Table S1 in Supplemental Material [48].

are known to have dissimilar errors [38]. We use here a fragment-based correction using three groups—(1) CH_3/CH_2 , (2) CH , and (3) C [38]—transforming Eq. (6) into Eq. (7):

$$\varepsilon_{T,\text{C}_a\text{H}_b\text{X}_c} = a_1\varepsilon_{\text{CH}_3/\text{CH}_2} + a_2\varepsilon_{\text{CH}} + a_3\varepsilon_{\text{C}} + c\varepsilon_{\text{CX}} - \frac{c}{2}\varepsilon_{\text{X}_2}. \quad (7)$$

In Eq. (7), a_1 is the number of primary and secondary C atoms, a_2 the number of tertiary C atoms, and a_3 the number of quaternary C atoms in the molecule, such that $a = a_1 + a_2 + a_3$ is the total number of C atoms in the halocarbon. A graphical representation of the groups in Eq. (7) is provided in Fig. 1. Let us consider the isomers 1,1,2-trifluoroethane and 1,1,1-trifluoroethane to illustrate how this assignment is made: 1,1,2-Trifluoroethane has one secondary carbon ($a_1 = 1$), one tertiary carbon ($a_2 = 1$), no quaternary carbons ($a_3 = 0$), and three C—F bonds ($c = 3$). 1,1,1-Trifluoroethane has one primary carbon ($a_1 = 1$), no tertiary carbon ($a_2 = 0$), one quaternary carbon ($a_3 = 1$), and three C—F bonds ($c = 3$).

After all error sources in the reactants and products of Eq. (1) have been accounted for, some residual errors with respect to experiments may persist. In practice, such residuals arise from the fact that the proposed corrections often correspond to mean values obtained from the average of

several compounds. These average corrections remove a large part of the total error but not all of it [$\Delta H_{i,\text{corr}}^0 \approx \Delta H_{i,\text{DFT}}^0 - \varepsilon_{T,i,\text{avg}}$, where $\varepsilon_{T,i,\text{avg}}$ is an average error], as seen in reactions involving nitrogen oxides or CO_2 reduction processes [38,43]. Hence, our corrections provide a simple and general way to minimize the residual errors of a dataset. If the final errors must be zero, then average corrections ought to be avoided, and individual corrections for each molecule should be applied instead (Table S2 in Supplemental Material [48]).

Herein, we propose two methods to determine the average corrections. Method I uses previously determined values for the CH_x errors [38] and calculates the CX errors solely from halomethane compounds (CH_yX_z , with y and z in the range from 1 to 4 and $y + z = 4$). Method II uses a simultaneous minimization of the MAE and the maximum absolute error (MAX) of our training dataset of 55 molecules to determine the CH_x and CX errors for each functional.

Importantly, the simplicity of methods I and II, built from only a small number of physically interpretable corrections, ensures their seamless integration into computational workflows. In practical terms, once the composition and structure of a halocarbon are specified, it is straightforward to compute appropriate corrections by summing the contributions of the carbon and halogen constituents. This

approach is particularly useful when experimental data are unavailable or when several dissimilar data are available.

C. Error correction methods

In method I the CX errors are found by use of (1) the functional-specific X_2 errors reported by Zapata *et al.* [32] and (2) the CH_y errors from the study of Urrego-Ortiz *et al.* [38]; see Table S3 in Supplemental Material [48]. The parameters for the TPSS, B3LYP and HSE06 functionals were not assessed by Urrego-Ortiz *et al.*, and hence were determined here by minimization of the residual error. In this case, the residual error results from applying all the corrections except ε_{CX} in Eq. (7). The CX errors were calculated as the average of these residual DFT errors.

In method II, the CH_y and CX errors were taken from a simultaneous minimization of the MAE and the MAX for each functional, with use of the values obtained from method I as an ansatz. The optimum values were taken as the solution on the Pareto front that minimized the Euclidean distance ε_{OBJ} from the utopia point [46]:

$$\varepsilon_{\text{OBJ}} = \sqrt{(\varepsilon_{\text{MAE}} - \varepsilon_{\text{MAE,opt}})^2 + (\varepsilon_{\text{MAX}} - \varepsilon_{\text{MAX,opt}})^2}. \quad (8)$$

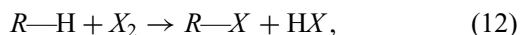
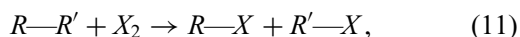
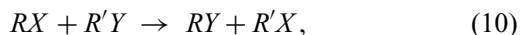
The utopia point ($\varepsilon_{\text{OBJ}} = 0$) is found when the MAE (ε_{MAE}) and the MAX (ε_{MAX}) are equivalent to MAE_{opt} ($\varepsilon_{\text{MAE,opt}}$) and MAX_{opt} ($\varepsilon_{\text{MAX,opt}}$), respectively. MAE_{opt} is the value of the mean absolute error for the minimization of residual errors with the MAE used as the objective function, and MAX_{opt} is the maximum absolute error of the optimization with only the MAX used as the objective function.

We note in passing that while higher levels of theory may calculate with greater accuracy certain properties of gas-phase species, advanced methods such as the random-phase approximation still have visible gas-phase and solid-state errors [76–79], and their computational cost for extended surfaces is so high that they are rarely used in heterogeneous (electro)catalysis, despite some interesting examples [79]. Instead, methods I and II provide simple semiempirical corrections to DFT-GGA functionals widely used in catalysis. We include some common meta-GGA and hybrid functionals to illustrate the fact that the errors are systematic. Our purpose is not to find the best functional for halogen thermochemistry but to show that all of them have sizable errors that can be swiftly corrected.

D. Validation set

A set of validation reactions that does not contain formation energies was created to validate the robustness of the proposed corrections and illustrate that they do not rely on incidental error cancellation. The validation set included 152 reactions, including halogen exchange [Eq. (9)], chain

redistribution [Eq. (10)], halogen addition [Eq. (11)], and halocarbon formation from hydrocarbons [Eq. (12)]:



where R and R' are different hydrocarbon or halocarbon chains, and X and Y are different halogen species. The reactions are shown in Table S4 in Supplemental Material [48]. These reaction classes help in making a thorough assessment of the corrections, as they feature differing levels of bonding information and, consequently, display differing extents of intrinsic error cancellation [80–83]. This diverse assortment of reactions allows a stringent assessment of the accuracy and transferability of the corrections [84].

III. RESULTS AND DISCUSSION

DFT calculations were performed with different functionals for the dataset of 55 halocarbons in Table S1 in Supplemental Material [48]. The experimental formation enthalpies $\Delta_f H_{\text{C}_a\text{H}_b\text{X}_c, \text{expt}}^0$ and those calculated from uncorrected DFT total energies are presented in Table S5 in Supplemental Material [48].

A. Error detection using method I

For method I, the error assessment was performed with only the data for the halomethanes of F, Cl, Br, and I (16 halocarbons in total). Initially, the total error $\varepsilon_{T, \text{C}_a\text{H}_b\text{X}_c}$ was calculated for each exchange-correlation functional. Subsequently, we used Eq. (7) to find ε_{CX} , taking into account the known values of $\varepsilon_{\text{CH}_3/\text{CH}_2}$, ε_{CH} , ε_{C} , and ε_{X_2} from the literature [32,38]. For each halogen type (F, Cl, Br, I), the DFT error was obtained as the average of the residual errors after corrections divided by the number of halogen atoms in the molecule, correlating the errors with the number of halogen substituents. Thus, the calculated ε_{CX} for method I represents the average of the four halomethanes, computed for each halogen and functional (Table S3 in Supplemental Material [48]). For instance, for the PBE functional, for CH_3F , CH_2F_2 , CHF_3 , and CF_4 , the CF errors are -0.09 , -0.10 , -0.09 , and -0.09 eV, respectively. Upon averaging of these four values, ε_{CF} is -0.09 eV.

The corrected formation enthalpies obtained with method I are reported in Table S6 in Supplemental Material [48]. The MAE for the PBE functional is 0.21 eV before the corrections and 0.06 eV after them, while the MAX is originally 0.69 eV and the corrections lower it to 0.18 eV. Moreover, the average of the MAEs for all functionals before application of method I was 0.35 eV and was

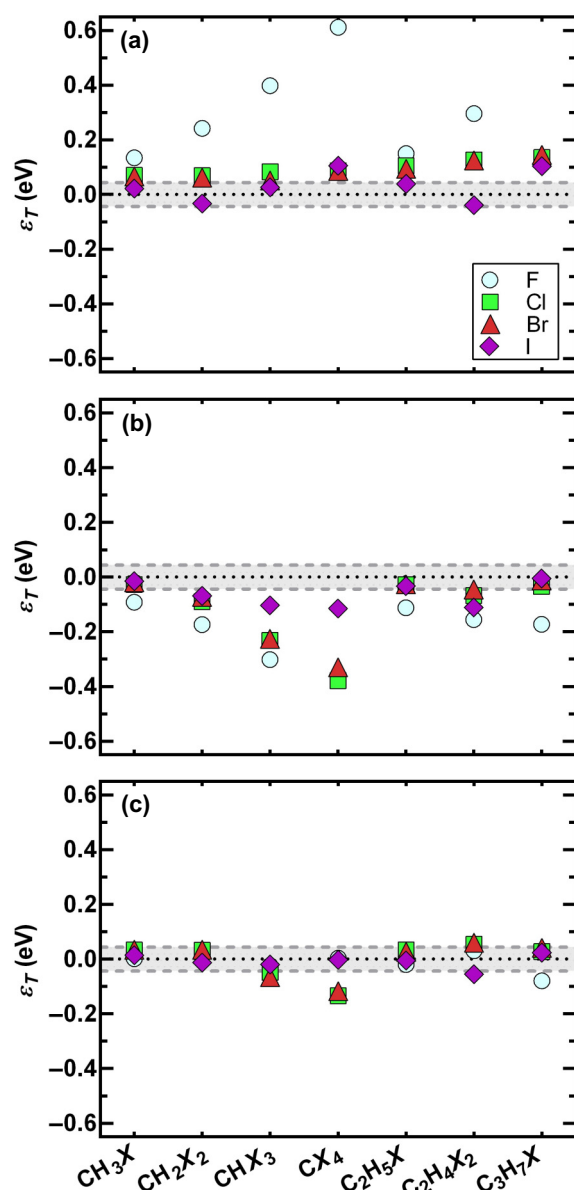


FIG. 2. Total errors for a series of halocarbons with one to three carbon atoms and different halogen substituents—F (circles), Cl (squares), Br (triangles), and I (diamonds)—calculated with the PBE functional. (a) Without any corrections, (b) upon application of the $\varepsilon_{\text{CH}_3/\text{CH}_2}$, ε_{CH} , ε_{C} , and ε_{X_2} corrections, and (c) after correction of all errors in Eq. (7) using method I. The dotted black line marks an errorless prediction, while the gray band corresponds to chemical accuracy (± 1 kcal/mol).

0.06 eV afterwards. The largest MAX was 1.57 eV before the corrections and was 0.23 eV after them, and the average of the MAXs was 1.00 eV before the corrections and was 0.19 eV afterwards. Hence, the beneficial effect of the corrections on halocarbon thermochemistry is statistically proven.

Figure 2 presents a comparison of the errors for the PBE functional with the use of cumulative corrections: First,

no corrections at all [Fig. 2(a)]. Then, X_2 and CH_y corrections [Fig. 2(b)]. Finally, X_2 , CH_y , and CX corrections [Fig. 2(c)] for 28 halocarbons that share the same backbone structure and differ only in the halogen substituent. The structural similarity of these series allows direct comparisons among the halogens. The uncorrected errors in Fig. 2(a) exhibit a clear increasing trend as a function of the size of the halogen ($\text{F} < \text{Cl} < \text{Br} < \text{I}$), a behavior that is effectively mitigated by the full correction scheme in Fig. 2(c).

The errors are consistently positive in Fig. 2(a), the only exceptions being for CH_2I_2 and $\text{C}_2\text{H}_4\text{I}_2$, which showed small negative errors. These positive errors indicate that the PBE functional typically overestimates the formation energies of haloalkanes. This behavior was observed for all the functionals studied except HSE06 (Figs. S1–S6 in Supplemental Material [48]). For that functional, the uncorrected residual errors were mostly negative, indicating systematic underestimation of the formation energies.

The uncorrected errors in Fig. 2(a) are generally larger for F-containing molecules and decrease with increasing halogen size. The MAEs in Fig. 2(a) are 0.28, 0.10, 0.09, and 0.05 eV for F-, Cl-, Br-, and I-containing halocarbons, respectively. This trend was also observed for the other GGA and meta-GGA functionals studied. However, for the scrutinized hybrid functionals this was not the case. For the B3LYP functional, the uncorrected MAEs of the halocarbons are 0.13 eV for F, and between 0.24 and 0.29 eV for Cl, Br, and I, while for the HSE06 functional, the uncorrected MAEs of all halogen-based compounds were 0.20–0.24 eV.

Figure 2(b) shows the errors after application of the carbon ($\varepsilon_{\text{CH}_3/\text{CH}_2}$, ε_{CH} , ε_{C}) and halogen (ε_{X_2}) corrections to the DFT formation energies. Halomethane errors become more negative with increasing number of X atoms, but except for F-containing molecules the trend does not seem to hold for larger halocarbons. Besides, we observe in Fig. 2(c), where the CX errors ε_{CX} are mitigated, that method I generally lowers the total errors, but some visible residual errors remain.

According to Table S2 in Supplemental Material [48], all the functionals except HSE06 generally display positive total errors, indicating that DFT functionals tend to underestimate the thermochemistry of halocarbons in a similar way. This is supported by the fact that ε_{CX} in Table S3 in Supplemental Material [48] is generally negative. Indeed, for the PBE functional we calculated that ε_{CF} , ε_{CCl} , ε_{CBr} , and ε_{CI} are -0.09 , -0.06 , -0.05 , and -0.03 eV, respectively. This decreasing trend as a function of the halogen size and electronegativity is observed in Table S3 in Supplemental Material [48] for the other functionals, and is in line with findings of a previous study, where the thermochemical errors for halogen compounds were found to correlate with the Pauling electronegativity [32]. Figure 3 shows a comparison of the errors of various

halogen compounds (X_2 , X , X^- , XX') obtained in a previous study and those of CX bonds as a function of the electronegativity. Note that for CX bonds we averaged the Pauling electronegativity of carbon (2.55) and the corresponding halogen (3.98 for F, 3.16 for Cl, 2.96 for Br, and 2.66 for I).

The good fit of the halogen errors within the previous trends shown in Fig. 3 indicates that, apart from method I, it would be possible to predict the errors on the basis of the electronegativity of the CX bonds. The errors predicted by the linear fit in Fig. 3(a) for the PBE functional are -0.15 , -0.06 , -0.04 , and 0.00 eV for ϵ_{CF} , ϵ_{CCl} , ϵ_{CBr} , and ϵ_{CI} , respectively. For comparison, the errors for the PBE functional with method I were -0.09 , -0.06 , -0.05 , and -0.03 eV, respectively. This simple and swift correction yields a decrease of the uncorrected MAE from 0.21 to 0.07 eV, while the MAX decreases from 0.69 to 0.24 eV. Although the decrease in the errors is not as pronounced as for method I (MAE of 0.06 eV and MAX of 0.18 eV), the applicability of a simple correction scheme based on the electronegativity beyond halogen-halogen bonds without requiring additional experimental data is encouraging.

It is worth highlighting that the linear trends in Fig. 3 and methods I and II can be used to collectively mitigate to a large extent inherent errors of DFT functionals for families of substances. However, each substance has its own functional-specific correction (Table S2 in Supplemental Material [48]). Application of those corrections to each species results in perfect agreement between the experimental and calculated energies for any substance.

Figure 3 suggests that the use of electronegativity as a descriptor for the errors improves the thermochemical predictions for gas-phase halocarbons. Figure S10 in Supplemental Material [48] shows that the average corrections for all the functionals studied can be determined as a function of the electronegativity of the halogens and halocarbons. However, those corrections were obtained for gas-phase halocarbon thermochemistry and may not be trivially extended to adsorbed species. In the adsorption energies, the total error can be broken down into gas-phase errors (to be corrected with the methods presented in this article) and adsorbed-phase errors, which require experimental adsorption data to be accurately determined for different adsorbents [40,85]. As the gas-phase and adsorbed-phase errors can be corrected independently, it is important to accurately assess both of them to predictively model adsorption-related phenomena.

Furthermore, method I uses halomethanes to obtain general corrections extrapolated to the rest of the dataset. It uses the errors found for the CH_3 groups in a previous study focused on N-containing species [38]. However, one may wonder whether incorporating the features of the current dataset, for instance, molecules with different degrees of halogenation bound to different sorts of C atoms

(tertiary, secondary, etc.), would lead to even smaller MAEs and MAXs.

B. Error detection using method II

The ϵ_{CH_3} and ϵ_{CX} values obtained with method I were used as an ansatz for the optimization procedure for method II. This approach refines the error predictions by adjusting the individual contributions from C-type environments and CX bonds in such a way that the overall predictive accuracy is maximized. By minimizing the MAE and the MAX simultaneously using Eq. (8), method II aligns more closely with the reference data, thereby improving its performance across a diverse set of halocarbons. The ansatzes derived from method I help ensure that the optimization converges rapidly and is physically meaningful [86].

An important issue of flexible models with more parameters, such as method II compared with method I, is the risk of overfitting, as the model might learn noise rather than actual physicochemical features of the dataset. To avoid this, we used the utopia point as the objective function since it provides a robust determination of the final parameters. However, there is still some dependency on the ansatzes: we tested the changes in the PBE parameters in method II starting from 0 as the initial guess for all the adjustable parameters, and the MAE and the MAX were 0.05 and 0.16 eV (compared with 0.04 and 0.11 eV, respectively, with use of the values obtained with method I as ansatzes). The average change in the parameters was approximately 0.02 eV compared with the original parameters, and the largest change was 0.05 eV for CH. All this indicates that the parameters of chemically intuitive method I are good ansatzes for method II.

Figure 4 provides a comparison of absolute residual errors for uncorrected DFT calculations and those corrected by method I and method II across the seven functionals studied. According to Table S12 in Supplemental Material [48], the “as is” DFT data exhibit the highest median errors and broadest interquartile ranges, suggesting considerable inaccuracy. Method I yields a substantial reduction in both the median error and the overall error dispersion. Further improvement is achieved with method II, as for each functional the error distribution of method II moved toward lower values. This is in the spirit of previous methods using chemical intuition as a starting point and then automatized optimizations to reach higher accuracy [46]. Here, method I offers satisfactory preliminary corrections using a localized model, while method II attains higher accuracy through its global optimization process.

Table I reports the ϵ_{CH_3} and ϵ_{CX} values obtained with method II. These can be used independently for DFT calculations of reaction energies in chemistry and (electro)catalysis. Table I outlines a compact and interpretable

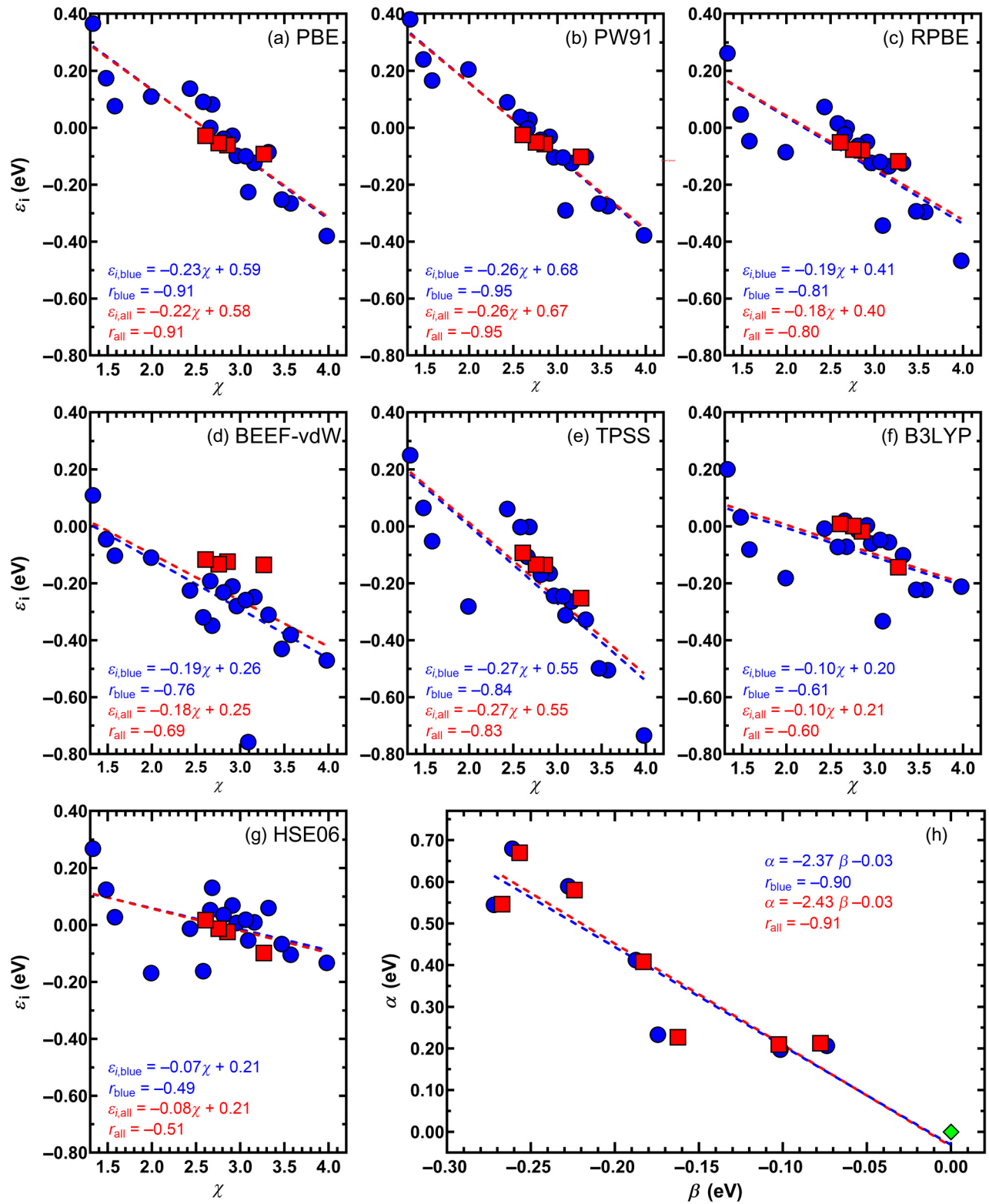


FIG. 3. Errors of halogen compounds X_2 , X , X^- , XX' from Ref. [32] (blue circles) together with the errors of CX bonds from method I (red squares) as a function of the electronegativity for the (a) PBE, (b) PW91, (c) RPBE, (d) BEEF-vdW, (e) TPSS, (f) B3LYP, and (g) HSE06 functionals. (h) Correlation between the slopes and offsets of the fits in (a)–(g) for the scrutinized functionals. The exact functional (in green) is included for comparison but was not used in the linear fits. The equation of the linear fit for the blue points and its corresponding correlation coefficient r are shown in blue. The fit and r in red correspond to the data for both the blue and the red points.

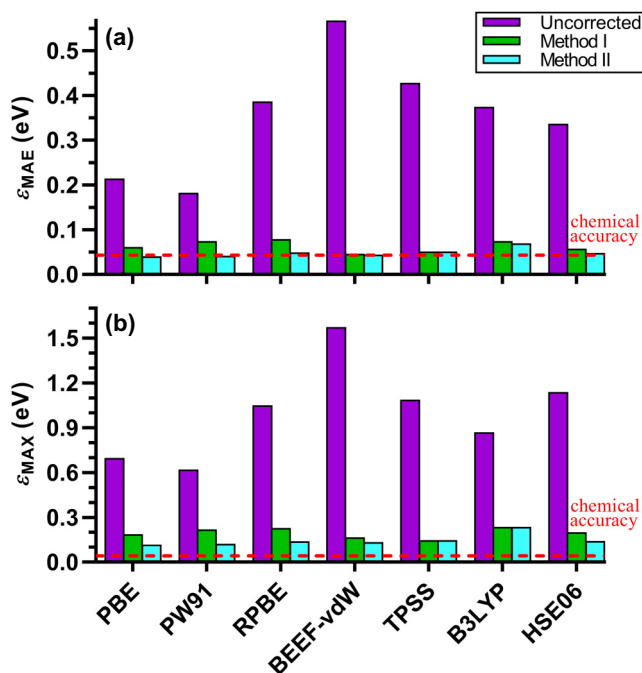


FIG. 4. Comparison of (a) the MAE and (b) the MAX of method I and method II with the baseline of uncorrected DFT results for seven different functionals. Chemical accuracy (1 kcal/mol) is shown as a dashed red line.

correction model that captures systematic DFT errors associated with various carbon environments and halogen substituents in halocarbons. Because the corrections are based on chemically meaningful descriptors, such as the type of C atoms (e.g., primary, secondary, etc.) and the identity of halogens (F, Cl, Br, I), they are transferable to structurally related molecules. This enables the application of the model beyond the original training set, allowing more accurate enthalpy predictions across a broader chemical space of halogen-based compounds. From Table I and

Table S3 in Supplemental Material [48], we conclude that no functional is simultaneously good at describing C—H, C—X, and X—X bonds and, on average, the lowest absolute errors are provided by the HSE06 functional and the highest are provided by the TPSS functional.

According to Table I, most DFT errors in C and CH are positive, while those in X_2 and CX bonds are negative. In general, the latter two errors are linearly related (see Fig. S9 in Supplemental Material [48]). For methods I and II, the largest errors are for F_2 , while those of other halogen-based compounds are not larger than -0.25 eV. The DFT errors vary as a function of the size of the halogens: Fig. S12 in Supplemental Material [48] shows for the PBE functional that larger halogens have smaller errors, such that the best initial DFT predictions are for I_2 and C—I bonds. However, we do not see a clear relationship between the dipole moments of the molecules and the errors (for the uncorrected and corrected results), as illustrated in Table S15 in Supplemental Material [48] for halomethanes. The errors do not decrease as the halogen content in halomethanes increases presumably because C—X and X—X bonds contribute similarly to the overall error in the formation energies, so their effects cancel out.

Furthermore, the errors calculated with method I are commensurate but not identical to those calculated with method II. The X_2 errors are the same for method I and method II as they come from previous work [32], and there are no significant differences between the errors calculated with methods I and II (see Table I and Table S3 in Supplemental Material [48]). The parity plot in Fig. S7 in Supplemental Material [48] shows that method II systematically improves agreement with experimental data by optimizing correction parameters. Most points (60%–71%) lie above the diagonal in Fig. S7 in Supplemental Material [48], showing that the residual errors decrease with method II for most molecules. A remarkable exception is the TPSS functional, where both methods yield the same

TABLE I. Gas-phase corrections (in electronvolts) for halocarbons found with method II for various functionals. The ϵ_{X_2} errors of Zapata *et al.* [32] are included for completeness. In each case, the third decimal place is shown in parentheses. The MAE is obtained from the results in Table S7.

Error	PBE	PW91	RPBE	BEEF-vdW	TPSS	B3LYP	HSE06
ϵ_{F_2}	−0.38(0)	−0.37(8)	−0.46(7)	−0.47(1)	−0.73(5)	−0.21(2)	−0.13(3)
ϵ_{Cl_2}	−0.12(3)	−0.12(4)	−0.13(5)	−0.24(8)	−0.26(4)	−0.05(6)	0.00(9)
ϵ_{Br_2}	−0.09(8)	−0.10(4)	−0.12(3)	−0.28(0)	−0.24(4)	−0.06(1)	0.00(7)
ϵ_{I_2}	0.00(0)	−0.00(2)	−0.02(4)	−0.19(2)	−0.10(7)	0.02(0)	0.05(2)
ϵ_{CH_3/CH_2}	0.05(1)	0.03(7)	0.10(4)	0.19(6)	0.12(0)	0.10(4)	−0.14(4)
ϵ_{CH}	0.14(8)	0.10(5)	0.22(5)	0.19(2)	0.24(8)	0.16(6)	−0.04(5)
ϵ_C	0.16(7)	0.12(6)	0.28(5)	0.21(8)	0.37(2)	0.45(7)	0.07(0)
ϵ_{CF}	−0.10(7)	−0.10(7)	−0.11(8)	−0.12(7)	−0.25(2)	−0.15(5)	−0.12(9)
ϵ_{CCl}	−0.05(3)	−0.04(1)	−0.05(3)	−0.11(6)	−0.13(6)	−0.00(6)	0.00(0)
ϵ_{CBr}	−0.04(7)	−0.03(9)	−0.06(6)	−0.13(0)	−0.13(4)	0.00(2)	0.00(1)
ϵ_{CI}	−0.04(0)	−0.03(3)	−0.04(2)	−0.12(5)	−0.09(3)	0.01(4)	0.02(6)
MAE	0.03(9)	0.04(0)	0.04(8)	0.04(2)	0.04(9)	0.06(8)	0.04(6)

corrections. This was possible because the CH_y errors in method I were not determined from the literature, as those values were not used in previous studies [32,38]. Instead, they were obtained by minimizing the error in a similar fashion to method I. Another exception was the BEEF-vdW functional, with only 47% of the molecules with a lower residual error in method II compared with method I. In this case, method II has a similar MAE to method I (0.04 eV) but the decrease in the MAX (from 0.16 to 0.13 eV) was obtained by redistribution of the residual error between the different molecules in the dataset.

These differences reflect the different design principles: method I is based on normalized average fitting parameters from a homogeneous subset (halomethanes), whereas method II performs a minimization of the MAE and the MAX over the full, 55-molecule training set, thereby capturing a wider variety of effects and delivering parameters that generalize across isomers, chain lengths, and functionalities. Thus, method II provides smaller residual errors and greater robustness, offering a more reliable basis for enthalpy predictions than the localized, empirically seeded method I.

Method I fits only the carbon-halogen parameters and takes the alkane errors from the literature. Thus, method I has four adjustable parameters for each functional. Method II uses those four parameters plus the three alkane parameters, so it has seven parameters. The differences between the predictive Akaike information criterion values of methods I and II are shown in Table S14 in Supplemental Material [48]. In general, method II should be preferred, as it provides a better trade-off between fit and complexity. However, for the BEEF-vdW, TPSS, and B3LYP functionals neither model is clearly preferable, and method I may be chosen in view of its simplicity.

In addition to the validation set of reactions described later, C_2F_6 ($\Delta_f H_{\text{C}_2\text{F}_6, \text{expt}}^0 = -13.91$ eV) was used independently of the original fitting set as a representative of purely predictive results on a small molecule with a large number of X atoms. The results showed that the residual errors decreased from 0.85 to 0.02 eV, from 0.78 to 0.03 eV, from 1.28 to 0.02 eV, from 1.07 to -0.02 eV, from 1.37 to -0.06 eV, from 0.52 to -0.10 eV, and from -0.13 to 0.10 eV for the PBE, PW91, RPBE, BEEF-vdW, TPSS, B3LYP, and HSE06 functionals, respectively. Hence, the corrections in Table I can aid in correcting the formation energies even for molecules outside the original fit for all functionals studied.

C. A glimpse at the chemical physics behind the corrections

Previous work [47] proposed that the trends in DFT errors may be connected to those in the formation energies themselves. In this vein, we observe in Fig. 5(a) that the experimental formation energies of halomethanes

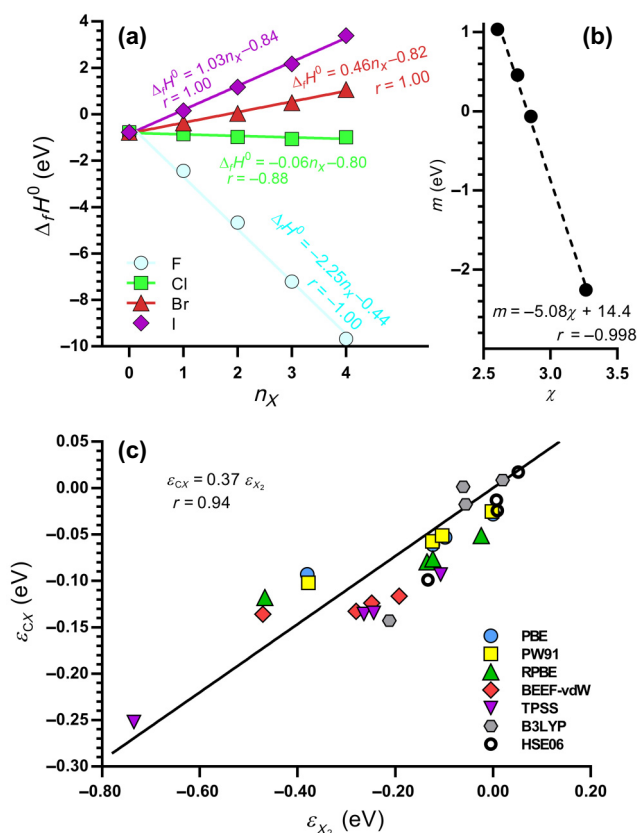


FIG. 5. (a) Experimental formation energies of halocarbons as a function of the number of halogen atoms, with the corresponding equation of the linear fit and the correlation coefficients. (b) Slopes of the linear fits in (a) as a function of the average electronegativity of the corresponding CX bonds. (c) Correlation between the X_2 and CX errors obtained with method I for the seven functionals studied.

are linearly related to the number of halogen atoms in the structure. Figure 5(a) shows that the offsets of the lines are close to the standard experimental formation energy of CH_4 (-0.77 eV), which has a halogen content of zero ($n_X = 0$). Interestingly, the slopes of the lines change depending on the halogen in the structure, and Fig. 5(b) shows a strong connection between the slopes and the electronegativity of the CX bonds. Therefore, halomethane thermochemistry seems to be modulated by the respective halogen electronegativity and abundance in each compound.

Since electronegativity appears to be a crucial parameter in the errors of CX , X_2 and XX' bonds [32], as shown in Figs. 3 and 5(a), there should be a relationship between X_2 and CX errors. This is exactly what is shown in Fig. 5(c). We note that the linear relationship in Fig. 5(c) stems from the electronegativity of the atoms involved in the chemical bonds, and can be used to predict CX errors using X_2 errors and vice versa.

The X_2 and CX errors for the PW91, B3LYP, and HSE06 functionals scale linearly as a function of those for the PBE functional (see Fig. S11 in Supplemental Material [48]). As the offsets in Fig. S11 in Supplemental Material [48] seem nearly null and functional independent and the slopes are positive, a large (small) error for the PBE functional corresponds to large (small) errors for the other functionals, hinting at systematic limitations (virtues) in these functionals. Specifically, for the PW91 functional vs the PBE functional, the slope is 1, evidencing their similar implementation and thermochemical predictions. For the B3LYP functional vs the PBE functional, the slope is 0.63, while for the HSE06 functional vs the PBE functional, the slope is 0.45. These slopes reflect the higher accuracy of hybrids with respect to GGAs, with the HSE06 functional being more accurate than the B3LYP functional for this family of compounds. The slopes also decrease depending on the amount of exact exchange (0 in the PBE and PW91 functionals, 20% in the B3LYP functional, and 25% in the HSE06 functional). Interestingly, the correlation coefficients decrease from 1.00 (PW91 functional vs PBE functional) to 0.88 (B3LYP functional vs PBE functional) and 0.76 (HSE06 functional vs PBE functional), confirming that functional similarity decreases as the amount of exact exchange increases.

D. Validation of the corrections

The reaction enthalpies of the validation reactions (Tables S4 and S8–S10 in Supplemental Material [48]) allow us to evaluate the suitability of our corrections to yield accurate thermochemical predictions without relying on error cancellation. Figure 6 compares the DFT uncorrected MAEs and MAXs with those obtained with use of the corrections of method I and method II. This provides an independent evaluation of the corrections in a different dataset where the formation enthalpies of halocarbons are not present.

For all functionals the corrections of methods I and II result in a decrease of the overall error. Before corrections, the uncorrected MAEs range from 0.07 to 0.12 eV, with MAXs as high as 0.73 eV, highlighting the unreliability of uncorrected DFT for certain reactions. Upon corrections, a general reduction in the errors is observed across all functionals, with MAEs reaching the scale of chemical accuracy and most MAXs below 0.20 eV. This significant improvement confirms that methods I and II successfully identify and remove systematic errors for all functionals. Interestingly, the correction schemes reorder the relative performance of the functionals: while the hybrid HSE06 functional exhibits the lowest uncorrected MAE and MAX, upon application of methods I and II, all functionals render similar results.

It is worth noting that the uncorrected MAE of the validation set is visibly lower than the corresponding

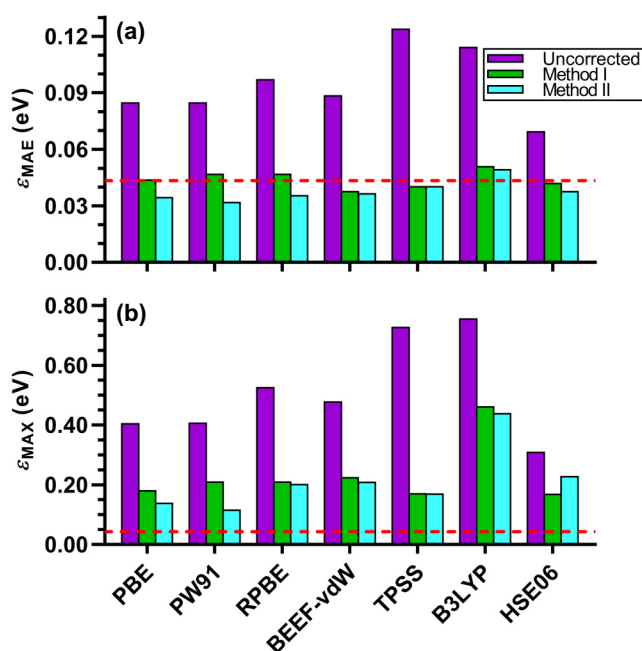


FIG. 6. Comparison of (a) the MAE and (b) the MAX for the reactions in the validation set for DFT without any corrections (purple bars) and after application of method I (green bars) and method II (cyan bars) for seven functionals. Chemical accuracy (1 kcal/mol) is shown as a dashed red line.

uncorrected errors for the formation enthalpies (Table S11 in Supplemental Material [48]). This is indicative of intrinsic error cancellation in the selected reaction sets, which can be ascertained by dividing the validation set into reaction classes. Figure 7 presents the average MAE for all the functionals according to the reaction classification described in Sec. II. The largest error cancellation is observed for the chain redistribution reactions, where the results of methods I and II are virtually equivalent to the uncorrected calculations, as the same corrections are present in the reactants and products. In other words, the same number and types of bonds are present on both sides of the reactions.

For halogen exchange reactions there is also a high degree of error cancellation, and the error corresponds to the difference between the CX and CY bond errors. The largest uncorrected error was observed for the halogenation reactions where the error corresponds to the highly correlated differences between X_2 and CX errors shown in Fig. 5. Although error cancellation for chain redistribution and halogenation reactions showed a large difference for the uncorrected calculations, around 0.11 eV on average, the difference for method II–corrected predictions was only 0.02 eV. This indicates that our corrections accurately predict various sorts of reaction energies without relying on error cancellation and avoiding the risk of increasing the errors instead of lowering them.

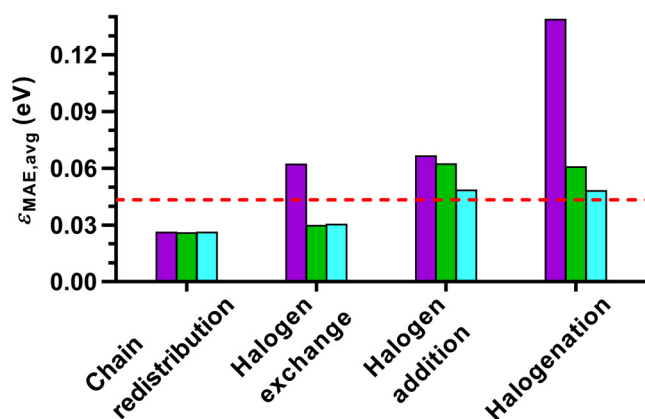


FIG. 7. Average MAE for all scrutinized functionals in the validation reactions according to their classification as halogen exchange, chain redistribution, halogen addition and halogenation reactions for DFT without any corrections (purple bars) and after application of method I (green bars) and method II (cyan bars). Chemical accuracy (1 kcal/mol) is shown as a dashed red line.

Finally, Table S11 in Supplemental Material [48] shows a systematic contraction of the MAX upon the corrections. For example, the MAX for the TPSS functional decreased from 0.73 to 0.17 eV. This error suppression across diverse reaction classes confirms that our correction schemes effectively avoid reliance on fortuitous error cancellation, yield statistically robust predictions, and are suitable for complex applications such as free energy landscapes or phase diagrams in electrocatalysis, where a single large deviation may compromise activity and stability forecasts [26].

As an additional internal validation of the results, we calculated the uncertainty as the $\pm$ standard deviation of the errors in method II by bootstrapping with 1000 iterations. To reduce the dependency on the initial values, we used a stochastic method for global optimization of the objective function instead of a reduced gradient algorithm (Tables S13 and S14 in Supplemental Material [48]). Bootstrapping shows similar results to those in Table I, and the average difference of these values relative to the bootstrap means is 0.014 eV. The errors exhibited small deviations across the bootstrap samples (0.023 eV, on average), indicating that the parameter estimates are well constrained by the data and remain stable under resampling. The highest deviations were observed for CH and C, presumably due to the smaller number of data points containing these fragments in the training set, leading to increased uncertainty in the bootstrap estimates and larger error bars. The MAE and MAX obtained from bootstrapping (Table S14 in Supplemental Material [48]) were smaller in all cases than those of the original training set (Fig. 4), indicating the robustness and stability of the fitting method. This suggests that the model is less affected by specific data points, as the resampling procedure averages out the influence of individual points.

Nevertheless, the determination of errors as a set of parameters is an ill-posed problem, such that it is possible to obtain different values depending on the training set used. If a set of reactions such as the validation set were used for training, the interactions that are not well described by DFT can be masked by error cancellation and the procedure could converge to different values. Hence, formation reactions are a more suitable training set for determining structurally additive error corrections, as they always have similar reactants with errors that can be detected and corrected, thereby minimizing the reliance on error cancellation.

IV. CONCLUSIONS

A chemically interpretable, group-additivity framework is proposed in this work to detect, quantify, and correct the structure-dependent, systematic errors of DFT for gas-phase formation enthalpies of halocarbons containing various amounts of F, Cl, Br, and I. We decomposed the total error into reactant (ϵ_{X_2}), carbon-type (ϵ_{CH_y}), and CX bond (ϵ_{CX}) contributions. Furthermore, we applied method I and method II to assess ϵ_{CX} . Method I is a chemically intuitive fit based on halomethanes and extrapolated to the rest of the halocarbons. Method II globally optimizes all parameters via a utopia-point minimization over a diverse 55-molecule training set. Both methods achieve substantial error suppression and close agreement with experimental data for most species, including subtle isomeric energy differences. The MAEs are reduced from approximately 0.35 eV to approximately 0.05 eV across seven common functionals, including GGA, metaGGA, and hybrid functionals. For the practical use of the corrections, if null residual errors are required, the exact corrections in Table S2 in Supplemental Material [48] should be used instead of method I or method II corrections, as exact corrections perfectly match the experimental data. For extensions to other halocarbons for which experimental data are unavailable, method II is advisable as it yields lower average errors than method I.

Interestingly, halocarbon thermochemistry is modulated by the electronegativity of CX bonds, in line with established trends for purely halogenic compounds. This descriptor can be extended to predict gas-phase errors of halocarbons outside the training set, but it has not been assessed for adsorbed species, where the chemical nature of solid adsorbents also plays a role.

Extensive validation on a set of approximately 150 reactions reveals a systematic contraction of the MAX and the MAE across all halocarbon families without relying on error cancellation. Our tabulated corrections and methods enable a swift and straightforward rectification of DFT outputs by fragment counting, offering a practical route to precise, cost-efficient thermochemistry modeling of

halogen and halocarbon-based processes in environmental remediation and catalysis.

ACKNOWLEDGMENTS

This work received financial support from Grants No. PID2024-158557OB-C22, No. PID2021-127957NB-I00, and No. TED2021-132550B-C21, which are funded by MICIU/AEI/10.13039/501100011033 and the European Union. The project that gave rise to these results also received the support of a Ph.D. fellowship from “la Caixa” Foundation (ID 100010434, fellowship code LCF/BQ/DI22/11940040). We thank Red Española de Supercomputación for supercomputing time on MareNostrum (Projects No. QHS-2025-3-0029, No. QHS-2025-2-0044, and No. QHS-2025-1-0024). F.C.V. also acknowledges financial support from the Basque Government through Grant No. IT1453-22 “Grupos Consolidados UPV/EHU del Gobierno Vasco” and the Elkartek program (Grant No. KK2025-00054). This research used resources of the Center for Functional Nanomaterials, which is a U.S. Department of Energy Office of Science Facility, and the Scientific Data and Computing Center, a component of the Computational Science Initiative, at Brookhaven National Laboratory under Contract No. DE-SC0012704. We also acknowledge financial support from Universidad EAFIT and the use of supercomputing resources of the Centro de Computación Científica Apolo at Universidad EAFIT.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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