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Highly accurate CCSD(T) homolytic Al–H bond dissociation enthalpies – chemical insights and performance of density functional theory

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ABSTRACT

We obtain gas-phase homolytic Al–H bond dissociation enthalpies (BDEs) at the CCSD(T)/CBS level for a set of neutral aluminium hydrides (which we refer to as the AlHBDE dataset). The Al–H BDEs in this dataset differ by as much as 79.2 kJ mol⁻¹, with $(H_2B)_2Al–H$ having the lowest BDE (288.1 kJ mol⁻¹) and $(H_2N)_2Al–H$ having the largest (367.3 kJ mol⁻¹). These results show that substitution with at least one $-AlH_2$ or $-BH_2$ substituent exerts by far the greatest effect in modifying the Al–H BDEs compared with the BDE of monomeric $H_2Al–H$ (354.3 kJ mol⁻¹). To facilitate quantum chemical investigations of large aluminium hydrides, for which the use of rigorous methods such as W2w may not be computationally feasible, we assess the performance of 53 density functional theory (DFT) functionals. We find that the performance of the DFT methods does not strictly improve along the rungs of Jacob's Ladder. The best-performing methods from each rung of Jacob's Ladder are (mean absolute deviations are given in parentheses): the GGA B97-D (6.9), the meta-GGA M06-L (2.3), the global hybrid-GGA SOGGA11-X (3.3), the range-separated hybrid-GGA CAM-B3LYP (2.1), the hybrid-meta-GGA ω B97M-V (2.5) and the double-hybrid methods mPW2-PLYP and B2GP-PLYP (4.1 kJ mol⁻¹).

Keywords: aluminium hydrides, bond dissociation energy, CCSD(T), density functional theory, DFT, free radicals, hydrogen storage, W2 theory.

Introduction

Neutral aluminium hydride reagents (i.e. R¹R²Al–H) are useful reagents in organic synthesis,^[1] and species such as alane (AlH₃) have also attracted interest as hydrogen storage materials, demonstrating potential application as a rocket propellant^[2] and as a hydrogen source for portable fuel cells.^[3,4] Besides the potential technological applications of alane, we note that attention has also been given to ways in which nonpolymerised forms of this reagent may be prepared and used in synthetic chemistry. Recently, a 1:2 alane arylphosphane adduct has been synthesised, which was shown to be able to release essentially free non-polymerised AlH₃, which could be used in reduction and hydroalumination reactions.^[5] Bulkier aluminium hydride species, such as diisobutylaluminium hydride (DIBAl-H), have been employed in effecting a wide range of reduction processes, including the (i) reduction of ketones and aldehydes to the corresponding alcohols, (ii) transforming α , β -unsaturated esters into the corresponding allylic alcohols^[6,7] and (iii) epoxide ring opening reactions.^[8] While the reactions of alkylsubstituted aluminium hydrides have received considerable attention, other aluminium hydride species have also been used in synthesis, albeit with much more limited scope to date. As one example, we note that Cl₂AlH has been employed for the ring-opening of 2-substituted 1,3-dioxolanes.^[9] In addition, there has been interest in the synthesis of other Al-H-containing species, and there has been success in generating and characterising species such as ClAlH₂.^[10]

Owing to the synthetic and technological applications of neutral aluminium hydrides, it would be insightful to have a greater understanding of some of the more salient thermodynamic properties of these compounds. One of the most fundamental thermochemical properties of such species, which has not yet received attention, are the homolytic Al–H bond dissociation enthalpies (BDEs) of such species (i.e. the energies associated with Eqn 1).

$$R^{1}R^{2}Al-H \rightarrow R^{1}R^{2}Al' + H'$$
(1)

Knowledge of how substituents affect the magnitude of the strength of Al-H bonds toward homolytic dissociation would be insightful, not least because such radical reactions may have industrial applications. For example, in the stabilisation of AlH₃ by species such as 2-mercaptobenzothiazole, a key step in the mechanism has been suggested to involve homolytic dissociation of the Al-H bond of AlH₃ to form the H₂Al radical.^[11] While there does not currently exist in the literature any systematic study of Al-H homolytic BDEs, we wish to note that numerous experimental and theoretical studies have been reported which have focussed on the synthesis and characterisation of a number of aluminium(II) radicals (i.e. of the type R^1R^2Al , which could be formed upon homolytic Al-H bond dissociation). The parent radical, H₂Al, has been synthesised and characterised by spectroscopic methods.^[12,13] A number of substituted aluminium-centred radicals have also been produced including: CH₃AlH,^[14] HAlNH₂,^[15–17] Al(NH₂)₂,¹⁷ HAlPH₂,^[18,19] HAlOH,^[20] Al $(OH)_2^{12}$ and HAlSH.^[21]

The present study addresses the gap in the literature concerning the extent to which substituents affect the strength of Al–H bonds toward homolytic dissociation. To achieve this, we report a high-level quantum chemical investigation (performed using the W2w thermochemical protocol), in which the gas-phase homolytic BDEs of a set of 18 aluminium hydrides (i.e. R¹R²Al–H) bearing a diverse range of substituents have been determined (which we refer to as the AlHBDE dataset). In addition, to facilitate future studies of the homolytic BDEs of larger aluminium hydrides, for which the use of the W2w thermochemical protocol is not computationally feasible, we also assess the performance of a wide range of contemporary density functional theory (DFT) methods to determine suitable lower-cost methods that could be applied for such a purpose.

Computational methods

The geometries of all species have been obtained at the B3LYP/AVTZ level of theory (where AVnZ denotes the use of aug-cc-pVnZ basis sets for hydrogen and first-row elements and aug-cc-pV(n + d)Z basis sets for second-row elements).^[22,23] The validity of each structure as being a minimum on the potential energy surface was confirmed by all real harmonic vibrational frequencies. Using the geometries obtained at the B3LYP/AVTZ level of theory, we then performed higher-level calculations employing the

W2w thermochemical protocol.^[24] To compute a W2w energy, several calculations must be performed. First, the underlying SCF/CBS energy is obtained using a two-point extrapolation of the form $E(L) = E_{\infty} + A/L^5$ in conjunction with the AVOZ and AV5Z basis sets. The following corrections were added to the underlying SCF/CBS energy: (i) $\Delta CCSD$ (obtained using a two-point extrapolation of the form $E(L) = E_{\infty} + A/L^3$ in conjunction with the AVQZ and AV5Z basis sets), (ii) $\Delta(T)$ (a correction for parenthetical triples excitations, obtained using a two-point extrapolation of the form $E(L) = E_{\infty} + A/L^3$ in conjunction with the AVTZ and AVOZ basis sets), (iii) a core-valence correction (Δ CV) obtained as the difference between the all-electron CCSD (T)/MTsmall energies (with the exception of second-row elements, in which the 1s electrons are frozen) and the corresponding frozen core calculations and (iv) a scalar relativistic correction (Δ Rel.), which is obtained by way of Douglass-Kroll-Hess (DKH) calculations^[25,26] and corresponds to the energy difference between a frozen-core DKH-CCSD(T)/MTsmall and regular CCSD(T)/MTsmall calculations. The final all-electron relativistic, bottom-of-thewell W2w energy is given by the following formula: $W2w_{rel,el} = SCF/CBS + \Delta CCSD + \Delta(T) + \Delta CV + \Delta Rel.$ To obtain energies at 298 K (i.e. BDE₂₉₈), the W2w values were amended by the inclusion of scaled ZPVE and $H_{\rm vib}$ contributions, both of which have been obtained at the B3LYP/AVTZ level of theory, and were scaled by 0.9884 and 0.9987, respectively.^[27]

We have additionally assessed a diverse array of different DFT functionals for their ability to compute gas-phase homolytic Al-H BDEs (in conjunction with the AVTZ and AVQZ basis sets), using the W2w non-relativistic bottom-ofthe-well BDEs as reference values. The DFT exchangecorrelation functionals considered in this study, ordered by their rung on Jacob's ladder, are the generalised gradient approximation (GGA) functionals: BLYP,^[28,29] B97-D,^[30] revPBE,^[33] PB86,^[29,34] HCTH407,^[31] PBE,^[32] and BPW91,^[29,35] the meta-GGA (MGGA) functionals: M06-L,^[36] TPSS,^[37] τ-HCTH,^[38] VSXC,^[39] M11-L,^[40] MN12-L,^[41] MN15-L,^[42] r²SCAN,^[43] and B97M-V,^[44] the hybrid-GGAs (HGGA): BH&HLYP,^[45] B3LYP,^[28,46,47] B3P86,^[34,46] B3PW91,^[35,46] PBE0,^[48] B97-1,^[49] X3LYP,^[50] SOGGA11-X,^[51] APF,^[52] and the range-separated functionals ω B97,^[53] ωB97X.^[53] ωB97X-V.^[54] N12-SX.^[55] CAM-B3LYP.^[56] the hybrid-meta GGAs (HMGGA): M05,^[57] M05-2X,^[58] M06,^[59] M06-2X,^[59] M08-HX,^[60] MN15,^[42] BMK,^[61] TPSSh,^[62] τ -HCTHh,^[38] PW6B95,^[63] and the range separated functionals MN12-SX, ^[55] M11, ^[64] ω B97M-V, ^[65] and the double hybrid (DH) functionals: B2-PLYP, ^[66] mPW2-PLYP, ^[67] B2GP-PLYP, ^[68] DSD-BLYP, ^[69] PWPB95, ^[70] DSD-PBEP86, ^[71,72] DSD-PBEB95,^[71] PBE0-DH,^[73] PBEQI-DH.^[74] Empirical D3 dispersion corrections^[75,76] were included using the Becke-Johnson^[77] damping potential (denoted by the suffix -D3). All calculations have been performed using the Gaussian 16 (rev. C.01) and ORCA 5.0 programs.^[78-81]

Results and discussion

General overview of the AIHBDE dataset

The full set of gas-phase homolytic Al-H BDEs (Eqn 1), which have been obtained in conjunction with the W2w thermochemical protocol, are provided in Table 1. In addition to reporting the final homolytic gas-phase Al-H BDEs at 298 K (i.e. BDE₂₉₈), we have also included the various contributions that lead to these values. These contributions include the underlying BDEs obtained using Hartree–Fock theory (Δ SCF), a correction for single and double excitations (Δ CCSD), a correction for the inclusion of quasi-perturbative triple excitations (Δ (T)), a core-valence correction (Δ CV), a scalar relativistic correction obtained within the Douglass-Kroll-Hess approximation (Δ Rel.), the zero-point vibrational energy contribution (Δ ZPVE) and finally, an enthalpy correction $(\Delta H_{\rm vib})$ at 298 K. The species have been selected such that there is a reasonable selection of electron-donating and electron-withdrawing substituents. From a general perspective, we note that the Al-H BDEs of the molecules in this dataset (at 298 K) differ by up to 79.2 kJ mol^{-1} . with $(H_2B)_2Al-H$ having the lowest BDE (288.1 kJ mol⁻¹), while (H₂N)₂Al-H is associated with the largest BDE $(367.3 \text{ kJ mol}^{-1})$. We note that the simplest molecule within this family, namely H₂Al-H, has a BDE of $354.3 \text{ kJ mol}^{-1}$. Prior to embarking on a more specific discussion concerning the effect of substituents in governing the magnitude of the Al–H BDEs, we make a few points to: (i) address the likely accuracy of the reported BDEs obtained at the W2w level by using an energy-based diagnostic for the importance of post-CCSD(T) contributions and (ii) examine the performance of the lower cost W1w thermochemical protocol, which may be applied to the high-level study of larger aluminium hydride species, for which the use of the more rigorous W2w protocol might be computationally prohibitive.

First, we wish to point out that the W2w thermochemical protocol, which in effect affords an energy at the all-electron CCSD(T) basis-set-limit level, does not include post-CCSD(T) corrections. In some systems, for example those that exhibit high degrees of non-dynamical correlation, post-CCSD(T) corrections can be of considerable magnitude and their exclusion can render any computed thermodynamic quantity substantially less accurate. To address the likely reliability of the CCSD(T) method in this context, an energy-based diagnostic, namely the percentage of the atomisation energy accounted for by parenthetical connected triple excitations, %TAE[(T)] has been developed.^[24,82] This diagnostic has been used previously for the purposes of validation of datasets of the BDEs of a range of other chemical bonds.^[83–87] It has been shown that for species with $\text{%TAE}[(T)] \leq 5\%$, post-CCSD(T) contributions are unlikely to exceed 2 kJ mol^{-1} . An analysis by Chan also supported the adoption of this recommended cutoff of $\leq 5\%$.^[88] As the %TAE[(T)] diagnostics of all molecules considered in this study are well below the 5% threshold (ranging from 0.1% in the case of AlH₃ and AlH₂ to 3.0% in

| Molecule | ΔSCF | ΔCCSD | Δ(Τ) | ΔCV | ΔRel. | ΔΖΡΥΕ | $\Delta H_{\rm vib}$ | BDE ₂₉₈ |
|--|-------|-------|------|------|-------|-------|----------------------|---------------------------|
| $(H_2B)_2AI-H(I)$ | 266.4 | 43.1 | -7.2 | -1.6 | -0.5 | -17.0 | 4.9 | 288.1 |
| $(H_2AI)_2AI-H$ (2) | 246.8 | 61.7 | -3.0 | -0.7 | -0.3 | -15.8 | 4.6 | 293.3 |
| (H ₂ B)HAI–H (3) | 296.7 | 42.5 | -5.6 | -1.8 | -0.6 | -20.6 | 6.3 | 317.0 |
| $(H_2AI)HAI-H$ (4) | 277.1 | 64.6 | -1.8 | -0.9 | -0.4 | -18.9 | 5.1 | 324.8 |
| $(H_2N)(H_2B)AI-H$ (5) | 305.8 | 43.7 | -5.5 | -1.6 | -0.5 | -20.1 | 5.7 | 327.4 |
| (H ₃ Si)HAI–H (6) | 282.3 | 79.1 | -0.3 | -0.4 | -0.4 | -20.0 | 5.4 | 345.7 |
| (PH ₂)HAI-H (7) | 285.5 | 79.2 | -0.7 | -0.4 | -0.5 | -20.1 | 5.4 | 348.5 |
| (SH)HAI-H (8) | 287.1 | 80.6 | -0.7 | -0.3 | -0.4 | -20.0 | 5.4 | 351.6 |
| CI(H)AI–H (9) | 288.1 | 81.1 | -0.6 | -0.5 | -0.5 | -20.8 | 5.5 | 352.4 |
| Cl ₂ Al–H (10) | 286.9 | 82.3 | -1.0 | -0.2 | -0.6 | -18.9 | 5.3 | 353.8 |
| H ₂ AI–H (II) | 288.5 | 82.4 | 0.0 | -0.3 | -0.3 | -21.7 | 5.7 | 354.3 |
| (OH)HAI-H (I2) | 290.9 | 80.9 | -0.9 | -0.3 | -0.3 | -21.1 | 5.6 | 354.9 |
| F(H)AI–H (13) | 290.3 | 82.0 | -0.7 | -0.4 | -0.4 | -21.2 | 5.6 | 355.2 |
| CH ₃ (H)AI–H (14) | 289.9 | 82.0 | -0.3 | -0.2 | -0.3 | -20.1 | 5.0 | 356.0 |
| (CN)(H)AI–H (I5) | 290.3 | 82.9 | -0.5 | -0.2 | -0.3 | -20.7 | 5.6 | 357.1 |
| (NH ₂)HAI–H (16) | 293.5 | 82.8 | -0.4 | +0.1 | -0.2 | -21.0 | 5.6 | 360.3 |
| F ₂ AI–H (17) | 290.2 | 85.8 | -1.1 | +0.1 | -0.3 | -19.4 | 5.4 | 360.7 |
| (H ₂ N) ₂ AI–H (18) | 298.2 | 84.2 | -0.7 | +0.6 | -0.2 | -21.1 | 6.2 | 367.3 |

Table I. Component breakdown and final W2w gas-phase homolytic AI-H BDEs (all components and energies are reported in kJ mol⁻¹).

the case of (CN)HAl), inclusion of post-CCSD(T) contributions are therefore unlikely to affect the BDEs to any significant extent. On this basis, it stands to reason that the W2w BDEs reported in this study are expected to be within chemical accuracy (i.e. with deviations below 1 kcal mol⁻¹) from reference values obtained at the full configuration interaction (FCI) infinite basis-set limit.^[89]

We have also sought to consider whether the W1w thermochemical protocol, which is less computationally demanding than W2w, and hence could be applied to the study of larger aluminium hydride species, would also result in reliable Al-H BDEs. W1w theory employs the AVTZ and AVOZ (rather than AVOZ and AV5Z) basis sets for the computation of the \triangle SCF and \triangle CCSD components, and the AVDZ and AVTZ (rather than AVTZ and AVQZ) basis sets are employed for the computation of the $\Delta(T)$ correction. Having performed this analysis (see the Supporting material for the non-relativistic bottom-of-the-well valence W1w BDEs and the values of the various contributions giving rise to these BDEs), we note that the differences between W2w and W1w are relatively small. First, we note that the W1w protocol systematically overestimates the Al-H BDEs compared with those obtained using the W2w protocol with an MD and MAD of +0.5 kJ mol⁻¹. Second, we note that the largest deviation, which amounts to 1.0 kJ mol^{-1} , was observed in the case of the BDE of (H₂B)₂Al-H. As a result of breaking down the BDE of this molecule into the individual components, we find that the deviation of 1.0 kJ mol^{-1} between the W1w and W2w value arises predominantly because of a larger difference in the $\Delta CCSD$ correction $(0.7 \text{ kJ mol}^{-1})$, with only a 0.3 kJ mol^{-1} difference in the underlying SCF energy and a difference of -0.1 kJ mol⁻¹ for the $\Delta(T)$ contribution.

Substituent effects in governing the magnitude of AI–H BDEs

Upon inspection of the AlHBDE dataset (Table 1), we note that, although the BDEs span a range of 79.2 kJ mol⁻¹, this relatively wide range belies the fact that upon exclusion of those molecules bearing at least one -BH2 or -AlH2 substituent (i.e. molecules 1-5) the resulting variation in BDEs amounts to 21.6 kJ mol^{-1} . Prior to discussing the BDEs of molecules 1-5, we note that, whereas substitution by thirdperiod elements (i.e. Si, P, S, and Cl) results in molecules that have lower Al-H BDEs than that of H₂Al-H, attachment of second-period elements (i.e. C, N, O, and F) serves to increase the Al-H BDEs. Of the species considered in this study, we note that (H₂N)₂Al-H is associated with the largest BDE (i.e. 13.0 kJ mol^{-1} higher than that of H₂Al–H). The finding that aluminium hydrides substituted by electrondonating substituents are not associated with significantly lower Al-H BDEs (and in the case of electron-donating groups belonging to the second period actually serve to increase the Al-H BDEs compared with that of H₂Al-H),

can be attributed, in part, to the fact that the resulting aluminium-centred radicals adopt electronic states that are σ rather than π . By performing NBO calculations at the B3LYP/AVTZ level of theory, we note that overlap of the lone-pairs (of the π -electron-donating substituents) and the formally vacant 3p orbitals of the central Al atoms in Al–H-containing precursor molecules are conserved in the resulting radicals, and consequently the radicals do not benefit from the stabilisation that might be expected to arise if overlap between the half-filled orbital on the aluminium and the lone pair of the donor substituents (for example, which has been noted previously in the case of C–H BDEs)^[90] were to occur.

As mentioned previously, the most dramatic substituent effects were observed in the case of molecules containing at least one -BH₂ or -AlH₂ substituent(s), with the magnitude of such effects being more pronounced in the case of the former. In this regard, we note that introduction of one -BH₂ substituent (as in (H₂B)HAl-H) serves to reduce the resulting Al-H BDE by 37.3 kJ mol^{-1} compared with that of H₂Al-H, while introduction of a single -AlH₂ substituent reduces the BDE by a smaller magnitude $(29.5 \text{ kJ mol}^{-1})$. The results of our computation for such species also indicate a sizable additive effect concerning the introduction of two such substituents, with the BDE of (H₂B)₂Al-H being 66.2 kJ mol⁻¹ lower than that of H₂Al-H (BDE = 354.3 kJ mol⁻¹) and the BDE of (H₂Al)₂Al–H being reduced by 61.0 kJ mol^{-1} compared with that of H₂Al–H. The significantly lower Al-H BDEs of molecules containing either -BH₂ or -AlH₂ substituent(s) may be attributed, at least in part, to the unpaired electron in each of the resulting radicals being delocalised onto either the substituent -BH2 or -AlH₂ groups (refer to the Supporting material for images of the SOMOs of the radicals resulting from the homolytic dissociation of the Al-H bonds of molecules 1-4). The extent of such delocalisation effects can be probed by way of Mulliken spin density calculations. For example, in (H₂B) HAl' (which adopts an almost planar structure, having a H-Al-B angle of 173.1° at the B3LYP/AVTZ level), we compute spin densities (at the ROHF/AVTZ level) of 0.437 for the boron atom and 0.531 for the aluminium atom. In a similar vein, we note that the (H₂B)₂Al radical, which adopts a planar structure with D_{2h} symmetry, is associated with spin densities of 0.194 on each of the substituent boron atoms and 0.607 on the central aluminium atom. Analogous effects, although of smaller magnitude, were also noted in the case of radicals containing at least one -AlH₂ substituent. In this regard, we compute a spin density of 0.140 on the -AlH₂ group of (H₂Al)HAl, while in the case of (H₂Al)₂Al, the substituent aluminium atoms are each associated with spin densities of 0.102. The reduced extent of delocalisation in the aluminiumsubstituted radicals may account, in part, for why these species have higher Al–H BDEs than the comparable $-BH_2$ substituted molecules.

Assessment of DFT methods for the computation of AI–H BDEs

Attention is now turned to considering the performance of a diverse array of lower-cost DFT methods for their ability to compute gas-phase homolytic Al–H BDEs (against the AlHBDE dataset). To assess these methods, we have utilised electronic non-relativistic bottom-of-the-well BDEs (i.e. those obtained according to $BDE_{NR,el} = \Delta SCF + \Delta CCSD + \Delta(T) + \Delta CV$). Table 2 gives the mean absolute deviations (MADs), mean deviations (MDs), largest deviations (LDs; the species that correspond to the largest deviation is given in bold) and the number of outliers (NOs, which constitute the number of species with an absolute deviation from the W2w reference value of ≥ 10 kJ mol⁻¹), in conjunction with both the AVTZ and AVQZ basis sets.

Prior to considering the performance of the functionals within each class, we make the following general points concerning the performance of these methods overall. First, the best-performing methods overall are CAM-B3LYP, M06-L, ω B97M-V and ω B97X-D, which in conjunction with the AVOZ basis set, are associated with MADs of 2.1, 2.3, 2.5 and 2.7 kJ mol⁻¹, respectively. Both CAM-B3LYP and ω B97X-D attain similar LDs of 4.1 and 4.3 kJ mol⁻¹, respectively, whereas wB97M-V attains a slightly higher LD of 7.1 kJ mol^{-1} (Table 2). Second, of the 53 functionals considered in this study, we note that in most of the cases, the use of the larger AVOZ basis set affords better performance than with the smaller AVTZ basis set. Having said that, the magnitude of these performance improvements is generally small for the conventional DFT methods (i.e. for the most part, being less than 1.0 kJ mol^{-1}). As expected, these differences can become more significant for the double-hybrid functional; for example, for the DSD-PBEP86 method, the difference reaches 2.6 kJ mol^{-1} . Of the seven functionals in which we note that using the smaller AVTZ basis set was found to offer better performance, the largest performance improvement was noted in the case of M06-2X (1.9 kJ mol^{-1}). Third, the overwhelming majority of the functionals systematically underestimate the BDEs. In this regard, only ten out of the 53 functionals assessed are associated with positive MDs. This finding, that the selected functionals tend to underestimate the Al-H BDEs, is consistent with previous studies that have demonstrated that DFT methods generally underestimate the BDEs of other bonds, for example, in the case of C-Cl,^[84] B-Cl,^[85] N-Br^[91] and S-F^[83] bonds. Fourth, for approximately 60% of the functionals considered in this study (in conjunction with the AVQZ basis set), their largest deviation was attributed to the computation of the Al-H BDE of molecule 1 (i.e. (BH₂)₂B-H).

We now turn our attention to considering the performance of the functionals within each family. These results will be discussed in the context of those values obtained in conjunction with the AVQZ basis set, not only as for the vast majority of the functionals use of this basis set affords better performance, but also because these values are closer to the basis-set-limit values for each functional. This is particularly true for the double-hybrid methods, which exhibit a substantially slower basis set convergence due to the MP2-like correlation term.^[92]

With the exception of B97-D, the GGA functionals show very poor performance with MADs between 15.0 (BP86) and 33.6 (revPBE) kJ mol⁻¹. B97-D performs considerably better but still results in a large MAD of 6.9 kJ mol^{-1} . The inclusion of the kinetic energy density in the functional form considerably improves the performance. With the exception of three functionals (r^2 SCAN, τ -HCTH and MN12-L) which attain MADs between 11.9 and 20.5 kJ mol^{-1} , the MGGAs attain MADs between 2.3 (M06-L) and 7.6 (B97M-V) $kJ mol^{-1}$. Of the considered HGGA methods, only one functional provides better performance than M06-L, namely the range-separated hybrid CAM-B3LYP with a MAD of merely 2.1 kJ mol^{-1} . This performance is followed by another range-separated hybrid, wB97X-D, which attains a MAD of 2.7 kJ mol^{-1} , respectively. We note that these long-rangecorrected functionals involve 65-100% exact exchange at long-range. The best-performing global hybrids are SOGGA11-X and BH&HLYP, with MADs of 3.3 and 3.8 kJ mol^{-1} , respectively. We note that these two methods involve 40-50% of exact exchange. The other global hybrids show relatively poor performance, with MADs ranging between 4.8 (B3P86) and 23.7 (PBE0) kJ mol⁻¹. The HMGGA methods do not result in better performance relative to the best-performing MGGA and HGGA methods. The best-performing HMGGA methods attain MADs of 2.5 (\u03c6B97M-V), 3.4 (M06), 3.7 (TPSSh) and 4.1 (BMK) $kJ mol^{-1}$. Thus, again we find that a range-separated HMGGA provides better performance than the global HMGGAs. Interestingly, the global HMGGA functionals involve a wide range of exact exchange amounts, ranging between 10% (TPSSh) and 42% (BMK). Somewhat surprisingly, the considered DHDFT methods also do not provide better performance relative to the best-performing MGGA and HGGA methods. The best-performing DHDFT methods are mPW2-PLYP and B2GP-PLYP with the same MAD of 4.1 kJ mol^{-1} . These results suggest that the performance for the Al-H BDEs does not strictly improve along the rungs of Jacob's Ladder.

Finally, it is of interest to examine the effect of adding an empirical dispersion correction on the performance of the DFT methods. For this purpose we consider the pairwise D3 dispersion correction. Table 3 gives an overview of the effect of adding the dispersion corrections for a selection of DFT methods. The tabulated values are the difference in MAD between the dispersion-uncorrected and dispersion-corrected functionals, namely Δ MAD = MAD(DFT) – MAD(DFT-D3). Therefore, a positive Δ MAD value indicates that adding the dispersion correction improves the overall performance of the functional. Inspection of Table 3 reveals that this is indeed the case for practically all of the considered DFT methods. With the exception of revPBE, the improvements

| Table 2. | Performance of various DF | T procedures (| (in conjunction | with the AV | TZ and A | AVQZ bas | is sets) | for the | calculation | of gas-pha | ase |
|-------------|-----------------------------|------------------|-----------------|---------------------------|----------|----------|----------|---------|-------------|------------|-----|
| homolytic / | Al–H bond dissociation ener | gies relative to | W2w values (in | n kJ mol ⁻¹). | | | | | | | |

| Туре ^А | Functional | | A | VTZ | | AVQZ | | | | | |
|-------------------|-----------------------------|------|-------|--------------------|----|------|-------|--------------------|----|--|--|
| | | MAD | MD | LD | NO | MAD | MD | LD | NO | | |
| GGA | revPBE | 34.3 | -34.3 | 46.3 (I) | 18 | 33.6 | -33.6 | 45.I (I) | 18 | | |
| | BPW91 | 31.5 | -31.5 | 44.5 (I) | 18 | 30.8 | -30.8 | 43.4 (I) | 18 | | |
| | PBE | 30.9 | -30.9 | 46.9 (I) | 18 | 30.2 | -30.2 | 45.6 (I) | 18 | | |
| | HCTH407 | 27.4 | -27.4 | 38.8 (I) | 18 | 26.6 | -26.6 | 37.5 (I) | 18 | | |
| | BLYP | 17.6 | -17.6 | 30.2 (I) | 18 | 16.9 | -16.9 | 28.6 (I) | 18 | | |
| | BP86 | 15.5 | -15.5 | 30.3 (I) | 18 | 15.0 | -15.0 | 29.1 (I) | 18 | | |
| | B97-D | 7.6 | -7.4 | 18.7 (I) | 3 | 6.9 | -6.6 | 17.7 (1) | 3 | | |
| MGGA | r ² SCAN | 21.4 | -21.4 | 31.6 (I) | 18 | 20.5 | -20.5 | 30.3 (I) | 18 | | |
| | <i>τ</i> -HCTH | 12.8 | -12.8 | 23.I (I) | 14 | 12.0 | -12.0 | 22.2 (I) | 14 | | |
| | MN12-L | 12.2 | +8.4 | 18.6 (I) | 15 | 11.9 | +8.4 | 21.8 (14) | 13 | | |
| | B97M-V | 7.1 | +1.4 | 19.3 (I) | 3 | 7.6 | +3.8 | 15.5 (1) | 3 | | |
| | VSXC | 6.9 | -5.0 | 25.2 (I) | 5 | 5.9 | -2.6 | 22.1 (I) | 4 | | |
| | MN15-L | 6.2 | +0.8 | 18.5 (I) | 2 | 5.8 | +0.7 | 18.7 (1) | 2 | | |
| | TPSS | 5.8 | -5.8 | 11.7 (1) | 2 | 5.4 | -5.4 | 11.1 (1) | I | | |
| | M06-L | 2.0 | -1.6 | 7.1 (I) | 0 | 2.3 | -2.2 | 7.9 (1) | 0 | | |
| HGGA | PBE0 | 24.5 | -24.5 | 31.5 (5) | 18 | 23.7 | -23.7 | 30.5 (5) | 18 | | |
| | APF | 22.6 | -22.6 | 29.2 (I) | 18 | 21.9 | -21.9 | 28.2 (5) | 18 | | |
| | APF-D | 21.7 | -21.7 | 28.4 (I) | 18 | 21.0 | -21.0 | 27.3 (I) | 18 | | |
| | B3PVV91 | 19.9 | -19.9 | 26.5 (I) | 18 | 19.3 | -19.3 | 25.4 (I) | 18 | | |
| | B97-1 | 13.2 | -13.2 | 20.6 (I) | 16 | 12.4 | -12.4 | 19.4 (I) | 16 | | |
| | ωB97 | 10.4 | +10.4 | 16.5 (18) | 7 | 11.6 | +11.6 | 17.2 (18) | П | | |
| | NI2-SX ^B | 10.9 | -10.6 | 23.7 (I) | 7 | 9.2 | -8.8 | 21.2 (1) | 5 | | |
| | X3LYP | 8.1 | -8.1 | 14.3 (I) | 2 | 7.4 | -7.4 | 12.8 (1) | I | | |
| | B3LYP | 7.9 | -7.9 | 14.2 (I) | 3 | 7.2 | -7.2 | 12.8 (1) | I | | |
| | B3P86 | 5.4 | -5.4 | 13.6 (1) | 2 | 4.8 | -4.8 | 12.5 (1) | 2 | | |
| | ω B97 Χ ^B | 3.1 | +3.1 | 8.5 (I) | 0 | 4.2 | +4.2 | 10.4 (1) | I | | |
| | BH&HLYP | 4.1 | -3.2 | 5.8 (10) | 0 | 3.8 | -2.4 | 5.8 (3) | 0 | | |
| | SOGGAII-X | 3.6 | -2.5 | 8.7 (I) | 0 | 3.3 | -2.1 | 8.0 (I) | 0 | | |
| | ω B97X-D^B | 3.2 | -3.1 | 5.1 (10) | 0 | 2.7 | -2.1 | 4.1 (12) | 0 | | |
| | ωB97X-V ^B | 3.3 | +3.3 | 10.4 (I) | I | 4.1 | +4.1 | 11.7 (1) | I | | |
| | CAM-B3LYP ^B | 2.5 | -2.3 | 4.6 (I3) | 0 | 2.1 | -1.5 | 4.3 (I3) | 0 | | |
| HMGGA | M06-2X | 15.3 | -15.3 | 20.7 (10) | 17 | 17.2 | -17.2 | 22.4 (I0) | 17 | | |
| | MII ^B | 9.6 | +9.6 | 36.6 (2) | 5 | 10.9 | +10.9 | 35.5 (2) | 5 | | |
| | τ -HCTHh | 11.4 | -11.4 | 20.8 (I) | 14 | 10.6 | -10.6 | 19.6 (1) | П | | |
| | PW6B95 | 10.7 | -10.7 | 19.3 (I) | 7 | 10.0 | -10.0 | 18.0 (1) | 4 | | |
| | PW6B95-D3 | 10.6 | -10.6 | 19.2 (I) | 6 | 9.9 | -9.9 | 17.9 (I) | 4 | | |
| | M05-2X | 8.0 | -7.7 | II.3 (5) | 6 | 8.5 | -8.4 | II.6 (5) | 7 | | |
| | M08-HX | 6.4 | +6.4 | II.8 (2) | I | 7.8 | +7.8 | II.5 (2) | 3 | | |

(Continued on next page)

| Table 2. | (Continued) |
|----------|-------------|
|----------|-------------|

| ТуреА | Type ^A Functional | | Α | VTZ | | AVQZ | | | | |
|-------|------------------------------|------|-------|--------------------|----|------|-------|--------------------|----|--|
| | | MAD | MD | LD | NO | MAD | MD | LD | NO | |
| | MN15 | 8.0 | -0.2 | 23.8 (I) | 4 | 5.9 | -1.9 | 21.8 (I) | 3 | |
| | ВМК | 4.4 | -4.4 | 9.3 (5) | 0 | 4.1 | -4.1 | 8.8 (5) | 0 | |
| | TPSSh | 4.2 | -4.2 | 7.3 (I) | 0 | 3.7 | -3.7 | 6.7 (I) | 0 | |
| | M06 | 4.2 | +4.0 | 9.7 (18) | 0 | 3.4 | +3.2 | 8.4 (I 8) | 0 | |
| | ωB97M-V ^B | 3.1 | +2.7 | 8.2 (18) | 0 | 2.5 | +2.2 | 7.I (I8) | 0 | |
| DH | PBE0-DH | 18.4 | -18.4 | 21.2 (5) | 18 | 17.2 | -17.2 | 19.8 (15) | 18 | |
| | PBEQI-DH | 15.0 | -15.0 | 16.1 (18) | 18 | 13.1 | -13.1 | 14.6 (17) | 18 | |
| | DSD-PBEP86 | 9.1 | -9.1 | . (0) | 2 | 6.5 | -6.5 | 8.4 (IO) | 0 | |
| | DSD-PBEB95 | 8.4 | -8.4 | 9.6 (10) | 0 | 5.8 | -5.8 | 7.8 (I7) | 0 | |
| | B2-PLYP | 7.3 | -7.3 | 10.1 (1) | I | 5.5 | -5.5 | 7.8 (I) | 0 | |
| | DSD-BLYP | 7.8 | -7.8 | 9.7 (17) | 0 | 5.4 | -5.4 | 8.0 (I7) | 0 | |
| | PWPB95 | 7.1 | -7.1 | 9.7 (I) | 0 | 5.4 | -5.4 | 7.6 (I) | 0 | |
| | B2GP-PLYP | 6.2 | -6.2 | 8.1 (10) | 0 | 4.1 | -4.1 | 6.3 (I7) | 0 | |
| | mPW2-PLYP | 5.7 | -5.7 | 7.5 (10) | 0 | 4.1 | -4.1 | 5.7 (10) | 0 | |

^AGGA, generalised gradient approximation; MGGA, meta-GGA; HGGA, hybrid-GGA; HMGGA, hybrid-meta-GGA; and DH, double hybrid. ^BRange separated XC functional.

| Table | 3. | Overview | of | the | effect | of | adding | а | D3 | dispersion |
|---------|-----|--------------|-----|------|--------|----|---------|-----|----|------------|
| correct | ion | on the perfo | orm | ance | of the | DF | T metho | ods | • | |

| Туре ^А | Functional | AVTZ | AVQZ |
|-------------------|--------------|------|------|
| GGA | revPBE | 1.4 | 1.4 |
| | PBE | 0.6 | 0.6 |
| | BLYP | 1.0 | 1.0 |
| | BP86 | 0.6 | 0.7 |
| MGGA | TPSS | 0.7 | 0.7 |
| HGGA | PBE0 | 0.5 | 0.5 |
| | B3PW91 | 0.8 | 0.9 |
| | B3LYP | 0.7 | 0.7 |
| HMGGA | PW6B95 | 0.1 | 0.1 |
| | ВМК | 0.0 | -0.I |
| | ωB97M-V | 0.2 | 0.2 |
| DH | B2-PLYP | 0.3 | 0.2 |

The tabulated values are $\Delta MAD = MAD(DFT) - MAD(DFT-D3)$ (in kJ mol⁻¹). A positive ΔMAD value indicates overall improvement in performance upon addition of the D3 dispersion correction.

^AGGA, generalised gradient approximation; MGGA, meta-GGA; HGGA, hybrid-GGA; HMGGA, hybrid-meta-GGA; and DH, double hybrid.

are relatively small and range between 0.1 (PW6B95) and 1.0 (BLYP) kJ mol⁻¹. Nevertheless, for functionals that are capable of sub-chemical accuracy, these corrections are statistically significant.

Conclusion

Using the high-level W2w thermochemical protocol, we have computed a dataset of gas-phase homolytic Al-H BDEs for a set of 18 neutral aluminium hydrides (which we refer to as the AlHBDE dataset). The intention of this study was two-fold. First, we wanted to investigate the magnitude by which substituents can induce variations in the Al-H BDEs. Second, we assess the performance of DFT functionals for their ability to compute accurate Al-H BDEs. In addressing the first aim of this study, we note that the Al-H BDEs of the species in this dataset span a range of 79.2 kJ mol^{-1} , with $(H_2B)_2Al-H$ having the lowest BDE $(288.1 \text{ kJ mol}^{-1})$ and $(H_2N)_2Al-H$ having the largest BDE $(367.3 \text{ kJ mol}^{-1})$. Of the selected substituents, both $-\text{AlH}_2$ and -BH₂ have by far the greatest effect in terms of altering the Al-H BDEs compared with that of the parent molecule H₂Al–H. In fact, when molecules containing at least one of these two substituents are removed from the set, the Al-H BDEs of the remaining 13 molecules span a smaller range of 21.6 kJ mol⁻¹. In terms of the second part of the study, our assessment of a broad range of DFT methods for the computation of Al-H BDEs (relative to the non-relativistic bottomof-the-well W2w reference values) reveals that M06-L and CAM-B3LYP result in the best overall performance with MADs of 2.3 and 2.1 kJ mol⁻¹, respectively. However, it should be noted that CAM-B3LYP is preferable since it results in a significantly smaller deviation of 4.3 kJ mol⁻¹ relative to the largest deviation of M06-L of 7.9 kJ mol $^{-1}$.

Supplementary material

Structural formulae for all aluminium hydrides investigated in the present study are provided in Supplementary Table S1. The geometries (in Cartesian coordinates) of all molecules investigated in this study (obtained at the B3LYP/ AVTZ level of theory) are provided in Supplementary Table S2. In addition, the non-relativistic bottom-of-thewell valence W1w Al–H BDEs, as well as the individual components leading to these values, are provided in Supplementary Table S3. Images of the SOMOs (obtained at the ROHF/AVTZ level of theory) for the radicals arising via the homolytic Al–H dissociation of molecules **1–4** are provided in Supplementary Table S4. Supplementary material is available online.

References

- Galatsis P, Sollogoub M, Sinay P. Diisobutylaluminum hydride. Encyclopedia of Reagents for Organic Synthesis. John Wiley & Sons, Ltd; 2008. doi:10.1002/047084289X.rd245.pub2
- [2] Weiser V, Eisenreich N, Koleczko A, Roth E. On the Oxidation and Combustion of AlH₃ a Potential Fuel for Rocket Propellants and Gas Generators. *Propellants Explos Pyrotech* 2007; 32: 213–221. doi:10.1002/prep.200700022
- [3] Graetz J, Reilly JJ, Yartys VA, Maehlen JP, Bulychev BM, Antonov VE, Tarasov BP, Gabis IE. Aluminum hydride as a hydrogen and energy storage material: Past, present and future. J Alloys Compd 2011; 509: S517–S528. doi:10.1016/j.jallcom.2010.11.115
- [4] Hua TQ, Ahluwalia RK. Alane hydrogen storage for automotive fuel cells – Off-board regeneration processes and efficiencies. *Int J Hydrog Energy* 2011; 36: 15259–15265. doi:10.1016/j.ijhydene. 2011.08.081
- [5] Anders M, Schwarzer A, Brendler E, Pollex R, Schumann E, Sandig-Predzymirska L, Kaiser S, Mertens F. Bis-(triphenylphosphane) Aluminum Hydride: A Simple Way to Provide, Store, and Use Non-Polymerized Alane for Synthesis. *ChemPlusChem* 2021; 86: 1193–1198. doi:10.1002/cplu.202100287
- [6] Wilson KE, Seidner RT, Masamune S. Selective reduction of 2-ene-1,4-diones and 2-en-1-ones with di-i-butylaluminium hydride. *J Chem Soc D* 1970; 213b–214. doi:10.1039/C2970000213B
- [7] Daniewski AR, Wojciechowska W. Synthesis of the corticoid side chain. J Org Chem 1982; 47: 2993–2995. doi:10.1021/jo00136a035
- [8] Lenox RS, Katzenellenbogen JA. Stereoselective method for the synthesis of both olefinic isomers from a single precursor. The Conjugate reduction of α,β-unsaturated epoxides. J Am Chem Soc 1973; 95: 957–959. doi:10.1021/ja00784a073
- [9] Morelli CF, Fornili A, Sironi M, Durì L, Speranza G, Manitto P. Evidence for a nucleophilic anti-attack on the cleaved C(2)–oxygen bond in Cl₂AlH-catalyzed ring-opening of 2-substituted 1,3dioxolanes. Tetrahedron Lett 2005; 46: 1837–1840. doi:10.1016/ j.tetlet.2005.01.108
- [10] Himmel HJ, Klaus C. Photolytically Induced Reaction of Monomeric AlCl with Dihydrogen in a Solid Ar Matrix at 12 K: Generation and Characterization of the Previously Unknown Monomeric Aluminium Hydride ClAlH₂. Z Anorg Allg Chem 2003; 629: 1477–1483. doi:10.1002/zaac.200300055
- [11] Ardis A, Natoli FJU (1974) Thermal Stability of Aluminium Hydride Through Use of Stabilizers, U.S. Patent and Trademark Office (U.S. Patent 3801707A).
- [12] Knight Jr LB, Woodward JR, Kirk TJ, Arrington CA. Electron spin resonance investigations of aluminum hydrides (AlH₂, AlHD, AlD₂), and aluminum hydroxides (Al(OH)₂, and Al(OD)₂) in neon matrixes at 4 K; comparisons with ab initio theoretical calculations. J Phys Chem 1993; 97: 1304–1311. doi:10.1021/ j100109a010
- [13] Pullumbi P, Mijoule C, Manceron L, Bouteiller Y. Aluminium, gallium and indium dihydrides. An IR matrix isolation and ab initio

study. Chem Phys 1994; 185: 13–24. doi:10.1016/0301-0104(94) 00110-3

- [14] Parnis JM, Ozin GA. Photochemical reactions of matrix-isolated aluminum atoms with methane and molecular hydrogen. 3. Structure, bonding and reactivity. J Phys Chem 1989; 93: 1220–1225. doi:10.1021/j100341a012
- [15] Lanzisera DV, Andrews L. Reactions of Laser-Ablated Aluminum Atoms with Ammonia. Infrared Spectra of HAlNH₂, AlNH₂, and HAlNH in Solid Argon. J Phys Chem A 1997; 101: 5082–5089. doi:10.1021/jp970560t
- [16] Himmel H-J, Downs AJ, Greene TM. Thermal and Photochemical Reactions of Aluminum, Gallium, and Indium Atoms (M) in the Presence of Ammonia: Generation and Characterization of the Species M·NH₃, HMNH₂, MNH₂, and H₂MNH₂. J Am Chem Soc 2000; 122: 9793–9807. doi:10.1021/ja001313x
- [17] Gaertner B, Himmel H-J. Structure and Bonding in the Aluminum Radical Species Al·NH₃, HAlNH₂, HAlNH₂·NH₃, and Al(NH₂)₂ Studied by Means of Matrix IR Spectroscopy and Quantum Chemical Calculations. *Inorg Chem* 2002; 41: 2496–2504. doi:10.1021/ic011292n
- [18] Himmel H-J, Downs AJ, Green JC, Greene TM. Compounds featuring a bond between a Group 13 (M) and a Group 15 element (N or P) and with the formulae H_mMNH_n and H_mMPH_n: structural aspects and bonding. *J Chem Soc Dalton Trans* 2001; 535–545. doi:10.1039/b008724f
- [19] Himmel H-J, Downs AJ, Greene TM. Reactions of aluminum, gallium, and indium (M) atoms with phosphine: generation and characterization of the species M·PH₃, HMPH₂, and H₂MPH. *Inorg Chem* 2001; 40: 396–407. doi:10.1021/ic000837v
- [20] Hauge RH, Kauffman JW, Margrave JL. Infrared matrix-isolation studies of the interactions and reactions of Group 3A metal atoms with water. J Am Chem Soc 1980; 102: 6005–6011. doi:10.1021/ ja00539a005
- [21] Zhao J, Wang Q, Yu W, Huang T, Wang X. M–S Multiple Bond in HMSH, H₂MS, and HMS Molecules (M = B, Al, Ga): Matrix Infrared Spectra and Theoretical Calculations. J Phys Chem A 2018; 122: 8626–8635. doi:10.1021/acs.jpca.8b08266
- [22] Dunning Jr TH. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J Chem Phys 1989; 90: 1007–1023. doi:10.1063/1.456153
- [23] Wilson AK, Woon DE, Peterson KA, Dunning Jr TH. Gaussian basis sets for use in correlated molecular calculations. IX. The atoms gallium through krypton. J Chem Phys 1999; 110: 7667–7676. doi:10.1063/1.478678
- [24] Karton A. A computational chemist's guide to accurate thermochemistry for organic molecules. WIREs Comput Mol Sci 2016; 6: 292–310. doi:10.1002/wcms.1249
- [25] Douglas M, Kroll NM. Quantum electrodynamical corrections to the fine structure of helium. Ann Phys 1974; 82: 89–155. doi:10.1016/0003-4916(74)90333-9
- [26] Hess BA. Applicability of the no-pair equation with free-particle projection operators to atomic and molecular structure calculations. *Phys Rev A* 1985; 32: 756–763. doi:10.1103/physreva. 32.756
- [27] Merrick JP, Moran D, Radom L. An evaluation of harmonic vibrational frequency scale factors. J Phys Chem A 2007; 111: 11683–11700. doi:10.1021/jp073974n
- [28] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 1988; 37: 785–789. doi:10.1103/physrevb. 37.785
- [29] Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A* 1988; 38: 3098–3100. doi:10.1103/physreva.38.3098
- [30] Grimme S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J Comput Chem 2006; 27: 1787–1799. doi:10.1002/jcc.20495
- [31] Boese AD, Handy NC. A new parametrization of exchangecorrelation generalized gradient approximation functionals. *J Chem Phys* 2001; 114: 5497–5503. doi:10.1063/1.1347371
- [32] Perdew JP, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple. *Phys Rev Lett* 1996; 77: 3865–3868. doi:10.1103/physrevlett.77.3865

- [33] Ernzerhof M, Perdew JP. Generalized gradient approximation to the angle- and system-averaged exchange hole. *J Chem Phys* 1998; 109: 3313–3320. doi:10.1063/1.476928
- [34] Perdew JP. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys Rev B* 1986; 33: 8822–8824. doi:10.1103/physrevb.33.8822
- [35] Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys Rev B* 1992; 46: 6671–6687. doi:10.1103/physrevb.46.6671
- [36] Zhao Y, Truhlar DG. A new local density functional for maingroup thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. J Chem Phys 2006; 125: 194101. doi:10.1063/1.2370993
- [37] Tao J, Perdew JP, Staroverov VN, Scuseria GE. Climbing the Density Functional Ladder: Nonempirical Meta–Generalized Gradient Approximation Designed for Molecules and Solids. *Phys Rev Lett* 2003; 91: 146401. doi:10.1103/physrevlett.91.146401
- [38] Boese AD, Handy NC. New exchange-correlation density functionals: The role of the kinetic-energy density. J Chem Phys 2002; 116: 9559–9569. doi:10.1063/1.1476309
- [39] van Voorhis T, Scuseria GE. A novel form for the exchangecorrelation energy functional. J Chem Phys 1998; 109: 400–410. doi:10.1063/1.476577
- [40] Peverati R, Truhlar DG. M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics. J Phys Chem Lett 2012; 3: 117–124. doi:10.1021/jz201525m
- [41] Peverati R, Truhlar DG. An improved and broadly accurate local approximation to the exchange–correlation density functional: The MN12-L functional for electronic structure calculations in chemistry and physics. *Phys Chem Chem Phys* 2012; 14: 13171–13174. doi:10.1039/c2cp42025b
- [42] Yu HS, He X, Li SL, Truhlar DG. MN15: A Kohn–Sham globalhybrid exchange–correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *Chem Sci* 2016; 7: 5032–5051. doi:10.1039/c6sc00705h
- [43] Furness JW, Kaplan AD, Ning J, Perdew JP, Sun J. Accurate and numerically efficient r²SCAN meta-generalized gradient approximation. J Phys Chem Lett 2020; 11: 8208–8215. doi:10.1021/acs. jpclett.0c02405
- [44] Mardirossian N, Head-Gordon M. Mapping the genome of metageneralized gradient approximation density functionals: The search for B97M-V. J Chem Phys 2015; 142: 074111. doi:10.1063/1. 4907719
- [45] Becke AD. A new mixing of Hartree–Fock and local densityfunctional theories. J Chem Phys 1993; 98: 1372–1377. doi:10.1063/1.464304
- [46] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 1993; 98: 5648–5652. doi:10.1063/ 1.464913
- [47] Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J Phys Chem 1994; 98: 11623–11627. doi:10.1021/j100096a001
- [48] Adamo C, Barone V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. J Chem Phys 1999; 110: 6158–6170. doi:10.1063/1.478522
- [49] Hamprecht FA, Cohen AJ, Tozer DJ, Handy NC. Development and assessment of new exchange-correlation functionals. J Chem Phys 1998; 109: 6264–6271. doi:10.1063/1.477267
- [50] Xu X, Zhang Q, Muller RP, Goddard WA. An extended hybrid density functional (X3LYP) with improved descriptions of nonbond interactions and thermodynamic properties of molecular systems. J Chem Phys 2005; 122: 014105. doi:10.1063/1. 1812257
- [51] Peverati R, Truhlar DG. Communication: A global hybrid generalized gradient approximation to the exchange-correlation functional that satisfies the second-order density-gradient constraint and has broad applicability in chemistry. *J Chem Phys* 2011; 135: 191102. doi:10.1063/1.3663871

- [52] Austin A, Petersson GA, Frisch MJ, Dobek FJ, Scalmani G, Throssell K. A Density Functional with Spherical Atom Dispersion Terms. J Chem Theory Comput 2012; 8: 4989–5007. doi:10.1021/ct300778e
- [53] Chai J-D, Head-Gordon M. Systematic optimization of long-range corrected hybrid density functionals. J Chem Phys 2008; 128: 084106. doi:10.1063/1.2834918
- [54] Mardirossian N, Head-Gordon M. ωB97X-V: A 10-parameter, range-separated hybrid, generalized gradient approximation density functional with nonlocal correlation, designed by a survivalof-the-fittest strategy. *Phys Chem Chem Phys* 2014; 16: 9904–99024. doi:10.1039/C3CP54374A
- [55] Peverati R, Truhlar DG. Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics. *Phys Chem Chem Phys* 2012; 14: 16187–16191. doi:10.1039/c2cp42576a
- [56] Yanai T, Tew DP, Handy NC. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem Phys Lett* 2004; 393: 51–57. doi:10.1016/j.cplett.2004.06.011
- [57] Zhao Y, Schultz NE, Truhlar DG. Exchange-correlation functional with broad accuracy for metallic and nonmetallic compounds, kinetics, and noncovalent interactions. J Chem Phys 2005; 123: 161103. doi:10.1063/1.2126975
- [58] Zhao Y, Schultz NE, Truhlar DG. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. J Chem Theory Comput 2006; 2: 364–382. doi:10.1021/ct0502763
- [59] Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor Chem Acc* 2008; 120: 215–241. doi:10.1007/s00214-007-0310-x
- [60] Zhao Y, Truhlar DG. Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. J Chem Theory Comput 2008; 4: 1849–1868. doi:10.1021/ct800246v
- [61] Boese AD, Martin JML. Development of density functionals for thermochemical kinetics. J Chem Phys 2004; 121: 3405–3416. doi:10.1063/1.1774975
- [62] Staroverov VN, Scuseria GE, Tao J, Perdew JP. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. J Chem Phys 2003; 119: 12129–12137. doi:10.1063/1.1626543
- [63] Zhao Y, Truhlar DG. Design of Density Functionals That Are Broadly Accurate for Thermochemistry, Thermochemical Kinetics, and Nonbonded Interactions. J Phys Chem A 2005; 109: 5656–5667. doi:10.1021/jp050536c
- [64] Peverati R, Truhlar DG. Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation. J Phys Chem Lett 2011; 2: 2810–2817. doi:10.1021/jz201170d
- [65] Mardirossian N, Head-Gordon M. ωB97M-V: A combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. *J Chem Phys* 2016; 144: 214110. doi:10.1063/1.4952647
- [66] Grimme S. Semiempirical hybrid density functional with perturbative second-order correlation. J Chem Phys 2006; 124: 034108. doi:10.1063/1.2148954
- [67] Schwabe T, Grimme S. Towards chemical accuracy for the thermodynamics of large molecules: new hybrid density functionals including non-local correlation effects. *Phys Chem Chem Phys* 2006; 8: 4398–4401. doi:10.1039/b608478h
- [68] Karton A, Tarnopolsky A, Lamère JF, Schatz GC, Martin JML. Highly Accurate First-Principles Benchmark Data Sets for the Parametrization and Validation of Density Functional and Other Approximate Methods. Derivation of a Robust, Generally Applicable, Double-Hybrid Functional for Thermochemistry and Thermochemical. J Phys Chem A 2008; 112: 12868–12886. doi:10.1021/jp801805p
- [69] Kozuch S, Gruzman D, Martin JML. DSD-BLYP: A General Purpose Double Hybrid Density Functional Including Spin Component Scaling and Dispersion Correction. J Phys Chem C 2010; 114: 20801–20808. doi:10.1021/JP1070852

- [70] Goerigk L, Grimme S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals – Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. J Chem Theory Comput 2011; 7: 291–309. doi:10.1021/ct100466k
- [71] Kozuch S, Martin JML. Spin-component-scaled double hybrids: An extensive search for the best fifth-rung functionals blending DFT and perturbation theory. J Comput Chem 2013; 34: 2327–2344. doi:10.1002/jcc.23391
- [72] Kozuch S, Martin JML. DSD-PBEP86: in search of the best doublehybrid DFT with spin-component scaled MP2 and dispersion corrections. *Phys Chem Chem Phys* 2011; 13: 20104–20107. doi:10.1039/c1cp22592h
- [73] Brémond E, Adamo C. Seeking for parameter-free double-hybrid functionals: The PBE0-DH model. J Chem Phys 2011; 135: 024106. doi:10.1063/1.3604569
- [74] Brémond É, Sancho-García JC, Pérez-Jiménez ÁJ, Adamo C. Communication: Double-hybrid functionals from adiabaticconnection: The QIDH model. J Chem Phys 2014; 141: 031101. doi:10.1063/1.4890314
- [75] Grimme S, Antony J, Ehrlich S, Krieg H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys* 2010; 132: 154104. doi:10.1063/1.3382344
- [76] Grimme S, Ehrlich S, Goerigk L. Effect of the damping function in dispersion corrected density functional theory. J Comput Chem 2011; 32: 1456–1465. doi:10.1002/jcc.21759
- [77] Becke AD, Johnson ER. A density-functional model of the dispersion interaction. J Chem Phys 2005; 123: 154101. doi:10.1063/1. 2065267
- [78] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, et al. Gaussian 16, Revision C.01. Wallingford, CT: Gaussian, Inc.; 2009.
- [79] Neese F. The ORCA program system. WIREs Comput Mol Sci 2012;2: 73–78. doi:10.1002/wcms.81
- [80] Neese F. Software update: the ORCA program system, version 4.0. WIREs Comput Mol Sci 2018; 8: e1327. doi:10.1002/wcms.1327
- [81] Neese F, Wennmohs F, Becker U, Riplinger C. The ORCA quantum chemistry program package. J Chem Phys 2020; 152: 224108. doi:10.1063/5.0004608

- [82] Karton A, Rabinovich E, Martin JML, Ruscic B. W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions. J Chem Phys 2006; 125: 144108. doi:10.1063/1.2348881
- [83] O'Reilly RJ, Balanay MP. A quantum chemical study of the effect of substituents in governing the strength of the S–F bonds of sulfenyl-type fluorides toward homolytic dissociation and fluorine atom transfer. *Chem Data Collect* 2019; 20: 100186. doi:10.1016/ j.cdc.2019.100186
- [84] Garifullina A, Mahboob A, O'Reilly RJ. A dataset of homolytic C–Cl bond dissociation energies obtained by means of W1w theory. *Chem Data Collect* 2016; 3–4: 21–25. doi:10.1016/j.cdc. 2016.07.003
- [85] Lu W, O'Reilly RJ. Homolytic B–Cl bond dissociation energies of chloroborane-type molecules. *Mong J Chem* 2022; 23: 9–18. doi:10.5564/mjc.v23i49.2016
- [86] Karton A, Sylvetsky N, Martin JML. W4-17: A diverse and highconfidence dataset of atomization energies for benchmarking high-level electronic structure methods. J Comput Chem 2017; 38: 2063–2075. doi:10.1002/jcc.24854
- [87] Karton A, Daon S, Martin JML. W4-11: A high-confidence benchmark dataset for computational thermochemistry derived from first-principles W4 data. *Chem Phys Lett* 2011; 510: 165–178. doi:10.1016/j.cplett.2011.05.007
- [88] Chan B. How to computationally calculate thermochemical properties objectively, accurately, and as economically as possible. *Pure Appl Chem* 2017; 89: 699–713. doi:10.1515/pac-2016-1116
- [89] Karton A. Chapter Three Quantum Mechanical Thermochemical Predictions 100 years after the Schrödinger Equation. Annu Rep Comput Chem 2022; 18: 123–166. doi:10.1016/bs.arcc.2022. 09.003
- [90] Menon AS, Henry DJ, Bally T, Radom L. Effect of substituents on the stabilities of multiply-substituted carbon-centered radicals. Org Biomol Chem 2011; 9: 3636–3657. doi:10.1039/ C10B05196B
- [91] O'Reilly RJ, Karton A. A dataset of highly accurate homolytic N-Br bond dissociation energies obtained by Means of W2 theory. *Int J Quantum Chem* 2016; 116: 52–60. doi:10.1002/qua.25024
- [92] Karton A, Martin JML. Basis set convergence of explicitly correlated double-hybrid density functional theory calculations. *J Chem Phys* 2011; 135: 144119. doi:10.1063/1.3647980

Data availability. The data that support the findings of this study are available in the supplementary material of this article and from the corresponding authors upon reasonable request.

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