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# N—H and N—Cl Homolytic Bond Dissociation Energies and Radical Stabilization Energies: An Assessment of Theoretical Procedures Through Comparison With Benchmark-Quality W2w Data

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**ABSTRACT:** The performance of a large variety of contemporary density functional theory (DFT), double-hybrid DFT, and high-level Gaussian-*n* (*Gn*) procedures has been evaluated for the calculation of bond dissociation energies (BDEs) and radical stabilization energies (RSEs) associated with N—X bonds (*X* = H, Cl). The chosen set of 62 N—X systems (31 N—H and 31 N—Cl) span a wide range of biologically relevant species. As reference values, we used benchmark-quality W2w data that we recently obtained as part of a systematic thermochemical study of substituent effects in these systems. Of the *Gn* schemes, the modified G4 procedures (G4-5H and G4(MP2)-6X) perform somewhat better than the corresponding standard G4 procedures for the N—X BDEs of these systems. For the N—H RSEs, G3X, G3X(MP2), G3X(MP2)-RAD, G4-5H, and G4(MP2)-6X emerge as excellent performers, with mean absolute deviations (MADs) from the benchmark W2w values of 0.9–1.4 kJ mol<sup>-1</sup>. However, for the N—Cl RSEs, G4 is the best performer, with an MAD of 1.7 kJ mol<sup>-1</sup>. The BDEs of both N—H and N—Cl bonds represent a challenge for DFT procedures. In particular, only a handful of functionals (namely, B3P86, M05-2X, M06-2X, and ROB2-PLYP) perform well, with MADs ≤ 4.5 kJ mol<sup>-1</sup> for both bond types. Nearly all of the considered DFT procedures perform signifi-

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cantly better for the computation of RSEs, due to a significantly larger degree of error cancellation compared with the BDEs. For the RSEs, BH&HLYP, M05-2X, M06, M06-2X, BMK, PBE0, B2-PLYP, B2GP-PLYP, B2T-PLYP, and ROB2-PLYP are the best performers, with MADs  $\leq 4.2$  kJ mol<sup>-1</sup>. Reliable values of N—H and N—Cl BDEs may be obtained by using the RSEs calculated by these functionals in conjunction with a thermochemical cycle involving an experimental (or high-level theoretical) BDE for the H<sub>2</sub>N—H or H<sub>2</sub>N—Cl bond. ©2011 Wiley Periodicals, Inc. *Int J Quantum Chem* 112: 1862–1878, 2012

**Key words:** density functional theory; Gaussian-*n* theory; nitrogen-centered radicals; bond dissociation energy; radical stabilization energy

## 1. Introduction

The N—Cl bond is a key functional group in organic and biological chemistry. For example, the nitrogen-containing functional groups of proteins and nucleobases are chlorinated *in vivo* by myeloperoxidase-derived hypochlorous acid. The nitrogen-centered radicals, formed by subsequent homolysis of the N—Cl bonds, are key intermediates in radical-mediated oxidative DNA damage, for example, covalent binding of the nucleobases to proteins or to other nucleobases [1]. For example, homolysis of the N—Cl bond in *N*-chloroadenine has been shown to initiate uridine dimer formation [2]. Nitrogen-centered radicals are also of synthetic importance [3], where they have been used in a number of cyclization processes [4] and homolytic amination reactions of aromatic molecules [4]. From an industrial perspective, *N*-chloro derivatives of amides, lactams, carbamates, and imides have been shown to be effective initiators for the metal-catalyzed living radical polymerization of methacrylates [5].

The homolytic bond dissociation energy (BDE) of the N—X bond (X = H, Cl) in RR'N—X is given by the energy change for the reaction:



Often one is interested not only in absolute BDEs but also in relative BDEs (e.g., the BDEs for RR'N—H and RR'N—Cl relative to those for the parent molecules NH<sub>3</sub> and NH<sub>2</sub>Cl, respectively). We have defined the relative BDEs for N—H and N—Cl species according to Eqs. (2) and (3), and refer to these as radical stabilization energies (RSEs):



N—H BDEs and RSEs have been the subject of numerous previous density functional theory

(DFT) and other theoretical investigations (see, e.g., Ref. [6] and references therein). However, these studies considered a relatively small number of exchange-correlation functionals and/or were limited to a small number of systems. As far as we are aware, N—Cl bonds have not been the subject of a benchmark DFT evaluation study. We have recently carried out a systematic study [7] of the effect of substituents on N—X homolytic BDEs and RSEs by means of the high-level *ab initio* W2w thermochemical protocol [8] for a diverse set of 31 N—H and 31 N—Cl species. The chosen set included species of biological, synthetic, and industrial importance. In this study, we use these W2w reference values to evaluate the performance of a variety of DFT procedures, including recently developed double-hybrid DFT (DHDFT) methods, as well as a number of composite thermochemical Gaussian-*n* (*Gn*) procedures.

## 2. Computational Methods

The DFT and *Gn* calculations were carried out with the Gaussian 09 program suite [9], with the exception of the DHDFT calculations, which were carried out with Gaussian 03 [10]. Unless otherwise noted, DFT calculations were performed using unrestricted procedures.

The DFT exchange-correlation functionals considered in this study (ordered by their rung on Jacob's ladder [11]) are: the local density approximation (LDA) SVWN5 [12]; variants of the pure generalized gradient approximation (GGA): BLYP [13, 14], BP86 [13, 15], PBE [16], HCTH407 [17], and B97-D [18]; the meta-GGAs (MGGAs): VSXC [19], TPSS [20],  $\tau$ -HCTH [21], and M06-L [22]; the hybrid-GGAs: PBE0 [23], B3PW91 [24, 25], B3P86 [15, 25], B97-1 [26], B98 [27], TPSSh [28], B3LYP [14, 25, 29], X3LYP [30], BH&HLYP [31],  $\omega$ B97 [32],  $\omega$ B97X [32], and  $\omega$ B97X-D [33]; the hybrid

meta-GGAs (HMGGAs): B1B95 [13, 34], BMK [35],  $\tau$ -HCTHh [21], M05 [36], M05-2X [37], M06 [38], M06-2X [38], and M06-HF [38]; and the DHDFT procedures: B2-PLYP [39], B2T-PLYP [40], B2K-PLYP [40], B2GP-PLYP [41], UB2-PLYP-09 [42], and ROB2-PLYP [42].

The performance of the DFT procedures with respect to basis set convergence was also investigated and was carried out in conjunction with the following basis sets: (i) the 6-31G(d), 6-31+G(d,p), 6-31+G(2df,p), 6-311+G(d,p), 6-311+G(2df,p), and 6-311+G(3df,2p) basis sets of Pople and co-workers and (ii) the  $A'VnZ$  ( $n = D, T, Q$ ) correlation-consistent basis sets of Dunning and co-workers (where  $A'VnZ$  indicates the combination of the regular cc-pVnZ basis sets [43] on H with aug-cc-pVnZ basis sets [44] on first-row atoms, and aug-cc-pV( $n+d$ )Z basis sets [45] on Cl). For the DHDFT procedures, we carried out all-electron (AE) calculations with the  $A'CVQZ$  core-valence basis set (where  $A'CVQZ$  denotes the combination of the regular cc-pVQZ basis set on H with the aug-cc-pwCVQZ core-valence weighted basis set [46] on all other atoms).

In addition, the performance of the composite thermochemical  $Gn$  procedures G3X [47], G3X(MP2) [48], G3X(MP2)-RAD [49], G4 [50], G4-5H [51], G4(MP2) [52], and G4(MP2)-6X [53] was also assessed.

Finally, we note that the geometries used for the DFT and  $Gn$  calculations throughout are the same as those used for the W2w reference energies (i.e., optimized at the B3LYP/ $A'$ VTZ level of theory).

## 3. Results and Discussion

### 3.1. W2w REFERENCE VALUES

Benchmark reference data have been taken from our previous study [7] and were obtained by means of W2w theory [8]. W2w represents a layered extrapolation to the relativistic, AE CCSD(T) basis-set limit and can achieve an accuracy in the  $\text{kJ mol}^{-1}$  range for molecules whose wave functions are dominated by dynamical correlation [54]. For a rigorous comparison with the DFT data, secondary effects that are not explicitly included in the DFT calculations, such as relativistic and zero-point vibrational energy (ZPVE) corrections, are excluded from the W2w reference

values. The resultant AE, nonrelativistic, vibrationless W2w reference BDEs are given in Table I.

The percentage of the total atomization energy accounted for by parenthetical connected triple excitations,  $\%TAE_c(T)$ , has been shown to be a reliable energy-based diagnostic for the importance of nondynamical correlation effects [55]. It has been suggested that  $\%TAE_c(T) < 2\%$  indicates systems that are dominated by dynamical correlation, while  $2\% < \%TAE_c(T) < 5\%$  indicates systems that include mild nondynamical correlation. The  $\%TAE_c(T)$  values for the systems considered in this study (Table I) indicate that they are either dominated by dynamical correlation or exhibit mild nondynamical correlation effects. In particular, the  $\%TAE_c(T)$  for the  $RR'N-H$ ,  $RR'N-Cl$ , and  $RR'N\cdot$  systems lie in the ranges 0.7–3.1%, 1.3–4.2%, and 0.6–3.7%, respectively.

### 3.2. PERFORMANCE OF DFT PROCEDURES FOR THE N–H AND N–Cl BDEs

#### 3.2.1. Standard Density Functional Theory Procedures

We begin by comparing the performance of a variety of DFT procedures in predicting the BDEs for the 62 N–X bonds considered in this work (31 N–H and 31 N–Cl bonds). The mean absolute deviations (MADs), mean deviations (MDs), largest deviations (LDs) in absolute value, and the number of systems with a deviation from the benchmark W2w values larger than  $10 \text{ kJ mol}^{-1}$  (number of outliers, NO) for the DFT procedures are presented in Table II. We make the following general observations: (i) With very few exceptions (most notably SVWN5 and M06-HF), all the functionals systematically underestimate the N–X BDEs (i.e., MDs are nearly always negative); (ii) of the pure DFT functionals, only the empirical semilocal BP86 performs acceptably well for both N–H and N–Cl bonds, with an overall MAD of  $9.3 \text{ kJ mol}^{-1}$ ; and (iii) the HMGGAs M05-2X, M06-2X, and BMK show good performance for both bond types. For the N–H BDEs, M06-2X gives the best performance (MAD =  $3.3 \text{ kJ mol}^{-1}$ ), while the M05-2X procedure is a close second, with an MAD of  $3.8 \text{ kJ mol}^{-1}$ . For the N–Cl BDEs, the M06 and BMK functionals offer the best performance, with MADs of 2.8 and  $3.0 \text{ kJ mol}^{-1}$ , respectively.

The only LDA functional subjected to assessment, namely SVWN5, substantially overestimates the BDEs of both bond types, and leads to large

TABLE I

Vibrationless, nonrelativistic W2w reference values for N—X bond dissociation energies (BDEs,  $\text{kJ mol}^{-1}$ ) and radical stabilization energies ( $\text{RSE}_{\text{NX}}$ ,  $\text{kJ mol}^{-1}$ ),  $\%TAE_e[\text{T}]$  diagnostics, and  $\langle S^2 \rangle$  values.

Structure	N—X BDE		$\text{RSE}_{\text{NX}}$		$\%TAE_e[\text{T}]$			$\langle S^2 \rangle^a$
	X = H	X = Cl	X = H	X = Cl	RR'NH	RR'NCI	RR'N·	
NH <sub>2</sub> X	483.6	274.7	0.0	0.0	1.3	2.8	1.4	0.760
NH <sub>3</sub> X <sup>+</sup>	560.6	291.4	-77.0	-16.7	0.7	1.3	0.6	0.761
MeNHX	451.4	264.7	32.2	10.0	1.3	2.0	1.3	0.762
MeNH <sub>2</sub> X <sup>+</sup>	501.3	251.0	-17.7	23.7	0.8	1.3	0.9	0.765
Me <sub>2</sub> NX	427.1	254.3	56.5	20.4	1.3	1.8	1.3	0.764
Me <sub>2</sub> NH <sub>2</sub> X <sup>+</sup>	462.4	226.2	21.2	48.5	0.9	1.3	1.0	0.767
H <sub>2</sub> C=CHNHX	403.5	201.1	80.1	73.6	1.7	2.3	1.9	0.959
F <sub>3</sub> CNHX	491.9	267.0	-8.3	7.7	2.5	3.2	2.8	0.760
ImidazoleNX	436.0	217.0	47.6	57.6	2.5	3.1	2.8	0.932
PyrroleNX	431.9	216.1	51.7	58.6	2.1	2.6	2.3	0.884
(XNH)CH <sub>2</sub> CO <sub>2</sub> H	456.7	261.3	26.9	13.4	2.2	2.7	2.3	0.762
HCONHX	511.4	288.3	-27.8	-13.6	2.3	3.2	2.8	0.944
MeCONHX	503.8	284.7	-20.2	-10.0	1.9	2.5	2.2	0.881
FCONHX	516.6	281.2	-33.0	-6.6	2.6	3.5	3.3	0.776
(NC)CONHX	521.1	290.9	-37.5	-16.2	3.1	3.8	3.7	1.073
HCONXMe	489.8	281.1	-6.2	-6.5	2.0	2.5	2.2	0.886
UreaN—X	490.0	275.9	-6.3	-1.2	2.3	3.0	2.7	0.777
(XNH)CH=NH	456.6	242.2	27.0	32.5	2.1	2.9	2.7	0.988
(XNH)(H <sub>2</sub> N)C=NH	457.5	248.1	26.1	26.6	2.2	2.9	2.7	0.968
(CHO) <sub>2</sub> NX	535.2	311.5	-51.6	-36.8	2.7	3.3	3.1	0.884
H <sub>2</sub> C=NX	401.8	234.4	81.8	40.3	1.9	3.1	2.2	0.930
MeCH=NX	407.6	240.5	76.0	34.2	1.6	2.3	1.7	0.903
(H <sub>2</sub> N)CH=NX	436.5	269.9	47.1	4.8	2.1	3.0	2.3	0.861
H(OH)C=NX	449.1	269.3	34.5	5.4	2.3	3.4	2.6	0.857
FCH=NX	455.7	258.4	27.9	16.2	2.5	3.7	2.9	0.886
(NC)CH=NX	423.2	242.4	60.5	32.3	3.0	3.9	3.3	1.177
Me <sub>2</sub> C=NX	407.8	241.8	75.8	32.9	1.6	2.0	1.6	0.885
Me(OH)C=NX	444.5	270.6	39.2	4.1	2.0	2.6	2.1	0.837
(H <sub>2</sub> N)C=NX	443.3	274.4	40.3	0.3	2.2	2.9	2.4	0.812
F <sub>2</sub> C=NX	475.2	260.6	8.4	14.1	3.0	4.2	3.6	0.841
F(OH)C=NX	474.9	273.0	8.7	1.7	2.7	3.8	3.1	0.813

<sup>a</sup> Obtained for RR'N· at the UHF/aug'-cc-pVTZ level of theory.

MADs of 41.4 and 93.5  $\text{kJ mol}^{-1}$  for X = H and Cl, respectively. Climbing up Jacob's ladder to include the reduced density gradient leads to a systematic underestimation of the N—H BDEs by all the considered GGAs, with BP86 attaining the smallest MAD (9.9  $\text{kJ mol}^{-1}$ , roughly half of that of the other GGAs). For the N—Cl bonds, although B97-D, BLYP, and HCTH407 systematically underestimate the BDEs, BP86 and PBE tend to overestimate them. The tendency of PBE to underbind the N—H bonds and to overbind the N—Cl bonds may be attributed to the different inconsistencies between the atomic and molecular energies observed for H and Cl for this functional [56].

Inclusion of the kinetic energy density results in the meta-GGA (MGGA) procedures. Without exception, the considered meta-GGAs underestimate the N—X BDEs of both bond types. For the N—H BDEs, all of the MGGAs perform relatively poorly, with MADs in the range of 19.5–25.7  $\text{kJ mol}^{-1}$ . For the N—Cl BDEs, the MADs lie in the range of 7.7–22.9  $\text{kJ mol}^{-1}$ , with M06-L giving the best performance. Alternatively, mixing of exact exchange results in the hybrid-GGA (HGGA) procedures. Again, all the hybrid-GGA procedures (with the exception of B3P86) systematically underestimate the BDEs, with MADs in the range of 3.3–21.0  $\text{kJ mol}^{-1}$  for the N—H species and 4.1–

TABLE II

Statistical analysis for the performance of unrestricted DFT procedures (in conjunction with the 6-311+G(3df,2p) basis set) for the calculation of N–X BDEs (X = H, Cl) relative to W2w reference values ( $\text{kJ mol}^{-1}$ ).

Method	Type <sup>a</sup>	N–H BDE				N–Cl BDE			
		MAD <sup>b</sup>	MD <sup>b</sup>	LD <sup>b</sup>	NO <sup>b</sup>	MAD	MD	LD	NO
SVWN5	LDA	41.4	41.4	60.3	30	93.5	93.5	110.6	31
B97-D	GGA	17.4	-17.4	30.5	29	24.2	-24.2	41.0	31
BLYP	GGA	24.6	-24.6	42.1	31	23.7	-23.7	44.3	30
HCTH407	GGA	19.3	-19.3	40.7	29	18.1	-18.1	47.4	24
PBE	GGA	19.2	-19.2	41.0	27	12.0	9.9	21.9	17
BP86	GGA	9.9	-9.6	29.9	11	8.6	2.5	22.2	13
VSXC	MGGA	19.5	-19.5	37.3	30	22.9	-22.9	42.9	30
$\tau$ -HCTH	MGGA	20.8	-20.8	40.0	30	13.7	-13.7	40.2	18
TPSS	MGGA	20.7	-20.7	33.4	30	11.6	-11.6	31.0	15
M06-L	MGGA	25.7	-25.7	43.5	31	7.7	-7.0	31.1	9
BH&HLYP	HGGA	21.0	-21.0	26.1	31	53.0	-53.0	61.2	31
B3LYP	HGGA	14.8	-14.8	28.3	28	26.9	-26.9	43.4	31
X3LYP	HGGA	14.4	-14.4	27.8	28	25.0	-25.0	41.1	31
TPSSh	HGGA	18.4	-18.4	29.5	29	17.3	-17.3	34.9	29
B3PW91	HGGA	15.9	-15.9	31.3	29	14.6	-14.6	35.1	26
B98	HGGA	15.2	-15.2	27.8	29	12.6	-12.6	29.3	21
$\omega$ B97	HGGA	11.2	-11.2	18.0	22	11.7	-11.7	19.8	20
$\omega$ B97X	HGGA	10.1	-10.1	18.9	18	10.3	-10.3	21.0	17
$\omega$ B97X-D	HGGA	8.3	-8.3	18.3	4	8.5	-8.5	21.8	8
PBE0	HGGA	17.2	-17.2	32.0	29	8.2	-8.1	27.7	8
B97-1	HGGA	18.2	-18.2	31.1	30	7.5	-7.2	24.4	7
B3P86	HGGA	3.3	-0.1	16.2	1	4.1	-2.5	23.0	3
M06-HF	HMGGA	16.8	16.8	31.0	28	22.2	22.2	38.2	27
M05	HMGGA	13.9	-13.9	28.6	26	13.3	-13.3	34.5	20
$\tau$ -HCTHh	HMGGA	18.9	-18.9	34.1	30	7.1	-6.8	26.4	7
B1B95	HMGGA	10.4	-10.4	26.5	15	5.0	-4.2	25.1	3
M06-2X	HMGGA	3.3	-1.9	8.0	0	4.5	4.4	11.9	4
M05-2X	HMGGA	3.8	-2.6	8.0	0	3.6	-2.2	7.5	0
BMK	HMGGA	6.3	-6.3	18.7	4	3.0	-2.0	17.1	2
M06	HMGGA	9.5	-9.5	24.2	7	2.8	-0.5	13.8	1

<sup>a</sup>LDA: local density approximation, GGA: generalized gradient approximation, HGGA: hybrid-GGA, MGGA: meta-GGA, HMGGA: hybrid-meta-GGA.

<sup>b</sup>MAD: mean absolute deviation, MD: mean deviation, LD: largest deviation (in absolute value), NO: number of outliers (defined as errors greater than  $10 \text{ kJ mol}^{-1}$  in absolute value).

$53.0 \text{ kJ mol}^{-1}$  for the N–Cl derivatives. It is instructive to compare the performance of the three hybrid functionals B3LYP, B3PW91, and B3P86, which combine Becke's three-parameter exchange functional with different gradient-corrected correlation functionals. For the N–H BDEs, these functionals give MADs of 14.8, 15.9, and  $3.3 \text{ kJ mol}^{-1}$ , respectively, while for the N–Cl BDEs they give MADs of 26.9, 14.6, and  $4.1 \text{ kJ mol}^{-1}$ , respectively. Thus, B3P86 is clearly superior to the other two functionals, having significantly smaller MADs. Note also that the num-

ber of species with deviations greater than  $10 \text{ kJ mol}^{-1}$  approaches the maximum possible value of 31 for B3LYP and B3PW91, while for B3P86 there is just one outlier in the set of N–H bonds and three outliers in the set of N–Cl bonds. In addition, B3P86 exhibits the desirable behavior of not being biased toward underestimation or overestimation of the BDEs, as demonstrated by MDs of  $-0.1$  (N–H) and  $-2.5$  (N–Cl)  $\text{kJ mol}^{-1}$ , respectively. This behavior parallels the better performance of BP86 compared with BLYP for the GGA functionals.



TABLE III

Statistical analysis for the performance of unrestricted (U) and restricted (R) formalisms for a subset of DFT procedures from Table II (in conjunction with the 6-311+G(3df,2p) basis set) for the calculation of N–X BDEs (X = H, Cl), relative to W2w reference values ( $\text{kJ mol}^{-1}$ ).

Functional	N–H BDE				N–Cl BDE			
	U		R		U		R	
	MAD	MD	MAD	MD	MAD	MD	MAD	MD
BP86	9.9	–9.6	7.0	–5.0	8.6	2.5	12.7	11.1
M06-L	25.7	–25.7	16.7	–16.7	7.7	–7.0	10.2	8.3
B3LYP	14.8	–14.8	8.4	–8.3	26.9	–26.9	15.7	–15.7
$\omega$ B97X-D	8.3	–8.3	4.0	–0.9	8.5	–8.5	4.9	3.5
PBE0	17.2	–17.2	9.6	–9.3	8.2	–8.1	7.6	5.8
B3P86	3.3	–0.1	7.6	6.7	4.1	–2.5	10.4	9.3
M06-HF	16.8	16.8	25.7	25.7	22.2	22.2	35.0	35.0
$\tau$ -HCTHh	18.9	–18.9	11.9	–11.9	7.1	–6.8	7.4	5.5
M06-2X	3.3	–1.9	4.8	4.5	4.5	4.4	14.6	14.6
M05-2X	3.8	–2.6	5.2	4.6	3.6	–2.2	9.2	9.2
BMK	6.3	–6.3	4.3	0.4	3.0	–2.0	8.8	8.2
M06	9.5	–9.5	3.7	–2.2	2.8	–0.5	10.4	10.0

Finally, we turn our attention to the HMGGGA functionals, which involve both exact exchange and the kinetic energy density. We note that B1B95, M06-2X, M05-2X, BMK, and M06 all give MADs smaller than  $10 \text{ kJ mol}^{-1}$  for the N–X BDEs. The best performers for the N–H bonds are M05-2X and M06-2X, with MADs of  $3.8$  and  $3.3 \text{ kJ mol}^{-1}$ , respectively, whereas for the N–Cl bonds, M05-2X, BMK, and M06 show the best performance, with MADs of  $3.6$ ,  $3.0$ , and  $2.8 \text{ kJ mol}^{-1}$ , respectively.

### 3.2.2. Unrestricted Versus Restricted Formalisms

The spin contamination of the underlying unrestricted Hartree–Fock (UHF) wavefunctions for the nitrogen-centered radicals considered here is reflected in  $\langle S^2 \rangle$  values of up to 1.18, compared with 0.75 for a pure doublet state (Table I). It is therefore of interest to compare the performance of restricted open-shell DFT with that of standard unrestricted DFT. We note that, although it has been suggested that DFT calculations on open-shell species should strictly be performed using an unrestricted formalism [57], the restricted open-shell formalism may perform better for certain types of systems and for more heavily parameterized functionals. As an example, in a previous investigation of the performance of the

unrestricted and restricted versions of BMK and MPWB1K for a set of 23 C–H BDEs of monosubstituted methyl radicals [58], it was found that, relative to W1 reference values, RMPWB1K and RBMK give excellent performance, with MADs of  $1.8$  and  $2.9 \text{ kJ mol}^{-1}$ , respectively, while the corresponding unrestricted procedures give MADs of  $5.9$  and  $4.8 \text{ kJ mol}^{-1}$ , respectively. Furthermore, while the unrestricted calculations tend to systematically underestimate the C–H BDEs, the restricted calculations have near-zero MDs. We show here that the restricted procedures also generally provide better performance for the N–H BDEs, whereas for the N–Cl BDEs the opposite seems to be the case.

Table III compares the MADs and MDs for a representative subset of 12 spin-unrestricted (designated by the prefix U) and restricted open-shell (designated with an R prefix) procedures for our test set of 31 N–H and 31 N–Cl BDEs. For the N–H BDEs (with the main exceptions being B3P86 and M06-HF), the restricted calculations result in MADs that are smaller by  $2.0$ – $9.0 \text{ kJ mol}^{-1}$  than those for the corresponding unrestricted calculations. In particular, RBMK,  $\omega$ RB97X-D, and RM06 emerge as the best RDFT performers, with MADs of  $4.3$ ,  $4.0$ , and  $3.7 \text{ kJ mol}^{-1}$ , respectively (compared with  $6.3$ ,  $8.3$ , and  $9.5 \text{ kJ mol}^{-1}$ , respectively, for the corresponding unrestricted variants). We also note that RBMK and  $\omega$ RB97-D

result in near-zero MDs of +0.4 and  $-0.9$  kJ mol<sup>-1</sup>, respectively. On the other hand, for B3P86 and M06-2X, the unrestricted procedures perform better than the restricted procedures, with MADs of 3.3 kJ mol<sup>-1</sup> in both cases, compared with 7.6 and 4.8 kJ mol<sup>-1</sup>, respectively.

For the N–Cl BDEs, the unrestricted procedures perform better than the corresponding restricted procedures, with the exception of B3LYP,  $\omega$ B97X-D, and PBE0. In particular, UBMK and UM06 give MADs of 3.0 and 2.8 kJ mol<sup>-1</sup>, respectively (compared with MADs of 8.8 and 10.4 kJ mol<sup>-1</sup> for the restricted procedures, respectively). We note that RB3P86 performs significantly worse than UB3P86 for both N–H and N–Cl BDEs. It is also of interest to note that RB3LYP is the only restricted open-shell procedure to underestimate the N–Cl BDEs, with an MD of  $-15.7$  kJ mol<sup>-1</sup>.

Finally, we note that the restricted formalisms tend to underestimate the BDEs to a smaller extent than the corresponding unrestricted formalisms. In fact, the MDs for the restricted procedures are systematically less negative or more positive than those of the corresponding unrestricted procedures by  $\sim 7$  (for the N–H BDEs) and  $\sim 12$  (for the N–Cl BDEs) kJ mol<sup>-1</sup>. Thus, in general, in cases where the unrestricted formalism underestimates the BDEs by amounts greater than these values, the restricted formalism is expected to perform better.

### 3.2.3. Basis Set Convergence

Table IV gives an overview of the basis set convergence for a selection of functionals for the N–H and N–Cl BDEs. The following basis sets are considered: (i) Pople's 6-31G(d), 6-31+G(d,p), 6-31+G(2df,p), 6-311+G(d,p), 6-311+G(2df,p), and 6-311+G(3df,2p) basis sets and (ii) Dunning's A'VDZ, A'VTZ, and A'VQZ basis sets. The largest basis set used is the A'VQZ basis set (of 6s5p4d3f2g and 7s6p5d3f2g quality on first- and second-row elements, respectively). We note that for both N–H and N–Cl BDEs, all the functionals converge quite smoothly along the series A'VDZ  $\Rightarrow$  A'VTZ  $\Rightarrow$  A'VQZ.

For the N–Cl BDEs, the 6-311+G(3df,2p) basis set systematically performs slightly better than the A'VQZ basis set. In particular, this basis set results in MADs that are 1–3 kJ mol<sup>-1</sup> smaller than those for the A'VQZ basis set (the main exception being M06-2X). It seems that for most of the functionals (again, except for M06-2X), the

Pople-style basis sets converge along the series: 6-31G(d), 6-31+G(d,p)  $\Rightarrow$  6-311+G(d,p)  $\Rightarrow$  6-31+G(2df,p), 6-311+G(2df,p)  $\Rightarrow$  6-311+G(3df,2p). The first three basis sets show poor performance, with MADs that are often more than 10 kJ mol<sup>-1</sup> greater than those obtained with 6-311+G(3df,2p). The 6-311+G(2df,p) basis set performs slightly better than 6-31+G(2df,p), with MADs lower by up to 1.0 kJ mol<sup>-1</sup>. However, this improvement in performance relative to the increase in computational cost does not seem to warrant its use. We also note that for most functionals, even the 6-311+G(2df,p) basis set gives MADs that are about 3 kJ mol<sup>-1</sup> higher than those obtained with 6-311+G(3df,2p). Thus, it seems from the above convergence patterns that the N–Cl BDEs are rather sensitive to the presence of the additional sets of d functions in the basis set. Finally, we note that, for most functionals, the MADs obtained with the A'VDZ and A'VTZ basis sets are 3.5–6.2 and 0.5–1.0 kJ mol<sup>-1</sup>, respectively, larger than the MADs for A'VQZ. We conclude that either a triple-zeta-valence basis set with three d-type polarization functions (i.e., 6-311+G(3df,2p)) or the Dunning-type A'VTZ basis set are adequate for the calculation of N–Cl BDEs. The performance of 6-311+G(3df,2p) is somewhat better than A'VTZ.

Basis set convergence for the N–H BDEs is faster than for the N–Cl BDEs. The MADs obtained for the A'VTZ basis set are generally within 0.1–0.5 kJ mol<sup>-1</sup> of those obtained for the A'VQZ basis set (three exceptions for which the difference reaches 0.9 kJ mol<sup>-1</sup> are  $\omega$ B97X-D,  $\tau$ -HCTHh, and M06-L). Two double-zeta-valence Pople-style basis sets that systematically perform better than the A'VQZ basis set are 6-31+G(d,p) and 6-31+G(2df,p). In general, these basis sets yield MADs that are 0.5–4.0 kJ mol<sup>-1</sup> lower than those of the A'VQZ basis set, with 6-31+G(2df,p) performing slightly better than 6-31+G(d,p). We also note that, for the N–H BDEs that involve only first-row elements, there is no longer a strong dependence on the presence of extra d functions in the basis set. The triple-zeta-valence 6-311+G(d,p) and 6-311+G(2df,p) basis sets give MADs that are 0.4–2.3 kJ mol<sup>-1</sup> higher relative to those obtained with A'VQZ, where the addition of the f function slightly increases the MADs. The 6-311+G(3df,2p) basis set results in MADs of 0.4–0.9 kJ mol<sup>-1</sup> higher than those obtained with A'VQZ and shows very similar performance to A'VTZ. We conclude by reiterating the good

**TABLE IV**  
**Basis set convergence for a selection of functionals for the N—X BDEs (X = H, Cl) (MADs relative to W2w reference values, kJ mol<sup>-1</sup>).**

Method	6-31G(d)		6-31+G(d,p)		6-31+G(2df,p)		6-311+G(d,p)		6-311+G(2df,p)		6-311+G(3df,2p)		AVDZ		AVTZ		AVQZ	
	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl	N—H	N—Cl
BLYP	36.3	32.3	23.2	39.9	22.4	26.4	25.4	40.3	26.0	27.0	24.6	23.7	29.1	28.9	24.2	26.2	23.7	25.2
BP86	20.4	10.7	8.8	15.0	8.2	8.7	10.4	14.9	11.0	8.3	9.9	8.6	14.0	9.2	9.6	8.6	9.3	8.6
TPSS	29.7	23.3	17.8	28.1	18.2	16.0	20.8	28.0	21.7	14.7	20.7	11.6	25.5	18.3	20.4	14.8	20.2	14.3
M06-L	35.1	20.3	22.7	22.6	22.4	12.3	26.6	22.0	27.5	10.6	25.7	7.7	26.6	15.5	26.0	10.1	25.9	9.3
B3LYP	26.2	37.6	13.4	43.4	12.9	30.2	15.6	43.7	16.2	30.1	14.8	26.9	19.6	33.4	14.5	29.4	14.0	28.3
TPSSh	27.3	29.5	15.4	33.8	15.9	21.7	18.6	33.6	19.5	20.3	18.4	17.3	23.1	24.4	18.2	20.4	17.9	19.9
B3PW91	26.1	27.5	14.0	31.7	13.8	18.7	16.3	31.7	17.1	17.6	15.9	14.6	20.4	21.7	15.8	17.3	15.3	16.6
B98	25.2	25.0	13.0	29.8	12.6	16.0	15.9	29.9	16.3	15.4	15.2	12.6	20.2	20.0	15.1	14.8	14.6	14.0
$\omega$ B97	19.5	23.3	7.3	28.0	7.0	14.1	11.9	29.2	12.6	14.5	11.2	11.7	15.0	17.8	11.3	13.9	10.8	12.5
$\omega$ B97X-D	17.0	21.4	5.3	25.7	4.8	11.8	9.0	26.2	9.5	11.5	8.3	8.5	12.5	15.7	8.6	11.5	7.7	10.9
PBE0	27.1	20.9	14.7	25.2	14.7	12.1	17.6	25.4	18.4	11.0	17.2	8.2	21.5	15.2	17.0	10.4	16.7	9.6
B97-1	28.2	19.6	15.8	24.4	15.4	10.4	18.9	24.7	19.3	9.9	18.2	7.5	23.0	14.5	18.1	9.4	17.6	8.6
B3P86	10.9	15.9	3.0	20.0	3.5	6.7	2.7	19.9	3.1	5.9	3.3	4.1	5.0	9.9	3.3	5.6	3.4	5.1
$\tau$ -HCTHh	28.2	19.2	16.2	23.7	16.0	10.3	19.4	24.0	20.0	9.9	18.9	7.1	24.2	12.9	19.0	9.8	18.1	9.0
M06-2X	11.7	7.9	2.9	12.8	2.8	3.2	3.6	14.0	4.0	3.5	3.3	4.5	7.1	3.5	3.1	3.3	3.2	3.8
BMK	16.7	15.2	6.1	19.6	4.8	3.6	7.3	20.2	7.6	4.4	6.3	3.0	9.5	12.0	6.2	4.1	6.4	4.2
M06	18.0	15.0	7.0	19.5	5.4	4.4	10.8	18.9	10.9	4.4	9.5	2.8	11.0	8.3	10.5	4.4	9.6	4.8



TABLE V

Statistical analysis of the performance of the double-hybrid DFT procedures for the N—X BDEs (X = H, Cl) relative to W2w reference values (kJ mol<sup>-1</sup>).

Functional	%HF	%MP2	Basis <sup>a</sup>	Core <sup>b</sup>	CBS <sup>c</sup>	N—H BDE				N—Cl BDE			
						MAD	MD	LD	NO	MAD	MD	LD	NO
B2K-PLYP	72	42	1	FC	×	4.2	-0.2	11.0	1	8.9	-8.7	16.6	14
B2K-PLYP	72	42	1	FC	✓	3.9	1.0	11.9	2	7.4	-6.8	16.0	8
B2K-PLYP	72	42	2	AE	×	4.2	0.1	11.5	2	6.7	-5.6	14.7	8
B2K-PLYP	72	42	2	AE	✓	4.0	1.4	12.4	3	5.5	-3.2	13.6	3
B2K-PLYP	72	42	3	FC	×	6.1	-5.1	12.2	8	10.5	-10.4	17.0	20
B2GP-PLYP	65	36	1	FC	×	4.0	-2.5	10.4	1	11.1	-11.1	19.7	21
B2GP-PLYP	65	36	1	FC	✓	3.7	-1.5	10.3	1	9.6	-9.6	19.3	16
B2GP-PLYP	65	36	2	AE	×	4.0	-2.2	10.6	1	8.2	-8.2	17.9	10
B2GP-PLYP	65	36	2	AE	✓	3.7	-1.2	10.4	1	6.6	-6.1	16.9	6
B2GP-PLYP	65	36	3	FC	×	7.0	-6.8	14.3	7	12.1	-12.1	19.6	22
UB2-PLYP-09	62	35	1	FC	×	3.9	-2.9	11.0	1	9.9	-9.9	18.9	17
UB2-PLYP-09	62	35	1	FC	✓	3.3	-1.1	10.3	1	8.4	-8.4	18.6	11
UB2-PLYP-09	62	35	3	FC	×	7.0	-6.9	14.9	6	10.7	-10.7	18.7	21
B2T-PLYP	60	31	1	FC	×	5.0	-4.6	12.8	2	14.3	-14.3	23.5	26
B2T-PLYP	60	31	1	FC	✓	4.5	-3.8	12.7	2	13.0	-13.0	23.2	25
B2T-PLYP	60	31	2	AE	×	4.9	-4.4	13.0	2	11.4	-11.4	21.6	21
B2T-PLYP	60	31	2	AE	✓	4.4	-3.5	12.8	2	9.7	-9.7	20.8	15
B2T-PLYP	60	31	3	FC	×	8.4	-8.4	16.3	9	14.7	-14.7	22.8	26
B2-PLYP	53	27	1	FC	×	6.2	-6.2	15.2	2	14.5	-14.5	24.8	28
B2-PLYP	53	27	1	FC	✓	5.7	-5.5	15.2	2	13.5	-13.5	24.6	25
B2-PLYP	53	27	2	AE	×	6.0	-5.9	15.4	2	11.7	-11.7	22.9	24
B2-PLYP	53	27	2	AE	✓	5.4	-5.2	15.3	2	10.2	-10.2	22.2	15
B2-PLYP	53	27	3	FC	×	9.6	-9.6	18.3	11	14.3	-14.3	23.7	26
ROB2-PLYP	59	28	1	FC	×	2.6	-0.4	8.9	0	6.8	-6.7	15.3	5
ROB2-PLYP	59	28	1	FC	✓	2.7	1.4	12.9	1	4.4	-3.8	13.0	1
ROB2-PLYP	59	28	3	FC	×	5.0	-4.7	11.5	1	8.4	-8.4	15.9	10

<sup>a</sup>Basis set 1 = A'VQZ, basis set 2 = A'CVQZ, basis set 3 = 6-311+G(3df,2p).

<sup>b</sup>FC = frozen core, AE = all electron.

<sup>c</sup>Combined with Petersson's CBS extrapolation of the MP2 correlation energy [59, 60].

performance of 6-31+G(2df,p) (or even 6-31+G(d,p)) for the calculation of N—H BDEs in structures containing only first-row elements.

### 3.2.4. Double-Hybrid Density Functional Theory Procedures

Table V gives the statistical analysis for the performance of DHDFT procedures. These occupy the fifth rung of Jacob's ladder as they use the virtual orbitals. Thus, the DH functionals mix exact Hartree-Fock exchange as well as MP2 correlation energies with the exchange-correlation energy of the underlying DFT functional. We have evaluated the performance of the DHDFT procedures with and without the frozen-core (FC) approximation and with and without the com-

plete basis set (CBS) extrapolation to the MP2 limit of Petersson and coworkers [59, 60].

Of the DH functionals, ROB2-PLYP shows the best performance for both the N—H and N—Cl BDEs. For the N—H BDEs, MADs of 2.7 and 2.6 kJ mol<sup>-1</sup> are obtained with and without the CBS extrapolation, respectively. For the N—Cl BDEs, MADs of 4.4 and 6.8 kJ mol<sup>-1</sup> are obtained with and without the CBS extrapolation.

Considering the N—H BDEs, it is evident that (i) the performance of all the functionals is relatively insensitive to the FC approximation and/or to the CBS extrapolation, (ii) compared with the "conventional" DFT functionals, ROB2-PLYP and B2K-PLYP are not biased toward underestimation of the BDEs (as indicated by small MD values), and (iii) all the unrestricted functionals show

TABLE VI

Statistical analysis of the performance of *Gn* methods for the calculation of N–H and N–Cl BDEs (kJ mol<sup>-1</sup>).

Method	N–H BDE				N–Cl BDE			
	MAD	MD	LD	NO	MAD	MD	LD	NO
G3X	3.4	-3.4	7.5	0	2.8	-2.6	5.6	0
G3X(MP2)-RAD	3.7	-3.7	6.8	0	1.8	-1.6	5.3	0
G3X(MP2)	4.4	-4.4	10.8	1	2.8	-2.5	7.1	0
G4	5.8	-5.8	11.3	1	5.3	-5.3	9.9	0
G4-5H	3.3	-3.3	7.1	0	3.0	-2.8	5.8	0
G4(MP2)	7.2	-7.2	15.8	4	5.3	-5.2	13.3	2
G4(MP2)-6X	2.9	-2.8	9.6	0	2.1	-1.4	7.4	0

fairly similar performance, with B2K-PLYP, B2GP-PLYP, and UB2-PLYP-09 being slightly better (MAD = 3.3–4.2 kJ mol<sup>-1</sup>) than B2-PLYP and B2T-PLYP (MAD ≈ 4.4–6.2 kJ mol<sup>-1</sup>).

For the N–Cl bonds, the MADs converge smoothly with each increase in the level of theory, that is, for each functional MAD(FC) > MAD(FC + CBS) > MAD(AE) > MAD(AE + CBS). Of the unrestricted procedures, B2K-PLYP shows the best performance, with MADs of 8.9, 7.4, 6.7, and 5.5 kJ mol<sup>-1</sup> for the above levels of theory, respectively, with UB2-PLYP-09 being a close second. B2-PLYP and B2T-PLYP show poorer performance, with MADs ranging between 10 and 14 kJ mol<sup>-1</sup>. We note that in a similar manner to most of the conventional DFT functionals, the DHs also tend to systematically underestimate the N–Cl bond energies.

Finally, due to the good performance of the 6-311+G(3df,2p) basis set for the conventional DFT procedures, we tested this basis set for the DHDFE procedures as well. For the N–H BDEs, the MADs are somewhat worse (by 1.9–3.4 kJ mol<sup>-1</sup>) than the A'VQZ results. In addition, the MDs indicate that the BDEs are now underestimated to a larger extent. However, for the N–Cl BDEs the performance of 6-311+G(3df,2p) is comparable to that of A'VQZ, with the largest increases in the MADs (of 1.0–1.6 kJ mol<sup>-1</sup>) observed for B2K-PLYP, B2GP-PLYP, and ROB2-PLYP.

### 3.3. PERFORMANCE OF *Gn* METHODS FOR THE N–H AND N–Cl BDEs

Table VI presents the statistical analysis of the performance of a selection of composite procedures of the *Gn* family, including G3X, G3X(MP2)-RAD, G3X(MP2), G4, G4-5H, G4(MP2), and G4(MP2)-6X. Note, that we are comparing nonrela-

tivistic, vibrationless *Gn* BDEs with nonrelativistic, vibrationless W2w reference values. Because our scaled B3LYP/A'VTZ ZPVEs and the ZPVEs used in the *Gn* methods (e.g., B3LYP/6-31G(2df,p)) are likely to be of similar quality, the use of a vibrationless comparison should be satisfactory.

A few general observations can be made about the N–Cl and N–H BDEs: (i) the *Gn* methods systematically underestimate the N–X BDEs; (ii) the G3X-type procedures and the modified G4-type procedures (G4-5H and G4(MP2)-6X) perform significantly better than G4 and G4(MP2); and (iii) overall the G3X(MP2)-RAD and G4(MP2)-6X procedures show the best performance. The good performance of G3X(MP2)-RAD is consistent with the very good performance shown by this procedure for C–H BDEs [58, 61].

For the N–H species, G4(MP2)-6X is the best performer (MAD = 2.9 kJ mol<sup>-1</sup>), and it is worth pointing out that this performance is significantly better than that of G4 (MAD = 5.8 kJ mol<sup>-1</sup>) or G4(MP2) (MAD = 7.2 kJ mol<sup>-1</sup>), and slightly better than that of the recent G4-5H procedure (MAD = 3.3 kJ mol<sup>-1</sup>). This is a useful result because G4(MP2)-6X is significantly cheaper in terms of computational cost than G4 or G4-5H. We find that G3X also performs better than G4 or G4-5H, with an MAD of 3.4 kJ mol<sup>-1</sup>. The low-cost G3X(MP2)-RAD procedure exhibits good performance (MAD = 3.7 kJ mol<sup>-1</sup>), and it is evident that use of the restricted open-shell formalism for the treatment of the radical species is advantageous, as G3X(MP2) (which uses an unrestricted formalism) exhibits a slightly poorer performance (MAD = 4.4 kJ mol<sup>-1</sup>).

For the N–Cl species, G3X(MP2)-RAD provides the best performance (MAD = 1.8 kJ mol<sup>-1</sup>), and again, because of the better treatment of

radical species, this is an improvement on G3X(MP2) (MAD = 2.8 kJ mol<sup>-1</sup>). The computationally more expensive G4 procedure, and its cheaper reduced-order variant G4(MP2), both exhibit somewhat poorer performance, with MADs of 5.3 kJ mol<sup>-1</sup>. The modified forms of G4 and G4(MP2), namely G4-5H and G4(MP2)-6X, offer significantly better performance, with MADs of 3.0 and 2.1 kJ mol<sup>-1</sup>, respectively.

### 3.4. PERFORMANCE OF DFT PROCEDURES FOR THE CALCULATION OF RSE<sub>NH</sub> AND RSE<sub>NCl</sub>

In Section 3.2, we have seen that the dissociation energies of N—H and N—Cl bonds to give nitrogen-centered radicals are, with few exceptions, significantly underestimated by DFT procedures. Furthermore, of the 30 tested DFT procedures, only three functionals (namely, M06-2X, B3P86, and M05-2X, see Table II) achieved MADs below the threshold of “chemical accuracy” (arbitrarily defined as 1 kcal mol<sup>-1</sup> or 4.2 kJ mol<sup>-1</sup>) for the N—H BDEs, and only four functionals (namely, M06, BMK, M05-2X, and B3P86) achieved this goal for the N—Cl BDEs.

In this section, we shall show that the RSEs, that is, the energies of reactions (2) and (3), are relatively well described by most DFT procedures, which is consistent with previous findings (see, e.g., Ref. 61 and references therein). This improvement in performance is mainly due to the fact that in the radical stabilization reaction larger molecular fragments are conserved on both sides of the reaction compared with the bond dissociation reaction. In this context, it is worth mentioning the recent work of Allen and coworkers [62], which discusses the concept of “hypohomodesmotic reactions.” These are reactions which, in addition to being isodesmic (that is, conserving numbers of each formal bond type), conserve the number of carbon atoms in each hybridization state and the hapticity (primary, secondary, tertiary, and quaternary). A consistent hierarchy of hydrocarbon reaction types was proposed that successively conserves larger molecular fragments: atomization > isogyric > isodesmic > hypohomodesmotic > homodesmotic > hyperhomodesmotic. This provides a sequence in which there is increasing cancelation of errors between reactants and products as the reaction hierarchy is traversed. Applying their definition of carbon-centered hypohomodesmotic reactions to nitrogen-centered species, we note that the radical sta-

bilization reactions (2) and (3) are hypohomodesmotic for all the N—H and N—Cl derivatives considered in this work.

The statistical analysis of the performance of various DFT procedures in calculating RSEs is presented in Table VII. For most DFT functionals, the MADs obtained for the RSEs are much smaller than those obtained for the BDEs (e.g., 30% of the MADs in Table II are smaller than 10 kJ mol<sup>-1</sup>, whereas in Table VII this number is increased to 80%). In particular, large improvements are observed for functionals that perform more poorly for the BDE. In general, the RSEs are overestimated across the board (positive MD values; with the notable exception of M06-HF).

For the N—H RSEs in Table VII, 11 functionals attain MADs below the threshold of chemical accuracy, namely the seven hybrid-GGAs BH&HLYP (2.5), TPSSH (4.1), B3PW91 (4.1),  $\omega$ B97X-D (3.0),  $\omega$ B97X (3.3),  $\omega$ B97 (3.3), and PBE0 (3.2), and the four hybrid meta-GGAs M06 (2.9), M06-2X (2.7), BMK (3.3), and M05-2X (2.9 kJ mol<sup>-1</sup>).

For the N—Cl RSEs, six functionals attain MADs below the chemical accuracy threshold, namely the hybrid-GGAs BH&HLYP (4.1) and PBE0 (4.2), and the same four hybrid meta-GGAs that achieved this goal for the N—H RSEs, specifically M06 (2.8), M05-2X (3.1), M06-2X (3.4), and BMK (4.0 kJ mol<sup>-1</sup>). Thus, these six functionals are suitable for the calculation of RSE<sub>NH</sub> and RSE<sub>NCl</sub>. It is also of general interest to note that five of these functionals involve high percentages of Hartree-Fock exchange (i.e., apart from M06, %HF  $\leq$  42).

Table VIII gives an overview of basis set convergence for the various functionals for the N—H and N—Cl RSEs. Quite remarkably (and in contrast to the behavior for the BDEs), the basis-set dependence almost entirely cancels for the RSEs. For the N—H RSEs, all the basis sets show very similar performance, except for the 6-31+G(d,p) basis set, which results in MADs 0.6–2.6 kJ mol<sup>-1</sup> higher than those obtained with the A'VQZ basis set. For the N—Cl RSEs, all the basis sets again show very similar performance, with the exception of 6-31G(d) and 6-31+G(d,p), which result in MADs 0.1–3.5 kJ mol<sup>-1</sup> higher than those obtained with A'VQZ. We note that in this case the 6-311+G(3df,2p) basis set tends to give MADs that are  $\sim$  1 kJ mol<sup>-1</sup> lower than those obtained with A'VQZ.

Table IX gives the statistical analyses for the RSEs calculated with the DHDFT procedures. We make two general observations: (i) in contrast to

TABLE VII

Statistical analysis of the performance of DFT procedures (in conjunction with the 6-311+G(3df,2p) basis set) for the calculation of N—H and N—Cl RSEs (relative to W2w reference values, kJ mol<sup>-1</sup>).

Method	Type <sup>a</sup>	N—H RSE				N—Cl RSE			
		MAD	MD	LD	NO	MAD	MD	LD	NO
SVWN5	LDA	17.0	16.8	55.1	18	11.0	8.5	48.8	13
B97-D	GGA	9.3	9.1	22.0	11	9.3	9.0	25.4	12
BLYP	GGA	10.9	10.7	27.9	11	12.0	11.6	31.8	15
HCTH407	GGA	11.2	11.0	32.1	14	12.3	12.2	41.0	15
PBE	GGA	10.4	10.2	31.6	12	9.3	8.3	34.4	13
BP86	GGA	10.4	10.2	30.1	12	9.8	9.1	33.5	14
VSXC	MGGA	10.0	9.7	27.2	13	6.6	-1.9	20.1	8
$\tau$ -HCTH	MGGA	10.7	10.6	29.5	13	12.1	12.1	38.2	14
TPSS	MGGA	6.2	5.0	17.5	8	7.7	5.7	25.0	11
M06-L	MGGA	5.8	4.9	22.5	4	5.8	1.1	25.2	4
BH&HLYP	HGGA	2.5	-2.1	7.6	0	4.1	3.3	11.4	1
B3LYP	HGGA	4.7	4.2	17.5	2	7.3	7.0	23.3	6
X3LYP	HGGA	4.4	3.8	17.0	2	6.7	6.3	22.2	5
TPSSh	HGGA	4.1	2.3	13.3	1	5.7	4.2	21.7	6
B3PW91	HGGA	4.1	3.3	18.5	2	5.7	5.3	25.6	5
B98	HGGA	5.4	5.2	17.6	2	8.2	8.0	24.5	7
$\omega$ B97	HGGA	3.3	2.7	9.3	0	5.0	3.8	11.8	2
$\omega$ B97X	HGGA	3.3	2.9	11.6	1	5.1	4.8	15.3	2
$\omega$ B97X-D	HGGA	3.0	2.5	12.3	1	5.2	5.0	18.2	3
PBE0	HGGA	3.2	2.0	16.7	2	4.2	3.4	22.9	3
B97-1	HGGA	6.0	5.8	18.5	4	8.4	8.3	25.2	9
B3P86	HGGA	4.5	3.8	19.8	2	5.3	5.0	25.3	4
M06-HF	HMGGA	8.9	-8.7	22.5	13	9.7	-5.5	21.3	12
M05	HMGGA	5.7	5.4	19.9	4	6.0	5.4	26.5	5
$\tau$ -HCTHh	HMGGA	7.4	7.2	22.2	9	8.9	8.8	28.1	11
B1B95	HMGGA	5.2	4.6	20.5	2	6.3	5.8	26.5	4
M06-2X	HMGGA	2.7	-1.9	9.5	0	3.4	-1.5	8.9	0
M05-2X	HMGGA	2.9	-0.2	7.4	0	3.1	0.4	6.1	0
BMK	HMGGA	3.3	1.8	14.1	1	4.0	3.6	18.6	2
M06	HMGGA	2.9	2.5	17.0	2	2.8	0.2	13.5	1

<sup>a</sup>LDA: local density approximation, GGA: generalized gradient approximation, HGGA: hybrid-GGA, MGGA: meta-GGA, HMGGA: hybrid-meta-GGA.

the BDE results, the differences between the AE and FC calculations with and without the CBS extrapolations are very small, that is, for all of the functionals: MAD(FC)  $\approx$  MAD(FC + CBS)  $\approx$  MAD(AE)  $\approx$  MAD(AE + CBS); (ii) in contrast to most of the functionals in Table VII, most DHs tend to underestimate the W2w reference RSEs (negative MDs).

Compared with the N—H BDEs (in Table V), noticeable improvements are observed for B2-PLYP (e.g., the MAD for the AE + CBS extrapolation is reduced from 5.4 to 2.4 kJ mol<sup>-1</sup>). However, the performance of B2K-PLYP, B2GP-PLYP, UB2-PLYP-09, and ROB2-PLYP slightly deteriorates (by  $\sim$  2 kJ mol<sup>-1</sup> for the former two and by  $\sim$  1 kJ mol<sup>-1</sup>

for the latter two). For the N—Cl bonds, however, performance is improved across the board. For the calculation of either RSE<sub>NH</sub> or RSE<sub>NCl</sub>, B2-PLYP shows the best performance, with MADs of 2.3–2.4 and 2.7–2.9 kJ mol<sup>-1</sup>, respectively. Furthermore, these narrow ranges illustrate the lack of sensitivity to the combination of basis set or core-electron treatment for these quantities.

### 3.5. PERFORMANCE OF *G*<sub>n</sub> METHODS FOR THE CALCULATION OF RSE<sub>NH</sub> AND RSE<sub>NCl</sub>

Table X presents the statistical analysis of the performance of the *G*<sub>n</sub> procedures for RSEs. The

**TABLE VIII**  
**Basis set convergence for DFT functionals for the calculation of  $RSE_{N-X}$  (X = H, Cl) (MADs relative to W2w reference values,  $\text{kJ mol}^{-1}$ ).**

Method	6-31G(d)		6-31+		6-311+		6-311+		6-311+		6-311+		6-311+		6-311+		6-311+	
	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl	N-H	N-Cl
BLYP	9.0	15.3	12.5	15.2	11.7	14.0	11.3	13.4	10.9	12.0	10.2	13.8	10.4	13.0	10.5	13.0	10.5	13.0
BP86	8.9	13.8	12.1	13.2	11.2	11.4	10.8	11.0	10.4	9.8	9.6	11.7	10.0	10.8	10.1	10.7	10.1	10.7
TPSS	5.7	10.8	7.2	10.3	6.6	8.9	6.3	8.5	6.2	7.7	6.4	9.3	6.1	8.5	6.0	8.3	6.0	8.3
M06-L	5.6	9.4	7.9	9.2	6.1	6.2	5.4	6.1	5.8	5.8	6.2	8.3	5.7	6.4	5.9	6.6	5.9	6.6
B3LYP	3.4	11.3	6.0	10.9	5.2	9.4	4.9	8.6	4.7	7.3	4.1	9.1	4.3	8.4	4.5	8.4	4.5	8.4
TPSSh	3.8	9.0	4.6	8.7	4.0	7.1	4.1	6.5	4.1	5.7	4.4	7.2	4.0	6.4	4.0	6.3	4.0	6.3
B3PW91	2.8	10.2	5.1	9.7	4.4	7.8	4.3	7.1	4.1	5.7	3.6	7.3	3.8	6.9	3.9	6.9	3.9	6.9
B98	3.9	12.4	6.8	12.0	5.9	10.3	5.7	9.6	5.4	8.2	4.8	10.1	4.9	9.3	5.0	9.2	5.0	9.2
$\omega$ B97	2.9	9.5	4.7	8.4	3.5	6.5	3.5	5.6	3.3	5.0	2.8	6.9	2.9	5.4	3.1	5.5	3.1	5.5
$\omega$ B97X-D	1.8	10.1	4.1	9.4	3.2	7.3	3.1	6.4	3.0	5.2	2.0	7.1	2.8	6.5	2.9	6.6	2.9	6.6
PBE0	2.0	8.1	4.1	7.6	3.5	6.0	3.4	5.4	3.2	4.2	3.1	5.3	3.0	5.1	3.1	5.1	3.1	5.1
B97-1	4.5	12.7	7.5	12.2	6.6	10.5	6.4	9.8	6.0	8.4	5.5	10.5	5.4	9.5	5.6	9.4	5.6	9.4
B3P86	3.1	9.9	5.6	9.4	4.8	7.4	4.7	6.7	4.5	5.3	3.8	7.1	4.2	6.5	4.3	6.5	4.3	6.5
$\tau$ -HCTHh	5.8	13.0	8.9	12.7	8.0	11.0	7.8	10.4	7.4	8.9	6.9	10.7	6.8	10.0	6.7	9.8	6.7	9.8
M06-2X	3.2	4.1	2.6	4.3	2.6	4.0	2.8	3.6	2.7	3.4	2.7	2.3	2.8	3.3	2.7	3.6	2.7	3.6
BMK	3.1	10.1	4.6	9.0	3.5	6.0	3.4	5.0	3.3	4.0	2.4	6.8	3.0	4.8	3.3	5.2	3.0	4.8
M06	3.2	7.9	5.0	6.6	3.0	3.2	2.9	3.0	2.9	2.8	3.4	4.8	2.6	2.7	2.5	3.1	2.6	2.7



TABLE IX

Statistical analysis of the performance of the double-hybrid DFT procedures for the N–X RSEs (X = H, Cl) (relative to W2w reference values, kJ mol<sup>-1</sup>).

Functional	Basis <sup>a</sup>	Core <sup>b</sup>	CBS <sup>c</sup>	N–H RSE				N–Cl RSE			
				MAD	MD	LD	NO	MAD	MD	LD	NO
B2K-PLYP	1	FC	×	5.8	-5.4	16.4	6	5.6	-5.0	16.6	6
B2K-PLYP	1	FC	✓	5.5	-4.9	15.7	5	5.3	-4.4	15.7	6
B2K-PLYP	2	AE	×	5.8	-5.3	16.5	5	5.9	-5.1	17.5	7
B2K-PLYP	2	AE	✓	5.5	-4.8	15.7	5	5.9	-5.1	16.8	7
B2K-PLYP	3	FC	×	5.5	-5.1	16.0	4	6.7	-6.7	18.8	9
B2GP-PLYP	1	FC	×	4.3	-3.5	12.3	3	4.0	-2.8	11.3	3
B2GP-PLYP	1	FC	✓	4.1	-3.0	11.9	3	3.8	-2.2	10.4	2
B2GP-PLYP	2	AE	×	4.3	-3.4	12.4	3	4.3	-2.9	12.2	3
B2GP-PLYP	2	AE	✓	4.0	-2.9	12.0	3	4.3	-2.9	11.5	3
B2GP-PLYP	3	FC	×	4.0	-3.2	11.7	3	4.8	-4.5	13.5	5
UB2-PLYP-09	1	FC	×	3.8	-2.7	11.5	1	3.6	-2.2	9.8	0
UB2-PLYP-09	1	FC	✓	3.6	-2.3	11.2	1	3.4	-1.7	9.5	0
UB2-PLYP-09	3	FC	×	3.5	-2.5	10.9	1	4.4	-3.9	11.9	4
B2T-PLYP	1	FC	×	3.3	-2.2	10.0	1	2.9	-1.1	8.1	0
B2T-PLYP	1	FC	✓	3.1	-1.8	9.7	0	2.9	-0.7	9.5	0
B2T-PLYP	2	AE	×	3.3	-2.2	10.2	1	3.2	-1.3	8.9	0
B2T-PLYP	2	AE	✓	3.1	-1.8	9.9	0	3.2	-1.3	9.9	0
B2T-PLYP	3	FC	×	3.1	-2.0	9.5	0	3.7	-2.8	9.8	0
B2-PLYP	1	FC	×	2.4	-0.6	8.5	0	2.7	0.5	10.8	1
B2-PLYP	1	FC	✓	2.3	-0.2	9.5	0	2.9	1.0	12.1	1
B2-PLYP	2	AE	×	2.4	-0.5	8.9	0	2.8	0.4	11.6	1
B2-PLYP	2	AE	✓	2.4	-0.2	9.9	0	2.8	0.4	12.5	1
B2-PLYP	3	FC	×	2.3	-0.3	8.4	0	2.8	-1.1	8.3	0
ROB2-PLYP	1	FC	×	3.1	-2.3	11.5	1	2.8	-1.1	9.4	0
ROB2-PLYP	1	FC	✓	3.2	-2.4	13.8	1	2.8	-0.7	11.4	1
ROB2-PLYP	3	FC	×	2.9	-2.1	11.0	1	3.2	-2.4	10.7	1

<sup>a</sup>Basis set 1 = A'VQZ, basis set 2 = A'CVQZ, basis set 3 = 6-311+G(3df,2p).

<sup>b</sup>FC = frozen core, AE = all electron.

<sup>c</sup>Combined with Petersson's CBS extrapolation of the MP2 correlation energy [59].

MADs associated with the RSE<sub>NH</sub> values are 1.6–3.1 kJ mol<sup>-1</sup> smaller than the MADs associated with the N–H BDEs calculated by the same methods (Table VI). We note that all the G3X-type procedures and the modified G4-type procedures (namely G4-5H and G4(MP2)-6X) show excellent performance, with MADs of 0.9–1.4 kJ mol<sup>-1</sup>. Furthermore, we also note the desirable near-zero MDs (between 0.0–0.5 kJ mol<sup>-1</sup> in absolute value) for these methods. For the N–Cl RSEs, the performance of G4 and G4(MP2) is markedly improved, and in particular, G4 emerges as the best performer with an MAD of 1.7 kJ mol<sup>-1</sup>.

### 3.6. CALCULATION OF N–H AND N–Cl BDEs VIA RSEs

We note that if an accurate BDE for the H<sub>2</sub>N–X (X = H, Cl) bond is available experimen-

tally (or from high-level ab initio calculations), then the BDE for any given RR'N–X system can be obtained via the calculated RSEs:

$$\text{BDE}(\text{NHRR}') = \text{BDE}(\text{H}_2\text{N–H}) - \text{RSE}_{\text{NH}} \quad (4)$$

$$\text{BDE}(\text{NCIRR}') = \text{BDE}(\text{H}_2\text{N–Cl}) - \text{RSE}_{\text{NCl}} \quad (5)$$

Given our finding that the RSE<sub>NH</sub> and RSE<sub>NCl</sub> values may be obtained to good accuracy using computationally inexpensive methods, such as many DFT or *Gn* procedures, this provides a cost-effective means of obtaining reliable BDEs. For example, if one uses nonrelativistic, vibrationless benchmark BDEs from W2w theory for the H<sub>2</sub>N–H and H<sub>2</sub>N–Cl bonds (483.6 and 274.4 kJ mol<sup>-1</sup>, respectively) [7], then the MAD, LD, and NO for BDEs

TABLE X

Statistical analysis of the performance of  $G_n$  methods for the calculation of N–H and N–Cl RSEs (relative to W2w reference values,  $\text{kJ mol}^{-1}$ ).

Method	N–H RSE				N–Cl RSE			
	MAD	MD	LD	NO	MAD	MD	LD	NO
G3X	1.0	0.0	4.1	0	3.3	–3.0	6.7	0
G3X(MP2)-RAD	0.9	–0.4	2.7	0	2.8	–2.7	6.3	0
G3X(MP2)	1.4	–0.3	6.1	0	3.0	–2.8	7.8	0
G4	2.7	2.7	8.0	0	1.7	0.2	4.9	0
G4-5H	1.0	–0.5	3.3	0	3.0	–3.0	7.3	0
G4(MP2)	4.4	4.3	12.8	1	3.1	2.5	10.5	1
G4(MP2)-6X	1.3	0.1	6.8	0	2.4	–2.0	6.3	0

derived via Eqs. (4) and (5) would be identical to those presented in Tables VII–X for the RSEs, except that the signs of the MDs would be reversed. Thus, each of these quantities would be significantly improved from their values when the BDEs are calculated directly. For the purpose of obtaining BDEs at 0 K in conjunction with RSEs, we suggest using the relativistic 0 K N–H and N–Cl BDEs from W4 theory:  $\text{BDE}(\text{H}_2\text{N–H}) = 443.6 \pm 0.7$  and  $\text{BDE}(\text{H}_2\text{N–Cl}) = 250.8 \pm 0.7 \text{ kJ mol}^{-1}$  [7].

#### 4. Conclusions

The performance of a variety of DFT and  $G_n$ -type procedures in predicting N–X BDEs is evaluated through comparison with high-level W2w values for a set of 31 N–H and 31 N–Cl BDEs. With regard to the calculation of BDEs from electronic energies obtained using  $G_n$  or DFT procedures, we draw the following conclusions:

- With very few exceptions, the DFT, DHDFT, and  $G_n$  procedures underestimate the N–H and N–Cl BDEs.
- Of the tested  $G_n$  methods, G4(MP2)-6X gives the best overall performance, with MADs of 2.9 and 2.1  $\text{kJ mol}^{-1}$  for the N–H and N–Cl BDEs, respectively.
- Considering both N–H and N–Cl BDEs, B3P86, M05-2X, and M06-2X show good performance, with MADs of 3.3, 3.8, and 3.3  $\text{kJ mol}^{-1}$ , respectively, for the N–H BDEs and 4.1, 3.6, and 4.5  $\text{kJ mol}^{-1}$ , respectively, for the N–Cl BDEs. In contrast, the ubiquitous B3LYP procedure shows MADs of 14.8 (N–H) and 26.9 (N–Cl)  $\text{kJ mol}^{-1}$ .

- For the N–Cl BDEs, the 6-311+G(3df,2p) basis set is found to give BDEs close to the basis-set limit. For the N–H BDEs, the 6-31+G(2df,p) basis set shows good performance.
- Of the DHDFT procedures, ROB2-PLYP displays the best overall performance, with MADs of 2.7 and 4.4  $\text{kJ mol}^{-1}$  for the N–H and N–Cl BDEs, respectively.

The radical stabilization reactions are hypohomodesmotic, and accordingly the RSEs are relatively well described by the  $G_n$  procedures or even by the DFT procedures. We make the following observations:

- The G3X-type procedures and the modified G4-type procedures (G4-5H and G4(MP2)-6X) show excellent performance for the N–H RSEs, with MADs of 0.9–1.4  $\text{kJ mol}^{-1}$ . However, for the N–Cl RSEs, G4 exhibits the best performance, with an MAD of 1.6  $\text{kJ mol}^{-1}$ .
- Considering both N–H and N–Cl RSEs, MADs below the threshold of chemical accuracy are obtained by six functionals, all of which (except for M06) involve relatively high percentages of Hartree–Fock exchange: BH&HLYP, M06, M05-2X, M06-2X, BMK, and PBE0.
- The RSEs converge very rapidly to the basis-set limit in the DFT calculations, such that even 6-31+G(2df,p) provides RSEs close to this limit for both types of bonds.
- Of the DHDFT procedures, B2-PLYP, ROB2-PLYP, and B2T-PLYP give the best performance, with MADs of 2.3–3.1 and 2.7–2.9 for the N–H and N–Cl RSEs, respectively.

- v. The good performance in calculating RSEs by computationally inexpensive methods such as the *Gn*-type and DFT procedures, provides a cost-effective means of calculating reliable BDEs via a thermochemical cycle.

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