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Supplemental Information

Generalized-gradient Approximation Exchange Functional with Near-best Semilocal Performance

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In this supplemental material we present:

a) Detailed analysis of the asymptotic behavior of the NCAP (nearly correct asymptotic potential) exchange potential;

b) Augmented versions of the tables that appear in the article to report the MD (Mean Deviation) in addition to the MAD (Mean Absolute Deviation);

c) Plot of satisfaction by NCAP of the global Lieb-Oxford[1] and Perdew *et al*.[2] bounds;

d) Comparison of NCAP-shifted HOMO eigenvalue with the system-dependent XC functional of Gledhill and Tozer[3] HOMO eigenvalues for small molecules;

e) Comparison of the NCAP HOMO and LUMO shifted eigenvalues with those from other XC functionals;

f) Results for the individual molecules of the test sets analyzed

a) Detailed analysis of the asymptotic behavior of the NCAP (nearly correct asymptotic potential) exchange potential

A GGA exchange energy functional usually is expressed in terms of an enhancement factor in the form[4]

$$E_X^{GGA}[n] = \int n(\mathbf{r})\,(\varepsilon_X^{LDA}(n(\mathbf{r}))\,F_X(s)\,d\mathbf{r} \quad . \tag{1}$$

Here $\varepsilon_X^{LDA}(n(\mathbf{r})) = A_X(n(\mathbf{r}))^{1/3}$ is the LDA for the exchange energy per particle, $A_X = -3(3\pi^2)^{1/3}/4\pi$, $n(\mathbf{r})$ is the electron number density, and $s(\mathbf{r}) = \left|\nabla n(\mathbf{r})\right| / 2k_F(\mathbf{r})n(\mathbf{r})$, is the exchange reduced density gradient with $k_F = (3\pi^2\, n(\mathbf{r}))^{1/3}$.

Since the X potential is given by

$$v_X^{GGA}([n];\mathbf{r}) = \frac{\delta E_X[n]}{\delta n(\mathbf{r})} \quad , \tag{2}$$

the general expression for the GGA X potential is

$$\begin{aligned} v_X^{GGA}([n];\mathbf{r}) &= A_X\, n(\mathbf{r})^{1/3}\left[\frac{4}{3}F_X(s)\right] \\ &+ A_X\, n(\mathbf{r})^{1/3}\left[-\frac{4}{3}s(\mathbf{r}) - \frac{1}{2k_F}\frac{\nabla^2 n(\mathbf{r})}{|\nabla n(\mathbf{r})|} + \frac{1}{2k_F}\frac{\nabla n(\mathbf{r})\cdot\nabla|\nabla n(\mathbf{r})|}{|\nabla n(\mathbf{r})|^2}\right]\frac{dF_X(s)}{ds} \quad . \\ &+ A_X\, n(\mathbf{r})^{1/3}\left[-\frac{1}{(2k_F)^2}\frac{\nabla n(\mathbf{r})\cdot\nabla|\nabla n(\mathbf{r})|}{|\nabla n(\mathbf{r})|\,n(\mathbf{r})} + \frac{4}{3}s(\mathbf{r})^2\right]\frac{d^2F_X(s)}{ds^2} \end{aligned} \tag{3}$$

The asymptotic behavior of v_X for a finite system arises only in part from the asymptotic behavior of the density[5-7], which very far away from the nucleus is dominated by the exponential decay,

$$n(r) \xrightarrow[r\to\infty]{} n_0\, e^{-\lambda r} \quad . \tag{4}$$

Using this expression for the density, and the corresponding expressions for the first derivative ($n'(r) \xrightarrow[r\to\infty]{} -\lambda\, n(r)$) and the second derivative ($n''(r) \xrightarrow[r\to\infty]{} \lambda^2\, n(r)$) of the density with respect to the distance r, Eq. (3) becomes

$$v_X^{GGA}([n];\mathbf{r}) \xrightarrow[r\to\infty]{} A_X\, n(r)^{1/3}\left[\frac{4}{3}F_X + \left(-\frac{4}{3}s(r) + \frac{1}{k_F r}\right)\frac{dF_X}{ds} + \frac{(s(r))^2}{3}\frac{d^2F_X}{ds^2}\right] \quad , \tag{5}$$

where $s \xrightarrow[r\to\infty]{} \lambda\, n^{-1/3}(r)/(2(3\pi^2)^{1/3})$. Notice that the $1/k_F r$ coefficient of dF_x/ds in Eq. (5) is structural in the sense that it arises from the Laplacian in spherical polar coordinates in such a fashion that the asymptotic behavior of the density appears only through the coefficient and the spherical symmetry assumed in Eq. (4).

Setting the right-hand side of Eq. (5) equal to $-1/r$ yields a differential equation for the large-r, hence large-s behavior of F_X. Consider what asymptotic potential behavior emerges from the structural contribution of Eq. (5). In conjunction with the simplest possible large-s form of $F_X^{GGA}(s)$, namely $F_X(s) \xrightarrow[s\to\infty]{} C_0\, s$ with C_0 a constant,[8] one gets

$$v_X^{GGA}([n];\mathbf{r}) \xrightarrow[r\to\infty]{} -\frac{3\,C_0}{4\,\pi}\frac{1}{r} \tag{6}$$

or $C_0 = 4\pi/3$ to deliver the desired X potential asymptotic decay. Note that this constant is completely independent of the density details, an explicit indication of the structural nature of this result.

Another possible solution for the asymptotic behavior of the enhancement factor is $F_X(s) \xrightarrow[s\to\infty]{} C_1\, s \ln s$. Substituting Eq. (4) in the natural logarithm of the reduced density gradient one finds that $\ln s \xrightarrow[r\to\infty]{} \lambda r/3 + \ln(\lambda/(2(3\pi^2 n_0)^{1/3}))$, so that Eq. (5) becomes

$$v_X^{GGA}([n];\mathbf{r}) \xrightarrow[r\to\infty]{} \frac{3\,C_1}{4\pi}\left(\frac{\lambda}{6} - \frac{1+C_A}{r}\right) \quad , \tag{7}$$

With the choice $C_1 = 4\pi/3$ and the recognition that

$$\lambda = 2\sqrt{-2\varepsilon_H} \quad , \tag{8}$$

where ε_H is the HOMO eigenvalue, the result is

$$v_X^{GGA}([n];\mathbf{r}) \xrightarrow[r\to\infty]{} \left(\frac{\sqrt{-2\varepsilon_H}}{3} - \frac{1+C_A}{r}\right) \quad , \tag{9}$$

where

$$C_A = \ln\left(\frac{\sqrt{-2\,\varepsilon_H}}{(3\pi^2 n_0)^{1/3}}\right) \quad . \tag{10}$$

The expression given in Eq. (9) is the same as Eq. (5) of the main paper. Recovery of the asymptotic behavior from an enhancement factor that goes as $s \ln s$ therefore also requires a reference energy shift. This shift has been discussed in a similar context[9-13] and is related to the derivative discontinuity of the KS potential.[14-18] We return to it below. Here we point out that the $-1/r$ contribution in Eq. (9) again is a structural contribution, while the contribution $-C_A/r$ comes from the asymptotic behavior of the density.

The required asymptotic form arises from any linear combination of the two asymptotic s dependences just discussed, $F_X(s) \xrightarrow[s\to\infty]{} C_0\, s$ and $F_X(s) \xrightarrow[s\to\infty]{} C_1\, s \ln s$ with $C_0 = C_1 = 4\pi/3$. Thus the new functional, denoted NCAP (Nearly Correct Asymptotic Potential) must have

$$F_x^{NCAP}(s) \xrightarrow[s\to\infty]{} \frac{4\pi}{3}\left[(1-\zeta)\, s \ln s - \zeta s\right] \quad , \tag{11}$$

that leads to

$$v_X^{GGA}([n];\mathbf{r}) \xrightarrow[r\to\infty]{} v_X^{NCAP}(\varepsilon_H,\, \zeta) - \frac{(1-\zeta)C_A}{r} - \frac{1-\zeta}{r} - \frac{\zeta}{r} \quad , \tag{12}$$

The constant $v_x^{NCAP}(\varepsilon_H,\, \zeta)$ is system-dependent, as denoted by its dependence on the HOMO eigenvalue of the NCAP potential.

On the other hand, the enhancement factor when $s \to 0$ is[19]

$$F_X^{NCAP}(s) \xrightarrow[s\to 0]{} 1 + \mu s^2 + \ldots \ , \tag{13}$$

where $\mu = 0.219514973$ corresponds to the PBE value.

Thus, a GGA enhancement factor which achieves these asymptotic properties and has the proper small-s limit, is (Eq. (8) of the article)

$$F_x^{NCAP}(s) = 1 + \mu \tanh(s) \sinh^{-1}(s) \frac{1 + \alpha((1-\zeta)\, s \ln(1+s) + \zeta\, s)}{1 + \beta \tanh(s) \sinh^{-1}(s)} \quad , \tag{14}$$

with $\alpha = 4\pi\beta/3\mu$, $\mu = 0.219514973$, $\beta = 0.018085697$, and $\zeta = 0.304121419$, all fixed through constraint satisfaction (see the details in the article).

b) Augmented versions of the tables that appear in the article to report the MD (Mean Deviation) in addition to the MAD (Mean Absolute Deviation

Table I. MD and MAD for the exchange, correlation and exchange-correlation energies of the noble gas atoms Ne, Ar, Kr, Xe in Hartrees.

	E_X		E_C		E_{XC}	
	MD	MAD	MD	MAD	MD	MAD
LSDA	4.35	4.35	–1.17	1.17	3.18	3.18
PBE	0.41	0.41	0.06	0.06	0.46	0.46
CAP	0.98	0.98	0.06	0.06	1.04	1.04
NCAP	0.20	0.20	–0.13	0.14	0.06	0.07
SCAN	–0.13	0.14	0.07	0.07	-0.07	0.08
B3LYP	0.38	0.38	–0.27	0.27	0.10	0.11
CAM-B3LYP	0.17	0.17	–0.16	0.16	0.02	0.02

Table II. MD and MAD for the heats of formation of the G3 set in kcal/mol (223 molecules), Barrier heights of the BH76 set of reactions in kcal/mol, binding energy of weakly bonded systems of the WB31 set in kcal/mol, bond distances of the T-96R set in Å and dipole moments of the Hait and Head-Gordon set in Debyes (144 molecules)*

	G3		BH		WB		BD		DM	
	MD	MAD	MD	MAD	MD	MAD	MD	MAD	MD	MAD
LSDA	–118.0	118.3	–14.4	15.5	3.5	3.6	-0.066	0.082	–0.051	0.159
PBE	-20.7	21.2	–8.4	9.9	0.80	1.6	0.018	0.018	–0.084	0.153
CAP	-0.4	9.2	–5.9	7.6	-2.3	2.7	0.022	0.022	–0.067	0.141
NCAP	-2.7	6.0	-6.4	8.0	–1.9	2.4	0.025	0.025	–0.076	0.143
SCAN	-3.7	5.1	–6.7	8.6	1.3	1.6	0.003	0.009	–0.020	0.089
B3LYP	4.8	5.7	-3.6	5.9	-0.3	1.2	0.005	0.011	–0.018	0.075
CAM-B3LYP	0.03	3.2	–3.2	3.7	0.1	1.0	0.003	0.014	0.030	0.067

*The original test set of Hait and Head-Gordon has 152 molecules. However in our calculations eight molecules (BH, CH, CH_2NH, CH_2-singlet, HOF, NaLi, O_3, and SiH) were excluded because independently of the XC functional, the calculations did not converge to the ground state.

Table III. Comparison of the HOMO eigenvalue with the experimental ionization potential[20-23] in eV for some of the noble gases. The values for NCAP correspond to the shifted exchange potential.

	Ne	Ar	Kr	Xe	MD	MAD
LSDA	13.56	10.40	9.42	8.42	-5.41	5.41
PBE	13.35	10.29	9.28	8.28	-5.57	5.57
CAP	13.11	10.13	9.15	8.17	-5.73	5.73
NCAP	21.19	17.44	16.19	14.92	1.57	1.76
SCAN	14.00	10.73	9.69	8.62	-5.11	5.11
B3LYP	15.65	11.67	10.47	9.28	-4.10	4.10
CAM-B3LYP	17.67	13.48	12.19	10.89	-2.31	2.31
Hartree-Fock	23.14	16.08	14.26	12.44	0.62	0.62
Exp. IP	21.57	15.76	14.00	12.13		

Table IV. MD and MAD for 17 valence and 23 Rydberg excitation energies in eV for a test set with four molecules. The values for NCAP correspond to the unshifted exchange potential.

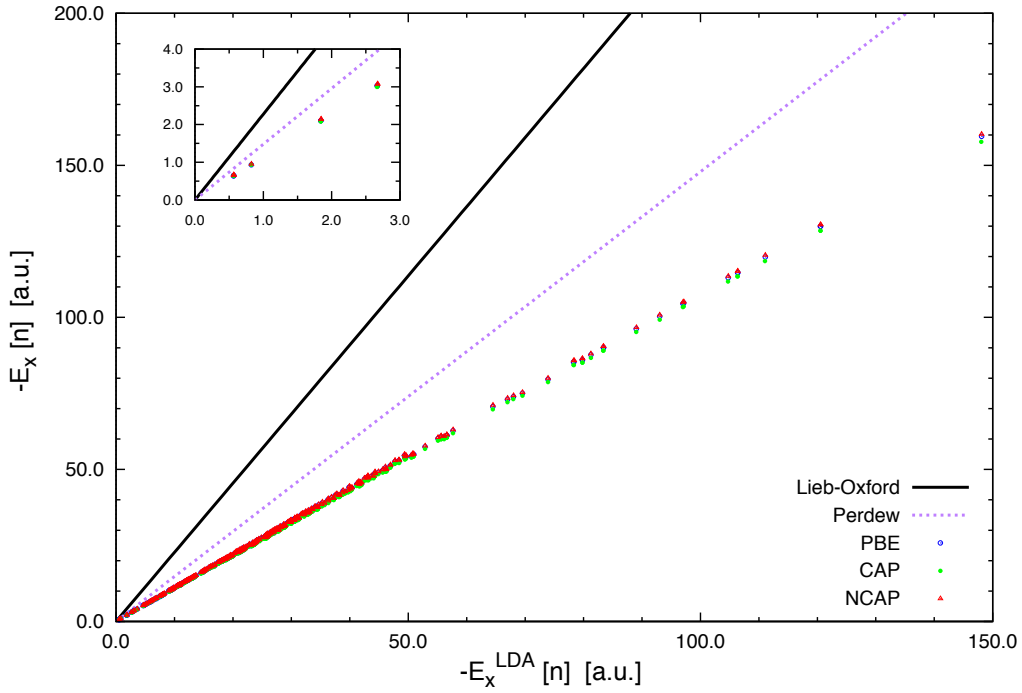
	Valence		Rydberg		Total	
	MD	MAD	MD	MAD	MD	MAD
LSDA	-0.16	0.30	-1.29	1.29	-0.81	0.87
PBE	-0.32	0.35	-1.47	1.47	-0.98	1.00
CAP	-0.28	0.32	-1.25	1.25	-0.84	0.86
NCAP	-0.20	0.26	-0.63	0.64	-0.45	0.48
B3LYP	–0.40	0.40	-0.88	0.88	-0.68	0.68
CAM-B3LYP	-0.41	0.42	–0.46	0.46	–0.44	0.44

c) Plot of satisfaction by NCAP of the global Lieb-Oxford[1] and Perdew *et al.*[2] bounds

Lieb-Oxford bound[1] $$E_X[n_\uparrow, n_\downarrow] \geq -1.679 \int d\mathbf{r}\, n^{4/3}(\mathbf{r})$$

Perdew et al. bound[2] $$E_X[n_\uparrow, n_\downarrow] \geq -1.092 \int d\mathbf{r}\, n^{4/3}(\mathbf{r})$$

The number of cases considered is 492. That total corresponds to the atoms and molecules in the test sets for the heats of formation (G3), barrier heights (BH), weakly bonded systems (WB), bond distances (BD), ionization potentials (IP), electron affinities (EA), proton affinities (PA), and frequencies (F). Specific atoms and molecules are listed in Section h) below.



d) Comparison of NCAP-shifted HOMO eigenvalue with the system-dependent XC functional of Gledhill and Tozer[3] HOMO eigenvalues for small molecules

Gledhill and Tozer[3] have recently developed an XC functional called ED (for electron deficient) based on density scaling considerations. It contains a Fermi-Amaldi term that leads to an X potential with the correct asymptotic behavior. This functional yields eigenvalues that lie close to the experimental ionization potentials. In the next table we compare the results with the eigenvalues from the shifted NCAP potential and from PBE. One can see that for both functionals, ED and NCAP, the HOMO eigenvalue gets closer to the exact vertical ionization potential.[24] Quantities in au.

Molecule	PBE	ED	NCAP	-IP
CH_4	-0.347	-0.506	-0.604	-0.526
CO	-0.332	-0.515	-0.588	-0.515
Cl_2	-0.268	-0.414	-0.501	-0.422
F_2	-0.347	-0.611	-0.579	-0.577
H_2O	-0.266	-0.466	-0.499	-0.464
HCl	-0.296	-0.425	-0.528	-0.469
HF	-0.355	-0.593	-0.611	-0.592
N_2	-0.377	-0.593	-0.634	-0.573
MAD	0.194	0.016	0.051	

e) Comparison of the NCAP HOMO and LUMO shifted eigenvalues with those from other XC functionals

In the following table one can see, for the noble gas atoms, that the NCAP shifted potential leads to LUMO eigenvalues that are negative, whereas in all the other functionals give positive LUMO eigenvalues. HOMO-LUMO eigenvalue differences are similar to those predicted by the other functionals. All quantities are in eV.

Atom		LSDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP	HF
He	H	-15.522	-15.763	-15.528	-24.278	-16.537	-18.004	-19.961	-24.979
	L	1.949	1.786	2.503	-5.353	6.077	1.817	2.443	3.201
Ne	H	-13.552	-13.347	-13.107	-21.19	-13.993	-15.649	-17.671	-23.141
	L	2.887	2.733	3.539	-3.994	3.432	2.807	3.413	4.173
Ar	H	-10.402	-10.285	-10.125	-17.444	-10.732	-11.67	-13.481	-16.082
	L	2.754	2.64	3.553	-3.494	3.642	2.869	3.647	4.708
Kr	H	-9.422	-9.28	-9.147	-16.186	-9.687	-10.473	-12.193	-14.263
	L	0.404	0.405	1.218	-5.822	1.355	0.675	1.544	2.798
Xe	H	-8.423	-8.281	-8.171	-14.922	-8.621	-9.278	-10.887	-12.439
	L	0.277	0.301	1.066	-5.729	1.214	0.566	1.396	2.542
Rn	H	-7.977	-7.83	-7.727	-14.337	-8.139	-8.747	-10.299	-11.646
	L	-0.205	-0.205	0.522	-6.015	0.660	0.008	0.694	1.543

f) Results for the individual molecules of the test sets analyzed

In the following tables we present the individual values for each one of the molecules in the different test sets.

All properties included in the G3/99 test set were calculated at the equilibrium B3LYP/631G(2df,p) structures using B3LYP/6-31G(2df,p) zero-point energies obtained with a frequency scale factor of 0.9854.

The experimental or computational data were taken from Refs. [25-42].

List of Tables

Table S1: Deviations of the standard enthalpies of formation for the molecules in the G3/99 set obtained with the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule	$\Delta_f H^o_{298}$	LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	LiH	33.3	-2.3	5.0	7.8	1.0	3.0	-0.0	-0.6
2	BeH	81.7	-9.3	-4.7	-4.3	-6.8	-9.5	-6.9	-6.9
3	CH	142.5	-8.3	-0.6	1.8	-2.7	2.3	-1.3	-0.5
4	$CH_2(^3B_1)$	93.7	-22.3	-4.1	-1.8	-5.1	-6.3	-1.8	-2.1
5	$CH_2(^1A_1)$	102.8	-17.5	2.2	6.3	-0.8	5.8	0.5	1.2
6	CH_3	35.0	-31.6	-2.5	2.5	-4.8	-4.7	-2.4	-3.0
7	CH_4	-17.9	-42.1	0.0	6.4	-2.9	0.7	-0.8	-1.7
8	NH	85.2	-11.3	-4.5	-1.2	-6.7	-0.8	-4.0	-3.1
9	NH_2	45.1	-25.2	-6.1	-0.4	-9.1	-1.8	-5.4	-4.6
10	NH_3	-11.0	-38.0	-2.9	4.1	-6.0	4.5	-1.9	-2.0
11	OH	9.4	-16.9	-2.7	-0.4	-3.5	-1.6	-1.1	-1.3
12	H_2O	-57.8	-32.4	-0.4	3.1	-1.0	4.6	2.9	1.9
13	FH	-65.1	-20.0	0.1	1.2	0.2	4.8	2.7	1.9
14	$SiH_2(^1A_1)$	65.2	-14.6	3.5	5.9	-1.4	2.2	-2.2	-1.9
15	$SiH_2(^3B_1)$	86.2	-16.4	-1.1	-0.6	-4.6	-7.7	-2.5	-2.8
16	SiH_3	47.9	-21.4	2.9	5.4	-3.2	-5.0	-3.2	-4.1
17	SiH_4	8.2	-25.3	8.3	12.5	0.2	-1.3	-1.9	-3.5
18	PH_2	33.1	-20.7	-1.6	0.9	-6.3	-3.4	-5.6	-5.2
19	PH_3	1.3	-27.8	2.7	6.1	-3.4	0.7	-2.7	-2.6
20	H_2S	-4.9	-23.7	0.5	2.2	-1.8	0.5	0.6	0.7
21	HCl	-22.1	-13.8	0.1	0.6	-0.5	1.5	1.5	1.5
22	Li_2	51.6	1.0	4.6	9.9	6.7	6.3	3.9	3.7
23	LiF	-80.1	-16.3	0.9	7.7	5.2	5.9	2.8	0.8
24	HCCH	54.2	-53.7	-8.9	1.2	-1.6	4.1	2.6	2.2
25	CH_2CH_2	12.5	-68.7	-8.1	3.9	-3.4	0.9	0.3	-1.0
26	CH_3CH_3	-20.1	-81.7	-4.9	8.8	-2.7	-0.8	0.6	-2.6
27	CN	104.9	-37.5	-15.8	-7.1	-8.7	4.4	2.3	5.6
28	HCN	31.5	-47.4	-13.2	-2.7	-6.8	5.8	-0.2	0.3
29	CO	-26.4	-39.4	-9.6	-3.1	-1.5	5.2	4.1	2.8
30	CHO	10.0	-53.9	-16.4	-8.8	-8.8	-3.1	-1.5	-2.2
31	CH_2O	-26.0	-59.7	-12.0	-3.3	-5.8	0.8	0.5	-0.5
32	CH_3OH	-48.0	-72.9	-6.9	4.0	-2.8	0.7	1.7	-1.3
33	N_2	0.0	-38.2	-14.7	-4.2	-9.3	10.0	-0.6	0.3
34	N_2H_4	22.8	-75.6	-13.4	1.4	-11.7	5.4	-4.4	-5.7
35	NO	21.6	-45.7	-19.3	-11.6	-12.6	2.0	-2.2	-2.2
36	O_2	0.0	-54.6	-23.6	-19.1	-15.3	-7.2	-3.5	-4.1
37	H_2O_2	-32.5	-65.3	-12.7	-4.6	-7.2	2.3	2.4	0.9
38	F_2	0.0	-39.7	-14.5	-10.8	-8.1	1.1	1.2	1.0
39	CO_2	-94.1	-83.6	-27.1	-16.6	-10.4	-3.4	1.6	0.3
40	Na_2	34.0	-3.3	-0.7	7.6	3.8	2.7	0.0	0.8
41	Si_2	139.9	-16.2	-6.7	-4.3	-3.4	0.1	5.5	11.5
42	P_2	34.3	-25.8	-4.2	-0.0	-1.9	4.8	1.6	6.4
43	S_2	30.7	-33.5	-13.7	-11.1	-7.5	-7.8	-1.7	1.4
44	Cl_2	0.0	-25.0	-7.9	-5.7	-1.9	-0.3	2.3	3.4
45	NaCl	-43.6	-5.4	4.1	7.3	6.9	2.2	5.7	4.5
46	SiO	-24.6	-30.7	-3.2	2.8	2.4	5.9	5.3	4.5
47	CS	66.9	-30.4	-8.3	-3.5	-1.7	4.1	5.1	7.8
48	SO	1.2	-41.6	-15.5	-11.3	-8.3	-5.9	-0.9	-0.5
49	ClO	24.2	-38.8	-16.3	-12.3	-9.6	-4.2	-1.1	0.0
50	ClF	-13.2	-33.2	-10.7	-7.4	-4.3	0.7	1.0	0.6

Table S1 – continued

51	Si_2H_6	19.1	-49.0	10.1	18.7	2.6	-5.9	-0.4	-3.9
52	CH_3Cl	-19.6	-52.2	-5.5	2.2	-1.6	-1.3	1.8	0.4
53	CH_3SH	-5.5	-62.4	-4.7	4.2	-2.1	-1.2	1.9	0.4
54	HOCl	-17.8	-45.8	-10.6	-5.3	-4.8	0.6	2.0	1.6
55	SO_2	-71.0	-75.5	-20.6	-11.8	-5.6	-0.1	8.5	7.7
56	BF_3	-271.4	-77.7	-11.0	3.2	11.1	0.3	6.1	-1.8
57	BCl_3	-96.3	-59.3	-13.6	-3.8	6.5	-8.7	8.4	5.6
58	AlF_3	-289.0	-54.7	0.6	14.1	17.7	5.6	11.0	3.0
59	$AlCl_3$	-139.7	-37.5	-0.9	7.4	14.6	-6.1	11.3	7.2
60	CF_4	-223.0	-122.9	-27.9	-11.3	3.0	-4.9	7.4	-3.8
61	CCl4	-22.9	-87.8	-21.5	-7.7	6.3	-3.5	15.9	13.0
62	COS	-33.1	-75.3	-26.2	-17.3	-10.9	-7.0	0.3	1.8
63	CS_2	28.0	-65.8	-23.8	-16.5	-9.9	-8.5	0.9	6.2
64	COF_2	-149.1	-100.8	-25.3	-11.9	-1.6	-0.9	7.5	1.5
65	SiF_4	-386.0	-80.9	2.3	19.9	27.2	8.4	17.4	5.4
66	SiCl4	-158.4	-59.7	-3.6	7.7	19.8	-6.7	19.1	13.9
67	N_2O	19.6	-90.7	-40.2	-26.3	-26.2	-1.2	-5.1	-1.7
68	NOCl	12.4	-74.7	-33.3	-22.6	-21.3	-4.8	-2.0	3.1
69	NF_3	-31.6	-107.0	-40.3	-26.0	-20.2	-6.2	-2.7	-6.3
70	PF_3	-229.1	-77.5	-10.3	2.9	8.0	4.1	6.8	-0.8
71	O_3	34.1	-95.0	-37.8	-28.2	-22.6	-1.1	6.5	9.7
72	F_2O	5.9	-78.0	-30.6	-22.1	-17.5	-4.6	-0.6	-1.3
73	ClF_3	-38.0	-102.2	-39.5	-27.9	-19.4	-11.7	-1.6	-2.3
74	CF_2CF_2	-157.4	-160.9	-47.3	-25.6	-8.8	-12.8	0.4	-9.7
75	CCl_2CCl_2	-3.0	-122.3	-35.0	-16.2	1.5	-10.7	13.7	10.3
76	CF_3CN	-118.4	-150.1	-41.9	-16.2	-5.0	-1.7	5.6	-2.9
77	CH_3CCH(propyne)	44.2	-96.3	-15.8	1.2	-3.2	0.8	2.5	0.1
78	CH_2CCH_2(allene)	45.5	-101.4	-20.6	-3.4	-7.8	-3.1	-1.0	-2.3
79	$C3H_4$(cyclopropene)	66.2	-101.4	-18.7	-2.7	-4.4	0.5	4.3	1.1
80	CH_3CHCH_2(propylene)	4.8	-109.8	-13.3	6.2	-3.0	-1.3	1.9	-1.8
81	$C3H_6$(cyclopropane)	12.7	-115.0	-15.4	2.9	-3.3	-3.0	3.5	-2.0
82	$C3H_8$(propane)	-25.0	-121.4	-9.0	12.6	-1.0	-2.1	3.0	-2.8
83	C_4H_6(1,3-butadien)	26.3	-137.8	-22.2	3.2	-3.8	-2.6	2.9	-0.3
84	C_4H_6(2-butyne)	34.8	-137.7	-21.7	2.3	-3.8	-1.5	3.5	-0.9
85	C_4H_6(methylene cyclopropane)	47.9	-147.1	-28.0	-4.4	-8.0	-6.9	1.4	-4.0
86	C_4H_6(bicyclobutane)	51.9	-147.2	-25.0	-2.1	-2.7	-4.0	8.6	1.2
87	C_4H_6(cyclobutene)	37.4	-142.7	-22.7	0.8	-2.0	-2.4	7.3	1.3
88	C_4H_8(cyclobutane)	6.8	-154.9	-19.1	6.7	-0.9	-4.4	6.7	-1.6
89	C_4H_8(isobutene)	-4.0	-150.2	-17.4	10.2	-1.0	-2.8	4.7	-1.6
90	C_4H_{10}(butane)	-30.0	-160.9	-12.9	16.6	0.8	-3.6	5.5	-2.8
91	C_4H_{10}(isobutane)	-32.1	-160.8	-11.9	18.2	2.3	-2.8	6.8	-1.8
92	C_5H_8(spiropentane)	44.3	-189.8	-32.0	-1.7	-4.4	-7.8	7.4	-2.5
93	C_6H_6(benzene)	19.7	-205.4	-42.2	-6.3	-3.8	-9.7	6.3	-0.5
94	CH_2F_2	-107.7	-80.5	-14.4	-2.9	-1.5	-1.6	2.0	-3.3
95	CHF_3	-166.6	-101.6	-21.3	-7.0	0.6	-3.1	4.6	-3.5
96	CH_2Cl_2	-22.8	-63.4	-11.0	-1.5	0.5	-1.9	5.7	3.9
97	$CHCl_3$	-24.7	-75.3	-16.4	-4.8	3.2	-2.8	10.5	8.2
98	CH_3NH_2(methylamine)	-5.5	-77.8	-8.1	6.1	-6.2	2.5	-1.3	-3.6
99	CH_3CN(acetronitrile)	18.0	-89.6	-19.8	-2.3	-8.2	2.8	-0.2	-1.7
100	CH_3NO_2(nitromethane)	-17.8	-142.1	-41.0	-19.9	-21.2	-5.6	-1.0	-3.4
101	CH_3ONO(methyl nitrite)	-15.9	-137.5	-38.7	-16.9	-19.8	-4.5	-0.2	-2.8
102	CH_3SiH_3(methyl silane)	-7.0	-63.0	5.2	16.7	2.5	-1.3	1.6	-2.2
103	HCOOH(formic acid)	-90.5	-96.2	-21.3	-7.7	-6.6	-2.2	2.7	-0.9
104	$HCOOCH_3$(methyl formate)	-85.0	-136.6	-26.7	-5.0	-6.9	-6.0	2.7	-3.3
105	CH_3CONH_2(acetamide)	-57.0	-142.0	-26.9	-2.0	-8.5	-2.9	0.9	-4.6
106	C_2H_4NH(aziridine)	30.2	-110.7	-19.9	-1.2	-8.5	-0.7	0.9	-3.2

Table S1 – continued

107	C_2N_2(cyanogen)	73.3	-97.0	-35.8	-14.3	-15.0	6.4	-0.6	2.0
108	$(CH_3)_2NH$(dimethylamine)	-4.4	-118.6	-13.0	9.3	-5.3	0.4	0.1	-4.7
109	$CH_3CH_2NH_2$(ethylamine)	-11.3	-118.9	-13.5	8.7	-5.7	-0.1	-0.1	-4.9
110	CH_2CO(ketene)	-11.4	-94.7	-25.7	-11.8	-10.8	-5.0	-1.2	-2.4
111	C_2H_4O(oxirane)	-12.6	-105.7	-19.3	-4.1	-6.1	-3.4	3.3	-1.1
112	CH_3CHO(acetaldehyde)	-39.7	-101.4	-17.6	-1.2	-5.6	-1.8	1.7	-1.7
113	HCOCHO(glyoxal)	-50.7	-118.7	-29.7	-10.6	-8.4	-1.8	3.1	-0.3
114	CH_3CH_2OH(ethanol)	-56.2	-113.0	-11.1	7.7	-1.3	-0.8	3.9	-1.8
115	CH_3OCH_3(dimethyl ether)	-44.0	-113.7	-12.2	7.0	-2.7	-2.6	2.2	-3.3
116	C_2H_4S(thiirane)	19.6	-95.5	-16.4	-2.9	-4.2	-4.4	4.1	1.6
117	$(CH_3)_2SO$(dimethyl sulfoxide)	-36.2	-135.9	-18.7	3.3	-2.4	-4.7	7.7	3.2
118	C_2H_5SH(ethanethiol)	-11.1	-101.8	-8.5	8.2	-0.2	-1.9	4.6	0.7
119	CH_3SCH_3(dimethyl sulfide)	-8.9	-101.9	-9.8	6.9	-1.7	-2.9	3.7	0.3
120	CH_2CHF(vinil fluoride)	-33.2	-91.6	-17.9	-3.4	-4.8	-3.0	0.2	-3.3
121	C_2H_5Cl(ethyl chloride)	-26.8	-92.0	-9.7	5.9	-0.1	-2.4	4.2	0.4
122	CH_2CHCl(vinyl chloride)	8.9	-85.2	-18.5	-5.1	-6.3	-5.6	-0.5	-2.3
123	CH_2CHCN(acrylonitrile)	43.2	-115.3	-26.9	-3.7	-7.5	3.7	2.5	1.4
124	CH_3COCH_3(acetone)	-51.9	-141.9	-21.8	2.5	-4.0	-3.6	4.0	-2.1
125	CH_3COOH(acetic acid)	-103.4	-136.2	-25.2	-3.9	-4.8	-3.9	5.0	-1.5
126	CH_3COF(acetyl fluoride)	-105.7	-123.0	-25.3	-6.4	-4.7	-4.2	3.9	-2.3
127	CH_3COCl(acetyl chloride)	-58.0	-115.5	-25.4	-7.3	-5.8	-5.9	4.5	1.3
128	$CH_3CH_2CH_2Cl$(propyl chloride)	-31.5	-131.8	-13.9	9.5	1.4	-4.1	6.5	0.1
129	$(CH_3)_2CHOH$(isopropanol)	-65.2	-153.2	-14.8	12.4	1.3	-2.2	6.9	-1.6
130	$C_2H_5OCH_3$(methyl ethyl ether)	-51.7	-154.1	-16.8	10.2	-1.5	-4.7	4.0	-4.1
131	$(CH_3)_3N$(trimethylamine)	-5.7	-160.0	-17.5	13.6	-3.4	-1.9	2.3	-5.4
132	C_4H_4O(furan)	-8.3	-171.0	-37.7	-11.0	-5.7	-8.1	6.2	-0.9
133	C_4H_4S(thiophene)	27.5	-158.1	-34.1	-9.4	-3.3	-7.6	8.8	4.4
134	C_4H_5N(pyrrole)	25.9	-177.6	-39.3	-9.2	-8.7	-6.1	2.9	-3.6
135	C_5H_5N(pyridine)	33.6	-202.2	-47.6	-11.2	-9.8	-8.4	2.6	-3.1
136	H_2	0.0	-3.5	4.9	4.2	-2.6	2.0	-0.6	0.4
137	SH	34.2	-12.6	-1.0	-0.0	-2.5	-1.6	-1.2	-1.0
138	$CCH(^2A',C_s)$	135.1	-42.9	-11.2	-3.4	-3.1	0.1	3.2	3.7
139	$CHCH_2(^2A',C_s)$	71.6	-62.1	-13.1	-2.6	-7.3	-5.7	-2.4	-3.1
140	$CH_3CO(^2A',C_s)$	-2.4	-95.2	-22.2	-7.1	-9.2	-5.8	-0.7	-3.5
141	$CH_2OH(^2A,C_1)$	-4.1	-67.2	-11.7	-2.0	-6.3	-4.4	-0.8	-3.5
142	$CH_3O(^2A',C_s)$	4.1	-59.8	-12.4	-2.7	-7.9	-6.6	-2.9	-4.7
143	$CH_3CH_2O(^2A'',C_s)$	-3.7	-100.2	-18.4	-0.8	-8.1	-9.2	-2.1	-6.4
144	$CH_3S(^2A',C_s)$	29.8	-53.2	-8.4	-0.3	-4.8	-4.8	-1.3	-2.6
145	$CH_3CH_2(^2A',C_s)$	28.9	-73.8	-8.8	3.5	-5.7	-6.9	-1.9	-4.5
146	$(CH_3)_2CH(^2A',C_s)$	21.5	-115.6	-14.5	5.5	-5.7	-9.0	-0.7	-5.6
147	$(CH_3)_3C$(t-butyl radical C_{3v})	12.3	-156.1	-18.5	9.6	-3.5	-9.8	2.4	-5.0
148	NO_2	7.9	-95.8	-42.5	-30.8	-27.3	-8.1	-5.1	-3.5
149	CH_2=C=$CHCH_3$ (1,2-butadiene)	38.8	-141.2	-25.1	-0.5	-6.9	-4.1	1.0	-2.4
150	CH_2=CH-$C(CH_3)$=CH_2 (isoprene)	18.0	-178.4	-25.8	7.9	-1.0	-3.9	6.3	0.2
151	C_5H_{10} (cyclopentane)	-18.3	-194.4	-20.9	13.4	3.9	-4.6	11.2	-0.2
152	C_5H_{12} (n-pentane)	-35.1	-200.3	-16.6	20.7	2.8	-4.6	8.3	-2.6
153	$C(CH_3)_4$ (neopentane)	-40.2	-199.8	-13.6	25.3	7.3	-2.9	12.0	0.2
154	C_6H_8 (1,3-cyclohexadiene)	25.4	-213.3	-34.7	3.5	1.0	-6.1	10.8	1.3
155	C_6H_8 (1,4-cyclohexadiene)	25.0	-212.9	-34.2	3.7	1.4	-5.6	11.0	1.0
156	C_6H_{12} (cyclohexane)	-29.5	-234.8	-23.6	19.6	7.8	-6.4	14.9	0.3
157	C_6H_{14} (n-hexane)	-39.9	-240.0	-20.7	24.5	4.5	-4.8	10.7	-2.7
158	C_6H_{14} (3-methyl pentane)	-41.1	-239.9	-18.8	27.6	7.4	-4.8	13.2	-0.7
159	$C_6H_5CH_3$ (toluene)	12.0	-245.6	-46.3	-2.6	-2.0	-11.3	9.2	-0.1
160	C_7H_{16} (n-heptane)	-44.9	-279.4	-24.5	28.6	6.4	-7.0	13.4	-2.6
161	C_8H_8 (1,3,5,7-cyclooctatetraene)	70.7	-270.2	-51.8	-1.2	0.5	-6.7	13.8	4.2
162	C_8H_{18} (n-octane)	-49.9	-318.9	-28.4	32.6	8.3	-9.0	16.0	-2.5

Table S1 – continued

163	$C_{10}H_8$ (naphthalene)	35.9	-341.6	-75.4	-14.8	-2.9	-19.8	13.9	2.2
164	$C_{10}H_8$ (azulene)	69.1	-343.1	-78.2	-17.6	-6.1	-19.2	14.1	6.4
165	CH_3COOCH_3 (methyl acetate)	-98.4	-175.7	-29.5	-0.1	-3.9	-6.8	6.1	-2.8
166	$(CH_3)_3COH$ (t-butanol)	-74.7	-192.7	-17.2	18.7	5.4	-3.0	11.3	-0.3
167	$C_6H_5NH_2$ (aniline)	20.8	-246.2	-52.6	-8.3	-8.1	-11.1	5.1	-3.2
168	C_6H_5OH (phenol)	-23.0	-239.9	-50.2	-9.3	-3.5	-11.6	9.6	0.5
169	CH_2=CH-O-CH=CH_2 (divinyl ether)	-3.3	-173.7	-31.6	-1.3	-5.3	-5.3	3.9	-2.4
170	C_4H_8O (tetrahydrofuran)	-44.0	-186.8	-24.4	7.2	1.8	-5.5	10.0	-1.2
171	C_5H_8O (cyclopentanone)	-45.9	-216.5	-35.4	1.3	-0.9	-8.0	10.7	-1.2
172	$C_6H_4O_2$ (1,4-benzoquinone)	-29.4	25.3	-60.9	-17.1	-6.0	-9.9	12.4	4.0
173	$C_4H_4N_2$ (pyrimidine)	46.8	-200.0	-54.1	-17.4	-17.0	-8.4	-2.4	-7.4
174	$(CH_3)_2SO_2$ (dimethyl sulfone)	-89.2	-168.3	-23.7	2.7	1.4	-7.3	14.2	6.0
175	C_6H_5Cl (chlorobenzene)	12.4	-217.8	-48.2	-10.6	-2.0	-11.9	10.0	2.7
176	NC-CH_2CH_2-CN (succinonitrile)	50.1	-174.6	-42.1	-5.6	-10.2	5.3	4.2	-0.1
177	$C_4H_4N_2$ (pyrazine)	46.9	-196.4	-50.5	-13.7	-13.5	-4.2	1.5	-3.1
178	CH_3COCCH (acetyl acetylene)	15.6	-153.3	-31.0	-3.5	-3.1	-0.2	8.3	3.9
179	CH_3-CH=CH-CHO (crotonaledehyde)	-24.0	-171.6	-32.8	-3.0	-7.2	-6.5	3.2	-2.3
180	$(CH_3CO)_2O$ (acetic anhydride)	-136.8	-237.9	-48.5	-9.0	-7.3	-10.7	8.3	-3.4
181	C_4H_6S (25-dihydrothiophene)	20.8	-165.1	-27.5	-0.5	-0.2	-5.8	9.6	2.8
182	$CH_3CH(CH_3)CN$ (2-methyl propanenitrile)	5.6	-165.9	-25.3	8.0	-2.2	2.4	7.1	0.5
183	CH_3-CO-CH_2CH_3 (methyl ethyl ketone)	-57.1	-181.8	-25.7	6.5	-2.0	-5.4	6.7	-2.2
184	$(CH_3)_2$CH-CHO (isobutyraldehyde)	-51.6	-178.9	-23.7	8.8	-0.0	-2.7	8.7	0.1
185	$C_4H_8O_2$ (1,4-dioxane)	-75.5	-220.9	-31.8	6.2	2.6	-8.7	11.6	-2.4
186	C_4H_8S (tetrahydrothiophene)	-8.2	-174.9	-21.0	8.5	4.1	-5.0	12.7	3.7
187	$(CH_3)_3C$-Cl (t-butyl chloride)	-43.5	-171.6	-15.7	17.0	6.6	-4.6	11.8	2.3
188	$CH_3CH_2CH_2CH_2Cl$ (n-butyl chloride)	-37.0	-170.6	-17.2	14.1	3.9	-3.8	9.7	0.8
189	C_4H_8NH (pyrrolidine)	-0.8	-192.4	-25.8	9.2	-1.3	-3.2	7.4	-3.1
190	$CH_3CH_2CH(NO_2)CH_3$ (2-nitrobutane)	-39.1	-260.9	-51.4	-5.7	-13.5	-9.3	8.2	-2.3
191	$CH_3CH_2OCH_2CH_3$ (diethyl ether)	-60.3	-193.4	-20.4	14.5	0.7	-5.1	6.8	-3.9
192	CH_3-$CH(OCH_3)_2$ (1,1-dimethoxy ethane)	-93.1	-221.1	-21.8	19.2	7.4	-1.7	14.9	1.5
193	$(CH_3)_3C$-SH (t-butanethiole)	-26.2	-181.5	-14.4	19.6	6.8	-3.8	12.7	3.0
194	$(CH_3CH_2S)_2$ (diethyl disulfide)	-17.9	-201.3	-22.5	12.9	3.0	-7.6	12.9	5.3
195	$(CH_3)_3C$-NH_2 (t-butylamine)	-28.9	-197.4	-18.2	21.2	2.4	-1.0	8.7	-2.2
196	$Si(CH_3)_4$ (tetramethyl silane)	-55.7	-175.6	-1.9	32.7	12.6	-0.4	14.7	3.8
197	C_5H_6S (2-methyl thiopehene)	20.0	-198.1	-38.4	-6.0	-1.9	-8.8	11.2	4.5
198	C_5H7N (N-methyl pyrrole)	24.6	-217.2	-43.2	-5.2	-7.1	-7.9	5.2	-3.8
199	$C_5H_{10}O$ (tetrahydropyran)	-53.4	-227.8	-27.5	13.1	5.4	-7.4	13.4	-0.9
200	$C_2H_5COC_2H_5$ (diethyl ketone)	-61.6	-222.2	-30.3	9.9	-0.7	-7.4	8.7	-2.8
201	$CH_3COOCH(CH_3)_2$ (isopropyl acetate)	-115.1	-255.3	-36.7	9.1	0.9	-8.4	11.9	-2.4
202	$C_5H_{10}S$ (tetrahydrothiopyran)	-15.2	-215.6	-24.5	13.9	7.2	-6.6	15.8	3.7
203	$C_5H_{10}NH$ (piperidine)	-11.3	-233.3	-28.8	15.1	2.3	-5.1	10.8	-2.9
204	$(CH_3)_3COCH_3$ (t-butyl methyl ether)	-67.8	-233.0	-21.4	23.2	7.0	-5.8	13.1	-1.2
205	$C_6H_4F_2$ (1,3-difluuorobenzene)	-73.9	-249.4	-59.6	-18.3	-4.1	-15.8	8.2	-3.1
206	$C_6H_4F_2$ (1,4-difluuorobenzene)	-73.3	-249.2	-59.5	-18.3	-4.0	-15.6	8.3	-3.0
207	C_6H_5F (fluorobenzene)	-27.7	-227.1	-50.6	-12.0	-3.7	-12.4	7.5	-1.5
208	$(CH_3)_2CHOCH(CH_3)_2$ (diisopropyl ether)	-76.3	-272.6	-26.2	25.9	7.5	-6.5	14.4	-2.2
209	PF_5	-381.1	-123.4	-10.6	10.8	23.4	4.2	18.2	2.5
210	SF_6	-291.7	-171.6	-32.4	-8.1	13.6	-9.8	20.3	2.2
211	P_4	14.1	-75.3	-19.5	-11.3	-3.9	-2.6	10.3	16.5
212	SO_3	-94.6	-110.4	-30.6	-18.2	-7.3	-5.0	11.9	9.5
213	SCl_2	-4.2	-47.4	-14.8	-9.6	-3.0	-4.6	4.1	6.2
214	$POCl_3$	-133.8	-88.5	-17.5	-3.9	7.4	-7.3	14.8	11.6
215	PCl_5	-86.1	-97.9	-21.9	-6.0	9.3	-14.2	17.7	15.6
216	SO_2Cl_2	-84.8	-115.6	-31.5	-17.2	-2.7	-10.8	15.2	13.8
217	PCl_3	-69.0	-59.9	-14.7	-5.5	1.7	-6.3	7.2	8.3
218	S_2Cl_2	-4.0	-75.8	-27.5	-19.3	-9.7	-12.7	2.4	7.3

Table S1 – continued

219	$SiCl_2$ ($^1A_1$)	-40.3	-35.0	-5.9	0.1	4.4	-2.6	5.7	5.8
220	CF_3Cl	-169.5	-115.8	-28.4	-12.3	1.7	-6.7	7.8	-1.3
221	C_2F_6	-321.3	-203.3	-46.6	-15.6	7.3	-10.6	13.2	-5.6
222	CF_3	-111.3	-97.4	-28.6	-16.1	-5.6	-9.7	0.5	-6.8
223	C_6H_5 (phenyl radical)	81.2	-199.1	-47.8	-13.6	-8.5	-16.4	3.5	-2.3

Table S2: Deviations of the ionization potential for the test set IP13/3 for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	C	259.7	9.3	6.3	2.9	5.6	9.7	6.2	6.7
2	S	238.9	3.6	0.4	-3.2	3.1	-0.4	3.4	3.1
3	SH	238.9	4.0	-0.4	-4.0	1.1	-0.1	1.8	1.7
4	Cl	299.1	5.2	0.2	-3.5	1.3	1.4	2.3	2.4
5	Cl_2	265.3	-1.6	-4.2	-7.5	-3.0	1.2	1.3	3.6
6	OH	299.1	9.0	4.2	-1.7	5.1	2.2	6.0	5.8
7	O	313.9	9.1	10.2	2.3	12.4	3.4	12.5	11.5
8	O_2	278.9	10.1	7.0	3.2	7.8	14.0	14.6	15.1
9	P	241.9	2.2	0.4	-1.6	-0.0	3.7	-2.0	-1.9
10	PH	234.1	3.5	2.5	0.2	2.4	6.5	0.9	1.0
11	PH_2	226.3	4.1	3.8	1.0	4.0	8.5	2.9	3.1
12	S_2	216.0	5.1	4.2	1.3	4.8	9.2	7.4	9.0
13	Si	187.9	2.0	1.3	-0.7	1.5	4.1	-0.6	-0.7

Table S3: Deviations of the electron affinities for the test set EA13/3 for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	C	29.1	12.0	7.0	3.8	6.7	4.6	2.3	1.4
2	S	47.9	6.9	1.8	-2.4	3.4	1.2	2.7	1.7
3	SH	53.3	6.0	0.4	-3.7	1.2	-1.4	0.6	-0.4
4	Cl	83.4	7.8	1.7	-2.3	2.4	1.2	2.2	1.6
5	Cl_2	55.6	9.7	12.2	7.2	14.5	14.3	16.3	14.5
6	OH	42.1	9.7	0.5	-4.5	1.1	-6.8	-1.5	-1.9
7	O	33.7	11.7	5.1	-1.2	6.2	0.0	3.7	3.3
8	O_2	10.8	1.5	-0.3	-6.3	1.4	-3.5	3.0	2.3
9	P	17.2	5.4	1.7	-2.3	4.9	-0.3	3.7	2.0
10	PH	23.2	4.9	0.2	-4.1	1.9	-1.7	1.3	-0.2
11	PH_2	29.4	3.8	-1.4	-5.5	-0.5	-4.0	-1.2	-2.4
12	S_2	38.5	2.1	-0.1	-4.1	1.4	-0.4	2.6	2.9
13	Si	31.9	4.3	2.0	0.1	2.5	3.2	-1.2	-2.5

Table S4: Deviations of the proton affinities for the test set PA8 for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	NH_3	211.9	-4.8	-1.3	1.3	0.5	0.0	-1.0	-2.1
2	H_2O	171.8	-4.5	-2.0	0.7	-0.3	-0.7	-2.1	-3.1
3	HCCH	156.6	-2.4	2.6	5.0	4.6	4.0	2.3	1.2
4	SiH_4	156.5	-8.6	-0.9	0.4	1.8	-2.4	-0.2	-2.9
5	PH_3	193.1	-9.0	-2.6	-0.7	-0.2	-0.4	-0.3	-1.1
6	H_2S	173.7	-5.9	-0.2	1.7	1.8	-0.0	-0.1	-1.8
7	HCl	137.1	-5.6	-0.7	1.4	1.1	-1.4	-1.8	-3.6
8	H_2	105.9	-4.3	-0.9	1.1	0.3	-1.4	-2.6	-4.0

Table S5: Deviations of the binding energies for the 31 weakly interacting systems for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	$(NH_3)_2$	3.15	3.32	1.08	-1.68	-1.27	1.21	0.39	0.90
2	$(HF)_2$	4.57	3.13	0.73	-2.17	-1.76	1.25	0.43	1.06
3	$(H_2O)_2$	4.97	4.46	1.56	-1.42	-1.07	1.86	1.03	1.75
4	NH_3-H_2O	6.41	5.62	2.23	-0.82	-0.51	2.11	1.35	2.03
5	$(HCONH_2)_2$	14.94	6.74	-0.20	-5.29	-4.77	1.18	-1.38	0.13
6	$(HCOOH)_2$	16.15	9.34	0.62	-4.32	-4.27	2.05	-0.54	1.36
7	C_2H_4-F2	1.06	3.93	2.30	-0.75	-0.22	1.98	0.55	0.23
8	NH_3-F2	1.81	6.99	4.66	1.39	1.89	3.65	1.98	1.46
9	C_2H_2-ClF	3.81	6.33	2.31	-1.47	-0.79	3.36	0.01	-0.26
10	HCN-ClF	4.86	4.97	1.09	-2.56	-1.93	0.72	-0.25	0.16
11	NH_3-Cl2	4.88	9.02	4.89	1.42	1.85	4.10	2.21	1.70
12	H_2O-ClF	5.36	7.10	2.98	-0.77	-0.21	3.41	1.26	1.62
13	NH_3-ClF	10.62	14.81	8.09	4.17	4.10	7.99	3.82	2.97
14	$(H_2S)_2$	1.66	2.29	0.53	-1.76	-1.47	-1.40	-0.40	-0.12
15	$(HCl)_2$	2.01	2.18	0.25	-2.23	-1.84	0.75	-0.54	-0.21
16	HCl-H_2S	3.35	3.94	1.29	-1.33	-1.05	0.53	0.00	0.23
17	CH_3Cl-HCl	3.55	3.13	0.02	-3.46	-2.87	1.85	-1.13	-0.61
18	HCN-CH_3SH	3.59	2.49	0.12	-2.96	-2.50	0.90	-0.81	-0.33
19	CH_3SH-HCl	4.16	5.83	2.00	-1.44	-1.13	2.33	0.18	0.54
20	HeNe	0.04	0.32	0.28	-0.41	-0.48	0.18	0.13	0.20
21	HeAr	0.06	0.48	0.40	-0.44	-0.49	0.67	0.18	0.29
22	Ne_2	0.08	0.18	0.15	-0.82	-0.86	0.19	-0.03	0.06
23	NeAr	0.13	0.20	0.06	-1.09	-1.08	0.14	-0.16	-0.04
24	CH_4-Ne	0.22	0.22	0.08	-1.25	-1.22	0.34	-0.20	-0.05
25	C_6H_6-Ne	0.47	0.52	-0.08	-2.69	-2.49	0.22	-0.58	-0.22
26	$(CH_4)_2$	0.51	0.47	-0.50	-2.96	-2.56	0.09	-1.03	-0.62

Table S5 – continued

27	$(C_2H_2)_2$	1.34	0.84	-0.24	-2.61	-2.21	-0.55	-0.81	-0.47
28	$(C_2H_4)_2$	1.42	1.20	-0.91	-4.71	-3.94	-0.85	-1.74	-1.04
29	Sandwich C_6H_6	1.81	-1.10	-3.80	-8.66	-7.90	-0.97	-4.49	-3.30
30	T-Shaped C_6H_6	2.74	0.13	-2.97	-7.06	-6.64	0.59	-3.35	-2.13
31	Parallel C_6H_6	2.78	-0.69	-4.30	-9.67	-8.85	-1.03	-5.18	-3.71

Table S6: Deviations of the FORWARD barrier heights of hydrogen transfer reactions for the HTBH38/04 test set for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	$H + HCl \rightarrow H_2 + Cl$	5.7	-8.9	-5.2	-3.7	-7.7	-7.5	-6.5	-4.7
2	$OH + H_2 \rightarrow H + H_2O$	5.7	-23.4	-11.5	-8.3	-6.8	-7.5	-4.8	-4.5
3	$CH_3 + H_2 \rightarrow H + CH_4$	12.1	-17.4	-8.2	-5.4	-3.8	-4.9	-3.3	-3.2
4	$OH + CH_4 \rightarrow CH_3 + H_2O$	6.7	-23.3	-11.8	-8.4	-7.4	-8.0	-4.3	-3.3
5	$H + H_2 \rightarrow H_2 + H$	9.6	-12.4	-5.9	-5.3	-7.0	-7.2	-5.3	-4.7
6	$OH + NH_3 \rightarrow H_2O + NH_2$	3.2	-27.2	-15.3	-11.6	-10.7	-10.6	-5.9	-3.6
7	$HCl + CH_3 \rightarrow Cl + CH_4$	1.7	-15.1	-7.5	-4.2	-3.7	-4.7	-3.1	-2.1
8	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	3.4	-23.7	-11.9	-8.3	-7.3	-8.0	-4.0	-2.8
9	$F + H_2 \rightarrow HF + H$	1.8	-24.7	-13.7	-10.0	-9.6	-8.9	-7.0	-6.3
10	$O + CH_4 \rightarrow OH + CH_3$	13.7	-23.2	-13.5	-9.6	-9.6	-11.2	-5.9	-4.7
11	$H + PH_3 \rightarrow PH_2 + H_2$	3.1	-10.5	-4.8	-3.9	-6.0	-6.1	-4.1	-3.0
12	$H + HO \rightarrow H_2 + O$	10.7	-12.8	-7.3	-6.7	-9.2	-7.6	-6.9	-5.2
13	$H + H_2S \rightarrow H_2 + HS$	3.5	-10.3	-4.7	-3.6	-5.8	-6.3	-4.0	-2.8
14	$O + HCl \rightarrow OH + Cl$	9.8	-32.6	-20.2	-15.7	-15.6	-14.0	-8.7	-5.5
15	$NH_2 + CH_3 \rightarrow CH_4 + NH$	8.0	-16.7	-7.6	-4.9	-3.6	-3.6	-2.1	-1.0
16	$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	7.5	-13.6	-4.9	-2.0	-0.7	-1.6	0.5	1.4
17	$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	10.4	-20.0	-8.9	-5.4	-4.1	-5.7	-1.6	-0.6
18	$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	14.5	-20.6	-10.1	-6.9	-5.6	-6.8	-3.2	-2.2
19	$C_5H_8 \rightarrow C_5H_8$	38.4	-13.4	-7.2	-7.6	-5.0	-4.6	0.4	2.1

Table S7: Deviations of the BACKWARD barrier heights of hydrogen transfer reactions for the HTBH38/04 test set for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	$H + HCl \rightarrow H_2 + Cl$	8.7	-19.0	-9.8	-7.1	-5.3	-7.9	-4.1	-3.5
2	$OH + H_2 \rightarrow H + H_2O$	21.2	-10.4	-8.0	-6.6	-10.9	-10.5	-8.3	-6.1
3	$CH_3 + H_2 \rightarrow H + CH_4$	15.3	-10.4	-5.9	-5.2	-8.3	-8.3	-5.7	-4.1
4	$OH + CH_4 \rightarrow CH_3 + H_2O$	19.6	-17.8	-11.2	-7.5	-7.5	-8.3	-6.1	-4.7
5	$H + H_2 \rightarrow H_2 + H$	9.6	-12.4	-5.9	-5.3	-7.0	-7.2	-5.3	-4.7
6	$OH + NH_3 \rightarrow H_2O + NH_2$	12.7	-24.2	-14.2	-10.3	-9.7	-10.0	-6.1	-3.9
7	$HCl + CH_3 \rightarrow Cl + CH_4$	7.9	-18.2	-9.7	-7.4	-5.9	-8.5	-3.1	-1.8
8	$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	19.9	-15.5	-9.6	-5.7	-5.9	-7.4	-4.7	-3.3
9	$F + H_2 \rightarrow HF + H$	33.4	-8.5	-9.1	-7.4	-12.7	-11.9	-10.6	-8.0
10	$O + CH_4 \rightarrow OH + CH_3$	8.1	-17.6	-8.9	-6.0	-5.0	-4.9	-3.9	-2.9
11	$H + PH_3 \rightarrow PH_2 + H_2$	23.2	-13.5	-4.9	-2.2	0.1	-3.6	-0.1	-0.3
12	$H + HO \rightarrow H_2 + O$	13.1	-25.4	-14.1	-10.4	-9.2	-10.5	-6.5	-6.2
13	$H + H_2S \rightarrow H_2 + HS$	17.3	-17.7	-7.8	-5.3	-2.3	-6.0	-1.4	-1.4

Table S7 – continued

14	$O + HCl \rightarrow OH + Cl$	10.4	-30.1	-18.0	-15.3	-13.2	-11.6	-6.7	-3.3
15	$NH_2 + CH_3 \rightarrow CH_4 + NH$	22.4	-19.8	-11.5	-7.8	-7.7	-9.9	-5.0	-3.7
16	$NH_2 + C_2H_5 \rightarrow C_2H_6 + NH$	18.3	-19.5	-10.5	-6.5	-6.3	-8.8	-3.5	-2.1
17	$C_2H_6 + NH_2 \rightarrow NH_3 + C_2H_5$	17.4	-14.7	-7.7	-4.2	-3.8	-5.6	-2.2	-0.8
18	$NH_2 + CH_4 \rightarrow CH_3 + NH_3$	17.8	-18.0	-10.5	-7.1	-6.6	-7.6	-4.7	-3.2
19	$C_5H_8 \rightarrow C_5H_8$	38.4	-13.4	-7.2	-7.6	-5.0	-4.6	0.4	2.1

Table S8: Deviations of the FORWARD barrier heights of non-hydrogen transfer reactions for the NHTBH38/04 test set for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	$H + N_2O \rightarrow OH + N_2$	18.14	-15.03	-7.66	-5.53	-8.35	-8.37	-6.31	-4.92
2	$H + FH \rightarrow HF + H$	42.18	-22.91	-14.24	-11.65	-13.85	-12.57	-10.37	-8.08
3	$H + ClH \rightarrow + HCl\ H$	18.00	-15.84	-8.31	-7.09	-8.67	-8.91	-5.51	-3.56
4	$H + FCH_3 \rightarrow HF + CH_3$	30.38	-16.36	-11.13	-8.60	-12.42	-9.70	-7.95	-4.36
5	$H + F_2 \rightarrow HF + F$	2.27	28.92	35.65	38.23	34.68	35.91	41.70	-6.96
6	$CH_3 + FCl \rightarrow CH_3F + Cl$	7.43	-17.97	-12.96	-7.97	-9.92	-11.41	-8.16	-4.05
7	$F^- + CH_3F \rightarrow FCH_3 + F^-$	-0.34	-17.84	-14.16	-8.45	-10.12	-13.31	-8.97	-7.66
8	$F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$	13.38	-8.19	-7.75	-7.13	-7.67	-7.11	-4.44	-2.61
9	$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	3.10	-12.54	-9.68	-4.97	-6.80	-9.59	-6.19	-2.77
10	$Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$	13.61	-7.79	-7.43	-6.65	-7.64	-6.73	-5.31	-1.73
11	$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	-12.54	-17.70	-14.10	-8.94	-10.63	-15.18	-9.97	-7.92
12	$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	2.89	-5.53	-5.30	-5.03	-5.63	-6.53	-4.18	-2.33
13	$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-2.78	-18.18	-14.35	-8.66	-10.13	-13.26	-8.97	-7.24
14	$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	10.96	-10.97	-10.56	-9.89	-10.20	-9.31	-6.24	-3.72
15	$H + N_2 \rightarrow HN_2$	14.69	-16.87	-9.38	-8.35	-10.01	-10.38	-7.06	-5.64
16	$H + CO \rightarrow HCO$	3.17	-10.91	-4.90	-3.89	-5.48	-6.84	-3.77	-3.06
17	$H + C2H_4 \rightarrow CH_3CH_2$	1.72	-7.14	-1.83	-0.70	-2.70	-6.19	-1.87	-1.51
18	$CH_3 + C2H_4 \rightarrow CH_3CH_2CH_2$	6.85	-12.50	-5.28	-1.55	-1.13	-6.19	-0.79	-0.22
19	$HCN \rightarrow HNC$	48.16	-3.24	-2.46	-2.96	-2.46	-1.72	-0.68	-0.98

Table S9: Deviations of the BACKWARD barrier heights of non-hydrogen transfer reactions for the NHTBH38/04 test set for the exchange-correlation functional shown in each column. All quantities are in kcal/mol.

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	$H + N_2O \rightarrow OH + N_2$	83.22	-51.21	-30.94	-27.84	-22.34	-18.60	-10.46	-6.56
2	$H + FH \rightarrow HF + H$	42.18	-22.91	-14.24	-11.65	-13.85	-12.57	-10.37	-8.08
3	$H + ClH \rightarrow HCl + H$	18.00	-15.84	-8.31	-7.09	-8.67	-8.91	-5.51	-3.56
4	$H + FCH_3 \rightarrow HF + CH_3$	57.02	-24.98	-15.83	-10.65	-10.48	-10.36	-8.14	-5.94

Table S9 – continued

5	$H + F_2 \rightarrow HF + F$	106.18	7.82	19.56	24.69	24.77	30.76	38.81	-9.14
6	$CH_3 + FCl \rightarrow CH_3F + Cl$	60.17	-22.45	-18.67	-14.24	-15.95	-14.65	-9.40	-3.60
7	$F^- + CH_3F \rightarrow FCH_3 + F^-$	-0.34	-17.84	-14.16	-8.45	-10.12	-13.31	-8.97	-7.66
8	$F^- \cdots CH_3F \rightarrow FCH_3 \cdots F^-$	13.38	-8.19	-7.75	-7.13	-7.67	-7.11	-4.44	-2.61
9	$Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$	3.10	-12.54	-9.68	-4.97	-6.80	-9.59	-6.19	-2.77
10	$Cl^- \cdots CH_3Cl \rightarrow ClCH_3 \cdots Cl^-$	13.61	-7.79	-7.43	-6.65	-7.64	-6.73	-5.31	-1.73
11	$F^- + CH_3Cl \rightarrow FCH_3 + Cl^-$	20.11	-10.55	-8.19	-3.06	-4.59	-5.19	-2.36	0.39
12	$F^- \cdots CH_3Cl \rightarrow FCH_3 \cdots Cl^-$	29.62	-6.89	-6.89	-5.80	-6.46	-4.03	-1.94	1.33
13	$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	17.33	-17.35	-14.21	-8.49	-10.46	-13.26	-8.33	-6.14
14	$OH^- \cdots CH_3F \rightarrow HOCH_3 \cdots F^-$	47.20	1.48	-2.86	-1.77	-4.18	-2.40	-0.63	2.52
15	$H + N_2 \rightarrow HN_2$	10.72	-1.57	-1.93	-1.86	-1.70	-1.20	-0.11	0.88
16	$H + CO \rightarrow HCO$	22.68	3.38	1.73	1.75	1.74	1.31	1.72	1.82
17	$H + C_2H_4 \rightarrow CH_3CH_2$	41.75	-2.35	-1.41	-0.61	-0.63	1.41	0.12	1.83
18	$CH_3 + C_2H_4 \rightarrow CH_3CH_2CH_2$	32.97	0.24	-3.05	-2.40	-5.14	-2.02	-3.36	0.35
19	$HCN \rightarrow HNC$	33.11	-2.24	-2.38	-2.68	-2.32	-0.76	0.45	0.95

Table S10: Deviations of the bond lengths for the test set T96-R for the exchange-correlation functional shown in each column. All quantities are in $\mathring{A}$

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	H_2	0.741	0.025	0.010	0.012	0.008	0.001	0.002	0.004
2	Li_2	2.673	0.045	0.065	0.120	0.085	0.082	0.037	0.013
3	LiH	1.595	0.011	0.012	0.024	0.016	0.007	-0.001	-0.008
4	LiF	1.564	-0.010	0.012	0.022	0.026	0.005	0.000	-0.006
5	LiCl	2.021	-0.016	0.004	0.019	0.023	0.006	0.000	-0.009
6	LiO	1.688	-0.011	0.011	0.022	0.026	0.005	-0.003	-0.011
7	Be2	2.440	-0.030	0.001	0.045	0.039	0.046	0.070	0.265
8	BeH	1.343	0.024	0.019	0.026	0.020	0.011	0.003	0.001
9	BeF	1.361	0.004	0.019	0.025	0.027	0.009	0.010	0.006
10	BeO	1.331	0.002	0.015	0.017	0.019	0.001	-0.005	-0.014
11	BeS	1.742	0.002	0.015	0.017	0.020	0.001	0.002	-0.011
12	B_2	1.590	0.016	0.029	0.038	0.037	0.028	0.022	0.017
13	BH	1.232	0.025	0.020	0.029	0.022	0.009	0.000	-0.003
14	BF	1.263	-0.002	0.013	0.018	0.020	0.002	0.002	-0.003
15	BF_3	1.313	-0.002	0.012	0.014	0.018	-0.001	0.003	-0.002
16	BCl	1.715	-0.005	0.016	0.024	0.027	0.004	0.006	-0.007
17	BCl_3	1.742	-0.012	0.006	0.008	0.015	-0.003	0.004	-0.004
18	BN	1.281	0.042	0.051	0.053	0.056	0.038	0.037	0.028
19	BO	1.204	0.001	0.010	0.012	0.014	0.000	-0.002	-0.007
20	BS	1.609	0.000	0.012	0.014	0.017	0.001	0.001	-0.009
21	C_2	1.242	0.151	0.162	0.167	0.167	0.006	0.005	0.000
22	CH	1.120	0.021	0.017	0.022	0.019	0.005	0.003	-0.000
23	CH_4	1.087	0.010	0.009	0.011	0.011	0.001	0.001	0.000
24	CF	1.272	-0.006	0.015	0.016	0.023	0.003	0.003	-0.004

Table S10 – continued

25	CF_4	1.323	-0.003	0.015	0.015	0.021	-0.001	0.003	-0.003
26	CCl	1.645	-0.010	0.015	0.017	0.026	0.006	0.011	-0.003
27	CCl_4	1.767	-0.009	0.015	0.014	0.026	0.003	0.014	-0.000
28	CN	1.172	-0.006	0.002	0.004	0.006	-0.009	-0.010	-0.017
29	CO	1.128	-0.000	0.008	0.010	0.012	-0.002	-0.003	-0.008
30	CO^+	1.115	-0.000	0.007	0.008	0.010	-0.005	-0.006	-0.011
31	CO_2	1.160	-1.160	0.011	0.012	0.015	-0.001	-0.000	-0.005
32	CP	1.562	-0.007	0.005	0.006	0.009	-0.010	-0.009	-0.021
33	CS	1.535	-0.002	0.011	0.013	0.016	-0.001	-0.003	-0.015
34	CS_2	1.553	-1.553	0.009	0.009	0.014	-0.002	0.000	-0.008
35	N_2	1.098	-0.003	0.005	0.006	0.007	-0.006	-0.007	-0.012
36	N_2^+	1.116	-0.010	-0.002	-0.001	0.001	-0.011	-0.012	-0.016
37	NH	1.036	0.019	0.015	0.017	0.016	0.004	0.005	0.002
38	NH^+	1.070	0.030	0.021	0.023	0.022	0.007	0.008	0.007
39	NF	1.317	-0.013	0.010	0.009	0.019	-0.001	0.001	-0.011
40	NCl	1.611	-0.019	0.007	0.008	0.018	0.004	0.009	-0.005
41	NO	1.151	-0.004	0.007	0.007	0.011	-0.004	-0.006	-0.012
42	NO^+	1.063	-0.001	0.007	0.007	0.009	-0.005	-0.007	-0.011
43	NS	1.494	-0.002	0.012	0.012	0.017	-0.002	-0.003	-0.015
44	O_2	1.208	-0.004	0.011	0.009	0.016	-0.002	-0.004	-0.013
45	O_2^+	1.116	-0.005	0.006	0.005	0.010	-0.007	-0.010	-0.017
46	OH	0.970	0.016	0.013	0.014	0.015	0.002	0.004	0.003
47	OH^+	1.029	0.027	0.019	0.019	0.019	0.005	0.009	0.008
48	OF	1.358	-0.026	0.001	-0.003	0.010	-0.007	-0.009	-0.023
49	F_2	1.412	-0.027	0.002	-0.004	0.010	-0.012	-0.015	-0.031
50	F_2^+	1.322	-0.030	-0.006	-0.011	0.001	-0.024	-0.029	-0.044
51	HF	0.917	0.014	0.013	0.013	0.014	0.003	0.005	0.004
52	HF^+	1.001	0.028	0.022	0.019	0.021	0.008	0.013	0.013
53	Na_2	3.079	-0.070	0.000	0.109	0.054	0.043	-0.009	-0.068
54	NaH	1.887	-0.015	0.006	0.030	0.021	0.006	-0.007	-0.020
55	NaF	1.926	-0.022	0.016	0.028	0.031	-0.002	0.002	-0.011
56	NaCl	2.361	-0.031	0.009	0.028	0.032	0.000	0.005	-0.011
57	NaO	2.052	-0.021	0.020	0.033	0.036	0.000	0.000	-0.016
58	MgH	1.730	0.023	0.027	0.030	0.030	0.013	0.012	0.001
59	MgF	1.750	0.006	0.032	0.035	0.041	0.012	0.019	0.009
60	MgCl	2.196	0.002	0.029	0.033	0.042	0.012	0.025	0.010
61	MgO	1.748	-0.022	0.002	0.004	0.010	-0.015	-0.009	-0.024
62	Al_2	2.466	-0.005	0.023	0.027	0.039	0.009	0.036	0.019
63	AlH	1.648	0.031	0.032	0.037	0.034	0.013	0.013	0.005
64	AlF	1.654	0.005	0.028	0.030	0.036	0.007	0.015	0.007
65	AlCl	2.130	0.006	0.032	0.033	0.044	0.012	0.029	0.013
66	AlO	1.618	-0.005	0.014	0.013	0.020	-0.001	0.007	-0.003
67	AlS	2.029	0.000	0.020	0.017	0.028	-0.000	0.015	-0.002
68	Si_2	2.246	-0.096	0.040	0.041	0.048	-0.096	-0.087	-0.111
69	SiH	1.520	0.025	0.025	0.029	0.027	0.009	0.009	0.003
70	SiH_4	1.480	0.013	0.013	0.017	0.014	0.001	-0.000	-0.003

Table S10 – continued

71	SiF	1.601	0.010	0.032	0.032	0.038	0.011	0.018	0.009
72	SiF_4	1.553	0.008	0.028	0.028	0.033	0.009	0.015	0.008
73	SiCl	2.058	0.002	0.027	0.025	0.037	0.011	0.026	0.011
74	SiCl	2.019	-0.003	0.021	0.021	0.031	0.004	0.017	0.004
75	SiN	1.572	-0.008	0.007	0.008	0.012	-0.005	-0.005	-0.015
76	SiO	1.510	0.005	0.019	0.019	0.023	0.003	0.002	-0.007
77	SiS	1.929	0.006	0.022	0.021	0.028	0.004	0.009	-0.009
78	P_2	1.893	-0.001	0.013	0.012	0.017	-0.005	-0.004	-0.024
79	P_4	2.210	-2.210	-0.001	-0.004	0.008	-0.014	-0.006	-0.029
80	PH	1.421	0.021	0.020	0.022	0.021	0.005	0.007	0.001
81	PF	1.589	0.007	0.029	0.028	0.036	0.009	0.016	0.006
82	PCl	2.015	-0.008	0.017	0.014	0.027	0.004	0.019	0.004
83	PN	1.491	-0.004	0.008	0.009	0.012	-0.006	-0.009	-0.021
84	PO	1.476	0.007	0.021	0.020	0.025	0.003	0.004	-0.007
85	S_2	1.889	0.007	0.022	0.020	0.030	0.006	0.014	-0.005
86	SH	1.341	0.018	0.016	0.017	0.018	0.004	0.006	0.001
87	SF	1.601	-0.003	0.022	0.018	0.030	0.002	0.009	-0.004
88	SF_6	1.561	-1.561	0.036	0.033	0.044	0.013	0.018	0.006
89	SO	1.481	0.009	0.024	0.023	0.030	0.005	0.009	-0.004
90	SO_3	1.420	0.009	0.024	0.023	0.029	0.004	0.006	-0.004
91	Cl_2	1.988	-0.007	0.017	0.012	0.031	0.009	0.023	0.004
92	Cl_2^+	1.891	0.003	0.023	0.018	0.032	0.008	0.018	-0.003
93	HCl	1.275	0.016	0.014	0.014	0.015	0.004	0.006	0.003
94	HCl^+	1.315	0.025	0.018	0.018	0.019	0.006	0.009	0.006
95	ClF	1.628	-0.004	0.023	0.018	0.033	0.005	0.012	-0.004
96	ClO	1.570	-0.015	0.013	0.009	0.023	0.007	0.009	-0.006

Table S11: Deviations of the harmonic vibrational frequencies for the test set T82-F for the exchange-correlation functional shown in each column. All quantities are in cm^{-1}

		Expt.	Deviation = Theory - Experiment						
	Molecule		LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
1	H_2	4401.2	-218.6	-85.8	-102.4	-75.5	22.1	17.2	7.6
2	Li_2	351.4	-17.8	-21.3	-33.5	-27.9	-19.2	-11.2	5.3
3	LiH	1405.7	-29.9	-28.5	-56.2	-39.8	-3.5	5.5	32.2
4	LiF	910.6	13.8	-16.4	-39.1	-40.9	-5.1	7.0	16.9
5	LiCl	643.0	10.6	-3.6	-19.0	-22.3	-7.0	2.5	14.9
6	LiO	814.6	3.7	-18.5	-35.0	-37.5	-8.0	8.7	30.3
7	LiNa	256.8	-4.4	-11.1	-21.5	-18.5	-10.2	-4.5	10.6
8	Be_2	267.9	99.9	78.7	62.5	52.8	60.6	9.8	-104.5
9	BeH	2060.8	-103.7	-86.3	-99.8	-92.6	-31.7	-23.4	-3.0
10	BeH^+	2221.7	-137.9	-112.5	-103.1	-93.0	-25.5	-41.2	-16.0
11	BeF	1247.4	-5.6	-41.2	-56.8	-62.3	-10.6	-11.5	6.2
12	BeCl	846.7	-16.4	-32.7	-41.1	-48.7	-24.7	-29.6	-11.4
13	BeO	1487.3	7.6	-33.2	-36.0	-45.6	29.0	40.1	85.2
14	BeS	997.9	-0.6	-20.4	-23.1	-31.2	21.0	2.8	42.9
15	B_2	1051.3	-15.1	-39.1	-53.9	-60.4	-46.6	-44.7	-36.9
16	BH	2366.9	-138.0	-124.4	-158.4	-136.5	-47.6	-15.6	21.5
17	BF	1402.1	4.7	-51.0	-66.6	-75.4	-2.3	-1.4	24.5
18	BCl	840.3	-2.7	-31.0	-38.6	-49.5	-3.7	-16.2	14.4
19	BN	1514.6	30.4	1.4	-4.3	-21.5	61.2	54.6	121.6
20	BO	1885.7	2.9	-38.5	-42.2	-57.3	16.6	30.5	69.3
21	BS	1180.2	2.9	-18.5	-19.5	-32.7	28.4	5.9	44.7
22	C_2	1854.7	45.2	2.2	-5.9	-22.1	44.6	23.0	49.9
23	CH	2858.5	-117.8	-127.1	-148.1	-146.9	-40.0	-35.8	14.4
24	CF	1308.1	24.4	-54.2	-54.8	-80.6	-3.8	-4.3	40.3
25	CN	2068.6	73.0	25.3	20.0	2.4	86.1	86.9	141.1
26	CO	2169.8	11.7	-40.2	-45.5	-60.8	41.6	44.4	88.3
27	CO^+	2214.2	37.7	-10.6	-10.1	-33.8	78.6	82.0	133.3
28	CP	1239.7	38.2	9.6	8.6	-5.5	48.2	46.0	89.9
29	CS	1285.2	5.7	-22.9	-24.2	-37.2	23.1	23.6	74.2
30	N_2	2358.6	43.7	-5.5	-7.7	-24.5	75.9	93.2	145.0
31	N_2^+	2207.0	114.4	58.8	55.7	34.4	119.1	127.7	167.5
32	NH	3282.3	-133.3	-109.1	-133.7	-130.4	-26.8	-28.3	21.1
33	NF	1141.4	52.9	-9.4	18.9	-35.5	23.4	27.1	71.4
34	NCl	828.0	53.4	8.8	10.1	-11.9	6.2	-2.8	28.7
35	NO	1904.2	56.0	-11.8	0.8	-36.1	56.9	73.1	129.2
36	NO^+	2376.4	42.2	-13.7	-12.7	-33.8	87.4	107.0	160.2
37	NS	1218.7	44.1	8.1	11.7	-21.8	43.2	39.0	92.2
38	O_2	1580.2	42.7	-21.9	-5.7	-48.2	46.4	59.4	125.7
39	O_2^+	1904.8	98.9	32.3	44.3	4.5	122.7	149.8	217.3
40	OH	3737.8	-143.0	-131.6	-127.9	-154.8	-7.5	-36.5	9.3
41	OH^+	3113.4	-211.4	-157.5	-146.9	-158.3	-40.4	-70.0	-49.7

Table S11 – continued

42	F_2	916.6	144.8	78.2	89.6	60.0	125.6	130.1	179.9
43	F_2^+	1073.3	142.2	76.5	91.5	56.0	132.0	158.4	222.2
44	HF	4138.3	-148.7	-158.6	-144.1	-177.6	-35.1	-50.9	-19.6
45	HF^+	3090.5	-222.4	-178.4	-144.9	-174.9	-61.9	-100.9	-91.5
46	Na2	159.1	3.8	-0.7	-10.5	-8.4	-0.2	-0.8	11.5
47	NaH	1172.2	-3.7	-23.7	-55.9	-42.5	13.8	11.4	39.5
48	NaF	535.7	15.9	-16.5	-31.2	-30.2	7.3	1.5	18.3
49	NaO	492.3	0.8	-24.1	-35.7	-33.2	0.8	-0.6	21.9
50	MgH	1495.2	-92.0	-88.3	-77.1	-88.3	-32.4	-49.1	-3.9
51	MgH^+	1699.1	-51.1	-46.4	-39.3	-42.9	20.6	10.8	63.2
52	MgO	784.8	57.4	19.9	17.1	7.1	50.9	34.8	70.2
53	MgS	528.7	15.5	-1.6	-0.8	-10.5	23.0	0.7	24.2
54	Al_2	350.0	13.0	-8.2	-7.4	-19.1	1.1	-23.7	-12.3
55	AlH	1682.6	-103.1	-100.2	-108.9	-109.9	-41.8	-46.8	-17.2
56	AlF	802.3	-18.8	-50.5	-54.2	-62.0	-10.8	-27.0	-9.8
57	AlCl	481.3	-7.1	-22.5	-22.3	-31.9	-4.2	-21.2	-7.0
58	AlO	979.2	25.6	-19.1	-14.9	-35.1	12.6	-23.0	1.1
59	AlS	617.1	2.5	-15.7	-9.2	-26.9	16.7	-16.9	5.7
60	Si_2	511.0	39.7	-26.2	-24.0	-33.8	51.9	37.9	68.7
61	SiH	2041.8	-79.5	-92.8	-97.2	-104.6	16.8	-39.4	1.9
62	SiH^+	2157.2	-133.8	-114.2	-120.3	-115.3	-50.7	-39.5	-5.4
63	SiF	857.2	-9.1	-45.4	-49.8	-62.9	-11.8	-24.5	-3.2
64	SiCl	535.6	6.5	-13.0	-9.9	-32.7	-11.6	-23.9	-5.2
65	SiN	1151.4	34.3	-1.6	-1.4	-15.2	27.7	29.5	64.1
66	SiO	1241.5	-12.3	-46.9	-45.5	-56.4	11.3	11.5	52.2
67	SiS	749.6	-9.4	-24.2	-21.8	-32.4	7.8	-2.6	33.2
68	P_2	780.8	15.8	1.4	4.1	-6.4	32.6	29.6	75.2
69	P_2^+	672.2	12.5	2.4	5.5	-5.5	108.5	99.4	137.2
70	PH	2365.2	-85.2	-78.5	-80.9	-92.5	23.3	-30.1	20.5
71	PF	846.8	0.7	-37.9	-33.4	-49.9	-0.1	-14.1	15.5
72	PCl	551.4	11.4	-19.2	-5.9	-24.4	-4.5	-17.9	5.3
73	PN	1337.2	34.9	2.3	4.2	-9.3	54.7	67.0	123.5
74	PO	1233.3	8.2	-27.3	-22.9	-48.1	22.2	22.8	68.2
75	S_2	725.6	-5.7	-19.4	-13.9	-33.7	10.6	-6.7	35.4
76	SO	1149.2	-2.2	-40.0	-32.3	-56.5	15.0	6.5	59.1
77	Cl_2	559.7	8.1	-16.7	-9.5	-31.2	-0.2	-16.2	15.1
78	Cl_2^+	645.6	3.5	-20.6	-15.2	-33.6	1.2	-8.6	32.6
79	HCl	2990.9	-101.6	-91.1	-87.5	-107.4	-15.0	-42.3	2.7
80	HCl+	2673.7	-139.7	-113.4	-106.4	-108.1	-37.1	-58.6	-19.5
81	ClF	786.1	22.3	-22.7	-13.7	-39.2	4.6	-0.6	38.3
82	ClO	853.8	64.3	9.5	19.1	-11.2	9.5	5.0	41.9

Table S12: Comparison of TDDFT valence and Rydberg excited states of small molecules with experimental values.

Molecule		Exp.	LDA	PBE	CAP	NCAP	B3LYP	CAM-B3LYP
N_2	V $^3\Pi_g$	8.04	7.57	7.41	7.42	7.54	7.59	7.70
	V $^3\Sigma_u^+$	7.75	7.91	7.55	7.51	7.74	7.11	6.98
	V $^3\Delta_u$	8.88	8.86	8.36	8.41	8.43	8.02	7.94
	V $^1\Pi_g$	9.31	9.06	9.10	9.13	9.14	9.26	9.38
	V $^3\Sigma_u^-$	9.67	9.69	9.69	9.76	9.72	9.35	9.23
	V $^1\Sigma_u^-$	9.92	9.69	9.69	9.76	9.72	9.35	9.23
	V $^1\Delta_u$	10.27	10.26	10.11	10.18	10.08	9.75	9.71
	R $^3\Sigma_g^+$	12.00	10.40	10.13	10.47	10.72	11.00	11.39
	R $^1\Sigma_g^+$	12.20	10.61	10.41	10.49	10.71	11.30	11.78
	V $^3\Pi_u$	11.19	10.40	10.43	10.51	10.64	10.68	10.81
CO	V $^3\Pi$	6.32	5.96	5.75	5.76	5.98	5.87	5.92
	V $^3\Sigma^+$	8.51	8.41	8.11	8.09	8.27	7.94	7.93
	V $^1\Pi$	8.51	8.17	8.25	8.29	8.32	8.40	8.47
	V $^3\Delta$	9.36	9.01	8.76	8.82	8.83	8.66	8.68
	R $^3\Sigma^+$	10.40	9.19	8.82	9.15	9.97	9.55	9.94
	R $^1\Sigma^+$	10.78	9.20	9.09	9.31	10.19	9.84	10.10
	R $^3\Sigma^+$	11.30	9.53	9.36	9.68	10.43	10.16	10.74
	R $^1\Sigma^+$	11.40	9.53	9.43	9.77	10.36	10.05	10.37
	R $^3\Pi$	11.55	9.58	9.44	9.38	10.36	10.27	10.86
	R $^1\Pi$	11.53	9.60	9.52	9.42	10.50	10.30	10.92
CH_2O	V $^3A_2$	3.50	3.06	3.06	3.12	3.18	3.19	3.17
	V $^1A_2$	3.94	3.67	3.80	3.86	3.87	3.91	3.91
	R $^3B_2$	6.83	5.76	5.56	5.90	6.34	6.28	6.66
	V $^3A_1$	5.53	6.24	5.81	5.81	5.95	5.47	5.38
	R $^1B_2$	7.09	5.82	5.72	6.06	6.45	6.40	6.81
	R $^3A_1$	7.79	6.45	6.29	6.27	7.02	7.13	7.59
	R $^1A_1$	7.97	6.46	6.36	6.28	7.02	7.19	7.67
	R $^3B_2$	7.96	6.55	6.39	6.56	7.27	7.08	7.42
	R $^1B_2$	8.12	6.57	6.46	6.64	7.31	7.15	7.56
	R $^1A_2$	8.38	6.73	6.63	6.94	7.94	7.43	7.88
C_2H_4	V $^3B_{1u}$	4.36	4.63	4.22	4.19	4.36	4.02	3.86
	R $^3B_{3u}$	6.98	6.50	6.25	6.65	7.07	6.47	6.77
	R $^1B_{3u}$	7.15	6.55	6.35	6.74	7.13	6.55	6.87
	R $^3B_{2g}$	7.79	6.97	6.73	7.02	7.74	7.02	7.46
	R $^1B_{2g}$	8.00	6.99	6.78	7.04	7.80	7.07	7.53
	R $^3B_{1g}$	7.79	6.95	6.76	7.08	7.20	7.03	7.39
	R $^1B_{1g}$	7.83	7.00	6.80	7.11	7.70	7.06	7.46
	R ^3A_g	8.15	7.30	7.00	7.19	7.76	7.33	7.73
	R ^1A_g	8.29	7.35	7.14	7.28	7.82	7.41	7.86
	V $^1B_{1u}$	7.66	7.35	7.24	7.35	7.48	7.31	7.41
	MAD		0.87	1.00	0.86	0.48	0.68	0.44

Table S13: Integrated errors of the density, IRD.

System	LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
Be^{0}	0.08200	0.03820	0.05286	0.04020	0.07395	0.04905	0.05518
B^{3+}	0.02959	0.01535	0.01145	0.00991	0.00690	0.01206	0.01234
B^{+}	0.05972	0.03291	0.04483	0.03762	0.05296	0.03597	0.04271
C^{4+}	0.02483	0.01278	0.00960	0.00830	0.00569	0.00991	0.00989
C^{2+}	0.05055	0.03429	0.04253	0.03847	0.04640	0.03492	0.04008
N^{5+}	0.02141	0.01097	0.00827	0.00718	0.00482	0.00841	0.00827
N^{3+}	0.04667	0.03555	0.04177	0.03951	0.04972	0.03519	0.03829
O^{6+}	0.01881	0.00960	0.00726	0.00635	0.00420	0.00729	0.00710
O^{4+}	0.04575	0.03672	0.04154	0.04011	0.04957	0.03629	0.03797
F^{7+}	0.01678	0.00853	0.00647	0.00571	0.00372	0.00643	0.00621
F^{5+}	0.04524	0.03778	0.04170	0.04062	0.05074	0.03744	0.03838
Ne^{8+}	0.01510	0.00766	0.00583	0.00523	0.00334	0.00577	0.00553
Ne^{6+}	0.04492	0.03865	0.04193	0.04109	0.04678	0.03849	0.03904
Ne^{0}	0.13244	0.09647	0.06856	0.08112	0.03530	0.07810	0.08692
AVE	0.04527	0.02967	0.03033	0.02867	0.03101	0.02824	0.03057

$$IRD = \int \left| \rho^{CCSD}(\mathbf{r}) - \rho(\mathbf{r}) \right| \, d\mathbf{r}$$

Table S14: Integrated errors of the gradient norm of the density, IRG.

System	LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
Be^{0}	0.32148	0.15586	0.16329	0.14952	0.15283	0.15260	0.17115
B^{3+}	0.27995	0.13499	0.10124	0.11185	0.07099	0.10827	0.11302
B^{+}	0.32027	0.15866	0.17119	0.16861	0.16502	0.14580	0.16478
C^{4+}	0.28719	0.13766	0.10372	0.11480	0.07130	0.10837	0.11207
C^{2+}	0.31616	0.17651	0.19061	0.20711	0.19854	0.16394	0.18120
N^{5+}	0.29200	0.13930	0.10585	0.11716	0.07111	0.10836	0.11094
N^{3+}	0.31129	0.20651	0.21966	0.24944	0.24461	0.19244	0.20932
O^{6+}	0.29556	0.14108	0.10752	0.11982	0.07172	0.10860	0.11098
O^{4+}	0.31063	0.24443	0.25376	0.29336	0.28723	0.22375	0.23915
F^{7+}	0.29870	0.14214	0.10866	0.12172	0.07179	0.10852	0.11063
F^{5+}	0.31849	0.28438	0.29100	0.33848	0.33656	0.26403	0.27666
Ne^{8+}	0.30194	0.14325	0.10966	0.12369	0.07183	0.10850	0.11015
Ne^{6+}	0.33743	0.32664	0.33233	0.38598	0.38924	0.30920	0.32142
Ne^{0}	0.79482	0.39219	0.35063	0.35448	0.18928	0.36127	0.38771
AVE	0.34185	0.19883	0.18637	0.20400	0.17086	0.17598	0.18708

$$IRG = \int \Big| |\nabla \rho^{CCSD}(\mathbf{r})| - |\nabla \rho(\mathbf{r})| \Big| \, d\mathbf{r}$$

Table S15: Integrated errors of the laplacian of the density, IRL.

System	LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
Be^{0}	1.44692	1.04009	0.85885	1.03432	0.73614	0.92486	0.98664
B^{3+}	1.85724	1.22618	0.94155	1.22268	0.75223	1.02842	1.09172
B^{+}	1.86723	1.40021	1.13998	1.43428	0.98158	1.16239	1.27241
C^{4+}	2.33148	1.52719	1.18051	1.52533	0.92163	1.25408	1.33137
C^{2+}	2.25021	1.80818	1.43609	1.87226	1.26014	1.43768	1.54428
N^{5+}	2.81362	1.85185	1.43880	1.85907	1.11607	1.50330	1.59419
N^{3+}	2.56208	2.28164	1.79885	2.36620	1.71454	1.78104	1.91733
O^{6+}	3.27420	2.12655	1.67398	2.13481	1.24281	1.70010	1.80530
O^{4+}	2.78548	2.71851	2.13803	2.89124	2.29757	2.12415	2.29946
F^{7+}	3.74831	2.42333	1.90895	2.44143	1.39873	1.91616	2.03899
F^{5+}	2.98291	3.25377	2.62453	3.56943	2.90243	2.56502	2.77868
Ne^{8+}	4.22930	2.72796	2.15488	2.76740	1.55506	2.14954	2.27676
Ne^{6+}	3.11869	3.89047	3.26628	4.36469	3.87346	3.16141	3.39101
Ne^{0}	7.21683	3.91080	3.60618	3.90698	2.42234	3.56509	3.78578
AVE	3.03461	2.29905	1.86910	2.38501	1.65534	1.87666	2.00814

$$IRL = \int \left| \nabla^2 \rho^{CCSD}(\mathbf{r}) - \nabla^2 \rho(\mathbf{r}) \right| \, d\mathbf{r}$$

Table S16: Dipole moment in Debye

System	CCSD(T)	LDA	PBE	CAP	NCAP	SCAN	B3LYP	CAM-B3LYP
AlF	1.4729	1.4606	1.3739	1.2423	1.3061	1.2985	1.4939	1.4880
BF	0.8194	1.0443	1.0485	1.1074	1.0894	1.0579	0.9503	0.9444
BH2Cl	0.6838	0.4274	0.4379	0.4408	0.4470	0.5430	0.5773	0.6465
BH2F	0.8269	0.6405	0.6182	0.5824	0.5902	0.6813	0.7520	0.7980
BHCl2	0.6684	0.4754	0.4815	0.4781	0.4867	0.5578	0.5893	0.6456
BHF2	0.9578	0.8070	0.7749	0.7412	0.7487	0.8275	0.8939	0.9347
CH2BH	0.6238	0.4875	0.5090	0.5055	0.5181	0.5647	0.6214	0.6834
CH2BOH	2.2558	2.2752	2.2669	2.2758	2.2739	2.3136	2.2876	2.3217
CH3BH2	0.5751	0.7750	0.7259	0.7398	0.7151	0.6942	0.6406	0.6247
CH3BO	3.6779	3.7078	3.6347	3.6307	3.6213	3.7727	3.8022	3.8670
CH3Cl	1.8981	1.8570	1.8196	1.8245	1.8156	1.9208	1.8683	1.9075
CH3F	1.8083	1.6871	1.6370	1.6116	1.6177	1.7025	1.7554	1.8086
CH3Li	5.8304	5.5105	5.4869	5.6440	5.6419	5.7662	5.6434	5.7096
CH3NH2	1.3876	1.3625	1.3181	1.3152	1.3126	1.3502	1.3626	1.4080
CH3OH	1.7091	1.6520	1.5951	1.5809	1.5813	1.6496	1.6746	1.7274
CH3SH	1.5906	1.6018	1.5730	1.5915	1.5729	1.6312	1.5718	1.5986
ClCN	2.8496	3.0215	2.9533	2.9392	2.9456	3.0000	3.0059	3.0205
ClF	0.8802	0.7674	0.7192	0.6881	0.6993	0.7978	0.8559	0.9169
CO	0.1172	0.2284	0.2239	0.2431	0.2280	0.1273	0.0871	0.0584
CS	1.9692	2.0942	2.0088	1.9871	1.9889	1.9506	1.9679	1.9747
CSO	0.7327	0.8549	0.7628	0.7253	0.7310	0.8002	0.8502	0.8357
FCN	2.1756	2.3299	2.3228	2.3403	2.3068	2.3381	2.2894	2.2983
FNO	1.6971	1.4491	1.4644	1.4407	1.4568	1.5349	1.5885	1.6377
H2O	1.8601	1.8555	1.7954	1.7958	1.7831	1.8400	1.8548	1.8948
H2O-H2O	2.7303	2.8164	2.7267	2.7288	2.7149	2.7546	2.7661	2.8002
H2O-NH3	3.5004	3.6276	3.5086	3.5073	3.4837	3.5311	3.5479	3.5998
H2S-H2S	0.9181	1.0981	1.0315	1.0359	1.0121	1.0176	0.9692	0.9571
H2S-HCl	2.1328	2.3792	2.2779	2.2905	2.2494	2.3041	2.2102	2.2045
HBH2BH	0.8429	0.9079	0.8614	0.8827	0.8479	0.8446	0.8145	0.8535
HBO	2.7322	2.6243	2.5855	2.5690	2.5784	2.7311	2.7863	2.8692
HBS	1.3753	1.2006	1.2268	1.2530	1.2509	1.4045	1.3928	1.5017
HCCCl	0.5009	0.2647	0.2646	0.2744	0.2663	0.3306	0.3503	0.4194
HCCF	0.7452	0.5155	0.4632	0.4412	0.4411	0.5506	0.6276	0.6942
HCHO	2.3927	2.2842	2.2376	2.2055	2.2110	2.3641	2.4017	2.4922
HCl	1.1055	1.1068	1.0681	1.0777	1.0591	1.1249	1.0850	1.1187
HCl-HCl	1.7766	1.8947	1.8196	1.8307	1.8050	1.8691	1.8022	1.8207
HCN	3.0065	3.0034	2.9427	2.9377	2.9371	3.0341	3.0362	3.0937
HCNO	2.956	2.4845	2.4233	2.4076	2.4103	2.5996	2.7592	2.9519
HCOF	2.1169	2.0312	1.9867	1.9756	1.9809	2.0948	2.1236	2.1863
HCONH2	3.9152	3.9059	3.8264	3.8457	3.8348	3.9415	3.9587	4.0305
HCOOH	1.3835	1.4175	1.4171	1.4375	1.4374	1.4812	1.4617	1.4772
HF	1.8059	1.7949	1.7455	1.7412	1.7328	1.7851	1.7998	1.8248
HF-HF	3.3991	3.4460	3.3552	3.3508	3.3390	3.4064	3.4215	3.4552

Table S16 – continued

HN3	1.6603	1.8209	1.7542	1.7606	1.7447	1.7479	1.7009	1.6801
HNC	3.0818	3.1358	3.0654	3.0803	3.0617	3.0530	3.0047	3.0146
HNCO	2.0639	2.0324	1.9660	1.9857	1.9520	2.0396	2.0453	2.0843
HOCl	1.5216	1.5306	1.4974	1.5031	1.4915	1.5321	1.5235	1.5409
HOCN	3.7998	3.9575	3.8703	3.9082	3.8971	3.9549	3.9149	3.9402
HOOH	1.5732	1.5681	1.5239	1.5190	1.5109	1.5533	1.5719	1.6003
LiBH4	6.1281	5.9096	5.9476	6.0182	6.0280	6.0738	6.0251	6.0483
LiCl	7.096	6.8277	6.8442	6.9350	6.9284	7.0322	6.9457	7.0052
LiCN	6.9851	6.8047	6.8165	6.9036	6.9086	6.9579	6.8966	6.9244
LiF	6.2879	6.0867	6.0935	6.1477	6.1478	6.2168	6.1915	6.2172
LiH	5.8286	5.6099	5.6155	5.7501	5.7669	5.8493	5.7254	5.7729
LiOH	4.5664	4.3194	4.3768	4.4652	4.4643	4.5098	4.4456	4.4543
N2H4	2.7179	2.7282	2.6368	2.6388	2.6237	2.6693	2.7014	2.7745
NaCl	9.0066	8.4917	8.4901	8.7538	8.7413	8.8427	8.6792	8.8073
NaCN	8.8903	8.5613	8.5643	8.7581	8.7559	8.8039	8.7082	8.7756
NaF	8.1339	7.7622	7.7239	7.8951	7.9036	7.9817	7.9369	8.0066
NaH	6.3966	5.6711	5.7562	6.1936	6.0641	6.3337	6.0291	6.2841
NaOH	6.769	6.4907	6.5523	6.6709	6.6791	6.6753	6.6325	6.6354
NH2Cl	1.9468	1.9478	1.9180	1.9293	1.9171	2.0039	1.9494	1.9706
NH2F	2.2688	2.2072	2.1472	2.1361	2.1337	2.2572	2.2575	2.3153
NH2OH	0.7044	0.6543	0.6306	0.6205	0.6247	0.7007	0.6913	0.7242
NH3	1.5289	1.5265	1.4748	1.4826	1.4683	1.5090	1.5203	1.5683
NH3-BH3	5.281	5.2789	5.2510	5.2855	5.2698	5.3152	5.2714	5.3069
NH3-NH3	2.1345	2.2229	2.1436	2.1474	2.1323	2.1623	2.1654	2.2036
NH3O	5.3942	5.1549	5.0477	5.0407	5.0382	5.1806	5.2447	5.4048
OCl2	0.5625	0.5154	0.4656	0.4546	0.4549	0.4942	0.5545	0.6083
P2H4	0.9979	1.0190	0.9672	1.0086	0.9549	1.0243	0.9347	1.0041
PH2OH	0.6836	0.6516	0.6610	0.6424	0.6675	0.6432	0.7182	0.7043
PH3	0.6069	0.6504	0.6025	0.6438	0.5917	0.6429	0.5568	0.6061
PH3O	3.7704	3.5852	3.4760	3.4500	3.4542	3.6008	3.7172	3.8596
S2H2	1.1425	1.1393	1.0913	1.1106	1.0811	1.1485	1.0971	1.1493
SCl2	0.3891	0.2953	0.2995	0.2782	0.2978	0.3439	0.3808	0.4049
SF2	1.0555	0.8444	0.7973	0.7481	0.7716	0.8564	1.0029	1.0681
SH2	0.9939	1.0114	0.9656	0.9884	0.9557	1.0126	0.9618	1.0075
SiH3Cl	1.3645	1.2625	1.2104	1.1960	1.1958	1.2488	1.2892	1.3484
SiH3F	1.3123	1.2394	1.1743	1.1354	1.1359	1.2030	1.2686	1.3123
SiO	3.1123	2.9840	2.9017	2.8195	2.8737	3.0029	3.2087	3.3328
SO2	1.6286	1.5218	1.4850	1.4437	1.4713	1.5389	1.6655	1.7371
AlH2	0.4011	0.3405	0.3481	0.3552	0.3795	0.3992	0.4482	0.4378
BeH	0.2319	0.1988	0.2434	0.2709	0.2766	0.2866	0.3050	0.2799
BH2	0.5004	0.5376	0.5102	0.5034	0.5050	0.4699	0.4921	0.5110
BN	2.0366	1.8504	1.8899	1.9384	1.8910	2.1672	2.1340	2.2778
BO	2.3171	2.2075	2.1837	2.1937	2.1836	2.3566	2.4217	2.5003
BS	0.7834	0.6130	0.6599	0.7174	0.6829	0.8825	0.8422	0.9445
C2H	0.7601	0.7798	0.7625	0.7466	0.7699	0.7514	0.7610	0.7629
C2H3	0.6867	0.7796	0.7214	0.7160	0.7178	0.6786	0.6984	0.7069

Table S16 – continued

C2H5	0.314	0.4465	0.3808	0.3722	0.3683	0.3319	0.3413	0.3368
CF	0.6793	0.9598	0.9422	0.9671	0.9549	0.8503	0.7727	0.7433
CF2	0.5402	0.7846	0.7623	0.8054	0.7846	0.7208	0.6212	0.6002
CH2F	1.3796	1.1652	1.1533	1.1391	1.1405	1.2648	1.3009	1.3583
CH2PH	0.8748	0.8986	0.8990	0.9460	0.9102	0.9951	0.8574	0.8587
CH2-t	0.5862	0.6244	0.5896	0.5815	0.5848	0.5636	0.5941	0.6149
CH3O	2.0368	2.3031	2.1216	2.0939	2.0870	2.0598	2.0916	2.1171
ClO2	1.8627	1.7008	1.6696	1.6400	1.6607	1.7237	1.8304	1.9069
CN	1.4318	1.1365	1.1546	1.1712	1.1283	1.4595	1.3667	1.5438
FCO	0.7678	0.7467	0.7572	0.7708	0.7630	0.8635	0.8306	0.8674
FH-BH2	2.973	3.1439	3.0208	2.9812	2.9699	2.9897	3.0340	3.0654
FH-NH2	4.6265	4.6736	4.5641	4.5629	4.5349	4.6489	4.6533	4.7182
FH-OH	3.3808	3.2260	3.2676	3.2834	3.2643	3.3917	3.4039	3.4433
H2CN	2.4939	2.5728	2.4666	2.4563	2.4523	2.5084	2.5015	2.5468
H2O-Al	4.3573	4.1925	4.2175	4.4188	4.3426	4.4480	4.2751	4.3717
H2O-Cl	2.2383	3.2621	3.1191	3.1602	3.1260	2.9277	2.7610	2.5301
H2O-F	2.1875	3.3489	3.1722	3.1600	3.1465	2.8458	2.8303	2.6667
H2O-Li	3.6184	1.7386	2.3975	3.1190	2.5400	2.7992	2.4949	3.1559
HCHS	1.7588	1.6660	1.6712	1.6957	1.6878	1.8378	1.7376	1.7818
HCO	1.6912	1.6015	1.5537	1.5429	1.5421	1.6793	1.7091	1.7877
HCP	0.3542	0.3455	0.3710	0.4229	0.3911	0.4530	0.3109	0.2825
HNO	1.6536	1.5716	1.4845	1.4728	1.4615	1.5600	1.6249	1.7210
HNO2	1.9345	1.9462	1.8829	1.8888	1.8757	1.9506	1.9564	1.9910
HNS	1.4062	1.3763	1.3359	1.3360	1.3282	1.3686	1.3802	1.4178
HO2	2.1659	2.3070	2.2112	2.2052	2.1955	2.1340	2.1803	2.1956
HPO	2.6291	2.3223	2.2390	2.1939	2.2155	2.3434	2.4871	2.6156
LiN	7.0558	6.5415	6.5489	6.7133	6.7297	6.8840	6.8172	6.9743
N2H2	2.8771	2.8730	2.7650	2.7625	2.7461	2.8025	2.8452	2.9288
NCl	1.1279	1.3736	1.2727	1.2292	1.2588	1.1267	1.1990	1.1832
NCO	0.7935	0.8677	0.8619	0.8630	0.8640	0.8641	0.7998	0.7793
NF	0.0671	0.3403	0.3136	0.3118	0.3197	0.1586	0.1385	0.0996
NF2	0.1904	0.0079	0.0318	0.0163	0.0268	0.1429	0.1664	0.1924
NH	1.5433	1.5308	1.4815	1.4776	1.4701	1.5281	1.5219	1.5624
NH2	1.7853	1.7833	1.7201	1.7227	1.7107	1.7644	1.7698	1.8209
NO	0.1271	0.2449	0.2292	0.2340	0.2294	0.1199	0.1152	0.0894
NO2	0.335	0.2802	0.2753	0.2619	0.2628	0.3100	0.3499	0.3885
NOCl	2.0773	1.6328	1.7388	1.7735	1.7777	1.8447	1.8005	1.8738
NP	2.8713	2.8142	2.7212	2.6711	2.6999	2.7648	2.9212	3.0457
NS	1.8237	1.8609	1.7674	1.7327	1.7460	1.7200	1.8324	1.8891
OCl	1.279	1.4566	1.3439	1.3130	1.3217	1.2061	1.3235	1.3351
OF	0.0205	0.2491	0.1938	0.1957	0.1721	0.0324	0.0140	0.0240
OF2	0.3252	0.2654	0.2795	0.2696	0.2788	0.3254	0.3315	0.3395
OH	1.655	1.6478	1.5940	1.5905	1.5824	1.6412	1.6452	1.6783
PCl	0.5657	0.2803	0.3086	0.2835	0.2924	0.4024	0.4695	0.5603
PF	0.8104	0.6045	0.5715	0.5171	0.5376	0.6164	0.7547	0.8114
PH	0.4375	0.4472	0.4202	0.4458	0.4138	0.4750	0.4007	0.4366

Table S16 – continued

PH2	0.5472	0.5786	0.5357	0.5713	0.5255	0.5891	0.5008	0.5473
PO	1.9617	1.8240	1.7658	1.7106	1.7407	1.8685	2.0303	2.1496
PO2	1.4426	1.2857	1.2608	1.2305	1.2374	1.3785	1.4312	1.5265
PPO	1.8812	1.7935	1.6797	1.6082	1.6429	1.7665	1.9464	2.0145
PS	0.6825	0.4795	0.4938	0.4737	0.4893	0.6027	0.6423	0.7491
SCl	0.069	0.2249	0.1797	0.1909	0.1853	0.0468	0.0361	0.0544
SF	0.8139	0.5677	0.5423	0.5011	0.5167	0.6300	0.7477	0.8212
SH	0.7727	0.7806	0.7449	0.7617	0.7377	0.7960	0.7462	0.7821
SO-trip	1.5606	1.4036	1.3581	1.3154	1.3329	1.3927	1.5320	1.6299
MAD		0.1589	0.1529	0.1413	0.1430	0.0892	0.0750	0.0670

Table S17: Static and dynamic polarizabilities in a.u.

System	Freq a.u.	Reff	LDA	PBE	CAP	NCAP
		MC-SCF				
H_2O	0.00	9.210	10.12	10.14	9.46	9.60
	0.05	9.284	10.22	10.25	9.55	9.70
	0.10	9.520	10.58	10.62	9.85	10.00
	0.15	9.960	11.33	11.41	10.45	10.62
	0.20	10.770	13.07	13.36	11.73	11.94
	0.25	12.560	174.40	-8.91	19.38	19.53
NH_3	0.00	13.880	14.83	14.75	13.80	14.01
	0.05	14.047	15.05	14.97	13.97	14.20
	0.10	14.600	15.80	15.74	14.57	14.82
	0.15	15.784	17.65	17.71	15.95	16.24
	0.20	18.840	29.24	34.42	21.04	21.33
CH_4	0.00	15.616	17.49	17.22	16.35	16.42
	0.05	15.740	17.66	17.39	16.49	16.56
	0.10	16.129	18.20	17.92	16.95	17.02
	0.15	16.836	19.22	18.93	17.80	17.87
	0.20	17.976	20.96	20.65	19.23	19.30
	0.25	19.798	24.12	23.82	21.71	21.74
	0.30	22.933	31.96	31.96	27.14	26.87
HF	0.00	5.324	5.89	5.94	5.56	5.62
	0.10	5.429	6.05	6.12	5.70	5.76
	0.20	5.795	6.68	6.79	6.23	6.30
	0.30	6.692	9.26	9.98	8.09	8.12
	0.40	17.012	6.68	7.09	5.50	5.33
H_2	0.00	5.203	5.56	5.34	5.20	5.20
	0.10	5.392	5.78	5.55	5.39	5.39
	0.20	6.061	6.59	6.31	6.08	6.08
	0.30	7.740	8.67	8.24	7.80	7.80
		CCSD				
N_2	0.0000	11.60	11.81	11.76	11.28	11.41
	0.0720	11.75	11.99	11.94	11.44	11.57
	0.0886	11.83	12.08	12.03	11.52	11.66
	0.0934	11.84	12.11	12.06	11.55	11.68
	0.0995	11.89	12.15	12.10	11.59	11.72
CO	0.0000	13.07	13.40	13.36	12.72	12.81
	0.0720	13.32	13.70	13.66	12.98	13.07
	0.0886	13.46	13.86	13.81	13.12	13.22
	0.0934	13.5	13.91	13.87	13.16	13.26
	0.0995	13.57	13.99	13.94	13.23	13.33
CO_2	0.0000	18.00	17.44	17.51	16.71	16.88
	0.0720	18.27	17.70	17.78	16.95	17.12
	0.0886	18.42	17.85	17.93	17.08	17.25

Table S17 – continued

	0.0934	18.46	17.89	17.98	17.13	17.30
	0.0995	18.53	17.96	18.04	17.18	17.36
Cl_2	0.0000	30.86	30.37	30.04	28.73	29.24
	0.0720	31.52	31.08	30.75	29.34	29.88
	0.0886	31.89	31.50	31.15	29.69	30.24
	0.0934	32.01	31.64	31.29	29.81	30.37
	0.0995	32.18	31.86	31.50	29.97	30.54
C_2H_2	0.0000	22.25	23.38	23.29	21.94	22.32
	0.0720	22.82	24.07	24.00	22.53	22.93
	0.0886	23.14	24.44	24.38	22.85	23.27
	0.0934	23.24	24.57	24.51	22.96	23.38
	0.0995	23.38	24.74	24.69	23.10	23.53
OCS	0.0000	35.71	34.08	34.01	32.37	32.90
	0.0720	36.80	35.11	35.04	33.27	33.84
	0.0886	37.36	35.67	35.60	33.77	34.36
	0.0934	37.57	35.86	35.79	33.93	34.53
	0.0995	37.88	36.12	36.05	34.16	34.77
CS_2	0.0000	59.15	54.40	54.25	51.56	52.46
	0.0720	62.04	56.89	56.74	53.79	54.77
	0.0886	63.77	58.31	58.16	55.05	56.08
	0.0934	64.40	58.80	58.65	55.49	56.52
	0.0995	65.20	59.48	59.33	56.09	57.15
MAD			4.44	2.25	1.92	1.74

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