Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for Localizing Electron Density Errors in Density Functional Theory

Rubén Laplaza, Victor Polo, Julia Contreras-García *

E-mail: contreras@lct.jussieu.fr

List of Tables

Computational details

All DFT calculations were performed using the Gaussian09 rev.D01 suite,[1] and therefore all the nomenclature and definitions correspond to those within this software. A total of 59 DFAs, as defined and available in the code, were considered across this work. 27 of them are pure DFAs, and 30 are hybrid DFAs including a percentage of exact exchange (HFX), and 2 are double-hybrids including second order perturbation theory contributions. All calculations were performed with the all electron quadruple-ξ aug-cc-pCVQZ[2,3] basis set. The complete list is as follows:

- G96LYP
- BVWN
- M06L
- M06
- M062X
- M06HF
- M05
- M052X
- M11
- N12SX
- MN12SX
- SOGGA11X
- PW91VWN
- TPSSh
- BMK
- BHandH
- BHandHLYP
- HSEH1PBE
- wB97XD
- LC-wPBE
- CAM-B3LYP
- APFD
- B2PLYP-FC
- mPW2PLYP-FC
- HSEVWN
- BRxVWN
- BPBE
- PW91PBE
- PBEPBE
- HSEPBE
- mPW1PBE
- mPW3PBE
- BPW91
- PW91PW91
- PBEPW91
- HSEPW91
- B3PW91
- mPW1PW91
- BLYP
- PW91LYP
- PBELYP
- HSELYP
- B3LYP
- mPW1LYP
- TPSSTPSS
- XAlphaXa
- BB95
- PW91B95
- PBEB95
- HSEB95
- SVWN
- PKZBPKZB
- B3P86
- PKZBKCIS
- BRxKCIS
- OVWN
- OPBE
- OLYP
- OB95

2D maps of N_2 for an assortment of DFAs

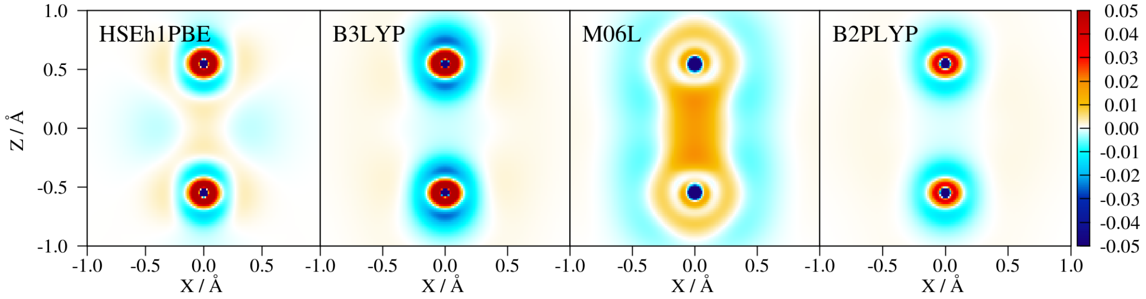


Figure S1: Electronic density difference ($\rho_{diff}(r)$) maps on the σ_v planes of the N_2 molecule at r_e. Methods are detailed in the top left corners, left to right: HSEh1PBE, B3LYP, M06L and B2PLYP-FC.

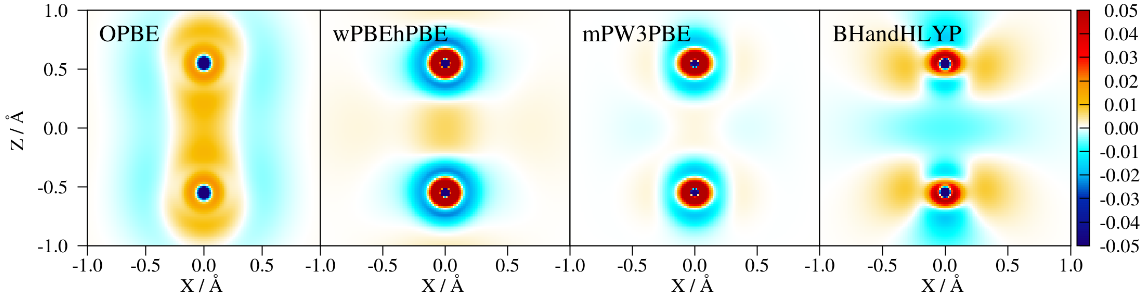


Figure S2: Electronic density difference ($\rho_{diff}(r)$) maps on the σ_v planes of the N_2 molecule at r_e. Methods are detailed in the top left corners, left to right: OPBE, wPBEhPBE, mPW3PBE and BHandHLYP.

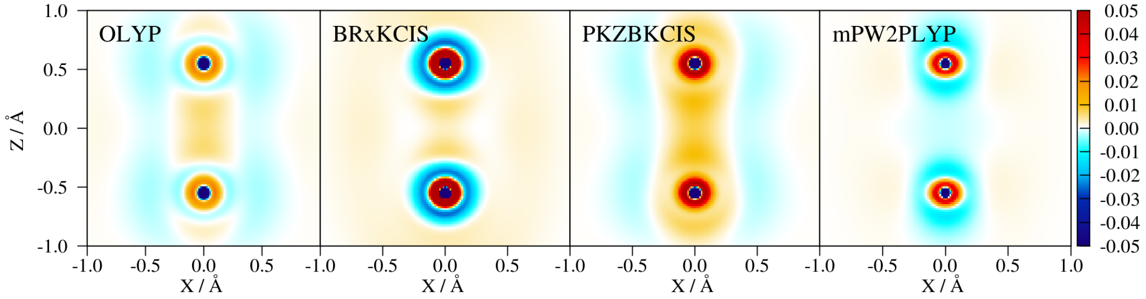


Figure S3: Electronic density difference ($\rho_{diff}(r)$) maps on the σ_v planes of the N_2 molecule at r_e. Methods are detailed in the top left corners, left to right: OLYP, BRxKCIS, PKZBKCIS and mPW2PLYP-FC.

On the topology of the Electron Localization Function

The determination of Ω_B disynaptic bonding basins is performed by computing the Electron Localization Function (ELF) as a scalar field expressed in a numerical grid, then finding all critical points on the field. Relative maxima in the grid (*attractors*) have associated basins that can be determined following gradient paths until boundaries between attractors are found, corresponding to minima or saddle points. Covalent bonds, as well as nuclei, have associated attractors and, consequently, basins.

In molecular systems the ELF partitioning is exhaustive but not always closed. Therefore, a numerical threshold based on the electron density is used to limit volumes whenever the function is asymptotically decaying (≤ 0.001 a.u.). For a more exhaustive methodological explanation, please refer to the Multiwfn 3.5 manual.[4] Note, however, that this is hardly important for the relatively confined bonding basins considered in this work, yet it can be an important precision if ELF basins related with bonds with hydrogen atoms are to be reported.

Molecular orbitals with occupation numbers $\neq 0$ are considered in every scalar field calculation, which are just canonical KS orbitals in closed-shell KS-DFT calculations, and the corresponding (weighted) Natural Orbitals in the case of post-HF calculations.

Additional information on the geometry of C_2H_6

The single C−C bond in ethane is unlike the triple bonds in the other molecule. In particular, HF calculations show that it has the highest bonding charge concentration, but not the shortest equilibrium bond length or highest harmonic frequency with respect to other methods. This is counterintuitive, and can only be understood by paying attention to the distortion on C−H bonds, which are shorter in HF and other high-HFX formulations like M06HF and BHandH. The effects of localization are shared between all the covalent bonds in the molecule, and sometimes may compensate and compete with each other.

In HF calculations, all covalent bonds in the system are overlocalized from the point of view of the density. Coherently, an increased (electronic) attractive force is exerted onto the nuclei involved in the bonding interaction. This leads to bond shortening in covalent diatomics. In the case of ethane, the bond shortening takes place primarily in the six C−H bonds, which can be exemplified by computing the electronic forces acting on nuclei as well as by the distances or harmonic frequencies associated with the C−H stretching. All in all, the molecule is *compressed* and forces are increased, in line with the observations for N_2 and CO. The shortening of these six bonds is energetically preferred over the shortening of the central C−C bond. The opposite is true for pure local DFAs, as reported in Tables S10 and S11.

Correlation between Λ_{diff} and the relative error with respect to the CCSD(T) references

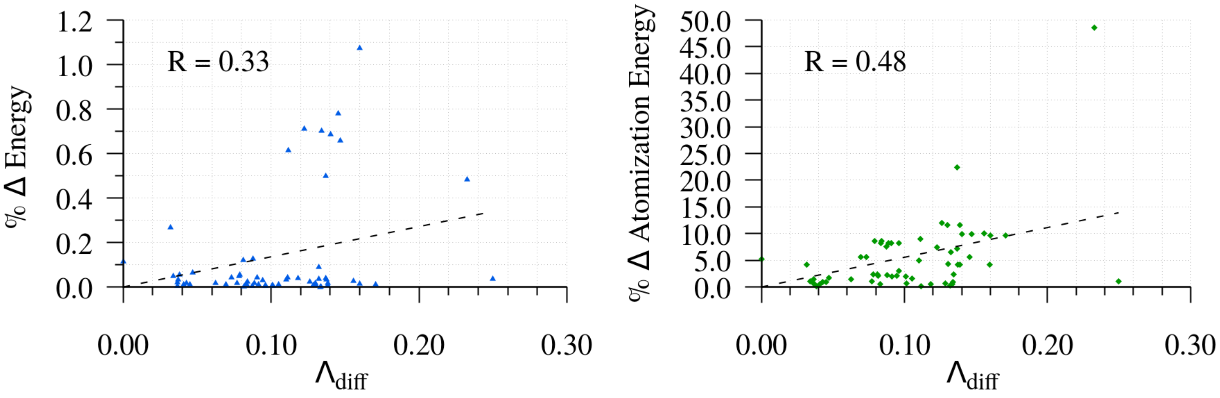


Figure S4: Correlation between Λ_{diff} and the relative error with respect to the CCSD(T) reference in several properties for the N_2 molecule at r_e for the DFA set. Least-squares fits are drawn as dashed black lines with their Pearson correlation coefficients (R) shown top left of each plot.

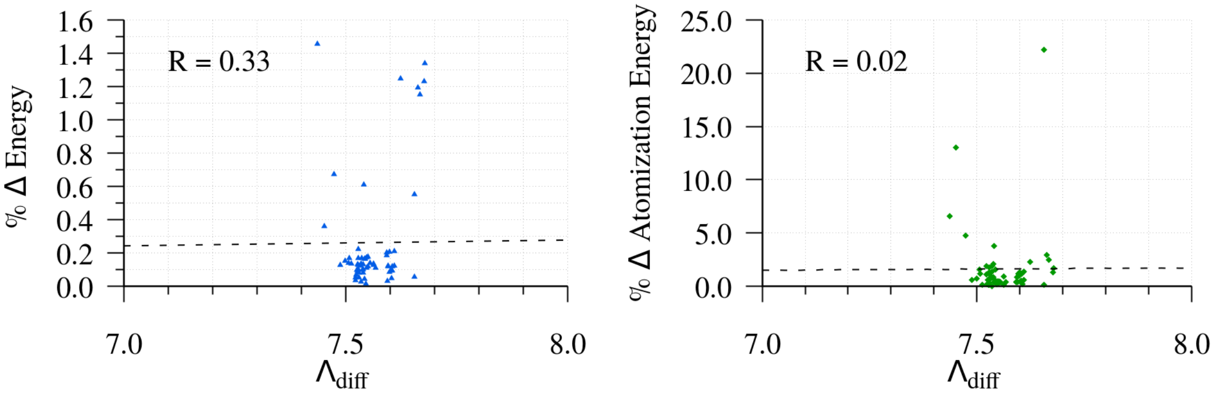


Figure S5: Correlation between Λ_{diff} and the relative error with respect to the CCSD(T) reference in several properties for the ethane C_2H_6 molecule at r_e for the DFA set. Least-squares fits are drawn as dashed black lines with their Pearson correlation coefficients (R) shown top left of each plot.

Custom DFAs

The BX-LYP single-parameter hybrid series of functionals were built using Gaussian09 rev.D01. Based on the three-parameter formulation of B3LYP as in the code, a simplified version was used in which the exchange-correlation energy takes the form:

$$E_{XC} = aE_X^{HF} + (1-a)(E_X^{Slater} + \Delta E_X^{B88}) + E_C^{LSDA} + (1-a)(E_C^{LYP} - E_C^{LSDA}) \tag{1}$$

The BX-LYP series takes a values ranging from 0.10 to 0.90, with the systematic nomenclature of B10%LYP, B20%LYP etc. up to B90%LYP. Analogously, the SX-VWN3 series takes the form:

$$E_{XC} = aE_X^{HF} + (1-a)E_X^{Slater} + E_C^{LSDA} \tag{2}$$

In which a takes values ranging from 0.10 to 0.90 with the systematic nomenclature of S10%VWN3 etc. Note that both series converge to the same result when $a \to 1$.

Table S1: Descriptors for the respective equilibrium geometries of CO. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, equilibrium distances (d_e) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol.

Method	Pop. Ω_b	Vol. Ω_b	d_e	ω_h	ΔE_{atom}
B10%LYP	3.0354	58.68	1.1297	2156.56	257.13
B20%LYP	3.0789	61.91	1.1243	2198.18	252.21
B30%LYP	3.1014	62.19	1.1192	2237.55	247.46
B40%LYP	3.1373	64.53	1.1145	2274.88	242.86
B50%LYP	3.1764	68.85	1.1101	2310.33	238.41
B60%LYP	3.2126	67.45	1.1059	2344.07	234.10
B70%LYP	3.2465	71.05	1.1020	2376.21	229.92
B80%LYP	3.2778	73.21	1.0983	2406.88	225.87
B90%LYP	3.3090	76.44	1.0948	2436.16	221.95

Table S2: Descriptors for the respective equilibrium geometries of N_2. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, equilibrium distances (d_e) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol.

Method	Pop. Ω_b	Vol. Ω_b	d_e	ω_h	ΔE_{atom}
B10%LYP	3.3836	130.12	1.0961	2384.84	233.93
B20%LYP	3.4491	137.88	1.0905	2433.30	227.36
B30%LYP	3.5089	154.31	1.0852	2479.45	220.97
B40%LYP	3.5625	171.13	1.0803	2523.53	214.74
B50%LYP	3.6160	188.38	1.0756	2564.97	208.68
B60%LYP	3.6704	191.54	1.0711	2605.34	202.77
B70%LYP	3.7376	208.29	1.0669	2644.11	197.01
B80%LYP	3.7903	225.35	1.0629	2681.40	191.39
B90%LYP	3.8366	241.96	1.0591	2717.32	185.90
S10%VWN3	3.4282	120.79	1.0899	2440.84	257.41
S20%VWN3	3.4863	136.14	1.0854	2480.35	247.51
S30%VWN3	3.5362	151.57	1.0811	2512.52	237.75
S40%VWN3	3.5831	156.25	1.0771	2553.82	228.14
S50%VWN3	3.6304	171.77	1.0732	2588.76	218.66
S60%VWN3	3.6803	188.03	1.0695	2622.46	209.30
S70%VWN3	3.7459	205.28	1.066	2655.00	200.08
S80%VWN3	3.7932	223.09	1.0626	2686.46	190.98
S90%VWN3	3.8358	240.42	1.0593	2716.90	181.99

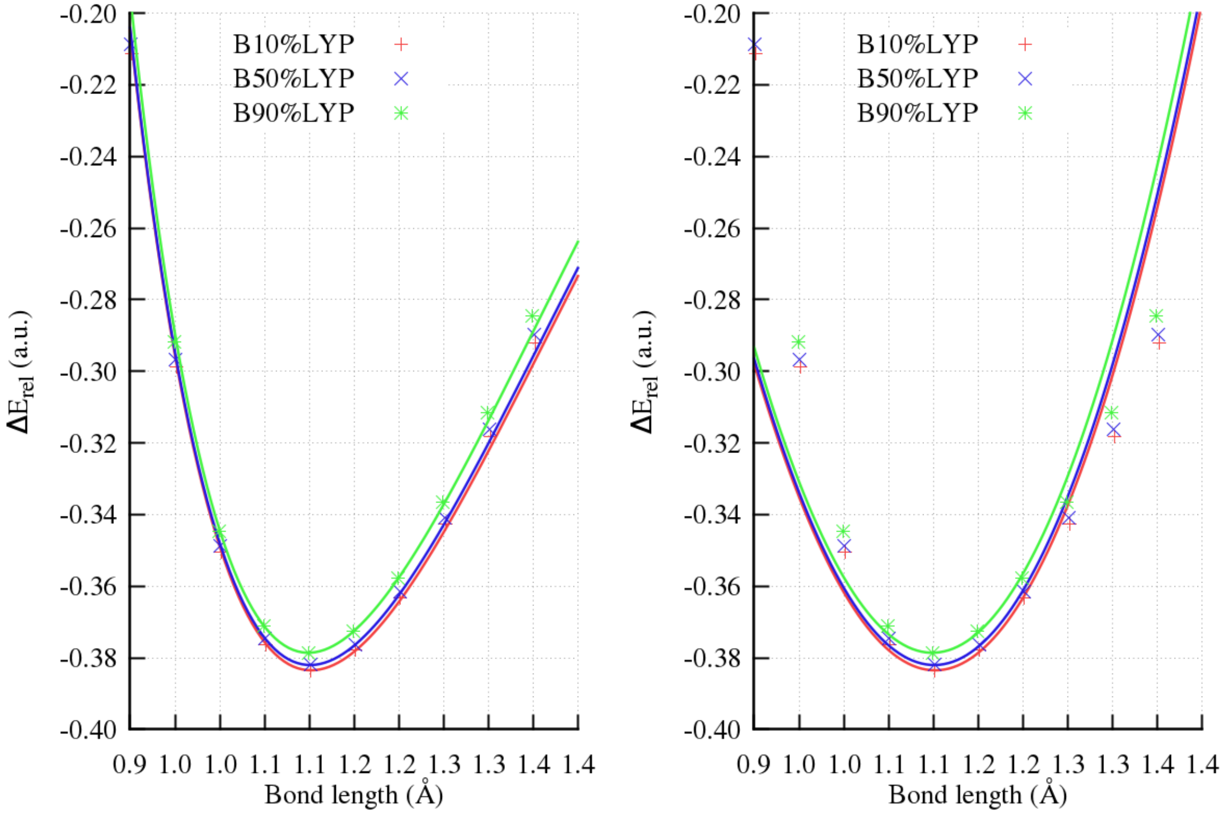
Morse potentials

A Morse potential of the form:

$$\mathcal{V}(x) = \mathcal{D}_e(1 - e^{\mathcal{A}(x-r_e)})^2 \tag{3}$$

was used to fit the data points of the stretching molecules in all graphics, given that r_e (equilibrium distance) and $\mathcal{D}_e$ (well depth) are known by calculation. Therefore, well amplitudes, $\mathcal{A}$, were the only parameter to fit by linear regression. Potential curves were offset with respect to their reference energies for representation purposes.

Figure S6: Dissociation curves for the N_2 molecule calculated with different methods. Data points have been fitted to a Morse potential (left) and a harmonic potential (right). ΔE_{rel} is the relative energy in atomic units with respect to the isolated atoms.



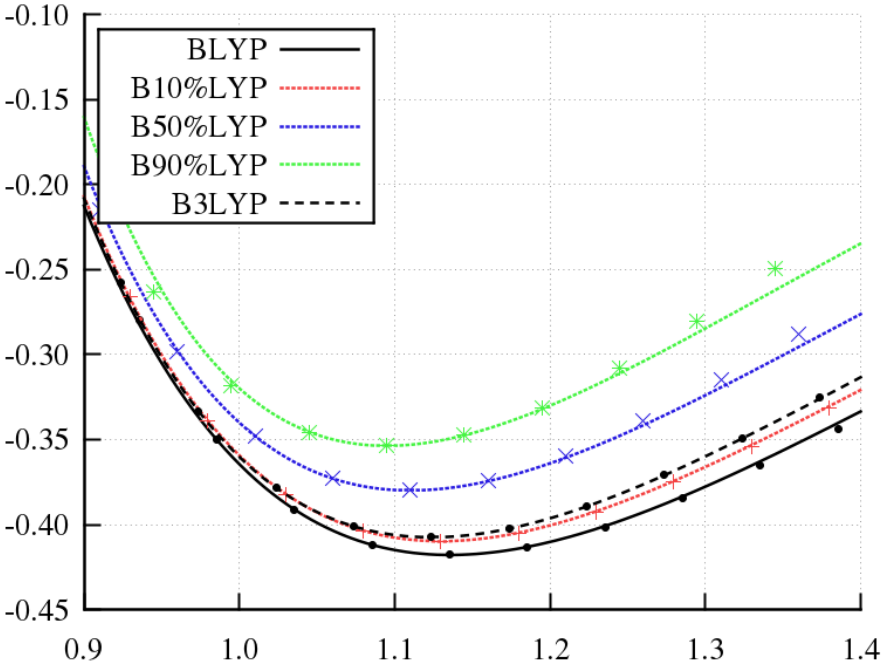


Figure S7: Dissociation curves for the CO molecule calculated with different methods. Data points have been fitted to a Morse potential. BLYP and B3LYP are shown in black solid and dashed lines respectively, and BX-LYP variants (B10%LYP, B50%LYP and B90%LYP) are shown in red, blue and green small lines respectively. ΔE_{rel} is the relative energy in atomic units with respect to the isolated atoms.

Table S3: Well amplitudes $\mathcal{A}$ in the Morse potential fits for dissociation curves with different methods for both the N_2 and CO molecules.

Molecule	N_2	CO
Method	$\mathcal{A}$	$\mathcal{A}$
BLYP	2.5742	2.2556
B3LYP	2.7966	2.3703
B10%LYP	2.7072	2.3192
B50%LYP	3.0946	2.5487
B90%LYP	3.4491	2.7466
B10%LYP//BLYP	2.5752	2.2662
B50%LYP//BLYP	2.5878	2.3222
B90%LYP//BLYP	2.6562	2.4001

References

(1) Frisch, M. J. et al. Gaussian 09, Revision D.01. Gaussian Inc. Wallingford CT 2009.

(2) Woon, D. E.; Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon. *J. Chem. Phys.* **1995**, *103*, DOI: `10.1063/1.470645`.

(3) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, DOI: `10.1063/1.456153`.

(4) Tian, L.; Feiwu, C. Multiwfn: A multifunctional wavefunction analyzer. *Journal of Computational Chemistry* **2011**, *33*, 580–592, DOI: `10.1002/jcc.22885`.

Table S4: Atomization energies (ΔE_{atom}) in kcal/mol, Λ_{diff} values in atomic units, and dipole moments ($\mathcal{D}$) in Debyes for the N_2, CO and C_2H_6 molecules in their respective CCSD(T) equilibrium geometries. (Part 1)

Molecule	N_2		CO			C_2H_6	
Method	ΔE_{atom}	Λ_{diff}	ΔE_{atom}	Λ_{diff}	$\mathcal{D}$	ΔE_{atom}	Λ_{diff}
G96LYP	235.89	0.1102	260.13	0.1180	0.184	700.42	7.6048
BVWN	241.23	0.1226	260.99	0.1268	0.162	718.13	7.6766
M06L	225.16	0.1322	259.04	0.1307	0.198	711.76	7.5917
M06	222.97	0.1012	259.79	0.1132	0.058	711.80	7.5671
M062X	227.11	0.0771	259.45	0.0755	0.011	710.00	7.5271
M06HF	227.13	0.2497	257.12	0.2564	-0.168	717.17	7.5081
M05	223.50	0.1332	257.97	0.1316	0.048	713.35	7.5257
M052X	225.87	0.1184	257.22	0.1168	-0.012	711.32	7.5280
M11	233.91	0.1386	259.31	0.1498	0.008	713.39	7.4877
N12SX	214.97	0.1303	253.81	0.1376	0.014	707.97	7.5622
MN12SX	223.09	0.1285	255.87	0.1288	-0.016	703.75	7.5386
SOGGA11X	228.23	0.1051	255.88	0.1104	0.022	710.95	7.5500
PW91VWN	247.00	0.1402	266.39	0.1449	0.155	729.86	7.6629
TPSSh	222.18	0.0340	250.23	0.0428	0.141	718.51	7.5994
BMK	229.41	0.0817	262.49	0.0684	0.056	712.29	7.5473
BHandH	224.83	0.1117	260.35	0.1165	-0.032	742.80	7.4739
BHandHLYP	207.72	0.0874	238.64	0.1108	-0.067	700.74	7.5958
HSEH1PBE	225.03	0.0383	254.83	0.0461	0.093	710.35	7.5245
wB97XD	225.88	0.0408	256.83	0.0508	0.093	712.00	7.5442
LC-wPBE	227.94	0.0626	257.79	0.0616	0.105	710.08	7.5132
CAM-B3LYP	229.09	0.0913	256.98	0.0936	0.054	715.35	7.5625
APFD	225.81	0.0370	255.80	0.0425	0.103	713.35	7.5281
B2PLYP-FC	231.34	0.0961	258.83	0.1189	0.145	710.31	7.6055
mPW2PLYP-FC	228.92	0.1011	257.09	0.1247	0.113	711.61	7.6026
HSEVWN	247.00	0.1468	265.08	0.1503	0.160	726.43	7.6672
BRxVWN	237.29	0.1455	264.27	0.1563	0.118	721.07	7.6783
BPBE	237.36	0.0693	263.81	0.0877	0.217	706.06	7.5397
PW91PBE	243.14	0.0835	269.24	0.1034	0.211	717.78	7.5266
PBEPBE	243.91	0.0791	269.11	0.0999	0.220	716.73	7.5223
HSEPBE	243.06	0.0906	267.90	0.1083	0.216	714.28	7.5299
mPW1PBE	222.63	0.0452	253.49	0.0500	0.091	708.11	7.5279
mPW3PBE	227.93	0.0366	257.82	0.0432	0.111	715.71	7.5332

Table S5: Atomization energies (ΔE_{atom}) in kcal/mol, Λ_{diff} values in atomic units, and dipole moments ($\mathcal{D}$) in Debyes for the N_2, CO and C_2H_6 molecules in their respective CCSD(T) equilibrium geometries. (Part 2)

Molecule	N_2		CO			C_2H_6	
Method	ΔE_{atom}	Λ_{diff}	ΔE_{atom}	Λ_{diff}	$\mathcal{D}$	ΔE_{atom}	Λ_{diff}
BPW91	237.34	0.0733	263.61	0.0908	0.214	706.99	7.5476
PW91PW91	243.12	0.0887	269.03	0.1068	0.207	718.72	7.5346
PBEPW91	243.89	0.0841	268.90	0.1032	0.216	717.67	7.5301
HSEPW91	243.05	0.0962	267.70	0.1120	0.212	715.23	7.5380
B3PW91	226.00	0.0366	255.89	0.0439	0.111	712.59	7.5432
mPW1PW91	222.58	0.0429	253.26	0.0509	0.088	708.99	7.5356
MP2-FC	236.31	0.0002	270.00	0.0621	0.271	707.84	7.6555
BLYP	240.67	0.1370	262.16	0.1426	0.181	704.62	7.6095
PW91LYP	246.42	0.1600	267.54	0.1654	0.174	716.22	7.5986
PBELYP	247.16	0.1559	267.37	0.1626	0.183	715.08	7.5936
HSELYP	246.39	0.1707	266.21	0.1758	0.179	712.71	7.6027
B3LYP	229.95	0.0783	255.65	0.0827	0.083	711.98	7.5923
mPW1LYP	225.84	0.0832	251.88	0.0872	0.054	706.40	7.5953
HF	115.40	0.2325	174.48	0.2848	-0.271	551.63	7.6555
TPSSTPSS	228.35	0.0470	254.36	0.0593	0.187	718.89	7.6091
XAlphaXa	215.13	0.1597	268.58	0.1792	0.230	662.39	7.4367
BB95	244.89	0.1113	271.30	0.1284	0.209	712.17	7.5509
PW91B95	250.63	0.1302	276.65	0.1470	0.202	723.71	7.5390
PBEB95	251.43	0.1263	276.53	0.1435	0.211	722.67	7.5344
HSEB95	250.60	0.1386	275.33	0.1528	0.207	720.25	7.5424
SVWN	274.82	0.1368	303.91	0.1584	0.218	801.31	7.4515
PKZBPKZB	229.91	0.0812	256.36	0.0875	0.225	710.32	7.5459
B3P86	234.08	0.0318	261.59	0.0404	0.102	735.93	7.5405
PKZBKCIS	229.55	0.0878	256.15	0.0957	0.222	695.76	7.5227
BRxKCIS	239.15	0.1323	271.06	0.1428	0.172	721.54	7.5281
OVWN	229.95	0.1343	258.14	0.1366	0.166	725.17	7.6243
OPBE	226.60	0.1337	261.19	0.1314	0.224	714.21	7.4992
OLYP	229.47	0.0946	259.25	0.1019	0.185	711.74	7.5550
OB95	233.96	0.1375	268.67	0.1404	0.214	720.12	7.5067
CCSD(T)	224.61	0.0000	257.25	0.0000	0.117	709.01	0.0000

Table S6: Descriptors for the respective equilibrium geometries of N_2. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, equilibrium distances (d_e) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol. (Part 1)

Method	Pop. Ω_b	Vol. Ω_b	d_e	ω_h	ΔE_{atom}
G96LYP	3.3020	108.25	1.1008	2340.92	235.90
BVWN	3.3077	108.69	1.0999	2343.26	241.23
M06L	3.5682	112.80	1.0951	2413.85	225.18
M06	3.6198	137.33	1.0884	2465.60	223.15
M062X	3.5724	180.76	1.0854	2512.34	227.42
M06HF	3.4571	190.74	1.0759	2615.55	228.11
M05	3.5265	159.81	1.0928	2447.22	223.56
M052X	3.4090	151.71	1.0829	2543.64	226.32
M11	3.4050	113.21	1.0835	2534.05	234.31
N12SX	3.4979	149.83	1.082	2501.05	215.45
MN12SX	3.6475	164.06	1.0869	2504.36	223.33
SOGGA11X	3.5808	163.80	1.0881	2516.18	228.43
PW91VWN	3.3099	116.77	1.099	2348.34	247.00
TPSSh	3.4568	144.80	1.0943	2418.89	222.21
BMK	3.5194	154.03	1.0894	2456.13	229.55
BhandH	3.6265	181.73	1.0746	2608.60	225.91
BhandHLYP	3.6139	187.06	1.0767	2585.54	208.61
HSEH1PBE	3.5089	151.68	1.0884	2480.19	225.20
wB97XD	3.4996	146.07	1.0871	2491.17	226.11
LC-wPBE	3.5550	168.10	1.0863	2520.45	228.21
CAM-B3LYP	3.5051	150.36	1.0855	2498.70	229.39
APFD	3.4987	150.91	1.0893	2471.40	225.95
B2PLYP-FC	3.3980	127.16	1.0977	2346.33	231.35
mPW2PLYP-FC	3.4361	136.91	1.0942	2383.69	228.95
HSEVWN	3.3178	113.13	1.0995	2347.16	247.00
BrxVWN	3.3877	121.91	1.0964	2386.26	237.30
BPBE	3.3339	114.79	1.1018	2350.17	237.38
PW91PBE	3.3361	123.31	1.101	2354.45	243.15
PBEPBE	3.3562	124.60	1.1022	2350.65	243.93
HSEPBE	3.3582	119.95	1.1015	2353.42	243.07
mPW1PBE	3.5105	154.42	1.0882	2481.43	222.82
mPW3PBE	3.4774	144.21	1.09	2459.18	228.05

Table S7: Descriptors for the respective equilibrium geometries of N_2. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, equilibrium distances (d_e) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol. (Part 2)

Method	Pop. Ω_b	Vol. Ω_b	d_e	ω_h	ΔE_{atom}
BPW91	3.3332	113.55	1.1014	2350.98	237.36
PW91PW91	3.3345	121.92	1.1006	2355.69	243.13
PBEPW91	3.3559	123.15	1.1018	2351.45	243.91
HSEPW91	3.3575	118.77	1.1011	2354.22	243.06
B3PW9	3.4770	143.37	1.09	2458.78	226.12
mPW1PW91	3.5079	153.23	1.0878	2482.51	222.78
MP2-FC	3.2911	103.13	1.1105	2201.86	236.53
BLYP	3.2994	113.55	1.1021	2333.24	240.69
PW91LYP	3.3009	121.40	1.1013	2337.51	246.43
PBELYP	3.3068	114.61	1.1025	2333.58	247.18
HSELYP	3.3102	111.06	1.1018	2336.38	246.41
B3LYP	3.4537	137.62	1.0901	2448.19	230.07
mPW1LYP	3.4769	154.70	1.0881	2468.18	226.03
HF	3.8509	258.21	1.0655	2729.25	117.62
TPSSTPSS	3.4027	139.29	1.0995	2367.54	228.35
XalphaXa	3.3504	111.54	1.0941	2392.73	215.16
BB95	3.3103	114.83	1.1018	2341.84	244.91
PW91B95	3.3120	115.41	1.101	2346.14	250.65
PBEB95	3.3176	115.96	1.1022	2342.36	251.46
HSEB95	3.3356	112.73	1.1015	2345.15	250.62
SVWN	3.3610	106.74	1.0937	2405.14	274.85
PKZBPKZB	3.3734	147.23	1.1087	2326.48	230.09
B3P86	3.4743	141.12	1.0893	2463.13	234.22
PKZBKCIS	3.3618	150.51	1.1088	2323.00	229.73
BrxKCIS	3.3993	121.52	1.0988	2385.94	239.15
OVWN	3.3896	144.95	1.0994	2368.13	229.95
OPBE	3.4163	163.17	1.1017	2372.51	226.62
OLYP	3.3832	150.89	1.1016	2357.41	229.49
OB95	3.3968	153.47	1.1016	2365.27	233.97
CCSD(T)	3.4074	143.46	1.0984	2346.79	224.61

Table S8: Descriptors for the respective equilibrium geometries of CO. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, equilibrium distances (d_e) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol. (Part 1)

Method	Pop. Ω_b	Vol. Ω_b	d_e	ω_h	ΔE_{atom}
G96LYP	2.9885	53.69	1.1344	2169.64	260.17
BVWN	2.9875	56.52	1.1337	2174.92	261.01
M06L	3.2405	80.34	1.1264	2231.17	259.05
M06	3.2279	89.13	1.1216	2268.34	259.88
M062X	3.1841	69.94	1.1193	2286.62	259.60
M06HF	2.9797	45.33	1.1119	2345.17	257.59
M05	3.1173	76.23	1.1267	2228.43	257.98
M052X	2.9914	54.66	1.1178	2297.91	257.42
M11	3.0239	65.90	1.1193	2286.33	259.45
N12SX	3.0901	64.41	1.1183	2294.32	253.98
MN12SX	3.2214	86.93	1.1214	2269.71	255.96
SOGGA11X	3.1734	72.88	1.1220	2264.93	255.96
PW91VWN	2.9912	55.58	1.1326	2183.06	266.41
TPSSh	3.0863	69.73	1.1283	2216.43	250.23
BMK	3.1930	72.24	1.1192	2287.44	262.64
BhandH	3.2369	71.16	1.1077	2379.06	261.07
BhandHLYP	3.1761	67.65	1.1110	2352.76	239.15
HSEH1PBE	3.1281	65.92	1.1219	2266.02	254.91
wB97XD	3.1353	69.73	1.1217	2267.40	256.92
LC-wPBE	3.1585	72.92	1.1207	2275.14	257.90
CAM-B3LYP	3.1289	66.14	1.1193	2286.71	257.12
APFD	3.1217	65.99	1.1228	2259.14	255.86
B2PLYP-FC	3.0717	63.66	1.1286	2213.65	258.83
mPW2PLYP-FC	3.0934	68.70	1.1256	2237.53	257.11
HSEVWN	2.9929	54.75	1.1332	2178.53	265.10
BrxVWN	3.0323	60.55	1.1303	2201.01	264.27
BPBE	3.0050	60.10	1.1352	2163.14	263.86
PW91PBE	3.0092	62.03	1.1342	2171.40	269.27
PBEPBE	3.0110	59.09	1.1353	2162.47	269.16
HSEPBE	3.0112	58.17	1.1347	2166.98	267.94
mPW1PBE	3.1249	71.11	1.1218	2266.82	253.57
mPW3PBE	3.1052	68.24	1.1235	2253.35	257.87

Table S9: Descriptors for the respective equilibrium geometries of CO. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, equilibrium distances (d_e) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol. (Part 2)

Method	Pop. Ω_b	Vol. Ω_b	d_e	ω_h	ΔE_{atom}
BPW91	3.0056	59.73	1.1349	2166.08	263.65
PW91PW91	3.0094	58.63	1.1338	2174.32	269.06
PBEPW91	3.0121	58.73	1.1350	2165.38	268.94
HSEPW91	3.0119	57.72	1.1344	2169.90	267.73
B3PW9	3.1043	64.86	1.1236	2252.97	255.94
mPW1PW91	3.1255	70.68	1.1214	2269.92	253.35
MP2-FC	3.0767	75.92	1.1348	2166.23	270.04
BLYP	2.9835	54.84	1.1355	2161.34	262.21
PW91LY	2.9891	56.54	1.1344	2169.46	267.57
PBELYP	2.9897	56.09	1.1356	2160.45	267.42
HSELYP	2.9913	55.63	1.1350	2164.92	266.25
B3LYP	3.0874	62.45	1.1237	2251.95	255.69
mPW1LYP	3.1014	63.45	1.1218	2266.82	251.96
HF	3.3040	74.56	1.1019	2426.46	175.70
TPSSTPSS	3.0401	66.20	1.1335	2176.55	254.38
XalphaXa	3.0548	60.50	1.1261	2233.34	268.59
BB95	2.9964	56.94	1.1354	2162.07	271.35
PW91B95	3.0012	58.73	1.1343	2170.37	276.68
PBEB95	3.0016	55.92	1.1355	2161.32	276.58
HSEB95	3.0019	55.03	1.1349	2165.77	275.37
SVWN	3.0607	59.65	1.1255	2237.59	303.93
PKZBPKZB	2.9957	62.78	1.1432	2103.75	256.61
B3P86	3.1057	64.30	1.1228	2258.76	261.65
PKZBKCIS	2.9859	62.01	1.1432	2103.71	256.40
BrxKCIS	3.0370	60.05	1.1322	2186.67	271.07
OVWN	2.9834	58.65	1.1336	2175.45	258.16
OPBE	3.0287	67.92	1.1354	2161.96	261.24
OLYP	3.0093	60.98	1.1354	2162.23	259.30
OB95	3.0188	64.59	1.1355	2161.04	268.72
CCSD(T)	3.0741	71.51	1.1294	2168.92	257.25

Table S10: Descriptors for the respective equilibrium geometries of C_2H_6. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, C−C equilibrium distances (d_e^{CC}) and C−H equilibrium distances (d_e^{CH}) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol. (Part 1)

Method	Pop. Ω_b	Vol. Ω_b	d_e^{CC}	d_e^{CH}	ω_h	ΔE_{atom}
G96LYP	1.7943	17.87	1.5362	1.0962	1015.80	89.18
BVWN	1.7944	17.99	1.5397	1.0910	1008.62	87.06
M06L	1.8043	17.38	1.5149	1.0881	1068.41	96.40
M06	1.7897	17.11	1.5154	1.0895	1067.58	96.46
M062X	1.7946	17.32	1.5230	1.0886	1049.91	97.94
M06HF	1.8126	17.94	1.5369	1.0854	1018.91	98.17
M05	1.7889	17.13	1.5184	1.0895	1060.42	94.10
M052X	1.7913	17.17	1.5239	1.0861	1048.89	97.77
M11	1.7958	17.46	1.5263	1.0923	1041.02	97.36
N12SX	1.8054	17.41	1.5153	1.0859	1068.74	97.93
MN12SX	1.8267	17.70	1.5167	1.0919	1063.79	97.41
SOGGA11X	1.8258	17.93	1.5237	1.0911	1047.39	99.18
PW91VWN	1.7933	17.86	1.5369	1.0907	1015.31	90.82
TPSSh	1.8148	17.95	1.5276	1.0919	1038.15	90.57
BMK	1.7937	17.48	1.5319	1.0905	1028.29	98.48
BhandH	1.8186	17.16	1.5031	1.0873	1098.29	105.14
BhandHLYP	1.8184	17.61	1.5172	1.0831	1064.96	89.52
HSEH1PBE	1.8136	17.63	1.5186	1.0912	1059.44	94.58
wB97XD	1.8072	17.55	1.5226	1.0899	1050.48	97.41
LC-wPBE	1.8120	17.52	1.5173	1.0899	1063.18	94.27
CAM-B3LYP	1.8078	17.53	1.5210	1.0892	1054.39	93.85
APFD	1.8111	17.72	1.5224	1.0918	1049.76	95.44
B2PLYP-FC	1.8024	17.64	1.5246	1.0886	1045.97	94.29
mPW2PLYP-FC	1.8044	17.60	1.5226	1.0874	1051.09	94.61
HSEVWN	1.7948	17.92	1.5378	1.0914	1012.95	89.67
BrxVWN	1.7897	18.40	1.5461	1.0879	993.98	86.79
BPBE	1.7996	17.81	1.5296	1.0980	1031.28	93.24
PW91PBE	1.7993	17.68	1.5269	1.0977	1037.79	97.10
PBEPBE	1.8006	17.75	1.5279	1.0988	1035.14	96.87
HSEPBE	1.8008	17.76	1.5278	1.0984	1035.55	95.94
mPW1PBE	1.8126	17.62	1.5190	1.0907	1058.63	93.87
mPW3PBE	1.8097	17.62	1.5205	1.0917	1054.72	94.78

Table S11: Descriptors for the respective equilibrium geometries of C_2H_6. Population of Ω_b in electrons, volume of Ω_b in a_o^{-3}, C−C equilibrium distances (d_e^{CC}) and C−H equilibrium distances (d_e^{CH}) in Å, harmonic frequencies (ω_h) in cm^{-1} and atomization energies (ΔE_{atom}) in kcal/mol. (Part 2)

Method	Pop. Ω_b	Vol. Ω_b	d_e^{CC}	d_e^{CH}	ω_h	ΔE_{atom}
BPW91	1.7991	17.80	1.5297	1.0973	1031.04	92.93
PW91PW91	1.7987	17.68	1.5271	1.0970	1037.56	96.79
PBEPW91	1.7998	17.74	1.5281	1.0982	1034.90	96.55
HSEPW91	1.8005	17.75	1.5279	1.0977	1035.31	95.63
B3PW9	1.8101	17.66	1.5214	1.0913	1052.72	93.28
mPW1PW91	1.8122	17.62	1.5191	1.0900	1058.63	93.55
MP2-FC	1.7951	17.47	1.5213	1.0875	1054.42	100.50
BLYP	1.7925	17.90	1.5382	1.0969	1011.02	90.47
PW91LY	1.7912	17.77	1.5355	1.0966	1017.47	94.21
PBELYP	1.7932	17.84	1.5366	1.0978	1014.72	93.95
HSELYP	1.7932	17.85	1.5364	1.0973	1015.08	93.05
B3LYP	1.8034	17.72	1.5268	1.0905	1039.79	91.71
mPW1LYP	1.8042	17.70	1.5262	1.0894	1041.47	91.11
HF	1.8369	18.10	1.5239	1.0835	1048.91	65.51
TPSSTPSS	1.8122	18.05	1.5319	1.0944	1027.17	90.57
XalphaXa	1.7981	17.19	1.5124	1.1039	1071.29	101.81
BB95	1.7979	17.72	1.5280	1.0961	1035.46	98.54
PW91B95	1.7952	17.60	1.5254	1.0958	1041.88	102.28
PBEB95	1.7983	17.67	1.5264	1.0970	1039.28	102.04
HSEB95	1.7983	17.67	1.5263	1.0965	1039.67	101.13
SVWN	1.8016	17.03	1.5062	1.0986	1087.43	117.93
PKZBPKZB	1.8088	18.15	1.5398	1.1040	1006.27	90.42
B3P86	1.8108	17.57	1.5190	1.0903	1058.62	95.98
PKZBKCIS	1.8019	18.02	1.5382	1.1032	1009.81	90.79
BrxKCIS	1.7896	18.16	1.5357	1.0943	1016.94	94.59
OVWN	1.8088	17.97	1.5303	1.0900	1031.22	88.71
OPBE	1.8161	17.82	1.5209	1.0970	1052.32	95.26
OLYP	1.8067	17.90	1.5288	1.0957	1033.67	92.15
OB95	1.8138	17.73	1.5189	1.0950	1057.58	100.81
CCSD(T)	1.7651	16.63	1.5231	1.0883	1024.52	91.51