Supporting Information for

"A first step towards Quantum Energy Potentials of Electron Pairs"

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CH_3–X ELF Basins

ELF at equilibrium

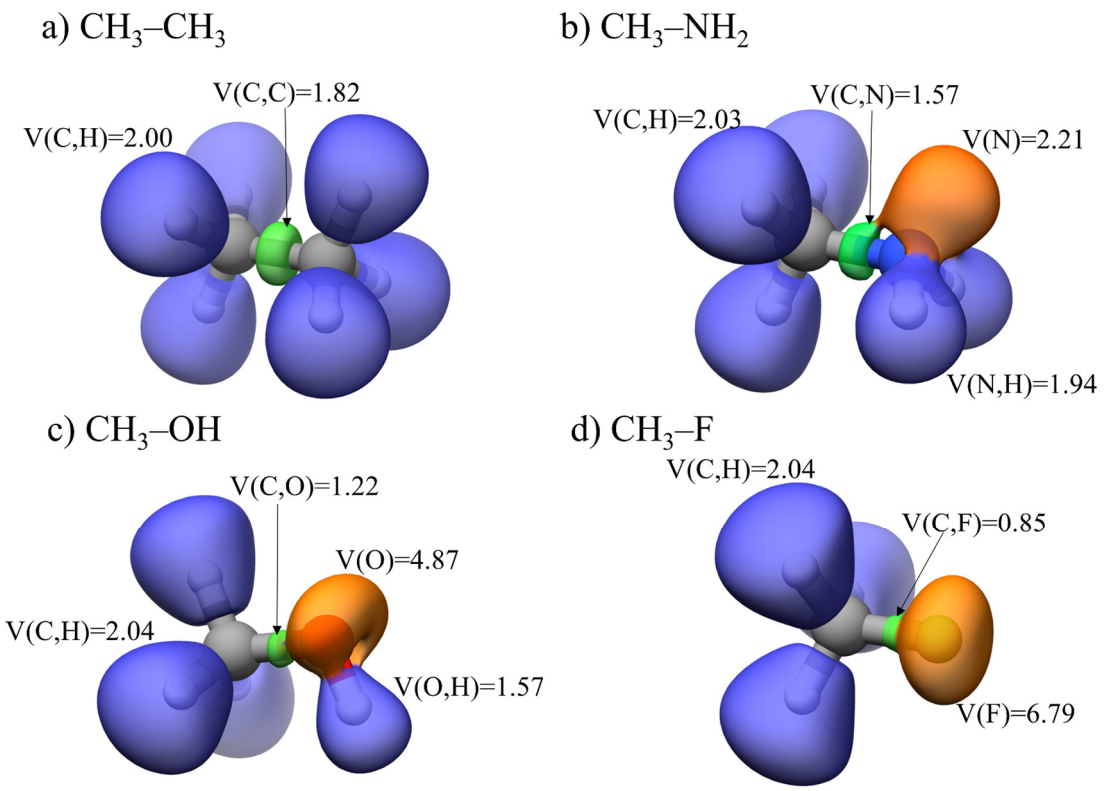

Figure S1. ELF basins (isovalue = 0.8) and populations for equilibrium geometries of a) CH_3–CH_3, b) CH_3–NH_2, c) CH_3–OH and d) CH_3–F. V(C,H) basins are shown in blue, V(C,X) in green, and V(N) in orange.

Evolution of populations and volumes

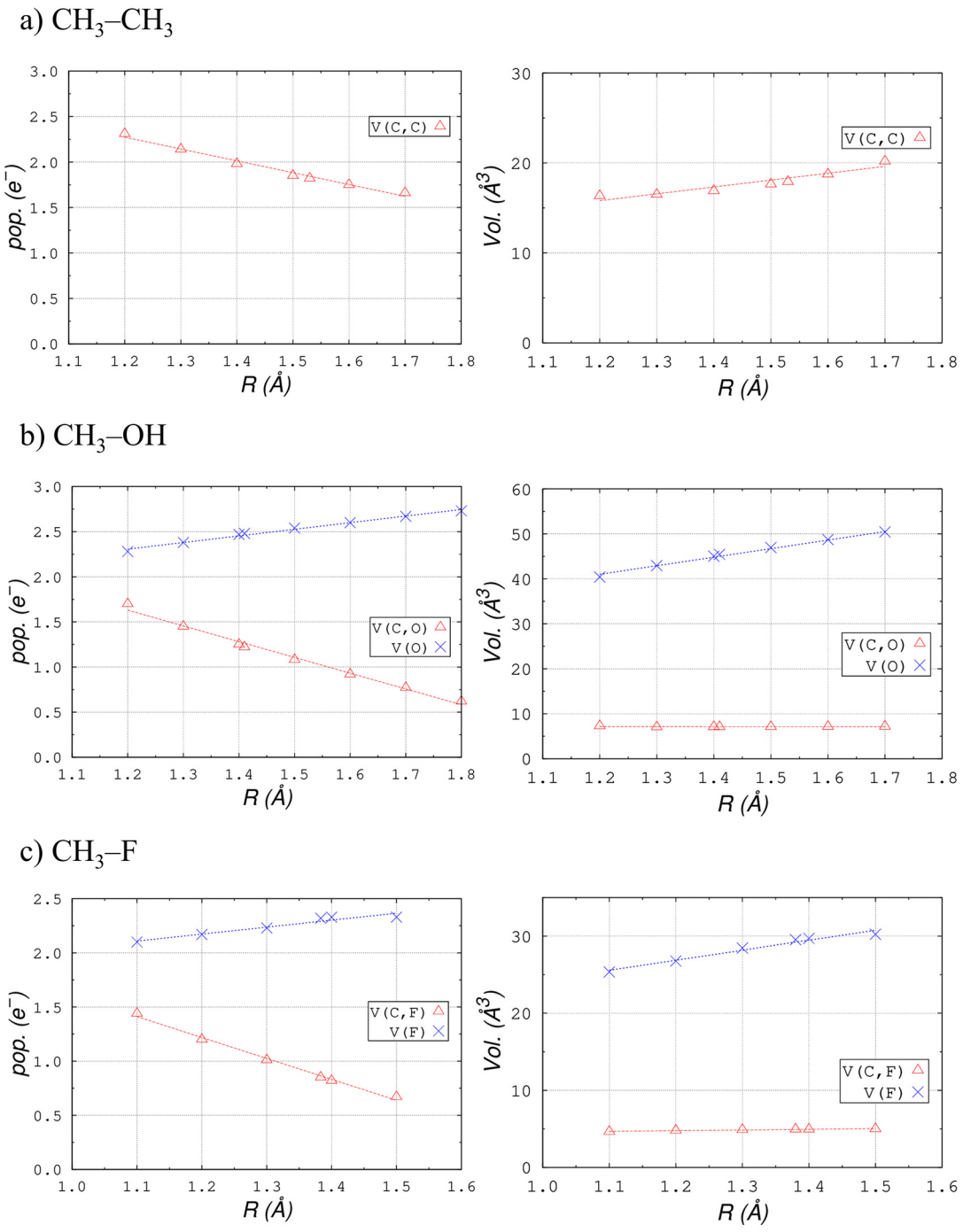

Figure S2. V(C,X) and V(X) populations and volumes for: a) CH_3–CH_3, b) CH_3–OH, and c) CH_3–F. Linear regression coefficients for populations: a) CH_3–CH_3, R^2 = 0.984 for V(C,C); b) CH_3–OH, R^2 = 0.989 for V(C,O) and 0.988 for V(O); c) CH_3–F, R^2 = 0.993 for V(C,F) and 0.934 for V(F). Linear regression coefficients for volumes: a) CH_3–CH_3, R^2 = 0.908 for V(C,C); b) CH_3–OH, R^2 = 0.993 for V(C,O) and 0.992 for V(O); c) CH_3–F, R^2 = 0.955 for V(C,F) and 0.969 for V(F).

CH_3–X R_B and R_{LP} as a function of R

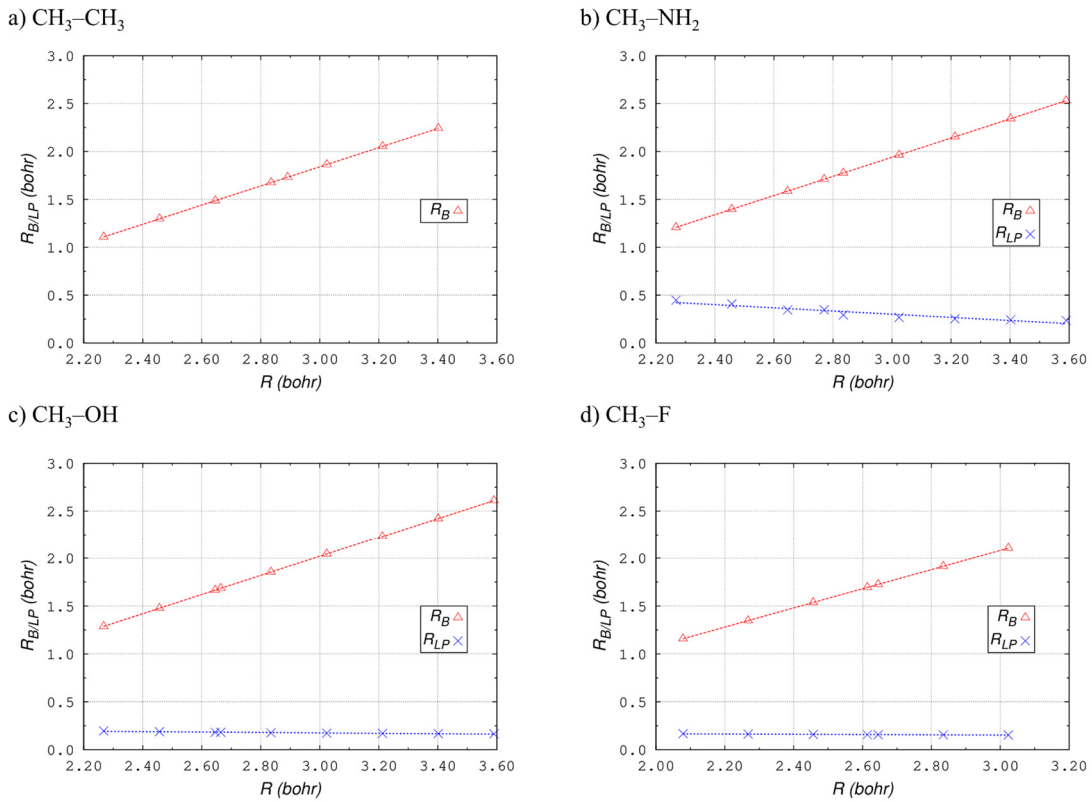

Figure S3. Bond and Lone Pair basin length as a function of the interatomic C–X distance for a) CH_3–CH_3, b) CH_3–NH_2, c) CH_3–OH, and d) CH_3–F. Linear regression coefficients for lone pairs: R^2 = 0.900 for CH_3–NH_2; 0.940 for CH_3–OH; and 0.961 for CH_3–F.

Computational details

Stability check

Kinetic energy C-N

Table S1. Kinetic energy (in a.u.) for CH_3–NH_2, as a function of the method.

R (Å)	$1/R^2$ (bohr^{-2})	HF			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	3.068	3.065	3.044	3.072
1.40	0.143	2.515	2.514	2.526	2.513
1.50	0.124	2.125	2.123	2.129	2.119
1.60	0.109	1.811	1.812	1.820	1.812
1.70	0.097	1.556	1.557	1.567	1.549
1.80	0.086	1.324	1.322	1.343	1.319
1.90	0.078	1.112	1.111	1.113	1.100
R (Å)	$1/R^2$ (bohr^{-2})	PBE			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	3.110	3.125	3.105	3.133
1.40	0.143	2.555	2.549	2.556	2.549
1.50	0.124	2.147	2.143	2.159	2.141
1.60	0.109	1.844	1.842	1.847	1.839
1.70	0.097	1.572	1.575	1.572	1.579
1.80	0.086	1.336	1.334	1.344	1.328
1.90	0.078	1.087	1.092	1.101	1.082
R (Å)	$1/R^2$ (bohr^{-2})	PBE0			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	3.086	3.107	3.087	3.124
1.40	0.143	2.535	2.535	2.541	2.534
1.50	0.124	2.136	2.135	2.139	2.133
1.60	0.109	1.827	1.825	1.837	1.821
1.70	0.097	1.569	1.568	1.569	1.562
1.80	0.086	1.323	1.329	1.328	1.329
1.90	0.078	1.090	1.091	1.093	1.088
R (Å)	$1/R^2$ (bohr^{-2})	B3LYP			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	3.089	3.127	3.108	3.129
1.40	0.143	2.540	2.540	2.548	2.538
1.50	0.124	2.138	2.137	2.148	2.137
1.60	0.109	1.830	1.828	1.845	1.823
1.70	0.097	1.570	1.566	1.576	1.565
1.80	0.086	1.342	1.330	1.341	1.333
1.90	0.078	1.091	1.097	1.101	1.098

The linear regression fittings for C-N bond kinetic energy are the following:

HF:

6-31G*(d):* $y = 21.816 \cdot x - 0.573;\ R^2 = 0.999$

6-311G*(d,p):* $y = 21.801 \cdot x - 0.573;\ R^2 = 0.999$

cc-PVDZ*:* $y = 21.542 \cdot x - 0.538;\ R^2 = 0.999$

cc-PVTZ*:* $y = 21.956 \cdot x - 0.593;\ R^2 = 0.999$

PBE:

6-31G*(d):* $y = 22.422 \cdot x - 0.623;\ R^2 = 0.999$

6-311G*(d,p):* $y = 22.482 \cdot x - 0.629;\ R^2 = 0.999$

cc-PVDZ*:* $y = 22.280 \cdot x - 0.602;\ R^2 = 0.999$

cc-PVTZ*:* $y = 22.631 \cdot x - 0.647;\ R^2 = 0.998$

PBE0:

6-31G*(d):* $y = 22.173 \cdot x - 0.607;\ R^2 = 0.999$

6-311G*(d,p):* $y = 22.322 \cdot x - 0.620;\ R^2 = 0.999$

cc-PVDZ*:* $y = 22.171 \cdot x - 0603;\ R^2 = 0.999$

cc-PVTZ*:* $y = 22.495 \cdot x - 0.640;\ R^2 = 0.998$

B3LYP:

6-31G*(d):* $y = 22.124 \cdot x - 0.596;\ R^2 = 0.999$

6-311G*(d,p):* $y = 22.472 \cdot x - 0.632;\ R^2 = 0.999$

cc-PVDZ*:* $y = 22.256 \cdot x - 0.602;\ R^2 = 0.999$

cc-PVTZ*:* $y = 22.476 \cdot x - 0.633;\ R^2 = 0.998$

Electrostatic interaction energy C-N

E_{intra} V(C-N)

Table S2. *E_{intra} V(C,N)* (in a.u.) for CH_3–NH_2, as a function of the method.

R (Å)	1/R (bohr^{-1})	HF			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	1.338	1.335	1.326	1.339
1.40	0.378	1.005	1.005	1.011	1.003
1.50	0.353	0.787	0.786	0.792	0.784
1.60	0.331	0.623	0.623	0.628	0.622
1.70	0.311	0.497	0.497	0.502	0.495
1.80	0.294	0.393	0.393	0.397	0.392
1.90	0.279	0.302	0.302	0.305	0.300
R (Å)	1/R (bohr^{-1})	PBE			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	1.372	1.386	1.371	1.391
1.40	0.378	1.032	1.030	1.036	1.029
1.50	0.353	0.805	0.804	0.810	0.802
1.60	0.331	0.639	0.638	0.643	0.636
1.70	0.311	0.506	0.506	0.509	0.505
1.80	0.294	0.396	0.395	0.399	0.393
1.90	0.279	0.294	0.294	0.296	0.292
R (Å)	1/R (bohr^{-1})	PBE0			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	1.357	1.368	1.354	1.376
1.40	0.378	1.021	1.020	1.025	1.019
1.50	0.353	0.797	0.796	0.801	0.794
1.60	0.331	0.631	0.630	0.636	0.627
1.70	0.311	0.501	0.501	0.504	0.499
1.80	0.294	0.391	0.391	0.394	0.390
1.90	0.279	0.294	0.294	0.295	0.292
R (Å)	1/R (bohr^{-1})	B3LYP			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	1.361	1.380	1.369	1.383
1.40	0.378	1.024	1.023	1.029	1.021
1.50	0.353	0.799	0.798	0.805	0.796
1.60	0.331	0.633	0.632	0.639	0.629
1.70	0.311	0.504	0.502	0.508	0.501
1.80	0.294	0.395	0.393	0.398	0.392
1.90	0.279	0.296	0.297	0.299	0.296

The linear regression fittings for intra-basin electrostatic energy in the C–N bond are the following:

HF:

6-31G*(d):* $y = 7.876 \cdot x - 1.940;\ R^2 = 0.983$

6-311G*(d,p):* $y = 7.857 \cdot x - 1.934;\ R^2 = 0.984$

cc-PVDZ*:* $y = 7.795 \cdot x - 1.911;\ R^2 = 0.986$

cc-PVTZ*:* $y = 7.885 \cdot x - 1.945;\ R^2 = 0.983$

PBE:

6-31G*(d):* $y = 8.181 \cdot x - 2.029;\ R^2 = 0.986$

6-311G*(d,p):* $y = 8.247 \cdot x - 2.050;\ R^2 = 0.983$

cc-PVDZ*:* $y = 8.159 \cdot x - 2.018;\ R^2 = 0.987$

cc-PVTZ*:* $y = 8.290 \cdot x - 2.065;\ R^2 = 0.982$

PBE0:

6-31G*(d):* $y = 8.075 \cdot x - 2.000;\ R^2 = 0.985$

6-311G*(d,p):* $y = 8.129 \cdot x - 2.018;\ R^2 = 0.983$

cc-PVDZ*:* $y = 8.049 \cdot x - 1.989;\ R^2 = 0.987$

cc-PVTZ*:* $y = 8.190 \cdot x - 2.038;\ R^2 = 0.982$

B3LYP:

6-31G*(d):* $y = 8.084 \cdot x - 2.000;\ R^2 = 0.985$

6-311G*(d,p):* $y = 8.187 \cdot x - 2.033;\ R^2 = 0.982$

cc-PVDZ*:* $y = 8.121 \cdot x - 2.008;\ R^2 = 0.985$

cc-PVTZ*:* $y = 8.208 \cdot x - 2.042;\ R^2 = 0.981$

E_{inter} C(C)-V(C,N)

Table S3. *E_{inter} C(C)-V(C,N)* (in a.u.) for CH_3–NH_2, as a function of the method.

R (Å)	1/R (bohr^{-1})	HF			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-5.340	-5.338	-5.333	-5.339
1.40	0.378	-4.532	-4.533	-4.551	-4.527
1.50	0.353	-3.918	-3.918	-3.936	-3.911
1.60	0.331	-3.416	-3.418	-3.439	-3.412
1.70	0.311	-3.003	-3.005	-3.027	-2.995
1.80	0.294	-2.644	-2.643	-2.666	-2.635
1.90	0.279	-2.310	-2.307	-2.330	-2.297
R (Å)	1/R (bohr^{-1})	PBE			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-5.412	-5.428	-5.333	-5.339
1.40	0.378	-4.598	-4.594	-4.551	-4.527
1.50	0.353	-3.976	-3.972	-3.936	-3.911
1.60	0.331	-3.475	-3.471	-3.439	-3.412
1.70	0.311	-3.051	-3.047	-3.027	-2.995
1.80	0.294	-2.676	-2.671	-2.666	-2.635
1.90	0.279	-2.311	-2.308	-2.330	-2.297
R (Å)	1/R (bohr^{-1})	PBE0			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-5.382	-5.395	-5.386	-5.401
1.40	0.378	-4.570	-4.567	-4.585	-4.563
1.50	0.353	-3.951	-3.948	-3.968	-3.942
1.60	0.331	-3.450	-3.445	-3.468	-3.438
1.70	0.311	-3.031	-3.027	-3.046	-3.019
1.80	0.294	-2.655	-2.653	-2.672	-2.645
1.90	0.279	-2.304	-2.301	-2.317	-2.289
R (Å)	1/R (bohr^{-1})	B3LYP			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-7.809	-7.895	-7.841	-7.908
1.40	0.378	-6.527	-6.523	-6.542	-6.520
1.50	0.353	-5.572	-5.570	-5.591	-5.569
1.60	0.331	-4.800	-4.796	-4.824	-4.785
1.70	0.311	-4.131	-4.124	-4.141	-4.122
1.80	0.294	-3.512	-3.496	-3.513	-3.500
1.90	0.279	-2.852	-2.867	-2.860	-2.866

Fittings for E_{inter} *C(C)-V(C,N)*:

HF:

6-31G*(d):* $y = -23.288 \cdot x + 4.231;\ R^2 = 0.997$

6-311G*(d,p):* $y = -23.296 \cdot x + 4.234;\ R^2 = 0.997$

cc-PVDZ*:* $y = -23.120 \cdot x + 4.158;\ R^2 = 0.998$

cc-PVTZ*:* $y = -23.365 \cdot x + 4.264;\ R^2 = 0.997$

PBE:

6-31G*(d):* $y = -23.749 \cdot x + 4.338;\ R^2 = 0.998$

6-311G*(d,p):* $y = -23.867 \cdot x + 4.379;\ R^2 = 0.997$

cc-PVDZ*:* $y = -23.120 \cdot x + 4.158;\ R^2 = 0.998$

cc-PVTZ*:* $y = -23.365 \cdot x + 4.264;\ R^2 = 0.997$

PBE0:

6-31G*(d):* $y = -23.608 \cdot x + 4.313;\ R^2 = 0.998$

6-311G*(d,p):* $y = -23.699 \cdot x + 4.345;\ R^2 = 0.997$

cc-PVDZ*:* $y = -23.557 \cdot x + 4.282;\ R^2 = 0.998$

cc-PVTZ*:* $y = -23.815 \cdot x + 4.389;\ R^2 = 0.997$

B3LYP:

6-31G*(d):* $y = -23.623 \cdot x + 4.313;\ R^2 = 0.998$

6-311G*(d,p):* $y = -23.763 \cdot x + 4.361;\ R^2 = 0.997$

cc-PVDZ*:* $y = -23.616 \cdot x + 4.291;\ R^2 = 0.997$

cc-PVTZ*:* $y = -23.827 \cdot x + 4.390;\ R^2 = 0.997$

E_{inter} C(N)-V(C,N)

Table S4. *E_{inter} C(N)-V(C,N)* (in a.u.) for CH_3–NH_2, as a function of the method.

R (Å)	1/R (bohr^{-1})	HF			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-7.740	-7.728	-7.681	-7.745
1.40	0.378	-6.459	-6.455	-6.477	-6.451
1.50	0.353	-5.532	-5.527	-5.545	-5.518
1.60	0.331	-4.764	-4.763	-4.775	-4.760
1.70	0.311	-4.106	-4.109	-4.123	-4.096
1.80	0.294	-3.504	-3.503	-3.524	-3.501
1.90	0.279	-2.917	-2.921	-2.921	-2.911
R (Å)	1/R (bohr^{-1})	PBE			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-7.849	-7.901	-7.833	-7.925
1.40	0.378	-6.557	-6.547	-6.563	-6.547
1.50	0.353	-5.592	-5.588	-5.612	-5.585
1.60	0.331	-4.821	-4.818	-4.831	-4.813
1.70	0.311	-4.131	-4.135	-4.138	-4.134
1.80	0.294	-3.497	-3.496	-3.511	-3.486
1.90	0.279	-2.825	-2.838	-2.837	-2.828
R (Å)	1/R (bohr^{-1})	PBE0			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-7.796	-7.842	-7.778	-7.886
1.40	0.378	-6.511	-6.511	-6.522	-6.509
1.50	0.353	-5.561	-5.559	-5.573	-5.556
1.60	0.331	-4.785	-4.781	-4.804	-4.773
1.70	0.311	-4.114	-4.114	-4.121	-4.105
1.80	0.294	-3.474	-3.482	-3.486	-3.481
1.90	0.279	-2.835	-2.846	-2.837	-2.836
R (Å)	1/R (bohr^{-1})	B3LYP			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.407	-7.809	-7.895	-7.841	-7.908
1.40	0.378	-6.527	-6.523	-6.542	-6.520
1.50	0.353	-5.572	-5.570	-5.591	-5.569
1.60	0.331	-4.800	-4.796	-4.824	-4.785
1.70	0.311	-4.131	-4.124	-4.141	-4.122
1.80	0.294	-3.512	-3.496	-3.513	-3.500
1.90	0.279	-2.852	-2.867	-2.860	-2.866

Fittings for E_{inter} *C(N)-V(C,N)*:

HF:

6-31G*(d):* $y = -36.780 \cdot x + 7.357;\ R^2 = 0.998$

6-311G*(d,p):* $y = -36.670 \cdot x + 7.322;\ R^2 = 0.998$

cc-PVDZ*:* $y = -36.406 \cdot x + 7.228;\ R^2 = 0.999$

cc-PVTZ*:* $y = -36.816 \cdot x + 7.375;\ R^2 = 0.998$

PBE:

6-31G*(d):* $y = -38.143 \cdot x + 7.779;\ R^2 = 0.998$

6-311G*(d,p):* $y = -38.338 \cdot x + 7.837;\ R^2 = 0.998$

cc-PVDZ*:* $y = -38.000 \cdot x + 7.120;\ R^2 = 0.999$

cc-PVTZ*:* $y = -38.544 \cdot x + 7.908;\ R^2 = 0.997$

PBE0:

6-31G*(d):* $y = -37.736 \cdot x + 7.670;\ R^2 = 0.998$

6-311G*(d,p):* $y = -37.920 \cdot x + 7.724;\ R^2 = 0.998$

cc-PVDZ*:* $y = -37.617 \cdot x + 7.624;\ R^2 = 0.999$

cc-PVTZ*:* $y = -38.218 \cdot x + 7.822;\ R^2 = 0.997$

B3LYP:

6-31G*(d):* $y = -37637 \cdot x + 7.619;\ R^2 = 0.998$

6-311G*(d,p):* $y = -38.094 \cdot x + 7.763;\ R^2 = 0.997$

cc-PVDZ*:* $y = -37.817 \cdot x + 7.664;\ R^2 = 0.998$

cc-PVTZ*:* $y = -38.160 \cdot x + 7.785;\ R^2 = 0.997$

Exchange–correlation energy

$E_{X\text{-}C}$ *C(C)-V(C,N)*

Table S5. $E_{X\text{-}C}$ *C(C)-V(C,N)* (in a.u.) for CH_3–NH_2, as a function of the method.

R (Å)	$1/R^2$ (bohr^{-2})	HF			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.062	-0.062	-0.062	-0.062
1.40	0.143	-0.051	-0.051	-0.052	-0.051
1.50	0.124	-0.043	-0.043	-0.043	-0.043
1.60	0.109	-0.036	-0.036	-0.037	-0.036
1.70	0.097	-0.031	-0.031	-0.032	-0.031
1.80	0.086	-0.027	-0.027	-0.027	-0.027
1.90	0.078	-0.023	-0.023	-0.024	-0.023
R (Å)	$1/R^2$ (bohr^{-2})	PBE			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.063	-0.063	-0.063	-0.063
1.40	0.143	-0.052	-0.052	-0.052	-0.052
1.50	0.124	-0.044	-0.044	-0.044	-0.043
1.60	0.109	-0.037	-0.037	-0.038	-0.037
1.70	0.097	-0.032	-0.032	-0.033	-0.032
1.80	0.086	-0.028	-0.028	-0.028	-0.028
1.90	0.078	-0.024	-0.024	-0.024	-0.023
R (Å)	$1/R^2$ (bohr^{-2})	PBE0			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.062	-0.062	-0.063	-0.062
1.40	0.143	-0.052	-0.052	-0.052	-0.051
1.50	0.124	-0.043	-0.043	-0.044	-0.043
1.60	0.109	-0.037	-0.037	-0.037	-0.037
1.70	0.097	-0.032	-0.032	-0.032	-0.032
1.80	0.086	-0.028	-0.028	-0.028	-0.027
1.90	0.078	-0.024	-0.024	-0.024	-0.023
R (Å)	$1/R^2$ (bohr^{-2})	B3LYP			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.062	-0.062	-0.063	-0.062
1.40	0.143	-0.052	-0.052	-0.052	-0.051
1.50	0.124	-0.043	-0.043	-0.044	-0.043
1.60	0.109	-0.037	-0.037	-0.037	-0.037
1.70	0.097	-0.032	-0.032	-0.032	-0.031
1.80	0.086	-0.027	-0.027	-0.028	-0.027
1.90	0.078	-0.023	-0.023	-0.024	-0.023

Fittings for Exchange–Correlation C(C)-V(C,N):

HF:

6-31G*(d):* $y = -0.436 \cdot x + 0.011;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.439 \cdot x + 0.011;\ R^2 = 0.999$

cc-PVDZ*:* $y = -0.434 \cdot x + 0.010;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.439 \cdot x + 0.012;\ R^2 = 0.999$

PBE:

6-31G*(d):* $y = -0.4377 \cdot x + 0.010;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.439 \cdot x + 0.011;\ R^2 = 0.999$

cc-PVDZ*:* $y = -0.437 \cdot x + 0.010;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.439 \cdot x + 0.011;\ R^2 = 0.999$

PBE0:

6-31G*(d):* $y = -0.436 \cdot x + 0.010;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.437 \cdot x + 0.011;\ R^2 = 0.999$

cc-PVDZ*:* $y = -0.439 \cdot x + 0.011;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.436 \cdot x + 0.011;\ R^2 = 0.999$

B3LYP:

6-31G*(d):* $y = -0.439 \cdot x + 0.011;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.438 \cdot x + 0.061;\ R^2 = 0.999$

cc-PVDZ*:* $y = -0.437 \cdot x + 0.060;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.439 \cdot x + 0.061;\ R^2 = 0.999$

$E_{X\text{-}C}$ C(N)-V(C,N)

Table S6. *$E_{X\text{-}C}$ C(N)-V(C,N)* (in a.u.) for CH_3–NH_2, as a function of the method.

R (Å)	$1/R^2$ (bohr^{-2})	HF			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.086	-0.086	-0.085	-0.086
1.40	0.143	-0.067	-0.067	-0.068	-0.067
1.50	0.124	-0.055	-0.055	-0.055	-0.055
1.60	0.109	-0.045	-0.045	-0.045	-0.045
1.70	0.097	-0.037	-0.037	-0.037	-0.036
1.80	0.086	-0.029	-0.029	-0.030	-0.029
1.90	0.078	-0.022	-0.022	-0.022	-0.022
R (Å)	$1/R^2$ (bohr^{-2})	PBE			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.087	-0.088	-0.087	-0.088
1.40	0.143	-0.069	-0.069	-0.069	-0.069
1.50	0.124	-0.055	-0.055	-0.056	-0.055
1.60	0.109	-0.046	-0.046	-0.046	-0.046
1.70	0.097	-0.037	-0.037	-0.036	-0.037
1.80	0.086	-0.029	-0.029	-0.029	-0.029
1.90	0.078	-0.021	-0.022	-0.022	-0.021
R (Å)	$1/R^2$ (bohr^{-2})	PBE0			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.086	-0.087	-0.086	-0.088
1.40	0.143	-0.068	-0.068	-0.068	-0.068
1.50	0.124	-0.055	-0.055	-0.055	-0.055
1.60	0.109	-0.045	-0.045	-0.046	-0.045
1.70	0.097	-0.037	-0.037	-0.037	-0.037
1.80	0.086	-0.029	-0.029	-0.029	-0.029
1.90	0.078	-0.021	-0.021	-0.021	-0.021
R (Å)	$1/R^2$ (bohr^{-2})	B3LYP			
		6-31G*(d)*	6-311G*(d,p)*	cc-PVDZ	cc-PVTZ
1.30	0.166	-0.086	-0.088	-0.087	-0.088
1.40	0.143	-0.068	-0.068	-0.069	-0.068
1.50	0.124	-0.055	-0.055	-0.055	-0.055
1.60	0.109	-0.045	-0.045	-0.046	-0.045
1.70	0.097	-0.037	-0.037	-0.037	-0.037
1.80	0.086	-0.030	-0.029	-0.029	-0.030
1.90	0.078	-0.021	-0.022	-0.022	-0.022

Fittings for Exchange–Correlation C(N)-V(C,N):

HF:

6-31G*(d):* $y = -0.706 \cdot x + 0.032;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.705 \cdot x + 0.032;\ R^2 = 0.999$

cc-PVDZ*:* $y = -0.695 \cdot x + 0.031;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.715 \cdot x + 0.033;\ R^2 = 0.999$

PBE:

6-31G*(d):* $y = -0.734 \cdot x + 0.035;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.731 \cdot x + 0.035;\ R^2 = 0.998$

cc-PVDZ*:* $y = -0.728 \cdot x + 0.034;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.738 \cdot x + 0.035;\ R^2 = 0.998$

PBE0:

6-31G*(d):* $y = -0.720 \cdot x + 0.034;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.729 \cdot x + 0.035;\ R^2 = 0.998$

cc-PVDZ*:* $y = -0.723 \cdot x + 0.034;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.734 \cdot x + 0.035;\ R^2 = 0.998$

B3LYP:

6-31G*(d):* $y = -0.714 \cdot x + 0.033;\ R^2 = 0.999$

6-311G*(d,p):* $y = -0.734 \cdot x + 0.035;\ R^2 = 0.998$

cc-PVDZ*:* $y = -0.726 \cdot x + 0.034;\ R^2 = 0.999$

cc-PVTZ*:* $y = -0.731 \cdot x + 0.035;\ R^2 = 0.998$

Integration errors

ELF-IQA integration errors were calculated as the difference between the reference DFT energy and the ELF-IQA energy. Notice that in all molecules, relative errors were lower than 1% but for Li_2, which presented a relative error of about 4.2%.

Table S7. DFT energy (computed at the B3LYP/6-31G(*d*) level of theory), ELF-IQA energy computed using B3LYP/6-31G(*d*) wavefunctions, integration error with respect to DFT calculations and relative integration error for the set of molecules considered in this work.

CH_3–CH_3				
R (Å)	E DFT (a.u.)	E ELF-IQA (a.u.)	ΔE (a.u.)	ΔE (%)
1.20	-79.7309	-79.1050	0.63	-0.78
1.30	-79.7910	-79.1681	0.62	-0.78
1.40	-79.8200	-79.2057	0.61	-0.77
1.50	-79.8299	-79.2150	0.61	-0.77
1.60	-79.8284	-79.2051	0.62	-0.78
1.70	-79.8200	-79.1952	0.62	-0.78
1.80	-79.8080	-79.1819	0.63	-0.78
1.53	-79.8304	-79.2060	0.62	-0.78
CH_3–NH_2				
R (Å)	E DFT (a.u.)	E ELF-IQA (a.u.)	ΔE (a.u.)	ΔE (%)
1.30	-95.8337	-95.1726	0.66	-0.69
1.40	-95.8507	-95.1947	0.66	-0.68
1.50	-95.8526	-95.1844	0.67	-0.70
1.60	-95.8460	-95.1882	0.66	-0.69
1.70	-95.8348	-95.1661	0.67	-0.70
1.80	-95.8214	-95.1501	0.67	-0.70
1.90	-95.8072	-95.1484	0.66	-0.69
1.47	-95.8497	-95.1939	0.66	-0.68
CH_3–OH				
R (Å)	E DFT (a.u.)	E ELF-IQA (a.u.)	ΔE (a.u.)	ΔE (%)
1.20	-115.6712	-114.9549	0.72	-0.62
1.30	-115.7043	-115.0152	0.69	-0.60
1.40	-115.7142	-115.0347	0.68	-0.59
1.50	-115.7112	-115.0398	0.67	-0.58
1.60	-115.7013	-115.0416	0.66	-0.57
1.70	-115.6877	-115.0305	0.66	-0.57
1.80	-115.6727	-115.0368	0.64	-0.55
1.90	-115.6573	-114.9960	0.66	-0.57
1.41	-115.7144	-115.0451	0.67	-0.58

CH_3–F				
R (Å)	E DFT (a.u.)	E ELF-IQA (a.u.)	ΔE (a.u.)	ΔE (%)
1.10	-139.6398	-138.9749	0.66	-0.48
1.20	-139.7030	-139.0135	0.69	-0.49
1.30	-139.7288	-139.0521	0.68	-0.48
1.40	-139.7337	-139.0445	0.69	-0.49
1.50	-139.7272	-139.0372	0.69	-0.49
1.60	-139.7146	-139.0368	0.68	-0.49
1.70	-139.6991	-138.9389	0.76	-0.54
1.38	-139.7339	-139.0410	0.69	-0.50

Evolution of the energetic terms and linear fittings

Electrostatic interaction energy

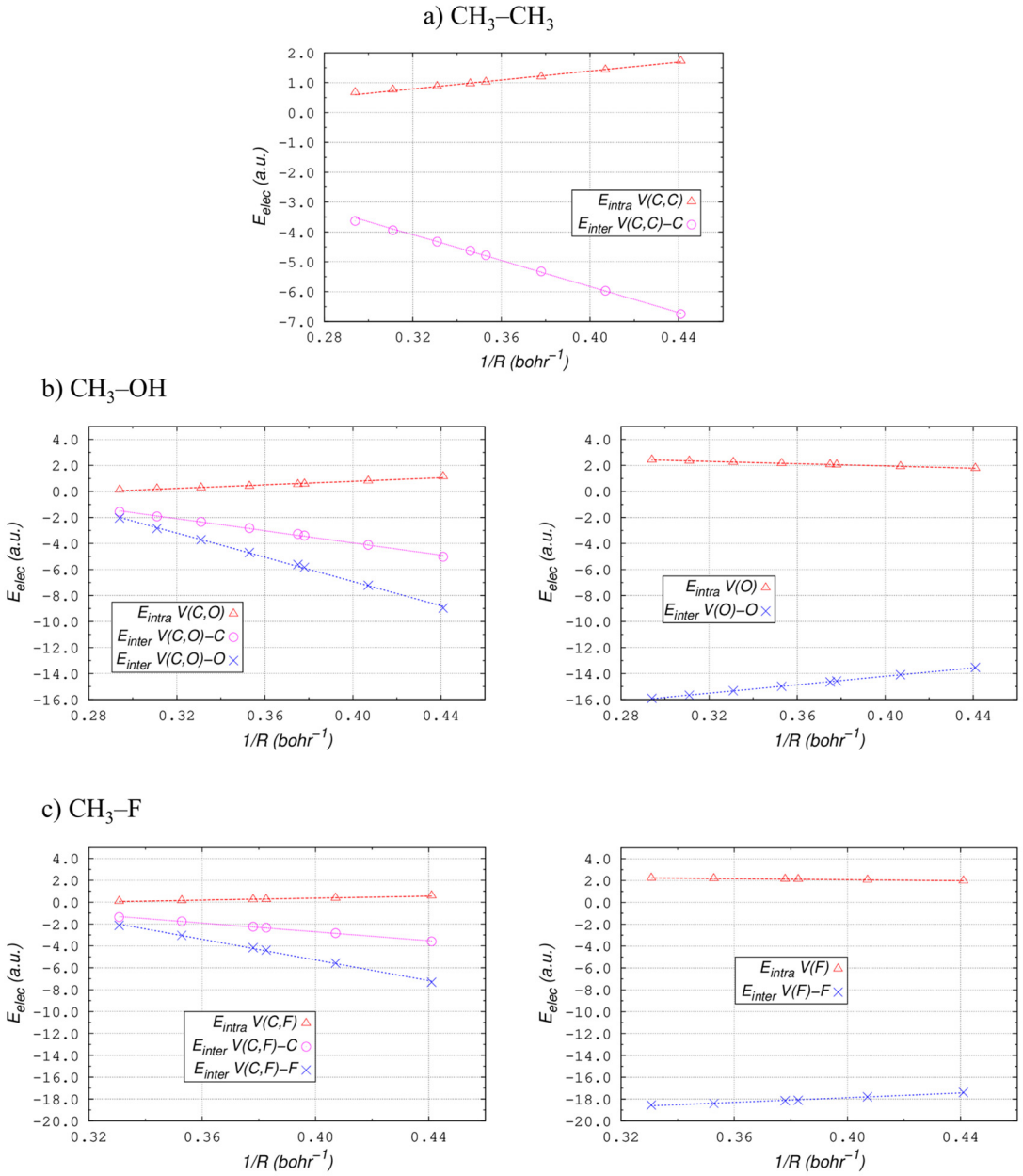

Figure S4. ELF-IQA computed classical electrostatic interaction energy (*intra* and *inter*) against *1/R* for a) CH_3–CH_3, b) CH_3–OH, and c) CH_3–F.

The linear regression fittings for CH_3–X set of molecules are the following:

CH_3–CH_3:

E_{intra} V(C,C): $y = 7.459 \cdot x - 1.595;\ R^2 = 0.995$

E_{inter} V(C,C)-C: $y = -21.717 \cdot x + 2.860;\ R^2 = 0.999$

CH_3–NH_2:

E_{intra} V(C,N): $y = 7.950 \cdot x - 1.966;\ R^2 = 0.978$

E_{inter} V(C,N)-C: $y = -23.366 \cdot x + 4.246;\ R^2 = 0.995$

E_{inter} V(C,N)-N: $y = -37.311 \cdot x + 7.535;\ R^2 = 0.996$

E_{intra} V(N): $y = -5.736 \cdot x\ +\ 3.509;\ R^2 = 0.989$

E_{inter} V(N)-N: $y = 20.609 \cdot x - 16.949;\ R^2 = 0.994$

CH_3–OH:

E_{intra} V(C,O): $y = 6.827 \cdot x - 1.951;\ R^2 = 0.972$

E_{inter} V(C,O)-C: $y = -23.329 \cdot x + 5.375;\ R^2 = 0.996$

E_{inter} V(C,O)-O: $y = -46.533 \cdot x + 11.693;\ R^2 = 0.999$

E_{intra} V(O): $y = -4.330 \cdot x\ +\ 3.690;\ R^2 = 0.999$

E_{inter} V(O)-O: $y = 16.219 \cdot x - 20.700;\ R^2 = 1.000$

CH_3–F:

E_{intra} V(C,F): $y = 4.498 \cdot x - 1.428;\ R^2 = 0.975$

E_{inter} V(C,F)-C: $y = -20.205 \cdot x + 5.369;\ R^2 = 0.997$

E_{inter} V(C,F)-F: $y = -47.220 \cdot x + 13.608;\ R^2 = 0.998$

E_{intra} V(F): $y = -2.382 \cdot x\ +\ 3.029;\ R^2 = 0.994$

E_{inter} V(F)-F: $y = 10.664 \cdot x - 22.138;\ R^2 = 0.988$

CH_3–X Interbasin Electrostatic interaction energy as a function of $q_1 \cdot q_2/R$

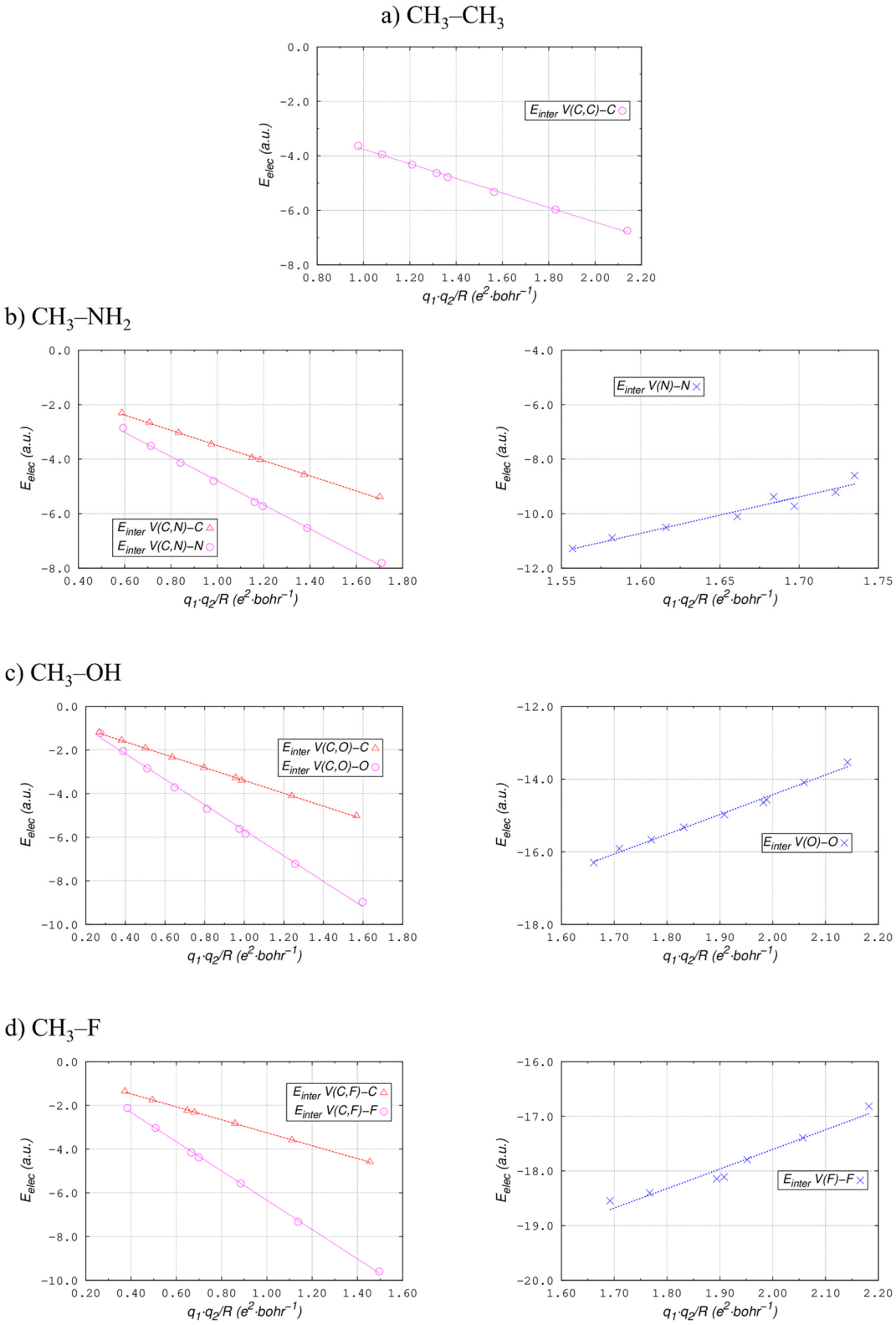

Figure S5. ELF-IQA computed classical electrostatic interaction energy (*intra* and *inter*) against $q_1 \cdot q_2/R$ for a) CH_3–CH_3, b) CH_3–NH_2, c) CH_3–OH, and d) CH_3–F.

The linear regression fittings for CH_3–X set of molecules are the following:

CH_3–CH_3:

E_{inter} *V(C,C)-C:* $y = -2.672 \cdot x - 1.085;\ R^2 = 0.998$

CH_3–NH_2:

E_{inter} *V(C,N)-C:* $y = -2.785 \cdot x - 0.712;\ R^2 = 0.999$

E_{inter} *V(C,N)-N:* $y = -4.422 \cdot x - 0.369;\ R^2 = 0.997$

E_{inter} *V(N)-N:* $y = 13.387 \cdot x - 32.141;\ R^2 = 0.956$

CH_3–OH:

E_{inter} *V(C,O)-C:* $y = -2.953 \cdot x - 0.441;\ R^2 = 1.000$

E_{inter} *V(C,O)-O:* $y = -5.851 \cdot x + 0.169;\ R^2 = 0.997$

E_{inter} *V(O)-O:* $y = 5.441 \cdot x - 25.311;\ R^2 = 0.992$

CH_3–F:

E_{inter} *V(C,F)-C:* $y = -2.960 \cdot x - 9.292;\ R^2 = 1.000$

E_{inter} *V(C,F)-F:* $y = -6.700 \cdot x + 0.358;\ R^2 = 0.999$

E_{inter} *V(F)-F:* $y = 3.581 \cdot x - 24.768;\ R^2 = 0.954$

Kinetic energy

Demonstration

Assuming a homogeneous electron gas kinetic energy density (Thomas-Fermi gas) within the basin, the kinetic energy would be given by:

$$T = C_F \int \rho^{5/3} dV = 4\pi C_F \int \left(\frac{q}{r^3}\right)^{5/3} r^2 dr = 4\pi C_F q^{5/3} \int \frac{1}{r^3} dr = \frac{-4\pi C_F q^{5/3}}{3} \frac{1}{r^2}$$

Where C_F is the Fermi Constant.

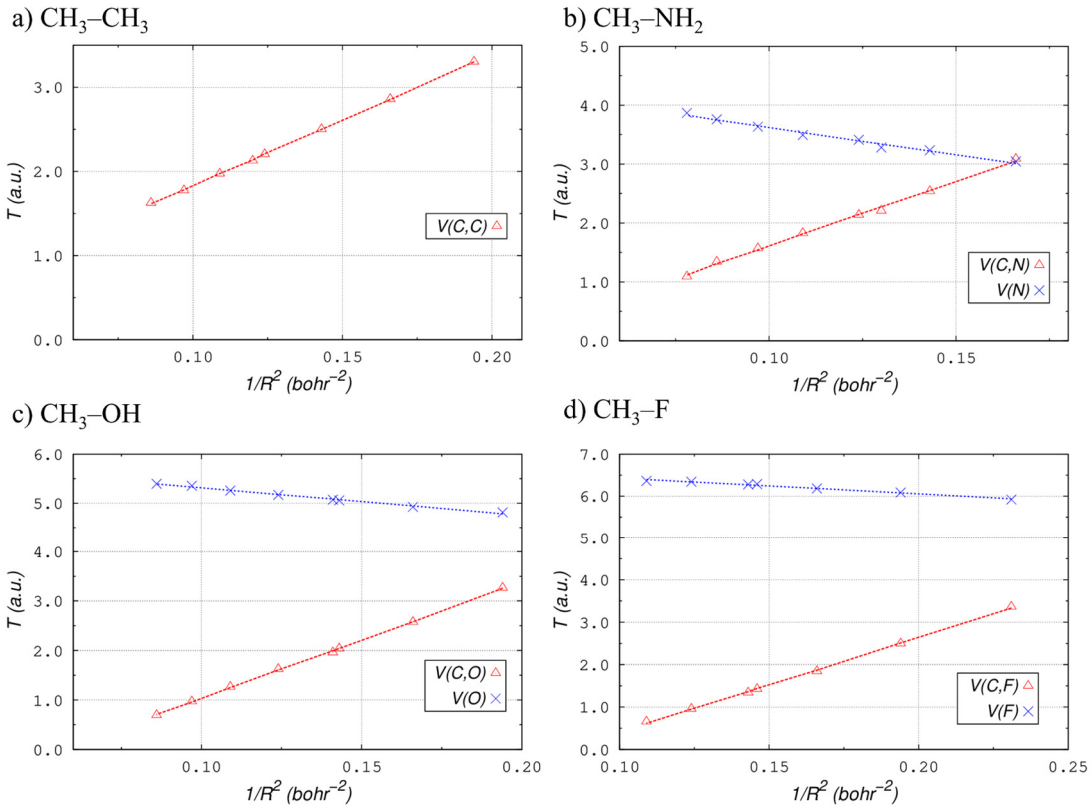

Figure S6. ELF-IQA computed bond kinetic energy against *1/R²* for V(C,X) and V(X) basins for a) CH_3–CH_3, b) CH_3–NH_2, c) CH_3–OH, and d) CH_3–F.

The linear regression fittings for CH_3-X set of molecules are the following:

CH_3–CH_3:

V(C,C): $y = 15.635 \cdot x + 0.264;\ R^2 = 1.000$

CH_3–NH_2:

V(C,N): $y = 21.946 \cdot x - 0.5854;\ R^2 = 0.997$

V(N): $y = -9.295 \cdot x + 4.551;\ R^2 = 0.984$

CH_3–OH:

V(C,O): $y = 23.582 \cdot x - 1.329;\ R^2 = 1.000$

V(O): $y = -5.629 \cdot x + 5.877;\ R^2 = 0.992$

CH_3–F:

V(C,F): $y = 22.259 \cdot x - 1.819;\ R^2 = 0.999$

V(F): $y = -3.754 \cdot x + 6.808;\ R^2 = 0.982$

Exchange-correlation

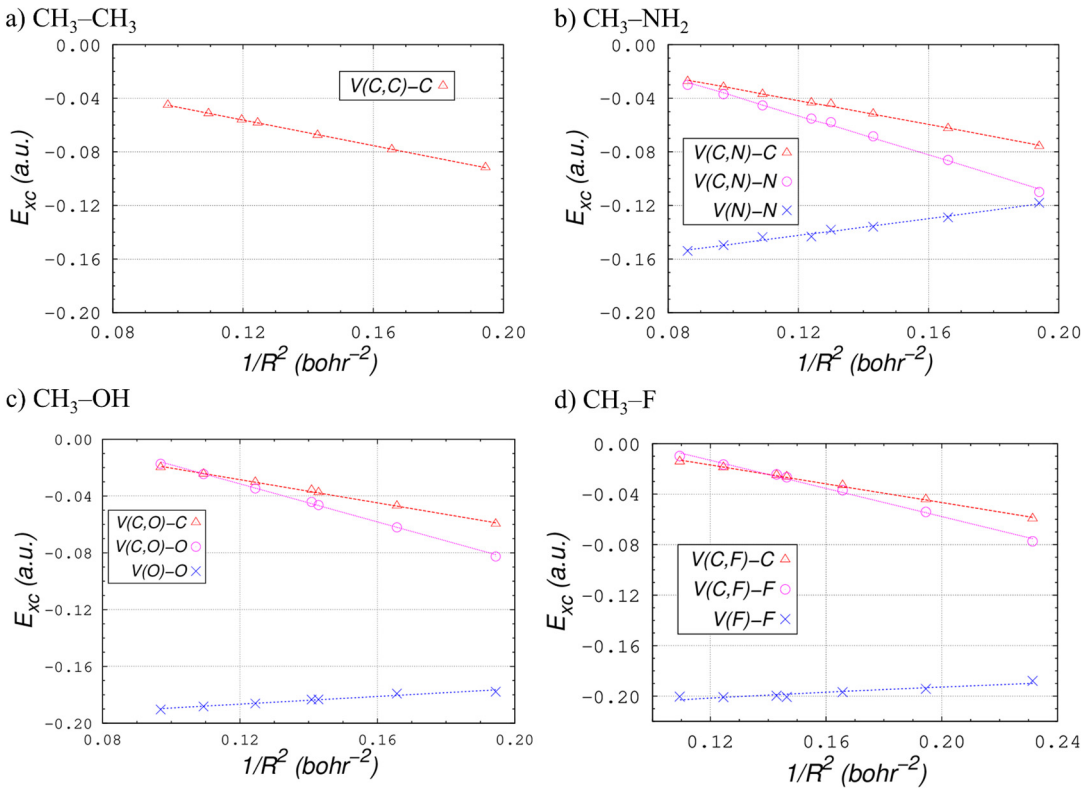

Figure S7. ELF-IQA computed exchange-correlation interaction energy between V(C,X) and V(X) basins and C and X atoms against *1/R* for a) CH_3–CH_3, b) CH_3–NH_2, c) CH_3–OH, and d) CH_3–F.

The linear regression fittings for CH_3-X set of molecules are the following:

CH_3–CH_3:

V(C,C)-C: $y = -0.360 \cdot x + 0.068;\ R^2 = 0.998$

CH_3–NH_2:

V(C,N)-C: $y = -0.329 \cdot x + 0.072;\ R^2 = 0.989$

V(C,N)-N: $y = -0.538 \cdot x + 0.132;\ R^2 = 0.986$

V(N)-N: $y = 0233 \cdot x - 0.223;\ R^2 = 0.980$

CH_3–OH:

V(C,O)-C: $y = -0.305 \cdot x + 0.077;\ R^2 = 0.989$

V(C,O)-O: $y = -0.502 \cdot x + 0.142;\ R^2 = 0.991$

V(O)-O: $y = 0.102 \cdot x - 0.222;\ R^2 = 0.980$

CH_3–F:

V(C,F)-C: $y = -0.301 \cdot x + 0.088;\ R^2 = 0.988$

V(C,F)-F: $y = -0.452 \cdot x + 0.144;\ R^2 = 0.983$

V(F)-F: $y = 0.087 \cdot x - 0.232;\ R^2 = 0.935$

Core Energies

Table S8. Total (kinetic, electrostatic and exchange-correlation) energies (in a.u.) for C and N cores in CH_3–NH_2.

R (Å)	Core C	Core N
1.2	37.322	51.318
1.3	37.284	51.293
1.4	37.265	51.288
1.5	37.256	51.297
1.6	37.254	51.317
1.7	37.256	51.334
1.8	37.259	51.354
1.9	37.261	51.368

BH_3–NH_3, BeH_2–NH_3, CH_3–Li and Li_2

Kinetic and exchange-correlation energy

Table S9. Kinetic and Exchange-Correlation energy (in a.u.) for BH_3–NH_3, BeH_2–NH_3, CH_3–Li and Li_2.

R (Å)	$1/R^2$ (bohr^{-2})	BH_3–NH_3		
		T V(B,N)	$E_{X\text{-}C}$ *V(B,N)-C(B)*	$E_{X\text{-}C}$ *V(B,N)-C(N)*
1.40	0.143	3.231	-0.038	-0.118
1.50	0.124	3.007	-0.029	-0.112
1.60	0.109	2.871	-0.021	-0.109
1.70	0.097	2.794	-0.016	-0.109
1.80	0.086	2.752	-0.011	-0.011
1.67	0.101	2.818	-0.017	-0.109
R (Å)	$1/R^2$ (bohr^{-2})	BeH_2–NH_3		
		T V(Be,N)	$E_{X\text{-}C}$ *V(Be,N)-C(Be)*	$E_{X\text{-}C}$ *V(Be,N)-C(N)*
1.50	0.124	3.169	-0.027	-0.125
1.60	0.109	3.053	-0.021	-0.122
1.70	0.097	2.987	-0.016	-0.120
1.80	0.086	2.927	-0.012	-0.118
1.90	0.078	2.866	-0.009	-0.117
1.79	0.087	3.010	-0.017	-0.122
R (Å)	$1/R^2$ (bohr^{-2})	CH_3–Li		
		T V(C,Li)	$E_{X\text{-}C}$ *V(C,Li)-C(C)*	$E_{X\text{-}C}$ *V(C,Li)-C(Li)*
1.70	0.097	1.997	-0.086	-0.043
1.80	0.086	1.853	-0.081	-0.037
1.90	0.078	1.726	-0.077	-0.031
2.00	0.070	1.616	-0.072	-0.027
2.10	0.063	1.508	-0.067	-0.023
2.20	0.058	1.415	-0.063	-0.019
2.30	0.053	1.330	-0.060	-0.016
1.98	0.071	1.632	-0.073	-0.028
R (Å)	$1/R^2$ (bohr^{-2})	Li_2		
		T V(Li,Li)	$E_{X\text{-}C}$ *V(Li,Li)-C(Li)*	
2.40	0.0486	0.000698	-0.0000790	
2.50	0.0448	0.000636	-0.0000730	
2.60	0.0414	0.000583	-0.0000680	
2.70	0.0384	0.000515	-0.0000610	
2.80	0.0357	0.000424	-0.0000510	
2.90	0.0333	0.000413	-0.0000510	
3.00	0.0311	0.000395	-0.0000490	
3.10	0.0291	0.000318	-0.0000410	
2.72	0.0378	0.000509	-0.0000600	

The linear regression fittings are the following:

BH_3–NH_3:

T V(B,N): $y = 8.596 \cdot x + 1.966;\ R^2 = 0.966$

$E_{X\text{-}C}$ V(B,N)-C(B): $y = -0.483 \cdot x + 0.031;\ R^2 = 0.999$

$E_{X\text{-}C}$ V(B,N)-C(N): $y = -0.189 \cdot x - 0.090;\ R^2 = 0.919$

BeH_2–NH_3:

T V(Be,N): $y = 6.286 \cdot x + 2.378;\ R^2 = 0.995$

$E_{X\text{-}C}$ V(Be,N)-C(Be): $y = -0.380 \cdot x - 0.020;\ R^2 = 0.998$

$E_{X\text{-}C}$ V(Be,N)-C(N): $y = -0.177 \cdot x - 0.103;\ R^2 = 0.985$

CH_3–Li:

T V(C,Li): $y = 15.157 \cdot x + 0.542;\ R^2 = 0.998$

$E_{X\text{-}C}$ V(C,Li)-C(C): $y = -0.603 \cdot x - 0.029;\ R^2 = 0.992$

$E_{X\text{-}C}$ V(C,Li)-C(Li): $y = -0.606 \cdot x + 0.016;\ R^2 = 1.000$

Electrostatic interaction energy

Table S10. Electrostatic energy, *intra* and *inter-basin* (in a.u.) for BH_3–NH_3, BeH_2–NH_3, CH_3–Li and Li_2.

R (Å)	1/R (bohr^{-1})	BH_3–NH_3		
		E_{intra} *V(B,N)*	E_{inter} *V(B,N)-C(B)*	E_{inter} *V(B,N)-C(N)*
1.40	0.378	1.430	-3.417	-8.915
1.50	0.353	1.290	-3.045	-8.454
1.60	0.331	1.195	-2.742	-8.157
1.70	0.311	1.135	-2.493	-7.988
1.80	0.294	1.103	-2.290	-7.916
1.67	0.317	1.153	-2.567	-8.039
R (Å)	1/R (bohr^{-1})	BeH_2–NH_3		
		E_{intra} *V(Be,N)*	E_{inter} *V(Be,N)-C(Be)*	E_{inter} *V(Be,N)-C(N)*
1.50	0.353	1.397	-1.918	-9.054
1.60	0.331	1.331	-1.768	-8.824
1.70	0.311	1.287	-1.641	-8.676
1.80	0.294	1.254	-1.529	-8.567
1.90	0.279	1.219	-1.425	-8.420
1.79	0.295	1.293	-1.650	-8.704
R (Å)	1/R (bohr^{-1})	CH_3–Li		
		E_{intra} *V(C,Li)*	E_{inter} *V(C,Li)-C(C)*	E_{inter} *V(C,Li)-C(Li)*
1.70	0.311	1.046	-5.659	-0.911
1.80	0.294	0.954	-5.361	-0.833
1.90	0.279	0.862	-5.065	-0.754
2.00	0.265	0.786	-4.807	-0.689
2.10	0.252	0.714	-4.544	-0.665
2.20	0.241	0.649	-4.302	-0.640
2.30	0.230	0.588	-4.068	-0.614
1.98	0.267	0.800	-4.852	-0.702
R (Å)	1/R (bohr^{-1})	Li_2		
		E_{intra} *V(Li,Li)*	E_{inter} *V(Li,Li)-C(Li)*	
2.40	0.220	0.000003	-0.000878	
2.50	0.212	0.000003	-0.000867	
2.60	0.204	0.000003	-0.000853	
2.70	0.196	0.000002	-0.000819	
2.80	0.189	0.000002	-0.000780	
2.90	0.182	0.000002	-0.000760	
3.00	0.176	0.000002	-0.000735	
3.10	0.171	0.000002	-0.000692	
2.72	0.194	0.000002	-0.000815	

The linear regression fittings are the following:

BH_3–NH_3:

E_{Inter} V(B,N): $y = 3.961 \cdot x - 0.092;\ R^2 = 0.977$

E_{Intra} V(B,N)-C(B): $y = -13.479 \cdot x + 1.698;\ R^2 = 0.998$

E_{Intra} V(B,N)-C(N): $y = -12.130 \cdot x - 4.234;\ R^2 = 0.950$

BeH_2–NH_3:

E_{Inter} V(Be,N): $y = 2.343 \cdot x + 0.563;\ R^2 = 0.991$

E_{Intra} V(Be,N)-C(Be): $y = -6.603 \cdot x + 0.414; R^2 = 0.998$

E_{Intra} V(Be,N)-C(N): $y = -8.269 \cdot x - 6.116; R^2 = 0.992$

CH_3–Li:

E_{Inter} V(C,Li): $y = 15.157 \cdot x + 0.542;\ R^2 = 0.998$

E_{Intra} V(C,Li)-C(C): $y = -0.603 \cdot x - 0.029;\ R^2 = 0.992$

E_{Intra} V(C,Li)-C(Li): $y = -0.606 \cdot x + 0.016;\ R^2 = 1.000$