Supporting Information:

Quantifying density errors in DFT

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Abstract

We argue that any general mathematical measure of density error, no matter how reasonable, is too arbitrary to be of universal use. However the energy functional itself provides a universal relevant measure of density errors. For the self-consistent density of any Kohn-Sham calculation with an approximate functional, the theory of density-corrected DFT provides an accurate, practical estimate of this ideal measure. We show how to estimate the significance of the density-driven error even when exact densities are unavailable. In cases with large density errors, the amount of exchange-mixing is often adjusted, but we show this is unnecessary. Many chemically relevant examples are given.

Table S1: Raw data (hartree unit) of Table 2 reactions. A denotes the self-consistent energy while A[B] indicate the A XC functional energy on the B density.

	Basis set	CCSD(T)	PBE	PBE[HF]	PBE[LDA]	LDA-LDA[HF]
			Atomization energies			
HCl	avtz	-0.169533	-0.168757	-0.168838	-0.169101	0.001369
LiH	avtz	-0.092863	-0.085228	-0.084342	-0.085322	-0.00041
NaCl	def2qzvp	-0.153433	-0.148332	-0.14747	-0.148595	0.000865
$CH_2(^3B_1)$	avtz	-0.306098	-0.309444	-0.307939	-0.309261	-0.002466
CH	def2qzvp	-0.132899	-0.134739	-0.133286	-0.134871	-0.002267
CH_2	avtz	-0.289941	-0.284622	-0.282914	-0.284712	-0.001818
NH	avtz	-0.131183	-0.140572	-0.138405	-0.140278	-0.003788
CH_4	avtz	-0.669995	-0.668623	-0.666526	-0.668757	-0.003043
			Reaction energies			
$HCl+CH_3 \rightarrow CH_4+Cl$	avtz	-0.009235	-0.006383	-0.005542	-0.006284	-0.002015
			Ionization energies			
C_2H_2	avtz	-0.417255	-0.413952	-0.414076	-0.414053	0.000427
He	av5z	-0.903258	-0.899157	-0.898393	-0.899018	-0.000754
			Double Ionization energies			
Ne^{6+}/Ne^{8+}	apwcv5z	16.383186	16.349979	16.348922	16.349618	0.001909
B^{+}/B^{3+}	apwcv5z	2.317662	2.311419	2.310388	2.311167	0.001726
N^{3+}/N^{5+}	apwcv5z	6.440821	6.424071	6.423054	6.423777	0.001836
O^{4+}/O^{6+}	apwcv5z	9.254418	9.232253	9.23122	9.231929	0.001867
			Electron affinity			
H	av5z	0.027434	0.038142	0.024903	0.038428	-0.020245
			Reaction barrier height			
$H+HF \rightarrow HF+H$	avtz	0.065745	0.042661	0.04819	0.042842	-0.007685
$CH_4+Cl \rightarrow HCl+CH_3$	avtz	0.009393	-0.003041	0.00289	-0.003021	-0.007117
$HCl+CH_3 \rightarrow CH_4+Cl$	avtz	0.000158	-0.009424	-0.002653	-0.009305	-0.009132
$H+N_2O \rightarrow OH+N_2$	avtz	0.028638	0.01585	0.034278	0.016122	-0.024065
$OH+N_2 \rightarrow H+N_2O$	avtz	0.130899	0.084667	0.11627	0.085134	-0.037827
			Dissociation of stretched molecules			
H_2^+ (at 5.0 $\AA$)	av5z	-0.000853	-0.080296	-0.075687	-0.080166	-0.001876
NaCl (at 6.0 $\AA$)	def2qzvp	-0.03112	-0.046999	-0.025567	-0.047334	-0.015427
NaCl (at 10.0 $\AA$)	def2qzvp	0.006041	-0.032528	0.012323	-0.03288	-0.03808
			Radical reaction energies			
$NH_2+H \rightarrow NH_3$	ccpvqz	0.171736	0.170535	0.171633	0.170877	-0.002073
$NHCH_3+H \rightarrow NH_2CH_3$	ccpvqz	0.164396	0.158323	0.162326	0.158904	-0.006435
$H+N_2O \rightarrow OH+N_2$	avtz	0.102261	0.068817	0.081992	0.069012	-0.013762
			High- and Low-spin energy difference			
$[Fe(NCH)_6]^{2+}$	ccpvtz	-0.042997	0.03314	-0.037168	0.032875	0.07818

BLYP[LDA]-BLYP[HF]	M06[LDA]-M06[HF]	B3LYP[LDA]-B3LYP[HF]	TPSS[LDA]-TPSS[HF]
Atomization energies			
0.000027	0.001026	-0.000016	-0.000761
-0.000946	-0.000674	-0.000429	-0.000076
-0.000984	0.003542	0.000042	-0.001626
-0.002788	-0.001335	-0.002276	-0.001191
-0.001981	-0.001189	-0.001288	-0.000105
-0.001901	-0.001416	-0.001146	-0.000957
-0.00296	-0.004751	-0.002043	-0.000439
-0.002233	-0.003132	-0.001523	-0.000807
Reaction energies			
-0.000118	-0.001809	0.000146	0.000512
Ionization energies			
-0.00019	-0.000322	-0.00003	-0.000384
-0.000903	0.000313	-0.000406	0.000381
Double Ionization energies			
0.000983	0.000921	0.000479	-0.000909
0.001071	0.000458	0.000609	-0.000752
0.001004	0.00081	0.000514	-0.000839
0.000992	0.00087	0.000496	-0.00087
Electron affinity			
0.014729	0.006554	0.002144	-0.531342
Reaction barrier height			
-0.005502	-0.006572	-0.00416	-0.004002
-0.006495	-0.00327	-0.003832	-0.004983
-0.006613	-0.005079	-0.003686	-0.004471
-0.018604	-0.017556	-0.014385	-0.014489
-0.031635	-0.021992	-0.022033	-0.02712
Dissociation of stretched molecules			
-0.00481	-0.003475	-0.003426	-0.005195
-0.025036	0.002629	-0.012526	-0.018138
-0.049757	-0.01084	-0.030944	-0.039961
Radical reaction energies			
-0.0007	-0.001665	-0.00038	0.000656
-0.003327	-0.001707	-0.001321	-0.001464
-0.013031	-0.004436	-0.007648	-0.012631
High- and Low-spin energy difference			
0.058537	0.032205	0.02358	0.057627

PBE0[LDA]-PBE0[HF]	M11[LDA]-M11[HF]	MN15[LDA]-MN15[HF]
Atomization energies		
-0.000486	-0.000176	0.000611
-0.000421	0.000299	0.000982
-0.000124	-0.000923	0.002604
-0.000727	-0.003614	0.00159
-0.000679	-0.001233	-0.000429
-0.000908	-0.000757	0.002455
-0.000615	-0.003433	-0.00196
-0.001343	-0.004113	0.003056
Reaction energies		
-0.000255	0.000142	-0.000091
Ionization energies		
0.000142	-0.00059	0.000766
-0.000072	0.000243	0.00091
Double Ionization energies		
-0.000012	0.000672	0.002019
0.000109	-0.001015	0.001067
0.000027	-0.000165	0.001163
0.000007	0.000167	0.001418
Electron affinity		
0.006487	-0.526112	-0.52694
Reaction barrier height		
-0.003291	-0.002516	-0.00454
-0.002474	-0.001235	-0.006774
-0.002729	-0.001093	-0.006865
-0.012047	-0.012252	-0.015042
-0.018277	-0.016883	-0.018798
Dissociation of stretched molecules		
-0.003008	-0.00096	-0.002291
-0.006988	0.01766	0.008025
-0.022779	0.019587	-0.002964
Radical reaction energies		
-0.000181	0.000897	-0.001641
-0.000561	0.001181	-0.002179
-0.00623	-0.004631	-0.003756
High- and Low-spin energy difference		
0.024793	-0.006387	0.031882