Supporting information to "Generalized Gradient Approximations of the Noninteracting Kinetic Energy from the Semiclassical Atom Theory: Rationalization of the Accuracy of the Frozen Density Embedding Theory for Nonbonded Interactions"

S. Laricchia[a], E. Fabiano[b], Lucian A. Constantin[a], F. Della Sala[b,a]
a) *Center for Biomolecular Nanotechnologies @UNILE*
Istituto Italiano di Tecnologia (IIT),
Via Barsanti, 73010 Arnesano (LE), Italy
b) *National Nanotechnology Laboratory (NNL), Istituto Nanoscienze-CNR,*
Via per Arnesano 16, 73100 Lecce, Italy

July 8, 2011

Table S1: Non-additive kinetic energy functionals $\tilde{T}_{\rm s}^{\rm nadd}[\tilde{\rho}_{\rm A}^{e}, \tilde{\rho}_{\rm A}^{e}]$ computed on embedded densities for subsystems corresponding to different KE GGA functionals for different interactions (weak, dipole, hydrogen-bonded systems). In each subgroups the systems are sorted according to the binding energy (reference values are reported in the text). All values are in mHa. The following shorthands have been used for the functional names: AK for APBEK; revAK for revAPBEK; AKi for APBEKint; revAKi for revAPBEKint.

Systems	GE2	revAKi	AKi	revAK	AK	Tw02	LC94
			Weak interaction				
He-Ne	-0.963	0.239	0.275	0.243	0.277	0.273	0.070
He-Ar	-0.938	0.286	0.328	0.289	0.330	0.325	0.112
$(Ne)_2$	-1.402	0.438	0.519	0.446	0.524	0.514	0.165
Ne-Ar	-1.414	0.583	0.688	0.591	0.693	0.681	0.285
CH_4-Ne	-1.636	0.601	0.719	0.612	0.726	0.712	0.267
C_6H_6-Ne	-3.000	1.684	2.086	1.719	2.111	2.066	1.004
$(CH_4)_2$	-2.282	1.940	2.370	1.976	2.394	2.347	1.327
			Dipole-dipole interaction				
$(H_2S)_2$	5.791	9.451	9.696	9.126	9.443	9.427	8.236
$(HCl)_2$	4.160	9.446	10.060	9.292	9.930	9.874	8.398
H_2S-HCl	14.160	18.936	19.274	18.299	18.768	18.759	17.053
CH_3Cl-HCl	8.068	16.342	17.417	16.077	17.201	17.105	14.741
CH_3SH-HCN	5.669	12.273	13.126	12.153	13.023	12.950	11.166
CH_3SH-HCl	22.300	28.930	29.345	27.867	28.518	28.515	25.999
			Hydrogen bond				
$(NH_3)_2$	2.748	8.807	9.742	8.853	9.779	9.684	8.077
$(HF)_2$	2.203	9.868	11.126	9.991	11.230	11.095	9.056
$(H_2O)_2$	4.387	12.138	13.467	12.241	13.556	13.419	11.335
NH_3-H_2O	9.838	17.951	19.433	18.015	19.494	19.351	17.155
HF-NCH	10.833	20.132	21.898	20.245	22.009	21.836	19.327
$(HCONH_2)_2$	24.819	42.180	45.371	42.130	45.343	45.048	40.188
$(HCOOH)_2$	38.355	58.470	62.516	58.502	62.583	62.213	56.634

Table S2: Other contributions to the energy error $\Delta W[\tilde{\rho}^e_{\rm A}, \tilde{\rho}^e_{\rm A}]$ computed on embedded densities for subsystems corresponding to different KE GGA functionals for different interactions (weak, dipole, hydrogen-bonded systems). In each subgroups the systems are sorted according to the binding energy (reference values are reported in the text). All values are in mHa. The following shorthands have been used for the functional names: AK for APBEK; revAK for revAPBEK; AKi for APBEKint; revAKi for revAPBEKint.

Systems	GE2	revAKi	AKi	revAK	AK	Tw02	LC94
			Weak interaction				
He-Ne	-0.161	-0.163	-0.157	-0.161	-0.156	-0.157	-0.168
He-Ar	-0.232	-0.238	-0.230	-0.235	-0.227	-0.228	-0.241
$(Ne)_2$	-0.312	-0.313	-0.296	-0.308	-0.293	-0.295	-0.317
Ne-Ar	-0.486	-0.488	-0.463	-0.479	-0.456	-0.459	-0.488
CH_4-Ne	-0.494	-0.499	-0.475	-0.492	-0.469	-0.472	-0.501
C_6H_6-Ne	-1.715	-1.769	-1.690	-1.746	-1.667	-1.678	-1.736
$(CH_4)_2$	-2.210	-2.387	-2.295	-2.357	-2.262	-2.275	-2.307
			Dipole-dipole interaction				
$(H_2S)_2$	-10.782	-10.095	-9.414	-9.601	-9.000	-9.087	-9.100
$(HCl)_2$	-9.324	-9.563	-9.093	-9.219	-8.781	-8.845	-8.770
H_2S-HCl	-19.779	-18.810	-17.702	-17.896	-16.918	-17.063	-16.947
CH_3Cl-HCl	-15.841	-16.626	-15.877	-16.054	-15.354	-15.450	-15.188
CH_3SH-HCN	-13.498	-13.685	-13.190	-13.330	-12.860	-12.934	-12.913
CH_3SH-HCl	-29.837	-28.588	-26.871	-27.136	-25.645	-25.859	-25.520
			Hydrogen bond				
$(NH_3)_2$	-9.429	-9.958	-9.700	-9.801	-9.540	-9.577	-9.510
$(HF)_2$	-8.631	-9.325	-9.078	-9.197	-8.940	-8.972	-8.871
$(H_2O)_2$	-11.737	-12.613	-12.334	-12.443	-12.152	-12.188	-12.028
NH_3-H_2O	-17.748	-18.710	-18.350	-18.452	-18.080	-18.129	-17.926
HF-NCH	-18.880	-20.058	-19.720	-19.813	-19.460	-19.503	-19.237
$(HCONH_2)_2$	-44.178	-47.125	-46.125	-46.333	-45.323	-45.456	-44.704
$(HCOOH)_2$	-57.303	-61.211	-60.171	-60.373	-59.291	-59.411	-58.346

Table S3: Embedding error on the energy ΔE and on the density ξ_v for hydrogen bond systems, using a revAPBEK kinetic energy functional with $\kappa_s = 1.0$

Systems	ΔE (mH)	ξ_v
$(NH_3)_2$	-0.332	1.67
$(HF)_2$	1.571	1.55
$(H_2O)_2$	0.627	1.99
NH_3-H_2O	0.511	3.10
HF-NCH	1.514	2.82
$(HCONH_2)_2$	-2.053	2.66
$(HCOOH)_2$	0.740	3.42
MAE	1.050	2.46
MARE(%)	9.29	

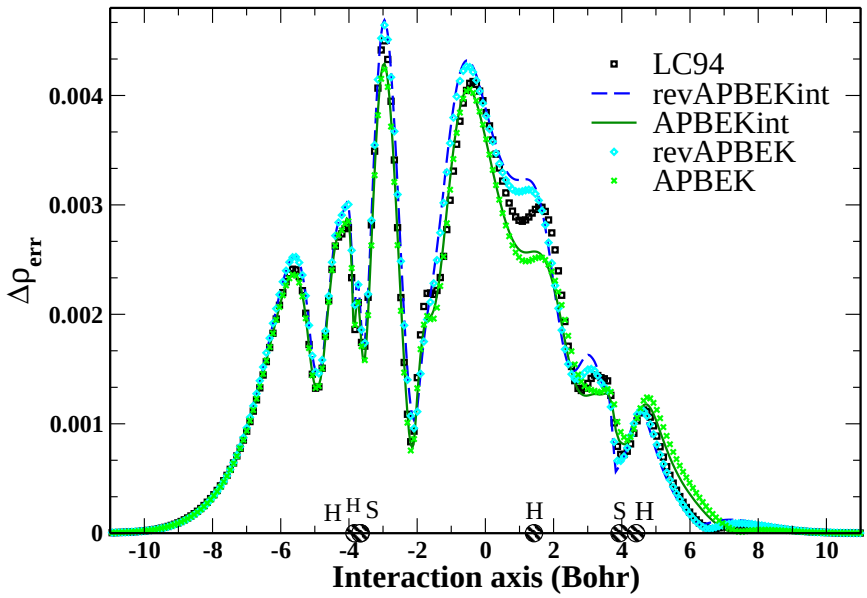

Figure S1: Plane averaged absolute error on the embedded valence density, i.e. $\int\int dxdy|\rho_{val}^{FDE}(\mathbf{r}) - \rho_{val}^{KS}(\mathbf{r})|$, where z in the interaction axis, for $H_2S - H_2S$ system.

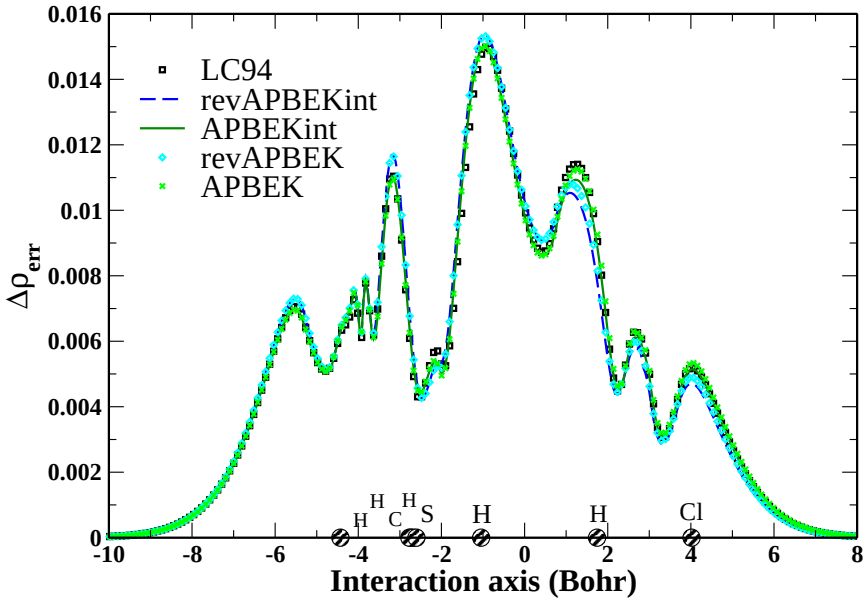

Figure S2: Same as in Fig. S1, for the $CH_3SH - HCl$ system.

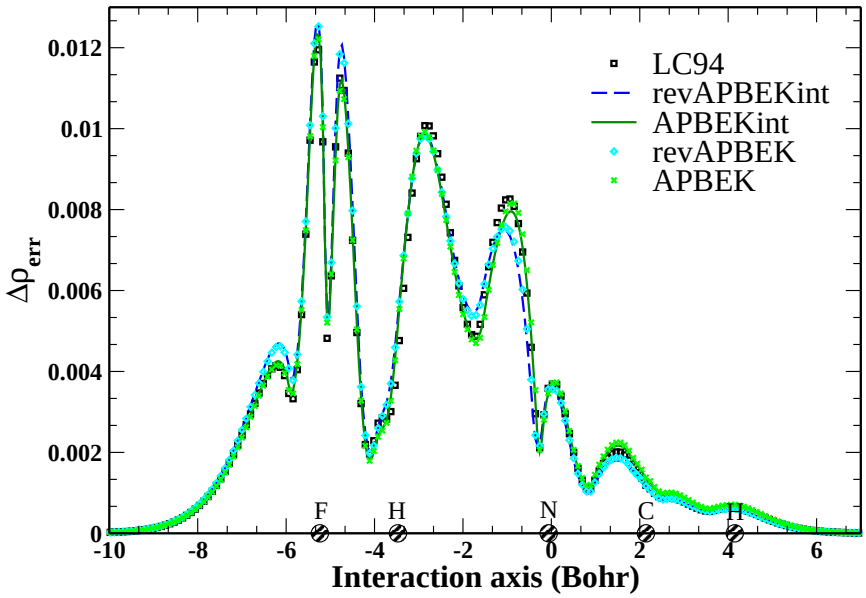

Figure S3: Same as in Fig. S1, for the $HF - NCH$ system.

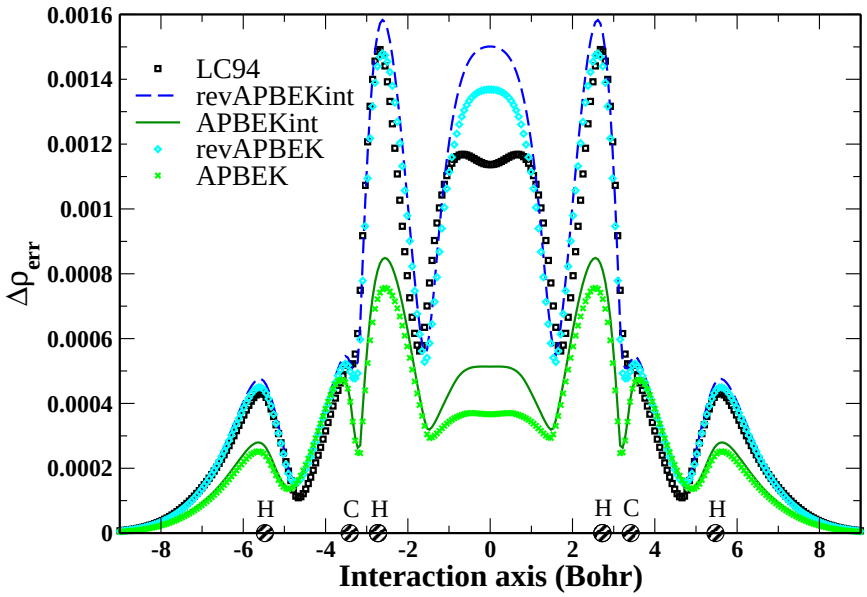

Figure S4: Same as in Fig. S1, for the $CH_4 - CH_4$ system. For weakly interacting systems the embedding errors on the density show larger deviations among different functionals. However for these systems the total error is one order of magnitue smaller than for DI or HB systems .