Supporting Information for "Restoring Size Consistency of Exchange-Correlation Functionals Constructed from the Adiabatic Connection"

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Mathematical forms of the used interpolation models

In this section we give mathematical forms of the used interpolation models for the AC integrand.

Interaction-Strength Interpolation (ISI):[1,2]

$$W_\lambda^{\mathrm{ISI}} = W_\infty[\rho] + \frac{X[\rho]}{\sqrt{1 + Y[\rho]\lambda} + Z[\rho]}, \tag{1}$$

where X, Y and Z are given by:

$$X = \frac{xy^2}{z^2}, \qquad Y = \frac{x^2y^2}{z^4}, \qquad Z = \frac{xy^2}{z^3} - 1 \tag{2}$$

with $x = -2W_0'[\rho]$, $y = W_\infty'[\rho]$, and $z = W_0[\rho] - W_\infty[\rho]$.

Revised Interaction-Strength Interpolation (rev-ISI):[3]

$$W_\lambda^{\mathrm{rISI}} = \frac{\partial}{\partial\lambda}\left(a^{\mathrm{rISI}}[\rho]\lambda\frac{b^{\mathrm{rISI}}[\rho]\lambda}{\sqrt{1+c^{\mathrm{rISI}}[\rho]\lambda}+d^{\mathrm{rISI}}[\rho]}\right), \tag{3}$$

with:

$$\begin{aligned} a^{\mathrm{rISI}}[\rho] &= W_\infty[\rho] \\ b^{\mathrm{rISI}}[\rho] &= -\frac{4W_0'[\rho]W_\infty'[\rho]^2}{(W_0[\rho]-W_\infty[\rho])^2} \\ c^{\mathrm{rISI}}[\rho] &= -\frac{8W_0'[\rho]^2W_\infty'[\rho]^2}{(W_0[\rho]-W_\infty[\rho])^4} \\ d^{\mathrm{rISI}}[\rho] &= -1-\frac{4W_0'[\rho]W_\infty'[\rho]^2}{(W_0[\rho]-W_\infty[\rho])^3}.e \end{aligned} \tag{4}$$

Seidl-Perdew-Levy (SPL):[4–6]

$$W_\lambda^{\mathrm{SPL}} = a^{\mathrm{SPL}}[\rho] + \frac{b^{\mathrm{SPL}}[\rho]}{\sqrt{1+c^{\mathrm{SPL}}[\rho]\lambda}} \tag{5}$$

with:

$$\begin{aligned} a^{\mathrm{SPL}}[\rho] &= W_\infty[\rho] \\ b^{\mathrm{SPL}}[\rho] &= W_0[\rho] - W_\infty[\rho] \\ c^{\mathrm{SPL}}[\rho] &= -\frac{2W_0'[\rho]}{W_0[\rho]-W_\infty[\rho]}. \end{aligned} \tag{6}$$

Liu-Burke (LB):[6,7]

$$W_\lambda^{\mathrm{LB}} = a^{\mathrm{LB}}[\rho] + b^{\mathrm{LB}}[\rho]\left(\frac{1}{(1+c^{\mathrm{LB}}[\rho]\lambda)^2} + \frac{1}{\sqrt{1+c^{\mathrm{LB}}[\rho]\lambda}}\right), \tag{7}$$

with:

$$\begin{aligned} a^{\mathrm{LB}}[\rho] &= W_\infty[\rho] \\ b^{\mathrm{LB}}[\rho] &= \frac{W_0[\rho] - W_\infty[\rho]}{2} \\ c^{\mathrm{LB}}[\rho] &= -\frac{4W_0'[\rho]}{5(W_0[\rho] - W_\infty[\rho])} \end{aligned} \tag{8}$$

Additional computational details

The point-charge-plus-continuum (PC) functional approximations to the strong coupling limit quantities are given by:[1]

$$W_\infty[\rho] = \int \left[A\rho(\mathbf{r})^{4/3} + B\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{4/3}}\right] \mathrm{d}\mathbf{r} \tag{9}$$

$$W_\infty'[\rho] = \int \left[C\rho(\mathbf{r})^{3/2} + D\frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{7/6}(\mathbf{r})}\right] \mathrm{d}\mathbf{r}. \tag{10}$$

The parameters $A = -1.451$, $B = 5.317 \times 10^{-3}$, and $C = 1.535$, are determined by the electrostatic arguments[1] and $D = -2.8957 \times 10^{-2}$ has been obtained by ensuring that the given approximation to $W_\infty'[\rho]$ is exact for the helium atom.[3] All interaction energies reported in the letter have been corrected for the basis-set superposition error. In all calculations (except for Kr which used an aug-cc-pV5Z basis set[8]) we used a basis set constructed adding selected s, p, d, and f functions to the aug-cc-pVQZ basis set[9,10] of each element. The list of additional functions is reported in Table S1.

Table S1: List of additional (Gaussian) basis functions used for each element.

Element	Basis function	
	type	Exponent
H	s	6.17937
	s	0.46550
	p	3.43000
	d	4.45300
He	s	19.0385
	s	2.0880
	p	16.1040
	p	2.4980
	d	12.4980
N	s	13.8234
	s	2.1950
	p	2.1480
	d	6.7170
C	s	9.9641
	s	1.6560
	p	1.5040
	d	4.5420
O	s	18.3030
	s	2.7760
	p	2.7320
	d	8.2530
Ne	s	29.0669
	s	4.3270
	p	4.2810
	d	13.3170
Ar	s	1.7580
	p	2.2450
	d	4.7760
	f	3.0582

Results for the S66 test set

TABLE S2: Signed errors in kcal/mol for the S66 test for all the AC-based functionals. Systems 1-23 have H-bond interaction, systems 24-46 dispersion, system 47-66 mixed characters.

num.	system	rev-ISI	ISI	SPL	LB
1	Water-Water	-0.064	-0.095	-0.161	-0.146
2	Water-MeOH	-0.141	-0.164	-0.213	-0.175
3	Water-MeNH2	-0.193	-0.210	-0.245	-0.189
4	Water-Peptide	-0.259	-0.294	-0.370	-0.334
5	MeOH-MeOH	-0.222	-0.239	-0.276	-0.225
6	MeOH-MeNH2	-0.364	-0.373	-0.393	-0.302
7	MeOH-Peptide	-0.417	-0.442	-0.495	-0.432
8	MeOH-Water	-0.124	-0.150	-0.204	-0.179
9	MeNH2-MeOH	-0.273	-0.287	-0.315	-0.261
10	MeNH2-MeNH2	-0.376	-0.380	-0.390	-0.293
11	MeNH2-Peptide	-0.484	-0.487	-0.494	-0.380
12	MeNH2-Water	-0.210	-0.223	-0.253	-0.180
13	Peptide-MeOH	-0.327	-0.336	-0.355	-0.272
14	Peptide-MeNH2	-0.470	-0.466	-0.460	-0.338
15	Peptide-Peptide	-0.549	-0.557	-0.575	-0.467
16	Peptide-Water	-0.156	-0.179	-0.226	-0.192
17	Uracil-Uracil	-0.649	-0.687	-0.767	-0.685
18	Water-Pyridine	-0.198	-0.209	-0.234	-0.169
19	MeOH-Pyridine	-0.296	-0.298	-0.301	-0.206
20	AcOH-AcOH	-0.481	-0.556	-0.713	-0.686
21	AcNH2-AcNH2	-0.679	-0.724	-0.819	-0.755
22	AcOH-Uracil	-0.550	-0.610	-0.739	-0.693
23	AcNH2-Uracil	-0.595	-0.647	-0.756	-0.699
24	Benzene-Benzene	0.268	0.354	0.531	0.854
25	Pyridine-Pyridine	0.350	0.448	0.652	0.998
26	Uracil-Uracil	-0.725	-0.617	-0.394	-0.002
27	Benzene-Pyridine	0.300	0.392	0.583	0.919
28	Benzene-Uracil	-0.180	-0.065	0.173	0.567
29	Pyridine-Uracil	-0.125	-0.015	0.214	0.594
30	Benzene-Ethene	0.010	0.046	0.120	0.306
31	Uracil-Ethene	-0.240	-0.205	-0.134	0.046
32	Uracil-Ethyne	-0.082	-0.056	-0.003	0.152
33	Pyridine-Ethene	0.019	0.059	0.143	0.337
34	Pentane-Pentane	-0.931	-0.913	-0.876	-0.634
35	Neopentane-Pentane	-0.671	-0.663	-0.649	-0.486

36	Neopentane-Neopentane	-0.498	-0.500	-0.502	-0.394
37	Cyclopentane-Neopentane	-0.630	-0.622	-0.605	-0.449
38	Cyclopentane-Cyclopentane	-0.736	-0.721	-0.690	-0.502
39	Benzene-Cyclopentane	-0.265	-0.215	-0.111	0.152
40	Benzene-Neopentane	-0.233	-0.202	-0.138	0.061
41	Uracil-Pentane	-0.905	-0.844	-0.718	-0.416
42	Uracil-Cyclopentane	-0.763	-0.707	-0.591	-0.322
43	Uracil-Neopentane	-0.660	-0.625	-0.552	-0.348
44	Ethene-Pentane	-0.411	-0.409	-0.406	-0.281
45	Ethyne-Pentane	-0.148	-0.144	-0.134	-0.018
46	Peptide-Pentane	-0.902	-0.875	-0.817	-0.578
47	Benzene-Benzene	0.005	0.039	0.107	0.287
48	Pyridine-Pyridine	-0.022	0.010	0.077	0.255
49	Benzene-Pyridine	-0.002	0.029	0.093	0.268
50	Benzene-Ethyne	0.119	0.125	0.137	0.238
51	Ethyne-Ethyne	0.037	0.023	-0.005	0.021
52	Benzene-AcOH	-0.192	-0.175	-0.140	0.002
53	Benzene-AcNH2	-0.239	-0.234	-0.222	-0.106
54	Benzene-Water	-0.091	-0.094	-0.100	-0.020
55	Benzene-MeOH	-0.197	-0.177	-0.135	0.023
56	Benzene-MeNH2	-0.178	-0.155	-0.108	0.056
57	Benzene-Peptide	-0.218	-0.175	-0.086	0.141
58	Pyridine-Pyridine	-0.299	-0.299	-0.299	-0.206
59	Ethyne-Water	0.019	-0.010	-0.071	-0.071
60	Ethyne-AcOH	-0.156	-0.180	-0.229	-0.177
61	Pentane-AcOH	-0.642	-0.629	-0.603	-0.441
62	Pentane-AcNH2	-0.758	-0.742	-0.709	-0.524
63	Benzene-AcOH	-0.176	-0.141	-0.070	0.123
64	Peptide-Ethene	-0.346	-0.345	-0.344	-0.233
65	Pyridine-Ethyne	-0.040	-0.054	-0.086	-0.047
66	MeNH2-Pyridine	-0.243	-0.220	-0.173	-0.008

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