Supporting Information for "Basis set convergence of the post-CCSD(T) contribution to noncovalent interaction energies"

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TABLE SI. Geometries of the weakly interacting complexes studied in this work as well as their benchmark frozen-core CCSD(T)/CBS interaction energies (in cm^{-1}). The numbers in brackets are literature references. If no reference is given, the CCSD(T)/CBS value was obtained in this work via an (aQZ,a5Z) extrapolation [(a5Z,a6Z) for H_2O–$H_2O(C_{2v})$ and both N_2–N_2 geometries]. The symbol R with no subscript denotes the distance between the centers of masses (COM) of the monomers.

System	Geometry	$E_{\rm int}^{\rm CCSD(T)/CBS}$	
He–He	$R = 5.6$ bohr	-7.4267	[1]
He–H_2	linear, $R = 6.4$ bohr, $r_{\rm HH} = 1.4487$ bohr	-10.592	[2]
H_2–H_2	T-shaped, $R = 6.4$ bohr, $r_{\rm HH} = 1.4487$ bohr	-38.290	[3]
He–LiH	linear He–LiH, $R_{\rm HeLi} = 3.97$ bohr, $r_{\rm LiH} = 3.0139$ bohr	-148.791	
LiH–LiH	antiparallel (rectangle) LiH-HLi 3.2631 bohr apart, $r_{\rm LiH} = 3.2627$ bohr	-16880.28	
Ne–Ne	$R = 3.1$ Å	-28.757	[4]
Ar–Ar	$R = 3.75$ Å	-97.445	[5]
He–C_3	T-shaped, $R = 6.75$ bohr, linear C_3 with $r_{\rm CC} = 2.414$ bohr	-26.93	[6]
Ne–HF	linear Ne–HF, R=6.068 bohr, $r_{\rm HF}$=1.7629 bohr [7]	-88.035	
Ar–HF	linear Ar–HF, R=6.474 bohr, $r_{\rm HF}$=1.7629 bohr	-216.323	
Ar–CH_4	A24 [8]	-138.853	[9]
H_2–HF	T-shaped, H of HF pointing towards the H_2 center of mass, R=5.403 bohr, $r_{\rm HF}$=1.7629 bohr, and $r_{\rm HH}$=1.4487 bohr	-396.037	
H_2–HCl	T-shaped, H of HCl pointing towards the H_2 center of mass, $R = 6.5$ bohr, $r_{\rm HCl} = 2.4086$ bohr, $r_{\rm HH} = 1.4487$ bohr	-206.09	[10]
H_2–CO	linear H_2-CO, R=7.922 bohr, $r_{\rm CO}$=2.1399 bohr [11], $r_{\rm HH}$=1.4487 bohr	-91.212	
H_2O–H_2O	A24 [8]	-1751.22	[9]
H_2O–H_2O	C_{2v} geometry (dipole moments of both molecules pointing in the same direction, molecular planes at 90° to each other) – see Supplementary Material	-1160.85	
N_2–N_2	slipped parallel (C_{2h}), R = 3.9938 Å, N-COM(this N_2)-COM(other N_2) angle= 50.08°, $r_{\rm NN} = 1.1014$ Å [12]	-108.64	
N_2–N_2	parallel (rectangle) N_2-N_2 3.7679 Å apart, $r_{\rm NN} = 1.1042$ Å	-79.53	
HF–HF	A24 [8]	-1598.03	[9]
NH_3–NH_3	A24 [8]	-1098.58	[9]
CH_4–CH_4	A24 [8]	-186.769	[9]

TABLE SII. The best estimates of the CCSD(T)/CBS, $\delta_{\rm T}$, $\delta_{\rm (Q)}$, $\delta_{\rm T+(Q)}$, and $\delta_{\rm Q}$ interaction energy contributions obtained as described in the text. The SCF, $\delta_{\rm MP2}$ = MP2−SCF, $\delta_{\rm CCSD}$ = CCSD−MP2, and $\delta_{\rm (T)}$ = CCSD(T)−CCSD interaction energy contributions, computed using the a(Q,5)Z extrapolation (except for SCF which was calculated in the a5Z basis and not extrapolated), are presented for comparison.

molecule	CCSD(T)/CBS	SCF	$\delta_{\rm MP2}$	$\delta_{\rm CCSD}$	$\delta_{\rm (T)}$	$\delta_{\rm T}$	$\delta_{\rm (Q)}$	$\delta_{\rm T+(Q)}$	$\delta_{\rm Q}$
He–He	-7.4267	6.415	-10.971	-1.648	-1.050	-0.213	-0.008	-0.221	-0.003
He–H_2	-10.592	10.958	-18.348	-1.199	-1.975	-0.377	-0.017	-0.394	-0.004
H_2–H_2	-38.290	20.150	-52.985	0.831	-6.368	-1.111	-0.109	-1.220	-0.031
He–LiH	-148.791	-122.913	-25.196	3.800	-4.483	-1.053	-0.073	-1.127	-0.029
LiH–LiH	-16880.28	-16249.840	-868.108	376.714	-139.046	-30.620	-3.062	-33.682	-0.504
Ne–Ne	-28.757	19.815	-37.905	-4.711	-6.232	-0.443	-0.102	-0.545	-0.007
Ar–Ar	-97.445	96.679	-211.285	44.603	-28.842	1.355	-1.908	-0.553	0.104
He–C_3	-26.93	33.724	-64.700	12.019	-7.729	0.477	-0.678	-0.201	0.021
Ne–HF	-88.035	27.020	-94.484	-2.209	-18.362	-0.883	-0.828	-1.711	0.028
Ar–HF	-216.323	61.446	-270.306	41.135	-48.597	0.013	-2.589	-2.577	-0.013
Ar–CH_4	-138.853	124.607	-273.452	44.683	-38.083	1.141	-2.305	-1.163	-0.121
H_2–HF	-396.037	-132.398	-252.799	31.763	-42.603	-2.899	-0.783	-3.682	-0.130
H_2–HCl	-206.09	81.295	-302.513	55.764	-41.565	-1.427	-2.149	-3.576	-0.010
H_2–CO	-91.212	24.713	-116.624	18.420	-17.721	-1.106	-1.259	-2.365	-0.045
H_2O–H_2O	-1751.22	-1281.470	-462.778	74.772	-85.557	2.392	-5.666	-3.273	0.106
H_2O–H_2O (C_{2v})	-1160.85	-869.454	-248.524	4.354	-47.675	0.735	-2.570	-1.835	-0.080
N_2–N_2	-108.64	77.657	-215.386	62.004	-31.554	4.029	-5.711	-1.682	1.462
N_2–N_2 (D_{2h})	-79.53	81.692	-194.235	62.113	-27.471	3.723	-4.749	-1.026	1.122
HF–HF	-1598.03	-1336.323	-227.817	12.208	-54.433	0.235	-4.040	-3.805	0.320
NH_3–NH_3	-1098.58	-515.370	-590.327	98.560	-92.755	3.357	-6.676	-3.319	0.003
CH_4–CH_4	-186.769	168.689	-342.081	35.736	-49.145	0.289	-3.316	-3.027	0.124

TABLE SIII. Anisotropy of the interaction energy contributions (in cm^{-1}) for the LiH–LiH complex. Three geometries are presented: antiparallel, collinear, and parallel (the corresponding Cartesian coordinates are listed in the Supporting Information). The columns marked "FC" and "AE" list frozen-core and all-electron results, respectively.

	antiparallel		collinear		parallel	
	FC	AE	FC	AE	FC	AE
			aDZ			
δ_{T}	-29.48	-29.23	-13.37	-13.45	-32.10	-32.24
$\delta_{(\mathrm{Q})}$	-1.17	-1.13	-0.75	-1.03	-2.68	-2.71
$\delta_{\mathrm{T}+(\mathrm{Q})}$	-30.65	-30.35	-14.13	-14.48	-34.78	-34.95
δ_{Q}	-0.21	-0.25	-0.31	-0.34	-0.11	-0.08
CCSD(T)	-15851.05	-15964.03	-8656.69	-8701.90	3759.53	3750.95
			aTZ			
δ_{T}	-35.06	-35.06	-13.93	-13.84	-31.57	-32.65
$\delta_{(\mathrm{Q})}$	-2.51	-2.88	-1.11	-1.34	-2.93	-3.22
$\delta_{\mathrm{T}+(\mathrm{Q})}$	-37.56	-37.94	-15.05	-15.18	-34.50	-35.87
δ_{Q}	-0.56		-0.42		-0.19	
CCSD(T)	-16689.70	-16931.65	-8718.38	-8802.70	3652.48	3630.34
			aQZ			
δ_{T}	-33.20	-33.70	-13.26	-13.19	-29.93	-31.19
$\delta_{(\mathrm{Q})}$	-2.83	-3.41	-1.18	-1.44	-3.01	-3.28
$\delta_{\mathrm{T}+(\mathrm{Q})}$	-36.03	-37.12	-14.44	-14.63	-32.93	-34.47
δ_{Q}	-0.50		-0.39		-0.17	
CCSD(T)	-16818.09	-17157.87	-8738.91	-8848.06	3636.57	3599.43
			aCVDZ			
δ_{T}	-29.82	-29.11	-13.38	-13.13	-31.90	-32.74
$\delta_{(\mathrm{Q})}$	-1.19	-1.46	-0.76	-0.91	-2.64	-2.84
$\delta_{\mathrm{T}+(\mathrm{Q})}$	-31.00	-30.57	-14.14	-14.04	-34.54	-35.59
δ_{Q}	-0.21	-0.26	-0.31	-0.32	-0.10	-0.02
CCSD(T)	-15928.41	-16057.43	-8664.37	-8711.06	3740.58	3711.67
			aCVTZ			
δ_{T}	-34.87	-35.03	-13.84	-13.78	-31.38	-32.61
$\delta_{(\mathrm{Q})}$	-2.53	-3.12	-1.13	-1.37	-2.91	-3.10
$\delta_{\mathrm{T}+(\mathrm{Q})}$	-37.40	-38.15	-14.97	-15.15	-34.28	-35.70
CCSD(T)	-16706.97	-16980.08	-8719.91	-8799.12	3646.66	3591.98
			aCVQZ			
δ_{T}	-32.99	-33.71	-13.18	-13.21	-29.85	-31.09
$\delta_{(\mathrm{Q})}$	-2.84	-3.60	-1.19	-1.49	-3.00	-3.21
$\delta_{\mathrm{T}+(\mathrm{Q})}$	-35.83	-37.31	-14.37	-14.70	-32.86	-34.30
CCSD(T)	-16826.97	-17185.19	-8741.18	-8841.57	3635.22	3573.98

TABLE SIV. Interaction energy contributions (in cm^{-1}) for the He–LiH and Ne–Ne complexes. The columns marked "FC" and "AE" list frozen-core and all-electron results, respectively.

Basis set	CCSD(T)		δ_T		$\delta_{(Q)}$		$\delta_{T+(Q)}$		δ_Q	
	FC	AE	FC	AE	FC	AE	FC	AE	FC	AE
					He–LiH					
6-31G*(0.25)	−12.718	−15.490	−0.522	−0.535	−0.030	−0.031	−0.552	−0.566	−0.007	−0.008
6-31G**(0.25,0.15)	−31.749	−36.440	−1.157	−1.171	−0.102	−0.106	−1.258	−1.276	−0.041	−0.041
aDZ	−98.359	−105.924	−1.063	−1.075	−0.054	−0.067	−1.117	−1.142	−0.025	−0.026
aTZ	−139.102	−158.345	−1.120	−1.234	−0.066	−0.074	−1.185	−1.308	−0.028	−0.030
aQZ	−147.367	−173.832	−1.105	−1.264	−0.071	−0.078	−1.176	−1.342	−0.029	−0.031
a5Z	−148.140	−176.679	−1.080	−1.246	−0.072	−0.078	−1.152	−1.324		
aCVDZ	−116.926	−126.543	−1.067	−1.084	−0.055	−0.057	−1.122	−1.141	−0.025	−0.026
aCVTZ	−140.329	−162.437	−1.121	−1.259	−0.067	−0.068	−1.187	−1.328	−0.028	−0.030
aCVQZ	−147.869	−175.107	−1.100	−1.277	−0.071	−0.073	−1.171	−1.350	−0.029	−0.031
					Ne–Ne					
6-31G*(0.25)	−16.806	−16.820	−0.108	−0.108	0.128	0.128	0.020	0.020	−0.013	−0.013
aDZ	−3.054	−3.075	−0.041	−0.039	0.033	0.033	−0.008	−0.006	−0.007	−0.007
aTZ	−16.671	−16.721	−0.269	−0.262	−0.027	−0.028	−0.296	−0.290		
aQZ	−22.958	−22.957	−0.373	−0.366	−0.070	−0.080	−0.443	−0.446		
a5Z	−25.753	−25.727	−0.407	−0.397						
aCVDZ	−3.125	−3.134	−0.041	−0.042	0.029	0.028	−0.012	−0.013	−0.007	−0.007
aCVTZ	−16.893	−16.802	−0.262	−0.257	−0.040	−0.053	−0.302	−0.310		
aCVQZ	−22.984	−22.947	−0.366	−0.353						

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