

# Supplementary material for “Spin-unrestricted random-phase approximation with range separation: Benchmark on atomization energies and reaction barrier heights”

Bastien Mussard,<sup>1,2,3, a)</sup> Peter Reinhardt,<sup>2,3</sup> János G. Ángyán,<sup>4,5</sup> and Julien Toulouse<sup>2,3, b)</sup>

<sup>1)</sup>*Sorbonne Universités, UPMC Univ Paris 06, Institut du Calcul et de la Simulation, F-75005, Paris, France*

<sup>2)</sup>*Sorbonne Universités, UPMC Univ Paris 06, UMR 7616, Laboratoire de Chimie Théorique, F-75005 Paris, France*

<sup>3)</sup>*CNRS, UMR 7616, Laboratoire de Chimie Théorique, F-75005 Paris, France*

<sup>4)</sup>*CRM2, Institut Jean Barriol, Université de Lorraine, F-54506 Vandœuvre-lés-Nancy, France*

<sup>5)</sup>*CRM2, Institut Jean Barriol, CNRS, F-54506 Vandœuvre-lés-Nancy, France*

The detailed results of the calculations on the AE49 and DBH24/08 datasets for the full-range and range-separated MP2, dRPA-I, and RPAX-SO2 methods at  $\mu = 0.5$  are reported

in Tables [I](#) and [II](#).

<sup>1</sup>R. Haunschild and W. Klopper, *J. Chem. Phys.* **136**, 164102 (2012).

<sup>2</sup>J. Zheng, Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.* **5**, 808 (2009).

---

<sup>a)</sup>Electronic mail: [bastien.mussard@upmc.fr](mailto:bastien.mussard@upmc.fr)

<sup>b)</sup>Electronic mail: [julien.toulouse@upmc.fr](mailto:julien.toulouse@upmc.fr)

TABLE I. Atomization energies (in kcal/mol) of the AE49 dataset (molecules of the G2-1 dataset except for the six molecules containing Li, Be, and Na) calculated by full-range HF+MP2, HF+dRPA-I, HF+RPAX-SO2 and range-separated RSH+MP2, RSH+dRPA-I, RSH+RPAX-SO2. The calculations were carried out using the cc-pVQZ basis set, MP2(full)/6-31G\* geometries, and with the srPBE functional and  $\mu = 0.5$  in the case of the range-separated calculations. The reference values are the non-relativistic FC-CCSD(T)/cc-pVQZ-F12 values of Ref. 1. For each method, the value with the largest absolute error is indicated in boldface.

	HF+			RSH+			Reference
	MP2	dRPA-I	RPAX-SO2	MP2	dRPA-I	RPAX-SO2	
CH <sub>2</sub> (singlet)	174.45	165.75	197.04	171.39	170.64	172.69	180.62
CH <sub>2</sub> (triplet)	188.70	181.63	201.41	190.84	189.71	191.31	189.74
CH <sub>3</sub> Cl	394.58	370.34	417.42	389.72	386.32	391.19	394.52
CH <sub>3</sub>	303.36	291.30	318.89	303.79	302.23	304.71	306.59
CH <sub>3</sub> SH	469.94	442.53	495.56	465.03	460.82	467.01	473.49
CH <sub>4</sub>	414.84	397.27	432.29	411.74	409.65	413.14	418.87
CH	76.38	74.13	85.21	79.46	79.19	80.04	83.87
Cl <sub>2</sub>	60.43	46.49	79.13	55.73	53.53	56.71	59.07
ClF	65.20	45.91	83.08	61.15	60.68	62.04	62.57
ClH	106.53	98.52	119.27	102.11	101.21	103.02	107.20
ClO	59.68	42.55	72.39	63.94	62.60	65.22	64.53
CN	168.84	141.95	164.00	176.12	173.99	177.86	180.06
CO <sub>2</sub>	<b>409.33</b>	350.00	413.15	395.12	392.37	396.91	388.59
CO	269.30	234.43	276.58	257.79	256.26	259.24	258.88
F <sub>2</sub>	42.18	15.59	59.82	36.60	36.99	37.84	38.75
FH	144.17	129.15	154.97	138.23	137.89	138.65	141.51
H <sub>2</sub> CCH <sub>2</sub>	561.39	528.59	582.70	556.69	552.92	558.80	561.34
H <sub>2</sub> CO	379.20	343.30	392.00	370.88	368.85	372.48	373.21
H <sub>2</sub> NNH <sub>2</sub>	432.47	394.47	431.32	432.36	429.67	434.62	436.70
H <sub>3</sub> CCH <sub>3</sub>	707.16	673.49	<b>735.15</b>	703.80	699.25	705.86	710.20
H <sub>3</sub> COH	513.32	477.43	534.34	507.36	504.60	509.06	511.83
HCCCH	409.59	373.19	419.99	401.10	397.40	403.34	402.76
HCN	319.26	279.53	312.96	308.30	305.60	310.48	311.52
HCO	285.80	252.01	291.99	280.35	278.63	281.90	278.28
HOCl	168.50	141.01	184.05	161.23	159.81	162.68	165.79
HOOH	272.51	232.25	286.06	263.66	262.62	265.56	268.65
N <sub>2</sub>	234.80	193.15	213.76	222.17	220.46	224.27	227.44
NH <sub>2</sub>	176.66	165.16	179.49	178.54	177.84	179.51	181.96
NH <sub>3</sub>	293.12	272.47	295.33	290.20	288.89	291.65	297.07
NH	78.57	74.39	80.62	82.08	81.82	82.54	82.79
NO	156.95	123.74	147.37	155.31	154.30	156.90	152.19
O <sub>2</sub>	126.53	92.04	113.98	124.06	123.31	126.00	120.54
OH <sub>2</sub>	233.83	212.21	243.34	226.55	225.77	227.54	232.56
OH	105.78	96.58	112.19	105.25	104.93	105.73	106.96
P <sub>2</sub>	113.59	88.61	105.38	106.63	99.52	107.19	115.95
PH <sub>2</sub>	144.95	141.41	152.46	146.95	146.30	147.68	153.97
PH <sub>3</sub>	230.24	222.62	241.82	229.63	228.31	230.84	241.47
S <sub>2</sub>	103.68	85.63	109.74	101.19	96.76	102.13	103.11
SC	175.16	146.58	186.41	164.13	159.64	166.22	170.98
SH <sub>2</sub>	178.55	168.10	194.48	174.35	172.84	175.82	183.30
Si <sub>2</sub> H <sub>6</sub>	519.18	504.65	556.67	<b>517.31</b>	<b>512.50</b>	<b>520.68</b>	535.47
Si <sub>2</sub>	59.29	50.71	67.94	72.31	69.20	75.82	73.41
SiH <sub>2</sub> (singlet)	145.90	141.61	165.21	143.64	142.93	145.89	153.68
SiH <sub>2</sub> (triplet)	128.93	126.44	141.38	129.82	128.58	131.14	133.26
SiH <sub>3</sub>	220.51	216.07	237.96	220.33	218.83	221.84	228.08
SiH <sub>4</sub>	314.28	307.46	336.62	311.98	310.07	313.73	324.59
SiO	200.09	165.92	203.39	187.97	185.75	190.47	192.36
SO <sub>2</sub>	270.73	<b>207.21</b>	269.30	249.24	245.56	251.39	259.77
SO	129.29	101.94	127.35	125.02	123.21	126.41	125.80
MAD	5.63	23.23	12.20	5.09	6.80	4.06	

TABLE II. Forward (F) and reverse (R) reaction barrier heights (in kcal/mol) of the DBH24/08 dataset calculated by full-range HF+MP2, HF+dRPA-I, HF+RPAX-SO2 and range-separated RSH+MP2, RSH+dRPA-I, RSH+RPAX-SO2. The calculations were carried out using the aug-cc-pVQZ basis set, QCISD/MG3 geometries, and with the srPBE functional and  $\mu = 0.5$  in the case of the range-separated calculations. The reference values are taken from Ref. 2. For each method, the value with the largest absolute error is indicated in boldface.

	HF+			RSH+			Reference
	MP2	dRPA-I	RPAX-SO2	MP2	dRPA-I	RPAX-SO2	
	F/R	F/R	F/R	F/R	F/R	F/R	F/R
Heavy-atom transfer							
H+N <sub>2</sub> O → OH+N <sub>2</sub>	35.94/89.26	28.20/ <b>100.80</b>	32.74/ <b>100.57</b>	18.11/74.67	18.00/76.40	17.92/74.43	17.13/82.47
H+ClH → HCl+H	22.79/22.79	24.07/24.07	23.33/23.33	19.07/19.07	19.36/19.36	18.44/18.44	18.00/18.00
CH <sub>3</sub> +FCl → CH <sub>3</sub> F+Cl	19.74/74.29	17.63/75.16	21.67/66.18	7.19/61.68	7.38/61.98	7.40/61.25	6.75/60.00
Nucleophilic substitution							
Cl <sup>-</sup> ⋯CH <sub>3</sub> Cl → ClCH <sub>3</sub> ⋯Cl <sup>-</sup>	14.64/14.64	15.92/15.92	15.05/15.05	15.12/15.12	15.85/15.85	14.76/14.76	13.41/13.41
F <sup>-</sup> ⋯CH <sub>3</sub> Cl → FCH <sub>3</sub> ⋯Cl <sup>-</sup>	4.59/28.88	4.78/33.98	4.35/33.29	4.43/30.70	4.62/31.50	4.09/30.43	3.44/29.42
OH <sup>-</sup> +CH <sub>3</sub> F → HOCH <sub>3</sub> +F <sup>-</sup>	-1.75/17.86	1.23/22.00	0.52/20.92	-2.33/20.59	-1.43/21.22	-2.60/19.81	-2.44/17.66
Unimolecular and association							
H+N <sub>2</sub> → HN <sub>2</sub>	27.60/8.06	22.54/12.53	23.36/12.59	13.23/12.66	13.34/12.59	12.81/12.47	14.36/10.61
H+C <sub>2</sub> H <sub>4</sub> → CH <sub>3</sub> CH <sub>2</sub>	9.32/46.54	6.67/48.13	7.80/49.83	2.38/45.29	2.62/45.24	2.20/44.74	1.72/41.75
HCN → HNC	34.46/ <b>52.09</b>	36.14/49.49	34.73/47.08	34.36/ <b>47.93</b>	34.85/ <b>48.15</b>	34.03/ <b>47.70</b>	48.07/32.82
Hydrogen transfer							
OH+CH <sub>4</sub> → CH <sub>3</sub> +H <sub>2</sub> O	7.66/25.01	13.65/24.16	9.28/25.55	4.63/18.62	4.77/18.82	4.14/18.16	6.70/19.60
H+OH → O+H <sub>2</sub>	17.56/15.58	15.42/20.08	16.13/15.90	12.44/8.22	12.07/8.03	11.88/7.64	10.70/13.10
H+H <sub>2</sub> S → H <sub>2</sub> +HS	6.42/16.36	7.18/20.71	6.32/15.59	4.28/15.00	4.42/15.89	3.84/14.29	3.60/17.30
MAD	6.17	6.95	6.40	2.94	3.01	2.83	