Correction to "Electronic Couplings for Charge Transfer across Molecule/Metal and Molecule/Semiconductor Interfaces: Performance of the Projector Operator-Based Diabatization Approach"

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POD electronic coupling values computed at hybrid-functional DFT level for He_2^+ (Table 1 in Ref. 1), Zn_2^+ (Table 2 in Ref. 1) and the HAB11 database (Table 3 in Ref. 1) are incorrect. The apparent "cluster boundary" calculations for B3LYP, PBE0, and PBE50, as described in the original manuscript, were erroneously carried out in periodic boundary conditions (PBC) where the long-range Hartree-Fock exchange (HFX) was screened using a large range-separation parameter $\omega = 14$ Bohr^{-1}. As a result, the global-hybrid functionals were in fact described as strongly-screened range-separated hybrid functionals with only a fraction of GGA exchange in the longe-range region (beyond ~0.07 Bohr) where the HFX, mixed with GGA exchange in the short-range, was attenuated. This incorrect setup yielded the values listed in the published article.

Recently, we have re-investigated the POD couplings on HAB7$^-$, HAB11, and new HAB79 datasets using the neutral-dimer approach in cluster boundary conditions.[2] Range-separated hybrid (RSH) functionals such as LRC-wPBEh and wB97X with mixed GGA and HF exchange in the short-range and pure HF in the long-range are the most accurate providing mean relative unsigned error ~5%. The corrected POD electronic coupling values for He_2^+, Zn_2^+, and HAB11 in cluster boundary conditions are summarized in Tables 1–3. Here, results are reported for a more diverse set of functionals than in the original publication, including GGA, hybrid, and range-separated hybrid functionals HSE06, LRC-wPBEh, and wB97X. The couplings reported here for GGA functionals differ somewhat from those reported in the original publication. This is because all calculations presented herein were carried out for charge-neutral dimers, consistent with the approach taken in Ref. 2, whereas previous calculations were carried out for dimers with a net charge of +1.

Table 1: POD Electronic Coupling $|H_{ab}|$ Values [meV] for He_2^+ Dimer Electron Self-Exchange and the Decay Rate Parameters β [Å^{-1}] Fitted to the $|H_{ab}| = Ae^{-\beta d/2}$ Function[a]

d[Å]	PBE	PBE0	HSE06	LRC-wPBEh	BLYP	B3LYP	wB97X	Ref[b]
2.5	168.59	171.99	171.31	180.49	168.17	172.36	185.40	195.93
3.0	56.30	55.64	55.24	60.15	55.86	55.98	60.72	60.81
4.0	6.05	5.56	5.47	6.34	5.97	5.65	6.08	5.52
4.5	0.57	0.50	0.48	0.57	0.57	0.51	0.51	0.44
β [Å^{-1}]	4.55	4.68	4.70	4.60	4.55	4.65	4.71	4.88

[a]The values are for coupling between the block-diagonalized HOMO-HOMO orbitals on charge-neutral dimers of donor and acceptor atoms. The all-electron wavefunctions were computed in Ahlrichs-def2-QZVP basis set. [b]FCI values from Ref 3.

Table 2: Electronic Coupling $|H_{ab}|$ Values [meV] for the Zn_2^+ Dimer Electron Self-Exchange and the Decay Rate Parameters β [Å^{-1}] Fitted to the $|H_{ab}| = Ae^{-\beta d/2}$ Function[a]

d[Å]	PBE	PBE0	HSE06	LRC-wPBEh	BLYP	B3LYP	wB97X	Ref[b]
5.0	73.3	84.7	80.1	107.0	70.1	79.6	121.0	173.7
6.0	22.6	25.3	23.6	32.1	21.7	24.2	34.7	56.0
7.0	6.5	7.1	6.5	8.8	6.4	6.9	8.8	15.5
β [Å^{-1}]	2.43	2.48	2.51	2.49	2.40	2.44	2.62	2.42

[a]The values are calculated as HOMO-HOMO coupling on neutral dimers using GTH pseudopotential for 18 core electrons and reoptimized TZVP-type basis set. [b]CASSCF(3,8)/aug-cc-pVTZ values from Ref. 3.

Table 3: Electronic Coupling H_{ab} Values [meV] for Organic-Dimer HAB11 Database Molecules and the Decay Rate Constants β [Å^{-1}] Fitted to the $H_{ab} = Ae^{-\beta d/2}$ Expression.[a]

dimer	d[Å]	PBE	PBE0	HSE06	LRC-wPBEh	BLYP	B3LYP	wB97X	Ref
ethylene	3.5	371.7	413.7	411.4	446.8	374.9	410.1	486.4	519.2[b]
	4.0	186.3	207.3	204.9	228.5	190.7	209.1	256.8	270.8[b]
	4.5	94.6	104.6	102.9	117.8	97.7	106.9	133.0	137.6[b]
	5.0	48.1	52.6	51.5	60.4	49.7	54.2	67.0	68.5[b]
	β [Å^{-1}]	2.72	2.75	2.77	2.67	2.69	2.70	2.64	2.70
acetylene	3.5	333.8	368.6	366.5	397.0	335.9	365.3	432.7	460.7[b]
	4.0	162.2	178.2	176.1	195.9	165.3	179.6	219.2	231.8[b]
	4.5	79.6	86.4	85.2	97.2	81.5	88.2	108.4	114.8[b]
	5.0	39.2	41.9	41.1	48.2	40.0	43.0	52.5	56.6[b]
	β [Å^{-1}]	2.86	2.90	2.92	2.81	2.83	2.85	2.81	2.80
cyclopropene	3.5	392.5	428.6	426.4	458.5	390.9	421.5	488.0	536.6[b]
	4.0	184.6	200.1	198.2	216.9	186.3	200.3	236.6	254.0[b]
	4.5	86.5	92.8	91.6	102.2	88.1	94.3	111.0	118.4[b]
	5.0	40.6	43.0	42.3	48.1	41.5	44.1	50.9	54.0[b]
	β [Å^{-1}]	3.03	3.07	3.08	3.01	2.99	3.01	3.01	3.06
cyclobutadiene	3.5	323.8	361.5	359.8	386.9	325.6	357.2	417.0	462.7[b]
	4.0	160.4	179.1	177.2	195.0	163.7	180.2	216.8	239.1[b]
	4.5	81.1	90.1	88.8	99.8	83.5	91.9	111.1	121.7[b]
	5.0	41.4	45.6	44.8	51.4	42.7	46.8	55.9	62.6[b]
	β [Å^{-1}]	2.74	2.76	2.78	2.69	2.71	2.71	2.28	2.67
cyclopentadiene	3.5	332.6	371.0	369.6	397.8	334.9	366.9	429.9	465.8[b]
	4.0	162.3	181.2	179.3	197.6	166.1	182.6	221.9	234.4[b]
	4.5	80.8	89.7	88.5	99.5	83.4	91.7	112.7	114.3[b]
	5.0	40.5	44.6	43.8	50.3	41.8	45.9	55.9	53.4[b]
	β [Å^{-1}]	2.80	2.82	2.84	2.76	2.77	2.77	2.72	2.89
furane	3.5	312.9	348.5	346.9	373.1	314.0	344.0	404.0	440.3[b]
	4.0	149.8	166.7	165.0	181.5	152.4	167.4	202.6	214.9[b]
	4.5	72.8	80.5	79.5	89.2	74.6	81.8	99.5	101.8[b]
	5.0	35.6	39.0	38.3	44.0	36.4	39.8	47.9	46.0[b]
	β [Å^{-1}]	2.90	2.92	2.94	2.85	2.87	2.87	2.84	3.01
pyrrole	3.5	324.1	361.3	359.8	387.8	325.2	356.4	419.3	456.3[b]
	4.0	158.3	176.4	174.5	192.6	161.2	177.2	215.8	228.6[b]
	4.5	78.7	87.2	86.0	96.9	80.7	88.7	109.2	111.3[b]
	5.0	39.4	43.2	42.5	48.9	40.3	44.2	54.1	52.2[b]
	β [Å^{-1}]	2.81	2.83	2.85	2.76	2.78	2.78	2.73	2.89
thiophene	3.5	333.7	371.9	370.5	398.9	334.4	366.2	429.4	449.0[c]
	4.0	159.6	177.9	176.0	194.1	162.6	178.6	217.4	218.9[c]
	4.5	77.6	85.9	84.8	95.5	79.7	87.5	108.0	106.5[c]
	5.0	38.0	41.7	41.0	47.1	38.9	42.7	52.3	54.4[c]
	β [Å^{-1}]	2.90	2.92	2.93	2.85	2.87	2.86	2.81	2.82
imidazole	3.5	308.0	342.7	341.1	367.2	309.6	338.9	398.1	411.6[c]
	4.0	147.9	164.4	162.7	179.2	150.8	165.4	200.1	202.6[c]
	4.5	72.2	79.7	78.7	88.4	74.0	81.1	98.6	99.1[c]
	5.0	35.4	38.7	38.1	43.7	36.2	39.6	47.6	49.7[c]
	β [Å^{-1}]	2.88	2.91	2.92	2.84	2.86	2.86	2.83	2.82
benzene	3.5	328.2	366.9	365.6	394.0	331.6	363.7	429.5	435.2[c]
	4.0	156.1	174.8	173.0	191.0	160.5	176.7	216.9	214.3[c]
	4.5	75.6	84.3	83.2	93.8	78.4	86.4	107.5	104.0[c]
	5.0	36.7	40.6	40.0	46.0	38.0	41.9	51.9	51.7[c]
	β [Å^{-1}]	2.92	2.93	2.95	2.86	2.89	2.88	2.82	2.85
phenol	3.5	254.4	293.5	292.4	313.3	258.1	290.2	341.8	375.0[c]
	4.0	115.6	134.1	132.8	145.7	119.3	135.2	165.7	179.6[c]
	4.5	53.6	62.3	61.5	68.9	55.8	63.6	79.0	85.2[c]
	5.0	25.0	29.1	28.6	32.7	25.9	29.7	36.8	41.3[c]
	β [Å^{-1}]	3.09	3.08	3.10	3.01	3.06	3.04	2.97	2.95

[a]The values are calculated as HOMO-HOMO coupling on neutral dimers using GTH pseudopotentials for core electrons and TZV2P basis set. [b] MRCI+Q values from Ref. 4. [c] NEVPT2 values from Ref. 4.

References

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