Electronic Supplementary Material (ESI) for Chemical Society Reviews.

Supporting Information

Energy Term (kcal/mol)	H_2O H_2O	H_2O MeOH	MeOH MeOH	H_2O H_3N	H_2O H_4N^+	H_2O Li^+	H_2O Na^+	H_2O K^+
ALMO EDA								
FRZ (ALMO)	-1.99	-0.10	0.21	-2.35	-12.84	-31.01	-23.34	-16.39
POL (ALMO)	-0.82	-0.98	-1.19	-1.60	-5.38	-7.22	-4.04	-2.63
CT (ALMO)	-5.93	-7.45	-7.10	-5.62	-10.02	-5.74	-4.48	-4.28
CT+BSSE (ALMO)	-2.11	-2.49	-2.77	-2.33	-7.20	-0.91	-0.87	-1.55
ΔE(BLYP)	-4.92	-3.57	-3.75	-6.28	-25.43	-39.14	-28.24	-20.56
DISP$^{(a)}$	-0.95	-1.96	-2.56	-1.16	-1.21	-0.10	-0.38	-0.63
ΔE(BLYP-D3)	-5.87	-5.53	-6.31	-7.44	-26.64	-39.23	-28.62	-21.19
NEDA								
ES (NEDA)	-12.04	-11.68	-12.20	-15.49	-31.70	-40.71	-31.74	-24.66
XC (NEDA)	-2.58	-3.17	-3.55	-3.12	-4.95	-3.73	-3.75	-3.24
POL (NEDA)	-1.08	-2.70	-4.02	-1.86	-5.07	-17.85	-15.57	-13.59
DEF (NEDA)	24.62	28.26	31.49	32.51	55.20	32.22	28.97	25.66
(SE (NEDA)$^{(b)}$)	0.51	1.37	2.01	0.93	2.67	8.97	7.82	6.89
CT (NEDA)	-13.84	-14.29	-15.49	-18.35	-38.90	-8.97	-5.89	-4.67
ΔE	-4.92	-3.58	-3.76	-6.30	-25.43	-39.04	-28.00	-20.51
POL + SE$^{(b)}$ (NEDA)	-0.57	-1.33	-2.01	-0.93	-2.40	-8.88	-7.75	-6.70
CORE (DEF + XC - SE$^{(b)}$)	21.53	23.72	25.93	28.46	47.58	19.52	17.40	15.53
EL (ES + POL + SE$^{(b)}$)	-12.61	-13.01	-14.21	-16.42	-34.10	-49.59	-39.49	-31.36

$^{(a)}$ The dispersion component DISP has been calculated as the Grimme D3 correction to the interaction energy.

$^{(b)}$ The self–energy component of NEDA does not contribute to ΔE.

Table 1: The BLYP/6-311G* level ALMO EDA and NEDA results performed on the BLYP-D3/6-311G* optimized geometries of test sets 1 and 2.

Energy Term (kcal/mol)	H_2O H_2O	H_2O MeOH	MeOH MeOH	H_2O H_3N	H_2O H_4N^+	H_2O Li^+	H_2O Na^+	H_2O K^+
SAPT(KS) DCBS								
E1(elst)	-12.04	-11.67	-12.18	-15.46	-31.74	-40.76	-32.25	-25.07
E1(exch)	13.65	14.87	15.68	18.06	25.13	16.53	11.76	10.51
E2(ind)	-6.59	-7.47	-8.12	-9.50	-17.53	-25.02	-21.47	-16.13
E2(exch-ind)	4.88	5.79	6.18	6.57	8.01	10.99	13.59	11.31
E2(disp)	-2.64	-4.01	-5.08	-3.98	-4.47	-0.58	-0.64	-2.28
E2(exch-disp)	0.84	1.16	1.30	1.27	0.91	0.09	0.21	0.53
E1 corrections	1.60	3.20	3.50	2.59	-6.61	-24.23	-20.49	-14.55
E2 corrections	-3.51	-4.52	-5.71	-5.65	-13.09	-14.52	-8.31	-6.57
SAPT(0) ΔE	-1.90	-1.32	-2.22	-3.05	-19.70	-38.75	-28.80	-21.12
SAPT(KS) MCBS								
E2(ind)$^{(a)}$	-0.99	-1.09	-1.28	-1.78	-7.34	-13.98	-7.19	-4.23
E2(exch-ind)$^{(a)}$	0.13	0.16	0.25	0.06	0.63	1.84	0.74	0.23
POL+EXCH (SAPT)$^{(a)}$	-0.85	-0.93	-1.03	-1.71	-6.72	-12.13	-6.45	-4.00
CT (SAPT)$^{(a)}$	-5.60	-6.38	-6.84	-7.73	-10.19	-11.04	-14.27	-11.90
CT EXCH (SAPT)$^{(a)}$	4.75	5.63	5.94	6.50	7.38	9.14	12.85	11.08
CT+EXCH (SAPT)$^{(a)}$	-0.85	-0.75	-0.90	-1.22	-2.81	-1.90	-1.42	-0.82

$^{(a)}$ The MCBS calculation of the 'E2(ind)' component is used as the SAPT polarization component, and the MCBS 'E2(exch-ind)' component is used as the SAPT exchange correction for polarization. The charge transfer component is calculated using these MCBS values and the equivalent DCBS values of these SAPT terms.

Table 2: The BLYP/6-311G* level DCBS and MCBS SAPT(KS) results performed on the BLYP-D3/6-311G* optimized geometries of test sets 1 and 2.

Energy Term (kcal/mol)	H_2O H_2O	H_2O MeOH	MeOH MeOH	H_2O H_3N	H_2O H_4N^+	H_2O Li^+	H_2O Na^+	H_2O K^+
KM EDA								
ES (KM)	-10.45	-9.40	-10.11	-14.84	-32.97	-44.14	-31.83	-23.66
EX (KM)	7.78	8.22	9.25	12.19	19.33	11.55	7.10	5.97
EX+BSSE (KM)	7.94	8.50	9.51	12.32	19.44	11.55	7.15	6.10
POL (KM)	-0.88	-0.95	-1.12	-1.60	-5.65	-9.37	-4.80	-2.96
CT (KM)	-2.59	-2.99	-3.06	-3.03	-6.52	-3.40	-2.06	-2.02
CT+BSSE (KM)	-1.60	-2.09	-2.22	-1.72	-5.22	-0.81	-0.24	-0.92
MIX (KM)	-0.08	-0.56	-0.52	0.15	1.38	3.29	1.52	0.83
MIX+BSSE (KM)	0.82	0.94	0.84	0.63	1.65	3.66	1.93	1.14
RVS EDA								
CEX (RVS)	-2.67	-1.17	-0.87	-2.65	-13.64	-32.59	-24.73	-17.68
POL (RVS)	-0.91	-1.04	-1.23	-1.70	-5.11	-6.61	-3.63	-2.38
CT+BSSE (RVS)[(a)]	-1.52	-2.35	-2.41	-1.41	-3.95	0.05	0.34	-0.48
MIX (RVS)	-0.02	-0.10	-0.11	-0.03	-0.33	-0.02	-0.03	-0.10
ΔE(RVS/KM)	-6.21	-5.68	-5.56	-7.13	-24.43	-42.07	-30.07	-21.84
ΔE(RVS)+BSSE(RVS)	-5.12	-4.66	-4.62	-5.79	-23.03	-39.17	-28.05	-20.64
ΔE(KM)+BSSE(KM)	-4.17	-3.01	-3.10	-5.21	-22.76	-39.12	-27.79	-20.30

[(a)] In the RVS EDA theory the charge transfer component includes a BSSE contribution implicitly. We have labelled this component 'CT+BSSE' to clarify this.

Table 3: The HF/6-311G* level KM EDA and RVS EDA results performed on the BLYP-D3/6-311G* optimized geometries of test sets 1 and 2.

Energy Term (kcal/mol)	H_4N^+ – Benzene	H_4N^+ – Thiophene	H_4N^+ – Furan	H_4N^+ – Pyrrole	Benzene – H_4N^+	Benzene – Li^+	Benzene – Na^+	Benzene – K^+
ALMO EDA								
FRZ (ALMO)	-2.62	-2.16	-1.21	-5.49	-2.62	-7.85	-9.16	-6.11
POL (ALMO)	-7.09	-6.91	-6.45	-7.67	-7.09	-20.84	-5.18	-2.83
CT (ALMO)	-6.92	-7.03	-7.21	-8.66	-6.92	-10.66	-4.13	-2.41
CT+BSSE (ALMO)	-6.30	-6.22	-6.45	-7.91	-6.30	-9.17	-3.24	-1.97
ΔE(BLYP)	-16.01	-15.28	-14.11	-21.07	-16.01	-37.87	-17.59	-10.90
DISP$^{(a)}$	-5.45	-5.12	-4.67	-4.64	-5.45	-0.32	-5.95	-7.82
ΔE(BLYP-D3)	-21.46	-20.41	-18.78	-25.72	-21.46	-38.19	-23.54	-18.72
NEDA								
ES (NEDA)	-14.38	-13.91	-12.62	-20.21	-14.38	-16.65	-10.35	-6.94
XC (NEDA)	-5.47	-5.18	-4.69	-5.49	-5.47	-5.01	-0.18	-0.22
POL (NEDA)	-18.03	-16.82	-14.12	-14.65	-18.03	-34.94	-8.65	-10.00
DEF (NEDA)	34.01	34.03	31.89	38.01	34.01	40.55	6.85	7.34
(SE (NEDA)$^{(b)}$)	9.14	8.52	7.13	7.43	9.14	17.58	4.34	5.03
CT (NEDA)	-12.33	-13.77	-14.70	-18.89	-12.33	-22.07	-5.36	-1.17
ΔE(BLYP)	-16.20	-15.64	-14.24	-21.22	-16.20	-38.12	-17.69	-10.98
POL + SE$^{(b)}$ (NEDA)	-8.89	-8.30	-6.99	-7.22	-8.89	-17.36	-4.31	-4.97
CORE (DEF + XC - SE$^{(b)}$)	19.40	20.33	20.07	25.09	19.40	17.96	2.33	2.09
EL (ES + POL + SE$^{(b)}$)	-23.27	-22.21	-19.61	-27.43	-23.27	-34.01	-14.66	-11.91

$^{(a)}$ The dispersion component DISP has been calculated as the Grimme D3 correction to the interaction energy.
$^{(b)}$ The self–energy component of NEDA does not contribute to ΔE.

Table 4: The BLYP/6-311G* level ALMO EDA and NEDA results performed on the BLYP–D3/6-311G* optimized geometries of test sets 3 and 4.

Energy Term (kcal/mol)	H_4N^+ – Benzene	H_4N^+ – Thiophene	H_4N^+ – Furan	H_4N^+ – Pyrrole	Benzene – H_4N^+	Benzene – Li^+	Benzene – Na^+	Benzene – K^+
SAPT(KS) DCBS								
E1(elst)	-14.39	-13.66	-12.65	-20.24	-14.39	-16.65	-10.41	-7.58
E1(exch)	13.34	13.38	12.96	16.66	13.34	12.66	0.91	0.61
E2(ind)	-19.03	-19.09	-16.92	-21.62	-19.03	-54.58	-11.93	-6.09
E2(exch-ind)	5.86	5.93	5.58	8.20	5.86	11.16	1.30	0.68
E2(disp)	-7.39	-7.09	-6.68	-7.79	-7.39	-1.06	-0.33	-1.25
E2(exch-disp)	0.83	0.80	0.75	1.03	0.83	0.08	0.02	0.04
E1 corrections	-1.05	-0.28	0.31	-3.58	-1.05	-3.99	-9.49	-6.97
E2 corrections	-19.73	-19.45	-17.27	-20.18	-19.73	-44.40	-10.95	-6.62
SAPT(0) ΔE	-20.78	-19.72	-16.96	-23.77	-20.78	-48.39	-20.44	-13.59
SAPT(KS) MCBS								
E2(ind)$^{(a)}$	-12.03	-12.30	-11.10	-13.20	-12.03	-38.90	-8.60	-4.69
E2(exch-ind)$^{(a)}$	0.62	0.93	0.98	1.32	0.62	2.87	0.04	0.00
POL+EXCH (SAPT)$^{(a)}$	-11.41	-11.38	-10.12	-11.88	-11.41	-36.03	-8.57	-4.69
CT (SAPT)$^{(a)}$	-7.00	-6.79	-5.82	-8.42	-7.00	-15.68	-3.33	-1.40
CT EXCH (SAPT)$^{(a)}$	5.24	5.01	4.60	6.88	5.24	8.29	1.26	0.68
CT+EXCH (SAPT)$^{(a)}$	-1.76	-1.78	-1.22	-1.54	-1.76	-7.39	-2.07	-0.72

$^{(a)}$ The MCBS calculation of the 'E2(ind)' component is used as the SAPT polarization component, and the MCBS 'E2(exch-ind)' component is used as the SAPT exchange correction for polarization. The charge transfer component is calculated using these MCBS values and the equivalent DCBS values of these SAPT terms.

Table 5: The BLYP/6-311G* level DCBS and MCBS SAPT(KS) results performed on the BLYP-D3/6-311G* optimized geometries of test sets 3 and 4.

Energy Term (kcal/mol)	H_4N^+ – Benzene	H_4N^+ – Thiophene	H_4N^+ – Furan	H_4N^+ – Pyrrole	Benzene – H_4N^+	Benzene – Li^+			Benzene – Na^+	Benzene – K^+
	6-311G*	6-311G*	6-311G*	6-311G*	6-311G*	BS1[a,b]	6-311G [a]	6-311G* [a]	6-311G*	6-311G*
KM EDA										
ES (KM)	-16.19	-15.00	-13.51	-21.78	-16.19	-22.61	-20.13	-22.61	-11.80	-8.41
EX (KM)	12.02	12.01	11.39	15.20	12.02	12.55	12.43	12.55	0.51	0.44
EX+BSSE (KM)	12.12	12.13	11.48	15.30	12.12	12.57	12.45	12.57	0.52	0.45
POL (KM)	-8.34	-8.05	-7.97	-9.96	-8.34	-25.86	-22.56	-410.54	-5.53	-4.70
CT (KM)	-5.57	-5.40	-5.66	-6.67	-5.57	-15.39	-15.34	-18.47	-4.59	-1.21
CT+BSSE (KM)	-5.26	-5.07	-5.29	-6.33	-5.26	-14.90	-14.86	-17.80	-4.10	-1.17
MIX (KM)	2.42	2.40	2.91	3.53	2.42	11.51	9.86	397.97	1.64	1.47
MIX+BSSE (KM)	2.62	2.68	3.13	3.76	2.62	11.79	10.23	398.24	1.80	1.51
RVS EDA										
CEX (RVS)	-4.17	-2.98	-2.12	-6.58	-4.17	-10.06	-7.70	-10.06	-11.29	-7.97
POL (RVS)	-7.16	-6.76	-6.33	-7.53	-7.16	-21.36	-18.33	-21.36	-5.45	-4.07
CT+BSSE (RVS)[c]	-3.68	-3.65	-3.73	-4.74	-3.68	-7.69	-9.02	-8.81	-2.45	-0.25
MIX (RVS)	-0.32	-0.29	-0.26	-0.44	-0.32	-0.01	0.00	-0.02	-0.01	-0.07
ΔE(RVS/KM)	-15.67	-14.04	-12.85	-19.67	-15.67	-39.80	-35.74	-41.09	-19.76	-12.40
ΔE(RVS)+BSSE(RVS)	-15.33	-13.68	-12.44	-19.29	-15.33	-39.12	-35.05	-40.25	-19.20	-12.36
ΔE(KM)+BSSE(KM)	-15.05	-13.32	-12.16	-19.01	-15.05	-39.01	-34.86	-40.15	-19.11	-12.32

[a] The geometry used for this calculation was obtained at the BLYP–D3/6-311G* level.

[b] The basis set BS1 is the 6-311G* basis set excluding d polarization function augmentation on lithium.

[c] In the RVS EDA theory the charge transfer component includes a BSSE contribution implicitly. We have labelled this component 'CT+BSSE' to clarify this.

Table 6: The HF/6-311G* level KM EDA and RVS EDA results performed on the BLYP-D3/6-311G* optimized geometries of test sets 3 and 4.

Energy Term (kcal/mol)	Benzene – T-shaped	Benzene – Parallel displaced	Benzene – Pyridine	Benzene – Pyrimidine	Benzene – DMA[a]	Benzene – Fluorobenzene	Benzene – Chlorobenzene	Benzene – Bromobenzene
ALMO EDA								
FRZ (ALMO)	2.11	5.30	4.88	4.23	4.25	2.49	2.44	2.30
POL (ALMO)	-0.15	-0.24	-0.23	-0.22	-0.42	-0.12	-0.10	-0.11
CT (ALMO)	-1.09	-1.44	-1.69	-1.87	-2.53	-1.27	-0.64	-0.85
CT+BSSE (ALMO)	-0.20	-0.11	-0.14	-0.21	-0.80	0.33	-0.27	-0.34
ΔE(BLYP)	1.76	4.94	4.51	3.80	3.04	2.70	2.08	1.85
DISP[b]	-4.82	-7.30	-7.58	-7.72	-8.98	-2.54	-3.50	-4.15
ΔE(BLYP-D3)	-3.06	-2.36	-3.07	-3.91	-5.94	0.15	-1.42	-2.30
NEDA								
ES (NEDA)	-2.18	-2.57	-3.47	-4.21	-5.60	0.19	-0.82	-1.50
XC (NEDA)	-2.46	-4.85	-5.19	-5.25	-4.92	-1.38	-1.53	-1.70
POL (NEDA)	-4.82	-11.91	-12.75	-13.08	-10.86	-2.41	-4.36	-5.74
DEF (NEDA)	14.13	29.12	31.52	32.47	31.44	7.69	10.02	12.23
(SE (NEDA)[c])	2.43	5.96	6.39	6.56	5.45	1.19	2.17	2.87
CT (NEDA)	-2.93	-4.85	-5.59	-6.11	-7.01	-1.42	-1.23	-1.44
ΔE(BLYP)	1.74	4.94	4.51	3.81	3.05	2.66	2.08	1.85
POL + SE[c] (NEDA)	-2.39	-5.95	-6.36	-6.52	-5.41	-1.22	-2.19	-2.87
CORE (DEF + XC - SE[c])	9.24	18.31	19.94	20.66	21.07	5.12	6.32	7.66
EL (ES + POL + SE[c])	-4.57	-8.52	-9.83	-10.73	-11.01	-1.03	-3.01	-4.37

[a] DMA is dimethylacetam*i.e.*

[b] The dispersion component DISP has been calculated as the Grimme D3 correction to the interaction energy.

[c] The self–energy component of NEDA does not contribute to ΔE.

Table 7: The BLYP/6-311G* level ALMO EDA and NEDA results performed on the BLYP-D3/6-311G* optimized geometries of test sets 5 and 6.

Energy Term (kcal/mol)	Benzene – T-shaped	Benzene – Parallel displaced	Benzene – Pyridine	Benzene – Pyrimidine	Benzene – DMA[a]	Benzene – Fluorobenzene	Benzene – Chlorobenzene	Benzene – Bromobenzene
SAPT(KS) DCBS								
E1(elst)	-2.18	-2.60	-3.51	-4.25	-5.63	0.20	-0.91	-1.50
E1(exch)	4.96	8.46	9.15	9.33	10.94	3.28	3.43	3.92
E2(ind)	-1.55	-4.26	-4.59	-4.77	-5.12	-1.16	-1.60	-2.51
E2(exch-ind)	1.32	3.90	4.29	4.48	4.58	0.97	1.42	2.26
E2(disp)	-7.25	-13.41	-14.06	-14.22	-13.97	-3.70	-4.69	-5.81
E2(exch-disp)	0.86	2.00	2.05	2.01	1.93	0.39	0.56	0.69
E1 corrections	2.78	5.86	5.65	5.08	5.32	3.48	2.52	2.42
E2 corrections	-6.62	-11.78	-12.31	-12.49	-12.57	-3.49	-4.31	-5.36
SAPT(0) ΔE	-3.84	-5.92	-6.66	-7.41	-7.26	-0.02	-1.79	-2.94
SAPT(KS) MCBS								
E2(ind)[b]	-0.24	-0.41	-0.34	-0.30	-0.56	-0.18	-0.14	-0.17
E2(exch-ind)[b]	0.06	0.04	0.03	0.03	0.09	0.01	0.00	0.00
POL+EXCH (SAPT)[b]	-0.18	-0.37	-0.31	-0.27	-0.47	-0.18	-0.13	-0.17
CT (SAPT)[b]	-1.31	-3.85	-4.25	-4.47	-4.56	-0.97	-1.46	-2.34
CT EXCH (SAPT)[b]	1.26	3.86	4.25	4.45	4.50	0.97	1.42	2.26
CT+EXCH (SAPT)[b]	-0.05	0.01	0.00	-0.01	-0.07	-0.01	-0.05	-0.08

[a] DMA is dimethylacetam*i.e.*

[b] The MCBS calculation of the 'E2(ind)' component is used as the SAPT polarization component, and the MCBS 'E2(exch-ind)' component is used as the SAPT exchange correction for polarization. The charge transfer component is calculated using these MCBS values and the equivalent DCBS values of these SAPT terms.

Table 8: The BLYP/6-311G* level DCBS and MCBS SAPT(KS) results performed on the BLYP–D3/6-311G* optimized geometries of test sets 5 and 6.

Energy Term (kcal/mol)	Benzene – T-shaped	Benzene – Parallel displaced	Benzene – Pyridine	Benzene – Pyrimidine	Benzene – DMA[a]	Benzene – Fluorobenzene	Benzene – Chlorobenzene	Benzene – Bromobenzene
KM EDA								
ES (KM)	-1.79	-0.73	-1.76	-2.67	-4.38	1.29	-0.11	-0.84
EX (KM)	3.46	6.17	6.79	6.96	7.49	1.94	2.45	2.94
EX+BSSE (KM)	3.56	6.53	7.15	7.30	7.73	2.08	2.54	3.04
POL (KM)	-0.20	-0.29	-0.25	-0.24	-0.50	-0.16	-0.11	-0.13
CT (KM)	-0.73	-1.40	-1.56	-1.67	-1.68	-0.80	-0.46	-0.54
CT+BSSE (KM)	-0.48	-0.93	-1.04	-1.13	-1.09	-0.33	-0.31	-0.41
MIX (KM)	0.07	0.17	0.15	0.16	0.09	0.03	0.04	0.08
MIX+BSSE (KM)	0.31	0.58	0.57	0.59	0.61	0.40	0.20	0.23
RVS EDA								
CEX (RVS)	1.67	5.44	5.04	4.29	3.10	3.23	2.35	2.10
POL (RVS)	-0.19	-0.34	-0.30	-0.27	-0.46	-0.21	-0.14	-0.15
CT+BSSE (RVS)[b]	-0.37	-0.69	-0.79	-0.88	-0.90	-0.25	-0.23	-0.30
MIX (RVS)	-0.02	0.02	-0.01	-0.02	-0.06	0.02	0.01	0.01
ΔE(RVS/KM)	0.81	3.93	3.38	2.53	1.01	2.31	1.82	1.51
ΔE(RVS)+BSSE(RVS)	1.09	4.43	3.94	3.12	1.68	2.79	1.99	1.66
ΔE(KM)+BSSE(KM)	1.40	5.17	4.67	3.86	2.38	3.29	2.21	1.88

[a] DMA is dimethylacetamide.

[b] In the RVS EDA theory the charge transfer component includes a BSSE contribution implicitly. We have labelled this component 'CT+BSSE' to clarify this.

Table 9: The HF/6-311G* level KM EDA and RVS EDA results performed on the BLYP-D3/6-311G* optimized geometries of test sets 5 and 6.