Electronic Supplementary Information

Intrinsic Dynamic and Static Nature of Each HB in the Multi-HBs between Nucleobase Pairs and its Behavior, Elucidated with QTAIM Dual Functional Analysis and QC Calculations

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Table S1. The interaction for multi-HB in Nu-Nu′ distances r_o(X, Y), evaluated with various methods.

AH-*-B in Nu-Nu′ (Symmetry: No)	r_o(X, Y)/(Å) MP2/BSS-A′ [a]	r_o(X, Y)/(Å) MP2/BSS-B′a [b]	r_o(X, Y)/(Å) MP2/BSS-B′b [c]	r_o(X, Y)/(Å) M06-2X/BSS-A [d]	r_o(X, Y)/(Å) M06-2X/BSS-C [e]	r_o(X, Y)/(Å) M06-2X/BSS-D [f]
N-*-HN in A-T (C_1: **1**)	1.7602	1.7527	1.7493	1.7775	1.7792	1.7765
NH-*-O in A-T (C_1: **2**)	1.8932	1.8861	1.8770	1.9343	1.9384	1.9372
CH-*-O in A-T (C_1: **3**)	2.7316	2.7138	2.7129	2.7452	2.7443	2.7441
NH-*-N in A-T (C_s: **4**)	1.7602	1.7527	1.7493	1.7741	1.7759	1.7736
NH-*-O in A-T (C_s: **5**)	1.8932	1.8861	1.8770	1.9367	1.9402	1.9382
CH-*-O in A-T (C_s: **6**)	2.7316	2.7138	2.7130	2.7357	2.7359	2.7376
NH-*-O in C-G (C_1: **7**)	1.7189	1.7104	1.7041	1.7490	1.7616	1.7625
N-*-HN in C-G (C_1: **8**)	1.8706	1.8677	1.8643	1.9020	1.9103	1.9073
O-*-HN in C-G (C_1: **9**)	1.8780	1.8687	1.8614	1.9017	1.9066	1.9102
NH-*-N in A-A (C_1: **10**)	1.9814	1.9722	1.9664	2.0308	2.0368	2.0347
CH-*-N in A-A (C_1: **11**)	2.4555	2.4455	2.4412	2.4942	2.4943	2.4956
N-*-HN in A-C (C_1: **12**)	1.8485	1.8451	1.8406	1.9124	1.9199	1.9172
NH-*-O in A-C (C_1: **13**)	1.7907	1.7823	1.7731	1.8261	1.8335	1.8372
N-*-HN in A-G (C_1: **14**)	1.8302	1.8241	1.8192	1.8793	1.8873	1.8769
NH-*-O in A-G (C_1: **15**)	1.8092	1.8019	1.7959	1.8520	1.8604	1.8624
CH-*-HN in A-G (C_1: **16**)	2.3914	2.3822	2.3798	2.3888	2.3893	2.4124
N-*-HN in A-U (C_1: **17**)	1.7579	1.7508	1.7472	1.7699	1.7713	1.7692
NH-*-O in A-U (C_1: **18**)	1.8952	1.8880	1.8796	1.9353	1.9390	1.9370
CH-*-O in A-U (C_1: **19**)	2.7262	2.7094	2.7076	2.7321	2.7315	2.7335
NH-*-N in C-C (C_1: **20**)	1.7613	1.7559	1.7522	1.7953	1.8008	1.7967
O-*-HN in C-C (C_1: **21**)	1.7432	1.7371	1.7270	1.7748	1.7868	1.7894
CH-*-O in C-C (C_1: **22**)	2.8352	2.8195	2.8203	2.8769	2.8763	2.8704
N-*-HN in C-T (C_1: **23**)	1.8406	1.8292	1.8292	1.9205	1.9309	1.9270
NH-*-O in C-T (C_1: **24**)	1.8204	1.8152	1.8059	1.8559	1.8629	1.8631
O-*-O in C-T (C_1: **25**)	3.5797	3.5675	3.5725	3.6389	3.6451	3.6532
N-*-HN in C-U (C_1: **26**)	1.8364	1.8258	1.8255	1.9091	1.9212	1.9172
NH-*-O in C-U (C_1: **27**)	1.8213	1.8159	1.8072	1.8521	1.8593	1.8591
O-*-O in C-U (C_1: **28**)	3.5543	3.5419	3.5456	3.6239	3.6285	3.6382
NH-*-O G-G (C_i: **29**)	1.6928	1.6888	1.6825	1.7240	1.7378	1.7344
O-*-HN G-G (C_i: **30**)	2.4331	2.4270	2.4259	2.4119	2.4150	2.4211
N-*-HN in G-T (C_1: **31**)	1.8277	1.8194	1.8164	1.8884	1.8964	1.9006
NH-*-O in G-T (C_1: **32**)	1.8359	1.8310	1.8218	1.8547	1.8622	1.8665
NH-*-O in G-U (C_1: **33**)	1.7486	1.7440	1.7353	1.7785	1.7882	1.7858
O-*-HN in G-U (C_1: **34**)	1.7607	1.7544	1.7468	1.8098	1.8222	1.8203
NH-*-O in T-T (C_1: **35**)	1.7857	1.7788	1.7723	1.8377	1.8450	1.8423
O-*-HN in T-T (C_1: **36**)	1.7857	1.7788	1.7724	1.8377	1.8450	1.8423
NH-*-O in T-T ([g]: **37**)	1.7858	1.7788	1.7722	1.8409	1.8483	1.8454
NH-*-O in T-U (C_1: **38**)	1.7783	1.7718	1.7649	1.8315	1.8392	1.8368
O-*-HN in T-U (C_1: **39**)	1.7940	1.7871	1.7809	1.8419	1.8488	1.8464
NH-*-O in U-U (C_1: **40**)	1.7863	1.7798	1.7733	1.8524	1.8584	1.8566
O-*-HN in U-U (C_1: **41**)	1.7863	1.7798	1.7733	1.8501	1.8561	1.8541
NH-*-O in U-U (C_s: **42**)	1.7863	1.7798	1.7733	1.8511	1.8567	1.8549
O-*-HN in U-U (C_s: **43**)	1.7863	1.7798	1.7733	1.8460	1.8526	1.8514

[a] BSS-A′: 6-311+G(3df,3pd). [b] BSS-B′a: 6-311+G(3df,3pd) for O, N, H, and 6-311+G(3d) for C. [c] BSS-B′b: 6-311+G(3df,3pd) for O, N, H, and 6-311+G(d) for C. [d] BSS-A: 6-311++G(3df,3pd). [e] BSS-C: 6-311++G(3df,3p). [f] 6-311++G(3d,3p). [g] The higher symmetry for T-T calculated with MP2/BSS-A′, MP2/BSS-B′a, MP2/BSS-B′b, M06-2X/BSS-A, M06-2X/BSS-C, and M06-2X/BSS-D are C_s, C_i, C_s, C_{2h}, C_{2h}, C_{2h} and C_{2h}, respectively.

Table S2. The ΔE_{ES} (kJ mol^{-1}) and ΔE_{ZP} (kJ mol^{-1}) values for Nu-Nu′, evaluated with various methods.

Compds (Symm)	ΔE_{ES}[a] MP2/BSS-A′[b]	ΔE_{ES}[a] MP2/BSS-B′a[c]	ΔE_{ZP}[a]	ΔE_{ES}[a] MP2/BSS-B′b[d]	ΔE_{ZP}[a]	ΔE_{ES}[a] M06-2X/BSS-A[e]	ΔE_{ZP}[a]	ΔE_{ES}[a] M06-2X/BSS-C[f]	ΔE_{ZP}[a]	ΔE_{ES}[a] M06-2X/BSS-D[g]	ΔE_{ZP}[a]
A-T (C_1)	–68.4	–70.3	–66.5	–71.3	–67.6	–58.9	–54.9	–58.7	–53.7	–58.8	–54.5
A-T (C_s)	–68.4	–70.3	–66.5	–71.3	–67.6	–59.1	–54.9	–58.9	–53.7	–59.0	–54.5
C-G (C_1)	–121.4	–123.5	–117.2	–125.0	–118.6	–113.6	–108.7	–113.3	–108.2	–112.3	–107.7
A-U (C_1)	–68.7	–70.6	–66.6	–71.4	–67.6	–59.6	–56.4	–59.4	–56.0	–59.5	–56.5
A-A (C_1)	–34.1	–35.4	–32.1	–35.8	–32.8	–26.6	–22.8	–26.5	–22.8	–26.7	–23.4
A-C (C_1)	–71.2	–73.1	–68.4	–74.2	–69.6	–60.1	–55.7	–59.9	–55.5	–59.8	–55.5
A-G (C_1)	–78.8	–80.5	–75.5	–81.2	–76.4	–68.7	–63.2	–68.5	–63.0	–68.7	–64.1
C-C (C_1)	–100.7	–102.6	–96.6	–104.2	–98.4	–91.3	–86.2	–90.9	–85.8	–91.1	–86.1
C-T (C_1)	–62.2	–64.0	–60.2	–64.8	–61.2	–52.7	–48.3	–52.5	–47.1	–52.6	–47.7
C-U (C_1)	–63.1	–64.9	–60.9	–65.5	–61.8	–54.0	–50.4	–53.8	–50.0	–53.9	–50.5
G-G (C_i)	–115.3	–117.1	–112.7	–118.3	–113.7	–109.4	–106.7	–108.8	–106.2	–107.8	–104.9
G-T (C_1)	–63.6	–65.4	–62.6	–66.3	–63.5	–54.9	–52.3	–54.7	–51.2	–54.0	–50.7
G-U (C_1)	–72.8	–74.2	–70.4	–75.4	–71.5	–65.1	–61.7	–64.9	–61.3	–64.9	–61.4
T-T (C_1)	–58.5	–60.0	–56.3	–61.6	–57.7	–50.1	–47.3	–50.0	–45.3	–50.3	–45.8
T-T (*h*)	–58.7	–60.0	–56.3	–61.6	–57.7	–50.0	–48.1	–50.0	–46.1	–50.2	–46.6
T-U (C_1)	–58.5	–59.9	–56.2	–61.2	–57.3	–50.8	–47.9	–50.7	–46.7	–51.0	–47.0
U-U (C_1)	–58.4	–59.8	–55.9	–60.8	–56.9	–49.3	–46.6	–49.3	–46.2	–49.5	–46.4
U-U (C_s)	–58.4	–59.8	–55.9	–60.8	–56.9	–49.5	–46.5	–49.4	–46.1	–49.6	–46.3

[a] The units of ΔE_{ES} and ΔE_{ZP} are given in kJ mol^{-1}. [b] BSS-A′: 6-311+G(3df,3pd). [c] BSS-B′a: 6-311+G(3df,3pd) for O, N, H, and 6-311+G(3d) for C. [d] BSS-B′b: 6-311+G(3df,3pd) for O, N, H, and 6-311+G(d) for C. [e] BSS-A: 6-311++G(3df,3pd). [f] BSS-C: 6-311++G(3df,3p). [g]6-311++G(3d,3p). [h] The higher symmetry for T-T calculated with MP2/BSS-A′, MP2/BSS-B′a, MP2/BSS-B′b, M06-2X/BSS-A, M06-2X/BSS-C, and M06-2X/BSS-D are C_s, C_i, C_s, C_{2h}, C_{2h}, C_{2h} and C_{2h}, respectively.

Table S3. The lengths of bond paths (r_{BP}) and the corresponding straight-line distances (R_{SL}) in each HB for Nu-Nu′, Evaluated with MP2/BSS-B′a.

AH-∗-B in Nu-Nu′ (symmetry: No.)	r_{BP}[a] (Å)	R_{SL}[b] (Å)	Δr[c] (Å)
N-∗-HN in A-T (C_1: **1**)	1.7785	1.7527	0.0258
NH-∗-O in A-T (C_1: **2**)	1.9156	1.8861	0.0295
CH-∗-O in A-T (C_1: **3**)	2.7494	2.7138	0.0356
NH-∗-N in A-T (C_s: **4**)	1.7785	1.7527	0.0258
NH-∗-O in A-T (C_s: **5**)	1.9156	1.8861	0.0295
CH-∗-O in A-T (C_s: **6**)	2.7495	2.7138	0.0357
NH-∗-O in C-G (C_1: **7**)	1.7393	1.7104	0.0289
N-∗-HN in C-G (C_1: **8**)	1.8938	1.8677	0.0261
O-∗-HN in C-G (C_1: **9**)	1.8971	1.8687	0.0284
NH-∗-N in A-A (C_1: **10**)	2.0004	1.9722	0.0282
CH-∗-N in A-A (C_1: **11**)	2.4675	2.4455	0.0220
N-∗-HN in A-C (C_1: **12**)	1.8716	1.8451	0.0265
NH-∗-O in A-C (C_1: **13**)	1.8116	1.7823	0.0293
N-∗-HN in A-G (C_1: **14**)	1.8501	1.8241	0.0260
NH-∗-O in A-G (C_1: **15**)	1.8308	1.8019	0.0289
CH-∗-HN in A-G (C_1: **16**)	2.5794	2.3822	0.1972
N-∗-HN in A-U (C_1: **17**)	1.7766	1.7508	0.0258
NH-∗-O in A-U (C_1: **18**)	1.9176	1.8880	0.0296
CH-∗-O in A-U (C_1: **19**)	2.7450	2.7094	0.0356
NH-∗-N in C-C (C_1: **20**)	1.7822	1.7559	0.0263
O-∗-HN in C-C (C_1: **21**)	1.7664	1.7371	0.0293
CH-∗-O in C-C (C_1: **22**)	2.8704	2.8195	0.0509
N-∗-HN in C-T (C_1: **23**)	1.8566	1.8292	0.0274
NH-∗-O in C-T (C_1: **24**)	1.8441	1.8152	0.0289
O-∗-O in C-T (C_1: **25**)	3.5785	3.5675	0.0110
N-∗-HN in C-U (C_1: **26**)	1.8531	1.8258	0.0273
NH-∗-O in C-U (C_1: **27**)	1.8448	1.8159	0.0289
O-∗-O in C-U (C_1: **28**)	3.5526	3.5419	0.0107
NH-∗-O G-G (C_i: **29**)	1.7152	1.6888	0.0264
O-∗-HN G-G (C_i: **30**)	2.4985	2.4270	0.0715
N-∗-HN in G-T (C_1: **31**)	1.8462	1.8194	0.0268
NH-∗-O in G-T (C_1: **32**)	1.8593	1.8310	0.0283
NH-∗-O in G-U (C_1: **33**)	1.7714	1.7440	0.0274
O-∗-HN in G-U (C_1: **34**)	1.7837	1.7544	0.0293
NH-∗-O in T-T (C_1: **35**)	1.8082	1.7788	0.0294
O-∗-HN in T-T (C_1: **36**)	1.8082	1.7788	0.0294
NH-∗-O in T-T (C_i: **37**)	1.8082	1.7788	0.0294
NH-∗-O in T-U (C_1: **38**)	1.8012	1.7718	0.0294
O-∗-HN in T-U (C_1: **39**)	1.8167	1.7871	0.0296
NH-∗-O in U-U (C_1: **40**)	1.8093	1.7798	0.0295
O-∗-HN in U-U (C_1: **41**)	1.8093	1.7798	0.0295
NH-∗-O in U-U (C_s: **42**)	1.8093	1.7798	0.0295
O-∗-HN in U-U (C_s: **43**)	1.8093	1.7798	0.0295

[a] The lengths of BPs. [b] Straight-line distances. [c] $\Delta r_{BP} = r_{BP} - R_{SL}$.

Table S4. QTAIM functions and QTAIM-DFA parameters for each HB of multi-HBs in nucleobase pairs, together with the nature of each HB, elucidated with MP2/BSS-B′b.[a,b]

AH-⁎-B in Nu-Nu′ (Symmetry: No.)	$\rho_b(\boldsymbol{r}_c)$ (au)	$c\nabla^2\rho_b(\boldsymbol{r}_c)$[c] (au)	$H_b(\boldsymbol{r}_c)$ (au)	$k_b(\boldsymbol{r}_c)$[d]	R[e] (au)	θ[f] (°)	C_{ii}[g] (unit[j])	θ_p[h] (°)	κ_p[i] (au^{-1})	Predicted Nature
N-⁎-HN in A-T (C_1: **1**)	0.0502	0.0093	–0.0147	–1.441	0.0173	147.6	3.13	182.6	6.5	*r*-CS/CT-TBP
NH-⁎-O in A-T (C_1: **2**)	0.0298	0.0116	–0.0014	–1.057	0.0117	96.9	5.63	146.7	106.3	*r*-CS/*t*-HB_{wc}
CH-⁎-O in A-T (C_1: **3**)	0.0060	0.0025	0.0006	–0.849	0.0025	75.3	16.27	81.9	69.8	*p*-CS/vdW
NH-⁎-N in A-T (C_s: **4**)	0.0502	0.0093	–0.0147	–1.441	0.0173	147.6	3.13	182.6	6.4	*r*-CS/CT-TBP
NH-⁎-O in A-T (C_s: **5**)	0.0298	0.0116	–0.0014	–1.057	0.0117	96.9	5.63	146.7	106.3	*r*-CS/*t*-HB_{wc}
CH-⁎-O in A-T (C_s: **6**)	0.0060	0.0025	0.0006	–0.849	0.0025	75.3	16.27	81.9	69.8	*p*-CS/vdW
O-⁎-HN in C-G (C_1: **7**)	0.0455	0.0136	–0.0099	–1.266	0.0168	126.0	3.16	169.6	10.9	*r*-CS/CT- MC
N-⁎-HN in C-G (C_1: **8**)	0.0380	0.0099	–0.0064	–1.245	0.0118	123.0	2.15	175.2	26.6	*r*-CS/CT- MC
NH-⁎-O in C-G (C_1: **9**)	0.0311	0.0119	–0.0020	–1.076	0.0120	99.4	4.03	149.6	91.6	*r*-CS/*t*-HB_{wc}
NH-⁎-N in A-A (C_1: **10**)	0.0292	0.0093	–0.0020	–1.095	0.0095	101.8	5.67	160.1	91.1	*r*-CS/CT- MC
CH-⁎-N in A-A (C_1: **11**)	0.0120	0.0045	0.0012	–0.841	0.0047	74.7	16.53	76.0	51.0	*p*-CS/vdW
N-⁎-HN in A-C (C_1: **12**)	0.0395	0.0101	–0.0074	–1.267	0.0125	126.1	3.67	174.5	21.0	*r*-CS/CT- MC
NH-⁎-O in A-C (C_1: **13**)	0.0372	0.0136	–0.0046	–1.145	0.0144	108.7	3.61	158.4	36.5	*r*-CS/CT- MC
N-⁎-HN in A-G (C_1: **14**)	0.0429	0.0097	–0.0094	–1.326	0.0135	134.1	3.50	179.0	9.5	*r*-CS/CT- MC
NH-⁎-O in A-G (C_1: **15**)	0.0366	0.0126	–0.0046	–1.154	0.0135	110.1	4.40	161.1	42.4	*r*-CS/CT- MC
CH-⁎-HN in A-G (C_1: **16**)	0.0056	0.0026	0.0009	–0.796	0.0027	71.3	30.25	78.4	108.3	*p*-CS/vdW
N-⁎-HN in A-U (C_1: **17**)	0.0505	0.0092	–0.0149	–1.446	0.0175	148.1	3.12	182.8	6.2	*r*-CS/CT-TBP
NH-⁎-O in A-U (C_1: **18**)	0.0295	0.0116	–0.0013	–1.053	0.0116	96.3	5.66	145.8	109.3	*r*-CS/*t*-HB_{wc}
CH-⁎-O in A-U (C_1: **19**)	0.0061	0.0025	0.0006	–0.850	0.0026	75.4	16.27	81.7	69.8	*p*-CS/vdW
NH-⁎-N in C-C (C_1: **20**)	0.0492	0.0099	–0.0137	–1.409	0.0170	144.2	2.61	180.7	4.5	*r*-CS/CT-TBP
O-⁎-HN in C-C (C_1: **21**)	0.0431	0.0133	–0.0084	–1.241	0.0157	122.4	3.77	168.3	15.7	*r*-CS/CT- MC
CH-⁎-O in C-C (C_1: **22**)	0.0050	0.0021	0.0006	–0.824	0.0022	73.3	14.38	83.4	57.2	*p*-CS/vdW
N-⁎-HN in C-T (C_1: **23**)	0.0406	0.0096	–0.0083	–1.303	0.0127	131.0	4.81	178.1	19.4	*r*-CS/CT- MC
NH-⁎-O in C-T (C_1: **24**)	0.0356	0.0126	–0.0040	–1.138	0.0132	107.7	4.66	159.4	49.7	*r*-CS/CT- MC
O-⁎-O in C-T (C_1: **25**)	0.0027	0.0013	0.0005	–0.762	0.0014	69.0	31.80	88.7	369.5	*p*-CS/vdW
N-⁎-HN in C-U (C_1: **26**)	0.0410	0.0096	–0.0086	–1.310	0.0128	131.9	4.76	178.5	12.3	*r*-CS/CT- MC
NH-⁎-O in C-U (C_1: **27**)	0.0354	0.0126	–0.0039	–1.135	0.0132	107.3	4.67	159.0	50.5	*r*-CS/CT- MC
O-⁎-O in C-U (C_1: **28**)	0.0029	0.0013	0.0005	–0.774	0.0014	69.7	30.68	89.8	344.2	*p*-CS/vdW
NH-⁎-O G-G (C_i: **29**)	0.0507	0.0137	–0.0127	–1.316	0.0187	132.8	2.83	172.2	8.1	*r*-CS/CT- MC
O-⁎-HN G-G (C_i: **30**)	0.0083	0.0044	0.0014	–0.804	0.0046	71.9	13.06	73.2	20.2	*p*-CS/vdW
N-⁎-HN in G-T (C_1: **31**)	0.0419	0.0100	–0.0089	–1.308	0.0134	131.6	3.88	177.2	16.0	*r*-CS/CT- MC
NH-⁎-O in G-T (C_1: **32**)	0.0343	0.0124	–0.0034	–1.120	0.0129	105.2	4.82	156.9	60.3	*r*-CS/CT- MC
NH-⁎-O in G-U (C_1: **33**)	0.0428	0.0139	–0.0077	–1.216	0.0159	118.9	3.02	165.9	19.4	*r*-CS/CT- MC
O-⁎-HN in G-U (C_1: **34**)	0.0411	0.0128	–0.0073	–1.221	0.0148	119.6	4.24	167.5	20.9	*r*-CS/CT- MC
NH-⁎-O in T-T (C_1: **35**)	0.0380	0.0130	–0.0053	–1.169	0.0141	112.1	4.23	163.7	32.2	*r*-CS/CT- MC
O-⁎-HN in T-T (C_1: **36**)	0.0380	0.0131	–0.0053	–1.169	0.0141	112.1	4.22	163.7	32.2	*r*-CS/CT- MC
NH-⁎-O in T-T (C_i: **37**)	0.0380	0.0131	–0.0053	–1.169	0.0141	112.1	4.22	163.7	28.4	*r*-CS/CT- MC
NH-⁎-O in T-U (C_1: **38**)	0.0387	0.0131	–0.0057	–1.178	0.0143	113.4	4.10	164.5	29.0	*r*-CS/CT- MC
O-⁎-HN in T-U (C_1: **39**)	0.0372	0.0130	–0.0048	–1.157	0.0138	110.4	4.35	162.4	36.2	*r*-CS/CT- MC
NH-⁎-O in U-U (C_1: **40**)	0.0379	0.0130	–0.0052	–1.166	0.0140	111.8	4.23	163.3	32.6	*r*-CS/CT- MC
O-⁎-HN in U-U (C_1: **41**)	0.0379	0.0130	–0.0052	–1.166	0.0140	111.8	4.23	163.3	32.6	*r*-CS/CT- MC
NH-⁎-O in U-U (C_s: **42**)	0.0379	0.0130	–0.0052	–1.166	0.0140	111.8	4.23	163.3	28.8	*r*-CS/CT- MC
O-⁎-HN in U-U (C_s: **43**)	0.0379	0.0130	–0.0052	–1.166	0.0140	111.8	4.23	163.3	28.8	*r*-CS/CT- MC

[a] BSS-B′b: 6-311+G(3df,3pd) for O, N, H, and 6-311+G(d) for C. [b] Data are given at BCPs. [c] $c\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, where $c = \hbar^2/8m$. [d] $k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$. [e] $R = (x + y)^{1/2}$, where (x, $y = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, $H_b(\boldsymbol{r}_c)$). [f] $\theta = 90^o - \tan^{-1}(y/x)$. [g] Compliance force constants. [h] $\theta_p = 90^o - \tan^{-1}(dy/dx)$. [i] $\kappa_p = |d^2y/dx^2|/[1 + (dy/dx)^2]^{3/2}$. [j] Å $mdyn^{-1}$.

Table S5. QTAIM functions and QTAIM-DFA parameters for each HB of multi-HBs in Some nucleobase pairs, together with the nature of each HB, evaluated with various basis sets for M06-2X Level.[a]

AH-∗-B in Nu-Nu′ (Symmetry: No.)	$\rho_b(\boldsymbol{r}_c)$ (au)	$c\nabla^2\rho_b(\boldsymbol{r}_c)^b$ (au)	$H_b(\boldsymbol{r}_c)$ (au)	$k_b(\boldsymbol{r}_c)^c$	R^d (au)	θ^e (°)	C_{ii}^f (unit[i])	θ_p^g (°)	κ_p^h (au^{-1})	Predicted Nature
M06-2X/BSS-A[j]										
N-∗-HN in A-T (C_1: **1**)	0.0470	0.0092	–0.0125	–1.404	0.0155	143.6	3.81	186.0	3.6	*r*-CS/CT-TBP
NH-∗-O in A-T (C_1: **2**)	0.0252	0.0115	0.0011	–0.949	0.0116	84.5	6.07	124.4	218.8	*p*-CS/*t*-HB$_{nc}$
CH-∗-O in A-T (C_1: **3**)	0.0055	0.0023	0.0007	–0.823	0.0024	73.3	20.49	78.9	103.9	*p*-CS/vdW
O-∗-HN in C-G (C_1: **7**)	0.0402	0.0137	–0.0061	–1.181	0.0150	113.9	3.88	174.8	36.4	*r*-CS/CT-MC
N-∗-HN in C-G (C_1: **8**)	0.0342	0.0103	–0.0037	–1.153	0.0110	109.8	2.22	178.1	45.3	*r*-CS/CT-MC
NH-∗-O in C-G (C_1: **9**)	0.0273	0.0121	0.0005	–0.981	0.0121	87.8	3.95	135.4	199.8	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in T-T (C_1: **35**)	0.0311	0.0133	–0.0008	–1.030	0.0133	93.6	5.50	153.4	126.8	*r*-CS/CT-MC
NH-∗-O in T-U (C_1: **38**)	0.0317	0.0133	–0.0011	–1.040	0.0134	94.7	4.84	155.8	118.0	*r*-CS/CT-MC
O-∗-HN in T-U (C_1: **39**)	0.0308	0.0132	–0.0007	–1.026	0.0132	93.0	4.76	152.4	133.2	*r*-CS/CT-MC
NH-∗-O in U-U (C_1: **40**)	0.0298	0.0132	–0.0001	–1.005	0.0132	90.6	4.97	147.3	152.1	*r*-CS/*t*-HB$_{wc}$
M06-2X/BSS-C[k]										
N-∗-HN in A-T (C_1: **1**)	0.0460	0.0107	–0.0097	–1.313	0.0144	132.3	4.04	184.0	11.6	*r*-CS/CT-TBP
NH-∗-O in A-T (C_1: **2**)	0.0248	0.0117	0.0015	–0.933	0.0118	82.8	5.91	112.1	164.8	*p*-CS/*t*-HB$_{nc}$
CH-∗-O in A-T (C_1: **3**)	0.0055	0.0023	0.0007	–0.815	0.0024	72.6	20.18	77.7	86.4	*p*-CS/vdW
O-∗-HN in C-G (C_1: **7**)	0.0381	0.0149	–0.0032	–1.097	0.0152	102.1	3.89	161.4	68.9	*r*-CS/CT-MC
N-∗-HN in C-G (C_1: **8**)	0.0329	0.0111	–0.0020	–1.083	0.0113	100.3	2.22	168.4	100.7	*r*-CS/CT-MC
NH-∗-O in C-G (C_1: **9**)	0.0268	0.0124	0.0010	–0.958	0.0124	85.4	3.89	120.4	170.2	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in T-T (C_1: **35**)	0.0302	0.0137	0.0003	–0.990	0.0137	88.9	5.26	136.8	150.2	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in T-U (C_1: **38**)	0.0307	0.0138	0.0001	–0.997	0.0138	89.7	4.58	139.1	146.5	*p*-CS/*t*-HB$_{nc}$
O-∗-HN in T-U (C_1: **39**)	0.0299	0.0136	0.0003	–0.988	0.0136	88.6	4.53	136.0	153.7	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in U-U (C_1: **40**)	0.0291	0.0136	0.0007	–0.972	0.0136	86.9	4.80	131.4	158.7	*p*-CS/*t*-HB$_{nc}$
M06-2X/BSS-C′[l]										
N-∗-HN in A-T (C_1: **1**)	0.0460	0.0107	–0.0097	–1.313	0.0144	132.3	4.03	184.0	11.6	*r*-CS/CT-TBP
NH-∗-O in A-T (C_1: **2**)	0.0248	0.0117	0.0015	–0.933	0.0118	82.8	5.91	112.2	164.1	*p*-CS/*t*-HB$_{nc}$
CH-∗-O in A-T (C_1: **3**)	0.0055	0.0023	0.0007	–0.814	0.0024	72.6	20.75	77.8	74.1	*p*-CS/vdW
O-∗-HN in C-G (C_1: **7**)	0.0381	0.0149	–0.0032	–1.097	0.0152	102.1	3.89	161.4	68.6	*r*-CS/CT-MC
N-∗-HN in C-G (C_1: **8**)	0.0330	0.0111	–0.0020	–1.083	0.0113	100.3	2.22	168.4	100.5	*r*-CS/CT-MC
NH-∗-O in C-G (C_1: **9**)	0.0268	0.0124	0.0010	–0.958	0.0124	85.4	3.90	120.4	170.3	*p*-CS/*t*-HB$_{nc}$
NH-∗-N in A-A (C_1: **10**)	0.0239	0.0097	0.0011	–0.938	0.0098	83.3	6.34	127.1	261.8	*p*-CS/*t*-HB$_{nc}$
CH-∗-N in A-A (C_1: **11**)	0.0106	0.0041	0.0014	–0.795	0.0044	71.2	18.21	70.6	35.0	*p*-CS/vdW
NH-∗-O in T-T (C_1: **35**)	0.0302	0.0137	0.0003	–0.990	0.0137	88.9	5.24	136.8	150.2	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in U-U (C_1: **40**)	0.0290	0.0135	0.0007	–0.973	0.0135	87.0	4.82	131.5	160.2	*p*-CS/*t*-HB$_{nc}$
M06-2X/BSS-D[m]										
N-∗-HN in A-T (C_1: **1**)	0.0459	0.0109	–0.0092	–1.299	0.0143	130.4	4.03	183.5	14.3	*r*-CS/CT-TBP
NH-∗-O in A-T (C_1: **2**)	0.0247	0.0117	0.0017	–0.922	0.0118	81.7	5.84	109.8	161.2	*p*-CS/*t*-HB$_{nc}$
CH-∗-O in A-T (C_1: **3**)	0.0055	0.0023	0.0007	–0.823	0.0024	73.3	20.41	78.6	90.7	*p*-CS/vdW
O-∗-HN in C-G (C_1: **7**)	0.0377	0.0150	–0.0027	–1.082	0.0152	100.1	3.87	158.9	73.6	*r*-CS/CT-MC
N-∗-HN in C-G (C_1: **8**)	0.0329	0.0112	–0.0017	–1.071	0.0114	98.7	2.29	167.4	104.5	*r*-CS/CT-MC
NH-∗-O in C-G (C_1: **9**)	0.0264	0.0123	0.0013	–0.944	0.0124	83.9	4.00	116.6	170.5	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in T-T (C_1: **35**)	0.0303	0.0137	0.0004	–0.983	0.0138	88.1	5.21	135.3	152.1	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in T-U (C_1: **38**)	0.0307	0.0138	0.0003	–0.990	0.0138	88.8	4.55	137.5	149.1	*p*-CS/*t*-HB$_{nc}$
O-∗-HN in T-U (C_1: **39**)	0.0299	0.0136	0.0005	–0.980	0.0137	87.8	4.50	134.5	155.9	*p*-CS/*t*-HB$_{nc}$
NH-∗-O in U-U (C_1: **40**)	0.0290	0.0136	0.0009	–0.965	0.0136	86.1	4.77	129.7	160.1	*p*-CS/*t*-HB$_{nc}$

[a] Data are given at BCPs. [b] $c\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, where $c = \hbar^2/8m$. [c] $k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$. [d] $R = (x + y)^{1/2}$, where $(x, y = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$. [e] $\theta = 90^o - \tan^{-1}(y/x)$. [f] Compliance force constants. [g] $\theta_p = 90^o - \tan^{-1}(dy/dx)$. [h] $\kappa_p = |d^2y/dx^2|/[1 + (dy/dx)^2]^{3/2}$. [i] Å mdyn^{-1}. [j] BSS-A: 6-311++G(3df,3pd). [k] BSS-C: 6-311++G(3df,3p). [l] BSS-C: 6-311++G(3df,3p).[m] 6-311++G(3d,3p).

Table S6. The structural parameters of the ΔE_{ES} and ΔE_{ZP} values and fractionalization of the total values of ΔE to each HB (ΔE_e), evaluated with MP2/BSS-A for the acetic acid dimer and the related species **I**–**III**, together with the C_{ii} values.[a]

Dimers (symm)	AH-∗-X	ΔE_{ES}[b] (kJ mol^{-1})	ΔE_{ZP}[c] (kJ mol^{-1})	ΔE_e (kJ mol^{-1})	C_{ii} (Å mdyn^{-1})
I (C_{2h})	OH-∗-O	-72.4	-66.2	-36.2	3.19
IIa (C_i)	NH-∗-O	-65.0	-55.3	-32.5	4.41
IIb (C_i)	NH-∗-S	-55.2	-49.0	-27.6	5.82
IIc (C_i)	NH-∗-Se	-55.6	-50.7	-27.8	5.93
III (C_1)	OH-∗-O	-70.6	-62.8	-43.1	3.01
	NH-∗-O			-27.5	4.72

[a]With the MP2/6-311++G(3df,3pd) method of the Gaussian 09 program. [b]The energies on the energy surface from the components (ΔE_{ES}) [= E_{ES}(HB) – E_{ES}(components)]. [c]The energies with the zero-point energy collections from the components (ΔE) [= E(HB) – E(components)].

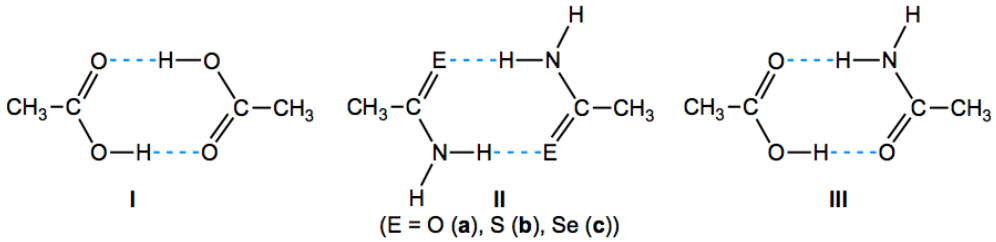


Chart S1. Structures of acetic acid dimer (**I**) and related species (**IIa**–**IIc** and **III**)

Table S7. The w'_{ij}/w_{ii} ratios for the interactions of each HB in Nu-Nu′ evaluated with CIV and POM of the under MP2/BSS-B′a.[a–c]

Interaction AH-∗-B (j)	$(w'_{1j}/w_1)_{CIV}$[d] (i = 1)	$(w'_{2j}/w_2)_{CIV}$[d] (i = 2)	$(w'_{3j}/w_3)_{CIV}$[d] (i = 3)	$(w'_{1j}/w_1)_{POM}$[d] (i = 1)	$(w'_{2j}/w_2)_{POM}$[d] (i = 2)	$(w'_{3j}/w_3)_{POM}$[d] (i = 3)
A-T (C_1)						
NH-∗-O (j = 1)	1.0000	0.1969	–0.2370	1.0000	0.1807	–0.2320
N-∗-HN (j = 2)	0.1058	1.0000	0.2774	0.1051	1.0000	0.2800
NH-∗-O (j = 3)	–0.6674	1.4505	1.0000	–0.6674	1.4909	1.0000
C-G (C_1)						
O-∗-HN (j = 1)	1.0000	0.4951	–0.0537	1.0000	0.5155	–0.0563
N-∗-HN (j = 2)	0.2589	1.0000	0.3481	0.2619	1.0000	0.3481
NH-∗-O (j = 3)	–0.0420	0.5204	1.0000	–0.0420	0.5291	1.0000
A-A (C_1)						
NH-∗-N (j = 1)	1.0000	–0.0076		1.0000	–0.0098	
N-∗-HC (j = 2)	–0.0204	1.0000		–0.0231	1.0000	
T-T (C_1)						
NH-∗-O (j = 1)	1.0000			1.0000		
(j = 2)	0.1126			0.1088		
U-U (C_1)						
NH-∗-O (j = 1)	1.0000			1.0000		
(j = 2)	0.1232			0.1194		

[a] BSS-B′a: The 6-311+G(3df,3pd) for O, N, H, and 6-311+G(3d) for C. [b] The w'_{ij}/w_i values are calculated at w = 0.05 (see eqns (5) and (13) in the text). [c] i and j for w'_{ij}/w_i represent the interaction in question and the other ones, respectively. [d] The w'_{ij}/w_i values are calculated with w = 0.05.

Table S8. The w'_{ij}/w_i ratios for the interactions of each HB in Nu-Nu′ evaluated with CIV and POM with M06-2X/BSS-C′.[a–c]

Interaction AH-∗-B (j)	$(w'_{1j}/w_1)_{CIV}$[d] (i = 1)	$(w'_{2j}/w_2)_{CIV}$[d] (i = 2)	$(w'_{3j}/w_3)_{CIV}$[d] (i = 3)	$(w'_{1j}/w_1)_{POM}$[d] (i = 1)	$(w'_{2j}/w_2)_{POM}$[d] (i = 2)	$(w'_{3j}/w_3)_{POM}$[d] (i = 3)
A-T (C_1)						
NH-∗-O (j = 1)	1.0000	0.1281	–0.2101	1.0000	0.0695	–0.2094
N-∗-HN (j = 2)	0.0877	1.0000	0.3095	0.0945	1.0000	0.3100
NH-∗-O (j = 3)	–0.7381	1.5903	1.0000	–0.7203	1.7082	1.0000
C-G (C_1)						
O-∗-HN (j = 1)	1.0000	0.5321	–0.0737	1.0000	0.5431	–0.0782
N-∗-HN (j = 2)	0.3031	1.0000	0.3685	0.3046	1.0000	0.3677
NH-∗-O (j = 3)	–0.0737	0.6455	1.0000	–0.0741	0.6553	1.0000
A-A (C_1)						
NH-∗-N (j = 1)	1.0000	–0.0008		1.0000	–0.0181	
N-∗-HC (j = 2)	0.0034	1.0000		–0.0185	1.0000	
T-T (C_1)						
NH-∗-O (j = 1)	1.0000			1.0000		
	–0.0008			0.0106		
U-U (C_1)						
NH-∗-O (j = 1)	1.0000			1.0000		
	0.0612			0.0559		

[a] BSS-B′a: The 6-311+G(3df,3pd) for O, N, H, and 6-311+G(3d) for C. [b] The w'_{ij}/w_i values are calculated with w = 0.05 and 0.1 (see eqns (5) and (13) in the text). [c] i and j for w'_{ij}/w_i represent the interaction in question and the other ones, respectively. [d] The w'_{ij}/w_i values are calculated with w = 0.05.

Table S9. QTAIM-DFA parameters for each HB of multi-HBs in Some nucleobase pairs, elucidated by employing the perturbed structures generated with CIV and POM methods, together with the nature of each HB and the differences between $\theta_{p:CIV}$ and $\theta_{p:POM}$, $\kappa_{p:CIV}$ and $\kappa_{p:POM}$, evaluated with M06-2X/BSS-C′.[a]

AH-∗-B in Nu-Nu′ (Symmetry: No.)	$\theta_{p:CIV}$ (°)	$\theta_{p:POM}$ (°)	$\Delta\theta_p$[b] (°)	$\kappa_{p:CIV}$ (au^{-1})	$\kappa_{p:POM}$ (au^{-1})	$\Delta\kappa_p$[c] (au^{-1})	Predicted Nature
N-∗-HN in A-T (C_1: **1**)	184.0	184.0	0.0	16.5	11.6	4.9	*r*-CS/CT-TBP
NH-∗-O in A-T (C_1: **2**)	112.1	112.2	–0.1	163.9	164.1	–0.2	*p*-CS/*t*-HB_{nc}
CH-∗-O in A-T (C_1: **3**)	77.8	77.8	0.0	75.9	74.1	1.8	*p*-CS/vdW
O-∗-HN in C-G (C_1: **7**)	161.4	161.4	0.0	74.6	68.6	6.0	*r*-CS/CT-MC
N-∗-HN in C-G (C_1: **8**)	168.4	168.4	0.0	109.8	100.5	9.3	*r*-CS/CT-MC
NH-∗-O in C-G (C_1: **9**)	120.4	120.4	0.0	171.9	170.3	1.6	*p*-CS/*t*-HB_{nc}
NH-∗-N in A-A (C_1: **10**)	127.1	127.1	0.0	268.0	261.8	6.2	*p*-CS/*t*-HB_{nc}
CH-∗-N in A-A (C_1: **11**)	70.5	70.6	–0.1	38.5	35.0	3.5	*p*-CS/vdW
NH-∗-O in T-T (C_1: **35**)	136.8	136.8	0.0	155.8	150.2	5.6	*p*-CS/*t*-HB_{nc}
NH-∗-O in U-U (C_1: **40**)	131.4	131.5	–0.1	164.5	160.2	4.3	*p*-CS/*t*-HB_{nc}

[a] BSS-C′: The 6-311+G(3df,3p) basis sets. [b] $\Delta\theta_p = \theta_{p:CIV} - \theta_{p:POM}$. [c] $\Delta\kappa_p = \kappa_{p:CIV} - \kappa_{p:POM}$.

Table S10. ΔE_{psi} (= $E_{\mathrm{psi}} - E_{\mathrm{o}}$) for A-T, C-G, A-A, T-T and U-U, calculated with M06-2X/BSS-C′.[a]

w	Δr (Å)	$\Delta E_{\mathrm{ES:CIV:}(j=1)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:POM:}(j=1)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:CIV:}(j=2)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:POM:}(j=2)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:CIV:}(j=3)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:POM:}(j=3)}$ (kJ mol^{-1})
A-T (C_1)							
–0.18897	–0.10000		0.58286		0.90317		0.16278
–0.10000	–0.05292	0.15228		0.23735		0.04437	
–0.09449	–0.05000		0.13653		0.20479		0.03676
–0.05000	–0.02646	0.03649		0.05592		0.01050	
–0.02500	–0.01323	0.00893		0.01365		0.00263	
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0.02500	0.01323	0.00866		0.01260		0.00236	
0.05000	0.02646	0.03413		0.04883		0.00945	
0.09449	0.05000		0.11552		0.16541		0.03413
0.10000	0.05292	0.13285		0.18457		0.03649	
0.18897	0.10000		0.44371		0.60912		0.12602
0.20000	0.10584	0.50593		0.68841		0.13968	
0.30000	0.15875	1.08302		1.50651		0.31480	
0.37794	0.20000		1.57793		2.19229		0.48834
0.40000	0.21167	1.83732		2.60187		0.57498	
0.50000	0.26459	2.75625		3.97606		0.91682	
0.56691	0.30000		3.12697		4.38984		1.07645
0.60000	0.31751	3.84006		5.62067		1.33402	
0.70000	0.37043	5.09793		7.55330		1.84415	
0.75589	0.40000		4.87293		7.00221		1.83522
0.80000	0.42334	6.56428		9.78078		2.46246	
0.90000	0.47626	8.28345		12.32042		3.19418	
0.94486	0.50000		6.71865		9.85613		2.76203
1.00000	0.52918	10.29327		15.18379		4.05824	
C-G (C_1)							
–0.18897	–0.10000		0.86642		1.39677		0.82703
–0.10000	–0.05292	0.23157		0.38674		0.22684	
–0.09449	–0.05000		0.05776		0.09714		0.05776
–0.05000	–0.02646	0.05592		0.09583		0.05540	
–0.02500	–0.01323	0.01365		0.02363		0.01365	
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
0.02500	0.01323	0.01313		0.02337		0.01313	
0.05000	0.02646	0.05198		0.09347		0.05225	
0.09449	0.05000		0.05251		0.09452		0.05251
0.10000	0.05292	0.20138		0.36810		0.20269	
0.18897	0.10000		0.68263		1.27074		0.69313
0.20000	0.10584	0.75903		1.42565		0.77951	
0.30000	0.15875	1.61600		3.12933		1.70579	
0.37794	0.20000		2.43384		4.77316		2.57299
0.40000	0.21167	2.72133		5.45605		2.92953	
0.50000	0.26459	4.03618		8.36143		4.40506	
0.56691	0.30000		4.83355		8.93458		5.24575
0.60000	0.31751	5.52930		11.79716		6.10140	
0.70000	0.37043	7.17208		15.72569		7.98940	
0.75589	0.40000		7.69009		13.06974		8.39110
0.80000	0.42334	8.94193		20.11422		10.04884	
0.90000	0.47626	10.82940		24.92728		12.26502	
0.94486	0.50000		10.77505		16.88459		11.80162
1.00000	0.52918	12.83318		30.13654		14.62036	

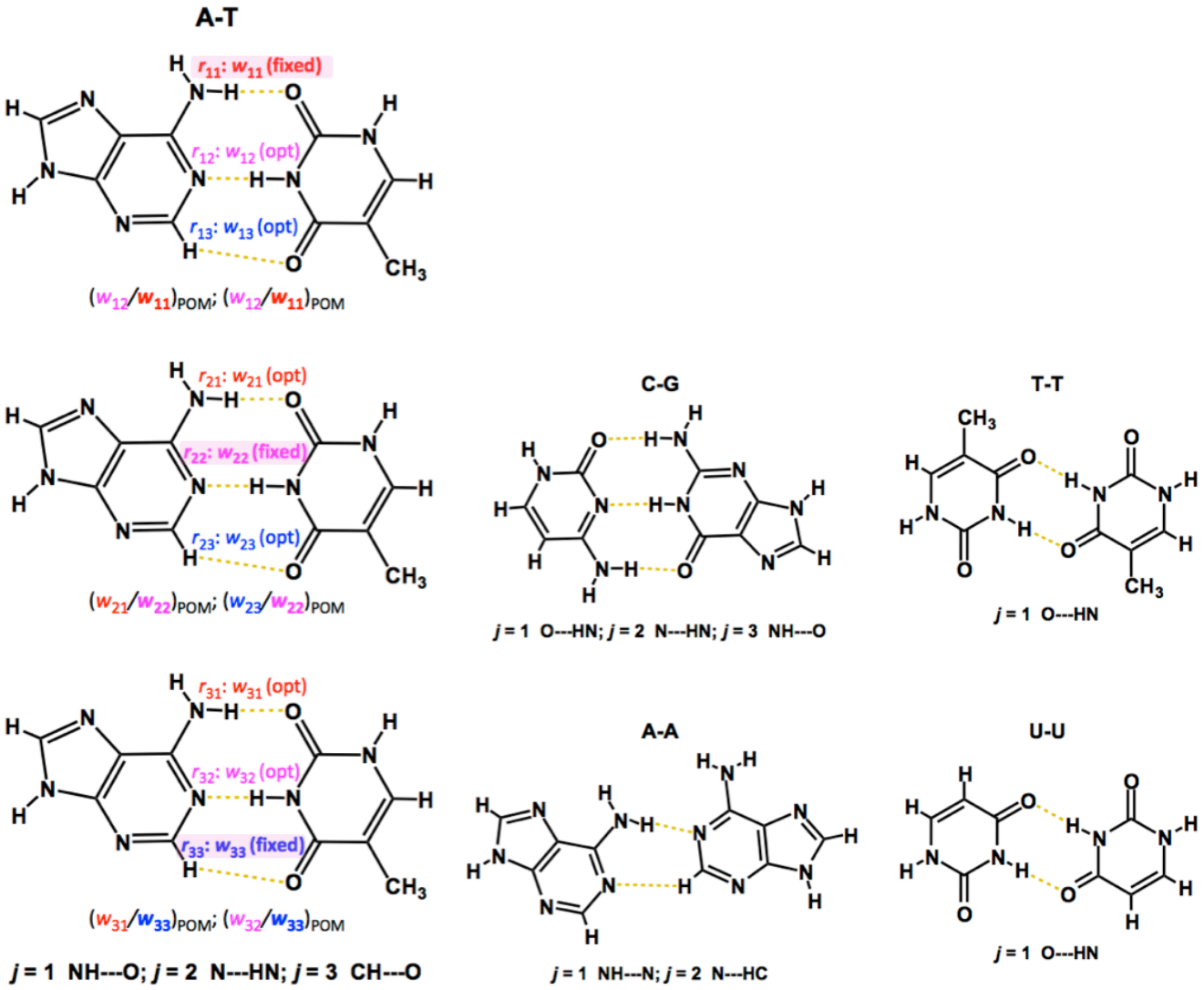
Table S10. Continued.

w	Δr (Å)	$\Delta E_{ES:CIV:(j=1)}$ (kJ mol^{-1})	$\Delta E_{ES:POM:(j=1)}$ (kJ mol^{-1})	$\Delta E_{ES:CIV:(j=2)}$ (kJ mol^{-1})	$\Delta E_{ES:POM:(j=2)}$ (kJ mol^{-1})	$\Delta E_{ES:CIV:(j=3)}$ (kJ mol^{-1})	$\Delta E_{ES:POM:(j=3)}$ (kJ mol^{-1})
A-A (C_1)							
–0.18897	–0.10000		0.51985		0.17328		
–0.10000	–0.05292	0.13495		0.05514			
–0.09449	–0.05000		0.12602		0.03676		
–0.05000	–0.02646	0.03177		0.01392			
–0.02500	–0.01323	0.00735		0.00394			
0.00000	0.00000	0.00000	0.00000	0.00000	0.00000		
0.02500	0.01323	0.00893		0.00158			
0.05000	0.02646	0.03439		0.00866			
0.09449	0.05000		0.10765		0.03938		
0.10000	0.05292	0.13154		0.03991			
0.18897	0.10000		0.42008		0.14703		
0.20000	0.10584	0.50147		0.18090			
0.30000	0.15875	1.10061		0.44686			
0.37794	0.20000		1.52016		0.47259		
0.40000	0.21167	1.94838		0.88847			
0.50000	0.26459	3.08759		1.59105			
0.56691	0.30000		3.03508		0.84541		
0.60000	0.31751	4.57677		2.66068			
0.70000	0.37043	6.50730		4.20789			
0.75589	0.40000		4.74953		1.23399		
0.80000	0.42334	8.99680		6.33244			
0.90000	0.47626	12.18232		9.15249			
0.94486	0.50000		6.51649		1.59630		
1.00000	0.52918	16.20616		12.80509			
T-T (C_1)							
–0.18897	–0.10000		0.56973				
–0.10000	–0.05292	0.16908					
–0.09449	–0.05000		0.14965				
–0.05000	–0.02646	0.04122					
–0.02500	–0.01323	0.01024					
0.00000	0.00000	0.00000	0.00000				
0.02500	0.01323	0.00998					
0.05000	0.02646	0.03965					
0.09449	0.05000		0.13915				
0.10000	0.05292	0.15412					
0.18897	0.10000		0.51197				
0.20000	0.10584	0.57498					
0.30000	0.15875	1.21561					
0.37794	0.20000		1.76959				
0.40000	0.21167	2.05603					
0.50000	0.26459	3.08523					
0.56691	0.30000		3.48141				
0.60000	0.31751	4.32000					
0.70000	0.37043	5.75956					
0.75589	0.40000		5.49255				
0.80000	0.42334	7.50158					
0.90000	0.47626	9.55026					
0.94486	0.50000		7.63758				
1.00000	0.52918	11.95364					

Table S10. Continued.

w	Δr (Å)	$\Delta E_{\mathrm{ES:CIV:}(j=1)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:POM:}(j=1)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:CIV:}(j=2)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:POM:}(j=2)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:CIV:}(j=3)}$ (kJ mol^{-1})	$\Delta E_{\mathrm{ES:POM:}(j=3)}$ (kJ mol^{-1})
U-U (C_1)							
–0.18897	–0.10000		0.66688				
–0.10000	–0.05292	0.18221					
–0.09449	–0.05000		0.16016				
–0.05000	–0.02646	0.04463					
–0.02500	–0.01323	0.01103					
0.00000	0.00000	0.00000	0.00000				
0.02500	0.01323	0.01103					
0.05000	0.02646	0.04253					
0.09449	0.05000		0.14440				
0.10000	0.05292	0.16331					
0.18897	0.10000		0.53823				
0.20000	0.10584	0.60859					
0.30000	0.15875	1.28571					
0.37794	0.20000		1.86936				
0.40000	0.21167	2.15790					
0.50000	0.26459	3.20337					
0.56691	0.30000		3.64682				
0.60000	0.31751	4.42029					
0.70000	0.37043	5.81995					
0.75589	0.40000		5.65795				
0.80000	0.42334	7.40811					
0.90000	0.47626	9.19660					
0.94486	0.50000		7.74260				
1.00000	0.52918	11.21587					

[a] BSS-C′: The 6-311+G(3df,3p) basis sets.



Scheme S1. Definition for j in w'_{ij}/w_i.

$$r_{i1} = r_{i1o} + w_{i1}a_o \quad \text{(S1)}$$

$$r_{i2} = r_{i2o} + w_{i2}a_o \quad \text{(S2)}$$

$$r_{i3} = r_{i3o} + w_{i3}a_o \quad \text{(S3)}$$

(i = 1, 2 and 3)

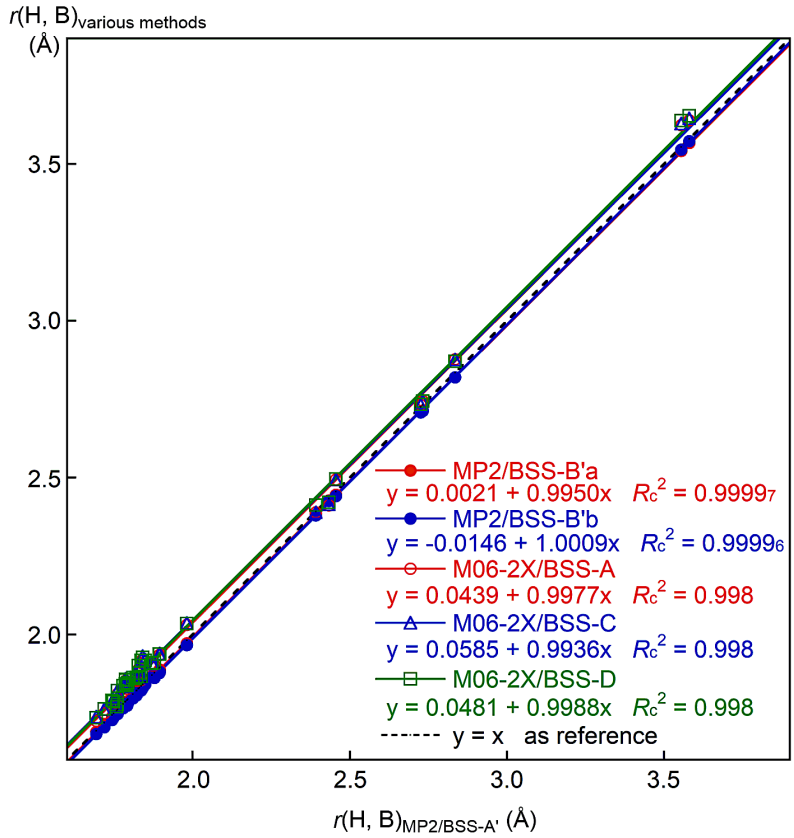


Fig. S1 Plots of r(H, B) for each HB in Nu-Nu′ calculated with various methods (r(H, B)$_{\text{various methods}}$) versus those with MP2/BSS-A′ (r(H, B)$_{\text{MP2/BSS-A′}}$).

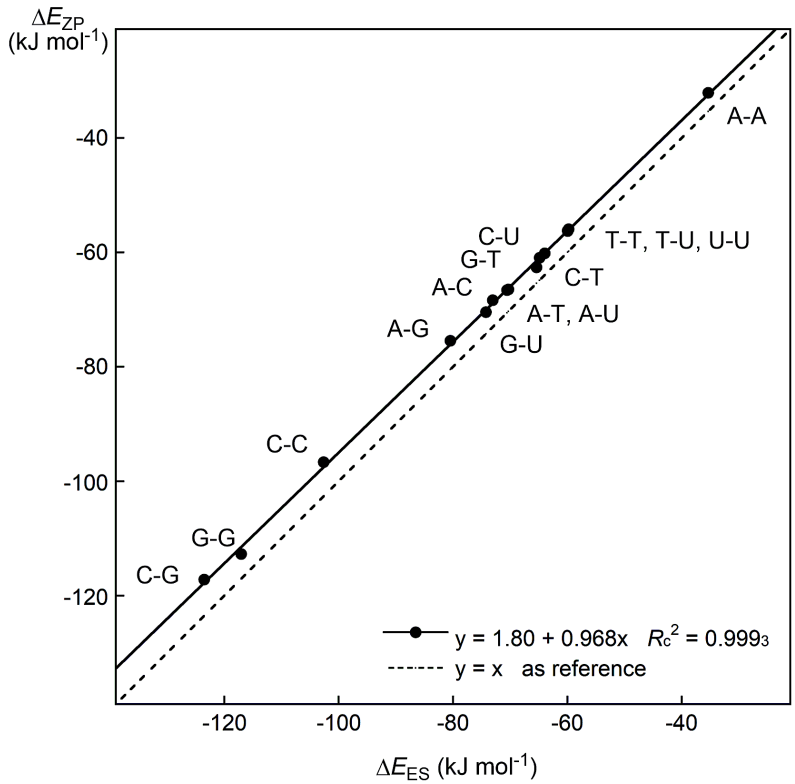


Fig. S2 Plot of ΔE_{ZP} versus ΔE_{ES}, together with ΔE_{ES} versus ΔE_{ES}, calculated with MP2/BSS-B′a.

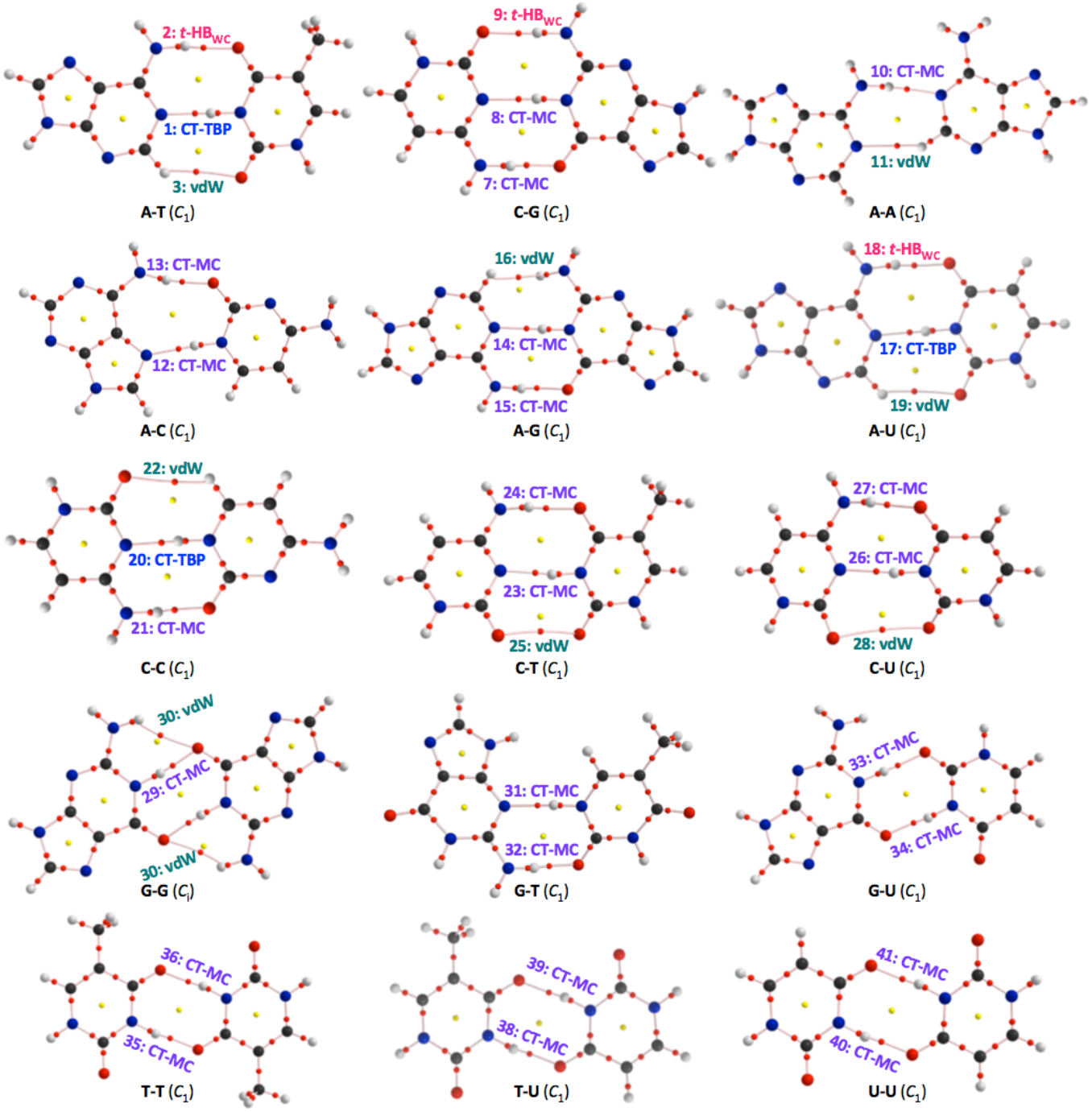


Fig. S3 Molecular graphs for nucleobase pairs, with numbers and predicted natures, evaluated with MP2/BSS-B′a. BCPs (bond critical points) are denoted by red dots, RCPs (ring critical points) by yellow dots, and BPs (bond paths) are by pink lines. Oxygen, nitrogen, carbon and hydrogen atoms are in red, blue, black and grey, respectively.

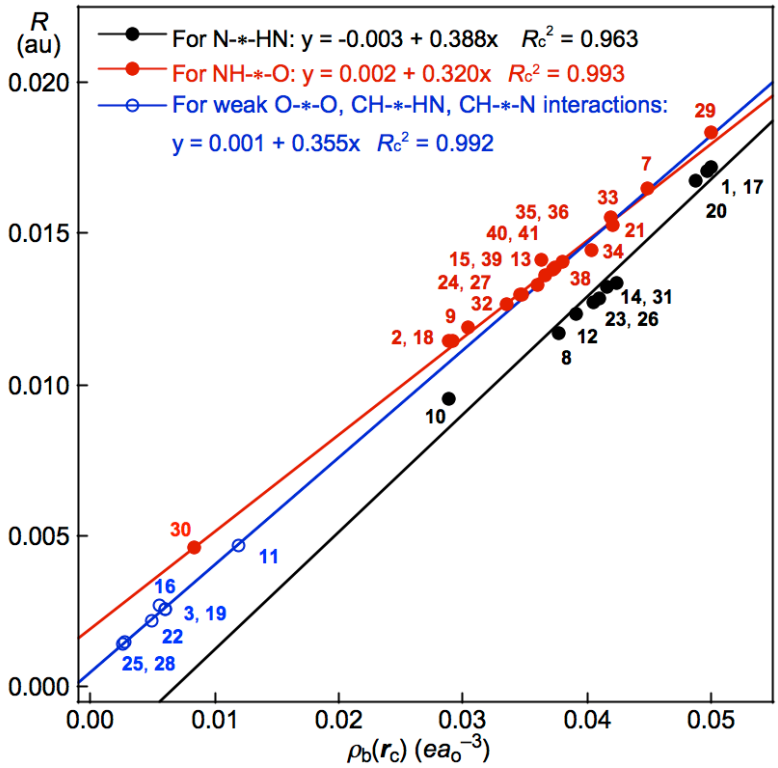


Fig. S4 Plots of R versus $\rho_b(r_c)$ for each HB in Nu-Nu′, calculated with MP2/BSS-B′a. While data for G(**A**) of NH-*-N are shown by black solid circles, those for G(**B**) of NH-*-O are by red solid circles, together with those for G(**C**) of CH-*-X (X = O, N and HN) and O-*-O by blue hole circles. Numbers for the interactions are the same as those in Table 2 and Fig. 4 of the text, respectively.

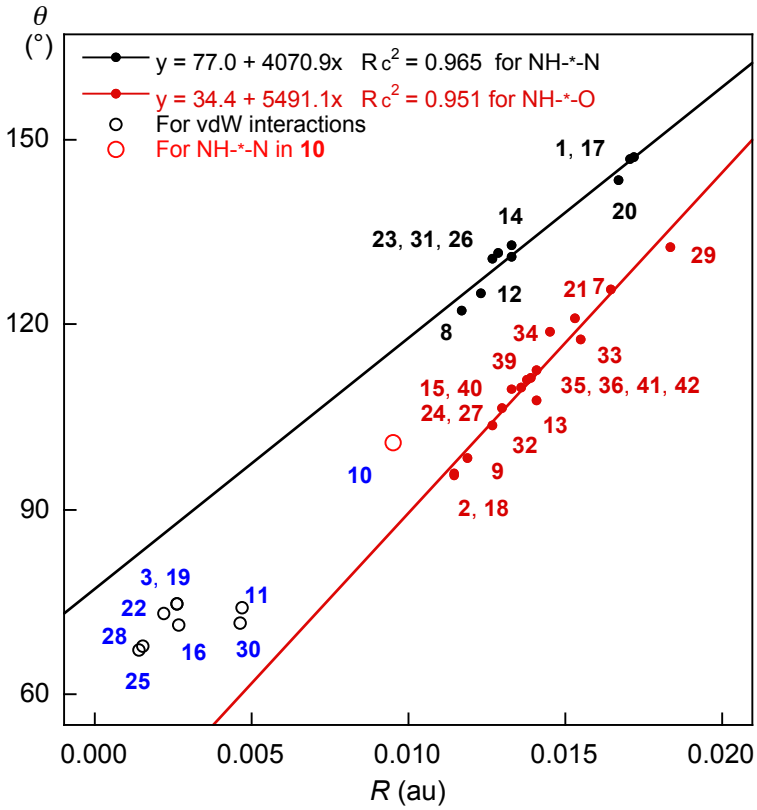


Fig. S5 Plots of θ versus R for Nu-Nu′, calculated with MP2/BSS-B′a, black line for θ versus R of N-*-HN (NH-*-N), CH-*-O, O-*-O and CH-*-HN, except for **10**: NH-*-N, red line for θ versus R of NH-*-O (O-*-HN) and CH-*-N, blue square digit for **10**: NH-*-N.

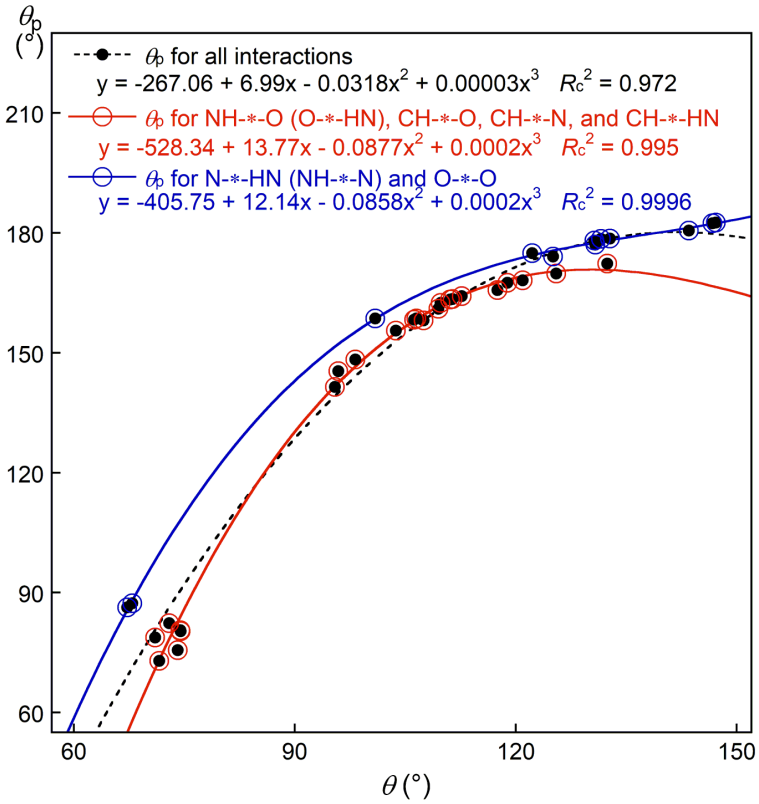


Fig. S6 Plots of θ_p versus θ for Nu-Nu′, calculated with MP2/BSS-B′a, black dot-line for θ_p versus θ of all interaction, red line for θ_p versus θ of NH-*-O (O-*-HN), CH-*-O, CH-*-N and CH-*-HN, blue line for θ_p versus θ of N-*-HN (NH-*-N) and O-*-O.

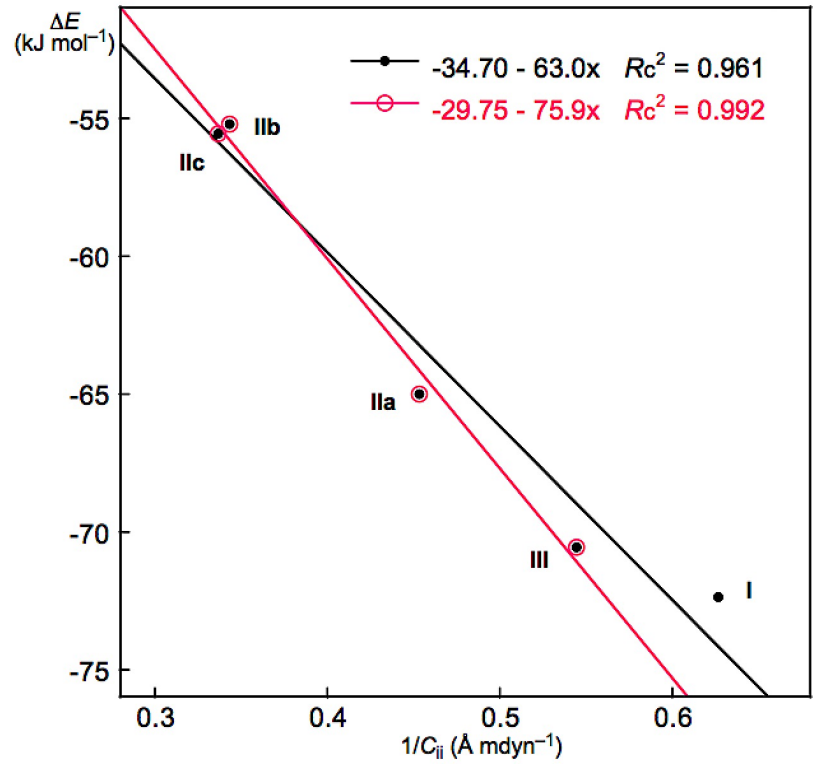


Fig. S7 Plots of ΔE versus $(1/C_{ii})$ in acetic acid dimer and the related species, calculated with MP2/BSS-A. See Table S6 and Chart S1 for the data and the structures of **I**–**III**. The correlation becomes better, if the data of **I**, of which ΔE value is largest in magnitude, is omitted from the correlation.

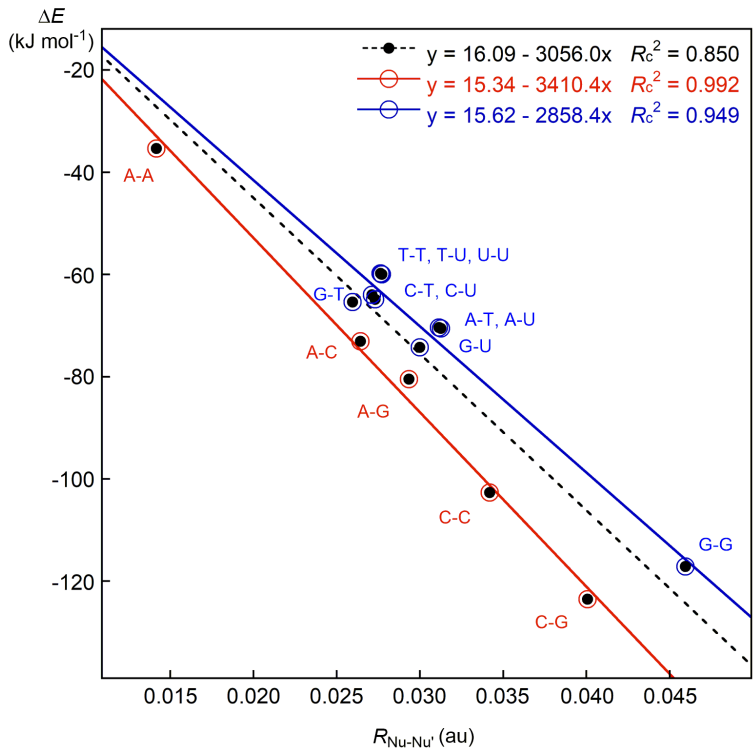


Fig. S8 Plots of ΔE versus $R_{\text{Nu-Nu}'}$ in Nu-Nu′, calculated with MP2/BSS-B′a.

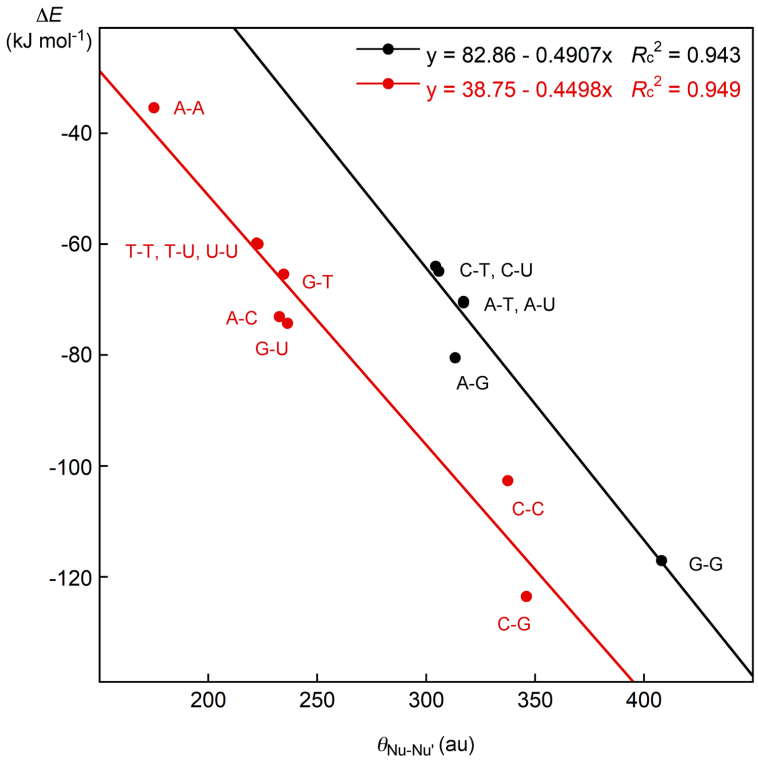


Fig. S9 Plots of ΔE versus $\theta_{\text{Nu-Nu}'}$ in Nu-Nu′, calculated with MP2/BSS-B′a.

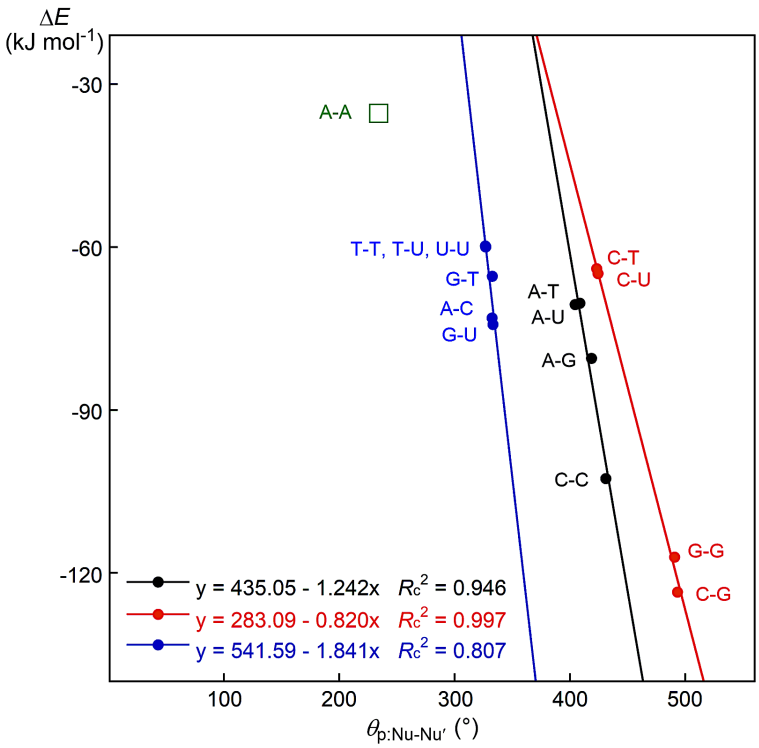


Fig. S10 Plots of ΔE versus $\theta_{\text{p:Nu-Nu}'}$ for Nu-Nu′, calculated with MP2/BSS-B′a.

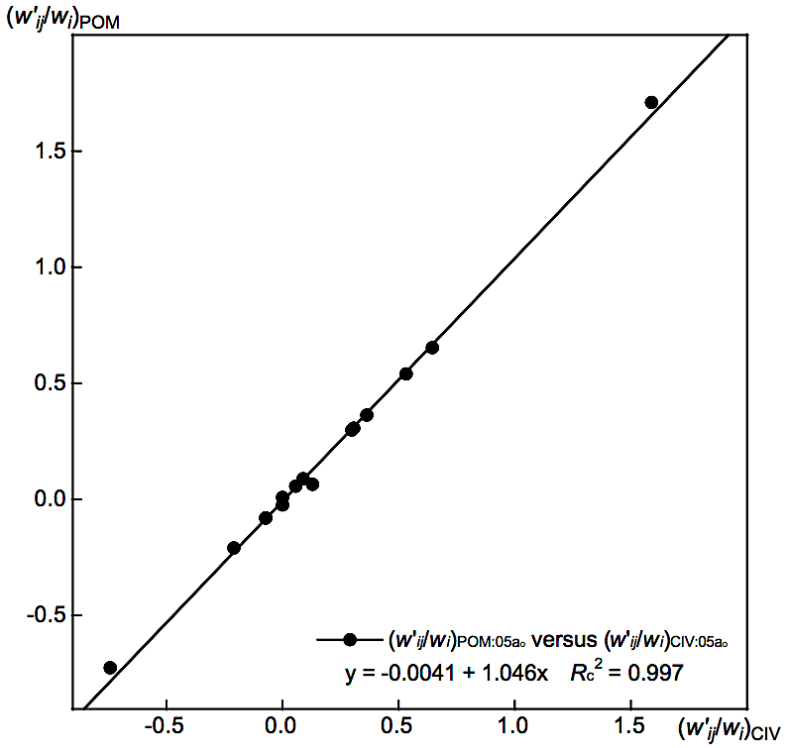


Fig. S11 Plot of $(w'_{ij}/w_i)_{\text{POM}}$ versus $(w'_{ij}/w_i)_{\text{CIV}}$ for each HB of multi-HB system in A-T, C-G, A-A, T-T and U-U, calculated with M06-2X/BSS-C′.

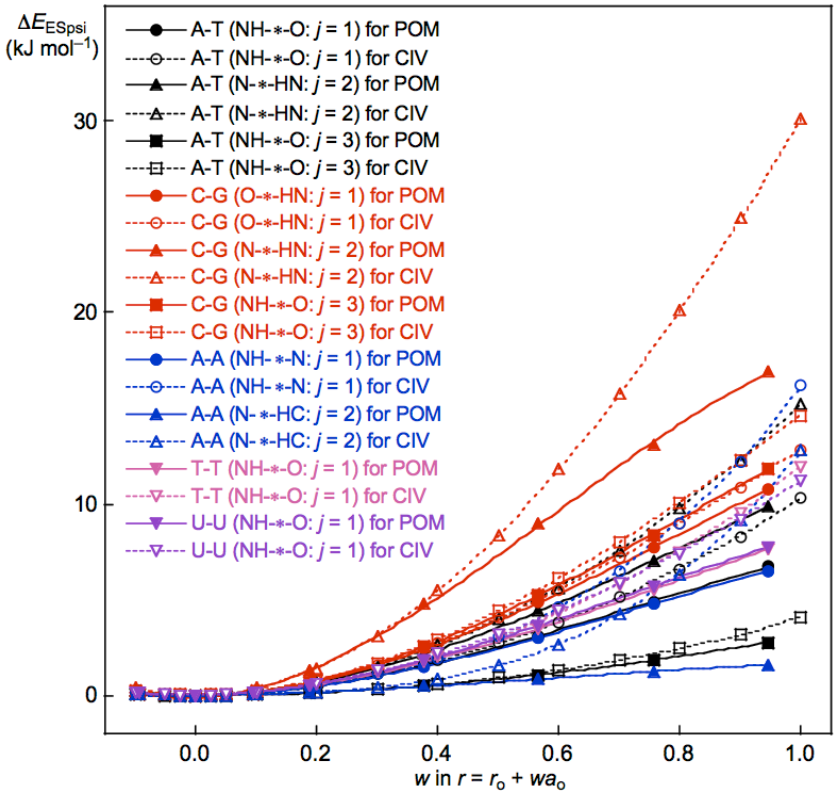


Fig. S12 Plots of $\Delta E_{\mathrm{ESpsi}}$ versus w_{ii} in $r = r_{\mathrm{o}} + w_{ii}a_{\mathrm{o}}$ for each HB in A-T, C-G, A-A, T-T and U-U calculated with CIV and POM of ModRedundant under M06-2X/BSS-C′.

Optimized structures given by Cartesian coordinates

Optimized structures given by Cartesian coordinates for examined molecules, together with the total energies with MP2/6-311+G(3df,3pd) method of the Gaussian 09 program, except for C of which calculations being performed with 6-311+G(3d). The optimized structures were confirmed by the frequency analysis.

MP2/BSS-B′a
Adduct Adenine-Thymine (A-T)
Symmetry C_1
energy MP2 = –919.708785 au
Standard orientation

7	0	-0.954261	0.379387	0.000000
6	0	-1.563985	1.583534	-0.000003
7	0	-2.869053	1.832451	-0.000003
6	0	-3.579511	0.699255	0.000000
6	0	-3.085775	-0.609960	0.000003
6	0	-1.680295	-0.749020	0.000004
7	0	-1.065488	-1.938158	0.000008
7	0	-4.942944	0.545718	0.000000
6	0	-5.196454	-0.798114	0.000004
7	0	-4.099539	-1.535285	0.000005
1	0	-0.894510	2.431662	-0.000005
1	0	-1.628754	-2.769727	0.000012
1	0	-0.048553	-1.992924	0.000010
1	0	-6.199405	-1.184799	0.000005
1	0	-5.618248	1.291992	-0.000001
1	0	0.798446	0.386080	-0.000001
7	0	1.845719	0.391873	-0.000002
7	0	3.813567	1.588918	-0.000009
6	0	2.431863	1.635088	-0.000008
8	0	1.807852	2.680713	-0.000012
6	0	2.482331	-0.832136	0.000002
8	0	1.834213	-1.880318	0.000006
6	0	3.940876	-0.793547	0.000000
6	0	4.690621	-2.088765	0.000006
6	0	4.536573	0.424455	-0.000005
1	0	4.272308	2.484722	-0.000014
1	0	5.762882	-1.914133	0.000004
1	0	4.428547	-2.678224	0.874567
1	0	4.428545	-2.678232	-0.874549
1	0	5.608747	0.541356	-0.000007

MP2/BSS-B′a
Adduct Adenine-Thymine (A-T)
Symmetry C_s
energy MP2 = –919.708785 au
Standard orientation

7	0	-0.756957	-0.693929	0.000000
6	0	-2.106449	-0.718627	0.000000
7	0	-2.898698	-1.785168	0.000000
6	0	-2.187818	-2.918099	0.000000
6	0	-0.794230	-3.043560	0.000000
6	0	-0.057169	-1.838798	0.000000
7	0	1.281022	-1.803002	0.000000

7	0	-2.643155	-4.212392	0.000000
6	0	-1.543711	-5.025645	0.000000
7	0	-0.402529	-4.359051	0.000000
1	0	-2.578537	0.253303	0.000000
1	0	1.784429	-2.672116	0.000000
1	0	1.773054	-0.911342	0.000000
1	0	-1.632220	-6.096906	0.000000
1	0	-3.608987	-4.495458	0.000000
1	0	0.000000	0.886902	0.000000
7	0	0.450703	1.832249	0.000000
7	0	0.229760	4.124961	0.000000
6	0	-0.413335	2.901166	0.000000
8	0	-1.626335	2.794612	0.000000
6	0	1.829785	1.872497	0.000000
8	0	2.491252	0.832680	0.000000
6	0	2.430023	3.202363	0.000000
6	0	3.922459	3.313468	0.000000
6	0	1.592840	4.268903	0.000000
1	0	-0.376985	4.927936	0.000000
1	0	4.232045	4.354812	0.000000
1	0	4.339042	2.820915	0.874559
1	0	4.339042	2.820915	-0.874559
1	0	1.954373	5.285030	0.000000

MP2/BSS-B′a
Adduct Cytosine-Guanine (C-G)
Symmetry C_1
energy MP2 = –935.765002 au
Standard orientation

7	0	-4.639318	0.474202	-0.050132
6	0	-4.937707	-0.865593	-0.088426
7	0	-3.863782	-1.628242	-0.071126
6	0	-3.278110	0.583805	-0.004052
7	0	-2.573325	1.732031	0.045222
6	0	-1.276117	1.515403	0.083989
7	0	-0.414739	2.551188	0.183115
7	0	-0.717360	0.264965	0.063505
6	0	-1.404434	-0.948530	0.016323
8	0	-0.785002	-2.017060	0.007807
6	0	-2.820121	-0.736859	-0.018633
1	0	-5.285505	1.245410	-0.050688
1	0	-5.951645	-1.219250	-0.128123
1	0	-0.814871	3.463076	0.055082
1	0	0.585457	2.426283	0.037187
1	0	0.311990	0.184561	0.065571
7	0	2.160545	-0.072176	-0.006947
6	0	2.906207	1.060467	-0.073822
7	0	4.294558	0.910121	-0.084204
8	0	2.432630	2.195022	-0.125329
6	0	2.734316	-1.273292	0.037373
7	0	1.939070	-2.338835	0.090585
6	0	4.165033	-1.431728	0.029366
6	0	4.907788	-0.297642	-0.032987
1	0	4.824721	1.765506	-0.132487
1	0	0.911571	-2.225021	0.069158
1	0	2.341041	-3.258184	0.116965
1	0	4.630473	-2.400008	0.068650
1	0	5.985070	-0.295035	-0.046064

MP2/BSS-B′a
Adduct Adenine-Adenine (A-A)
Symmetry C_1
energy MP2 = –932.821002 au
Standard orientation

7	0	-1.788124	-0.992480	0.401771
6	0	-2.700097	-1.981461	0.450132
7	0	-4.017743	-1.907098	0.264450
6	0	-4.395377	-0.653599	-0.001001
6	0	-3.570659	0.473258	-0.083554
6	0	-2.192329	0.257157	0.138842
7	0	-1.298683	1.260585	0.108658
7	0	-5.655724	-0.171034	-0.255299
6	0	-5.533974	1.173638	-0.472672
7	0	-4.288949	1.606758	-0.378490
1	0	-2.305281	-2.962970	0.667674
1	0	-1.618899	2.162331	-0.198549
1	0	-0.300752	1.061017	0.172953
1	0	-6.386143	1.789692	-0.696046
1	0	-6.501511	-0.715734	-0.276319
1	0	0.613419	-1.314083	0.070385
7	0	1.585811	0.489197	0.232751
6	0	1.588198	-0.849128	0.035131
7	0	2.640831	-1.632874	-0.185332
6	0	3.779887	-0.938340	-0.194222
6	0	3.926039	0.441223	-0.002439
6	0	2.737316	1.161241	0.220780
7	0	2.734326	2.508806	0.384176
7	0	5.062553	-1.391168	-0.375140
6	0	5.888228	-0.304976	-0.283894
7	0	5.242820	0.825839	-0.057572
1	0	3.617740	2.950675	0.575810
1	0	1.912409	2.921074	0.791622
1	0	6.954185	-0.394773	-0.389994
1	0	5.331628	-2.347021	-0.539957

MP2/BSS-B′a
Adduct Adenine-Cytosine (A-C)
Symmetry C_1
energy MP2 = –860.609707 au
Standard orientation

1	0	-0.327809	-1.879665	-0.011674
7	0	-3.583904	-1.733546	0.023652
6	0	-4.612367	-0.873475	0.023528
7	0	-4.579355	0.459978	0.010803
6	0	-3.320934	0.901400	-0.001626
6	0	-2.147560	0.137159	-0.001998
6	0	-2.322901	-1.271803	0.010160
7	0	-1.314076	-2.145192	0.010110
7	0	-2.888247	2.206131	-0.016592
6	0	-1.529097	2.182997	-0.024663
7	0	-1.036444	0.952843	-0.016127
1	0	-5.593628	-1.324372	0.034815
1	0	-1.560146	-3.120375	0.013892
1	0	-0.942754	3.083854	-0.037164
1	0	-3.482426	3.018598	-0.020945
8	0	1.452302	-1.798081	-0.045597
7	0	1.792708	0.439975	-0.001919

6	0	2.262878	-0.873003	-0.024160
7	0	3.615659	-1.056895	-0.015523
6	0	4.421235	-0.016587	0.005385
7	0	5.755643	-0.271375	-0.032148
6	0	3.964693	1.339242	0.029019
6	0	2.612416	1.507360	0.025243
1	0	0.768943	0.572016	-0.007160
1	0	6.031236	-1.229184	0.105875
1	0	6.407870	0.446593	0.224327
1	0	4.637269	2.177790	0.040330
1	0	2.138967	2.476216	0.041356

MP2/BSS-B′a
Adduct Adenine-Guanine (A-G)
Symmetry C_1
energy MP2 = –1007.974268 au
Standard orientation

7	0	5.307451	0.292382	-0.174030
6	0	5.529171	-1.044541	0.039602
7	0	4.414172	-1.725494	0.213644
6	0	3.956789	0.486813	-0.131762
7	0	3.310816	1.661639	-0.316534
6	0	2.014877	1.523426	-0.205599
7	0	1.196785	2.626229	-0.300297
7	0	1.383290	0.345421	0.054082
6	0	1.995792	-0.905923	0.203652
8	0	1.313209	-1.911796	0.386584
6	0	3.423967	-0.782125	0.110606
1	0	5.996135	1.008914	-0.332415
1	0	6.520481	-1.458795	0.057286
1	0	1.664693	3.422969	-0.702876
1	0	0.278191	2.456206	-0.680186
1	0	0.352829	0.364869	0.181025
7	0	-1.465998	0.428841	0.303833
6	0	-2.162973	1.560347	0.541753
7	0	-3.476243	1.747003	0.483651
6	0	-4.108964	0.617962	0.142662
6	0	-3.527843	-0.626926	-0.119718
6	0	-2.119699	-0.703952	-0.018287
7	0	-1.441176	-1.833325	-0.237974
7	0	-5.454270	0.404359	-0.013632
6	0	-5.614707	-0.911985	-0.349394
7	0	-4.473063	-1.573300	-0.423371
1	0	-1.567768	2.417369	0.825117
1	0	-1.972155	-2.668696	-0.415841
1	0	-0.444702	-1.900964	-0.009020
1	0	-6.586092	-1.335868	-0.528642
1	0	-6.178087	1.093501	0.106188

MP2/BSS-B′a
Adduct Adenine-Uracil (A-U)
Symmetry C_1
energy MP2 = –880.488228 au
Standard orientation

7	0	-0.630964	-0.291627	-0.000008
6	0	-1.131422	-1.545255	-0.000026
7	0	-2.408987	-1.909448	-0.000037

6	0	-3.217621	-0.844020	-0.000027
6	0	-2.842252	0.503869	-0.000008
6	0	-1.454777	0.767739	0.000001
7	0	-0.948942	2.006962	0.000018
7	0	-4.589237	-0.812406	-0.000031
6	0	-4.961240	0.503589	-0.000018
7	0	-3.934224	1.335352	-0.000003
1	0	-0.389395	-2.330646	-0.000032
1	0	-1.584219	2.784932	0.000023
1	0	0.058693	2.152849	0.000022
1	0	-5.994599	0.799554	-0.000019
1	0	-5.195539	-1.615756	-0.000042
1	0	1.113539	-0.142995	0.000003
7	0	2.157815	-0.056540	0.000009
7	0	4.226558	-1.084908	0.000015
6	0	2.848501	-1.243633	0.000006
8	0	2.319980	-2.339329	-0.000003
6	0	2.684896	1.222620	0.000021
8	0	1.945980	2.205650	0.000024
6	0	4.137168	1.285141	0.000030
6	0	4.846730	0.132744	0.000027
1	0	4.755879	-1.940897	0.000013
1	0	4.619957	2.244251	0.000040
1	0	5.923983	0.109686	0.000034

MP2/BSS-B′a
Adduct Cytosine-Cytosine (C-C)
Symmetry C_1
energy MP2 = –788.395311 au
Standard orientation

7	0	-1.146017	-0.227485	-0.000288
6	0	-1.805630	0.994024	0.001109
8	0	-1.141103	2.038401	0.004160
7	0	-3.168278	0.975406	0.004872
6	0	-3.803527	-0.179892	-0.003705
7	0	-5.164434	-0.127763	-0.047980
6	0	-3.147497	-1.447758	-0.007761
6	0	-1.783263	-1.411240	-0.003685
1	0	-0.108353	-0.197404	0.001973
1	0	-5.574737	0.773002	0.133642
1	0	-5.693661	-0.938122	0.218013
1	0	-3.687404	-2.377323	-0.021699
1	0	-1.147221	-2.282983	-0.004798
7	0	1.643041	-0.071092	0.003734
6	0	2.262694	-1.284243	0.003597
7	0	3.665458	-1.262969	-0.000318
8	0	1.671345	-2.355369	0.006588
6	0	2.323878	1.068625	-0.000185
7	0	1.624326	2.203508	0.000012
6	0	3.763286	1.087735	-0.004327
6	0	4.389608	-0.117530	-0.004254
1	0	4.114308	-2.164843	-0.000591
1	0	0.590969	2.170706	0.001654
1	0	2.102960	3.085365	-0.004405
1	0	4.323261	2.005419	-0.007463
1	0	5.461985	-0.223634	-0.007266

MP2/BSS-B′a
Adduct Cytosine-Thymine (C-T)
Symmetry C_1
energy MP2 = –847.480698 au
Standard orientation

7	0	-2.978566	1.680608	-0.446903
6	0	-1.593887	1.609363	-0.431806
8	0	-0.888512	2.550931	-0.724723
7	0	-1.122467	0.366477	-0.058393
6	0	-1.872273	-0.763218	0.192839
8	0	-1.328136	-1.845665	0.429559
6	0	-3.320276	-0.597715	0.159733
6	0	-4.182916	-1.781304	0.468233
6	0	-3.803931	0.627592	-0.160627
1	0	-3.352796	2.577377	-0.708757
1	0	-0.093095	0.277250	0.056836
1	0	-5.235006	-1.517148	0.406890
1	0	-3.981008	-2.590628	-0.228422
1	0	-3.970981	-2.156201	1.466034
1	0	-4.861346	0.834212	-0.212498
7	0	1.684107	-0.098386	0.272449
6	0	2.491398	0.966938	0.581897
7	0	3.851270	0.828388	0.237195
8	0	2.112985	1.989483	1.120022
6	0	2.182116	-1.208342	-0.249231
7	0	1.329836	-2.217350	-0.483962
6	0	3.574845	-1.355601	-0.576061
6	0	4.374711	-0.288945	-0.314706
1	0	4.429532	1.623936	0.455830
1	0	0.368174	-2.146983	-0.142067
1	0	1.676331	-3.094057	-0.826156
1	0	3.969199	-2.257201	-1.008629
1	0	5.432314	-0.279320	-0.522247

MP2/BSS-B′a
Adduct Cytosine-Uracil (C-U)
Symmetry C_1
energy MP2 = –808.260401 au
Standard orientation

7	0	3.454521	-1.118197	-0.380667
6	0	2.066336	-1.209948	-0.404817
8	0	1.492794	-2.216307	-0.758966
7	0	1.436756	-0.052539	0.004695
6	0	2.033994	1.152383	0.325062
8	0	1.352310	2.144617	0.586814
6	0	3.486229	1.143119	0.321889
6	0	4.136652	0.009530	-0.029289
1	0	3.937503	-1.953644	-0.666302
1	0	0.400976	-0.095611	0.089745
1	0	4.014464	2.038406	0.590356
1	0	5.211451	-0.063435	-0.056771
7	0	-1.410632	0.046589	0.266745
6	0	-2.081919	-1.125973	0.504974
7	0	-3.444834	-1.138210	0.145848
8	0	-1.583775	-2.121929	0.993372
6	0	-2.037679	1.113567	-0.203322
7	0	-1.315921	2.231875	-0.368936
6	0	-3.434405	1.104430	-0.545727

6	0	-4.097785	-0.065694	-0.354720
1	0	-3.921742	-2.009931	0.312407
1	0	-0.357750	2.263610	-0.012388
1	0	-1.765811	3.076630	-0.668597
1	0	-3.933664	1.972600	-0.936255
1	0	-5.143836	-0.194786	-0.580057

MP2/BSS-B′a
Adduct Guanine-Guanine (G-G)
Symmetry C_i
energy MP2 = –1083.124286 au
Standard orientation

7	0	4.555241	2.906066	0.017867
6	0	5.268101	1.732989	0.010055
7	0	4.496361	0.665712	-0.018756
6	0	3.231306	2.574253	-0.009808
7	0	2.191725	3.435206	-0.011167
6	0	1.041138	2.806481	-0.044137
7	0	-0.128067	3.499099	-0.111230
7	0	0.913770	1.447883	-0.060791
6	0	1.950287	0.521683	-0.050021
8	0	1.697202	-0.692233	-0.051227
6	0	3.221965	1.174455	-0.032166
1	0	4.920948	3.843544	0.035469
1	0	6.342478	1.723199	0.026345
1	0	-0.074682	4.473440	0.127767
1	0	-0.987382	3.012745	0.094280
1	0	-0.056484	1.079203	-0.050107
8	0	-1.697202	0.692233	0.051227
6	0	-1.950287	-0.521683	0.050021
7	0	-4.555241	-2.906066	-0.017867
6	0	-5.268101	-1.732989	-0.010055
7	0	-4.496361	-0.665712	0.018756
6	0	-3.231306	-2.574253	0.009808
7	0	-2.191725	-3.435206	0.011167
6	0	-1.041138	-2.806481	0.044137
7	0	0.128067	-3.499099	0.111230
7	0	-0.913770	-1.447883	0.060791
6	0	-3.221965	-1.174455	0.032166
1	0	-4.920948	-3.843544	-0.035469
1	0	-6.342478	-1.723199	-0.026345
1	0	0.074682	-4.473440	-0.127767
1	0	0.987382	-3.012745	-0.094280
1	0	0.056484	-1.079203	0.050107

MP2/BSS-B′a
Adduct Guanine-Thymine (G-T)
Symmetry C_1
energy MP2 = –994.842973 au
Standard orientation

7	0	-1.900110	2.032126	-0.671355
6	0	-3.097003	2.703800	-0.598522
7	0	-4.085548	1.933265	-0.196219
6	0	-2.142175	0.741072	-0.295935
7	0	-1.225615	-0.260556	-0.237340
6	0	-1.749045	-1.412327	0.128438
7	0	-0.958182	-2.501443	0.264468

7	0	-3.074383	-1.551414	0.425009
6	0	-4.085236	-0.545910	0.412029
8	0	-5.222185	-0.832472	0.721189
6	0	-3.504888	0.705994	-0.006319
1	0	-1.022442	2.399090	-0.999710
1	0	-3.177947	3.745276	-0.849806
1	0	-0.031009	-2.465694	-0.164867
1	0	-1.392687	-3.405788	0.317464
1	0	-3.418267	-2.454594	0.720957
7	0	1.617462	-0.111438	-0.069684
6	0	2.264240	-1.254557	-0.438818
8	0	1.682192	-2.280315	-0.783797
7	0	3.633578	-1.162817	-0.389172
6	0	4.407810	-0.064645	0.002817
8	0	5.624956	-0.132204	-0.003235
6	0	3.630008	1.104520	0.403558
6	0	4.371534	2.322596	0.857130
6	0	2.277612	1.016178	0.345733
1	0	0.585889	-0.129529	-0.129439
1	0	4.141088	-1.994745	-0.658074
1	0	3.681381	3.116439	1.128138
1	0	4.995038	2.088008	1.715739
1	0	5.031156	2.678958	0.070404
1	0	1.640534	1.838121	0.635322

MP2/BSS-B′a
Adduct Guanine-Uracil (G-U)
Symmetry C_1
energy MP2 = –955.625708 au
Standard orientation

7	0	-4.728759	-0.438129	-0.036134
6	0	-4.520006	-1.794484	-0.042806
7	0	-3.242035	-2.114301	-0.022014
6	0	-3.500853	0.157529	-0.007233
7	0	-3.259835	1.489187	0.002919
6	0	-1.977936	1.748685	0.035694
7	0	-1.538466	3.043324	0.118316
7	0	-1.004725	0.795650	0.045717
6	0	-1.193182	-0.590729	0.022692
8	0	-0.220482	-1.344058	0.021469
6	0	-2.593092	-0.906316	0.000923
1	0	-5.611513	0.044949	-0.045180
1	0	-5.335993	-2.493306	-0.062950
1	0	-2.224998	3.729822	-0.145800
1	0	-0.595737	3.228286	-0.185614
1	0	-0.023171	1.100937	0.051893
8	0	1.622552	1.668990	-0.050067
6	0	2.566480	0.874655	-0.033125
7	0	3.862654	1.330298	-0.047045
7	0	2.432118	-0.477756	-0.000155
6	0	4.809716	-0.840845	0.005469
6	0	4.955844	0.500237	-0.027556
6	0	3.472119	-1.426499	0.021680
8	0	3.226469	-2.614811	0.050970
1	0	3.966404	2.330736	-0.067102
1	0	1.461810	-0.846323	0.010108
1	0	5.659028	-1.498107	0.020530
1	0	5.914656	0.990729	-0.040511

MP2/BSS-B′a
Adduct Thymine-Thymine (T-T)
Symmetry C_1
energy MP2 = –906.579293 au
Standard orientation

7	0	4.015925	1.146546	-0.000002
6	0	2.738262	1.677898	-0.000003
8	0	2.524131	2.872592	-0.000008
7	0	1.752782	0.711995	-0.000002
6	0	1.928195	-0.657822	0.000001
8	0	0.960875	-1.421081	0.000001
6	0	3.307088	-1.129628	0.000004
6	0	3.554832	-2.605584	0.000007
6	0	4.289372	-0.195693	0.000002
1	0	4.757614	1.826811	-0.000004
1	0	0.778429	1.048474	-0.000003
1	0	4.620367	-2.817193	0.000008
1	0	3.102298	-3.065835	0.874188
1	0	3.102299	-3.065839	-0.874172
1	0	5.335205	-0.459133	0.000002
8	0	-0.960869	1.421073	0.000002
6	0	-1.928192	0.657817	0.000001
7	0	-1.752783	-0.712001	-0.000002
7	0	-4.015931	-1.146540	-0.000003
6	0	-2.738270	-1.677898	-0.000004
8	0	-2.524146	-2.872593	-0.000007
6	0	-3.307082	1.129631	0.000003
6	0	-3.554818	2.605587	0.000007
6	0	-4.289372	0.195701	0.000001
1	0	-4.757624	-1.826800	-0.000005
1	0	-0.778432	-1.048484	-0.000002
1	0	-4.620352	2.817202	0.000008
1	0	-3.102282	3.065834	0.874189
1	0	-3.102281	3.065839	-0.874172
1	0	-5.335204	0.459145	0.000001

MP2/BSS-B′a
Adduct Thymine-Thymine (T-T)
Symmetry C_i
energy MP2 = –906.579293 au
Standard orientation

7	0	-4.015964	-1.146453	0.000012
6	0	-2.738318	-1.677844	0.000005
8	0	-2.524228	-2.872546	0.000000
7	0	-1.752805	-0.711976	0.000002
6	0	-1.928186	0.657844	-0.000002
8	0	-0.960837	1.421071	0.000001
6	0	-3.307066	1.129697	0.000010
6	0	-3.554746	2.605663	0.000007
6	0	-4.289379	0.195792	0.000021
1	0	-4.757673	-1.826696	0.000000
1	0	-0.778457	-1.048468	-0.000001
1	0	-4.620274	2.817298	0.000018
1	0	-3.102167	3.065894	0.874180
1	0	-3.102190	3.065881	-0.874185
1	0	-5.335206	0.459258	0.000045

7	0	4.015964	1.146453	-0.000012
6	0	2.738318	1.677844	-0.000005
8	0	2.524228	2.872546	0.000000
7	0	1.752805	0.711976	-0.000002
6	0	1.928186	-0.657844	0.000002
8	0	0.960837	-1.421071	-0.000001
6	0	3.307066	-1.129697	-0.000010
6	0	3.554746	-2.605663	-0.000007
6	0	4.289379	-0.195792	-0.000021
1	0	4.757673	1.826696	0.000000
1	0	0.778457	1.048468	0.000001
1	0	4.620274	-2.817298	-0.000018
1	0	3.102190	-3.065881	0.874185
1	0	3.102167	-3.065894	-0.874180
1	0	5.335206	-0.459258	-0.000045

MP2/BSS-B′a
Adduct Thymine-Uracil (T-U)
Symmetry C_1
energy MP2 = –867.358642 au
Standard orientation

7	0	3.911513	-0.902912	-0.000005
6	0	2.702004	-1.575208	-0.000001
8	0	2.623854	-2.786120	-0.000005
7	0	1.613636	-0.726225	0.000001
6	0	1.633803	0.654430	0.000001
8	0	0.586690	1.304334	0.000005
6	0	2.950508	1.278705	-0.000001
6	0	3.030278	2.773207	0.000000
6	0	4.031846	0.461440	-0.000004
1	0	4.725184	-1.495226	-0.000018
1	0	0.684114	-1.170497	0.000004
1	0	4.065200	3.103444	-0.000003
1	0	2.528841	3.179550	-0.874216
1	0	2.528848	3.179549	0.874221
1	0	5.041273	0.841200	-0.000007
8	0	-1.012856	-1.730906	0.000017
6	0	-2.055421	-1.079095	0.000009
7	0	-2.027544	0.305394	-0.000001
7	0	-4.330297	0.504905	-0.000006
6	0	-3.107410	1.162574	-0.000008
8	0	-3.021762	2.372153	-0.000016
6	0	-3.382970	-1.667276	0.000010
6	0	-4.464111	-0.854075	0.000004
1	0	-5.135371	1.108813	-0.000020
1	0	-1.093961	0.743507	-0.000001
1	0	-3.478399	-2.736618	0.000018
1	0	-5.475465	-1.225760	0.000005

MP2/BSS-B′a
Adduct Uracil-Uracil (U-U)
Symmetry C_1
energy MP2 = –828.137946 au
Standard orientation

7	0	4.173591	0.304066	-0.000025
6	0	3.022992	1.081394	-0.000011
8	0	3.059027	2.293170	0.000005

7	0	1.862235	0.336588	-0.000018
6	0	1.751406	-1.043499	-0.000039
8	0	0.648772	-1.588064	-0.000033
6	0	3.013012	-1.761919	-0.000046
6	0	4.170350	-1.061328	-0.000042
1	0	5.035201	0.824174	-0.000021
1	0	0.978016	0.866215	-0.000006
1	0	3.000535	-2.835420	-0.000055
1	0	5.139271	-1.532681	-0.000050
8	0	-0.648771	1.588063	0.000012
6	0	-1.751405	1.043499	0.000013
7	0	-1.862234	-0.336588	0.000006
7	0	-4.173592	-0.304066	0.000042
6	0	-3.022992	-1.081394	0.000019
8	0	-3.059027	-2.293170	0.000013
6	0	-3.013013	1.761919	0.000045
6	0	-4.170351	1.061327	0.000054
1	0	-5.035201	-0.824175	0.000053
1	0	-0.978017	-0.866216	-0.000009
1	0	-3.000536	2.835420	0.000058
1	0	-5.139272	1.532681	0.000074

MP2/BSS-B′a
Adduct Uracil-Uracil (U-U)
Symmetry C_s
energy MP2 = –828.137946 au
Standard orientation

7	0	0.680045	-4.129027	0.000000
6	0	1.350196	-2.912876	0.000000
8	0	2.560270	-2.839240	0.000000
7	0	0.503525	-1.824191	0.000000
6	0	-0.880934	-1.838554	0.000000
8	0	-1.522925	-0.789650	0.000000
6	0	-1.482381	-3.159928	0.000000
6	0	-0.680050	-4.249206	0.000000
1	0	1.275899	-4.940101	0.000000
1	0	0.951068	-0.895724	0.000000
1	0	-2.552616	-3.244538	0.000000
1	0	-1.061905	-5.256762	0.000000
8	0	1.522930	0.789653	0.000000
6	0	0.880937	1.838557	0.000000
7	0	-0.503521	1.824191	0.000000
7	0	-0.680050	4.129026	0.000000
6	0	-1.350196	2.912873	0.000000
8	0	-2.560270	2.839232	0.000000
6	0	1.482380	3.159934	0.000000
6	0	0.680045	4.249209	0.000000
1	0	-1.275907	4.940098	0.000000
1	0	-0.951063	0.895722	0.000000
1	0	2.552614	3.244548	0.000000
1	0	1.061897	5.256766	0.000000

Appendix

QTAIM Dual Functional Analysis (QTAIM-DFA)

The bond critical point (BCP; ∗) is an important concept in QTAIM. The BCP of $(\omega, \sigma) = (3, -1)$[SA1] is a point along the bond path (BP) at the interatomic surface, where charge density $\rho(\boldsymbol{r})$ reaches a minimum. It is donated by $\rho_b(\boldsymbol{r}_c)$, so are other QTAIM functions, such as the total electron energy densities $H_b(\boldsymbol{r}_c)$, potential energy densities $V_b(\boldsymbol{r}_c)$ and kinetic energy densities $G_b(\boldsymbol{r}_c)$ at the BCPs. A chemical bond or interaction between A and B is denoted by A–B, which corresponds to the BP between A and B in QTAIM. We will use A-∗-B for BP, where the asterisk emphasizes the presence of a BCP in A–B.

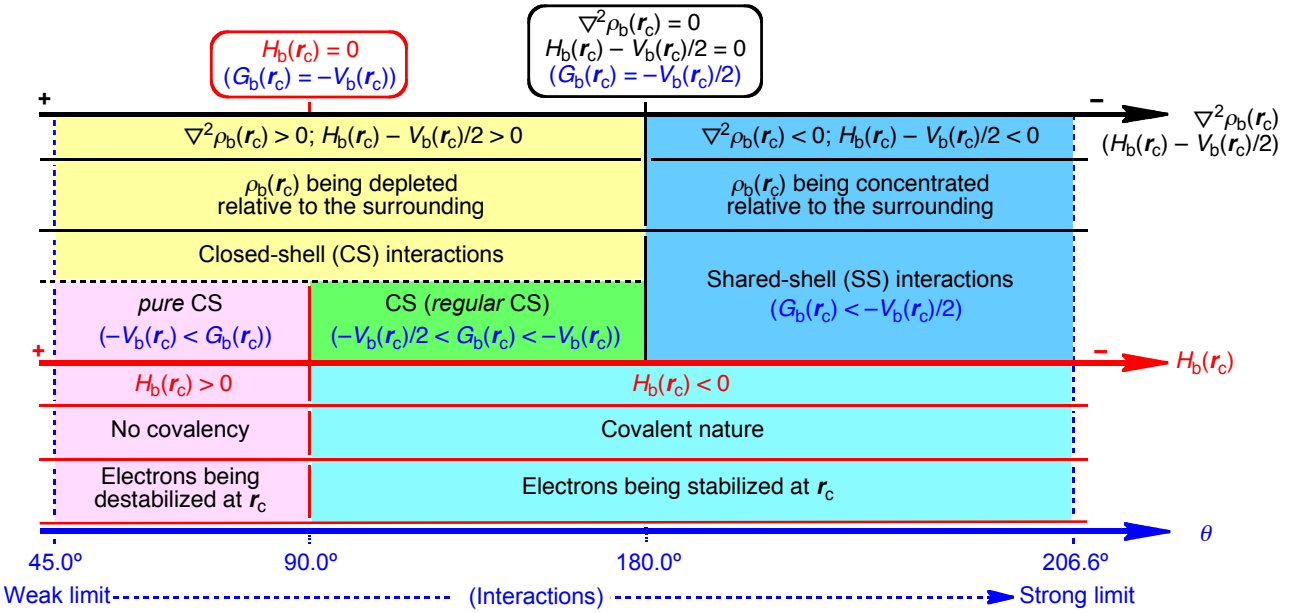
The sign of the Laplacian $\rho_b(\boldsymbol{r}_c)$ ($\nabla^2\rho_b(\boldsymbol{r}_c)$) indicates that $\rho_b(\boldsymbol{r}_c)$ is depleted or concentrated with respect to its surrounding, since $\nabla^2\rho_b(\boldsymbol{r}_c)$ is the second derivative of $\rho_b(\boldsymbol{r}_c)$. $\rho_b(\boldsymbol{r}_c)$ is locally depleted relative to the average distribution around $\boldsymbol{r}_c$ if $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, but it is concentrated when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$. Total electron energy densities at BCPs ($H_b(\boldsymbol{r}_c)$) must be a more appropriate measure for weak interactions on the energy basis.[SA1–SA8] $H_b(\boldsymbol{r}_c)$ are the sum of kinetic energy densities ($G_b(\boldsymbol{r}_c)$) and potential energy densities ($V_b(\boldsymbol{r}_c)$) at BCPs, as shown in eqn (SA1). Electrons at BCPs are stabilized when $H_b(\boldsymbol{r}_c) < 0$, therefore, interactions exhibit the covalent nature in this region, whereas they exhibit no covalency if $H_b(\boldsymbol{r}_c) > 0$, due to the destabilization of electrons at BCPs under the conditions.[SA1] Eqn (SA2) represents the relation between $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$, which is closely related to the virial theorem.

$$H_b(\boldsymbol{r}_c) = G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c) \quad \text{(SA1)}$$

$$(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 \quad \text{(SA2)}$$

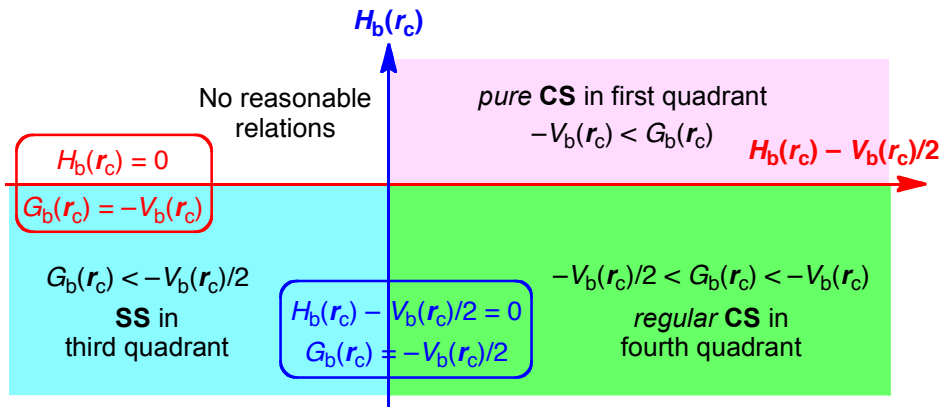
$$= G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2 \quad \text{(SA2')}$$

Interactions are classified by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Interactions in the region of $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ are called shared-shell (SS) interactions and they are closed-shell (CS) interactions for $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$. $H_b(\boldsymbol{r}_c)$ must be negative when $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$, since $H_b(\boldsymbol{r}_c)$ are larger than $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$ by $V_b(\boldsymbol{r}_c)/2$ with negative $V_b(\boldsymbol{r}_c)$ at all BCPs (eqn (SA2)). Consequently, $\nabla^2\rho_b(\boldsymbol{r}_c) < 0$ and $H_b(\boldsymbol{r}_c) < 0$ for the SS interactions. The CS interactions are especially called *pure* CS interactions for $H_b(\boldsymbol{r}_c) > 0$ and $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$, since electrons at BCPs are depleted and destabilized under the conditions.[SA1a] Electrons in the intermediate region between SS and *pure* CS, which belong to CS, are locally depleted but stabilized at BCPs, since $\nabla^2\rho_b(\boldsymbol{r}_c) > 0$ but $H_b(\boldsymbol{r}_c) < 0$.[SA1a] We call the interactions in this region *regular* CS,[SA4,SA5] when it is necessary to distinguish from *pure* CS. The role of $\nabla^2\rho_b(\boldsymbol{r}_c)$ in the classification can be replaced by $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, since $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c) = H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (eqn (SA2)). Scheme SA1 summarizes the classification.



Scheme SA1. Classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$, together with $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$.

We proposed QTAIM-DFA by plotting $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ (= $(\hbar^2/8m)\nabla^2\rho_b(\boldsymbol{r}_c)$),[SA4a] after the proposal of $H_b(\boldsymbol{r}_c)$ versus $\nabla^2\rho_b(\boldsymbol{r}_c)$.[SA4b] Both axes in the plot of the former are given in energy unit, therefore, distances on the (x, y) (= $(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$ plane can be expressed in the energy unit, which provides an analytical development. QTAIM-DFA incorporates the classification of interactions by the signs of $\nabla^2\rho_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c)$. Scheme SA2 summarizes the QTAIM-DFA treatment. Interactions of *pure* CS appear in the first quadrant, those of *regular* CS in the fourth quadrant and SS interactions do in the third quadrant. No interactions appear in the second one.



Scheme SA2. QTAIM-DFA: Plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for Weak to Strong Interactions.

In our treatment, data for perturbed structures around fully optimized structures are also employed for the plots, together with the fully optimized ones (see Fig. SA1).[SA4–SA8] We proposed the concept of the "dynamic nature of interaction" originated from the perturbed structures. The behavior of interactions at the fully optimized structures corresponds to "the static nature of interactions", whereas that containing perturbed structures exhibit the "dynamic nature of interaction" as explained below. The method to generate the perturbed structures is discussed later. Plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are analyzed

employing the polar coordinate (R, θ) representation with (θ_p, κ_p) parameters.[SA4a,SA5–SA8] Fig. SA1 explains the treatment. R in (R, θ) is defined by eqn (SA3) and given in the energy unit. Indeed, R does not correspond to the usual interaction energy, but it does to the local energy at BCP, expressed by $[(H_b(\boldsymbol{r}_c))^2 + (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)^2]^{1/2}$ in the plot (cf: eqn (SA3)), where $R = 0$ for the enough large interaction distance. The plots show a spiral stream, as a whole. θ in (R, θ) defined by eqn (SA4), measured from the y-axis, controls the spiral stream of the plot. Each plot for an interaction shows a specific curve, which provides important information of the interaction (see Fig. SA1). The curve is expressed by θ_p and κ_p. While θ_p, defined by eqn (SA5) and measured from the y-direction, corresponds to the tangent line of a plot, where θ_p is calculated employing data of the perturbed structures with a fully-optimized structure and κ_p is the curvature of the plot (eqn (SA6)). While (R, θ) correspond to the static nature, (θ_p, κ_p) represent the dynamic nature of interactions. We call (R, θ) and (θ_p, κ_p) QTAIM-DFA parameters, whereas $\rho_b(\boldsymbol{r}_c)$, $\nabla^2\rho_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $V_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ belong to QTAIM functions. $k_b(\boldsymbol{r}_c)$, defined by eqn (SA7), is an QTAIM function but it will be treated as if it were an QTAIM-DFA parameter, if suitable.

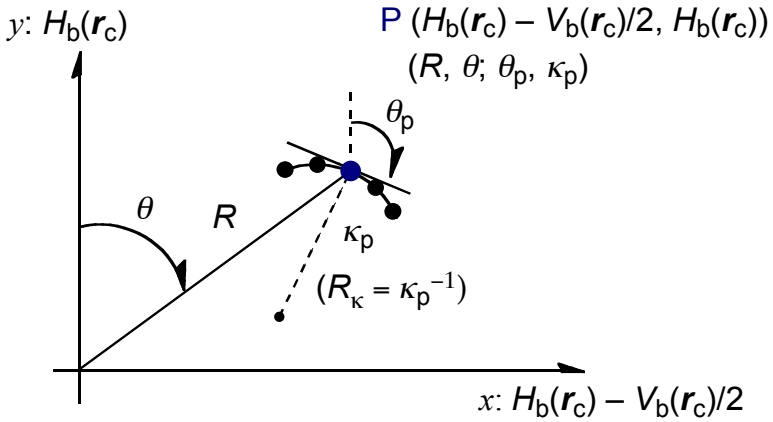


Fig. SA1 Polar (R, θ) coordinate representation of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, with ($\theta_p$, κ_p) parameters.

$$R = (x^2 + y^2)^{1/2} \quad \text{(SA3)}$$

$$\theta = 90^\circ - \tan^{-1}(y/x) \quad \text{(SA4)}$$

$$\theta_p = 90^\circ - \tan^{-1}(\mathrm{d}y/\mathrm{d}x) \quad \text{(SA5)}$$

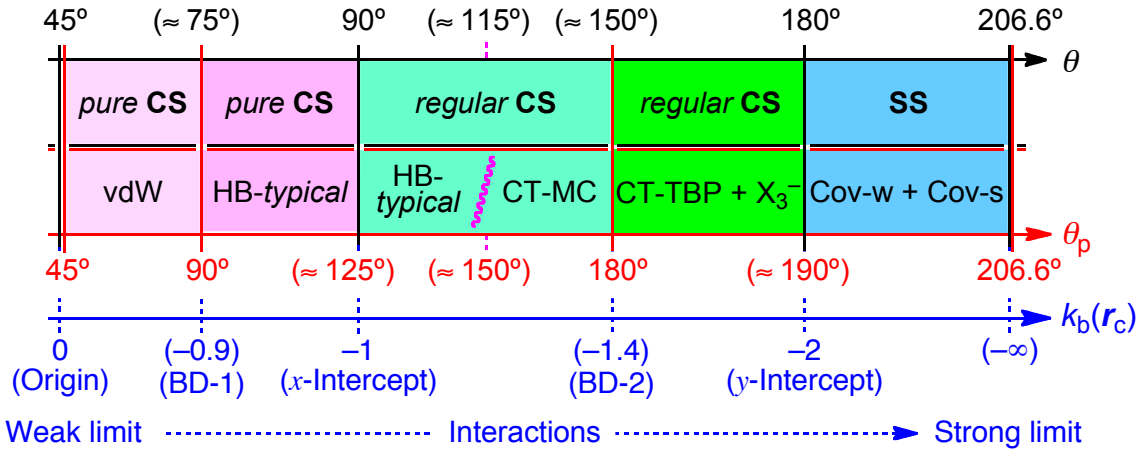
$$\kappa_p = |\,\mathrm{d}^2y/\mathrm{d}x^2|\,/[1 + (\mathrm{d}y/\mathrm{d}x)^2]^{3/2} \quad \text{(SA6)}$$

$$k_b(\boldsymbol{r}_c) = V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c) \quad \text{(SA7)}$$

where $(x, y) = (H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2, H_b(\boldsymbol{r}_c))$

Criteria for Classification of Interactions: Behavior of Typical Interactions Elucidated by QTAIM-DFA

$H_b(\boldsymbol{r}_c)$ are plotted versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ for typical interactions in vdW (van der Waals interactions), HBs (hydrogen bonds), CT-MCs (molecular complexes through charge transfer), X_3^- (trihalide ions), CT-TBPs (trigonal bipyramidal adducts through charge-transfer), Cov-w (weak covalent bonds) and Cov-s (strong covalent bonds).[SA4–SA8] Rough criteria are obtained by applying QTAIM-DFA, after the analysis of the plots for the typical interactions according to eqns (SA3)–(SA7). Scheme SA3 shows the rough criteria, which are accomplished by the θ and θ_p values, together with the values of $k_b(\boldsymbol{r}_c)$. The criteria will be employed to discuss the nature of interactions in question, as a reference.



Scheme SA3. Rough classification and characterization of interactions by θ and θ_p, together with $k_b(\boldsymbol{r}_c)$ (= $V_b(\boldsymbol{r}_c)/G_b(\boldsymbol{r}_c)$).

Characterization of interactions

The characterization of interactions is explained employing $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$. The wide range of the perturbed structures were generated by partially optimizing $r(^2Cl\text{-}^3Cl)$ in $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$, assuming the $C_{\infty v}$ symmetry, with $r(^1Cl\text{-}^2Cl)$ being fixed in the wide range. The partial optimization method is called POM.[SA4b,SA5] The QTAIM functions, such as $V_b(\boldsymbol{r}_c)$, $G_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ are calculated at BCPs for the wide varieties of the perturbed structures of $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$. $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ and $H_b(\boldsymbol{r}_c)$ are plotted versus the interaction distances $r(^1Cl\text{-}^2Cl)$ in the perturbed structures of $[^1Cl\text{-}^2Cl\text{-}^3Cl]^-$, in the wide range. Fig. SA2 shows the plots. Each plot is analyzed using a regression curve of the ninth function and the first derivative of each regression curve is obtained. As shown in Fig. SA2, the maximum value of $H_b(\boldsymbol{r}_c)$ ($dH_b(\boldsymbol{r}_c)/dr = 0$) is defined as the borderline between vdW and t-HB interactions. Similarly, the maximum value of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ ($d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/dr = 0$) does to the borderline between CT-MC and CT-TBP. However, it seems difficult to find a characteristic point corresponding to the borderline between *t*-HB and CT-MC in nature. Therefore, the borderline is tentatively given by $\theta_p = 150°$ based on the expectation form the experimental results, where θ_p is defined by $[90° - \tan^{-1}[dH_b(\boldsymbol{r}_c)/d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]]$ in the plot of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$. The proposed classification and characterization of interactions, by means of the QTAIM functions of $H_b(\boldsymbol{r}_c)$, $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$, $G_b(\boldsymbol{r}_c)$ and/or $V_b(\boldsymbol{r}_c)$, are summarized in Table SA1. The plot of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ versus w in Fig. SA2 is essentially the same as that of $\nabla^2\rho_b(\boldsymbol{r}_c)$ versus d(H---F) in X–H---F–Y, presented by Espinosa and co-workers.[SA9]

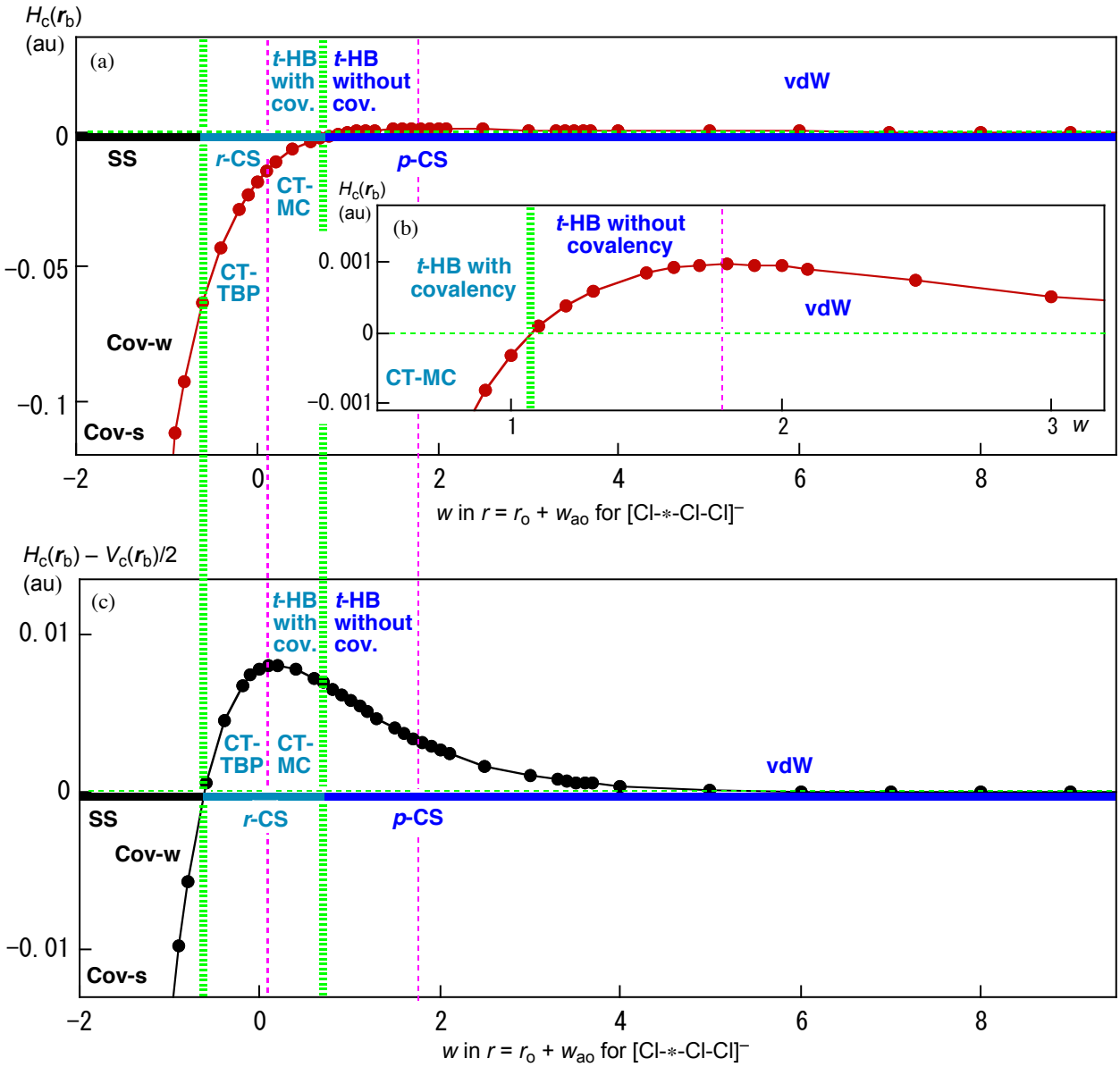


Fig. SA2 Plot of $H_b(\boldsymbol{r}_c)$ versus w in $r(^1\text{Cl-}^2\text{Cl}) = r_o(^1\text{Cl-}^2\text{Cl}) + wa_o$ for $^1\text{Cl-}^2\text{Cl-}^3\text{Cl}^-$ (a) with the magnified picture of (a) (b) and that of $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ versus w (c). Typical hydrogen bonds without covalency and typical hydrogen bonds with covalency are abbreviated as *t*-HB without cov. and *t*-HB with cov., respectively, whereas Cov-w and Cov-s stand for weak covalent bonds and strong covalent bonds, respectively.

Table SA1. Proposed definitions for the classification and characterization of interactions by the signs $H_b(\boldsymbol{r}_c)$ and $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$ and their first derivatives, together with the tentatively proposed definitions by the characteristic points on the plots of $H_b(\boldsymbol{r}_c)$ versus $H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2$. The tentatively proposed definitions are shown by italic. The requirements for the interactions are also shown.

ChP/Interaction	Requirements by $H_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$	Requirements by $G_b(\boldsymbol{r}_c)$ and $V_b(\boldsymbol{r}_c)$
Origin	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 = 0$; $H_b(\boldsymbol{r}_c) = 0$	$G_b(\boldsymbol{r}_c) = 0$; $V_b(\boldsymbol{r}_c) = 0$
vdW	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) > 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c)/d(-r) > -dV_b(\boldsymbol{r}_c)/d(-r)$
Borderline (BD-1)	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) = 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c)/d(-r) = -dV_b(\boldsymbol{r}_c)/d(-r)$
t-HB$_{\text{with no covalency}}$	$H_b(\boldsymbol{r}_c) > 0$; $dH_b(\boldsymbol{r}_c)/d(-r) < 0$	$G_b(\boldsymbol{r}_c) > -V_b(\boldsymbol{r}_c)$; $dG_b(\boldsymbol{r}_c) < -dV_b(\boldsymbol{r}_c)$
Borderline (*x*-intercept)	$H_b(\boldsymbol{r}_c) = 0$ ($\theta_p^a = 125^o$)	$G_b(\boldsymbol{r}_c) = -V_b(\boldsymbol{r}_c)$ ($\theta_p^a = 125^o$)
t-HB$_{\text{with covalency}}$	$H_b(\boldsymbol{r}_c) < 0$; ($125^o <$) $\theta_p^a < 150^o$	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$; ($125^o <$) $\theta_p^b < 150^o$
Borderline (Tentative)	*$\theta_p^a = 150^o$*	*$\theta_p^b = 150^o$*
CT-MC	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) > 0$;	$dG_b(\boldsymbol{r}_c) > dV_b(\boldsymbol{r}_c)/2$;
	$150^o < \theta_p^a < 180^o$	$150^o < \theta_p^a < 180^o$
Borderline (BD-2)	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) = 0$	$2dG_b(\boldsymbol{r}_c)/d(-r) = -dV_b(\boldsymbol{r}_c)/d(-r)$
	($H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 > 0$; $H_b(\boldsymbol{r}_c) < 0$)	($-V_b(\boldsymbol{r}_c)/2 < G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
CT-TBP with X_3^-	$d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)/d(-r) < 0$	$2dG_b(\boldsymbol{r}_c)/d(-r) < -dV_b(\boldsymbol{r}_c)/d(-r)$
	($H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 > 0$; $H_b(\boldsymbol{r}_c) < 0$)	($-V_b(\boldsymbol{r}_c)/2 < G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
Borderline (*y*-intercept)	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 = 0$ ($H_b(\boldsymbol{r}_c) < 0$)	$G_b(\boldsymbol{r}_c) = -V_b(\boldsymbol{r}_c)/2$ ($G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)$)
Cov-w	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 < 0$; *$R^c < 0.15$ au*	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)/2$; *$R^c < 0.15$ au*
Borderline (Tentative)	*$R^c = 0.15$ au*	*$R^d = 0.15$ au*
Cov-s	$H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2 < 0$; *$R^c > 0.15$ au*	$G_b(\boldsymbol{r}_c) < -V_b(\boldsymbol{r}_c)/2$; *$R^d > 0.15$ au*

[a] $\theta_p = 90^o - \tan^{-1}[dH_b(\boldsymbol{r}_c)/d(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]$, $\theta_p = 125^o$ is tentatively given for $\theta = 90^o$, where θ is defined by $90^o - \tan^{-1}[H_b(\boldsymbol{r}_c)/(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)]$ with $H_b(\boldsymbol{r}_c) = 0$. [b] $\theta_p = 90^o - \tan^{-1}[d(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))/d(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)]$, $\theta_p = 125^o$ is tentatively given for $\theta = 90^o$, where θ is defined by $90^o - \tan^{-1}[(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))/(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)]$ with $(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)) = 0$]. [c] $R = [(H_b(\boldsymbol{r}_c) - V_b(\boldsymbol{r}_c)/2)^2 + (H_b(\boldsymbol{r}_c))^2]^{1/2}$. [d] $R = [(G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c)/2)^2 + (G_b(\boldsymbol{r}_c) + V_b(\boldsymbol{r}_c))^2]^{1/2}$.

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