

Supplemental Tables and Figures

to accompany

“Why does the optimal tuning method of the range separation parameter of a long-range corrected density functional fail in intramolecular charge transfer excitation calculations?”

by

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Molecules

Table S1. Intramolecular CT excitation energy between electron-donating orbital corresponding to -NH₂ and electron-withdrawing orbitals corresponding to various electron acceptors (eV). Values in parentheses are errors of CT excitation energies from EOM-CCSD.

<i>n</i>	Distance R(Å)	-X	EOM-CCSD (cc-pVTZ)	EOM-CCSD (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	HF	B3LYP	BLYP
2	6.19	-NH ₂	5.81	5.78 (-0.02)	5.42 (-0.39)	5.03 (-0.78)	5.69 (-0.12)	5.11 (-0.70)	4.86 (-0.94)
	6.12	-OH	5.97	5.98 (0.02)	5.59 (-0.38)	5.42 (-0.54)	5.86 (-0.10)	5.25 (-0.71)	5.02 (-0.95)
	5.29	-Cl	5.66	5.81 (0.15)	5.44 (-0.22)	5.18 (-0.48)	5.70 (0.04)	5.00 (-0.66)	4.86 (-0.80)
	6.16	-CHO	4.88	4.99 (0.11)	4.80 (-0.08)	4.59 (-0.29)	5.10 (0.22)	4.50 (-0.38)	4.30 (-0.58)
	6.14	-CN	5.08	5.18 (0.11)	4.94 (-0.14)	4.76 (-0.32)	5.16 (0.08)	4.67 (-0.41)	4.50 (-0.58)
	6.12	-NO ₂	4.53	4.67 (0.14)	4.49 (-0.04)	4.26 (-0.27)	4.89 (0.36)	4.05 (-0.49)	3.80 (-0.73)
3	8.65	-NH ₂	5.00	5.12 (0.11)	4.71 (-0.29)	4.41 (-0.59)	4.91 (-0.09)	4.25 (-0.75)	4.11 (-0.89)
	8.57	-OH	5.14	5.25 (0.11)	4.82 (-0.32)	4.55 (-0.60)	5.02 (-0.13)	4.38 (-0.77)	4.19 (-0.95)
	7.76	-Cl	4.94	5.05 (0.11)	4.68 (-0.26)	4.55 (-0.55)	4.87 (-0.06)	4.25 (-0.69)	4.02 (-0.92)
	8.61	-CHO	4.34	4.43 (0.10)	4.20 (-0.14)	3.94 (-0.40)	4.42 (0.09)	3.81 (-0.53)	3.60 (-0.74)
	8.60	-CN	4.45	4.54 (0.09)	4.28 (-0.16)	4.04 (-0.40)	4.47 (0.02)	3.93 (-0.52)	3.75 (-0.70)
	8.57	-NO ₂	4.09	4.20 (0.11)	3.99 (-0.09)	3.72 (-0.36)	4.28 (0.19)	3.50 (-0.58)	3.25 (-0.83)
4	11.11	-NH ₂	4.50	4.60 (0.10)	4.20 (-0.30)	3.88 (-0.62)	4.35 (-0.15)	3.72 (-0.79)	3.49 (-1.02)
	11.03	-OH	4.61	4.71 (0.10)	4.28 (-0.32)	3.96 (-0.65)	4.43 (-0.18)	3.80 (-0.81)	3.57 (-1.04)
	10.22	-Cl	4.44	4.53 (0.09)	4.17 (-0.27)	3.85 (-0.59)	4.32 (-0.12)	3.68 (-0.76)	3.45 (-0.99)
	11.06	-CHO	3.96	4.06 (0.09)	3.79 (-0.17)	3.49 (-0.48)	3.97 (0.00)	3.32 (-0.64)	3.09 (-0.87)
	11.05	-CN	4.03	4.12 (0.08)	3.85 (-0.19)	3.56 (-0.47)	4.00 (-0.03)	3.41 (-0.62)	3.21 (-0.82)
	11.03	-NO ₂	3.76	3.86 (0.10)	3.64 (-0.13)	3.34 (-0.43)	3.85 (0.09)	3.10 (-0.66)	2.84 (-0.92)
5	13.57	-NH ₂			3.83	3.47			
	13.50	-OH			3.9	3.53			
	12.69	-Cl			3.81	3.44			
	13.52	-CHO			3.5	3.15			
	13.51	-CN			3.54	3.2			
	13.48	-NO ₂			3.37	3.03			
6	16.03	-NH ₂			3.56	3.17			
	15.96	-OH			3.61	3.22			
	15.15	-Cl			3.53	3.12			
	16.07	-CHO			3.28	2.88			
	15.97	-CN			3.31	2.91			
	15.94	-NO ₂			3.17	2.78			
7	18.39	-NH ₂			3.34	2.9			
	18.42	-OH			3.39	2.97			
	17.61	-Cl			3.33	2.88			
	18.43	-CHO			3.12	2.67			
	18.42	-CN			3.13	2.7			
	18.39	-NO ₂			3.02	2.58			
8	20.96	-NH ₂			3.18	2.7			
	20.88	-OH			3.21	2.74			
	20.08	-Cl			3.16	2.68			
	20.89	-CHO			2.98	2.5			
	20.88	-CN			2.99	2.52			
	20.85	-NO ₂			2.89	2.42			

Table S2. Intermolecular CT excitation energy from electron-donating orbital corresponding to NH₃ to electron-withdrawing orbitals corresponding to various electron acceptors (eV). Values in parentheses are errors of CT excitation energies from EOM-CCSD.

n	Distance R(Å)	HX	EOM-CCSD (cc-pVTZ)	EOM-CCSD (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	HF	B3LYP	BLYP
2	6.19	NH ₃	11.13	11.93 (0.80)	11.06 (-0.07)	11.11 (-0.01)	12.42 (1.29)	7.09 (-4.04)	5.47 (-5.66)
	6.12	H ₂ O	11.03	11.66 (0.64)	10.77 (-0.26)	10.83 (-0.20)	12.29 (1.26)	6.77 (-4.26)	5.09 (-5.93)
	5.29	HCl	10.34	10.51 (0.17)	10.18 (-0.16)	10.24 (-0.10)	11.65 (1.31)	5.79 (-4.55)	4.39 (-5.94)
	6.16	CH ₂ O	9.72	9.90 (0.18)	9.34 (-0.38)	9.26 (-0.46)	11.63 (1.91)	4.41 (-5.31)	2.55 (-7.17)
	6.14	HCN	11.43	11.78 (0.34)	10.97 (-0.46)	11.05 (-0.39)	13.09 (1.65)	6.15 (-5.29)	4.34 (-7.09)
	6.12	HNO ₂	8.79	8.99 (0.20)	8.03 (-0.76)	8.03 (-0.76)	10.32 (1.53)	3.24 (-5.55)	1.56 (-7.23)
3	8.65	NH ₃	11.71	12.57 (0.86)	11.65 (-0.07)	11.71 (0.00)	13.05 (1.34)	7.22 (-4.49)	5.57 (-6.15)
	8.57	H ₂ O	11.63	12.34 (0.70)	11.37 (-0.26)	11.50 (-0.14)	12.95 (1.31)	6.84 (-4.80)	5.11 (-6.52)
	7.76	HCl	10.91	11.18 (0.27)	10.76 (-0.15)	10.82 (-0.09)	12.32 (1.41)	6.12 (-4.79)	4.40 (-6.51)
	8.61	CH ₂ O	10.35	10.54 (0.18)	9.93 (-0.42)	9.93 (-0.42)	12.23 (1.88)	4.52 (-5.83)	2.53 (-7.82)
	8.60	HCN	12.02	12.36 (0.34)	11.53 (-0.49)	11.53 (-0.49)	13.65 (1.63)	6.20 (-5.81)	4.28 (-7.74)
	8.57	HNO ₂	9.4	9.59 (0.19)	8.65 (-0.75)	8.65 (-0.75)	10.96 (1.55)	3.36 (-6.04)	1.55 (-7.85)
4	11.11	NH ₃	12.08	12.93 (0.85)	12.02 (-0.06)	12.08 (0.00)	13.41 (1.33)	7.27 (-4.81)	5.54 (-6.54)
	11.03	H ₂ O	12.02	12.71 (0.69)	11.76 (-0.26)	11.88 (-0.13)	13.33 (1.31)	6.88 (-5.13)	5.08 (-6.93)
	10.22	HCl	11.33	11.59 (0.26)	11.18 (-0.15)	11.25 (-0.08)	12.75 (1.42)	6.19 (-5.14)	4.37 (-6.96)
	11.06	CH ₂ O	10.71	10.90 (0.19)	10.28 (-0.43)	10.28 (-0.43)	12.58 (1.87)	4.59 (-6.13)	2.53 (-8.18)
	11.05	HCN	12.35	12.69 (0.34)	11.85 (-0.50)	11.99 (-0.36)	13.98 (1.63)	6.25 (-6.10)	4.26 (-8.10)
	11.03	HNO ₂	9.75	9.94 (0.19)	8.99 (-0.76)	8.99 (-0.76)	11.30 (1.55)	3.42 (-6.33)	1.54 (-8.21)
5	13.57	NH ₃	12.3	13.15 (0.85)	12.25 (-0.05)	12.31 (0.01)	13.63 (1.33)	7.30 (-5.00)	5.52 (-6.78)
	13.50	H ₂ O	12.25	12.94 (0.69)	11.99 (-0.25)	12.12 (-0.13)	13.56 (1.31)	6.91 (-5.34)	5.06 (-7.19)
	12.69	HCl	11.58	11.84 (0.25)	11.44 (-0.14)	11.51 (-0.08)	13.01 (1.43)	6.23 (-5.36)	4.36 (-7.22)
	13.52	CH ₂ O	10.94	11.13 (0.19)	10.50 (-0.44)	10.50 (-0.44)	12.81 (1.87)	4.63 (-6.31)	2.53 (-8.41)
	13.51	HCN	12.57	12.91 (0.34)	12.07 (-0.51)	12.21 (-0.36)	14.20 (1.62)	6.29 (-6.29)	4.25 (-8.33)
	13.48	HNO ₂	9.98	10.17 (0.19)	9.21 (-0.77)	9.21 (-0.77)	11.52 (1.55)	3.47 (-6.51)	1.54 (-8.44)
6	16.03	NH ₃	12.45	13.30 (0.85)	12.40 (-0.05)	12.46 (0.01)	13.78 (1.33)	7.32 (-5.13)	5.51 (-6.94)
	15.96	H ₂ O	12.4	13.09 (0.69)	12.15 (-0.25)	12.28 (-0.12)	13.72 (1.31)	6.93 (-5.47)	5.05 (-7.36)
	15.15	HCl	11.76	12.01 (0.25)	11.62 (-0.14)	11.68 (-0.07)	13.19 (1.43)	6.25 (-5.50)	4.35 (-7.41)
	16.07	CH ₂ O	11.11	11.30 (0.19)	10.67 (-0.44)	10.67 (-0.44)	12.98 (1.87)	4.66 (-6.45)	2.53 (-8.58)
	15.97	HCN	12.73	13.07 (0.34)	12.22 (-0.51)	12.37 (-0.37)	14.36 (1.62)	6.32 (-6.42)	4.24 (-8.49)
	15.94	HNO ₂	10.12	10.32 (0.20)	9.31 (-0.81)	9.31 (-0.81)	11.63 (1.51)	3.46 (-6.66)	1.52 (-8.60)
7	18.39	NH ₃	12.56	13.41 (0.85)	12.51 (-0.05)	12.57 (0.01)	13.89 (1.33)	7.33 (-5.23)	5.50 (-7.06)
	18.42	H ₂ O	12.52	13.21 (0.69)	12.27 (-0.25)	12.39 (-0.12)	13.83 (1.31)	6.95 (-5.57)	5.04 (-7.48)
	17.61	HCl	11.88	12.14 (0.25)	11.75 (-0.14)	11.81 (-0.07)	13.32 (1.43)	6.28 (-5.61)	4.35 (-7.54)
	18.43	CH ₂ O	11.23	11.41 (0.19)	10.78 (-0.45)	10.78 (-0.45)	13.09 (1.87)	4.69 (-6.54)	2.53 (-8.69)
	18.42	HCN	12.85	13.19 (0.34)	12.34 (-0.51)	12.48 (-0.37)	14.47 (1.62)	6.34 (-6.51)	4.24 (-8.61)
	18.39	HNO ₂	10.24	10.44 (0.20)	9.43 (-0.81)	9.43 (-0.81)	11.75 (1.51)	3.49 (-6.75)	1.52 (-8.72)
8	20.96	NH ₃	12.64	13.49 (0.85)	12.60 (-0.05)	12.66 (0.01)	13.97 (1.33)	7.34 (-5.30)	5.49 (-7.16)
	20.88	H ₂ O	12.6	13.29 (0.69)	12.36 (-0.25)	12.48 (-0.12)	13.92 (1.31)	6.96 (-5.65)	5.03 (-7.57)
	20.08	HCl	11.98	12.23 (0.25)	11.84 (-0.14)	11.91 (-0.07)	13.41 (1.43)	6.29 (-5.69)	4.34 (-7.64)
	20.89	CH ₂ O	11.32	11.51 (0.19)	10.87 (-0.45)	10.87 (-0.45)	13.19 (1.87)	4.71 (-6.61)	2.54 (-8.78)
	20.88	HCN	12.94	13.28 (0.34)	12.43 (-0.51)	12.57 (-0.37)	14.56 (1.62)	6.36 (-6.58)	4.24 (-8.70)
	20.85	HNO ₂	10.34	10.54 (0.20)	9.53 (-0.81)	9.53 (-0.81)	11.85 (1.51)	3.51 (-6.83)	1.53 (-8.81)

Table S3. Intramolecular orbital energy gaps between electron-donating orbital corresponding to -NH₂ and electron-withdrawing orbitals corresponding to various electron acceptors (eV).

<i>n</i>	Distance R(Å)	-X	HF	HF (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	B3LYP	BLYP
2	6.19	-NH ₂	11.25	11.27	10.06	8.90	4.83	3.34
	6.12	-OH	11.45	11.50	10.27	9.18	4.98	3.46
	5.29	-Cl	11.16	11.30	10.12	8.96	4.88	3.39
	6.16	-CHO	10.35	10.38	9.26	8.19	4.26	2.88
	6.14	-CN	10.50	10.55	9.46	8.38	4.42	3.03
	6.12	-NO ₂	10.14	10.17	8.99	8.04	4.00	2.65
3	8.65	-NH ₂	9.86	9.92	8.93	7.61	4.01	2.69
	8.57	-OH	10.02	10.06	9.07	7.83	4.11	2.76
	7.76	-Cl	9.85	9.90	8.93	7.62	4.02	2.70
	8.61	-CHO	9.20	9.21	8.26	7.03	3.55	2.33
	8.60	-CN	9.29	9.32	8.39	7.16	3.66	2.42
	8.57	-NO ₂	9.01	9.02	8.04	6.85	3.36	2.17
4	11.11	-NH ₂	8.99	9.01	8.16	6.73	3.46	2.25
	11.03	-OH	9.10	9.12	8.26	6.82	3.53	2.30
	10.22	-Cl	8.96	8.98	8.14	6.72	3.45	2.25
	11.06	-CHO	8.43	8.44	7.60	6.25	3.09	1.96
	11.05	-CN	8.50	8.51	7.69	6.35	3.16	2.03
	11.03	-NO ₂	8.26	8.26	7.40	6.11	2.93	1.84
5	13.57	-NH ₂			7.62	6.05		
	13.50	-OH			7.69	6.12		
	12.69	-Cl			7.59	6.03		
	13.52	-CHO			7.13	5.65		
	13.51	-CN			7.19	5.72		
	13.48	-NO ₂			6.94	5.51		
6	16.03	-NH ₂			7.21	5.59		
	15.96	-OH			7.28	5.65		
	15.15	-Cl			7.18	5.46		
	16.07	-CHO			6.78	5.13		
	15.97	-CN			6.82	5.19		
	15.94	-NO ₂			6.60	5.01		
7	18.39	-NH ₂			6.91	5.11		
	18.42	-OH			6.96	5.26		
	17.61	-Cl			6.87	5.08		
	18.43	-CHO			6.51	4.79		
	18.42	-CN			6.55	4.84		
	18.39	-NO ₂			6.34	4.68		
8	20.96	-NH ₂			6.67	4.78		
	20.88	-OH			6.71	4.82		
	20.08	-Cl			6.62	4.76		
	20.89	-CHO			6.30	4.49		
	20.88	-CN			6.33	4.53		
	20.85	-NO ₂			6.13	4.39		

Table S4. Intermolecular orbital energy gaps between electron-donating orbital corresponding to NH₃ and electron-withdrawing orbitals corresponding to various electron acceptors (eV).

<i>n</i>	Distance R(Å)	HX	HF	HF (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	B3LYP	BLYP
2	6.19	NH ₃	15.02	15.76	13.59	13.65	7.36	5.39
	6.12	H ₂ O	15.00	15.56	12.93	12.99	7.64	5.07
	5.29	HCl	13.91	14.60	12.43	12.49	6.45	4.39
	6.16	CH ₂ O	13.90	14.12	11.59	11.51	4.86	2.55
	6.14	HCN	15.35	15.73	13.22	13.30	6.59	4.34
	6.12	HNO ₂	12.57	12.54	10.27	10.27	3.69	1.56
3	8.65	NH ₃	14.76	15.90	13.35	13.42	7.56	5.56
	8.57	H ₂ O	14.71	15.64	13.14	13.26	7.18	5.11
	7.76	HCl	14.19	14.63	12.62	12.68	6.49	4.40
	8.61	CH ₂ O	13.87	14.09	11.56	11.56	4.84	2.53
	8.60	HCN	15.28	15.66	13.15	13.15	6.53	4.28
	8.57	HNO ₂	12.59	12.56	10.28	10.28	3.69	1.55
4	11.11	NH ₃	14.72	15.87	13.33	13.39	7.53	5.54
	11.03	H ₂ O	14.68	15.60	13.11	13.23	7.15	5.08
	10.22	HCl	14.17	14.60	12.59	12.66	6.46	4.37
	11.06	CH ₂ O	13.86	14.09	11.55	11.55	4.84	2.53
	11.05	HCN	15.26	15.64	13.12	13.27	6.50	4.26
	11.03	HNO ₂	12.57	12.54	10.26	10.26	3.68	1.54
5	13.57	NH ₃	14.70	15.84	13.32	13.38	7.51	5.52
	13.50	H ₂ O	14.65	15.57	13.09	13.21	7.13	5.06
	12.69	HCl	14.15	14.58	12.58	12.64	6.45	4.36
	13.52	CH ₂ O	13.86	14.08	11.55	11.55	4.84	2.53
	13.51	HCN	15.25	15.63	13.11	13.25	6.50	4.25
	13.48	HNO ₂	12.57	12.54	10.26	10.26	3.68	1.54
6	16.03	NH ₃	14.68	15.82	13.30	13.36	7.50	5.51
	15.96	H ₂ O	14.63	15.55	13.07	13.20	7.11	5.05
	15.15	HCl	14.14	14.57	12.57	12.63	6.44	4.35
	16.07	CH ₂ O	13.86	14.09	11.55	11.55	4.84	2.53
	15.97	HCN	15.25	15.63	13.11	13.25	6.49	4.24
	15.94	HNO ₂	12.52	12.49	10.20	10.20	3.64	1.52
7	18.39	NH ₃	14.67	15.81	13.29	13.35	7.49	5.5
	18.42	H ₂ O	14.62	15.54	13.06	13.19	7.1	5.04
	17.61	HCl	14.14	14.57	12.56	12.63	6.44	4.35
	18.43	CH ₂ O	13.87	14.09	11.55	11.55	4.84	2.53
	18.42	HCN	15.25	15.63	13.11	13.25	6.49	4.24
	18.39	HNO ₂	12.52	12.49	10.2	10.2	3.64	1.52
8	20.96	NH ₃	14.66	15.8	13.29	13.35	7.48	5.49
	20.88	H ₂ O	14.61	15.53	13.05	13.18	7.1	5.03
	20.08	HCl	14.13	14.56	12.56	12.62	6.43	4.34
	20.89	CH ₂ O	13.87	14.09	11.55	11.55	4.84	2.54
	20.88	HCN	15.25	15.63	13.11	13.25	6.49	4.24
	20.85	HNO ₂	12.53	12.5	10.21	10.21	3.65	1.53

Table S5. Intramolecular exciton binding energies between electron-donating orbital corresponding to -NH₂ and electron-withdrawing orbitals corresponding to various electron acceptors (eV).

<i>n</i>	Distance R(Å)	-X	EOM-CCSD (cc-pVTZ)	EOM-CCSD (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	HF	B3LYP	BLYP
2	6.19	-NH ₂	-5.44	-5.49	-4.64	-3.87	-5.56	0.27	1.52
	6.12	-OH	-5.49	-5.51	-4.68	-3.76	-5.59	0.27	1.56
	5.29	-Cl	-5.50	-5.49	-4.68	-3.78	-5.46	0.12	1.46
	6.16	-CHO	-5.47	-5.40	-4.46	-3.59	-5.26	0.24	1.42
	6.14	-CN	-5.42	-5.37	-4.52	-3.63	-5.34	0.25	1.47
	6.12	-NO ₂	-5.60	-5.50	-4.50	-3.78	-5.25	0.05	1.15
3	8.65	-NH ₂	-4.86	-4.80	-4.22	-3.19	-4.95	0.24	1.42
	8.57	-OH	-4.87	-4.80	-4.25	-3.28	-5.00	0.27	1.43
	7.76	-Cl	-4.91	-4.85	-4.25	-3.22	-4.98	0.23	1.32
	8.61	-CHO	-4.86	-4.78	-4.07	-3.09	-4.77	0.25	1.27
	8.60	-CN	-4.85	-4.78	-4.11	-3.12	-4.82	0.27	1.33
	8.57	-NO ₂	-4.92	-4.83	-4.05	-3.13	-4.73	0.14	1.08
4	11.11	-NH ₂	-4.49	-4.41	-3.96	-2.86	-4.64	0.25	1.23
	11.03	-OH	-4.49	-4.41	-3.98	-2.86	-4.67	0.27	1.27
	10.22	-Cl	-4.52	-4.45	-3.97	-2.88	-4.65	0.23	1.20
	11.06	-CHO	-4.47	-4.38	-3.81	-2.77	-4.47	0.23	1.13
	11.05	-CN	-4.47	-4.40	-3.84	-2.79	-4.50	0.25	1.17
	11.03	-NO ₂	-4.49	-4.40	-3.76	-2.77	-4.41	0.17	1.00
5	13.57	-NH ₂			-3.78	-2.58			
	13.50	-OH			-3.80	-2.59			
	12.69	-Cl			-3.78	-2.60			
	13.52	-CHO			-3.63	-2.50			
	13.51	-CN			-3.66	-2.52			
	13.48	-NO ₂			-3.57	-2.48			
6	16.03	-NH ₂			-3.66	-2.43			
	15.96	-OH			-3.67	-2.43			
	15.15	-Cl			-3.64	-2.35			
	16.07	-CHO			-3.50	-2.26			
	15.97	-CN			-3.52	-2.28			
	15.94	-NO ₂			-3.43	-2.24			
7	18.39	-NH ₂			-3.56	-2.21			
	18.42	-OH			-3.57	-2.30			
	17.61	-Cl			-3.54	-2.21			
	18.43	-CHO			-3.40	-2.12			
	18.42	-CN			-3.41	-2.14			
	18.39	-NO ₂			-3.32	-2.09			
8	20.96	-NH ₂			-3.49	-2.08			
	20.88	-OH			-3.50	-2.09			
	20.08	-Cl			-3.46	-2.08			
	20.89	-CHO			-3.32	-1.99			
	20.88	-CN			-3.33	-2.01			
	20.85	-NO ₂			-3.24	-1.96			

Table S6. Intermolecular exciton binding energies between electron-donating orbital corresponding to NH₃ and electron-withdrawing orbitals corresponding to various electron acceptors. (eV).

n	Distance R(Å)	HX	EOM-CCSD (cc-pVTZ)	EOM-CCSD (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	HF	B3LYP	BLYP
2	6.19	NH ₃	-3.89	-3.84	-2.53	-2.54	-2.60	-0.27	0.08
	6.12	H ₂ O	-3.98	-3.90	-2.16	-2.16	-2.71	-0.87	0.02
	5.29	HCl	-3.57	-4.09	-2.25	-2.26	-2.26	-0.66	0.01
	6.16	CH ₂ O	-4.18	-4.21	-2.25	-2.25	-2.27	-0.45	0.00
	6.14	HCN	-3.92	-3.95	-2.25	-2.25	-2.27	-0.45	0.00
	6.12	HNO ₂	-3.78	-3.55	-2.24	-2.24	-2.25	-0.45	0.00
3	8.65	NH ₃	-3.04	-3.33	-1.71	-1.71	-1.71	-0.33	0.00
	8.57	H ₂ O	-3.08	-3.30	-1.77	-1.77	-1.77	-0.35	0.00
	7.76	HCl	-3.28	-3.46	-1.86	-1.86	-1.87	-0.37	0.00
	8.61	CH ₂ O	-3.52	-3.55	-1.63	-1.63	-1.64	-0.32	0.00
	8.60	HCN	-3.27	-3.31	-1.62	-1.62	-1.63	-0.32	0.00
	8.57	HNO ₂	-3.18	-2.97	-1.62	-1.62	-1.63	-0.32	0.00
4	11.11	NH ₃	-2.65	-2.94	-1.31	-1.31	-1.31	-0.26	0.00
	11.03	H ₂ O	-2.66	-2.89	-1.35	-1.35	-1.35	-0.27	0.00
	10.22	HCl	-2.84	-3.01	-1.41	-1.41	-1.42	-0.28	0.00
	11.06	CH ₂ O	-3.15	-3.19	-1.27	-1.27	-1.28	-0.25	0.00
	11.05	HCN	-2.90	-2.95	-1.27	-1.27	-1.28	-0.25	0.00
	11.03	HNO ₂	-2.83	-2.61	-1.27	-1.27	-1.28	-0.25	0.00
5	13.57	NH ₃	-2.40	-2.69	-1.07	-1.07	-1.07	-0.21	0.00
	13.50	H ₂ O	-2.40	-2.63	-1.09	-1.09	-1.09	-0.22	0.00
	12.69	HCl	-2.57	-2.75	-1.13	-1.13	-1.14	-0.22	0.00
	13.52	CH ₂ O	-2.92	-2.95	-1.05	-1.05	-1.05	-0.21	0.00
	13.51	HCN	-2.67	-2.72	-1.04	-1.04	-1.05	-0.21	0.00
	13.48	HNO ₂	-2.60	-2.38	-1.05	-1.05	-1.05	-0.21	0.00
6	16.03	NH ₃	-2.23	-2.52	-0.90	-0.90	-0.90	-0.18	0.00
	15.96	H ₂ O	-2.23	-2.46	-0.92	-0.92	-0.92	-0.18	0.00
	15.15	HCl	-2.38	-2.56	-0.95	-0.95	-0.95	-0.19	0.00
	16.07	CH ₂ O	-2.75	-2.79	-0.88	-0.88	-0.89	-0.18	0.00
	15.97	HCN	-2.51	-2.56	-0.89	-0.89	-0.89	-0.18	0.00
	15.94	HNO ₂	-2.40	-2.17	-0.89	-0.89	-0.89	-0.18	0.00
7	18.39	NH ₃	-2.11	-2.40	-0.78	-0.78	-0.78	-0.16	0.00
	18.42	H ₂ O	-2.10	-2.33	-0.79	-0.79	-0.79	-0.16	0.00
	17.61	HCl	-2.25	-2.43	-0.82	-0.82	-0.82	-0.16	0.00
	18.43	CH ₂ O	-2.64	-2.68	-0.77	-0.77	-0.77	-0.15	0.00
	18.42	HCN	-2.40	-2.44	-0.77	-0.77	-0.77	-0.15	0.00
	18.39	HNO ₂	-2.28	-2.05	-0.77	-0.77	-0.77	-0.15	0.00
8	20.96	NH ₃	-2.02	-2.31	-0.69	-0.69	-0.69	-0.14	0.00
	20.88	H ₂ O	-2.01	-2.24	-0.70	-0.70	-0.70	-0.14	0.00
	20.08	HCl	-2.15	-2.34	-0.72	-0.72	-0.72	-0.14	0.00
	20.89	CH ₂ O	-2.55	-2.58	-0.68	-0.68	-0.68	-0.14	0.00
	20.88	HCN	-2.31	-2.35	-0.68	-0.68	-0.68	-0.14	0.00
	20.85	HNO ₂	-2.19	-1.96	-0.68	-0.68	-0.68	-0.14	0.00

Table S7. Orbital energy gap, CT excitation energy and exciton binding energy (eV) of intra- and intermolecular CT excitations from -NH₂ (NH₃) to -NO₂ (HNO₂) with $n=4$ in a change in μ value.

μ	Intermolecular CT			Intramolecular CT			Local		
	Orbital energy gap	CT excitation energy	Exciton binding energy	Orbital energy gap	CT excitation energy	Exciton binding energy	Orbital energy gap	CT excitation energy	Exciton binding energy
0.00	1.54	1.54	0.00	1.84	2.84	1.00	5.35	5.63	0.28
0.01	1.84	1.54	-0.30	2.15	2.84	0.69	5.68	5.65	-0.03
0.02	2.15	1.57	-0.58	2.45	2.84	0.40	5.99	5.66	-0.33
0.03	2.45	1.64	-0.81	2.73	2.85	0.12	6.29	5.66	-0.64
0.04	2.75	1.77	-0.98	3.01	2.87	-0.13	6.58	5.65	-0.94
0.05	3.04	1.94	-1.10	3.26	2.89	-0.37	6.87	5.64	-1.23
0.06	3.34	2.16	-1.18	3.50	2.92	-0.58	7.14	5.62	-1.52
0.07	3.63	2.41	-1.22	3.72	2.95	-0.77	7.41	5.61	-1.80
0.08	3.92	2.67	-1.25	3.93	2.98	-0.95	7.67	5.59	-2.07
0.09	4.20	2.94	-1.26	4.13	3.01	-1.12	7.92	5.58	-2.34
0.10	4.48	3.21	-1.27	4.31	3.04	-1.28	8.16	5.56	-2.60
0.11	4.75	3.48	-1.27	4.49	3.06	-1.42	8.40	5.55	-2.85
0.12	5.02	3.75	-1.27	4.65	3.09	-1.56	8.63	5.54	-3.08
0.13	5.27	4.00	-1.27	4.81	3.11	-1.69	8.85	5.54	-3.31
0.14	5.53	4.26	-1.27	4.95	3.14	-1.82	9.06	5.53	-3.53
0.15	5.77	4.50	-1.27	5.10	3.16	-1.94	9.27	5.53	-3.74
0.16	6.01	4.74	-1.27	5.23	3.18	-2.05	9.47	5.54	-3.93
0.17	6.24	4.97	-1.27	5.36	3.20	-2.16	9.67	5.55	-4.12
0.18	6.46	5.19	-1.27	5.48	3.22	-2.26	9.85	5.56	-4.29
0.19	6.68	5.41	-1.27	5.60	3.24	-2.36	10.03	5.57	-4.46
0.20	6.89	5.62	-1.27	5.71	3.26	-2.45	10.21	5.59	-4.62
0.21	7.09	5.82	-1.27	5.82	3.28	-2.53	10.38	5.61	-4.77
0.22	7.28	6.01	-1.27	5.92	3.30	-2.62	10.54	5.64	-4.91
0.23	7.47	6.20	-1.27	6.01	3.32	-2.70	10.70	5.67	-5.04
0.24	7.65	6.38	-1.27	6.11	3.34	-2.77	10.85	5.69	-5.16
0.25	7.82	6.55	-1.27	6.20	3.35	-2.84	11.00	5.73	-5.27
0.26	7.99	6.72	-1.27	6.28	3.37	-2.91	11.14	5.76	-5.38
0.27	8.15	6.88	-1.27	6.36	3.39	-2.97	11.28	5.80	-5.48
0.28	8.30	7.03	-1.27	6.44	3.40	-3.03	11.41	5.83	-5.58
0.29	8.45	7.18	-1.27	6.51	3.42	-3.09	11.54	5.87	-5.67
0.30	8.59	7.32	-1.27	6.58	3.44	-3.15	11.66	5.91	-5.75
0.31	8.72	7.45	-1.27	6.65	3.45	-3.20	11.78	5.95	-5.83
0.32	8.85	7.58	-1.27	6.72	3.47	-3.25	11.89	5.99	-5.90
0.33	8.98	7.70	-1.27	6.78	3.48	-3.30	12.00	6.03	-5.97
0.34	9.09	7.82	-1.27	6.84	3.49	-3.34	12.11	6.07	-6.03
0.35	9.21	7.94	-1.27	6.89	3.51	-3.38	12.21	6.11	-6.09
0.36	9.32	8.05	-1.27	6.95	3.52	-3.42	12.30	6.15	-6.15
0.37	9.42	8.15	-1.27	7.00	3.53	-3.46	12.40	6.20	-6.20
0.38	9.52	8.25	-1.27	7.05	3.55	-3.50	12.49	6.24	-6.25

0.39	9.62	8.35	-1.27	7.09	3.56	-3.53	12.58	6.28	-6.30
0.40	9.71	8.44	-1.27	7.14	3.57	-3.57	12.66	6.32	-6.34
0.41	9.80	8.53	-1.27	7.18	3.58	-3.60	12.74	6.35	-6.39
0.42	9.89	8.61	-1.27	7.22	3.59	-3.63	12.82	6.39	-6.42
0.43	9.97	8.69	-1.27	7.26	3.60	-3.66	12.89	6.43	-6.46
0.44	10.05	8.77	-1.27	7.30	3.61	-3.69	12.96	6.47	-6.50
0.45	10.12	8.85	-1.27	7.33	3.62	-3.71	13.03	6.50	-6.53
0.46	10.19	8.92	-1.27	7.37	3.63	-3.74	13.10	6.54	-6.56
0.47	10.26	8.99	-1.27	7.40	3.64	-3.76	13.16	6.57	-6.59
0.48	10.33	9.05	-1.27	7.43	3.64	-3.79	13.22	6.60	-6.62
0.49	10.39	9.12	-1.27	7.46	3.65	-3.81	13.28	6.64	-6.64
0.50	10.45	9.18	-1.27	7.49	3.66	-3.83	13.34	6.67	-6.67

Table S8. Molecular orbitals corresponding to intramolecular CT excitations from -NH₂ and various electron acceptor. (H is HOMO and L is LUMO)

<i>n</i>	-X	EOM-CCSD (cc-pVTZ)	EOM-CCSD (cc-pVDZ)	LC-BLYP ($\mu=0.47$)	OT-LC-BLYP	HF	B3LYP	BLYP
2	-NH ₂	H \rightarrow L +3	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L +3	H \rightarrow L	H \rightarrow L
	-OH	H \rightarrow L +2	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L +2	H \rightarrow L	H \rightarrow L
	-Cl	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-CHO	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H -1 \rightarrow L
	-CN	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-NO ₂	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
3	-NH ₂	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-OH	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-Cl	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-CHO	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-CN	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-NO ₂	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
4	-NH ₂	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-OH	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-Cl	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-CHO	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-CN	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
	-NO ₂	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L	H \rightarrow L
5	-NH ₂			H \rightarrow L	H \rightarrow L			
	-OH			H \rightarrow L	H \rightarrow L			
	-Cl			H \rightarrow L	H \rightarrow L			
	-CHO			H \rightarrow L	H \rightarrow L			
	-CN			H \rightarrow L	H \rightarrow L			
	-NO ₂			H \rightarrow L	H \rightarrow L			
6	-NH ₂			H \rightarrow L	H \rightarrow L			
	-OH			H \rightarrow L	H \rightarrow L			
	-Cl			H \rightarrow L	H \rightarrow L			
	-CHO			H \rightarrow L	H \rightarrow L			
	-CN			H \rightarrow L	H \rightarrow L			
	-NO ₂			H \rightarrow L	H \rightarrow L			
7	-NH ₂			H \rightarrow L	H \rightarrow L			
	-OH			H \rightarrow L	H \rightarrow L			
	-Cl			H \rightarrow L	H \rightarrow L			
	-CHO			H \rightarrow L	H \rightarrow L			
	-CN			H \rightarrow L	H \rightarrow L			
	-NO ₂			H \rightarrow L	H \rightarrow L			
8	-NH ₂			H \rightarrow L	H \rightarrow L			
	-OH			H \rightarrow L	H \rightarrow L			
	-Cl			H \rightarrow L	H \rightarrow L			
	-CHO			H \rightarrow L	H \rightarrow L			
	-CN			H \rightarrow L	H \rightarrow L			
	-NO ₂			H \rightarrow L	H \rightarrow L			

Table S9. Molecular orbitals corresponding to intramolecular CT excitations from NH₃ and various electron acceptor. (H is HOMO and L is LUMO)

[illegible]

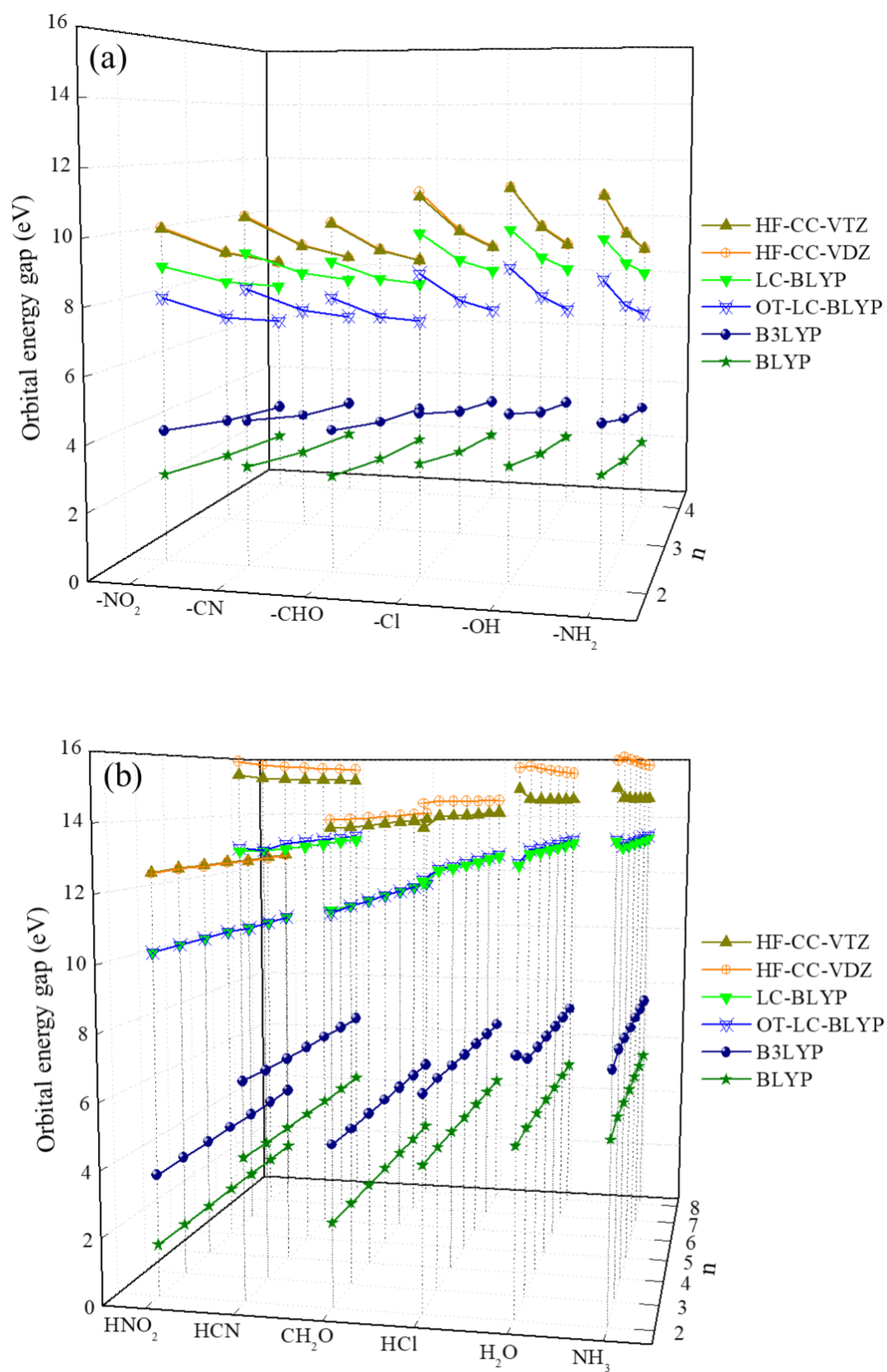


Figure S1. Orbital energy gaps corresponding to (a) intramolecular and (b) intermolecular CT excitations between electron-donating and electron-withdrawing orbitals calculated using HF, LC-BLYP, OT-LC-BLYP, B3LYP and BLYP.

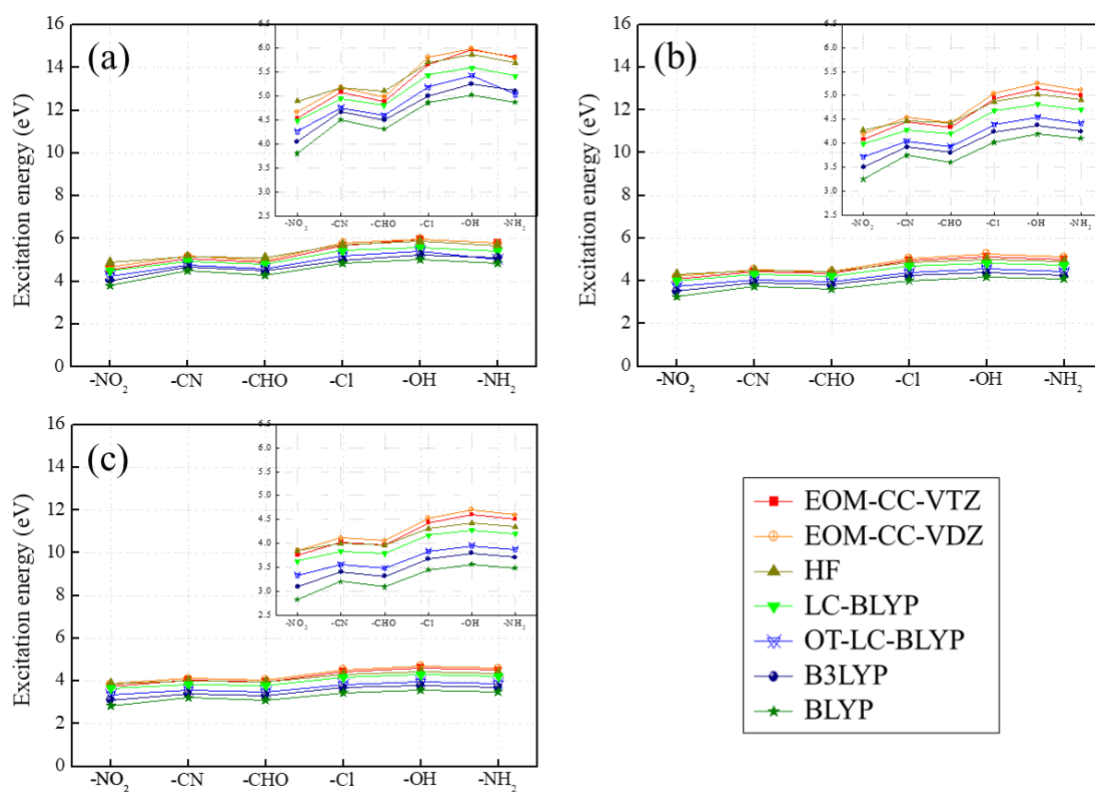


Figure S2. Intramolecular CT excitation energies from electron-donating to electron-withdrawing orbitals with (a) $n=2$, (b) $n=3$, and (c) $n=4$ calculated using EOM-CCSD, HF, LC-BLYP, OT-LC-BLYP, B3LYP and BLYP.

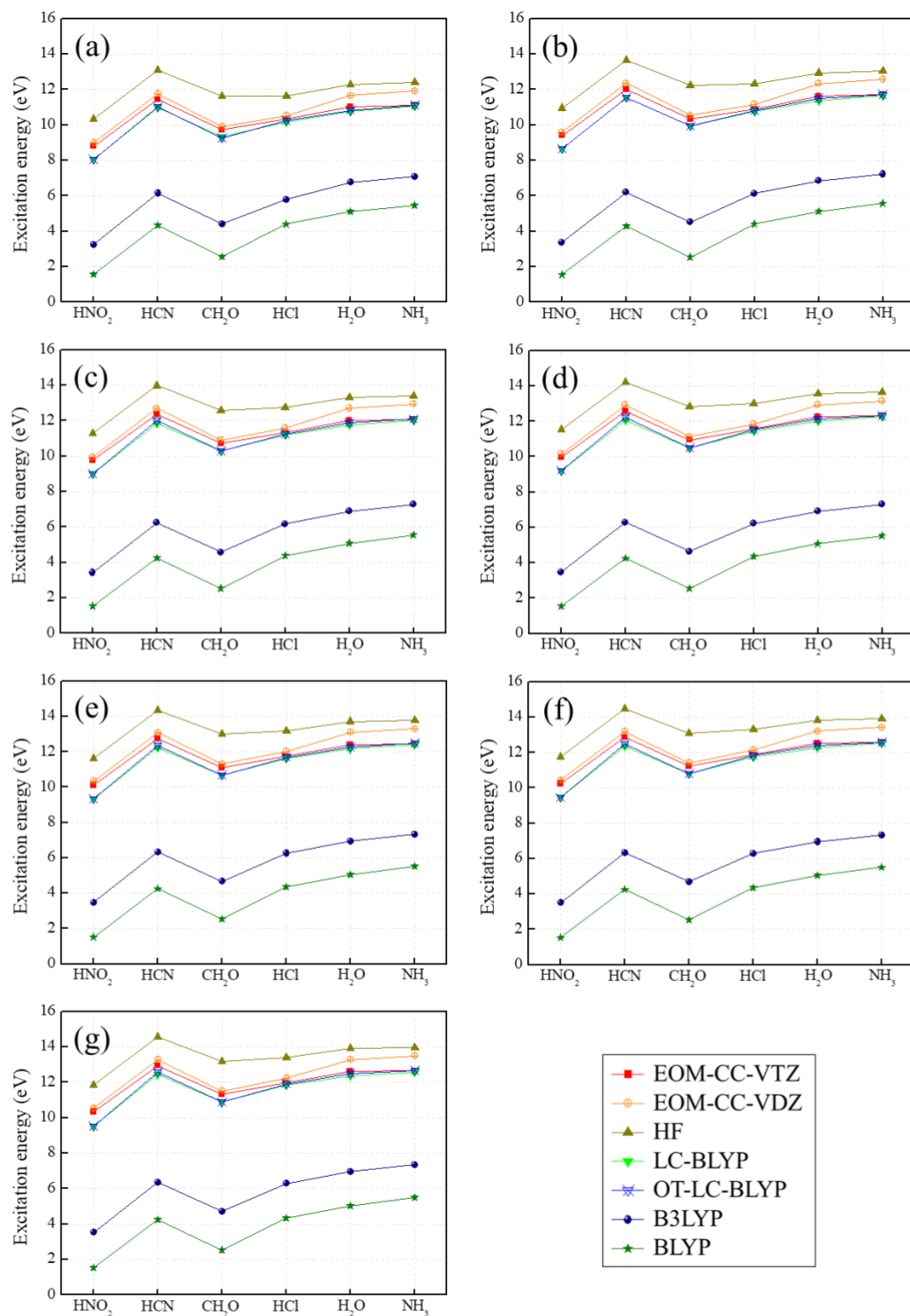


Figure S3. Intermolecular CT excitation energies from electron-donating to electron-withdrawing orbitals with (a) $n=2$, (b) $n=3$, (c) $n=4$, (d) $n=5$, (e) $n=6$, (f) $n=7$, and (g) $n=8$ calculated using EOM-CCSD, HF, LC-BLYP, OT-LC-BLYP, B3LYP and BLYP.

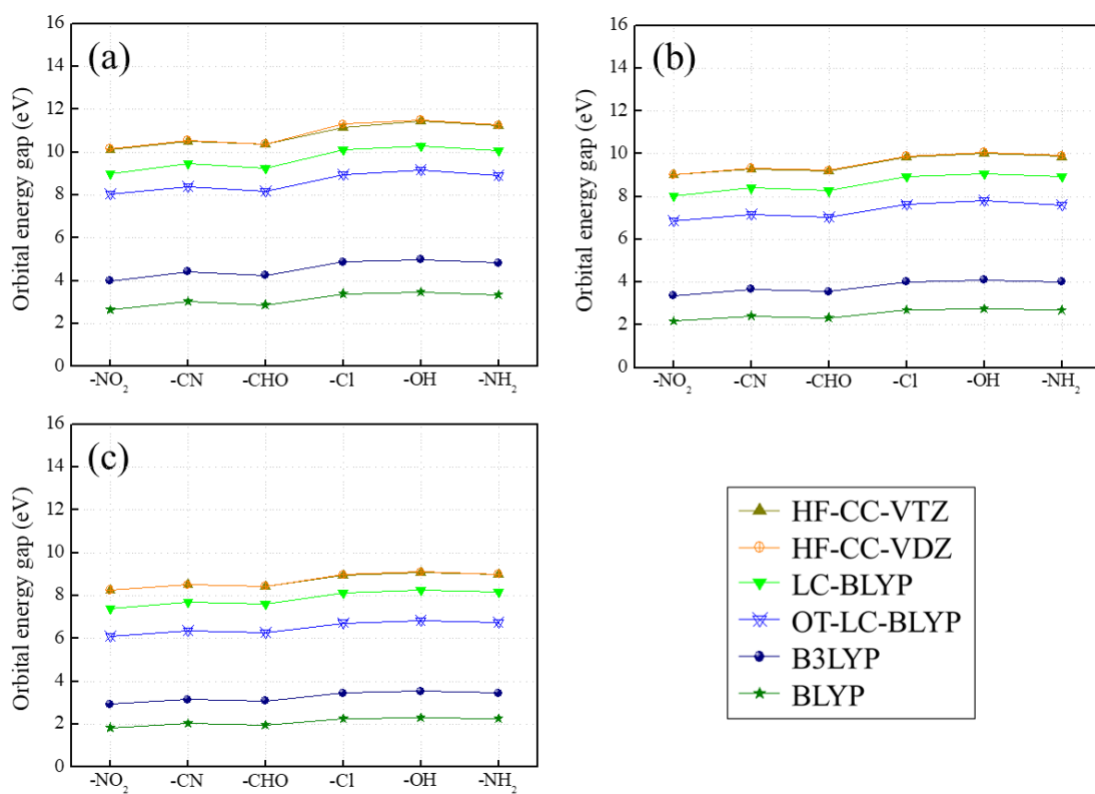


Figure S4. Orbital energy gaps between electron-donating and electron-withdrawing orbitals in intramolecular CT excitations with (a) $n=2$, (b) $n=3$, and (c) $n=4$ calculated using HF, LC-BLYP, OT-LC-BLYP, B3LYP and BLYP.

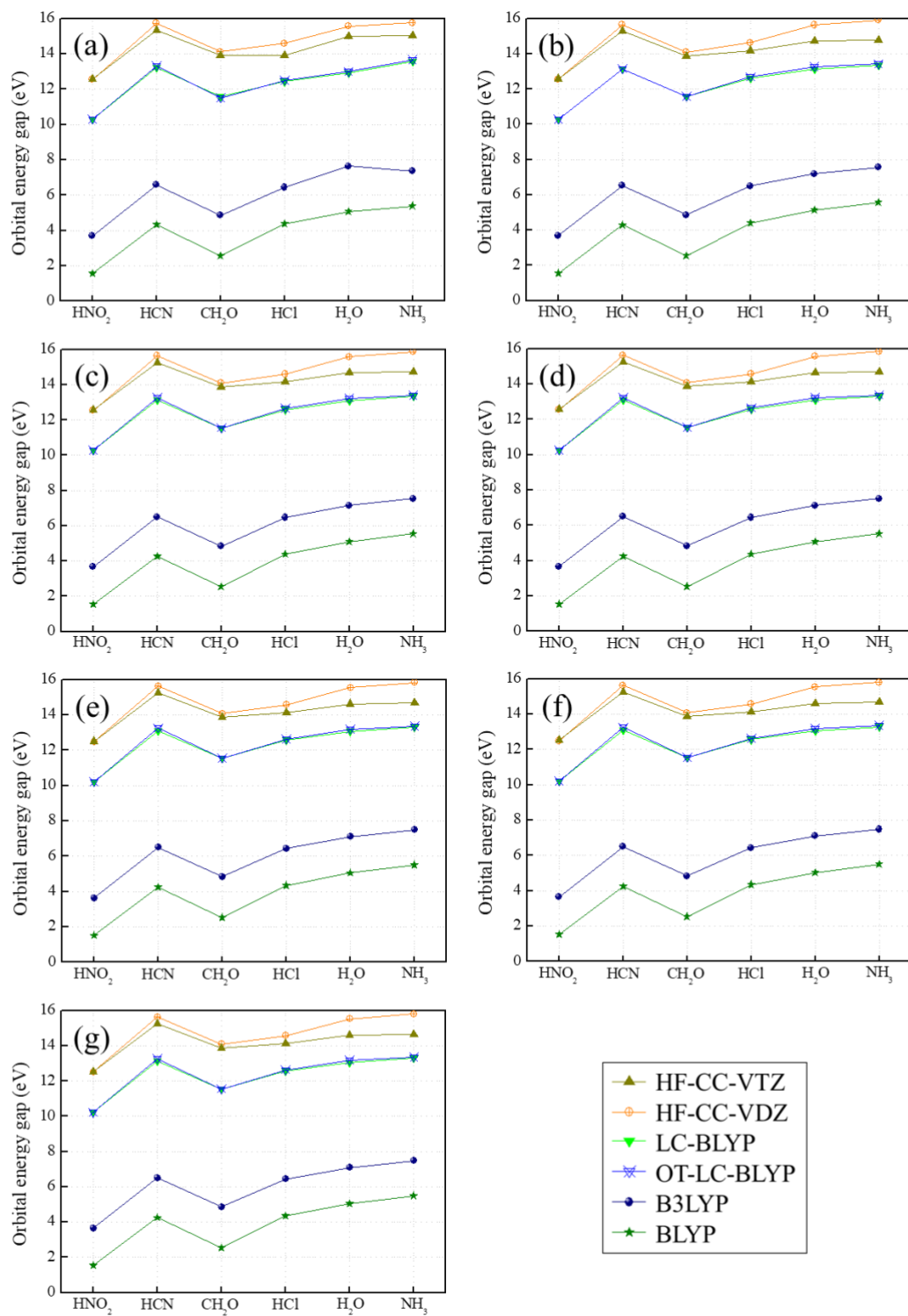


Figure S5. Orbital energy gaps between electron-donating and electron-withdrawing orbitals of intermolecular CT excitations with (a) $n=2$, (b) $n=3$, (c) $n=4$, (d) $n=5$, (e) $n=6$, (f) $n=7$, and (g) $n=8$ calculated using HF, LC-BLYP, OT-LC-BLYP, B3LYP and BLYP.

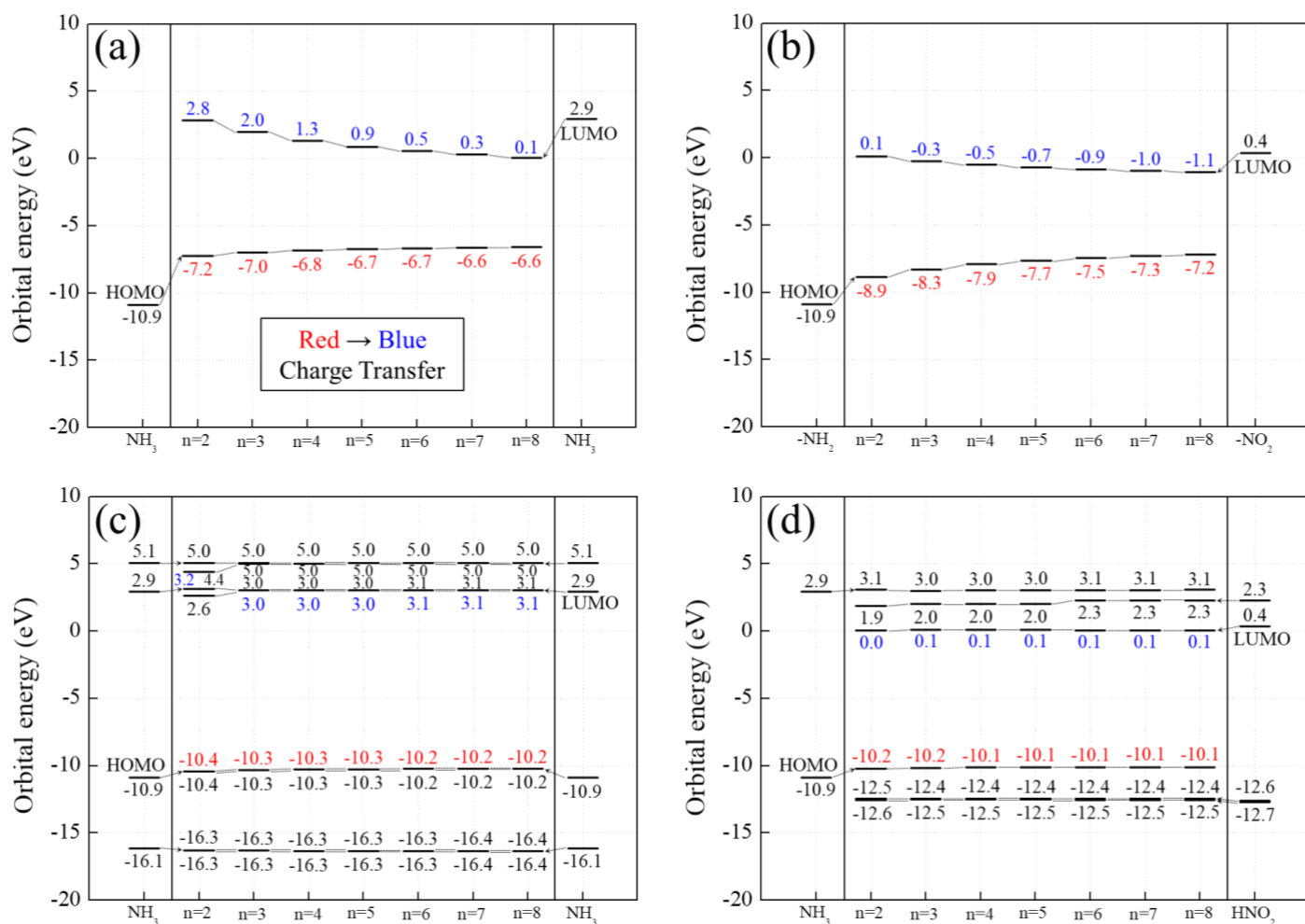


Figure S6. Intramolecular HOMO and LUMO energies of (a) $\text{H}_2\text{N}-(\text{CH}=\text{CH})_n-\text{NH}_2$ and (b) $\text{H}_2\text{N}-(\text{CH}=\text{CH})_n-\text{NO}_2$ and intermolecular HOMO and LUMO energies of (c) $\text{H}_2\text{N}-\text{H} \cdots \cdots \text{H}-\text{NH}_2$ and (d) $\text{H}_2\text{N}-\text{H} \cdots \cdots \text{H}-\text{NO}_2$ with regard to n calculated using LC-BLYP. The HOMO and LUMO energies of NH_3 molecule in (a) and (c) and the HOMO energy of NH_3 and the LUMO of HNO_2 in (b) and (d) are displayed in both sides.

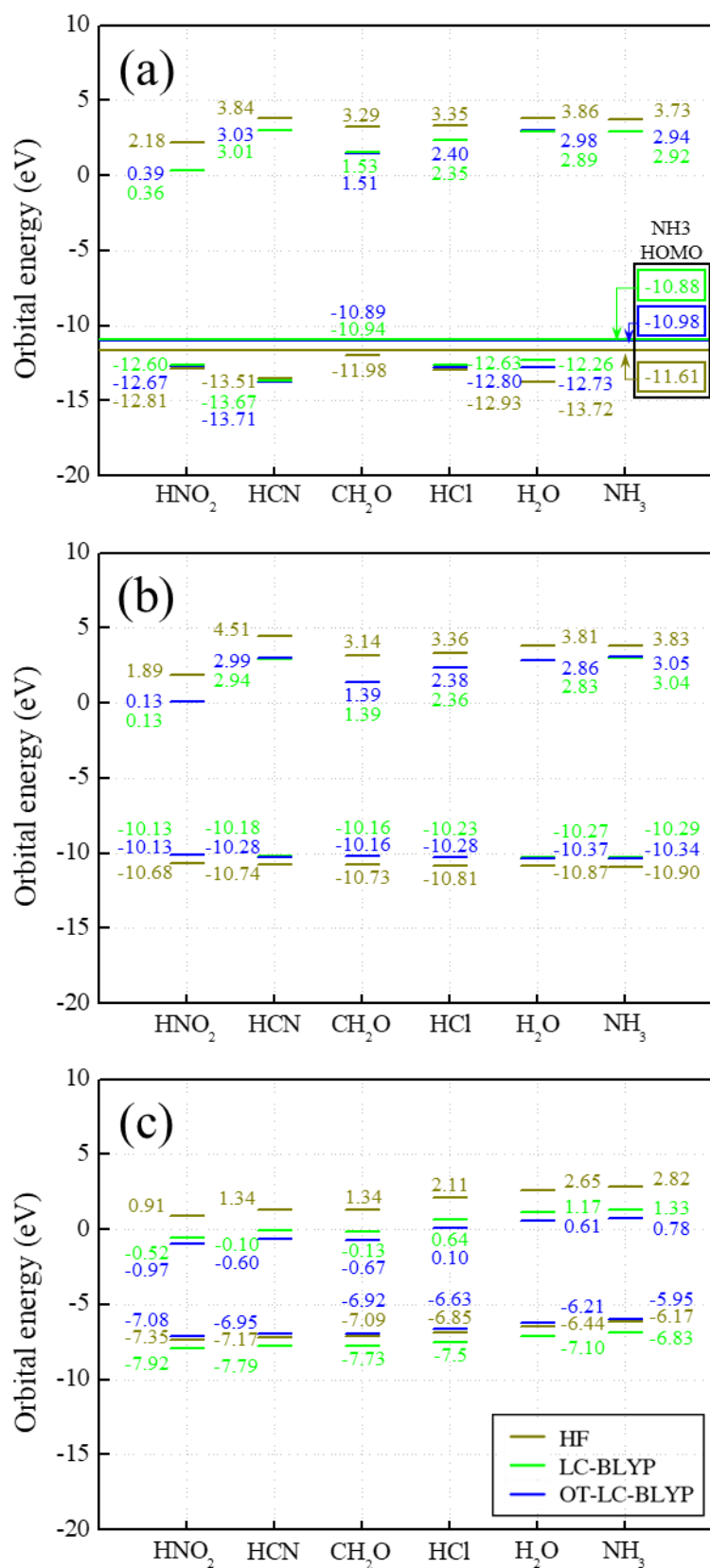


Figure S7. (a) HOMO and LUMO energies of electron acceptors as single molecule of (HX) (b) HOMO and LUMO energies of their combination with NH₃ molecule for intermolecular CT excitations [H₂N-H.....H-X] (n=4), (c) HOMO and LUMO energies for intramolecular CT excitations [H₂N-(CH=CH)_n-NO₂] (n=4).

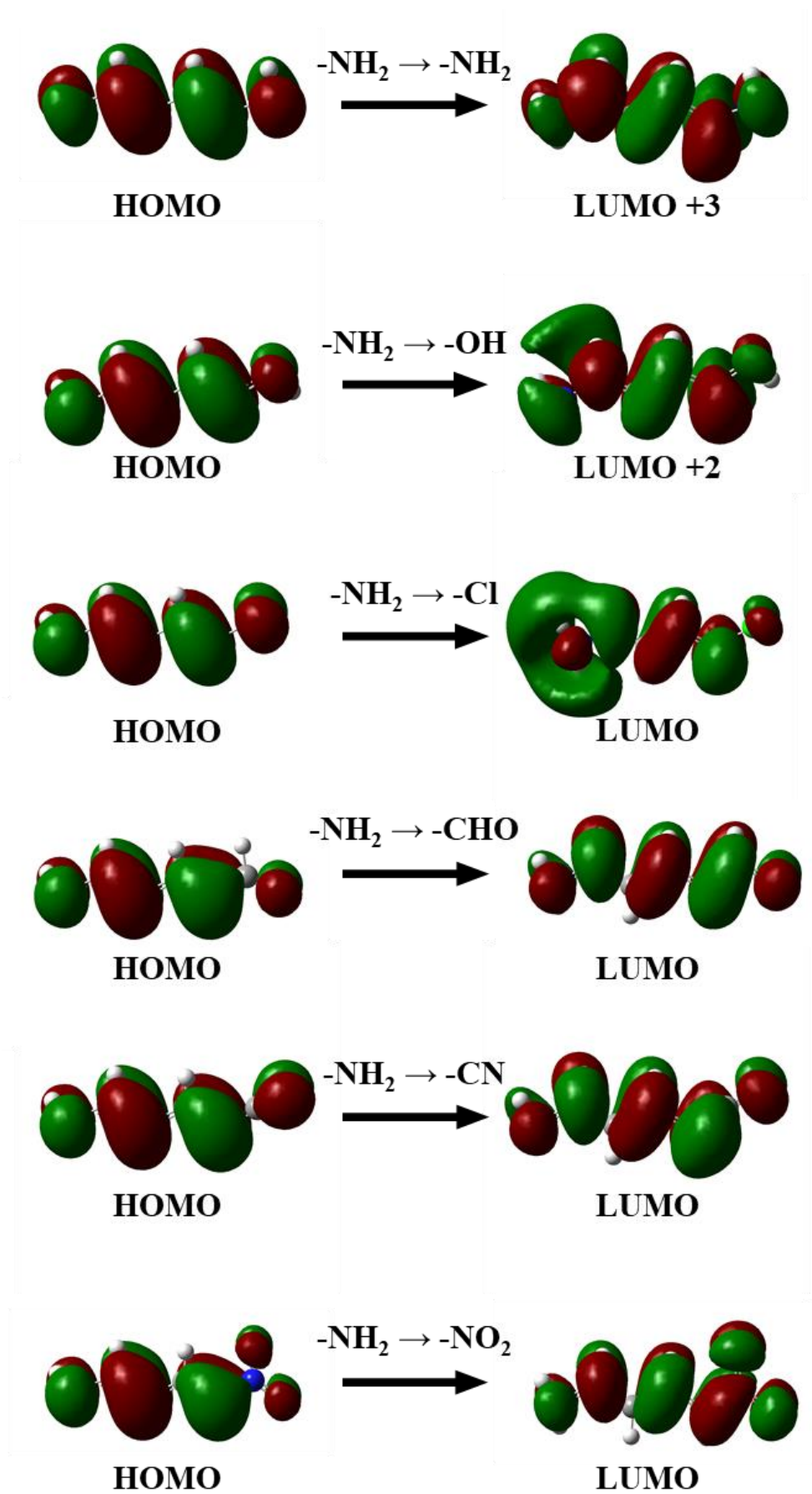


Figure S8. MO shapes of intramolecular CT excitations from -NH_2 to various electron acceptors with $n=2$ calculated using HF.

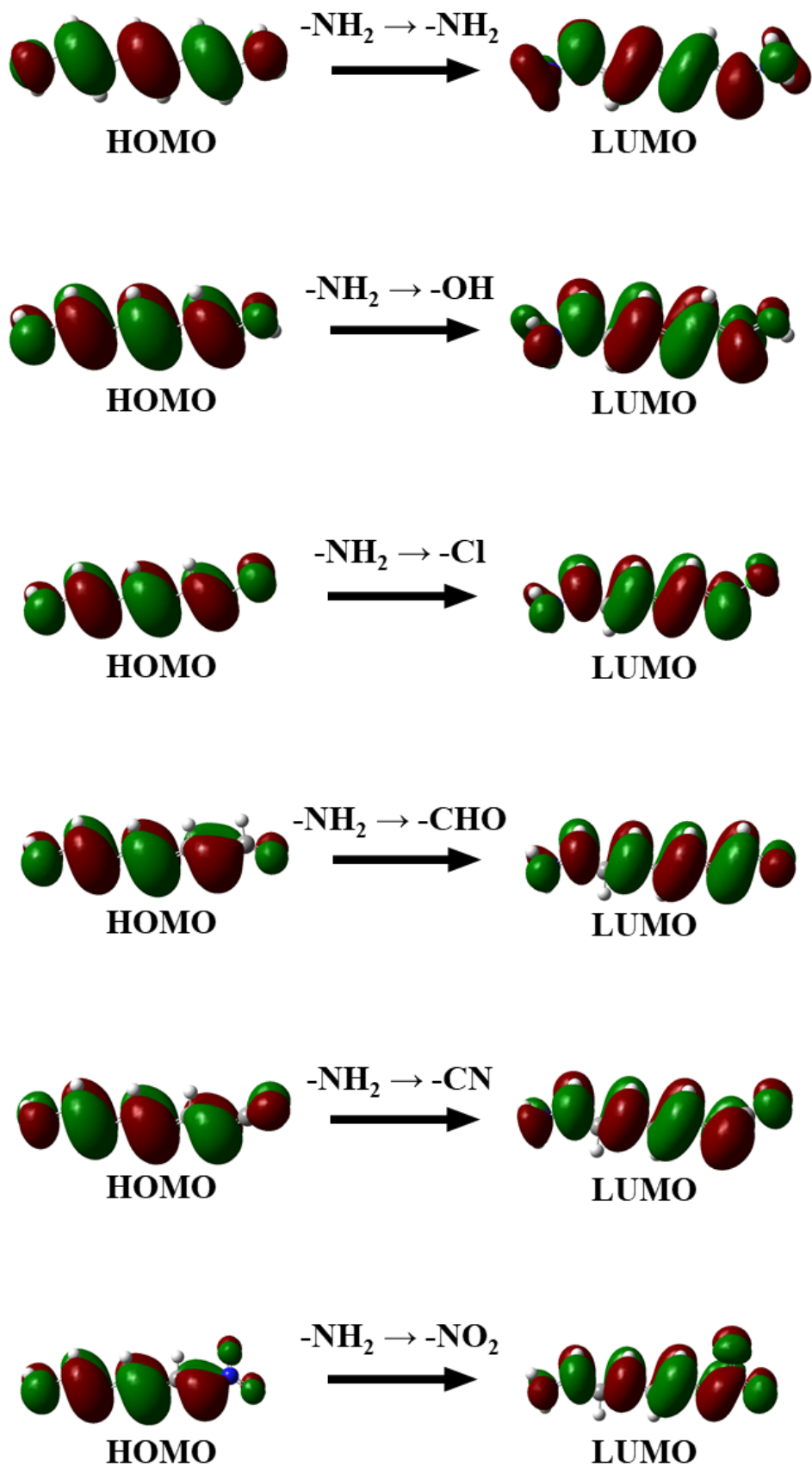


Figure S9. MO shapes of intramolecular CT excitations from $-\text{NH}_2$ to various electron acceptors with $n=3$ calculated using HF.

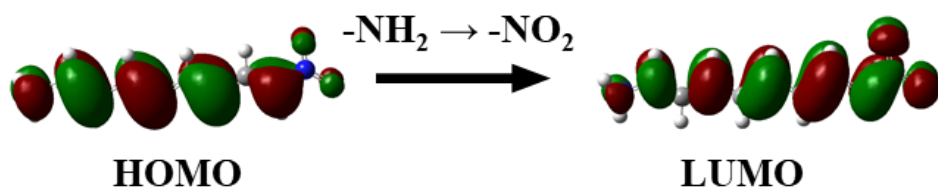
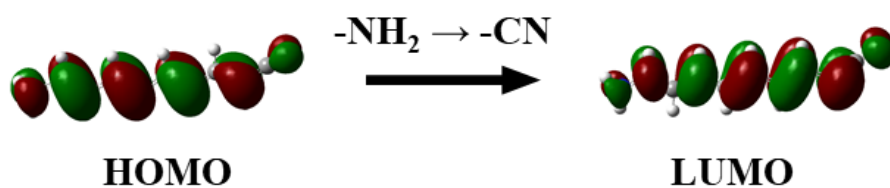
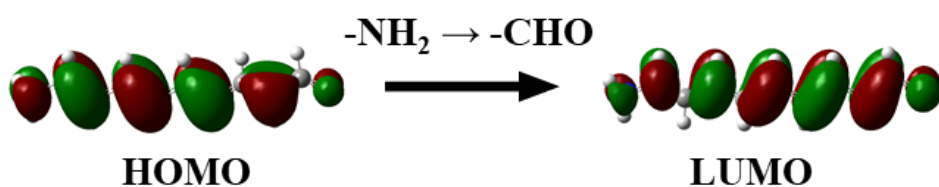
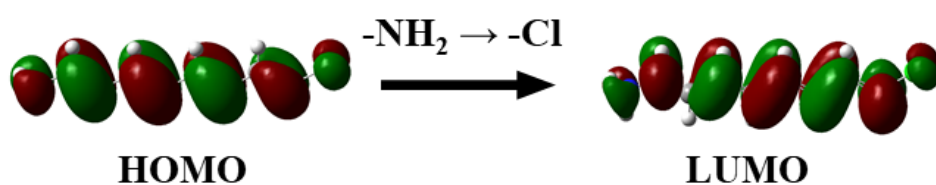
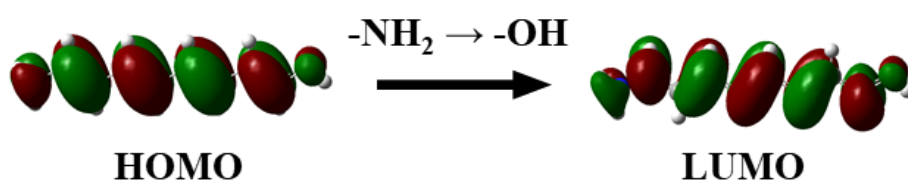
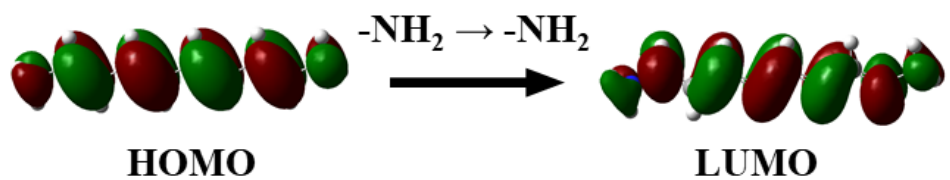


Figure S10. MO shapes of intramolecular CT excitations from -NH₂ to various electron acceptors with $n=4$ calculated using HF.

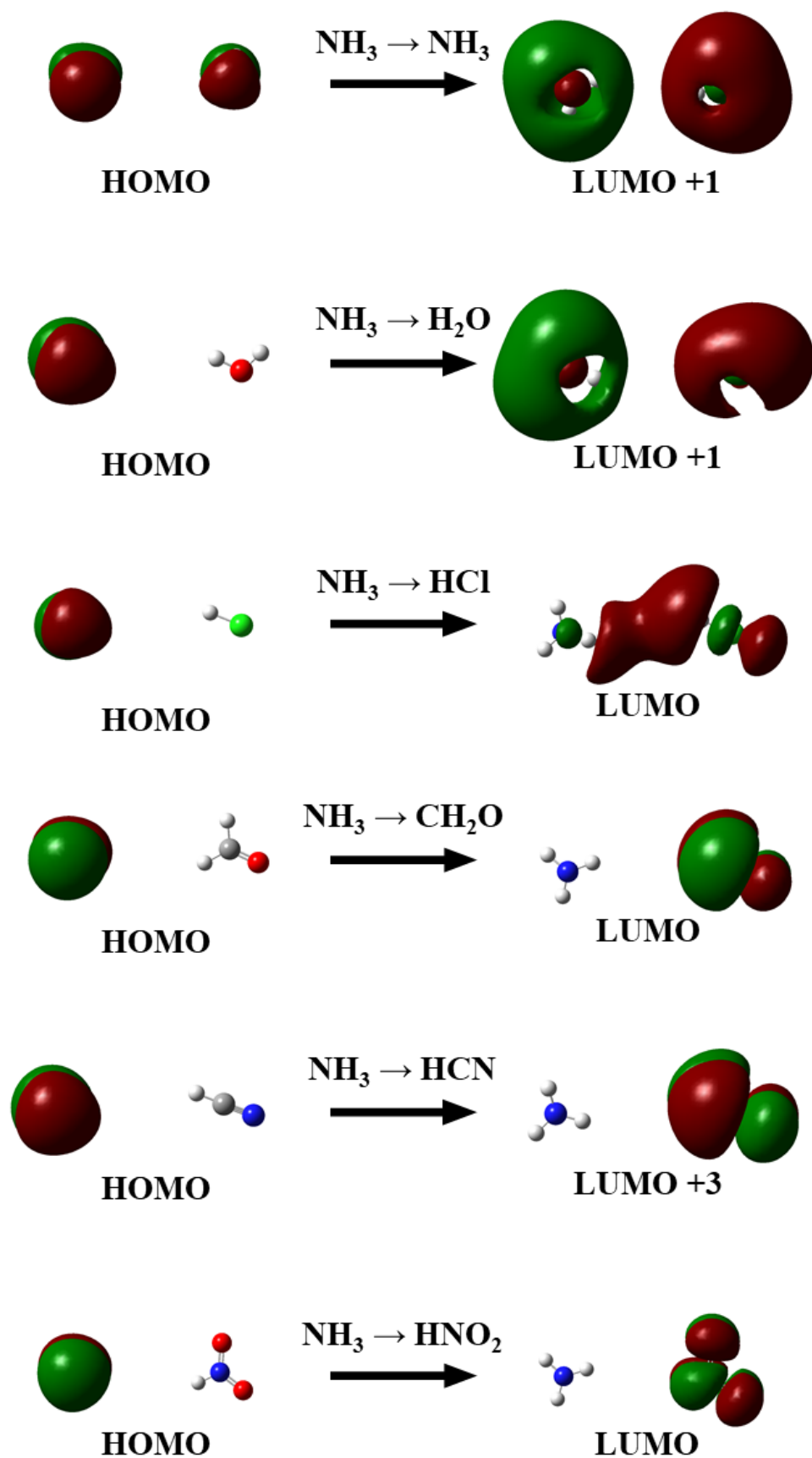


Figure S11. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=2$ calculated using HF.

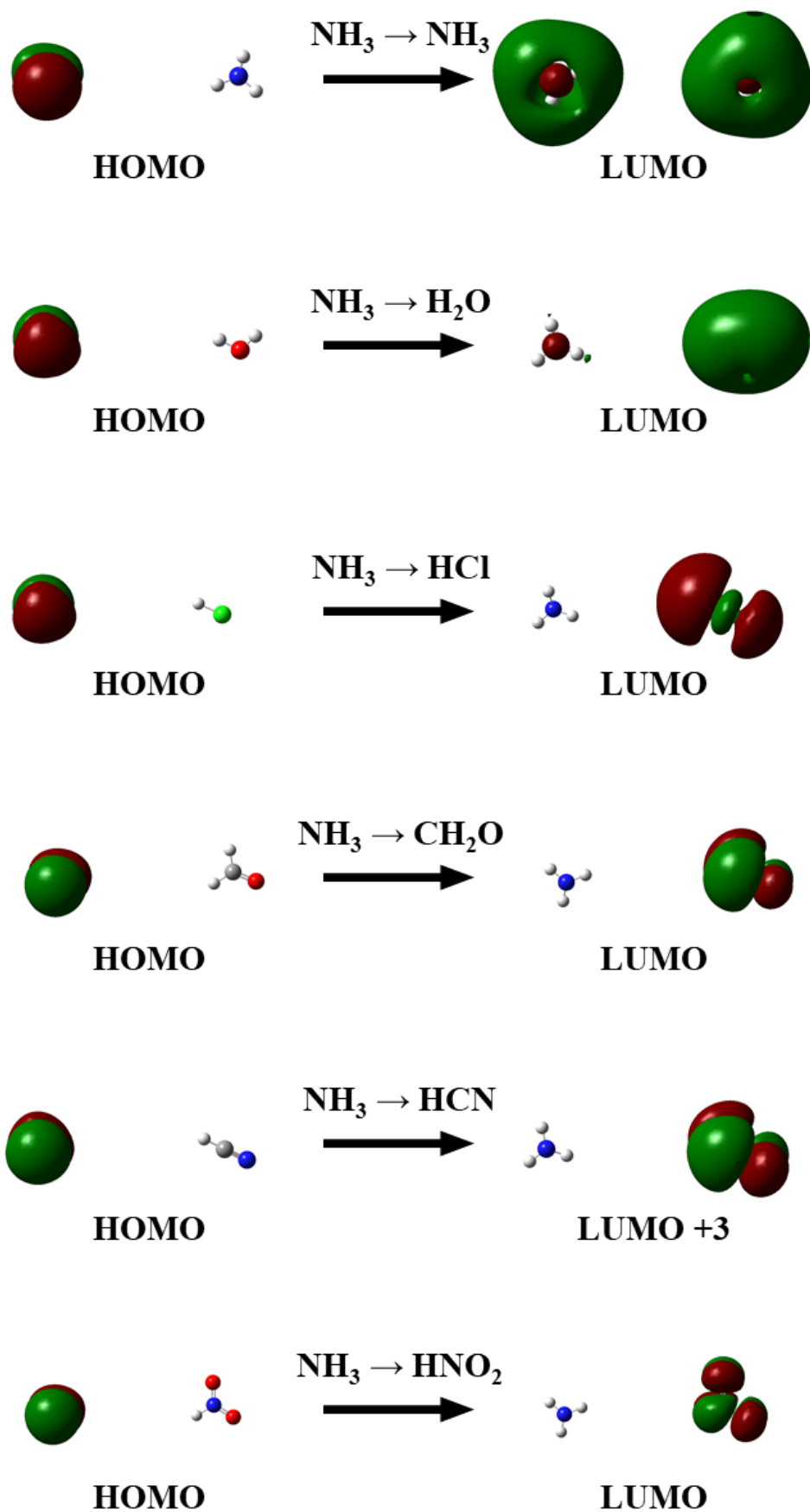


Figure S12. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=3$ calculated using HF.

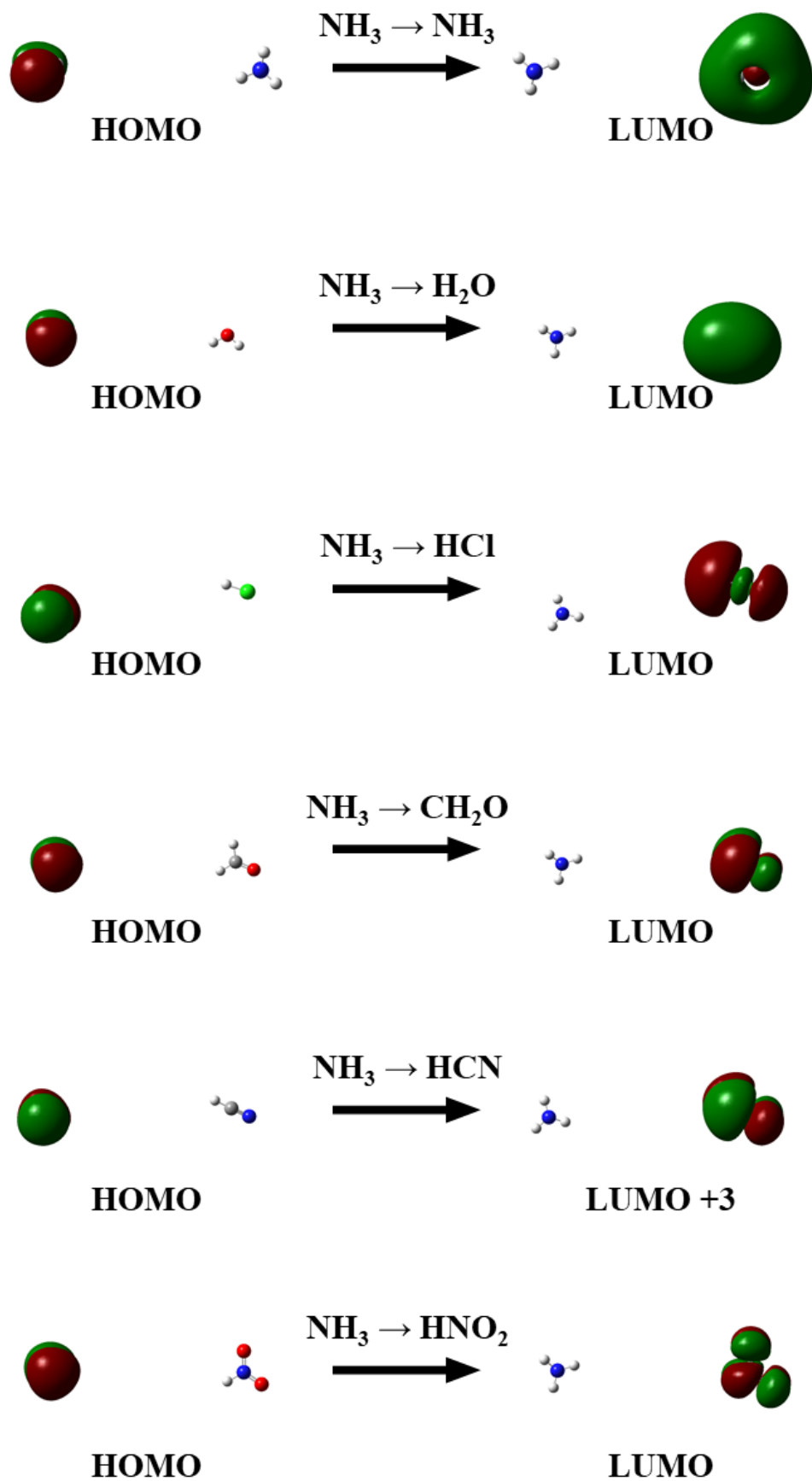


Figure S13. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=4$ calculated using HF.

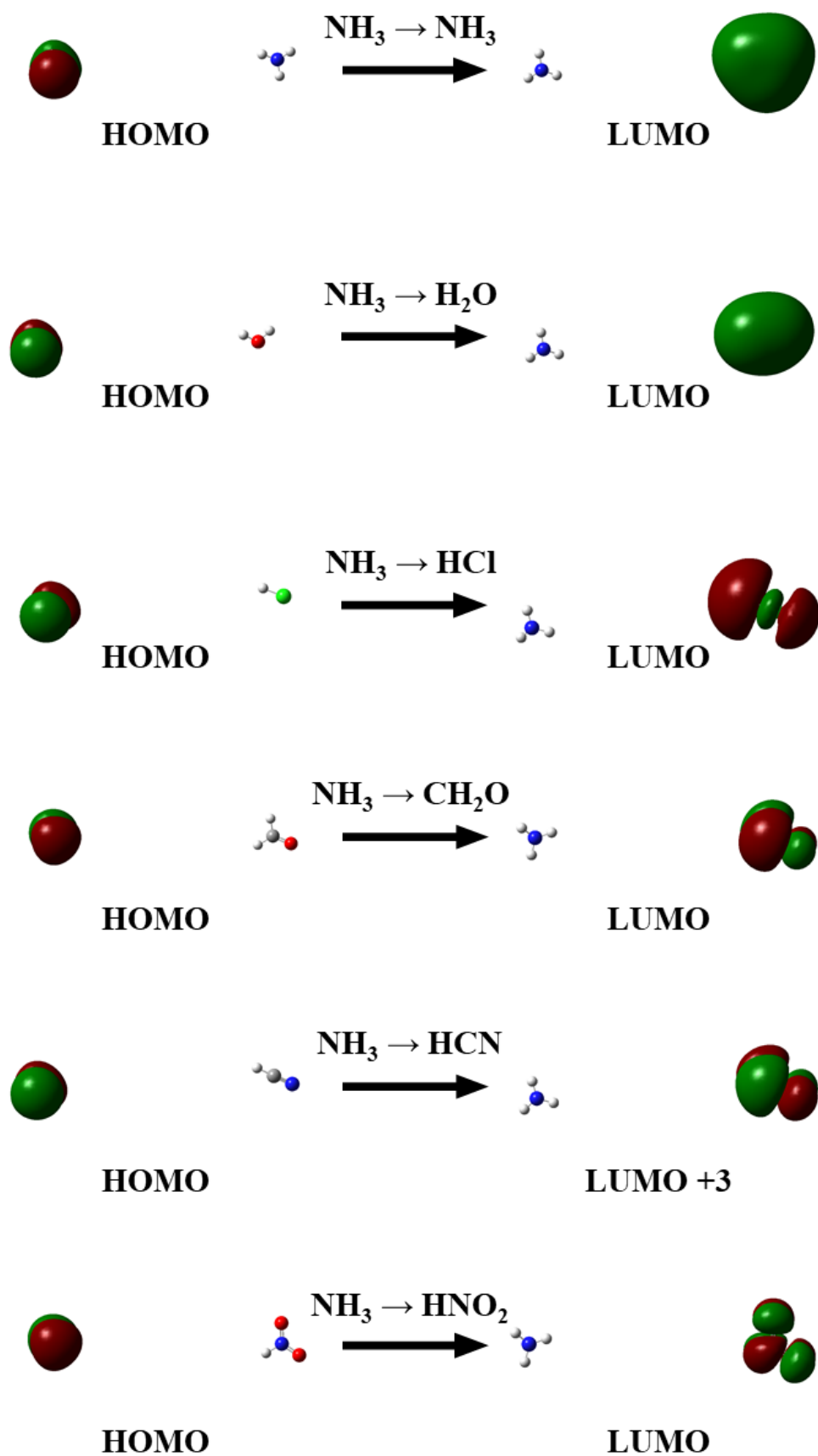


Figure S14. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=5$ calculated using HF.

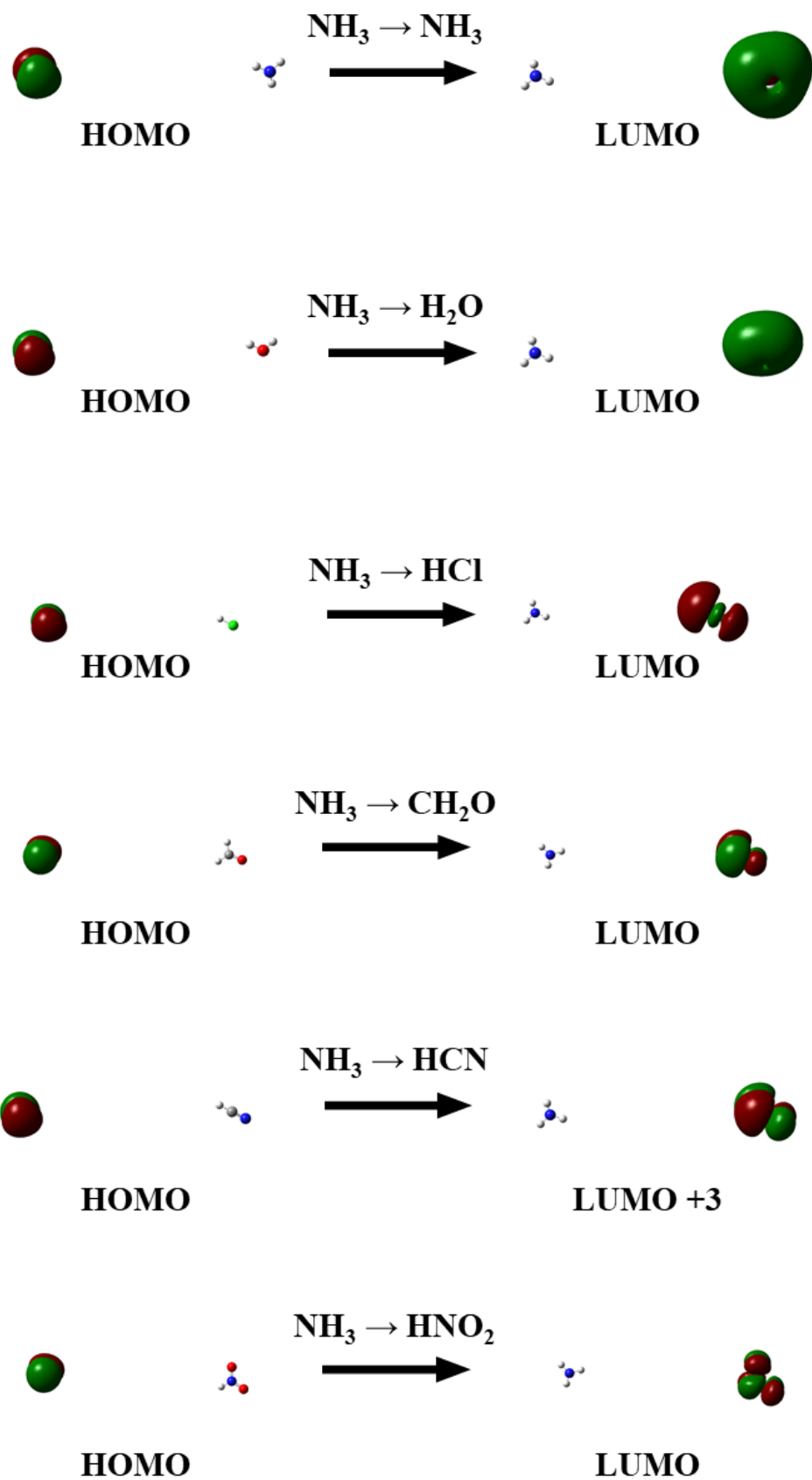


Figure S15. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=6$ calculated using HF.

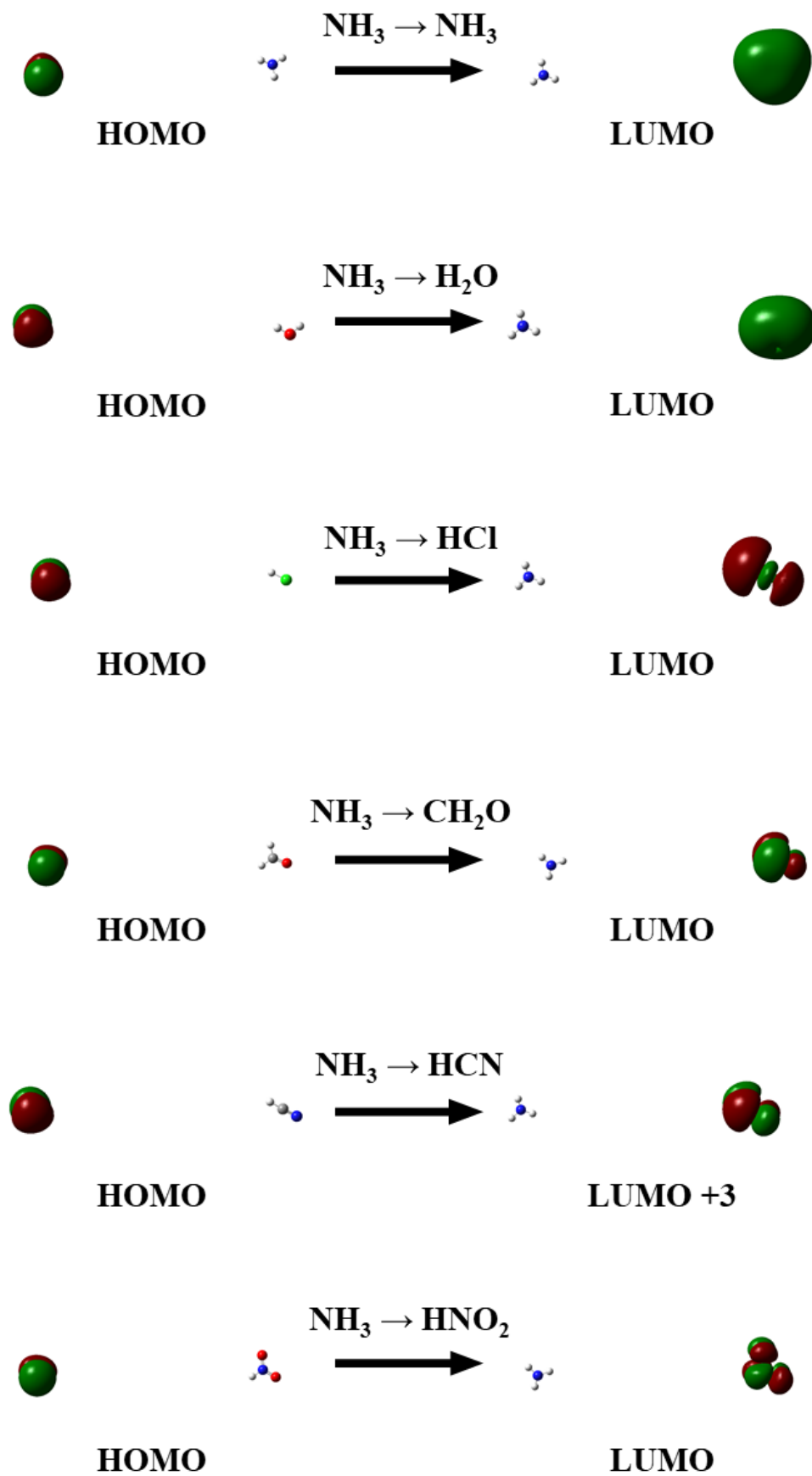


Figure S16. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=7$ calculated using HF.

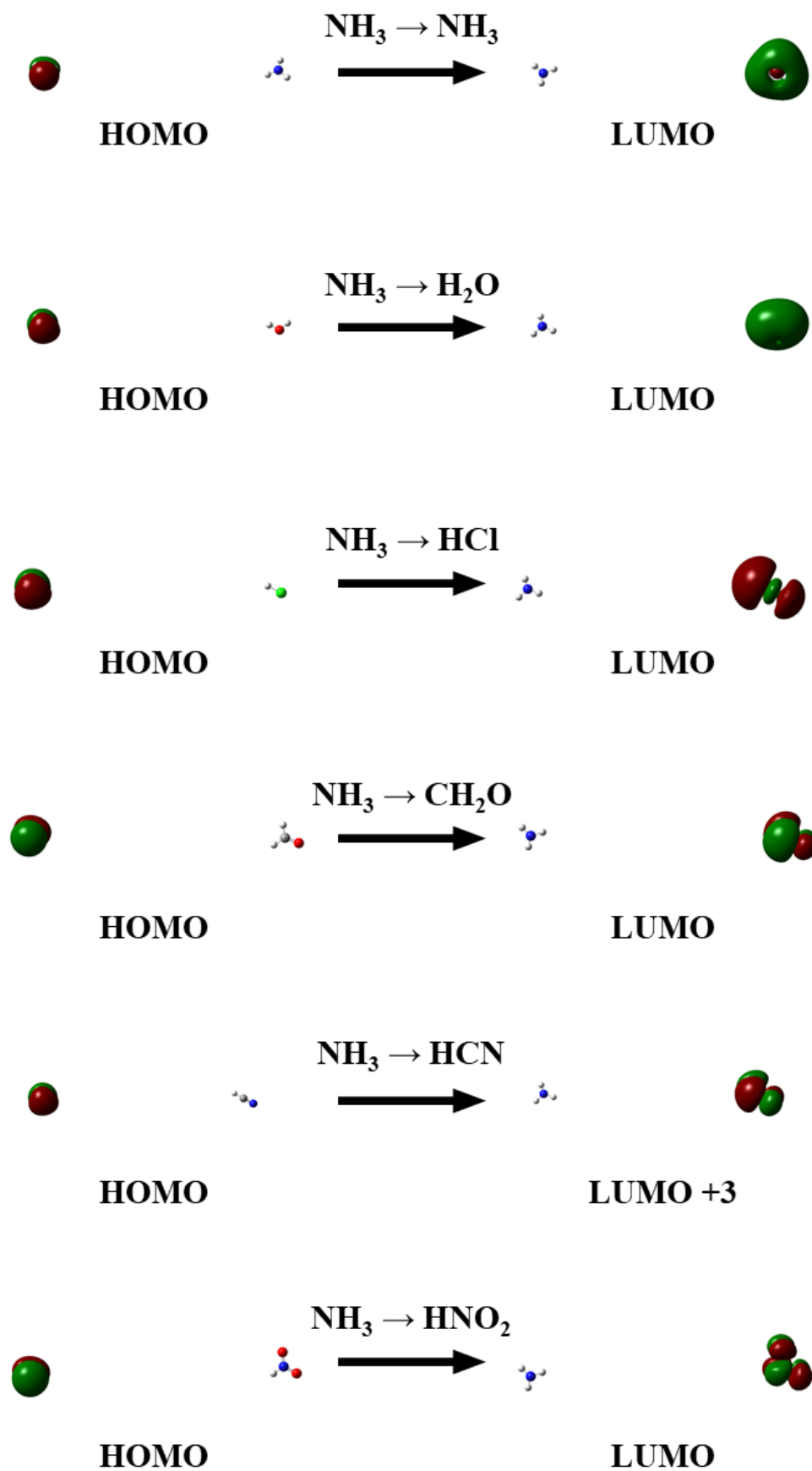


Figure S17. MO shapes of intermolecular CT excitations from NH_3 to various electron acceptors with $n=8$ calculated using HF.