Supporting Information

Interacting Quantum Atoms (IQA) and Relative Energy Gradient (REG) Study of the Halogen Bond with explicit Analysis of Electron Correlation

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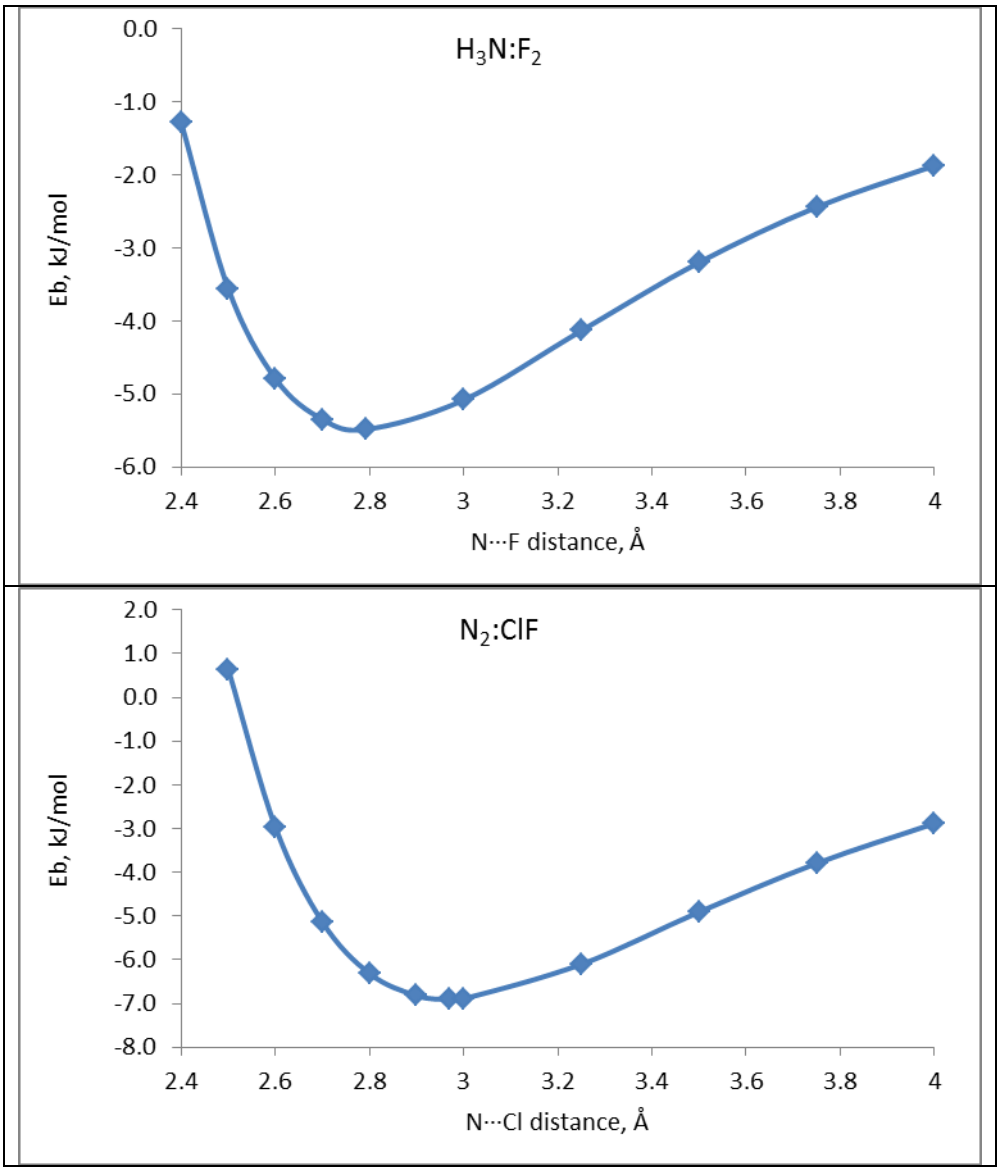
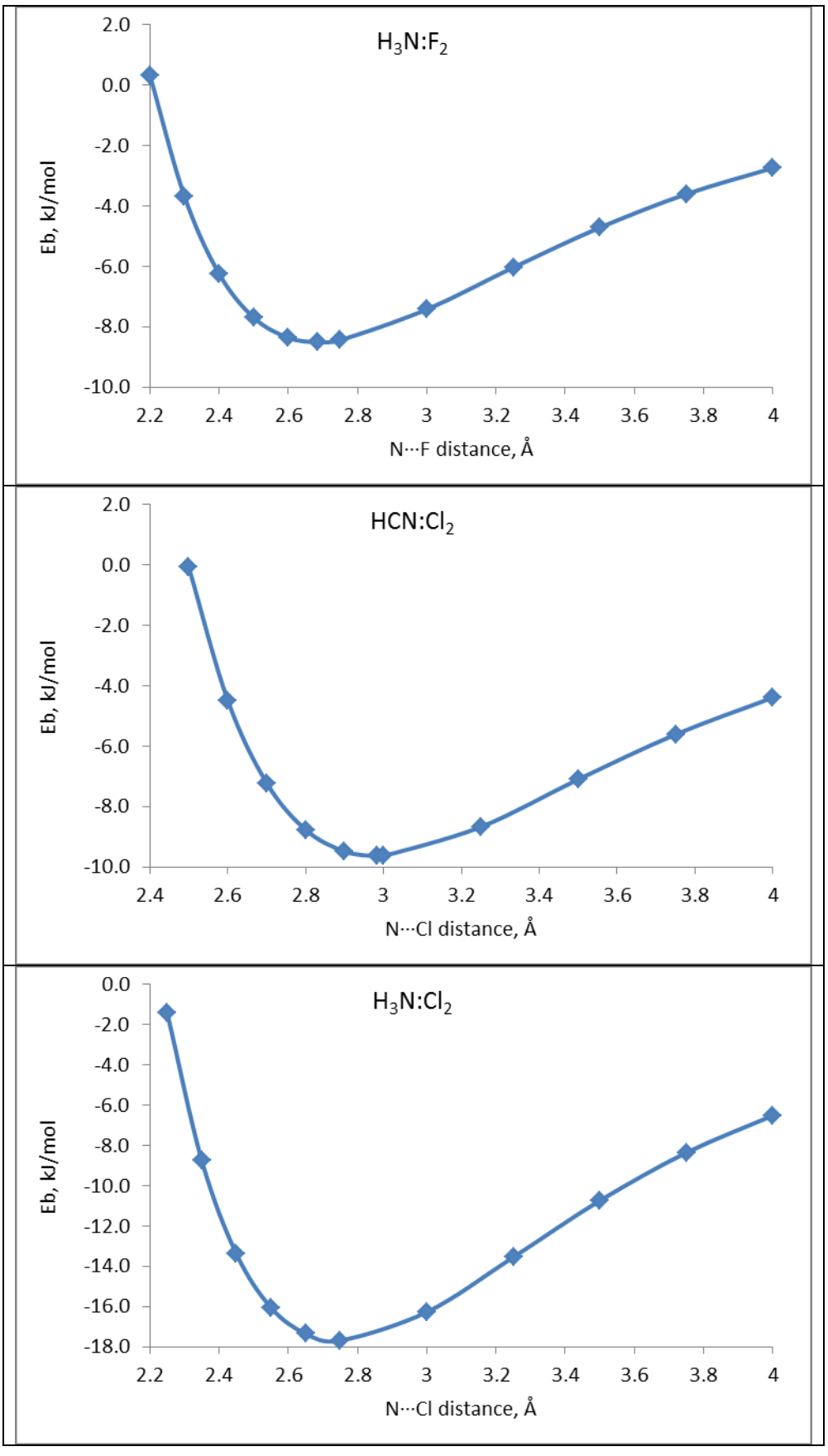
Pg. 22 **Figure S4.** Charge transfer profiles for all 7 complexes. The overall net charge of the halogen molecule in plotted (in e) versus the N…X distance (in Å).

Figure S1. Energy profiles calculated at MP4(SDQ)/6-31+G(2d,2p) level for all 7 complexes.




H3N:F2
Eb, kJ/mol
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
N···F distance, Å
HCN:Cl2
Eb, kJ/mol
2.0
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
N···Cl distance, Å
H3N:Cl2
Eb, kJ/mol
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
-12.0
-14.0
-16.0
-18.0
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
N···Cl distance, Å

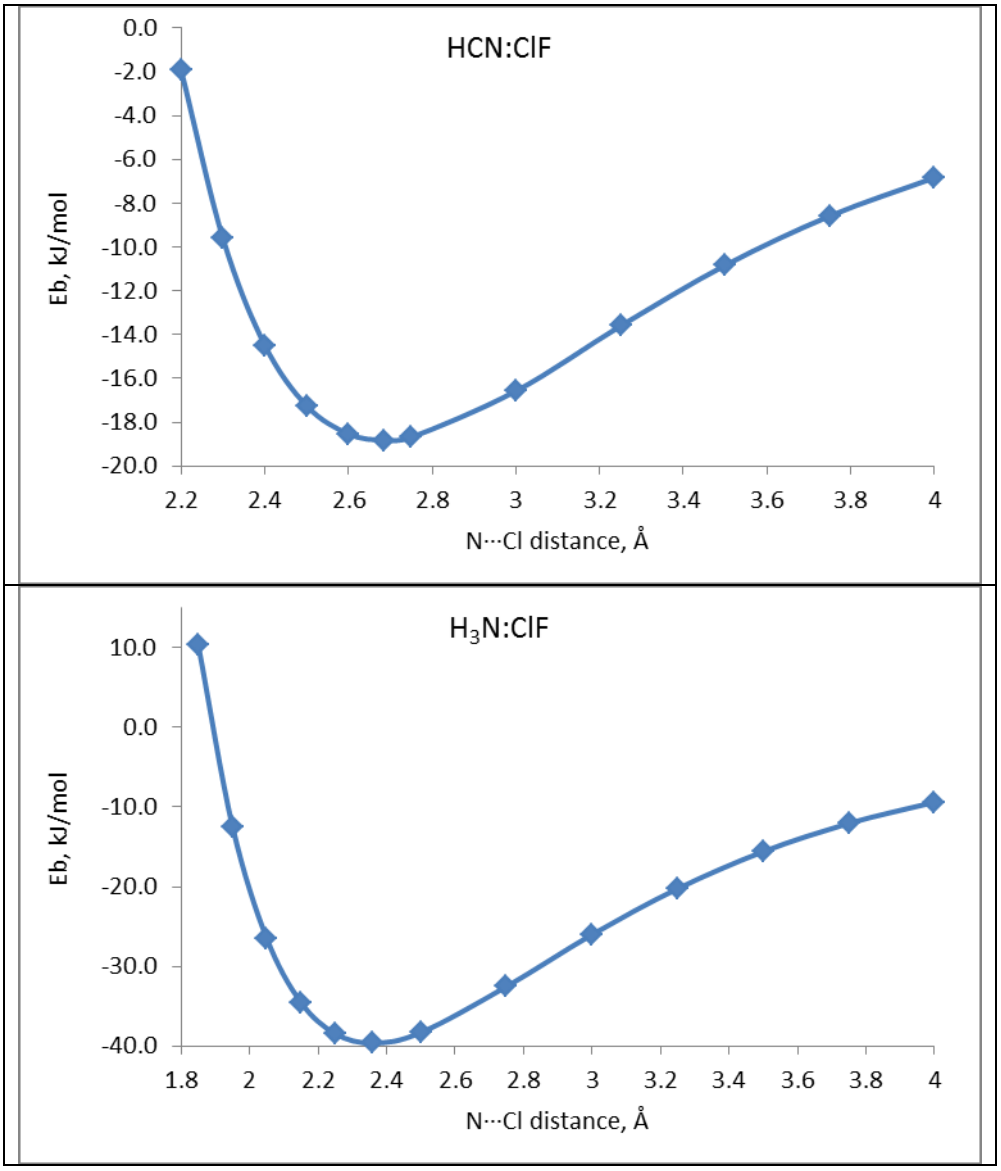
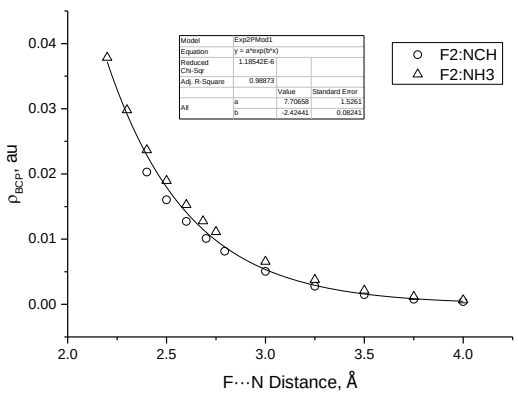
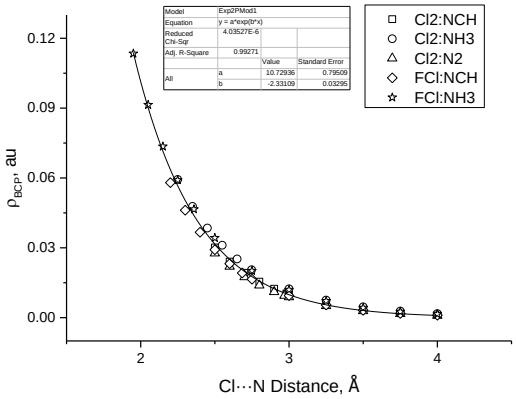

HCN:ClF
Eb, kJ/mol
0.0
-2.0
-4.0
-6.0
-8.0
-10.0
-12.0
-14.0
-16.0
-18.0
-20.0
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
N···Cl distance, Å
H3N:ClF
Eb, kJ/mol
10.0
0.0
-10.0
-20.0
-30.0
-40.0
1.8
2
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
N···Cl distance, Å

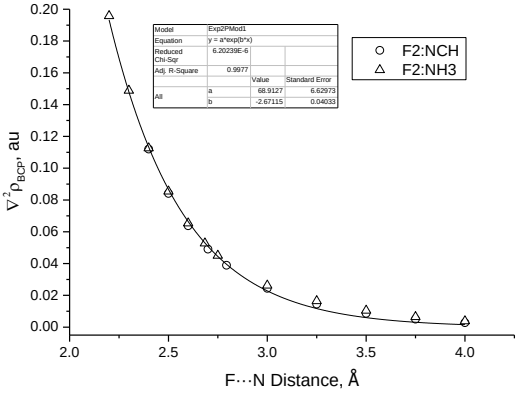
Table S1. Energy range of the energy profiles and the corresponding (atomic integration) errors calculated as the difference between the sum of the IQA terms and the original *ab initio* energy (kJ mol^{-1}).

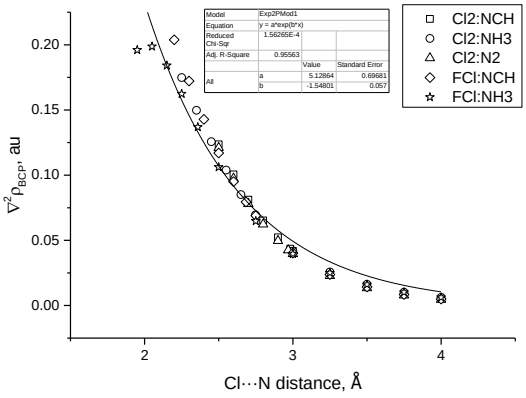
Complexes	Energy Range	Hartree-Fock energy		Correlation contribution	
		Max-Error	Min-Error	Max-Error	Min-Error
$HCN:F_2$	4.2	0.07	0.06	2.0	1.6
$H_3N:F_2$	8.8	0.07	0.05	-0.2	-0.9
$HCN:Cl_2$	9.6	0.00	-0.02	-3.0	-4.6
$H_3N:Cl_2$	9.6	0.00	-0.03	3.3	2.2
N_2:ClF	7.6	0.02	0.00	-0.7	-3.0
HCN:ClF	16.9	0.04	0.02	-1.9	-4.7
H_3N:ClF	30.2	0.08	-0.03	-1.0	-4.5

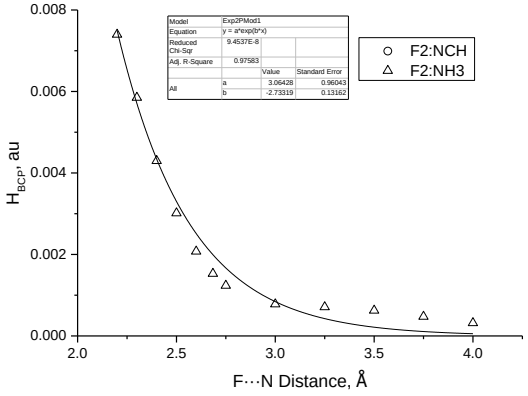
Figure S2. Evolution of ρ_{BCP}, $\nabla^2\rho_{BCP}$ and H_{BCP} along the energy profiles of all seven complexes.











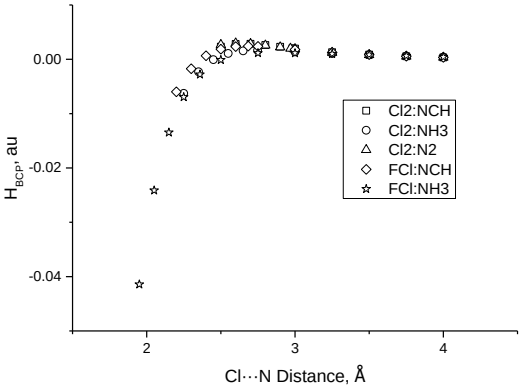


Table S2

Level 1 REG analysis of the energy profiles of all seven complexes based on the **total atomic energies** (E_{IQA}^{A}) ranked by their REG values. The atomic labelling should be clear from the common core scheme X1-X2···N3-etc. Note that in Table 3 of the main text, which summarises this Table, X1 is referred to as X_{outer}, and X2 as X_{inner}.

$HCN:F_2$

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_f2	2.94	0.97		EIQA_f1	3.60	0.98
EIQA_n3	1.87	0.99		EIQA_n3	1.02	0.98
EIQA_c4	0.78	0.96		EIQA_h5	-0.23	-0.99
EIQA_h5	0.17	0.97		EIQA_c4	-1.25	-0.99
EIQA_f1	-3.08	-0.96		EIQA_f2	-3.34	-0.98

$H_3N:F_2$

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_f2	3.54	0.97		EIQA_f1	4.00	0.97
EIQA_n3	1.83	0.99		EIQA_n3	0.28	0.70
EIQA_h5	0.72	1.00		EIQA_h5	-0.36	-0.97
EIQA_h4	0.72	1.00		EIQA_h6	-0.36	-0.97
EIQA_h6	0.72	1.00		EIQA_h4	-0.36	-0.97
EIQA_f1	-3.72	-0.98		EIQA_f2	-3.74	-0.97

$HCN:Cl_2$

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_cl2	2.95	0.97		EIQA_cl1	3.55	0.97
EIQA_c4	1.92	0.97		EIQA_n3	2.50	0.99
EIQA_h5	0.45	0.97		EIQA_h5	-0.56	-0.98
EIQA_n3	-0.07	-0.22		EIQA_c4	-2.50	-0.97
EIQA_cl1	-3.40	-0.98		EIQA_cl2	-2.78	-0.95

H_3N:Cl_2

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_cl2	2.56	0.96		EIQA_cl1	3.49	0.95
EIQA_h6	1.35	0.98		EIQA_n3	1.70	0.98
EIQA_h4	1.35	0.98		EIQA_h6	-0.79	-0.94
EIQA_h5	1.35	0.98		EIQA_h5	-0.79	-0.94
EIQA_n3	-0.17	-0.72		EIQA_h4	-0.79	-0.94
EIQA_cl1	-4.49	-0.97		EIQA_cl2	-2.51	-0.94

N_2:ClF

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_n4	1.55	0.97		EIQA_n3	1.50	1.00
EIQA_n3	1.41	1.00		EIQA_f1	1.24	0.94
EIQA_cl2	0.55	0.96		EIQA_cl2	-0.27	-0.71
EIQA_f1	-1.64	-0.98		EIQA_n4	-2.42	-0.98

HCN:ClF

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_c4	2.33	0.98		EIQA_n3	2.29	1.00
EIQA_h5	0.60	0.98		EIQA_f1	0.88	0.94
EIQA_n3	0.48	0.97		EIQA_cl2	0.23	0.98
EIQA_cl2	-0.30	-0.99		EIQA_h5	-0.57	-0.98
EIQA_f1	-1.27	-0.97		EIQA_c4	-2.38	-0.98

H_3N:ClF

SEG1				SEG2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
EIQA_h6	1.35	0.97		EIQA_n3	1.38	1.00
EIQA_h5	1.35	0.97		EIQA_cl2	0.89	0.92
EIQA_h4	1.35	0.97		EIQA_f1	0.68	0.95
EIQA_n3	-0.03	-0.68		EIQA_h6	-0.84	-0.95
EIQA_f1	-0.86	-0.96		EIQA_h5	-0.84	-0.95
EIQA_cl2	-1.70	-0.95		EIQA_h4	-0.84	-0.95

Table S3

Level 2 REG analysis of the energy profile of all seven complexes based on the **total interatomic** V_{inter}^{AB} **and intra-atomic energies** (E_{intra}^{A}) ranked by their REG values. The atomic labelling should be clear from the common core scheme X1-X2···N3-etc. Note that in Table 4 of the main text, which summarises this Table, X1 is referred to as X_{outer}, and X2 as X_{inner}.

$HCN:F_2$

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	6.36	0.98		Inter_f2_n3	6.47	0.94
Intra_f2	6.27	0.97		Intra_f1	3.48	0.97
Inter_f2_c4	1.43	0.98		Inter_n3_c4	0.54	0.98
Inter_f1_n3	1.02	0.99		Inter_f1_c4	0.45	0.86
Inter_f1_f2	0.99	0.99		Inter_n3_h5	0.25	1.00
Intra_c4	0.83	0.96		Inter_f1_h5	0.09	0.93
Inter_c4_h5	0.37	0.97		Inter_f1_n3	-0.06	-0.27
Inter_f2_h5	0.11	0.98		Intra_h5	-0.09	-0.99
Intra_h5	0.07	0.97		Inter_f2_h5	-0.10	-0.98
Inter_n3_h5	-0.13	-0.97		Inter_f1_f2	-0.15	-0.72
Inter_f1_h5	-0.15	-0.98		Inter_c4_h5	-0.51	-0.99
Inter_n3_c4	-0.70	-0.97		Intra_c4	-0.89	-0.99
Inter_f1_c4	-1.24	-0.98		Inter_f2_c4	-1.14	-0.98
Intra_f1	-3.39	-0.97		Intra_n3	-2.62	-0.90
Inter_f2_n3	-9.22	-0.97		Intra_f2	-5.93	-0.96

$H_3N:F_2$

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	6.65	0.99		Inter_f2_n3	7.46	0.94
Intra_f2	6.14	0.97		Intra_f1	4.17	0.97
Inter_f1_f2	3.48	1.00		Inter_f1_h6	0.34	0.91
Inter_f1_n3	1.83	0.99		Inter_f1_h4	0.34	0.91
Inter_f2_h6	0.54	0.99		Inter_f1_h5	0.34	0.91
Inter_f2_h5	0.54	0.99		Inter_n3_h6	0.01	0.12
Inter_f2_h4	0.54	0.99		Inter_n3_h5	0.01	0.12
Intra_h5	0.54	1.00		Inter_n3_h4	0.01	0.12

Intra_h6	0.54	1.00		Intra_h5	-0.17	-0.98
Intra_h4	0.54	1.00		Intra_h6	-0.17	-0.98
Inter_h4_h6	0.53	1.00		Intra_h4	-0.17	-0.98
Inter_h5_h6	0.53	1.00		Inter_h5_h6	-0.18	-0.97
Inter_h4_h5	0.53	1.00		Inter_h4_h5	-0.18	-0.97
Inter_n3_h4	-0.37	-0.97		Inter_h4_h6	-0.18	-0.97
Inter_n3_h6	-0.37	-0.97		Inter_f2_h4	-0.37	-0.97
Inter_n3_h5	-0.37	-0.97		Inter_f2_h6	-0.37	-0.97
Inter_f1_h4	-0.88	-0.99		Inter_f2_h5	-0.37	-0.97
Inter_f1_h5	-0.88	-0.99		Inter_f1_n3	-0.48	-0.82
Inter_f1_h6	-0.88	-0.99		Inter_f1_f2	-0.82	-0.86
Intra_f1	-5.04	-0.98		Intra_n3	-3.25	-0.93
Inter_f2_n3	-10.34	-0.98		Intra_f2	-6.55	-0.96

HCN:Cl_2

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_cl2	6.50	0.97		Inter_cl2_n3	11.87	0.96
Intra_n3	6.35	0.98		Inter_n3_c4	4.34	0.98
Inter_cl2_c4	3.60	0.98		Intra_cl1	3.40	0.96
Intra_c4	1.75	0.97		Inter_cl1_c4	0.97	0.93
Inter_cl1_n3	1.66	0.99		Inter_n3_h5	0.86	0.98
Inter_c4_h5	0.96	0.97		Inter_cl1_h5	0.14	0.94
Inter_cl1_cl2	0.32	1.00		Inter_cl1_cl2	0.01	0.40
Inter_cl2_h5	0.30	0.98		Intra_h5	-0.26	-0.98
Intra_h5	0.21	0.98		Inter_cl2_h5	-0.33	-0.97
Inter_cl1_h5	-0.20	-0.98		Inter_cl1_n3	-0.78	-0.90
Inter_n3_h5	-0.58	-0.97		Inter_c4_h5	-1.28	-0.98
Inter_cl1_c4	-1.67	-0.98		Intra_c4	-2.47	-0.98
Inter_n3_c4	-2.58	-0.97		Inter_cl2_c4	-4.05	-0.97
Intra_cl1	-3.46	-0.98		Intra_n3	-5.72	-0.96
Inter_cl2_n3	-11.35	-0.97		Intra_cl2	-6.60	-0.95

H_3N:Cl_2

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	7.78	0.98		Inter_cl2_n3	10.54	0.94
Intra_cl2	6.30	0.96		Intra_cl1	3.58	0.94
Inter_cl1_n3	2.58	0.98		Inter_n3_h5	1.23	0.97

Inter_cl1_cl2	1.72	0.99		Inter_n3_h4	1.23	0.97
Inter_cl2_h6	1.51	0.98		Inter_n3_h6	1.23	0.97
Inter_cl2_h5	1.51	0.98		Inter_cl1_h6	0.46	0.89
Inter_cl2_h4	1.51	0.98		Inter_cl1_h5	0.46	0.89
Inter_h5_h6	0.97	0.98		Inter_cl1_h4	0.46	0.89
Inter_h4_h6	0.97	0.98		Inter_cl1_cl2	-0.51	-0.84
Inter_h4_h5	0.97	0.98		Intra_h6	-0.53	-0.94
Intra_h6	0.97	0.98		Intra_h5	-0.53	-0.94
Intra_h4	0.97	0.98		Intra_h4	-0.53	-0.94
Intra_h5	0.97	0.98		Inter_h5_h6	-0.56	-0.94
Inter_cl1_h4	-1.12	-0.98		Inter_h4_h5	-0.56	-0.94
Inter_cl1_h5	-1.12	-0.98		Inter_h4_h6	-0.56	-0.94
Inter_cl1_h6	-1.12	-0.98		Inter_cl1_n3	-1.04	-0.88
Inter_n3_h4	-1.59	-0.98		Inter_cl2_h4	-1.08	-0.96
Inter_n3_h5	-1.59	-0.98		Inter_cl2_h6	-1.08	-0.96
Inter_n3_h6	-1.59	-0.98		Inter_cl2_h5	-1.08	-0.96
Intra_cl1	-4.97	-0.97		Intra_n3	-4.91	-0.94
Inter_cl2_n3	-13.74	-0.97		Intra_cl2	-5.95	-0.94

N_2:ClF

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	5.56	0.98		Inter_cl2_n3	9.93	0.96
Intra_cl2	4.59	0.97		Inter_f1_cl2	1.21	0.98
Intra_n4	1.17	0.97		Inter_f1_n4	1.03	0.98
Inter_cl2_n4	1.06	0.96		Intra_f1	0.53	0.89
Inter_n3_n4	0.33	0.97		Inter_n3_n4	-0.36	-0.97
Inter_f1_n3	0.06	0.74		Inter_f1_n3	-0.84	-1.00
Inter_f1_cl2	-0.43	-0.89		Intra_n4	-1.83	-0.98
Inter_f1_n4	-0.58	-0.96		Inter_cl2_n4	-1.94	-0.98
Intra_f1	-1.16	-0.99		Intra_n3	-2.82	-0.91
Inter_cl2_n3	-8.71	-0.97		Intra_cl2	-4.86	-0.95

HCN:ClF

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	7.81	0.98		Inter_cl2_n3	13.03	0.97
Inter_cl2_c4	4.01	0.97		Inter_n3_c4	4.35	0.98

Intra_cl2	3.14	0.97		Inter_f1_c4	3.39	0.99
Intra_c4	2.42	0.97		Intra_f1	0.91	0.94
Inter_f1_n3	2.03	0.96		Inter_n3_h5	0.84	0.98
Inter_f1_cl2	1.39	1.00		Inter_f1_h5	0.40	0.99
Inter_c4_h5	1.28	0.97		Inter_f1_cl2	0.10	0.57
Inter_cl2_h5	0.39	0.97		Intra_h5	-0.27	-0.97
Intra_h5	0.30	0.98		Inter_cl2_h5	-0.54	-0.99
Inter_f1_h5	-0.31	-0.97		Inter_c4_h5	-1.30	-0.98
Inter_n3_h5	-0.75	-0.97		Intra_c4	-2.68	-0.97
Intra_f1	-1.72	-0.98		Intra_cl2	-3.19	-0.96
Inter_f1_c4	-2.22	-0.97		Inter_f1_n3	-3.93	-0.99
Inter_n3_c4	-3.25	-0.96		Intra_n3	-4.89	-0.95
Inter_cl2_n3	-12.71	-0.97		Inter_cl2_c4	-5.81	-0.99

H_3N:ClF

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	7.15	0.96		Inter_cl2_n3	9.80	0.97
Inter_f1_cl2	4.09	0.96		Intra_f1	1.27	0.93
Inter_f1_n3	1.47	0.96		Inter_n3_h4	1.27	0.97
Inter_cl2_h4	1.28	0.97		Inter_n3_h5	1.27	0.97
Inter_cl2_h5	1.28	0.97		Inter_n3_h6	1.27	0.97
Inter_cl2_h6	1.28	0.97		Inter_f1_h6	0.87	0.98
Intra_h6	0.92	0.96		Inter_f1_h4	0.87	0.98
Intra_h5	0.92	0.96		Inter_f1_h5	0.87	0.98
Intra_h4	0.92	0.96		Intra_h5	-0.64	-0.95
Inter_h5_h6	0.91	0.96		Intra_h4	-0.64	-0.95
Inter_h4_h6	0.91	0.96		Intra_h6	-0.64	-0.95
Inter_h4_h5	0.91	0.96		Inter_h4_h5	-0.66	-0.95
Intra_cl2	0.39	0.99		Inter_h5_h6	-0.66	-0.95
Inter_f1_h4	-0.98	-0.96		Inter_h4_h6	-0.66	-0.95
Inter_f1_h6	-0.98	-0.96		Inter_cl2_h4	-1.22	-0.99
Inter_f1_h5	-0.98	-0.96		Inter_cl2_h6	-1.22	-0.99
Inter_n3_h6	-1.24	-0.95		Inter_cl2_h5	-1.22	-0.99
Inter_n3_h5	-1.24	-0.95		Intra_cl2	-1.30	-1.00
Inter_n3_h4	-1.24	-0.95		Inter_f1_cl2	-1.76	-0.88
Intra_f1	-2.17	-0.96		Inter_f1_n3	-2.04	-0.99
Inter_cl2_n3	-12.11	-0.97		Intra_n3	-4.41	-0.94

Table S4

Level 3 REG analysis of the energy profile of all seven complexes based **on the total intra-atomic energy E_{intra}^{A}, and the interatomic atomic energies V_{cl} (electrostatic), V_x (exchange) and V_c correlation (overall 4 possible energy types)**, ranked by their REG values. The atomic labelling should be clear from the common core scheme X1-X2···N3-etc. Note that in Table 5 of the main text, which summarises this Table, X1 is referred to as X_{outer}, and X2 as X_{inner}.

HCN:F_2

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	6.36	0.98		Vx_f2_n3	4.81	0.93
Intra_f2	6.27	0.97		Intra_f1	3.48	0.97
Vx_f1_f2	2.52	0.98		Vcl_f2_n3	1.66	0.97
Vcl_f2_c4	1.57	0.98		Vcl_n3_c4	0.94	0.99
Vcl_f1_n3	1.44	0.98		Vcl_f1_f2	0.94	0.95
Intra_c4	0.83	0.96		Vc_f2_n3	0.89	0.97
Vx_n3_c4	0.46	0.97		Vcl_f1_c4	0.44	0.86
Vcl_c4_h5	0.30	0.97		Vcl_n3_h5	0.30	1.00
Vc_f1_n3	0.18	0.96		Vx_f1_n3	0.26	0.93
Vcl_f2_h5	0.12	0.98		Vc_f1_c4	0.16	0.98
Vc_f2_c4	0.10	0.95		Vx_f2_c4	0.11	0.94
Vx_c4_h5	0.08	0.98		Vcl_f1_h5	0.09	0.93
Vc_n3_c4	0.07	0.97		Vc_f1_h5	0.03	0.99
Intra_h5	0.07	0.97		Vx_f2_h5	0.01	0.96
Vx_n3_h5	0.03	0.96		Vx_f1_c4	0.01	0.88
Vc_n3_h5	0.03	0.97		Vx_f1_h5	0.00	0.94
Vc_c4_h5	0.01	0.96		Vc_c4_h5	-0.02	-0.99
Vc_f2_h5	0.00	-0.03		Vc_n3_h5	-0.02	-0.90
Vx_f1_h5	0.00	-0.98		Vc_f1_f2	-0.02	-0.98
Vx_f2_h5	-0.01	-0.96		Vc_f2_h5	-0.02	-1.00
Vx_f1_c4	-0.02	-0.98		Vx_n3_h5	-0.04	-0.98
Vc_f1_h5	-0.02	-0.95		Vc_n3_c4	-0.04	-0.87
Vc_f1_f2	-0.07	-1.00		Vx_c4_h5	-0.08	-0.98
Vc_f1_c4	-0.11	-0.96		Intra_h5	-0.09	-0.99
Vx_f2_c4	-0.15	-0.97		Vcl_f2_h5	-0.11	-0.98
Vcl_f1_h5	-0.15	-0.98		Vc_f2_c4	-0.18	-0.99
Vcl_n3_h5	-0.16	-0.97		Vc_f1_n3	-0.27	-0.98
Vx_f1_n3	-0.42	-0.97		Vcl_f1_n3	-0.31	-0.72
Vc_f2_n3	-0.75	-0.96		Vx_n3_c4	-0.40	-0.98

Vcl_n3_c4	-1.16	-0.97		Vcl_c4_h5	-0.43	-0.99
Vcl_f1_c4	-1.22	-0.98		Intra_c4	-0.89	-0.99
Vcl_f1_f2	-1.54	-0.98		Vx_f1_f2	-1.09	-0.92
Vcl_f2_n3	-2.02	-0.98		Vcl_f2_c4	-1.26	-0.97
Intra_f1	-3.39	-0.97		Intra_n3	-2.62	-0.90
Vx_f2_n3	-7.20	-0.97		Intra_f2	-5.93	-0.96

H_3N:F_2

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Vx_f1_f2	6.80	0.99		Vx_f2_n3	5.65	0.93
Intra_n3	6.65	0.99		Intra_f1	4.17	0.97
Intra_f2	6.14	0.97		Vcl_f2_n3	1.81	0.96
Vcl_f1_n3	2.61	0.99		Vcl_f1_f2	1.60	0.93
Vcl_f2_h6	0.62	0.99		Vc_f2_n3	0.60	0.97
Vcl_f2_h5	0.62	0.99		Vx_f1_n3	0.36	0.92
Vcl_f2_h4	0.62	0.99		Vcl_f1_h6	0.33	0.91
Vx_n3_h6	0.61	1.00		Vcl_f1_h4	0.33	0.91
Vx_n3_h4	0.61	1.00		Vcl_f1_h5	0.33	0.91
Vx_n3_h5	0.61	1.00		Vcl_n3_h4	0.26	0.98
Intra_h5	0.54	1.00		Vcl_n3_h6	0.26	0.99
Intra_h6	0.54	1.00		Vcl_n3_h5	0.26	0.98
Intra_h4	0.54	1.00		Vc_f1_f2	0.06	0.78
Vcl_h4_h6	0.51	1.00		Vx_f2_h4	0.06	0.94
Vcl_h5_h6	0.51	1.00		Vx_f2_h5	0.06	0.94
Vcl_h4_h5	0.51	1.00		Vx_f2_h6	0.06	0.94
Vc_f1_n3	0.21	0.99		Vc_f1_h5	0.05	0.97
Vc_n3_h4	0.06	0.96		Vc_f1_h6	0.05	0.97
Vc_n3_h5	0.06	0.96		Vc_f1_h4	0.05	0.97
Vc_n3_h6	0.06	0.96		Vx_f1_h5	0.01	0.89
Vx_h4_h5	0.02	1.00		Vx_f1_h4	0.01	0.89
Vx_h4_h6	0.02	1.00		Vx_f1_h6	0.01	0.89
Vx_h5_h6	0.02	1.00		Vc_h5_h6	0.00	-0.61
Vc_h4_h6	0.01	1.00		Vc_h4_h6	0.00	-0.61
Vc_h5_h6	0.01	1.00		Vc_h4_h5	0.00	-0.61
Vc_h4_h5	0.01	1.00		Vc_f2_h4	0.00	-0.29
Vx_f1_h6	-0.02	-0.99		Vc_f2_h5	0.00	-0.29
Vx_f1_h4	-0.02	-0.99		Vc_f2_h6	0.00	-0.29
Vx_f1_h5	-0.02	-0.99		Vx_h5_h6	-0.01	-0.94
Vc_f2_h5	-0.03	-0.99		Vx_h4_h5	-0.01	-0.94
Vc_f2_h6	-0.03	-0.99		Vx_h4_h6	-0.01	-0.94

Vc_f2_h4	-0.03	-0.99		Vc_n3_h4	-0.06	-0.95
Vc_f1_h5	-0.05	-0.97		Vc_n3_h5	-0.06	-0.95
Vc_f1_h6	-0.05	-0.97		Vc_n3_h6	-0.06	-0.95
Vc_f1_h4	-0.05	-0.97		Vcl_h5_h6	-0.17	-0.98
Vx_f2_h6	-0.07	-0.98		Vcl_h4_h5	-0.17	-0.98
Vx_f2_h5	-0.07	-0.98		Vcl_h4_h6	-0.17	-0.98
Vx_f2_h4	-0.07	-0.98		Intra_h5	-0.17	-0.98
Vc_f2_n3	-0.43	-0.95		Intra_h6	-0.17	-0.98
Vc_f1_f2	-0.43	-1.00		Intra_h4	-0.17	-0.98
Vx_f1_n3	-0.78	-0.99		Vc_f1_n3	-0.18	-0.97
Vcl_f1_h4	-0.86	-0.99		Vx_n3_h5	-0.25	-0.96
Vcl_f1_h5	-0.86	-0.99		Vx_n3_h6	-0.25	-0.96
Vcl_f1_h6	-0.86	-0.99		Vx_n3_h4	-0.25	-0.96
Vcl_n3_h4	-0.98	-1.00		Vcl_f2_h4	-0.42	-0.97
Vcl_n3_h6	-0.98	-1.00		Vcl_f2_h6	-0.42	-0.97
Vcl_n3_h5	-0.98	-1.00		Vcl_f2_h5	-0.42	-0.97
Vcl_f2_n3	-2.28	-0.98		Vcl_f1_n3	-0.84	-0.87
Vcl_f1_f2	-3.32	-0.99		Vx_f1_f2	-2.42	-0.91
Intra_f1	-5.04	-0.98		Intra_n3	-3.25	-0.93
Vx_f2_n3	-8.06	-0.98		Intra_f2	-6.55	-0.96

HCN:Cl_2

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_cl2	6.50	0.97		Vx_cl2_n3	6.07	0.95
Intra_n3	6.35	0.98		Vcl_cl2_n3	5.80	0.97
Vcl_cl2_c4	3.76	0.98		Vcl_n3_c4	5.43	0.98
Vcl_cl1_n3	1.94	0.98		Intra_cl1	3.40	0.96
Intra_c4	1.75	0.97		Vcl_cl1_c4	0.96	0.93
Vx_cl1_cl2	1.68	0.99		Vcl_n3_h5	0.93	0.98
Vx_n3_c4	0.97	0.98		Vc_cl2_n3	0.88	0.97
Vcl_c4_h5	0.78	0.97		Vcl_cl1_cl2	0.83	0.95
Vcl_cl2_h5	0.31	0.98		Vx_cl1_n3	0.25	0.96
Intra_h5	0.21	0.98		Vx_cl2_c4	0.14	0.95
Vx_c4_h5	0.18	0.98		Vcl_cl1_h5	0.14	0.94
Vc_cl1_n3	0.11	0.97		Vc_cl1_c4	0.11	0.98
Vx_n3_h5	0.06	0.97		Vc_n3_c4	0.03	0.99
Vc_cl2_c4	0.05	0.94		Vc_cl1_h5	0.02	0.98
Vc_n3_h5	0.02	0.98		Vx_cl1_c4	0.01	0.91
Vc_c4_h5	0.02	0.97		Vx_cl2_h5	0.01	0.96
Vc_n3_c4	0.00	0.69		Vc_cl1_cl2	0.01	0.49
Vx_cl1_h5	0.00	-0.98		Vx_cl1_h5	0.00	0.91

Vc_cl2_h5	-0.01	-1.00		Vc_cl2_h5	-0.01	-0.99
Vx_cl2_h5	-0.01	-0.97		Vc_n3_h5	-0.01	-0.91
Vc_cl1_h5	-0.01	-0.96		Vc_c4_h5	-0.03	-0.98
Vx_cl1_c4	-0.02	-0.99		Vx_n3_h5	-0.08	-0.97
Vc_cl1_c4	-0.06	-0.96		Vc_cl2_c4	-0.14	-0.99
Vc_cl1_cl2	-0.09	-1.00		Vc_cl1_n3	-0.17	-0.98
Vx_cl2_c4	-0.16	-0.98		Vx_c4_h5	-0.21	-0.98
Vcl_cl1_h5	-0.20	-0.98		Intra_h5	-0.26	-0.98
Vx_cl1_n3	-0.28	-0.98		Vcl_cl2_h5	-0.34	-0.97
Vc_cl2_n3	-0.61	-0.96		Vx_cl1_cl2	-0.82	-0.93
Vcl_n3_h5	-0.64	-0.97		Vcl_cl1_n3	-1.03	-0.91
Vcl_cl1_cl2	-1.36	-0.99		Vcl_c4_h5	-1.07	-0.98
Vcl_cl1_c4	-1.65	-0.98		Vx_n3_c4	-1.09	-0.97
Intra_cl1	-3.46	-0.98		Intra_c4	-2.47	-0.98
Vcl_n3_c4	-3.56	-0.97		Vcl_cl2_c4	-4.19	-0.97
Vcl_cl2_n3	-4.91	-0.97		Intra_n3	-5.72	-0.96
Vx_cl2_n3	-6.43	-0.97		Intra_cl2	-6.60	-0.95

$H_3N{:}Cl_2$

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	7.78	0.98		Vx_cl2_n3	5.80	0.93
Intra_cl2	6.30	0.96		Vcl_cl2_n3	4.74	0.96
Vx_cl1_cl2	4.74	0.99		Intra_cl1	3.58	0.94
Vcl_cl1_n3	3.08	0.98		Vcl_n3_h5	1.84	0.96
Vcl_cl2_h6	1.60	0.98		Vcl_n3_h4	1.84	0.96
Vcl_cl2_h5	1.60	0.98		Vcl_n3_h6	1.84	0.96
Vcl_cl2_h4	1.60	0.98		Vcl_cl1_cl2	1.27	0.90
Vx_n3_h4	1.05	0.98		Vcl_cl1_h6	0.46	0.89
Vx_n3_h6	1.05	0.98		Vcl_cl1_h5	0.46	0.89
Vx_n3_h5	1.05	0.98		Vcl_cl1_h4	0.46	0.89
Intra_h6	0.97	0.98		Vc_cl2_n3	0.45	0.97
Intra_h4	0.97	0.98		Vx_cl1_n3	0.30	0.92
Intra_h5	0.97	0.98		Vc_cl1_cl2	0.07	0.79
Vcl_h5_h6	0.93	0.98		Vx_cl2_h5	0.06	0.92
Vcl_h4_h6	0.93	0.98		Vx_cl2_h4	0.06	0.92
Vcl_h4_h5	0.93	0.98		Vx_cl2_h6	0.06	0.92
Vc_cl1_n3	0.13	0.97		Vc_cl1_h5	0.03	0.96
Vx_h4_h6	0.04	0.98		Vc_cl1_h6	0.03	0.96
Vx_h4_h5	0.04	0.98		Vc_cl1_h4	0.03	0.96
Vx_h5_h6	0.04	0.98		Vc_cl2_h4	0.02	0.83

Vc_n3_h4	0.03	0.92		Vc_cl2_h5	0.02	0.83
Vc_n3_h5	0.03	0.92		Vc_cl2_h6	0.02	0.83
Vc_n3_h6	0.03	0.92		Vx_cl1_h5	0.01	0.89
Vc_h5_h6	0.01	0.96		Vx_cl1_h4	0.01	0.89
Vc_h4_h5	0.01	0.96		Vx_cl1_h6	0.01	0.89
Vc_h4_h6	0.01	0.96		Vc_h5_h6	-0.01	-0.93
Vx_cl1_h5	-0.01	-0.98		Vc_h4_h5	-0.01	-0.93
Vx_cl1_h4	-0.01	-0.98		Vc_h4_h6	-0.01	-0.93
Vx_cl1_h6	-0.01	-0.98		Vx_h4_h6	-0.02	-0.94
Vc_cl1_h4	-0.02	-0.95		Vx_h5_h6	-0.02	-0.94
Vc_cl1_h5	-0.02	-0.95		Vx_h4_h5	-0.02	-0.94
Vc_cl1_h6	-0.02	-0.95		Vc_n3_h5	-0.04	-0.92
Vc_cl2_h5	-0.05	-0.97		Vc_n3_h6	-0.04	-0.92
Vc_cl2_h6	-0.05	-0.97		Vc_n3_h4	-0.04	-0.92
Vc_cl2_h4	-0.05	-0.97		Vc_cl1_n3	-0.10	-0.95
Vx_cl2_h4	-0.09	-0.98		Intra_h6	-0.53	-0.94
Vx_cl2_h6	-0.09	-0.98		Intra_h5	-0.53	-0.94
Vx_cl2_h5	-0.09	-0.98		Intra_h4	-0.53	-0.94
Vc_cl2_n3	-0.25	-0.92		Vcl_h5_h6	-0.54	-0.95
Vc_cl1_cl2	-0.33	-0.99		Vcl_h4_h5	-0.54	-0.95
Vx_cl1_n3	-0.51	-0.97		Vcl_h4_h6	-0.54	-0.95
Vcl_cl1_h4	-1.10	-0.98		Vx_n3_h5	-0.61	-0.94
Vcl_cl1_h5	-1.10	-0.98		Vx_n3_h4	-0.61	-0.94
Vcl_cl1_h6	-1.10	-0.98		Vx_n3_h6	-0.61	-0.94
Vcl_n3_h4	-2.64	-0.98		Vcl_cl2_h4	-1.14	-0.95
Vcl_n3_h5	-2.64	-0.98		Vcl_cl2_h6	-1.14	-0.95
Vcl_n3_h6	-2.64	-0.98		Vcl_cl2_h5	-1.14	-0.95
Vcl_cl1_cl2	-3.02	-0.98		Vcl_cl1_n3	-1.34	-0.89
Intra_cl1	-4.97	-0.97		Vx_cl1_cl2	-1.78	-0.89
Vcl_cl2_n3	-5.52	-0.97		Intra_n3	-4.91	-0.94
Vx_cl2_n3	-8.22	-0.97		Intra_cl2	-5.95	-0.94

N_2:ClF

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	5.56	0.98		Vx_cl2_n3	6.98	0.95
Intra_cl2	4.59	0.97		Vcl_cl2_n3	2.95	0.99
Vx_f1_cl2	2.01	0.98		Vcl_f1_cl2	2.59	0.96
Vcl_cl2_n4	1.36	0.97		Vc_cl2_n3	1.05	0.97
Intra_n4	1.17	0.97		Vcl_f1_n4	1.01	0.98
Vx_n3_n4	0.50	0.99		Intra_f1	0.53	0.89

Vcl_f1_n3	0.31	0.94		Vx_cl2_n4	0.28	0.95
Vc_n3_n4	0.24	0.96		Vx_f1_n3	0.25	0.96
Vc_f1_n3	0.12	0.96		Vc_f1_n4	0.17	0.98
Vc_cl2_n4	0.04	0.90		Vc_f1_cl2	0.13	0.95
Vx_f1_n4	-0.03	-0.98		Vx_f1_n4	0.01	0.91
Vc_f1_n4	-0.09	-0.95		Vcl_n3_n4	-0.09	-0.98
Vcl_n3_n4	-0.17	-1.00		Vc_cl2_n4	-0.20	-0.99
Vc_f1_cl2	-0.19	-0.98		Vc_f1_n3	-0.22	-0.98
Vx_f1_n3	-0.25	-0.97		Vx_n3_n4	-0.27	-0.92
Vx_cl2_n4	-0.30	-0.97		Vc_n3_n4	-0.29	-0.96
Vcl_f1_n4	-0.55	-0.96		Vcl_f1_n3	-1.09	-0.99
Vc_cl2_n3	-0.69	-0.96		Vx_f1_cl2	-1.38	-0.94
Vcl_cl2_n3	-1.10	-0.94		Intra_n4	-1.83	-0.98
Intra_f1	-1.16	-0.99		Vcl_cl2_n4	-2.21	-0.98
Vcl_f1_cl2	-2.44	-0.97		Intra_n3	-2.82	-0.91
Vx_cl2_n3	-7.61	-0.97		Intra_cl2	-4.86	-0.95

HCN:ClF

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	7.81	0.98		Vcl_cl2_n3	7.93	0.99
Vcl_cl2_c4	4.22	0.97		Vcl_n3_c4	5.50	0.98
Intra_cl2	3.14	0.97		Vx_cl2_n3	5.10	0.94
Vx_f1_cl2	3.12	0.98		Vcl_f1_c4	3.38	0.99
Intra_c4	2.42	0.97		Vcl_f1_cl2	1.78	0.97
Vcl_f1_n3	2.30	0.96		Intra_f1	0.91	0.94
Vx_n3_c4	1.40	0.98		Vcl_n3_h5	0.91	0.98
Vcl_c4_h5	1.04	0.97		Vc_cl2_n3	0.57	0.97
Vcl_cl2_h5	0.40	0.97		Vcl_f1_h5	0.40	0.99
Intra_h5	0.30	0.98		Vx_f1_n3	0.17	0.94
Vx_c4_h5	0.23	0.98		Vc_f1_cl2	0.14	0.94
Vc_f1_n3	0.09	0.97		Vx_cl2_c4	0.12	0.94
Vx_n3_h5	0.07	0.97		Vc_n3_c4	0.07	0.99
Vc_n3_h5	0.02	0.97		Vc_f1_c4	0.06	0.98
Vc_c4_h5	0.02	0.96		Vc_f1_h5	0.01	0.98
Vc_cl2_c4	0.01	0.94		Vx_f1_c4	0.01	0.90
Vx_f1_h5	0.00	-0.98		Vx_cl2_h5	0.01	0.95
Vc_f1_h5	-0.01	-0.95		Vc_cl2_h5	0.00	0.41
Vx_cl2_h5	-0.01	-0.98		Vx_f1_h5	0.00	0.91
Vc_cl2_h5	-0.02	-0.98		Vc_n3_h5	-0.01	-0.86
Vx_f1_c4	-0.02	-0.99		Vc_c4_h5	-0.03	-0.98

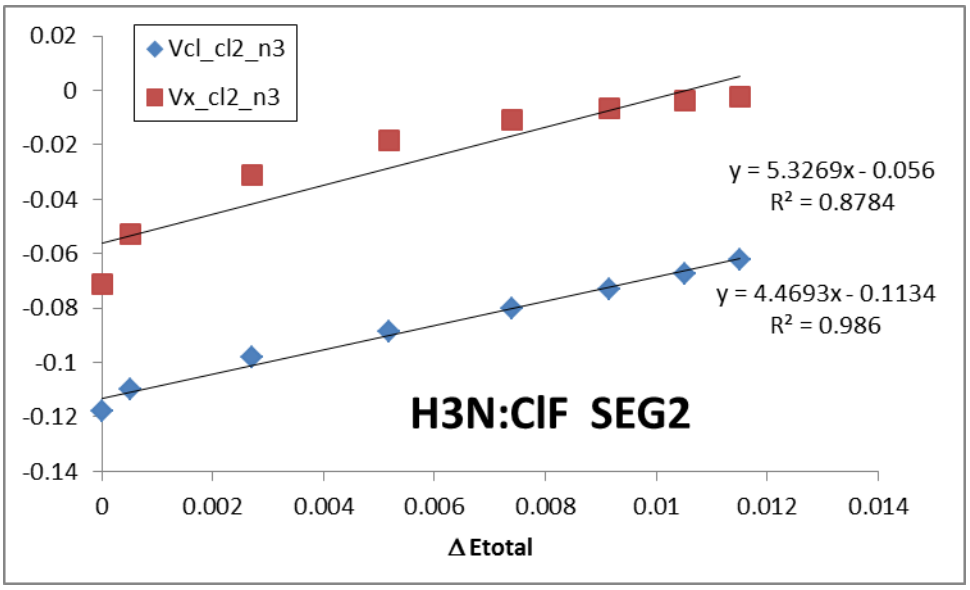
Vc_f1_c4	-0.04	-0.95		Vc_cl2_c4	-0.05	-1.00
Vc_n3_c4	-0.08	-0.99		Vx_n3_h5	-0.07	-0.97
Vx_cl2_c4	-0.21	-0.98		Vc_f1_n3	-0.10	-0.98
Vc_f1_cl2	-0.25	-0.98		Vx_c4_h5	-0.21	-0.97
Vx_f1_n3	-0.27	-0.98		Intra_h5	-0.27	-0.97
Vcl_f1_h5	-0.31	-0.97		Vcl_cl2_h5	-0.55	-0.99
Vc_cl2_n3	-0.40	-0.94		Vcl_c4_h5	-1.08	-0.98
Vcl_n3_h5	-0.82	-0.97		Vx_n3_c4	-1.15	-0.97
Intra_f1	-1.72	-0.98		Vx_f1_cl2	-1.68	-0.94
Vcl_f1_cl2	-1.73	-0.97		Intra_c4	-2.68	-0.97
Vcl_f1_c4	-2.20	-0.97		Intra_cl2	-3.19	-0.96
Vcl_n3_c4	-4.65	-0.96		Vcl_f1_n3	-4.10	-0.99
Vcl_cl2_n3	-5.07	-0.97		Intra_n3	-4.89	-0.95
Vx_cl2_n3	-7.64	-0.98		Vcl_cl2_c4	-5.93	-0.99

H_3N:ClF

SEG-1				SEG-2		
TERM	**REG**	**R**		**TERM**	**REG**	**R**
Intra_n3	7.15	0.96		Vx_cl2_n3	5.33	0.94
Vx_f1_cl2	4.43	0.96		Vcl_cl2_n3	4.47	0.99
Vcl_f1_n3	1.70	0.96		Vcl_n3_h6	1.96	0.97
Vcl_cl2_h4	1.37	0.97		Vcl_n3_h4	1.96	0.97
Vcl_cl2_h5	1.37	0.97		Vcl_n3_h5	1.96	0.97
Vcl_cl2_h6	1.37	0.97		Intra_f1	1.27	0.93
Vx_n3_h5	0.98	0.96		Vcl_f1_h6	0.87	0.98
Vx_n3_h6	0.98	0.96		Vcl_f1_h4	0.87	0.98
Vx_n3_h4	0.98	0.96		Vcl_f1_h5	0.87	0.98
Intra_h6	0.92	0.96		Vcl_f1_cl2	0.73	1.00
Intra_h5	0.92	0.96		Vc_cl2_n3	0.24	0.99
Intra_h4	0.92	0.96		Vx_f1_n3	0.23	0.93
Vcl_h5_h6	0.88	0.96		Vc_f1_cl2	0.19	0.92
Vcl_h4_h6	0.88	0.96		Vx_cl2_h5	0.06	0.93
Vcl_h4_h5	0.88	0.96		Vx_cl2_h4	0.06	0.93
Intra_cl2	0.39	0.99		Vx_cl2_h6	0.06	0.93
Vc_cl2_n3	0.07	0.95		Vc_cl2_h4	0.03	0.92
Vc_f1_n3	0.07	0.91		Vc_cl2_h5	0.03	0.92
Vx_h5_h6	0.03	0.95		Vc_cl2_h6	0.03	0.92
Vx_h4_h5	0.03	0.95		Vc_f1_h5	0.02	0.98
Vx_h4_h6	0.03	0.95		Vc_f1_h6	0.02	0.98
Vc_h5_h6	0.00	0.85		Vc_f1_h4	0.02	0.98
Vc_h4_h5	0.00	0.85		Vx_f1_h5	0.01	0.91

Vc_h4_h6	0.00	0.85		Vx_f1_h4	0.01	0.91
Vc_n3_h6	0.00	0.61		Vx_f1_h6	0.01	0.91
Vc_n3_h5	0.00	0.61		Vc_h5_h6	-0.01	-0.96
Vc_n3_h4	0.00	0.58		Vc_h4_h5	-0.01	-0.96
Vx_f1_h5	-0.01	-0.94		Vc_h4_h6	-0.01	-0.96
Vx_f1_h6	-0.01	-0.94		Vc_n3_h6	-0.02	-0.93
Vx_f1_h4	-0.01	-0.94		Vc_n3_h5	-0.02	-0.93
Vc_f1_h5	-0.01	-0.88		Vc_n3_h4	-0.02	-0.93
Vc_f1_h6	-0.01	-0.88		Vx_h5_h6	-0.03	-0.96
Vc_f1_h4	-0.01	-0.88		Vx_h4_h6	-0.03	-0.96
Vc_cl2_h5	-0.04	-0.94		Vx_h4_h5	-0.03	-0.96
Vc_cl2_h6	-0.04	-0.94		Vc_f1_n3	-0.07	-0.95
Vc_cl2_h4	-0.04	-0.94		Vcl_h4_h5	-0.64	-0.95
Vx_cl2_h6	-0.09	-0.96		Vcl_h5_h6	-0.64	-0.95
Vx_cl2_h4	-0.09	-0.96		Vcl_h4_h6	-0.64	-0.95
Vx_cl2_h5	-0.09	-0.96		Intra_h5	-0.64	-0.95
Vx_f1_n3	-0.23	-0.91		Intra_h4	-0.64	-0.95
Vc_f1_cl2	-0.33	-0.96		Intra_h6	-0.64	-0.95
Vcl_f1_cl2	-0.34	-0.95		Vx_n3_h5	-0.69	-0.95
Vcl_f1_h4	-0.97	-0.96		Vx_n3_h4	-0.69	-0.95
Vcl_f1_h6	-0.97	-0.96		Vx_n3_h6	-0.69	-0.95
Vcl_f1_h5	-0.97	-0.96		Vcl_cl2_h4	-1.28	-0.99
Intra_f1	-2.17	-0.96		Vcl_cl2_h6	-1.28	-0.99
Vcl_n3_h6	-2.23	-0.96		Vcl_cl2_h5	-1.28	-0.99
Vcl_n3_h5	-2.23	-0.96		Intra_cl2	-1.30	-1.00
Vcl_n3_h4	-2.23	-0.96		Vcl_f1_n3	-2.27	-0.99
Vcl_cl2_n3	-3.61	-0.97		Vx_f1_cl2	-2.49	-0.92
Vx_cl2_n3	-8.50	-0.97		Intra_n3	-4.41	-0.94

Figure S3. Relation between the total energy of H_3N:ClF (relative to the energy minimum, in Hartree), and the electrostatic (red) and exchange (blue) energy contributions (relative to the energy minimum, in Hartree) for the (top) **full** complex formation energy segment (SEG2) and the (bottom) **long-range-only** part of the complex formation segment.



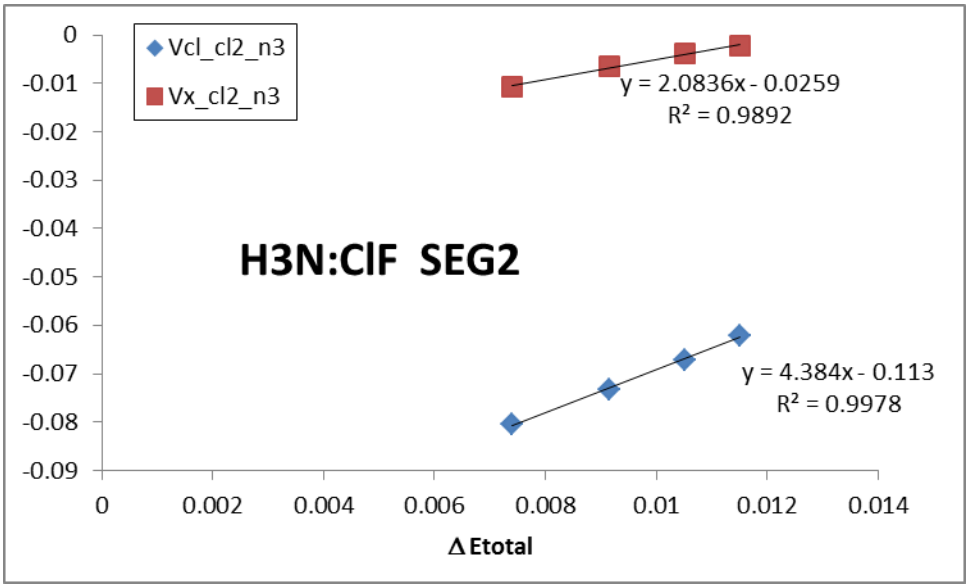
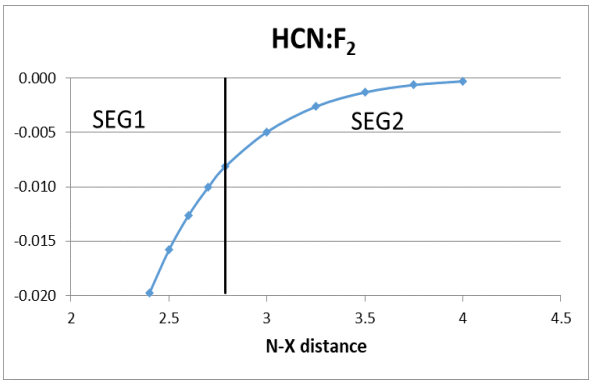
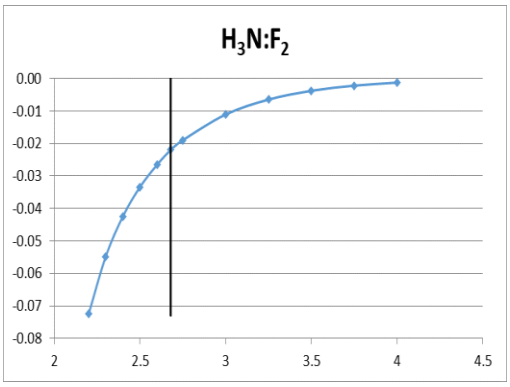
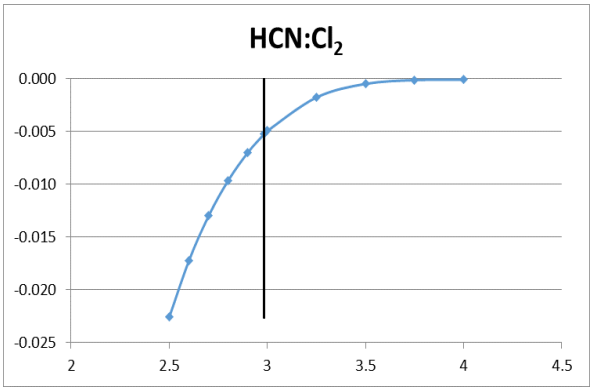
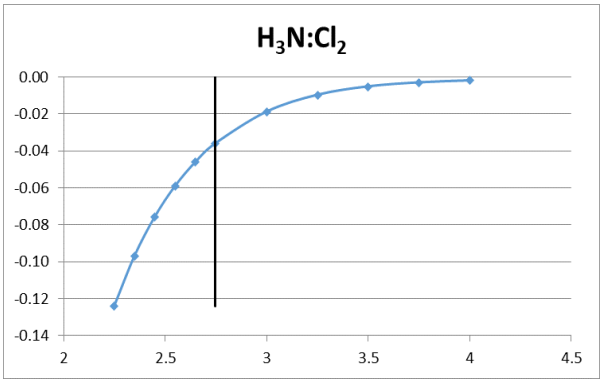
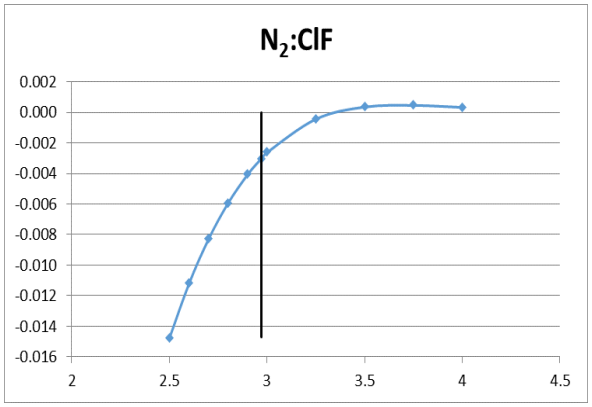
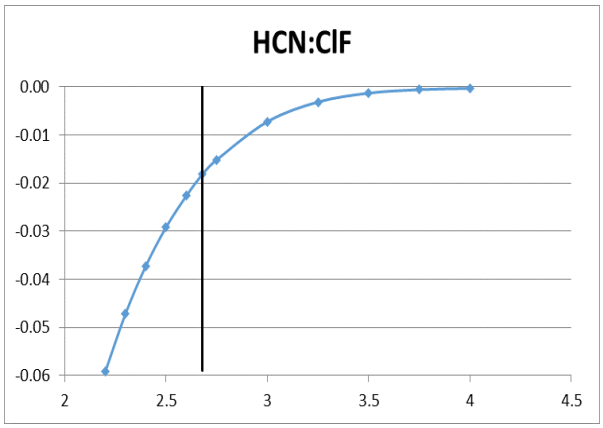
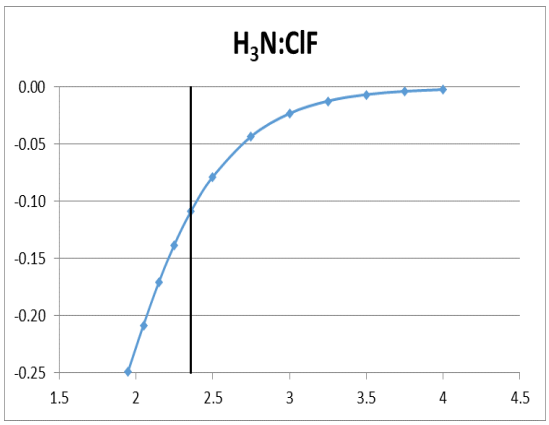



Figure S4. Charge transfer profiles for all 7 complexes. The overall net charge of the halogen molecule is plotted (in *e*) *versus* the N…X distance (in Å). The bold vertical line marks the equilibrium distance.