Supporting Information:

A simple model for halogen bond interaction energies

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1 Additional files

The supporting information for this paper also includes Cartesian coordinates of the geometries for all complexes calculated at the CCSD(T)-F12b/VTZ-(PP)-F12 level. These can be found in xyz_files.zip, and are labelled as donor-acceptor.xyz. In addition to this, all data including energies, separations, and SAPT energy decompositions can be found in CSV format in the datasets folder.

2 Model parameters

Table S1: Parameters for all molecules in the fitting and validation sets, as fitted to the Linear ($c + X_i + B_j$) and Pn (cX_iB_j/R_{ij}^n) models for $n = 0$ and 4, plus the second components additional to $P0$ for the fitting set. The parameters for the Linear model have units kcal mol^{-1}, while those for the Pn models are dimensionless.

	Model			
	Linear	$P0$ (1st comp.)	$P0$ (2nd comp.)	$P4$
c / kcal mol^{-1}	-10.638	59.0032	2.0114	3327.9474 Å^4
		Halogen bond donors (X_i)		
Br_2	6.902	0.2193	0.0008	0.2461
I_2	6.633	0.2298	0.1685	0.3254
BrI	4.854	0.3075	0.1092	0.3682
ClBr	5.749	0.2699	-0.0181	0.2707
ClI	3.630	0.3601	0.1637	0.3974
HBr	10.116	0.0767	0.3269	0.1709
HI	9.251	0.1132	0.4858	0.2560
FCl	4.822	0.3148	-0.5345	0.2215
FBr	1.199	0.4688	-0.4426	0.3306
FI	1.129	0.5143	0.3288	0.4600
F_2	—	0.0654	—	0.0621
Cl_2	—	0.1560	—	0.1845
CF_3Cl	—	0.1145	—	0.1651
CF_3Br	—	0.1607	—	0.2336
CF_3I	—	0.2132	—	0.3343
		Lewis bases (B_j)		
H_2O	0.060	-0.3062	-0.4056	-0.2947
CH_2O	-0.435	-0.3323	-0.5090	-0.3056
HCN	0.338	-0.2942	-0.4518	-0.3050
CH_2S	-0.298	-0.4948	0.5020	-0.5623
H_3N	-3.028	-0.6034	0.3373	-0.4416
H_2S	-4.871	-0.3169	-0.0810	-0.4643
CH_3OH	—	-0.4110	—	-0.3749
C_2H_4	—	-0.2991	—	-0.4215
PH_3	—	-0.4340	—	-0.5713
Oxirane	—	-0.4500	—	-0.3883
Thiirane	—	-0.6169	—	-0.7500

3 Benchmark data

Table S2: Benchmark interaction energies and intermolecular separations for all complexes in the fitting set, calculated at the CCSD(T)-F12b level, using VnZ-(PP)-F12 basis sets with n =T, Q, then extrapolated to the complete basis set (CBS) limit.

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
Br_2	H_2O	-3.8419	-3.9210	-3.9921	2.7918
Br_2	CH_2O	-4.2728	-4.3744	-4.4417	2.7498
Br_2	HCN	-3.5401	-3.6164	-3.6564	2.8888
Br_2	CH_2S	-6.1036	-6.3054	-6.4191	2.9106
Br_2	H_3N	-7.5249	-7.7032	-7.8103	2.5978
Br_2	H_2S	-3.8056	-3.9349	-4.0340	3.1139
BrI	H_2O	-5.4232	-5.5715	-5.6662	2.8270
BrI	CH_2O	-5.8785	-6.0623	-6.1818	2.7870
BrI	HCN	-5.1428	-5.2901	-5.3502	2.9059
BrI	CH_2S	-8.2224	-8.5285	-8.7127	2.9786
BrI	H_3N	-10.6429	-10.9145	-11.0522	2.6468
BrI	H_2S	-5.2709	-5.4977	-5.6757	3.1616
ClBr	H_2O	-4.6916	-4.7942	-4.8878	2.7210
ClBr	CH_2O	-5.1168	-5.2433	-5.3495	2.6806
ClBr	HCN	-4.3855	-4.4841	-4.5602	2.8043
ClBr	CH_2S	-7.3457	-7.5954	-7.7604	2.8393
ClBr	H_3N	-9.8411	-9.5377	-9.7964	2.5147
ClBr	H_2S	-4.6112	-4.7727	-4.9153	3.0396
ClI	H_2O	-6.3655	-6.5372	-6.6436	2.7691
ClI	CH_2O	-6.8421	-7.0511	-7.1863	2.7284

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
ClI	HCN	-6.1381	-6.3114	-6.4094	2.8244
ClI	CH_2S	-9.5909	-9.9361	-10.1441	2.9202
ClI	H_3N	-12.1499	-12.7710	-12.9422	2.5984
ClI	H_2S	-6.2173	-6.4724	-6.6566	3.1017
FBr	H_2O	-7.7928	-7.9483	-8.0540	2.5098
FBr	CH_2O	-8.3791	-8.5617	-8.6728	2.4727
FBr	HCN	-7.5666	-7.7198	-7.7957	2.5351
FBr	CH_2S	-13.7768	-14.1416	-14.3436	2.5672
FBr	H_3N	-16.2278	-16.5119	-16.6741	2.3288
FBr	H_2S	-8.6066	-8.8705	-9.0320	2.7558
FCl	H_2O	-5.1525	-5.2673	-5.3642	2.5436
FCl	CH_2O	-5.6393	-5.7812	-5.8504	2.5009
FCl	HCN	-4.6893	-4.7895	-4.8186	2.6361
FCl	CH_2S	-9.2779	-9.6040	-9.7814	2.5432
FCl	H_3N	-11.2460	-11.5080	-11.6510	2.2979
FCl	H_2S	-5.0616	-5.2499	-5.3684	2.8153
FI	H_2O	-9.1483	-9.3364	-9.4488	2.6238
FI	CH_2O	-9.7722	-9.9998	-10.1249	2.5856
FI	HCN	-9.2663	-9.4621	-9.5521	2.6203
FI	CH_2S	-14.1216	-14.4855	-14.7128	2.7601
FI	H_3N	-17.5111	-17.7972	-17.9678	2.4910
FI	H_2S	-9.4824	-9.7728	-9.9585	2.9236
HBr	H_2O	-1.6186	-1.6472	-1.6863	3.1170
HBr	CH_2O	-2.0259	-2.0761	-2.1098	3.1073

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
HBr	HCN	-1.3849	-1.4160	-1.4358	3.2459
HBr	CH_2S	-2.0516	-2.1235	-2.1869	3.5617
HBr	H_3N	-2.1777	-2.2158	-2.2630	3.1711
HBr	H_2S	-1.2610	-1.3118	-1.3850	3.6497
HI	H_2O	-2.4349	-2.4892	-2.5437	3.1716
HI	CH_2O	-2.7394	-2.8288	-2.9012	3.1550
HI	HCN	-2.1656	-2.2217	-2.2469	3.3079
HI	CH_2S	-2.7576	-2.8800	-2.9785	3.5957
HI	H_3N	-3.4603	-3.5322	-3.5956	3.1870
HI	H_2S	-1.8085	-1.8954	-1.9960	3.7103
I_2	H_2O	-4.1494	-4.2639	-4.3428	2.9328
I_2	CH_2O	-4.5490	-4.6960	-4.7586	2.9026
I_2	HCN	-3.8630	-3.9756	-4.0238	3.0358
I_2	CH_2S	-6.0726	-6.3194	-6.4631	3.1096
I_2	H_3N	-7.8713	-8.0852	-8.1777	2.7577
I_2	H_2S	-3.8799	-4.0572	-4.2030	3.3021

Table S3: Benchmark interaction energies and intermolecular separations for all complexes in the validation set, calculated at the CCSD(T)-F12b level, using VnZ-(PP)-F12 basis sets with n =T, Q, then extrapolated to the complete basis set (CBS) limit.

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
Br_2	CH_3OH	-5.0287	-5.1541	-5.2323	2.6899
Br_2	C_2H_4	-3.7104	-3.8254	-3.9146	2.9910
Br_2	Oxirane	-5.6765	-5.8206	-5.8875	2.6500
Br_2	Thiirane	-8.2632	-8.5190	-8.6439	2.8300
Br_2	PH_3	-4.6340	-4.8342	-4.9656	2.9931
BrI	CH_3OH	-7.1368	-7.3433	-7.4563	2.7176
BrI	C_2H_4	-5.1315	-5.3210	-5.4264	3.0297
BrI	Oxirane	-7.8167	-8.0455	-8.1642	2.6800
BrI	Thiirane	-10.6422	-10.9888	-11.1907	2.9200
BrI	PH_3	-7.3208	-7.6582	-7.8735	2.9785
CF_3Br	H_2O	-2.9002	-2.9924	-3.0885	2.9805
CF_3Br	CH_2O	-3.0021	-3.1036	-3.1522	2.9529
CF_3Br	HCN	-2.7189	-2.8343	-2.9039	3.0909
CF_3Br	CH_2S	-2.8829	-2.9214	-2.9566	3.3642
CF_3Br	H_3N	-4.1070	-4.2079	-4.2452	2.9761
CF_3Br	H_2S	-2.0900	-2.1329	-2.1385	3.4972
CF_3Cl	H_2O	-2.0648	-2.1000	-2.1304	2.9740
CF_3Cl	CH_2O	-2.1391	-2.1968	-2.2315	2.9761
CF_3Cl	HCN	-1.9093	-1.9962	-1.9845	3.1199
CF_3Cl	CH_2S	-1.9582	-1.9971	-1.9935	3.4216
CF_3Cl	H_3N	-2.6339	-2.7442	-2.7958	3.0638
CF_3Cl	H_2S	-1.3055	-1.3335	-1.3303	3.5215

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
CF_3I	H_2O	-3.8391	-3.9324	-4.0488	3.0373
CF_3I	CH_2O	-3.9364	-4.0559	-4.1539	3.0070
CF_3I	HCN	-3.6191	-3.6620	-3.7221	3.1466
CF_3I	CH_2S	-3.9782	-4.0395	-4.1556	3.3727
CF_3I	H_3N	-5.9030	-6.0767	-6.0802	2.9755
CF_3I	H_2S	-2.8629	-2.9587	-3.0251	3.5357
Cl_2	H_2O	-2.7537	-2.8180	-2.8901	2.8129
Cl_2	CH_2O	-3.1310	-3.2206	-3.3098	2.7639
Cl_2	HCN	-2.5028	-2.5669	-2.6117	2.9220
Cl_2	CH_2S	-3.7399	-3.8878	-4.0147	3.0271
Cl_2	H_3N	-4.7486	-4.8782	-4.9920	2.6798
Cl_2	H_2S	-2.3817	-2.4815	-2.5937	3.2143
ClBr	CH_3OH	-6.0779	-6.2318	-6.3677	2.6213
ClBr	C_2H_4	-4.4620	-4.6038	-4.7632	2.9072
ClBr	Oxirane	-6.7351	-6.9074	-7.0029	2.5800
ClBr	Thiirane	-9.8033	-10.1132	-10.2986	2.7600
ClBr	PH_3	-6.2842	-6.5689	-6.7874	2.8564
ClI	CH_3OH	-8.2494	-8.4824	-8.6225	2.6660
ClI	C_2H_4	-6.0967	-6.3150	-6.4556	2.9524
ClI	Oxirane	-8.9928	-9.2495	-9.3813	2.6300
ClI	Thiirane	-12.1645	-12.5513	-12.7742	2.8700
ClI	PH_3	-9.3373	-9.7514	-10.0326	2.8795
F_2	H_2O	-1.1819	-1.2099	-1.1811	2.6797
F_2	CH_2O	-1.3849	-1.4208	-1.3936	2.6374

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
F_2	HCN	-1.0667	-1.0980	-1.0443	2.7864
F_2	CH_2S	-1.4760	-1.5378	-1.3273	2.9570
F_2	H_3N	-1.7479	-1.8047	-1.8122	2.6465
F_2	H_2S	-0.9219	-0.9681	-0.9196	3.1155
FBr	CH_3OH	-10.1710	-10.3846	-10.4893	2.4124
FBr	C_2H_4	-8.5519	-8.7757	-8.9776	2.5800
FBr	Oxirane	-10.8586	-11.0873	-11.2010	2.3900
FBr	Thiirane	-16.5434	-16.9315	-17.1503	2.5600
FBr	PH_3	-17.7896	-18.3404	-18.6330	2.4275
FCl	CH_3OH	-6.7744	-6.9431	-7.0366	2.4309
FCl	C_2H_4	-4.7305	-4.8832	-4.9648	2.7090
FCl	Oxirane	-7.5136	-7.7026	-7.7848	2.3900
FCl	Thiirane	-12.5737	-12.9532	-13.1533	2.4800
FCl	PH_3	-19.4629	-20.1680	-20.5098	2.1836
FI	CH_3OH	-11.6800	-11.9266	-12.0636	2.5342
FI	C_2H_4	-9.8331	-10.0767	-10.2350	2.7230
FI	Oxirane	-12.4674	-12.6461	-12.7146	2.5100
FI	Thiirane	-16.6852	-17.0694	-17.3095	2.7600
FI	PH_3	-15.7366	-16.2000	-16.4779	2.6932
HBr	CH_3OH	-2.1593	-2.2142	-2.2589	3.0800
HBr	C_2H_4	-1.3662	-1.4131	-1.4593	3.4907
HBr	Oxirane	-2.6990	-2.7682	-2.7953	3.0500
HBr	Thiirane	-2.7476	-2.8322	-2.8858	3.5100
HBr	PH_3	-1.1722	-1.2197	-1.2824	3.7351

		Interaction energy (kcal/mol)			
Donor	Acceptor	TZ	QZ	CBS	R (Å)
HI	CH_3OH	-3.0784	-3.1681	-3.2477	3.1139
HI	C_2H_4	-0.8654	-1.9653	-2.0276	3.5646
HI	Oxirane	-3.6338	-3.7440	-3.7930	3.0900
HI	Thiirane	-3.6600	-3.8012	-3.8874	3.5400
HI	PH_3	-1.7449	-1.8277	-1.9236	3.7794
I_2	CH_3OH	-5.4471	-5.6118	-5.6749	2.8300
I_2	C_2H_4	-3.7945	-3.9458	-4.0294	3.1767
I_2	Oxirane	-6.1282	-6.3174	-6.4275	2.7900
I_2	Thiirane	-8.1057	-8.3927	-8.5773	3.0300
I_2	PH_3	-4.6140	-4.8402	-5.0019	3.2075

4 DFT results for all systems

Table S4: Interaction energies and intermolecular separations for all complexes in the fitting and validation sets, calculated using the M06-2X and ωB97xD density functionals with the aVTZ(-PP) basis set. The CCSD(T)-F12b/CBS benchmarks are shown for comparison.

		Interaction energy (kcal/mol)			R (Å)		
Donor	Acceptor	CBS	M06-2X	ωB97xD	CBS	M06-2X	ωB97xD
Br_2	H_2O	-3.9921	-4.2000	-3.7100	2.7918	2.7805	2.7901
Br_2	CH_2O	-4.4417	-4.4500	-3.7300	2.7498	2.7530	2.7735
Br_2	HCN	-3.6564	-3.4300	-3.0200	2.8888	2.8729	2.8976
Br_2	CH_2S	-6.4191	-6.5800	-5.6100	2.9106	2.9178	2.9789
Br_2	H_3N	-7.8103	-7.6700	-7.8400	2.5978	2.6329	2.6378
Br_2	H_2S	-4.0340	-4.2800	-3.6400	3.1139	3.1316	3.1568
Br_2	CH_3OH	-5.2323	-5.1300	-4.6600	2.6899	2.7205	2.7233
Br_2	C_2H_4	-3.9146	-4.3000	-3.6300	2.9910	2.9959	3.0504
Br_2	Oxirane	-5.8875	-5.4200	-4.7800	2.6500	2.7040	2.7077
Br_2	Thiirane	-8.6439	-8.4600	-7.1800	2.8300	2.8381	2.9241
Br_2	PH_3	-4.9656	-5.3100	-4.5300	2.9931	2.9420	3.0312
BrI	H_2O	-5.6662	-6.2300	-5.5900	2.8270	2.8218	2.8366
BrI	CH_2O	-6.1818	-6.3600	-5.5900	2.7870	2.8002	2.8169
BrI	HCN	-5.3502	-5.4200	-4.9500	2.9059	2.9074	2.9019
BrI	CH_2S	-8.7127	-8.6200	-7.8600	2.9786	2.9778	3.0380
BrI	H_3N	-11.0522	-11.0400	-11.0700	2.6468	2.6644	2.6953
BrI	H_2S	-5.6757	-5.7700	-5.2600	3.1616	3.2015	3.2249
BrI	CH_3OH	-7.4563	-7.4800	-6.9100	2.7176	2.7446	2.7622
BrI	C_2H_4	-5.4264	-5.8300	-5.2600	3.0297	3.0698	3.1134
BrI	Oxirane	-8.1642	-7.6800	-7.0300	2.6800	2.7317	2.7476

		Interaction energy (kcal/mol)			R (Å)		
Donor	Acceptor	CBS	M06-2X	ωB97xD	CBS	M06-2X	ωB97xD
BrI	Thiirane	-11.1907	-10.6800	-9.7200	2.9200	2.9356	3.0100
BrI	PH_3	-7.8735	-8.0800	-7.2000	2.9785	2.9377	3.0494
CF_3Br	H_2O	-3.0885	-2.9900	-2.4000	2.9805	2.9167	3.0023
CF_3Br	CH_2O	-3.1522	-3.0700	-2.3600	2.9529	2.9224	3.0086
CF_3Br	HCN	-2.9039	-2.4700	-2.1000	3.0909	3.0545	3.1542
CF_3Br	CH_2S	-2.9566	-3.0700	-2.4600	3.3642	3.3500	3.4420
CF_3Br	H_3N	-4.2452	-4.1600	-3.9700	2.9761	2.9626	2.9862
CF_3Br	H_2S	-2.1385	-2.0900	-1.7600	3.4972	3.4370	3.5675
CF_3Cl	H_2O	-2.1304	-1.9100	-1.2900	2.9740	2.9336	3.1213
CF_3Cl	CH_2O	-2.2315	-2.0700	-1.3500	2.9761	2.9184	3.1270
CF_3Cl	HCN	-1.9845	-1.5400	-1.1600	3.1199	3.1269	3.1199
CF_3Cl	CH_2S	-1.9935	-1.9700	-1.3900	3.4216	3.3851	3.5588
CF_3Cl	H_3N	-2.7958	-2.5100	-1.8800	3.0638	3.0491	3.0799
CF_3Cl	H_2S	-1.3303	-1.1600	-0.8700	3.5215	3.4760	3.7571
CF_3I	H_2O	-4.0488	-4.2200	-3.6000	3.0373	2.9707	3.0462
CF_3I	CH_2O	-4.1539	-4.2300	-3.5100	3.0070	2.9727	3.0480
CF_3I	HCN	-3.7221	-3.5400	-3.1800	3.1466	3.1103	3.1919
CF_3I	CH_2S	-4.1556	-4.2900	-3.7700	3.3727	3.4175	3.4682
CF_3I	H_3N	-6.0802	-6.0900	-6.0300	2.9755	2.9781	3.0099
CF_3I	H_2S	-3.0251	-2.8100	-2.6700	3.5357	3.5224	3.5549
Cl_2	H_2O	-2.8901	-3.0000	-2.3800	2.8129	2.7676	2.7947
Cl_2	CH_2O	-3.3098	-3.2800	-2.4400	2.7639	2.7480	2.7717
Cl_2	HCN	-2.6117	-2.3300	-1.8300	2.9220	2.8633	2.9327
Cl_2	CH_2S	-4.0147	-4.3100	-3.5200	3.0271	3.0268	3.0051

		Interaction energy (kcal/mol)			R (Å)		
Donor	Acceptor	CBS	M06-2X	ωB97xD	CBS	M06-2X	ωB97xD
Cl_2	H_3N	-4.9920	-5.1000	-5.0900	2.6798	2.6926	2.6558
Cl_2	H_2S	-2.5937	-2.8400	-2.1500	3.2143	3.1358	3.1871
ClBr	H_2O	-4.8878	-5.1800	-4.8100	2.7210	2.7197	2.7092
ClBr	CH_2O	-5.3495	-5.3800	-4.8200	2.6806	2.6973	2.6800
ClBr	HCN	-4.5602	-4.4100	-4.1000	2.8043	2.8018	2.7995
ClBr	CH_2S	-7.7604	-8.0800	-7.4200	2.8393	2.8165	2.8632
ClBr	H_3N	-9.7964	-9.6100	-10.2300	2.5147	2.5416	2.5332
ClBr	H_2S	-4.9153	-5.1500	-4.7700	3.0396	3.0670	3.0381
ClBr	CH_3OH	-6.3677	-6.2600	-5.9500	2.6213	2.6516	2.6312
ClBr	C_2H_4	-4.7632	-5.1500	-4.6300	2.9072	2.9389	2.9508
ClBr	Oxirane	-7.0029	-6.4800	-6.0500	2.5800	2.6317	2.6216
ClBr	Thiirane	-10.2986	-10.1800	-9.2800	2.7600	2.7620	2.8173
ClBr	PH_3	-6.7874	-8.3300	-6.9700	2.8564	2.7056	2.8327
ClI	H_2O	-6.6436	-7.3500	-6.7500	2.7691	2.7653	2.7711
ClI	CH_2O	-7.1863	-7.4600	-6.7800	2.7284	2.7429	2.7430
ClI	HCN	-6.4094	-6.5700	-6.1800	2.8244	2.8366	2.8244
ClI	CH_2S	-10.1441	-10.1600	-9.6600	2.9202	2.9130	2.9593
ClI	H_3N	-12.9422	-13.0100	-13.3000	2.5984	2.6076	2.6272
ClI	H_2S	-6.6566	-6.7700	-6.5100	3.1017	3.1446	3.1142
ClI	CH_3OH	-8.6225	-8.7600	-8.2900	2.6660	2.6900	2.6948
ClI	C_2H_4	-6.4556	-6.8400	-6.4000	2.9524	3.0116	3.0287
ClI	Oxirane	-9.3813	-8.9300	-8.3800	2.6300	2.6815	2.6847
ClI	Thiirane	-12.7742	-12.2800	-11.6400	2.8700	2.8853	2.9360
ClI	PH_3	-10.0326	-10.1800	-9.7600	2.8795	2.8555	2.9071

		Interaction energy (kcal/mol)			R (Å)		
Donor	Acceptor	CBS	M06-2X	ωB97xD	CBS	M06-2X	ωB97xD
F_2	H_2O	-1.1811	-0.9100	-0.5300	2.6797	2.7640	2.9669
F_2	CH_2O	-1.3936	-1.1800	-0.5900	2.6374	2.6896	2.9039
F_2	HCN	-1.0443	-0.6800	-0.4500	2.7864	2.8142	3.2600
F_2	CH_2S	-1.3273	-1.7200	-1.1600	2.9570	2.8565	2.8556
F_2	H_3N	-1.8122	-1.5400	-1.3900	2.6465	2.5976	2.5858
F_2	H_2S	-0.9196	-0.9200	-0.4400	3.1155	3.0288	3.4271
FBr	H_2O	-8.0540	-8.6600	-8.1900	2.5098	2.5262	2.5055
FBr	CH_2O	-8.6728	-9.0100	-8.4600	2.4727	2.4896	2.4560
FBr	HCN	-7.7957	-7.9200	-7.6000	2.5351	2.5657	2.5216
FBr	CH_2S	-14.3436	-14.9500	-14.3400	2.5672	2.5567	2.5763
FBr	H_3N	-16.6741	-17.0400	-17.1900	2.3288	2.3210	2.3510
FBr	H_2S	-9.0320	-9.3500	-9.0000	2.7558	2.7542	2.7806
FBr	CH_3OH	-10.4893	-10.4500	-10.1000	2.4124	2.4550	2.4254
FBr	C_2H_4	-8.9776	-9.2000	-8.8400	2.5800	2.6370	2.6435
FBr	Oxirane	-11.2010	-10.5800	-10.1500	2.3900	2.4395	2.4150
FBr	Thiirane	-17.1503	-16.9600	-16.2400	2.5600	2.5723	2.5934
FBr	PH_3	-18.6330	-18.4800	-18.0400	2.4275	2.4578	2.4615
FCl	H_2O	-5.3642	-5.7300	-5.1400	2.5436	2.5486	2.5295
FCl	CH_2O	-5.8504	-6.0600	-5.3300	2.5009	2.5095	2.4808
FCl	HCN	-4.8186	-4.8500	-4.1900	2.6361	2.6382	2.6114
FCl	CH_2S	-9.7814	-9.5300	-9.9300	2.5432	2.5829	2.5635
FCl	H_3N	-11.6510	-11.2800	-12.1600	2.2979	2.3276	2.3175
FCl	H_2S	-5.3684	-5.6100	-5.4000	2.8153	2.8998	2.8280
FCl	CH_3OH	-7.0366	-7.0000	-6.4800	2.4309	2.4760	2.4473

		Interaction energy (kcal/mol)			R (Å)		
Donor	Acceptor	CBS	M06-2X	ωB97xD	CBS	M06-2X	ωB97xD
FCl	C_2H_4	-4.9648	-5.4900	-4.9200	2.7090	2.7716	2.7314
FCl	Oxirane	-7.7848	-7.2500	-6.6300	2.3900	2.4637	2.4254
FCl	Thiirane	-13.1533	-11.9700	-12.1600	2.4800	2.5462	2.5370
FCl	PH_3	-20.5098	-12.5900	-15.3900	2.1836	2.4017	2.3239
FI	H_2O	-9.4488	-10.6100	-9.6300	2.6238	2.6296	2.6323
FI	CH_2O	-10.1249	-10.8400	-9.8200	2.5856	2.5881	2.5935
FI	HCN	-9.5521	-10.1300	-9.4900	2.6203	2.6421	2.6135
FI	CH_2S	-14.7128	-14.8300	-14.4900	2.7601	2.7534	2.7764
FI	H_3N	-17.9678	-18.5000	-18.3100	2.4910	2.4970	2.5157
FI	H_2S	-9.9585	-10.2400	-9.8600	2.9236	2.9413	2.9587
FI	CH_3OH	-12.0636	-12.5900	-11.6600	2.5342	2.5545	2.5678
FI	C_2H_4	-10.2350	-10.7600	-10.0700	2.7230	2.7539	2.7845
FI	Oxirane	-12.7146	-12.6300	-11.7300	2.5100	2.5392	2.5599
FI	Thiirane	-17.3095	-16.9900	-16.3700	2.7600	2.7675	2.7964
FI	PH_3	-16.4779	-16.7100	-16.3600	2.6932	2.6910	2.7069
HBr	H_2O	-1.6863	-1.6400	-1.3500	3.1170	3.0990	3.1837
HBr	CH_2O	-2.1098	-2.1100	-1.5000	3.1073	3.0373	3.2076
HBr	HCN	-1.4358	-1.1200	-0.9500	3.2459	3.2292	3.3407
HBr	CH_2S	-2.1869	-2.1500	-1.6500	3.5617	3.4726	3.6390
HBr	H_3N	-2.2630	-2.2100	-2.1400	3.1711	3.1390	3.1610
HBr	H_2S	-1.3850	-1.2900	-1.0600	3.6497	3.5685	3.7291
HBr	CH_3OH	-2.2589	-2.2100	-1.7800	3.0800	3.0420	3.1518
HBr	C_2H_4	-1.4593	-1.3900	-1.3100	3.4907	3.3660	3.5608
HBr	Oxirane	-2.7953	-2.7900	-2.0700	3.0500	2.9803	3.1519

		Interaction energy (kcal/mol)			R (Å)		
Donor	Acceptor	CBS	M06-2X	ωB97xD	CBS	M06-2X	ωB97xD
HBr	Thiirane	-2.8858	-3.0000	-2.2900	3.5100	3.4367	3.5847
HBr	PH_3	-1.2824	-1.0400	-0.9700	3.7351	3.6220	3.8136
HI	H_2O	-2.5437	-2.6000	-2.3300	3.1716	3.1078	3.2275
HI	CH_2O	-2.9012	-2.9200	-2.3900	3.1550	3.1085	3.2429
HI	HCN	-2.2469	-2.0100	-1.9000	3.3079	3.2749	3.3323
HI	CH_2S	-2.9785	-2.9900	-2.5700	3.5957	3.5526	3.6615
HI	H_3N	-3.5956	-3.5600	-3.7200	3.1870	3.1914	3.2087
HI	H_2S	-1.9960	-1.9200	-1.8100	3.7103	3.6288	3.7578
HI	CH_3OH	-3.2477	-3.2500	-2.9200	3.1139	3.0720	3.1494
HI	C_2H_4	-2.0276	-2.0900	-2.1100	3.5646	3.4740	3.6015
HI	Oxirane	-3.7930	-3.7200	-3.1900	3.0900	3.0375	3.1435
HI	Thiirane	-3.8874	-3.9600	-3.4400	3.5400	3.5377	3.6203
HI	PH_3	-1.9236	-1.7200	-1.7600	3.7794	3.6918	3.8325
I_2	H_2O	-4.3428	-4.7700	-4.2200	2.9328	2.9053	2.9364
I_2	CH_2O	-4.7586	-4.9200	-4.2100	2.9026	2.8896	2.9288
I_2	HCN	-4.0238	-3.9600	-3.5900	3.0358	2.9992	3.0453
I_2	CH_2S	-6.4631	-6.3800	-5.6800	3.1096	3.1377	3.1994
I_2	H_3N	-8.1777	-8.2200	-8.3300	2.7577	2.7830	2.7978
I_2	H_2S	-4.2030	-4.3300	-3.8900	3.3021	3.3225	3.3671
I_2	CH_3OH	-5.6749	-5.7700	-5.2900	2.8300	2.8396	2.8578
I_2	C_2H_4	-4.0294	-4.4000	-3.9500	3.1767	3.1732	3.2721
I_2	Oxirane	-6.4275	-6.0400	-5.4600	2.7900	2.8337	2.8503
I_2	Thiirane	-8.5773	-8.1000	-7.3200	3.0300	3.0676	3.1151
I_2	PH_3	-5.0019	-4.9300	-4.5800	3.2075	3.2227	3.2690

Table S5: Interaction energies and intermolecular separations for all complexes involving the set of larger molecules, calculated using M06-2X/aVTZ-(PP). The larger molecules comprise the donors C_6F_5X, where X is Cl, Br, or I, and the acceptors glycine (Gly), valine (Val), leucine (Leu), and sulphoximine (Sulphox). Also given for the purposes of parametrisation (see the Jupyter notebook) are their interactions with the molecules from the fitting set, calculated at the same level of theory.

Donor	Acceptor	E (kcal/mol)	R (Å)
Br_2	Gly	-5.1300	2.7520
Br_2	Val	-5.8100	2.7510
Br_2	Leu	-6.4300	2.7570
Br_2	Sulphox	-6.3600	2.7740
BrI	Gly	-7.4900	2.7780
BrI	Val	-8.3400	2.7760
BrI	Leu	-8.8200	2.7740
C_6F_5Br	H_2O	-3.0000	2.9030
C_6F_5Br	CH_2O	-3.2300	2.9190
C_6F_5Br	HCN	-2.4500	3.0400
C_6F_5Br	CH_2S	-3.2900	3.3590
C_6F_5Br	H_3N	-4.1500	2.9520
C_6F_5Br	H_2S	-0.9700	3.4960
C_6F_5Br	Gly	-3.6600	2.8920
C_6F_5Br	Val	-4.6100	2.9010
C_6F_5Br	Leu	-4.9700	2.9280
C_6F_5Br	Sulphox	-4.0500	2.9980
C_6F_5Cl	H_2O	-1.7200	2.9360
C_6F_5Cl	CH_2O	-2.2200	3.0470
C_6F_5Cl	HCN	-1.3400	3.1440
C_6F_5Cl	CH_2S	-2.2800	3.4020

Donor	Acceptor	E (kcal/mol)	R (Å)
C_6F_5Cl	H_3N	-2.2500	3.0540
C_6F_5Cl	H_2S	-0.5100	3.5150
C_6F_5Cl	Gly	-2.4900	2.9240
C_6F_5Cl	Val	-3.7500	3.1420
C_6F_5Cl	Leu	-5.1200	3.1580
C_6F_5Cl	Sulphox	-3.3200	3.3180
C_6F_5I	H_2O	-4.3600	2.9530
C_6F_5I	CH_2O	-4.4200	2.9540
C_6F_5I	HCN	-3.6600	3.0780
C_6F_5I	CH_2S	-4.4700	3.4000
C_6F_5I	H_3N	-6.2800	2.9640
C_6F_5I	H_2S	-1.4400	3.5610
C_6F_5I	Gly	-5.1800	2.9440
C_6F_5I	Val	-6.2200	2.9530
C_6F_5I	Leu	-6.4500	2.9590
C_6F_5I	Sulphox	-5.9600	2.9890
ClBr	Gly	-6.3900	2.6680
ClBr	Val	-7.1000	2.6860
ClBr	Leu	-7.6500	2.6700
ClBr	Sulphox	-7.6600	2.6750
ClI	Gly	-8.9400	2.7060
ClI	Val	-9.7800	2.7180
ClI	Leu	-10.2800	2.6970
ClI	Sulphox	-10.7800	2.6690
FBr	Gly	-10.0800	2.4990

Donor	Acceptor	E (kcal/mol)	R (Å)
FBr	Val	-10.8800	2.4960
FBr	Leu	-11.3100	2.4860
FBr	Sulphox	-14.2900	2.3650
FCl	Gly	-6.9300	2.5290
FCl	Val	-7.6900	2.5300
FCl	Leu	-8.0900	2.5220
FCl	Sulphox	-9.6500	2.4380
FI	Gly	-12.4000	2.5880
FI	Val	-13.3000	2.5800
FI	Leu	-13.8200	2.5710
FI	Sulphox	-16.2700	2.5120
HBr	Gly	-2.2800	3.0380
HBr	Val	-3.0100	3.1080
HBr	Leu	-3.1700	3.0460
HBr	Sulphox	-3.1500	3.2210
HI	Gly	-3.3200	3.1020
HI	Val	-4.1800	3.0960
HI	Leu	-3.2500	3.0860
HI	Sulphox	-3.9900	3.2720
I_2	Gly	-5.8000	2.8720
I_2	Val	-6.6700	2.8830
I_2	Leu	-7.0800	2.8640
I_2	Sulphox	-6.8700	2.8960

5 Additional figures

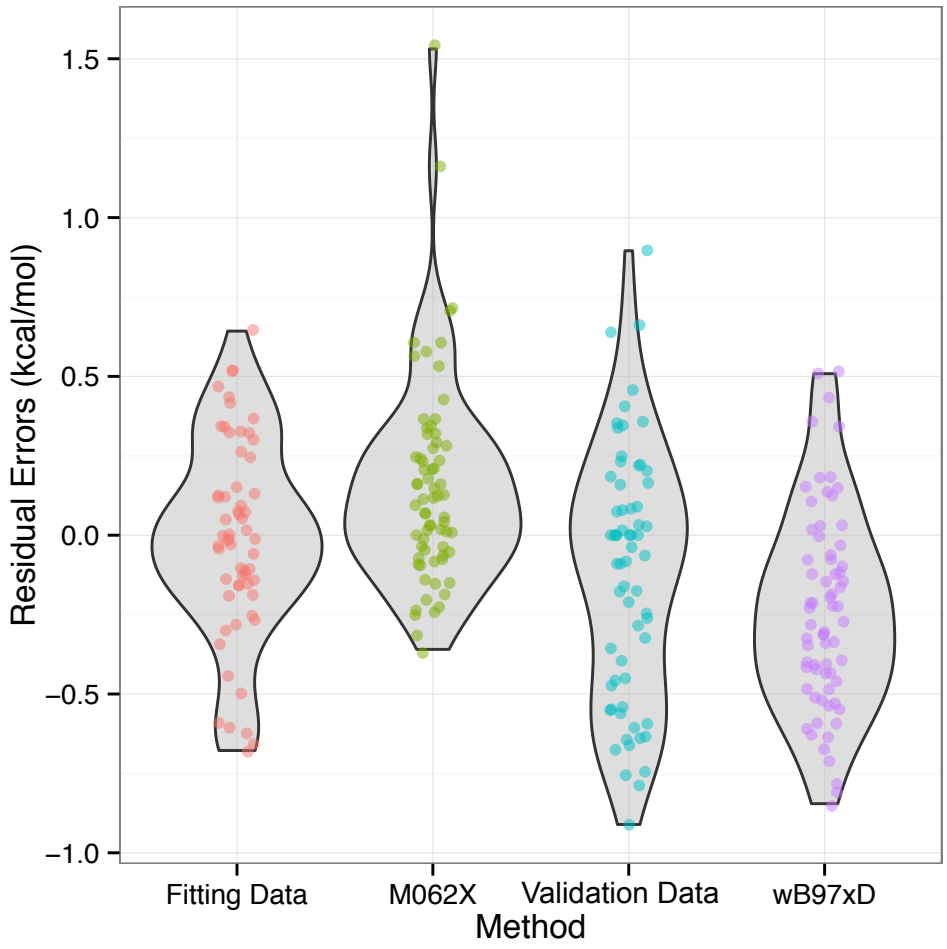

Figure S1: Violin plots of the error distributions of the $P0$ model, M06-2X/aVTZ, and ωB97xD/aVTZ, compared to CCSD(T)-F12b/CBS results. The model is split into data from the fitting and validation sets. The shape of the violin shows where the density of errors is concentrated, such that an ideal distribution would be a very short, wide density centred on the origin.

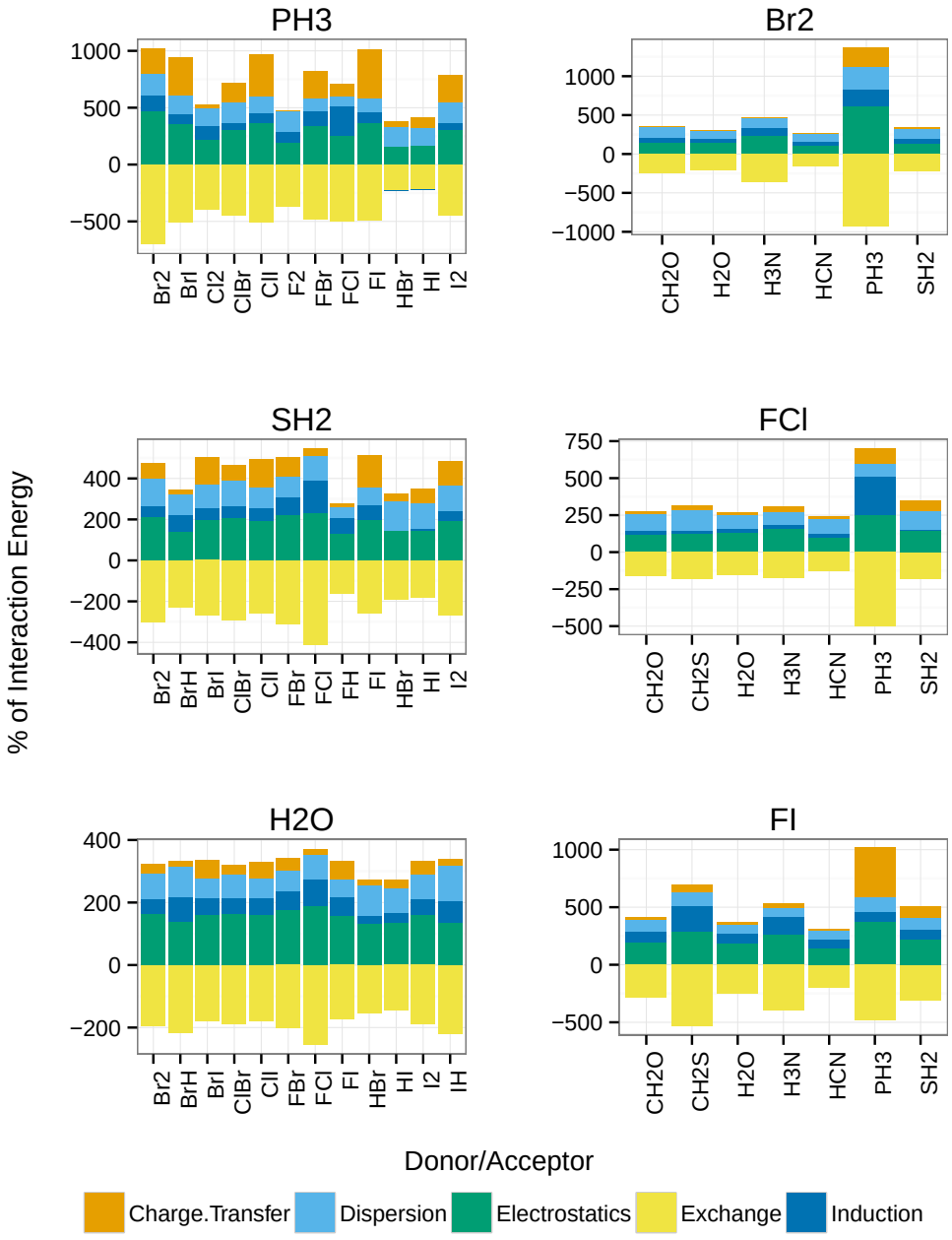

Figure S2: The SAPT decompositions as a percentage relative to the interaction energy, for 3 donors and 3 acceptors. For the right hand column, the percentage charge transfer jumps in all instances for the PH_3 acceptor, particularly in the case of FI. In the left hand column, the charge transfer contributions are far greater for phosphine than for the other two, and those for SH_2 are similarly larger than for H_2O. The numerical data can be found in the fitting_set.csv dataset.