Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Spurious proton transfer in hydrogen bonded dimers

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Table S1: Hydrogen bond strength, E_{hb} (in kcal/mol). Energies are basis set superposition error corrected

System	Method	aug-cc-PVYZ		System	Method	aug-cc-PVYZ	
		Y = D	Y = T			Y = D	Y = T
	PBE-D3	-4.77	-4.82		PBE-D3	pt	pt
	SCAN-D2	-5.05	-5.13		SCAN-D2	pt	-5.91
	SCAN-L-D2	-5.31	-5.98		SCAN-L-D2	pt	pt
	M06-L-D3	-4.16	-4.29		M06-L-D3	-5.12	-5.25
	PBE0-D3	-4.94	-4.97		PBE0-D3	-6.80	-6.95
$(HCN)_2$	PBE0	-4.55	-4.57	$(HSiN)_2$	PBE0	-6.21	-6.36
	HSE03-D3	-4.64	-4.68		HSE03-D3	-6.16	-6.31
	$HSE03_{NW}$-D3	-4.75	-4.80		$HSE03_{NW}$-D3	-6.22	-6.39
	HSE06-D3	-4.63	-4.67		HSE06-D3	-6.17	-6.32
	LC-PBE-D3	-6.08	-6.06		LC-PBE-D3	-9.37	-9.52
	M06-2x-D3	-4.45	-4.52		M06-2x-D3	-6.53	-6.77
	MP2	-4.46	-4.70		MP2	-3.01	-3.50
	PBE-D3	pt	pt		PBE-D3	pt	pt
	SCAN-D2	pt	-6.22		SCAN-D2	pt	pt
	SCAN-L-D2	pt	pt		SCAN-L-D2	pt	pt
	M06-L-D3	-5.10	-5.02		M06-L-D3	pt	pt
	PBE0-D3	-6.59	-6.65		PBE0-D3	pt	pt
$(HGeN)_2$	PBE0	-5.89	-5.95	$(HSnN)_2$	PBE0	pt	pt
	HSE03-D3	-5.93	-6.00		HSE03-D3	pt	pt
	$HSE03_{NW}$-D3	-6.07	-6.15		$HSE03_{NW}$-D3	pt	pt
	HSE06-D3	-5.94	-6.00		HSE06-D3	pt	pt
	LC-PBE-D3	-9.17	-9.22		LC-PBE-D3	pt	pt
	M06-2x-D3	-6.12	-6.41		M06-2x-D3	-5.50	-5.87
	MP2	-2.77			MP2	-3.13	-2.52

Basis set from "Basis Set Exchange" database. A New Basis Set Exchange: An Open, Up-to-date Resource for the Molecular Sciences Community. Benjamin P. Pritchard, Doaa Altarawy, Brett Didier, Tara D. Gibson, Theresa L. Windus. J. Chem. Inf. Model. 2019, 59(11), 4814-4820.

Table S2: Hydrogen bond distance, d_{hb} (in Å).

System	Method	aug-cc-PVYZ		System	Method	aug-cc-PVYZ	
		Y = D	Y = T			Y = D	Y = T
	PBE-D3	2.15	2.18		PBE-D3	pt	pt
	SCAN-D2	2.15	2.18		SCAN-D2	pt	1.63
	SCAN-L-D2	2.09	2.11		SCAN-L-D2	pt	pt
	M06-L-D3	2.15	2.15		M06-L-D3	2.03	2.07
	PBE0-D3	2.15	2.18		PBE0-D3	1.94	1.95
$(HCN)_2$	PBE0	2.16	2.19	$(HSiN)_2$	PBE0	1.95	1.96
	HSE03-D3	2.20	2.22		HSE03-D3	1.99	2.01
	$HSE03_{NW}$-D3	2.18	2.21		$HSE03_{NW}$-D3	1.92	1.93
	HSE06-D3	2.19	2.22		HSE06-D3	2.00	2.02
	LC-PBE-D3	2.04	2.07		LC-PBE-D3	1.81	1.82
	M06-2x-D3	2.20	2.22		M06-2x-D3	2.09	2.10
	MP2	2.18	2.19		MP2	2.25	2.23
	PBE-D3	pt	pt		PBE-D3	pt	pt
	SCAN-D2	pt	1.57		SCAN-D2	pt	pt
	SCAN-L-D2	pt	pt		SCAN-L-D2	pt	pt
	M06-L-D3	1.98	2.03		M06-L-D3	pt	pt
	PBE0-D3	1.90	1.91		PBE0-D3	pt	pt
$(HGeN)_2$	PBE0	1.92	1.93	$(HSnN)_2$	PBE0	pt	pt
	HSE03-D3	1.95	1.97		HSE03-D3	pt	pt
	$HSE03_{NW}$-D3	1.83	1.85		$HSE03_{NW}$-D3	pt	pt
	HSE06-D3	1.96	1.98		HSE06-D3	pt	pt
	LC-PBE-D3	1.82	1.83		LC-PBE-D3	pt	pt
	M06-2x-D3	2.12	2.11		M06-2x-D3	2.02	1.96
	MP2	2.15			MP2	2.02	1.74

Basis set from "Basis Set Exchange" database.

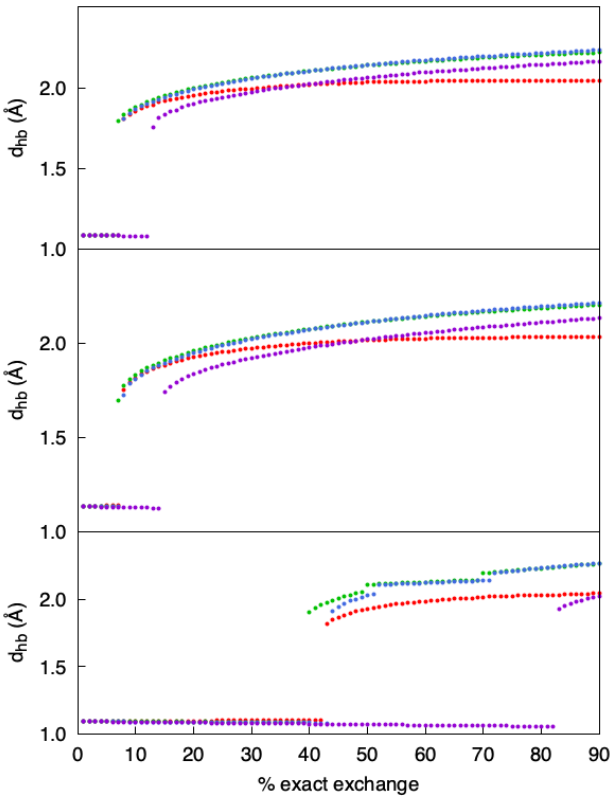

Figure S1: Change in the hydrogen bond distance, d_{hb}, with respect to the amount of exact exchange, ex, in m-PBE0 (red), m-HSE06 (green), m-HSE03 (blue) and m-HSE03$_{NW}$ (magenta) for $(HSiN)_2$ (top), $(HGeN)_2$ (middle) and $(HSnN)_2$ (bottom).

Table S3: Bond distance d_{X-H}, in Å, and deviation, in percentage, with respect to the MP2 value.

System	Method	% ex	d_{X-H}	Deviation (%)
	PBE	0	1.076	0.7
		10	1.073	0.5
HCN	m-HSE06-D3	20	1.070	0.2
		40	1.065	-0.3
	MP2	100	1.068	0.0
	PBE	0	1.504	1.1
		10	1.497	0.6
HSiN	m-HSE06-D3	20	1.491	0.2
		40	1.479	-0.6
	MP2	100	1.488	0.0
	PBE	0	1.538	1.3
		10	1.530	0.7
HGeN	m-HSE06-D3	20	1.525	0.4
		40	1.513	-0.4
	MP2	100	1.519	0.0
	PBE	0	1.703	2.9
		10	1.695	2.4
HSnN	m-HSE06-D3	20	1.688	2.0
		40	1.676	1.3
	MP2	100	1.655	0.0

Table S4: $X-H$ stretching frequency, ν_{X-H} in cm^{-1}, and deviation, in percentage, with respect to the MP2 value.

System	Method	% ex	ν_{X-H}	Deviation (%)
HCN	PBE	0	3360.3	-2.8
	m-HSE06-D3	10	3398.9	-1.7
		20	3435.9	-0.6
		40	3502.9	1.3
	MP2	100	3456.8	0.0
HSiN	PBE	0	2097.5	-5.0
	m-HSE06-D3	10	2154.2	-2.5
		20	2189.1	-0.9
		40	2264.9	2.6
	MP2	100	2208.4	0.0
HGeN	PBE	0	2057.1	-6.0
	m-HSE06-D3	10	2133.6	-2.5
		20	2166.4	-1.0
		40	2235.7	2.1
	MP2	100	2188.8	0.0
HSnN	PBE	0	1829.7	-12.5
	m-HSE06-D3	10	1848.5	-11.6
		20	1895.3	-9.4
		40	1982.3	-5.2
	MP2	100	2091.7	0.0

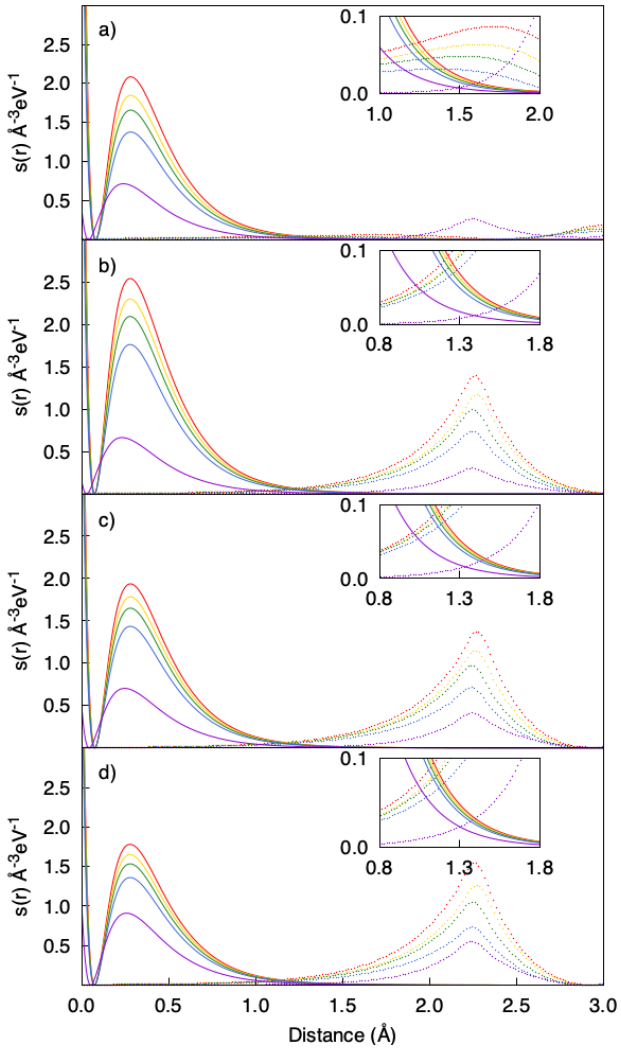

Figure S2: Local softness, $s(\mathbf{r})^-$ (solid lines) and $s(\mathbf{r})^+$ (dotted lines), of the HXN isolated molecules. Considering HXN oriented as in Fig. 3 of the main tex, $s(\mathbf{r})^+$ is shifted to the right along along the $d_{N\cdots H}$ line. Red PBE calculations, yellow m-HSE06 with 10% of xc, green m-HSE06 with 20% of ex, blue m-HSE06 with 40% of ex, magenta MP2 calculations. a) HCN, b) HSiN, c) HGeN, d) HSnN.