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Accurately extracting the signature of intermolecular interactions present in the NCI plot of the reduced density gradient versus electron density †

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Electronic Supplementary Information (ESI)

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1 2D plots (δg^{inter}, δk^{inter}) for the water dimer

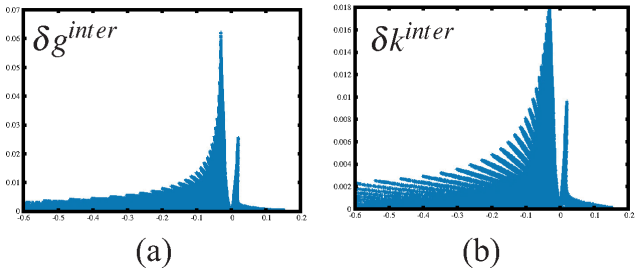

Fig. S 1 Comparison between the δg^{inter} and δk^{inter} 2D plots versus the signed electron density ($sign(\lambda_2)\rho$) for the water dimer at equilibrium geometry.

2 Water dimer (equilibrium geometry); 3D plot of (a) δs^{inter}, (b) δs^{inter} and δg^{inter}

Figure S2(a) highlights why δs is not an appropriate descriptor to describe weak molecular interactions. Figure S2(b) demonstrates that the more convex form observed for δg compared to δs originates from the specific mathematical form of δs (by dividing by $\rho^{4/3}$).

Panel (a) of this Figure shows the δs^{inter} isosurfaces calculated for the water dimer at equilibrium geometry. As can be seen, in addition to the usual small isosurface (blue) featuring the interaction between H and O atoms, a large ring appears around it associated to very small ED values. This last isosurface corresponds to the large and sharp peak always observed in the δs^{inter} 2D plot representation. A careful analysis shows that it has nothing to do with BCP and does not correspond to the hydrogen bond interaction. It rather denotes the existence of points, within the "interaction corridor" where the drop in ED gradient, though small, is greater than the very low ED at those points far from the atoms. In such regions, the denominator ($\rho^{4/3}$) decays faster than the numerator ($|\nabla\rho^{IGM}| - |\nabla\rho|$). As a consequence, the δs^{inter} value increases dramatically. The presence of this artifact at low ED values plagues the analysis of weak molecular interactions within the IGM model. This demonstrates that the δs^{inter} descriptor is not appropriate to describe weak molecular interaction, due to its mathematical form.

In panel (b), the δg^{inter} isosurface (purple) is displayed and superimposed on the δs^{inter} representation (yellow). As can be seen, the δg^{inter} is located exactly at the same place than

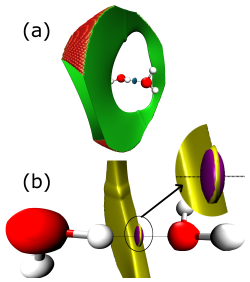

Fig. S 2 Water dimer at equilibrium geometry (a) $\delta s^{inter} = 0.85 a.u.$ isosurface, color coding in the ED range $-0.05 < sign(\lambda_2)\rho < +0.05$ a.u. (b) $\delta s^{inter} = 0.85 a.u.$ isosurface (yellow) superimposed on the $\delta g^{inter} = 0.04 a.u.$ isosurface (purple);

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the δs^{inter} isosurface (the one corresponding to the hydrogen bond), in the middle of the H$\cdots$O hydrogen bond. But mostly, δs^{inter} is narrower (a yellow slice slightly exceeds the convex δg^{inter} isosurface). In the case of δg^{inter}, no extra-ring is observed, thanks to the simple mathematical form of the δg^{inter} descriptor. This Figure clearly shows that not dividing by $\rho^{4/3}$ ($\delta g^{inter} = |\nabla^{IGM}\rho(r)| - |\nabla\rho(r)|$) leads to a broader and slightly convex isosurface (purple) compared to the isosurface (yellow) obtained with:

$$\delta s^{inter} = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla^{IGM}\rho(r)| - |\nabla\rho(r)|}{(\rho(r))^{4/3}}$$

Therefore, the narrow central yellow isosurface observed for the hydrogen bond in the δs representation does not result from the IGM model (used to get δs), but rather from the specific mathematical form of δs that reinforces points where ED is low.

3 Relationship between δk and δg at bond critical point

Using the simple exponential model of two interacting atoms A and B (equations 6 and 7 in the manuscript), a linear relationship can be established at BCP : $\delta k = \delta g \times \frac{\alpha}{4(1+\frac{\alpha}{\beta})}$.

4 DFT functional dependency of electron density at bond critical point for four dimers

The geometry of each dimer was obtained using four different DFT functionals and the basis set 6-311++G**.

Table S 1 H-bond length d and properties at the bond critical point (ρ, δg^{inter} and δk^{inter} in a.u.) obtained using three different DFT functionals

Complex		d(Å)	ρ	δg^{inter}	δk^{inter}
$PH_3\cdots H_2O$	B3LYP	2.65	0.016	0.027	0.054
	M06-2X	2.61	0.016	0.028	0.053
	wB97XD	2.62	0.016	0.028	0.053
$H_2O\cdots H_2O$	B3LYP	1.93	0.032	0.060	0.148
	M06-2X	1.92	0.032	0.063	0.152
	wB97XD	1.92	0.032	0.066	0.153
$HCN\cdots HF$	B3LYP	1.84	0.044	0.090	0.189
	M06-2X	1.85	0.043	0.087	0.183
	wB97XD	1.85	0.044	0.087	0.185
$HF\cdots NH_3$	B3LYP	1.68	0.063	0.121	0.258
	M06-2X	1.69	0.061	0.119	0.253
	wb97XD	1.68	0.061	0.119	0.254