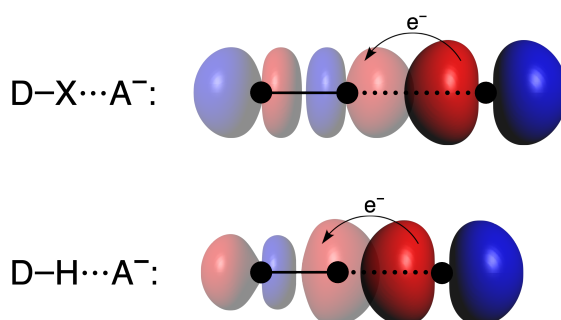


Halogen Bonds and the σ -Hole Myth

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I will discuss the nature of strong halogen bonds as compared to hydrogen bonds, based on extensive computational analyses of the structure and bonding mechanism in trihalides $\text{DX}\cdots\text{A}^-$ and the analogous hydrogen-bonded complexes $\text{DH}\cdots\text{A}^-$ ($\text{D}, \text{X}, \text{A} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) using relativistic density functional theory [1]. The vast series of model systems provide a set of consistent data from which reliable trends in structure and stability can be inferred over a large range of systems. But the main objective, as mentioned above, is to achieve a detailed understanding of the nature of halogen bonds, how they resemble but also how they differ from the better-understood hydrogen bonds.



Thus, we present an accurate, causal physical model of the halogen bond based on quantitative Kohn-Sham molecular orbital (MO) theory, energy decomposition analyses (EDA) and Voronoi deformation density (VDD) analyses of the charge distribution [2, 3]. It appears that the halogen bond in $\text{DX}\cdots\text{A}^-$ arises not only from classical electrostatic attraction but also receives substantial stabilization from HOMO–LUMO interactions between the lone pair of A^- and the σ^* orbital on D-X (see illustration). In the course of my talk, I will address the idea of the σ -hole bond, a myth that is still being proliferated in parts of the scientific community.

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