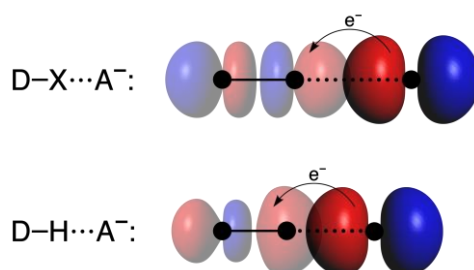


## Halogen Bonding versus Hydrogen Bonding: A Molecular Orbital Perspective.

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I will present the results of an extensive computational analyses of the structure and bonding mechanism in trihalides  $\text{DX}\cdots\text{A}^-$  and the analogous hydrogen-bonded complexes  $\text{DH}\cdots\text{A}^-$  ( $\text{D}, \text{X}, \text{A} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) obtained using relativistic density functional theory (DFT) at ZORA-BP86/TZ2P. One purpose of these computations has been to obtain a set of consistent data from which reliable trends in structure and stability can be inferred over a large range of systems.



The main objective is however 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 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. 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  $\text{A}^-$  and the  $\sigma^*$  orbital on  $\text{D-X}$ .

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