σ-Hole Interactions: A Physical Interpretation

P. Politzer[1,2*] and J. Murray[1,2]

[1]*Department of Chemistry, University of New Orleans, New Orleans, LA 70148, USA*
[2]*CleveTheoComp, 1951 W 26th Street, Suite 409, Cleveland, OH 44113, USA*

*Author for correspondence e-mail: ppolitze@uno.edu

The anisotropic electronic densities of covalently-bonded Group IV-VII atoms frequently give rise to regions of positive electrostatic potential on the extensions of single covalent bonds to these atoms. Through such positive "σ-holes", the atoms can interact attractively and highly directionally with negative sites such as the lone pairs of Lewis bases, anions, π electrons, etc. [1,2]. In the case of Group VII, this is called "halogen bonding". Hydrogen bonding can be viewed as a less directional subset of σ-hole interactions. Since positive σ-holes often exist in conjunction with regions of negative potential, such atoms can also interact favorably with positive sites. In accordance with the Hellmann-Feynman theorem, all of these interactions are purely Coulombic in nature (which encompasses polarization and dispersion). The strength of σ-hole bonding increases with the magnitudes of the potentials of the positive σ-hole and the negative site.

References

1. P. Politzer and J. S. Murray, ChemPhysChem, 14, 2013, 278-294.
2. P. Politzer, J. S. Murray and T. Clark, Physical Chemistry Chemical Physics, 15, 2013, 11178-11189.