Electron Density as a Probe of Inter- and Intra-Molecular Bonds

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The fact that two negatively charged electrons could come together to form a bond between two, otherwise neutral, atoms has led to a lot of confusion and excitement among physicists and chemists. This was originally suggested by Lewis and Langmuir more than a century ago and is well understood in terms of the quantum physics that developed a decade later. However, chemical bonding continues to fascinate and confuse experts and novice alike. None other than the Nobel laureate Roald Hoffman wrote that philosophy of physics is different from philosophy of chemistry and it appears to have been mostly influenced by the conviction that 'physics' cannot explain 'chemical bond'! Most chemists grew up equating 'chemical bond' to a 'covalent bond', which caused more confusion and needless debate. Though ionic bonding is taught from high school, chemical bonding continued to imply a 'covalent bond' for most chemists. This contributed to the debate and confusion in the literature about the hydrogen bond, which controls the properties of the molecules of life, water and DNA. For several decades hydrogen 'bonding' was thought to be just electrostatic 'interaction', as everyone from Pauling was convinced that hydrogen could have only one 'chemical bond'. It took nearly a century of contributions from many experimental and theoretical scientists to realize that hydrogen 'bonding' is not just electrostatic 'interaction'. Non-covalent 'interaction' was introduced to describe hydrogen 'bonding' and other intermolecular interactions. In 2011, IUPAC came up with a new definition of hydrogen bonding, following our initiative. The decade that followed saw the discussion on intermolecular bonding expand to include more and more elements in the periodic table. Our laboratory relied on accurate structures of weakly bound complexes of H_2O/H_2S determined by the pulsed nozzle Fourier transform microwave spectrometer.[1] While microwave spectroscopy could give the coordinates of each atom in a complex, it does not give direct information about which of the atoms are bonded. We relied on the quantum theory of atoms in molecules (AIM) for identifying all the inter- and intra-molecular bonds.[2] The combination of microwave spectroscopy and AIM theory has helped us understand intermolecular bonds formed by all elements in the periodic table. We suggest a classification of all intermolecular bonds as Non-covalent bonds (shared-shell) and non-covalent bonds (Closed-shell).[3] This talk will summarize our understanding of intermolecular bonds.

Reference:

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2. A. Shahi and E. Arunan, "Hydrogen bonding, halogen bonding and lithium bonding: An atoms in molecule and natural bond orbital perspective towards conservation of total bond order, inter- and intra-molecular bonding", Phys. Chem. Chem. Phys. 16, 22935-22952 (2014).

3. Arijit Das and E. Arunan, “Unified classification of non-covalent bonds formed by main group elements: a bridge to chemical bonding” *Phys. Chem. Chem. Phys.* **25**, 22583-22594 (2023). A perspective published and highlighted on the front cover.