Revisiting the Structure and Bonding of H_3^+ in QTAIM

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Whenever the structure of a molecule is discussed, automatically the concept of the chemical bond is taking into consideration to distinguish the pair of atoms with mutual interactions. The topological features of electron density of H_3^+ (singlet, D_{3h}) calculated based on modern wavefunction[1, 2] and density functional[2] models show that the bond paths connect each hydrogen nucleolus to the non-nuclear attractor (NNA) at the center of the molecule. In this circumstance the atomic basins (an object with nucleolus and portion of electron density around it) do not share any inter-atomic surfaces (IAS), thus the idea of mutual interacting atoms is lost in this simple molecule. Also the two terminal points of each bond path are hydrogen nucleolus (Z=+1) and NNA (Z=0), the latter is not considering as the atom in chemistry.

It seems that the two concepts, i.e. bonding and structure that successfully have been preserved and redefined within the QTAIM theory for many different types of molecules, both become ambiguous concepts in this simple tri-atomic molecule.

Since the methods of generating and analyzing the electron density have been developed significantly, in addition to the rapid growth of computational resources, systematic study on bonding and structure of H_3^+ to its most accurate theoretical level is now feasible.

The outstanding generalization of QTAIM beyond the Born-Oppenheimer approximation[3] is also another fundamental advance in this field which allows the analysis of both the electronic and nuclear wavefunctions together. The method has been successfully applied to diatomic molecules and more general pictures of bonding and structure concepts have been presented[3].

References

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