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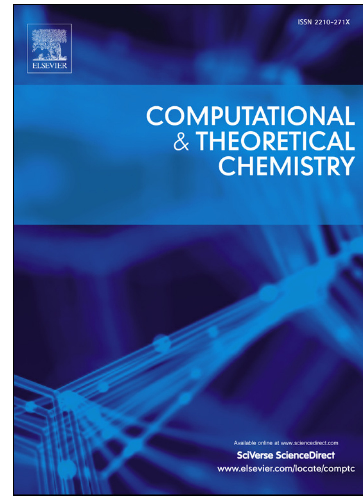

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A view of covalent and ionic bonding from Maximum Probability Domains

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Abstract

Connecting the accurate Quantum Mechanics to the chemical view is the first of foremost purposes of interpretative methods in general, and topological analysis in particular. In this field of methods, the Maximum Probability Domains (MPD) analysis, is conceptually appealing but has not been extensively applied yet. In this study we provide the general vision coming out from MPD on the two main family of bonds: polar-covalent and ionic bonds. An interesting picture arises concerning the MPD solution associated to covalent bonds, displaying a prolate shape that extends preferentially in the orthogonal direction to the bond axis, and not along it. The polarity of the bond only affects marginally the domain shape, though further probability analysis seems to allow quantifying it. Concerning the ionic bond, a resonating picture emerges, which is compatible, and refines, the usual electrostatic vision of two oppositely-charged atoms in interaction.

Keywords: Topological analysis, Chemical bonding, Real space technique

1. Introduction

In his 1916 seminal paper *The atom and the molecule*, G. N. Lewis [1] introduced his original model of the cubical atom and electron pairing to rationalize bonding in molecules. This model, supplemented by Langmuir's octet rule [2] can be considered as the foundation of the modern chemical alphabet, and as such it determines the way chemists see and think the concept of chemical bond. Later, Linus Pauling, in the first of his famous series of articles on the nature of the chemical bond [3], connected the recently developed quantum theory with the Lewis model, and presented the electron-pair bond (the covalent bond in modern terms) and the ionic bond as the two extreme cases of bonding mechanisms which can lead to a two electron chemical bond between two atoms. As depicted in scheme 1a, in Pauling's electron-pair bond the stabilization comes from spin-exchange resonance energy of the two singlet-coupled electrons, which is a purely quantum effect, whereas for the ionic bond (scheme 1b) it is the classical electrostatic interaction between the two ions that drives the stabilization. Much more

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