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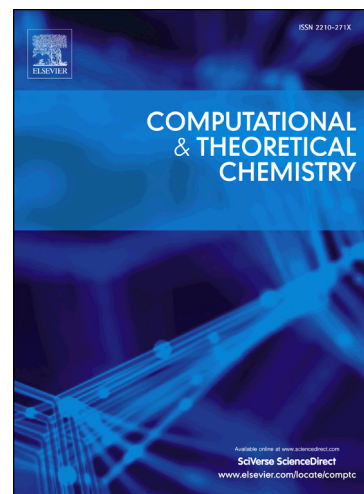
In Search of an Intrinsic Chemical Bond

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Abstract

The chemical bond, as a link between atoms, is an intrinsic property of the charge density. However, bond energy, which is commonly seen as the energy difference between a molecular state and an arbitrary dissociated state, depends extrinsically on the charge density. This view of a bond as a natural link possessing properties that are externally determined is at best clumsy, and often leads to contradictory interpretations as to the origins of the structure and properties of molecules and solids. Ideally, one would like to uncover an intrinsic property of the chemical bond that gives similar information content as that provided by bond energy. To this end, we report on our ongoing work exploring the intrinsic geometry imposed on the charge density by mapping it onto the smallest volumes bounded by zero flux surfaces in the gradient of the charge density. These natural volume elements of the the Quantum Theory of Atoms in Molecules have well defined properties, and hence, this mapping produces a set of property distributions with a quantifiable geometric structure that varies from molecule to molecule. Here, we examine the intrinsic geometry of the kinetic energy distribution for a series of homonuclear dimers and compare the geometric properties of these distributions with the bond energies of the same dimers.

Keywords: QTAIM, Kinetic Energy Density, Bond Bundle, Charge Density Distribution, Density Functional Theory

1. Introduction

Chemistry is the study of atoms and bonds. The Quantum Theory of Atoms and Molecules (QTAIM) [1] provides a rigorous and well studied representation of an atom in terms of the intrinsic topology and geometry of the charge density. However, save for an early attempt to define the properties of bonded fragments [2], the original formulation of QTAIM offered no means to access bond properties [1]. Thus, while QTAIM revealed that an atom with well-defined properties

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