Identifying Strong Covalent Interactions with Pauli Principle

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ABSTRACT

As one of the most widely used chemical concepts whose origin can be traced back to Lewis theory of bonding a century ago, a covalent bond involves sharing one or more pairs of electrons. A strong covalent interaction (SCI) is such a covalent bond that two or more electron pairs are shared, yielding a double, triple, quadruple bond, etc. Despite its ubiquity and usefulness, a robust and generally applicable approach to accurately identify strong covalent interactions and determine their bond orders is still lacking. Here, an SCI index is proposed from density functional theory using the Pauli energy, which is the contribution of the Pauli Exclusion Principle to the kinetic energy. Illustrative examples from organic, inorganic, and organometallic systems were provided. Its close relationship with the electron localization function (ELF) was elucidated. Both ELF and SCI generate similar results. Two complexes with a quintuple metal-metal bond have been confirmed. A stronger than quintuple bond has been proposed. This work should provide a reliable approach to determine bond orders for strong covalent interactions in complex systems, and meanwhile pinpoint the physiochemical origin and rationalizes the usefulness of both SCI and ELF. These tools can be applied to many other systems in many different fields to effectively appreciate strong covalent interactions.