

A Valence Bond Interpretation of 4 Electron, 3 Center σ Systems

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Four electron σ systems centered on three atoms (4e/3c units) have been studied using valence bond (VB) methods. The molecules studied were comprised of different combinations of C, O, and N with hydrogens added to preserve the 4e/3c unit. Prior to VB calculations, geometric parameters were optimized at the B3YLP/6-31G** level. After freezing the σ systems, VB structures were generated for the σ systems of each molecule by using the Breathing Orbital Valence Bond (BOVB) method. It was concluded that for all structures the importance of the VB structures depends on three factors; namely, electronegativity, charge separation, and spin pairing. In addition, different structures were combined in order to determine contributions to the total bond energy. It was determined that stabilization from mixing in ionic structures has a small role in the bond energy. This is because 4e/3c σ systems are more diffuse than the two atom sigma system previously studied in which the mixing in of ionic structures greatly lowers bond energy.