A QUANTUM CHEMICAL STUDY OF XH AND XH₂ (X=Be,C,N,O): 2s² RECOUPLED PAIR BONDING

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High level MRCI and RCCSD(T) calculations using large correlation consistent basis sets were used to study the low-lying states of the XH and XH₂ hydrides of the first row p block elements. Recoupled pair bonding is found in states such as the BeH X²Σ⁺ ground state, the BH a′Π excited state, the CH a″Σ⁻ excited state, the NH A′Π excited state, and OH ²Δ and ³Σ⁺ excited states. The 2s² recoupled bonding exhibited by these elements is similar to, but quantitatively different from, the 3p²/3s² recoupled pair bonding of the second row late p block elements (P, S, Cl). The differences arise from the well-understood distinction between the orbitals involved in recoupling. One of the dissimilarities between the two groups of elements is how favorable it is to form the second bond via covalent or recoupled pair bonding. In SF₂ and ClF₂, forming two recoupled pair bonds from the 3p² pair is more stable than forming one recoupled bond and one covalent bond due to the antibonding character of the singly occupied orbital containing the electron left over from recoupling; using this orbital to form a second bond reduces the antibonding character and stabilizes the molecule. In B and C, the recoupled 2s² pair is a set of lobe orbitals, and there is less driving force to bond to the second lobe than to the singly occupied 2p orbital that is also present. The X²A₁ ground state of BH₂ and the X²B₁ ground state of CH₂ are both therefore bent at about 130° with bonding that represents a linear combination of one recoupled bond and one covalent bond (the X¹Σ⁺ ground state of BeH₂ is linear with two recoupled bonds because there is only one electron available in BeH(X²Σ⁺)).