ABSTRACT

The thesis begins with an introduction to the evolution of various theories of chemical bonding with its application to polyhedral bonding. The quantitative tools used to study the various systems discussed in the thesis and the qualitative ideas of electron counting rules are discussed in Chapter 1.

Polyhedral boranes have always been a fascination for chemists despite the complexity of the structural patterns they exhibit. A great advancement in the development of polyhedral boranes began with the formulation of Wade's rule. The \( n+1 \) skeletal electron pair rule by Wade could account for the bonding in many existing monopolyhedral boranes. Some condensed polyhedral boranes known at that time required additional parameters to be incorporated into Wade's rule. With an enormous number of such condensed systems emerging, an extension of Wade's rule became essential. The \( n+m \) rule invented by Balakrishnaraj and Jemmis could throw light in many of these systems where sharing of more than one atom is involved. Single vertex bridged complexes needed an additional refinement of the \( n+m \) rule which resulted in a generalized \( mno \) rule. This rule helped to bring many diverse systems together. Chapter 2 discusses the rule in detail illustrating it using known examples. Justification of the rule based on molecular orbital theory is provided. Application of the \( mno \) rule in solving an error in an edge shared macropolyhedral borane is also given.

The condensation of two polyhedral boranes can occur by the sharing of one or more atoms. A survey of the experimental structures suggested the interactions between the non-bonded atoms on adjacent polyhedra as one of the factors affecting the stability of a macropolyhedral borane. The nature of such interactions are looked at in detail, first
with all-boron systems and then with heavy atom substitution, both main group and transition metals, to understand the effect of hetero atoms on them and forms Chapter 3 of the thesis.

The bonding in tubular boranes starting from the very common dianions $B_nH_n^{2-}$ ($n=6, 7, 10, 12$) are explored which also helped in examining the explanations given by Wade for the $n+1$ rule. As the analysis on the nature of bonding between the rings showed that five membered stacking are more preferred, mini-nanotubes like $B_{17}H_{17}^{2-}$, $B_{22}H_{22}^{2-}$, $B_{27}H_{27}^{2-}$ and an infinite extension of $B_5H_5$ rings in a staggered form are studied. These give a generalized picture and forms the subject matter of Chapter 4.

The application of $mno$ rule in an extended system based on polyhedra is examined in Chapter 5 by designing an edge shared system with simple pentagonal pyramid units. The resulting 3-D boride network require metal ions to attenuate their charge requirements and density functional theory based computations using plane wave basis are employed for the detailed study of the system. The studies show that the $mno$ rule has many more promising potentials to be put into use in extended systems involving any polyhedral borane as the repeating unit.