

题目:

New Chemical Concepts Arising from Theoretical Analysis

摘要:

This talk will consist of three exemplary cases which we recently studied based on the block-localized wavefunction (BLW) method which is a variant of ab initio valence bond (VB) theory.

- 1) The activation of CO by a non-metal catalyst, namely $B_2(NHC^R)_2$. The ground state of B_2 is of a single bond, but its third excited state of a triple bond has two significant σ -holes. The strong electrostatic attraction of the σ -holes with two NHC^R molecules can compensate the state excitation energy. Still, only one of the two π bonds of diboryne ($B\equiv B$) fits to one of the degenerate LUMOs of CO. When CO approaches $B_2(NHC^R)_2$, however, we identify a HOMO-LUMO swap. Subsequently, both HOMO and HOMO-1 of $B_2(NHC^R)_2$ can effectively interact with the two π^* orbitals of CO, resulting in the ultimate activation of CO.
- 2) The origin of the resonance-enhanced (RAHB) and resonance-inhibited (RIHB) hydrogen bond. BLW optimizations can result in optimal yet resonance-quenched structures with related physicochemical properties. Thus, correlation between π resonance and the strength of intramolecular RAHBs can be explored. We confirmed that π resonance unanimously reduces the bonding distance, strengthens the bonding and red-shifts the D-H vibrational frequency. By merging two malonaldehyde molecules, we also showed that intramolecular hydrogen bonds may be cooperative or anticooperative, depended on their relative orientations, and there is the RIHB concept as well.
- 3) The π - π repulsion in conjugated systems. We demonstrated that in conjugated systems, apart from the much familiar π conjugation which is stabilizing, there is also strong π - π repulsion which is a kind of intramolecular strain.

莫亦荣，1982 进入厦门大学，后一直在化学系就读，师从张乾二教授，主攻价键理论及其应用，并于 1992 年获博士学位。曾获德国科学交流和洪堡基金会基金资助，在 Schleyer 和 Peyerimhoff 小组工作。1998 至 2001 年，在美国明尼苏达大学化学系高加力教授小组工作。2001 年至 2002 年，在美国 Xencor 公司任计算生物科学家。2002 年 8 月起，在美国 Western Michigan 大学化学系任教。2003 年起为厦门大学化学化工学院闽江讲座教授，并入选福建省百人计划。