

Charge Distribution and Structure of Maximum Spin Li_nX ($n=2-7$, $\text{X}=\text{Li}$ and Na) Clusters

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Clusters are nano-sized materials between isolated molecules and condensed macroscopic states. Some of the fundamental problems which one would like to understand about clusters are their structures, relative stabilities, and their asymptotic behaviors as the clusters grow to condensed macroscopic states. Theoretical calculations take an important key role in understanding experimental observations due to lacking of direct experimental information available on their geometries. The alkali aggregates are among the better known micro-clusters, both experimentally and theoretically. Most of the studies of alkali clusters [1] focused on the ground state which is low-spin and bonded by electron pairing. Recently the non-pair Cs_2 ($^3\Sigma_u^+$) dimer was probed by experimental photo-association spectroscopy and found to be weakly bound relative to the two separated ground state atoms. According to both molecular orbital and valence bond theories, singlet electron-pairing is a fundamental form of bonding in the ground state of closed-shell molecules whereas triplet coupling is associated with a repulsive anti-bonding interaction. This paradigm seems breakdown as we observed the situation on non-pair electron in Cs_2 ($^3\Sigma_u^+$) dimer. The theoretical studies further showed that their bonding energy rise quite steeply as the high-spin $n+1\text{Li}_n$ clusters increase in size, reaching 0.5 eV/atom for $^{13}\text{Li}_{12}$ despite the lack of any electron pairs between the atoms [2-5]. These types of clusters are higher in energy than the corresponding lowest-spin states but stable with respect to isolated lithium atoms. This is quite a surprising result as the triplet state of H_2 is not bound. Owing to the novelty of this no-pair ferromagnetic-bonding and its occurrence in alkali clusters, it is interest to probe the nature of this bonding and structural characteristics by theoretical means. Until now some geometrical configurations of maximum-spin pure lithium clusters have been well studied, however the geometrical and stable information of mixed lithium clusters has remained unknown. This paper describes the structures and charge distributions of maximum-spin mixed lithium species, which are devoid of electron pairs but nevertheless are strongly bonded.

In this work the structure optimizations were performed in the local spin density approximation (LSDA) with the exchange-correlation functional of Becke's 3 parameter

functional and Perdew 91 expression (B3PW91). All-electron basis sets 6-311G(d) were employed. After optimizations, partial charges were obtained from Natural Population Analysis (NPA). The NPA solves most of the problems of the Mulliken scheme by construction of a more appropriate set of atomic basis functions, and so the atomic charges from NPA are reliable and usually independent of the basis sets. The same functional and basis set were used for frequency analysis in order to be able to distinguish between stable structures and transition structures. Our results revealed that all Li_nX clusters can be derived from substitutions of the peripheral Li atoms with X atoms in the Li_{n+1} ($n=2-7$). Atomic charges depend on its position and ability to obtain/lose electron. Na and K atom bears the most positive charges, which is different from the charge distributions in the low-spin mixed lithium clusters [1]. Larger heter-atoms favor to occupy outer positions in order to decrease geometrical reconstruction. The maximum-spin bimetallic clusters remain more three-dimensional geometries than their corresponding low-spin states. In various mixed maximum-spin lithium species, Li_3X and Li_2X^+ clusters are predicted to be more stable with respect to other clusters in this series, which is difficult to understand and not related with the open- or closed-shells of valence electrons similar to the situation in the low-spin clusters. Their odd-even fluctuation of stability tends to gradually decrease with the increase in the size of these clusters.

References

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