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某些镧系化合物化学键特性的**INDO**研究

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摘要 本文用INDO方法研究了不同价态镧系化合物的成键性质和4f轨道在成键中的作用,结果表明,镧系化合物的成键受许多因素, 如价态、半径、配位数、空间构型等影响。不同配体与镧系元素成键的强度差别较大; 高价态的共价性大于低价态的; 配位数低的大于配位数高的。某些特殊构型的镧系化合物除σ键外, 还形成重叠较好的π配键,使Ln-L键共价性大大增强。4f轨道在成键中的作用比5d的少得多, 三价(二价态)的4f轨道基本定域(<0.1%), 四价态的4f轨道对成键的贡献明显增大, 可接近1%。

关键词 分子轨道 化学键 INDO法 镧系元素化合物

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Study on bonding and 4f orbital effect of lanthanide compounds

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Abstract The bonding and the 4f orbital effect of lanthanide elements at different valence state in their compounds have been studied by INDO method. The bonding of lanthanide compounds is affected by many factors, such as valence state, ionic radius, ligand, coordinate no., space configuration etc. The strength of bonds composed of different ligands with lanthanide is distinctly different. The covalence of Ln-L bonds of lanthanide ions at high valence state in their compounds is larger than that at low valence state. Teh covalency at low coordinate no. is larger than that at high coordinate no. Some lanthanide compounds with special configuration, besides s bond, can form pp-dp dative bond with much overlap, which makes the Ln-L bond increase markedly. The effect of 4f orbitals on bonding is far less than that of 5d orbitals. The Ln 4f orbitals at 3 or 2 valence state may be considered to be essentially localized while the contribution of 4f orbitals on bonding in 4 valent Ce compounds increases obviously, up to 1%.

Key words MOLECULAR ORBIT CHEMICAL BONDS LANTHANIDE SERIES COMPOUNDS

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