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镧系元素**4f**轨道在成键中的作用的理论研究

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摘要 用密度泛函方法在冻结或不冻结4f轨道的条件下计算一系列含镧系元素双原子 分子，对结果进行分析，得出以下结论：镧系元素4f轨道按传统的化学键理论观点 是不直接参与成键的，
但对成键有一定作用：通过与匹配物的轨道混合使键长变短 ，键能增加，
一般可达百分之几。随着镧系原子序数的增加4f轨道对成键的贡献减 少。电负性高或价态高的匹配物对4f轨道的作用较强，4f轨道对成键的影响比较大 。对于重镧系元素，匹配物不是F或O时，
4f轨道对成键的贡献相当小，可以看成芯 轨道，但对于轻稀土，
在比较精确的计算中则应作为价轨道处理。镧系元素与氟结 合时，只有对靠近Yb的重镧系元素才可以把4f当作芯轨道，而与氧结合时即使对于 YbO把Yb4f作为芯轨道仍会带来较大误差。

关键词 镧系元素 化学键 分子轨道理论

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Theoretical Study on the Role of Lanthanide 4f Orbitals in Bonding

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Abstract A series of diatomic molecules containing lanthanides (Ln) are studied by means of density functional calculations with or without the Ln 4f orbitals frozen. Based on analysis of the calculated results the following can be concluded. The Ln 4f orbitals do not directly participate in bonding from the view-point of traditional bonding theory, but may influence the bonding to a certain extent through mixing a little match orbitals into the localized 4f orbitals and mixing some 4f component into the delocalized molecular orbitals, causing the bond lengths shortened and the bonding energy increased by about several hundredths in general. The contribution of 4f orbitals lessens with the increase of the atomic number of lanthanides. The matches with higher electronegativity or higher valences act on the 4f orbitals more strongly, resulting in larger influence of the 4f orbitals on bonding. Except for the matches being F or O, the 4f orbitals contribute to bonding quite small for the heavy lanthanides, and they can be considered as core orbitals, but they should be considered as valence orbitals in accurate calculations for the light lanthanides. In lanthanide fluorides the 4f orbitals can be treated as core orbitals only for the heavier lanthanides near Yb, while in lanthanide oxides sensible errors may occur if the 4f orbitals are dealt with as core orbitals even for YbO.

Key words LANTHANON CHEMICAL BONDS MOLECULAR ORBITAL THEORY

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