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FULL PAPERS

X-H (X = C, N, O, Si, P, S) 键离解能计算的密度泛函方法研究

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摘要 使用了不同密度泛函方法计算X-H (X = C, N, O, Si, P, S) 键离解能，并分析不同密度泛函方法的计算精度。研究发现大多数密度泛函方法包括B3LYP, B3P86, B3PW91, G96LYP, PBE1PBE，和BH&HLYP都明显低估键离解能13-25 kJ/mol。该现象与是否使用无限基组无关，因为即使使用无限基组键离解能仍然被低估。因此密度泛函方法不适合用于键离解能的估算。其中B3P86方法的偏差最小。进一步分析表明，使用限制性开壳层计算并无任何优势，在大多数情况下非限制性开壳层计算实际上比限制性开壳层计算要好。最后，我们发现了密度泛函方法对键离解能的低估是系统的，因此建议利用校准后的UDFT/6-311++G(d, p)方法计算化学键离解能。

关键词 密度泛函理论,键离解能,基组, B3P86方法

分类号

Density Functional Method Studies of X—H (X＝C, N, O, Si, P, S) Bond Dissociation Energies

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Abstract The performances of the density functional theory (DFT) methods in calculating X—H bond dissociation energies (BDE, X＝C, N, O, Si, P, S) were evaluated. It was found that most DFT methods including B3LYP, B3PW91, G96LYP, PBE1PBE and BH&HLYP significantly underestimated the X—H BDE by as much as 13—24 kJ/mol. The underestimation is not due to the use of finite basis set, because the DFT methods still significantly underestimate the X—H BDE with the complete basis set. Therefore, these DFT methods can not be used to calculate the BDE directly. Nevertheless, the B3P86 method shows very small underestimation for the X—H BDE. Further analysis suggests that there be no advantage for using the restricted open-shell DFT methods. The unrestricted DFT methods actually perform slightly better than the restricted open-shell DFT methods in most cases. Finally, it was found that the underestimation by the DFT methods was largely systematic. The use of the calibrated UDFT/6-311＋＋G(d, p) method was recommended to calculate the X—H BDE.

Key words density functional theory bond dissociation energy basis set B3P86 method

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