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研究简报

硝酰胺二聚体静电能和交换能的理论计算

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摘要 根据对称性匹配微扰理论, 并运用多个微扰和非微扰方法, 计算了硝酰胺二聚体在不同分子间距(R)时静电能和交换能. 这些具有轨道弛豫的静电能不仅含有第4级单、双、四和三重激发态项, 而且含有CCSD的第5级和更高级的能量项. 同时发现: 第4级的三重激发态能量项比第5级和更高级的能量项之和还重要. 求得的含有分子内电子相关效应的交换能达到了CCSD水平.
用于计算交换能关联校正项的单对交换近似在硝酰胺二聚体的范德华最小距离0.42 nm附近区域才较合理. 在R为0.32～1.42 nm范围, 静电能与R的关系有两种: 一是在小于等于0.47 nm时, ($R^{-7.64}$; 二是大于0.47 nm时, ($R^{-3.97}$. 交换能具有明显的短程作用特点, 其与R间的关系为指数衰减: 21.061exp(−R/0.318). 最后发现: 在硝酰胺二聚体中, 分子内的电子相关效应对和的影响很显著.

关键词 静电能 交换能 分子间作用 硝酰胺
分类号

Theoretical Calculation of Electrostatic Energy and Exchange Energy between Two Interacting Nitramide Molecules

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Abstract The electrostatic and exchange energies between two interacting nitramide molecules at several intermolecular separations (R) were derived based upon symmetry-adapted perturbation theory (SAPT) and using perturbative and nonperturbative methods. The obtained electrostatic energies with orbital relaxation not only include the fourth order contributions with single, double, quadruple and triple excitations, but also contain fifth and higher order contributions from CCSD theory. It was found that the fourth order triple excitation term is more important than the sum of these fifth and higher order contributions. The derived exchange energies with intramonomer correlation effects arrive at CCSD level. The single exchange approximation used for computing correlation corrections to exchange energy was found to be reasonable only in the region near the Van der Waals minimum distance of 0.42 nm for nitramide dimer. The R-dependency of the electrostatics has two different stages with R from 0.32 to 1.42 nm, ($R^{-7.64}$ for R less than 0.47 nm, inclusively; and ($R^{-3.97}$ for R over 0.47 nm. The exchange energy takes on a clear characteristic of short-range interaction, R-dependency of which is in the formula of 21.061exp(−R/ 0.318). The influence of intramonomer electron correlation on and was also found to be remarkable in the dimer system.

Key words electrostatic energy exchange energy intermolecular interaction nitramide

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