

# Towards Understanding the Nature of Internal Rotation Barriers with a New Energy Partition Scheme: Ethane and n-Butane

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## Abstract

Based on an alternative energy partition scheme where density-based quantification of the steric effect was proposed [S.B. Liu, *J. Chem. Phys.* 126, 244103 (2007)], the origin of the rotation barrier height between the eclipsed and staggered conformers of ethane and n-butane is systematically investigated in this work. The new definition is repulsive, exclusive, and extensive, and is intrinsically related to Bader's atoms in molecules approach. Two kinds of differences, adiabatic and vertical, are considered in this work, where in the former category the two conformers are in their respectively optimized geometry whereas in the latter case fixed bond lengths and angles are employed. We find that in the adiabatic case the eclipsed conformer possesses a larger steric repulsion than the staggered conformer for both molecules, but in the vertical cases the staggered conformer retains a larger steric repulsion. For ethane, a strong correlation relationship between the total energy difference and the fermionic quantum energy difference is discovered. This linear relationship, however, is not valid for n-butane, whose behaviors in energy component differences are found to be more complicated. The impact of basis set and density functional choices on energy components from the new energy partition scheme has been investigated, as has its comparison with another definition of the steric effect in the literature in terms of the natural bond orbital analysis through the Pauli Exclusion Principle.